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INHIBITION OF NATURAL GAS HYDRATES

by

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ABSTRACT

An experimental apparatus for the study of gas hydrate formation and inhibition up to pressures of 1100 psia was designed, constructed and consequently tested. A high pressure liquid level gauge with sight glasses is used as equilibrium cell.

The vapor, liquid water, hydrate equilibrium lines for pure cyclopropane and pure methane were reproduced within 3% of the published data (49,15). The equilibrium data for cyclopropane, in the presence of 5 molar methanol-water solution was extended up to the quadruple point where four phases (vapor, liquid water + inhibitor, liquid hydrocarbon, hydrate) are present.

A computer alogarithm to predict the dissociation pressures of gas hydrates in presence of inhibitors, based on a modification by Menten (75) of the Parrish and Prausnitz (54) model was written and tested.

TABLE OF CONTENTS

TABLE OF CONTENTS (CONT.)

LIST OF FIGURES

LIST OF TABLES

LIST OF TABLES (CONT.)

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TO MY PARENTS, AURELIO AND ELISA

AND

TO MY WIFE RHONDA

INTRODUCTION

The demand for a large energy supply has been steadily increasing during this century and in the past decade man has had to look for new and innovative alternatives since the reserves of the traditional energy supplier, oil, have become limited and have been involved in the world's politics as a weapon against the industrialized countries. Hydrates of natural gases are one of the latest alternatives since only in the early 1970's large formations were found in the permafrost regions and in the ocean sediments. The existence of hydrates was first shown in 1811 by Sir Humphrey Davy but only in 1934 an extensive research began.

Natural gas hydrates are nonstochiometric inclusion compounds in which a guest gas molecule is held by van der Waals forces in a metastable crystal lattice, constructed by water molecules. The crystal structure is stabilized by the presence of the guest molecule. Industry has considered hydrates a problem since they are responsible for pipeline plugging and most of the past research dealt with methods of prediction of condition formation and different ways of inhibition. Several prediction models have been postulated and as of today the most widely used are those of Parrish (54) and of Robinson (52,57). Both models are

based on statistical mechanics and the only difference between them is the inclusion of theoretical interaction constant by Robinson.

In the field of prevention of hydrate formation, the methods most commonly used are:

1) dehydration of the gas phase,
2) addition of inhibitor like an alcohol or an electrolyte,
3) modification of temperature or pressure so the formation condition is not present anymore.

While the first one requires large volumes of gas to be processed and the third one is limited by operational condition, the addition of an inhibitor is considered the most flexible alternative. In order to calculate the amount of inhibitor required, industry uses a procedure obtained by Jacoby (34) based on the results of Hammerschmidt's investigation in the 1930's. Only in 1979, Menten (75) proposed a new method, based on a modification of Parrish's model, which seems to obtain predictions eight times more accurate than Hammerschmidts.

The main objective of this work is to continue the study of hydrate inhibition by building an apparatus to study hydrate equilibria at high pressure and to test Menten's model for hydrates of gas mixtures.

Literature Review:

A) History of gas hydrates

Gas hydrate form part of the large family of compounds called clathrates. A common feature of all clathrates is the fact that they are formed by a host lattice, by itself thermodynamically unstable, which is stabilized by inclusion of a second component. The forces binding this component are similar in nature to intermolecular forces in liquids. Therefore, gas hydrates can be regarded as a solid solution of the second component in the host lattice.

The existence of hydrates was first discovered in 1811 by Sir Humphrey Davy and twenty years later Faraday studied the hydrates of chlorine gas. In the second half of the nineteenth century in Europe, a group of French scientists, among them Villard (1,2,3,4) and De Forcrand(5,6),discovered and collected data on many additional hydrates, including CO_2, CS_2, C_2H_2, NH_3, CH_4, C_2H_6, C_2H_4, C_3H_8, N_2O, Ar, Kr, Xe.

At this point, the interest on hydrates was only in the academic community but towards the 1930's, due to the fact that the gas and oil industry had to go to higher pressures in their pipelines, and that the occurrence of pipeline freezing had become a common source of annoyance, several studies were started to determine the causes of these problems. In 1934 E. G. Hammerschmidt (7,9,16,17,19)

discovered that natural gas hydrates were responsible for the plugging of lines. Subsequently he published a series of articles describing the reason for the formation, different ways of avoiding it, and the first equation for their prediction. His studies were verified by an investigation sponsored by the U. S. Bureau of Mines and the American Gas Association under the supervision of Deaton and Frost (10, 11, 15, 22). At the same time, several other investigators like Bechtold, Wilcox, Carson and Katz (14,20,13,23,24,21) started studying the formation of hydrates in the laboratory in order to get a better understanding of their occurence under operating conditions and to find other methods for predicting their formation.

Only in the 1950's the molecular structure of hydrates was determined as a result of the investigations of von Stackelberg, Claussen, Mueller, Marsh and Pauling (27, 28,29,30,31,32,33). Due to their crystal-like structure van der Waals and Platteeuw (38,39,40) were able to apply statistical mechanics and derived a series of fundamental equations based on the Lenard-Jones Devonshire cell theory.

In the 1960's Kobayashi and coworkers (43,44,45,46) studied the presence of hydrates at extremely high pressures and temperature and then determined parameters for the

statistical model. McKoy and Sinanoglu (48) compared the results of the prediction of hydrate formation using the statistical mechanics model based on different potentials, concluding that the Kihara potential gave the best results.

In the early 1970's, hydrate fields were discovered in the permafrost regions and in the ocean sediments, making hydrates a possible alternate energy resource. Therefore, a new field of research was open and investigators, such as Katz, Billy and Dick, Franklin (68,71,69) studied the formation of hydrates and their prediction in nature. At this point the Russian scientific body suddenly began publishing a large amount of knowledge particulary in the area of the occurrence and use of hydrates in nature. (e.g. Makogon (53)).

During this period the research on the more traditional area of hydrates investigation did not stop. In 1972 Parrish and Prausnitz (54) used the van der Waals and Platteeuw approach with several modifications to derive a new model for the prediction of mixture of gas hydrate formation. In 1974 Katz and Holder (68,74) published the results of their studies on the formation of hydrates by liquid hydrocarbons and Bishnoi (70) began studying the kinetics of hydrate formation.

Since then studies have been carried out by other researchers, such as Kobayashi, Holder, Parrish, Robinson, and Sloan (59,63,65,67,56,61,52,57,62,64) on hydrate formation, water content of gas forming hydrates, and thermodynamic parameters for prediction.

B) Nature and structure of gas hydrates.

Gas hydrates can be formed by pure gases or a mixture of gases. Regardless of the number of components in the gas phase, hydrates are non-stochiometric inclusion compounds, in which the included, "guest," gas molecules are held by van der Waals forces in a metastable crystal lattice, which is constructed from water molecules. The "host" molecules are held together by hydrogen bonding. Depending on components of the gas phase, gas hydrates crystallize in either of two cubic structures (I and II).

The unit cell of structure I is illustrated in Fig. 1. It contains 46 water molecules which enclose two types of cavities. The smaller cavities are located at the vertices and center of the unit cell. Each small cavity is formed by a pentagonal dodecahedral structure of 20 water molecules. The remaining six water molecules form bridges between the dodecahedral arrays in such a way to form a second type of cavity: a tetrakaidecahedron having two opposite hexagonal faces and twelve pentagonal faces.

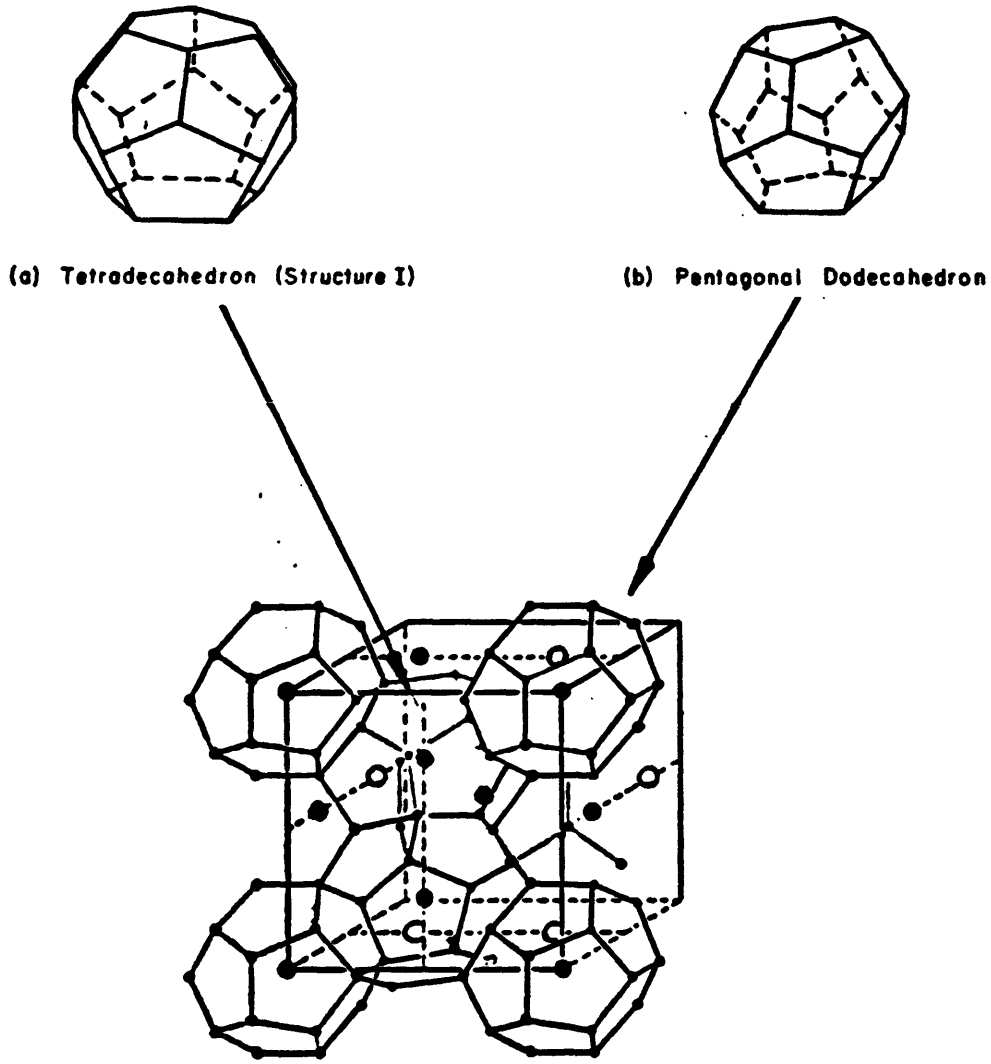

FIG. 1 HYDRATE LATTICE OF STRUCTURE I

The molecules of gases bound in structure I hydrates are relatively small (e.g. CH_4, C_2H_4, X_e) and in general occupy both types of cavities but some such as C_2H_6 occupy only the large cavities.

The unit cell of the hydrates crystallizing in Structure II is much more complex and is shown in Fig. 2. It contains 136 water molecules which also form two types of cavities. The smaller ones are distorted pentagon dodecahedra. The large cavities are formed by a hexadecahedron structure of 28 water molecules. Hydrates of structure II are formed only by molecules which are too large to be accommodated in structure I. This means that they can only occupy the larger cavities. (e.g. C_3H_8).

Since the pentagonal dodecahedron cavity is common to both structures, it can be considered as the basis or backbone of the hydrate crystal. In Fig. 3 this cavity is depicted, each ball representing an oxygen atom. Each line shown has a physical meaning: two represent chemically reacted hydrogen atoms, the third one a hydrogen bond. A fourth line, not shown, represents a second hydrogen bond which connects the cavity to other cavities so that structures I and II can be formed.

Table 1 summarizes the principal properties of gas hydrates.

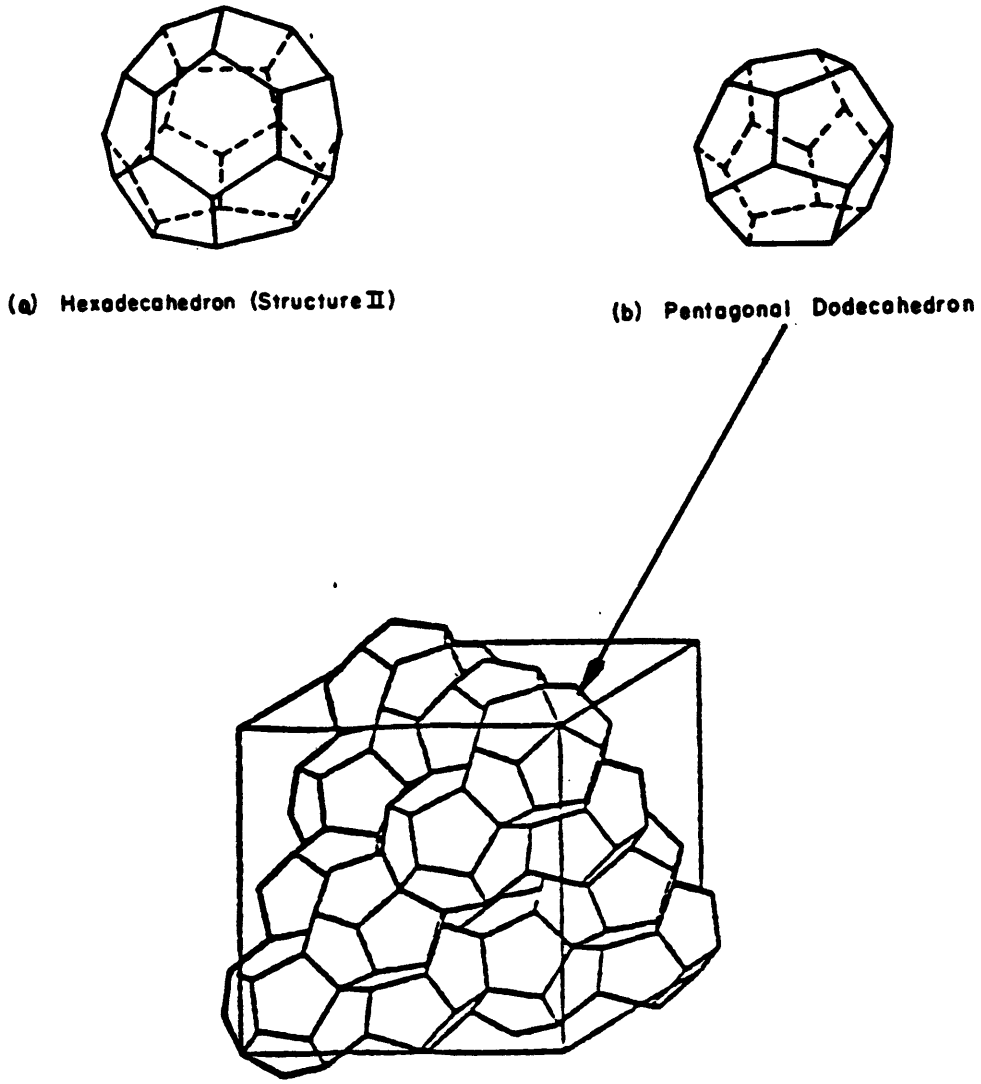

FIG. 2 HYDRATE LATTICE OF STRUCTURE II

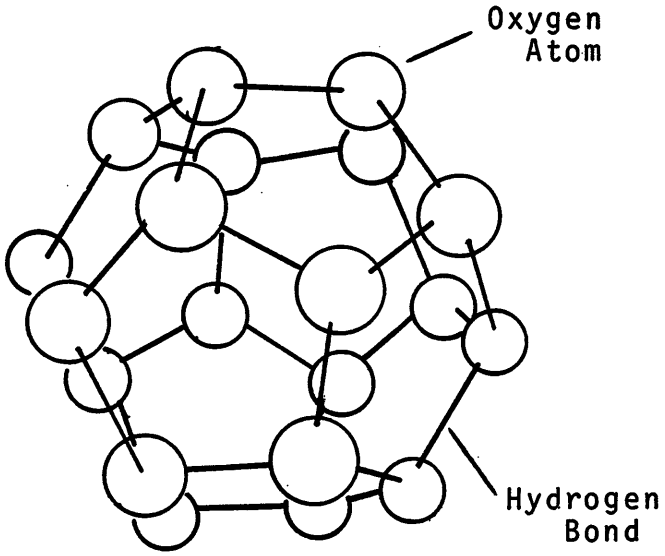

FIG. 3 HYDRATE LATTICE OF PENTAGONAL CAVITY

Table 1

HYDRATE LATTICE PROPERTIES

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

C) Hydrate prediction, equations and models.

After the discovery by Hammerschmidt in 1934 that, hydrates were the cause of pipeline freezing, a great effort was undertaken by the scientific community to investigate the properties and behavior of these new compounds. At the same time, the oil and gas industry had a special interest in a way of predicting hydrate formation.

As it usually happens when dealing in a new area of research, the first prediction methods were obtained by fitting data to empirical equation.

Hammerschmidt (7) determined the following relationship:

$$T = 8.9\ P^{\cdot 285} \qquad (1)$$

T = Temperature, F^{o}

P = Absolute pressure, lbs/sq.inch.

Its major drawback was the lack of a parameter which would express the effect of the forming gas composition.

Subsequently, Deaton and Frost (11) were able to come up with a relation that resolved the Hammerschmidt's shortcomings and expressed the equation:

$$T = a + 33.5 \log P \qquad (2)$$

T = Temperature, F

P = Absolute pressure, lbs/sq inch

a = constant, varies with type of gas, value -42.8 to -32.1

All of these first expressions were not general relations and applied mainly to natural gases or light hydrocarbons.

In 1939, Wilcox, Carson and Katz (23), developed an empirical method for predicting formation conditions which was based on the use of vapor solid equilibrium constants, Kv-s, in a manner similar to the vapor liquid equilibrium constants. The conditions of hydrate formation from a multicomponent gaseous mixture are calculated using the same method as for dew point calculations:

$$\Sigma z_i = 1.0 = \sum_i Y_i / K_{vs,i} \qquad (3)$$

Y_i = mole fraction of i in gas phase

Z_i = mole fraction of i in solid phase

The values of the solid-vapor equilibrium constants were obtained from ternary mixture data and for non-forming gases, the constant was assumed equal to infinity. This method is still widely used. In fact, charts of vapor-solid equilibrium constants can be found in the Technical Data Book of the American Petroleum Institute and in the GPSA data book. In more recent years Katz (68) has extended this method to the four phase hydrate equilibrium between vapor, liquid water, mixture of hydrates formers, and solid hydrate phase. Using the relation

$$K_{L\text{-}V_i} = y_i/x_i \tag{4}$$

equation (3) becomes

$$\Sigma_i z_i = \Sigma_i x_i \cdot K_{v\text{-}L,i}/K_{v\text{-}si} = 1.0 \tag{5}$$

and four phase hydrate condition can be predicted.

Even though the method of Katz and coworkers represent a great step forward in the prediction of hydrate conditions, there are two serious problems within it:

1) As in the liquid-vapor equilibrium constants, the $K_{v\text{-}s}$ values are assumed to be functions of temperature and pressure only. However, they have been shown to be highly dependent on the composition of the forming gases by Marshall and Kobayashi (45).

2) Using this approach, the formation of two different hydrate structures, I and II, cannot be taken into account because it is a macroscopic method without a molecular theory basis.

Another macroscopic method was proposed in 1968 by McLeod and Campbell (47) when reporting the results of their study on hydrate formation by natural gas mixtures at high pressures.

The basis of this method is in fact that the slope of the hydrate equilibrium curve at any given temperature between 6000 and 10,000 psia is almost constant and its average value is .0666. Furthermore, the quantity $\Delta H_{v-s}/ZR$ is considered as a constant function of pressure and gas type only.

Therefore, using a modified Clapeyron equation, the following equality holds:

$$\frac{d\ln P}{dT} = \frac{\Delta H_{v-s}}{ZRT^2} = \frac{}{T^2} = .0666 \qquad (6)$$

where C_i = Factor equal to $\Delta H_{v-s}/ZR$

ΔH_{v-s} = Latent heat of phase transformation

Z = Compressibility factor

T = Temperature, R^o

P = Absolute pressure, lbs/sq inch

In the case the forming gas is a mixture, Raoult's Law is assumed. Therefore, the constant value is calculated by using:

$$C_{MIX} = \sum_i c_i x_i \qquad (7)$$

The structure of hydrates had to be determined in order for a model based on molecular theory to be proposed. Therefore, when von Stackelberg, Claussen and Pauling et al (27,28,29,30,31,32,33) obtained such information, through x-ray diffraction van der Waals and Platteeuw (38,39, 40) were finally able to postulate a statistical model which relates the dissociation pressure and temperature to the chemical potential difference between the empty and filled hydrate lattice. The prediction method was derived from a simple model which corresponds to the three dimensional generalization of ideal localized adsorption, and the following assumptions were the basis for such analysis:

1) The contribution of the "host" (encaging) molecules to the free energy is independent of the mode of occupation of the cavities by the "guest" molecules. This implies that the spectrum of the host lattice is not affected by the presence of the solute molecules.

2) The encaged molecules are localized in the cavities and a cavity can never hold more than one solute molecule.

3) The mutual interaction of solutes molecules is neglected, therefore, the partition function for the molecule in its cage is independent of the number and types of solute molecule present.

4) Classical statistic are valid.

The properties of the hydrates were obtained using partition functions for solvent and solute which were derived by recognizing the similarity between the probability of finding an x amount of balls in an x number of boxes and the probability of finding a solute molecule in an enclosing lattice.

The final equations obtained were:

$$\Delta\mu_W^H = \mu_{H_2O}^B - \mu_{H_2O}^H = - RT\sum_m \nu_m \ln (1 - \sum_J \Theta_{mj}) \qquad (8)$$

$\mu_{H_2O}^B$ = chemical potential of pure H_2O in empty lattice

$\mu_{H_2O}^H$ = chemical potential of pure H_2O in filled hydrate lattice

R = Gas constant 1.987 cal/mole

T = Temperature, K^o

ν_m = number of cavities of type m per water molecule

Θ_m = fraction of type m cavities occupied by gas component ℓ

$$2) \quad \Theta_{ML} = C_{ML} f_L/(1 + \sum_J C_{Mj} f_j) \qquad (9)$$

where C_{ML} is the Langmuir constant and f is the fugacity of the gas component. The fugacity is then related to the

mole fraction in the gas phase and to the total pressure by

$$f_L = y_L \phi_L P \qquad (10)$$

Analyzing equations 8 and 9 once temperature and pressure are given, the fugacity can be calculated using an equation of state, ν_m is determined by the structure type; therefore, the only unknown is the Langmuir constant. This constant C_j, represents the H_2O-gas interaction in the cavity; in order to determine its value, van der Waals and Platteeuw used the cell theory introduced by Lennard-Jones and Devonshire for the study of liquids. The cell theory can be applied to hydrates because all cavities are approximately spherical and their walls consist of a relatively large number of atoms. Therefore, it is possible to suppose that the field of force acting on a solute molecule in its cage has a spherical symmetry. Furthermore two more assumptions have to be made:

1) The solute molecule can rotate freely in their cavities; in other words, the rotational partition function for the motion in the cavity is the same as that in the perfect gas.

2) The potential energy of a solute molecule at a distance r from the center of its cage is given by the spherical symmetrical potential w(r) proposed by Leonard-Jones and Devonshire.

Even though these last two assumptions seem very similar to the former ones, they are much more restrictive since only monoatomic gases as A, Kr, Xe and to a somewhat lesser extent the almost spherical molecules CH_4, CF_4, SF_6 satisfy them.

The L-J-D method assumes that the average contribution to the potential energy due to the interaction of solute molecule with any of the elements constituting the wall of its cage can be described by the force law:

$$\rho\ (R) = 4\varepsilon_o \{(\sigma/R)^{12} - (\sigma/R^6)\ \} \qquad (11)$$

R = Distance between solute molecule and particular elements of wall considered

σ = Distance for which attraction and rejection are in balance $\rho = 0$

ε = Value of $-\rho(R)$ corresponding to the strongest attraction which occurs at $R = 2\sigma$

which is independent of the shape and size of interacting molecules.

The interactions are summed over all the molecules distributed over the surface of a sphere and the resulting field within the sphere, averaged over all orientations, is given by:

$$w(r) = w(0) + (z\varepsilon_o/a^2) \left| 22(\sigma/a)^{12} - 10\,(\sigma/a)^6 \right| \; r^2 + O(r^4) \qquad (12)$$

ε_o = value of $-\rho(R)$ corresponding to the strongest attraction which at $R = 2\sigma$

σ = distance for which attraction and rejection are in balance.

Z = number of lattice molecules in the wall of cavity.

$w(0)$ = potential at center of cavity

a = core radius

Finally the relation determining the Langmuir constant is expressed by:

$$C(T) = \frac{4\pi}{kT} \int \exp \left| -w\,(r)/kT \right| r^2 \sigma r \qquad (13)$$

The agreement between the calculated dissociation pressure using this model and the experimental values is quite good for monoatomic gases but it deteriorates as the molecules become larger and less spherical. According to van der Waals and Platteeuw (39,40) the reasons for such results could be found in (1) the hindered rotation of non-spherical molecules in their cavities, (2) in the failure of the central field approximation in describing the interaction between solute molecule and a molecule in the lattice; and (3) hindered rotation of the molecule in its cavity.

Only years later another reason was found, which could explain some of the discrepancy between calculated and observed values

> "The numerical values in the calculation were derived from bromine hydrates which do not form either structure I or II (72)."

Once this first microscopic model was established, many investigators set out to improve it.

In 1963, McKoy and Sinanoglu (48) published the results of their study which considered different molecular potentials in the van der Waals and Platteeuw model. Using the following three different potential in the L-J-D cell model:

1) L-J-D 12-6 2) Kihara 3) L-J-D 28-7

and several statistic calculations they were able to conclude that

1) To a good approximation the chemical potential of the lattice is independent of solute occupation of the cavity.
2) The encaged molecule is confined pretty much to the center of the cell and does not collide with the wall.
3) The shape and size effect of the solute molecule in determining the force field in the cavity cannot be neglected.

As a result of the last conclusion, the Kihara potential, which assigns a core to each molecule and therefore includes the effect of the finite size of the molecules on their interaction, allows to obtain improved dissociation pressures for rodlike molecules as N_2, O_2, C_2H_6 and NO_2. Furthermore McKoy and Sinanoglu were able to determine that dissociation pressures are more sensitive to the parameters of the intermolecular potentials than are second virial coefficient data from which these parameters are determined.

During the same period, Nagata and Kobayashi (43) studied the hydrates of methane following the same approach as van der Waals and Platteeuw. Instead of using estimated L-J parameters, they fitted such parameters directly to the V-L-H equilibrium data. Furthermore, they introduced the concept of a reference hydrate which made the calculation of the chemical potential difference, of a given hydrate along its three phase line, easier.

In 1972, Parrish and Prausnitz (54) came up with a slightly more complex method that was based on van der Waal's and Platteuw's model. They used Kihara parameters in determining the cell potential which was expressed by:

$$w(r) = 27\varepsilon \left| \frac{\sigma^{12}}{R^{11}r} \left(\partial^{10} + \frac{a\,\sigma^{11}}{R}\right) - \frac{\sigma^{6}}{R^{5}r} \left(\partial^{4} + \frac{a}{R}\,\partial^{5}\right) \right| \qquad (14)$$

where

$$\partial^{\nu} = \left|(1-r/R - a/R)^{-N} - (1 + r/R - a/R)^{-N}\right|/N \qquad (15)$$

ε = characteristic energy

a = core radius

z = coordination number

R = cell radius of the cavity

N = 4,5,10,11

They kept the rest of statistical model equations as before. The Kihara parameters used, were determined from single and binary gas dissociation conditions and then used to predict dissociation conditions.

In their model, Parrish and Prausnitz did not calculate the dissociation pressure for a given temperature directly from the results fo the statistical method. They used a thermodynamic approach to phase equilibrium, and were able to determine the same quantity $\Delta\mu_w^{\partial}$ or $\Delta\mu_w^{L}$, depending if ice or liquid water is present, through two different paths:

A) van der Waals and Platteauw model

B) Thermodynamic derivation

The dissociation pressure was then determined forcing the difference in the values of the chemical potentials,

calculated using the two different paths, to zero by iterating on pressure.

The thermodynamic analysis used to obtain $\Delta\mu_w^L$ or $\varepsilon\,\Delta\mu_w^\alpha$ is as follows:

At equilibrim $P^\alpha = P^\beta = P^\gamma$ (16a)

$T^\alpha = T^\beta = T^\gamma$ (16b)

$\mu^\alpha = \mu^\beta = \mu^\gamma$ (16c)

Therefore in the case of hydrate and ice

$$\mu_w^H (T,P,) = \mu_w^\alpha (T,P) \quad (17)$$

μ_w^H = Chemical potential of water in hydrate phase

μ_w^α = Chemical potential of water in ice phase

and if liquid water is present

$$\mu_w^H (T,P,) = \mu_w^L (T,P) + RT \ln x_w \quad (18)$$

μ_w^L = Chemical potential of pure water in liquid phase

x_w = Water mole fraction

If we define

$$\Delta\mu_w^\alpha = \mu_w^\beta - \mu_w^\alpha \quad (19a)$$

$$\Delta\mu_w^L = \mu_w^\beta - \mu_w^L \quad (19b)$$

where μ^β = chemical potential of pure water in the empty lattice

and rewrite equation (8) for any number of gas components

$$\Delta\mu_w^H = \mu_w^B - \mu_w^H = - RT\Sigma_m \nu_m \ln (1 - (\Sigma C_{mj}\phi_j y_j P) \quad (20)$$

Then by substituting (20) into (19a) and (19b) finally by using 17 and 18:

$$\Delta\mu_w^\alpha = RT\Sigma\nu_m \ln(1 + \Sigma Cm_j\Phi_j y_j P) \quad (21a)$$

$$\Delta\mu_w^L = RT \{\Sigma \nu_m \ln (1-\Sigma Cm_j\phi_j y_j P) + \ln x_w\} \quad (21b)$$

So far the relations for $\Delta\mu_w^\alpha$ and $\Delta\mu_w^L$ are obtained using only the results of the statistical model and some basic thermodynamic laws; this representing path A. Path B is developed by using the fact that the effect of pressure and temperature on the chemical potential difference can also be calculated by using a total differential such as:

$$d\Delta\mu = (\partial\Delta\mu/\partial T)_p dT + (\partial\Delta\mu/\partial P)_T dP \quad (22)$$

where $\Delta_y = \Delta_{yw}$ or Δ_{yw}^L, the chemical potential difference of water in the empty hydrate and water in the ice ( ) or in liquid (L) phase.

and by using thermodynamic relations

$$d\Delta\mu = (-\Delta H/T) dT + \Delta V\, dP \quad (23)$$

dividing equation 23 by RT, the following equation is obtained

$$d(\Delta\mu/RT) = -(\Delta H/RT^2) dT + (\Delta V/RT) dP \quad (24)$$

where ΔH and ΔV are the molar enthalpy and molar volume difference between hydrate and the coexisting phase ice or water depending on the use.

For ice $\Delta H = \Delta h_{0,0}^{\beta-\alpha}$ = molar enthalpy difference between hydrate and ice (25)

$\Delta V = \Delta V_{0,0}^{\beta-\alpha}$ = molar volume difference between empty hydrate and ice (26)

For liquid water

$\Delta H = \Delta h_{0,0}^{\beta-\alpha} + \Delta h_w^f$ = molar enthalpy difference between empty hydrate and water (27)

$\Delta V = \Delta V_{0,0}^{\beta-\alpha} + \Delta V_w^f$ Molar volume difference between empty hydrate and water (28)

$\Delta h_w^f = \Delta h_o^f + \int_{T_o}^{T} \Delta cp_w \, dT$ = enthalpy difference between ice and liquid water and freezing point (29)

Δv_w^f = volume difference between ice and liquid water

$\Delta cp_w = \Delta cp_w^o - a(T - T_o)$ = difference in heat capacity between ice and water

Once $\Delta\mu_{0,0}^{\beta-\alpha}$ is found experimentally, using a reference hydrate, equation 23 is integrated and the results are:

for ice

$$\Delta\mu_w^{\alpha}(T,Pr)/RT = \Delta\mu_w^{\alpha}(To, Pr_o)/RTo - \int_{To}^{T} \Delta h_{0,0}^{\beta-\alpha}/RT^2 dT +$$

$$\int_{Pat_{OC}}^{Pat} \Delta V_{0,0}^{\beta-\alpha}/RT \; dP \qquad (30a)$$

for water

$$\Delta\mu_w^{L}(T,Pr)/RT = \Delta\mu_w^{L}(To,Pr_o)/RT_o - \int_{To}^{T}(\Delta h_{0,0}^{\beta-\alpha} + \Delta h_w^{f})/RT^2 \; dT +$$

$$\int_{Pat\ OC}^{Pat\ T}(\Delta V_{0,0}^{\beta-\alpha} + \Delta V_w^{f})/RT \; dP \qquad (30b)$$

Since the integration is carried out along the three phase equilibrium line which is univarient, equations 30a and 30b can be simplified

$$\Delta\mu_w^{\alpha}(T,Pr)/RT = \Delta\mu_w^{\alpha}(To,Pr_o)/RT_o - \int_{T_o}^{T} \Delta h_{o,o}^{\beta-\alpha}/RT_2 dT +$$

$$\int_{T_o}^{T} (\Delta v_{o,o}^{\beta-\alpha}/RT)\frac{dP}{dT} \; dT \qquad (31a)$$

$$\Delta\mu_w^{L}(T,Pr)/RT = \Delta\mu_w^{L}(To,Pr_o)/RT_o - \int_{To}^{T}(\Delta h_{o,o}^{\beta-\alpha} + \Delta h_w^{f})/RT_2 dT$$

$$+ \int_{To}^{T}\left(\frac{\Delta v_{o,c}^{\beta\ \alpha} + \Delta v_w^{f}}{RT}\right)\frac{dP}{dT} \; dT \qquad (31b)$$

where

T = Temperature, K^o

Pr = Reference Pressure, atms

$\Delta\mu_w^{\alpha}$ (To,Pr_o) = $\Delta\mu_{o,o}^{\beta-\alpha}$ + $\Delta v_{o,o}^{\beta-\alpha}$ Pr =

$\Delta\mu_w^{L}$ (To,Pr_o) = $\Delta\mu_{o,o}^{\beta-\alpha}$ + ($\Delta v_{o,o}^{\beta-\alpha}$ + Δv_w^{f}) Pr =

To = 273.15K

Finally $\Delta\mu_{w(T,Pr)}^{\beta-a} \varepsilon\ \Delta\mu_{w(T,Pr)}^{\beta-L}$ are brought to the equilibrium pressure using the following equations:

for ice: $\Delta\mu_w^{\alpha}(T,P) = \Delta\mu_w^{\alpha}(T,Pr) + \Delta v_{o,o}^{\beta-\alpha}\ (P-Pr)$ (33a)

for liquid water: $\Delta\mu_w^{L}(T,P) = \Delta\mu_w^{L}\ (T,Pr) + (\Delta v_{o,o}^{\beta-\alpha} + \Delta v^{f})$ +

$(P-Pr)$ (33b)

To obtain the hydrate dissociation pressure the difference between the $\Delta\mu_w^{\alpha}$ (T,P) or $\Delta\mu_w^{L}$(T,P) calculated by equations (21a) and (33a) or (21b) and (33b) depending if ice or liquid water is present, is forced to zero by iterating on pressure. This procedure is possible since once the temperature is fixed, all the equations are only a function of pressure. The pressure at which the difference between the $\Delta\mu_w$(T,P) is then taken as the equilibrium value.

The Parrish and Prausnitz (54) scientific contribution at this time was not only a model suitable for computer use. They extended the concept of reference hydrates to both structure, and expressed the reference hydrate pressure as:

$$\ln Pr = Ar + Br/T + Cr \ln T \qquad (34)$$

The reference hydrates for each structure are given in table 2.

Parrish and Prausnitz also developed empirical relations of the type:

$$Cml\ (T) = (Ame/T)\exp\ (Bml/T) \qquad (35)$$

Cml = Langmuir constant

Aml = constant obtained by fitting equilibrium data

Bml = constant obtained by fitting equilibrium data

which enabled the calculation of the Langmuir constants in the temperature range 260-300K without having to use equations 14 & 13. They calculated the Kihara parameters for 15 hydrates forming gases and new values for $\Delta\mu^{\beta-\alpha}_{o,o}$, the chemical potential difference between empty hydrate and ice were calculated.

Several years later, Ng & Robinson (52,57) modified the Parrish and Prausnitz program in order to obtain more

TABLE 2

REFERENCE HYDRATES

Temperature (K)	Structure I	Structure II
273.15	Xenon	Bromochloro-Fluoromethane
273.15	Methane	Natural Gas Hydrate

consistent predictions specifically for the case in which the forming gas is a mixture of gases.

The computer program was modified first by adding a proportionality constant, which has not a theoretical foundation, to the equation of the chemical potential difference derived from the statistical model.

Ng and Robinson modified equation for multicomponent mixtures is:

$$\Delta\mu_w^L = RT \quad \pi_j\{1+3\ (\alpha_j-1)Y_j^2 - 2(\alpha_j - 1)\ Y_j^3\} \ * \sum_m \nu_m \ln\ (1 + \sum_j C_{mj} f_j) + \ln X_w \qquad (36)$$

where

α_j = mole fraction of the componet j.

Y_j = mole fraction of the component j.

Secondly the fugacities were evaluated by using the Peng-Robinson equation of state.

Therefore the improved predictions of this program are a result of both changes and cannot be directly compared to Parrish's and Prausnitz's since their fugacities had been calculated by using the Chueh-Prausnitz eq. a less accurate equation but the best available at the time.

In 1980, Dhamawardhana (76), found experimentally the values of $\Delta\mu_o^{\beta-\alpha}$ and $\Delta h_o^{\beta-\alpha}$ and using a computer program similar to Parrish and Prausnitz in which fugacities could be calculated by one of the following equation of states:

1) Soave-Redlich-Kwong
2) Peng-Robinson

obtained new sets of Kihara parameters for the most common hydrate forming gases.

The set of parameters corresponding to the Peng-Robinson Equation of State was then chosen on the basis of being able to reproduce three phase equilibrium state for binary mixtures of gases more accurately than the others.

D) Inhibitors

The primary factors responsible for the formation of natural gas hydrates are pressure, temperature and gas composition. Since pressures and temperatures are dictated by circumstances, the only means available to the gas industry to avoid line obstructions caused by these compounds lies in changing the composition of the gas stream. This may be done by either removing certain constituents or by adding others.

In practice the gas stream composition is changed by removing water vapor in dehumidifying or dehydration plants. However, this method has the limitation that it can only be applied to large volumes of gas; therefore, it is only used in main lines leaving the gathering systems, supplying these lines, unprotected.

In the case of changing the gas stream composition by adding certain compounds, the gas industry employs alcohols, electrolytes and glycols. Inhibitor use at first was limited to the removal of hydrates obstruction, but lately, inhibitors have been added to lines to prevent hydrate formation. The compounds used as inhibitors must meet the following requirements (53):

1) The substance must effectively power the temperature of hydrate formation.

2) It must have a low freezing point.

3) It must be unreactive with natural gas components.

4) It must be soluble in water.

5) It must have low viscosity.

6) It must not be toxic.

7) It must have a low cost.

The choice of inhibitor is made empirically since no quantitative mechanism by which inhibitors prevent hydrate formation has been reported in the literature. Qualitatively the behavior of inhibitors like alcohols and gycols can be explained by the effect that these compounds have on the hydrogen bonds of the water molecules.

Studies on the effect of inhibitors started in 1937 when J. T. Russell (12), published the results of his research on the inhibiting effect of ammonia. According to Russell, a concentration of 42 ppm of ammonia was enough to prevent hydrate formation in the natural gas he used in his experiments and consequently in the field testing. His investigative shortcomings were: 1) the fact that the analysis of the natural gas was not given and 2) that no relation between amount of inhibitor and the lowering of the freezing point was developed.

Several years later Hammerschmidt (15) investigated the freezing point lowering of hydrate formation of a natural

gas using ethanol, methanol, n-propanol and ammonia in solution varying in concentration from 5 to 20 weight percent. As in Russell's case, no analysis of the natural gas used is given by Hammerschmidt, and no experimental data are shown. Instead several graphs of dissociation pressure vs temperature for the different solutions and an equation relating the amount and type of inhibitor to the lowering of the formation point are given. This relation is expressed by the formula:

$$d = (2335\ W)/(100M - MW) \qquad (37)$$

where $d = {}^{o}F$ lowering of freezing point of the gas hydrate

M = Molecular weight of the antifreeze

W = Weight percent antifreeze compound

2335 = constant

The constant is the average value obtained from more than 100 experimental determinations. The effectiveness of the different inhibitors is also discussed, and the inhibitors are ranked in decreasing order as: ammonia, methanol, ethanol, n-proponal, ammonium bicarbonate, acetone. Regarding ammonia, Hammerschmidt's observations are totally contrary to Russell's since he observed the the formation of solid compounds, carbonates of ammonia,

when carbon dioxide is present in the gas; therefore, the use of ammonia as an inhibitor is discouraged.

In later years, Powell (18) continued Hammerschmidt's work, while Miller and Strong (8) determined the effect of acetone, methanol, ethanol and potassium hydroxide on propane hydrates. Kobayashi (87) determined experimentally the hydrate decomposition conditions for methane, ethane and two natural gases with solutions of ethanol and sodium chloride brine. He also tried to predict the effect of sodium chloride, dissolved in water, on the condition of methane hydrate formation, using the concept of chemical equilibria. He concluded that at that time there were not enough thermodynamic and vapor-liquid equilibrium data to enable calculation of the hydrate formation conditions, and furthermore, that some of his assumptions in calculating the fugacities might cause large errors in the predicted dissociation pressure.

During the same period another investigator, A. P. Pieron (26), using the reaction equation for hydrate formation.

$$A + nH_2O \rightleftharpoons A \cdot n\,H_2O \qquad (38)$$

where A = hydrate forming gas

n = number of water molecules per mole of A in hydrate

and the chemical equilibrium concept was able to derive the following equation:

$$nR\ln a_{H_2O}/a'_{H_2O} = \mu A n H_2O - \mu A - n\cdot\mu^{o}H_2O \; T/T - A\cdot n\, H_2O - \mu A - N\cdot\mu^{o}H_2O \; To/To \quad (39)$$

where $a'H_2O$ = activity of water at To

To = equilibrium temperature of third component at To

$a\ H_2O$ = Activity of water at T

T = equilibrium temperature

which is simplified by using the relation $\frac{\partial(\mu/T)}{\partial T} + -\Delta h^{-}/T^{2}$ first to

$$nRT\ln a_{H_2O}/a'_{H_2O} = \Delta H^{*} \; 1/T - 1/To \quad (40)$$

and then by assuming:

1) ΔH^{*} independent of temperature and presence of inhibitor
2) The activity coefficient of water is equal to 1.0
3) The mole fraction of third component is small enough such that:

$$\ln (1-X_{T.C}) = -X_{T.C}$$

to $\Delta T = - \frac{nR\ To^2}{\Delta H}$ (41)

where ΔT = equilibrium temperature lowering in C^o

n = number of moles water per mole of hydrate

R = gas constant (1.987×10^{-3} Kcal/mole ^oK)

ΔH = heat of formation of one mole of hydrate at temperature To

$X_{T.C}$ = mole fraction in water layer

If the weight percent and molecular weight of the inhibitor are substituted for the mole fraction, $\Delta H'$ calculated using an approximate equation, and To assumed equal to an average value from Hammerschmidt ( ) then equation becomes

$$\Delta T = (2232W)/M\ (100 - W) \quad (42)$$

ΔT = lowering of freezing point of hydrate formation, F^o.

Comparing equation (42) with Hammerschmidt's, both equations are of the same form and the difference in constants is only 4%, which is quite remarkable considering the different nature of both derivations. On the other hand, this theoretical equation does not represent any improvement over Hammerschmidt's.

From Pieron's work to 1979, no one had postulated another equation relating inhibitors' properties to temperature lowering of hydrate formation; in fact, industry is

currently using a procedure deviced by Jacoby (34), in 1955, which is based on Hammerschmidt's equation, his vapor to liquid composition ratio of methanol in natural gas data and on Katz vapor-solid constant.

In 1979, P. Menten, (75) in order to take into account the presence of inhibitors, modified the equation for the chemical potential difference between water in the empty lattice and in the liquid phase, obtained from statistical mechanics, within the Parrish and Prausnitz model. The modified equation appears as follows:

$$\Delta\mu_w^L(T,P) - RT \sum_m \nu_m \ln (1+C_m f) + RT \ln (\gamma_W x_W) \qquad (43)$$

where R = gas constant, 1.987 cal/mole

T = temperature K^o

ν_m = number of cavaties of type m per water molecule

C_m = Langmuir constant

f = fugacity

γ_W = activity coefficient of water

W = mole percent of water in liquid phase

The activity coefficient γ_W, obtained from the Wilson equation, takes care of the presence of the inhibitor in the water, while in case of a volatile inhibitor, the gas fugacity must be modified accordingly.

This new model has only been used for the prediction of the effect of inhibitors on pure gas hydrate formation conditions producing results eight times more accurate than Hammerschmidts.

One purpose of this work was to investigate how accurate this model can predict the formation condition for hydrates of gas mixtures.

5) Experimental Apparatus

Experimental apparati similar to the one used in this study have been used successfully for high pressure equilibrium studies throughout the scientific community (13,23, 73,74). A modification has been made in order to allow a faster and more precise way of sampling the phases at equilibrium. The apparatus and the laboratory facilities are shown in Figs. 4 and 5. For a clearer description, the apparatus is presented under the following separate subsections:

1) Equilibrium cell, which allows the hydrate forming phase and water take brought into contact.

2) Mixing system which allows the liquid and gas phases to obtain better contact.

3) Temperature measuring and control system which measures the temperature in the equilibrium cell and controls it by means of a temperature bath.

4) Pressure measuring system which measures the pressure in the equilibrium cell.

5) Liquid and gas charging system which allows the equilibrium cell to be filled with the required components of each phase.

6) Chromatograph which allows the sampling of the different phases in the equilibrium cell.

FIG. 4 LISTING

1. Gas Mixture Cylinder
2. High Pressure Helium Cylinder
3. Positive Displacement Pump
4. Low Pressure Gauge
5. High Pressure Gauge
6. Temperature Probes Digital Readouts
7. Recorder
8. Temperature Control for Bath
9. Vacuum Pump
10. Cooling Unit
11. Main Power Sitchboard
12. Mixer
13. Equilibrium Cell
14. Electric Motor for Mixing System
15. Chromatograph Control Panel
16. Constant Temperature Bath

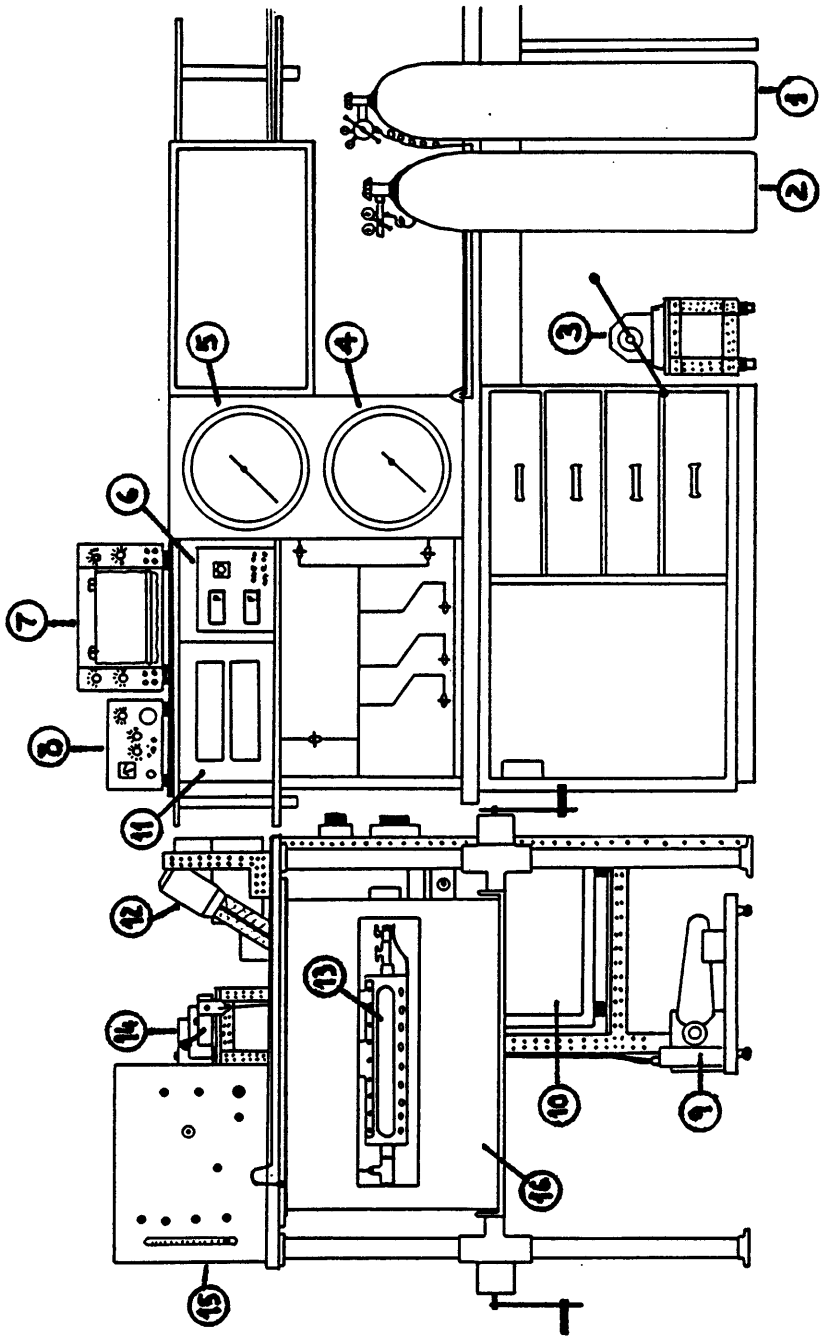

FIG. 4 EXPERIMENTAL APPARATUS

FIG. 5 LISTING

1. High Pressure Gauge (0 - 2000 Psia)
2. Low Pressure Gauge (0 - 1000 Psia)
3. Gas Mixture Cylinder
4. High Pressure Helium
5. Positive Displacement Pump
6. Vacuum Pump
7. Burette for Liquid Phase Storage
8. Cold Trap
9. Base Heater
10. Constant Temperature Bath
11. Electric Motor
12. Cooling Coil
13. Equilibrium Cell
14. Controlled Heater
15. Temperature Control
16. Platinum Resistance Thermometer
17. High Purity Helium Cylinder

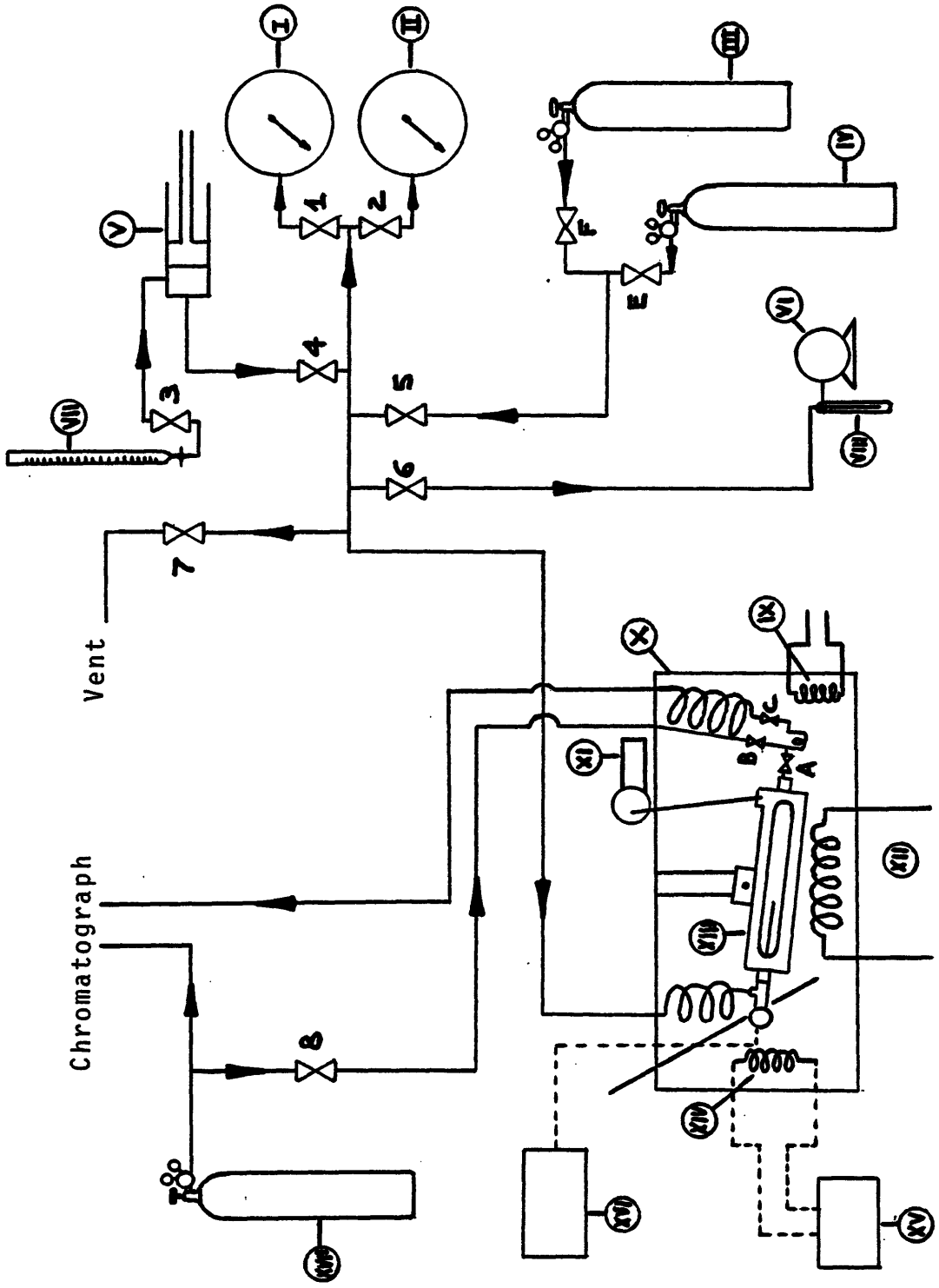

FIG. 5 APPARATUS FLOW DIAGRAM

7) Vacuum system.

1. Equilibrium cell: (Figure 6)

The equilibrium cell, a standard heavy duty, high pressure liquid level gage is a Jerguson single section transparent glass model, series T-30, whose pressure rating at 100°F is 2000 psi. The outside dimensions of the gage are: length 15 3/8, height 3 1/4", width 4 7/16, while the visible section of the glass measures 12 5/8" x 5/8". The gage has a one piece liquid chamber, machined from a solid bar of cold rolled steel, two interchangeable sectional steel gage covers, four gaskets and a set of two glasses. All the parts are tightly locked over the liquid chamber with special bolts and nuts. Special low flow Teflon gaskets are used on the liquid chamber side in order to prevent the leakage of gas by diffusion through the gaskets. Two 1/2" N.P.T. female end connections are welded over the gage outlets.

One end of the cell is connected to the rest of the apparatus by 1/8" stainless steel tubing and a platinum resistance thermometer is inserted in the gage through the same end. At the other outlet, by means of a series of globe valves, a sample of the cell contents can be withdrawn and directly run through the chromatograph.

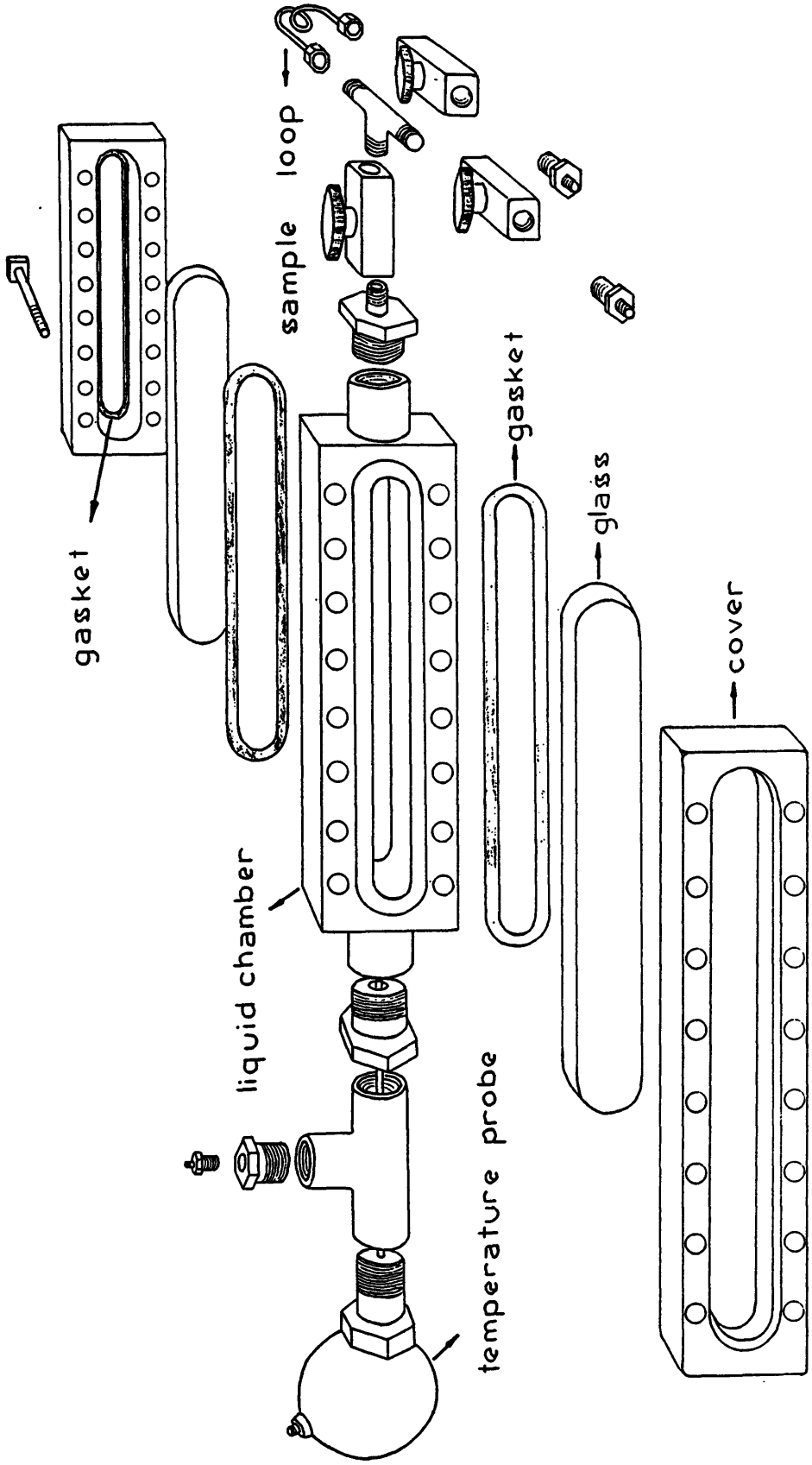

FIG. 6 EQUILIBRIUM CELL DETAILS

2. Mixing system

A pair of custom made stainless steel brackets is attached to the top part of the gage by the same bolts which hold it together. On the brackets two steel bearings, one per bracket, are mounted in such a way to allow the gage to be suspended from a steel rod and to rock up to an angle of 35^{o} on its lonitudinal axis. Figure 7 shows the supporting assembly.

A steel cable connects the gage to a bearing mounted on the shaft of a 1/2 hp electric motor. The speed at which the shaft is rotating is controlled by a gear box.

3. Temperature measuring and control system.

To measure the temperature inside the cell, an Omega, Platinum Resistance thermometer, type PR 12, is inserted in the liquid chamber of the cell. The leads are insulated with TFE Teflon, and a high temperature epoxy is used as moisture sealant. A 1/8" stainless steel sheath, pressure tight, covers the leads up to the connection head. (Figure 6). The Platinum Resistance thermometer is connected to a digital readout. The accuracy of the instrument in the temperature range 0-30 C^{o} is 1.0% and the calibration is given in Appendix A.

To control the temperature, a constant temperature bath of a 45% diethyl glycol-water mixture is used. The solution is contained in a 36" long, 16" wide and 24" high

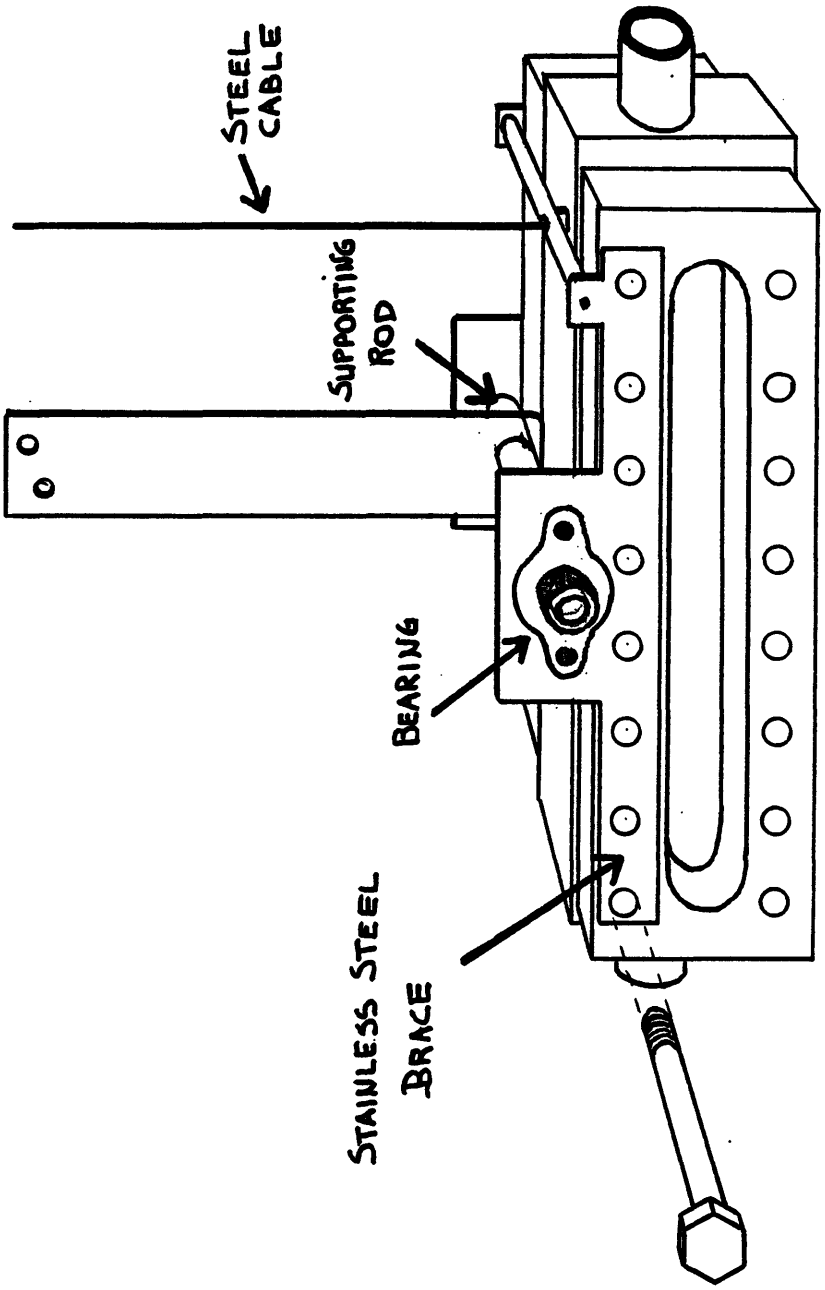

FIG. 7 EQUILIBRIUM CELL ROCKING ASSEMBLY

galvanized steel tank of 1/8" thickness. Two 25 3/4" long and 6 1/4" high windows of 1/8" thick plexiglass are located in the front and back sides of the tank to allow visual observation of the cell and its contents.

As a safety measure a mirror arrangement is set up so that observation can be done without standing directly in front of the cell. The tank is insulated all around, except for the window areas, by two layers of 1/2" thick insulation and by a wood casing. The bath can be raised and lowered by a winch and pulley assembly (See Fig. 8).

The temperature of the bath is kept at the desired value by the use of a refrigeration coil of a single stage cooling unit, with a capacity of 850 watts, a base 2000 watts immersion heater, manually controlled by á variac and by a 500 watts similar heater connected to a temperature controller. The heater response is proportional to the temperature difference between the set point valve and the temperature in the bath which is measured by a resistance thermometer contained in a stainless steel, copper nickel plated sheath.

The mixture in the bath is mixed by two stirrers which as for the heaters end cooling coil, are situated so to allow an unhindered view of the cell. The temperature of the bath is monitored by several iron-constantan on thermocouples to ensure proper mixing of the fluid.

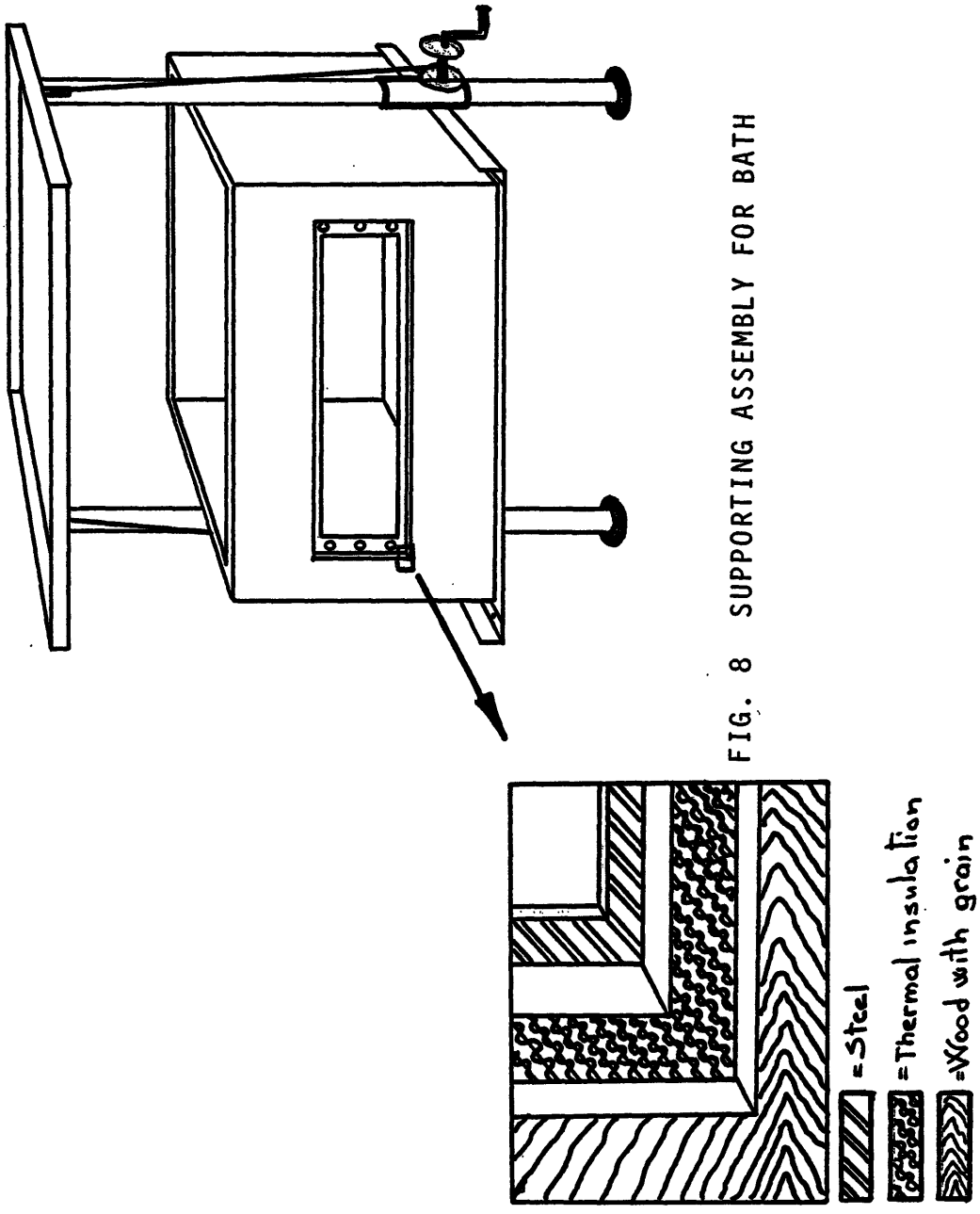

FIG. 8 SUPPORTING ASSEMBLY FOR BATH

4. Pressure measuring system.

The pressure in the apparatus is measured by two Heise, Bourdon tube gauges, type CM, with pressure ranges of 0-1000 psi and 0-2000 psi.

The gauges are operated by the effect of internal pressure on a Bourdon tube which is oval in cross section and bent into a circular arc. The pressure within the tube tends to straighten it and the motion of the free end of the tube is transmitted to the graduated dial. Both gauges read gauge pressure, but when they were calibrated, the graduated dials were adjusted so that absolute pressure could be read directly. The accuracy of the gauges is 1.0% of the full scale including the effect of hysterisis, and no compensation for temperature effects is required since both gauges are operating within the limits (-25^{o}F to 125^{o}) of the built in thermal compensator. Calibration curves for both gauges are in Appendix A.

5. Liquid and gas charging systems.

The liquid phase is stored in a 500 ml graduated buret which through 12" of tygon tubing, a union bonnet lift check valve, pressure rating of 6000 psi at 70^{o}F., and a 90^{9} bend made with 1/4" 316 s.s. is connected to a positive displacement pump. The pump is a Ruska model, type 2250-801, with a pressure rating of 8000 psi. This type of

pump works on the principle of volume displacement. A plunger of given diameter is forced into the liquid fill cylinder by a measuring screw. The volume displaced is shown on a linear scale in cubic centimeters. (Figure 9). The pump is connected to the equilibrium cell by an assembly of 1/8" 316 s.s. tubing and 1/8" Nupro s.s.-2BJ shut-off valves. All fittings are of the Swagelock type.

The gas phase, in contrast, is stored in commercial gas cylinders of different types and sizes depending on the contents and their properties. The gases are charged into the system by means of pressure regulators choosen according to the guidelines of the Matheson Gas Company.

For the cyclopropane experiment a regulator model 510 which allowed a discharge pressure of up to 120 psig was used. For the natural gas mixture runs a new regulator model 4-/I, with a discharge pressure of 1000 psig, had to be used. The gases are introduced into the cell through the same tubing and valves assembly used for the liquid phase.

6. Chromatograph

The chromatograph is not commercially available. Instead it was put together using a thermal conductivity cell

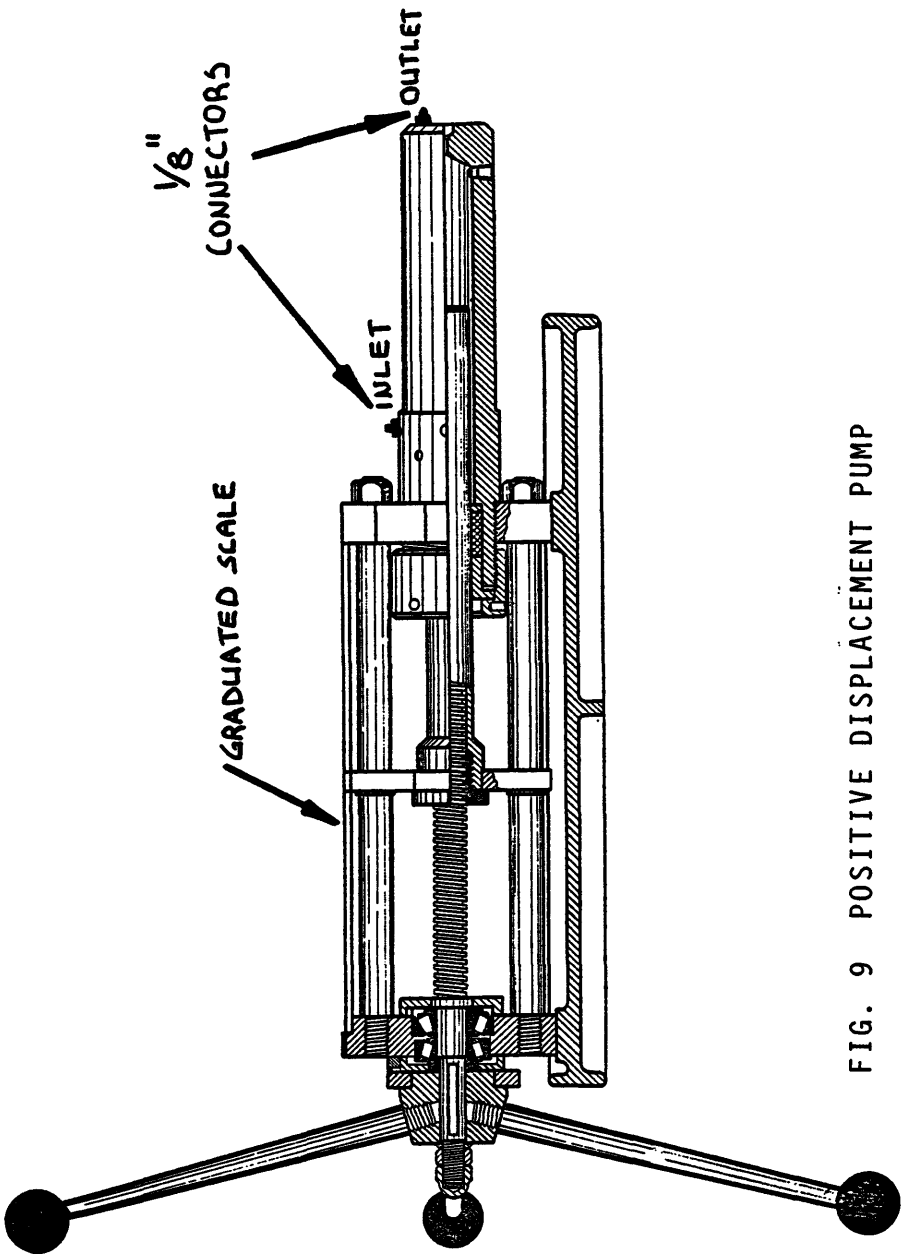

FIG. 9 POSITIVE DISPLACEMENT PUMP

detector, a voltage regulator power supply control, a variable input recorder and a 3' long, 1/8" diameter column. The thermal conductivity cell is a model 10-077 by Gow Mac consisting of a metal tube with two pair of bore holes in which four Rhenium-Tungsten filament are placed. All four filaments are swept by a gas flow in such a way that one pair only is in contact with the carrier gas, while the other can receive the column effluent. The filaments are heated by the power supply control and are connected electrically into a Wheatstone bridge. The elements lose heat to the block depending upon the thermal conductivity of the gas. Therefore, when the carrier gas passes through both sets of filaments the network is balanced and the electrical output is zero. When the sample exiting the column passes through a pair of elements the temperature and resistence changes produce an imbalance on the bridge which is monitored by the recorder.

The column is made by using standard 1/8" copper tubing packed with Poropak compound made by Hewlett Packard and is immersed in a portable constant temperature bath set to maintain a temperature of 115^{o}F.

7) Vacuum System

Vacuum was supplied to the equilibrium cell and

chromatograph by a Duo-Seal Vacuum pump.

Two acetone-dry ice cold traps were used to avoid condesable vapor from going into the pump. The reason for two cold traps is the fact that water trapped in the system, when loading the cell, accumulates at the bottom of the trap and freezes, clogging the line. Therefore, the first trap is a regular boiling flask where most of the water is collected and can freeze without clogging the line.

6) Experimental Procedures

The experimental determination of hydrate formation conditions required the following sequential steps, (refer to Figure 5 for flow diagram).

1) The equilibrium cell and connecting tubing are pressurized with helium to about 100 psig by opening valves 1,2, and 5 and then closing 5.

2) The valves to the pressure gauges (1 & 2) are closed in order to prevent liquid from getting trapped in the Bourdon tubes. The rest of the system is then vented by opening valve #7.

3) The tubing and cell are washed several times with distilled water. This is accomplished by pumping through valve 4, 120 ml of double distilled water, using the positive displacement pump, and allowing the cell to rock for 15 to 20 minutes. The system is then flushed with helium (valves 5 & E are open) forcing as much water as possible out through the sample port connection and vent (valves A, B, C and 7 are open and then closed).

4) The cold traps are loaded with the dry ice-acetone mixture so that the temperature is lowered to -80F maximum.

5) The vacuum pump is turned on and valve 6 is open allowing the system to be evacuated. Vacuum is maintained

for 15-20 minutes. Valve 6 is then closed, valves 1 and 2 are slowly opened and then the system is vented through valve 7. Valve 6 is reopened and vacuum is maintained for 20-30 minutes.

At this point the cell is ready to be loaded with the liquid phase, stored in the 500 ml graduated burette. For the runs in which an inhibitor was used, the methanol solution was made up by weighting the desired amounts of water and alcohol with a Mettler balance. To check the concentration of the refractive index the solution was measured before and after the experimental run.

6) The positive displacement pump is charged allowing the liquid to enter the cylinder. Usually 200 ml were introduced in the pump. Using the pump 80 ml of liquid are introduced in the system through valve 4 so that the cell liquid chamber is 30%-60% full.

7) The liquid in the cell is deareated. In the case of pure water, vacuum is pulled on the system until water starts boiling and is left on for several minutes. When the methanol-water solution is used, the cell temperature is lowered until solution freezes completely and then vacuum is pulled (see step 5).

8) The system is triple diluted with the gas to be used. The triple dilution is obtained by the following procedure:

A) Pressurize system to desired pressure by closing valve E, opening F and 5 and adjusting the regulator of the storage cylinder.

B) Allow gas to remain in cell for 10 minutes, then open valve 7 and vent system until pressure is equal to 15 psia.

C) Open valve 6 and pull vacuum.

Repeat steps A,B, and C three times. When a volatile inhibitor is present the above procedure has to be carried out while the solution is still frozen.

At this point the system is ready to be pressurized to the required value for the particular run. The temperature is increased so that the liquid phase is present and a value several degrees (5-10^{o}F) above the hydrate formation temperature is reached.

9) The cell is pressurized to a value higher than the highest required hydrate formation pressure, as the system must be supersaturated to form hydrates. (see step 8).

10) The initial conditions are recorded, then the mixing system is turned on while cooling is started. Temperature and pressure are recorded at regular time intervals throughout the cooling cycle. Pressure decreases slowly as the temperature drops until hydrates form, then it starts decreasing at a much faster rate. The cell contents have to be several degrees (usually 4-5 ^{o}F) below the hydrate

formation temperature before hydrates will appear. After a sizable amount of hydrates is formed, the heaters are turned on.

11) The rate of heating is decreased to a value of .1 - .2 F/hour as the temperature increases and when the last hydrate crystals disappear the temperature is kept constant for six hours while the pressure is monitored for any change. This temperature and its corresponding pressure are then recorded as the three phases equilibrium conditions.

12) The pressure is dropped to the next desired value and step 10 to 11 are repeated.

During the low pressure runs, the pressure drop was achieved by opening the cell sample-port valves A and C and allowing the desired amount of gas to leave the cell and to be sent directly to the chromatograph.

At high pressures, a sample of the gas phase was first introduced by opening valve A into the sample loop, then valve A is closed and valve C is opened sending the sample to the chromatograph. The pressure in then reduced to the desired value by opening valve 7.

Detailed instructions for the use of the chromatograph are in Appendix D.

7) Experimental Results

To test the apparatus several vapor-liquid water-hydrate equilibrium curves were obtained experimentally and compared to data in the literature.

For the low pressure range, 0-100 psia, the three phase data by Hafeman and Miller (49) for cyclopropane and pure water were reproduced while the equilibrium line data by Menten (75) for cyclopropane and a 16.5 weight percent methanol-water solution was extended to the quadruple point where vapor-liquid hydrocarbon-liquid water and hydrate coexist. These results are given in table 3 and plotted in Figure 11. The solid lines were generated using the computer program HYD2.FOR which can be found in Appendix C.

For the high pressure range, above 300 psia, the data by Deaton and Frost (22) for methane and pure water was reproduced in the temperature range 273.70-279.15K. Higher temperature could not be achieved due to the limitation posed by the pressure of the storage cylinder (700 psia).

These results are given in table 4 and plotted in Figure 12.

TABLE 3

EXPERIMENTAL VALUES OF DISSOCIATION

CONDITIONS OF CYCLOPROPANE HYDRATES

Liquid Phase Composition Wt% CH_3OH	Temperature (K)	Pressure (KPA)
0.0	289.65	570.89
	281.09	192.38
	278.93	145.45
	276.15	103.06
16.5	282.76	466.10
	278.20	288.78
	276.17	216.52

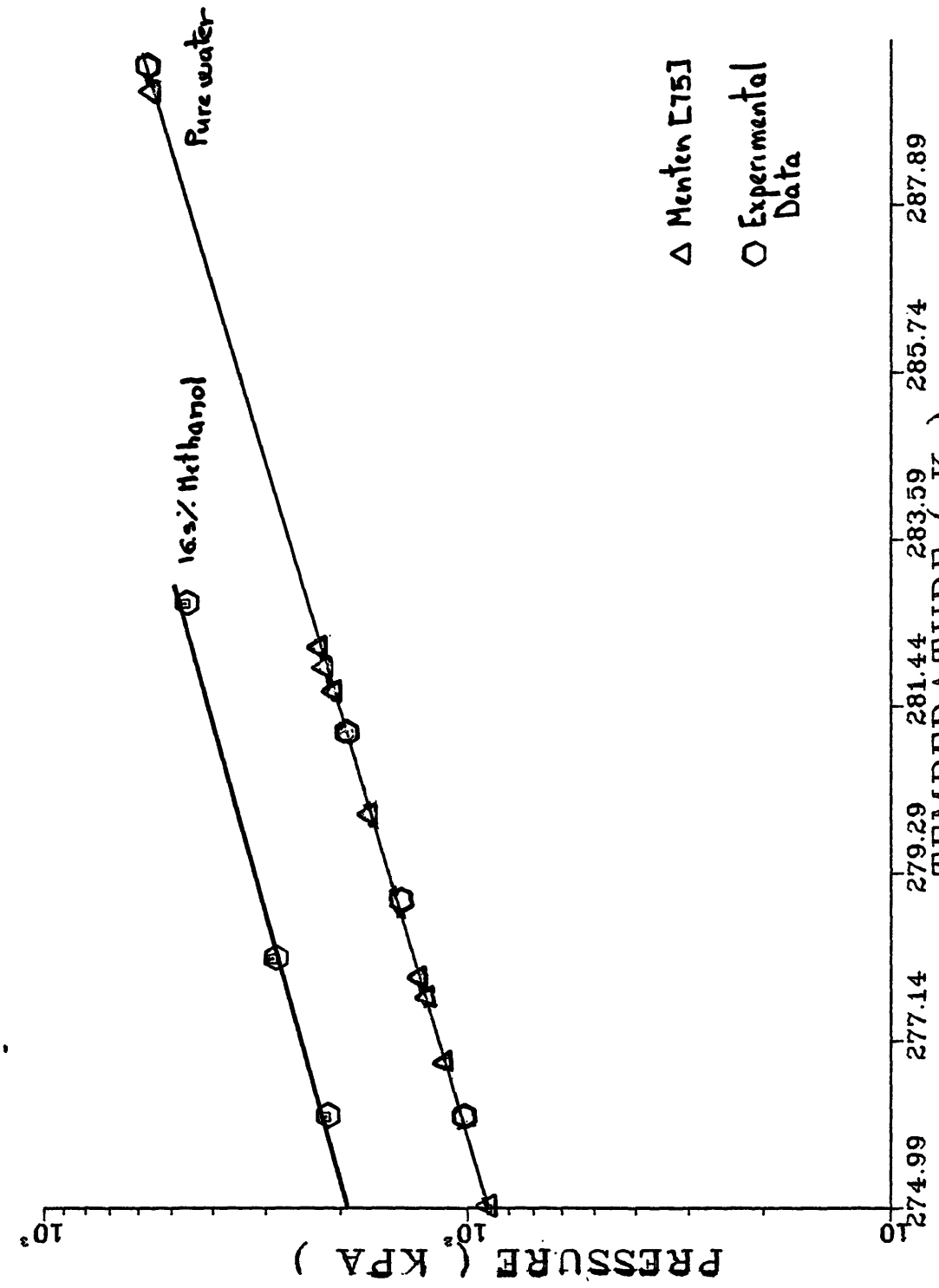

FIG. 10 EXPERIMENTAL RESULTS AT LOW PRESSURE

TABLE 4

EXPERIMENTAL VALUES OF DISSOCIATION

CONDITIONS OF METHANE HYDRATES

Temperature (K)	Pressure (KPA)
279.28	4738.00
278.28	4225.00
273.83	2723.42

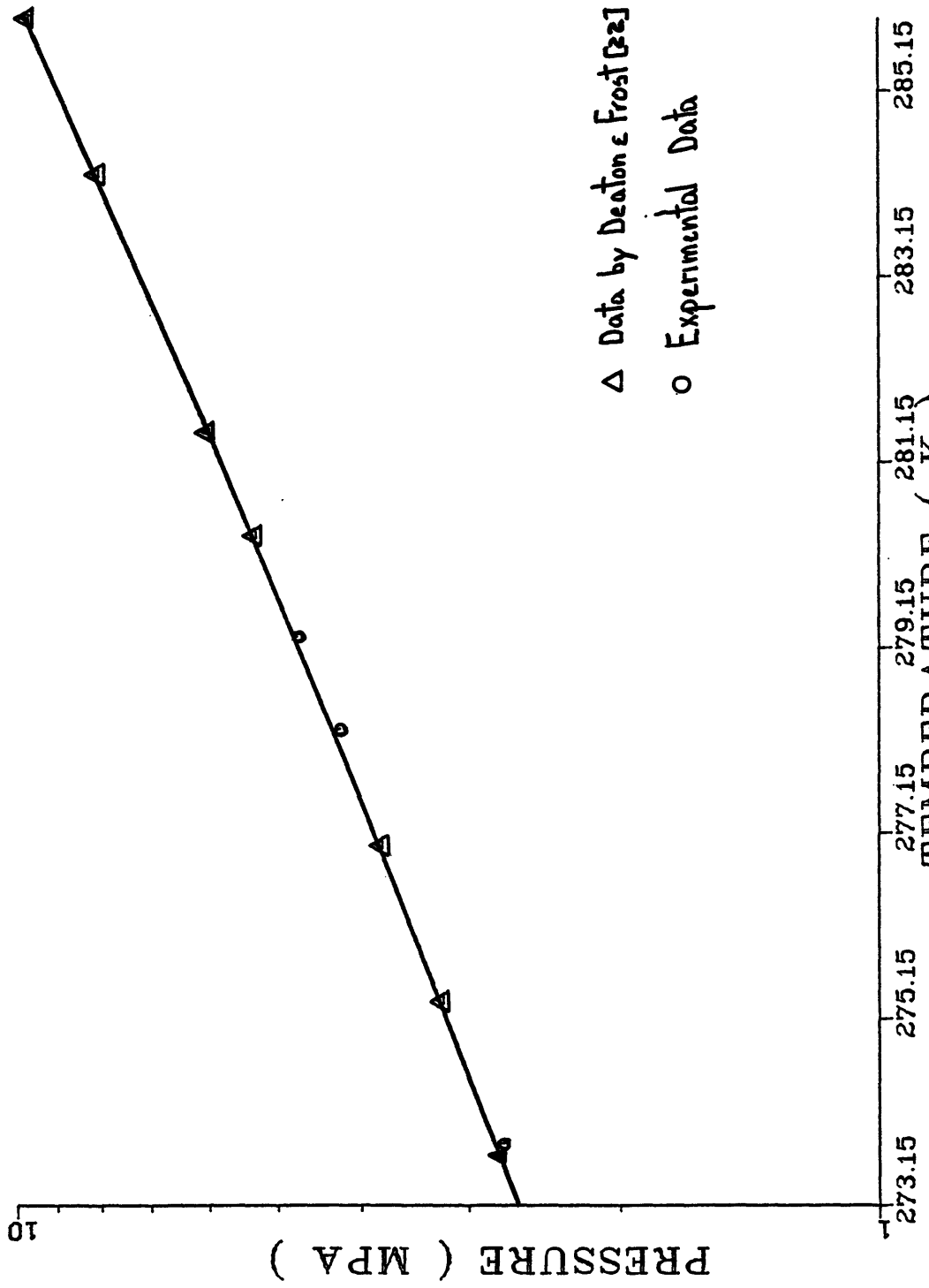

FIG. 11 EXPERIMENTAL RESULTS AT HIGH PRESSURE

DISCUSSION

The results of the cyclopropane-pure water hydrate experiment are compared in table 5 to the experimental values obtained by Hafemann and Miller (49), and fall within a 3% error margin. The accuracy of the previously taken data is not known, but Miller has been quoted by Zerpa (75) to consider a 2% error, extremely good.

For the cyclopropane -5M methanol-water solution results, the only source of comparison is the data obtained by Menten (76), at a lower temperature range. Therefore, the best line through her data was obtained by linear regression and extrapolated. In order to have an idea of how accurate this extrapolation would be, the values of temperature and pressure corresponding to the intersection of the vapor-liquid water-hydrate equilibrium line with the cyclopropane vapor pressure curve were calculated by simultaneously solving the two equations. These values represent the formation conditions for a quadruple point, which in the presence of a pure gas, is determined by fixing one variable, as the phase rule equation shows:

$$F = C + 2 - P = 1$$

where F = degree of freedom

C = number of components = 3 (cyclopropane, water, methanol)

P = phases = 4

At these conditions the four phases present are: gas, liquid hydrocarbon, liquid water, and hydrate and by choosing the composition, temperature and pressure are fixed.

To be able to use the vapor pressure equilibrium curve for pure cyclopropane the assumption that almost no water or methanol would dissolve in the gas phase had to be made. The solubility of water in hydrocarbons has been investigated by McKetta and Katz (80) and in the desired temperature range the amount of water dissolved is of the order of less than .004 mole fraction while according to Menten (76), the amount of methanol is between .008 and .006 mole fraction, therefore justifying the assumption made. The experimental values obtained are shown in table 5 and fall within a 3% error, and the experimental quadruple point is within 2.5% of the mathematically predicted value. The results of the high pressure testing with methane are also given in table 5, and, as in the previous cases, fall within the 3% error margin, showing a consistent error throughout the whole pressure range.

TABLE 5

COMPARISON BETWEEN EXPERIMENTAL DATA AND LITERATURE VALUES

Components	Temperature (K)	Exp.Press (KPA)	Ref.Press (KPA)	% DIFF
Cyclopropane,	289.65	570.89	587.95	2.989
Pure water	281.09	192.38	196.25	2.009
	278.93	145.45	148.79	2.291
	276.15	103.06	104.26	1.164
Cyclopropane	282.76	466.10	476.41[1]	2.212
16.5 %Wt.	278.20	288.78	296.00[1]	2.501
CH_3OH	276.17	216.52	216.66	.068
Methane,	279.28	4738.00	4826.33	1.998
Pure water	278.28	4225.00	4350.00	2.960
	273.83	2723.42	2804.77	2.987

[1]These values were obtained by extrapolation of the published data.

In order to test the validity of the modification made by Menten (75) in Parrish and Prausnitz model to take in account the presence of inhibitors, first the effects of different thermodynamic parameters on the predictions of dissociation pressure at a given temperature were examined, then these results were compared to those obtained using Dharmawardhana's alogarithm.

In table 7 the results of the effect of using a different equation of state in calculating the fugacity and of using the data fitted equation instead of the statistical model to obtain the Langmuir constant are shown. In the second column the experimental values of dissociation pressure for hydrates of methane gas in the presence of a 15% by weight ethanol-water mixture (Kobayashi (87)) are given. The third and fourth columns are the predicted values using the Pitzer-Curl correlation or the Peng-Robinson equation to calculate the fugacity. As expected the effects of using a more accurate equation of state are more noticeable at high pressures. The use of different methods to obtain the Langmuir constant did not produce any changes in the predictions as it is shown by comparing the values of columns four and five with those of columns two and three.

One of the limitations of Menten's alogarithm as it was written, consisted in the fact that it could only be

TABLE 6

COMPARISON BETWEEN PARRISH'S AND DHAMAWARDHANA'S PARAMETERS FOR METHANE

	Parrish	Dharmawardhana
$\Delta\mu(T_oP_o)$*1 cal/gm mole	302	310
$\Delta\mu(T_oP_o)$*1 cal/gm mole	275	332
Kihara Parameters:	153.17	156.72
e/k	3.2398	3.2000
σ	.3000	.3834
a		
Constants in Langmuir Equation (35):		
Small Cavity		
AML	.0037237	.0027711
BML	2708.8	2752.8047
Large Cavity		
AML	.018372	.014865
BML	2737.9	2878.0682

*1 Methane when pure will form structure I hydrates only therefore the values corresponds to this structure only.

TABLE 7

EFFECT OF DIFFERENT THERMODYNAMIC PARAMETERS ON THE DISSOCIATION CONDITION PREDICTIONS OF METHANE - 15% ETHANOL - WATER SOLUTION HYDRATES

Temp. (K)	Exp. Pres. (MPA)	Pres. 1 (MPA)	Pres. 2 (MPA)	Pres. 3 (MPA)	Pres. 4 (MPA)	P% (EXP-1)	P% (EXP-2)
273.26	3.378	3.648	3.749	3.648	3.749	7.40	9.89
277.21	5.468	5.472	5.669	5.472	5.669	0.07	3.54
279.43	7.060	6.890	7.194	6.890	7.194	2.47	1.86
281.09	8.356	8.207	8.613	8.207	8.613	1.82	2.98
284.71	13.658	12.767	13.375	12.767	13.375	6.97	2.11

TABLE 8

COMPARISON BETWEEN DISSOCIATION PRESSURE PREDICTED USING PARRISH'S PARAMETERS OR DHARMAWARDHANA'S FOR HYDRATES OF METHANE IN PRESENCE OF 15% ETHANOL-WATER SOLUTION

TEMP. (K)	EXP. PRES. (MPA)	PRES. 1 (MPA)	PRES. 5 (MPA)	PRES. 6 (MPA)	PRES. 7 (MPA)	PRES.8 (MPA)	P % (EXP-5)	P % (EXP-7)	P % (EXP-8)
273.26	3.378	3.648	3.242	3.242	3.141	4.268	4.18	7.53	20.85
277.21	5.468	5.472	4.864	4.864	4.661	6.419	12.43	17.31	14.81
279.43	7.060	6.890	6.181	6.181	5.877	8.184	14.28	20.13	13.73
281.09	8.356	8.207	7.295	7.295	6.991	9.997	14.53	19.50	16.48
284.71	13.658	12.767	11.146	11.146	10.538	14.479	22.60	29.67	5.62

was written, consisted in the fact that it could only be used to predict hydrate formation conditions for pure gases. Therefore Dharmawardhana's computer program, which could be used for gas mixtures, was modified so it could take into account the presence of inhibitors. If the same equation of state, method of calculating the Langmuir constant, $\Delta\mu o^{\beta-\alpha}$, $\Delta h_o^{\beta-\alpha}$, and Kihara parameters are used in both programs, the same predictions for dissociation pressures are obtained, showing that the programs are equivalent. Table 8 gives the values of this comparison in columns four and five.

In columns three and five the effect of using different sets of $\Delta\mu o^{\beta-\alpha}$, $\Delta h_o^{\beta-\alpha}$, and Kihara parameters is shown. As it can be seen the differences in predicted values are much greater than any of the previous differences due to changes in other quantities. The parameters used correspond to those calculated by Parrish and those obtained by Dharmawardhana. The letter found $\Delta\mu o^{\beta-}$, the chemical potential difference of water in the empty hydrate lattice and of water in the ice phase, and $\Delta h_o^{\beta-}$, the molar enthalpy difference in the same two previous phases, experimentally and then obtained the Kihara parameters by regressing on three phases equilibrium data for binary mixtures.

Since the calculation of these parameters is dependent on what equation of state is used, Dharmawardhana compared the results obtained by using the following equations of state:

1) Soave Redlich Kwong
2) Peng Robinson

and chose those from the second since allowed him to fit the available data the best. Parrish's, and instead were calculated values obtained by fitting all the available three phases equilibrium data for pure gases and the Kihara constant were calculated using the Soave Redlich Kwong equation to obtain fugacities and regressing on the same data used to find the two previous constants. Table 6 summarizes the values for these parameters for methane hydrates found by the two researchers.

The predicted dissociation pressures using Dharmawardhana parameters are in much greater error then when Parrish's values are used and do not show any appreciable improvement over Hammerschmidt's values, shown in column seven. Columns five and six instead show the effect of using a data fitted equation versus the statistical model in calculating the Langmuir constant. Very large differences are obtained in the predictions which could not be

differences are obtained in the predictions which could not be explained.

As a result of this first analysis, the model was found to be very dependent on the values of $\Delta\mu_o^{\beta-\alpha}$, $\Delta h_o^{\beta-\alpha}$, and the Kihara parameters. Better results should be expected while predicting dissociation conditions for pure gases by using Parrish's parameters because of how they were obtained.

To further test the validity of the modification proposed by Menten, confidential data obtained from Exxon for a gas mixture of 88% methane and 12% propane for three different methanol water solutions was predicted. These predictions were compared to Hammerschmidt's and in almost every instance the older empirical method estimates the formation conditions much more closely. For the two lower methanol concentrations the older method predicts the equilibrium conditions within a 20% error while the values obtained using the computer program increase with pressure from a 25% error up to 40%.

In order to establish if the large error in prediction using the modified Dharmawardhana's alogarithm is due to the model itself not being capable of predicting formation conditions accurately when inhibitors are present or to the parameters used, the prediction for pure water was forced

to coincide with the experimental values and the difference between experimental and predicted curves at a given pressure was subtracted from the rest of the predicted curves. As a result of this procedure it would seem that at low methanol concentrations, the model would predict more accurately while at higher concentrations the prediction is in the same range as Hammerschmidts. No explanation could be found for the behavior of the model at high inhibitor concentrations, by analyzing the values of parameters such as fugacity, and activity coefficient. At this point it would seem that the modification to take in account the presence of inhibitors in hydrates of gas mixtures is not a great improvement with respect to Hammerschmidt's prediction, and that the formation condition for hydrates that crystalize in structure I are predicted more accurately than for structure II.

In order to ensure the above conclusions more experimental data on natural gas hydrates in presence of inhibitors should be taken keeping in mind that both type of structures should be investigated.

CONCLUSIONS

1.) An apparatus has been constructed and tested successfully on single components for measurements of three and four phases hydrate inhibition.

2.) A computer program, which combines the results of Dhamarwardhana (77) and Menten (76) has been written and tested.

3.) Tests using the above program show accurate predictions for inhibition of hydrates of pure components in structure I, but less accurate predictions for inhibitors of hydrates from gas mixture forming structure II. The reason for this inaccuracy is not certain.

4.) Very few data are available for hydrate inhibition of mixture forming structure II hydrates.

RECOMMENDATIONS

1.) More data are needed on inhibition of gas mixture hydrates, particularly those forming structure II.

2.) With more data, the reasons for the model's inaccuracy should be investigated thoroughly, e.g. with respect to gas and liquid phase composition.

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APPENDIX A:

Calibration

The two Heise guages were calibrated at the Bureau of Standards in Boulder against a dead weight gauge, in such a way that absolute pressure could be read directly.

The Heise gauge was connected to a helium cylinder and to one side of the pressure sensor membrane. The other side of the membrane was attached to the Ruska pump and dead weight.

The gauge was pressurized to the desired values, unbalancing the sensor's membrane, which was then balanced by using the Ruska pump and the dead weight gauge.

The results of the calibration are shown in Figure 15 and table 10.

A second degree polynomial was fitted to both sets of data and the resulting equations are:

0-2000 Psia

$$P_{actual} = 2.2608350 + .9965814\ P_{gauge} + .000007\ P^2_{gauge}$$

0-1000 Psia

$$P_{actual} = .6801342 + .9936020\ P_{gauge} + .0000073\ P^2_{gauge}$$

P_{actual} = True pressure, Psia

P_{gauge} = Pressure reading on gauge, Psia

TABLE 9

HEISE GAUGES CALIBRATION RESULTS

Pressure Gauge Range	Gauge Press. (PSIA)	True Press. (PSIA)	P%
0 - 1000	994.0	992.0	.201
	821.4	821.9	.012
	749.0	749.4	.053
	599.0	599.6	.100
	398.5	398.2	.075
	201.3	202.1	.397
0 - 2000	1960.0	1963.7	.189
	1815.0	1818.9	.215
	1614.0	1618.1	.254
	1423.0	1427.7	.330
	1214.0	1218.0	.329
	987.0	992.0	.506
	818.5	821.5	.366
	747.0	749.4	.321
	597.0	599.2	.368
	397.0	398.2	.302
	200.0	202.1	1.050

The RTD Platinum Resistance was calibrated against a Doric high accuracy Platinum resistance thermometer, previously calibrated at the Bureau of Standards by Johnson (78). The results of the calibration are given in table 11 and Figure 17. A second degree polynomial was fitted to the data and the resulting equation is:

$$T_{actual} = -17.72517 + .557394\ T_{RTD} + .0000045\ T_{RTD}^2$$

T_{actual} = True temperature, C^o

T_{RTD} = Reading obtained from RTD thermometer F^o

TABLE 10

RTD PLATINUM RESISTANCE THERMOMETER

CALIBRATION RESULTS

Reference Temp. (C)	True Temp. (C)	RTD Temp. (F)	T% *1
30.13	30.14	85.80	.535
20.22	20.25	68.13	.477
10.18	10.21	50.07	.621
0.19	0.20	32.15	.656
- 9.53	- 9.55	14.67	.920

*1 Percent difference between true temperature and RTD reading.

*2 The true temperature was obtained by using the equation:

$$T - t = .994377*10^{-2} + .29582*10^{-2}*t + -.66030*10^{-4}*t^2 - .17229*10^{-3}*t^3 + + .27143*10^{-7}*t^4$$

given by Johnson (77).

T = true temperature C

t = doric temperature C

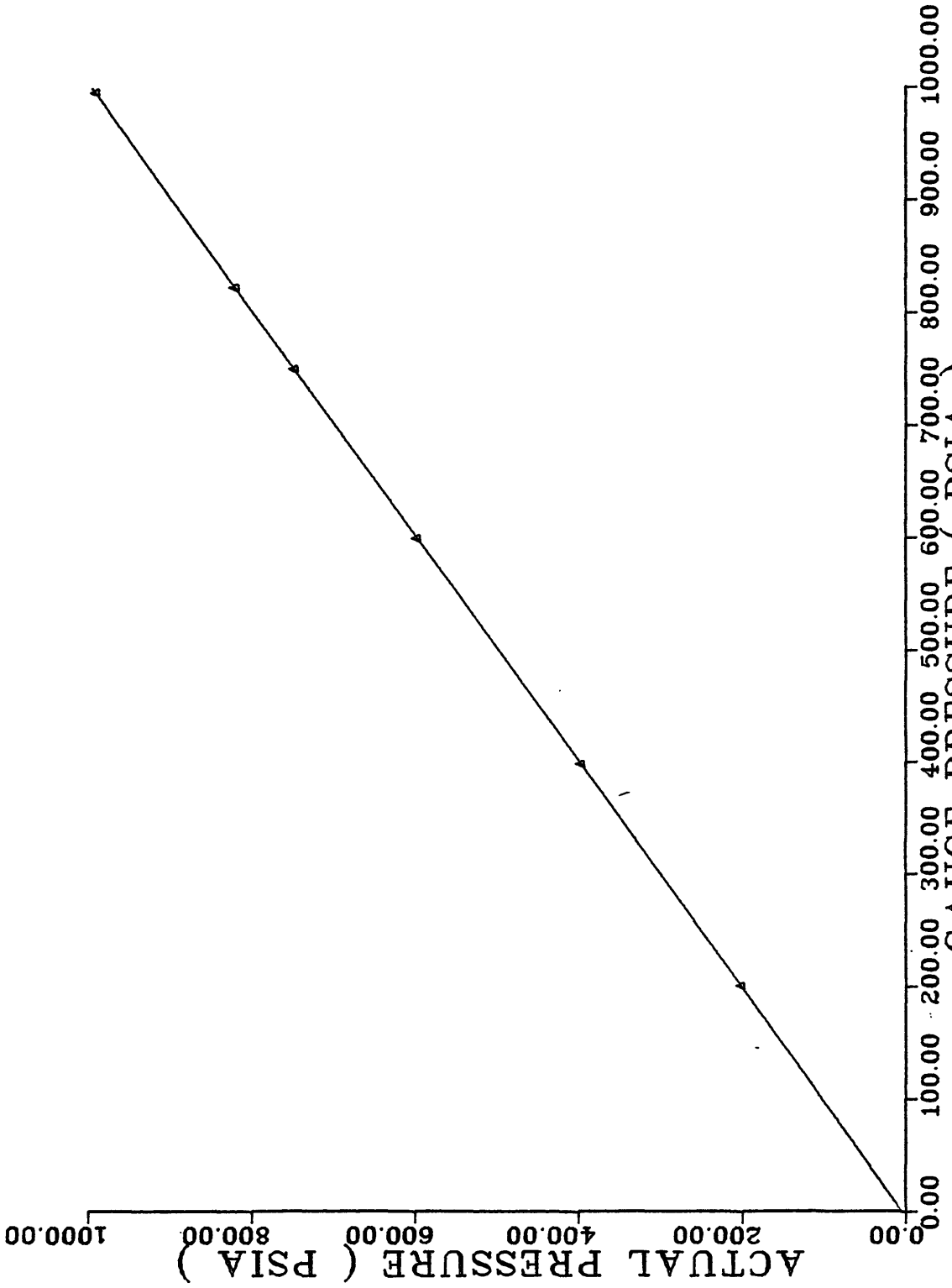

FIG. 12 CALIBRATION CURVE FOR 0-1000 PSIA HEISE GAUGE

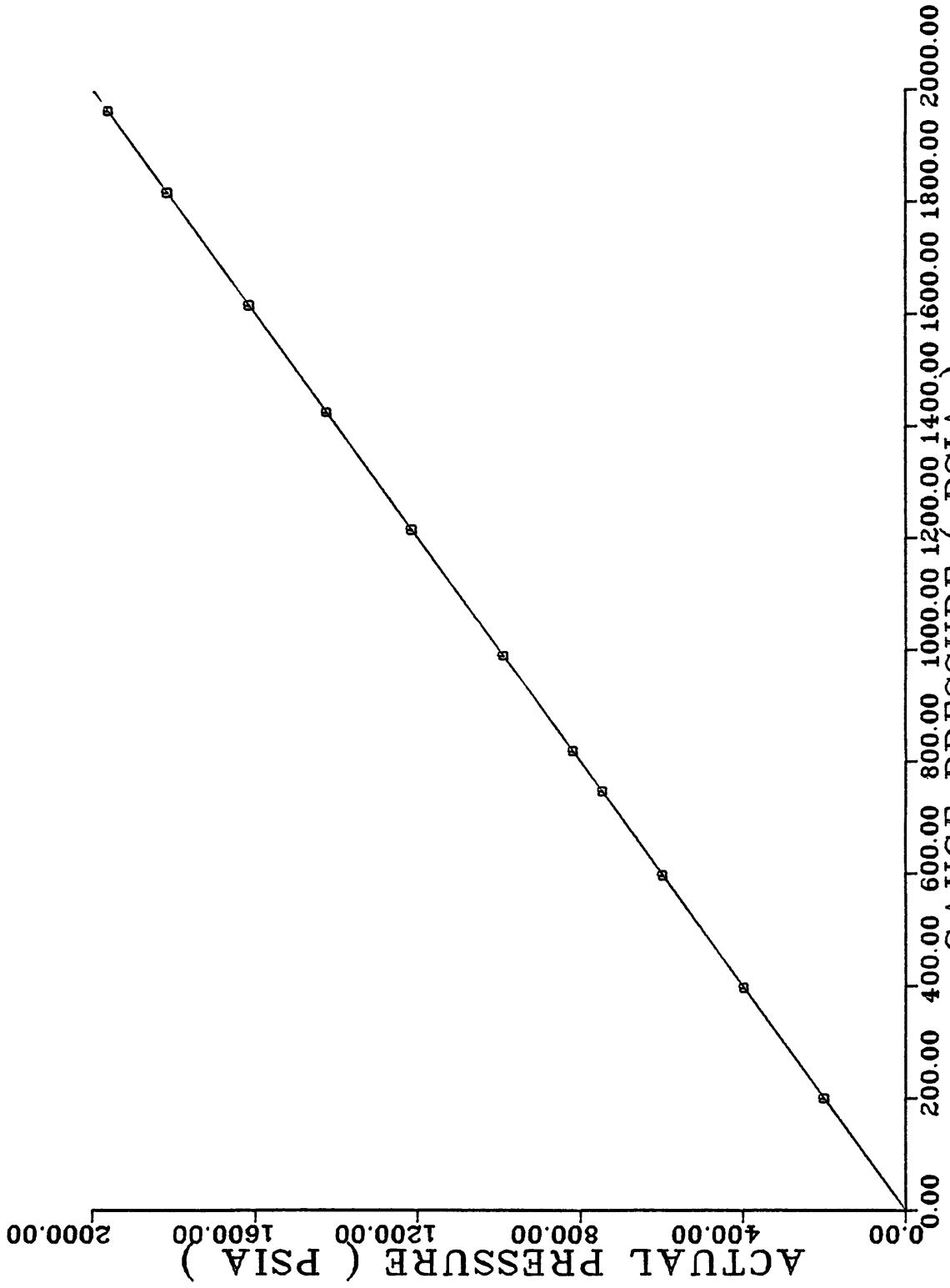

FIG. 13 CALIBRATION CURVE FOR 0-2000 PSIA HEISE GAUGE

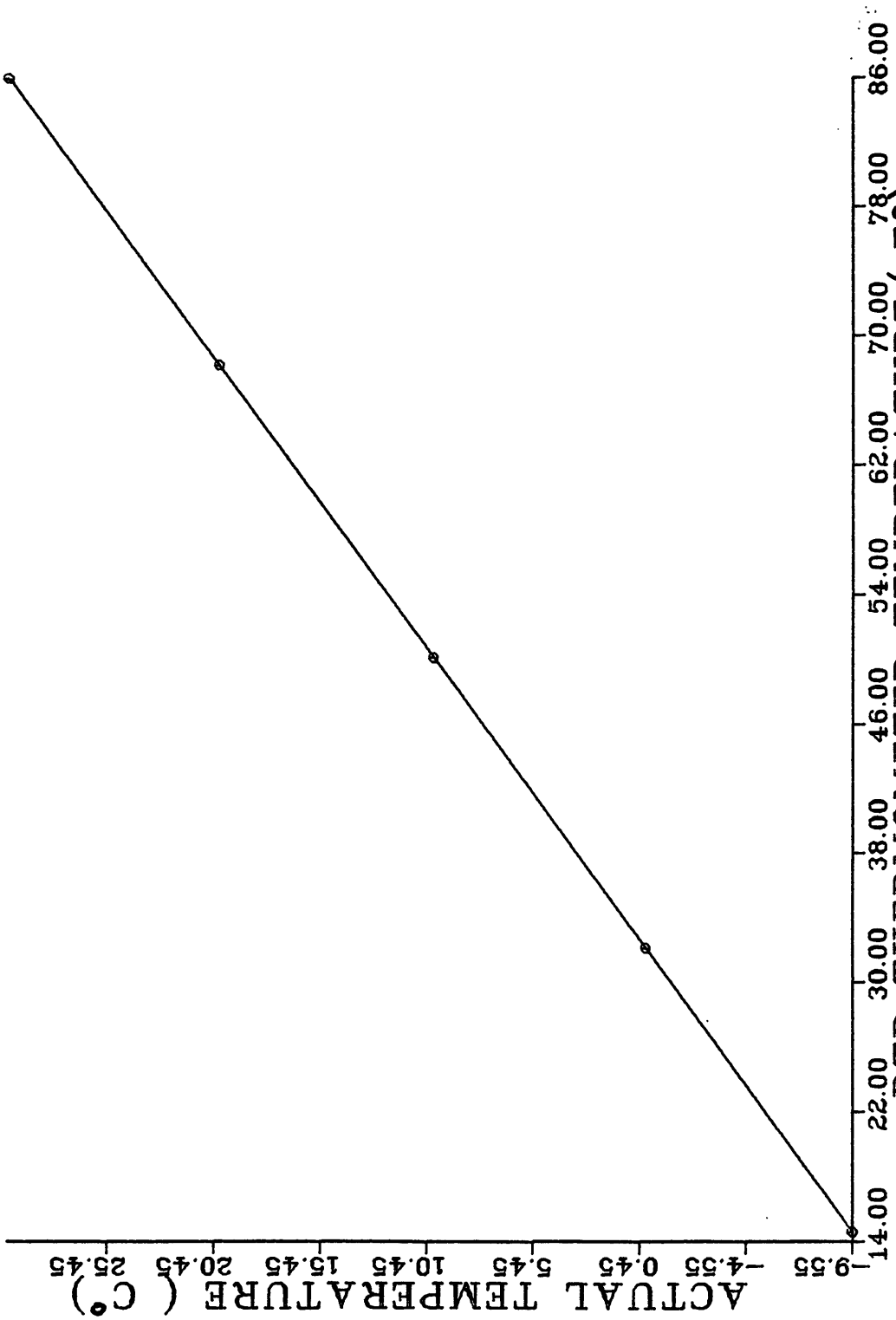

FIG. 14 CALIBRATION CURVE FOR PLATINUM RESISTANCE THERMOMETER

Primary Data

The following equations were obtained by fitting the literature data with a third degree polynomial

A) Cyclopropane - pure water. (Hafemann & Miller (49))

$$\log P = 302.5206 - 3.3044T + .0119121T^2 - 000014T^3$$

P = absolute pressure KPA

T = temperature K^o

B) Methane - pure water (Deaton & Frost (22))

$$\log P = 219.7814 - 2.352851T + .0082614T^2 - .0000095T^3$$

P = absolute pressure MPA

T = temperature K^o

C) Cyclopropane - SM Methanol-water (Menten (75))

$$\log P = .04969T - 11.38$$

TABLE 11

PRIMARY DATA FOR CYCLOPROPANE AND METHANE HYDRATES

Components	Temperature (K)	Exp. Press. (KPA)
Cyclopropane, pure water	289.65	570.89
	281.09	192.38
	278.93	145.45
	276.15	103.06
Cyclopropane	282.76	466.10
16.5 % Wt.	278.20	288.78
CH_3OH	276.17	216.52
Methane,	279.28	4738.00
pure water	278.28	4225.00
	273.83	2723.42

Computer Program

The computer program used in basically the same as Dharmawrdhana's, with several modifications in the way of inputing data and parameters needed for the calculations. The program calculates the dissociation pressure for three phase equilibria given temperature and a first guess of pressure.

The program is made up of a main alogarithm which calls the following subroutines:

A) Subroutine AMUC: Calculates $\Delta\mu$ (T,P) using a equation (31b)

B) Subroutine LANG: Calculates the Langmuir constants using the statistical model.

C) Subroutine LANG 2: Calculates the Langmuir constants using equation (35)

D) Subroutine PENG Calculates fugacities for gas phase component using the Peng-Robinson equation.

E) Subroutine VCube: Solve a third degree equation

F) Subroutine Act: Calculates the activity of water in the absence of inhibitor

G) Subroutine Wilson: Calculates the activity of water in the presence of inhibitors.

H) Subrountine Data: Store all the data needed for the program

The data stored in subroutine H are:

1) Critical temperature, pressure, volume, accentric factor
2) Solubility parameter for the equation used in subroutine Act
3) Kihara parameters
4) What type of cavity will be filled by the guest molecule in the crystal lattice.
5) Volume and corresponding temperature of inhibitors in order to obtain an expression for volume as a function of temperature
6) Interaction parameters for the Wilson equation.

These values are passed from subroutine data to the rest of the program by means of common statements which pass only the individual data required in a specific subroutine. For example:

Common/Pendat/TC, PC, VC, W

allows the values of critical temperature, pressure volume and accentric factor to be sent to subroutine Peng only. The first three characters of the work enclosed between bars indicates to what subroutine the data are sent.

The computer program has been modified so it has become interactive, therefore, the rest of the parameters needed can be entered through a terminal. The information required is asked by the computer and typical values or explanations are given so that the question are self explanatory.

The papers used as references for the program are listed at the beginning of the alogarithm.

A general flowchart of the program, which has been called FYD.FOR, is given in Figure 18, and a list of the main variables follows.

A second program was used during the testing of the modification proposed by Menten and this alogarithm corresponds to the one found in Menten's thesis under the name MU02.FOR but altered so that hydrates formation condition of methane in presence of a ethanol-water solution could be predicted. A flow chart is given in Figure 19 and a list of variables and a copy of the program follows:

LIST OF VARIABLES FOR COMPUTER PROGRAM HYD.FOR

NCOMP = Type of components (also used as a counter for reading data)

PINCX = Pressure increment

NHY = Hydrate structure

NN = Number of data points to estimate

EP = Kihara parameter ε/K

SIGP = Kihara parameter σ } Must be read in for each

CP = Kihara parameter a component

SO1 = Constant used in solubility equation

SO2 = Constant used in solubility equation

SO3 = Constant used in solubility equation } read in as

SO4 = Constant used in solubility equation an array (10)

TC = Critical temperature

PC = Critical pressure

VC = Critical volume

W = Acentric factor

Y = Mole fractions in vapor phase

NR = Type of convergency 0 = secant method;

= 1 = Newton Raphson

PEXP = Pressure input at the beginning of program

P = First guess for dissociation pressure

T = Temperature at which dissociation pressure is to be found

CL = Langmuir constants

ACTI = RT ln X_w

CSML = Cm*fugacity for each component, depends on structure and for small cavities

CSMLS = Cm*fugacity for each component in case of a mixture, depends on structure and for small cavities

CLG = Same as CSML but for large cavities

CLGS = Same as CSMLS but for large cavities

DEL = Difference between $\Delta\mu$ from statistical mechanics and from thermodynamics

DMCAL = $\Delta\mu$ from thermodynamics

AMU = $\Delta\mu$ from statistical mechanics

PR = Equilibrium pressure for reference hydrate calculated using data fitted equation.

VINT =
VINT1 = } Variables used to evaluate volume integral
VINT2 =

V = Number of cavities of type m per molecule of in hydrate

AR,BR,CR = Constants in equilibrium pressure equation for reference hydrate.

DV = $\Delta V_o^{\beta-\alpha}$

DH $\Delta\eta_o^{\beta-\alpha}$

DM = $\Delta\mu_o^{\beta-\alpha}$

TO = 273.15K

DMUO = $\Delta\mu_o^{\beta-\alpha}$ at To,Pr

HINT = Enthalpy integral

DMPR = $\Delta\mu_W^L$ (T,Pr)

DMU2 = $\Delta\mu_W^L$ (T,P)

A = Cell radius

Z = Coordination number of cavity type m

BK = Boltzman constant

PHI = Fugacity

TR = Reduced temperature

PR = Reduced pressure

CG = Empirical binary interaction coefficient

R = Gas constant

VL = Liquid molar volume calculated using $V^L = a + b^T + c^{T2}$ (equation 1)

V1,V2,V3 = Pure components liquid molar volume used in above equation to determine constant

T1,T2,T3 = Temperature corresponding to each of the above molar volumes

A3,B3,C3 = Constants for equation 1 when three molar volumes are given

A2,B2 = Constants for equation 1 when two molar volumes are given

PAIN = Empirical energy term used to determine binary constant in Wilson

X = Mole fraction of components in liquid phase

XLAMDA = Binary constant in Wilson equation

GAMMA = Activity coefficient calculated by Wilson equation

TERM1 =

TERM2 = Dummy variables used to calculate C3.

TERM3 =

TERM4 =

NCOMPL = Number of components in liquid phase

SUMX = Sum of liquid mole fractions

XLSUM = Sum of logarithmic terms in Wilson equation

XSUM1 = Sum of non-logarithmic terms in Wilson equation

XSUM = Sum in the denominator of non-logarithmic terms

NCOMP1 = NCOMPL - 1

This is not a complete list of all the variables in the alogarithm since a lot of terms correspond to equations or variables defined in the articles referenced in the beginning of the program listing. However, this list, plus the articles is all that is needed to become thoroughly familiar with the computer program.

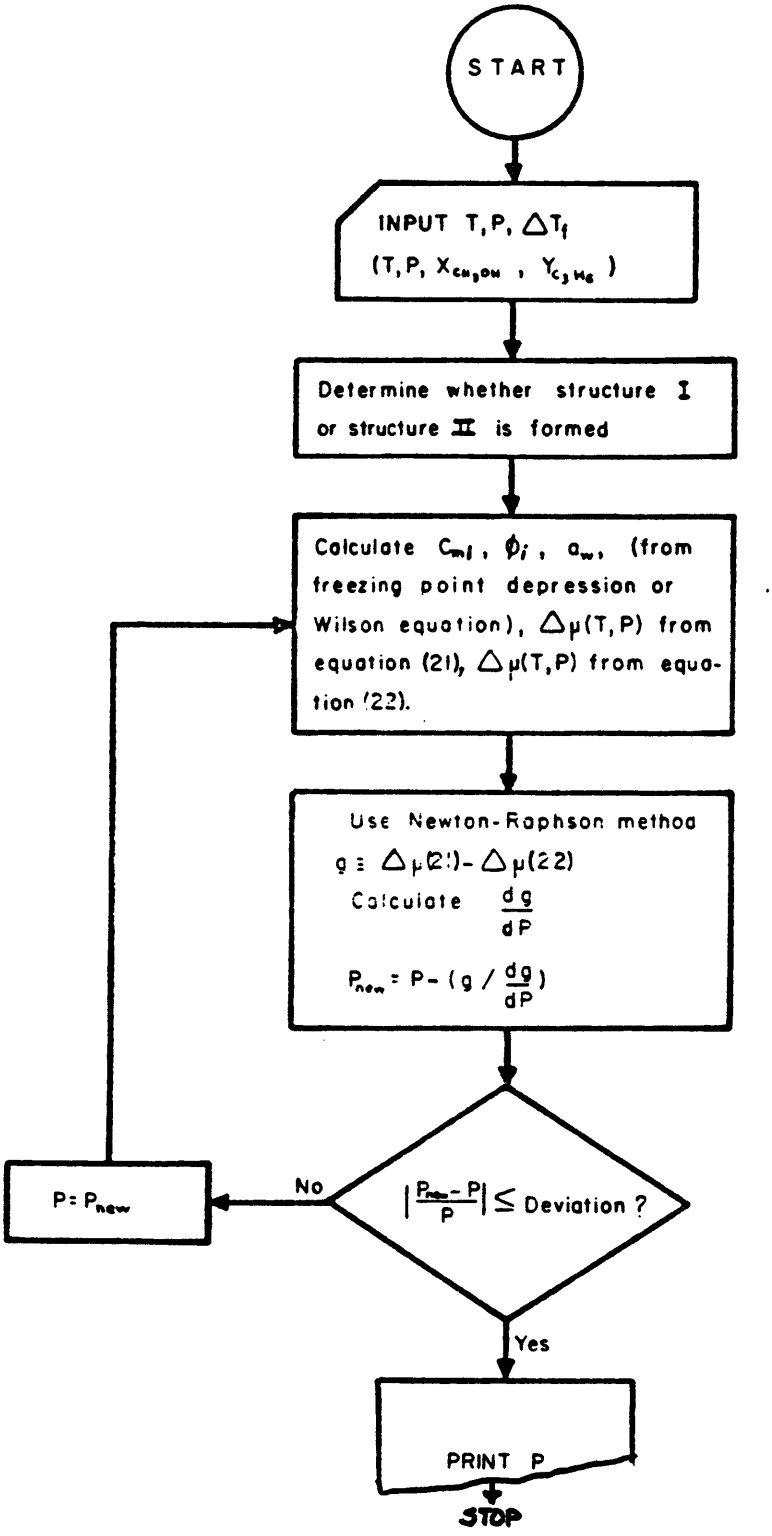

FIG. 15 FLOWCHART FOR COMPUTER PROGRAM PPME.FOR

TABLE 12

PARAMETERS USED IN COMPUTER PROGRAM

Thermodynamic Constants:

	Structure I	Structure II
	Cal/gm mole	Cal/gm mole
$\Delta\mu^{\beta-\alpha}_{0,0}$	310 ± 6	224 ± 7
$\Delta h^{\beta\ \alpha}_{0,0}$	332 ±12	245 ± 10

Kihara Parameters:

Component	ε/k K	σ Å	a Å
Methane	156.72	3.2000	0.3834
Ethane	177.01	3.2444	0.5651
Propane	208.45	3.3111	0.6502

Constants for Langmuir equation:

	Small Cavities of Structure I		Large Cavities of Structure I	
Gas	A * 10^3	B	A * 10^2	B
Methane	2.7711	2752.8047	1.4865	2878.0682
Ethane	0.0	0.0	0.4071	3820.7119
Propane	0.0	0.0	0.0	0.0

	Small Cavities of Structure II		Large Cavities of Structure II	
Methane	2.1778	2713.4259	6.6777	2310.0682
Ethane	0.0	0.0	2.9157	3277.9254
Propane	0.0	0.0	1.3212	4506.9810

CHROMATOGRAPH
OPERATIONAL PROCEDURE *1

1) Check the level of dry ice-acetone mixture in cold trap.
2) Turn vacuum pump on (switch #8), open valves #16 & 15, (manometer Hg level = 12").
3) Open chromatographic He cylinder valve, set pressure at 90 psig.
4) Open completely valves #9 & 17, by using valve #12, adjust helium flow so that the flowmeter shows a reading of 5½.
5) Wait 5 minutes, then turn on the thermoconductivity cell power supply, column temp, bath and mixer (switches #3,1,4).

   NEVER TURN ON POWER SUPPLY IF HELIUM FLOW IS NOT ON.
6) Set therm. cell power supply volt range to the 10-20 reading and turn the current knob until the Ammeter reads 280 mA.
7) Turn chart record (switch #2).
8) Open valve #13 and push in sampling valve knob, wait until manometer Hg level returns to 12".
9) Pull out sampling valve knob, close valves #I3 then #16.

---

*1 flow diagram Figure 19

FIGURE 17 LISTING

A. Thermoconductivity Cell

B. Gas Flowmeter

C. Sampling Valve

D. Constant Temperature Bath

E. Packed Column

F. Vacuum Pump

G. Manometer

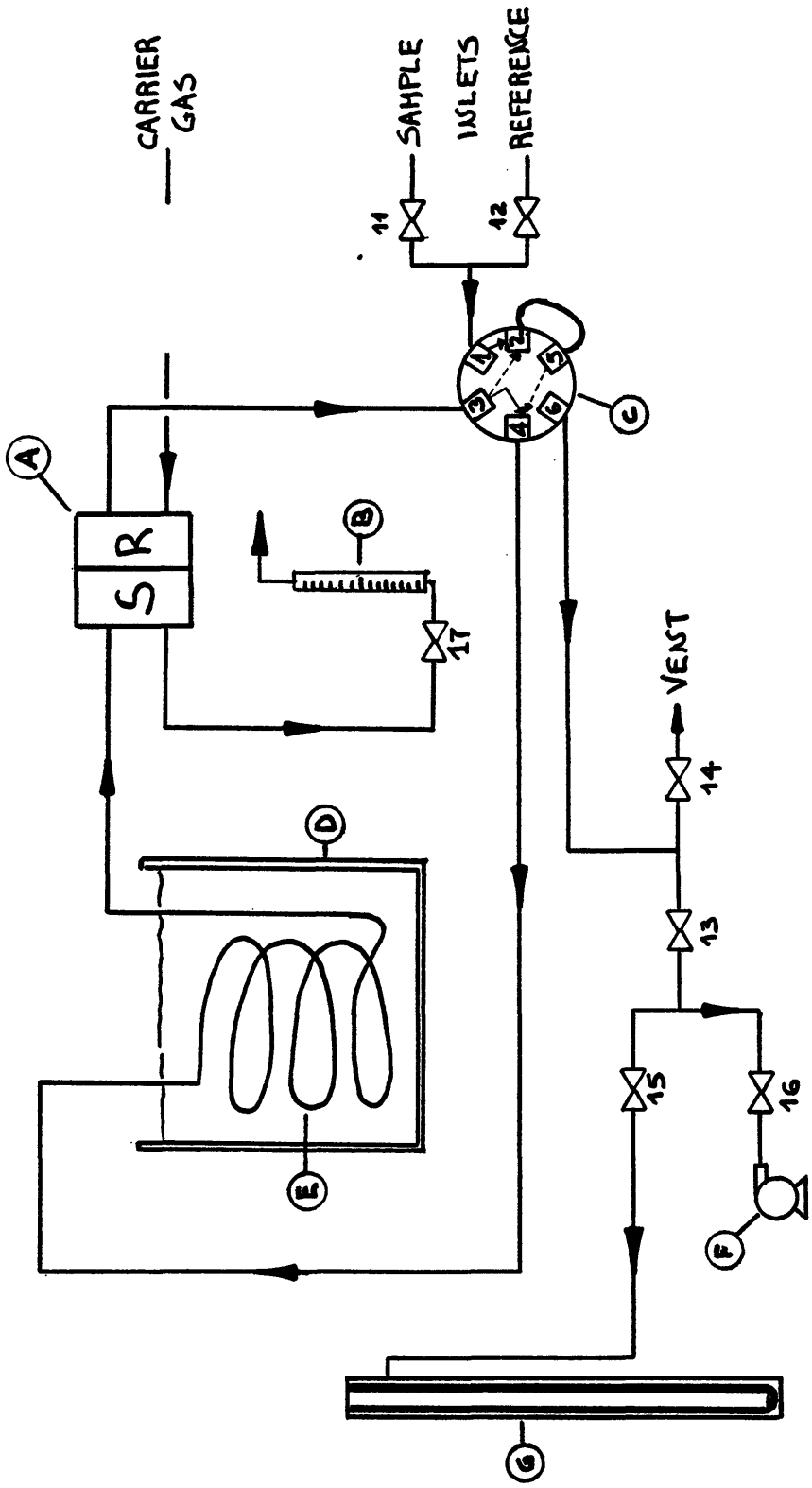

FIG. 16 CHROMATOGRAPH FLOW DIAGRAM

10) Open valve #11, then by slowly opening valve #13 drop Hg level in manometer to 7" then close valves #13 and #11.

11) Push in sampling valve knob, check response being recorded on chart, wait 1 minute then pull out knob. This step completes the analysis of the sample; the following steps will prepare the chromatograph to receive another sample. (This procedure will allow to flush the chromatograph when connected to the sampling loop of the high pressure cell, in other cases the sampling line has to be connected to a He source in order to be able to follow the below outlined procedure).

12) Open valve #8, while chekcing the flowmeter so that a reading of 5½ is kept. (Use valve #13 to keep reading). (By opening valve #8 He sweeps the sampling line).

13) Open valves B and C, inside temperature bath, open valve #11 and push in sampling valve knob.

14) Wait 5 minutes, close valves #8 and B.

15) Open valves #16 and 13, wait until Hg level is back to 12".

16) Close valves C and #11.

17) Go to step 9 if another sample is to be analyzed.

SHUT OFF PROCEDURE

1) Turn off the therm. cell power supply (switch #3) make sure voltage switch is back to off position and that current knob is turned counter clockwise all the way.
2) Turn off chart recorder, column temp. bath and mixer (switches #2,1,4).
3) Close valves #11, 10, 16, 13, pull out sample valve knob. Shut off vacuum pump.
4) Close chromatographic He cylinder, let flowmeter reading go to 0 and then close valves #9, 13, 17.

1) NEVER CLOSE He CYLINDER IF THERMOCONDOCTIVITY CELL POWER IS ON.
2) DO NOT LEAVE CHROMATOGRAPH ON OVER NIGHT OR FOR LONG PERIODS OF TIME.

```
C
C      COMPUTER FILE NAME : HYD.FOR
C
C
C      FOR REFERENCE:
C
C
C     1) DISSOCIATION PRESSURE OF GAS HYDRATES FORMED BY GAS MIXTURES,
C          W.R. PARRISH & J.M. PRAUSNITZ, IND. ENG. CHEM. PROCESS
C          DEVELOP., VOL 11 NO. 1, 1972
C
C     2) A NEW TWO CONSTANT EQUATION OF STATE, D.Y. PENG & D.B. ROBIN-
C          SON, IND. CHEM. FUND., VOL 15 NO.1,1976
C
C     3) EXPERIMENTAL THERMODYNAMIC PARAMETERS FOR THE PREDICTION OF
C          NATURAL GAS HYDRATES DISSOCIATION CONDITIONS,
C          P.B. DHAMAWARDHANA, W.R. PARRISH & E.D. SLOAN, IND. CHEM.
C          FUND., VOL 19 NO.4, 1980
C
C     4) EFFECTS OF INHIBITORS ON HYDRATE FORMATION, P.D. MENIEN,
C          W.R. PARRISH & E.D. SLOAN, IND. ENG. CHEM. PROCESS DES.
C          DEVELOP., VOL 20 NO. 2, 1981
C
C     5) PREDICTION OF TERNARY VAPOR-LIQUID EQUILIBRIA FROM BINARY
C          DATA, M.J. HOLMES & M. VAN WINKLE, IND. ENG. CHEMISTRY,
C          VOL 62 NO. 1, 1970
C
C     6) LOW - PRESSURE SOLUBILITY OF GASES IN LIQUID WATER,
C          E. WILHELM, R. BATTINO, R.J. WILCOCK, CHEMICAL REVIEWS,
C            1977, VOL. 77, NO. 2
C
C
C
C
C      THIS COMPUTER PROGRAM PREDICT FORMATION PRESSURE FOR HYDRATES
C      GIVEN A TEMPERATURE AND A FIRST GUESS FOR PRESSURE.
C
C
C
C
      DIMENSION CL(4,10),PHI(10),Y(10),DMU(2),
     1   EP(10),SIGP(10),CP(10),CB(4,10),
     2   TC(10),PC(10),VC(10),W(10),SO1(10),SO2(10),SO3(10),SO4(10),
     3   D(2),VU(2),VL(2),V1(10),V2(10),V3(10),T1(10),T2(10),T3(10),
     4   A3(10),B3(10),C3(10),A2(10),B2(10),AVL(10),PAIN(10,10),X(10),
     5   XLAMDA(10),GAMMA(10),TERM1(10),TERM2(10),TERM3(10),TERM4(10),
     6   ACTC(10)
C
C
C
C
      COMMON NHY
```

```
      COMMON/LANDAT/EP,SIGP,CP,CB
      COMMON/WILDAT/V1,V2,V3,T1,T2,T3,PAIN
      COMMON/PENDAT/TC,PC,VC,W
      COMMON/ACTDAT/SO1, SO2, SO3, SO4
C
C
C     THE STATEMENTS STARTING AT LINE      TO LINE
C     ALLOW THE INPUT OF ALL THE NECESSARY DATA
C     FOR RUNNING THE PROGRAM.
C
C
C
C
      WRITE (4,901)
901   FORMAT('0',2X,' DO YOU WANT THE RESULTS TO BE STORED IN ',
     1   ' A DATA FILE ? '/5X,'( DATA FILE NAME = FOR10.DAT )')
      READ (4,902)  IANS1
902   FORMAT(A3)
C
      WRITE (4,903)
903   FORMAT('0',2X,' WHAT KIND OF CONVERGENCY METHOD DO YOU WANT ?',
     1   /8X,'( SECANT METHOD : TYPE 0 )'/8X,'( NEWTON-RAPHSON : ',
     2   'TYPE 1 )')
      READ (4,1001) NR
C
      WRITE (4,904)
904   FORMAT('0',2X,' WHAT IS THE VALUE OF THE CONVERGENCE CRITERIA',
     1   ' ?')
      READ (4,1001) CC
C
      WRITE (4,905)
905   FORMAT ('0',2X,' WHAT PRESSURE INCREMENT IS TO BE USED ?')
      READ (4,1001) PINCX
C
      WRITE (4,900)
900   FORMAT('0',2X,' HOW MANY DATA POINTS DO YOU WANT TO ESTIMATE ?')
      READ(4,1001) NN
1001  FORMAT(G)
C
      WRITE(4,1009)
1009  FORMAT('0',2X,' WHAT STRUCTURE IS EXPECTED TO FORM ?')
      READ (4,1001) NHY
C
      WRITE (4,1000)
1000  FORMAT('0',2X,' WHAT ARE THE GAS PHASE COMPONENTS ?'/7X,
     1   'METHANE = 1'/7X,'ETHANE = 2'/7X,'PROPANE = 3'/7X,
     2   'N-BUTANE = 4'/7X,'I-BUTANE = 5'/7X,'PENTANE = 6'/7X,
     3   'NITROGEN = 7'/7X,'CARBON DIOXIDE = 8'/7X,
     4   'HYDROGEN SULFIDE = 9')
      READ (4,1001) NCOMP
```

```
C
      WRITE (4,1004)
1004  FORMAT('0',2X,' HOW MANY COMPONENTS IN THE LIQUID PHASE ?')
      READ (4,1001) NCOMPL
C
C
      IF (NCOMPL .EQ. 1) GO TO 99
C
C
      WRITE (4,1006)
1006  FORMAT('0',2X,' WHAT ARE THE LIQUID MOLE FRACTIONS ?'/7X,
     1   'X(1) = METHANOL'/7X,'X(2) = WATER')
      READ (4,1005) X(1),X(2)
1005  FORMAT(2G)
C
C
C
C
C
C
C     STARTING POINT FOR THE CALCULATIONS OF THE
C     DISSOCIATION PRESSURE OF HYDRATES.
C
C
C
 99   DO 1 IX=1,NN
C
      IF ( IX .EQ. 1) GO TO 100
      WRITE (4,1010)
1010  FORMAT ('0',2X,' HAVE THE GAS MOLE FRACTIONS CHANGED ?')
      READ (4,902) IANS2
C
      IF ( IANS2 .EQ. 'NO' ) GO TO 101
 100  WRITE (4,1002)
1002  FORMAT('0',2X,' WHAT ARE THE GAS PHASE MOLE FRACTIONS ?')
      READ (4,1003) Y(1),Y(2),Y(3),Y(4),Y(5),Y(6),Y(7),Y(8),Y(9)
1003  FORMAT(9G)
C
 101  IF ( IX .EQ. 1 .OR. NCOMPL .EQ. 1 ) GO TO 102
      WRITE (4,1011)
1011  FORMAT ('0',2X,' HAVE THE LIQUID MOLE FRACTIONS CHANGED ?')
      READ (4,902) IANS3
C
      IF ( IANS3 .EQ. 'NO' ) GO TO 102
C
      WRITE (4,1006)
      READ (4,1005) X(1) , X(2)
C
C
 102  WRITE (4,1007)
1007  FORMAT('0',2X,' WHAT ARE THE DISSOCIATION TEMPERATURE &'/
```

```
     1   2X,'THE FIRST GUESS FOR THE DISSOCIATION PRESSURE ?')
      READ (4,1005) T , P
C
C     SUBROUTINE DATA STORES SOME OF THE PHYSICAL
C     PROPERTIES OF THE DIFFERENT COMPONENTS
C     PRESENT IN THE GAS AND LIQUID PHASES.
C
C
C
C
      CALL DATA
C
C
      DS=.0
      NG=NG+1
      NSF=0
C     NR=0
      NEWPT=0
      PEX=P
      P=P/14.696
      I=(T-32.)*5./9.+273.15
530   CONTINUE
C
C
      CALL LANG(T,CL,NCOMP)
C
C
      CL(4,4)=4.040815/T*EXP(2687.9744/T)
      CL(4,5)=7.046619/T*EXP(3083.9044/T)
C
C
      IF ( NCOMPL .GT.1) CALL WILSON (NCOMPL,X,T,ACTI)
C
      IF ( NCOMPL .EQ. 1) CALL ACT ( T, ACTI2, NCOMP,Y)
C
C
      WRITE (4,42)
42    FORMAT('0',6X,'TEMPERATURE',3X,'EXP. PRESSURE',6X,
     1   'EST. PRESSURE')
C
111   CONTINUE
C
C
C
C
      DO 660 K=1,2
C
C
112   CALL PENG(T,P,NCOMP,Y,PHI)
C
      CALL AMUC(T,P,AMU)
```

```
C
C
      IF(NHY.GT.1) GO TO 18
C
C
      DO 17 I=1,NCOMP
      IF(Y(I).EQ..0) GO TO 610
      CSML=CL(1,I)*PHI(I)
      CSMLS=CSMLS+CSML
      CLG=CL(2,I)*PHI(I)
      CLGS=CLG+CLGS
610   CONTINUE
C
C
17    CONTINUE
      AM1=2.*ALOG(1.+CSMLS)/46.
      AM2=6.*ALOG(1.+CLGS)/46.
C
C
      IF ( NCOMPL .EQ. 1) ACTI = ACTI2
C
C
      DMCAL=(AM1+AM2)*1.987*T+ACTI
      CSMLS=.0
      CLGS=.0
      GO TO 20
C
C
18    DO 19 I=1,NCOMP
      IF(Y(I).EQ..0) GO TO 620
      CSML=CL(3,I)*PHI(I)
      CSMLS=CSMLS+CSML
      CLG=CL(4,I)*PHI(I)
      CLGS=CLG+CLGS
620   CONTINUE
C
C
19    CONTINUE
      AM1=16.*ALOG(1.+CSMLS)/136.
      AM2=8.*ALOG(1.+CLGS)/136.
      DMCAL=(AM1+AM2)*1.987*T+ACTI
      CSMLS=.0
      CLGS=.0
20    DEL=AMU-DMCAL
      IF(NR.EQ.1) GO TO 702
694   CONTINUE
      D(K)=DEL
662   DPS=ABS(DEL)*100./AMU
      IF(DPS.LT.CC) GO TO 80
      P=P+PINCX
660   CONTINUE
```

```
C
C
C      CONVERGENCE BY SECANT METHOD
C
C
       DPS=(DEL/AMU*100)
       IF(ABS(DPS).LT.CC) GO TO 80
       NEWPT=NEWPT+1
       IF(NEWPT.EQ.1) GO TO 800
       NTEST=DS/ABS(DS)+DEL/ABS(DEL)
       IF(NTEST.EQ.0) GO TO 702
       IF(ABS(DEL).GT.ABS(DS)) GO TO 703
800    PS=P
       DS=DEL
       P=P-DEL/((D(2)-D(1))/PINCX)
       K=0
C
C
       GO TO 111
C
C
80     T=(T-273.15)*9./5.+32.
       P=P*14.696
       DPSUM=DPSUM+ABS(PEX-P)
C
       WRITE(4,43)T,PEX,P
43     FORMAT(1X,3(F15.3,X))
C
       TSI = ( T - 32.) * 5./9. + 273.15
       PEXSI = PEX * 6.894757293
       PSI = P * 6.894757293
C
       IF ( IANS1 .EQ. 'YES' ) WRITE (10,42)
       IF ( IANS1 .EQ. 'YES' ) WRITE (10,43) TSI , PEXSI , PSI
C
C
7      K=0
       N=0
C      NR=0
       NC1=0
       NU1=0
       NUM=0
 NU=0
       NRC=0
C
1      CONTINUE
C
C
C
       PDMN=DPSUM/NN
       WRITE(4,34)PDMN
```

```
34    FORMAT(1X,F10.2)
      STOP
C
C
C     CONVERGENCE BY NEWTON-RAPHSON METHOD.
C
C
702   CONTINUE
      DEL=AMU-DMCAL
      DPS=ABS(DEL)*100./AMU
      IF(NR.EQ.1) GO TO 51
51    IF(DPS.LT.CC) GO TO 80
      DSAVE=DEL
52    FORMAT(1X,2(F10.3,X))
      NR=1
      NRC=1+NRC
      IF(NRC.GT.1) GO TO 668
      U1=DEL
      U2=DS
      U3=P
      U4=PS
      GO TO 690
668   U2=DEL
      U4=P
      NUM=DEL/ABS(DEL)
      IF(NUM)670,672,676
670   U1=AMAX1(VU(1),VU(2))
      GO TO 675
676   U1=AMIN1(VU(1),VU(2))
      GO TO 675
672   WRITE(4,681)
681   FORMAT(1X,'CHECK CONVERGENCE')
      STOP
C
C
675   CONTINUE
      DO 682 II=1,2
      IF(U1.EQ.VU(II)) U3=VL(II)
682   CONTINUE
690   P=(U1*U4-U2*U3)/(U1-U2)
      VU(1)=U1
      VU(2)=U2
      VL(1)=U3
      VL(2)=U4
C
C
      GO TO 111
C
C
703   T=(T-273.15)*9./5.+32.
      P=PS*14.696
```

```
      WRITE (4,42)
      WRITE(4,43)T,PEX,P
C
      TSI = ( T - 32.) * 5./9. + 273.15
      PEXSI = PEX * 6.894757293
      PSI = P  * 6.894757293
C
      IF ( IANS1 .EQ. 'YES' ) WRITE (10,42)
      IF ( IANS1 .EQ. 'YES' ) WRITE (10,43) TSI , PEXSI , PSI
C
C
      GO TO 7
      STOP
      END
```

```
      SUBROUTINE AMUC(T,P,DMU2)
C
C     SUBROUTINE AMUC CALCULATES DELTAMU USING ITS TOTAL
C     DIFFERENTIAL.
C
C
C
      COMMON NHY
C
C
C
      PR(X)=EXP(AR+BR/X+CR*ALOG(X))
      VINT=0.0
      VINT1=0.0
      VINT2=0.0
10    FORMAT(3F)
      IF(NHY.GT.1) GO TO 20
C     CALCULATE STRUCTURE I PROPERTIES
      V=6./46.
      GO TO 30
C     CALCULATE STRUCTURE II PROPERTIES
20    V=8./136.
30    CONTINUE
      IF(NHY.GT.1) GO TO 60
C     CALCULATE STRUCTURE I PROPERTIES
      AR=-1212.2
      BR=44344.0
      CR=187.719
      DV=4.598
      IF(T.LT.273.15)DV=3.
      DH=332.
      DM=310.
      GO TO 70
C     CALCULATE STRUCTURE II PROPERTIES
60    AR=-1023.14
      BR=34984.3
      CR=159.923
      DV=4.998
      IF(T.LT.273.15)DV=3.4
      DH=245.
      DM=224.
70    TO=273.15
C
C
C     CALCULATE MUO/RTO AT PO,TO
      DMUO=(DM+DV*PR(TO)*.0242152)/(1.987*TO)
C
C
C     CALCULATE ENTHALPY INTEGRAL
      HINT=(1./1.987)*(DH*(1./T-1./TO)+2616.398*(1./T-
     11./TO)+20.6166*ALOG(T/TO)-.021163*(T-TO))
```

```
      IF(T.LT.273.15) HINT=1.*DH*(1./T-1./273.15)/1.987
C
C
C     CALCULATE VOLUME INTEGRAL
      N=ABS(273.15-T)
      DO 40 I=1,N+1
      DT=1.
      TI=TI+DT
      IF(I.EQ.1)TI=TO
      DPRDT=((-BR/TI+CR)/TI)*PR(TI)
      VINT1=(DPRDT/TI)*(DV/82.056)
      VINT=.5*(VINT1+VINT2)+DT*VINT
      VINT2=VINT1
40    CONTINUE
      IF(T.LT.273.15)VINT=-VINT
      DMPR=(DMUO+HINT+VINT)*1.987*T
115   FORMAT(1X,F15.2)
      DMU2=DMPR+DV*.0242152*(P-PR(T))
      RETURN
      END
```

```
      SUBROUTINE LANG(T,CL,NCOMP)
C
C     SUBROUTINE LANG CALCULATES THE LAGMUIR CONSTANT USING
C     KIHARA PARAMETERS.
C
C
      DIMENSION A(4),Z(4),CB(4,10),KS(10),CL(4,10),
     1X(20),WT(20),SIGP(10),EP(10),CP(10)
C
C
      COMMON/LANDAT/EP,SIGP,CP,CB
C
C
      NPT=10
      NP=5
C
C
      DATA(X(J),WT(J),J=6,10)/.1488743389,.29552422147,
     1.4333953941,.2692667193,.6794095683,.2190
     2863625,.86506336627,.1494513492,.9739065285,
     3.0666713443/
      DATA (A(I),Z(I),I=1,4)/3.95,20.,4.3,24.,3.91,20.,4.73,
     128./
      DATA PI,BK/3.1416,1.3804E-16/
C
C
      DO 22 J=1,NP
      X(J)=-X(NPT-J+1)
      WT(J)=WT(NPT-J+1)
22    CONTINUE

      KBLOW=0
      DO 5 J=1,NCOMP
      DO 1 I=1,4
1     CL(I,J)=.0
      C=CP(J)
      EK=EP(J)
      EC=EP(J)*BK
      RC=SIGP(J)*1.122462
      DO 5 I=1,4
      IF (CB(I,J).LT.1.) GO TO 5
      RCA=RC/A(I)
      CA=C/A(I)
C     NEWTON RAPSON METHOD FOR FINDING LIMITS , YL
C     FIRST GUESS S=.4
      S=.4
      RCA6=RCA**6
      RCA12=RCA**12
      DO 2 N=1,20
      IF (S.GT.1.0.OR.S.LE.0.0) GO TO 6
      UM=1./(1.-S-CA)
```

```
      UP=1./(1.+S-CA)
      UM5=UM**5
      UP5=UP**5
      DA4=UM5+UP5
      DA5=UM5*UM+UP5*UP
      DB6=DA4+CA*DA5
      UM11=UM**11
      UP11=UP**11
      DA10=UM11+UP11
      DA11=UM11*UM+UP11*UP
      DB12=DA10+CA*DA11
      DB=RCA12*DB12-2.*RCA6*DB6
      A10=UM11/UM-UP11/UP
      A11=UM11-UP11
      B12=(.1*A10+CA*A11/11.0)
      A4=UM5/UM-UP5/UP
      A5=UM5-UP5
      B6=A4/4.+CA*A5/5.
      B=RCA12*B12-2.*RCA6*B6
      W=Z(I)*EK/(2.*S*T)*B
      DWY=-W/S+Z(I)*EK*DB/(2.*S*T)
      DS=S-(W-10.)/DWY
      IF(ABS((DS-S)/DS).LT.0.01) GO TO 3
2     S=DS
3     YL=S
C     GAUSSIAN INTEGRATION
      P=2.*PI*A(I)**3/(T*136.2)*YL
      SQ=.0
      DO 4 N=1,NPT
      Y=YL*(X(N)+1.)/2.
      UP=1./(1.+Y-CA)
      UM=1./(1.-Y-CA)
      UP5=UP**5
      UM5=UM**5
      A4=UM5/UM-UP5/UP
      A5=UM5-UP5
      B6=A4/4.+CA*A5/5.
      UP11=UP**11
      UM11=UM**11
      A10=UM11/UM-UP11/UP
      A11=UM11-UP11
      B12=(.1*A10+CA*A11/11.)
      B=RCA12*B12-2.*RCA6*B6
      W=Z(I)*EK/(2.*Y*T)*B
4     SQ=SQ+EXP(-W)*Y**2*WT(N)
      CL(I,J)=P*SQ
270   FORMAT(1X,4(F10.5,X))
5     CONTINUE
      RETURN
6     KBLOW=2
      WRITE(4,7)
```

```
 7      FORMAT(1X,'PROBLEM BLOW UP')
        RETURN
        END
```

```
      SUBROUTINE PENG(T,P,NCOMP,Y,PHI)
C
C     SUBROUTINE PENG CALCULATES THE FUGACITY OF A MIXTURE OF
C     GASES USING THE PENG - ROBINSON EQUATION.
C
      DIMENSION TC(10),PC(10),W(10),B(10),PHI(10),VC(10),AK(10)
     1,A(100,100),Y(10),TR(10),PR(10),CG(100,100)
C
C
      COMMON/PENDAT/TC,PC,VC,W
C
C
      DATA CG(1,7),CG(1,8),CG(1,9),CG(2,7),CG(2,8),CG(2,9),
     1CG(3,7),CG(3,8),CG(3,9),CG(4,7),CG(4,8),CG(4,9),
     2CG(5,7),CG(5,8),CG(5,9),CG(6,7),CG(6,8),CG(6,9),
     3CG(7,8),CG(7,9),CG(8,9)/.036,.1,.085,.05,.13,.084,
     4.08,.135,.075,.09,.13,.06,.095,.13,.05,.095,.125,.065,
     5-.02,.18,.1/
      R=82.056
      ID=-1
C
C
      DO 97 I=1,NCOMP
      DO 97      J=1,NCOMP
      CG(J,I)=CG(I,J)
      A(I,J)=.0
      AM=.0
      BM=.0
      B(I)=.0
      AK(I)=.0
97    CONTINUE
      DO 1 I=1,NCOMP
      TR(I)=T/TC(I)
      IF(Y(I).EQ..0) GO TO 149
      PR(I)=P/PC(I)
      A(I,I)=.45724*(R*TC(I))**2/PC(I)
      B(I)=.0778*R*TC(I)/PC(I)
      AK(I)=.37464+1.54226*W(I)-.26992*W(I)**2
      AK(I)=(1.+AK(I)*(1.-SQRT(TR(I))))**2
      A(I,I)=AK(I)*A(I,I)
149   CONTINUE
1     CONTINUE
      DO 2 I=1,NCOMP
      DO 2 J=1,NCOMP
      IF(Y(J).EQ..0) GO TO 145
      IF(Y(I).EQ..0) GO TO 145
      A(I,J)=(1.-CG(I,J))*SQRT(A(I,I)*A(J,J))
145   CONTINUE
2     CONTINUE
      DO 4 I=1,NCOMP
      IF(Y(I).LE..0) GO TO 41
```

```
41      CONTINUE
        BM=BM+B(I)*Y(I)
4       CONTINUE
        DO 75       I=1,NCOMP
        AK(I)=.0
75      CONTINUE
        DO 3 J=1,NCOMP
        DO 3 I=1,NCOMP
        IF(Y(I).EQ..0) GO TO 148
        IF(Y(J).EQ..0) GO TO 148
        AK(J)=Y(I)*A(I,J)+AK(J)
148     CONTINUE
3       CONTINUE
        DO 6 J=1,NCOMP
        AK(J)=2.*AK(J)
6       CONTINUE
 DO 5 I=1,NCOMP
 DO 5 J=1,NCOMP
        AM=AM+Y(I)*Y(J)*A(I,J)
5       CONTINUE
        CALL VCUBE(AM,BM,P,R,T,V,Z,ID)
        AB=AM*P/(R*T)**2
        BB=BM*P/(R*T)
        DO 62       I=1,NCOMP
        IF(Y(I).EQ..0) GO TO 61
        A1=B(I)*(Z-1.)/BM
        A2=ALOG(Z-BB)
        A3=AB/(2*SQRT(2.)*BB)
        A4=AK(I)/AM-B(I)/BM
        A5=ALOG((Z+2.414*BB)/(Z-.414*BB))
        PHI(I)=A1-A2-A3*A4*A5
        PHI(I)=EXP(PHI(I))
        PHI(I)=PHI(I)*Y(I)*P
61      CONTINUE
62      CONTINUE
        RETURN
        END
```

```
      SUBROUTINE VCUBE(A,B,P,R,T,V,Z,ID)
C
C     SUBROUTINE VCUBE SOLVES A THIRD DEGREE EQUATION
C
C
      D=B-R*T/P
      E=-(3.*B*B+2.*R*T*B/P-A/P)
      F=B*B*B+(R*T*B*B-A*B)/P
      G=(3.*E-D*D)/3.
      H=-(9.*D*E-27.*F-2.*D*D*D)/27.
      IF(G**3./27.+H*H/4..LE.0.) GO TO 10
      S=-H/2.+SQRT(G**3./27.+H*H/4.)
      TT=-H/2.-SQRT(G**3./27.+H*H/4.)
      IF(S)5,6,6
    5 S=-((-S)**(1./3.))
      GO TO 7
    6 S=(S)**(1./3.)
    7 IF(TT)8,9,9
    8 TT=-(-TT)**(1./3.)
      GO TO 15
    9 TT=(TT)**(1./3.)
C     SINGLE REAL ROOT
   15 V=S+TT-D/3.
      GO TO 40
   10 THETA = (ACOS(-.5*H/SQRT(-G**3/27.)))/3.
      V1=2.*SQRT(-G/3.)*COS(THETA)
      V2=2.*SQRT(-G/3.)*COS(THETA+2.0944)
      V3=2.*SQRT(-G/3.)*COS(THETA+4.1888)
      IF(ID)20,30,30
C     TAKE LARGEST V FOR VAPOR
   20 V=AMAX1(V1,V2,V3)-D/3.
      GO TO 40
C     TAKE SMALLEST V FOR LIQUID
30    V=AMIN1(V1,V2,V3)-D/3.
40    Z=P*V/(R*T)
      RETURN
```

```
      SUBROUTINE ACT  (T, ACTI2, NCOMP, Y)
C
C     SUBROUTINE ACT CALCULATES THE ACTIVITY COEFFICENT
C     OF WATER  IN THE ABSCENCE OF AN INHIBITOR.
C
      DIMENSION SO1(10),SO2(10),SO3(10),SO4(10),X(10),
     1   Y(10)
C
C
      COMMON/ACTDAT/ SO1, SO2, SO3, SO4
C
C
      DO 1 I=1 , NCOMP
C
      IF ( I .EQ. 6 ) GO TO 2
C
      X(I) = SO1(I) + SO2(I)/T + SO3(I)*ALOG(T) + SO4(I)*T
C
      X(I) = EXP(X(I)/1.9872)
C
      IF ( Y(I) .EQ. 0.0 ) X(I) = 0.0
      XSUM = XSUM + X(I)
C
 2    XX = 0.0
C
1     CONTINUE
C
      XW = 1. - XSUM
C
      ACTI2 = 1.9872 * T * ALOG(XW)
C
      XSUM = 0.0
C
      IF ( T .LT. 273.15 ) ACTI2 = 0.0
C
      RETURN
```

```
      SUBROUTINE WILSON (NCOMPL,X,T,ACTI)
C
C
C     THIS SUBROUTINE CALCULATES THE ACTIVITY
C     COEFFICENT USING WILSON'S EQUATION
C
C
      DIMENSION V1(10),V2(10),V3(10),T1(10),T2(10),T3(10),
     1   A3(10),B3(10),C3(10),A2(10),B2(10),AVL(10),PAIN(10,10),
     2   X(10),XLAMDA(10,10),GAMMA(10),TERM1(10),TERM2(10),TERM3(10),
     3   TERM4(10),ACTC(10)
C
C
      COMMON/WILDAT/V1,V2,V3,T1,T2,T3,PAIN
C
      SUMX = 0.0
C
      DO 121 I=1,NCOMPL
      SUMX = SUMX + X(I)
121   CONTINUE
C
C
      DO 111 I=1 , NCOMPL
      IF (V3(I) .LE. 0.0 ) GO TO 1000
      TERM1(I) = (T3(I)-T1(I))*(V2(I)-V1(I))
      TERM2(I) = (V3(I)-V1(I))*(T2(I)-T1(I))
      TERM3(I) = (T2(I)**2.-T1(I)**2.)*(T3(I)-T1(I))
      TERM4(I) = (T3(I)**2.-T1(I)**2.)*(T2(I)-T1(I))
C
      C3(I) = (TERM1(I)-TERM2(I))/(TERM3(I)-TERM4(I))
      B3(I) = ((V2(I)-V1(I))-(C3(I)*(T2(I)**2.-T1(I)**2.)))/
     1   (T2(I)-T1(I))
      A3(I) = V1(I) - B3(I)*T1(I) - C3(I)*(T1(I)**2.)
C
C
      GO TO 1001
C
 1000 IF (V2(I) .LE. 0.0) GO TO 1003
C
      B2(I) = (V2(I)-V1(I))/(T2(I)-T1(I))
      A2(I) = V1(I) - B2(I)*T1(I)
C
 1001 IF (V3(I) .LE. 0.0) AVL(I) = A2(I) + B2(I)*T
      IF (V3(I) .GT. 0.0) AVL(I) = A3(I) + B3(I)*T + C3(I)*(T**2.)
C
      GO TO 111
C
 1003 AVL(I) = V1(I)
C
111   CONTINUE
C
```

```
C
C
      DO 118 I=1 , NCOMPL
      PAIN(I,I) = 0.0
118   CONTINUE
C
      DO 122 I=1,NCOMPL
      DO 123 J=1 , NCOMPL
      XLAMDA(I,J) = (AVL(J)/AVL(I))*EXP(-PAIN(I,J)/(1.9872*T))
123   CONTINUE
122   CONTINUE
C
      DO 114 I=1 , NCOMPL
      XLSUM = 0.0
      XSUM1 = 0.0
      DO 115 J=1 , NCOMPL
C
      XLSUM = XLSUM + X(J)*XLAMDA(I,J)
      XSUM2 = 0.0
C
      DO 116 M=1 , NCOMPL
      XSUM2 = XSUM2 + X(M)*XLAMDA(J,M)
116   CONTINUE
C
      XSUM1 = XSUM1 + (X(J)*XLAMDA(J,I))/XSUM2
115   CONTINUE
C
      XLSUM = XLSUM/SUMX
C
      GAMMA(I) = EXP(1. - XSUM1)/XLSUM
C
C
      ACTC(I) = GAMMA(I) * X(I)
C
C
114   CONTINUE
C
C
      ACTI = 1.9872 * T * ALOG(ACTC(2))
C
C
      RETURN
      END
```

```
      SUBROUTINE DATA
C
C     SUBROUTINE DATA STORES ALL THE VALUES OF THE
C     DIFFERENT PARAMETERS & CONSTANT NEEDED
C     THROUGHOUT THE PROGRAM.
C
C     THE VARIABLES ARE STORE IN SUCH A WAY
C     THAT FOR EACH COMPOUNP ALL THE VALUES
C     ARE LISTED.
C
C
      DIMENSION EP(10),SIGP(10),CP(10),CB(4,10),V1(10),
     1   V2(10),V3(10),T1(10),T2(10),T3(10),PAIN(10,10),TC(10),
     2   PC(10),VC(10),W(10),SO1(10),SO2(10),SO3(10),SO4(10)
C
C
      COMMON NHY
      COMMON/LANDAT/EP,SIGP,CP,CB
      COMMON/WILDAT/V1,V2,V3,T1,T2,T3,PAIN
      COMMON/PENDAT/TC,PC,VC,W
      COMMON/ACTDAT/ SO1, SO2, SO3, SO4
C
C
C
C     1) METHANE.
C
      DATA EP(1),SIGP(1),CP(1)/156.72,3.2000,.3834/
      DATA CB(1,1),CB(2,1),CB(3,1),CB(4,1)/20.,20.,20.,20./
      DATA TC(1),PC(1),VC(1),W(1)/190.60,45.4,99.0,.008/
      DATA SO1(1),SO2(1),SO3(1),SO4(1)/-365.183,18106.7,49.7554,
     1   -0.000285033/
C
C
C
C     2) ETHANE
C
      DATA EP(2),SIGP(2),CP(2)/177.01,3.2444,.5651/
      DATA CB(1,2),CB(2,2),CB(3,2),CB(4,2)/0.0,20.,0.0,20./
      DATA TC(2),PC(2),VC(2),W(2)/305.4,48.2,148.0,.098/
      DATA SO1(2),SO2(2),SO3(2),SO4(2)/-533.392,26565.,74.624,
     1   -0.00457313/
C
C
C
C
C
C     3) PROPANE.
C
      DATA EP(3),SIGP(3),CP(3)/208.45,3.3111,.6502/
      DATA CB(1,3),CB(2,3),CB(3,3),CB(4,3)/0.0,0.0,0.0,20./
      DATA TC(3),PC(3),VC(3),W(3)/369.8,41.9,203.,.152/
```

```
      DATA SO1(3),SO2(3),SO3(3),SO4(3)/-628.866,31638.4,88.0808,
     1   0.0/
C
C
C
C
C
C     4) METHANOL.
C
      DATA V1(1),V2(1),V3(1)/39.556,44.874,57.939/
      DATA T1(1),T2(1),T3(1)/273.15,373.15,473.15/
      DATA PAIN(1,2),PAIN(2,1)/205.30,482.16/
C
C
C
C
C
C     5) WATER.
C
      DATA V1(2),V2(2),V3(2)/18.060,18.278,18.844/
      DATA T1(2),T2(2),T3(2)/277.13,323.15,373.15/
C
C
C
C
C
      RETURN
      END
```

```
      DIMENSION AML(2), BML(2),CML(2),CL(4,10),PHI(10),Y(10),
     1   EP(10),SIGP(10),CP(10),CB(4,10),TC(10),PC(10),VC(10),
     2   W(10)
      COMMON/LANDAT/EP,SIGP,CP,CB
      COMMON/PENDAT/TC,PC,VC,W
C
C
      PR(X) = EXP(AR+BR/X+CR*ALOG(X))
5     WRITE (4,15)
15    FORMAT( '  INPUT T IN K, P IN MMHG,X1 MOLE FRACT.OF MEOH,'
     1   'Y MOLE FRACTION OF C-C3 ')
      READ (4,10) T,P, X1, Y(1)
10    FORMAT(4G)
C
      P = P/760.
C
      WRITE (4,16)
16    FORMAT ('0',2X,' INPUT PRESSURE INCREMENT & NO OF POINTS',
     1   ' TO BE PLOTTED ')
C
      READ (4,17) PINCX , N
17    FORMAT (2G)
C
C     WRITE (4,901)
C 901 FORMAT ('0',2X,' PRESSURE ',8X,' G ', 8X,' DMU1 ',
C     1  8X,' DMU2 ')
C
C
C
      WRITE (4,850)
850   FORMAT('0',2X,'WHAT IS THE VALUE OF NCOMP ?'/5X,
     1   '(TYPE 1 FOR METHANE)' )
C
      READ(4,851) NCOMP
851   FORMAT(G)
C
      WRITE (4,852)
852   FORMAT('0',2X,'DO YOU WANT TO USE THE STAT.MECH.MODEL',
     1   /,3X,'TO CALCULATE THE LANGMUIR CONSTANT ?'/5X,
     2   ' ( TYPE 1 IF SO )')
C
      READ (4,851) IANS
C
      WRITE (4,853)
853   FORMAT('0',2X,' DO YOU WANT TO USE THE P-R EQUATION',/3X,
     1   'TO CALCULETA THE FUGACITY ?',/5X,'( TYPE 1 IF SO )')
C
      READ (4,851) IANS1
C
C
      IF ( T .EQ. 0.0 ) GO TO 50
```

```
      X2 = 1.0 - X1
C
C
      CALL DATA
C
C
C     STRUCTURE 1 PROPERTIES
      AML(1) = .0027711
      AML(2) = .014865
      BML(1) =  2752.8047
      BML(2) =  2878.0682
C
C
      DO 900 I = 1,2
C
      CML(I) = AML(I)/T * EXP(BML(I)/T)
C
 900  CONTINUE
C
      IF ( IANS .EQ. 1 ) CALL LANG ( T,CL,NCOMP)
C
C
      WRITE (4,3000) CML(1),CML(2),CL(1,1),CL(2,1)
3000  FORMAT(4G)
C
C
      DO 400 L = 1 , N
C
C
      IF (IANS1 .EQ. 1) CALL PENG (T,P,NCOMP,Y,PHI)
      IF (IANS1 .EQ. 1) GO TO 999
C
C
C
C     CALCULATE FUGACITY USING PITZER - CURL CORRELATION
      TCP = 190.6
      TRP = T/ TCP
      WP = .007
      PCP = 45.4
      R = 82.056
      B =(.083 - .422/(TRP**1.6)+WP*(.139-.172/(TRP**4.2)))*R*TCP/PCP
      PHI(1) = EXP((P*B)/(R*T))
C
C
C     CALCULATE ACTIVITY
C
C
 999    VLH2 = 22.8868 - .0364168 * T + 6.65578E-5 * T **2.
        VLET = 53.7004 -  .031108 * T + 1.600E-4 * T **2.
      DE12 = VLH2/VLET*EXP(-382.30/(1.987*T))
      DE21 = VLET/VLH2*EXP(-955.45/(1.987*T))
```

```
      GAMM = EXP (-ALOG(X2+DE21*X1)-X1*(DE12/(X1+DE12*X2)-DE21
     1   /(DE21*X1+X2)))
      A = X2 * GAMM
C     IF ( T .LT. 274.61) GO TO 60
C     CALCULAT STRUCTURE 1 PROPERTIES
      AR = -1212.2
      BR = 44344.0
      CR = 187.719
      DV = 4.598
      DH = 332.0
      DM = 310.0
 70   TO = 273.15
C     CALCULATEMUO/RTO AT PO & TO.
      DMUO = (DM+DV*PR(TO)*.0242152)/(1.987*TO)
C     CALCULATE ENTHALPY INTEGRAL
C
      HINT=(1./1.987)*(DH*(1./T-1./TO)+2616.398*(1./T-
     11./TO)+20.6166*ALOG(T/TO)-.021163*(T-TO))
C
C
C     CALCULATE VOLUME INTEGRAL
C
C
      VINT = 0.0
      VINT1 = 0.0
      VINT2 = 0.0
C
C
      N=ABS(273.15-T)
      DO 40 I=1,N+1
      DT=1.
      TI=TI+DT
      IF(I.EQ.1)TI=TO
      DPRDT=((-BR/TI+CR)/TI)*PR(TI)
      VINT1=(DPRDT/TI)*(DV/82.056)
      VINT=.5*(VINT1+VINT2)+DT*VINT
      VINT2=VINT1
40    CONTINUE
C
C
      IF ( IANS .EQ. 1) GO TO 860
C
      CSML = CML(1) * PHI(1) * P * Y(1)
      CLG = CML(2)  * PHI(1) * P * Y(1)
C
      GO TO 861
C
C
 860  CSML = CL(1,1) * PHI(1) * P * Y(1)
      CLG = CL(2,1) * PHI(1) * P * Y(1)
C
```

```
C
C
 861   AM1 = 2. * ALOG(1.+CSML)/46.
       AM2 = 6.* ALOG (1.+CLG)/46.
C
C
       DMPR=(DMUO+HINT+VINT)*1.987*T
       DMU1 = 1.987*T*((AM1+AM2)+ALOG(A))
       DMU2 = DMPR+DV*.0242152*(P-PR(T))
       G = DMU2 - DMU1
       DIFF = ABS ( G/DMU2) * 100.
C
C
       WRITE (11,250) P , G , DIFF ,PHI(1),A,DMU1,DMU2
250    FORMAT(7G)
       P = P + PINCX
C
C
C      WRITE (11,2000) P , DMU2 ,DMPR,DMUO,HINT,VINT
C 2000    FORMAT(6G)
C
C
C
400    CONTINUE
C
C
       GO TO 5
C
C
 50    STOP
       END
```

```
      SUBROUTINE LANG(T,CL,NCOMP)
C
C
C     SUBROUTINE LANG CALCULATES THE LAGMUIR CONSTANT USING
C     KIHARA PARAMETERS.
C
C
      DIMENSION A(4),Z(4),CB(4,10),KS(10),CL(4,10),
     1X(20),WT(20),SIGP(10),EP(10),CP(10)
C
C
      COMMON/LANDAT/EP,SIGP,CP,CB
C
C
      NPT=10
      NP=5
C
C
      DATA(X(J),WT(J),J=6,10)/.1488743389,.29552422147,
     1.4333953941,.2692667193,.6794095683,.2190
     2863625,.86506336627,.1494513492,.9739065285,
     3.0666713443/
      DATA (A(I),Z(I),I=1,4)/3.95,20.,4.3,24.,3.91,20.,4.73,
     128./
      DATA PI,BK/3.1416,1.3804E-16/
C
C
      DO 22 J=1,NP
      X(J)=-X(NPT-J+1)
      WT(J)=WT(NPT-J+1)
22    CONTINUE

      KBLOW=0
      DO 5 J=1,NCOMP
      DO 1 I=1,4
1     CL(I,J)=.0
      C=CP(J)
      EK=EP(J)
      EC=EP(J)*BK
      RC=SIGP(J)*1.122462
      DO 5 I=1,4
      IF (CB(I,J).LT.1.) GO TO 5
      RCA=RC/A(I)
      CA=C/A(I)
C     NEWTON RAPSON METHOD FOR FINDING LIMITS , YL
C     FIRST GUESS S=.4
      S=.4
      RCA6=RCA**6
      RCA12=RCA**12
      DO 2 N=1,20
      IF (S.GT.1.0.OR.S.LE.0.0) GO TO 6
```

```
      UM=1./(1.-S-CA)
      UP=1./(1.+S-CA)
      UM5=UM**5
      UP5=UP**5
      DA4=UM5+UP5
      DA5=UM5*UM+UP5*UP
      DB6=DA4+CA*DA5
      UM11=UM**11
      UP11=UP**11
      DA10=UM11+UP11
      DA11=UM11*UM+UP11*UP
      DB12=DA10+CA*DA11
      DB=RCA12*DB12-2.*RCA6*DB6
      A10=UM11/UM-UP11/UP
      A11=UM11-UP11
      B12=(.1*A10+CA*A11/11.0)
      A4=UM5/UM-UP5/UP
      A5=UM5-UP5
      B6=A4/4.+CA*A5/5.
      B=RCA12*B12-2.*RCA6*B6
      W=Z(I)*EK/(2.*S*T)*B
      DWY=-W/S+Z(I)*EK*DB/(2.*S*T)
      DS=S-(W-10.)/DWY
      IF(ABS((DS-S)/DS).LT.0.01) GO TO 3
2     S=DS
3     YL=S
C     GAUSSIAN INTEGRATION
      P=2.*PI*A(I)**3/(T*136.2)*YL
      SQ=.0
      DO 4 N=1,NPT
      Y=YL*(X(N)+1.)/2.
      UP=1./(1.+Y-CA)
      UM=1./(1.-Y-CA)
      UP5=UP**5
      UM5=UM**5
      A4=UM5/UM-UP5/UP
      A5=UM5-UP5
      B6=A4/4.+CA*A5/5.
      UP11=UP**11
      UM11=UM**11
      A10=UM11/UM-UP11/UP
      A11=UM11-UP11
      B12=(.1*A10+CA*A11/11.)
      B=RCA12*B12-2.*RCA6*B6
      W=Z(I)*EK/(2.*Y*T)*B
4     SQ=SQ+EXP(-W)*Y**2*WT(N)
      CL(I,J)=P*SQ
270   FORMAT(1X,4(F10.5,X))
5     CONTINUE
      RETURN
6     KBLOW=2
```

```
      *PITE(4,7)
7     FORMAT(1X,'PROBLEM BLOW UP')
      RETURN
      END
```

```
      SUBROUTINE PENG(T,P,NCOMP,Y,PHI)
C
C
C     SUBROUTINE PENG CALCULATES THE FUGACITY OF A MIXTURE OF
C     GASES USING THE PENG - ROBINSON EQUATION.
C
C
      DIMENSION TC(10),PC(10),W(10),B(10),PHI(10),VC(10),AK(10)
     1,A(100,100),Y(10),TR(10),PR(10),CG(100,100)
C
C
      COMMON/PENDAT/TC,PC,VC,W
C
C
      DATA CG(1,7),CG(1,8),CG(1,9),CG(2,7),CG(2,8),CG(2,9),
     1CG(3,7),CG(3,8),CG(3,9),CG(4,7),CG(4,8),CG(4,9),
     2CG(5,7),CG(5,8),CG(5,9),CG(6,7),CG(6,8),CG(6,9),
     3CG(7,8),CG(7,9),CG(8,9)/.036,.1,.085,.05,.13,.084,
     4.08,.135,.075,.09,.13,.06,.095,.13,.05,.095,.125,.065,
     5-.02,.18,.1/
      R=82.056
      ID=-1
C
C
      DO 97 I=1,NCOMP
      DO 97      J=1,NCOMP
      CG(J,I)=CG(I,J)
      A(I,J)=.0
      AM=.0
      BM=.0
      B(I)=.0
      AK(I)=.0
97    CONTINUE
      DO 1 I=1,NCOMP
      TR(I)=T/TC(I)
      IF(Y(I).EQ..0) GO TO 149
      PR(I)=P/PC(I)
      A(I,I)=.45724*(R*TC(I))**2/PC(I)
      B(I)=.0778*R*TC(I)/PC(I)
      AK(I)=.37464+1.54226*W(I)-.26992*W(I)**2
      AK(I)=(1.+AK(I)*(1.-SQRT(TR(I))))**2
      A(I,I)=AK(I)*A(I,I)
149   CONTINUE
1     CONTINUE
      DO 2 I=1,NCOMP
      DO 2 J=1,NCOMP
      IF(Y(J).EQ..0) GO TO 145
      IF(Y(I).EQ..0) GO TO 145
      A(I,J)=(1.-CG(I,J))*SQRT(A(I,I)*A(J,J))
145   CONTINUE
2     CONTINUE
```

```
      DO 4 I=1,NCOMP
      IF(Y(I).LE..0) GO TO 41
41    CONTINUE
      BM=BM+B(I)*Y(I)
4     CONTINUE
      DO 75       I=1,NCOMP
      AK(I)=.0
75    CONTINUE
      DO 3 J=1,NCOMP
      DO 3 I=1,NCOMP
      IF(Y(I).EQ..0) GO TO 148
      IF(Y(J).EQ..0) GO TO 148
      AK(J)=Y(I)*A(I,J)+AK(J)
148   CONTINUE
3     CONTINUE
      DO 6 J=1,NCOMP
      AK(J)=2.*AK(J)
6     CONTINUE
 DO 5 I=1,NCOMP
 DO 5 J=1,NCOMP
      AM=AM+Y(I)*Y(J)*A(I,J)
5     CONTINUE
      CALL VCUBE(AM,BM,P,R,T,V,Z,ID)
      AB=AM*P/(R*T)**2
      BB=BM*P/(R*T)
      DO 62       I=1,NCOMP
      IF(Y(I).EQ..0) GO TO 61
      A1=B(I)*(Z-1.)/BM
      A2=ALOG(Z-BB)
      A3=AB/(2*SQRT(2.)*BB)
      A4=AK(I)/AM-B(I)/BM
      A5=ALOG((Z+2.414*BB)/(Z-.414*BB))
      PHI(I)=A1-A2-A3*A4*A5
      PHI(I)=EXP(PHI(I))
61    CONTINUE
62    CONTINUE
      RETURN
      END
```

```
      SUBROUTINE VCUBE(A,B,P,R,T,V,Z,ID)
C
C
C     SUBROUTINE VCUBE SOLVES A THIRD DEGREE EQUATION
C
C
      D=B-R*T/P
      E=-(3.*B*B+2.*R*T*B/P-A/P)
      F=B*B*B+(R*T*B*B-A*B)/P
      G=(3.*E-D*D)/3.
      H=-(9.*D*E-27.*F-2.*D*D*D)/27.
      IF(G**3./27.+H*H/4..LE.0.) GO TO 10
      S=-H/2.+SQRT(G**3./27.+H*H/4.)
      TT=-H/2.-SQRT(G**3./27.+H*H/4.)
      IF(S)5,6,6
    5 S=-((-S)**(1./3.))
      GO TO 7
    6 S=(S)**(1./3.)
    7 IF(TT)8,9,9
    8 TT=-(-TT)**(1./3.)
      GO TO 15
    9 TT=(TT)**(1./3.)
C     SINGLE REAL ROOT
   15 V=S+TT-D/3.
      GO TO 40
   10 THETA = (ACOS(-.5*H/SQRT(-G**3/27.)))/3.
      V1=2.*SQRT(-G/3.)*COS(THETA)
      V2=2.*SQRT(-G/3.)*COS(THETA+2.0944)
      V3=2.*SQRT(-G/3.)*COS(THETA+4.1888)
      IF(ID)20,30,30
C     TAKE LARGEST V FOR VAPOR
   20 V=AMAX1(V1,V2,V3)-D/3.
      GO TO 40
C     TAKE SMALLEST V FOR LIQUID
30    V=AMIN1(V1,V2,V3)-D/3.
40    Z=P*V/(R*T)
      RETURN
      END
```

```
      SUBROUTINE DATA
C
C
C     SUBROUTINE DATA STORES ALL THE VALUES OF THE
C     DIFFERENT PARAMETERS & CONSTANT NEEDED
C     THROUGHOUT THE PROGRAM.
C
C     THE VARIABLES ARE STORE IN SUCH A WAY
C     THAT FOR EACH COMPOUNP ALL THE VALUES
C     ARE LISTED.
C
C
      DIMENSION EP(10),SIGP(10),CP(10),CB(4,10),V1(10),
     1   V2(10),V3(10),T1(10),T2(10),T3(10),PAIN(10,10),TC(10),
     2   PC(10),VC(10),W(10),SO1(10),SO2(10),SO3(10),SO4(10)
C
C
      COMMON NHY
      COMMON/LANDAT/EP,SIGP,CP,CB
      COMMON/WILDAT/V1,V2,V3,T1,T2,T3,PAIN
      COMMON/PENDAT/TC,PC,VC,W
      COMMON/ACTDAT/ SO1, SO2, SO3, SO4
C
C
C
C     1) METHANE.
C
      DATA EP(1),SIGP(1),CP(1)/153.17,3.2398,.300/
      DATA CB(1,1),CB(2,1),CB(3,1),CB(4,1)/20.,20.,20.,20./
      DATA TC(1),PC(1),VC(1),W(1)/190.60,45.4,99.0,.008/
      DATA SO1(1),SO2(1),SO3(1),SO4(1)/-365.183,18106.7,49.7554,
     1   -0.000285033/
C
C     THE FOLLOWING DATA IS BASED ON DHARMAWARDHANA DATA
C
C     2) ETHANE
C
      DATA EP(2),SIGP(2),CP(2)/177.01,3.2444,.5651/
      DATA CB(1,2),CB(2,2),CB(3,2),CB(4,2)/0.0,20.,0.0,20./
      DATA TC(2),PC(2),VC(2),W(2)/305.4,48.2,148.0,.098/
      DATA SO1(2),SO2(2),SO3(2),SO4(2)/-533.392,26565.,74.624,
     1   -0.00457313/
C
C
C
C
C
C     3) PROPANE.
C
      DATA EP(3),SIGP(3),CP(3)/208.45,3.3111,.6502/
      DATA CB(1,3),CB(2,3),CB(3,3),CB(4,3)/0.0,0.0,0.0,20./
```

```
      DATA TC(3),PC(3),VC(3),W(3)/369.8,41.9,203.,.152/
      DATA SO1(3),SO2(3),SO3(3),SO4(3)/-628.866,31638.4,88.0808,
     1   0.0/
C
CC
CC
CC
CC
C     4) METHANOL.
C
      DATA V1(1),V2(1),V3(1)/39.556,44.874,57.939/
      DATA T1(1),T2(1),T3(1)/273.15,373.15,473.15/
      DATA PAIN(1,2),PAIN(2,1)/205.30,482.16/
C
CC
CC
CC
C     5) WATER.
C
      DATA V1(2),V2(2),V3(2)/18.060,18.278,18.844/
      DATA T1(2),T2(2),T3(2)/277.13,323.15,373.15/
C
CC
CC
C     6) ETHANOL
C
C     DATA V1(1),V2(1),V3(1)/57.141,60.356,64.371/
C     DATA T1(1),T2(1),T3(1)/273.15,323.15,373.15/
C     DATA PAIN(1,2),PAIN(2,1)/382.30,955.45/
CC
CC
CC
C
      RETURN
      END
```