T-1975

AN APPARATUS FOR THE MEASUREMENT OF HYDRATE PROPERTIES AND THE MEASUREMENT OF CYCLOPROPANE SOLUBILITY IN POTASSIUM CHLORIDE SOLUTIONS

by

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T-1975

A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirement for the degree of Master of Science.

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ABSTRACT

An experimental apparatus capable of making accurate measurements of cyclopropane hydrate forming conditions and cyclopropane solubility in water and KCl solutions was designed, constructed, and tested. The basic unit is an equilibrium cell with sight glasses; an ultrasonic device is used to promote agitation.

Temperatures were measured with a platinum resistance thermometer, calibrated against a standard Leeds and Northrup platinum thermometer. Pressures were measured with a Barocel pressor sensor and read with an electronic manometer. Gas volume measurements were made with two Volumetric volumeter units. Step by step operating procedures are presented for use by future operators.

The solubility data was taken at 0, 3, and 5°C and at KCl concentrations of 0.0, 0.5, 1.1, 1.5, and 10 g/l. These solubility measurements will be used for further hydrate work. The estimated accuracy of the solubility measurements was to within 1.023 percent.

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ACKNOWLEDGMENTS

I would like to express my sincere appreciation to the following persons and organizations:

Professor Dendy Sloan, for his valuable guidance and encouragement during the research at Colorado School of Mines.

Dr. William Parrish for his helpful suggestions during this research.

Professors V.F. Yesavage and A.J. Kidnay, for their participation as members of the thesis committee.

Fundacion Gran Mariscal de Ayacucho-Venezuela, for their financial support of my graduate studies.

National Science Foundation, for their financial support of this research.

Deborah, for her time proof-reading.

My family, for their patience and encouragement throughout my graduate studies.

INTRODUCTION

The solubility of gases in liquids is an area of active interest from both the theoretical and practical standpoints. A knowledge of the solubility of gases is of practical importance in various industrial applications. The more important uses are in the gas-liquid separation processes of absorption and stripping. Another more specific application is in the experimental study of gas hydrate dissociation conditions, where reliable solubility data are required.

The Parrish and Prausnitz (25) model for hydrate dissociation requires the composition of the hydrate for basic model parameters. In order to determine the quantity of gas going into the hydrate structure, the quantity of gas remaining in the liquid (gas solubility) must be determined. The computer model of Parrish and Prausnitz which incorporates solubility and hydrate composition has been adapted to the Colorado School of Mines DEC-10 System, and is included in Appendix D.

The primary objective of this work was to design and construct an experimental apparatus capable of making accurate measurements of gas-hydrate compositions.

The secondary objective was to measure the solubility of cyclopropane in salt solutions of KCl in a range of 0 to 1.5 g/l with 10 g/l solution as a check point. The temperature considered was in a range where cyclopropane gas-hydrates are known to form. These measurements will be used in the near future to experimentally determine cyclopropane hydrate composition.

I. LITERATURE SURVEY

1. Henry's Law

The solubility of a gas in a liquid is determined by the equations of phase equilibrium. If a gaseous phase and a liquid phase are in equilibrium, then for any component i, the fugacities in both phases must be the same:

$$f_i^g = f_i^l \tag{1}$$

Equation (1) is of little use unless something can be said about how the fugacity of component i in each phase is related to the temperature, pressure, and composition of that phase. Considering the fugacity of a component i (a gas) when it dissolves in a liquid solvent, equation (1) can be simplified with further assumptions. Usually the solubility of a gas in a liquid is proportional to its partial pressure in the gas phase, provided the partial pressure is not large. The equation which describes this observation is commonly known as Henry's law:

$$\lim_{X_i \to 0} \frac{f_i}{X_i} = \lim_{X_i \to 0} \frac{P_i}{X_i} = K_i \tag{2}$$

$$\text{or } P_i = Y_i P_T = K_i X_i \qquad (3)$$

Henry's law is strictly applicable only in the extrapolation to infinite dilution (27), that is, where the solubility and the partial pressure of the solute are small.

The assumptions on which Equation (2) and (3) are based can be readily recognized by comparison with Equation (1). The left-hand side of Equation (3) shows that in Henry's law the gas phase is assumed to be ideal and thus the fugacity is replaced by the partial pressure. The right hand side of Equation (3) shows that the fugacity in the liquid phase is assumed to be proportionality is taken as an empirically determined factor, K_i. This factor K_i depends only on the nature of solute and solvent and on the temperature. The thermodynamic significance of this constant can be established by comparing the liquid fugacity as given by Henry's law with that obtained in the conventional manner using the concept of an activity coefficient γ_i and some standard state fugacity $f_i°$:

$$f_i^l = K_i X_i = \gamma_i X_i f_i° \qquad (4)$$

$$\text{Thus } K_i = \gamma_i f_i° \qquad (5)$$

where i stands for solute. At a given temperature, pressure, and binary system, the standard state fugacity is a constant and does not depend on the solute mole fraction in the liquid phase. Since K_i does not depend on X_i, it follows from Equation (4) that the activity coefficient γ_i must also be independent of X_i. It is this feature, the constancy of the activity coefficient, which contains the essential assumption of Henry's law (27) and which allows its use at concentrations greater than infinite dilution. Many times in solubility measurements K_i is inverted since pressure is the independent variable to give:

$$X_i = K_i' P_i \tag{6}$$

$$\text{where } K_i' = 1/K_i \tag{7}$$

In this work K_i', the inverted Henry's constant, will be used.

2. Review of Experimental Methods for Gas Solubility Measurements

Earlier reviews (2, 19) described many different methods for determining the solubility of gases in liquids. Yet, the development of new approaches and equipment continues unabated. Some methods are simple, using commercially available glassware, and others are complex and costly, for example, the Van Slyke method (20) which uses mass spectrophotometry.

Physical methods may be divided into two broad classifications:

1) Saturation methods wherein a previously degassed solvent is saturated with a gas under conditions in which the necessary pressures, volumes, and temperatures, may be determined.

2) Extraction methods wherein the dissolved gas in a previously saturated solution is removed under conditions in which the pressure, volume, and temperature may be determined.

Markham and Kobe (22) designed an Ostwald-type apparatus to measure the solubility of carbon dioxide and nitrous oxide in aqueous salt solutions. The principle of the Ostwald method is that a measured volume of gas is brought in contact with a measured quantity of gas-free liquid. Equilibrium is established by agitation and the volume of gas remaining is measured after the system pressure has come to equilibrium. The change in volume gives the amount dissolved by the liquid.

The apparatus used in this experiment is based on the same principle as the apparatus of Markham and Kobe. This is the method most readily used with the hydrate formation apparatus. The method involves allowing the pressure to equilibrate at constant volume, then changing the volume (and the number of moles) and allowing the pressure to re-equilibrate.

II. EXPERIMENTAL EQUIPMENT

A photograph of the equipment is presented in Figure 1. A schematic diagram of the experimental system is shown in Figure 2. A description of the individual components of the system are presented here under the following separate subsections:

1. The Equilibrium Cell - where cyclopropane and KCl solutions are brought into contact with each other.

2. The Liquid Charging System - which determines the quantity of KCl solution in the system.

3. The Pressure Measuring System - a constant volume means of determining pressure.

4. The Temperature Measuring and Control System - which measures the temperature in the equilibrium cell and controls the bath temperature.

5. The Conductivity Measuring System - which measures changes in conductance of the solutions.

6. The Ultrasonic Agitation System - which generates the necessary agitation to promote rapid equilibrium.

7. The Vacuum System.

FIGURE 1. OVERALL VIEW OF THE EXPERIMENTAL EQUIPMENT

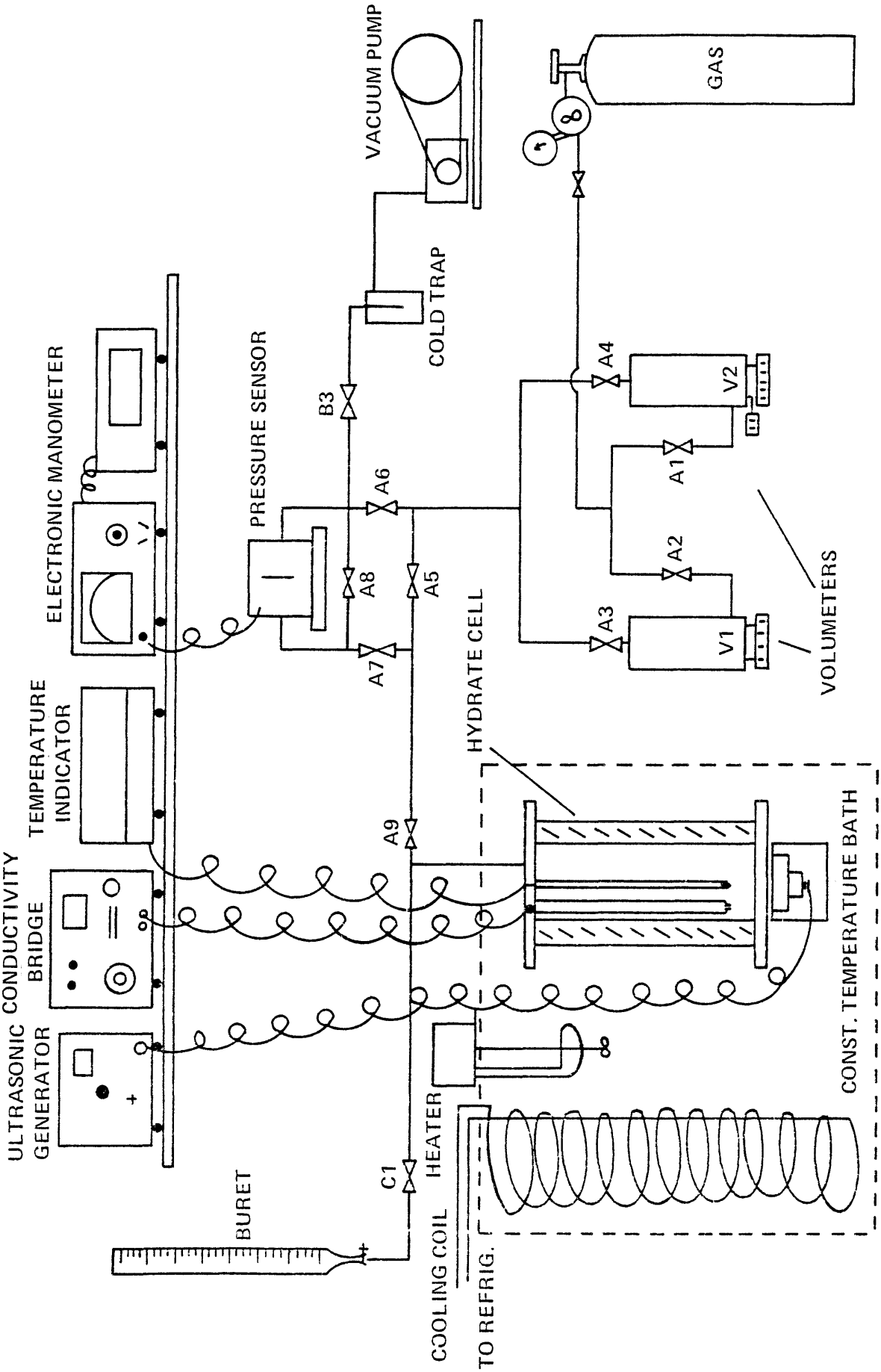


FIGURE 2 – EXPERIMENTAL APPARATUS FOR THE FORMATION OF HYDRATES AND MEASUREMENT OF CYCLOPROPANE SOLUBILITY IN SALT SOLUTIONS

1. The Equilibrium Cell

The Equilibrium Cell was a cylindrical cell in which solubilities were measured. It is shown in Figures 3 and 4. This same cell will be used for hydrate measurements. The cell dimensions were: 2 inch ID cylindrical bore and 5 inches long. It was constructed of a bearing bronze alloy (83% Cu, 7% tin, 7% lead, 3% zinc), with a tensile strength of 40,000 psia. The design pressure was in excess of 1,000 psia for operating temperatures from -30°C to 100°C. Closures on the cell were made of Type 410 stainless steel. Each closure was removable and was attached with six 3/8 inch bolts. Rubber 'O' ring gaskets were used as seals on the top and bottom closures. Two sight glass windows (see Figure 4) were built on opposite sides of the cell in order to observe the hydrate formation. The windows were 1/4 inch plexiglass with teflon gasket seals. Each window was attached with twelve 1/8 inch bolts. The ultrasonic transducer that produced agitation of the liquid in the cell was bolted to the outside of the lower plate. This was covered by a 3 inch ID aluminum cover.

The cell was connected to the gas inlet valve by means of a 1/4 inch copper tubing. This same inlet was connected to the liquid inlet valve. The platinum resistance thermometer was connected to the upper plate of the cell by an

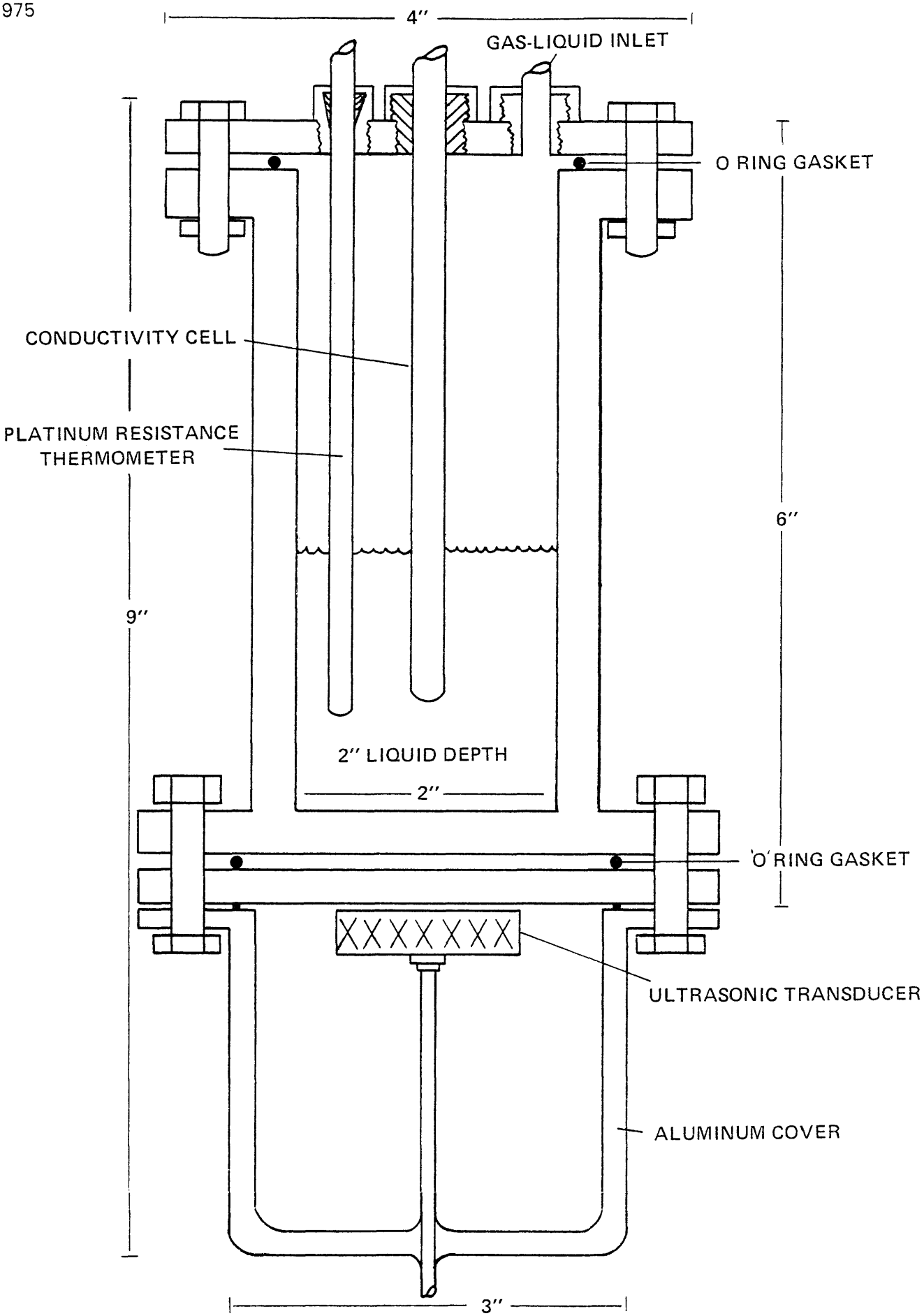


FIGURE 3 – SCHEMATIC DRAWING OF THE EQUILIBRIUM CELL

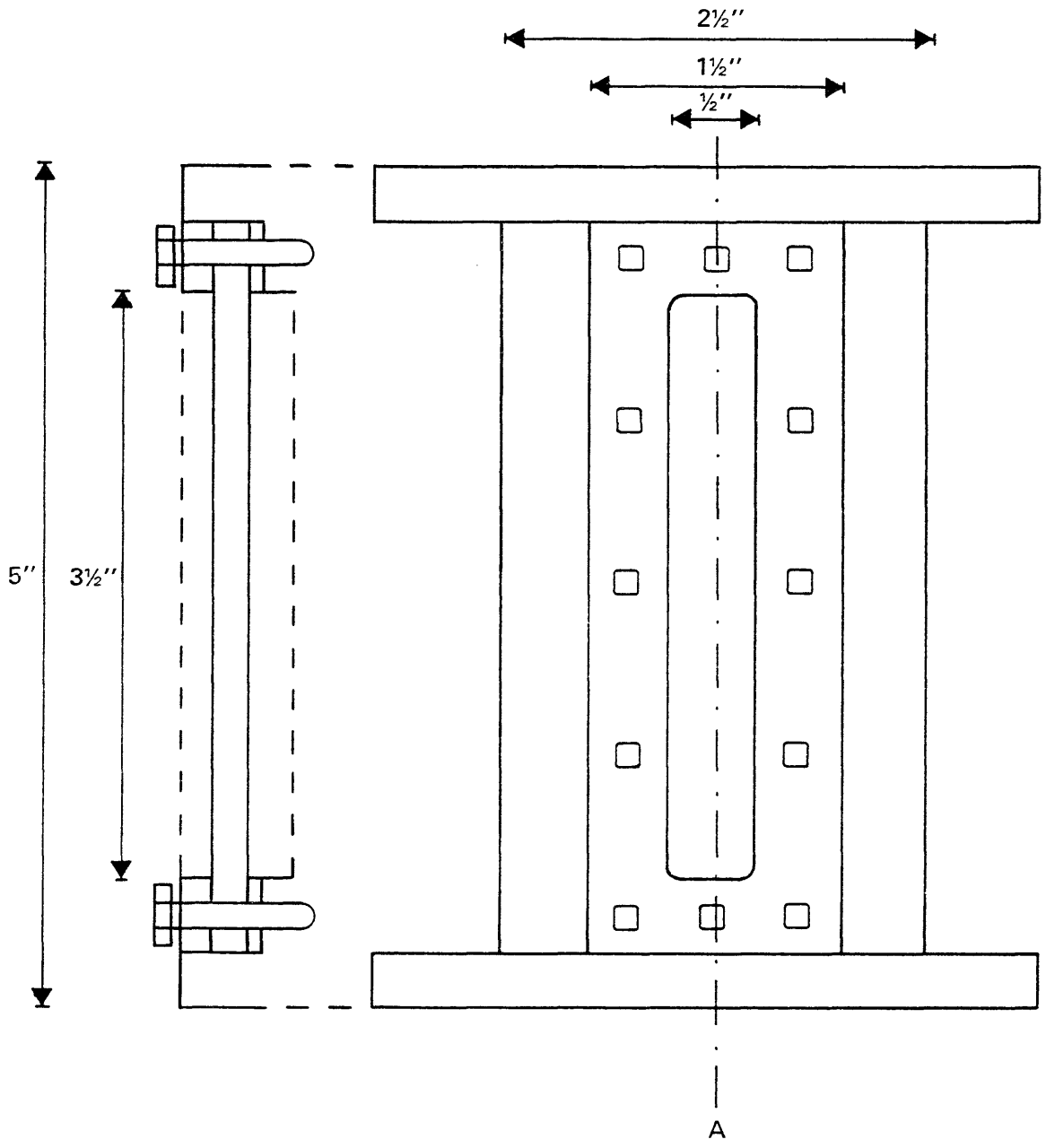


FIGURE 4 – SCHEMATIC DRAWING OF THE EQUILIBRIUM CELL WINDOWS

Omegalock compression fitting.

The cell was supported by means of three 4 1/2 inch long bolts standing on a plexiglass box. This 147 cu. in. box was constructed mainly for bath fluid displacement.

2. Liquid Charging System

Water or salt solution was charged to the evacuated cell from the 250 ml buret with graduations of 1.0 ml shown in Figure 2. The buret was open to the atmosphere and connected to a bellows seal valve and tubing assembly by approximately six inches of 1/4 inch Tygon tubing. The remaining tubing throughout the entire experimental apparatus was 1/4 inch copper tubing. The valves of the assembly were commercial, 1/4 inch Nupro B4-H bellows valves. All of the valves in the system were the same except the two metering valves at the volumeter inlet. The Brass fittings were commercial Swagelok fittings.

3. Gas Charging System

The equipment used in charging the cell with gas (see Figure 2) consisted of the gas cylinder, a pressure regulator, two Volumetrics volumeters and an assembly of valves and tubing connected to the equilibrium cell. The cyclopropane cylinder was a size D cylinder from Matheson Gas Company. The gas analysis which was provided by Matheson Co., was as follows:

Carbon Dioxide	<	1 ppm
Air	<	50 ppm
Propylene	<	1230 ppm
Allene	<	100 ppm
Cyclopropane	=	balance

The regulator was a pressure regulator with a 35 psig outlet pressure gauge. A Matheson pressure needle valve model 100S was used to control the flow of gas to the system. The gas charged to the system was measured with a Model VM volumeter and a Model V-1R volumeter made by Volumetric Company of California (see Figure 5). Both volumeters provide an accuracy of $\pm$ .15% of reading. The calibrations checks are shown in Appendix A. Tubing was connected to the volumeters by two 1/4 inch B-OVS2 Whitey regulating valves. The volumes of all gas lines were measured.

4. Pressure Measuring System

The pressure measuring system consisted of a Barocel pressure sensor, an electronic manometer, and the tubing which connected the sensor with the equilibrium cell. The pressure sensor was a Barocel Model 570 shown in Figure 6 which is intended for general purpose gaging, differential or absolute pressure measurements. The sensor consists of a sealed diaphragm which changes position (and capacitance)

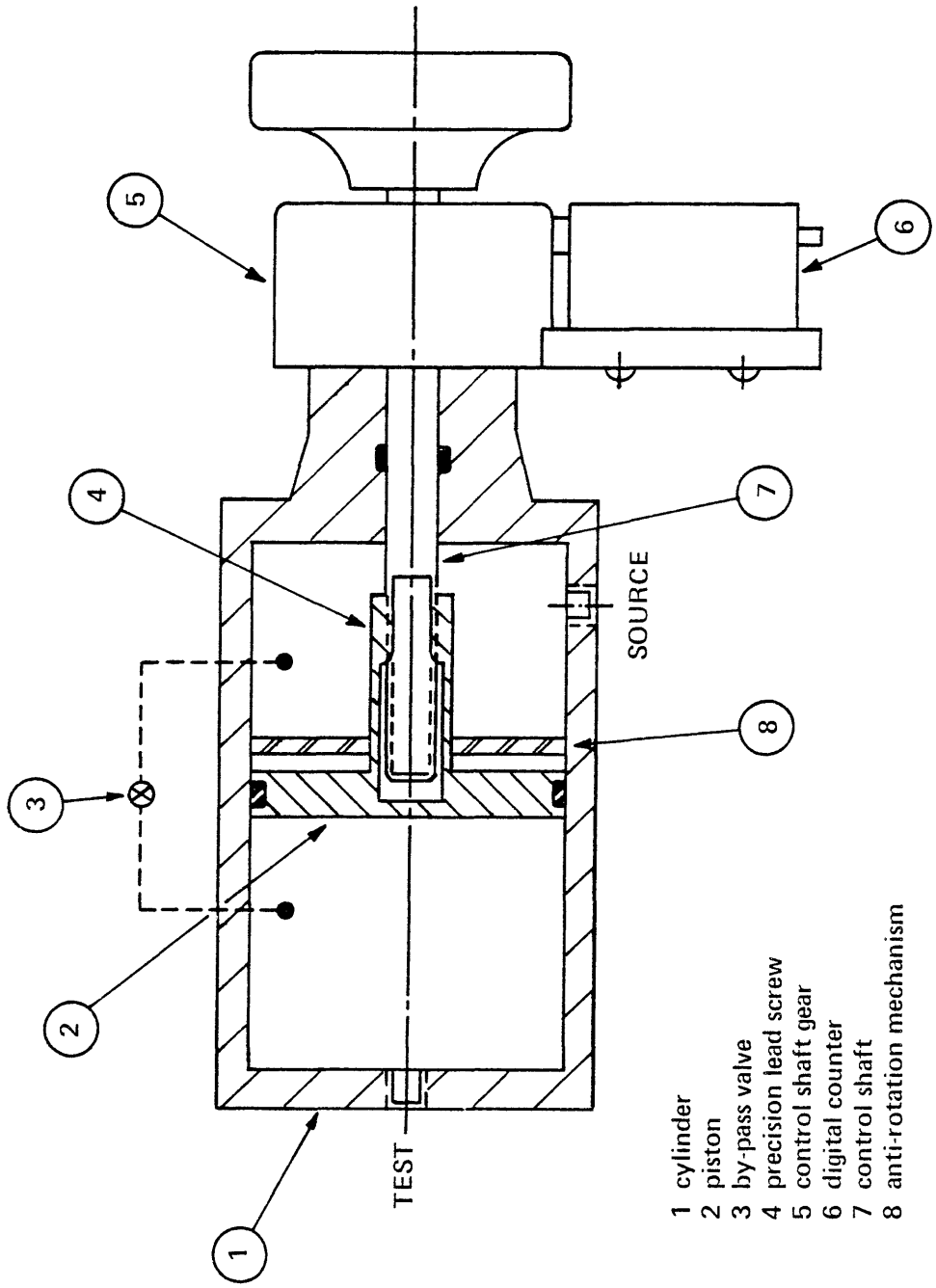
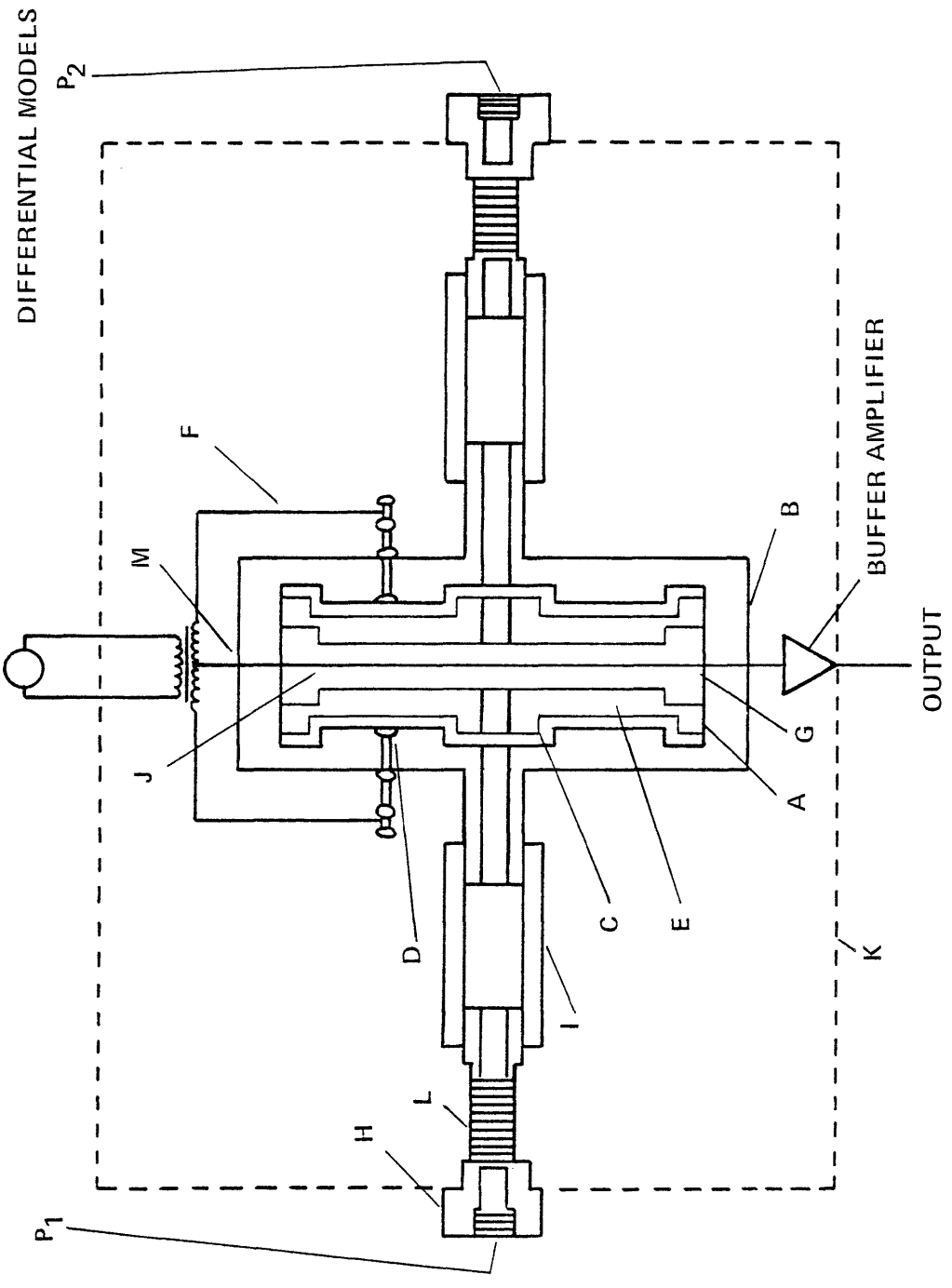


FIGURE 5 – VOLUMETRIC VOLUMETER. SCHEMATIC DIAGRAM

FIGURE 6 – BAROCEL PRESSURE SENSOR. SCHEMATIC DIAGRAM



A SUBSTRATE SUPPORT
B SEALED METAL HOUSING
C SCREEN
D JUMPER WIRE
E CERAMIC SUBSTRATE
F FILM TERMINATION
G METAL FILM
H PRESSURE PORT
I CERAMIC COUPLING
J DIAPHRAGM
K EXTERNAL HOUSING
L STRAIN RELIEF
M TIG WELD

between two plates with pressure changes. The sensor has a range from 0 to 2,000 Torr. The overall accuracy is ± .25% of reading in addition to ± .02% of operating scale. The resolution is 0.001 Torr on the most sensitive scale.

The sensor is mounted on a Type 525 thermal base used to stabilize the temperature at 105°F or 180°F. The latter temperature was used to accelerate degassing. The electronic manometer was Type 1173 with analog display and with a one volt output connected to a digital voltmeter with four and a half digits. The Barocel and the electronic manometer were purchased from Datametrics and the digital voltmeter was obtained from Digitac. The Barocel sensor was calibrated against a Mercury manometer with graduations of 0.1 mm Hg. The results of the calibrations are shown in Table A-2. The interconnecting tubing between the sensor and the cell was commercial 1/4 inch copper tubing.

5. Temperature Measuring and Control System

The temperature in the cell was sensed with a 6 1/2 inch long Omega Type PR-11 platinum resistance thermometer. The output was read with a digital temperature indicator Model DS-100-T5 purchased from Doric Scientific. The temperature range was from -23°C to 80°C with an overall accuracy of ± 0.02°C. The platinum resistance thermometer was calibrated

against a Leeds and Northrup platinum resistance thermometer traceable to the National Bureau of Standards. The corrected temperature was used in the experiment. The results of the calibrations are shown in Table A-1.

The temperature bath was constructed of 1/2 inch plexiglass with dimensions as follows: 13 inches long, 7 1/2 inches wide, and 17 inches high, having a capacity of approximately 5 1/2 gallons. The outer wall was insulated with 1 inch Armoflex foam. The bath fluid was Dow-Corning 200 Silicone fluid with a freezing point of -40°F and viscosity of five centistokes at 0°C. This fluid was used mainly because it is a good dielectric. The temperature of the bath was controlled by a combined circulating and immersed thermostat which supplied heat from a 750 watt heater. The bath was circulated by a small 10^{1}/min capacity pump which was attached to the thermomix controller. The thermomix controller was a Model 1440-GKU purchased from VWR Scientific.

The refrigeration system was a Model PCC-24A-3 Blue M hermetic refrigerator with 1/2 HP compressor and 3500 BTU/HR removal capacity. The temperature range was -23°C to room temperature with control within $\pm$ .15°C. The Freon-12 refrigerant emerged through a thermostatic expansion valve and flowed through a 7/16 inch OD, 16 inch high stainless steel coil wound on a 7 inch OD mandrel. The refrigerator

was equipped with a hot gas by-pass system to minimize undershooting and to allow better control of the cooling capacity. With the refrigerator and the separate controller the bath could be controlled to ± 0.02°C at 0°C.

6. Conductivity Measuring System

The conductances of the salt solution were measured with a conductivity cell connected to a Beckman Conductivity Bridge Model No. RC19. The conductivity cell Model No. DEL-K-1 with constant K = 1, was connected to the upper closure of the equilibrium cell by means of a specially machined swagelock connector with two 'O' ring seals.

The accuracy of the cell is 1.0% and the accuracy of the bridge is 0.25% of reading and can be used in the range of 0.1 micro mho to 0.1 mho. With this instrument, resistance can be measured in the range of 100 ohms to 10 megohms.

7. Ultrasonic Agitation System

The ultrasonic agitation system consisted of an ultrasonic transducer attached to the lower plate of the equilibrium cell and connected to an ultrasonic generator with a 25 foot waterproof cable. The transducer assembly consisted of a steel back block, a pair of lead zirconate titanate ferroelectric elements with a connector tab and an aluminum front block. These were held together by a center bolt under

high tension. The teflon-coated connector wires and the cable comprised the electrical parts.

The generator was a solid-state module which operated from a commercial 120 V, 60 H_z electrical outlet. The generator allowed the resonant frequency of the dynamic unit to control it, and it usually operated at about 24.5 KH_z. The power output maximum was about 75 watts. This was regulated by an external Variac. The power varied with the depth of the liquid and an abrupt change in current was noticed when the transducer began producing cavitation. The ultrasonic unit was assembled by Bliss Sonic Company in Fayetteville, Pennsylvania. The ultrasonic unit was designed for optimum efficiency with 2 1/2 inches of liquid water in the cell.

8. Vacuum System

The vacuum system consisted of a Welch-Duo-Seal Vacuum pump, Model 1399, rated at 1.5×10^{-3} mm Hg ultimate pressure which was connected to the equilibrium cell via 1/4 inch copper tubing and a 7/16 ID rubber vacuum hose.

A liquid nitrogen cold trap was used to prevent condensable vapor from going into the pump. The discharge of the vacuum system was vented to the atmosphere outside the building.

III. EXPERIMENTAL PROCEDURE

The procedure was, in general, to determine the number of initial gas moles in the system from the volumeters through valve A9; then the final moles in the cell and volumeters were determined at the final pressure. The number of moles of gas dissolved was the difference in the above values.

1. Initially, the liquid in the system from the previous run was removed from the equilibrium cell. The volume of liquid was collected in a 200 milliliter graduated cylinder. The equilibrium cell was then cleaned and dryed with a heat gun. The gas was removed from the system and condensed in the cold trap.
2. The cell was submerged in the bath and connected to the liquid and gas charging system. The cell was then evacuated and pressurized to about 20 psia with cyclopropane for leak checks. The cell was evacuated again in preparation for the solution's charge to remove any residual air.
3. The salt solutions were made up by adding distilled water (carbon dioxide free) to a known amount of KCl (reagent grade). After the salt was in the flask, water was added to the 1 liter mark.

4. Gas inlet valve A9 in Figure 2 was closed. Two hundred milliliters of solution were then charged to the evacuated cell from the 250 milliliter buret through the liquid feed valve (valve c1). The air dissolved in the solution was eliminated by freezing the solvent and pumping out the gas. The process of thawing and freezing was repeated twice in an hour. This method of degassing gives good results since the amount of lost solvent was only 0.5 ml as determined by cold trap weighings.
5. After determining the temperature at which the first run would be made, the thermocontrol was set and the system was cooled down by the refrigeration coils in the bath until the set point temperature of the thermocontrol was reached. Then the ultrasonic oscillator was turned on for good mixing.
6. The vapor pressure of the solution was measured. Next, a pressure was chosen which insured that the system would be in the two phase gas-liquid region, below the gas liquid hydrate equilibrium conditions. The procedure to introduce the gas into the system was as follows: valve A9 and

and A5 (figure 2) were closed and valves A7 and A8 were opened to the vacuum system and the liquid vapor remaining in the line to the sensor was evacuated. Then cyclopropane gas was admitted to the volumeters through valves A1 and A2. Then valve A8 was closed and valve A5 was opened so that the gas filled the lines up to the desired total pressure. After five minutes, the total pressure and ambient temperature were measured. Then valve A9 was opened and gas was admitted to the cell and began dissolving in the solution.

7. Pressure was recorded at half hour intervals until no noticeable change was observed. Usually, the system reached equilibrium using ultrasonics after four hours. The final pressure and temperature of the system was measured at this point.
8. The same procedure was repeated at a higher pressure within the two phase gas-liquid region. The pressure was increased by advancing the V_2 volumeter and the change in volume was measured with the micrometer counter in the V_2 volumeter. The pressure was measured every half hour, again, until the system

reached equilibrium conditions. The final pressure and temperature were, again, measured at this point. Conductance was also measured at several equilibrium conditions.

9. Finally, the cell was disconnected and prepared to be charged with a new solution. The same procedure was followed for each successive run.

IV. EXPERIMENTAL RESULTS

Henry's constants and solubility data were determined for cyclopropane in pure water and salt solutions of KCl at concentrations of 0.0, 0.5, 1.1, 1.5, and 10 g/l, at temperatures of 0, 3, and 5°C. The lower concentrations will be needed for future hydrate work. The experimental data for each isotherm are tabulated in Tables 1, 2, and 3 and presented graphically in Figure 7, 8, and 9. The primary data and solubilities for each experimental run are tabulated in Appendix E. Figures 7 and 8 present the natural logarithm of the inverted Henry's constant expressed in mole fraction/mm Hg cyclopropane versus reciprocal temperature $(K)^{-1}$ at constant salt concentrations. Partial pressures are defined here as total pressure minus water vapor pressure ($P_T - P°_{H_2O}$). In Figure 9 the natural logarithm of the inverted Henry's constant against salt concentration is presented with temperature parameters.

The lines through the data in Figures 7, 8, and 9 were generated with a least square fit, resulting in the following equation:

TABLE 1

Experimental Values of Inverted Henry's Constants for 0°C Isotherm

Run	T °C	P^V mm Hg	C g/l	P_i mm Hg	$K_i' \times 10^7$ mole fract / mm Hg	P_i mm Hg	$K_i' \times 10^7$ mole fract / mm Hg
5	0.08	4.618	0.00	246.5	7.770	295.6	7.769
7	0.01	4.619	0.00	45.5	3.908	90.0	6.939
7	0.01	4.619	0.00	131.0	7.700	--	--
2	0.01	4.614	0.510	315.0	7.690	--	--
1	0.02	4.612	1.098	284.3	7.625	344.3	7.630
3	0.08	4.610	1.518	230.5	7.589	356.0	7.590
4	0.07	4.389	10.090	201.8	6.870	330.5	6.880

TABLE 2

Experimental Values of Inverted Henry's Constants for 3°C Isotherm

Run	T °C	P^V mm Hg	C g/l	P_i mm Hg	$K_i' \times 10^7$ mole fract / mm Hg	P_i mm Hg	$K_i' \times 10^7$ mole fract / mm Hg
12	3.05	5.692	0.000	350.0	6.717	519.4	6.716
13	3.01	5.688	0.508	390.3	6.656	600.3	6.650
14	3.05	5.686	1.125	429.3	6.603	646.1	6.601
15	3.02	5.670	1.505	369.5	6.578	683.3	6.570
16	3.09	5.654	10.020	389.4	5.922	625.0	5.920

TABLE 3

Experimental values of Inverted Henry's Constants for 5°C Isotherm

Run	T C°	P^V mm Hg	C g/l	P_i mm Hg	$K_i' \times 10^7$ mole fract / mm Hg	P_i mm Hg	$K_i' \times 10^7$ mole fract / mm Hg
6	5.06	6.548	0.00	649.0	6.069	729.5	6.079
8	5.05	6.544	0.486	429.5	6.030	550.6	6.029
9	5.01	6.539	1.085	320.4	5.997	548.0	6.000
10	5.02	6.523	1.508	398.5	5.965	671.9	5.970
11	5.01	6.505	10.012	465.5	5.353	742.6	5.348

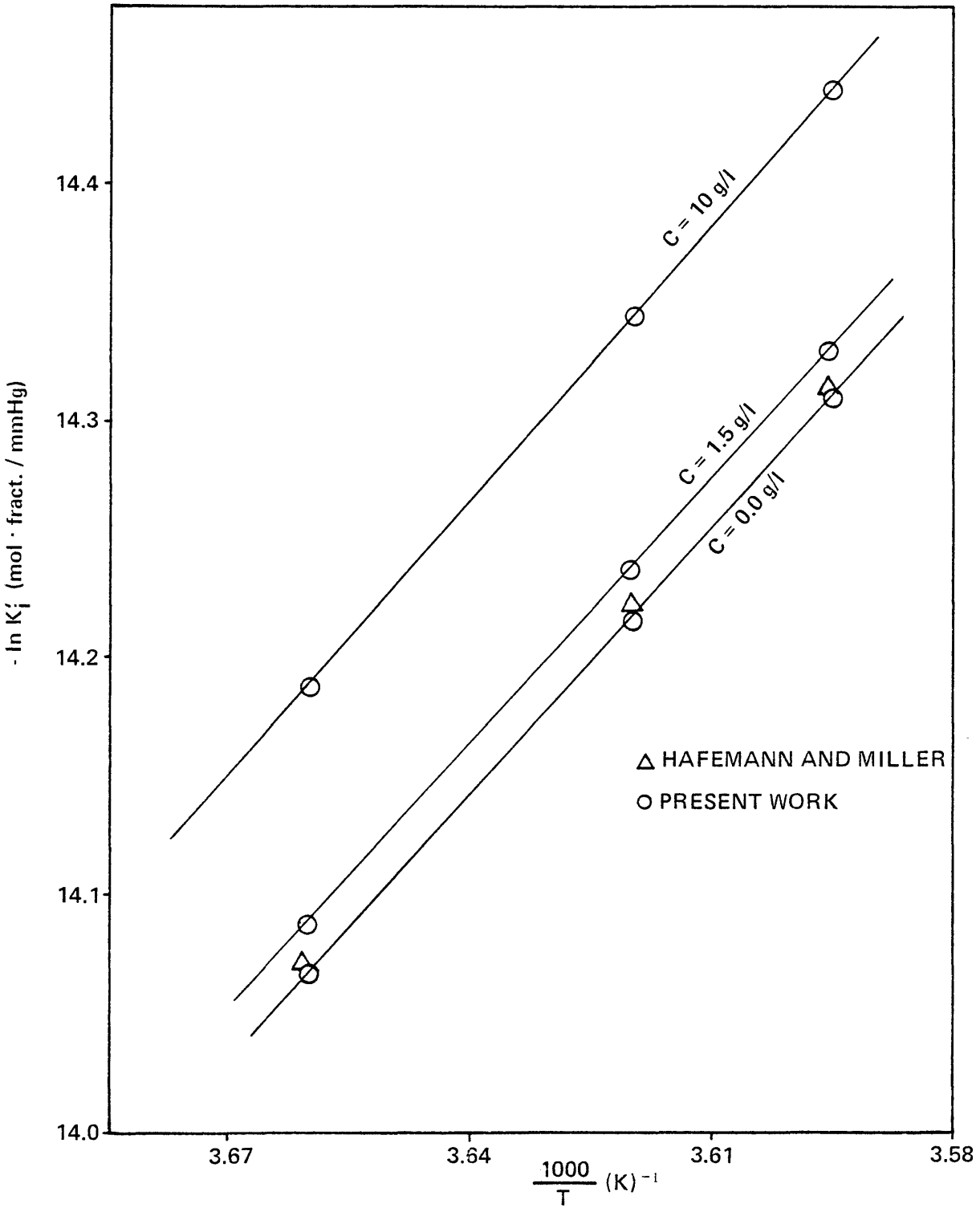


FIGURE 7 – INVERTED HENRY'S CONSTANTS OF CYCLOPROPANE IN KCL SOLUTIONS AS A FUNCTION OF TEMPERATURE

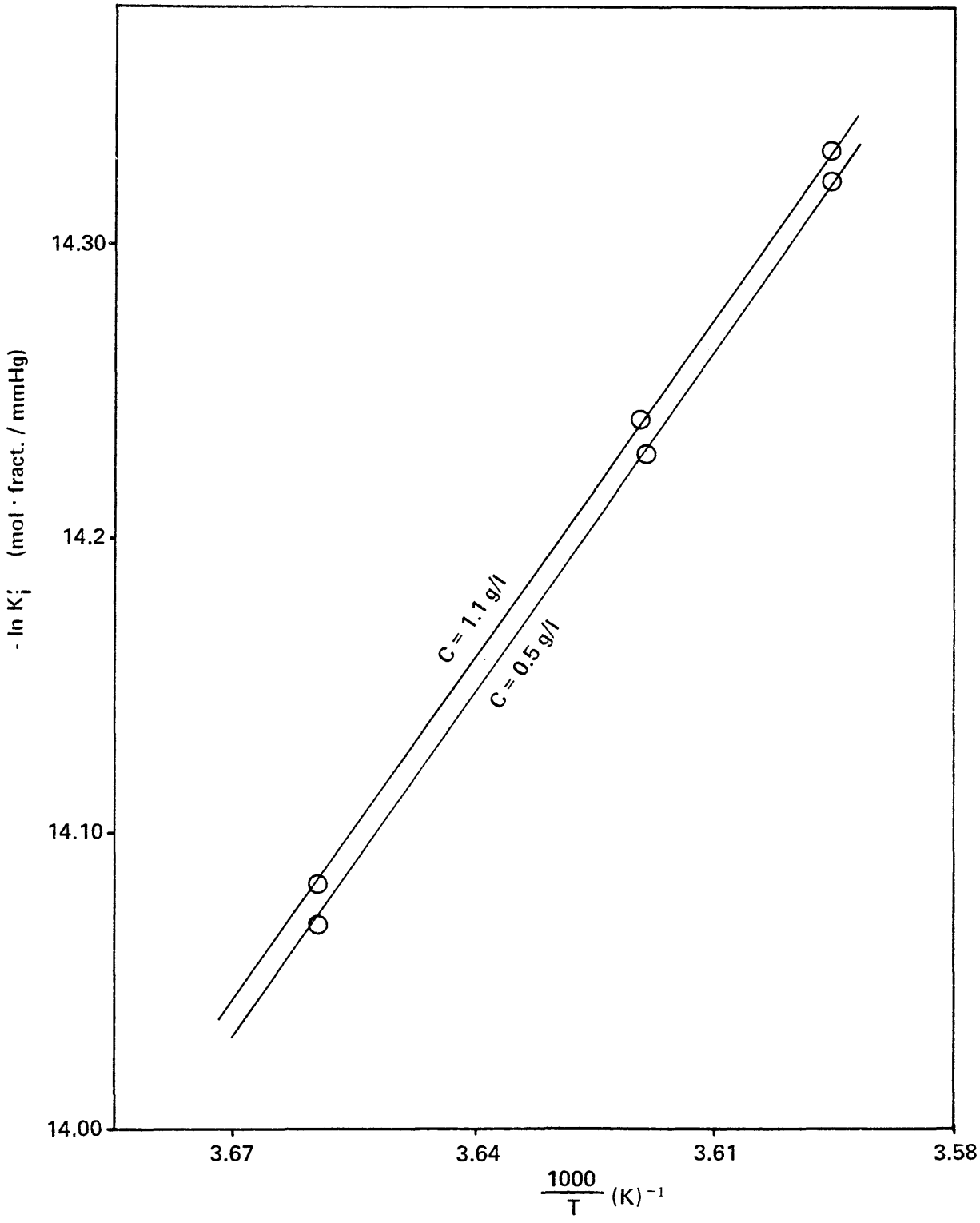


FIGURE 8 – INVERTED HENRY'S CONSTANTS OF CYCLOPROPANE IN KCL SOLUTIONS AS A FUNCTION OF TEMPERATURE

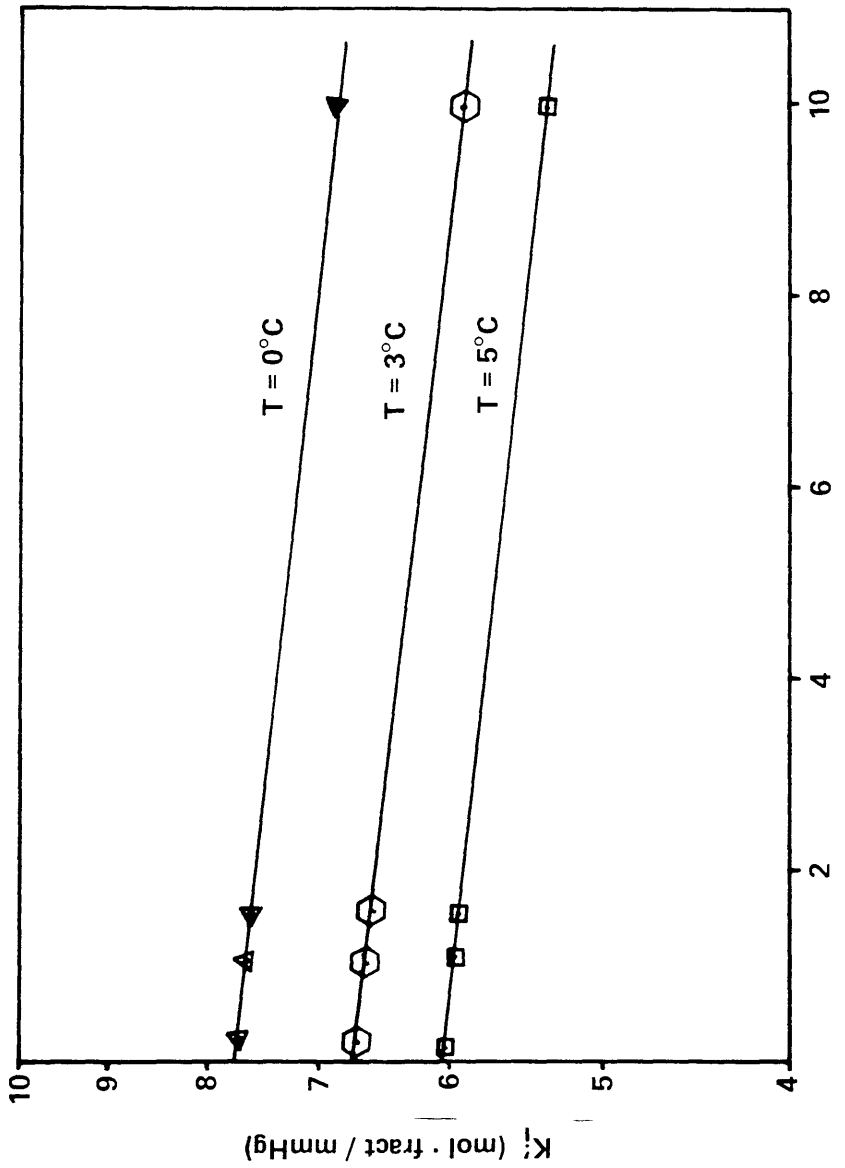


FIGURE 9 – INVERTED HENRY'S CONSTANTS OF CYCLOPROPANE AS A FUNCTION OF SALT CONCENTRATION

$$\ln K_i' = -50.609 + \frac{4700.5}{T} + 3.446 \ln T$$

$$-(9.94\times10^{-2} - \frac{10.332}{T} - 8.80\times10^{-3} \ln T)\times C \quad (8)$$

where K_i' is in mole fract./mm Hg

T is in °K,

and C is in g/l.

V. DISCUSSION

From the experimental results of this study, the solubility data of cyclopropane as a function of temperature and salt concentrations, behave in a regular manner. The values for Henry's constant are in good agreement with the values reported by Hafemann and Miller (14) within about +1.57%. Miller (23) indicated that the accuracy of his data is unknown, but that he would be pleased if it were better than 2%. The solubility of cyclopropane in pure water has been measured by Inga and McKetta (17) at pressures of 14.7 to 619.9 psia and temperatures of 70 to 220°F. If the results of this study at low temperatures are extrapolated to 70°F the values of Inga and McKetta agree within -2.6%. A previous study by Allott and Stewart (1) on the solubilities of inhaled anaesthetics in water at 37°C produce solubility coefficients 6% greater than those reported here, using extrapolated data of the present work.

In determining the extent to which Henry's law applies for each temperature, it may be noted that the cyclopropane

solubility in water and salt solutions is directly proportional to the partial pressure of cyclopropane. Figure 10 shows that this fact agrees well with the two extreme sets of data at different temperatures and salt concentration.

All of the cyclopropane-water data reported here were correlated with Equation (8). The constants of this equation were determined by a linear least-squares procedure. The maximum deviation of any of the data from the equation is $\pm$ 0.28%. Equation (8) makes use of the temperature dependence of the intergrated Van't Hoff equation and the salinity dependence of the Sctehenon relation (5) (i.e., that the logarithm of the solubility is a linear function of salt concentration). Also, it has been shown that this kind of equation represents accurately the solubilities of Helium and Neon in water and sea water (30), and the solubility of butane in salt solutions of NaC_1 (28).

A comparison of the prediction of Equation (8) with the experimental data is shown in Figures 7, 8, and 9. The solubility of cyclopropane decreases with increasing temperature and with increasing salt concentration. The reduction of solubility with increasing salt concentration is

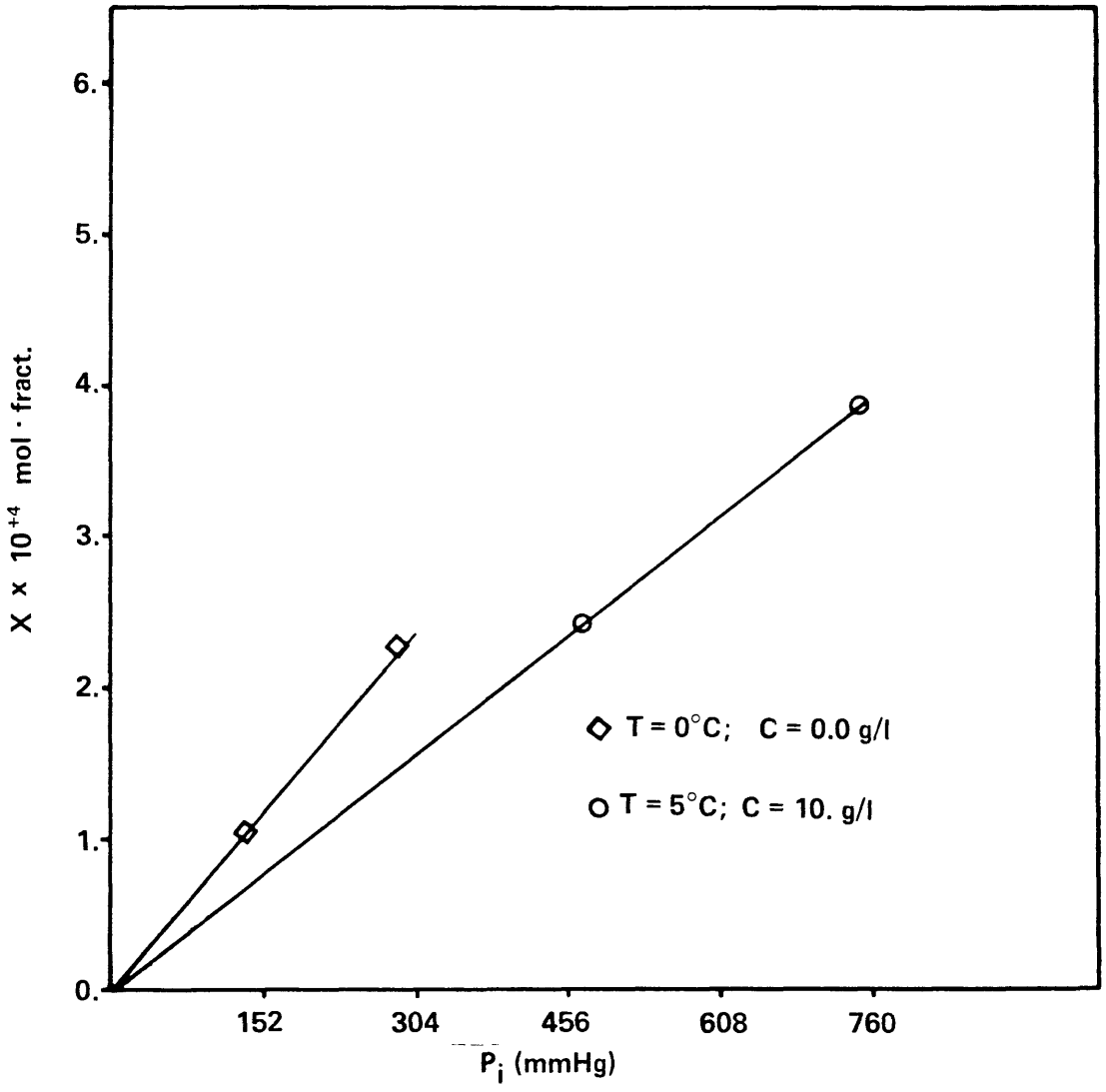


FIGURE 10 – SOLUBILITY OF CYCLOPROPANE AS FUNCTION OF PARTIAL PRESSURE

consistent with the effect of salt addition on the solubility of gases in water observed by Weiss (30) and by Rice (28). Apparently, the salt ions associate with several water molecules, effectively reducing the number of water molecules available for dissolving the cyclopropane. This salt effect has been explained to a great extent by different theories (19).

The vapor pressure of pure water was measured and agreed with values in literature (31) within + 0.4% which represents an error in temperature of +0.02°C. The vapor pressures are shown in Tables 1, 2, and 3 along with the solubility data.

At very low total pressure, a small deviation from a straight line becomes visible in moles of gas dissolved versus partial pressure as shown in Figure 11 and Table 1. In appendix B calculations are presented to show that this low pressure deviation is a result of neglecting the amount of water vapor in the lines leading to the equilibrium cell. At higher pressure this effect is negligible.

The activity and activity coefficients of water in KCl solutions were studied. The results of the calculations are shown in Table 4. The activity and activity coefficients are defined by the following equations:

$$a_i = \frac{f_i}{f_i^\circ} \qquad (11)$$

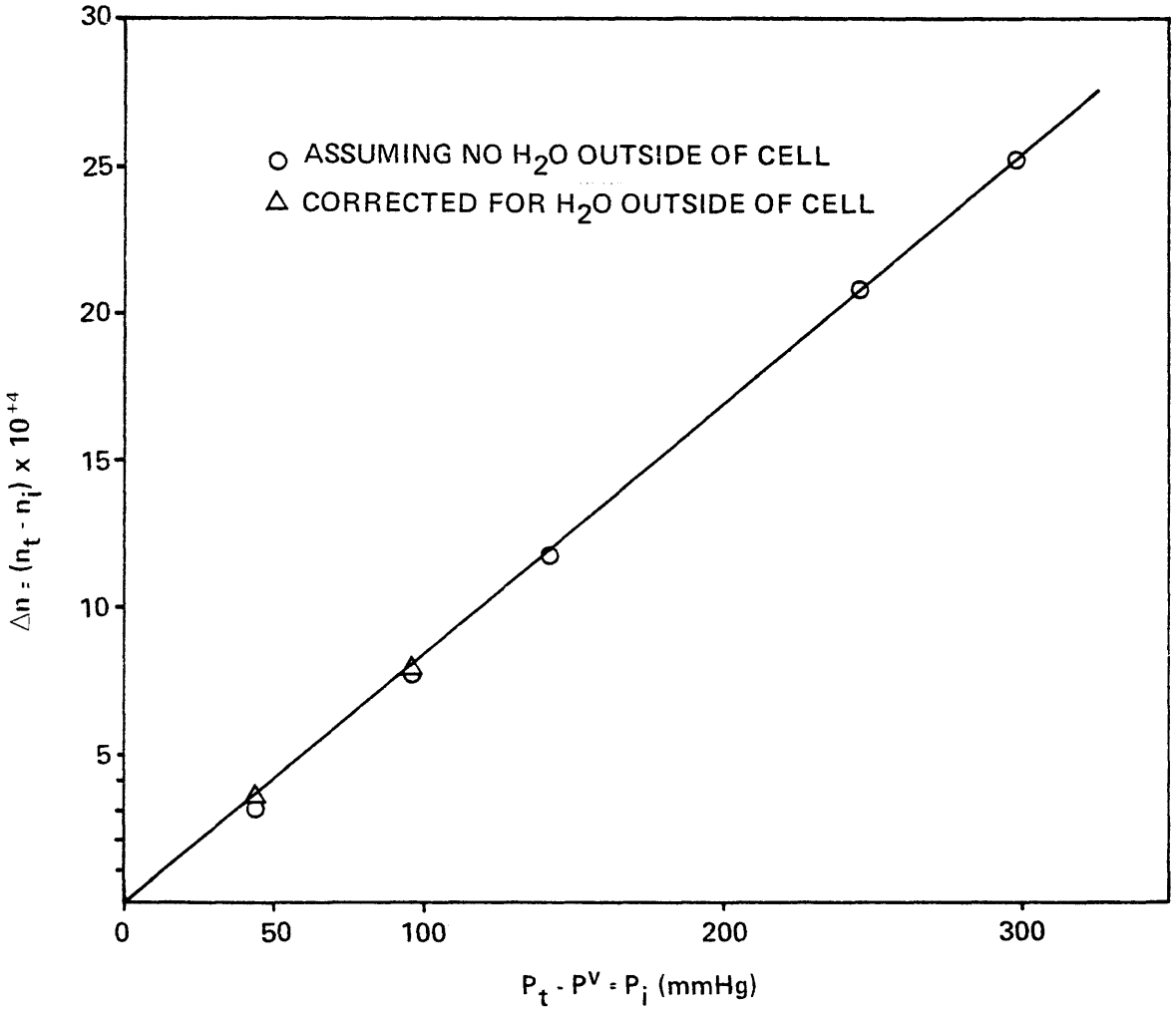


FIGURE 11 – MOLES OF GAS DISSOLVED VERSUS PARTIAL PRESSURE CYCLOPROPANE

TABLE 4

Values of Activity and Activity Coefficients for KCl Solutions

T °C	p^V mm Hg	$X_S x10+4$ KCl mol fract.	a activity	γ acti. coeff.
0.0	4.618	0.0000	1.0000	1.000
	4.614	1.191	0.9990	0.9991
	4.612	2.622	0.9981	0.9989
	4.602	3.574	0.9965	0.9968
	4.589	23.784	0.9937	0.9950
3.0	5.692	0.000	1.0000	1.0000
	5.688	1.191	0.9991	0.9993
	5.686	2.622	0.9989	0.9991
	5.670	3.574	0.9961	0.9964
	5.654	23.784	0.9931	0.9954
5.0	6.548	0.000	1.0000	1.0000
	6.541	1.191	0.9990	0.9991
	6.539	2.622	0.9986	0.9988
	6.523	3.574	0.9963	0.9966
	6.505	23.784	0.9934	0.9957

$$\gamma_i = \frac{f_i}{X_i f_i^\circ} \tag{12}$$

$$f_i = y_i \phi_i P_T \tag{13}$$

Sometimes the vapor deviates significantly from the perfect gas law and the fugacity must be calculated by methods described in literature (18, 27).

In other cases at sufficiently low pressure, the vapor may be assumed to be a perfect gas, and $\phi_i = 1$, so $f_i^\circ = P_i^\circ$ and $f_i = P_i$. Under the conditions of this experiment the water vapor may be taken as a perfect gas, so that the total pressure of water salt solution becomes a particularly convenient measure of water's activity. The vapor pressure of KCl is low enough to assume that the vapor phase is pure water.

The third column in Table 4 gives the values of $a_i = P_i/P_i^\circ$ measured at several values of mole fraction and temperature. The fourth column gives γ_i; the difference of γ_i from unity shows the degree of departure from a perfect solution.

The cyclopropane heat of solution can be obtained by taking the derivative of Equation (8) with respect to 1/T according to the following expression (25):

$$\left(\frac{\partial \ln X_i}{\partial\, 1/T}\right)_{P,C} = -\frac{\Delta H}{R} \tag{14}$$

since the inverted Henry's constant, K', is mole fraction/mm Hg, we can write for cyclopropane in pure water:

$$\left(\frac{\partial \ln K_i'}{\partial\, 1/T}\right)_{P,C} = \frac{-\Delta H}{R} = 4700.5 - 3.446T \qquad (15)$$

At T = 0°C and P_T = 760 mm Hg, the cyclopropane heat of solution divided by the universal gas constant is 3759.23 K.

An error analysis, provided in Appendix B, indicated that the inverted Henry's Constants should be good to within 1.1 percent.

VI. CONCLUSIONS

1. An apparatus has been designed and built for the measurements of cyclopropane water solubility and formation of cyclopropane hydrates.

2. Solubilities of cyclopropane in pure water and KCl solutions have been measured within the pressure-temperature range of cyclopropane hydrate formation with an estimated accuracy within 1.023 percent.

3. The experimental results for cyclopropane water solubility confirm the validity of Henry's law in the range of temperature and pressure studied.

4. The data of cyclopropane solubility reported here has been fitted to an equation in temperature and salinity. The equation fits the values with an estimated accuracy of 0.28 percent.

VII. RECOMMENDATIONS

1. It is recommended that the apparatus and the solubility data reported here be used for determining hydrate composition.

2. It is recommended that solubility data be determined at higher temperatures.

3. It is recommended that solubilities of cyclopropane in intermediate concentrations (e.g. 2.5, 5.0, 7.5 g/l) of KCl solutions be studied.

4. It is recommended that solubility data at constant temperature be determined at different pressures in order to check the effect of water vapor in the lines at other conditions.

5. It is recommended that the agitation be adjusted for the height of liquid in the cell if extensive solubility studies are continued.

NOMENCLATURE

a = activity of water in salt solutions

C = KCl composition in g/l

f_i^l, f_i^g, f_i^o = fugacity of liquid, gas, and pure component

K_i = Henry's constant (mm Hg /mol fract)

K_l' = Inverted Henry's constant (mol fract/mm Hg)

n_s = moles of salt solution in the cell

n_f = final number of moles of gas at equilibrium

n_T = initial total number of moles of gas

Δn = number of moles of gas dissolved ($n_T - n_f$)

H = number of counts in the volumeter

P_i = partial pressure of gas

P^V = vapor pressure of solution

P^o = vapor pressure of pure water

P_T = total pressure of gas

P_f = final pressure of gas at equilibrium

R = universal constant of gases

T = temperature in the cell

Ta = ambient temperature

V_T = total volume in the lines and volumeters

V_V = total volume in the vapor space

V_C = volume of the cell

X_i = mole fraction of gas dissolved

Y_i = mole fraction of gas in vapor phase

Greek Letters

γ_i = activity coefficient of water in salt solutions

ϕ = fugacity coefficients

Superscripts

o = pure vapor pressure

g = gas phase

l = liquid phase

v = vapor phase

Subscripts

a = ambient temperature

i = component i

g = gas component

f = final condition

T = total pressure or volume

APPENDICES

APPENDIX A

1. Calibration of the Platinum Resistance Thermometer

The platinum resistance thermometer was calibrated against a standard Leeds and Northrup platinum thermometer which was referenced against an N.B.S. previous standard (1968-IPTS). Resistances were measured with a Fluke multimeter. The range of calibration was from -23°C to 60°C. The results of the calibration are shown in Table A1. The procedure used to calibrate the systems platinum resistance thermometer is outlined below. The silicone fluid was incorporated as a multitemperature bath in which both thermometers were immersed.

Procedure: The calibrated thermometer used as a standard, was inserted into the bath. Then, the thermometer to be calibrated was inserted to the same depth. The leads of the calibrated thermometer were connected to a Fluke meter and the leads of the thermometer to be calibrated were connected to the electronic indicator. The temperature in the bath was set with the thermocontroller. Once it stabilized, values for both thermometers were recorded. During the

TABLE A1

Results of Platinum Resistance Thermometer Calibrations.

Standard Platinum Thermometer (°C)	Platinum Resistance Thermometer (°C)
-9.301	-9.370
-8.355	-8.405
-7.731	-7.780
-6.492	-6.430
-5.112	-5.140
-3.985	-4.015
-2.745	-2.770
-1.281	-1.315
-0.025	-0.040
+0.910	+0.930
+1.963	-2.000
+3.183	+3.225
+4.029	+4.050
+5.279	+5.290
+6.030	+6.020
+7.378	+7.360
+8.069	+8.050
+9.093	+9.075
+10.227	+10.200
+19.837	+19.745
+25.301	+25.225
+29.684	+29.540
+35.920	+35.830
+40.019	+39.900
+46.661	+44.520
+50.127	+49.960
+54.743	+54.575
+59.966	+59.750
+65.169	+64.890
+70.317	+70.000
+75.405	+75.055

calibration of the thermometers a cycling effect of $\pm$ .02K was noticed in the temperatures. The median value was used for the purpose of calibration.

Once the temperatures were read, the bath was set at a new temperature and the procedure was repeated for the whole range.

2. Calibration of the Pressure Sensor and Electronic Manometer

The pressure sensor and electronic manometer were calibrated against a mercury manometer which had graduations of 0.01 mm Hg. The range of pressure was from 5 to 2000 Torr. The results of the calibration are shown in Table A2. The procedure used to calibrate the pressure measuring system is outlined below. A schematic diagram of the pressure calibration system is shown in Figure A-1.

Procedure: Initially the sensor and electronic manometer were connected to the tubing assembly and Mercury manometer. An initial test for leaks was performed. The range multiplier in the electronic manometer was set at the zero position and the zero position was adjusted with the control in the near panel. Then the range multiplier was set at full scale position and adjusted to 100 percent output with a control on the rear panel. The system was evacuated, the heating base was set at 180°F and degassing continued for two hours.

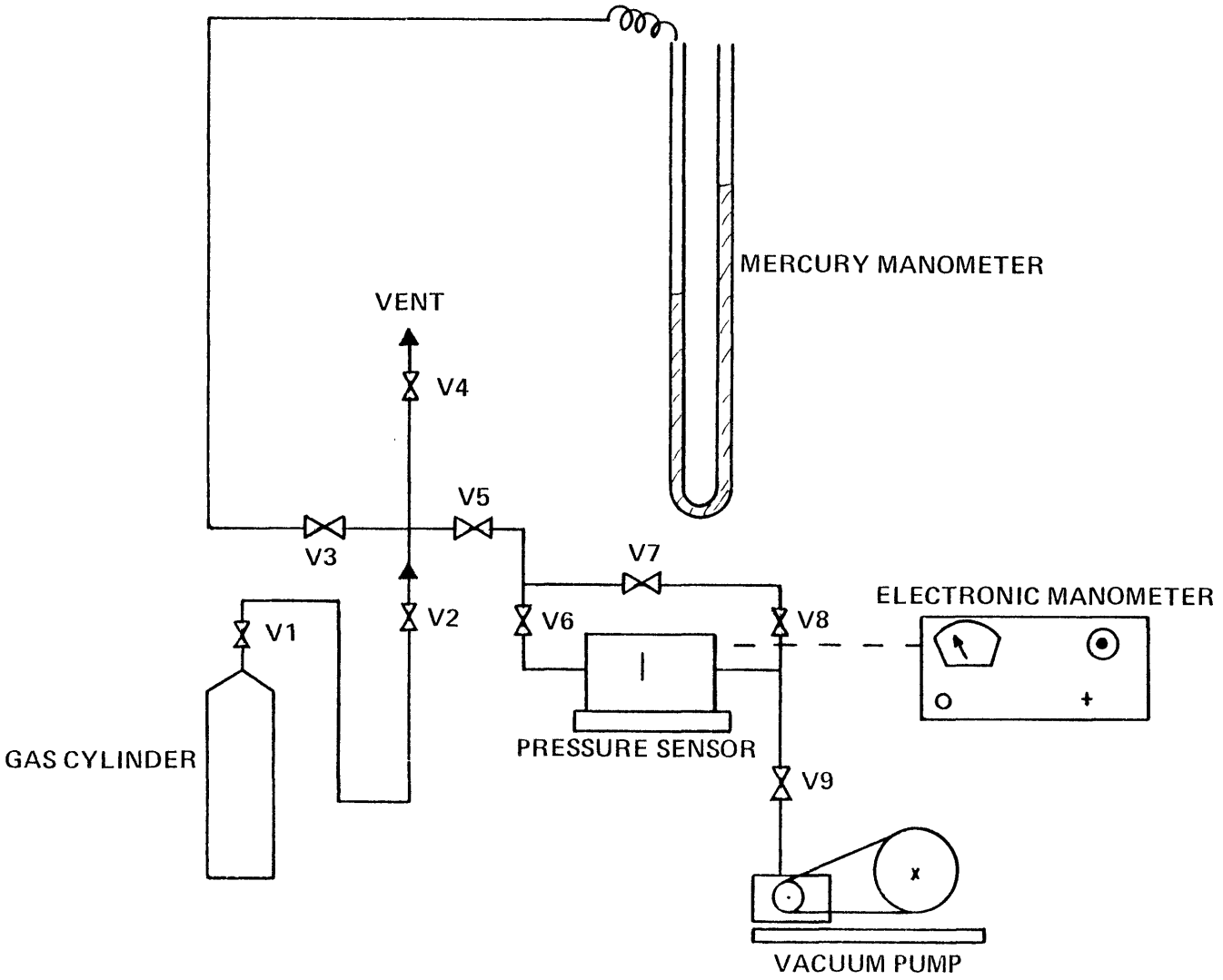


FIGURE A1 – PRESSURE CALIBRATION SYSTEM

TABLE A2

Results of the Barocel Pressure Sensor Calibrations

Mercury Manometer (mm Hg corrected to 0°C)		Pressure Sensor (mm Hg)
5.2		5.21
15.6		15.60
25.3		25.35
49.6		50.00
52.7		52.66
201.6		201.70
595.9		597.10
609.6	(barometric pressure at 22.8°C)	609.60
726.2		725.10
898.2		897.80
949.8		950.30
992.2		992.80
1081.8		1081 10
1168.7		1168.70
1468.9		1469.10

A vacuum pump was used to evacuate the system. Since the tubing produced a small pressure drop with the range multiplier at the most sensitive position, the sensor zero was used to adjust zero.

The measurements were started at low values of absolute pressure. Valves V2 & V4 were closed and the system was evacuated (see Figure A1). Pressures from 5 Torr to atmospheric were generated by opening valve V4 to vent. Pressure from atmospheric to 3000 Torr were generated with a pressurized cylinder of helium. At each data point, the pressure was recorded by reading the Mercury manometer and the electronic manometer. The readings in the Mercury manometer were corrected to 0°C. The barometric pressure and room temperature were recorded during the experiment.

3. Volumeter System Calibration

The volume of the volumeters was determined by Helium expansion from the volumeter to the initially evacuated expansion cylinder of known volume.

$$V_{volumeter} = \frac{(P_{after\ expansion})}{P_{before\ expansion} - P_{after\ expansion}} V_{cylinder}$$

$$= \frac{(465\ mm\ Hg)}{(1240-465)mm\ Hg} \times (326.8\ ml) = 196.08\ ml$$

Another expansion gave a value of 196.08 ml. The number of counts determined for the whole volume was 9570 with 300 counts per turn. The volume displaced per turn (300 counts) was 6.147 ml.

APPENDIX B

Data Reduction and Error Analysis

Sample Calculation

Run 5. Cyclopropane-water at 273.15K

1. Cyclopropane

P_T = 373.8 mm Hg

Ta = 300 K (27°C)

V_T = 511.61 cc (volume of tubing and volumetrics; see auxiliary calculations

V_V = 88.54 cc (volume of vapor space and correction; see auxiliary calculations

Moles of gas charged are determined from initial P.V.T. measurements.

$$N_T = \frac{(373.8)(511.61)}{(760)(72.05)(300)} = 0.01022$$

Correction for non-ideality

$$Z = 1+\left(\frac{BP_C}{RT_C}\right)\frac{P_r}{T_r} \qquad \text{(B-1)}$$

P_r = 0.00907 P_T = 373.8 mm Hg P_C = 54.2 atm

T_r = 0.75 Ta = 300 K T_C = 397.4 K

Using Pitzer correlations (26) get second Virial coefficient

$$\left(\frac{BP_C}{RT_C}\right) = -0.481$$

$$Z = 1 + (-0.481)\frac{(0.00907)}{(0.75)} = 0.9941$$

Real number of moles charged = $(0.9941)^{-1}(0.01022) = 0.01028$

2. Water

Charge = 201.0 cc at 27°C

Density (26) = 0.99656 g/m

Weight charged = (201)(0.99656) = 200.3

Moles charged NS = $\frac{200.3}{18.016}$ = 11.118 moles

3. Gas dissolved and inverted Henry's law at first pressure

P^V = 4.618 mm Hg

P_f = 251.2 mm Hg

T = 273.15 K

Correction for nonidealities using the same procedure as the preceeding section, get Z_i, and Z_2 at 273.15K and 300 K

Z_1 = 0.9953

Z_2 = 0.9950

Moles of gas at equilibrium assuming that there is water vapor diffusion in the vapor space to value A9, and the diffusion in the rest of the system is negligible

$$n_f = \frac{(P_f - P^V)\ V_V}{760\ RT\ (Z_1)} + \frac{P_f\ V_T}{(760)\ RT_a\ (Z_2)} \qquad \text{(B-2)}$$

$$n_f = \frac{(251.2 - 4.618)(88.54)}{760\ (82.05)(273.15)(0.9953} + \frac{281.2(511.61)}{760(82.05)(300)(0.9960)}$$

$n_f = 0.008149$

moles of gas dissolved

$\Delta n = n_T - n_f = 0.01028 - 0.008149 = 0.002131$

$$\text{mole fraction } X = \frac{\Delta n}{\Delta n + n_s} = \frac{0.002131}{0.002131+11.118} = 0.000019167$$

$$\text{Henry's constant } K' = \frac{X}{P_g} = \frac{0.00019167}{246.5} = 7.774 \times 10^{-7}$$

4. Gas dissolved and inverted Henry's constants at second pressure

$P_f = 300.2$ mm Hg

$T = 273.15$ K

Total volume:

Number of counts $N = 6220$

One turn = 300 counts = 6.147 cc

$$\Delta V = 6220\ \frac{6.147}{300} = 127.45 \text{ cc}$$

$V_T = 511.61 - 127.45$ cc $= 384.16$ cc

Correction for non-idealities

$Z_1 = 0.9943$

$Z_2 = 0.9950$

$$n_f = \frac{(295.7)(88.54)}{760\ (82.05)(273.15)(0.9943)} + \frac{(330.2)(384.14)}{(760)(72.05)(300)(0.985)}$$

$n_f = 0.007725$

$\Delta n = n_T - n_f = 0.0128 - 0.007725 = 0.002555$

$X = 2.2975 \times 10^{-4}$

$K' = \frac{X}{P_g} = 7.769 \times 10^{-7}$ (mot fract/mm Hg)

Corrections for water vapor in gas phase at low pressures.

$P_T = 62.66$ mm Hg $\quad T = 0°C$

$P^V = 4.618$ mm Hg

$p_f = 50.2$ mm Hg

$$n_T = \frac{P_T V_T}{RT\ 760} = \frac{62.66 \times 511.61}{(760)(82.05)(273.15)} = 0.001882$$

$$n_f = \frac{(P_V - P^V)V_V}{760\ RT} + \frac{P_f V_T}{760\ RT_a} \qquad \text{(B-2)}$$

$$n_f = \frac{(45.59)(88.54)}{(760)982.65)(273.15)} + \frac{50.2(511.61)}{760x(82.05)(300)} = 0.00160$$

moles of gas dissolved

$\Delta n = n_T - n_f = 0.001882 - 0.00160 = 0.000198$

This value is lower than expected because assumption made in Equation (B-2) doesn't hold any longer. The mole fraction of water vapor represents 9.1% so the diffusion in the lines is higher. Doing the calculation using partial pressure of gas as $(P_f - P^V)$ for the entire system we get

n_f = 0.001492 moles of gas

Δn = 0.000390 moles of gas

This value is expected according to Henry's law.

Auxiliary Calculations

a. Equilibrium Cell (by water displacement)

$$\frac{280.00\ g}{0.9965\ g/ml} = 280.98\ ml$$

b. Tubing from equilibrium cell to valve A-9,

(by calculations from tubing diameter and length).

7.57 ml

c. Free volume of tubing from cell to volumeters

by Helium compression in volumeter V2 (see Figure 2).

P (mm Hg)	ΔV (counts)	ΔV (ml)
731.1	0	0
828.0	4575	93.74

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$V_1 = V_{tub} + V_{cell} + V_{vol} = \frac{\Delta V}{(1-P_1/P_2)} = \frac{93.74}{(1-\frac{731.0}{828.0})}$$

$$= 800.15$$

$$V_{tub} = V_i - V_{vol} - V_{cell} = 800.15 - 418.12 - 288.54$$

$$= 83.49\ ml$$

Error Analysis

The accuracy of the experiment was determined by studying the possible source of error in some important variables as follows:

Temperature error in the cell was $\pm$ 0.02 °C.

Room temperature could be estimated to 0.1°C.

Degassing of the solution produced 0.5 ml of solution lost.

The liquid changed to cell could be estimated to 0.5 ml.

Measurements of volume could be estimated to 0.12%.

Pressure error was estimated to 0.25%.

The absolute error can be calculated from the following equations.

$$K_i = f(X_1, X_2, \ldots) \tag{B-3}$$

$$\Delta K_i' = \sum_i \frac{\partial f}{\partial X_i} \Delta X \tag{B-4}$$

and since the inverted Henry's constant K_i' is the variable of study:

$$K_2' = f\ (P_T, P^V, V_V, V_T, T, T_a, P_f, V_{H_2O}, W_S)$$

$$K_i' = \frac{\frac{n_i - n_f}{n_T}}{P_f - P^V}$$

$$= \frac{\frac{P_T V_T}{RTa} - \frac{(P_f - P^V)V_v}{RTC} - \frac{P_f V_T}{RTa}}{(P_f - P^V)(n_{H_2O} + n_s)} \tag{B-5}$$

Let $n_{H_2O} + n_S = N$

Substituting (B-5) in (B-4) and solving for K_i'

$$\Delta K_i' = \frac{V_T}{(P_f-P^V)N}\Delta P_T + \left\{\frac{P_T V_T}{N(P_f-P_V)^2} - \left[\frac{-RT_C N(P_f-P^V)V_V + V_V(P_f-P_V)}{N^2R^2T_C{}^2(P_f-P^V)^2}\right.\right.$$

$$\left.\left.\frac{RT_C N}{}\right] - \frac{P_f V T}{RT_a N(P_f-P_v)^2}\right\}\Delta P^V - \frac{(P_f-P^V)\ \Delta V^V}{RT_C(P_f-P^V)N}$$

$$+\left[\frac{P_T}{(P_f-P^V)N} - \frac{P_f}{RT_0 N(P_f-P^V)}\right]\ \Delta V^T - K_i' N\left(\frac{\rho}{18}\Delta V_{H_2O} + \frac{1}{75}\ \Delta W_S\right)/\left(\frac{\rho}{18}V_{H_2O} + \frac{W_S}{75}\right)^2$$

$$+\frac{P_f V_T\ \Delta T_a}{RN(P_f-P^V)T_a{}^2} + \left\{-\frac{P_T V_T}{N(P_f-P_V)^2} - \left[\frac{RT_C(P_f-P_V)N\ V_V - (P_f-P^V)V_V RT_C N}{R^2T_C{}^2N^2(P_f-P_V)^2}\right]\right.$$

$$\left.-\left[\frac{R\ T_a N(P_f-PV)V_T - P_f V_T RT_a N}{R^2T_a{}^2N^2(P_f-P^V)^2}\right]\right\}\ \Delta P_f \qquad \text{(B-6)}$$

The absolute error introduced by the measured parameters is demonstrated by substituting the numerical values of the run number 7 in the equation (B-6).

The estimated absolute error was $7.058597*10^{-9}$ mole fract/mm Hg which gives a percentage error of 1.023 percent.

APPENDIX C

Suppliers of Major Equipment

Equipment	Model	Supplier
1. Barocel Pressure Sensor	570	Datametrics 340 Fordham Rd Wilmigton, Mass 01887
2. Electronic Monometer	1173	
3. Conductivity Bridge	RC-19	Beckman Instruments Cedar Brove, NJ 07009
4. Circulator thermomix	1440BKU	VWR Scientific Co. 3700 Havana Denver, Colorado 80207
5. Digital Voltmeter	--	United System Corp. 4950 East Enaus Denver, Colorado 80222
6. Fittings (Swagelock)	--	Denver Valve and Fittings 970 Simms Denver, Colorado 80215
7. Equilibrium Cell	--	Golden Tool and Machine Co. 1600 W. 5th Ave. Golden, Colorado 80401
8. Platinum Resistance Thermometer	PR-11	Omega Engineering P. O. Box 4047 Stanford, Connecticut 06907

9. Platinum Resistance Thermometer Indicator	PRT05	Doric Scientific 3883 Ruffin Road San Diego, CA 92123
10. Refrigeration Unit		Blue M Electric Co. Blue Island, IL 60406
11. Ultrasonic System	--	Bliss Sonic Co. P. O. Box 142 Fayetteville, PA 17222
12. Volumetrics	VM1	Volumetrics 1025 Silver Vitae Ingelwood, CA 90301
13. Vacuum Pump	1399A	Sargent Welch Scientific 4040 Dahlia Street Denver, CO 80207

APPENDIX D

COMPUTER PROGRAM FOR HYDRATE CALCULATIONS

The computer program HYDMIX calculates hydrate-formation conditions in moist gas mixtures. The method of solution uses the statistical thermodynamic theory of van der Waals and Platteeuw; the paper by Parrish and Prausnitz describes the basic algorithm used here.

The program is written in FORTRAN 10. It is easy to use, normally requiring four simple data cards in addition to temperatures, pressure, and gas compositions. HYDMIX can be used to calculate hydrate-formation conditions in gas mixtures contining up to ten components (excluding water).

The program tends to calculate too high a pressure at a given temperature. For design purposes, conservative estimates of the program's reliability are that it predicts pressures 20 percent too high and temperatures 3°F too high. These errors are roughly comparable to the estimated errors for the commonly used K-factor correlations.[1] However, HYDMIX

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[1]American Petroleum Institute Technical Data Book Petroleum Refining, (1966); Section 9, page 38.

has two major advantages in that it can be used --

1. To calculate hydrate-formation conditions over an extended temperature range (250-300°K) and pressure range (0-10,000 psia).
2. To predict hydrate formation conditions in mixtures containing nonhydrate-forming gases.

In the data deck, integer data are read in on a 1013 format and real data, with one possible exception, are read in on a 7F format. The data cards, in sequence, are:

1. The number of components, excluding water, NCOMP.
2. The title of the problem, TITLE (Format 13A5).
3. The component numbers, KC, as given in Table D-1. The numbers are used to fetch parameters for estimating physical properties of the gases and the hydrate phase. All hydrate-forming gases (KC>0) must be listed before the other components ($KC \geq 0$).

If any components are present but not listed in Table D-1, their value of KC is zero and they are listed last on card 3. Each of these components require three additional cares:

3(a) The critical pressure, PCO (atm), critical volume (cc/gmol), critical temperature, TCO (°K), acentric factor, ω, two correction factors for the modified Redlich-Kwong equation, C1RKV and C2RKV (corresponding to Ω_1 and Ω_2; Chueh and

Prausnitz, 1968), molecular weight, AMOLWT and the components name COMPA and COMPB. The card format if 7F, 2A5.

3(b) The parameters for estimating gas solubility in water at a given temperature, T (°K), AS, BS, CS (Morrison, 1952), and any pressure, P(atm) at a given temperature, SLOPE. If the partial molar volume at infinite dilution of the gas in water, v (assumed temperature independent) is known, SLOPE = 4.5×10^{-3} v , where v is in cc/gmol. Otherwise, SLOPE is the slope of the $\log_{10}$ f/x versus P/T lines, where f is the fugacity (atm) of the gas and x is the mole fraction of the gas in water (See Prausnitz, 1969).

3(c) The factors used to correct the geometric mean assumption for calculating critical temperatures of binary mixtures, CORRV (corresponding to k_{12}; Chueh and Prausnitz, 1968). CORRV for NCOMP pairs (k_{12} = 0.0 for the pure component "pair") containing the component are required.

4. The control parameter for the dimension of the temperature, KT (KT equals 1, 2, 3, or 4 for °F, °R, °C, °K, respectively); for the dimension of the pressure, KP

TABLE D-1

COMPONENTS AND THEIR COMPONENT

NUMBERS AS NEEDED IN PROGRAM HYDMIX

Hydrate-Forming Gases		Non Hydrate-Forming Gases	
Component	Component Number (KC)	Component	Component Number (KC)
Methane	1	Hydrogen	-1
Ethane	2	Helium	-2
Ethylene	3	n-Butane	-3
Propane	4	n-Pentane	-4
Propylene	5	Isopentane	-5
Isobutane	6	n-Hexane	-6
Carbon Dioxide	7	Cyclohexane	-7
Nitrogen	8	n-Heptane	-8
Hydrogen Sulfide	9		
Oxygen	10		
Cyclopropane	11		
Argon	12		
Krypton	13		
Xenon	14		

(KP equals 0 or 1 for atm or psia, respectively); for calculating the hydrate phase composition (water-free basis) KY (KY = 1 for composition calculation); and for a temperature calculation at a given pressure KTC.[1] (KTC 0 for temperature calculation.)

5. The gas phase composition Y (mole percent or mole fraction) and the control parameter CC. If CC is greater than 1.0, more than one temperature-pressure calculation will be made for the given gas composition.
6. The temperature TS, and pressure PS. If a temperature calculation is to be made (KTC<0), TS is an initial guess of the temperature. A first guess for PS is optional if a pressure calculation is being made (KTC≥0).

Blank cards end a series of calculations. For example, if CC is greater than 1.0, one blank card ends the reading of TS and PS, a second (and third if NCOMP 6) blank card stops the reading of gas compositions. The next blank card stops the program (sets NCOMP = 0).

Complete listings follow, containing the main program MYDMIX and the subroutines DATAP, DPCHECK, GAUSS, DPCALC, BLAT, PHIMIX and DUBEQN. An example data input and printed output are included.

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[1]HYDMIX calculates pressures directly but temperatures indirectly by guessing temperatures and solving for pressure. Therefore, unless only two or three temperature calculations are needed for a given gas composition, it is more efficient to solve several constant temperature problems. The results can be interpolated to get the temperatures at the given pressures.

```
      COMPUTER PROGRAM HYDMIX.F10

      CALCULATION OF HYDRATE FORMATION CONDITIONS FROM GAS
      MIXTURES

      COMPONENT AND COMPONENT NUMBER,
      HYDRATE-FORMING GASES, LIST FIRST
      METHANE   =1   ETHANE    =2  2   ETHENE    =  3
      PROPANE      =   4    PROPENE      =   5   ISOBUTANE  =   6
      CARB. DOX.    =   7     NITROGEN        =  8   HYD. SULF =9
      OXYGEN      = 10  CYCLOPROPANE = 11   ARGON    =12
      KRYPTON    = 13   XENON      = 14  SUL.HEXFL.      = 15
      NONHYDRATE-FORMING GASES LISTED IN DATAP, LOAD NEXT
      HYDROGEN     =-1  HELIUM      =-2   N-BUTANE    = -3
      ISOBUTANE    = -4   N-PENTANE    =-5   ISOPENTANE   = -6
    ISOPENTANE    = -6  N-HEXANE     = -7  CYCLOHEXANE   = -8
    N-HEPTANE    = -9
    LOAD UNLISTED GASES LAST (KC=0)


        DIMENSION CA(4,10), CB(4,10), TITLE(13), KC(10)

        COMMON/PHIB/NCOMP,Y(10),TCO(10),AMOLWT(10),PCO(10),C1RKV
        2(10),C2RKV(10),TCOIJ(10,10),AMWTIJ(10,10),PCOIJ(10,10)
        2,CORRV(10,10),COMPA(10),COMPB(10),VCO(10),W(10),WIJ(
        310,10),ZCOIJ(10,10),VCOIJ(10,10),KQM(10)/HYD/KIND
        4,KBLOW,NCD,KS(10),CL(4,10),AP(6,10),TM(10),NSFI,NSFII,
        5NHF/GAS/F(10),AS(10),BS(10),CS(10),SLOPE(10)/CONST/R,
        6GASR,T0/GS/NPT,X(20),WT(20)/SCRACH/XM(10),YH(4,10),SYH(4)/LAT
        7/NU(4),IS,IF
        REAL NU
        DATA R,GASR,T0/1.987,82.057,273.161/
        DATA NP,NP1,NPT,(X(J),WT(J),J=6,10)/5,6,10,0.14887
        143389,0.2955242247,0.4333953941,0.2692667193,0.679409
        25683,0.2190863625,0.8650633667,0.1494513492,0.973
        39065285,0.0666713443/
1       DO 2 J=1,NP
        X(J)=-X(NPT-J+1)   10-5 = -5
2       WT(J)=WT(NPT-J+1)                    -6
3       WRITE(7,44)
        READ(2,45) NCOMP
        IF(NCOMP.LE.0) STOP
        READ(2,46) (TITLE(J),J=1,13)
        READ(2,45) (KC(J),J=1,NCOMP)
        CALL DATAP (KC,CA,CB)
        IF(NCD.EQ.NCOMP)GO TO 6
        NCD1=NCD+1
        DO 5 J=NCD1,NCOMP
      KS(J)=0
        DO 4 I=1,4
1       CL(I,J)=0.0
        READ(2,48) PCO(J),VCO(J),TCO(J),W(J),C1RKV(J),C2R
        1KV(J),AMOLWT(J),COMPA(J),COMPB(J)
        READ(2,49)AS(J),BS(J),CS(J),SLOPE(J)
5       READ(2,49)(CORRV(J,JJ),JJ=1,NCOMP)
        CORRV(J,J)=0.0
4       CONTINUE
        NCOMP1=NCOMP-1
        DO 7 I=1,NCOMP1
```

```
      I1=I+1
      DO 7 J=I1,NCOMP                                                  67

      CORRV(I,J)=CORRV(J,I)
7     CONTINUE
      DO 8 I=1,NCOMP1
      I1=I+1
      DO 8 J=I1,NCOMP
      WIJ(I,J)=(W(I)+W(J))*0.5
      ZCOIJ(I,J)=0.291-0.08*WIJ(I,J)
      VCOIJ(I,J)=((VCO(I)**(1.0/3.0)+VCO(J)**(1.0/3.0))
     1**3)/8.0
      TCOIJ(I,J)=((TCO(I)*TCO(J))**0.5)*(1.0-CORRV(I,J))
      PCOIJ(I,J)=ZCOIJ(I,J)*GASR*TCOIJ(I,J)/VCOIJ(I,J)
       AMWTIJ(I,J)=2.0/(1.0/AMOLWT(I)+1.0/AMOLWT(J))
8     CONTINUE
      READ(2,45)KT,KP,KY,KTC
C     SET KY .NE. 0 FOR HYDRATE COMPOSITION CALCULATION
C     SET KTC .GT. 0 TO CALCULATE TEMPERATURE, A GUESS FOR
C     T IS REQUIRED IF KTC .GT. 0
      GO TO (9,10,11,12),KT
9        TP=1HF
      GO TO 13
10    TP=1HR
      GO TO 13
11    TP=1HC
      GO TO 13
12    TP=1HK
13    PP=4HATM
      IF(KP.EQ.1) PP=4HPSIA
      NPROB=0
      WRITE(7,50)NCOMP,(TITLE(J),J=1,13),TP,PP
      IF(KY.NE.0) GO TO 14
      WRITE(7,51)
      GO TO 15
4     WRITE(7,52)
;      SET CC =2. TO RUN A SERIES OF P-T CALC.
;      BEFORE CHANGING COMPOSITIONS
5     READ(2,49) (Y(J),J=1,NCOMP),CC
      PS=Y(1)
      DO 16 J=2,NCOMP
6     PS=PS+Y(J)
      IF (PS.LT.1.0E-4) GO TO 3
      IF (PS.LT.1.1) GO TO 18
      DO 17 J=1,NCOMP
7     Y(J)=0.01*Y(J)
8     CONTINUE
9     READ(2,49) TS,PS
      IF(ABS(TS+PS).LT.1.0E-6) GO TO 15
      NPROB=NPROB+1
      WRITE(7,47)NPROB,TS,PS
      T=TS
      P=PS
      GO TO ( 20,21,22,23), KT
0     T=T+459.69
1     T=T/1.8
      GO TO 23
2     T=T+T0
3     IF (KP.EQ.1) P=PS/14.696
      DO 29 K=1,20
```

```
      PX=P
      TX=T
      CALL DPCHEK(T,P)
      IF (KBLOW.GT.Ø) GO TO 35
      IF ((ABS(T-28Ø.)).GT.2Ø.Ø) GO TO 25
      DO 24 J =1,NHF
      DO 24 I=1,4
24    CL(I,J)=CA(I,J)/T*EXP(CB(I,J)/T)
      GO TO 26
25    CALL GAUSS (CB,T)
      IF(KBLOW.GT.Ø) GO TO 35
26    CALL DPCALC (T,P)
      IF (KBLOW.GT.Ø) GO TO 35
      IF (KTC.EQ.Ø) GO TO 3Ø
      DEV=(P-PX)/PX
      IF (ABS(DEV).LT.1.ØE-4)GO TO 3Ø
      IF (K.GT.1)GO TO 27
      DPDT=Ø.5*(PX-P)/ABS(PX-P)
      GO TO 28
27    DPDT=ALOG(P/P1)/(T-T1)
28    P1=P
      T1=T
29    T=T+ALOG(PX/P)/DPDT
      WRITE(7,54) PX,DEV
      GO TO 35
3Ø    GO TO (31,32,33,34), KT
31    T=T*1.8-459.69
      GO TO 34
32    T=T*1.8
      GO TO 34
33    T=T-273.15
      GO TO 34
34    IF (KP.EQ.1) P=P*14.696
      WRITE(7,53) T,P
      IF(KY.GT.Ø) GO TO 36
35    WRITE(7,55)(COMPA(J),COMPB(J),Y(J),J=1,NCOMP)
      GO TO 42
C     CALCULATION OF HYDRATE COMPOSITION
36    DO 37 I=IS,IF
      SYH(I)=1.Ø
      DO 37 J=1,NHF
      YH(I,J)=CL(I,J)*F(J)
37    SYH(I)=SYH(I)+YH(I,J)
      SXM=Ø.Ø
      DO 39 J=1,NHF
      XM(J)=1.ØE-8
      DO 38 I=IS,IF
      YH(I,J)=YH(I,J)/SYH(I)
38    XM(J)=XM(J)+NU(I)*YH(I,J)
39    SXM=SXM+XM(J)
      DO 4Ø J=1,NHF
4Ø    XM(J)=XM(J)/SXM
      NHF1=NHF+1
      DO 41 J=NHF1,NCOMP
     XM(J)=Ø.Ø
      WRITE(7,43) (COMPA(J),COMPB(J),Y(J),XM(J),J=1,NCOMP)
42    IF (CC.GT.Ø.Ø5)GO TO 19
      GO TO 15
```

```
43        FORMAT (40X,2A6,F6.4,F8.4)
44        FORMAT (1H1)
45        FORMAT (15I)
46        FORMAT (13A5)
47        FORMAT (1H0,I5,4X,9HESTIMATED,F7.1,F9.1)
48        FORMAT (7F)
49        FORMAT (7F)
50        FORMAT (1H1,37HCALCULATIO OF GAS HYDRATE FORMATION ,
          135HCONDITIONS FOR A MIXTURE CONTAINING, I3,11H COMP
          2ONENTS/1X,13A5///3X,7HPROBLEM,11X,5HTEMP.,4X,6HPRESS.,
          318X,11HCOMPOSITION/3X,6HNUMBER,12X,5HDEG. ,A1,4X,A4,
          419X,13HMOLE FRACTION)
51        FORMAT(1H0,58X,3HGAS/40X,9HCOMPONENT,9X,5HPHASE)
52        FORMAT(1H0,52X,3HGAS,4X,7HHYDRATE/40X,9HCOMPONENT,3X,
          12(9HPHASE    ))
53        FORMAT(10X,10HCALCULATED,F6.1,F9.1)
54        FORMAT(39H0 NO CONVERGENCE IN TEMP. CALC. FOR P =,
          1F7.2,32H ATM. THE PRESSURE DIFFERENCE IS,E11.3)
55        FORMAT(40X,2A6,F11.4)
          END


          SUBROUTINE DATAP (KC,CA,CB)

           TABLES OF PARAMETERS REQUIRED IN HYDMIX

          DIMENSION KC(1),CA(4,10),CB(4,10),TCOD(30),AMOWTD
          1(30),PCOD(30),C1RKVD(30),C2RKVD(30),KSD(30),CAD(80),
          2CBD(80),APD(120),ASD(30),BSD(30),CSD(30),SLOPED(30),
          3COMPAD(30),COMPBD(30),WD(30),C(900),VCOD(30)
          4,TMD(20),SIGD(20),ED(20),CD(20)
          COMMON/PHIB/NCOMP,Y(10),TCO(10),AMOLWT(10),PCO(10),
          1C1RKV(10),C2RKV(10),TCOIJ(10,10),AMWTIJ(10,10),PCOIJ
          2(10,10),CORRV(10,10),COMPA(10),COMPB(10),VCO(10),
          3W(10),FILA(310)/HYD/KIND,KBLOW,NCD,KS(10),CL(4,10),
          4AP(6,10),TM(10),NSFI,NSFII,NHF/GAS/F(10),AS(10),BS(10)
          5,CS(10),SLOPE(10)/KIHARA/SIG(10),E(10),CP(10)
          DATA (KSD(J),J=1,30),(APD(J),J=1,120)/30*0,120*0.0/
          DATA (ASD(J),BSD(J),CSD(J),SLOPED(J),J=1,30)/120*0./


                            METHANE
          DATA COMPAD(1),COMPBD(1)/6HMETHAN,6HE      /
          DATA PCOD(1),VCOD(1),TCOD(1),WD(1),C1RKVD(1),C2RKVD(1),
          1AMOWTD(1)/45.80,99.50,190.70,.013,.4278,.0867,16.04/
          DATA KSD(1),ASD(1),BSD(1),CSD(1),SLOPED(1)/1,77.067,40
          190.0,26.20,.20/
          DATA (APD(K),K=1,6)/2.2988136E+01,-8.1905829E+03,7.64
          126122E+05,1.2953706E+02,-6.2092897E+04,7.5382975E+06/
          DATA TMD(1),(CAD(K),CBD(K),K=1,4)/90.0,3.7236928E-03,
          12.7887926E+03,1.8371958E-02,2.7379222E+03,2.9560021
          2E-03,2.6951133E+03,7.6068205E-02,2.2027552E+03/
          DATA SIGD(1),ED(1),CD(1)/3.2398,153.17,.3000/


                           ETHANE
          DATA COMPAD(2),COMPBD(2)/6HETHANE,6H      /
          DATA PCOD(2),VCOD(2),TCOD(2),WD(2),C1RKVD(2),C2RKVD(2),
          1AMOWTD(2)/48.20,148.00,305.40,.105,.4340,.0880,30.07/
          DATA KSD(2),ASD(2),BSD(2),CSD(2),SLOPED(2)/1,87.699,4730
```

```
     1.0,29.67,.48/
     DATA (APD(K),K=7,12)/8.4299910E+00,-6.2496322E+02,-3.
     14253895E+05,1.6686460E+02,-8.1804756E+04,1.0010425E+07/
     DATA TMD(2),(CAD(K),CBD(K),K=5,8)/277.75,0.,0.,6.626441
     18E-03,3.6437872E+03,0.,0.,3.9652678E-02,3.0611476E+03/
     DATA SIGD(2),ED(2),CD(2)/3,326064,174.661,.400000/
C
C
C                          ETHYLENE
C
     DATA COMPAD(3),COMPBD(3)/6HETHYLE,6HNE    /
     DATA PCOD(3),VCOD(3),TCOD(3),WD(3),C1RKVD(3),C2RKVD(3)
     1,AMOWTD(3)/50.50,124.00,238.10,0.085,.4323,.0876,
     228.05/
     DATA KSD(3),ASD(3),BSD(3),CSD(3),SLOPED(3)/1,69.697,
     13900,0,23.70,.25/
     DATA (APD(K),K=13,18)/2.2341478E+02,-1.173
     11126E+05,1.5502043E+7,1.2953706E+2,-6.2092897E+04,7.5
     2382975E+06/
     DATA TMD(3),(CAD(K),CBD(K),K=9,12)/973.15,8.3039818E-04
     1,2.3969642E+03,5.4486550E-03,3.6638280E+03,6.4093
     247E-04,2.0425537E+3,3.4940143E-02,3.1071246E+03/
     DATA SIGD(3),ED(3),CD(3)/3.294103,172.869,.470000/
C
C
C                          PROPANE
C
     DATA COMPAD(4),COMPBD(4)/6HPROPAN,6HE     /
     DATA PCOD(4),VCOD(4),TCOD(4),WD(4),C1RKVD(4),C2RKVD(4),
     1AMOWTD(4)/42.00,200.00,369.90,.152,.4380,.0889,44.09/
     DATA KSD(4),ASD(4),BSD(4),CSD(4),SLOPED(4)/2,-0.,-0.,
     1-0.,-0./
     DATA (APD(K),K=19,24)/2.5931555E+01,-1.0426912E+04,9.53
     137258E+05,2.6353301E+02,-1.2824351E+05,1.5406803E+07/
     DATA TMD(4),(CAD(K),CBD(K),K=13,16)/278.55,6*0.,1.2353
     1352E-02,4.4060762E+03/
     DATA SIGD(4),ED(4),CD(4)/3,3030,200.94,0,68/
C
C
C                          PROPYLENE
C
     DATA COMPAD(5),COMPBD(5)/6HPROPYL,6HENE   /
     DATA PCOD(5),VCOD(5),TCOD(5),WD(5),C1RKVD(5),C2RKVD(5)
     1,AMOWTD(5)/45.40,181.00,365.10,.139,.4370,.0889,

     242.08/
     DATA KSD(5),ASD(5),BSD(5),CSD(5),SLOPED(5)/2,-.133
     1,4.6,-0.,-0./
     DATA (APD(K),K=25,30)/-0.,-0.,-0.,-1.3064921
     1E+02,8.9934878E+04,-1.4701707E+07/
     DATA TMD(5),(CAD(K),CBD(K),K=17,20)/274.11,6*0.,2.0174
     2574E-02,4.0057213E+03/
     DATA SIGD(5),ED(5),CD(5)/3,230370,202.418,,650000/
C
C
C                          ISOBUTANE
C
     DATA COMPAD(6),COMPBD(6)/6HISOBUT,6HANE   /
     DATA PCOD(6),VCOD(6),TCOD(6),WD(6),C1RKVD(6),C2RKVD(6)
     1,AMOWTD(6)/36.00,263.00,408.10,.187,.4420,.0898,
     258.12/
     DATA KSD(6),ASD(6),BSD(6),CSD(6),SLOPED(6)/2,-0.,-0.,
     1-0.,-0./
     DATA (APD(K),K=31,36)/-4.7072893E+02,2.6122400E+05,-3.6
```

```
1226320E+07,-1.4799849E+02,9.7898654E+04,-1.569287E+07/
DATA TMD(6),(CAD(K),CBD(K),K=21,24)/275.05,6*0.,1.6010
1649E-02,4.4486183E+03/
DATA SIGD(6),ED(6),CD(6)/3,124441,220.519,,800000/


              CARBON DIOXIDE
DATA COMPAD(7),COMPBD(7)/6HCARB. ,6HDIOX, /
DATA PCOD(7),VCOD(7),TCOD(7),WD(7),C1RKVD(7),C2RKVD(7)
1,AMOWTD(7)/72,90,94.00,304.20,.225,.4470,.0911,44.01/
DATA KSD(7),ASD(7),BSD(7),CSD(7),SLOPED(7)/1,51.375,328
10.0,17.48,.17/
DATA (APD(K),K=37,42)/-0.,-0.,-0.,2.4093647E*02,-1.224
11477E+05,1.5648717E+07/
DATA TMD(7),(CAD(K),CBD(K),K=25,28)/283.09,1,1978208E-
103,2.8605527E+03,8.507036E-03,3.2779273E+03,9.0912169E-04,2,69
254530E+03,4.8261746E-02,2.5718249E+03/
DATA SIGD(7),ED(7),CD(7)/2,968077,169.089,,720000/


                        NITROGEN
DATA COMPAD(8),COMPBD(8)/6HNITROG,6HEN    /
DATA PCOD(8),VCOD(8),TCOD(8),WD(8),C1RKVD(8),C2RKVD(8)
1,AMOWTD(8)/33.50,90.10,126.20,.040,.4290,.0870,28.10/
DATA KSD(8),ASD(8),BSD(8),CSD(8),SLOPED(8)/1,81.328
1,4160.0,27.70,.14/
DATA (APD(K),K=43,48)/3.7416622E+01,-1.5323224E+04,1.76
164516E+06,5.1422017E+01,-1.7567227E+04,1.3404491E+06/
DATA TMD(8),(CAD(K),CBD(K),K=29,32)/973.15,3.80868
145E-03,2.2054811E+03,1.8420332E-02,2.3012642E+03,
23.0283638E-03,2.1750261E+03,7.5148805E-02,1.8605
3879E+03/
DATA SIGD(8),ED(8),CD(8)/3.219893,127.949,,35000/


                  HYDROGEN SULFIDE
DATA COMPAD(9),COMPBD(9)/6HHYD. S,6HULFIDE/
DATA PCOD(9),VCOD(9),TCOD(9),WD(9),C1RKVD(9),C2RKVD(9)
1,AMOWTD(9)/38.90,95.00,373.60,.100,.4340,.0882,34.08/
DATA KSD(9),ASD(9),BSD(9),CSD(9),SLOPED(9)/1,53.29,3264
1.9,18.468,.15/
DATA (APD(K),K=49,54)/7.2178431E+00,-1.0501658E+
13,-2.5678014E+05,6.5701635E+01,-2.8206677E+04,2.79
297385E+06/
DATA TMD(9),(CAD(K),CBD(K),K=33,36)/302.65,3.0343126E-
103,3.7360128E+03,1.6740531E-02,3.6108936
2E+03,2.3757661E-03,3.7505670E+03,7.3631407E-02,2.854
31339E+03/
DATA SIGD(9),ED(9),CD(9)/3.155830,205.848,,360000/


                        OXYGEN
DATA COMPAD(10),COMPBD(10)/6HOXYGEN,6H    /
DATA PCOD(10),VCOD(10),TCOD(10),WD(10),C1RKVD(10),C2RKVD(10)
1,AMOWTD(10)/50.10,74.40,154.80,.021,.4278,.086
27,32.00/
DATA (APD(K),K=55,60)/1.3830332E+01,-3.0864257
1E+03,1.6311569E+05,1.1904532E+02,-5.4570848E+04,6.381
20284E+06/
DATA KSD(10),ASD(10),BSD(10),CSD(10),SLOPED(10)/1,69,0
```

```
      130,23.5,2.94,,14/
      DATA TMD(10),(CAD(K),CBD(K),K=37,40)/308,,1.73629E-2,2.2893
     1E+3,5.7732E-2,1.9354E+3,1.44306E-2,2.3826E+3,1.538
     220E-2,1.5187E+3/
      DATA SIGD(10),ED(10),CD(10)/2.7673,166.37,0.360/
C
C                        CYCLOPROPANE
C     DATA COMPAD(11),COMPBD(11)/6HCYCOPR,6HOPANE /
      DATA PCOD(11),VCOD(11),TCOD(11),WD(11),C1RKVD(11),C2RKV
     882,42.
     208/
      DATA KSD(11)/1/
      DATA (APD(K),K=61,66)/1.1108020E+01,-3.0698191E+03,-2.
     15920052E+04,-1.0537367E+03,5.9264677E+05,-8.3296480E07/
      DATA TMD(11),(CAD(K),CBD(K),K=41,44)/290,,0.,0.,1.
     14486318E-03,4.5794507E+03,0.,0.,1.3136414E-02,4.6533
     2503E+03/
C
C
C                          ARGON
C     DATA COMPAD(12),COMPBD(12)/6HARGON ,6H      /
      DATA PCOD(12),VCOD(12),TCOD(12),WD(12),C1RKVD(12),
     1C2RKVD(12),AMOWTD(12)/48.00,75.20,151.00,-.002,.4278
     2,.0867,39.94/
      DATA KSD(12),ASD(12),BSD(12),CSD(12),SLOPED(12)/1,60.
     1272,3290.0,20.50,,13/
      DATA TMD(12),(CAD(K),CBD(K),K=45,48)/700,,2.5779112E-02
     1,2.2269542E+03,7.5412939E-02,1.9180952E+03,2.1892273
     2E-02,2.3151161E+03,1.8660433E-01,1.5387055E+03/
      DATA SIGD(12),ED(12),CD(12)/2.943366,170.501,.184000/
C
C
C                          KRYPTON
C
      DATA PCOD(13),VCOD(13),TCOD(13),WD(13),C1RKVD(13),C2R
     1KVD(13),AMOWTD(13)/54.30,92.20,209.40,0.,,4278,.086
     17,83.70/
      DATA KSD(13),ASD(13),BSD(13),CSD(13),SLOPED(13)/1,60,43
     14,3410.0.20.50,.15/
      DATA TMD(13),(CAD(K),CBD(K),K=49,52)/700,,1.6862029
     1E-02,2.8404923E+03,5.7202128E-02,2.4466135E+03,1.399
     22616E-02,2.9478150E+03,1.5472212E-01,1.9491895E+03/
      DATA SIGD(13),ED(13),CD(13)/2.973892,198.143,.230000/
C
C
C                          XENON
C     DATA COMPAD(14),COMPBD(14)/6HXENON ,6H      /
      DATA PCOD(14),VCOD(14),TCOD(14),WD(14),C1RKVD(14),C2R
     1KVD(14),AMOWTD(14)/58.00,118.80,289.75,.002,.4278,. .
     20867,131.30/
      DATA KSD(14),ASD(14),BSD(14),CSD(14),SLOPED(14)/
     11,60,434,3410.0,20.50,.15/
      DATA TMD(14),(CAD(K),CBD(K),K=53,56)/700,,4.0824807E-03
     1,3.6063281E03,2.0657075E-02,3.4132764E+03,3.2288266E-
     203,3.6466751E+03,8.3579978E-02,2.7090814E+03/
      DATA SIGD(14),ED(14),CD(14)/3.190545,201.340
     1,.282000/
```

```
                    SULFUR HEXAFLUORIDE
      DATA COMPAD(15),COMPBD(15)/6HSULF. ,6HHEXAF./
      DATA PCOD(15),VCOD(15),TCOD(15),WD(15),C1RKVD(15),C2
     1RKVD(15),AMOWTD(15)/37.11,199.00,318.70,.190,.4278,
     2.0867,146.05/
      DATA KSD(15),ASD(15),BSD(15),CSD(15),SLOPED(15)/2,0.,
        1-0.,=0.,-0./
      DATA TMD(15),(CAD(K),CBD(K),K=57,60)/0.,6
     1*0.,7.3561084E-03,4,7443114E+03/
      DATA SIGD(15),ED(15),CD(15)/3.273865,201.215,.810000/


                          HYDROGEN
      DATA COMPAD(30),COMPBD(30)/6HHYDROG,6HEN    /
      DATA PCOD(30),VCOD(30),TCOD(30),WD(30),C1RKVD(30),
     1C2RKVD(30),AMOWTD(30)/20.20,51.50,43.60,0.,.4278,.0
     2867,2.00/


                          HELIUM
      DATA COMPAD(29),COMPBD(29)/6HHELIUM,6H      /
      DATA PCOD(29),VCOD(29),TCOD(29),WD(29),C1RKVD(29),
     1C2RKVD(29),AMOWTD(29)/6.67,37.50,10.47,0.,.4278,.086
     27,4.00/
     DATA KSD(29),ASD(29),BSD(29),CSD(29),SLOPED(29)/0,58.9
     187,2740.0,20.50,.13/


                          N-BUTANE
      DATA COMPAD(28),COMPBD(28)/6HN-BUTA,6HNE    /
      DATA PCOD(28),VCOD(28),TCOD(28),WD(28),C1RKVD(28),C2
     1RKVD(28),AMOWTD(28)/37.47,255.00,425.16,.200,.4450,.0
     1906,58,24/


                          ISOBUTENE
      DATA COMPAD(27),COMPBD(27)/6HISOBUT,6HENE   /
      DATA PCOD(27),VCOD(27),TCOD(27),WD(27),C1RKVD(27)
     1,C2RKVD(27),AMOWTD(27)/39.70,240.00,419.60,.190,.44
     220,.0902,56.11/


                          N-PENTANE
      DATA COMPAD(26),COMPBD(26)/6HN-PENT,6HANE   /
      DATA PCOD(26),VCOD(26),TCOD(26),WD(26),C1RKVD(26),C2
     1RKVD(26),AMOWTD(26)/33.25,304.00,496.60,.25
     22,.4510,.0919,72.15/


                          ISOPENTANE
      DATA COMPAD(25),COMPBD(25)/6HISOPEN,6HTANE  /
      DATA PCOD(25),VCOD(25),TCOD(25),WD(25),C1RKVD(25),C2
     1RKVD(25),AMOWTD(25)/33.37,306.00,460.39,.215,.4450,
     2.0906,72.15/
```



```
                          N-HEXANE
      DATA COMPAD(24),COMPBD(24)/6HN-HEXA,6HNO    /
            DATA PCOD(24),VCOD(24),TCOD(24),WD(24),C1RKVD
     1(24),C2RKVD(24),AMOWTD(24)/29.30,370.00,507.40,
```

```
2.298,.4570,,0935,86.18/

                        CYCLOHEXANE
DATA COMPAD(23),COMPBD(23)/6HCYCLOH,6HEXANE /
DATA PCOD(23),VCOD(23),TCOD(23),WD(23),C1RKVD(23)
1,C2RKVD(23),AMOWTD(23)/40.20,308.00,553.40,.209,
2.4440,,0903,84.16/

                        N-PENTANE
DATA COMPAD(22),COMPBD(22)/6HN-HEPT,6HANE   /
DATA PCOD(22),VCOD(22),TCOD(22),WD(22),C1RKVD(22),C2
1RKVD(22),AMOWTD(22)/27.00,432.00,540.20,.349,
2.4680,,0952,100.21/

                    K12 CORRECTION FACTORS
DATA (C(J),J=1,900)/900*0.0/
DATA (C(J),J=2,30)/2*1.,2*2,4.,5.,3.,5.,3.,2*2.,1.,2.,
16.,6*0,0,10.,2*8.,2*6.,2*4.,2*3./
DATA (C(J),J=33,60)/3*0.,1.,8.,5.,6.,5.,0.,2*3.,
12.,6.,6*0.,4.,2*3.,2*2.,2*1.,2*5./
DATA (C(J),J=64,90)/2*0.,1.,6.,4.,5.,4.,0.,3.,5.,2.,
13.,6*0,,4.,3*3.,2.,2*1.,2*5./
DATA (C(J),J=95,120)/2*0.,11.,9.,8.,9.,0.,6.,5.,
12*3.,6*0.,2.,1.,1.,0.,2*1.,0.,2*5./
DATA (C(J),J=126,150)/0.,10.,7.,2*7.,0.,6.,5.,2*3.
1,6*0.,2.,2*1.,0.,3*1.,2*7./
DATA (C(J),J=157,180)/16.,12.,9.,9.,2*6.,5.,2*
13.,13*0.,2*7./
DATA (C(J),J=188,210)/6.,8.,2.,9.,2*6.,2*5.,6*0
1.,3*20.,2*18.,4*16./
DATA (C(J),J=219,240)/8.,2*5.,2*6.,2*5.,6*0.,20.,2*16.
1,2*14.,2*12.,2*16./
DATA (C(J),J=250,270)/10.,9.,3*12.,10.,6*0.,16.,15.,13
1.,2*1.,2*9.,2*20./
DATA (C(J),J=281,300)/9.,3*1.,5.,6*0.,3*16.,2*13.,2*12.
1,2*15./
  DATA (C(J),J=312,330)/2*5.,3.,5.,6*0.,2.,2*1.,0.,2*1.,0.
  1,2*7./
  DATA (C(J),J=343,360)/3.,5.,10.,6*0.,3*9.,2*7.,4*5./
  DATA (C(J),J=374,390)/1.,3.,6*0.,3*9.,2*7.,4*5./
  DATA (C(J),J=405,420)/3.,6*0.,5*5.,4*3./

  DATA (C(J),J=442,450)/9*10./
  DATA (C(J),J=659,660)/2*20./
  DATA (C(J),J=689,690)/2*20./
  DATA (C(J),J=719,720)/2*15./
  DATA (C(J),J=749,750)/2*15./
  DATA (C(J),J=779,780)/2*15./
  DATA (C(J),J=809,810)/2*13./
  DATA (C(J),J=839,840)/2*13./
  DATA C(870)/10./
  CORRV(30,30)=0.0
  NSFI=0
  NSFII=0
  DO 6 J=1,NCOMP
  IF (KC(J))1,7,2
1 KC(J)=31+KC(J)
2 K=KC(J)
  PCO(J)=PCOD(K)
```

```
      VCO(J)=VCOD(K)
      TCO(J)=TCOD(K)
      W(J)=WD(K)
      C1RKV(J)=C1RKVD(K)
      C2RKV(J)=C2RKVD(K)
      AMOLWT(J)=AMOWTD(K)
      KS(J)=KSD(K)
      AS(J)=ASD(K)
       BS(J)=BSD(K)
       CS(J)=CSD(K)
      SLOPE(J)=SLOPED(K)
      COMPA(J)=COMPAD(K)
      COMPB(J)=COMPBD(K)
      IF (KS(J).LT.1) GO TO 6
     SIG(J)=SIGD(K)
      E(J)=ED(K)
      CP(J)=CD(K)
      TM(J)=TMD(K)
      NS=6*(K-1)+1
      NF=6*K
      L=0
      DO 3 I=NS,NF
      L=L+1
    AP(L,J)=APD(I)
      NS=4*(K-1)+1
      NF=4*K
      L=0
      DO 4 I=NS,NF
      L=L+1
      CA(L,J)=CAD(I)
4     CB(L,J)=CBD(I)
      IF (KS(J).EQ.2)GO TO 5
      NSFI=NSFI+1

      GO TO 6
5     NSFII=NSFII+1
6     CONTINUE
      NCD=NCOMP
      GO TO 8
7     NCD=J-1
8     CORRV(NCD,NCD)=0.0
      NCD1=NCD-1
      DO 10 J=1,NCD1
      CORRV(J,J)=0.0
      K=KC(J)
      J1=J+1
      DO 10 JJ=J1,NCD
      KK=KC(JJ)
      IF(KK.GT.K) GO TO 9
      CORRV(JJ,J)=C(30*(KK-1)+K)*0.01
      GO TO 10
9     CORRV(JJ,J)=C(30*(K-1)+KK)*0.01
10    CORRV(J,JJ)=CORRV(JJ,J)
      NHF=NSFI+NSFII
      RETURN
      END


      SUBROUTINE DPCHEK(T,P)
      COMMON/PHIB/NC,Y(10),FILP(800)/HYD/KIND,KB,JYM,KS(10),
```

```
      1CL(4,10),AP(6,10),TM(10),NSFI,NSFII,NHF
      KB=0
      NSFI=0
      NSFII=0
      NHFP=0
      Y1=0.0
      Y2=0.0
      DO 1 J=1,NHF
      IF(Y(J).GT.1.E-6) NHFP=NHFP+1
      IF (T.GT.TM(J)) KB=KB+1
      IF (KS(J).EQ.1) Y1=Y1+Y(J)
      IF (KS(J).EQ.2) Y2=Y2+Y(J)
1     CONTINUE
      IF (Y1.GT.1.0E-8) NSFI=1
      IF (Y2.GT.1.0E-8) NSFII=1
      KIND=1
      IF (NSFII.EQ.1) KIND=2
      IF (KB.LT.NHFP) GO TO 2
      WRITE(7,4)
      RETURN
2     NT=0
      KB=0
      IF(P.GT.0.0001) RETURN
      IF (T.GT.T0) NT=3
      PG=0.0
      YS=0.0
      PM=0.0
      DO 3 J=1,NHF
      PS=0.0
      PS=AP(NT+1,J)+AP(NT+2,J)/T+AP(NT+3,J)/(T*T)
      PS=EXP(PS)
      IF (PS.GT.PM)PM=PS
      PG=PG+Y(J)*PS
      YS=YS+Y(J)
3     CONTINUE
      IF (PG.GT.PM) PG=PM
      P=PG/YS
      RETURN
C
C
4     FORMAT (41H NO HYDRATE WILL FORM AT THIS TEMPERATURE)
      END


      SUBROUTINE DPCALC (T,P)

C
C     CALCULATION OF THE PRESSURE FOR A GIVEN TEMPERATURE
C
      COMMON /PHIB/NC,Y(10),FILB(800)/HYD/KIND,KBLOW,NJMAX,KS
     1(10),CL(4,10),AP(6,10),TM(10),NFI,NFII,NHF/GAS/
     2F(10),A(10),B(10),C(10),SLOPE(10)/LAT/NU(4),NS,NF/SCRA
     3CH/PHI (10),SC(4),FS(10),FILS(30)/CONST/R,GASR,T0
      REAL NU
      DATA (NU(I),I=1,4)/0.043478,0.13043,0.11765,0.058823/
      PSAVE=1.0E+08
      ERR1=1.0
      ERR2=1.0
      RT=R*T
      IF(KIND.EQ.2) GO TO 2
```

```
1       DV=0.1113
        IF(T.LT.T0) DV=0.0726
        NS=1
        NF=2
        GO TO 3
2       DV=0.1210
        IF(T.LT.T0) DV=0.0823
        NS=3
        NF=4
3       CALL BLAT (T,B0,P0)
        PG=P
        DEVM=0.01
C       START OF OUTER LOOP
4       DO 13 M=1,30
        CALCULATE FUGACITY COEFFICIENTS
        CALL PHIMIX (T,P,PHI)
        DO 5 J=1,NC
5       F(J)=PHI(J)*Y(J)*P
C       ESTIMATE GAS SOLUBILITY
        IF (T.LT.T0) GO TO 7
        XW=1.0

        DO 6 J=1,NC
        IF(A(J).LT.0.001) GO TO 6
        S=10.0**(-A(J)+B(J)/T+C(J)*ALOG10(T))
        X=(S/22414.6)/(1000./18.02+S/22414.6)
        HX=10.0**(SLOPE(J)*(P/T-1./T)-ALOG10(X))
        XW=XW-F(J)/HX
6       CONTINUE
7       XW =ALOG(XW)
        DO 8 I=NS,NF

        DO 8 J=1,NHF
        SC(I)=SC(I)+CL(I,J)*Y(J)*PHI(J)
55      FORMAT(8X,3E12.4,3I6)
8       CONTINUE
        PS=P
C       START OF INNER LOOP
        DO 11 MM=1,10
        GP=0.0
        G=0.0
        DO 10 I=NS,NF
        G=G+NU(I)*ALOG(1.0+SC(I)*PS)
        GP=GP+NU(I)*SC(I)/(1.0+SC(I)*PS)
10      CONTINUE
        G=B0+(PS-P0)*DV/RT-G-XW
        GP=DV/RT-GP
         P=PS-G/GP
        DEV=ABS((P-PS)/PS)
        IF (DEV.LT.DEVM)GO TO 12
        IF (P.LT.0.0) P=0.5*PS
11      PS=P
        IF (PSAVE.LT.0.99E+8) GO TO 17
        IF (KIND.EQ.2.AND.NFI.GT.0) GO TO 14
        ERR1=ERR1/2.
        IF (DEV.LT.ERR1) GO TO 9
        WRITE (4,20)DEV
        KBLOW=1
        RETURN
12      D=ABS((P-PG)/PG)
```

```
      IF (D,LT.Ø.ØØ1) GO TO 14
      DEVM=Ø.1*D
      IF (DEVM.GT.Ø.Ø1) DEVM=Ø.Ø1
13    PG=P
      IF (PSAVE.LT.Ø,998E+8)GO TO 17
      ERR2=ERR2/2.Ø
      IF(D.LT.ERR2)GO TO 4
      IF(KIND.EQ.2.AND.NFI.GT.Ø) GO TO 14
      WRITE(7,19) D
      KBLOW=1

14    CONTINUE
      IF (KIND.EQ.1) GO TO 16
     CHECK TO SEE IF HYDRATE I IS PRESENT
      IF (NFI.EQ.Ø) RETURN
      PSAVE=P
      NS=1
      NF=2
      KIND=1
      DO 15 J=1,NC
15    FS(J)=F(J)
      GO TO 1
16    IF (P,LT.PSAVE) RETURN
17    KIND=2
      NS=3
      NF=4
      P=PSAVE
      DO 18 J=1,NC
18    F(J)=FS(J)
      RETURN
C
C
19    FORMAT (52H PROBLEM DID NOT CONVERGE IN OUTER LOOP,
      1 DEVIATION =,E11.3)
2Ø    FORMAT( 52H PROBLEM DID NOT CONVERGE IN INNER LOOP,
      1 DEVIATION =,E11.3)
      END


      SUBROUTINE BLAT (T,BØ,PØ)
      DIMENSION A(15), SH(2), SMU(3)
      COMMON /HYD/ KIND,KBLOW,NJMAX,KS(1Ø),CL(4,1Ø),AP(6,1Ø),TM(1Ø)
      1,NFI,NFII,NHF/GS/NPT,X(2Ø),WT(2Ø)/CONST/R,GASR,TICE
      DATA TH,H, DAH,DBH/291.,-2616.398,Ø.2Ø6166E+2,-Ø.211
      1634E-1/
      DATA SH(1),SH(2),SMU(1),SMU(2)/275.66,193.Ø,3Ø2.Ø1,211./
      DATA (A(J),J=1,15)/23.Ø439,-3357.57,-1.85,-12
      112.2,44344.Ø,187.719,11.5115,-4Ø92.37,Ø.316Ø33,
      2-1Ø23.14,34984.3,159.923,4Ø71.64,-193428.8,-599.755/
      PR=Ø.Ø
      TØ=TICE
      TMU=SMU(KIND)
      HO=SH(KIND)
      DVL=Ø.Ø387
      IF (KIND.EQ.2) GO TO 1
      NT=3
      DVO=Ø.Ø726
      GO TO 3
1     DVO=Ø.Ø823
      IF (T,LE.TH) GO TO 2
```

```
      PR=79,5065
      TMU=320.902
      T0=TH
      NT=12
      GO TO 4
    NT=9
3     IF(T.GT.T0) GO TO 4
      DVL=0.0
      NT=NT-3
4     A1=A(NT+1)
      A2=A(NT+2)
      A3=A(NT+3)
      PICE=EXP(A1+A2/T0+A3*ALOG(T0))
      TMUO=(TMU+(DVO*DVL)*(PICE-PR))/T0
      P0=EXP(A1+A2/T+A3*ALOG(T))
      PINT=0.0
      DO 5 NG=1,NPT
      TI=(T*(X(NG)+1.0)-T0*(X(NG)-1.0))/2.0
      PI=EXP(A1+A2/TI+A3*ALOG(TI))
      DPDT=PI*(A3-A2/TI)/TI
      GI=DPDT*WT(NG)/TI
5     PINT=PINT+GI
      HINT=HO*(1.0/T-1.0/T0)
      IF(T.GT.T0)HINT=HINT*DAH*ALOG(T/T0)+DBH*(T-T0)-H*(1.0
     1/T-1.0/T0)
      B0=(TMUO+(T-T0)/2.0*(DVL+DVO)*PINT+HINT)/R
      RETURN
      END


      SUBROUTINE PHIMIX( T,P,PHI)
      DIMENSION PHI(10),PC(10),VC(10),TC(10),A(4),Z(3),ARKV
     1(10,10),BRKV(10),AIRKV(10),PHILN(10),TCIJ(10,10),PCIJ
     2(10,10)
      COMMON /PHIB/ NCOMP,Y(10),TCO(10),AMOLWT(10),
     1PCO(10),C1RKV(10),C2RKV(10),TCOIJ(10,10),AMWTIJ(10,10),
     2PCOIJ(10,10)/CONST/R,GASR,T0
      RT=GASR*T
    DO 1 I=1,NCOMP
      PC(I)=PCO(I)/(1.0+44.2/(AMOLWT(I)*T))
      TC(I)=TCO(I)/(1.0+21.8/(AMOLWT(I)*T))
      ARKV(I,I)=C1RKV(I)*GASR**2*(TC(I)**2.5)/PC(I)
      BRKV(I)=C2RKV(I)*GASR*TC(I)/PC(I)
      IF (I.EQ.NCOMP) GO TO 2
      I1=I+1
      DO 1 J=I1,NCOMP
      TCIJ(I,J)=TCOIJ(I,J)/(1.0+21.8/(AMWTIJ(I,J)*T))
      PCIJ(I,J)=PCOIJ(I,J)/(1.0+44.2/(AMWTIJ(I,J)*T))
      ARKV(I,J)=(C1RKV(I)+C1RKV(J))*0.5*GASR**2*TCIJ(I,J)**2
     1.5/PCIJ(I,J)
*     ARKV(J,I)=ARKV(I,J)
1      CONTINUE
2     CONTINUE
      AMRKV=0.0
      BMRKV=0.0
      DO 3 I=1,NCOMP
      AIRKV(I)=0.0
      BMRKV=BMRKV+Y(I)*BRKV(I)
      DO 3 J=1,NCOMP
3     AIRKV(I)=AIRKV(I)+Y(J)*ARKV(I,J)
```

```
      A(1)=1.Ø
      A(2)=-1.Ø
      PBRT=P*BMRKV/RT
     ABRT=AMRKV/(BMRKV*GASR*T**1,5)
      A(3)=PBRT*(ABRT-1.Ø-PBRT)
      A(4)=-ABRT*(PBRT**2.Ø)
      CALL CUBEQN(MTYPE,Z,A)
      IF(MTYPE)4,5,5
4     ZV=AMAX1(Z(1),Z(2),Z(3))
      GO TO 6
5     ZV=Z(1)
6     VV=ZV*RT/P
      QVVB=ALOG(VV/(VV-BMRKV))
      Q1VB=1.Ø/(VV-BMRKV)
      Q2RTB=2.Ø/(GASR*T**1,5*BMRKV)
      QVBV=ALOG((VV+BMRKV)/VV)
      QARTB=AMRKV/(GASR*T**1,5*BMRKV**2.Ø)
      QBVB=BMRKV/(VV+BMRKV)
      DO 7 I=1,NCOMP
      PHILN(I)=QVVB+BRKV(I)*Q1VB-AIRKV(I)*Q2RTB*QVBV+BR
      1KV(I)*QARTB*(QVBV-QBVB)-ALOG(ZV)
7     PHI(I)=EXP(PHILN(I))
      RETURN
      END


      SUBROUTINE CUBEQN (MTYPE,Z,A)
      DIMENSION A(4),Z(3),B(3)
      B(1)=A(2)/A(1)
      B1OV3=B(1)/3,
      B(2)=A(3)/A(1)
      B(3)=A(4)/A(1)
      ALF=B(2)-B(1)*B1OV3
      BET=2,Ø*B1OV3**3-B(2)*B1OV3+B(3)
      BETOV2=BET/2.Ø
      ALFOV3=ALF/3.Ø
      CUAOV3=ALFOV3**3
      SQBOV2=BETOV2**2
      DEL=SQBOV2+CUAOV3
      IF(DEL)9,1,4
1     MTYPE=Ø
      GAM=SQRT(-ALFOV3)
      IF(BET)3,3,2
2     Z(1)=-2.Ø*GAM-B1OV3
      Z(2)=GAM-B1OV3
      Z(3)=Z(2)
      GO TO 13
3     Z(1)=2.Ø*GAM-B1OV3
      Z(2)=-GAM-B1OV3
      Z(3)=Z(2)
      GO TO 13
    MTYPE=1
      EPS=SQRT(DEL)
      TAU=-BETOV2
      RCU=TAU+EPS
      SCU=TAU-EPS
      SIR=1,Ø
      SIS=1,Ø
      IF(RCU)5,6,6
```

```
5       SIR=-1.Ø
6       IF(SCU)7,8,8
7       SIS=-1.Ø
8       R=SIR*(SIR*RCU)**Ø.33333333
        S=SIS*(SIS*SCU)**Ø.33333333
        Z(1)=R+S-B1OV3
        Z(2)=-(R+S)/2.Ø-B1OV3
        Z(3)=Ø.8660254Ø*(R-S)
        GO TO 13
9       MTYPE=-1
        QUOT=SQBOV2/CUAOV3
        ROOT=SQRT(-QUOT)
        IF(BET)11,1Ø,1Ø
1Ø      PEI=(1.5707963+ATAN(ROOT/SQRT(1.Ø-ROOT**2)))/3.Ø
        GO TO 12
11      PEI=ATAN(SQRT(1.Ø-ROOT**2)/ROOT)/3.Ø
12      FACT=2.Ø*SQRT(-ALFOV3)
        Z(1)=FACT*COS(PEI)-B1OV3
        Z(2)=FACT*COS(PEI+2.Ø943951)-B1OV3
        Z(3)=FACT*COS(PEI+4.1887902)-B1OV3
13      RETURN
        END


        SUBROUTINE GAUSS (CB,T)
C
C       CALCULATION OF LANGMUIR CONSTANTS USING GAUSSIAN
C       INTEGRATION
C
        DIMENSION A(4),Z(4),CB(4,1Ø)
        COMMON /HYD/ KIN,KBLOW, NCD,KS(1Ø),CL(4,1Ø),FIL(72)
        1,NHF/GS/NPT,X(2Ø),WT(2Ø)/KIHARA/SIGP(1Ø),EP(1Ø),CP(1Ø)
        DATA PI,BK/3.1416,1.3804E-16/
        DATA (A(I),Z(I),I=1,4)/3.95,2Ø.Ø,4.3Ø,24.Ø,3.91,2Ø.Ø
        1,4.73,28.Ø/
        KBLOW=Ø
        DO 5 J=1,NHF
        DO 1 I=1,4
1       CL(I,J)=Ø.Ø
        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.Ø) GO TO 5
        RCA=RC/A(I)
        CA=C/A(I)
C       NEWTON RAPHSON METHOD FOR FINDING INTEGRATION LIMIT,
C       YL  FIRST GUESS S=Ø.4

        S=Ø.4
        RCA6=RCA**6
        RCA12=RCA**12
        DO 2 N=1,2Ø
        IF (S.GT.1.Ø.OR.S.LE.Ø.Ø) GO TO 6
        UM=1.Ø/(1.Ø-S-CA)
        UP=1.Ø/(1.Ø+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*DB12-2.0*RCA6*DB6
      A10=UM11/UM-UP11/UP
      A11=UM11-UP11
      B12=(0.1*A10+CA*A11/11.0)
      A4=UM5/UM-UP5/UP
      A5=UM5-UP5
      B6=A4/4.0+CA*A5/5.0
      B=RCA12*B12-2.0*RCA6*B6
      W=Z(I)*EK/(2.0*S*T)*B
      DWY=-W/S+Z(I)*EK*DB/(2.0*S*T)
      DS=S-(W-10.0)/DWY
      IF (ABS((DS-S)/DS).LT.0.01) GO TO 3
2     S=DS
3     YL=S
C     GAUSSIAN INTEGRATION
      P=2.0*PI*A(I)**3./(T*136.2)*YL
      SQ=0.0
      DO 4 N=1,NPT
      Y=YL*(X(N)+1.0)/2.0
      UP=1.0/(1.0+Y-CA)
      UM=1.0/(1.0-Y-CA)
      UP5=UP**5
      UM5=UM**5
      A4=UM5/UM-UP5/UP
      A5=UM5-UP5
      B6=A4/4.0+CA*CA*A5/5.0
      UP11=UP**11
      UM11=UM**11
      A10=UM11/UM-UP11/UP
      A11=UM11-UP11
      B12=(0.1*A10+CA*A11/11.0)
      B=RCA12*B12-2.0*RCA6*B6
      W=Z(I)*EK/(2.0*Y*T)*B
4     SQ=SQ+EXP(-W)*Y**2*WT(N)
      CL(I,J)=P*SQ
5     CONTINUE
      RETURN
6     KBLOW=2
      WRITE(7,7)J
      RETURN
C
C
7     FORMAT(10H COMPONENT,I2,35H CAUSED PROBLEM TO BLOW UP IN GAUSS)
      END
```

*** SAMPLE PROBLEM * DATA DECK ***

```
YDRATE DATA OF ROBINSON + HUTTON,J CAN PET TECH 7,1(1967)
,7,9
,1,0,0
2,0,22.3,5,7,2,0
0.0,360,0
0.0,765,0
,0,0.0
2.5,22.0,5,5
4.0,1095.0
2.3,22.2,5,5
9.0,1742.0
,0,0.0,0.0,0.0
```

HYDRATE DATA OF ROBINSON + HUTTON, J CAN PET TECH 7,1(1967)

	PROBLEM NUMBER		TEMP. DEG. F	PRESS. PSIA	COMPONENT	COMPOSITION MOLE FRACTION GAS PHASE
	1	ESTIMATED	50.0	360.0		
		CALCULATED	50.0	396.2		
						0.7200
						0.2230
						0.0570
	2	ESTIMATED	60.0	765.0		
		CALCULATED	60.0	772.4		
						0.7200
						0.2230
						0.0570
0	3	ESTIMATED	64.0	1095.0		
		CALCULATED	64.0	1085.2		
						0.7250
						0.2200
						0.0550
0	4	ESTIMATED	69.0	1742.0		
		CALCULATED	69.0	1784.2		
						0.7230
						0.2220
						0.0550

APPENDIX E

Primary Data

Run #	T °C	C g/l	P^V mm Hg	P_T mm Hg	P_f mm Hg	N counts	P_f mm Hg
1	0.10	1.1	4.612	431.6	289.0	6443	349.0
2	0.08	0.5	4.616	478.6	320.0	-	-
3	0.10	1.5	3.510	349.2	235.1	13020	361.0
4	0.05	10.0	4.589	302.0	236.5	14160	335.1
5	0.08	0.0	4.618	373.8	252.2	6220	300.2
6	5.00	0.0	6.548	934.8	655.6	4068	736.1
7	0.1	0.0	4.619	69.28	50.2	18616	94.6
8	5.00	0.5	6.544	471.9	436.1	7729	557.0
9	5.01	1.1	6.541	465.9	327.0	14770	208.8
10	5.02	1.5	6.538	579.9	410.0	14370	678.5
11	5.05	10.0	6.505	662.4	472.0	13000	749.0
12	3.05	0.0	5.692	518.2	355.7	11830	521.1
13	3.05	0.5	5.688	576.0	396.0	12710	606.0
14	3.01	1.1	5.685	632.0	435.0	12165	652.1
15	3.09	1.5	5.670	544.7	375.0	16580	689.0
16	3.05	10.0	5.396	565.3	395.1	13020	619.3

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