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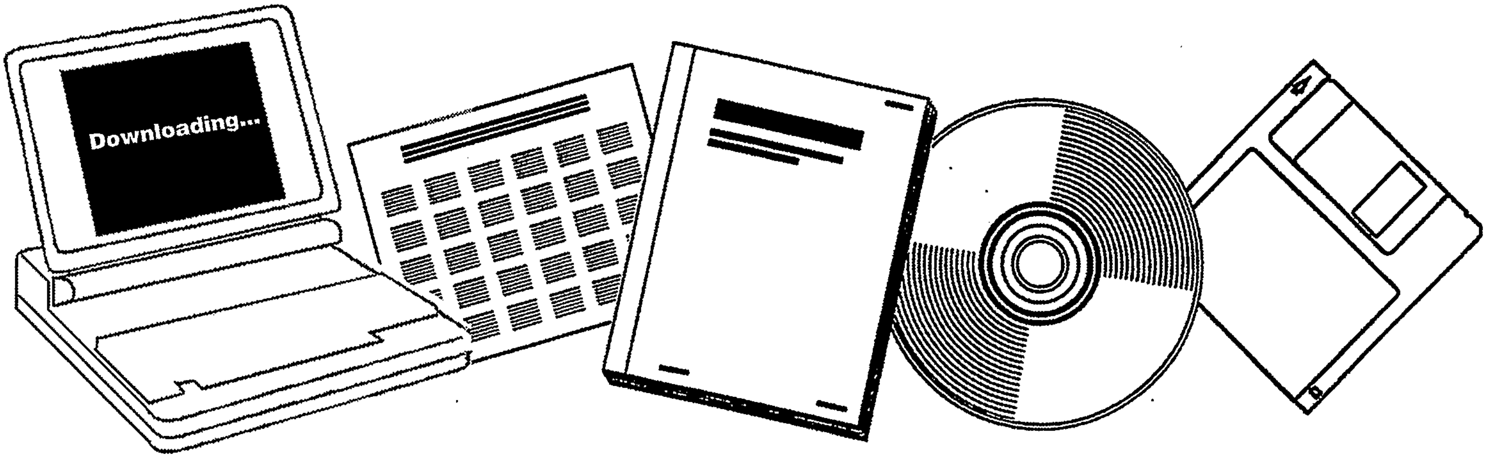
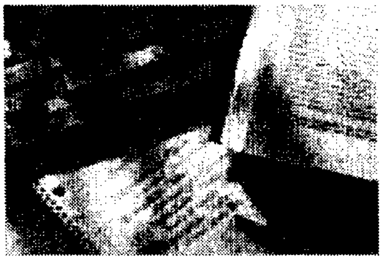
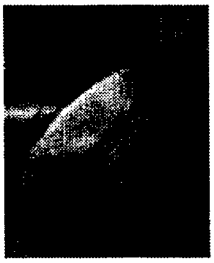
AUTOMATION OF A HYDROGEN PROBE FOR DETERMINATION OF HYDROGEN SOLUBILITIES IN COAL LIQUIDS SOLVENTS

PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL
AND PETROLEUM ENGINEERING

1987







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by

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Finally, I would like to acknowledge the support that my wife, Paola, gave me during the hard times.

This work is dedicated to my Wife and Son

ABSTRACT

Signature

AUTOMATION OF A HYDROGEN PROBE FOR DETERMINATION OF HYDROGEN SOLUBILITIES IN COAL LIQUID SOLVENTS

Carlos R. Alonso Karlezi

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The Hydrogen Probe Equipment developed in our laboratory, was automatized in order to improve the data adquisition of the variables involved in the process as are temperatures, pressures and the time of travel for the mercury bead. The equipment was tested by studing the hydrogen-tetralin, hydrogen-tetralin-methane and hydrogen-tetralin-ethane systems.

A 300-ml autoclave equipped with a magnetically driven agitator was used as a equilibrium cell. The in-situ hydrogen probe was used to measure the hydrogen partial pressure in the mentioned systems.

The partial pressure of methane was varied from 0 to 1000 psi while the temperature was 325 °C and 375 °C. The ethane partial pressure was varied from 0 to 585 psi and the temperature was 360 °C and 395 °C. For the hydrogen-tetralin system, the temperature was 350 °C and 390 °C.

Results from the hydrogen-tetralin system show good agreement when compared with literature data. As they show, the hydrogen solubility of hydrogen in tetralin increase when the temperature and pressure are increased. For the ternary systems, it was found that the hydrogen solubility in tetralin increased when the partial pressure of the third component added (methane or ethane) was increased and the partial pressure of hydrogen was held constant.

The experimental values for the K-value for hydrogen and tetralin where compared with the predicted value by using the correlations proposed by Chao and Seader in 1961 for tetralin and the correlation proposed by Sebastian et al. in 1980 for hydrogen. The experimental values show a good agreement with the predicted values by using these correlations.

Besides the experimental work done, a commercial equipment of the hydrogen probe system was constructed to be used in the plant that Catalytic Inc. operates in Wilsonville, Alabama.

DESCRIPTORS

Ethane

Hydrogen

Methane

Phase Equilibria

Commercial H_2 Probe

Hydrogen Probe

Computer control system

Microflowmeter

Tetralin

Toepler pump

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

A	Logarithmic mean surface area of the nickel tube, m
C_d	Dissolved concentration of hydrogen, kgmole/m^3
D	Diffusivity constant
E	Activation Energy
$H_2(g)_1$	Hydrogen concentration on side 1, kgmole/m^3
$H_2(g)_2$	Hydrogen concentration on side 2, kgmole/m^3
$H_2(s)_1$	Hydrogen adsorbed on side 1, kgmole/m^3
$H_2(s)_2$	Hydrogen adsorbed on side 2, kgmole/m^3
K	K-value (= y/x)
k_p	Mass transfer coefficient, Kgmole/m^2/sec/$MPa^{0.5}$
K_d	Solubility constant
N_d	Rate of diffusion, kgmole/m^2/sec
P_1	Hydrogen pressure inside the probe, MPa
P_2	Hydrogen pressure outside the probe, MPa
Q	Hydrogen permeation flow, m^3/sec (NTP)
R	Universal constant of the gases
T	Temperature
x	Mole fraction on the liquid phase
X	Thickness of the nickel tube
y	Mole fraction on the gas phase

Greeks

ϕ	Permeability constant, m^3(NTP)/sec/m^2/$MPa^{0.5}$

1. INTRODUCTION

Coal liquefaction has been used to provide a liquid fuel for its use on industrial and non-industrial equipment. The process of coal liquefaction increases the H/C ratio of the coal by the addition of hydrogen. This is neccesary since the coal has a much lower H/C ratio than liquid hydrocarbons and crude oil.

The study of coal liquefaction is complicated by the fact that coal is not a single molecule but an abundance of various molecules and several impurities. The behavior of hydrogen in coal liquids plays an important role in the design and development of coal liquefaction processes. Several mixtures containing typical hydrocarbon components have been used to model coal liquid. By using these mixtures, studies have been completed in the determination of the effects of hydrogen on coal liquid constituents.

The hydrogen solubility in tetralin in the systems hydrogen-tetralin, hydrogen-tetralin, methane and hydrogen-tetralin-ethane was investigated in this work. Tetralin is a good coal liquid model and it is able to penetrate the coal interstices and thus increases the surface area.

The experiments were performed in a 300-cc, high temperature and pressure batch-stirred reactor equipped with temperature controlling devices. A hydrogen probe was used to determine the hydrogen partial pressure in the system. The experiments were carried out over a temperature range between 598 and 668 ^{o}K and pressures up to 17 MPa.

The hydrogen probe equipment was first made automatic so that the experimental studies would have a more reliable and accurate data adquisition system. The computer based designed system accomplish these objectives.

Also a commercial hydrogen probe was built to be employed in the pilot plant of

Catalytic Inc. in Wilsonville, Alabama. Preliminary results show that the equipment is working for the purposes for which it was designed.

2. BACKGROUND

2.1 LITERATURE REVIEW

2.1.1 Effect of Pressure and Temperature on Hydrogen Solubilities

The study of the effect of pressure and temperature on the solubility of hydrogen in different solvents is well documented. Lin et al.(1)* have shown that the hydrogen solubility in SRC II liquid increases when the temperature is increased. The same effect is observed when the pressure of the system is increased. Ohsima et al.(2) determined that the hydrogen concentration in coal derived liquid increases proportional with the hydrogen partial pressure and with the square of the system temperature. Ding et al.(3) have shown that the hydrogen solubility in SRC II liquid increases to a maximum with temperature and the decreases. Harrison et al.(4) determined solubilities of hydrogen in different solvents, as are tetralin, SRC II middle distillate and SRC II heavy distillate. They found that hydrogen is more soluble when pressure and temperature are increased.

Prather et al.(5) used temperatures between 100 and 400 °C and pressures between 3.44 MPA (500 psi) and 20.68 MPa (3000 psi) to determine the solubility of hydrogen in creosote oil. They found that the hydrogen solubility was more appreciable increased when the temperature was increased. Data from a pilot plant obtained from Exxon and Gulf(6) shown that the solubility of hydrogen tends to increase when the pressure is increased. Kara et al.(7) investigated the hydrogen-tetralin system. Their results show that the hydrogen solubility in tetralin increases with both temperature and pressure with temperatures up to 640 °K, and then the hydrogen solubility decreases. Also they found that the solubility of hydrogen in hydrotreated SRC II liquid increases when total pressure is increased.

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* Parenthical references placed superior to the line of text refer to the bibliography

Simnick et al.[8], using a flow type apparatus, investigated the hydrogen-tetralin system at temperatures between 189.6 °C and 399.1 °C and pressures between 20 and 250 atm. Their results shown that the hydrogen solubility increased with temperature and pressure. In another study, Simnick et al.[9], using the same flow type apparatus as in their previous work studied vapor-liquid equilibria of ternary mixtures of hydrogen-methane- tetralin. Their results show that if the concentration of methane is increased in the gas feed, the solubility of hydrogen in tetralin decreased. Also they observed that the hydrogen solubility in tetralin increased when the temperature and total pressure increased.

2.1.2 Solubility of hydrogen in organic solvents

The same behavior for the hydrogen solubility that was observed for coal liquids is observed in organics. Brunner[10] investigated the hydrogen solubility in 10 differents organic solvents. He found that the solubility of hydrogen decreased when the partial pressure of hydrogen was held constant. Using temperatures up to 440 °C and pressures up to 2500 bars, Seward et al.[11] showed that the hydrogen concentration in water increases when the pressure is increased. The hydrogen solubility in diphenilmethane was found to increase with pressure and especially with temperature by Simnick et al.[12] More data by Simnick are found for the system methane-quimoline[13], hydrogen-mxylene and hydrogen- m-cresol[14].

Lin et al.[15] have obtained data for the system hydrogen-hexadecane and methane-n-hexadecane. As methane concentration is increased, Sagara et al.[16] have shown that hydrogen solubility in ethylene decreases. Ding[17] found that hydrogen concentration in coal liquid decreases when the methane partial pressure is increased.

Using a dynamic flow type equilibirum cell, Thompson and Edmister[18] studied vapor-liquid equilibria for hydrogen-bencene and hydrogen- cyclohexane at pressures up to 100 MPa (1000 atm) and temperatures from 298 to 673 °K. Brainard[19] found that the addition of cyclohexane to the quaternary system of hydrogen-bencene-cyclohexane-n-hexane will decrease hydrogen solubility in benzene.

The concentration of hydrogen in methanol was found to decrease due to the presence of reaction species from the hydrogenation of p–nitrotoluene in studies by Choudhanry et al.(20) Benham et al.(21) showed that the solubility of hydrogen in hydrocarbons decreases with decreases in temperature.

More data on systems containing hydrogen are found in the following references:

- Silver(22); ternary and quaternary systems of hydrogen, n–hexane, cyclohexane and benzene at 311 and 367 °K and pressures of 1000 and 2000 psi.

- Oliphant et al.(23); ternary system hydrogen– tetralin–mxylene and hydrogen–tetralin–m–xylene.

2.2 THEORETICAL BASIS FOR NICKEL PROBE

2.2.1 Hydrogen Permeation through Nickel

The permeation of hydrogen through metals has been studied for more than fifty years. The permeation has been shown to be atomic in nature(24). Among the features of hydrogen permeation in and through metals is the finding that 10 to 15 times higher permeation factor are obtained when compared with oxygen and nitrogen permeation at the same temperature.

Nickel was chosen to built the hydrogen probe because of its mechanical stability, chemical inertness and reasonable permeability. Gala(25) was the first to test this metal in the development of a hydrogen probe applied to coal liquefaction processes.

It has been postulated that the sequence of steps that represents the hydrogen permeation through nickel membrane is as follows(26):

1. Physical adsorption of hydrogen on the metal surface.

2. Dissociation of hydrogen into its atomic form and dissolution into the bulk metal.

3. Diffusion of the dissolved atomic hydrogen through the metal structure.

4. Combination of the dissolved atomic atoms into the hydrogen molecule at the other side of the nickel surface.

5. Desorption of the adsorbed molecular hydrogen from the metal surface into the bulk phase.

Among the five steps just mentioned, the diffusion one is the lowest step in all the process(27,36,37,38), so the overall permeation rate is determined by the rate of diffusion. The previous mechanism yields to an expression for hydrogen permeation rate through a nickel membrane as follows;

$$Q = \{(K_d \times D \times A)/(X)\} (P_1^{0.5} - P_2^{0.5}) \qquad (2\text{-}1)$$

In this expression, Q is the volumetric permeation rate of hydrogen through the nickel wall; D is the diffusivity constant; K_d is a solubility constant; A is the logarithmic mean surface area of the nickel probe; P_1 and P_2 are the hydrogen partial pressures inside and outside the probe respectively and X is the wall thickness of the nickel tube. A detail explanation of how equation 2.1 was developed is explained in appendix A.

Some investigations of hydrogen permeation through nickel at high pressures have been reported in the literature (28,29). Experimental studies of hydrogen permeation through a nikel probe over a wide range of pressure and temperature and the development of an unique in-situ nickel probe has been conducted in our laboratory.(17,25,30,31,32)

2.2.2 Permeability Coefficient of Hydrogen Through Nickel

If equation 2.1 is observed, it can be noticed that there are two terms that can be considered as one, these are the solubility constant, K_d, and the permeability coefficient, D. This combined new term is called the permeability coefficient and can be expressed as the product of these two terms as follows;

$$\phi = K_d * D \tag{2-2}$$

Both, the diffusivity and solubility constants follow an Arrenihus type of temperature dependency:

$$K_d = K_o \exp\ [-E_k/RT] \tag{2-3}$$

$$D = D_o \exp\ [-E_d/RT] \tag{2-4}$$

Therefore, the permeability coefficient may be written like:

$$\phi = K_d D = K_o D_o \exp(-(E_k+E_d)/RT) \tag{2-5}$$

$$\phi = \phi_o \exp(-E/RT) \tag{2-6}$$

In this equation, E represents the activation energy and T the temperature in degrees Kelvin. The logarithm of the permeability coefficient is a linear function of the reciprocal of the temperature, so:

$$\ln\phi = \ln\phi_o - E/RT \tag{2-7}$$

The values of the slope, E/R and the values of $\ln(\phi_o)$ can be determined experimentally by measuring the hydrogen permeation at a fixed temperature and knowing all the geometric data for the nickel tube and the pressures inside and outside the probe.

3. EXPERIMENTAL

The laboratory set-up is shown in figure 3.1. The experimental equipment consists of four different sections: (1) high pressure section, (2) sampling system and low pressure section, (3) control system and (4) electrical panel.

3.1 HIGH PRESSURE SECTION

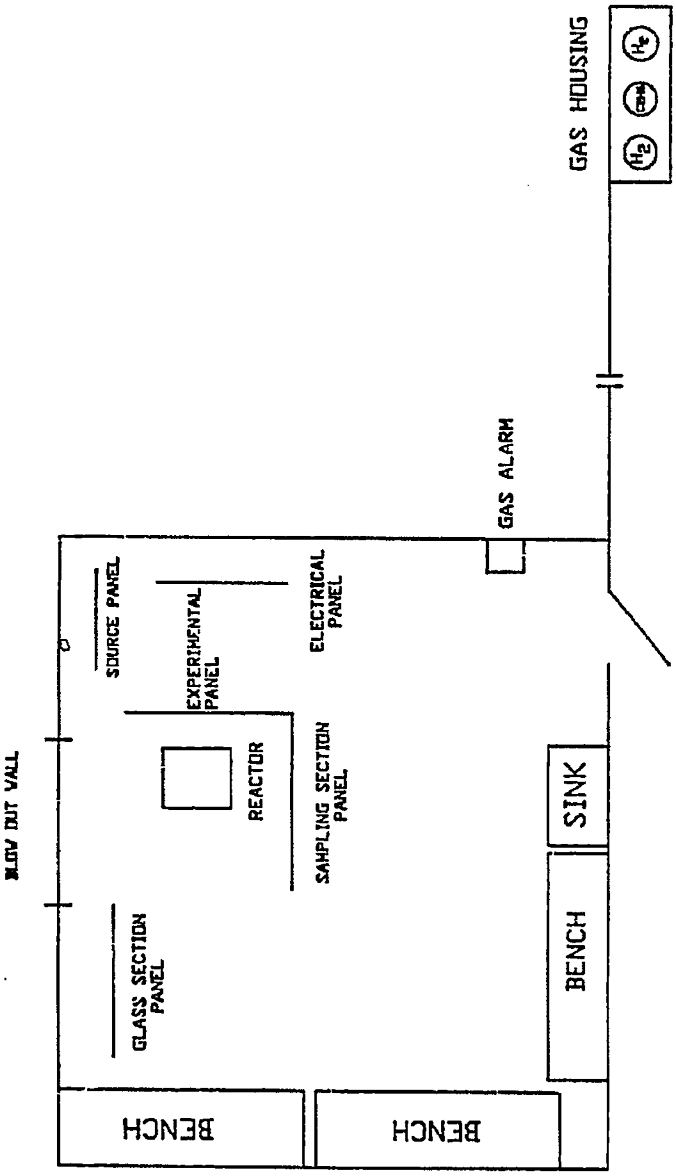
This section was designed for being used with high temperatures and pressures and consists of a source section, a stirred equilibrium cell, a high pressure microflowmeter and two hydrogen probes.

3.1.1 Source Section

This section is used to provide the high pressure gases; helium, hydrogen, methane and ethane, and the liquid solvent, tetralin to the equilibrium cell and the microflowmeter. The gases have different uses: helium (41 MPa (6000 psig) and 99.995% purity) is used for pressure testing of the equipment while hydrogen (41 MPa (6000 psig) and 99.995 % purity), methane (17 MPa (2500 psig) and 99.9% purity), ethane (17 MPa (2500 psig) and 99.9% purity) and the solvent, tetralin (99.99% purity) are used for the equilibrium studies. All four gases were provided by the Harvey Company and the tetralin by Fisher Scientific.

The gas cylinders are placed outside the laboratory for safety reasons. From the cylinders to the source panel inside the laboratory, 1/8" O.D. stainless steel tubing, rated at 69 MPa (10,000 psig) at room temperature, was used. In the source panel, each line has its own pressure gauge, so the pressure in each line is known. Two of the lines, hydrogen and helium, go into a surge tank located behind the source panel, while the methane (or ethane) line is bypassed from the panel and goes directly to the

Figure 3-1: LABORATORY SET-UP



equilibrium cell. This procedure was employed in order to use the methane (or ethane) efficiently. The flow rates of each gas are controlled by using needle valves which are rated to 41 MPa (6,000 psig). The surge tank is used to have a high pressure reservoir of gas, so the cylinder is not exposed directly to the system. The pressure in the surge tank is monitored by using a Heise gauge which has a range from 0 to 5000 psia with divisions of 5 psi. A pressure transducer is installed in the same line as it is the Heise gauge.

The liquid feed container is located over the equilibrium cell. This is a one-liter expansion cylinder and it is connected directly to the reactor. Tetralin is introduced in this cylinder and then it is charged into the reactor by opening a Jamesbury air-actuated ball valve that allows the solvent to flow into the reactor. The source section is schematically shown in figure 3.2.

3.1.2 Equilibrium Cell

A 300 cc autoclave, made of 316 stainless steel is employed as the equilibrium cell. This autoclave was purchased from Autoclave Enginneers Inc. and is designed to withstand pressures up to 37 MPa (5,400 psig) at 650°F. Figure 3.3 shows a schematic drawing of the equilibrium cell.

The equilibrium cell is equipped with gas and liquid inlets, sampling ports for the liquid and gas phases, a bottom port used to remove the liquid from the reactor and a rupture disk that blows up when the pressure inside the reactor exceds 5,000 psi. Inside the cell there are two probes (one for the liquid phase and another for the gas phase), two type K-thermocuples that measure the temperatures in the liquid and gas phases and a variable speed magnetically driven agitator.

All the lines are made from 1/8" O.D. 304 stainless steel tubing. The only exception is the solvent charging line that was made of 1/4" O.D. 304 stainless steel tubing.

Figure 3-2: SOURCE SECTION

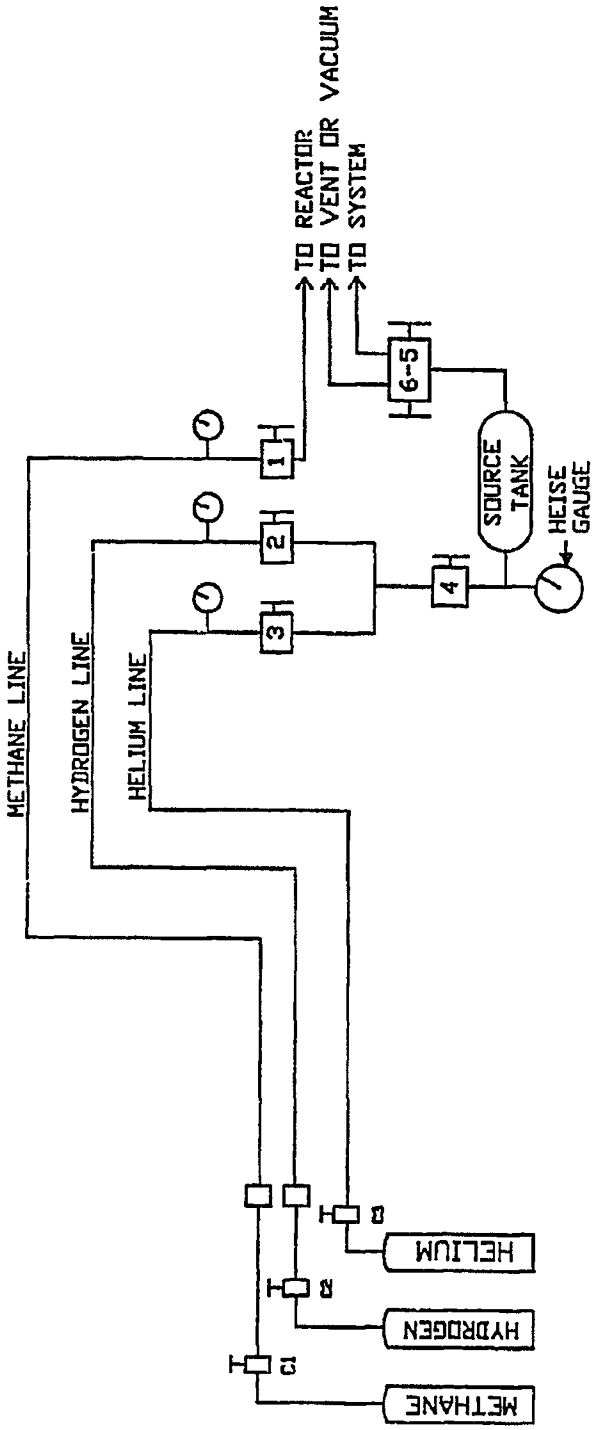
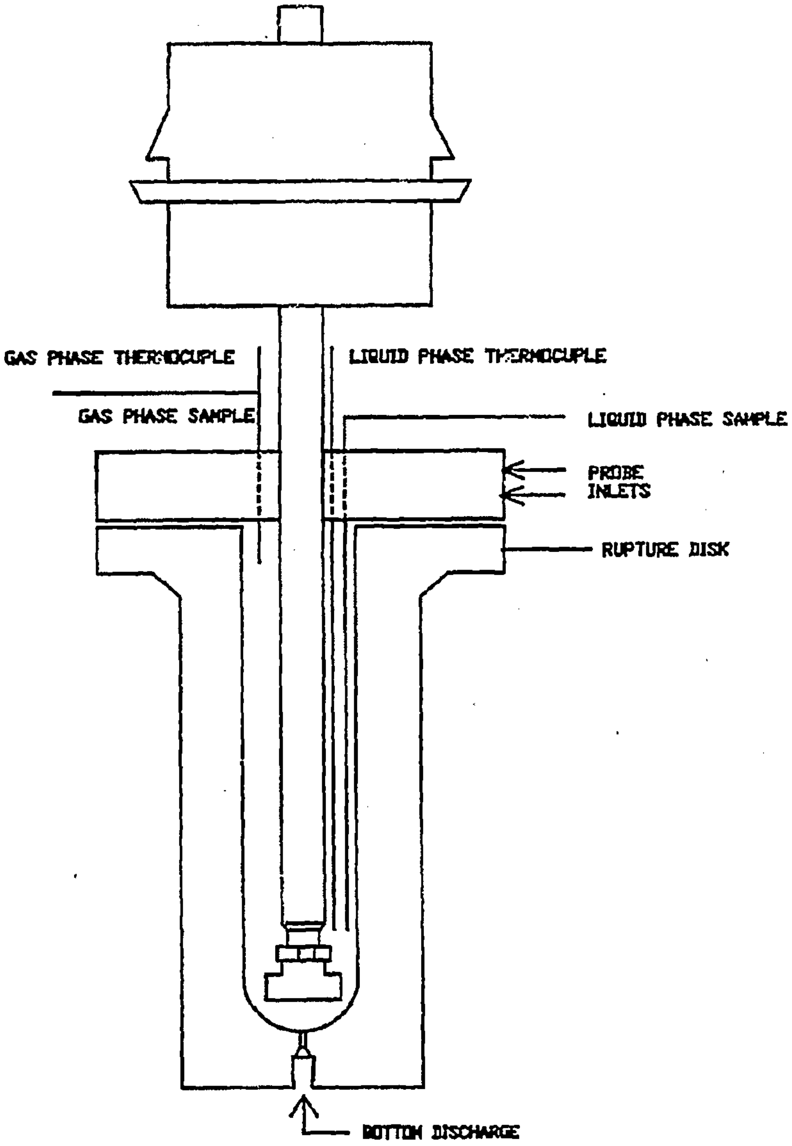


Figure 3-3: EQUILIBRIUM CELL



The pressure inside the reactor is read by a Heise gauge via a pressure transducer that reduces the thermal effects on the pressure readings. This transducer transmits the pressure of the reactor by compressing a viscous fluid, so the reactor pressure can be read without thermally damaging the Heise gauge's bourdon tube. The Heise gauge can read pressures up to 5,000 psia and has divisions of 2 psi. Also a pressure transducer is connected to the same line as is the Heise gauge in order to have a signal suitable for feeding into the computer that controls the system. A schematic drawing of this part of the system is shown in figure 3.4.

The reactor is placed in a 1 ft^3 aluminum box which is filled with 1/4" O.D. balls (provided by Abbot Ball Co.). Encircling the reactor there are eight heaters that supplied 1.6 KW of energy to the system in order to heat the interior of the cell. The heaters were provided by Chromalox. The temperature inside the cell is controlled within 1°K deviation from the set point by using a Thermo-Electric Slectrol$^{(tm)}$, proportional controller which has a range from 0 to 1999 °F. The aluminum box is encased with 1" thick Duraboard insulation, provided by Fibrefrax. This type of heating system is needed because the conventional heater system supplied with the autoclave does not provided isothermal heating. This heating unit is shown schematically in figure 3.5.

3.1.3 High Pressure Microflowmeter

Since there is not a commercial flowmeter capable of measuring flow rates of 10^{-10} m^3/s, a micro-flowmeter was developed in our laboratory in order to accomplish this task(25). The micro-flowmeter consists in a high pressure cast iron cage (provided by Fisher & Porter Co.), a six-port air-actuated-valve (provided by Valco), two four-way solenoid valves (provided by Humphrey Co.), a capillary tube, two lasers with their receivers, a Heise gauge, a pressure transducer and the hydrogen probes (figure 3.6).

This flowmeter is used to measure the hydrogen permeation rate by recording the time required for a mercury bead to travel a specific length of the capillary tube which has a diameter of $1.0 \cdot 10^{-3}$ m approximately. The flowmeter is rated to work at pressures up to 35 MPa (5,000 psi) at room temperature.

Figure 3-4: HIGH PRESSURE SECTION

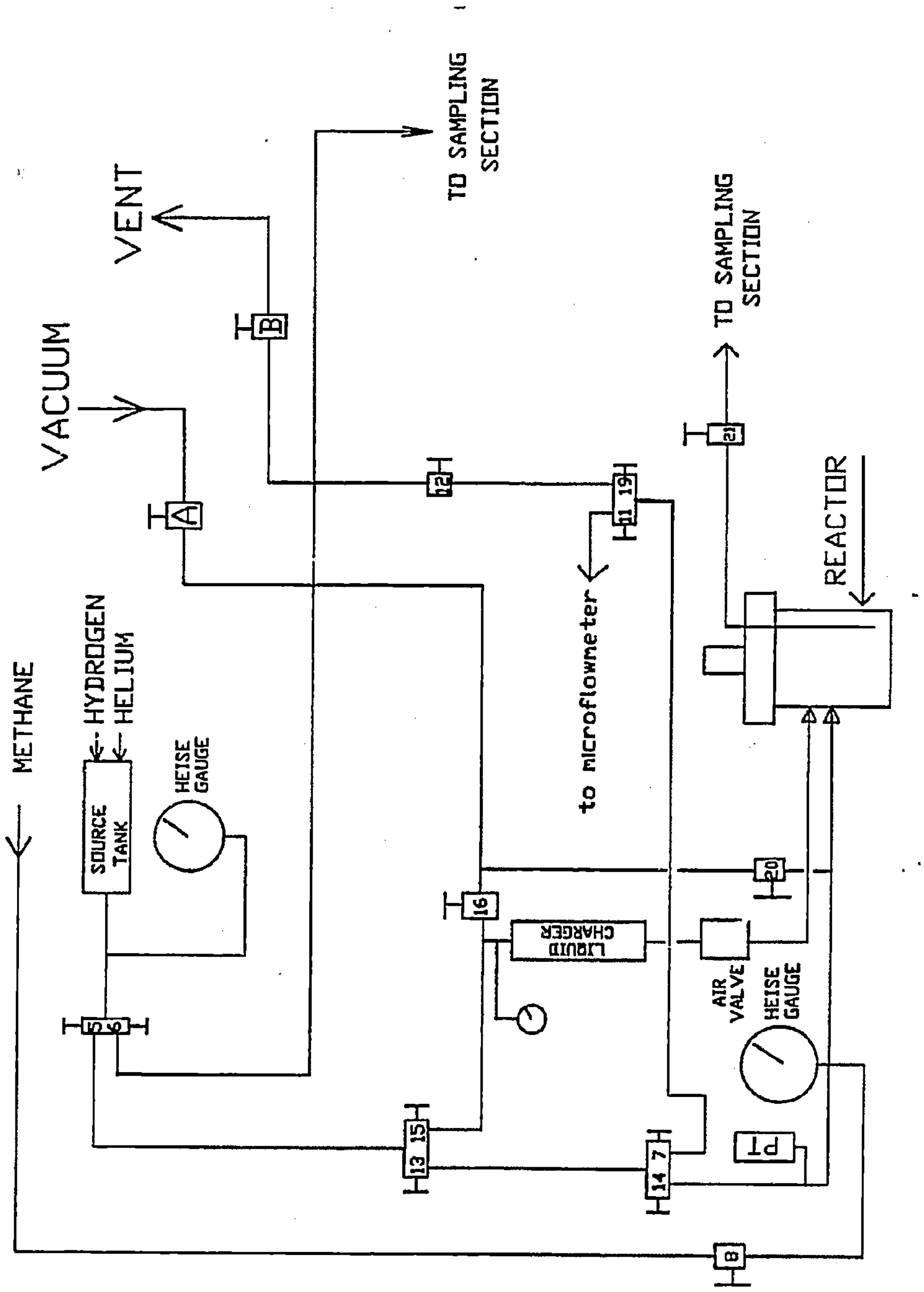


Figure 3-5: HEATING UNIT

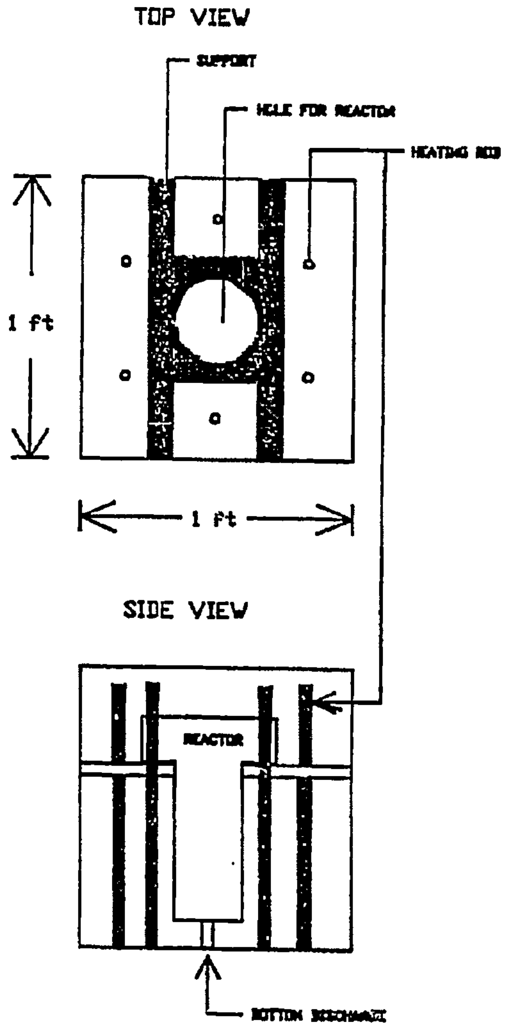
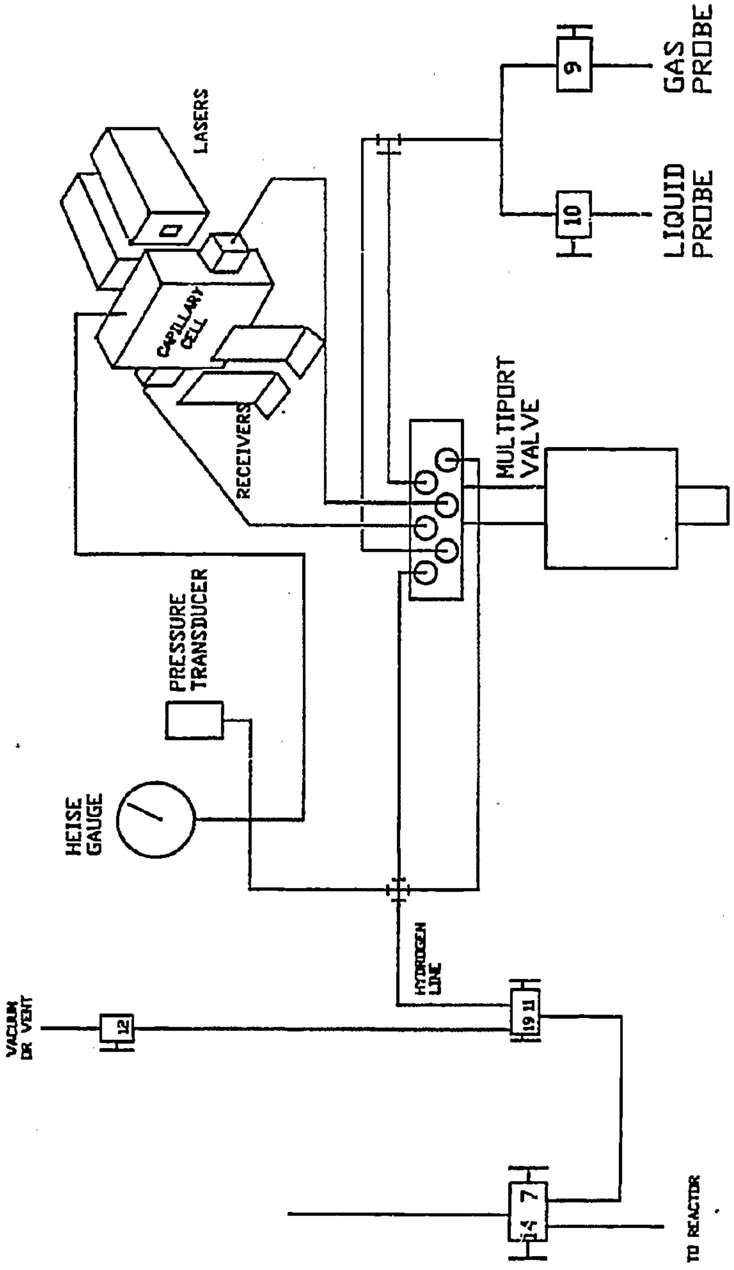


Figure 3-6: MICROFLOWMETER



A pressure line equalize the pressure inside and outside the capillary tube, so the cast iron housing and the capillary tube are at the same pressure at all times.

The capillary tube was secured and sealed within the cage by using two O-rings, which created a tight seal and isolated the capillary from the gauge. The capillary tube was constructed following the drawing shown in figure 3.7.

One of the most important parts of the microflowmeter is a 4-way multiport valve that allows the mercury bead to flow in one direction and then change its flow direction to the opposite side. This valve was constructed especially for this purposes by Valco Co. and it is air-actuated. The time sequence that this valve does is shown in figure 3.8.

3.1.4 Hydrogen Probe

The in-situ hydrogen probe was developed and constructed in our laboratory. This unique technique was suggested by Chiang and Klinzing(33) for continually in-situ monitoring of hydrogen partial pressure in a hydrogen bearing multicomponent systems. Since the first unit was constructed, some changes have been made mainly in the support system of the probe, resulting in the present unit. A schematic drawing for the probe support is shown in figure 3.9.

The hydrogen probe is made of a piece of approximately 10 m of nickel tube which has a wall thickness of $1.27*10^{-4}$ m and an O.D. of $3.76*10^{-4}$ m. The nickel tube is wrapped around a hexagonal frame which uses 4/40 threaded rod and four supports. The probe is connected to the microflowmeter via the six-port valve. The probes can withstand a pressure differential of 24 MPa (3,500 psi) at 850°F. A drawing showing a side view for the actual probe is shown in figure 3.10.

The nickel tube was manufactured by Handy & Harman Co. and its composition is shown on table 3.1.

Figure 3-7: CAPILLARY TUBE

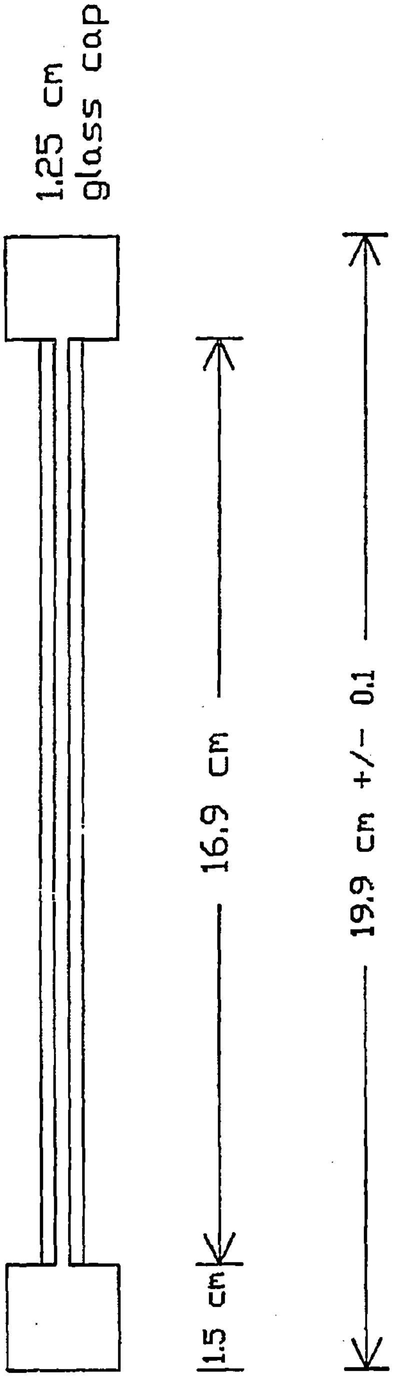


Figure 3-8: 6-PORT VALVE SEQUENCE

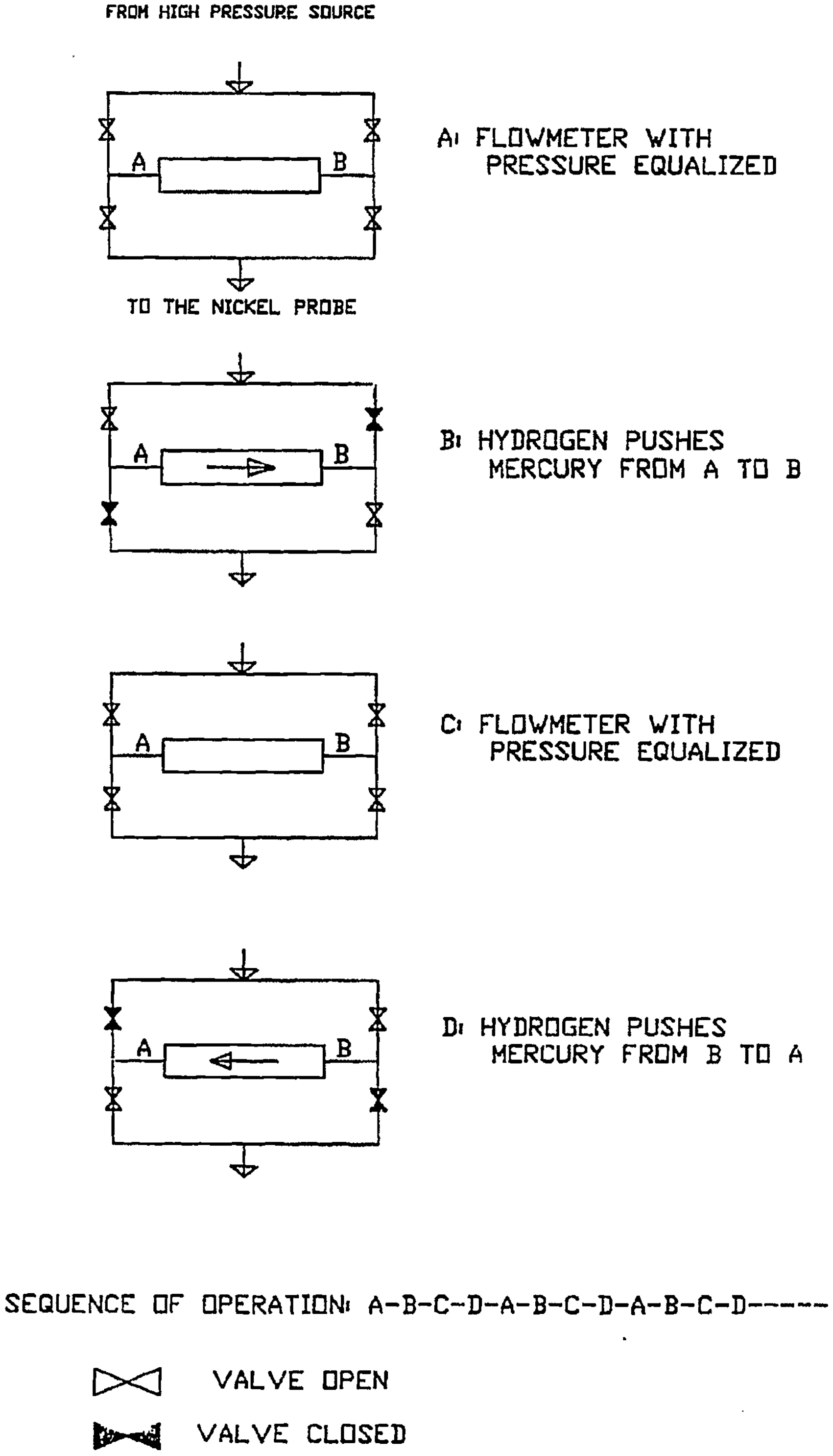
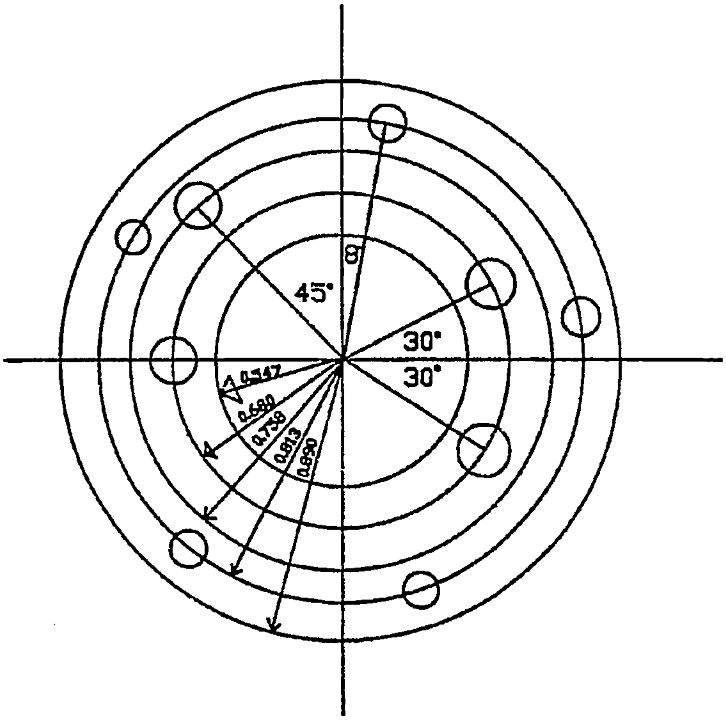


Figure 3-9: SUPPORT FOR THE PROBE



All holes in the 0.813" line are 4/40
Other holes are 1/8" .

Figure 3-10: SIDE VIEW FOR THE PROBE

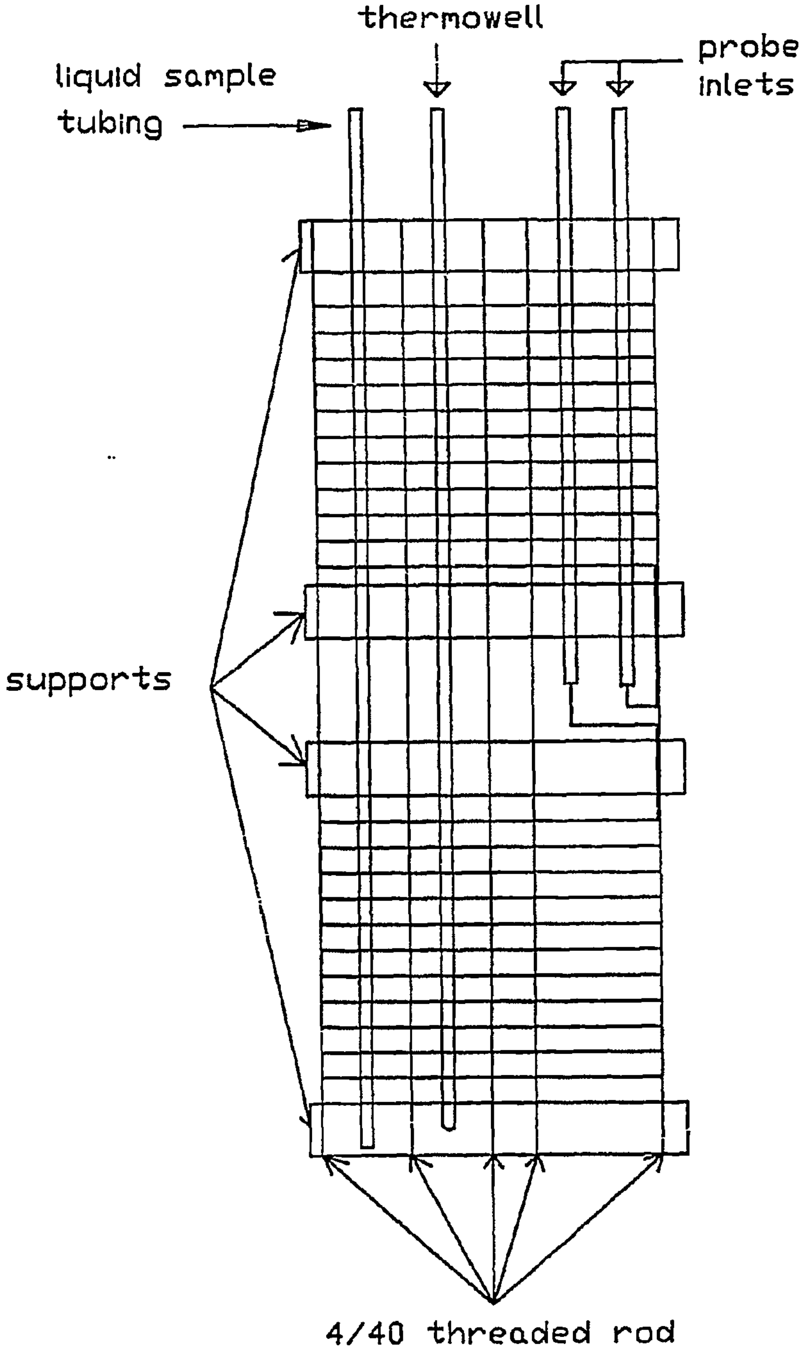


Table 3-1: COMPOSITION OF THE NICKEL TUBE

ELEMENT	WEIGHT %
Ni	99.44
Mn	0.29
S	0.002
Si	0.02
C	0.06
Fe	0.17
Cu	0.03

3.2 LOW PRESSURE SECTION

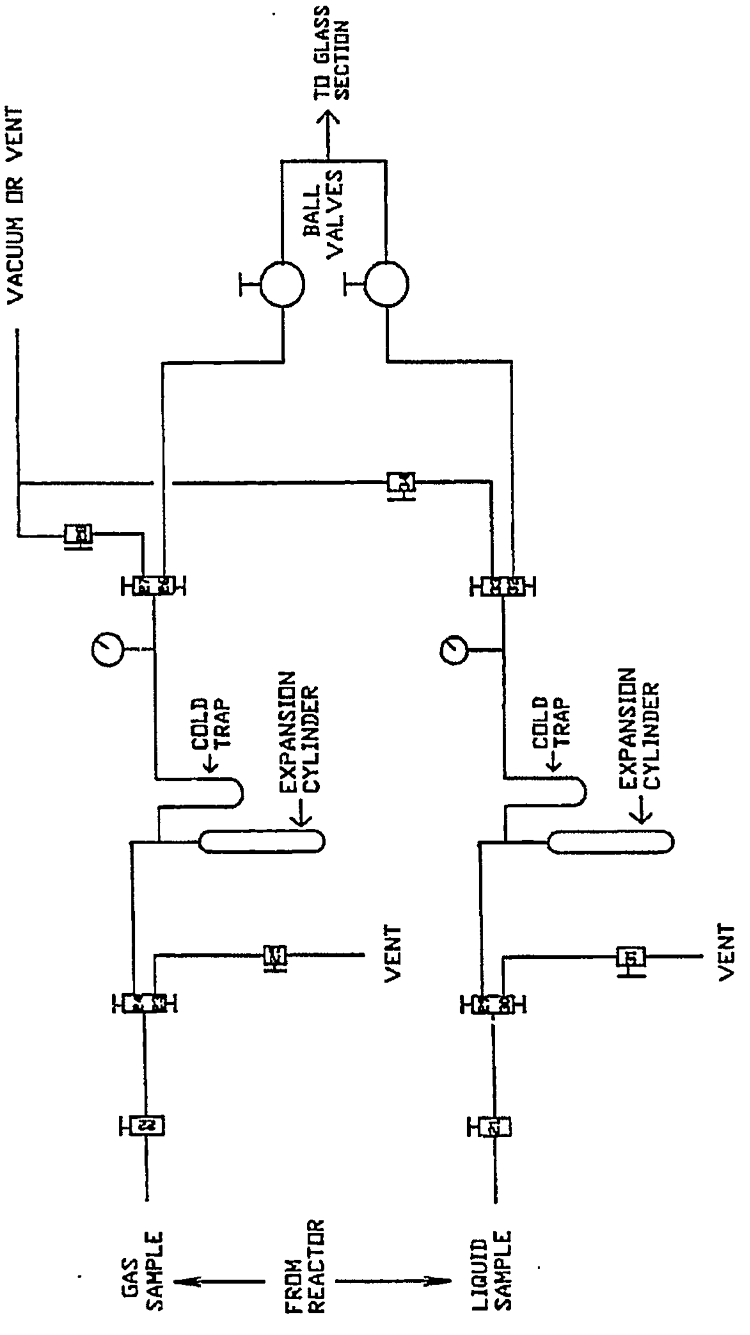
The low pressure section is designed for withdrawing samples from the equilibrium cell. Samples can be removed from the gas phase, the liquid phase or from both.

3.2.1 Liquid and Gas Phase Sampling Section

There are two different withdrawal systems conected to the equilibrium cell. One is for the liquid phase and the other for the gas phase. These two systems, though differents, have similar designs. Figure 3.11 shows these systems.

The sample is trapped between two locking autoclave valves (numbers 21 and 29–30 in figure 3-11). The first two samples of the liquid phase are vented and the subsequent is carried to an expansion cylinder where the light and heavy components are separated. Right after the expansion cylinder, which is standing upright, there is a cold trap, which is cooled by using liquid nitrogen which is placed in a Dewar flask. Once the two phases are in equilibrium inside the expansion cylinder, a Toepler pump is used to transfer the gas phase from the cylinder to the glass section, where the sample is hold in a sample flask. After the transfer is completed, the gas sample is analyzed in a gas chromatograph.

Figure 3-11: SAMPLE WITHDRAWAL SYSTEM



3.2.2 Toepler pump

A toepler pump is used to transfer the gas phase from the expansion cylinder to a glass section. The toepler pump used in this system was provided by Eck & Krebs Co. and it was specially designed with a piston volume of 500 ml. The way that this pump operates is explained in detail in appendix B. A diagram showing this pump is in figure 3.12.

The glass section, where the Toepler pump is located is shown in detail in figure 3.13.

3.2.3 Gas Chromatograph

A Perkin–Elmer Sigma 1–B gas chromatograph is used to analyze the samples that are transfer to the glass section. A thermo–conductivity–detector (TCD) method was employed in this study. Two 10–feet 1/8" O.D. Carbosieve–II columns were used to do the analysis of the sample due to the ability of the columns to separate light hydrocarbons and permanent gases. The columns were supplied by Supelco.

The carrier gas used was a mixture of 9% of hydrogen in helium. This was employed because a M–shape peak is obtained for hydrogen when helium is used as a carrier gas (34,35). The mixture used as a carrier gas, 9% of hydrogen in helium, was provided by the Harvey Co.

Two purifiers were installed between the carrier gas cylinder and the gas chromatograph. One is an oxygen purifier and the other is a filter that removes the humidity

Figure 3-12: TOEPLER PUMP

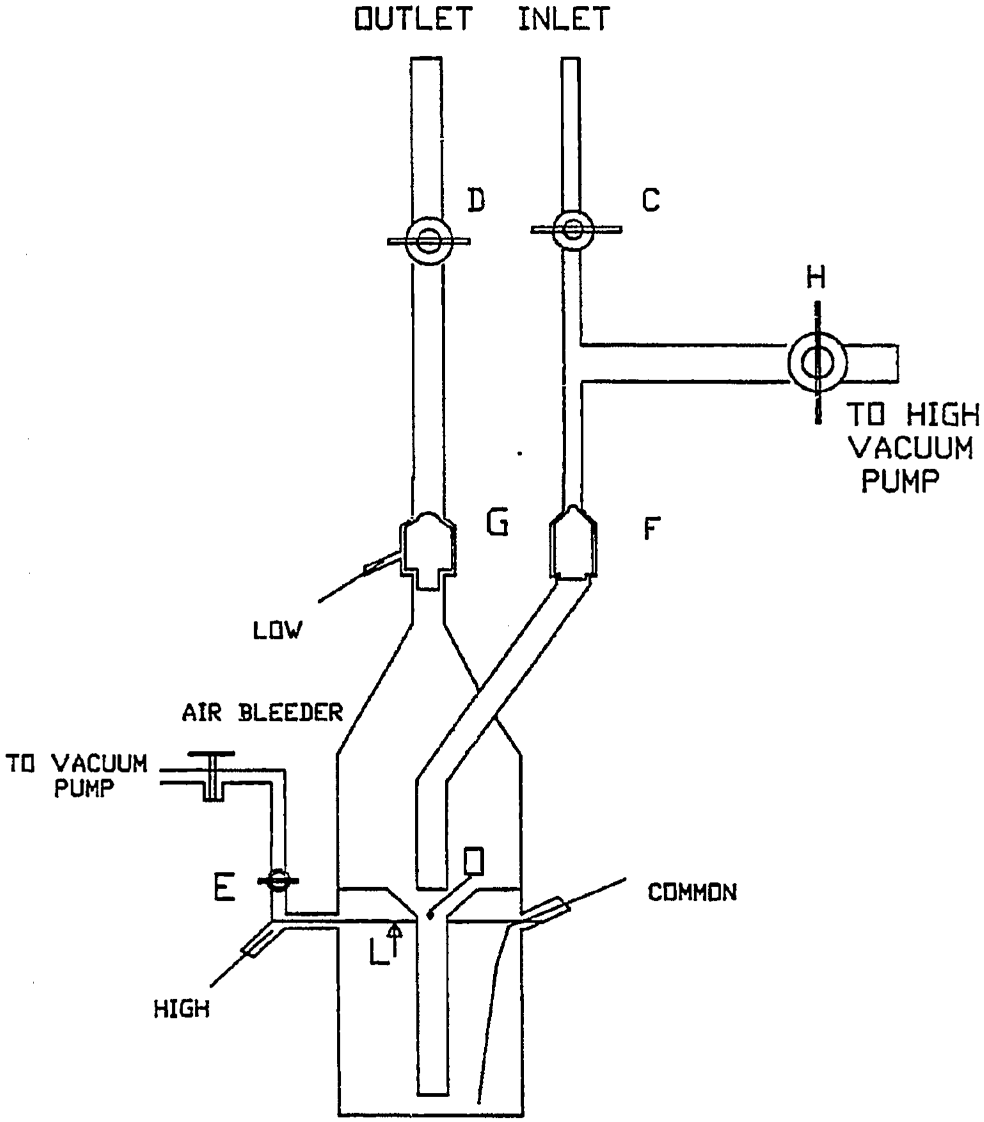
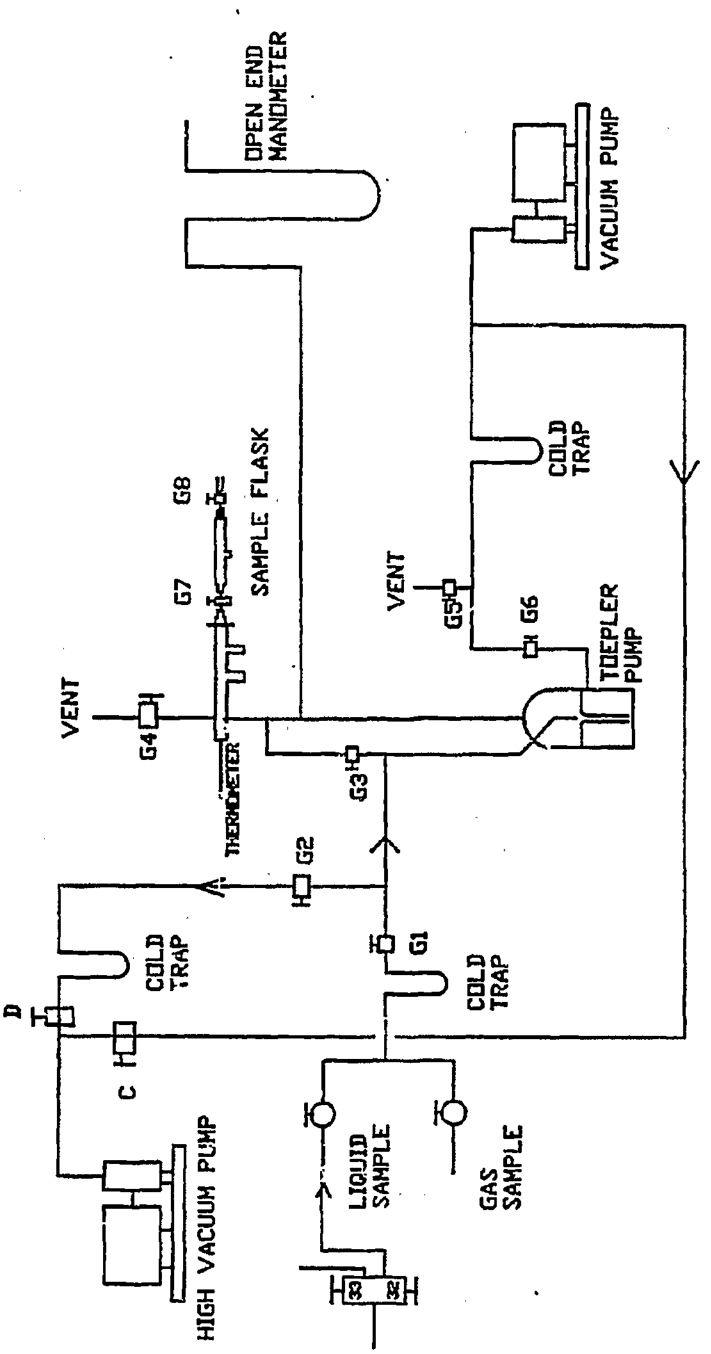


Figure 3-13: GLASS SECTION



3.3 CONTROL SYSTEM

A computer control system was built and installed to have a better control of the entire system as well as a better record of the data. The complete system consists of a basic-computer/controller, a 12 bit-16 channel A/D board and a printer. The computer runs a control program that is able to make the multi-port valve switch from one position to another. Also the computer reads 8 different channels on the A/D board, each one of these is a different signal coming from the system. The printer prints an output after each sequence is completed.

3.3.1 Basic Computer/Controller

The BCC52 computer/controller, provided by Micromint Inc., is a single board controller/development system. The board has the 8052AH-Basic chip, 48 Kbytes of RAM/EPROM, a 2764/128 EPROM programmer, 3 parallel ports, a serial terminal port with auto baud rate selection and a serial print port.

The BCC52 is based on the 8052AH-basic chip which is a preprogrammed version of the Intel 8052AH microcontroller. The 8052AH is the latest and the newest on Intel's 8 bit controller chip series. This contains 8 Kbytes of on-chip ROM, 256 Kbytes of RAM, three 16 bit counter/timers, 6 interrupts and 32 I/O lines. In the 8052AH-Basic, the ROM is a masked Basic interpreter and the I/O lines are redefined to address data and control lines.

Unlike most one-shot Eprom programmers that fill the entire content of an Eprom regardless of the application program size, BCC52 treats the Eprom as write once mass storage. This means that when a basic application program is saved to Eprom, it is tagged with an identifying ROM number and stored only in the amount of space required to fit the program. Additional application programs can be stored to the same Eprom until all the available space is used. A 21128 Eprom affords 16 Kbytes of mass storage space.

Another feature of the BCC52 computer/controller is an inside real time clock which has a resolution of 5 miliseconds.

All the features mentioned above make this computer a good non-expensive alternative for the purpose of controlling the system.

3.3.2 A/D Board

The A/D board used in our system is the model BCC30. This is a 16 channel (8 channel differential input), 12 bit plus sign, -5 to +5 volts, 10,000 samples/sec. BCC52/MMZ8 bus compatible board.

This A/D board can either be configured as 16 independent single ended input channels or 8 differential input channels. Single or differential operation is determined by the placement of one jumper in the board. For our purposes, differential input result in a better way to measure the differents channels that are being used.

3.3.3 Printer

The printer used in the system is the MTPI-GNS. The printer consists of a data memory for one line of text, character generator, print timing controller, print driver and data receiver.

Some of its features are:

1. Double width printing
2. Standard upright printing and inverted printing selectable by DIP switches
3. Printing of character sets of seven countries
4. Receiving all input data as bit image graphics data and printing it by DIP selection

5. Test printing.

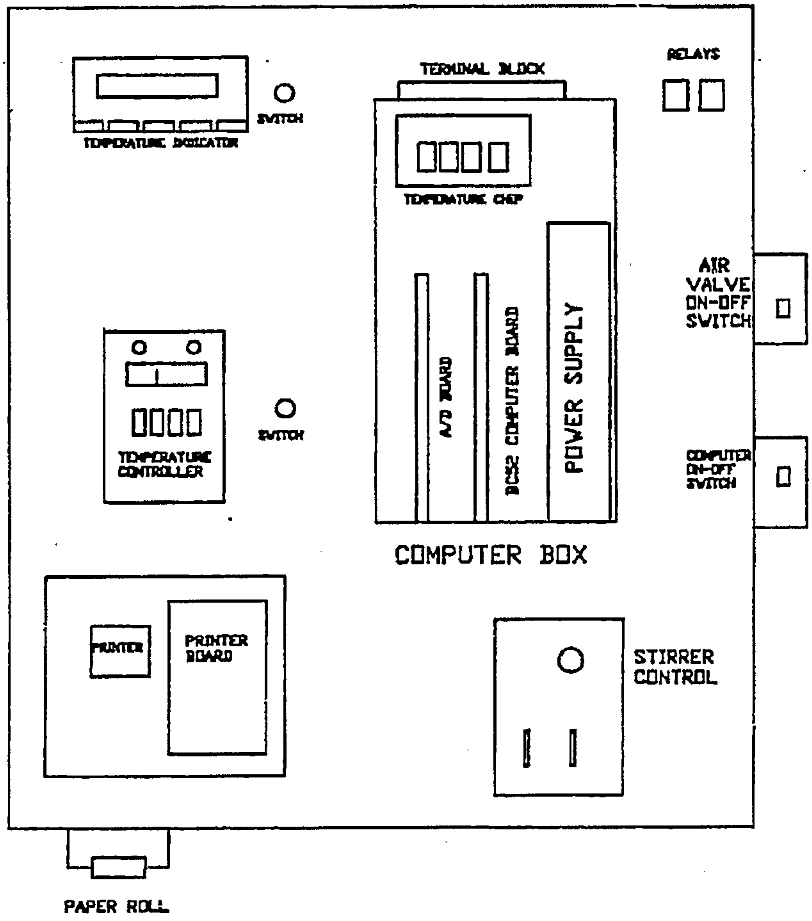
3.3.4 Control Programs

In order to have the control system working, a control program was written and saved in an Eprom. The program and its block diagram are shown in appendix C, where it is explained in all its different functions. Also a small program that allows reading of 8 channels is shown in the same appendix.

3.4 ELECTRICAL PANEL

The electrical panel is located far from the reactor in order to avoid any possibility of an explosion by a spark that may come from the panel. In this panel there are all the controls needed for use the entire equipment; (1)stirrer control, supplied by Emerson Industrial Controls, which control the turn on and off of the stirrer as well as its velocity; (2) the Doric trendicator, that reads the thermocouple and displays the value of the temperature of the heating unit; (3) A Thermo-electric Slectroi proportional heating control unit that controls the oven temperature by reading a type K thermocuple; (4) The ASCO solenoids switch,that drives the Jamesbury valve of the liquid charging unit by switching the air line pressure; (5) a box that contains the BCC52 computer/controller, the A/D board, four AD595AQ chips that are used for the thermocuples in order to have a signal for the A/D board, and the power supply used to give power to the control system; and (6) the printer. A schematic drawing is shown in figure 3.14.

Figure 3-14: ELECTRICAL PANEL



3.5 OPERATIONAL PROCEDURES

3.5.1 Equipment Calibration

3.5.1.1 Thermocuples read by the computer. The computer reads four different thermocuples coming from the system. These are the temperatures of the gas and liquid phase inside the reactor and two thermocuples for the room temperature. Since the distance between each thermocuple and the A/D board is different, the reading was slightly different, so a calibration was carried out. All four thermocuples were placed in cold water and the value that the computer read was recorded. After this, all four thermocuples were placed in hot water. After this, a small correction for each thermocuple was incorporated to the control program, so each one of them would read the same value for a temperature when located in the same place.

3.5.1.2 Heise Gauges. There are three Heise gauges that are used in the system, one is located in the source panel and reads the pressure of the source tank, the second gauge reads the pressure of the micro flowmeter and the third one the pressure inside the reactor. In order to check these Heise gauges, all three were connected in paralel, which means that all three were reading the same pressure. This can be done by properly opening some valves in the system. After a known pressure was set, the reading on all three was checked. It was found that each gauge was reading the correct value for the pressure.

3.5.1.3 Pressure Transducers. The calibration of the pressure transducers was done by charging the reactor and microflowmeter with helium. After a few minutes, when each system was equilibrated, the pressure on the Heise gauges was recorded as well as the pressure read by the computer. After this, the pressure was changed and the procedure repeated. A plot between the real pressure and the one read by the computer was drawn and the linear equation resulting was incorporated to the control program in order to correct this difference. Since the reading of voltages by the computer has some fluctuations, an average of 50 reading was taken for each pressure used to do the calibration.

3.5.1.4 Glass Section Volume. The volume of the glass section is of main interest since it will be used to calculate the number of moles of gas that were transferred from the expansion cylinder. In order to get the volume of this section the following procedure was performed: a vacuum was pulled on the section. While doing this, a sample flask with a well known volume was open to the atmosphere and the atmospheric pressure was taken. The pressure inside the glass section was taken after the mercury manometer was in equilibrium. The sample flask was closed and connected to the glass section. When the section was isolated from the vacuum, the valve of the flask was opened and the air that was inside the flask was allowed to go into the glass section volume. After the pressure was stabilized inside the glass section, this was recorded. By applying ideal gas law, the volume of the glass section including the sample flask can be known.

3.5.1.5 Gas Chromatograph. The response of the detector of the gas chromatograph to certain gases was calibrated by using calibration gases. Tha gases used were hydrogen, methane, ethane, oxygen and nitrogen (provided by Alltech). A plot of the response of the chromatograph, showed as area versus the volume of gas injected, was obtained for each gas. This is carried out because when a mixture of any of this gases is analyzed, the area of each peak will be given by the chromatograph, so the volume of each gas in the sample will be known. The least square method was used to correlate this data. The temperature and time program used in the Gas chromatograph are shown in appendix D.

3.5.2 Leak Test

In this work it is absolutely neccesary to have the system leak-free in order to avoid any possible explossion that may occur by ignition of the hydrogen utilized in the system. Therefore, before starting the experiments and after all the system is set-up, a pressure test should be carried on. Helium was used to do the pressure tests.

3.5.2.1 High pressure Section. The pressure used in the reactor and the microflowmeter rarely exceed of 20 MPa (3,000 psi). For this reason, the pressure test was carried on with pressures up to 24 MPa (3,500 psi). In order to have a reliable pressure test, the system was pressurized and kept at that level of pressure for at least 12 hours. Temperatures and pressures were recorded at the beginning and at the end of that period of time since a change on the temperature will produce a change in the pressure.

3.5.2.2 Low Pressure Section. A very small leak could mean a significant error in the final calculation of the number of moles of gas transferred to this section, so the leak test has to be done very carefully in this section. High vacuum was pulled on the system and the system was kept isolated for at least 4 hours. Pressure, temperature and atmospheric pressure were recorded each half hour in order to observe changes.

3.5.2.3 Gas Chromatograph. The line coming from the gas carrier cylinder to the chromatogarph was checked for possible leaks since a small leak may cause a shift in the base line when the chromatograph is running. The gas chromatograph operates at 75 psi, so the test was carried on with pressures up to 100 psi.

3.5.3 Conditioning

3.5.3.1 Probe Conditioning. The conditioning of the probe is very important since oxygen and carbon may affect the rate of permeation of hydrogen. Also oxygen can cause embrittlement and cracking if it is incorporated into the nickel grain boundary, so the removal of oxygen and carbon before doing any experiment is very important. Some methods to condition the probe before starting the experiments are found in the literature(25,30,31,32). The method used in this experiment was to pressurize the probe to 3,5 MPa (500 psi), heat up the reactor 650°F and keep there for at least 10 hours. After that, vacuum was pulled on the probe. After keeping the probe under vacuum for at least one hour, hydrogen was charged again to a pressure of 10 MPa (1,500 psi). After this the probe was ready to use.

3.5.3.2 Capillary Conditioning. The capillary tube made for the microflowmeter is shown in figure 3.7. In its initial condition, the inside wall is so rough that the mercury beam can not flow smoothly through the tube. The capillary was roughened by using a 0.011" diameter steel wire with the aid of wetted 200 mesh carbon silicate. Once the interior is roughened, it is cleaned with acetone and dried by using dust chaser to remove any posible particle from the interior of the capillary. The capillary is then ready to use when a mercury bead can flow smoothly within the tube.

3.5.3.3 Gas Chromatograph. Before using the gas chromatograph, the flow of carrier gas in both chanels should be checked. The flowrate of carrier gas was 30 ml/min.

After the flows are set, the column must be conditioned in order to remove any strange material from its interior. For this the chromatograph oven is heated up to 225°C and kept at that temperature for 16 hours. This procedure must be repeated each time that the interior of the column is in contact to the atmosphere or when foreign compounds are inside the column.

The detector needs to be on at least 45 minutes before any sample is injected to the chromatograph. The equipment can be checked by running a blank sample which should produce a constant base line.

3.5.4 Vacuum and Vent

Vacuum is pull out in the entire section before charging any gas or liquid to it. Tha vacuum pump is connected to the system via a 1/2 " O.D. stainless steel tubing. The vacuum may be directed to three different directions. The first one goes to the high pressure system and the sampling section while the other two goes to the glass section. In order to have the vaccum connected to each one of this directions, three valves, one in each line, are used. In order to have the vacuum on the high pressure and sampling sections, valve A (see figure 3.4) should be opened.

For the glass section, valves C and D (figure 3.13) must be opened. Valve C connects the lower part of the Toepler pump to the vacuum line while valve D connects the glass section to the vacuum line For venting the high pressure and sampling systems, valve B (figure 3.4) must be opened.

In order to have a special part of the equipment in vacuum while the other is under pressure, adittional valves should be opened or closed. For details, the schematic figures of the section in particular must be observed.

3.5.5 Pressurization of the Source Section

In order to pressurize this section (see figure 3.2) with hydrogen or helium, vacuum must be pulled out before. Every valve in this section, 2 to 5, must be openned. By opening valve 6, vacuum is pulled on the system and it is up to valves C2 and C3, which must be closed. After wait for at least 10 minutes, valve 6 is closed and the gas to used, helium or hydrogen is allow to enter this section by opening the properly valve (C2 or C3). Valve 5 can be used to vent this section too.

3.5.6 Pressurization of the Equilibrium Cell

After having this cell under vacuum for at least 15 minutes, valves 5 (from the source section) and 13 must be opened. In this way, the gas to used is in valve 14 (see figure 3.4). By closing valve 20, the equilibrium cell is isolated from the vacuum, so if valve 14 is opened, tha gas begins to fill the reactor. When the desired pressure is reached, valve 14 is closed, so the reactor is kept isolated under pressure.

3.5.7 Pressurization of the Microflowmeter

Before pull vacuum or pressurize this section, the mercury bead should be inserted in the capillary tube. When this is done and the multiport valve checked to be on the mid-position, the system is ready to work with. This section, microflowmeter and the probes, should be under vacuum for at least one hour since the time needed to evacuate the probes is much higher due to the dimension of the nickel tube. Vacuum is pulled out on this section by opening valve 12 (figure 3.6). By openig valves 9 and

10, the probes are under vacuum too. Valves 11 and 19 are always open. After the time required for the vacuum, valve 12 is closed and the hydrogen (or helium) is allowed to go into this section by openning valve 7 (figures 3.4 and 3.6). When the desired pressure is reached, valve 7 is closed.

3.5.8 Charging liquid into the cell

In order to put the liquid inside the reactor without opening it, a liquid charger is used. This charger is a one-liter sampling cylinder. The liquid can be introduced into this cylinder by using a syringe or a wash bottle. Once the liquid is inside, the cylinder should be connected back to the system. After the system is set-up, vacuum should be pulled out on this cylinder for at least 5 minutes. The vacuum is connected to the charger by opening valve 16 (figure 3.4). After closing valve 16, valve 15 is open, so hydrogen is allowed to go into the charger. When the pressure inside the charger is at least 2.5 times the presure in the equlibrium cell, valve 15 is closed. The Jamesbury air valve is now open and the liquid falls into the reactor. After the transfer is completed, the air valve is closed. It is recomended the pressure inside the reactor not to be more than 500 psi when liquid is being charging into the cell.

3.5.9 Charging other gases into the cell

If gases other than hydrogen are going to be used in the experiments, the reactor should be at a pressure lower than the gas cylinder to be used. Valve 8 (figure 3.4) is the one used to charge the gas to the equilibrium cell.

3.5.10 Sampling

Since both sample lines work in the same way, the explanation to be given here will be for the liquid phase sampling system. The sampling system (figure 3.11) must be under vacuum for at least 5 minutes before the sample is taken. Valves 29, 34 and 33 must be opened while valves 21, 30 and 32 must be closed. Then valve 29 is closed, valve 21 is open for five seconds and then closed. The sample is held between valves

21 and 29–30. Valve 30 now is open in order to vent the sample. After closing valve 30 again, valve 21 is open again for another five seconds, and then closed. By doing this a second sample is held between valves 21 and 29–30, which is vent again by repeating the procedure just mentioned. A third sample is taken, but instead of venting this, it is expanded into the expansion cylinder by opening valve 23. Before doing the expansion of the sample, valves 33 and 34 must be closed and the cold trap must have liquid nitrogen around it.

3.5.11 Transfering the Sample

When the sample has been expanded, the gas phase of the sample must be transferred to the glass section (figure 3.13). Before doing the transfer, vacuum should be pulled on this section. When pulling the vacuum, valves G4, G5, G8, C, D and 32 (see figure 3.11) must be closed. All other valves must be open. Then valves C and D are open slowly and at the same time in order to begin to pull vacuum in the entire section. After at least 10 minutes, valves C, D, G2 and G6 must be closed. Then valve 32 is opened slowly so the sample begins to be tranferred. Valve G3 is then closed and G6 is open slowly in order to have the Toepler pump working satisfactorily. The transfer is completed after 20 minutes of having the Toepler pump working. The bleed valve (G5) is not opened completely; it is opened until a smooth operation of the Toepler pump is obtained. Instructions of the operation for the Toepler pump are in Appendix B.

3.5.12 Analysis of the sample

After the transference is completed, valve G6 is closed, so the Toepler pump stops working. Then valve 32 is closed so the sample is hold in the sample flask, which can be removed from the glass section and brought to the gas chromatograph, where the sample is analyzed.

3.6 EXPERIMENTAL PROCEDURES

3.6.1 Hydrogen Permeation Experiments

In these experiments, hydrogen is charged into the reactor and the microflowmeter. The equilibrium cell is heated up to the desired temperature. The pressure in the microflowmeter is set in 3,000 psi. After waiting some time to reach the thermal equilibrium inside the reactor, the probe is connected to the microflowmeter by openning valves 9 or 10 (depending of what probe is going to be used; liquid or gas phase) and the control program is started. After obtaining at least 8 points with constant conditions (temperature, pressures and time of travel of the mercury), the control program is stopped and the temperature inside the reactor is increased to a new value. After waiting for thermal equilibrium inside the cell, the program is started again. This procedure is repeated for each temperature to be studied. Equation 2-1 is used to calculate the value of the permeability coefficient, ϕ, at different temperatures.

3.6.2 Solubility of Hydrogen in Tetralin

In order to determine the solubility of hydrogen in tetralin at a fixed temperature, 150 ml of tetralin is charged to the reactor, which is already at the desired temperature. The hydrogen pressure inside the reactor is fixed at a specific value. After waiting for equilibrium, a sample is withdrawn from the liquid phase and expanded in the sampling cylinder. The gas phase is then transferred to the glass section. The pressure before and after the transfer must be recorded.

The total number of tetralin moles is known by weighting the expansion cylinder and cold trap just after the expansion. After cleaning the inside of the expansion system, these units are weighed again, so the number of moles of tetralin can be determined. At the same time, by knowing the pressure in the glass section before and after the transfer, its volume and the temperature, the total number of hydrogen moles is known. With these two values, the hydrogen mole fraction in the liquid phase is determined.

3.6.3 Effect of Methane in Hydrogen Solubility in Tetralin

The procedure to follow in these experiments is very similar to the one explained in the section 3.6.2. The only difference is that the hydrogen pressure inside the equilibrium cell is kept constant at all times. The methane partial pressure is changed after each run.

The way to ensure that the hydrogen partial pressure is the same in all the experiments is by using the microflowmeter, which needs to show the same time of travel for the mercury bead under different methane partial pressures. The sample is taken in the same way that was mentioned before. The difference in the gas being transferred from the expansion cylinder is that this gas phase contains a mixture of hydrogen and methane. The number of moles calculated as was explained in the preceding paragraph corresponds to the total number of moles in the gas phase. The composition of hydrogen and methane are determined by analyzing the sample in the gas chromatograph.

For use of ethane instead of methane, the procedure is the same as explained above.

3.7 COMMERCIAL EQUIPMENT

3.7.1 Use of the Apparatus

A commercial equipment was built to be used in a Liquefaction Pilot Plant operated by Catalytic Inc. located in Wilsonville, Alabama. The unit will determine the partial pressure of hydrogen in a gas stream that comes from the hydrogen catalytic reactor. The temperature in this stream is close to 700 °F and the pressure approximately 2700 psi. The approximate percentage of hydrogen is 85 to 93%.

3.7.2 Construction of the Equipment

The commercial unit has identical equipment to the one being used it the University laboratory. The details of each component were explained in sections 3.1 to 3.4.

In order to install the equipment in the plant, a number of modifications and precautions were taken. The unit where the equipment is located is classified as Division I, Class I according with safety regulations. In order to meet these specifications, the equipment was separated in three distinct parts. Each part is housed in a 7/8" wall thickness aluminum box which meets the safety standards.

The first box contains the two laser beams that are used to determine the time of travel of the mercury bead inside the capillary tube. This box has a 115 V input and no hydrogen is present in this box.

The second box contains the capillary cell and the multiport valve. The capillary cell has the capillary tube with the mercury bead in it. Hydrogen is used inside the capillary cell and the multiport valve.

The third box contains all the electronics used in the system. It contains the laser receivers, two solenoids valves (that works with the multiport valve), and two relays. Also the box has a terminal block that has all the connections for sending and receiving signals from the computer. Details of each box are shown in figures 3.15 to 3.20.

Each box has windows in order to have light communication with the laser, hydrogen flowmeter and the sensors. These windows are 1" x 8" and are covered with 1/2" thick explosion-proof glass bolted to the apertures. All three units have nitrogen purges in them.

All three boxes are mounted on a welded base and aligned in order to insure a direct light path between the laser outputs and the light sensors through the glass capillary containing the mercury droplet. A 2-D drawing showing the entire system is shown in figure 3.21.

The computer system is mounted inside its own box. This box contains an internal power supply, a BC52 computer/controller, a 12-bit 16-channel A/D converter, a printer interface card, a voltage regulator card, two thermocuple transducers, a terminal block and a fan. The control program used in this system is shown in appendix E. The schematic drawing of this box is shown in figure 3.22.

3.7.3 Location of the Equipment

The entire system, boxes and the probe are located on the 5th floor of a metallic structure which supports the hydrogen catalytic reactor. A 2-dimensional drawing showing where the system is located is shown in figure 3.23.

3.7.4 Operation Instructions

A complete set of instructions is shown in appendix F.

Figure 3-15: LASERS BOX: TOP VIEW

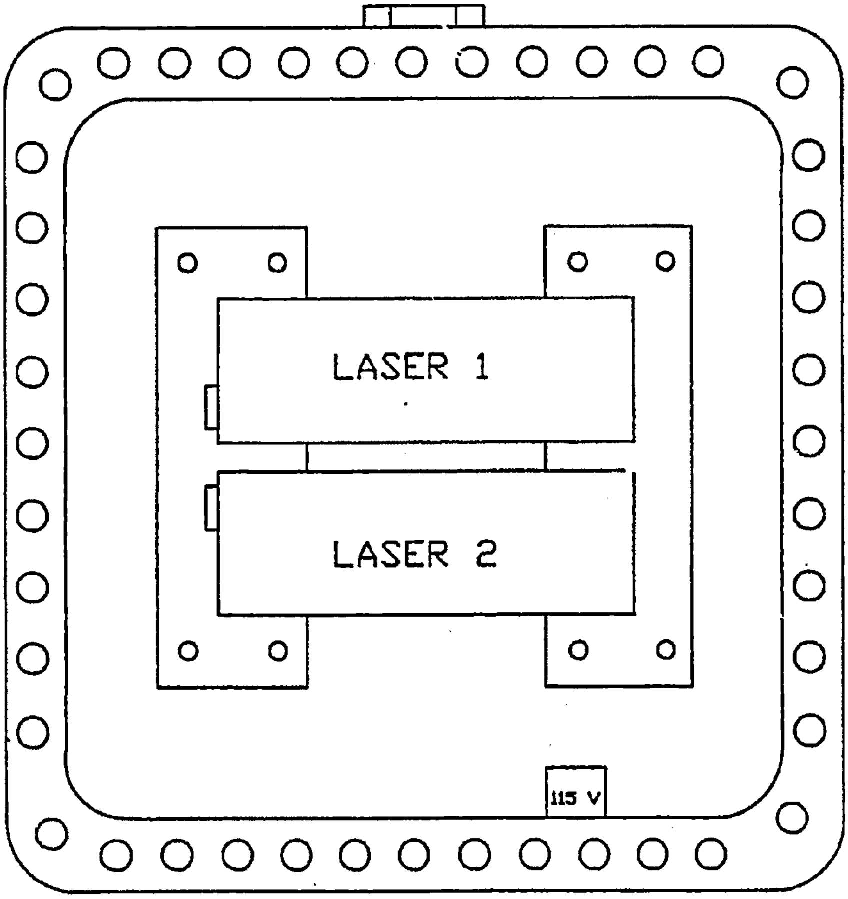
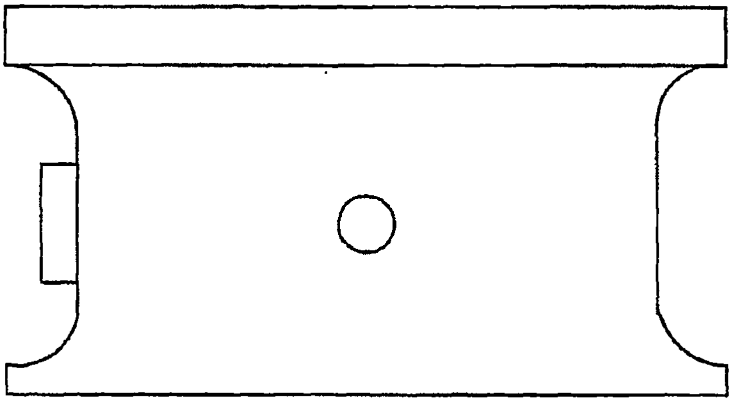
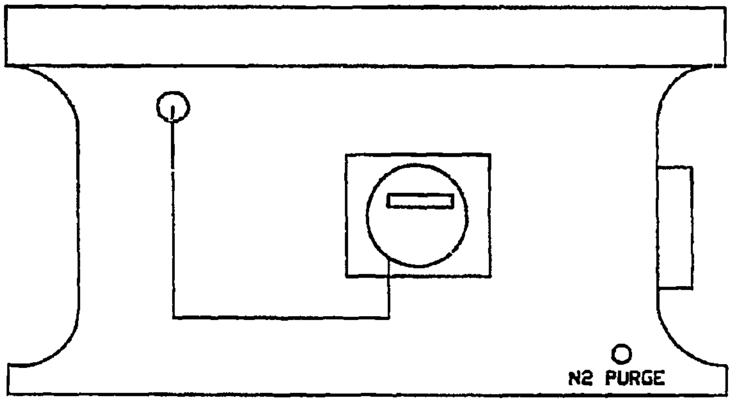


Figure 3-16: LASERS BOX: SIDE AND BACK VIEWS



LASERS' BOX: FRONT VIEW



LASERS' BOX: BACK VIEW

Figure 3-17: CELL BOX: TOP VIEW

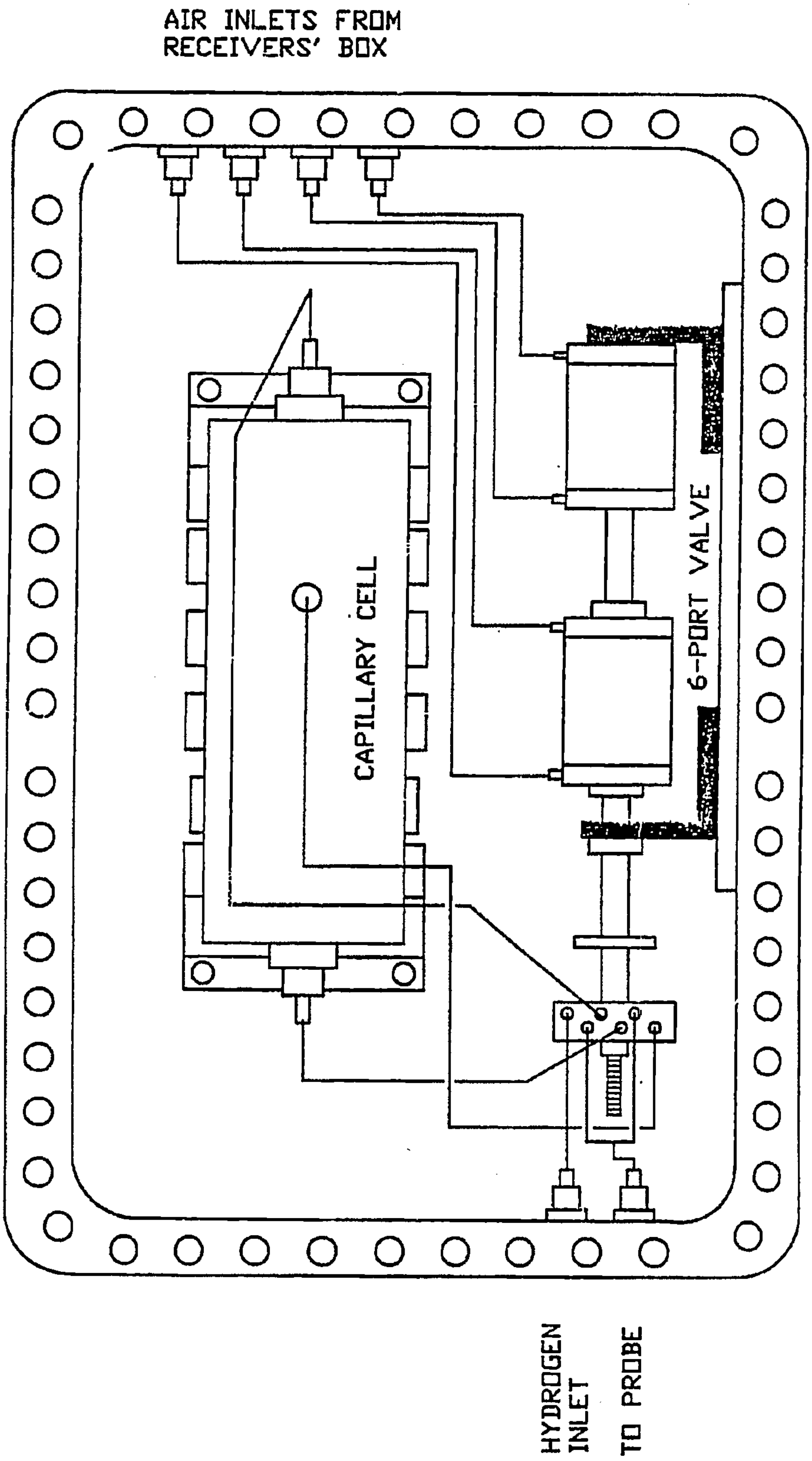
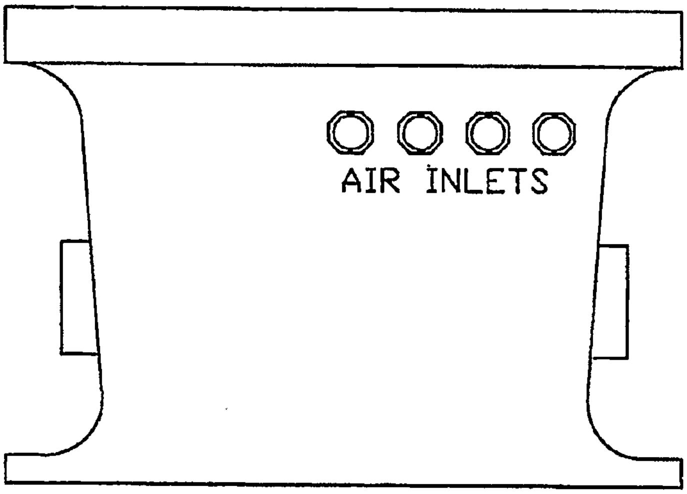
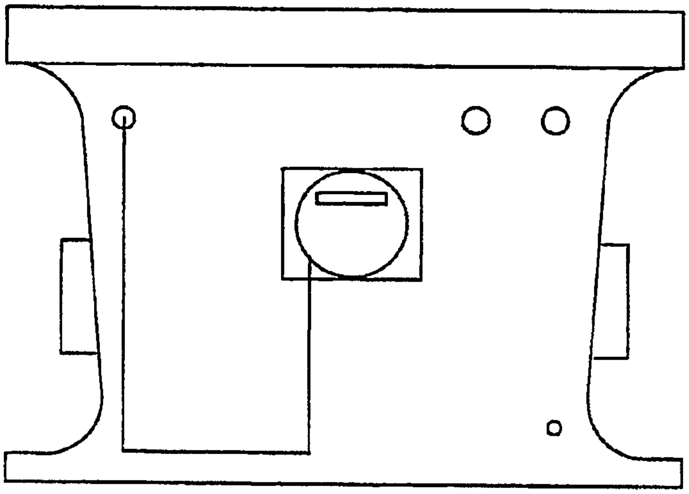


Figure 3-18: CELL BOX: SIDE AND BACK VIEWS



CELL'S BOX: FRONT VIEW



CELL'S BOX: BACK VIEW

Figure 3-19: RECEIVERS BOX: TOP VIEW

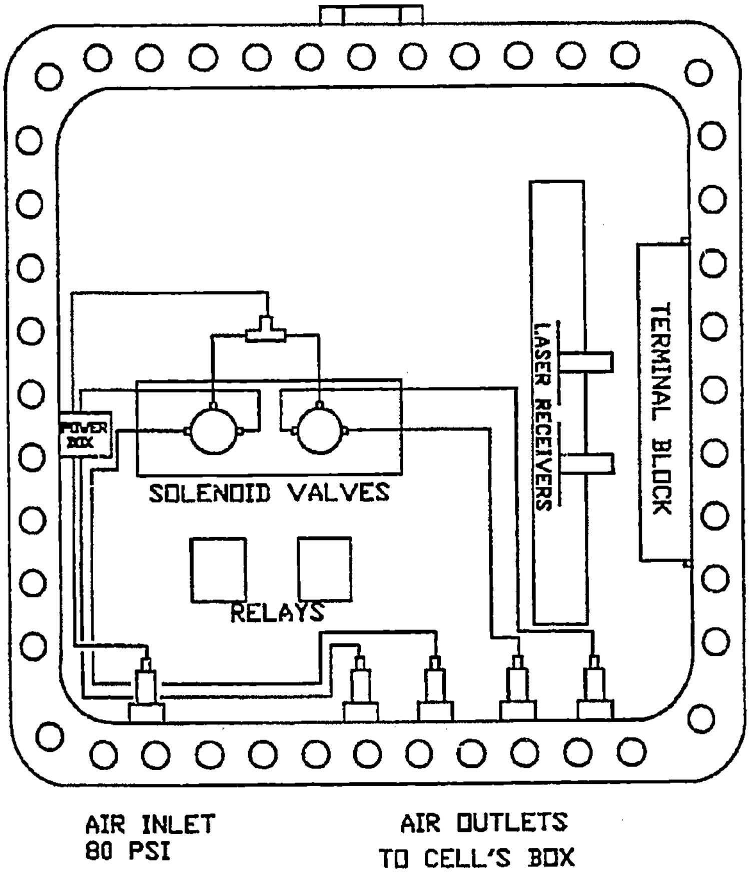
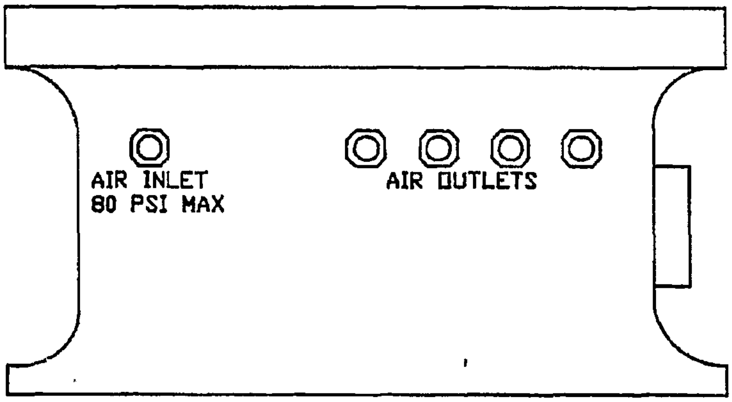
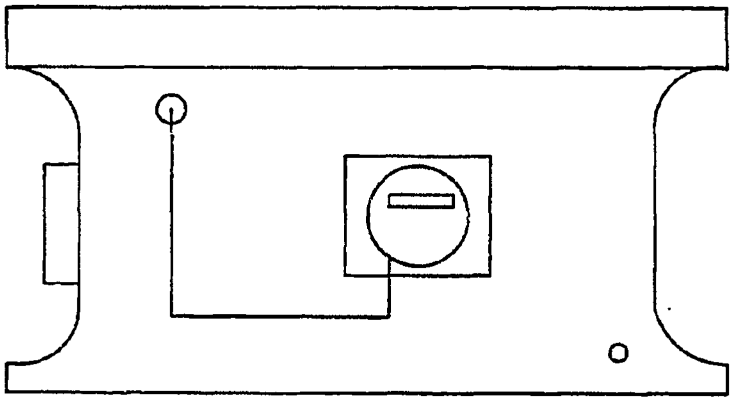


Figure 3-20: RECEIVERS BOX: SIDE AND BACK VIEWS



RECEIVERS' BOX: FRONT VIEW



RECEIVERS' BOX: BACK VIEW

Figure 3-21: 2-D DRAWING FOR THE ENTIRE SYSTEM

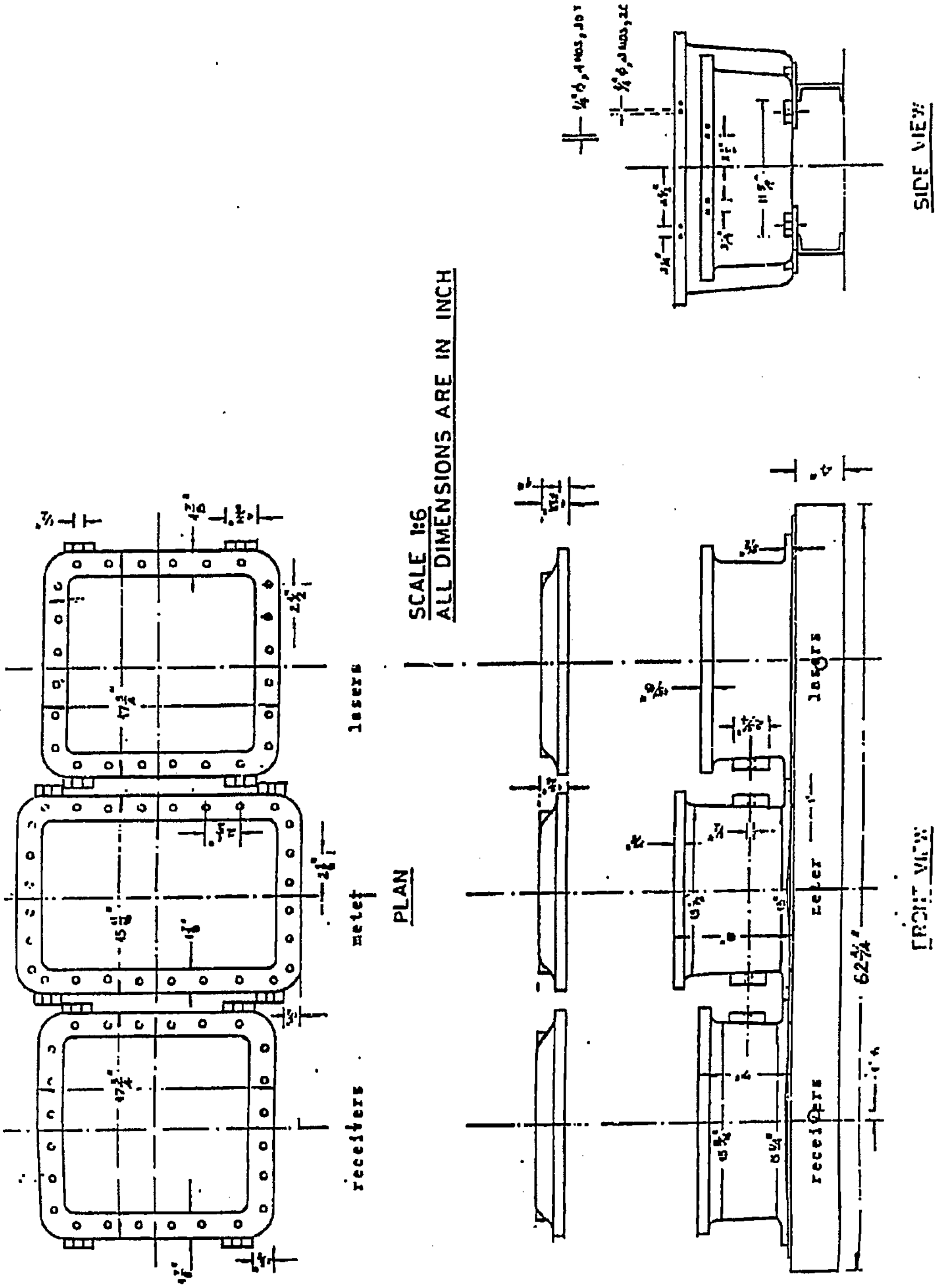
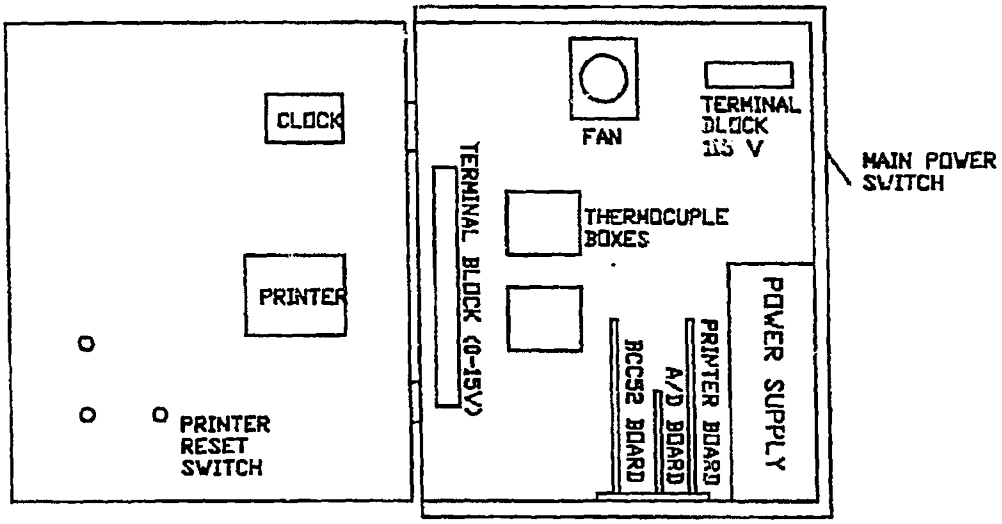
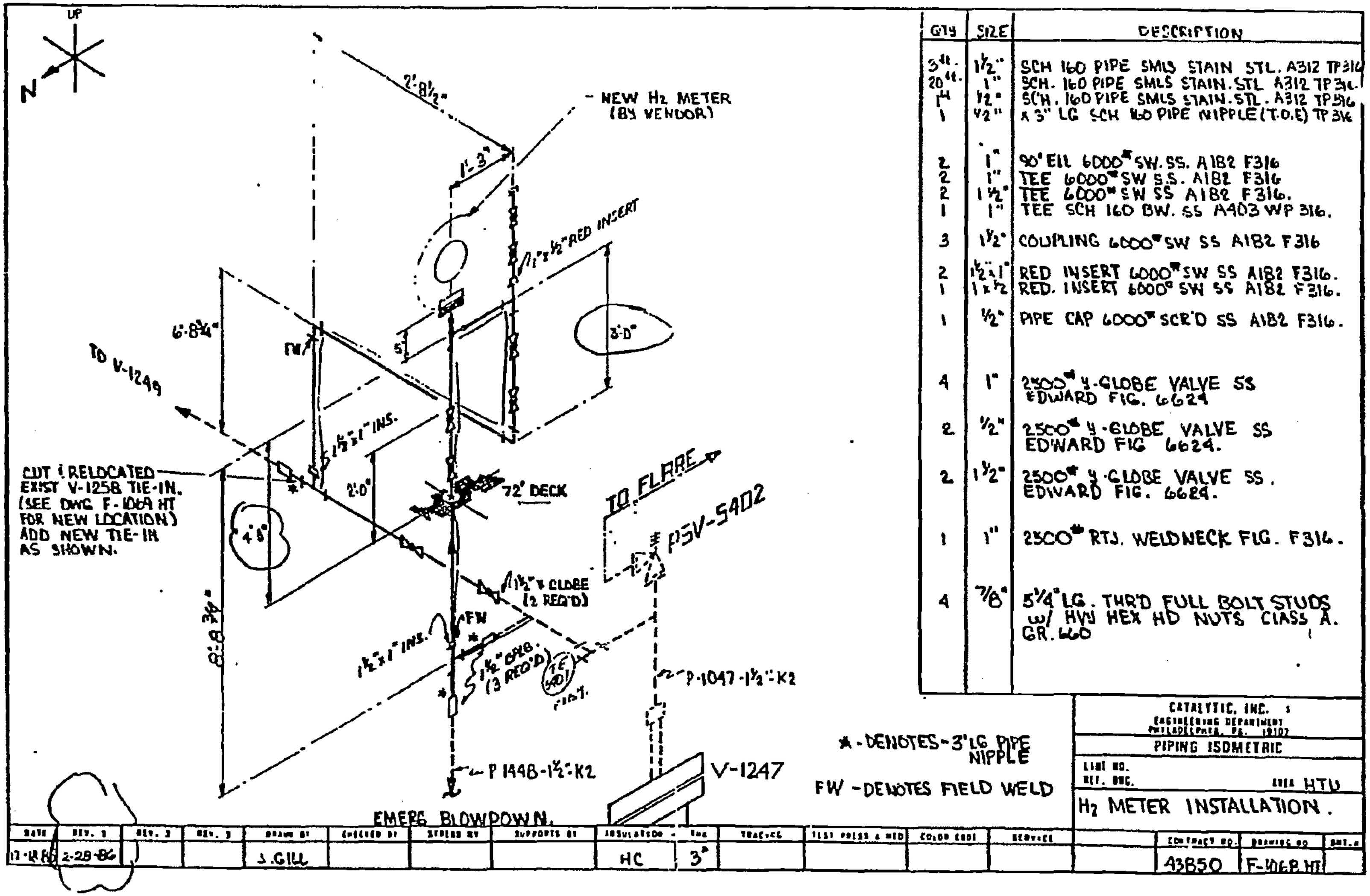


Figure 3-22: COMPUTER BOX





QTY	SIZE	DESCRIPTION
3 ft.	1½"	SCH 160 PIPE SMLS STAIN STL. A312 TP316
20 ft.	1"	SCH. 160 PIPE SMLS STAIN. STL A312 TP316.
1'	½"	SCH. 160 PIPE SMLS STAIN. STL. A312 TP316
1	½"	x 3" LG SCH 160 PIPE NIPPLE (T.O.E) TP316
2	1"	90° ELL 6000# SW. SS. A182 F316
2	1"	TEE 6000# SW S.S. A182 F316
2	1½"	TEE 6000# SW SS A182 F316.
1	1"	TEE SCH 160 BW. SS A403 WP 316.
3	1½"	COUPLING 6000# SW SS A182 F316
2	1½"x1"	RED INSERT 6000# SW SS A182 F316.
1	1x½	RED. INSERT 6000# SW SS A182 F316.
1	½"	PIPE CAP 6000# SCR'D SS A182 F316.
4	1"	2500# Y-GLOBE VALVE SS EDWARD FIG. 6624
2	½"	2500# Y-GLOBE VALVE SS EDWARD FIG 6624.
2	1½"	2500# Y-GLOBE VALVE SS. EDWARD FIG. 6624.
1	1"	2500# RTJ. WELDNECK FLG. F316.
4	7/8"	5¼" LG. THR'D FULL BOLT STUDS w/ HVY HEX HD NUTS CLASS A. GR. 660

Figure 3-23: LOCATION OF THE SYSTEM

4. EXPERIMENTAL RESULTS

4.1 ANCILLARY RESULTS

This section shows the results for a set of preliminary determinations, which are needed prior to the beginning of the final set of experiments.

4.1.1 Gas Chromatograph Calibration

The gas chromatograph was calibrated by using the following gases supplied by Alltech: hydrogen, methane, ethane, oxygen and nitrogen. For each one of these gases, a linear equation was obtained by using the least squares method. Appendix G shows the experimental data and corresponding figure for each calibration.

The equations obtained by doing this were:

H_2 : Area = Vol * 7.422 - 0.075

N_2 : Area = Vol * 261.8 - 0.601

O_2 : Area = Vol * 226.5 - 2.750

CH_4 : Area = Vol * 197.0 - 0.005

C_2H_6 : Area = Vol * 333.1 - 0.003

In these equations, "Area" represents the Area that the integrator produces for each peak and "Vol" represents the volume injected of each gas in ml.

4.1.2 Pressure Transducer Calibration

The two pressure tranducers used in the system were calibrated as was explained in paragraph 3.5.1.3. Tables with the values for each calibration and their plots are shown in appendix H. The linear equations obtained for each transducer are:

Reactor Pressure Tranducer:

$$A.P. = (R.P. - 13.85)/1.019$$

Microflowmeter Presure Transducer:

$$A.P. = (R.P. - 23.38)/1.023$$

where A.P. = Actual Pressure
R.P. = Pressure read by the transducer

4.1.3 Volume

4.1.3.1 Sample Flask. The volume of each sample flask used in this work was calibrated. The values for these two flasks are;

Number 1: 135.9 [ml]

Number 2: 136.2 [ml]

4.1.3.2 Glass Section. The volume of the glass section was calculated as was explained in paragraph 3.5.1.4. The volume for the entire section starting at valve 32 (figure 3.13) was calculated to be 1229.5 [ml].

Experimental values for these determinations are shown in appendix I.

4.1.3.3 Diameter of Capillary Tube. The diameter of the capiallary tube used for the mercury movement was calculated to be $1.12*10^{-3}$ m. Details of these calculations are shown in appendix I.

4.2 RESULTS

This section conatins the results for the solubility experiments. The experiments considered here are the following: (1) Permeability coefficient for the nickel probes constructed for this work, (2) Solubility of hydrogen in tetralin at two different temperatures and (3) Solubility of hydrogen in tetralin at two different temperatures under the presence of ethane and methane at hydrogen partial pressure constant at about 950 psi. The experimental data obtained for each set of experiments is shown in appendix J and a sample calculation is shown in appendix K.

4.2.1 Permeability Coefficient

The results given in this section were obtained by the procedure detailed in section 3.6.1. The procedure was repeated for the liquid and the gas probes, so an equation for each one was developed.

The final results are shown in table 4.1 and figures 4.1 to 4.3.

4.2.2 Hydrogen Solubility in Tetralin

The final data for the solubility of hydrogen in tetralin at a constant temperature and varying the hydrogen partial pressure in the reactor, are shown in tables 4.2 and 4.3 and in figure 4.4.

The procedure followed to get these results is explained in section 3.6.2.

Table 4-1: Hydrogen Permeation Runs

LIQUID PHASE PROBE

TEMPERATURE [^{o}C]	PERMEABILITY COEFFICIENT [$m^3/s/m/(MPa)^{1/2}]*10^{11}$
327.8	32.014
346.2	44.916
361.0	57.906
374.4	69.934
397.5	90.534
425.2	132.810

GAS PHASE PROBE

TEMPERATURE [^{o}C]	PERMEABILITY COEFFICIENT [$m^3/s/m/(MPa)^{1/2}]*10^{11}$
326.9	35.231
342.9	46.071
345.2	44.183
361.1	56.405
375.3	71.764
396.8	95.280

Figure 4-1: PERMEABILITY COEFFICIENT FOR LIQUID PHASE PROBE

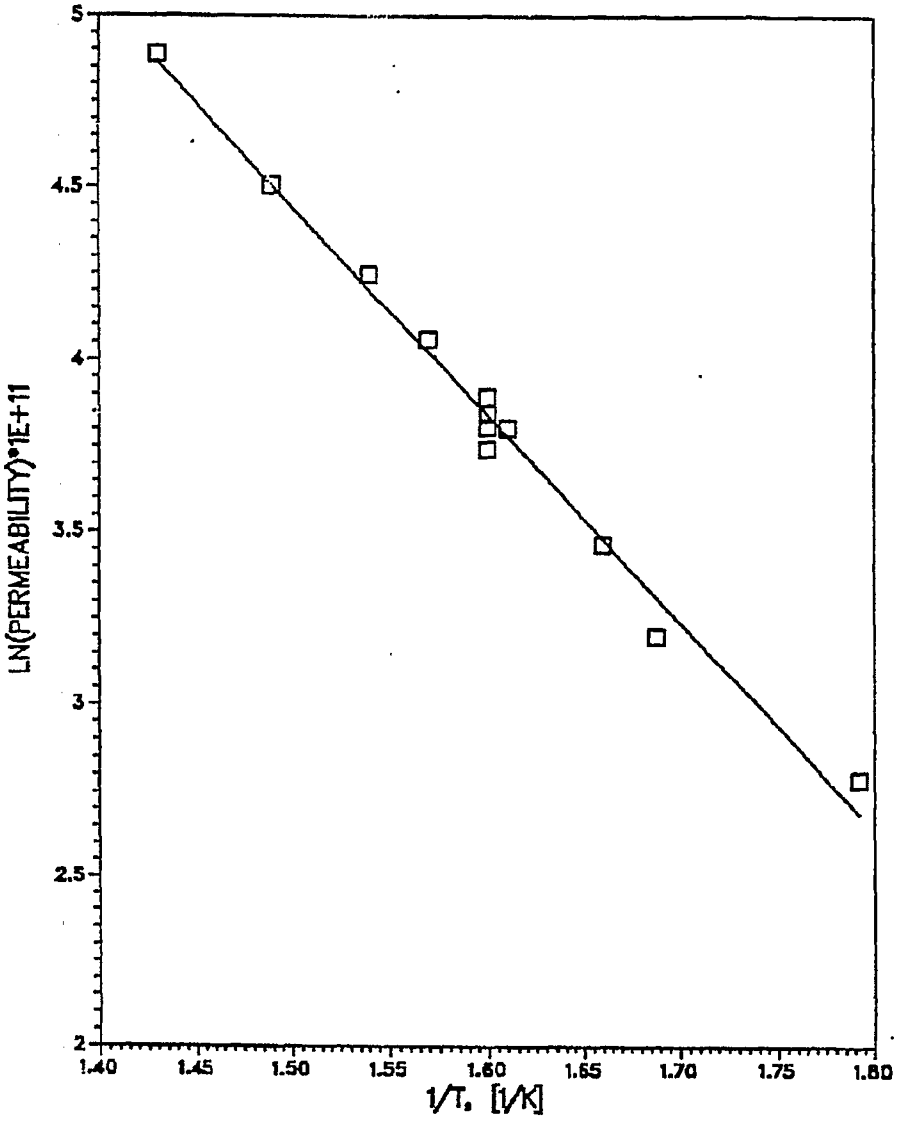


Figure 4-2: PERMEABILITY COEFFICIENT FOR GAS PHASE PROBE

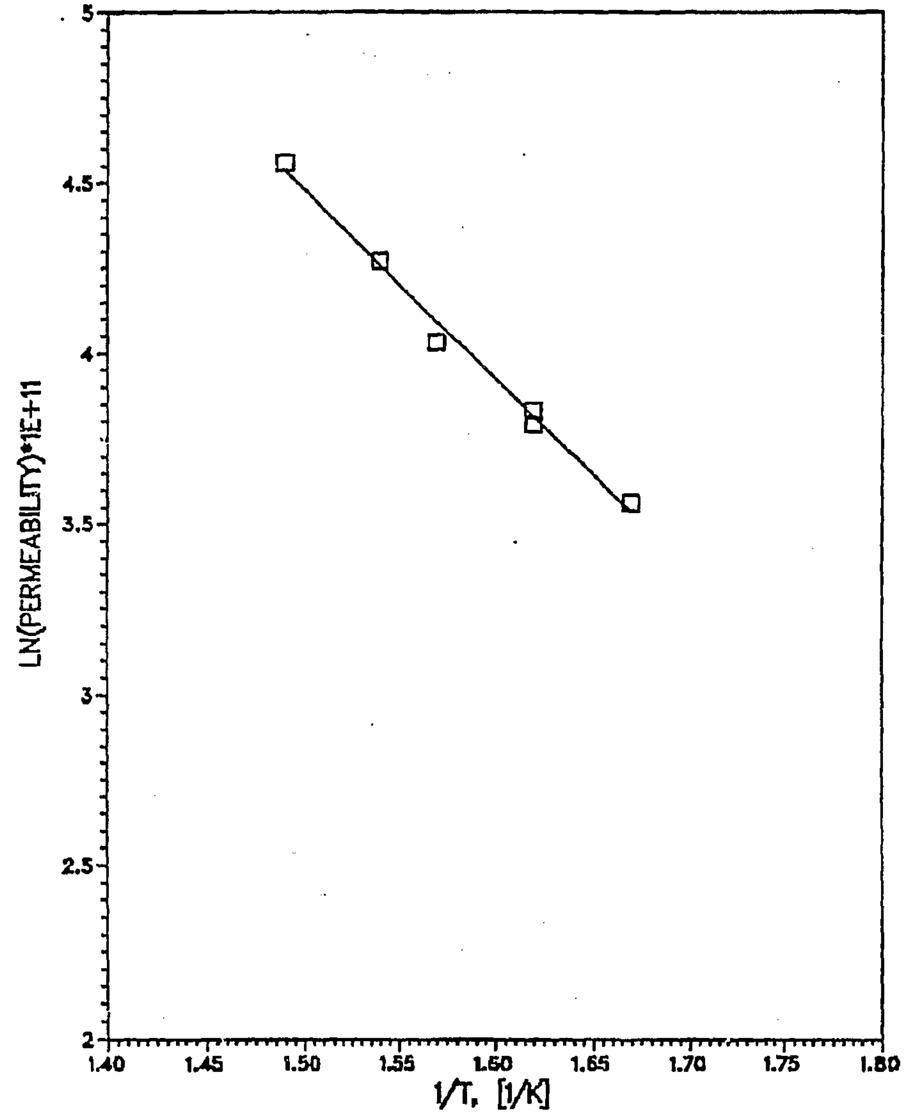


Figure 4-3: PERMEABILITY COEFFICIENT FOR LIQUID AND GAS PHASE PROBES

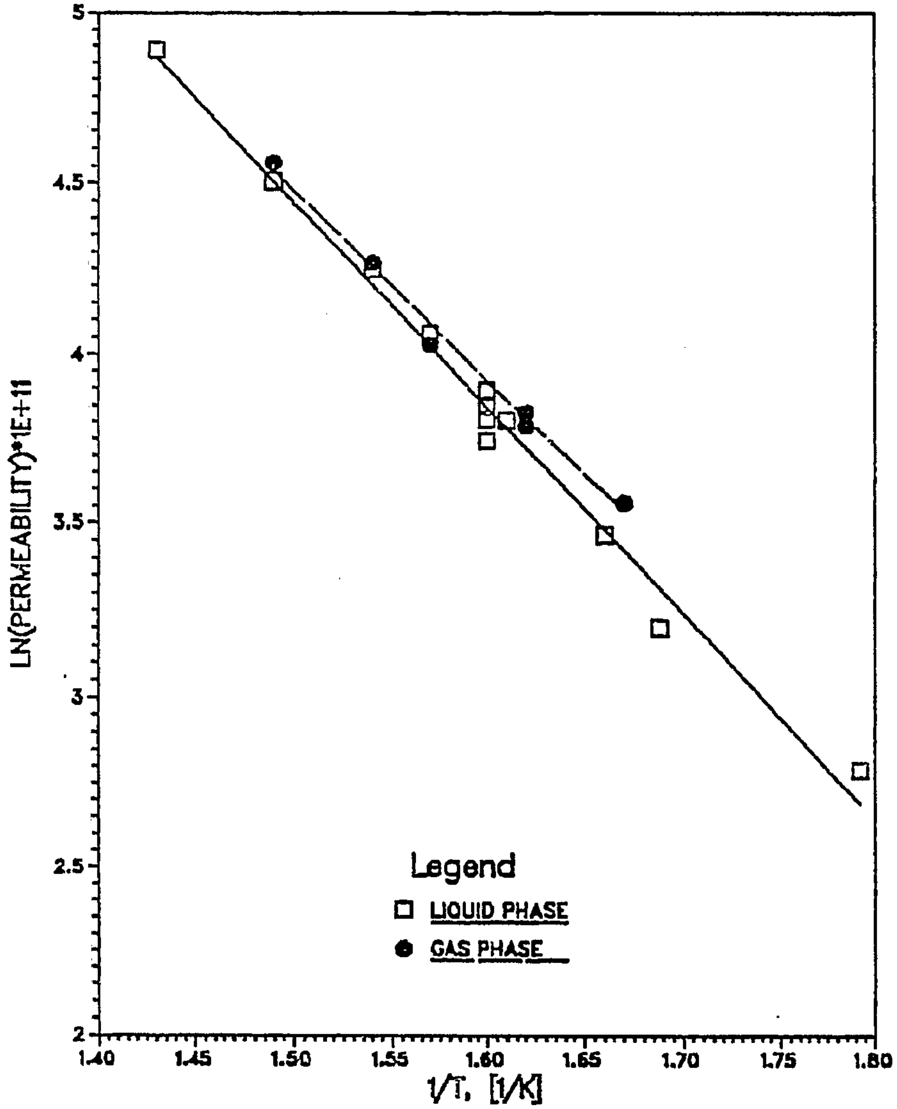


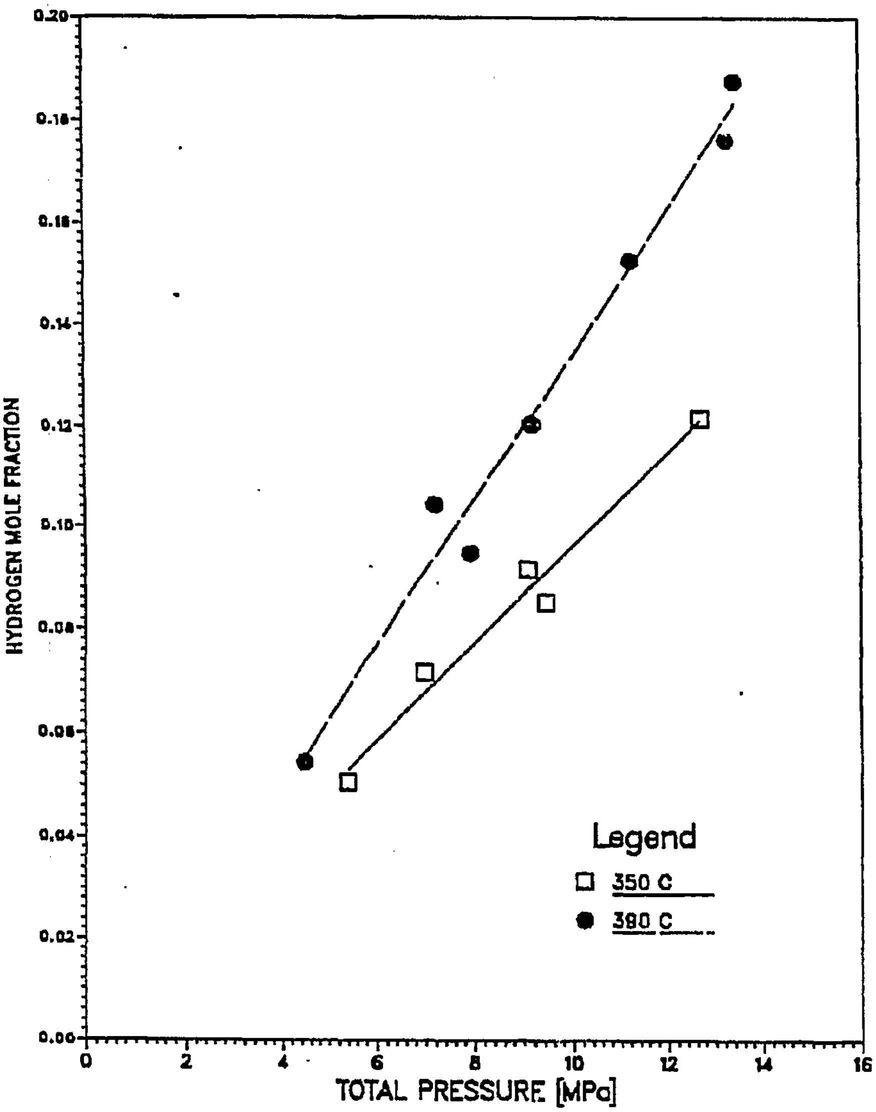
Table 4-2: System Hydrogen-Tetralin at 350 °C

EXP. #	PRESSURE[MPa]			LIQUID MOLE FRACTION	
	TOTAL	HYDROGEN	TETRALIN	HYDROGEN	TETRALIN
1	5.41	4.24	1.17	0.0505	0.9495
2	9.46	8.29	1.17	0.0851	0.9149
3	12.69	11.52	1.17	0.1217	0.8783
4	9.09	7.90	1.19	0.0916	0.9084
5	7.00	5.81	1.19	0.0716	0.9284

Table 4-3: System Hydrogen-Tetralin at 390 °C

EXP. #	PRESSURE[MPa]			LIQUID MOLE FRACTION	
	TOTAL	HYDROGEN	TETRALIN	HYDROGEN	TETRALIN
1	4.48	2.58	1.90	0.0544	0.9456
2	7.21	3.78	1.90	0.1045	0.8955
3	7.93	6.01	1.92	0.0948	0.9052
4	9.18	7.24	1.94	0.1207	0.8793
5	11.23	9.30	1.93	0.1528	0.8472
6	13.45	11.50	1.95	0.1878	0.8122
7	13.26	11.33	1.93	0.1764	0.8234

Figure 4-4: SYSTEM HYDROGEN-TETRALIN



4.2.3 Hydrogen Solubility in Tetralin under the presence of Methane

The final results for the runs for the hydrogen solubility in tetralin under the presence of methane are shown in this section. The procedure followed in order to obtained these results is explained in section 3.6.3

Tables 4.4 and 4.5 and figures 4.5 to 4.7 show these results.

Table 4-4: System Hydrogen-Tetralin-Methane at 325 °C

EXP.	PRESSURE[MPa]			LIQUID PHASE MOLE FRACTION		
#	HYDROGEN	METHANE	TETRALIN	HYDROGEN	METHANE	TETRALIN
1	6.27	----	0.85	0.08163	---	0.9384
2	7.25	0.38	0.85	0.07078	0.01532	0.9139
3	7.11	1.68	0.85	0.07243	0.04530	0.8823
4	6.98	2.98	0.85	0.08603	0.04685	0.8671
5	7.09	4.23	0.85	0.09554	0.04171	0.8628
6	7.32	5.43	0.85	0.10871	0.02632	0.8650

4.2.4 Hydrogen Solubility in Tetralin under the presence of Ethane

The value for the mole fraction of hydrogen, ethane and tetralin at two temperatures is shown in tables 4.6 and 4.7. The experimental procedure used is the same as that for the experiments using methane (see 3.6.3.). Figures 4.8 to 4.10 show these results.

4.2.5 K-Value for Each Experiment

The K-value was calculated by using the formula y/x. The value for the liquid molar fraction, x, was obtained directly from the final results of each set of experiments while the value for the gas phase mole fraction was obtained by assuming that the gas phase behaves as an ideal gas. The K-values obtained in this way are

Table 4-5: System Hydrogen-Tetralin-Methane at 375 °C

EXP.	PRESSURE[MPa]			LIQUID PHASE MOLE FRACTION		
#	HYDROGEN	METHANE	TETRALIN	HYDROGEN	METHANE	TETRALIN
1	3.65	----	1.57	0.0795	---	0.9205
2	6.25	1.88	1.57	0.0858	0.01674	0.8973
3	6.19	3.48	1.57	0.1194	0.03748	0.8530
4	5.61	7.03	1.57	0.1692	0.02295	0.8078
5	5.81	2.53	1.55	0.1042	0.02834	0.8675
6	6.65	5.19	1.56	0.1456	0.02945	0.8249
7	6.83	5.27	1.56	0.1635	0.03171	0.8047
8	5.91	7.30	1.58	0.1711	0.03605	0.7972
9	6.45	3.49	1.58	0.1321	0.03950	0.8284
10	6.25	2.87	1.55	0.1192	0.03060	0.8514

Figure 4-5: SYSTEM HYDROGEN-TETRALIN-METHANE
Hydrogen Mole Fraction

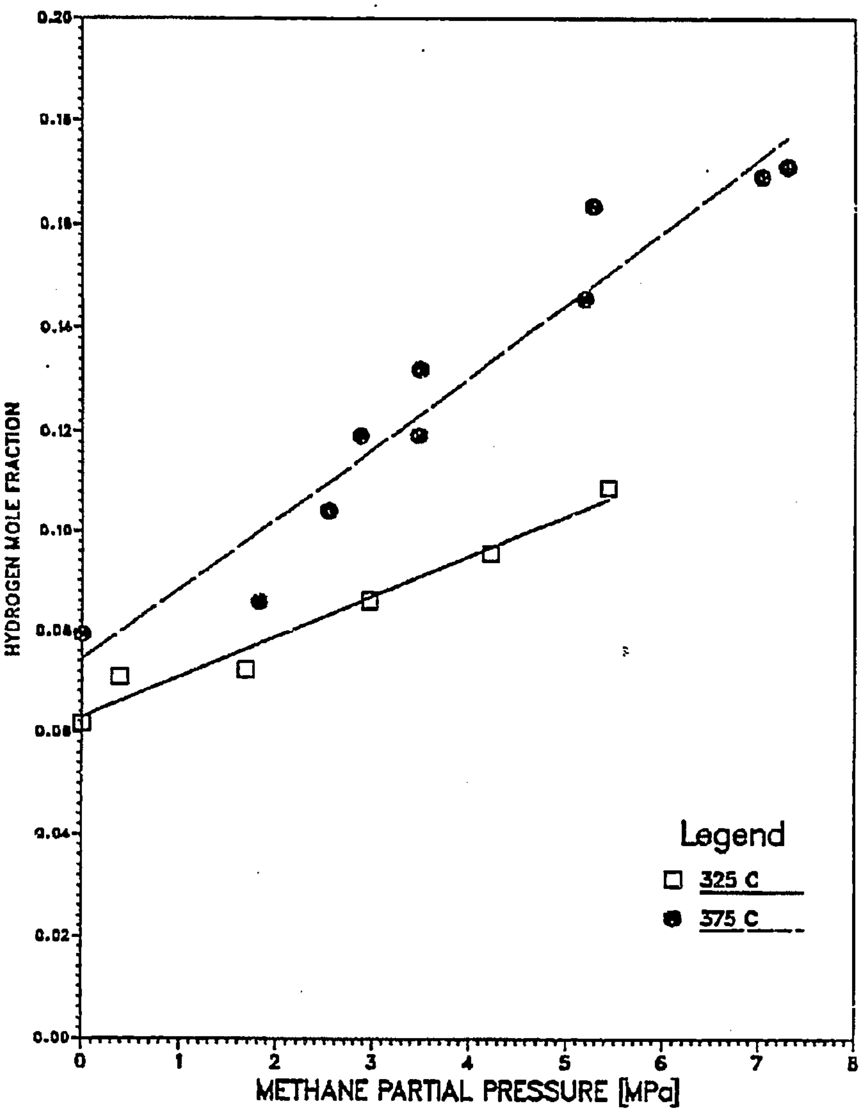


Figure 4-6: SYSTEM HYDROGEN-TETRALIN-METHANE
Methane Mole Fraction-Liquid Phase

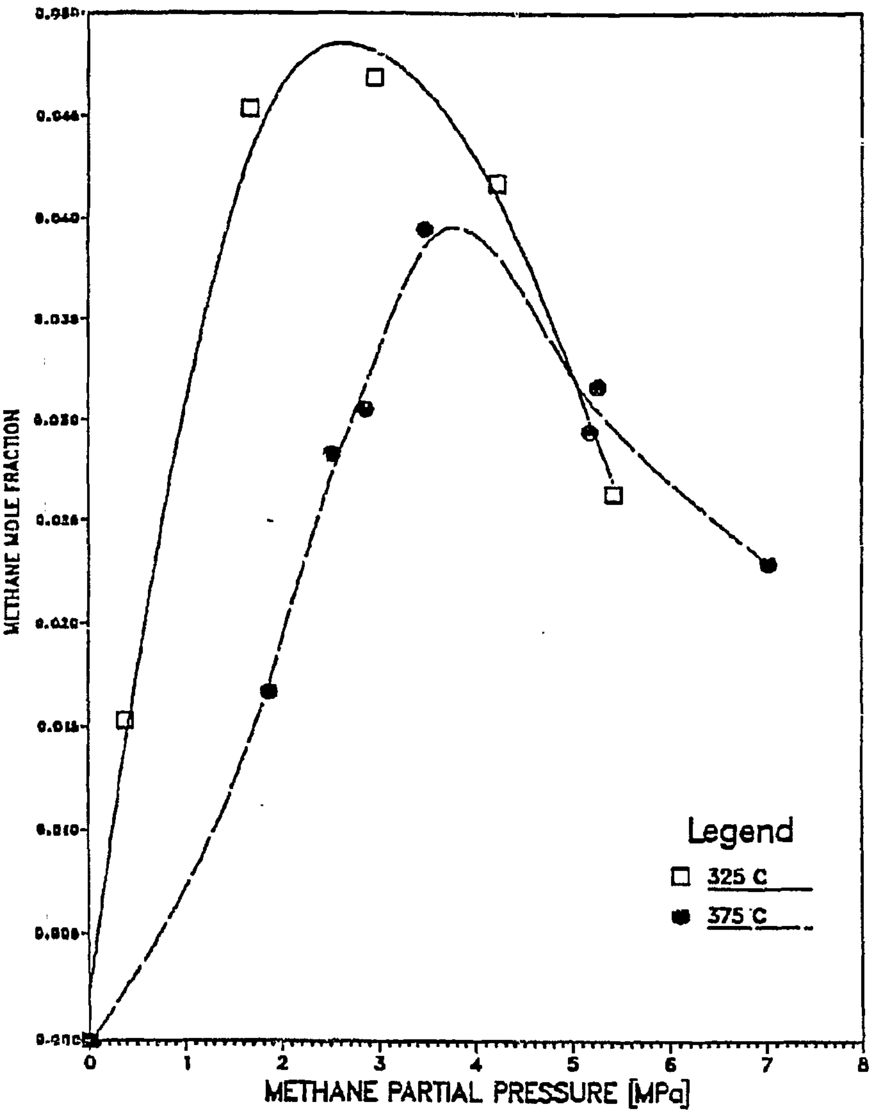


Figure 4-7: SYSTEM HYDROGEN-TETRALIN-METHANE
Tetralin Mole Fraction-Liquid Phase

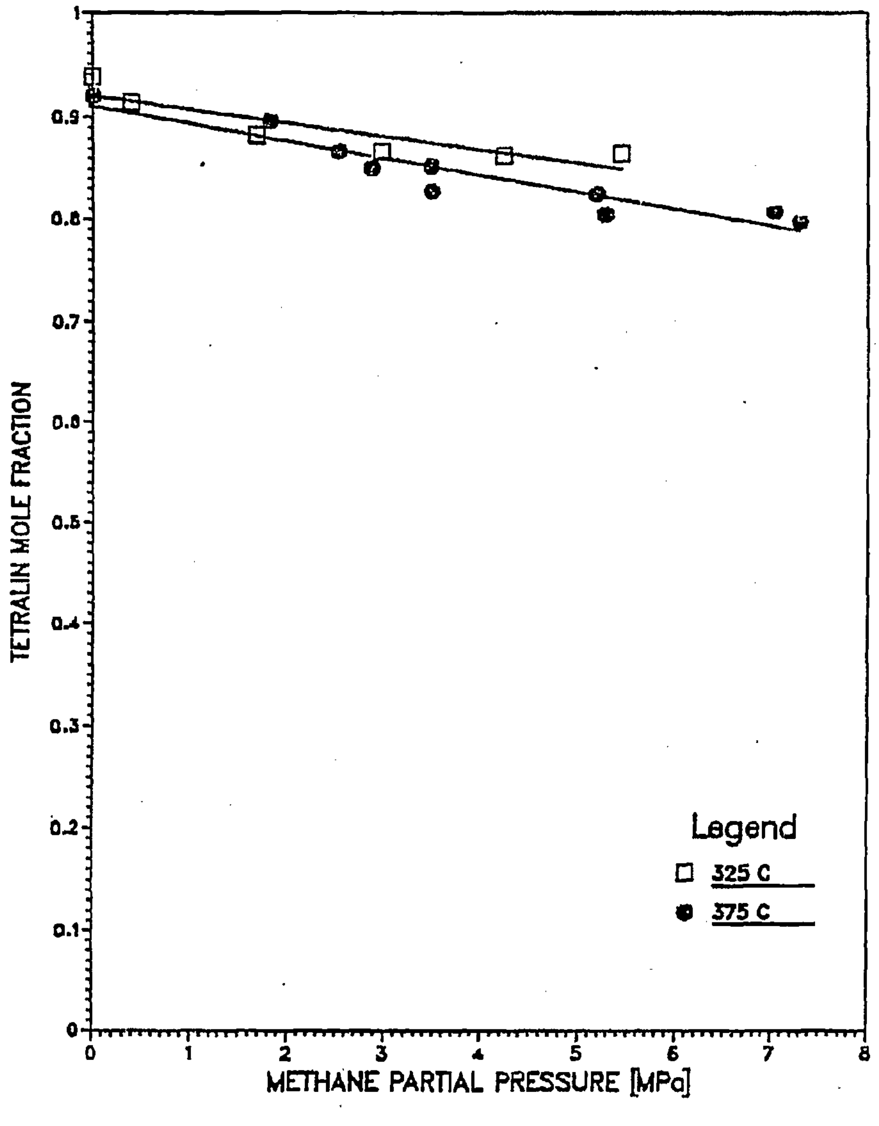


Table 4-6: System Hydrogen-Tetralin-Ethane at 360 °C

EXP.	PRESSURE[MPa]			LIQUID PHASE MOLE FRACTION		
#	HYDROGEN	ETHANE	TETRALIN	HYDROGEN	ETHANE	TETRALIN
1	8.18	----	1.33	0.07585	---	0.9242
2	6.43	0.05	1.35	0.07706	0.00142	0.9215
3	6.74	0.25	1.36	0.07770	0.00386	0.9186
4	6.48	0.85	1.34	0.08050	0.00303	0.9165
5	6.63	1.37	1.35	0.08105	0.00317	0.9158
6	6.53	2.59	1.34	0.08417	0.00304	0.9128
7	6.52	3.78	1.33	0.08802	0.00295	0.9087

Table 4-7: System Hydrogen-Tetralin-Ethane at 395 °C

EXP.	PRESSURE[MPa]			LIQUID PHASE MOLE FRACTION		
#	HYDROGEN	ETHANE	TETRALIN	HYDROGEN	ETHANE	TETRALIN
1	7.14	----	2.03	0.1382	---	0.8618
2	7.18	0.50	2.01	0.1405	0.00498	0.8545
3	7.31	1.03	2.03	0.1451	0.00943	0.8454
4	7.14	4.01	2.03	0.1880	0.00785	0.8081

Figure 4-8: SYSTEM HYDROGEN-TETRALIN-ETHANE
Hydrogen Mole Fraction-Liquid Phase

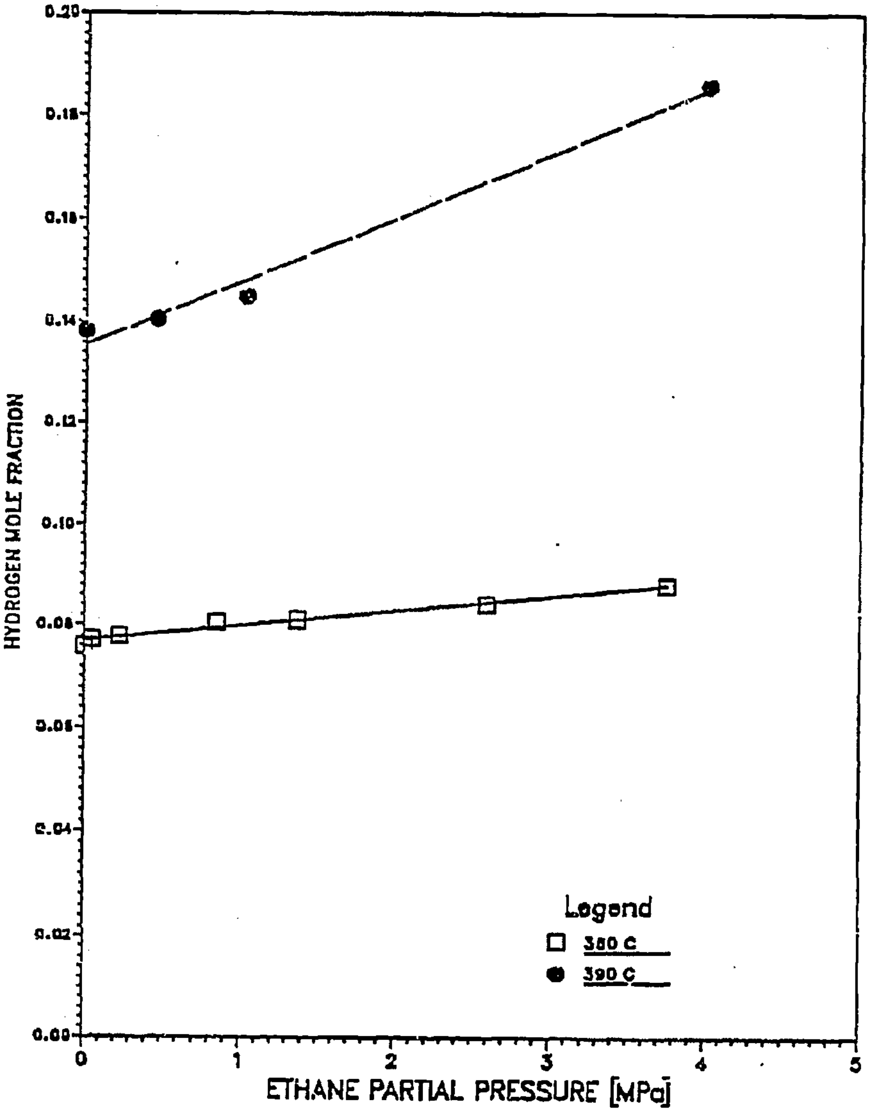


Figure 4-9: SYSTEM HYDROGEN-TETRALIN-ETHANE
Ethane Mole Fraction-Liquid Phase

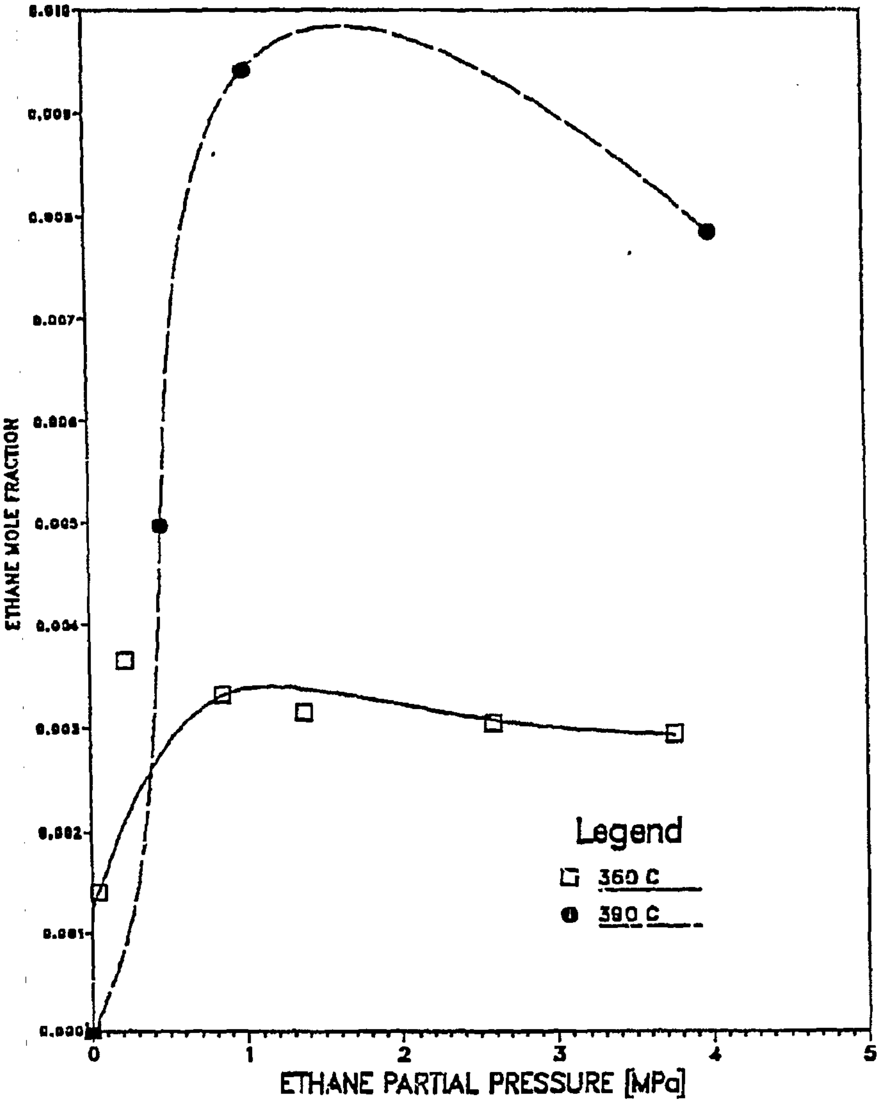
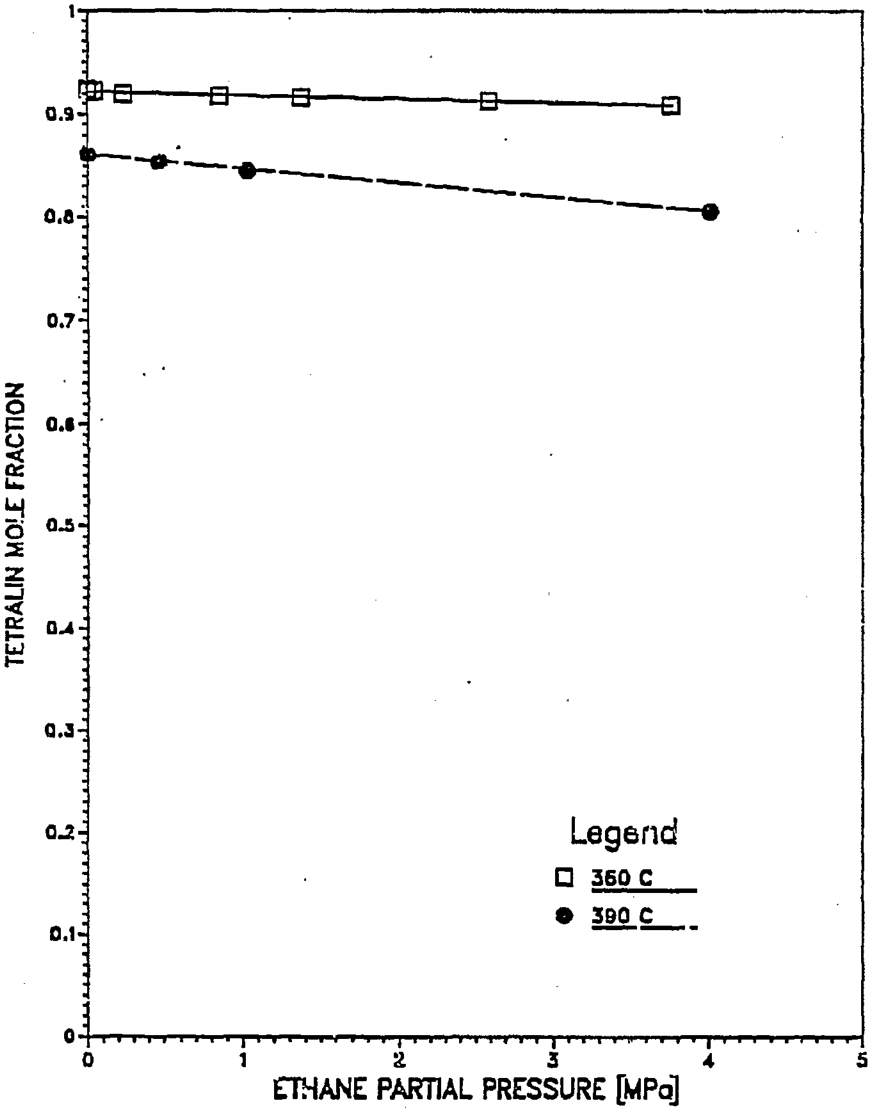


Figure 4-10: SYSTEM HYDROGEN-TETRALIN-ETHANE
Tetralin Mole Fraction-Liquid PHase



tabulated in the following tables. Tables 4.8 to 4.13 and figures 4.11 to 4.18 show these results.

Table 4-8: System Hydrogen-Tetralin at 350 °C
K-value

TOTAL PRESSURE [MPa]	K-VALUE	
	HYDROGEN	TETRALIN
5.41	15.52	0.228
6.99	11.59	0.183
9.09	9.49	0.144
8.46	10.29	0.135
12.69	7.46	0.105

Table 4-9: System Hydrogen-Tetralin at 390 °C
K-values

TOTAL PRESSURE [MPa]	K-VALUE	
	HYDROGEN	TETRALIN
4.48	10.59	0.449
7.21	7.05	0.294
7.93	7.99	0.268
9.18	6.54	0.240
11.23	5.42	0.203
13.45	4.55	0.178
13.26	4.84	0.177

Table 4-10: System Hydrogen-Tetralin-Methane at 325 °C
K-values

TOTAL PRESSURE [MPa]	K-VALUE		
	HYDROGEN	METHANE	TETRALIN
7.12	14.29	----	0.127
8.47	11.29	6.54	0.110
9.64	9.49	4.96	0.098
10.79	6.99	6.82	0.091
12.18	5.68	9.29	0.081
13.59	4.63	----	0.072

Table 4-11: System Hydrogen-Tetralin-Methane at 375 °C
K-values

TOTAL PRESSURE		K-VALUE	
[MPa]	HYDROGEN	METHANE	TETRALIN
8.22	10.18	----	0.208
9.70	7.51	11.59	0.179
9.89	5.64	9.03	0.181
10.67	4.92	8.78	0.171
11.24	4.62	11.27	0.163
13.40	3.41	13.14	0.141
13.67	3.06	12.17	0.142
14.77	2.34	15.65	0.132

Table 4-12: System Hydrogen-Tetralin-Ethane at 360 °C
K-values

TOTAL PRESSURE		K-VALUE	
[MPa]	HYDROGEN	ETHANE	TETRALIN
7.52	10.85	----	0.192
7.83	10.67	3.73	0.187
8.33	10.41	7.69	0.177
8.67	9.29	32.26	0.168
9.35	8.75	45.12	0.158
10.46	7.42	81.67	0.140
11.61	6.38	92.47	0.126

Table 4-13: System Hydrogen-Tetralin-Ethane at 395 °C
K-values

TOTAL PRESSURE		K-VALUE	
[MPa]	HYDROGEN	ETHANE	TETRALIN
9.17	5.64	----	0.257
9.65	5.29	9.47	0.244
10.38	4.58	10.57	0.232
13.18	2.92	38.71	0.191

Figure 4-11: SYSTEM HYDROGEN-TETRALIN
K-value for Hydrogen

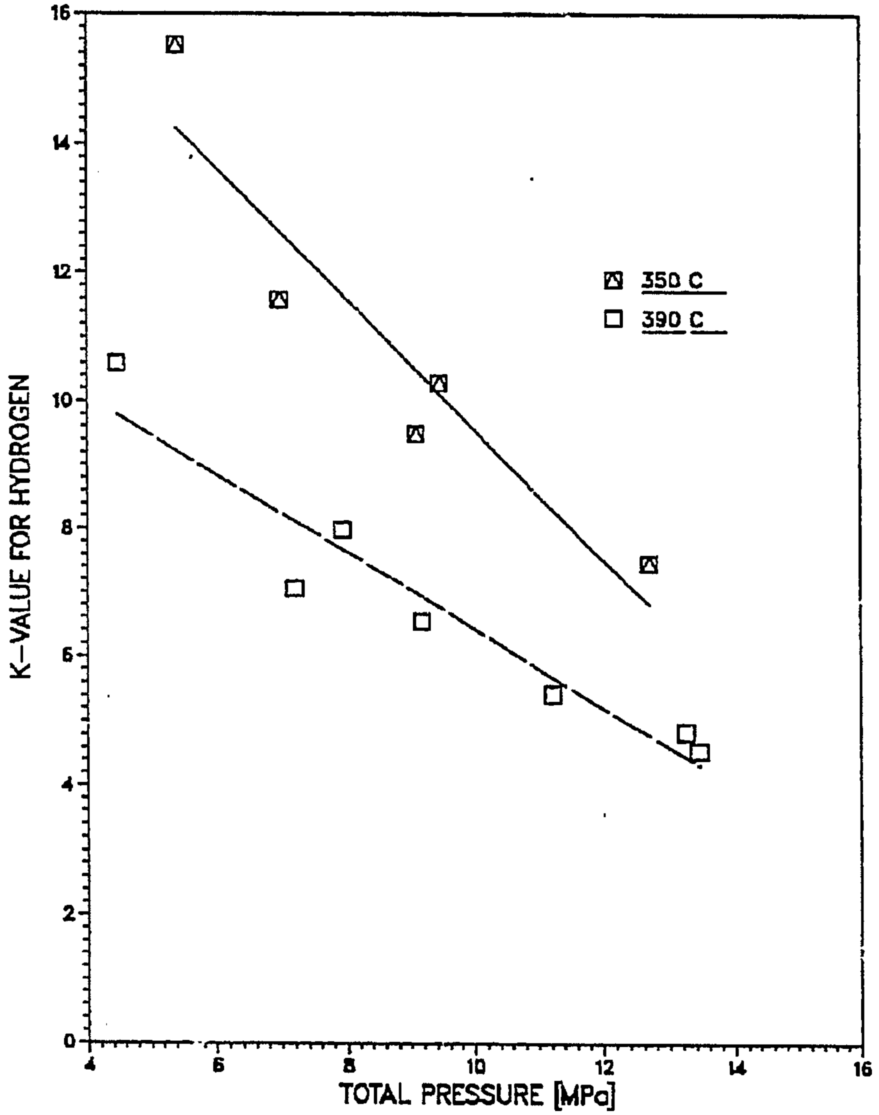


Figure 4-12: SYSTEM HYDROGEN-TETRALIN
K-value for Tetralin

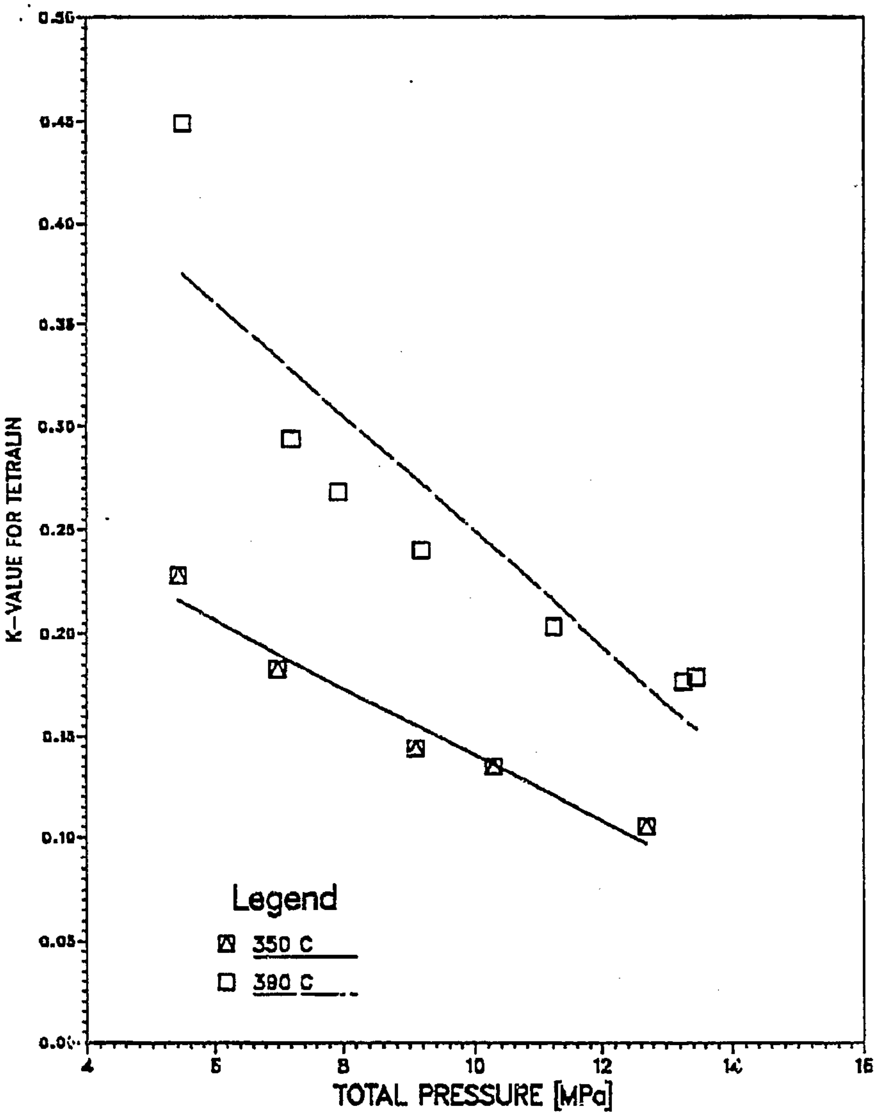


Figure 4-13: SYSTEM HYDROGEN-TETRALIN-METHANE
K-value for Hydrogen

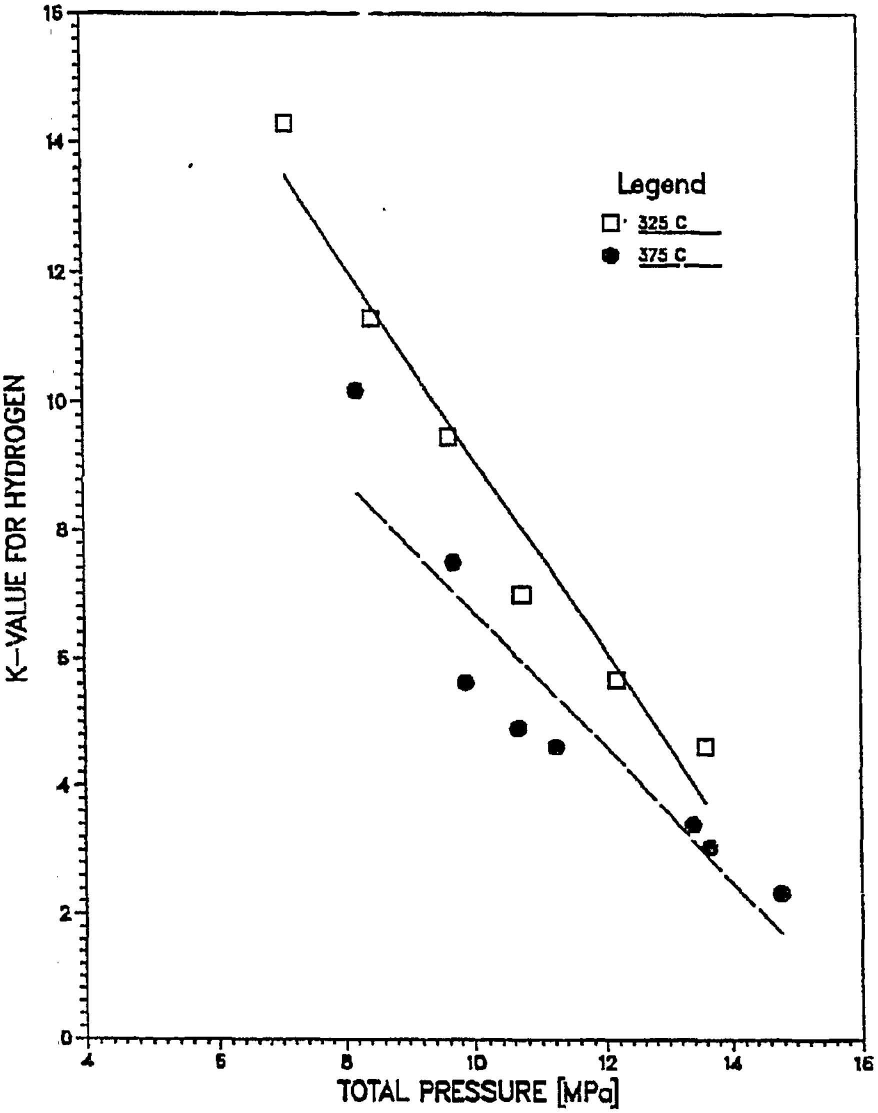


Figure 4-14: SYSTEM HYDROGEN-TETRALIN-METHANE
K-value for Methane

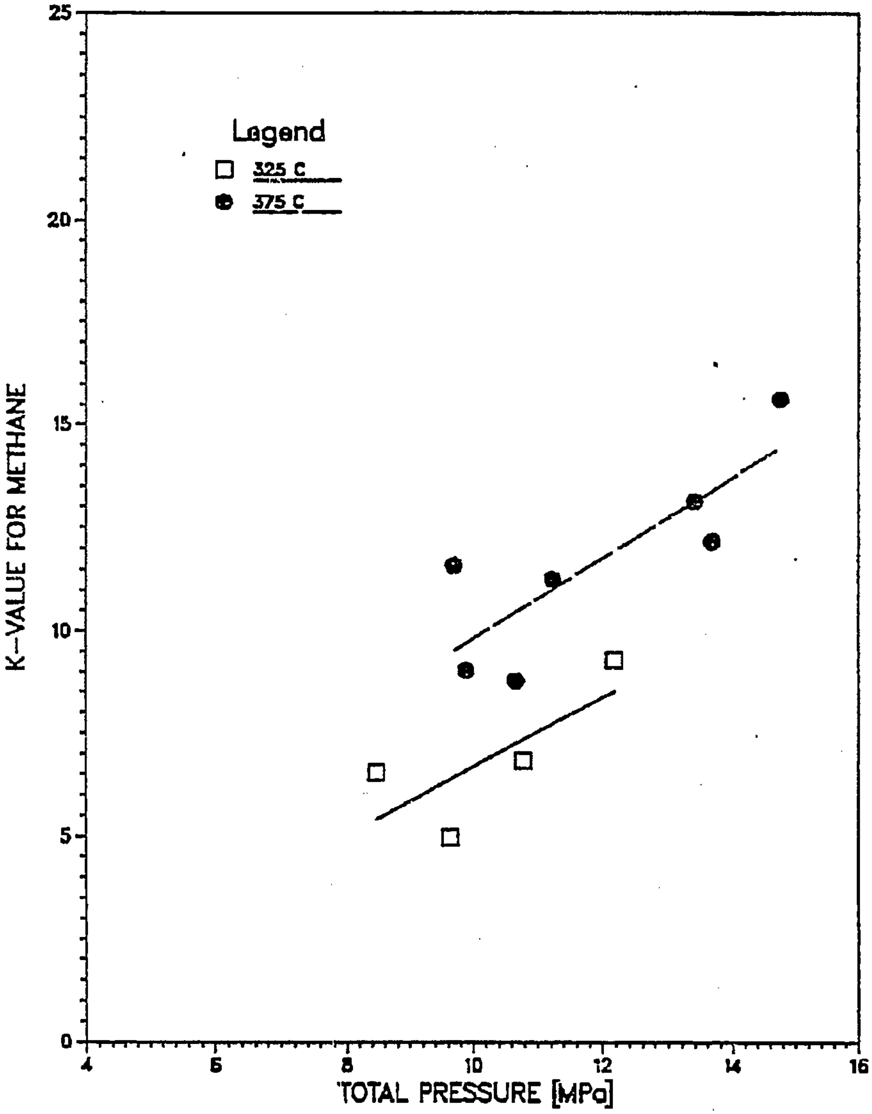


Figure 4-15: SYSTEM HYDROGEN-TETRALIN-METHANE
K-value for Tetralin

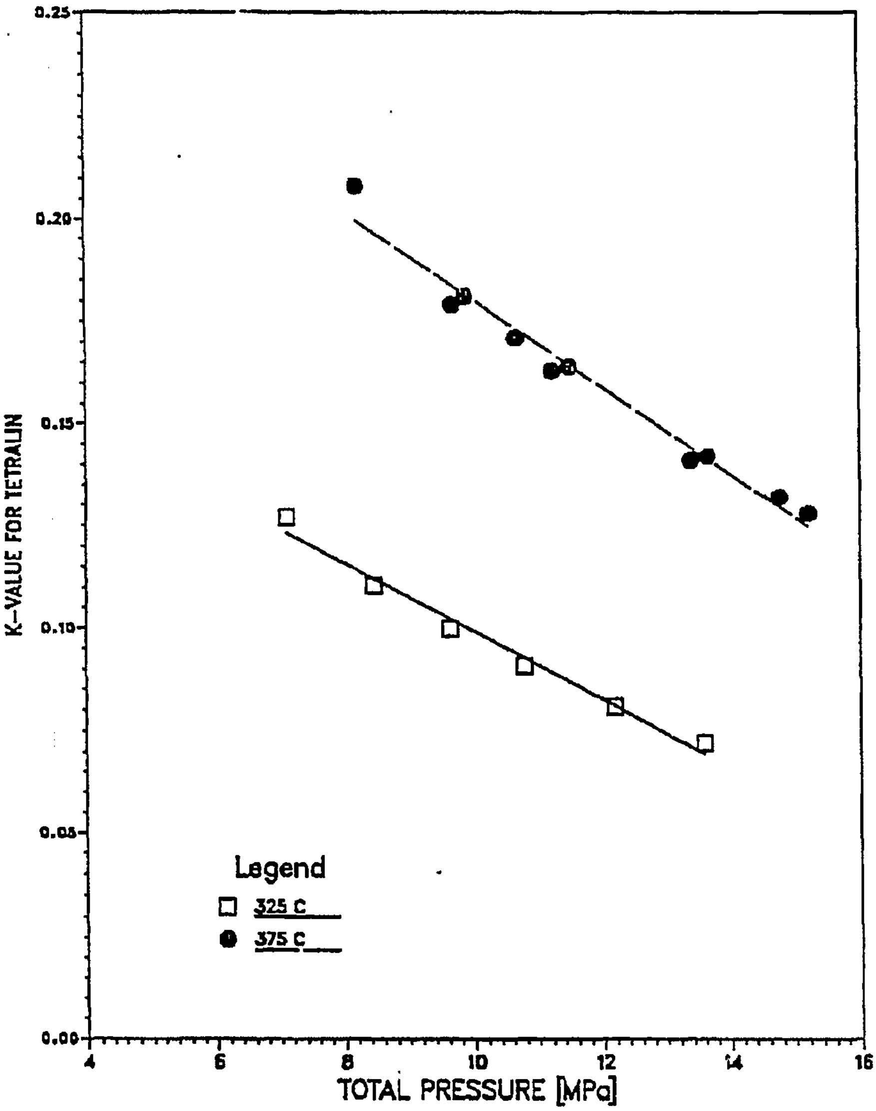


Figure 4-16: SYSTEM HYDROGEN-TETRALIN-ETHANE
K-value for Hydrogen

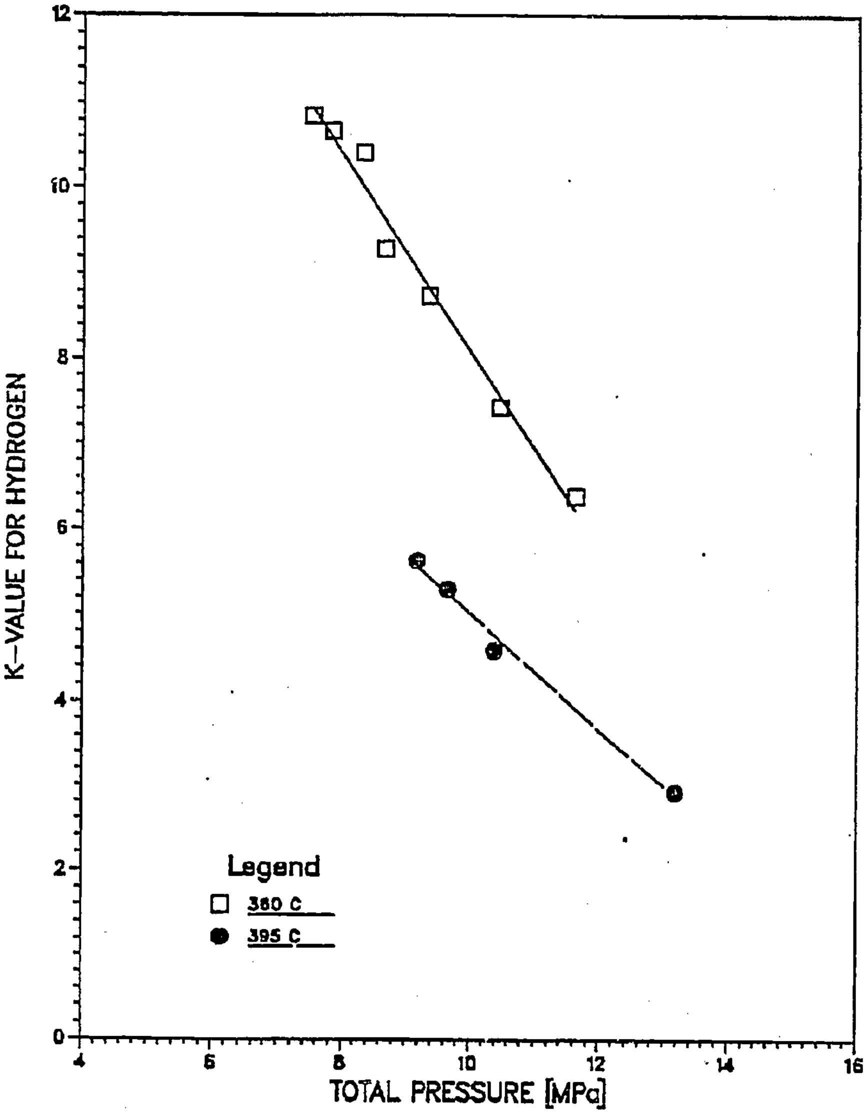


Figure 4-17: SYSTEM HYDROGEN-TETRALIN-ETHANE
K-value for Ethane

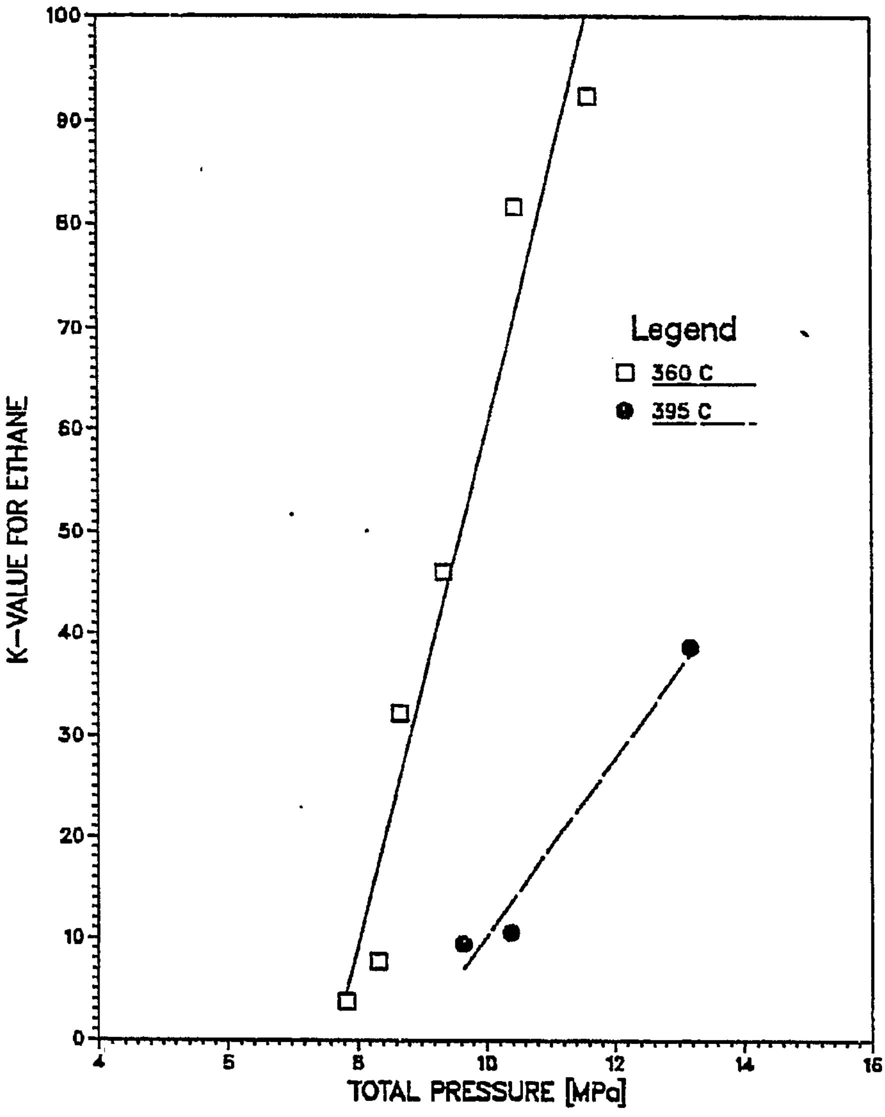
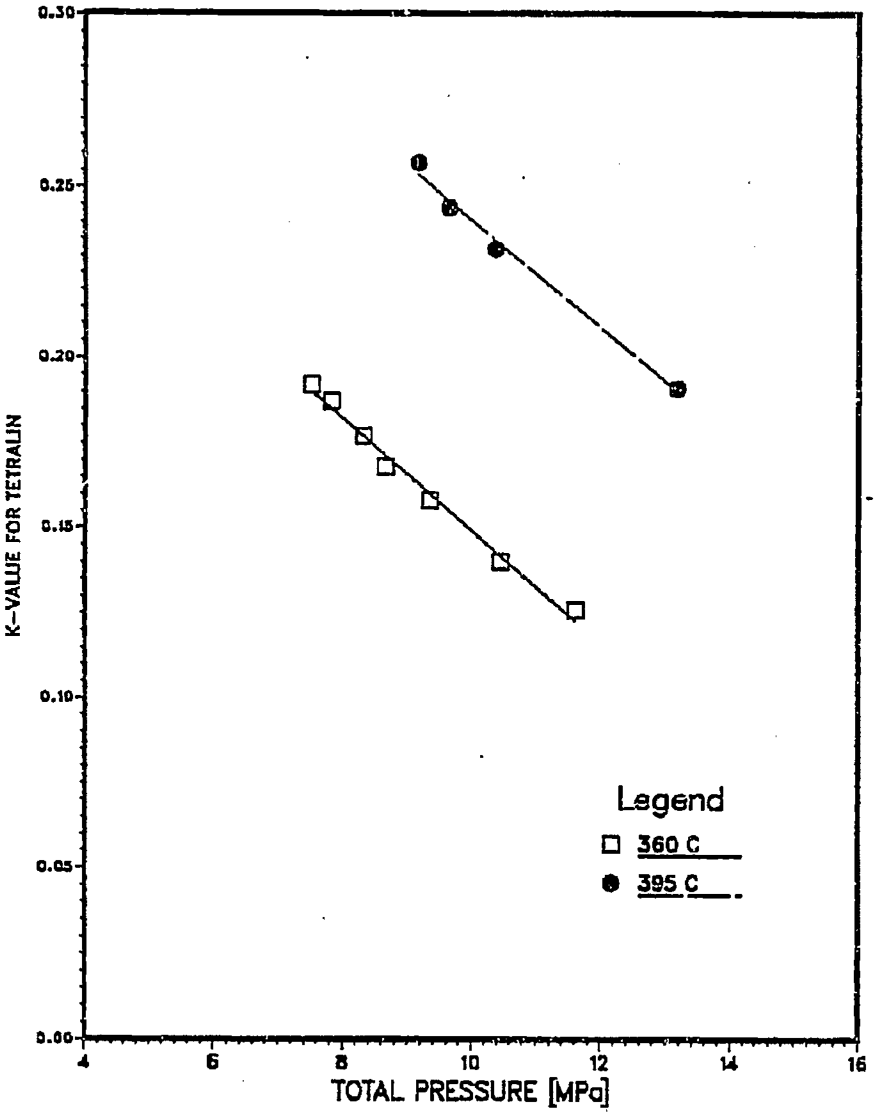


Figure 4-18: SYSTEM HYDROGEN-TETRALIN-ETHANE
K-value for Tetralin



5. Analysis of Results

5.1 VAPOR PRESSURE OF TETRALIN

An inspection of the tetralin vapor pressure when no methane nor ethane are present in the system, shows that the experimental values for the vapor pressure of tetralin are in good agreement with the equation presented by Kara et al.(31) (see appendix K). The equation is:

$$\log P = -2549(+/-\ 235)/T - 1.022(+/-0763)*10^{(-3)}T + 7.804(+/-0.854) \qquad (5-1)$$

where P is in KPa

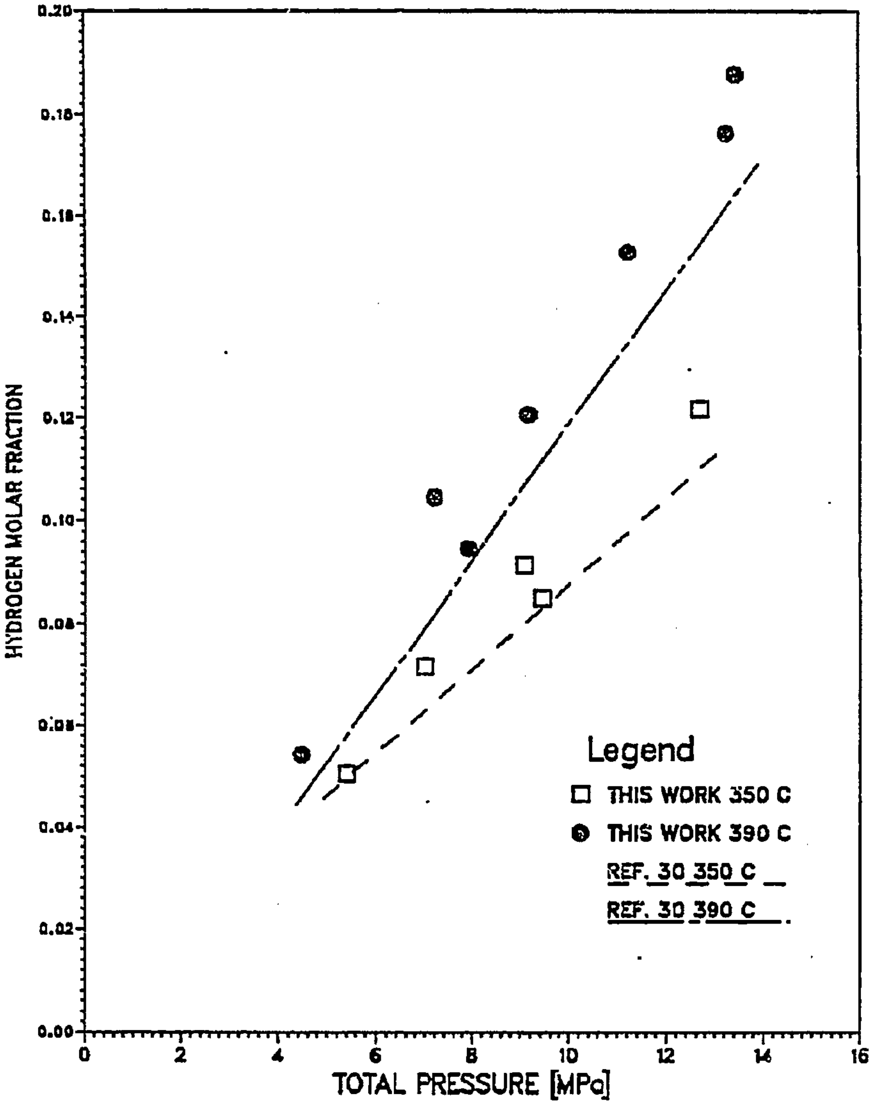
T is in °K

5.2 SYSTEM HYDROGEN-TETRALIN

The experimental data for the system hydrogen-tetralin were compared to that of Sung(30). Figure 5.1 shows this comparison. It can be noticed that there is a good agreement between the experimental data of this work and Sung's data. The results obtained in this work show up to 15% higher values than Sung's results. This difference can be possibly explained because of the existence of experimental problems in the sampling section due to weighing inaccuracies and residual liquid on the sampling lines.

The major problem occured when the amount of liquid was weighed in order to obtain the number of liquid moles in the sample. The weight of the system that held the liquid sample (expansion cylinder and cold trap) was too heavy, about 2 kilograms, so an analytical balance could not be used. The weight of the sample was no more than 2 grams. This caused the difference in weight of the cylinder and the sample to

Figure 5-1: SYSTEM HYDROGEN-TETRALIN
Hydrogen Mole fraction
(Comparison with Literature Data)



be small so the error generated was about 10% in the number of moles of liquid. A Ohaus[(tm)] digital pan balance was used in this study. Its accuracy was 0.1 grams. The other problem was the residual liquid held in the sampling lines which caused the weight of liquid to appear to be less than the actual value. These experimental problems cause less amounts of liquid to be measured than was actually present, so the mole fraction of hydrogen will appear to be larger than the actual values.

Besides these experimental problems, it can be noticed that the slope of the figure 5.1 shows good agreement with Sung's results. For this reason the experimental results were considered suitable for analysis.

It can be observed that when the temperature of the system was increased, the hydrogen solubility in tetralin was also increases. The same effect was observed when the pressure of the system was increased. This behavior of the hydrogen solubility was measured by numerous investigators and they obtained similar findings.(8,30,31,32)

5.3 SYSTEM HYDROGEN-TETRALIN-METHANE

Figures 4.2 to 4.4 present the liquid mole fraction for hydrogen, tetralin and methane in the liquid phase.

It can be noticed that the hydrogen solubility in tetralin increases when the methane partial pressure is increased and the hydrogen partial pressure is held constant (figure 4.2). At the same time, if the temperature is increased, the hydrogen solubility increases as is also seen in the binary system, hydrogen–tetralin. This behavior for hydrogen is different when coal liquid is used instead of tetralin as the solvent. Ding(17) has shown that when the methane partial pressure is increased, the hydrogen solubility decreases. This difference may be because of the different nature of the solvent used. Tetralin is a pure compound while coal liquids contains mixtures of many compounds. These difference in the composition may affect the behavior of hydrogen in the respective liquids.

For tetralin, the liquid mole fraction tends to decrease when the methane partial pressure is increased. At this condition the total system pressure increases. When the temperature is increased, the tetralin mole fraction decreases. These results for tetralin mole fraction follows normal behavior.

The solubility of methane in tetralin shows a different behavior pattern when the partial pressure of methane is increased. The mole fraction of methane in the liquid increases up to a maximun and then decreases. When the temperature is increased, the similar maximun was observed, but the mole fraction decreases in absolute value. This phenomena of a decrease in the mole fraction with temperature was noticed by Ramanujan et al. (39) when studing the systems of methane-aromatic oil and methane-toluene.

5.4 SYSTEM HYDROGEN-ETHANE-TETRALIN

The same behavior pattern for hydrogen solubility observed in the hydrogen-tetralin-methane system was also observed in the hydrogen-tetralin-ethane system. Figure 4.5 shows the hydrogen mole fraction in the liquid phase. As can be observed, the hydrogen solubility increases when the partial pressure of ethane is increased and the hydrogen partial pressure is held constant. The increase of temperature causes the hydrogen solubility to increase.

The tetralin mole fraction also had the same behavior as before. The increase in ethane partial pressure causes the tetralin mole fraction to decrease. The tetralin mole fraction decreases when the temperature increases as was expected.

The ethane mole fraction also shows a maximum with ethane partial pressure. The decrease in the case of ethane is not as strong as in the case of methane (figure 4.6). The effect of temperature on the solubility of ethane was found to be the inverse to that of methane. When the temperature is increased, the mole fraction of ethane in the liquid phase increased. This increase may be due to the mole fraction of ethane in tetralin which is one order of magnitude less than that of methane.

5.5 K-VALUES

The K-values were calculated for the systems hydrogen-tetralin, hydrogen-tetralin-methane and hydrogen-tetralin-ethane. The value for the gas phase was calculated assuming that the gas phase behaves as an ideal gas.

The K-value for hydrogen and tetralin in every system follows the usual behavior. This means that the K-value decreases with total pressure (figures 4.8,4.10,4.12,4.13,4.15). The effect of the temperature on the K-value shows that when the temperature is increased the K-value increases for hydrogen. The opposite effect is observed for tetralin, that is the K-value decreases when the temperature increases. For methane and ethane, the K-values increase with pressure.

The K-values for hydrogen and tetralin were found to follow a similar pattern with temperature and pressure. Figure 5.2 and 5.3 present the K-value for hydrogen from the systems containing methane and ethane. It can be observed that the K-values decreases with temperature as expected and that the third component (methane or ethane) only affect the slope of the data. If the system hydrogen-tetralin is included in the plot, it can be observed that the same pattern results (figure 5.4). The slope in the hydrogen-tetralin system is different from the other systems. This may be because of the third component present in the other systems.

The K-value of tetralin had the same effect with temperature as shown in figure 5.5. These comparison of K-value behaviors show the consistency of the experimental data obtained during this investigation.

Since methane and ethane are part of an homologous series, it is expected that the K-value for hydrogen and tetralin will not change dramatically when methane is interchanged for ethane. Figures 5.2 to 5.5 emphasizes this finding.

Figure 5-2: K-VALUE FOR HYDROGEN
AT DIFFERENT TEMPERATURES
(From systems with methane and ethane)

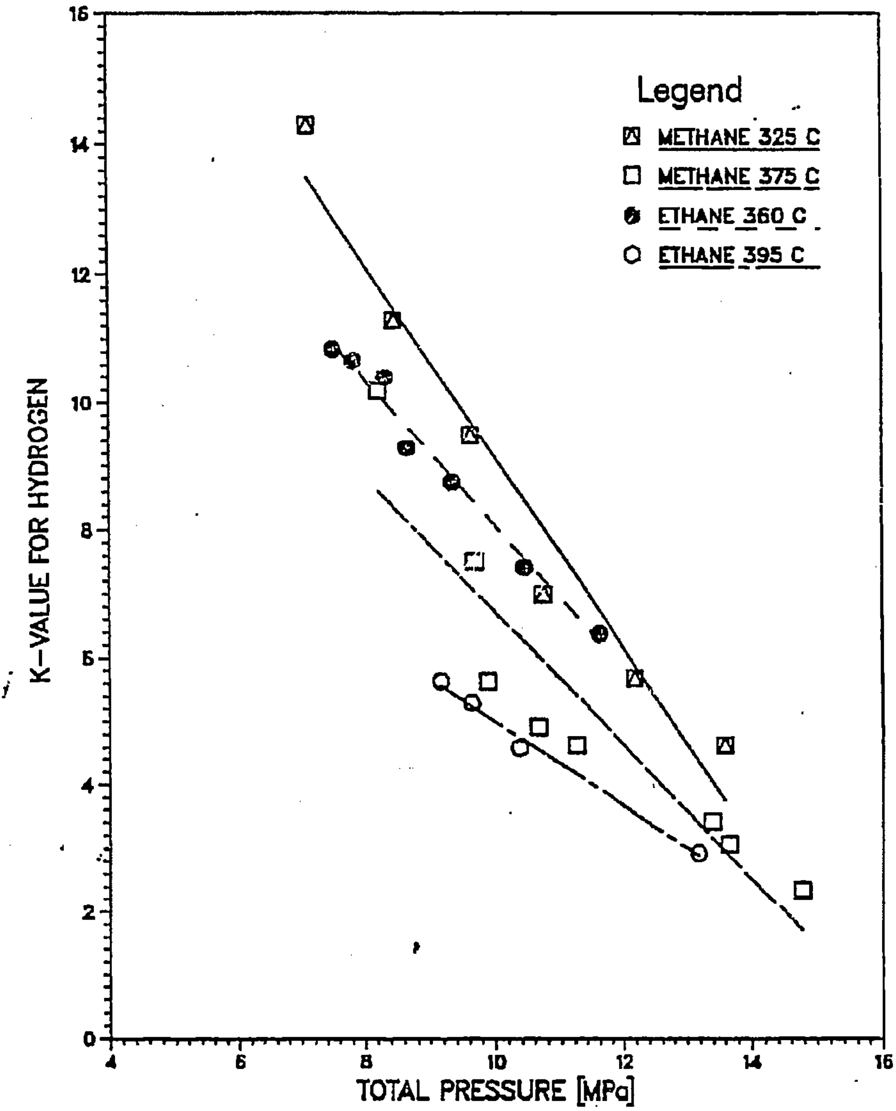


Figure 5-3: K-VALUE FOR HYDROGEN
AT DIFFERENT TEMPERATURES
(From systems with methane and ethane
No data shown)

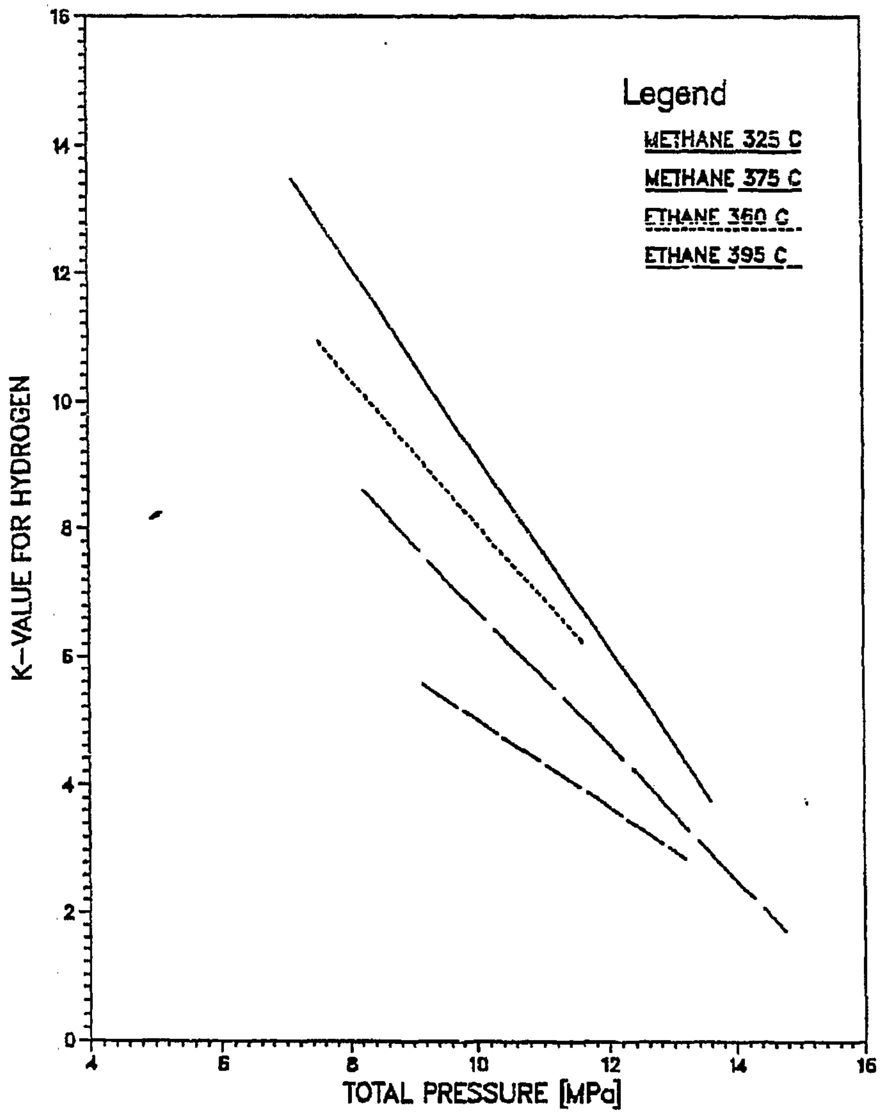


Figure 5-4: (K-VALUE FOR HYDROGEN
AT DIFFERENT TEMPERATURES
(From all systems studied)

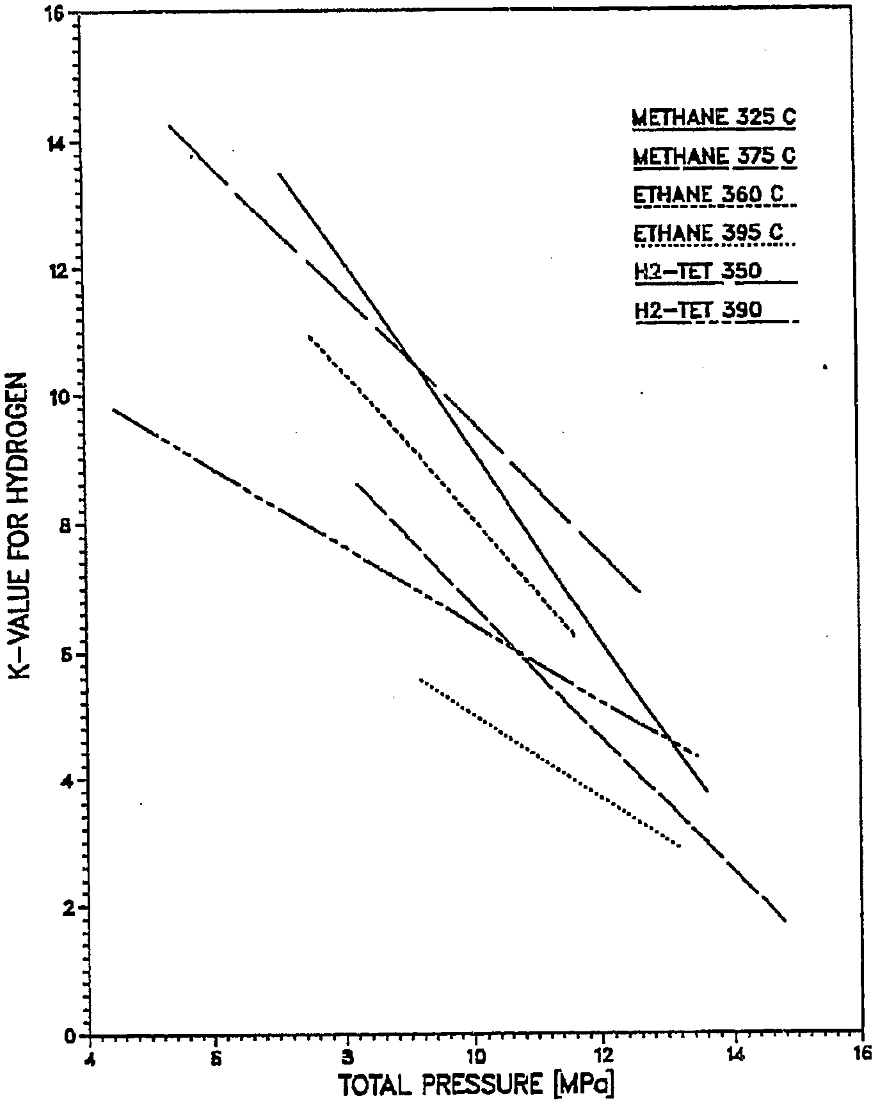
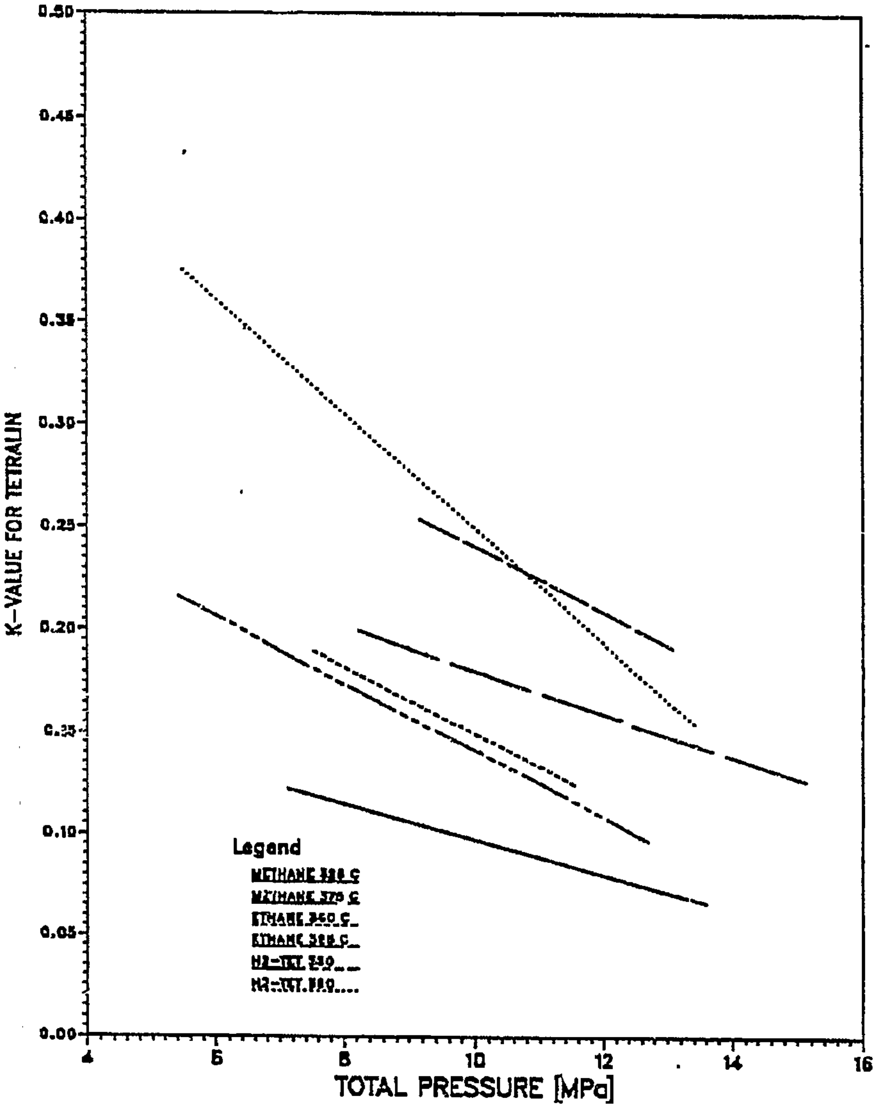


Figure 5-5: K-VALUE FOR TETRALIN
AT DIFFERENT TEMPERATURES
(From all systems studied)



5.5.1 Prediction of K-values

There are several correlations that may predicts K-values for hydrogen and tetralin in binary and ternary systems. Two equations were used in this study to predict the K-value for hydrogen and tetralin in the systems hydrogen-tetralin, hydrogen-tetralin-methane and hydrogen-tetralin-ethane.

The first equation was the one developed by Chao and Seader (40) in 1961. This equation predicts the K-value for each one of the components in hydrocarbon systems but it has some restrictions for its use mainly concerning temperatures and pressures. It has been demonstrated in the literature that this equation generates a large error in its use with hydrogen (100% some times) but that it can be used for tetralin with confidence.

The second correlation used was that developed by Sebastian et al. (41) in 1980. This correlation is suitable only for hydrogen in binary and ternary systems. The correlation can be used between 310 and 700 °K and pressures up to 30 MPa. Since the conditions used in this work are within the mentioned range, the correlation was used to predict the K-values in the three systems studied. Details of the correlations are given in appendix L.

For each of the above correlations, the experimental values for the liquid mole fraction, x, and the calculated values for the vapor mole fraction, y, for each component was used.

Figures 5.6 to 5.13 show the comparison between the experimental K-values and the ones calculated by the use of the correlation. Tables with this comparison are shown in appendix L.

5.5.1.1 K-value for Hydrogen. The K-value hydrogen at 350 °C is predicted accurately within 8% for the system hydrogen-tetralin. However at 390 °C, the value predicted is larger than the experimental value (figure 5.6).

For the systems containing a third component, the prediction is generally larger than the experimental value (figure 5.7 to 5.10). This difference is up to 22%. The best prediction for a ternary system is for the one using ethane at 360 °C (figure 5.10), which has a difference within 20%. In most cases, the diference between the predicted and calculated value is higher at higher pressures.

5.5.1.2 K-value for tetralin. The K-value for tetralin is predicted accurately in all three system studied as it can be observed in figures 5.11 to 5.13. The larger difference between the experimental and calculated values is observed at higher pressures as it was observed for hydrogen.

These results show that the experimental K-values for hydrogen and tetralin are predicted well by the use of two correlations found in the literature.

The difference observed between the predicted value and the experimental may be due to several reasons. The most important are:

1. Assumption of ideal gas behavior in the gas phase.

2. Experimental error in the sampling system.

3. Assumption in the correlations.

Figure 5-6: SYSTEM HYDROGEN-TETRALIN
K-value Comparison for Hydrogen

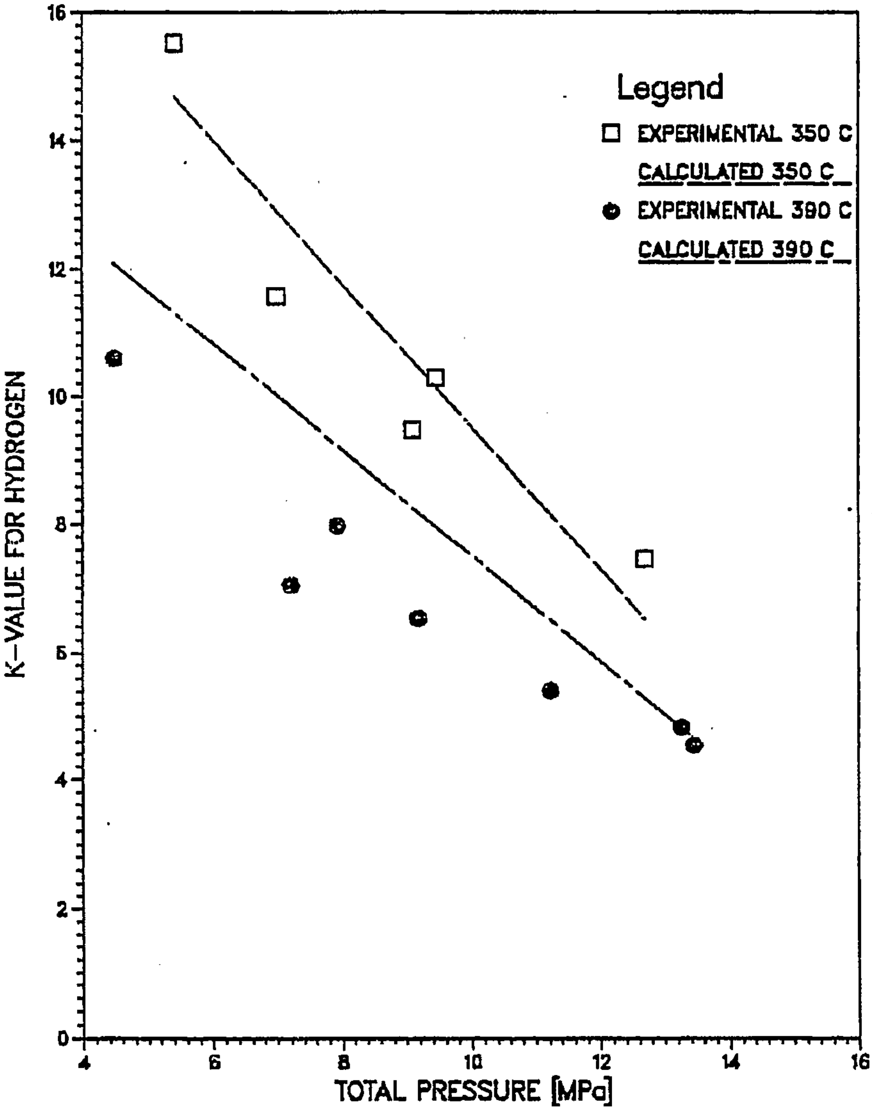


Figure 5-7: SYSTEM HYDROGEN-TETRALIN-METHANE
K-value Comparison for Hydrogen at 325 °C

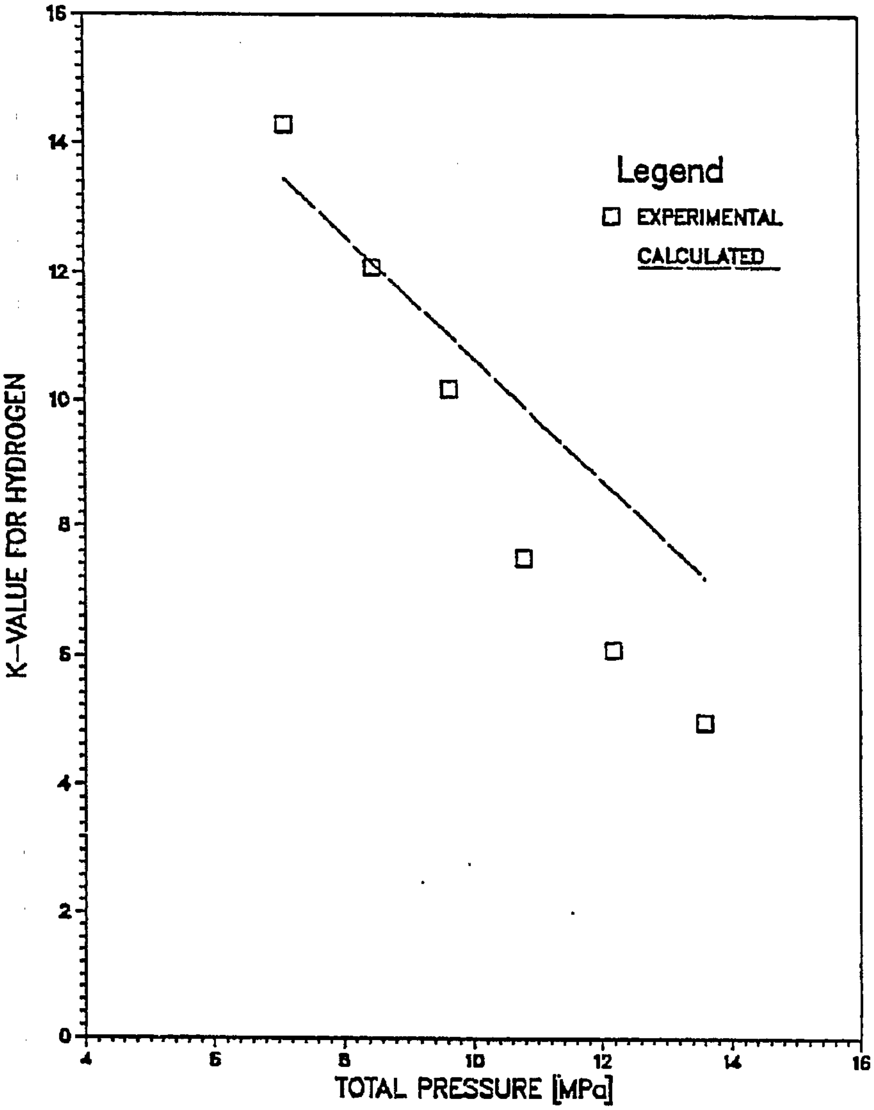


Figure 5-8: SYSTEM HYDROGEN-TETRALIN-METHANE
K-value Comparison for Hydrogen at 375 °C

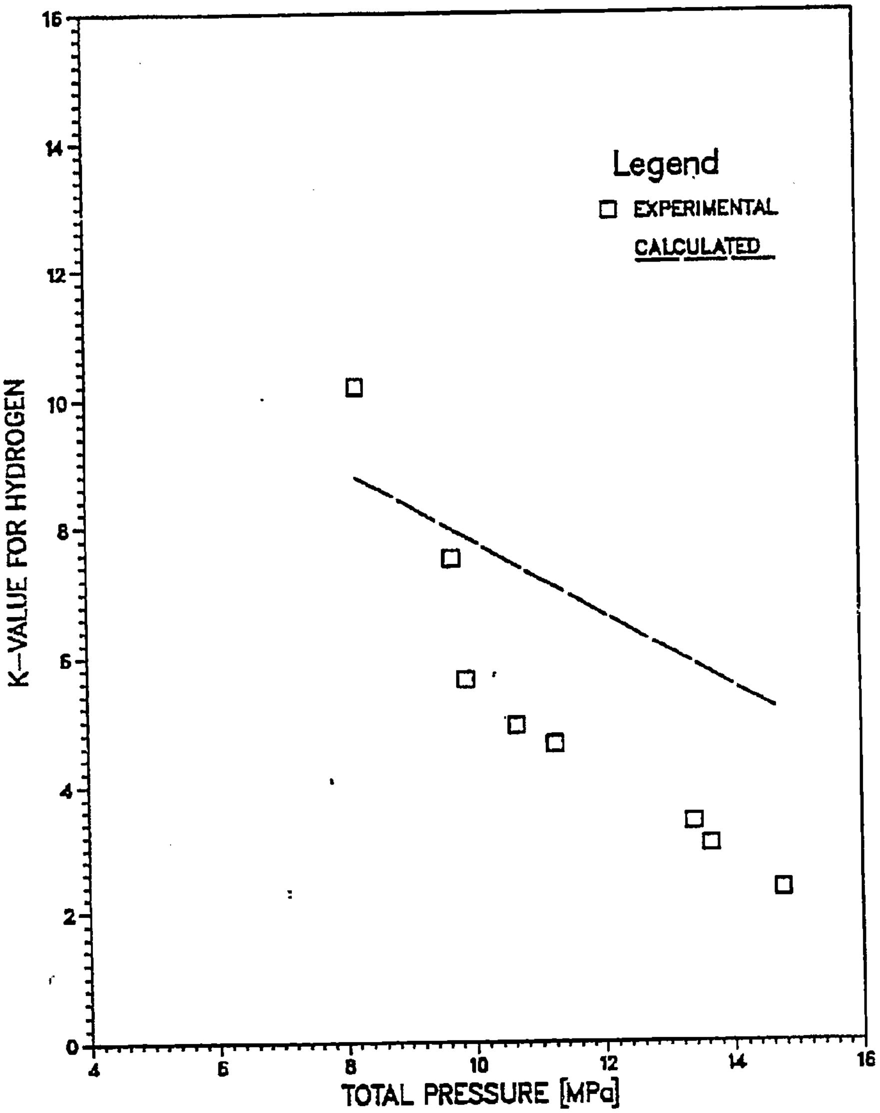


Figure 5-9: SYSTEM HYDROGEN-TETRALIN-ETHANE
K-value Comparison for Hydrogen at 360°C

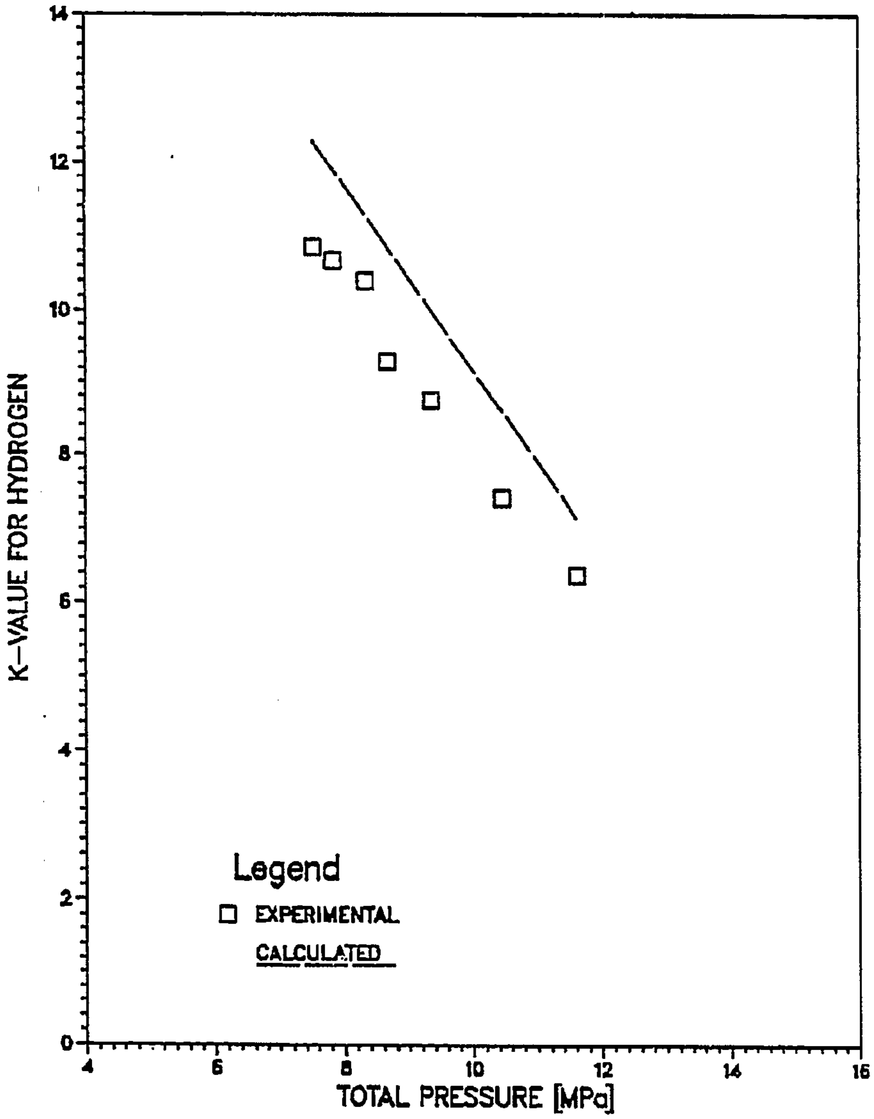


Figure 5-10: SYSTEM HYDROGEN-TETRALIN-ETHANE
K-value Comparison for Hydrogen at 395°C

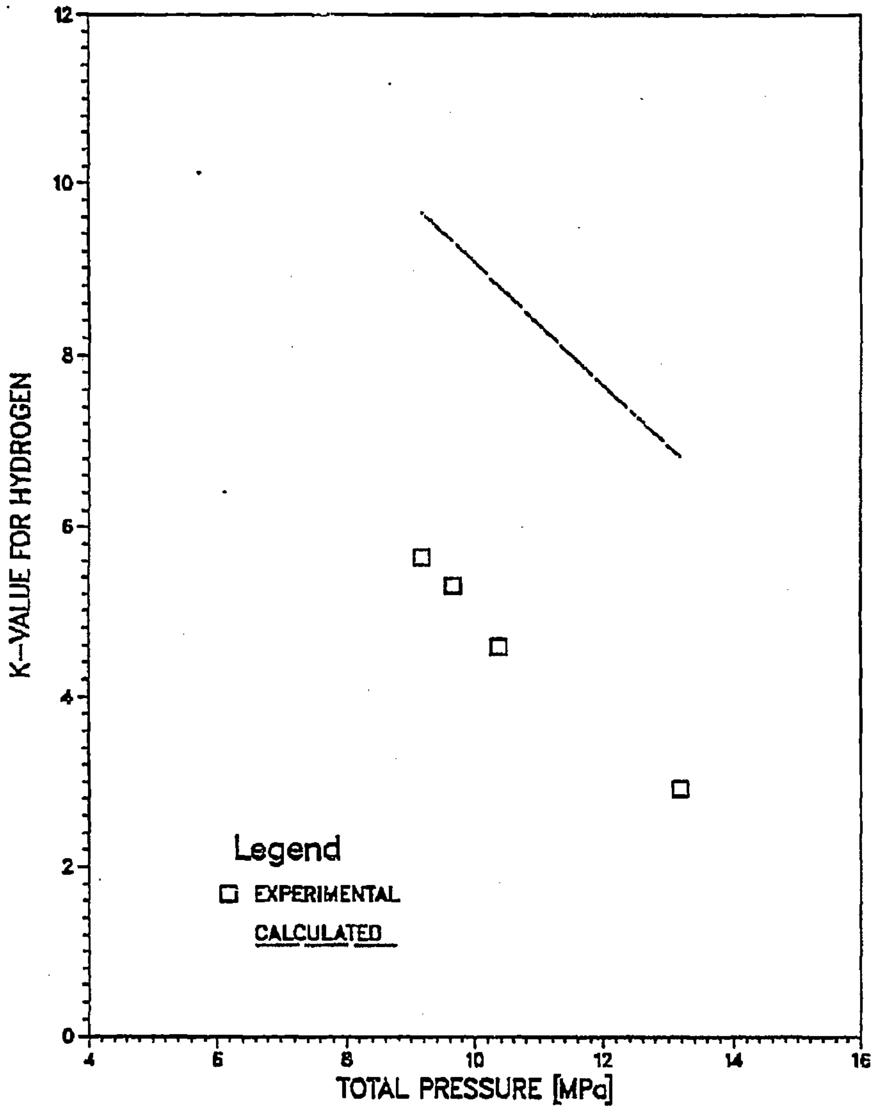


Figure 5-11: SYSTEM HYDROGEN-TETRALIN
K-value Comparison for Tetralin

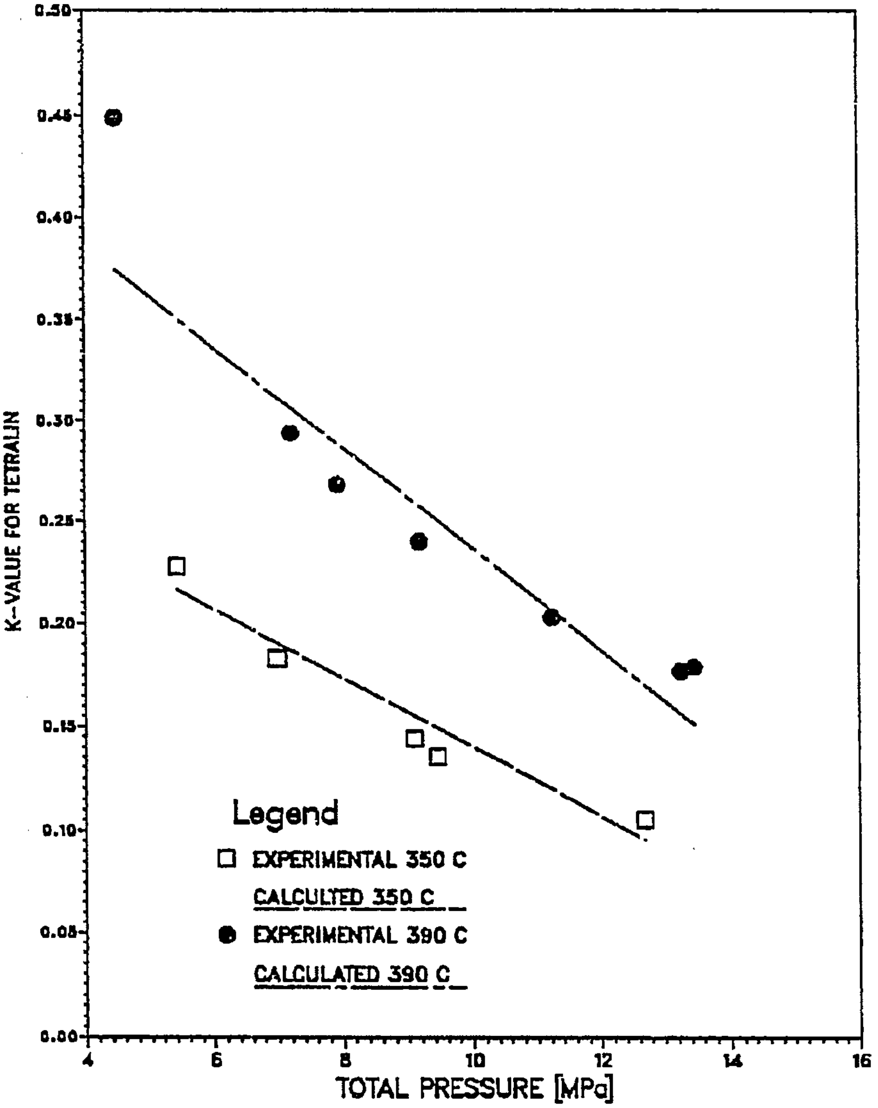


Figure 5-12: SYSTEM HYDROGEN-TETRALIN-METHANE
K-value Comparison for Tetralin

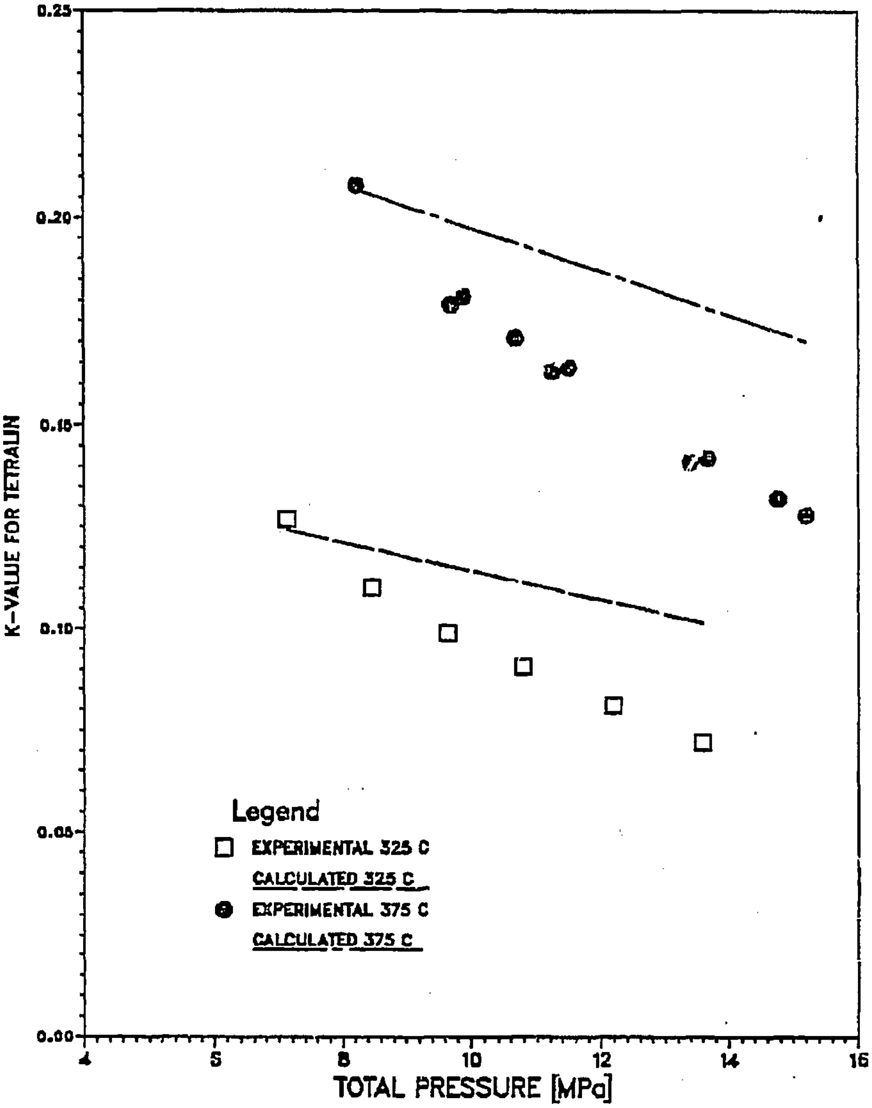
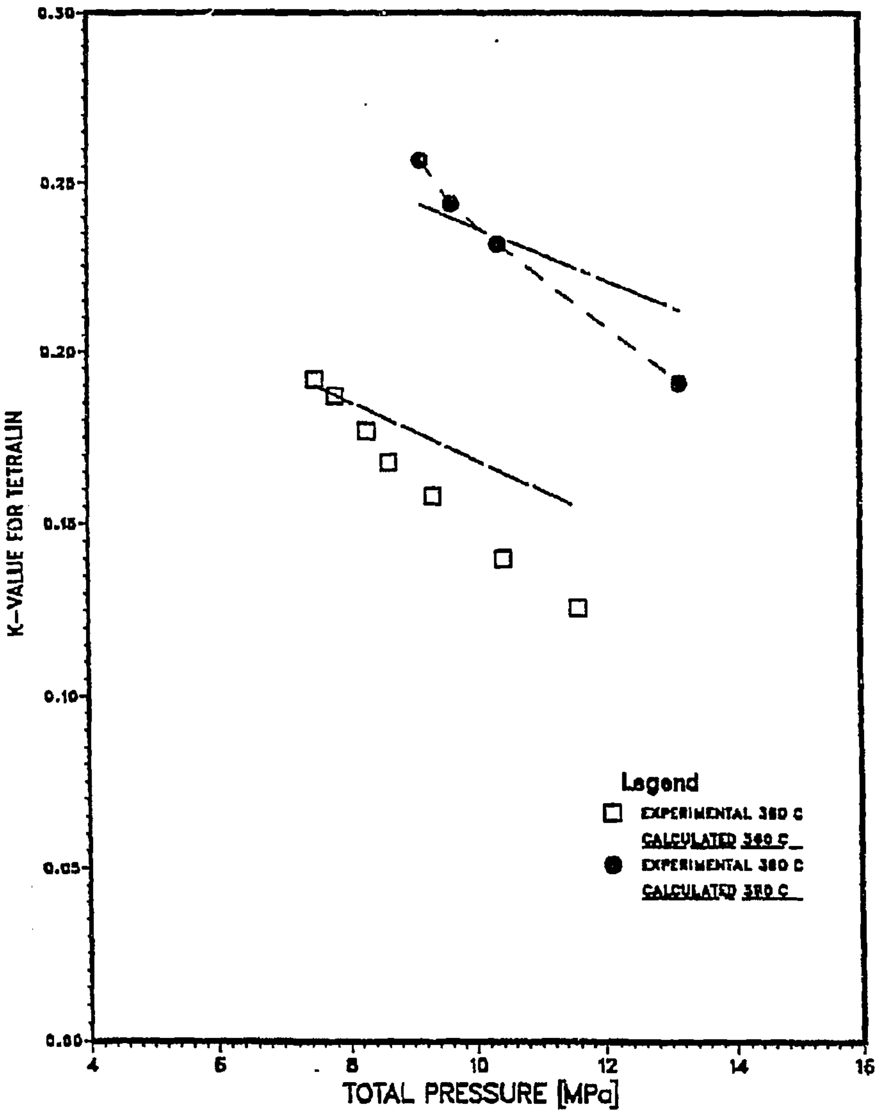


Figure 5-13: SYSTEM HYDROGEN-TETRALIN-ETHANE
K-value Comparison for Tetralin



5.6 RESULTS FROM COMMERCIAL EQUIPMENT

Some preliminary results were obtained in Wilsonville by using the equipment build at the University. The detail of the calculations are shown in appendix M.

The value for the hydrogen partial pressure calculated by using the experimental results obtained in the plant is close to 30 psi. This value is too small when compared with the real value (between 2000 and 2500 psi). The reason for this may be due to two problems. The first problem is the existence of a leak between the equipment and the probe that may produce a short time for the travel of the mercury bead. The second problem is that the real temperature near the probe is not the temperature that the computer is reading. This problem of the temperature is probably since the thermocuple that the computer is reading is located 4 ft before the probe and a value for another thermocuple located 10 ft after the probe. These thermocuples read a difference of 200°F in temperature. These two problems will be solved by checking for leaks in the probe and by installing a thermocuple close to the probe. The control system probed to be working well.

6. CONCLUSIONS

6.1 AUTOMATION OF HYDROGEN PROBE

The automation of the hydrogen probe was found to be useful for the experimental purposes for which it was designed. The computer control system allowed one to have a very accurate measurement of the variables involved in the process i.e. the temperatures, the pressures and the time of travel for the mercury bead.

6.2 EXPERIMENTAL RESULTS

The experimental results obtained in this study shows that the solubility of hydrogen in tetralin increased when the system temperature is increased. Also the solubility increased when the pressure increased.

For ternary systems it was found that the solubility of hydrogen increased in tetralin when the partial pressure of methane is increased and the partial pressure of hydrogen was held constant. The same effect is observed in the ternary system hydrogen–tetralin–ethane. The solubility of tetralin has the contrary effect, the solubility decreases when the partial pressure of methane (or ethane) is increased.

The behavior of the solubility of methane (or ethane) in tetralin can not be explained with the normal theory of solubilities. Thus no general conclusion for the solubility of methane or ethane in tetralin can be made.

The prediction of the K–values for hydrogen and tetralin in all three systems by using two correlations taken from the literature agree with the experimental values obtained in this study. It has to be recognized that the correlation uses some parameters that are difficult to estimate. This may generate some error in the value predicted. At the same time, the experimental error might affect the results but this will not be large enough to change the results dramatically.

6.3 COMMERCIAL EQUIPMENT

Preliminary tests of the commercial equipment contructed in our laboratory show that the equipment is adequate to operate in a commercial plant for the determination of hydrogen concentration.

7. RECOMMENDATIONS

The recommendations for further users of this equipment can be divided in two kind: Equipment and Experimental.

7.1 EQUIPMENT

- Since the adquisition of variables was improved by the computerization of the system, it is highly recommended to re-design the sampling section in order to minimize the possible experimental error. Some changes that may be done are:

1. Shorten lines in the sampling system.

2. Use of bigger diameter for the tubing.

3. Isolate the lines in order to avoid the condensation of the sample.

- In order to know the amount of moles in the glass section, the volume of this section has to be known. The actual value used was 1229.5 ml. The recommendation is to decrease this volume so the pressure of the sample inside this section after the transfer will be larger than it actually is. The way to reach this objective is by keeping valve G3 (figure 3.13) closed after the transfer of the sample from the expansion cylinder is completed. This increase in the pressure of the sample will facilitate the detection of the components by the gas chromatograph and will minimize the error in reading the manometer.

- It is very important to have a very well ventilated laboratory since the experiments require the use of some toxic fumes such as mercury and tetralin.

- Change the open-end manometer actually used for a closed-end manometer. In this way the changes in the atmospheric pressure will not affect the readings of pressures.

- Installation of a filter in the gas line that goes to the reactor.

- Try to increase the height of the heater box wall.

7.2 EXPERIMENTAL

- In order to get very reliable data on vapor-liquid equilibria it will be neccesary to obtain samples from the liquid and gas phase. The sampling of the liquid phase alone is useful only when the solubility is required.

APPENDIX A.

DEVELOPMENT OF EQUATION FOR HYDROGEN PERMEATION

The sequence of steps by which hydrogen permeation takes place is as follows:

1.- Hydrogen is physically adsorbed on the metal surface from the gas phase.

$$H_2(g)_1 \longleftrightarrow H_2(s)_1 \qquad \text{(A-1)}$$

$$N_{H_1} = k_p * [H_2(g)_1 - H_2(s)_1] \qquad \text{(A-2)}$$

where k_p is the mass transfer coefficient.

2.- Hydrogen is dissociated into its atomic form and dissolved into the metal.

$$H_2(s)_1 \longrightarrow 2H(s)_1 \qquad \text{(A-3)}$$

which is described by Sievert's Law;

$$C_{d_1} = K_d * [H(s)_1]^{1/2} \qquad \text{(A-4)}$$

where C_{d_1} is the dissolved concentration of hydrogen and K_d is the solubility constant.

3.- The dissolved hydrogen diffuses through the metal structure.

This step needs of the following assumptions:

- the diffusivity is constant

- the rate of diffusion is small

- steady state has been achieved

The rate of flow in one dimension can be modeled by

$$N_d = -D * [dC_d/dx] \qquad \text{(A-5)}$$

where

N_d = rate of diffusion
D = diffusivity
x = direction of flow
C_d = hydrogen concentration at x

Considering a thin film, the boundary conditions are:

$x = 0 \qquad C_d = C_{d_1}$

$x = l \qquad C_d = C_{d_2}$

where C_{d_2} = hydrogen concentration at $x = l$, (l = thickness)

Integration yields to the following expression;

$$N_d = D * [C_{d_1} - C_{d_2}]/l \qquad \text{(A-6)}$$

4.- The dissolved hydrogen atoms combine on the other side of the metal to form the hydrogen molecule.

$$2H(s)_2 \longrightarrow H_2(s)_2 \qquad \text{(A-7)}$$

The partial pressure that the molecules would exert if desorbed can be related to the concentration in the metal. This is, by using Sievert's law:

$$C_{d_2} = k_d * [H(s)_2]^{1/2} \qquad \text{(A-8)}$$

where $H(s)_2$ = dissolved concentration of hydrogen

5.- The hydrogen molecule desorbs from the surface

$$H_2(s)_2 \longrightarrow H_2(g)_2 \tag{A-9}$$

$$N_{H_2} = k_p^{'} * [H_2(s)_2 - H_2(g)_2] \tag{A-10}$$

where:

N_{H_2} = molar flux of hydrogen

k_p = mass transfer coefficient

Through experimentation(27,35,36,37) it has been shown that the diffusion step is the rate limiting and therefore controls the permeation of hydrogen through the nickel wall. All other steps are in equilibrium and the resistance to adsorption and desorption are so small that:

$$H_2(g)_1 = H_2(s)_1 \tag{A-11}$$

$$H_2(g)_2 = H_2(s)_2 \tag{A-12}$$

Combining equations 2,6,8,11 and 13, the hydrogen flow can be expressed as:

$$N_t = (D\ K_d/l) * (H_2(g)_1^{0.5} - H_2(g)_2^{0.5}) \tag{A-13}$$

The constants D and K_d can be combined to form the permeability factor as follows:

$$\phi = D * K_d * (22.4) \tag{A-14}$$

So the final expression for the hydrogen permeation equation is as follows:

$$Q = (\phi * A/X) * (P_1^{0.5} - P_2^{0.5}) \quad \text{(A-15)}$$

APPENDIX B.

INSTRUCTIONS FOR TOEPLER PUMP OPERATION

The following instructions are based on figure 3.12.

Fill Toepler pump to level "L" with mercury.

Pump operation should be checked before opening stopcock "C" and "D" for gas transfer. To do this, evacuate the upper cell of the Toepler pump by means of a high vacuum pumping system connected through stopcock "H" while evacuating the lower cell by means of a pump connected through stopcock "E". Close the air bleeder valve while evacuating the system and pump equally on both the upper and the lower cells. The mercury should not move while pumping.

When evacuating, close the high vacuum system by means of stopcock "H", shut off the vacuum pump and open the air bleeder valve to allow air to enter through stopcock "E".

Adjust the bleeder valve, so mercury rises SLOWLY into the top section of the Toepler Pump. As mercury fills the top cell of the pump, float "G" will open and float "F" will close. When the mercury rises past "G" and connects to the "L" and "O" lead of the relay, the vacuum pump should start. This vacuum pump should have enough capacity to pump the air out of the lower cell of the Toepler pump while the bleeder valve is steel allowing air to enter the system.

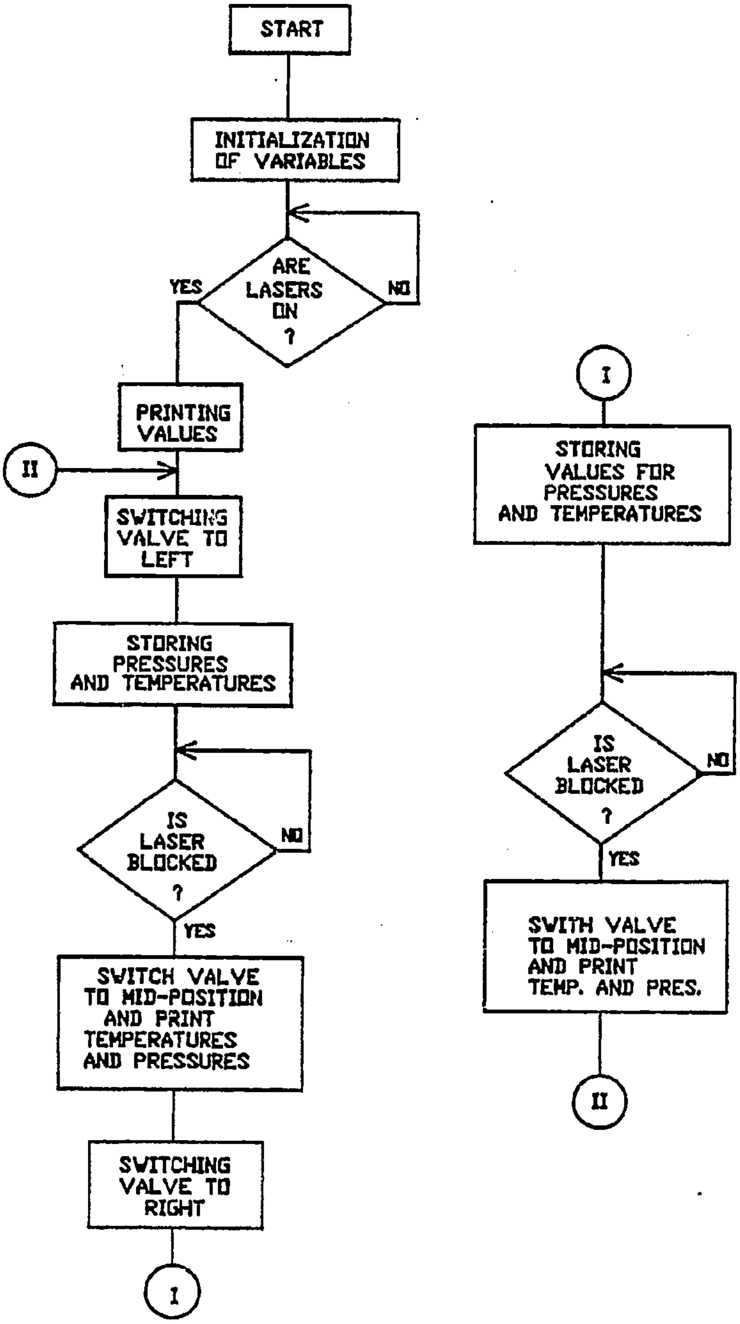
As the mercury falls past "G" this valve should close and retain enough mercury to form a gas tight seal. As the mercury drops, valve "F" should open, this will allow gas to reenter the top cell of the Toepler pump when mercury drops below "O". When the mercury falls completely into the lower cell, it should connect th the high lead of the relay and shut off the vacuum pump. The common lead of the relay should always be in contact with the mercury in the Toepler pump.

If the Toepler pump operates satisfactorily, open stopcock "C" and "D" to begin gas transfer. The pumping rate can be controlled by means of bleeder valve. Care must be taken that this valve is not open too far, as this would keep the vacuum pump from removing enough air in the lower cell to allow mercury to contact the "high" lead to the relay. The pump should cycle every two to four minutes.

APPENDIX C.

CONTROL PROGRAMS FOR UNIVERSITY EQUIPMENT

Figure C-1: BLOCK DIAGRAM FOR CONTROL PROGRAM



CONTROL PROGRAM FOR UNIVERSITY EQUIPMENT

...Initialization of the program...

```
10      BAUD 75
20     XBY(0C803H)=80H
30     XBY(0C801H)=0
40     XBY(0C802H)=0
50     TIME=0
```

...checking if the lasers are ON before going any further in the program...

```
60      DO
70      GOSUB 1200
75      UNTIL A(4)>1.0.AND.A(5)>1.0
```

...when the lasers are checked to be on, the program prints the values for temperatures and pressures of the system...

```
80      GOSUB 1600
90      PRINT #USING(###.#),"LIQ. TEMP. =",A(0)
100     GOSUB 1500
110     PRINT #USING(###.#),"GAS TEMP.  =",A(1)
120     GOSUB 1500
130     PRINT #USING(###.#),"LASER TEMP.=",A(2)
140     GOSUB 1500
150     PRINT #USING(###.#),"ROOM TEMP. =",A(3)
155     GOSUB 1500
160     PRINT #""
```

...resetting auxiliary variables used as additive variables; B(0), B(1), B(2), B(3), B(6), B(7) and B(10) used as a counter...

```
170   B(0)=0
175   B(1)=0
180   B(2)=0
185   B(3)=0
190   B(6)=0
195   B(7)=0
200   B(10)=1
```

...switching the valve to get a flow position; in this case the flow will be from left to right,,,

```
210   XBY(0C802H)=2
220    GOSUB 1500
```

...printing direction of flow...

```
225    PRINT #"HG TO RIGHT"
227    GOSUB 1500
```

...checking if the right laser is blocked by the mercury drop...

```
230    GOSUB 1200
240    IF A(5)<1.0 THEN  GOTO 260
```

...if the right laser is blocked, the program goes to line 260, otherwise keeps checking the laser ...

```
250    GOTO 230
```

...when the right laser is blocked, the program begins looking for the same laser to be unblocked...

```
260    GOSUB 1200
270    IF A(5)>1.0 THEN  GOTO 290
```

...when the right laser is unblocked, the program goes to line 290, otherwise keeps looking for this to occurs...

```
280    GOTO 260
```

...when the laser is unblocked, the program waits about 10% of the time of travel of the mercury before switching to mid-position...

```
290   X=(TIME*0.1)/1.651E-03
292    GOSUB 1700
```

...switching to mid-position,,,

```
294   XBY(0C801H)=2
295    GOSUB 1500
```

...printing the location of the mercury bead...

```
296    PRINT #"HG IN RIGHT"
298    GOSUB 1500
```

...taking some averages for the values that the computer read while the mercury was travelling from one side to the other...

```
300   A(0)=B(0)/B(10)
305   A(1)=B(1)/B(10)
```

```
310   A(2)=B(2)/B(10)
315   A(3)=B(3)/B(10)
320   A(6)=B(6)/B(10)
325   A(7)=B(7)/B(10)
```

...the program sends this averages to subroutine 1600, where the linear correlations in order to get the actual values for temperatures and pressures are...

```
330    GOSUB 1600
```

...printing...

```
340    PRINT #USING(####.#),"TIME=",TIME,"[SEC]"
350    GOSUB 1500
360    PRINT #USING(###.#),"LIQ. TEMP. =",A(0)
365    GOSUB 1500
370    PRINT #USING(###.#),"GAS TEMP.  =",A(1)
375    GOSUB 1500
380    PRINT #USING(###.#),"LASER TEMP.=",A(2)
385    GOSUB 1500
390    PRTNT #USING(###.#),"ROOM TEMP. =",A(3)
395    GOSUB 1500
400    PRINT #USING(####),"MICRO PRES.=",A(6)
405    GOSUB 1500
410    PRINT #USING(####),"REAC. PRES.=",A(7)
415    GOSUB 1500
420    PRINT #""
```

...resetting auxiliary variables...

```
430   B(0)=0
435   B(1)=0
440   B(2)=0
445   B(3)=0
450   B(6)=0
455   B(7)=0
460   B(10)=0
470   TIME=0
480   DBY(71)=1
```

...switching flow direction to flow position: Right to Left...

```
490   XBY(0C802H)=0
```

...checking for the right laser to be blocked...

```
500    GOSUB 1200
510    IF A(5)<1.0 THEN  GOTO 530
```

...if the right laser is blocked, programs goes to 530, otherwise stays in line 500-510...

```
520     GOTO 500
```

...when the right laser is blocked, the computer clock starts...

```
530     CLOCK 1
```

...printing direction of flow...

```
535     PRINT #"HG TO LEFT"
540     GOSUB 1500
```

...reading values for voltages corresponding to temperatures and pressures...

```
550     GOSUB 1200
555    B(0)=B(0)+A(0)
560    B(1)=B(1)+A(1)
565    B(2)=B(2)+A(2)
570    B(3)=B(3)+A(3)
575    B(6)=B(6)+A(6)
580    B(7)=B(7)+A(7)
585    B(10)=B(10)+1
```

...checking for the left laser to be blocked by the mercury bead...

```
590     IF A(4)<1.0 THEN  GOTO 610
600     GOTO 550
```

...when the left laser is blocked, the computer clock stops...

```
610     CLOCK 0
```

...checking if the left laser is unblocked...

```
620     GOSUB 1200
630     IF A(4)>1.0 THEN  GOTO 650
```

...when it is unblocked, the program goes to 650, if not goes to 620...

```
640     GOTO 620
```

...after the mercury unblocked the left laser, the program has a delay time before switching the valve to mid-position...

```
650  X=(TIME*0.1)/1.651E-03
655   GOSUB 1700
```

...switching the valve to mid-position...

```
660  XBY(0C801H)=0
670   GOSUB 1500
```

...printing location of the mercury...

```
675   PRINT #"HG IN LEFT"
680   GOSUB 1500
```

...taking averages of the values read by the computer during the travel of the mercury...

```
690  A(0)=B(0)/B(10)
695  A(1)=B(1)/B(10)
700  A(2)=B(2)/B(10)
705  A(3)=B(3)/B(10)
710  A(6)=B(6)/B(10)
715  A(7)=B(7)/B(10)
```

...sending averages to subroutine 1600 to get actual values for pressures and temperatures...

```
720   GOSUB 1600
```

...printing...

```
730   PRINT #USING(####.#),"TIME=",TIME,"[SEC]"
740   GOSUB 1500
750   PRINT #USING(###.#),"LIQ. TEMP. =",A(0)
760   GOSUB 1500
770   PRINT #USING(###.#),"GAS TEMP.  =",A(1)
780   GOSUB 1500
790   PRINT #USING(###.#),"LASER TEMP.=",A(2)
800   GOSUB 1500
810   PRINT #USING(###.#),"ROOM TEMP. =",A(3)
820   GOSUB 1500
830   PRINT #USING(####),"MICRO PRES.=",A(6)
840   GOSUB 1500
850   PRINT #USING(####),"REAC. PRES.=",A(7)
860   GOSUB 1500
870   PRINT #""
```

...resetting auxiliary variables...

```
880   B(0)=0
885   B(1)=0
890   B(2)=0
895   B(3)=0
900   B(6)=0
905   B(7)=0
910   B(10)=0
920   TIME=0
930   DBY(71)=1
```

...switching valve to flow from left to right...

```
940   XBY(0C802H)=2
950    GOSUB 1500
```

...checking if the left laser is unblocked...

```
960    GOSUB 1200
970    IF A(4)<1.0 THEN  GOTO 990
```

...when it is unblocked, the program goes to line 990, otherwise remains reading in line 960...

```
980    GOTO 960
```

...when the left laser is unblocked, the computer clock starts...

```
990    CLOCK 1
```

...printing direction of flow for the mercury...

```
995    PRINT #"HG TO RIGHT"
1000   GOSUB 1500
```

...reading and storageing values for volatges corresponding to temperatures and pressures...

```
1010   GOSUB 1200
1015  B(0)=B(0)+A(0)
1020  B(1)=B(1)+A(1)
1025  B(2)=B(2)+A(2)
1030  B(3)=B(3)+A(3)
1035  B(6)=B(6)+A(6)
1040  B(7)=B(7)+A(7)
1045  B(10)=B(10)+1
```

...checking if the right laser is blocked by the mercury...

```
1050   IF A(5)<1.0 THEN  GOTO 1070
1060   GOTO 1010
```

...when the right laser is blocked, the computer clock stops...

```
1070   CLOCK 0
```

...the program goes to line 260 and the complete program from 260 to line 1080 is repeated again...

```
1080   GOTO 260
1090   GOTO 1730
```

SUBROUTINE 1200: This subroutine is used for the computer for reading the 8 ports of the A/D board that have the values for voltages corresponding to temperatures and pressures.

```
1200  N=55296
1210   FOR A=0 TO 7
1220   GOSUB 1300
1230   NEXT A
1240   RETURN
1300  XBY(N)=A+8
1310  XBY(N)=A
1320  D1=XBY(N) : D2=XBY(N)
1330  R=0.0012207
1340   IF D1>=240 THEN  GOTO 1400
1350  A(A)=R*((D1*256)+D2)
1360   RETURN
1400  D1=255-D1 : D2=255-D2
1410  A(A)=-1*R*((D1*256)+D2)
1420   RETURN
```

SUBROUTINE 1500: This is a subroutine for having a delay time while the computer is printing the output after each sequence. Also is used for a delay time after switching the multi-port valve.

```
1500   FOR Z=1 TO 500
1510   NEXT Z
1520   RETURN
```

SUBROUTINE 1600: This subroutine has the linear equations used to convert voltages to actual values of pressures and temperatures.The variables used here are A(0) to A(4) for temperatures; A(5) and A(6) for laser receivers and A(7) and A(8) for pressures.

```
1600   FOR A=0 TO 3
1610  A(A)=A(A)*100
1620   NEXT A
1630  A(0)=A(0)-0.95
1640  A(1)=A(1)+1.65
1650  A(2)=A(2)-0.05
1660  A(3)=A(3)-1.35
1670  A(6)=(A(6)*1000-23.3819)/1.0226
1680  A(7)=(A(7)*1000-13.8502)/1.0192
1690   RETURN
```

SUBROUTINE 1700: This subroutine has the delay time used before switching the valve to mid position after the laser is unblocked.

```
1700   FOR C=1 TO X
1710   NEXT C
1720   RETURN
1730   END
```

PROGRAM THAT READS A/D BOARD PORTS

This program is in charge of reading the 8 ports used in the A/D Board that has the values of voltages read by the computer.

```
10      BAUD 75
20     XBY(0C803H)=80H
30     XBY(0C801H)=0
40     XBY(0C802H)=0
50      GOSUB 1200
60      PRINT USING(#.###),A(0),A(1),A(2),A(3),A(4),A(5),
        A(6),A(7)
70      GOTO 50
80      END
```

The subroutine 1200 asks for the subroutine 1300 that actually does the job of read all the ports.

```
1200  N=55296
1210   FOR A=0 TO 7
1220   GOSUB 1300
1230   NEXT A
1240   RETURN
```

Subroutine 1300 actually reads all 8 ports. If the value to read is negative, the program calculates the value by using subroutine 1400.

```
1300  XBY(N)=A+8
1310  XBY(N)=A
1320  D1=XBY(N) : D2=XBY(N)
1330  R=.0012207
1340   IF D1>=240 THEN  GOTO 1400
1350  A(A)=R*((D1*256)+D2)
1360   RETURN
```

This subroutine is used in case that the value read is negative

```
1400  D1=255-D1 : D2=255-D2
1410  A(A)=-1*R*((D1*256)+D2)
1420   RETURN
```

APPENDIX D.
GAS CHROMATOGRAPH PROGRAMS

```
LST!

METHOD    1


ANALYZER CONTROL

INJ TEMP     250
DET ZONE 1,2     250   250
AUX TEMP       25
FLOW A,B     30   30
INIT OVEN TEMP,TIME      50    8

DATA PROC

STD WT,SMP WT      0.0000    1.0000  0
FACTOR,SCALE        1   0
TIMES     8.00    0.00  327.67  327.67  327.67  327.67
SENS-DET RANGE    100   50    0.00    2   0   0
UNK,AIR    1.000    0.00
TOL       0.0000   0.050     1.0
REF PK    0.000    0.00    0.00    0.00
STD NAME

EVENT CONTROL

ATTN-CHART-DELAY      2    5    0.01

  TIME  DEVICE    FUNCTION NAME
   2.00 ZERO   Z   1
   3.00 ATTN   A    5
   3.10 ZERO   Z   1
```

```
LST2

METHOD    2


ANALYZER CONTROL

INJ TEMP     250
DET ZONE 1.2     250    250
AUX TEMP      25
FLOW A.B     30    30
INIT OVEN TEMP.TIME      50     7

TEMP  RATE  TIME
 225   32.0    2

DATA PROC

STD WT.SMP WT      0.0000     1.0000  0
FACTOR.SCALE        1    0
TIMES     14.46    0.00  327.67  327.67  327.67  327.67
SENS-DET RANGE     100   50     0.00     2    0    0
UNK.AIR     1.000     0.00
TOL        0.0000    0.050      1.0
REF PK     0.000     0.00     0.00     0.00
STD NAME

EVENT CONTROL

ATTN-CHART-DELAY       2     5     0.01

   TIME  DEVICE     FUNCTION NAME
    2.00 ZERO    Z    1
    3.50 ATTN    A     5
    3.60 ZERO    Z    1
    9.50 ATTN    A     4
    9.60 ZERO    Z    1
```

```
LST3

METHOD   3


ANALYZER CONTROL

INJ TEMP     250
DET ZONE 1,2     250    250
AUX TEMP       25
FLOW A,B     30   30
INIT OVEN TEMP,TIME      50     7

TEMP  RATE  TIME
 225   32.0   15

DATA PROC

STD WT,SMP WT      0.0000     1.0000  0
FACTOR,SCALE         1   0
TIMES     27.46     0.00  327.67  327.67  327.67  327.67
SENS-DET RANGE     100    50     0.00     2    0    0
UNK,AIR    1.000    0.00
TOL        0.0000    0.050      1.0
REF PK     0.000     0.00     0.00     0.00
STD NAME

EVENT CONTROL

ATTN-CHART-DELAY       2     5     0.01

  TIME  DEVICE    FUNCTION NAME
   2.00 ZERO   Z   1
   3.50 ATTN   A    5
   3.60 ZERO   Z   1
   9.50 ATTN   A    4
   9.60 ZERO   Z   1
```

APPENDIX E.

CONTROL PROGRAM FOR COMMERCIAL EQUIPMENT

CONTROL PROGRAM FOR WILSONVILLE

...Initialization of the program...

```
10     BAUD 75
20    XBY(0C803H)=80H
30    XBY(0C801H)=0
40    XBY(0C802H)=0
```

...goto 1900, where the valve initialization sequence is done...

```
45     GOSUB 1900
```

...resetting external clock...

```
50    XBY(0C800H)=0
60    XBY(0C800H)=255
```

...resetting auxiliary variables (TIME and A(9))...

```
61    TIME=0
62    A(9)=0
```

...checking if the lasers are on before going any further...

```
65     DO
70     GOSUB 1200
75     UNTIL A(2)>1.5.AND.A(3)>1.5
```

...when lasers are checked to be on, the program prints out values for temperatures and the microflowmeter pressure...

```
80     GOSUB 1600
90     PRINT #USING(###.#),"REAC. TEM.=",A(0)
100    GOSUB 1500
110    PRINT #USING(###.#),"BOX TEMP. =",A(1)
120    GOSUB 1500
130    PRINT #USING(####),"MICRO PRES. =",A(4)
135    GOSUB 1500
140    PRINT #""
145    GOSUB 1500
```

...resetting auxiliar variables, B(0), B(1), B(4) and B(10)...

```
150   B(0)=0
160   B(1)=0
```

```
164   B(4)=0
170   B(10)=1
```

...checking if the "REVERSE START" swith is off...

```
172    IF A(5)<3 THEN  GOTO 180
```

...If the "REVERSE START" switch is on goes to the following sequence...

...set auxiliary variable A(9) to be 1

```
174   A(9)=1
```

...switch the valve to the other mid-position...

```
175   XBY(0C802H)=2
176   XBY(0C801H)=2
```

...send the program to line 390...

```
177    GOTO 390
```

...If the "REVERSE START" switch is off, the valve switch to flow position, in this case the mercury bead travels from right to left...

```
180   XBY(0C802H)=2
182    GOSUB 1500
```

...printing direction of travelling for the mercury bead...

```
185    PRINT #"HG TO LEFT"
187    GOSUB 1500
```

...checking for the LEFT laser to be blocked A(2)...

```
190    GOSUB 1200
200    IF A(2)<1.5 THEN  GOTO 220
210    GOTO 190
```

...When the left laser is blocked, the program cheks the laser to be unblocked again...

```
220    GOSUB 1200
230    IF A(2)>1.5 THEN  GOTO 250
240    GOTO 220
```

...when the laser is unblocked, the program waits about 10% of the travelling time before switching the valve to mid-position...

```
250   X=(TIME*0.1+0.005385)/1.651E-03
252    GOSUB 1800
```

...when the delay time is over, the valve switch to mid-position...

```
254   XBY(0C801H)=2
255    GOSUB 1500
```

...printing location of the mercury bead...

```
256    PRINT #"HG IN LEFT"
257    GOSUB 1500
```

...taking averages for the voltages that the computer read during the time of travelling...

```
260   A(0)=B(0)/B(10)
270   A(1)=B(1)/B(10)
274   A(4)=B(4)/B(10)
```

...the computer send this averages to subroutine 1600 in order to use the linear correlations to get the values for temperatures and pressures...

```
280    GOSUB 1600
```

...printing values...

```
290    PRINT #USING(#####.#),"TIME=",TIME,"SEC"
300    GOSUB 1500
310    PRINT #USING(###.#),"REAC. TEM.=",A(0)
320    GOSUB 1500
330    PRINT #USING(###.#),"BOX TEMP. =",A(1)
340    GOSUB 1500
350    PRINT #USING(####),"MICRO PRES. =",A(4)
360    GOSUB 1500
370    PRINT #""
380    GOSUB 1500
```

...resetting values for counters...

```
390   B(0)=0
400   B(1)=0
404   B(4)=0
410   B(10)=0
```

...resetting value for the time variable...

```
420   TIME=0
```

...resetting external clock...

```
430   XBY(0C800H)=0
440   DBY(71)=1
```

...switching the valve so the mercury begins travelling from left to right...

```
450   XBY(0C802H)=0
```

...if the program get to this line by using the "REVERSE START" switch, (means that A(9) was equal to 1) it jumps all the lines from 455 to 508...

```
455    IF A(9)=1 THEN  GOTO 509
```

...If the program came here by following the normal procedure (means that A(9) was equal to 0, the program follows lines 460 to end...

...checking if the left laser is ublocked...

```
460    GOSUB 1200
470    IF A(2)<1.5 THEN  GOTO 490
480    GOTO 460
```

...when the left laser, A(2), is blocked, both clocks start...

```
490    CLOCK 1
500   XBY(0C800H)=1
```

...printing direction for the mercury bead...

```
505    PRINT #"HG TO RIGHT"
507    GOSUB 1500
```

...resetting A(9) to be equal to zero...

```
509   A(9)=0
```

...reading values for volatges of temperatures and pressures while the mercury bead is travelling...

```
510    GOSUB 1200
```

...storaging values for voltages by using auxiliary variables B's...

```
520   B(0)=B(0)+A(0)
530   B(1)=B(1)+A(1)
534   B(4)=B(4)+A(4)
540   B(10)=B(10)+1
```

...checkig if the "NORMAL STOP" switch is off...

```
550    IF A(6)<3 THEN  GOTO 580
```

...if the "NORMAL STOP" switch is on, the program goes to subroutine 1700 where the instruction for the normal detention of the program are...

```
560    GOSUB 1700
570    GOTO 1030
```

...if the "NORMAL SWITCH" is off, the program continues its normal procedure...

...checking if the right laser, A(3), is blocked...

```
580    IF A(3)<1.5 THEN  GOTO 600
590    GOTO 510
```

...if the right laser is blocked, both clocks stop...

```
600    CLOCK 0
610   XBY(0C800H)=255
```

...checking the right laser, A(3), to be unblocked...

```
620    GOSUB 1200
630    IF A(3)>1.5 THEN  GOTO 650
640    GOTO 620
```

...when the right laser is unblocked, a delay time is wait before switching the valve to the mid-position...

```
650   X=(TIME*0.1+0.005385)/1.651E-03
652    GOSUB 1800
```

...switching the valve to mid-position...

```
654   XBY(0C801H)=0
655    GOSUB 1500
```

...printing the location of the mercury bead...

```
656    PRINT #"HG IN RIGHT"
657    GOSUB 1500
```

...taking averges for the voltages that the computer read during the travelling of the mercury bead...

```
660   A(0)=B(0)/B(10)
670   A(1)=B(1)/B(10)
674   A(4)=B(4)/B(10)
```

...sending these averages to the subroutine 1600 in order to get the actual values for temperatures and pressures...

```
680    GOSUB 1600
```

...printing the values for temperatures, pressures and the time of travelling...

```
690    PRINT #USING(#####.#),"TIME=",TIME,"SEC"
700    GOSUB 1500
710    PRINT #USING(###.#),"REAC. TEM.=",A(0)
720    GOSUB 1500
730    PRINT #USING(###.#),"BOX TEMP. =",A(1)
740    GOSUB 1500
750    PRINT #USING(####),"MICRO PRES. =",A(4)
760    GOSUB 1500
770    PRINT #""
780    GOSUB 1500
```

...resetting auxiliary variables...

```
790   B(0)=0
800   B(1)=0
804   B(4)=0
810   B(10)=0
```

...resetting value for the time variable and for the external clock...

```
820   TIME=0
830   XBY(0C800H)=0
840   DBY(71)=1
```

...switching the valve to flow position, moving from right to left...

```
850   XBY(0C802H)=2
```

...checkig if the right laser is blocked...

```
860    GOSUB 1200
870    IF A(3)<1.5 THEN  GOTO 890
880    GOTO 860
```

...when it is blocked, both clocks start...

```
890    CLOCK 1
900   XBY(0C800H)=1
```

...printing direction of traveling for the mercury bead...

```
905    PRINT #"HG TO LEFT"
907    GOSUB 1500
```

...adding new values for voltages to the old value, so an average can be taking at the end of the travelling...

```
910    GOSUB 1200
920   B(0)=B(0)+A(0)
930   B(1)=B(1)+A(1)
934   B(4)=B(4)+A(4)
940   B(10)=B(10)+1
```

...checking if the "NORMAL STOP" switch is off...

```
950    IF A(6)<3 THEN  GOTO 980
960    GOSUB 1700
970    GOTO 1030
```

...if the "NORMAL STOP" switch is off, the program continues...

...checking for the left laser to be blocked again...

```
980    IF A(2)<1.5 THEN  GOTO 1000
990    GOTO 910
```

...if it is blocked, both clocks stop...

```
1000   CLOCK 0
1010  XBY(0C800H)=255
```

...sending the program to line 220, so the program is repeated one more time...

```
1020   GOTO 220
1030   END
```

...SUBROUTINE 1200: IN CHARGE OF READING THE A/D BOARD...

```
1200  N=55296
1210   FOR A=0 TO 7
1220   GOSUB 1300
1230   NEXT A
1240   RETURN
1300  XBY(N)=A+8
1310  XBY(N)=A
1320  D1=XBY(N) : D2=XBY(N)
1330  R=0.0012207
1340   IF D1>=240 THEN  GOTO 1400
1350  A(A)=R*((D1*256)+D2)
1360   RETURN
1400  D1=255-D1 : D2=255-D2
1410  A(A)=-1*R*((D1*256)+D2)
1420   RETURN
```

...SUBROUTINE 1500: IN CHARGE OF HAVING A DELAY TIME FOR THE PRINTING...

```
1500   FOR Z=1 TO 600
1510   NEXT Z
1520   RETURN
```

...SUBROUTINE 1600: IT HAS THE LINEAR CORRELATIONS FOR TEMPERATURES AND PRESSURES...

```
1600  A(0)=(147.079*A(0)-144.763)*1.8+32
1610  A(1)=(149.275*A(1)-148.864)*1.8+32
1620  A(4)=(A(4)-1)*1250
1630   RETURN
```

...SUBROUTINE 1700: IN CHARGE OF STOPPING THE PROGRAM WHEN THE "NORMAL STOP" SWITCH IS TURNED ON...

```
1700   FOR C=1 TO 600
1710   NEXT C
1720   GOSUB 1900
1730  XBY(0C800H)=255
1740   PRINT #"SYSTEM STOP AT"
1750   PRINT #,TIME,"[SEC]"
1760   RETURN
```

...SUBROUTINE 1800: IT HAS THE DELAY TIME BEFORE SWITCHING THE VALVE TO MID-POSITION...

```
1800   FOR C=1 TO X
1810   NEXT C
1820   RETURN
```

...SUBROUTINE 1900: IT CONATINS THE NORMAL SEQUENCE NEEDED FOR THE VALVE TO OPERATE SATISFACTORILY...

```
1900  XBY(0C801H)=0
1905   GOSUB 1500
1910  XBY(0C802H)=0
1915   GOSUB 1500
1920  XBY(0C802H)=2
1925   GOSUB 1500
1930  XBY(0C801H)=2
1935   GOSUB 1500
1940  XBY(0C802H)=0
1945   GOSUB 1500
1950  XBY(0C801H)=0
1955   GOSUB 1500
1960   RETURN
```

APPENDIX F.

INSTRUCTIONS FOR OPERATION OF COMMERCIAL EQUIPMENT

INSTRUCTION FOR OPERATING HYDROGEN PROBE

1. Generalities

The purpose of the equipment installed at the pilot plant in Wilsonville, Alabama is to determine the partial pressure of hydrogen in a gas stream.

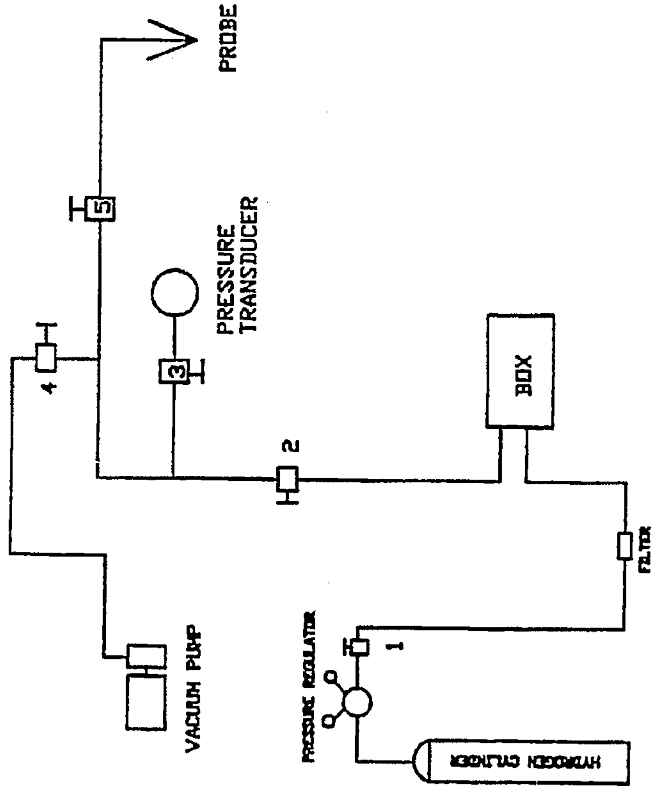
The equipment consists in three boxes, one probe and one computer box that controls the entire system. The first box contains the laser beams. The second box contains the capillary cell where the mercury bead flows from one side to the other inside a capillary tube, and the multiport valve that allows the mercury to change the flow direction. The third box contains two laser receivers, two solenoid valves, two relays and a terminal block.

The computer box, located in a room besides the control room, has a power supply, a BC52 computer/control board, an A/D board, a printer card, a external clock and a fan.

2. Operation of the system

A schematic drawing of the system is shown in figure 1. The system may be shown as a hydrogen cylinder, a box, a pressure transducer and a probe. The system uses 5 external valves numbered from 1 to 5 in the mentioned figure.

SCHEMATIC OF THE SYSTEM INSTALLED IN ALABAMA



The system works in the following way: Hydrogen should be charged in the entire system from the cylinder to the probe at a certain pressure. The probe should be at a certain temperature in order to have a permeation between the inside and the outside of the probe. When the permeation begins, the microflowmeter can be turned on, so the mercury will travel from side to side and the computer will record the time needed for the travelling. By applying formula 1, the partial pressure outside the probe can be calculated.

$$Q = [(\phi * A)/X] * (\sqrt{P1} - \sqrt{P2}) \qquad (1)$$

Where Q = hydrogen permeation rate in (m^3/s at NTP conditions)

ϕ = permeation coefficient (m^3(NTP)/m/sec/(MPa)$^{1/2}$)

A = logarithmic mean surface area of the probe (m^2)

X = thickness of the nickel wall (m)

P1 = Pressure inside the probe (MPa)

P2 = pressure outside the probe (MPa)

Some constants for this equations are:

Q = Volume of the capillary/TIME of travelling

Volume of the capillary = $\pi * Dc^2 *$lenght/4

length = length of the travelling = $5.398*10^{-2}$ (m)

Dc = diameter of the capillary = $0.112*10^{-2}$ (m)

X = $1.27*10^{-4}$ (m) = thickness of the nickel tube

OD Ni = $3.96*10^{-4}$ (m)

ID Ni = $1.42*10^{-4}$ (m)

LMD Ni = log mean diameter = $2.477 * 10^{-4}$ (m)

A = π * (length of nickel) * LMD (m^2)

= $\exp(-6003/TK + 13.45)*10^{-11}$

where TK is the temparature of the probe in ^{o}K.

By using equation 1, and knowing the physical dimensions for the nickel tube, the temperature at which the probe is and the pressure inside the microflowmeter, the pressure of hydrogen outside the probe can be calculated.

3. Operational Hints

Before presenting the operational hints, a description for the external valves used in the system will be given.

- Valve # 1 connects the cylinder, after the regulator, with the system.
- Valve # 2 is located after the boxes and can isolated the boxes from the pressure transducer and the probe.
- Valve # 3 connects the main line coming from the boxes and goes to the probe with the pressure transducer.
- Valve # 4 connetcs the vacuum pump from the hydrogen line.

- Valve # 5 can isolated the probe from the rest of the system.

3.1 Insertion of the mercury bead in the capillary cell

In order to put the mercury bead inside the capillary cell, two methods can be followed. The first one is to remove the cell and insert the mercury with the cell not in place. To do this, the 1/8" line that connects both ends of the cell should be disconnected. Then the screws that hold the cell to the box's floor must be unscrewed and the cell can be removed. With the cell out of the box, the capillary tube can be removed and the mercury inserted into it. After this the procedure should be repeated in reverse. What this means is that the cell has to be screwed to the box and the 1/8" tubing re-located in its position.

The second procedure does not require taking the cell out of the box. One side of the cell should be removed from the 1/8" tubing. Then the special syringe is used. The nickel tube of the syringe that is used as a needle is inserted into the hole left by removal of the 1/8 tubing. A mirror and a flashlight must be used in order to see how far the nickel tube is inserted into the capillary. When the nickel tubing is approximated at mid-point of the capillary, the mercury is inserted from the syringe. The size of the mercury drop should not be greater than 0.5 inches in length. When this operation is completed, the syringe is removed and the 1/8" tubing re-inserted in the cell.

The first procedure mentioned (complete removal of the cell) means that the lasers have to be re-adjusted after the cell is re-screwed into the box since the capillary tube was moved. The second procedure is most recommended since no further adjustment of the laser has to be done.

3.2 Vacuum to the system

It is very important that vacuum is pulled on the system since a small amount of air will cause problems in the operation of the microflowmeter. In order to pull a vacuum, valves 1, 2 and 5 should be open, while valve 4 and 3 should be closed. The pressure regulator from the hydrogen cylinder is closed at this time. The vacuum pump is turned on and then the valve number 4 is opened VERY SLOWLY. When the first sign of vacuum appears on the system, the opening of valve 4 should be stopped for at least 1 minute. After this time, valve 4 can be opened all the way but very slowly. The mercury bead may have a slight movement when the vacuum begins to be applied.

The vacuum in the system has to be pulled for at least 2 hours since the dimensions of the nickel tubing are very small.

3.3 Pressurizing the system

After the evacution is completed, hydrogen is inserted in the system. This step is <u>very important</u> and must be permormed carefully. The way to do this is as follows: Closed valve 4, so the vacuum pump is isolated from the system. Open the pressure regulator very, very slowly. When the first signs of pressure appears to be on the system, stop turning the regulator for at least 2 minutes. Then keep increasing the pressure up to 100 psi. At this point, valve 3 (from the pressure transducer) can be opened. After this, the pressure can be increased up to 3,000 psi. It should be noted that it is essential to increase the pressure up to 700 psi very slowly; after 700 psi is reached in the regulator, the pressure can be increased more rapidly.

3.4 Starting operation of the system

After the pressure is set at 3,000 psi, it is recomended to wait for at least 5 hours before starting the system. This is due to the slow hydrogen movement into the nickel tubing. After this time is over, the system is ready to start operating.

1.- Check to see if the lasers are on.

2.- Check if the multiport valve has enough pressure to operate (80 psi).

3.- Turn on the computer.

3.5 Additional comments

The multiport valve, by the way that is contructed, has one right sequence where the mercury has no movement when pulling a vacuum or pressurizing the system and has one wrong sequence that may cause the mercury to jump to one side when vacuum or pressure are on the system. The right sequence is as follows:

- Originally, both solenoid valves are off which means in terms of computer:

```
XBY(0C802H) = 0
XBY(0C801H) = 0
```

- To get movement to the left side, solenoid 2 has to be activated:

```
XBY(0C802H) = 2
```

- To get a mid-position, solenoid 1 should be activated:

```
XBY(0C801H) = 2
```

- To return flow to the right side, solenoid 2 has to be deactivated:

```
XBY(0C802H) = 0
```

- To get another mid-position, solenoid 1 has to be deactivated;

```
XBY(0C801H) = 0
```

After following this sequence, the valve is in a good mid-position that allows pulling vacuum or pressurized the system and the mercury will not move at all.

There are two ways to get this sequence done before starting, these are: (1) by using the computer program
(2) by typing on the Tandy keyboard

1.0 By using the computer program

The computer program has one instruction in line 45 that sends the program to subroutine 1900. In this subroutine the sequence just explained is followed, so the valve can get to the right mid-position with no problems. In order to get this sequence operating, the lasers should be OFF and the main power switch located on the side of the control box turned on for 1 minute and then turned off again.

2.0 Manual operation

The computer has to be turned on and at then, CONTROL C must by typed on the board. The symbol > will appear on the screen. Then the following sequence must be typed:

```
XBY(0C803H) = 80H
XBY(0C802H) = 2
XBY(0C801H) = 2
XBY(0C802H) = 0
XBY(0C801H) = 0
```

Then the computer can be turned off, and the vacuum and pressurization of the system can be done.

APPENDIX G.

EXPERIMENTAL VALUES FOR GC CALIBRATION

GAS = HYDROGEN

VOLUME[ml]	AREA
0.0	0.0
0.02	0.035
0.04	0.0162
0.05	0.2027
0.06	0.2896
0.08	0.4457
0.10	0.577
0.15	0.9714
0.20	1.2396
0.30	2.090
0.35	2.4314
0.40	3.1206

GAS = METHANE

VOLUME[ml]	AREA
0.0	0.0
0.1	17.25
0.2	41.04
0.3	56.85
0.35	69.79
0.25	49.72
0.15	30.35
0.05	10.72

GAS = ETHANE

VOLUME[ml]	AREA
0.0	0.0
0.05	16.76
0.10	33.09
0.15	50.08

GAS = OXYGEN

VOLUME[ml]	AREA
0.0	0.0
0.05	10.16
0.10	24.89
0.15	29.20
0.20	36.74
0.25	48.01
0.30	62.41
0.35	71.79
0.40	90.62
0.50	115.05

GAS = NITROGEN (0-0.1 ml)

VOLUME[ml]	AREA
0.0	0.0
0.02	1.74
0.02	2.225
0.04	5.235
0.06	9.44
0.08	13.98
0.10	19.37
0.10	18.72
0.09	17.70
0.05	6.58
0.03	3.48

GAS = NITROGEN (0-0.5 ml)

VOLUME[ml]	AREA
0.0	0.0
0.05	13.52
0.10	26.91
0.15	35.76
0.20	46.64
0.25	55.21
0.30	64.92
0.35	82.31
0.40	101.12
0.45	113.27
0.50	120.74
0.03	6.87
0.07	17.11
0.09	24.69
0.27	67.75
0.04	9.78

Figure G-1: GC CALIBRATION FOR HYDROGEN

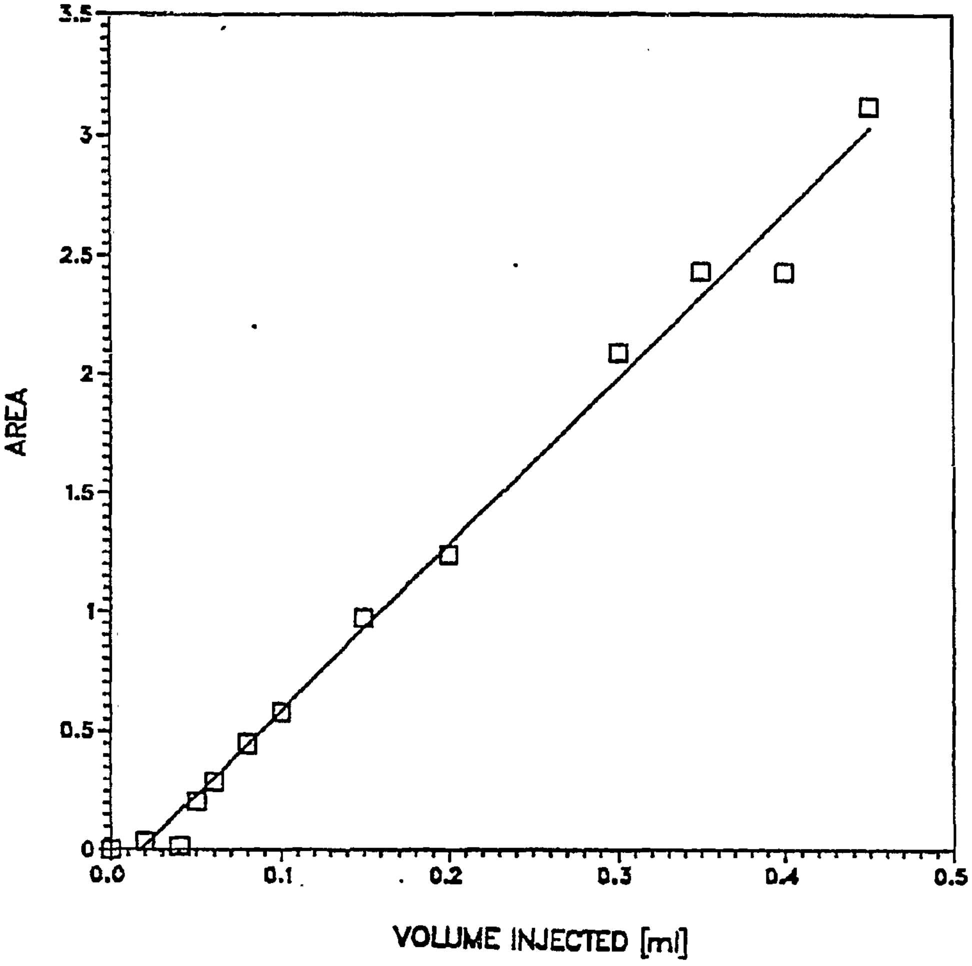


Figure G-2: GC CALIBRATION FOR METHANE

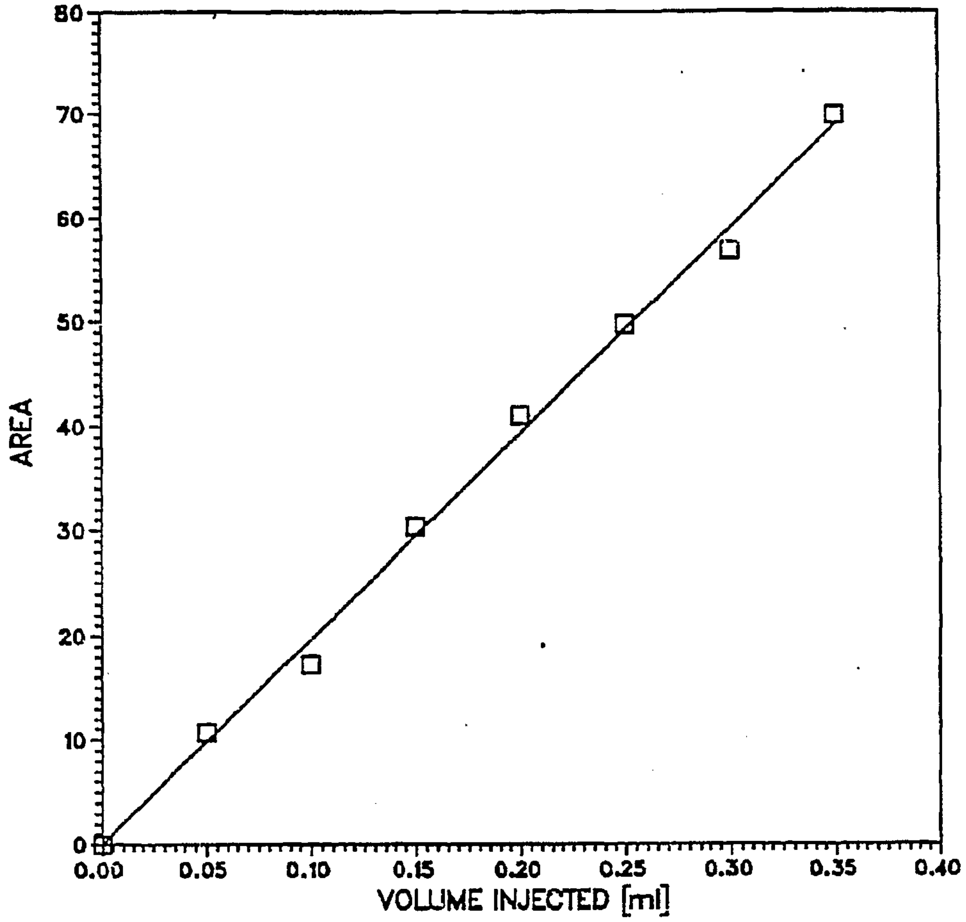


Figure G-3: GC CALIBRATION FOR ETHANE

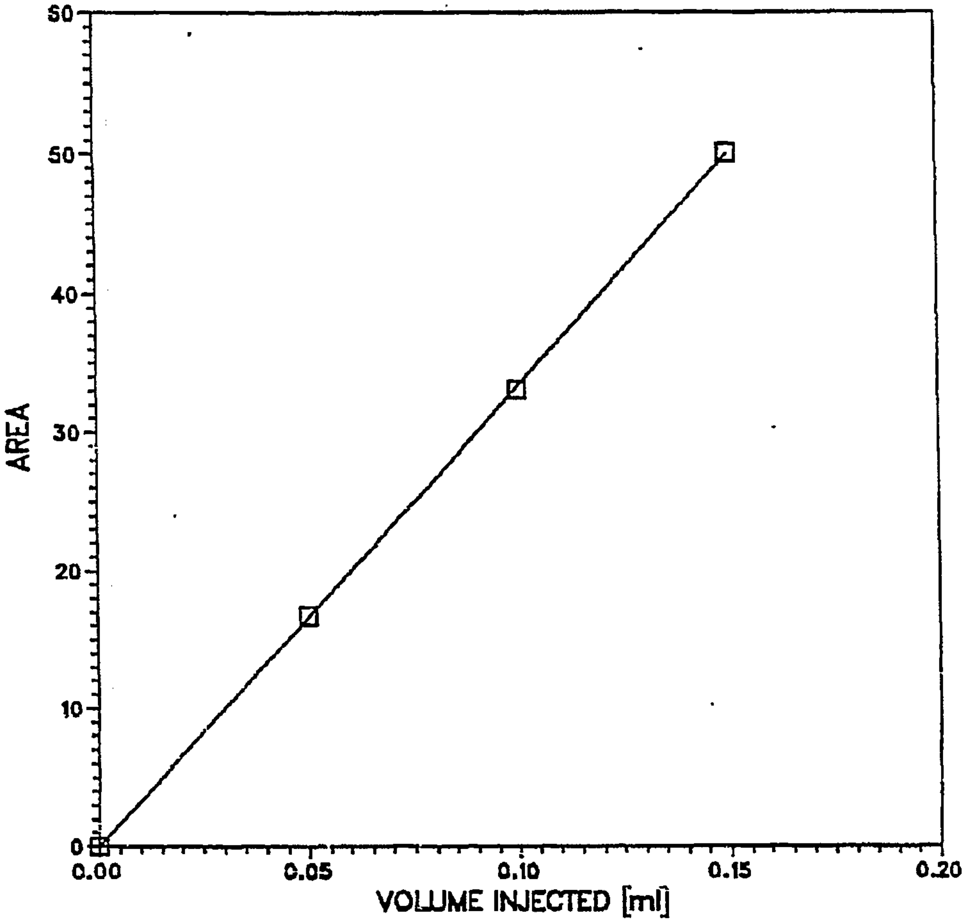


Figure G-4: GC CALIBRATION FOR OXYGEN

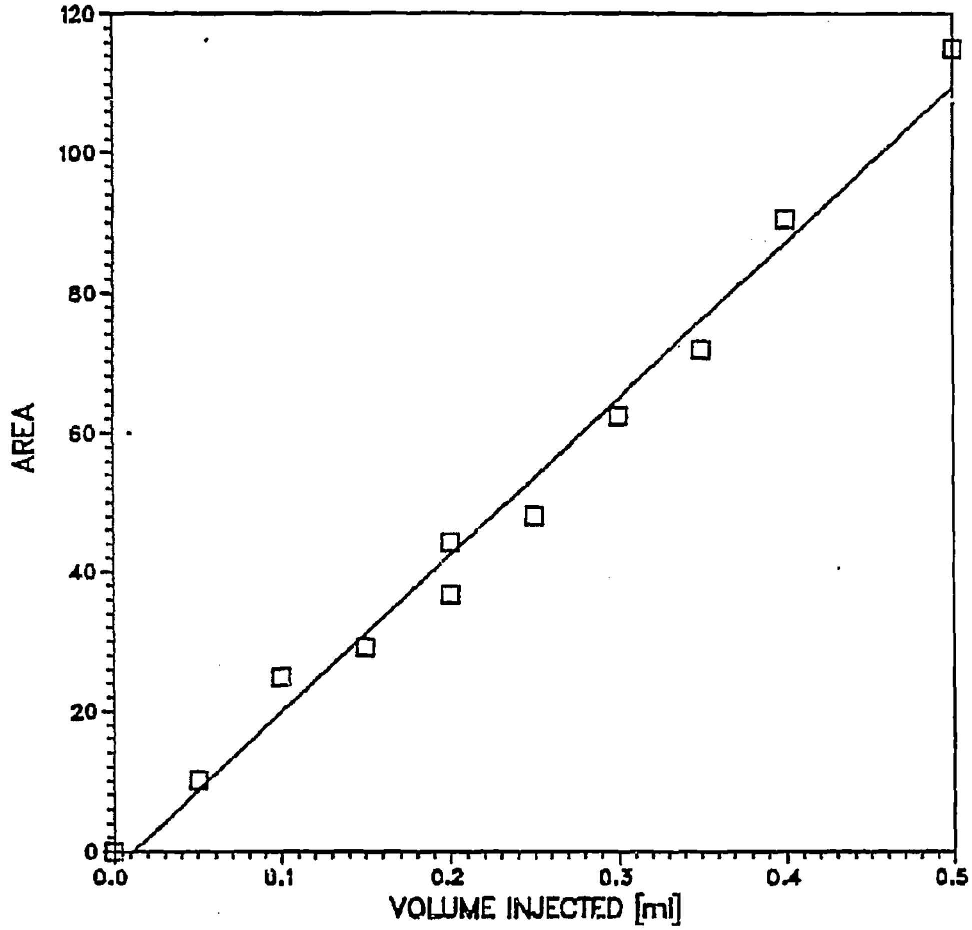


Figure G-5: GC CALIBRATION FOR NITROGEN
RANGE = 0 --> 0.1 ml

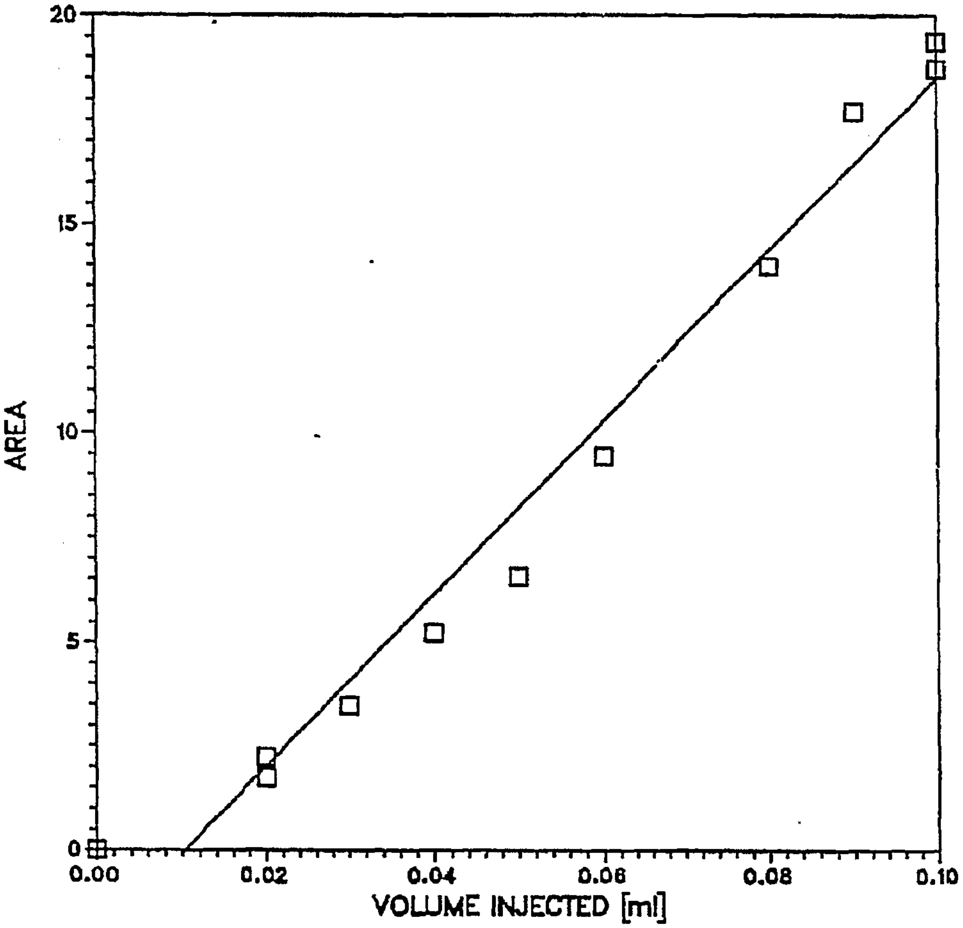
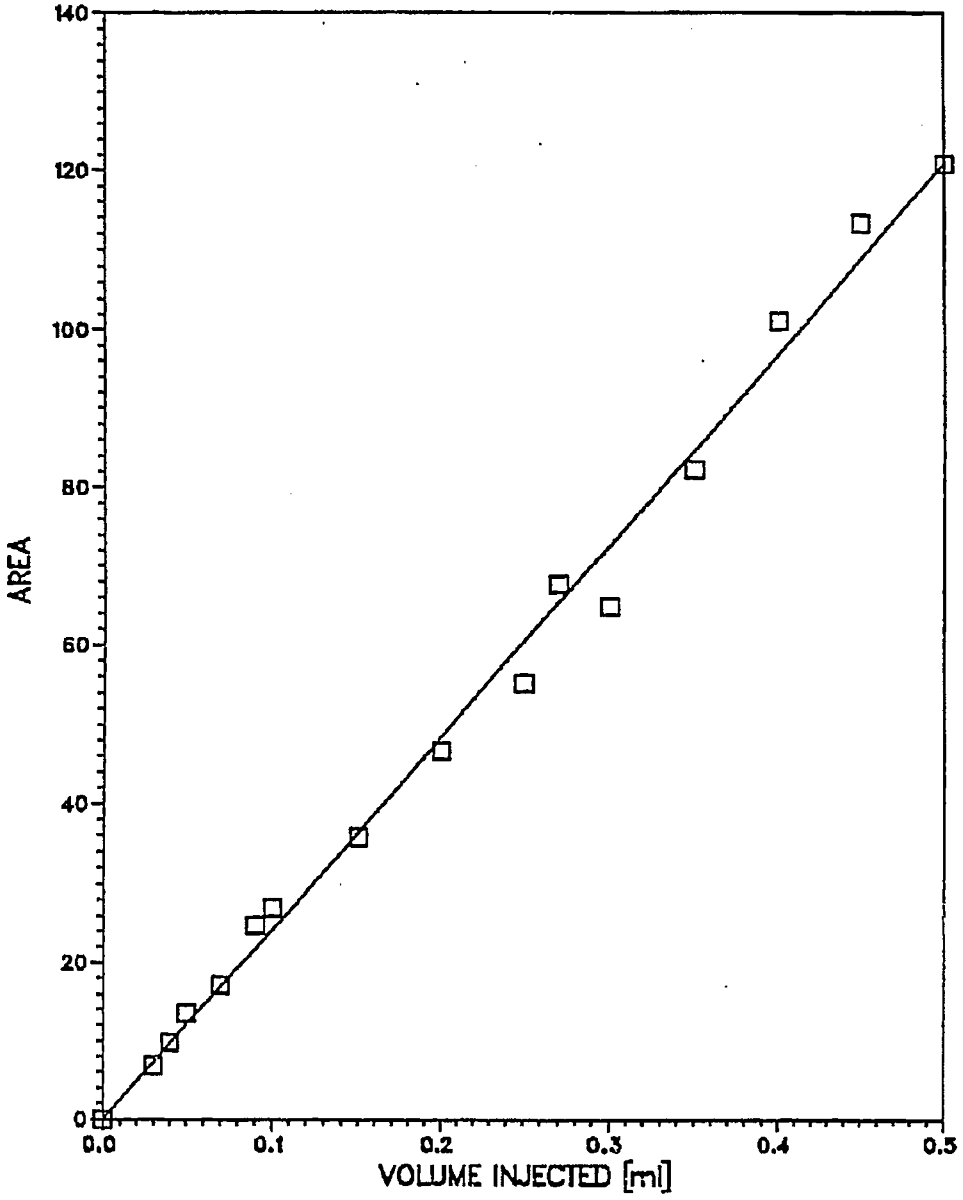


Figure G-6: GC CALIBRATION FOR NITROGEN
RANGE = 0 --> 0.5 ml



APPENDIX H.

PRESSURE TRANSDUCER CALIBRATION

MICROFLOWMETER P.T. CALIBRATION

HEISE GAUGE	[psi]	TRANSDUCER
2830		2910
3290		3384
2765		2847
2515		2597
2275		2353
2004		2076
1755		1821
1507		1570
1250		1307
1000		1049
743		785
500		536
398		429
300		330
200		225
100		122
47		65
1085		1134

REACTOR P.T. CALIBRATION

HEISE GAUGE	[psi]	TRANSDUCER
2828		2892
2764		2829
2517		2578
2277		2336
2006		2060
1755		1805
1510		1555
1252		1292
1000		1036
745		774
502		526
399		421
302		322
201		217
100		114
48		59
660		686

Figure H-1: MICROFLOWMETER PRESURE TRANSDUCER CALIBRATION

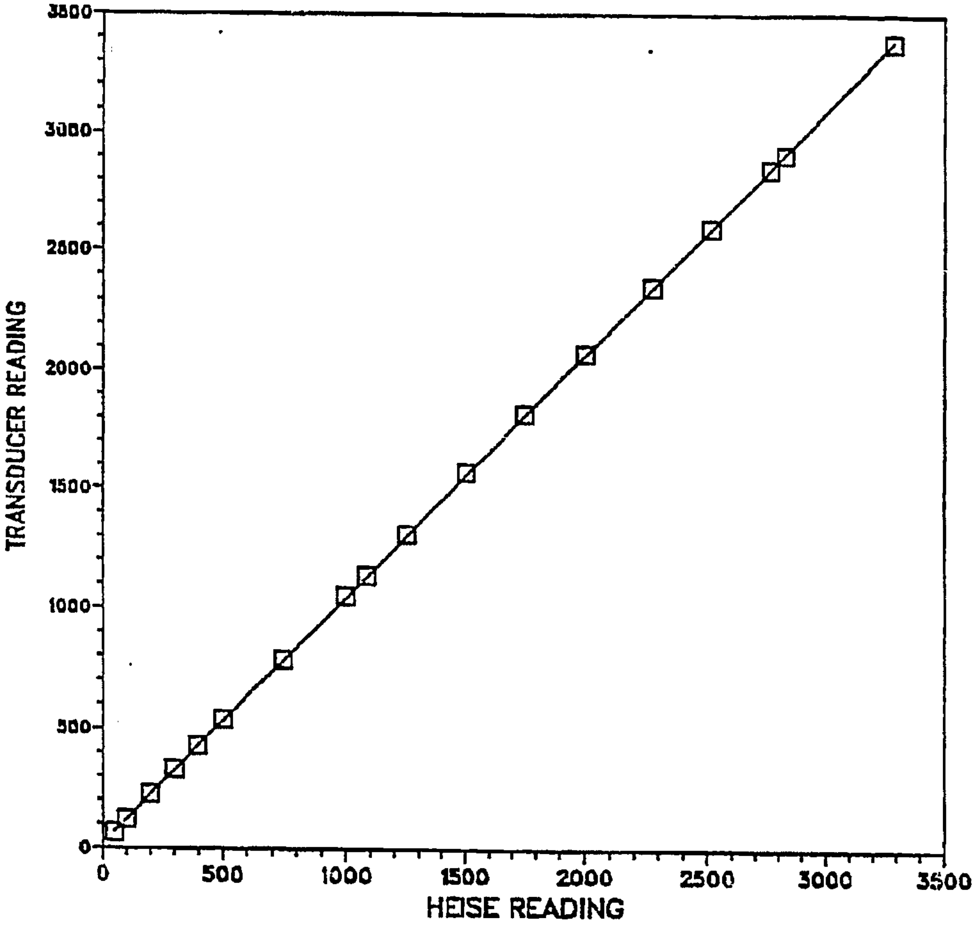
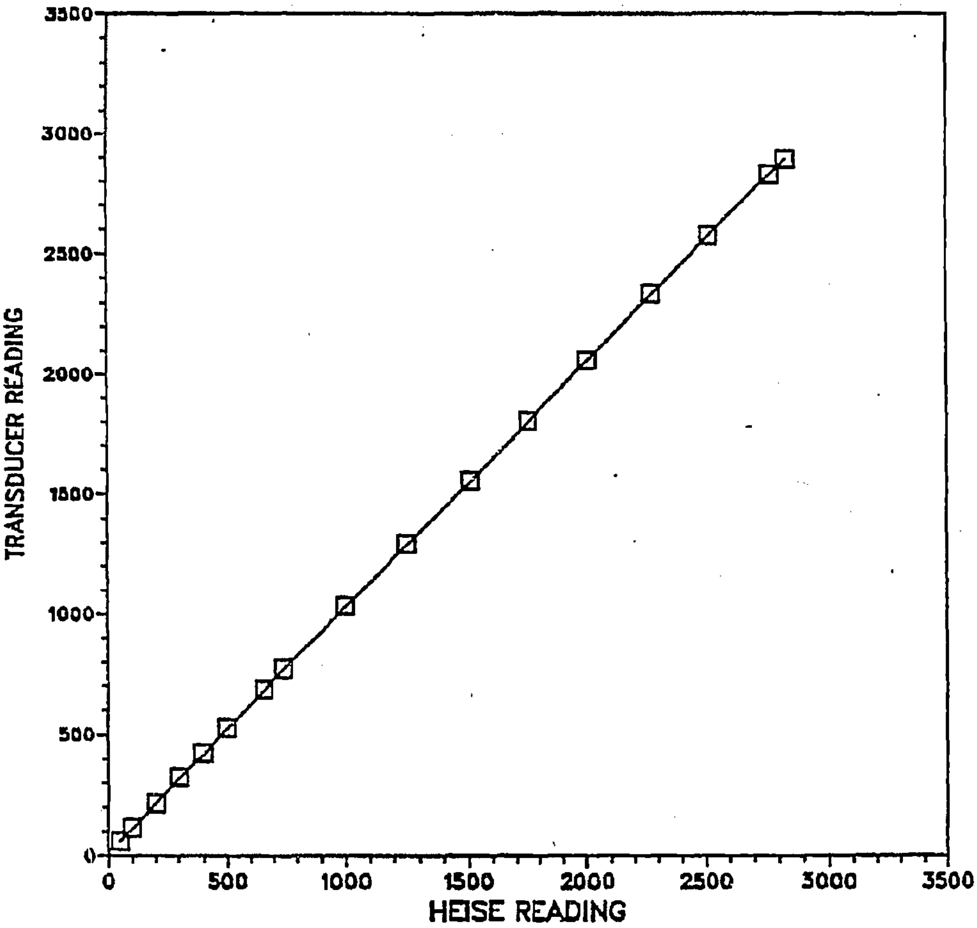


Figure H-2: REACTOR PRESSURE TRANSDUCER CALIBRATION



APPENDIX I.

EXPERIMENTAL DATA FOR VOLUME AND DIAMETER

I.1 SAMPLE FLASK VOLUME

Number	Wt. w/o water[g]	Wt. with water[g]	Temp [°C]
1	133.43	268.84	26.9
2	134.75	270.54	26.9

I.2 GLASS SECTION VOLUME

Pressure before inlet of air [cm Hg]	Pressure after inlet of air [cm Hg]	Temperature of the air [°C]
73.30	73.10	24
73.30	73.10	24
73.30	73.05	24

I.3 CAPILLARY DIAMETER

Length of the mercury [in]	Weight of the mercury [g]
2 1/16	0.7040
1 9/16	0.5457
2 13/16	0.9613
2 14/16	0.9899
1 11/16	0.5837

APPENDIX J.

EXPERIMENTAL DATA

Table J-1: System Hydrogen-Tetralin at 350 °C

	PRESSURE[psi]		TEMPERATURE[°C]					
EXP.#	REACTOR	MICRO.	LIQUID	GAS	ROOM	TIME [Sec]	ΔP [cm Hg]	LIQUID WEIGHT [g]
1	757	3000	351.7	348	24	--	1.30	2.12
2	1350	3000	351.8	347	24	--	2.00	1.87
3	1840	2781	351.8	347.2	24	435.8	2.97	1.86
4	1317	2768	351.8	347.2	24	278.4	2.40	1.90
5	1015	2763	352.2	347.5	24	223.4	1.65	1.86

Table J-2: System Hydrogen-Tetralin at 390 °C

	PRESSURE[psi]		TEMPERATURE[°C]					
EXP.#	REACTOR	MICRO.	LIQUID	GAS	ROOM	TIME [Sec]	ΔP [cm Hg]	LIQUID WEIGHT [g]
1	650	2751	389.5	389.2	23	86.1	1.10	1.66
2	1046	2750	389.3	390.0	23	110.7	2.10	1.57
3	1148	2808	392.4	387.5	24	86.7	2.00	1.66
4	1331	2778	393.5	388.5	24	138.0	2:55	1.61
5	1629	2793	392.9	388.1	24	167.5	2.95	1.40
6	1951	2947	394.1	389.5	24	212.4	3.85	1.45
7	1923	2942	392.5	388.4	23	202.0	3.15	1.28

Table J-3: System Hydrogen-Tetralin-Methane at 325 °C

EXP.#	PRESSURE[psi] REACTOR	MICRO.	TEMPERATURE[°C] LIQUID	GAS	ROOM	TIME [Sec]	ΔP [cm Hg]	LIQUID WEIGHT [g]
1	1033	2986	325.7	323.1	25	399.7	1.20	1.58
2	1228	2983	326.1	323.6	25	416.4	1.80	1.66
3	1398	2985	326.0	323.1	25	412.6	2.50	1.63
4	1565	2986	326.3	323.2	25	406.5	2.90	1.65
5	1766	2989	326.1	323.1	25	411.7	3.00	1.64
6	1972	2987	326.5	323.2	26	418.4	3.0	1.67

Table J-4: System Hydrogen-Tetralin-Methane at 375 °C

EXP.#	PRESSURE[psi] REACTOR	MICRO.	TEMPERATURE[°C] LIQUID	GAS	ROOM	TIME [Sec]	ΔP [cm Hg]	LIQUID WEIGHT [g]
1	1407	2989	374.4	369.6	25	180.9	2.50	1.88
2	1630	2995	374.5	369.7	25	179.1	3.10	1.56
3	2205	2992	374.7	370.2	25	186.0	2.65	1.58
4	1434	2969	373.4	368.9	24	176.3	2.35	1.34
5	1944	2980	374.1	369.8	24	189.1	3.25	1.33
6	2151	2980	373.9	369.7	25	193.0	3.45	1.20
7	2142	2983	373.9	369.8	25	175.6	3.75	1.28
8	1667	2993	374.1	369.6	23	185.9	3.00	1.26
9	1548	2971	374.0	369.7	23	183.6	2.70	1.36

Table J-5: System Hydrogen-Tetralin-Ethane at 360 °C

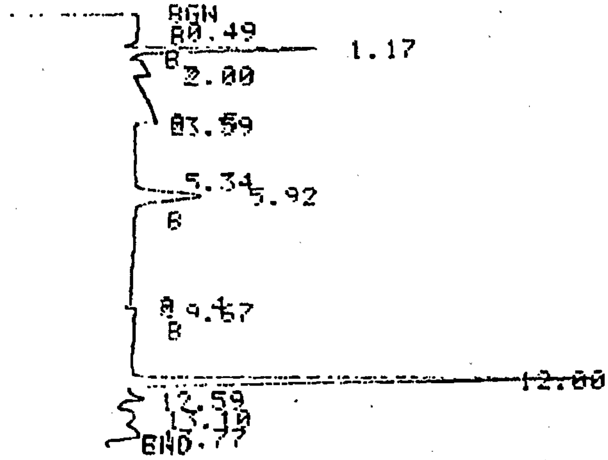
EXP.#	PRESSURE[psi] REACTOR	PRESSURE[psi] MICRO.	TEMPERATURE[°C] LIQUID	TEMPERATURE[°C] GAS	TEMPERATURE[°C] ROOM	TIME [Sec]	ΔP [cm Hg]	LIQUID WEIGHT [g]
1	1090	2991	360.0	357.3	25	216.1	1.55	1.64
2	1135	2992	362.5	357.6	27	218.4	1.60	1.63
3	1208	2998	362.7	357.9	27	223.8	1.65	1.62
4	1356	2993	362.4	357.4	28	222.2	1.80	1.84
5	1517	2990	361.0	357.2	28	223.1	1.65	1.55
6	1684	2993	359.1	358.4	28	223.9	1.85	1.59

Table J-6: System Hydrogen-Tetralin-Ethane at 395 °C

EXP.#	PRESSURE[psi] REACTOR	PRESSURE[psi] MICRO.	TEMPERATURE[°C] LIQUID	TEMPERATURE[°C] GAS	TEMPERATURE[°C] ROOM	TIME [Sec]	ΔP [cm Hg]	LIQUID WEIGHT [g]
1	1330	2981	396.4	394.0	26	91.3	3.05	1.65
2	1400	2990	396.7	392.1	25	92.9	2.97	1.56
3	1505	2993	396.6	394.3	25	93.0	3.20	1.52
4	1912	2995	397.7	393.1	26	91.0	4.25	1.56

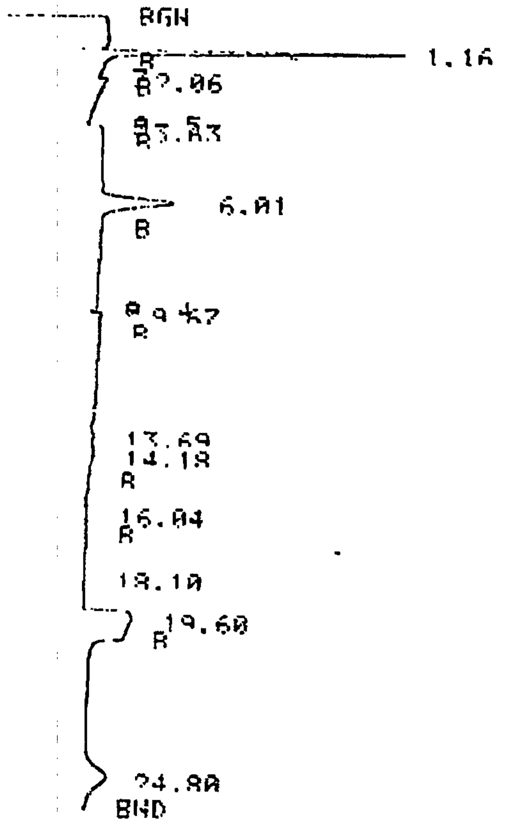
Figure J-1: TYPICAL CHROMATOGRAM FOR HYDROGEN-METHANE

```
ANAL  1  DET    1  METH    2       2  FILE   82

RUN      12  METHANE AT 325 C

SENSITIVITIES   100  50
```



```
ANAL  1  DET    1  METH    2       2  FILE   82

RUN      12  METHANE AT 325 C 18 : 26.0   5 /  9 / 87

SENSITIVITIES   100  50

   TIME        AREA  BC     RRT       RF           C   NAME

   0.49     0.0000        0.049    1.000      0.0000 !
   1.17     0.6614        0.117    1.000      3.5510 !  0.0993
   2.00     0.0291 V      0.200    1.000      0.1564 !
   3.59     0.1103 V      0.359    1.000      0.5926 !
   5.34     0.0533 T      0.534    1.000      0.2864 !
   5.92     5.0376        0.592    1.000     27.0448 ! (0.0233)
   9.67     0.3323        0.967    1.000      1.7841 !
  12.00     9.4988 T      1.200    1.000     50.9956 !  0.0982
  12.59     0.6238 T      1.259    1.000      3.3490 !
  13.10     0.9641 T      1.310    1.000      5.1760 !
  13.77     1.3158        1.377    1.000      7.0642 !  ______
                                                         0 1563
```

Figure J-2: TYPICAL CHROMATOGRAM FOR HYDROGEN-ETHANE



```
ANAL  1  DET    1  METH    3      3  FILE   58

RUN     14  EXP WITH ETHANE 20 :  2.0   5 / 14 / 87

SENSITIVITIES   100  50

  TIME       AREA   BC     RRT      RF          C   NAME

  1.16     0.8677         0.116   1.000      7.7155 !
  2.06     0.0307         0.206   1.000      0.2735 !
  3.63     0.1052         0.363   1.000      0.9356 !
  6.01     5.2777         0.601   1.000     46.9283 !
  9.67     0.3022         0.967   1.000      2.6874 !
 13.69     0.0939 T       1.369   1.000      0.8355 !
 14.18     0.2619         1.418   1.000      2.3287 !
 16.04     0.0721         1.604   1.000      0.6416 !
 18.10     0.0189 V       1.810   1.000      0.1686 !
 19.60     2.4796         1.960   1.000     22.0486 !
 24.80     1.7360         2.480   1.000     15.4367 !
```

APPENDIX K.
SAMPLE CALCULATION

The sample calculation is based on the data for the system hydrogen-tetralin-ethane at 360 °C. The point considered was the base point when no ethane was present in the reactor.

Experimental data

Reactor pressure	1090 psi
Flowmeter pressure	2991 psi
Room temperature	25.1 °C
Liquid phase temp.	360.0 °C
Gas phase temp.	357.3 °C
Time of travel for Hg	216.6 sec

ΔP for sample in glass section: 1.55 cm Hg

Weight of the liquid phase sample : 1.64 gr

Calculations

Pressure of hydrogen from equation 2.1 : 897 psi

Vapor pressure of tetralin (by difference) : 1090 - 897 = 207 psi

Vapor pressure of tetralin (by equation 5-1) : 193 psi

These results show a good agreement between the experimental value for the tetralin vapor pressure and the one calculated by using equation 5-1.

moles of gas transfered from expansion cylinder: $n_T = PV/RT$

$$n_T = ((1.55/76)*1229.5)/(82.05*(273.16+27))$$

$$n_T = 1.0182 \times 10^{-3}$$

moles of tetralin: $n_t = m/MW$

$$n_t = 1.64/132.196$$

$$n_t = 1.241 \times 10^{-2}$$

Mole fraction of hydrogen in the liquid: $x_{H_2} = n_T/(n_T+n_t)$

$$x_{H_2} = 1.0182x10^{-3}/(1.0182x10^{-3}+1.241x10^{-2})$$

$$x_{H_2} = 0.07585$$

Mole fraction of tetralin in the liquid: $x_{tet} = 1 - x_{H_2}$

$$x_{tet} = 1 - 0.07585$$

$$x_{tet} = 0.92415$$

When a third component, methane or ethane is used, n_T represents the total number of moles in the gas phase. The porcentage of each gas, hydrogen and methane (or ethane) are obtained from the analysis done in the gas chromatograph. With this porcentages, the number of moles of hydrogen and methane (or ethane) are known and the mole fraction of theses compound in the liquid is calculated in the same way as shown before.

APPENDIX L.
K-VALUE COMPARISON

L.1 CORRELATION USED FOR TETRALIN

The correlation used for tetralin was the one propesed by Chao and Seader[40] in 1961. The correlation is:

$$K_i = (\nu^{o} * \gamma)/(\phi)$$

The values for ν^{o}, γ and ϕ are obtained from the following relations:

$$\log(\nu^{o}) = \log(\nu^{(0)}) + \log(\nu^{(1)})$$

Correlations for $\log(\nu^{(0)})$ and $\log(\nu^{(1)})$ are found in the mentioned paper.

$$\ln(\gamma_i) = V_i(\delta_i - \bar{\delta})^{0.5}/RT$$

and $\bar{\delta}$ is given by:

$$\bar{\delta} = (\mathrm{SUM}\ x_i V_i \delta_i)/(\mathrm{SUM}\ x_i V_i)$$

The value for ϕ is calculated by using the Redlich and Kwong equation of state.

The second correlation used, developed by Sebastian et. al.[41] is as follows:

$$\ln(f/x) = \ln(f/x)_{p=0} + p\bar{V}/(RT)$$

equations for $\ln(f/x)_{p=0}$ and $\bar{V}$ are given in the mentioned paper.

The results of the comparison are given in the following tables.

Table L-1: System Hydrogen-Tetralin
K-value for hydrogen at 350 °C

PRESSURE[MPa]	Kexp	Kcalc	%Diff
5.41	15.52	14.28	1.2
6.99	11.59	12.42	6.7
9.09	9.49	9.82	3.4
9.46	10.29	9.52	8.1
12.69	7.46	7.35	1.5

Table L-2: System Hydrogen-Tetralin
K-value for tetralin at 350 °C

PRESSURE[MPa]	Kexp	Kcalc	%Diff
5.41	0.228	0.229	0.5
6.99	0.183	0.184	0.5
9.09	0.144	0.134	2.0
9.46	0.132	0.129	4.8
12.69	0.105	0.130	26.6

Table L-3: System Hydrogen-Tetralin
K-value for hydrogen at 390 °C

PRESSURE[MPa]	Kexp	Kcalc	%Diff
4.48	10.59	13.58	22.0
7.21	7.05	9.07	22.3
7.93	7.99	8.42	5.1
9.18	6.54	7.39	11.5
11.23	5.42	6.21	12.7
13.45	4.55	5.32	14.5
13.26	4.84	4.92	10.5

Table L-4: System Hydrogen-Tetralin
K-value for tetralin at 350 °C

PRESSURE[MPa]	Kexp	Kcalc	%Diff
4.48	0.449	0.421	6.7
7.21	0.294	0.256	4.3
7.93	0.258	0.262	2.3
9.18	0.240	0.233	3.0
11.23	0.203	0.197	3.0
13.45	0.179	0.172	4.1
13.26	0.177	0.173	2.3

Table L-5: System Hydrogen-Tetralin-Methane
K-value for hydrogen at 325 °C

PRESSURE[MPa]	Kexp	Kcalc	%Diff
7.12	14.29	14.08	1.5
8.47	11.29	11.97	5.7
9.64	9.49	9.62	10.3
10.79	6.99	9.51	26.5
12.18	5.68	8.52	33.3
13.59	4.63	7.70	39.9

Table L-6: System Hydrogen-Tetralin-Methane
K-value for tetralin at 325 °C

PRESSURE[MPa]	Kexp	Kcalc	%Diff
7.12	0.127	0.131	2.8
8.47	0.111	0.117	5.1
9.64	0.099	0.110	10.0
10.79	0.091	0.108	16.1
12.18	0.081	0.105	23.1
13.59	0.072	0.107	32.6

Table L-7: System Hydrogen-Tetralin-Methane
K-value for hydrogen at 375 °C

PRESSURE[MPa]	Kexp	Kcalc	%Diff
8.22	10.18	9.22	10.4
9.70	7.51	7.81	3.8
15.20	2.57	5.26	51.1
9.89	5.64	7.71	26.8
13.40	3.41	5.89	42.1
14.77	2.34	5.35	56.3
11.49	4.25	6.71	36.7
10.67	4.92	7.19	31.6

Table L-8: System Hydrogen-Tetralin-Methane
K-value for tetralin at 375 °C

PRESSURE[MPa]	Kexp	Kcalc	%Diff
8.22	0.208	0.213	2.3
9.70	0.179	0.211	15.2
15.20	0.128	0.176	27.3
9.89	0.181	0.200	9.5
13.40	0.141	0.176	19.9
13.67	0.142	0.175	18.9
14.77	0.132	0.182	27.5
11.49	0.164	0.165	0.6
10.67	0.171	0.191	10.5

Table L-9: System Hydrogen-Tetralin-Ethane
K-value for hydrogen at 360 °C

PRESSURE[MPa]	Kexp	Kcalc	%Diff
7.52	10.85	12.58	13.8
7.83	10.67	12.24	12.8
8.33	10.41	11.58	10.1
8.67	9.29	11.11	16.4
9.35	8.75	10.35	15.5
10.46	7.42	9.28	20.0
11.61	6.38	8.40	24.0

Table L-10: System Hydrogen-Tetralin-Ethane
K-value for tetralin at 360 °C

PRESSURE[MPa]	Kexp	Kcalc	%Diff
7.52	0.192	0.194	1.0
7.83	0.187	0.189	1.1
8.33	0.177	0.165	2.2
8.67	0.168	0.162	5.6
9.35	0.158	0.155	7.6
10.46	0.140	0.164	14.6
11.61	0.126	0.144	20.3

Table L-11: System Hydrogen-Tetralin-Ethane
K-value for hydrogen at 395 °C

PRESSURE[MPa]	Kexp	Kcalc	%Diff
9.17	5.64	9.73	42.0
9.65	5.29	9.30	43.1
10.38	4.85	8.72	44.4
13.18	2.92	6.84	57.3

Table L-12: System Hydrogen-Tetralin-Ethane
K-value for tetralin at 395 °C

PRESSURE[MPa]	Kexp	Kcalc	%Diff
9.17	0.257	0.244	5.3
9.65	0.244	0.237	3.0
10.38	0.232	0.229	1.3
13.18	0.191	0.193	9.9

APPENDIX M.

EXPERIMENTAL DATA FROM WILSONVILLE

The experimental data taken with the equipment installed in Wilsonville are:

Pressure inside microflowmeter	2820 psi = 19.44 MPa
Temperature of the stream	703.7 °F
Box temperature	99.4 °F
Time of travel for mercury	54 sec

The values for the data of the system are:

Length of Nickel	34'8"
Capillary volume	5.318×10^{-8} m^3
Logartihmic mean area	8.851×10^{-3}

Permeability coefficient equation:

$$\phi = 7.508 \times 10^{-6} \times \exp(-6008/TK)$$

where TK is the temperature in °K

ϕ is the permeability coefficient in $m^3/sec(NTP)/m/MPa^{0.5}$

Calculated values

$\phi = 64.56 \times 10^{-11}$

$Q(NTP) = Vc/time = 5.318 \times 10^{-8}/54 * (2820/14.696) * (530/559.4)$

$= 1.791 \times 10^{-7}$

$\Delta P = (1.791 \times 10^{-7} \times 1.27 \times 10^{-4})/(8.851 \times 10+[-3] \times 64.56 \times 10^{-11})$

$= 3.981$

$= (19.44)^{0.5} - P_2^{0.5} = 3.981$

$P_2^{0.5} = 0.428$ MPa

$P_2 = 0.183$ MPa = 26.6 psi

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