

VISCOSITY OF SELECTED HYDROCARBONS

SATURATED WITH GAS

By

DULAIHAN KHULAIWI AL-HARBI

Bachelor of Science
Pennsylvania State University
University Park, Pennsylvania
1970

Master of Science
Pennsylvania State University
University Park, Pennsylvania
1975

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the Degree of
DOCTOR OF PHILOSOPHY
May, 1982



VISCOSITY OF SELECTED HYDROCARBONS
SATURATED WITH GAS

Thesis Approved:

G. N. Maddox

Thesis Adviser

John Huber

J. E. Francis

Norman N. Durbin

Norman N. Durbin

Dean of the Graduate College

ACKNOWLEDGMENTS

I wish to express my deepest appreciation and thanks to my advisor Dr. R. N. Maddox for his excellent guidance, patience, and understanding throughout the course of this work. I would also like to express my appreciation to the members of my advisory committee, Dr. K. J. Bell, Dr. J. H. Erbar, and Dr. G. J. Mains for their valued suggestions.

Many thanks to the University of Petroleum and Minerals, Dhahran, Saudi Arabia for the financial support and encouragement throughout the years of my graduate studies.

I would like to thank, Dr. Faisal Al-Juwaihel, Dr. Saed Akashah, Suleiman Diab, Beleid Kuwairi, Khaled Gasem, Daniel Chen, and Mahmoud Rahman for their unforgettable friendship, encouragement, and valuable suggestions. I also thank Mr. Ross Fox of the Fluid Properties Laboratory for his invaluable technical assistance.

My father, mother, and brothers deserve my deepest appreciation for their constant support, encouragement, and understanding.

Last but not least, many thanks to Fahad Al-Hubdan for his unforgettable assistance in using TSO and correlating the data.

TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION	1
II. LITERATURE SURVEY	3
Hydraulic Pressure Effect	3
Solubility Pressure Effects	7
Kinematic Viscometer	9
III. EXPERIMENTAL APPARATUS	11
Viscometer	11
Pressure Cell	14
Temperature Control	18
Pressure Distribution System	19
IV. EXPERIMENTAL PROCEDURES	21
Calibration of Viscometer	21
Preparation of Experimental Apparatus	23
Operation	24
Materials Tested	26
V. RESULTS AND DISCUSSION	27
Results	27
Discussion	43
Correlation of Viscosity Data	48
VI. CONCLUSIONS AND RECOMMENDATIONS	52
BIBLIOGRAPHY	53
APPENDIX A - COMPARISON BETWEEN PURE ABSOLUTE LIQUID VISCOSITY AND ABSOLUTE LIQUID VISCOSITY UNDER GAS PRESSURE	56
APPENDIX B - EXAMPLE RAW DATA	66
APPENDIX C - CALIBRATION OF EQUIPMENT	69

LIST OF TABLES

Table	Page
I. Pressure Cell Seals	18
II. Reliability of Experimental Data for n-Heptane at Atmospheric Pressure	22
III. Assurance of Reaching Equilibrium Between Normal- Heptane and Carbon Dioxide--as an Example	25
IV. Test Material Specification	26
V. Experimental and Calculated Viscosity of Normal- Heptane Under Carbon Dioxide Gas Pressures	28
VI. Experimental and Calculated Viscosity of Normal- Heptane Under Hydrogen Gas Pressures	31
VII. Experimental and Calculated Viscosity of Normal- Heptane Under Nitrogen Gas Pressures	33
VIII. Experimental and Calculated Viscosity of Cyclo- Hexane Under Carbon Dioxide Gas Pressures	35
IX. Experimental and Calculated Viscosity of Cyclo- Hexane Under Hydrogen Gas Pressures	39
X. Experimental and Calculated Viscosity of Cyclo- Hexane Under Nitrogen Gas Pressures	40
XI. Experimental and Calculated Viscosity of Benzene Under Carbon Dioxide Gas Pressures	41
XII. Experimental and Calculated Viscosity of Benzene Under Hydrogen Gas Pressures	44
XIII. Experimental and Calculated Viscosity of Benzene Under Nitrogen Gas Pressures	45
XIV. Summary of Results of Nonlinear Least Square Fitting Using MARQ	51
XV. Effect of Nitrogen Gas Pressure on the Absolute Viscosity of n-Heptane	57

Table :	Page
XVI. Effect of Hydrogen Gas Pressure on the Absolute Viscosity of n-Heptane	58
XVII. Effect of Carbon Dioxide Gas Pressure on the Absolute Viscosity of n-Heptane	59
XVIII. Effect of Carbon Dioxide Gas Pressure on the Absolute Viscosity of Cyclohexane	60
XIX. Effect of Nitrogen Gas Pressure on the Absolute Viscosity of Cyclohexane	61
XX. Effect of Hydrogen Gas Pressure on the Absolute Viscosity of Cyclohexane	62
XXI. Effect of Carbon Dioxide Gas Pressure on the Absolute Viscosity of Benzene	63
XXII. Effect of Hydrogen Gas Pressure on the Absolute Viscosity of Benzene	64
XXIII. Effect of Nitrogen Gas Pressure on the Absolute Viscosity of Benzene	65
XXIV. Experimental Measurements of Benzene Kinematic Viscosity Under Hydrogen Gas Pressure	67
XXV. Kinematic Viscometer Calibrations	71
XXVI. Calibration Measurements With Degased Distilled Water	72
XXVII. Calibration of HTL Pressure Gauge	73
XXVIII. Calibration Data for Pressure Cell Thermocouple	74

LIST OF FIGURES

Figure	Page
1. Zeitfuchs Capillary Viscometer	12
2. Support for Zeitfuchs Capillary Viscometer	13
3. Pressure Cell	15
4. View Port Details	16
5. Pressure Cell Top Flange and Viscometer Connections	17
6. Schematic Diagram of the Kinematic Viscometer Experimental Apparatus	20
7. Kinematic Viscosity of n-Heptane Under Carbon Dioxide Pressure	29
8. Kinematic Viscosity of n-Heptane Under Hydrogen Gas Pressure	32
9. Kinematic Viscosity of n-Heptane Under Nitrogen Gas Pressure	34
10. Kinematic Viscosity of Cyclohexane Under Carbon Dioxide Gas Pressure	36
11. Kinematic Viscosity of Cyclohexane Under Hydrogen Gas Pressure	37
12. Kinematic Viscosity of Cyclohexane Under Nitrogen Gas Pressure	38
13. Kinematic Viscosity of Benzene Under Carbon Dioxide Gas Pressure	42
14. Kinematic Viscosity of Benzene Under Nitrogen Gas Pressure	46
15. Kinematic Viscosity of Benzene Under Hydrogen Gas Pressure	47
16. Calibration Curve of the Pressure Cell Thermocouple	75

CHAPTER I

INTRODUCTION

Viscosity is an important design parameter in many engineering and scientific areas, such as fluid flow, heat and mass transfer operations. A thorough survey of the published literature reveals that most viscosity data reported are incomplete in the sense that they do not cover a wide range of temperatures. There is comparatively less literature data on the effect of pressure on liquid viscosity.

This study was conducted to determine the effect of gas pressures on liquid viscosity. Two types of hydrocarbon liquid-gas systems were studied:

1. A hydrocarbon liquid-inert gas system, and
2. A hydrocarbon liquid-soluble gas system.

The hydrocarbon test liquids used were n-heptane, cyclohexane, and benzene, and the inert gases were nitrogen and hydrogen. The soluble gas was carbon dioxide. Gas pressures ranged from 200 psig to 700 psig while temperatures were varied from room temperature up to 220°F.

A capillary viscometer was used to obtain the experimental kinematic liquid viscosities under gas pressures at various temperatures. The data points were tested for consistency by using a correlation that had been developed by FPRI and had been proven to fit viscosity data of pure and mixed hydrocarbon liquids into a straight line.

The densities of the equilibrium liquid were obtained via the OSU/GPA method. The compositions of the equilibrium liquid-gas mixture, needed for the OSU/GPA method, were obtained by an appropriate equation of state. The equation of state was chosen for each binary mixture on the basis of comparison of calculated and experimental vapor-liquid equilibrium compositions. The equation of state giving the best reproduction of experimental measurements was used for each mixture. The densities and equilibrium liquid gas compositions were obtained using the GPA K&H computer program (35). The absolute viscosities were then calculated from the experimental kinematic viscosities and the calculated densities.

CHAPTER II

LITERATURE SURVEY

The effect of pressure on the viscosity of pure liquid and liquid mixtures has been the object of research for many years. The pressure effect on viscosity, unlike temperature effect, depends upon the molecular structure of liquids.

This survey covers two areas of pressure effect research: investigations where the pressure was supplied by the fluid under test--hydraulic, and investigations where compressed gases were used to supply the system pressure--compression.

Hydraulic Pressure Effect

McLeod (22) proposed and tested an expression for pure component viscosity as a function of temperature, which he later modified to include pressure effect. His model showed reasonable agreement with experimental data. The model was empirical and required regression of six constants from the data.

Bridgman (8, 9) used a falling object viscometer to study the effect of pressure of 43 pure liquids at temperatures of 30^o and 75^oC and pressures up to 12000 kg/cm². He observed that the behavior of viscosity with pressure was a strong function of molecular structure. No correlation for the pressure effect on viscosity was tried.

Dow (12) used a falling object viscometer to obtain data on the effect of pressure on the viscosity of liquid mixtures at temperatures of 30° and 75°C, and pressures up to 12000 kg/cm². The viscosity of non-polar liquid mixtures increased linearly with pressure. The viscosity of polar liquids showed a nonlinear dependence on pressure.

Sage and Lacey (28) studied the effect of pressure on the viscosity of liquid n-pentane, gaseous methane, and two natural gas mixtures. The temperature range of the n-pentane data was 100° to 200°F and pressures up to 1500 psia. Viscosity increased linearly with pressure.

Sage and Lacey (29) used a rolling ball viscometer to study the effect of pressure on the viscosity of liquid propane. Viscosity increased linearly with pressure up to a reduced pressure of 0.9.

Sage, Yale, and Lacey (30) studied the effect of pressure on the viscosity of n-butane and iso-butane throughout the gaseous region at temperatures from 100° to 220°C. The liquid phase viscosity of these liquids was also determined throughout this temperature interval and pressures from vapor pressure to 2000 psi. No pressure-viscosity correlation was given.

Bicher and Katz (6) studied the effect of pressure on the viscosity of methane, propane, and four of their binary mixtures (20, 40, and 80 mole percent methane). A pressure range of 400 to 5000 psi was covered with temperatures ranging from 77° to 437°F. Their data indicated a linear behavior of viscosity with pressure.

Smith and Brown (32) used a rolling ball viscometer to obtain the viscosity of ethane and propane in the temperature range of 15° to 200°C at pressures from 100 to 5000 psi. They correlated their experimental data and literature data using a corresponding state technique. The

parameter μ/\sqrt{M} , where μ is absolute viscosity and M is molecular weight, was plotted as a function of the reduced pressure and temperature. The correlation fitted the data reasonably well.

Hubbard and Brown (16) used a rolling ball viscometer to study the effect of pressure on the viscosity of n-pentane. The temperature range of the study was from 25° to 250°C, and the pressure range was from atmospheric to 1000 psi. The viscosity of n-pentane increased linearly with increase in pressure. The viscosity of n-pentane under pressure was also studied by Reamer and coworkers (26).

Greist, Webb, and Schiessler (15) used a rolling ball viscometer to obtain the viscosity of seven pure hydrocarbons having 25 or 26 carbon atoms and three binary mixtures of them. The compounds included isoparaffinic, cycloparaffinic, and aromatic types. The pressure range of this study was from one atmosphere to 3450 bars at 37.8°, 60.0°, 98.8°, and 135.0°C. The effect of pressure on viscosity was found to be dependent on molecular structure. For saturated compounds, at constant temperature, an approximate linear relationship was found between $\log \mu$ and

$$\left[\left(\frac{V}{V_0} \right)^4 - \left(\frac{V}{V_0} \right)^2 \right]$$

where μ is absolute viscosity, and V , V_0 are the specific volumes at pressure P and pressure P_0 , respectively.

Gambill (14) reported an empirical relationship for the effect of pressure on the kinematic viscosity of petroleum-derived lubricating oils, which was emphasized as being only approximate:

$$\left[\frac{\partial \ln \eta}{\partial P} \right]_T = 5 \times 10^{-6} \left[\frac{\partial \ln (\eta)}{\partial \left(\frac{1}{T} \right)} \right]_P$$

where

η = kinematic viscosity, centistokes;

T = temperature, degree K; and

P = pressure, atm.

When the pressure is more than 1000 atmospheres, $\log \mu$ is a linear function of $1/P$.

Eakin et al. (13) studied the effect of pressure on the viscosity of liquid, gas, and dense fluid ethane. The pressure range for this study was from atmospheric to 10,000 psia, and temperature ranged from 77° to 220°F. The viscosity increased linearly with pressure.

Agaev and Bolubev (1) used a falling object viscometer to study the effect of pressure on the liquid viscosity of n-pentane, n-heptane, and n-octane. Their data were tabulated as functions of temperature and pressure. Temperature ranged from 25° to 275°C and pressure 1 to 500 atmospheres. Their data showed a linear increase of viscosity with pressure up to the critical pressure, where nonlinearity occurred.

Babb and Scott (2) determined the viscosity of n-pentane, i-butane, n-butane, propane, propylene, and freon-12 at 30°C and pressures from 2 to 12 Kbar. Their data showed an exponential behavior of viscosity with pressure. There were no attempts from their part to fit their data to any model.

Isakova and Oshueva (17) used a capillary viscometer to determine the viscosity of methanol at temperatures of 20° and 160°C at pressures ranging from atmospheric to 250 Kg/cm². Their data showed a linear increase of viscosity with increase in pressure.

Chandhuri, Stager, and Mathur (11) studied the effect of pressure on the viscosity of liquid aldehydes from atmospheric pressure to 20,000

psig. The logarithm of the ratio of the absolute viscosity at a pressure P to the viscosity at atmospheric conditions was found to be a linear relationship with pressure. The relationship $\mu = \mu_0 \exp (mP)$ was suggested, where

μ = absolute viscosity at P , CP;

μ_0 = absolute viscosity at atmospheric pressure, CP;

P = pressure, psi; and

m = slope of resulting line when $\log (\mu/\mu_0)$ is plotted against pressure.

Brazier and Freeman (7) measured the effect of pressure on the viscosity of n-pentane, n-hexane, cyclopentane, methyl-cyclohexane, and 2,2-dimethylbutane (DMB) at 30°C and pressures up to 4 Kbar. They found that the smaller the compressibility of the liquid, the greater was the effect of pressure on viscosity with the exception of DMB, where viscosity increased abnormally rapidly with pressure.

Solubility Pressure Effects

Lewis (21) studied the viscosity of liquids containing dissolved gases. Liquids included carbon tetrachloride, methyl-alcohol, benzene, acetone, and ether. The gases used were sulfur dioxide and chlorine. The pressure applied to the system was not specified. Most of the viscosity measurements were taken at room temperature. His data indicated viscosity varied nonlinearly with the amount of gas dissolved in the liquid.

Simon and Graue (31) studied the effect of carbon dioxide pressure on the viscosity of nine crude oils. The range of temperature was 100°

to 250°F and pressure up to 2300 psia. Their data showed that viscosity decreased as carbon dioxide pressure was increased.

Bennett (4) studied binary mixtures of n-nonane saturated with methane gas along isotherms over a temperature range of -30 to 78°F. The pressure range was from the vapor pressure of the solvent to 1200 psi. His results showed that viscosity decreased exponentially with pressure at low temperatures and approached linearity at high temperatures.

Bagzis (3) studied the viscosity of n-decane, n-hexane, and a binary mixture of n-butane and n-decane saturated with methane over a pressure range between solvent vapor pressure and 1200 psia. A system of n-decane saturated with ethane was also studied. His results showed that the saturated liquid viscosity was more greatly affected by pressure at low temperatures than at high temperatures. The viscosity of n-hexane decreased exponentially as the methane gas pressure was increased at low temperatures and approached linearity at high temperatures.

Rudolf (27) studied the effect of methane gas pressure on the viscosity of lean absorber oils. The temperature range of his study was from -26° to 77°F at pressures from atmospheric to 1000 psia. The viscosity of lean oils decreased exponentially with increase of methane gas pressure at low temperatures and approached linearity at high temperatures.

McCoy (23) studied the effect of pressure on the viscosity of n-octane and a binary mixture of n-octane and nitrogen, helium, hydrogen, argon, or methane. The temperature range for this study was from 98° to 155°F, and pressures from atmospheric to 1000 psia. The reader is referred to his thesis for more details.

Miller and Jones (24) studied the effect of carbon dioxide gas pressure on the viscosity of heavy oils. Oil gravity ranged from 10° to 17° API. The pressure range of this study was from 200 to 5000 psi at temperatures of 75°, 140°, and 200°F. Their results indicated that viscosity decreased with increase of carbon dioxide pressure.

Kinematic Viscometer

Bird, Stewart, and Lightfoot (5) present the following result of the derivation of Poisseuille's Law for Newtonian fluids flowing inside tubes:

$$Q = \frac{\pi(\Delta P)}{8\mu L} r^4 \quad (1)$$

Van Waser et al. (34) showed that this relationship could be applied to capillary viscometer measurements provided that the following substitutions were made: $\Delta P = \rho gh$ and $Q = V/t$. In addition, if the effect of kinetic energy is considered in the derivation of Poisseuille's Law, the form of Equation (1) becomes:

$$\mu = \frac{\pi r^4 \rho g h t}{8LV} - \frac{\xi PV}{8\mu L t} \quad (2)$$

Noting that the kinematic viscosity η , is equal to μ/ρ , the following expression may be obtained:

$$\eta = \frac{\pi r^4 g h t}{8LV} - \frac{\xi V}{8\pi L t} \quad (3)$$

Equation (3) can be written as:

$$\eta = K_1 t - \frac{K_2}{t} \quad (4)$$

in which K_1 is characteristic of a given viscometer and K_2 is reported by Cannon, Manning, and Bell (10) and Van Waser (34) to be a function of Reynold's number.

The difficulty in the evaluation of K_2 reported by Johnson, LeTourneau, and Matteson (18) suggests that the best solution to this problem is to design a viscometer to make K_2 as small as possible. The Zeitfuchs style viscometer was found to have a constant K_2 small enough to give a correction for kinetic energy of about 0.03 percent (10). Neglecting this small term, Equation (4) may be written in the following form:

$$\eta = K_1 t \quad \text{or} \quad \eta = Kt \quad (5)$$

Equation (5) served as the basis for the viscosity measurements made during this study. K was determined by measuring the efflux time, t , of fluid of known kinematic viscosity, η . Once K was determined, the kinematic viscosity of a test fluid was found by measuring the efflux time for the test fluid.

Johnson, LeTourneau, and Matteson evaluated the Zeitfuch's capillary viscometer and reported that the crossarm design of the instrument virtually eliminated errors that could be introduced by the difference in surface tension between the calibration and test liquids.

CHAPTER III

EXPERIMENTAL APPARATUS

The apparatus employed was basically the same as constructed by Bennett (4). The reader is referred to his thesis for a more detailed description of the experimental equipment.

The apparatus consisted primarily of the capillary viscometer, the pressure cell, the constant temperature bath, the flow system used to move the test fluid through the capillary tube, and the instrumentation used to measure temperature, pressure, and efflux time of the test fluid. Other equipment used included a refrigeration system, temperature controller, and vacuum pump.

Viscometer

A Zeitfuchs cross-arm capillary viscometer (Figure 1) was used to make kinematic viscosity measurements. Manufactured by the Cannon Instrument Company, the viscometer had a one-piece glass body with a stainless steel metal support (Figure 2) attached with Sauereisen sealing cement. The viscometer consisted of a reservoir, cross-arm, reverse bend capillary tube, measuring bulb, and metal support.

The liquid sample was held in the reservoir at a depth specified by the height of the reverse bend prior to entry into the capillary tube. The liquid sample was transported to the capillary tube via the cross-arm. The capillary tube had a measuring bulb with scribed lines above

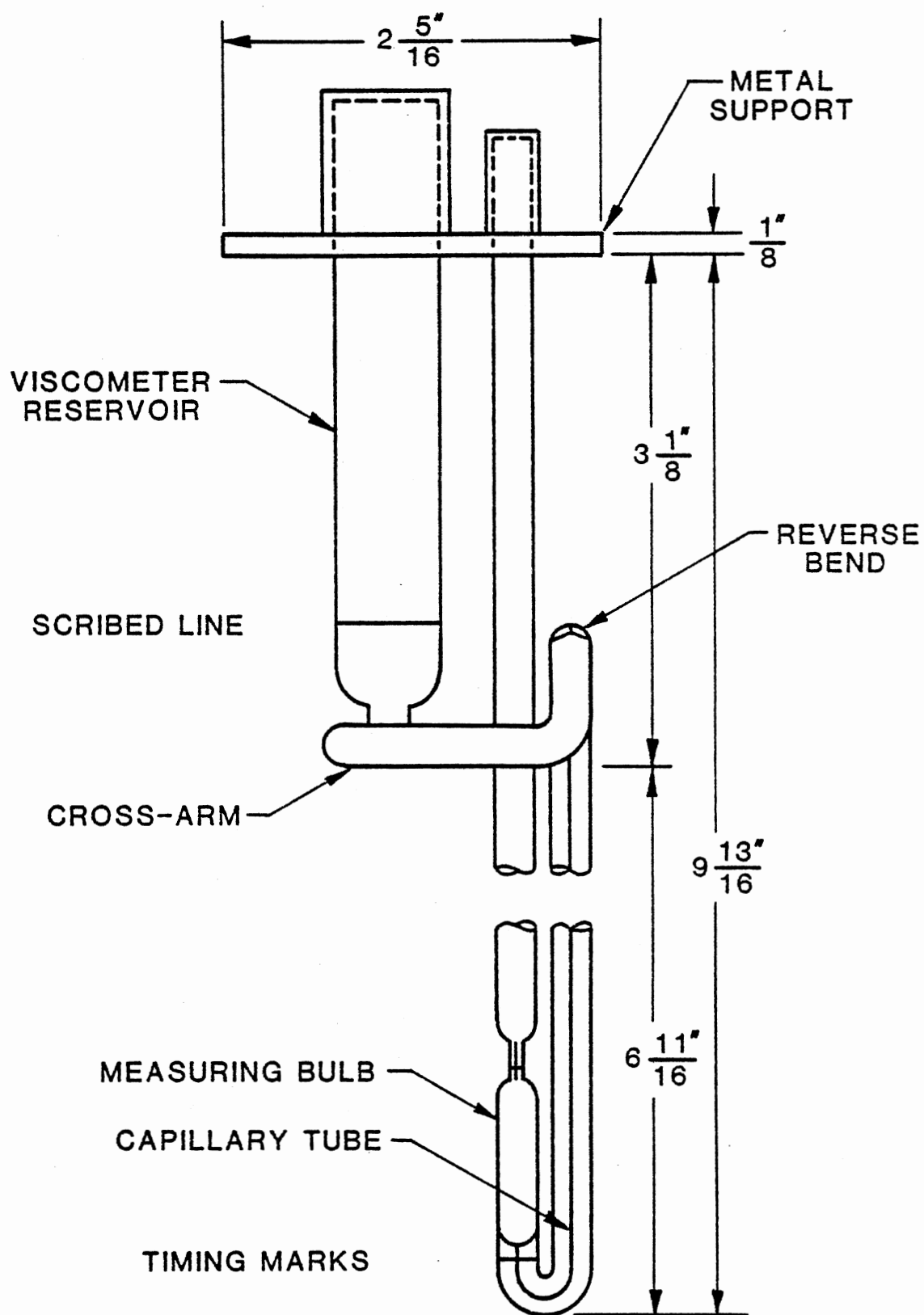
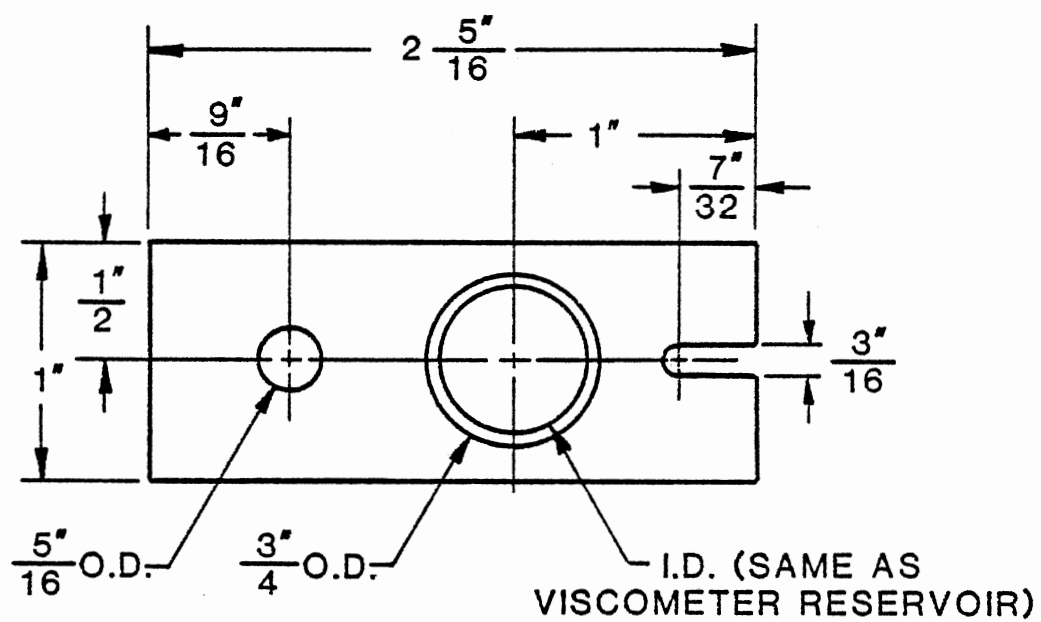


Figure 1. Zeitfuchs Capillary Viscometer



MATERIAL: 304 STAINLESS STEEL

Figure 2. Support for Zeitfuchs Capillary Viscometer

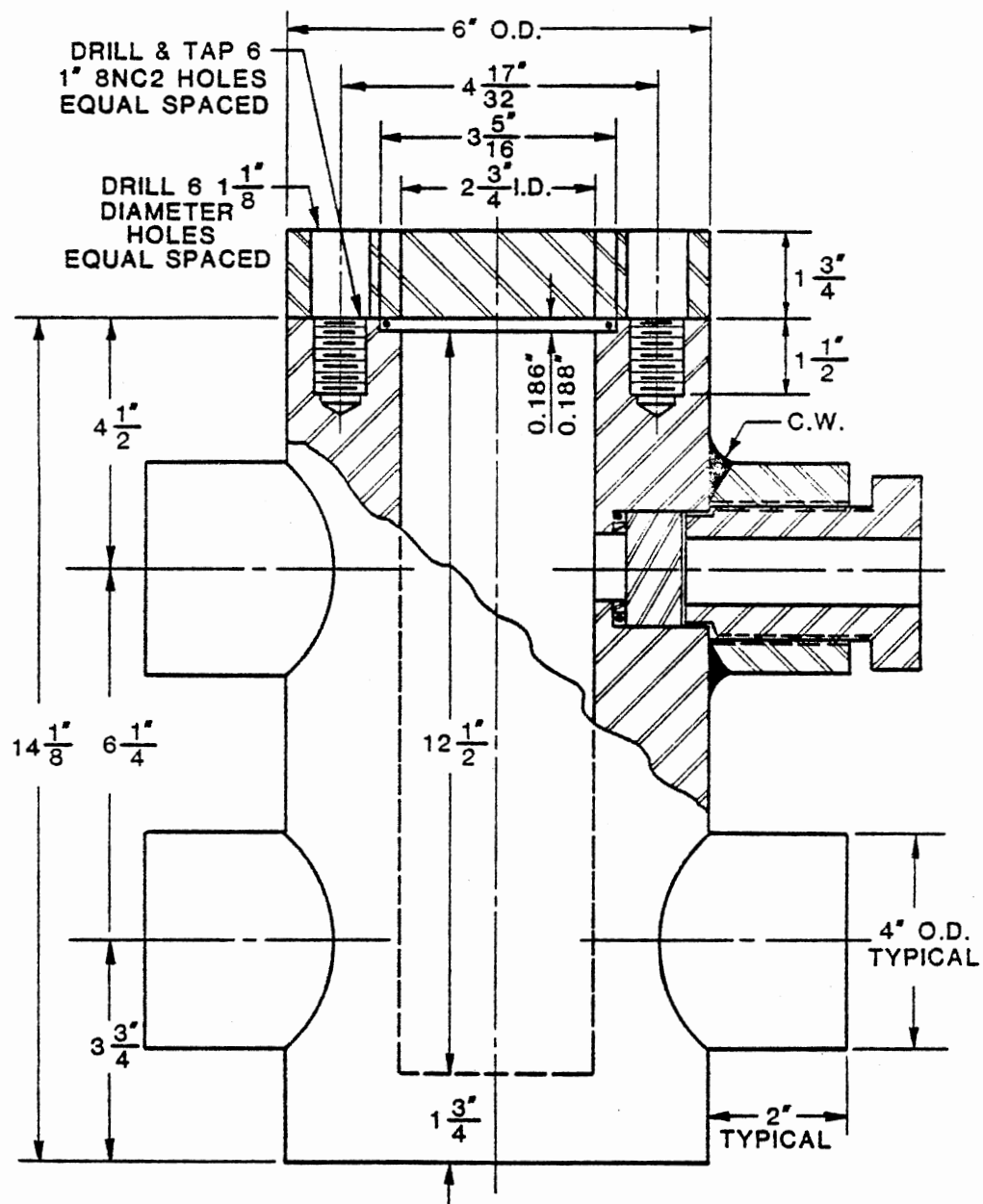
and below the body of the bulb. These scribed lines served as timing marks for obtaining the time necessary for the fluid to fill the bulb. The metal support served as a mounting bracket to hold the viscometer in place within the pressure cell.

Pressure Cell

The pressure cell (Figure 3) contained the viscometer during operation and allowed observation of the viscometer reservoir and measuring bulb. The pressure cell served to maintain the desired pressure on the liquid sample during viscosity measurements.

Observation of the viscometer inside the pressure cell was accomplished through four glass view ports (Figure 4) installed in the sides of the pressure cell. The windows in the observation ports were made of fused quartz. All observations were made through a 14-power cathetometer, as recommended by Bagzis (3), to see the fluid movement within the very fine capillary tube.

The heavy cell body and top were constructed of 304 stainless steel. A tight seal was obtained by the use of teflon O-rings in all view port assemblies and the top of the cell body seal. Table I illustrates the types and sizes of O-rings used in the pressure cell. The cell body and top flange assembly are shown in Figure 5. Eight 5/8-inch diameter bolts secured the top flange to the pressure cell body. McCoy (23) inserted a 1/8-inch stainless steel tube from the top flange into the reservoir of the viscometer. This tube served to fill the viscometer reservoir with test fluid and remove excess sample.



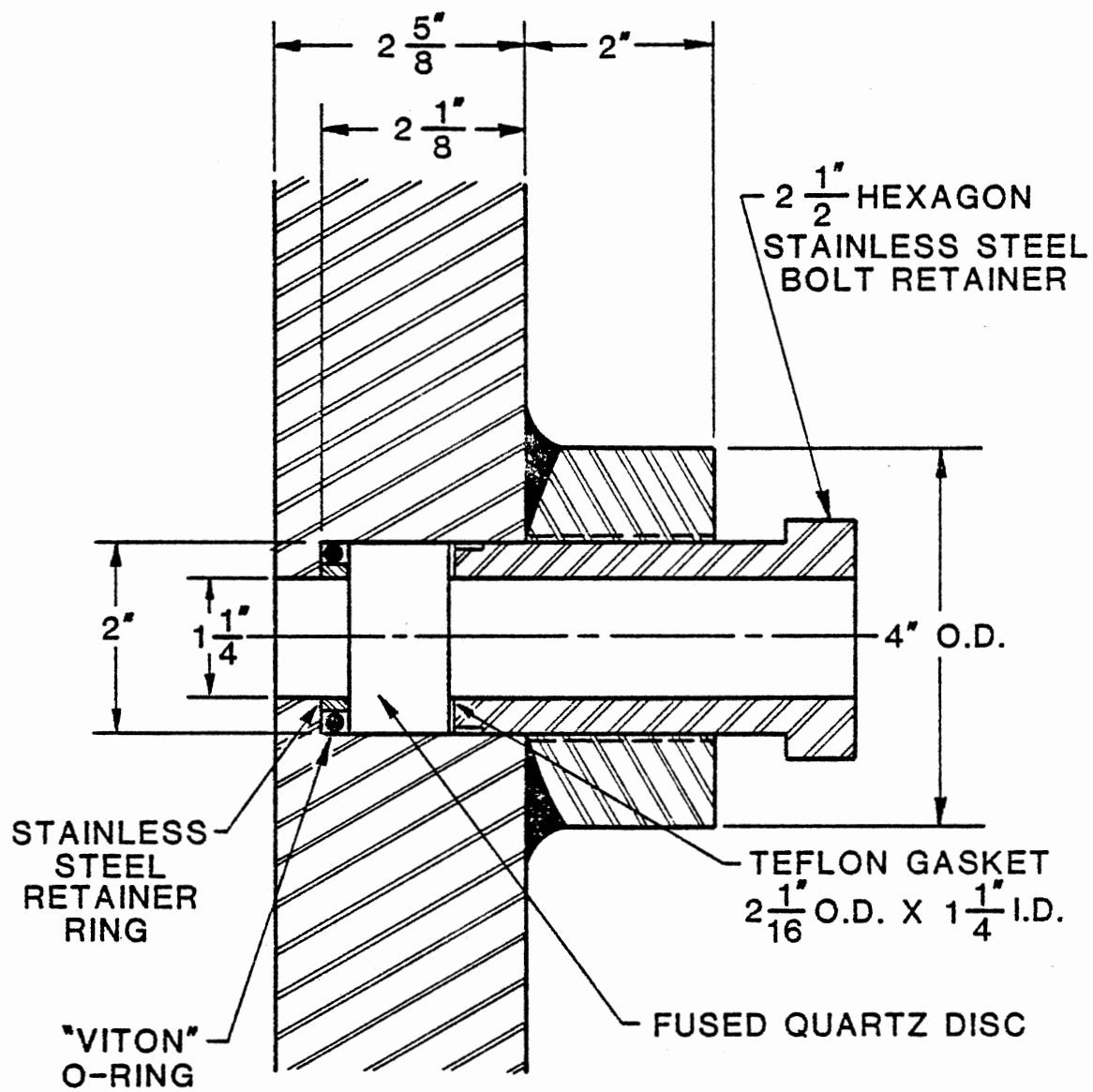


Figure 4. View Port Details

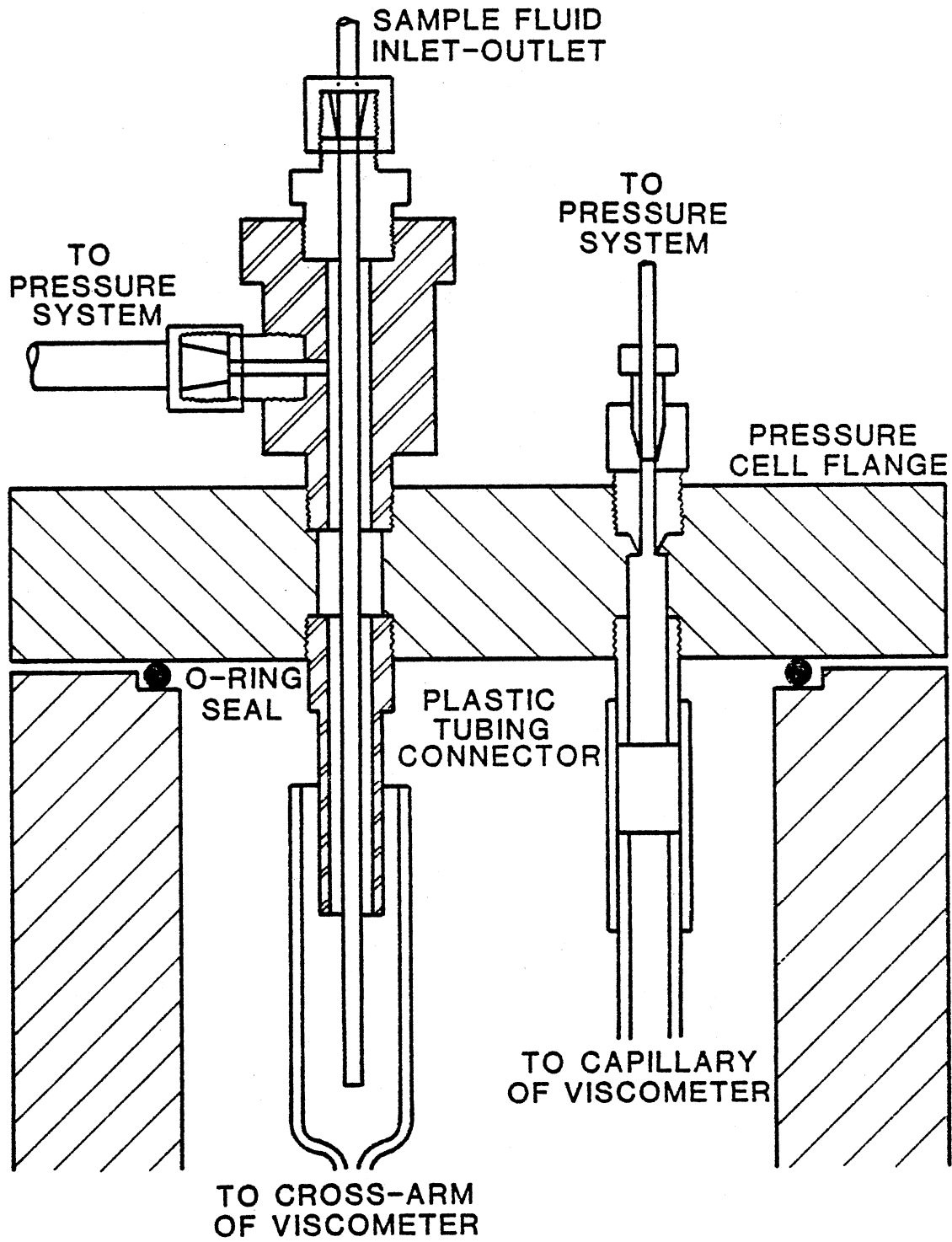


Figure 5. Pressure Cell Top Flange and Viscometer Connections

Temperature Control

A constant temperature bath surrounded the pressure cell. A Fisher proportional temperature controller (Model No. 22, Serial No. 946) was used to control the bath temperature. The controller had a temperature range of 0°C to 250°C with an accuracy of $\pm 0.01^\circ\text{C}$ and a repeatability of $\pm 0.02^\circ\text{C}$. The temperature controller had two controlled electrical outlets, each rated for 750 watts capacity. Two immersion heaters each of 500 watts capacity were used. The bath fluid for ambient and higher temperatures was General Electric Type SF 1154 silicone oil. This fluid had excellent optical characteristics across a wide temperature range. This was very important in order to watch the movement of the test fluid through the viscometer reservoir, capillary, and measuring bulb.

For temperatures below ambient the bath fluid was 1-propanol. An FTS System Inc. Flexo-Cool liquid cooling system (Model No. FC-50-55-P10A, Serial No. FC-1-81-74) was used.

TABLE I
PRESSURE CELL SEALS

Seal Type	Inside Diameter (in.)	Outside Diameter (in.)	Compound	Seal Co. Int.* Part No.
O-Ring	2.975	3.395	Teflon	2-337
O-Ring	1.600	2.020	Teflon	2-326
Washer	---	---	Teflon	---

*Seal Company Interprise, Oklahoma City, Oklahoma.

Pressure Distribution System

The pressure distribution system (Figure 6) served to introduce the test gas into the pressure cell, control the liquid level in the viscometer, and measure the total pressure exerted on the liquid sample.

The in-line pressure controller and the Ruska screw pump were used to move the liquid sample through the cross-arm to the capillary tube of the viscometer. The in-line pressure controller was used mainly at low pressures while the Ruska screw pump was used at high pressures.

Removal of the air from all portions of the pressure distribution system was accomplished by a Duo-Seal vacuum pump prior to filling the pressure cell and viscometer with sample liquid.

Two pressure gauges were used to measure the system pressure, an HTL Bourdon tube gauge graduated in 5 psi increments from 0 psig to 2000 psig was used for pressure measurements. For vacuum and low pressure, an Ascroft-American Duragauge graduated in 1/2 psi increments from 0 psig to 100 psig and in 1/2 inch of mercury increments from 0 to 30 inches of mercury vacuum was used.

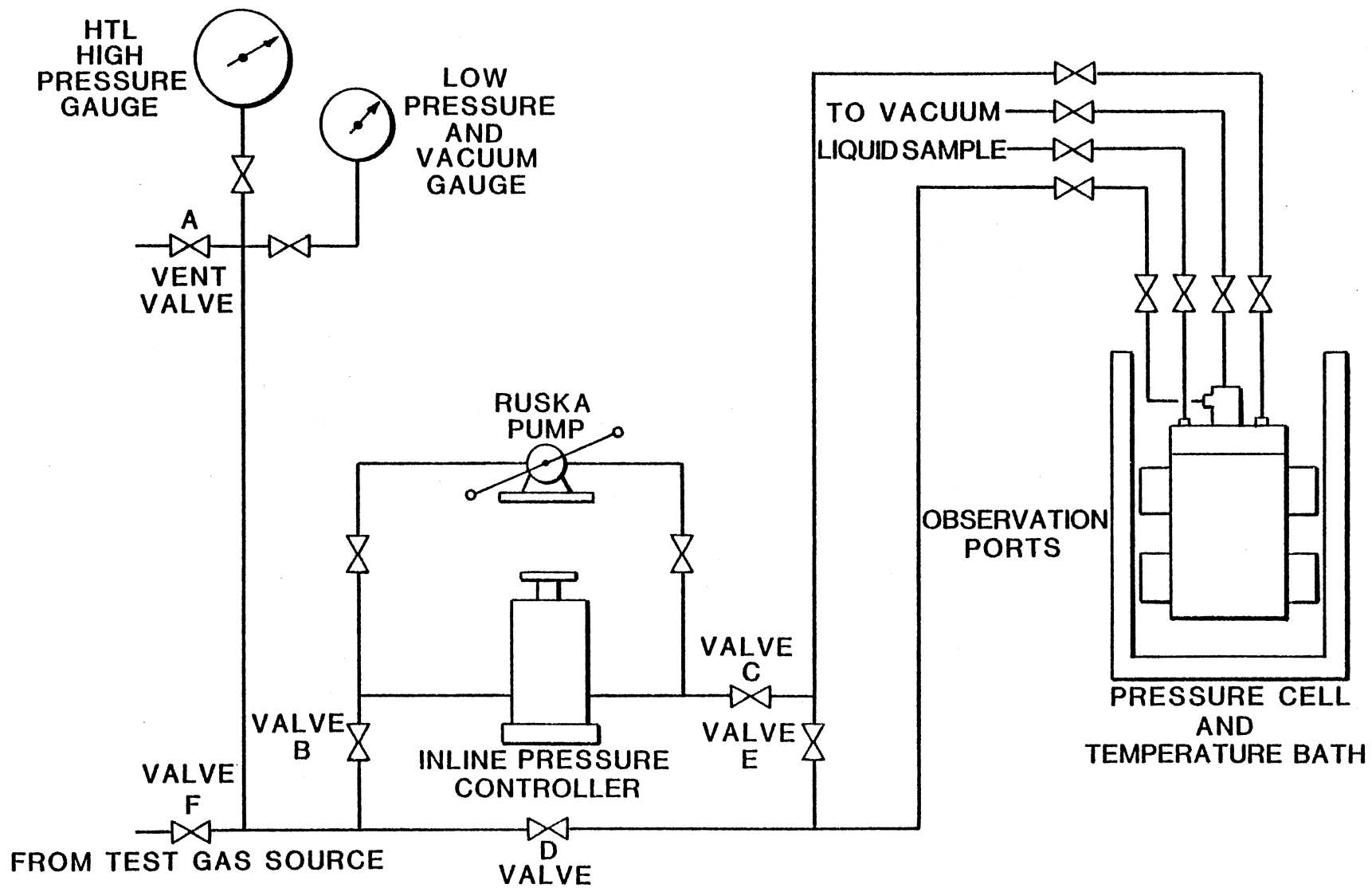


Figure 6. Schematic Diagram of the Kinematic Viscometer Experimental Apparatus

CHAPTER IV

EXPERIMENTAL PROCEDURES

Calibration of Viscometer

The cleanliness of the viscometer was very important, and traces of any previous compounds made it very difficult to obtain reproducible results. Before use, the viscometer was thoroughly cleaned by three alternating washings with absolute ethanol, distilled water, and acetone; then it was purged with dry air until there were no traces of liquid. The viscometer reservoir was filled with degased distilled water to the prescribed level and secured to the pressure cell top flange. After the top flange was bolted to the pressure cell body and external connections were made, the cell was jacked up and lowered into the constant temperature bath and the bath was filled with bath fluid. The final external connections were made and a slight suction was applied to the capillary outlet tube to start the calibration fluid flowing down the capillary tube. After the flow had been initiated, it would continue due to siphon action. Two coupled electric timers were used to measure the time necessary to fill the measuring bulb from the lower to the upper timing marks. The electric timers were manufactured by the Standard Electric Time Company. One timer has divisions of 1/100 of a second with a total measurable time of 60 seconds. The other timer had divisions of 1/100 minutes with a total measurable time of one hour. After a measurement was completed, a slight pressure was applied to the capillary outlet tube to

reverse flow. When the calibration fluid had completely returned to the viscometer reservoir, the measurement process was repeated several times until consecutive bulb fill times agreed within a fraction of a second.

The first measurement was conducted with a dry capillary and was not recorded. Subsequent measurements were made with the capillary tube wetted from previous measurements. Bennett (4) made an extensive study using a wetted Zeitfuchs capillary viscometer and found that the wetted capillary measurements were reproducible. To ensure that this operator was making the correct measurements with as true an accuracy as the equipment allowed, several runs were made at atmospheric pressure for n-heptane and were compared with API Project 44 Data (36). The results in Table II show agreement within less than 1 percent for all data points taken on n-heptane.

TABLE II
RELIABILITY OF EXPERIMENTAL DATA FOR N-HEPTANE
AT ATMOSPHERIC PRESSURE

Temperature °F	Experimental Kinematic Viscosity CS	API Project 44 Kinematic Viscosity (36) CS	Percent Error
77.41	0.5859	0.5811	-0.80
98.46	0.5204	0.5255	0.90
124.08	0.4658	0.4696	0.38

The viscometer measuring bulb and reservoir were illuminated by a 15 watt mercury lamp. Observations of the bulb were made through a 14-power cathetometer. All calibration measurements were conducted under conditions identical to experimental techniques. The flow times and viscometer constants are tabulated in Appendix B. The distilled water density was taken from Abul-Hamayel (37), and viscosity data were obtained from Kestin, Sokolov, and Wakeham (20).

Preparation of Experimental Apparatus

After dismantling the equipment, the viscometer was thoroughly cleaned. The viscometer was attached to the pressure cell top flange. The top flange was bolted securely to the pressure cell body and the external piping connections were made. The flow system was checked for leaks with compressed nitrogen gas. After the system was found to be pressure tight, the pressure cells and flow system were vented, the vacuum pump was started, and the system was evacuated to approximately 28 inches of mercury. The system was pressurized to approximately 30 psig with test gas. The procedures of evacuating and pressurizing with test gas were repeated three times. These procedures were necessary to remove all traces of air from the system.

After the sweeping procedure had been completed, the pressure cell was evacuated to approximately 28 inches of mercury. A graduated flask of test liquid was attached to the pressure cell top flange. The appropriate valves were opened and the test liquid was allowed to fill the viscometer reservoir. The pressure cell was then pressurized slowly with the test gas until the desired pressure was reached. The pressure cell was isolated from the flow system by closing all valves leading

from the top flange. The appropriate pipe connections were unscrewed and the pressure cell was jacked up and lowered into the constant temperature bath. Bath fluid was added until the cell was immersed.

The pipes leading out of the top flange were reconnected into the pressure flow system. Prior to opening the valves leading to the cell, the sweeping procedures were performed on the pressure flow lines. The temperature controller was set to the desired temperature and the pressure cell was allowed to stand until the desired temperature was reached. The system was then allowed to attain equilibrium.

Operation

To start a kinematic viscosity measurement, all system valves were closed except valves C and D (Figure 6). The Ruska screw pump or the in-line pressure controller was used to decrease the pressure slightly on the capillary exit tube, causing the test fluid to flow into the capillary tube. After flow had been initiated valve C was closed, and valve E was opened to equalize the pressure across the ends of the viscometer. The electric timers were turned on when the flowing fluid reached the lower timing mark on the viscometer measuring bulb, and the timers were turned off when the fluid reached the upper timing mark, and the time was recorded. At the end of the measurement, valve E was closed and valve C was opened. The pressure on the outlet tube was increased slightly by the use of the Ruska screw pump or the in-line pressure controller, which caused the test fluid to return to the viscometer reservoir. Measurements were repeated until successive flow times remained consistent. When the flow times remained constant for several measurements, equilibrium was assumed. Table III is included here as an

example. The pressure could then be changed and a new series of measurements taken. After completing an isotherm, the temperature was raised, time was allowed for equilibrium to be reached, and a new isotherm was started.

TABLE III
ASSURANCE OF REACHING EQUILIBRIUM BETWEEN NORMAL-
HEPTANE AND CARBON DIOXIDE--AS AN EXAMPLE

Time (p.m.)	Run No.	Temperature (m.v.)	Pressure (psig)	Flow Time (min:sec)
1:30	1	4.840	310	3:05.67
	2	4.840	310	3:28.00
	3	4.840	310	3:22.24
	4	4.841	310	3:45.55
	5	4.841	310	3:12.50
3:30	1	4.840	310	3:45.37
	2	4.840	310	4:18.12
	3	4.840	310	4:06.42
	4	4.840	310	4:07.14
	5	4.841	310	4:11.35
6:20	1	4.840	310	4:11.99
	2	4.840	310	4:07.13
	3	4.840	310	4:09.30*
	4	4.841	310	4:10.30*
	5	4.842	310	4:10.00*
	6	4.840	310	4:10.26

*Equilibrium assumed.

After completing the required measurements, the bath fluid was drained and the pressure cell was depressured and removed from the bath. The apparatus could then be dismantled, cleaned, and recharged for another series of measurements.

Materials Tested

The materials tested, their purities and suppliers are listed in Table IV.

TABLE IV
TEST MATERIAL SPECIFICATION

Material	Supplier	Grade	Min. Purity (Mol Percent)
N-Heptane	Phillips Petroleum Co.	Pure	99.00
Cyclohexane	Phillips Petroleum Co.	Pure	99.00
Benzene	Phillips Petroleum Co.	Pure	99.00
Hydrogen	Linde Specialty Gases	Commercial	99.95
Nitrogen	Matheson Gas Product	Matheson	99.99
Methane	Phillips Petroleum Co.	Pure	99.00
Carbon Dioxide	Sooner Supplies, Inc.	Pure	99.50

CHAPTER V

RESULTS AND DISCUSSION

Results

The kinematic viscosities of n-heptane, cyclohexane, and benzene were measured under several gas pressures. Gases used were carbon dioxide, nitrogen, and hydrogen.

Table V contains experimental kinematic viscosities of n-heptane under carbon dioxide gas pressures ranging from 310 to 700 psig and temperatures from 71.87° to 215.3°F for each pressure. Figure 7 is a plot of the kinematic viscosity as a function of the reciprocal of the absolute temperature for each pressure. The saturated liquid densities for n-heptane/carbon dioxide gas mixtures were calculated using the GPA K&H computer program (35). Liquid compositions were obtained via the BWR equation of state because it predicted the experimental compositions more accurately, and the density was then calculated using the OSU/GPA method. The absolute viscosities were calculated using these densities and the experimental kinematic viscosities. Densities and absolute viscosities are shown in Table V.

Kinematic viscosities and absolute viscosities for the n-heptane/carbon dioxide system decreased with increasing carbon dioxide gas pressure. The effect of gas pressure on viscosity decreases as the temperature increases, as shown in Figure 7.

TABLE V
 EXPERIMENTAL AND CALCULATED VISCOSITY OF NORMAL-HEPTANE
 UNDER CARBON DIOXIDE GAS PRESSURES

Pressure psig	Temperature °F	Kinematic Viscosity cs	Density* g/cc	Absolute Viscosity cp
310	71.87	0.4640	0.7192	0.3337
	126.91	0.3975	0.6883	0.2736
	169.65	0.3473	0.6527	0.2267
	215.30	0.2960	0.6234	0.1845
510	71.87	0.3801	0.7468	0.2838
	126.91	0.3535	0.6945	0.2455
	169.65	0.3060	0.6625	0.2027
	215.30	0.2745	0.6301	0.1730
700	71.87	0.3420	0.7617	0.2605
	126.91	0.3154	0.7098	0.2239
	169.65	0.2850	0.6723	0.1916
	215.30	0.2590	0.6367	0.1649

*Calculated by OSU/GPA method using SHBWR equation of state to determine liquid composition.

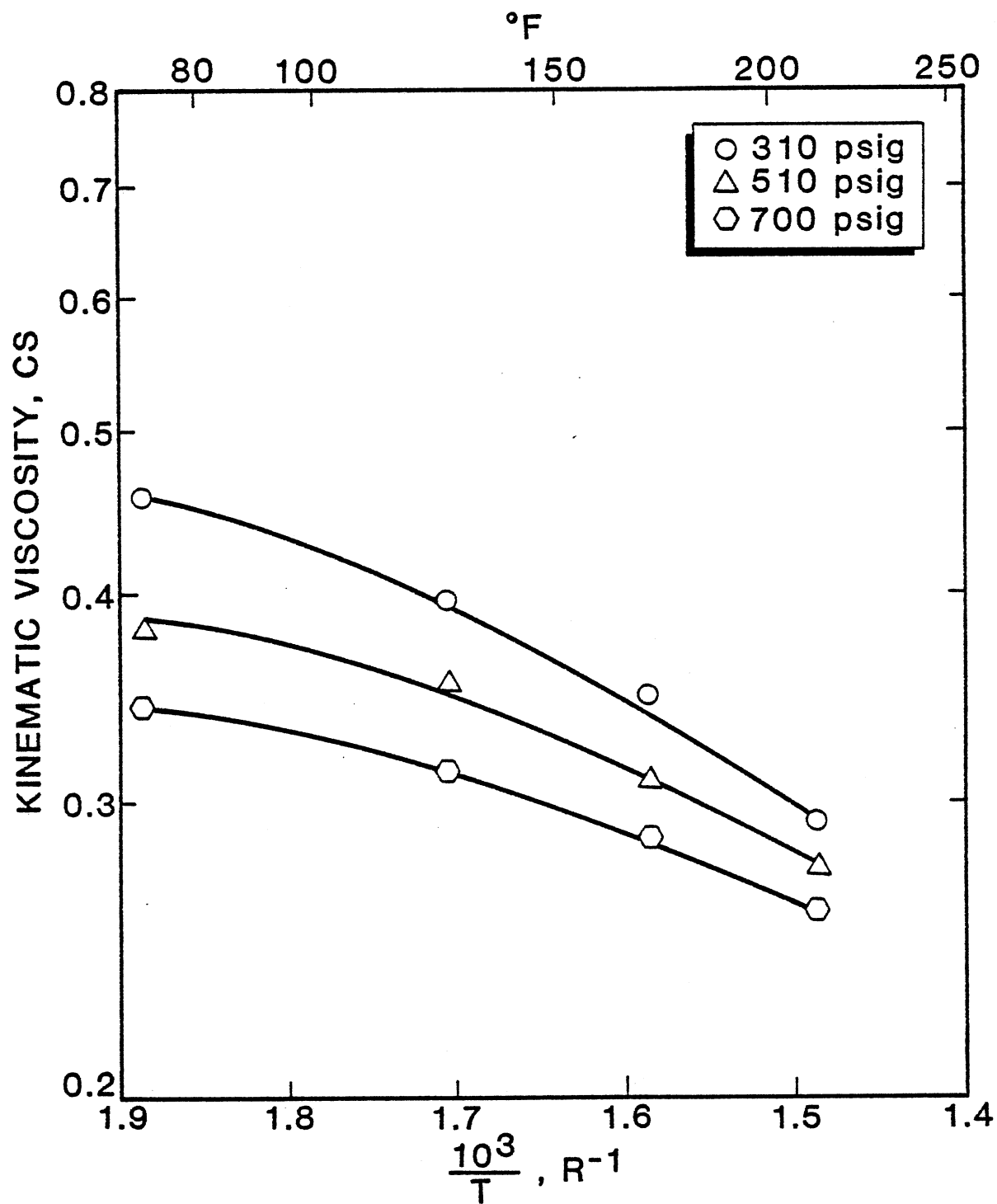


Figure 7. Kinematic Viscosity of n-Heptane Under Carbon Dioxide Pressure

The effect of hydrogen gas pressure on the kinematic viscosity of n-heptane is shown in Table VI. Kinematic viscosity tends to increase slightly with increase in hydrogen gas pressure, as shown in Figure 8. The kinematic viscosity of n-heptane under nitrogen gas pressure is shown in Table VII. The results are plotted in Figure 9 as isotherms. As in the case of hydrogen gas pressure, saturated liquid densities for the n-heptane/hydrogen and the n-heptane/nitrogen systems were calculated along with the absolute viscosities. The results are reported in Tables VI and VII, respectively. Hydrogen gas and nitrogen gas pressures affected the absolute viscosity of n-heptane in the same manner as they did the kinematic viscosity.

The kinematic viscosity of cyclohexane under carbon dioxide gas pressure is shown in Table VIII. The results are plotted in Figure 10 as a function of pressure for each temperature. The kinematic viscosity of the cyclohexane-carbon dioxide system decreases with increase in carbon dioxide gas pressure. The effect of carbon dioxide gas pressure on viscosity tends to decrease as the pressure increases.

The effect of the pressure of hydrogen and nitrogen gases on the kinematic viscosity of cyclohexane are shown in Figures 11 and 12, respectively. Kinematic viscosity increased slightly as the pressure increased in both cases. Saturated liquid densities and absolute viscosities were calculated and are presented in Tables IX and X.

The kinematic viscosity of benzene under carbon dioxide gas pressure was measured. The results, along with the calculated densities and absolute viscosities, are shown in Table XI. The effect of carbon dioxide gas pressure on the viscosity of benzene is shown in Figure 13. The viscosity of benzene decreases with the increase in carbon dioxide gas

TABLE VI
 EXPERIMENTAL AND CALCULATED VISCOSITY OF NORMAL-HEPTANE
 UNDER HYDROGEN GAS PRESSURES

Pressure psig	Temperature °F	Kinematic Viscosity cs	Density* g/cc	Absolute Viscosity cp
200	73.77	0.6053	0.6844	0.4143
	114.84	0.4936	0.6641	0.3278
	148.20	0.4588	0.6468	0.2968
	186.23	0.3795	0.6263	0.2377
400	73.77	0.6128	0.6822	0.4181
	114.84	0.5130	0.6615	0.3394
	148.20	0.4652	0.6441	0.2996
	186.20	0.3901	0.6233	0.2431
600	73.77	0.6200	0.6799	0.4216
	114.84	0.5253	0.6589	0.3462
	148.20	0.4783	0.6414	0.3068
	186.23	0.4100	0.6202	0.2543

*Calculated via OSU/GPA using SRK to obtain liquid compositions.

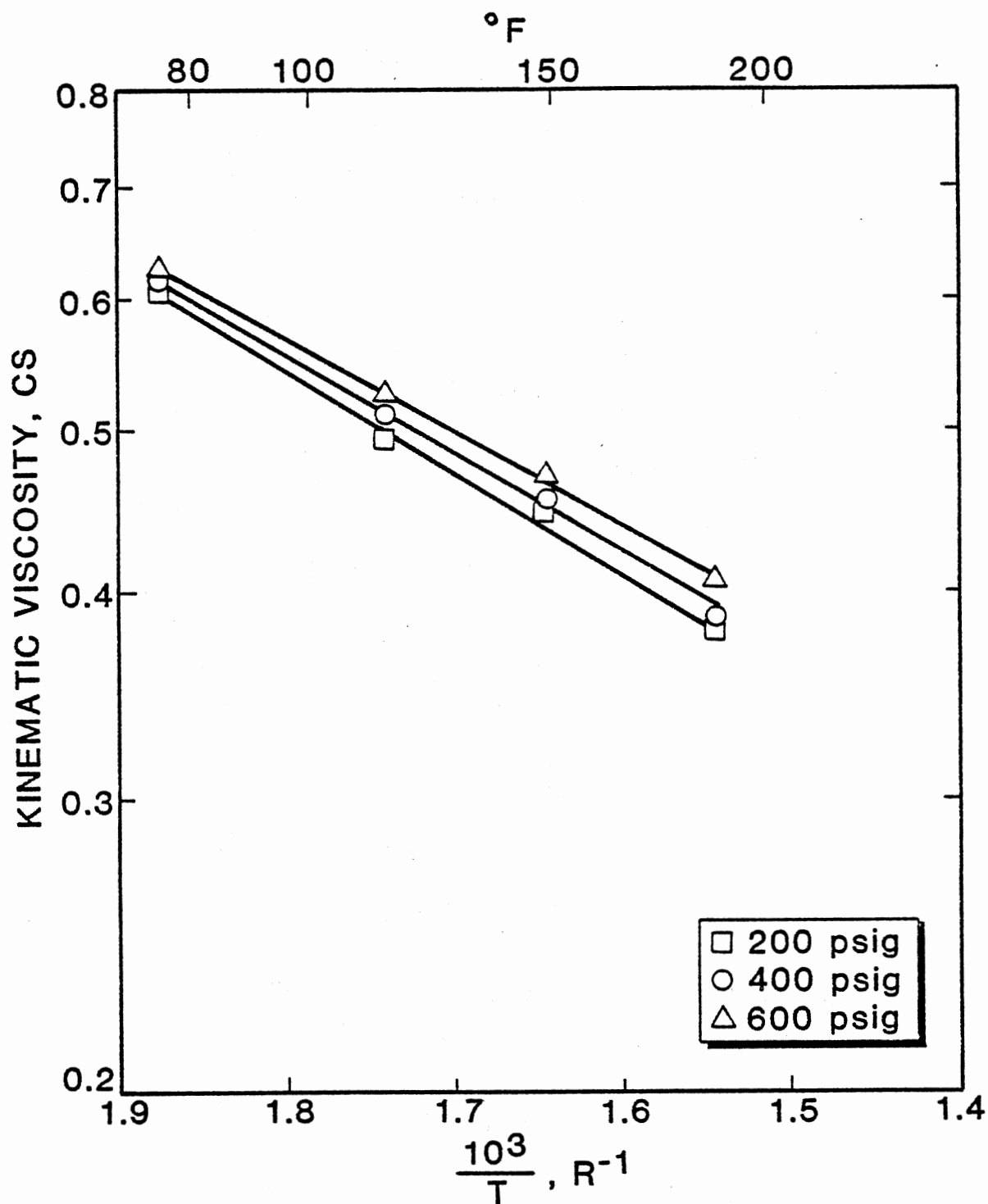


Figure 8. Kinematic Viscosity of n-Heptane Under Hydrogen Gas Pressure

TABLE VII
 EXPERIMENTAL AND CALCULATED VISCOSITY OF NORMAL-HEPTANE
 UNDER NITROGEN GAS PRESSURES

Temperature °F	Pressure psig	Kinematic Viscosity cs	Density* g/cc	Absolute Viscosity cp
97.02	200	0.5300	0.6739	0.3572
	400	0.5572	0.6723	0.3746
	600	0.5655	0.6707	0.3793
	800	0.5785	0.6692	0.3872
	1000	0.5821	0.6676	0.3886
166.90	200	0.3786	0.6380	0.2416
	400	0.4093	0.6361	0.2603
	600	0.4164	0.6342	0.2641
	800	0.4200	0.6322	0.2655
	1000	0.4224	0.6305	0.2663

*Calculated by OSU/GPA method using SRK equation of state for liquid composition.

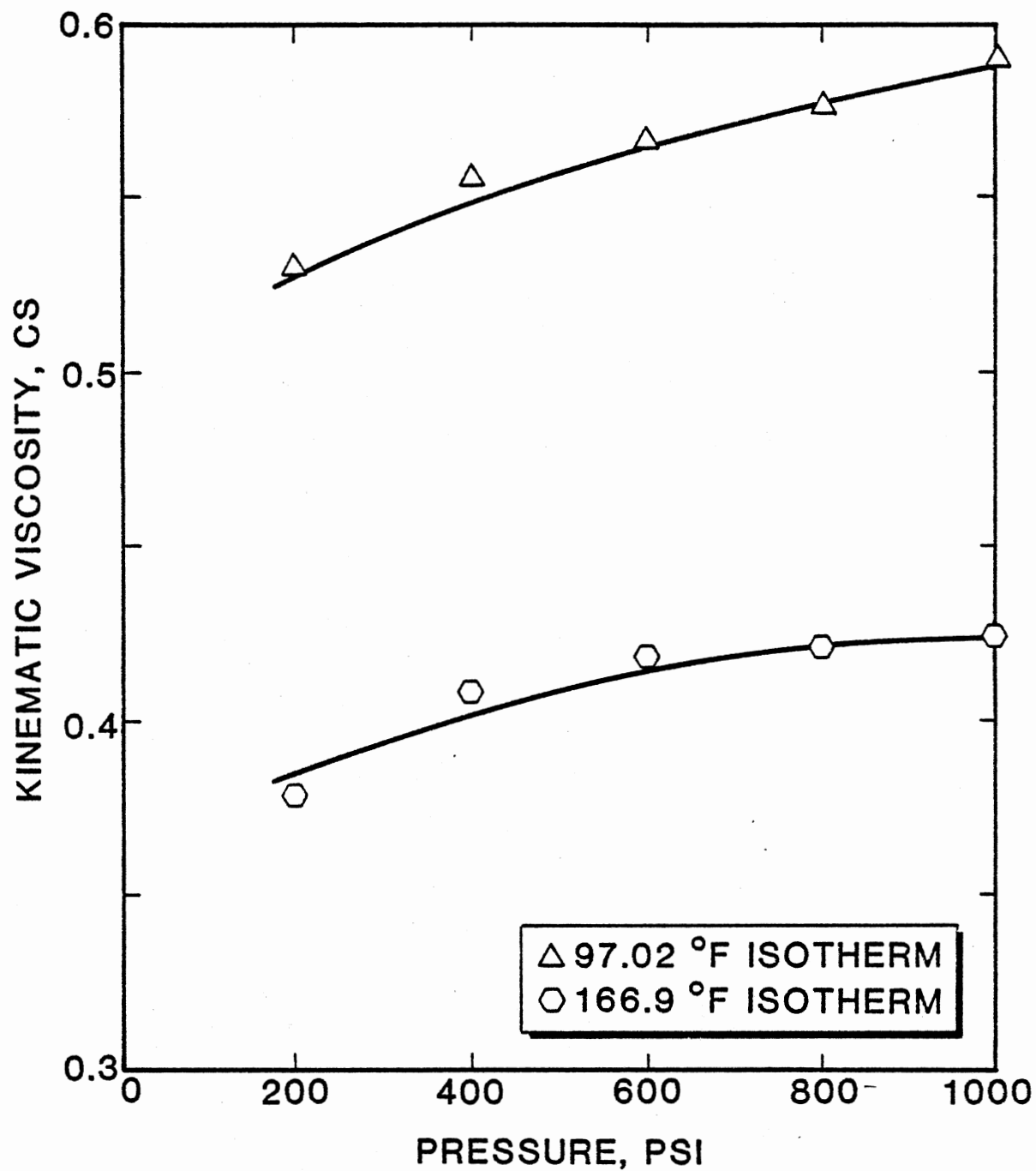


Figure 9. Kinematic Viscosity of n-Heptane Under Nitrogen Gas Pressure

TABLE VIII

EXPERIMENTAL AND CALCULATED VISCOSITY OF CYCLOHEXANE
UNDER CARBON DIOXIDE GAS PRESSURES

Pressure psig	Temperature °F	Kinematic Viscosity cs	Density* g/cc	Absolute Viscosity cp
210	88.13	0.8183	0.8357	0.6838
	116.10	0.7075	0.8063	0.5705
	157.91	0.5700	0.7703	0.4391
	174.20	0.5143	0.7575	0.3896
410	88.13	0.6423	0.8667	0.5567
	116.10	0.6143	0.8393	0.5156
	157.91	0.5227	0.7913	0.4136
	174.20	0.4858	0.7753	0.3766
600	88.13	0.5200	0.8674	0.4510
	116.10	0.5089	0.8472	0.4311
	157.91	0.4962	0.8104	0.4021
	174.20	0.4284	0.7932	0.3398

*Calculated by OSU/GPA method using SHBWR equation of state for liquid compositions.

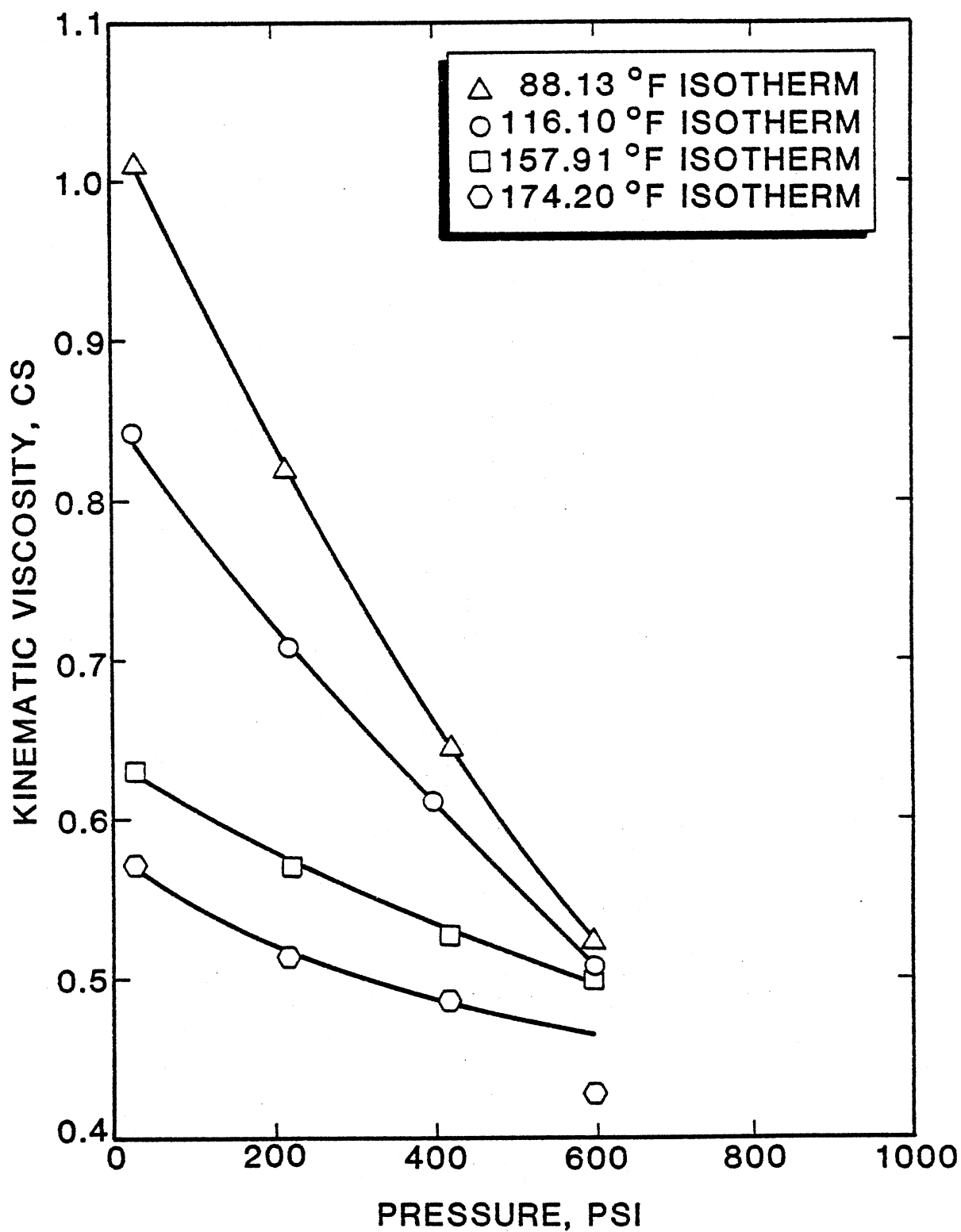


Figure 10. Kinematic Viscosity of Cyclohexane Under Carbon Dioxide Gas Pressure

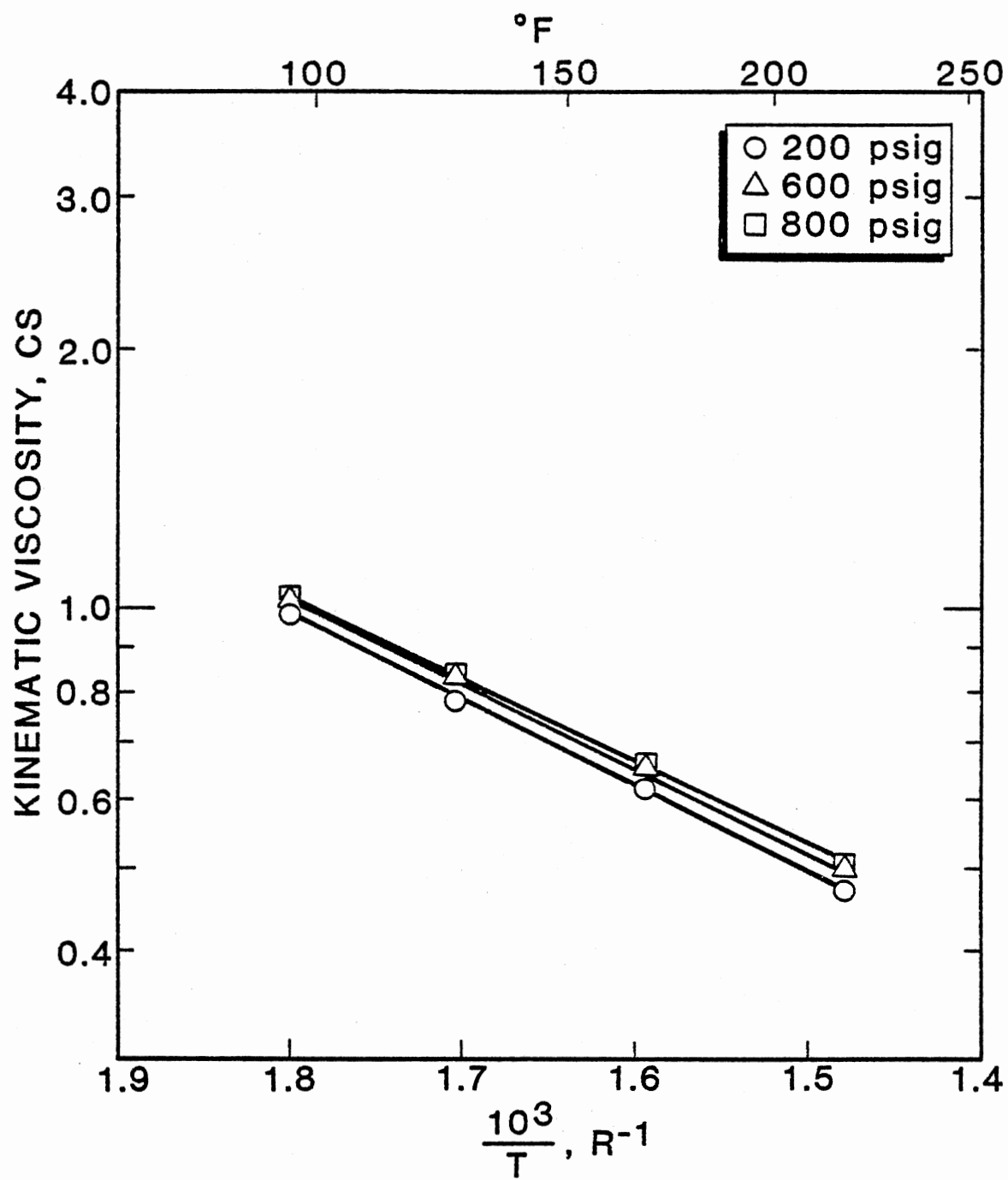


Figure 11. Kinematic Viscosity of Cyclohexane Under Hydrogen Gas Pressure

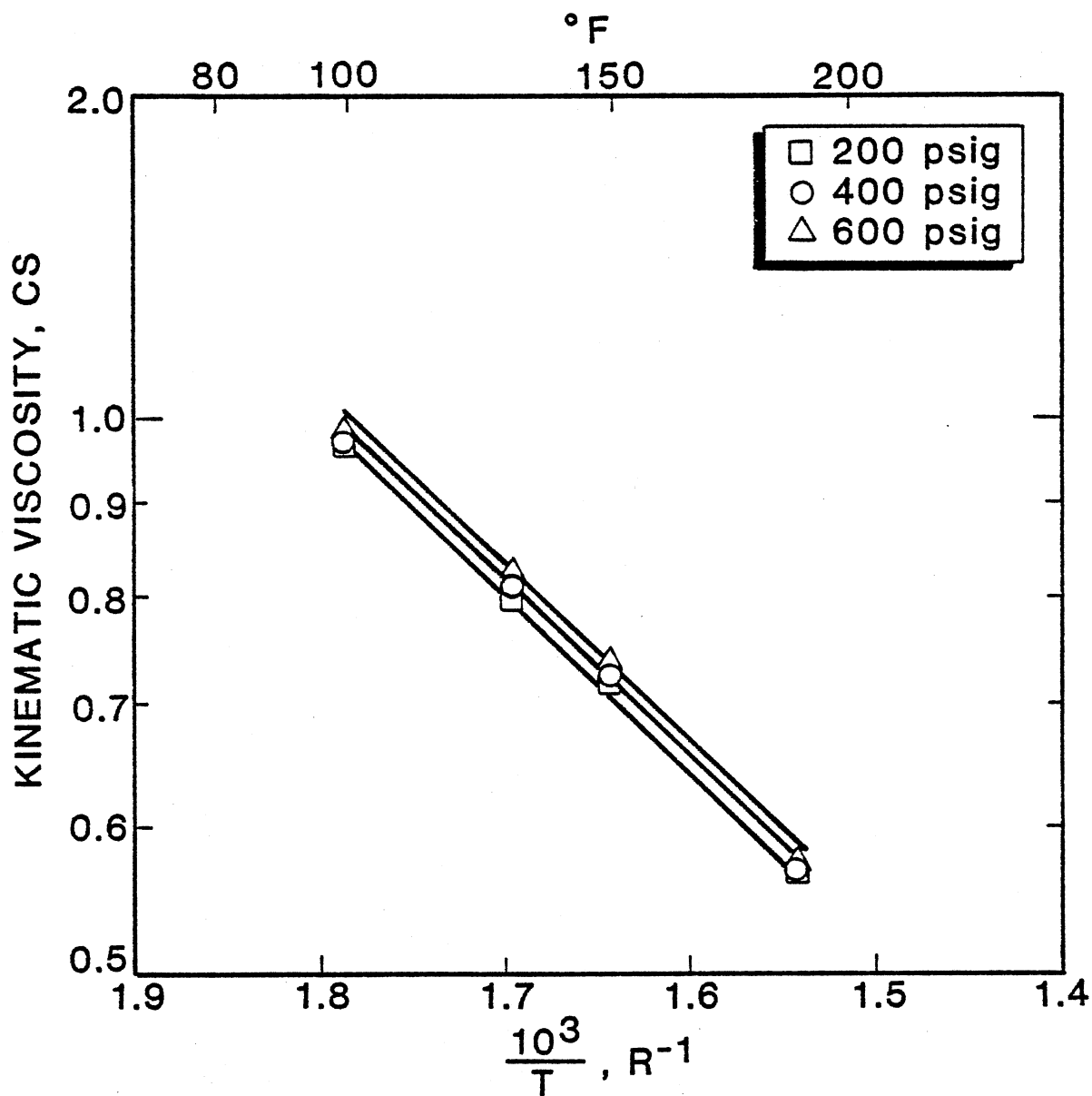


Figure 12. Kinematic Viscosity of Cyclohexane Under Nitrogen Gas Pressure

TABLE IX
 EXPERIMENTAL AND CALCULATED VISCOSITY OF CYCLO-HEXANE
 UNDER HYDROGEN GAS PRESSURES

Pressure psig	Temperature °F	Kinematic Viscosity cs	Density* g/cc	Absolute Viscosity cp
200	99.13	0.9650	0.7760	0.7514
	129.20	0.7950	0.7620	0.6058
	148.07	0.7135	0.7512	0.5360
	186.40	0.5625	0.7290	0.4100
400	99.13	0.9723	0.7764	0.7490
	129.07	0.8142	0.7600	0.6188
	148.07	0.7300	0.7580	0.5533
	186.40	0.5684	0.7266	0.4130
600	99.13	0.9750	0.7750	0.7556
	129.07	0.8265	0.7580	0.6265
	148.07	0.7398	0.7471	0.5527
	186.40	0.5720	0.7242	0.4142

*Calculated by OSU/GPA method using SRK equation of state for liquid composition.

TABLE X
 EXPERIMENTAL AND CALCULATED VISCOSITY OF CYCLOHEXANE
 UNDER NITROGEN GAS PRESSURES

Pressure psig	Temperature °F	Kinematic Viscosity cs	Density* g/cc	Absolute Viscosity cp
200	96.17	0.9852	0.7807	0.7692
	125.06	0.7824	0.7650	0.5986
	166.48	0.6253	0.7415	0.4636
	214.90	0.4715	0.7126	0.3360
400	96.17	0.9957	0.7799	0.7766
	125.06	0.7980	0.7637	0.6095
	166.48	0.6188	0.7400	0.4579
	214.90	0.4755	0.7109	0.3380
600	96.17	1.0073	0.7783	0.7840
	125.06	0.8210	0.7622	0.6258
	166.48	0.6288	0.7386	0.4644
	214.90	0.4762	0.7093	0.3378
800	96.17	1.0040	0.7772	0.7803
	125.06	0.8210	0.7612	0.6249
	166.48	0.6332	0.7371	0.4668
	214.90	0.4784	0.7077	0.3386

*Calculated via OSU/GPA method using SRK equation of state to obtain liquid compositions.

TABLE XI

EXPERIMENTAL AND CALCULATED VISCOSITY OF BENZENE
UNDER CARBON DIOXIDE GAS PRESSURES

Pressure psig	Temperature °F	Kinematic Viscosity cs	Density* g/cc	Absolute Viscosity cp
200	68.29	0.5647	0.8892	0.5021
	105.60	0.4637	0.8578	0.3977
	140.81	0.4183	0.8315	0.3478
	184.51	0.3554	0.8023	0.2791
400	68.29	0.4306	0.9295	0.4002
	105.60	0.4228	0.8821	0.3730
	140.81	0.3926	0.8491	0.3334
	184.51	0.3412	0.8143	0.2779
600	68.29	0.2817	0.9500	0.2676
	105.60	0.3563	0.9109	0.3246
	140.81	0.3417	0.8687	0.2968
	184.51	0.3156	0.8281	0.2614

*Calculated by OSU/GPA method using Grayson-Steed equation of state for liquid composition.

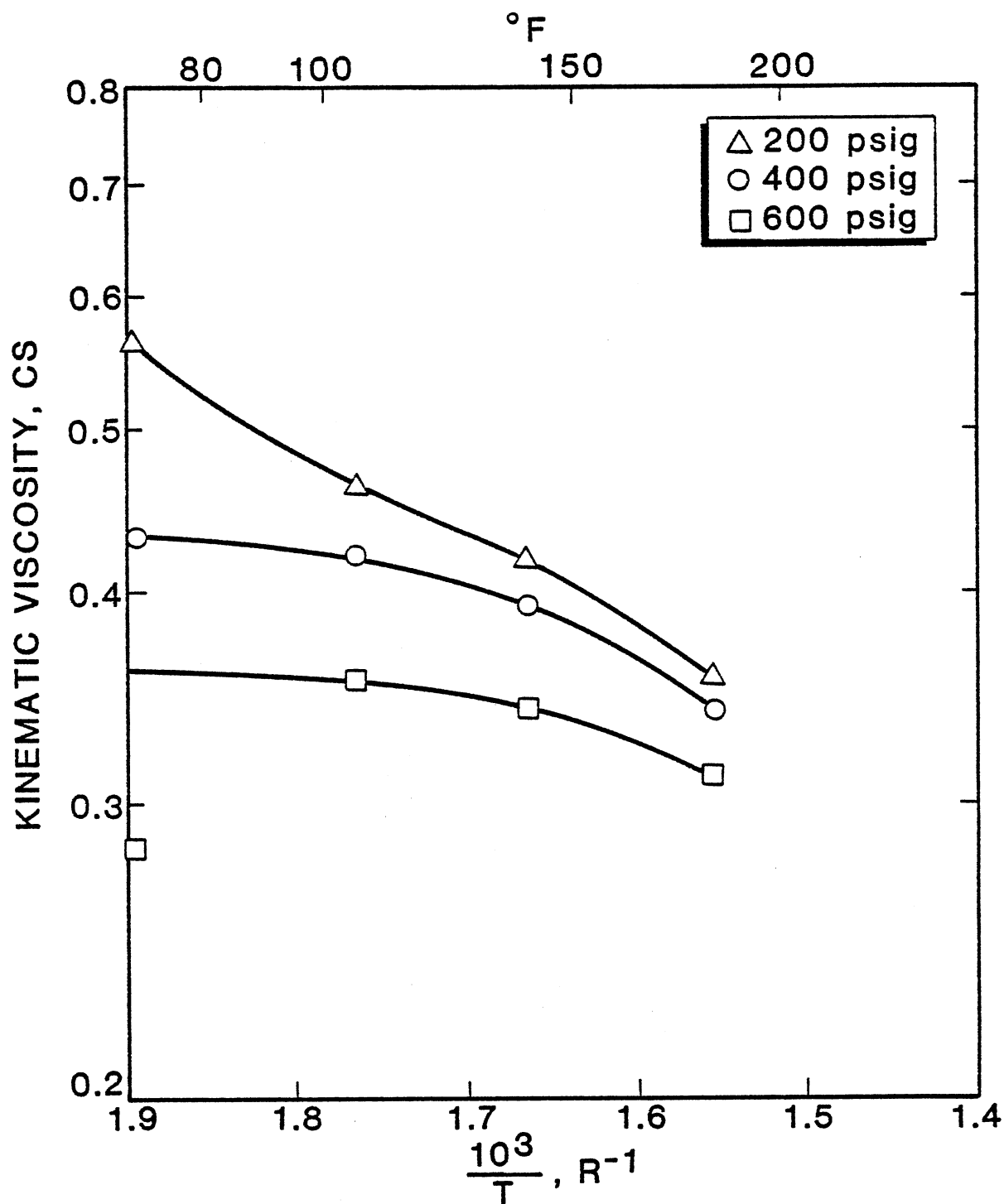


Figure 13. Kinematic Viscosity of Benzene Under Carbon Dioxide Gas Pressure

pressure. These results are similar to the ones previously obtained for n-heptane and cyclohexane under carbon dioxide gas pressures.

The effect of hydrogen and nitrogen gas pressures on the kinematic viscosity of benzene was measured. The results are shown in Tables XII and XIII, respectively. Figure 14 shows the effect of hydrogen gas pressure on the kinematic viscosity of benzene. The effect of nitrogen gas pressure on the kinematic viscosity of benzene is shown in Figure 15.

Discussion

The absolute viscosity of pure benzene and n-heptane has been reported by Vargaftik (27) to increase linearly with pressure. For 50 atmosphere pressure, which is the maximum pressure for this study, the viscosity increased by 6 percent for pure benzene and about 5 percent for pure n-heptane. The effect of pressure on the pure viscosity of pure cyclohexane is expected to follow the same trends.

The effect of solubility of carbon dioxide gas on the viscosity of crude oil was discussed by Simon and Graue (31), and more recently by Miller and Jones (24). Their results indicate that absolute viscosity decreases with increase in solubility of carbon dioxide gas.

In this study the kinematic viscosities of n-heptane, cyclohexane, and benzene were measured under three pressures of carbon dioxide gas at several temperatures. Because in all cases the solubility of carbon dioxide gas increases with increasing pressure and decreases with temperature (19, 25, 33), and the density of the hydrocarbon-carbon dioxide mixtures increases with increase in carbon dioxide gas pressure (see Tables V, VII, and XI), the absolute viscosities decreased as the pressure of carbon dioxide gas was increased. The decrease in absolute

TABLE XII
 EXPERIMENTAL AND CALCULATED VISCOSITY OF BENZENE
 UNDER HYDROGEN GAS PRESSURES

Pressure psig	Temperature °F	Kinematic Viscosity cs	Density* g/cc	Absolute Viscosity cp
200	77.57	0.7099	0.8514	0.6044
	99.77	0.6101	0.8392	0.5120
	135.48	0.4864	0.8193	0.3985
	163.14	0.4385	0.8033	0.3522
400	77.57	0.7271	0.8502	0.6182
	99.77	0.6113	0.8381	0.5132
	135.48	0.5043	0.8179	0.4125
	163.14	0.4389	0.8017	0.3519
600	77.57	0.7289	0.8491	0.6189
	99.77	0.6225	0.8368	0.5210
	135.48	0.5036	0.8164	0.4111
	163.14	0.4411	0.8001	0.3529

*Calculated by GPA/OSU method using SRK equation of state for liquid composition.

TABLE XIII
 EXPERIMENTAL AND CALCULATED VISCOSITY OF BENZENE
 UNDER NITROGEN GAS PRESSURES

Pressure psig	Temperature °F	Kinematic Viscosity cs	Density* g/cc	Absolute Viscosity cp
200	77.82	0.6902	0.8517	0.5878
	125.64	0.5128	0.8254	0.4233
	149.79	0.4442	0.8116	0.3605
	184.94	0.3783	0.7911	0.2993
400	77.82	0.7059	0.8509	0.6006
	125.64	0.5278	0.8246	0.4355
	149.79	0.4594	0.8107	0.3724
	184.94	0.3862	0.7900	0.3051
600	77.82	0.7164	0.8502	0.6091
	125.64	0.5339	0.8238	0.4398
	149.79	0.4671	0.8097	0.3782
	184.94	0.3949	0.7890	0.3116

*Calculated via OSU/GPA method using SRK to determine liquid compositions.

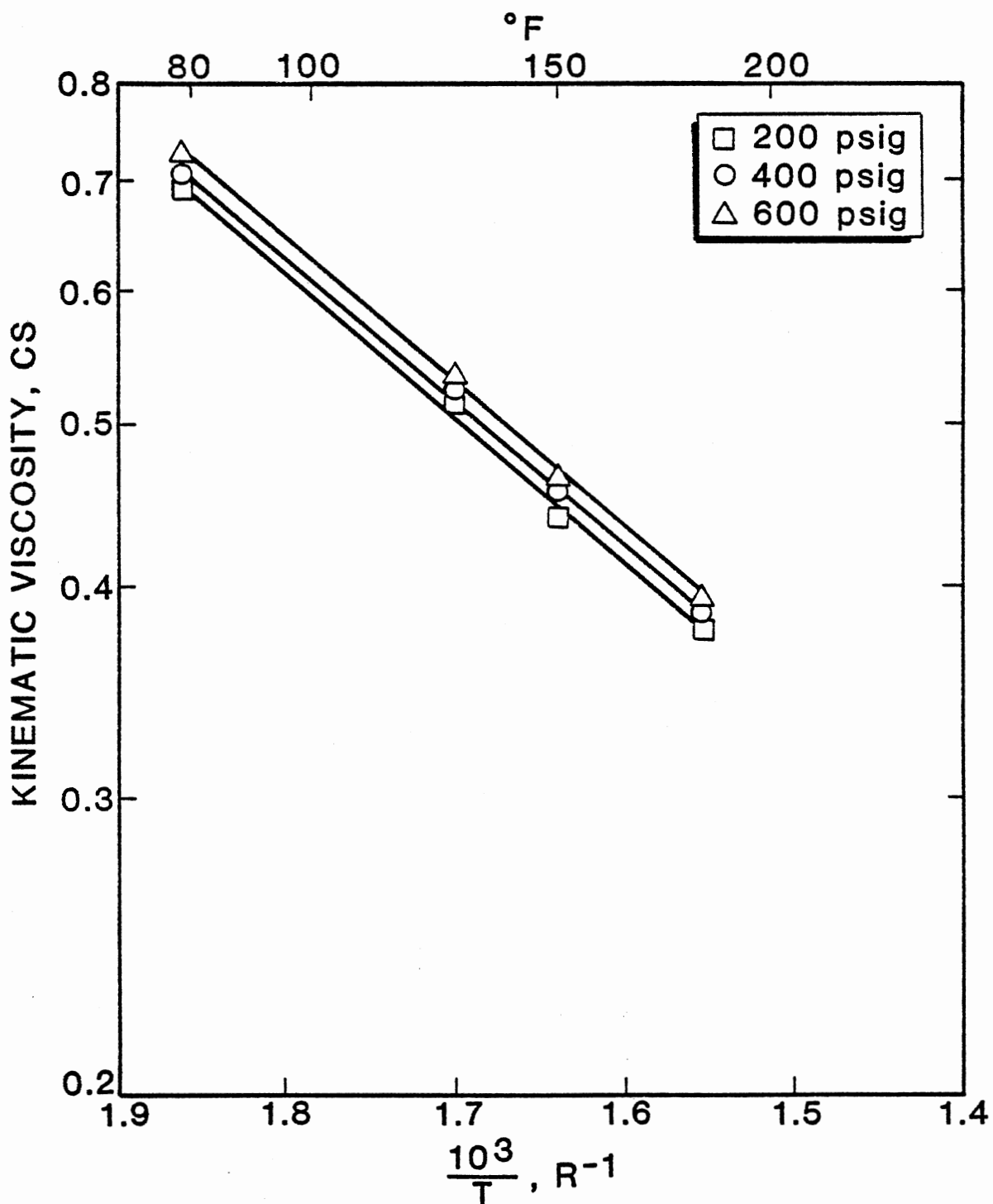


Figure 14. Kinematic Viscosity of Benzene Under Nitrogen Gas Pressure

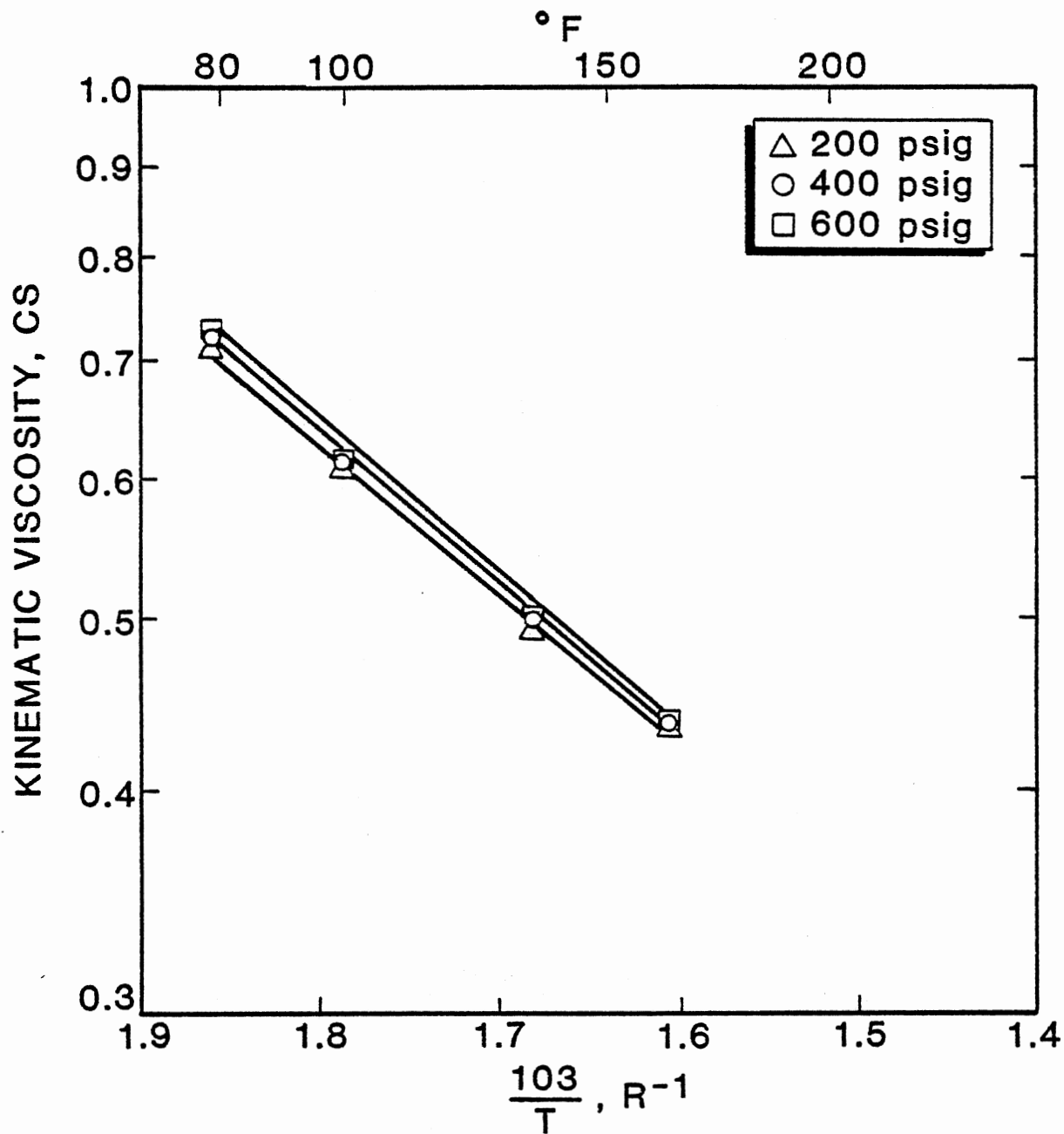


Figure 15. Kinematic Viscosity of Benzene Under Hydrogen Gas Pressure

viscosity ranged from a low of about 9 percent at 169.65°F and 310 psig to a high of 36 percent at 71.87°F and 700 psig for n-heptane, as shown in Table XVII. For cyclohexane the decrease in absolute viscosity ranged from 5 percent to 44 percent (see Table XVIII) and for benzene it ranged from 7 percent to 58 percent (see Table XXI).

The solubility of hydrogen gas or nitrogen gas in n-heptane, cyclohexane, or benzene is reported to be very small (19, 25, 33). The change in absolute viscosity due to solubility effects will be small compared to the pressure effect. Since increasing the pressure will increase the absolute viscosity while increasing the solubility will decrease the absolute viscosity, one will anticipate that the effect of hydrogen gas solubility or nitrogen gas solubility on the absolute viscosity will not offset the pressure effect. The comparison between the pure liquid absolute viscosity at atmospheric pressure and the absolute viscosity of liquid under hydrogen or nitrogen gas pressure for n-heptane, cyclohexane and benzene are shown in Appendix A.

Correlation of Viscosity Data

Absolute liquid viscosity may be correlated using a form of the Andrade equation (39):

$$\mu_L = f(P) e^{B_1/T} \quad (6)$$

where

μ_L = absolute liquid viscosity, CP;

$f(P)$ = a function of pressure;

B_1 = assumed to be constant; and

T = absolute temperature, R.

In our study $f(P)$ was found to be linear in pressure and has the form:

$$f(P) = B_2 P + B_3 \quad (7)$$

where P is pressure in psia, and B_2, B_3 are constants. The relationship between pressure and solubility, at constant temperature, was also found to be linear:

$$P = f'(T) x_2 + B_4 \quad (8)$$

where

P = pressure, psia;

$f'(T)$ = function of temperature; and

x_2 = solubility of gas in liquid, mole percent.

In our study, $f'(T)$ was found to be linear in temperature and takes the form:

$$f'(T) = B_5 T + B_6 \quad (9)$$

where B_5, B_6 are constants, and T is absolute temperature, R. Substituting Equation (9) into Equation (8):

$$P = B_5 x_2 T + B_6 x_2 + B_4 \quad (10)$$

Substituting Equation (10) into Equation (7) and combining constants:

$$f(P) = B_7 x_2 T + B_8 x_2 + B_3 \quad (11)$$

Substituting Equation (11) into Equation (6):

$$\mu_L = (A_1 + A_2 x_2 T + A_3 x_2) e^{A_4/T} \quad (12)$$

where $A_1, A_2, A_3,$ and A_4 are constants.

A computer program that uses a nonlinear least square fitting (37) was used to fit our data, for each compound, to Equation (12). A summary of the results of the fit is indicated in Table XIV. As indicated in Table XIV, Equation (12) was found to fit the effect of gas solubility on the liquid viscosity with a maximum average absolute deviation of 3.8 percent.

TABLE XIV
 SUMMARY OF RESULTS OF NONLINEAR LEAST
 SQUARE FITTING USING MARQ

Compound	Total No. of Points in Data	AAPD*	Maximum Positive Percent Deviation	Maximum Negative Percent Deviation
n-Heptane	31	3.800	+9.870	-10.08
Benzene	35	2.187	2.914	- 9.70
Cyclohexane	33	1.909	5.380	- 2.93

*AAPD (absolute average percent deviation) is defined as:

$$\text{AAPD} = \frac{1}{N} \sum_{i=1}^n \left| \left(\frac{\text{fitted viscosity} - \text{exp. viscosity}}{\text{exp. viscosity}} \right) \times 100 \right|$$

where N is total number of points.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

This study was performed to determine the effect of gas pressures on the viscosity of selected hydrocarbons. The following conclusions were apparent:

1. For all the hydrocarbons studied, the viscosity decreased with increase in carbon dioxide pressure. The decrease in viscosity was higher at low temperatures than it was at high temperatures. This was due to the decrease in solubility of carbon dioxide gas as temperature was increased.

2. Viscosity increased slightly with increase in hydrogen or nitrogen gas pressure. The increase was lower than otherwise expected from the pure pressure effect.

3. Absolute viscosities were found to fit the following equation reasonably well:

$$\mu_L = (A_1 + A_2 X_2 T + A_3 X) \text{ EXP } \left(\frac{A_4}{T} \right)$$

Since the range of pressure used in this study was moderate, higher pressures are recommended for future investigations, especially for hydrogen and nitrogen gases.

BIBLIOGRAPHY

- (1) Agaev, N. A., and I. F. Golubev, *Gazovaya Prom*, 8(5), 45 (1963).
- (2) Babb, S. E., Jr., and G. J. Scott, *J. Chem. Phys.*, 40(12), 3666 (1964).
- (3) Bagzis, L. D., M.S. thesis, Oklahoma State University, Stillwater, Oklahoma, May, 1971.
- (4) Bennett, S. E., M.S. thesis, Oklahoma State University, Stillwater, Oklahoma, August, 1969.
- (5) Bird, R. B., W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, New York: John Wiley and Sons, 1963.
- (6) Bitcher, L. B., Jr., and D. L. Katz, *Ind. Eng. Chem.*, 35, 754 (1943).
- (7) Brazier, D. W., and G. R. Freeman, *Can. J. Chem.*, 47 (6), 893 (1969).
- (8) Bridgman, P. W., *Proc. Natl. Acad. Sci.*, 11, 603 (1925).
- (9) Bridgman, P. W., *Proc. Am. Acad. Arts. Sci.*, 61, 57 (1926).
- (10) Cannon, M. R., R. E. Manning, and J. D. Bell, *Anal. Chem.*, 32, 355 (1960).
- (11) Chandhuri, P. M., R. A. Stager, and G. P. Mathur, J., *Chem. Eng. Data*, 13(1), 9 (1968).
- (12) Dow, R. B., *J. Appl. Phys.*, 6, 71 (1935).
- (13) Eakin, B. E., K. E. Starling, J. P. Dolan, and R. T. Ellington, *J. Chem. Eng. Data*, 7(1), 33 (1962).
- (14) Gambel, W. R., *Chem. Eng.*, Feb. 9, 1959, pp. 123-126.
- (15) Greist, E. M., W. Webb, and R. W. Schiessler, *J. Chem. Phys.*, 29 (4), 711 (1958).
- (16) Hubbard, R. M., and G. G. Brown, *Ind. Eng. Chem.*, 35, 1276 (1943).
- (17) Isakova, N. P., and L. A. Oshueva, *Zh. Fiz. Khim.*, 40(5), 1130 (1966).

- (18) Johnson, J. F., R. L. LeTourneau, and R. Matteson, *Anal. Chem.* 24, 1505 (1952).
- (19) Kalra, H., H. Kubota, D. B. Robinson, and H. J. Ng, *Am. Chem. Soc.*, 23(4), 317 (1978).
- (20) Kestin, J. K., M. Sokolov, and W. A. Wakeham, *J. Phys. Chem. Ref. Data*, 7(3), 941 (1978).
- (21) Lewis, J. R., *J. Am. Chem. Soc.*, 47, 626 (1925).
- (22) MacLeod, D. B., *Trans. Faraday Soc.*, 19, 6 (1923).
- (23) McCoy, D. D., Ph.D. thesis, Oklahoma State University, Stillwater, Oklahoma, May, 1976.
- (24) Miller, S. J., and R. A. Jones, *Oil and Gas J.*, July 6, 1981.
- (25) Ohgaki, K., and T. Katayama, *J. Chem. Eng. Data*, 21(1), 53 (1976).
- (26) Reamer, H. H., G. Cokelet, and B. H. Sage, *Anal. Chem.*, 31, 1422 (1959).
- (27) Rudolf, H. E., M.S. thesis, Oklahoma State University, Stillwater, Oklahoma, 1973.
- (28) Sage, B. H., and W. N. Lacey, *Ind. Eng. Chem.*, 30, 829 (1938).
- (29) Sage, B. H., and W. N. Lacey, *Trans. Am. Inst. Mining Met. Eng.*, 127, 118 (1938).
- (30) Sage, B. H., W. D. Yale, and W. N. Lacey, *Ind. Eng. Chem.*, 31, 223 (1939).
- (31) Simon, R., and D. J. Graue, *J. Petr. Tech.*, Jan. 1965.
- (32) Smith, A. S., and G. G. Brown, *Ind. Eng. Chem.*, 35(6), 705 (1943).
- (33) Thompson, E. T., and W. C. Edmister, *A.I.Ch.E. J.*, 11 (3), 457 (1965).
- (34) Van Wazer, J. R., J. W. Lyons, K. Y. Kim, and R. E. Colwell, *Viscosity and Flow Measurements*, New York: Interscience Publishers, 1963.
- (35) _____, G. P. A. KSH Computer Program, Tulsa, Oklahoma, 74013.
- (36) _____, API Research project 44, Petroleum Research Lab., Carnegie Institute.
- (37) Chandler, J. P., MARQ, A.N.S.I. Standard Fortran, Dept. of Computation Sciences, Oklahoma State University, Stillwater, Oklahoma.

- (38) Abul-Hamayel, M., Ph.D. Dissertation, Oklahoma State University, Stillwater, Oklahoma, 1979.
- (39) Andrade, E. N. Dac, Endeavour 13, 177 (1954).
- (40) Vargaftik, N. B., Tables of the Thermophysical Properties of Liquids, 2nd Ed. New York: John Wiley and Sons, 1975.

APPENDIX A

COMPARISON BETWEEN PURE ABSOLUTE LIQUID VISCOSITY
AND ABSOLUTE LIQUID VISCOSITY
UNDER GAS PRESSURE

TABLE XV
 EFFECT OF NITROGEN GAS PRESSURE ON THE ABSOLUTE
 VISCOSITY OF N-HEPTANE

Temperature °F	Pressure psig	Absolute Pure Viscosity cp	Absolute Viscosity Under Gas Pressure cp	Change cp	%
97.02	200	.3544	.3572	.0028	.79
	400		.3746	.0202	5.69
	600		.3793	.0249	7.02
	800		.3872	.0328	9.25
	1000		.3886	.0342	9.65
116.90	200	.2518	.2526	.0008	.30
	400		.2603	.0085	3.30
	600		.2641	.0123	4.88
	800		.2655	.0137	5.44
	1000		.2663	.0145	5.75

TABLE XVI
 EFFECT OF HYDROGEN GAS PRESSURE ON THE
 ABSOLUTE VISCOSITY OF N-HEPTANE

Pressure psig	Temperature °F	Absolute Pure Viscosity cp	Absolute Viscosity Under Gas Pressure cp	Change cp	%
200	73.77	.4051	.4118	.0067	1.56
	114.84	.3223	.3261	.0038	1.18
	148.20	.2738	.2959	.0221	8.07
	186.23	.2321	.2373	.0052	2.24
400	73.77	.4051	.4135	.0084	2.07
	114.84	.3223	.3367	.0144	4.46
	148.20	.2738	.2979	.0241	8.80
	186.23	.2321	.2423	.0102	4.40
600	73.77	.4051	.4149	.0098	2.42
	114.84	.3223	.3423	.0200	6.20
	148.20	.2738	.3042	.0304	11.10
	186.23	.2321	.2530	.0209	9.00

TABLE XVII

EFFECT OF CARBON DIOXIDE GAS PRESSURE ON THE ABSOLUTE
VISCOSITY OF N-HEPTANE

Pressure psig	Temperature °F	Absolute Pure Viscosity*	Absolute Viscosity Under Gas Pressure	Change cp	%
310	71.87	.4098	.3337	-.0761	-18.57
	126.91	.3032	.2736	-.0296	- 9.76
	169.65	.2488	.2265	-.0223	- 8.96
	215.30	.2071	.1845	-.0226	-10.91
510	71.87	.4098	.2838	-.1260	-30.75
	126.91	.3032	.2455	-.0577	-19.03
	169.65	.2488	.2027	-.0461	-18.52
	215.30	.2071	.1730	-.0341	-16.46
700	71.87	.4098	.2605	-.1493	-36.43
	126.91	.3032	.2239	-.0793	-26.15
	169.65	.2488	.1916	-.0572	-22.99
	215.30	.2071	.1649	-.0377	-18.20

*Viscosities of pre n-heptane at one atmosphere were used as a reference point.

TABLE XVIII
 EFFECT OF CARBON DIOXIDE GAS PRESSURE ON THE ABSOLUTE
 VISCOSITY OF CYCLOHEXANE

Pressure psig	Temperature °F	Viscosity cp	Absolute Viscosity Under Gas Pressure cp	Change cp	%
210	88.13	.8067	.6838	-.1229	-15.23
	116.10	.6353	.5705	-.0648	-10.19
	157.91	.4629	.4391	-.0239	- 5.06
	174.20	.4138	.3896	-.0242	- 5.84
410	88.13	.8067	.5567	-.2500	-30.99
	116.10	.6353	.5156	-.1197	-18.84
	157.91	.4629	.4136	-.0493	-10.65
	174.20	.4138	.3766	-.0372	- 8.98
600	88.13	.8067	.4510	-.3557	-44.09
	116.10	.6353	.4311	-.2042	-32.14
	157.91	.4629	.4021	-.0608	-31.13
	174.20	.4138	.3391	-.0747	-18.05

TABLE XIX
EFFECT OF NITROGEN GAS PRESSURE ON THE ABSOLUTE
VISCOSITY OF CYCLOHEXANE

Pressure psig	Temperature °F	Absolute Pure Viscosity cp	Absolute Viscosity Under Gas Pressure cp	Change cp	%
200	96.17	.7513	.7692	.0179	2.38
	125.06	.5914	.5986	.0072	1.22
	166.48	.4361	.4636	.0276	6.30
	214.90	.3203	.3360	.0157	4.90
400	96.17	.7513	.7766	.0253	3.36
	125.06	.5914	.6095	.0181	3.06
	166.48	.4361	.4579	.0218	4.99
	214.90	.3203	.3380	.0177	5.53
600	96.17	.7513	.7840	.0327	4.35
	125.06	.5914	.6258	.0344	5.82
	166.48	.4361	.4644	.0283	6.49
	214.90	.3203	.3378	.0175	5.46
800	96.17	.7513	.7803	.0290	3.85
	125.06	.5914	.6249	.0335	4.45
	166.48	.4361	.4668	.0307	7.03
	214.90	.3203	.3386	.0183	5.70

TABLE XX

EFFECT OF HYDROGEN GAS PRESSURE ON THE ABSOLUTE
VISCOSITY OF CYCLOHEXANE

Pressure psig	Temperature °F	Pure Absolute Viscosity cp	Absolute Viscosity Under Gas Pressure cp	Change cp	%
200	99.13	.7323	.7414	.0091	1.24
	129.20	.5731	.6058	.0327	5.70
	148.07	.4968	.5360	.0392	7.89
	186.40	.3819	.4100	.0281	7.30
400	99.13	.7323	.7490	.0160	2.28
	129.20	.5731	.6188	.0457	7.97
	148.07	.4968	.5533	.0565	11.37
	186.40	.3819	.4130	.0311	8.14
600	99.13	.7323	.7556	.0233	3.18
	129.20	.5731	.6265	.0534	9.32
	148.07	.4968	.5527	.0559	11.25
	186.40	.3819	.4142	.0323	8.45

TABLE XXI

EFFECT OF CARBON DIOXIDE GAS PRESSURE ON THE ABSOLUTE
VISCOSITY OF BENZENE

Pressure psig	Temperature °F	Pure Absolute Viscosity cp	Absolute Viscosity Under Gas Pressure cp	Change cp	%
200	68.29	.6414	.5021	-.1393	-21.72
	105.60	.4866	.3977	-.0889	-18.26
	140.81	.3869	.3478	-.0391	-10.10
	184.51	.3014	.2791	-.0223	- 7.39
400	68.29	.6414	.4002	-.2412	-37.60
	105.60	.4866	.3730	-.1136	-23.34
	140.81	.3869	.3334	-.0536	-13.83
	184.51	.3014	.2779	-.0235	- 7.79
600	68.29	.6414	.2676	-.3744	-58.37
	105.60	.4866	.3246	-.1620	-33.29
	140.81	.3869	.2968	-.0901	-23.28
	184.51	.3014	.2614	-.0400	-13.27

TABLE XXII
 EFFECT OF HYDROGEN GAS PRESSURE ON THE ABSOLUTE
 VISCOSITY OF BENZENE

Pressure psig	Temperature °F	Pure Absolute Viscosity cp	Absolute Viscosity Under Gas Pressure cp	Change cp	%
200	77.57	.5966	.6044	.0078	1.310
	99.77	.5086	.5120	.0034	0.668
	135.48	.3999	.3985	-.0014	-0.350
	163.14	.3391	.3522	.0131	3.800
400	77.57	.5966	.6182	.0216	3.620
	99.77	.3086	.5132	.0046	0.900
	135.48	.3999	.4125	.0125	3.150
	163.14	.3391	.3519	.0128	3.770
600	77.57	.5966	.6189	.0223	3.730
	99.77	.3086	.5210	.0124	2.430
	135.48	.3999	.4111	.0112	2.800
	163.14	.3391	.3529	.0138	4.060

TABLE XXIII
 EFFECT OF NITROGEN GAS PRESSURE ON THE ABSOLUTE
 VISCOSITY OF BENZENE

Pressure psig	Temperature °F	Pure Absolute Viscosity cp	Absolute Viscosity Under Gas Pressure cp	Change cp	%
200	77.82	.5955	.5878	.0077	1.290
	125.64	.4256	.4233	.0023	0.540
	149.79	.3665	.3605	.0060	1.640
	184.94	.3007	.2993	.0014	0.460
400	77.82	.5955	.6006	+.0051	0.856
	125.64	.4256	.4355	.0099	2.320
	149.79	.3665	.3724	.0059	1.610
	184.94	.3007	.3051	.0044	1.460
600	77.82	.5955	.6091	.0136	2.280
	125.64	.4256	.4398	.0142	3.330
	149.79	.3665	.3782	.0117	3.190
	184.94	.3007	.3116	.0109	3.620

APPENDIX B

EXAMPLE RAW DATA

TABLE XXIV

EXPERIMENTAL MEASUREMENTS OF BENZENE KINEMATIC
VISCOSITY UNDER HYDROGEN GAS PRESSURE

Cell Temperature (mV)	Cell Pressure (psi)	Atmospheric Pressure (Hg)	Flow Time		Kinematic Viscosity (cs)
			Min:Sec	Sec	
<u>T = 77.57°F</u>					
1.560	200	28.98	10:00.66	600.66	0.7106
1.560	200		9:59.50	599.50	0.7092
<u>1.560</u>	<u>200</u>		10:00.15	<u>600.15</u>	<u>0.7099</u>
Av 1.560	200	28.98		600.103	0.7099
1.560	400	29.00	10:14.47	614.47	0.7269
1.560	400		10:14.77	614.77	0.7272
<u>1.560</u>	<u>400</u>	<u>29.00</u>	10:14.60	<u>614.60</u>	<u>0.7271</u>
Av 1.560	400	29.00		614.6133	0.7271
1.563	600	29.00	10:16.50	616.50	0.7293
1.563	600		10:15.83	615.83	0.7285
<u>1.563</u>	<u>600</u>		10:16.00	<u>616.00</u>	<u>0.7287</u>
Av 1.563	600	29.00		616.11	0.7289
<u>T = 99.77°F</u>					
2.085	200	29.06	8:35.40	515.40	0.6097
2.085	200		8:36.00	516.00	0.6104
2.085	200		8:34.90	515.90	0.6103
<u>2.085</u>	<u>200</u>	<u>29.06</u>	8:35.50	<u>515.50</u>	<u>0.6098</u>
Av 2.085	200	29.06		515.70	0.6101
2.085	400	29.06	8:36.04	516.04	0.6105
2.085	400		8:37.00	517.00	0.6116
2.085	400		8:37.00	517.00	0.6116
<u>2.085</u>	<u>400</u>	<u>29.06</u>	8:37.14	<u>517.14</u>	<u>0.6118</u>
Av 2.085	400	29.06		516.795	0.6113
2.085	600	29.07	8:45.68	525.68	0.6219
2.085	600		8:46.33	526.33	0.6226
<u>2.085</u>	<u>600</u>	<u>29.07</u>	8:46.60	<u>526.60</u>	<u>0.6230</u>
Av 2.085	600	29.07		526.203	0.6225

TABLE XXIV (Continued)

Cell Temperature (mV)	Cell Pressure (psi)	Atmospheric Pressure (Hg)	Flow Time		Kinematic Viscosity (cs)
			Min:Sec	Sec	
<u>T = 135.48°F</u>					
2.925	200	29.1	6:51.43	411.43	0.4867
2.925	200		6:50.90	410.90	0.4861
2.925	200		6:51.00	411.00	0.4862
<u>2.925</u>	<u>200</u>	<u>29.1</u>	6:51.20	<u>411.20</u>	<u>0.4864</u>
Av 2.925	200	29.1		411.133	0.4864
2.920	400	29.1	7:06.93	426.93	0.5051
2.920	400		7:05.92	425.92	0.5039
<u>2.920</u>	<u>400</u>	<u>29.1</u>	7:05.96	<u>425.96</u>	<u>0.5039</u>
Av 2.920	400	29.1		426.27	0.5043
2.920	600	29.1	7:06.62	426.62	0.5047
2.920	600		7:05.04	425.04	0.5028
<u>2.920</u>	<u>600</u>	<u>29.1</u>	7:05.43	<u>425.43</u>	<u>0.5033</u>
Av 2.920	600	29.1		425.697	0.5036
<u>T = 163.14°F</u>					
3.572	200	29.1	6:10.50	370.50	0.4383
3.572	200		6:10.90	370.90	0.4388
3.572	200		6:10.20	370.20	0.4379
<u>3.572</u>	<u>200</u>	<u>29.1</u>	6:11.00	<u>371.00</u>	<u>0.4389</u>
Av 3.572	200	29.1		370.65	0.4385
3.572	400	29.05	6:11.33	371.33	0.4393
3.572	400		6:10.75	370.75	0.4386
<u>3.572</u>	<u>400</u>		6:11.00	<u>371.00</u>	<u>0.4389</u>
Av 3.572	400	29.05		371.026	0.4389
3.570	600	29.05	6:12.50	372.50	0.4407
3.570	600		6:13.02	373.02	0.4413
3.572	600		6:13.30	373.30	0.4404
<u>3.572</u>	<u>600</u>	<u>29.05</u>	6:13.80	<u>373.80</u>	<u>0.4422</u>
Av 3.572	600	29.05		372.905	0.4411

APPENDIX C

CALIBRATION OF EQUIPMENT

Viscometer Calibration

The cross arm viscometer required a capillary constant to calculate the test fluid kinematic viscosity from experimental flow time measurements. Water, a fluid of known density and absolute viscosity, was used as the calibration fluid.

Distilled water was degased before it was used as a calibration fluid. The degassing process required rapid boiling in an apparatus consisting of a boiling flask with vented condenser for approximately one hour. After boiling, the water temperature was maintained above 180°F for an additional hour to ensure that all dissolved gases were removed. Only one cross arm viscometer was used throughout this study.

The method of Kestin, Sokolov, and Wakeham (20) was used to find the absolute viscosity of distilled water at each calibration temperature; their correlation is:

$$\log \left\{ \frac{\mu(t)}{\mu(20^\circ\text{C})} \right\} = \left\{ 1.2378 - 1.303 \times 10^{-3} (20 - t) \right. \\ \left. + 3.06 \times 10^{-6} (20 - t)^2 \right. \\ \left. + 2.55 \times 10^{-8} (20 - t)^3 \right\} \\ - 8^\circ\text{C} \leq t \leq 150^\circ\text{C}$$

where

$\mu(t)$ = absolute viscosity of distilled water at desired temperature, CP;

$\mu(20)$ = absolute viscosity of distilled water at 20°C = 1.002 CP;

and

t = temperature, °C.

The density of distilled water was calculated using Abul-Hamayel's correlation (38):

$$\rho = 0.999986 + 0.1890 \times 10^{-4} (t) - 0.5886 \times 10^{-5} (t^2) + 0.1548 \times 10^{-7} (t^3)$$

where t is temperature ($^{\circ}\text{C}$), and ρ is density (gm/cm^3). The value of the capillary constant, K , used during this study was 1.18305×10^{-3} , which is the average of the calibration values in Table XXV. Table XXVI shows the calibration measurements for the distilled degased water.

TABLE XXV
KINEMATIC VISCOMETER CALIBRATIONS

Temperature $^{\circ}\text{F}$	Time sec	Absolute Viscosity CP	Density gm/ml	Kinematic Viscosity CS	Calibration Constants (CS/sec) $\times 10^3$
79.82	725.11	0.8594	0.9966	0.8623	1.1892
88.10	665.50	0.7778	0.9953	0.7815	1.1743
98.10	588.78	0.6951	0.9935	0.6996	1.1882
119.60	479.45	0.5595	0.9887	0.5659	1.1803

Calibration of Pressure Gauge

Calibration of the system pressure gauge used during this study was done using a Ruska Model 2400HL dead weight pressure system. The accuracy of this equipment (manufacturer specification) was a minimum of 0.01 percent of reading up to 12140 psi.

TABLE XXVI

CALIBRATION MEASUREMENTS WITH DEGASED DISTILLED WATER

Cell Temperature m. v.	Atmospheric Pressure mmHg	Flow Time	
		min:sec	sec
1.613	740.6	12:05.11	725.11
1.613		12:05.10	725.10
1.613		12:05.09	725.09
<u>1.613</u>	<u>740.6</u>	12:05.12	<u>725.12</u>
Av 1.613	740.6		725.105
Temperature = 79.82°F			
1.810	744.8	11:05.30	665.30
1.815		11:05.40	665.40
1.810		11:05.98	665.98
1.810		11:05.00	665.00
<u>1.810</u>	<u>744.8</u>	11:05.90	<u>665.90</u>
1.810	744.8		665.51
Temperature = 88.10°F			
2.045	740.90	9:48.75	588.75
2.045		9:48.70	588.70
2.050		9:48.70	588.70
<u>2.045</u>	<u>740.90</u>	9:49.00	<u>589.00</u>
2.046	740.90		588.78
Temperature = 98.10°F			
2.552	739.80	7:59.40	479.40
2.552		7:59.30	479.30
2.552		7:59.50	479.50
<u>2.552</u>	<u>739.80</u>	7:59.60	<u>479.60</u>
2.552	739.80		479.45
Temperature = 119.60°F			

The pressure gauge calibrated was HTL Industrial Products high pressure gauge (Part No. 101FTM13A41, Serial No. 579108). The calibrated data are tabulated in Table XXVII.

TABLE XXVII
CALIBRATION OF HTL PRESSURE GAUGE

Dead Weight Tester (psig)	Pressure Gauge (psig)
206	206
306	305
406	405
606	605
806	802
1006	1000

Thermocouple Calibrations

The chromel-alumel thermocouple used during the operation of the kinematic viscometer was calibrated against a N.B.S. calibrated Leeds and Northrup Corporation platinum resistance thermometer (Serial No. 1761202). The range of temperatures covered by the calibration was from room temperature to 495°F. Two readings were taken at each temperature with the thermocouple referenced to an ice bath. Table XXVIII contains the tabulated data. Figure 16 is a graphical presentation of the arithmetic average of thermocouple readings for each temperature. The calibration was checked periodically to ensure that there was no change in thermocouple readings of temperature.

TABLE XXVIII

CALIBRATION DATA FOR PRESSURE CELL THERMOCOUPLE

Actual Temperature ($^{\circ}\text{C}$)	Actual Temperature ($^{\circ}\text{F}$)	Thermocouple Reading (mv)
24.449	76.010	1.523
48.639	119.550	2.537
57.429	135.372	2.925
70.250	158.450	3.451
80.890	177.602	3.900
97.556	207.600	4.660
108.234	226.821	5.050
120.835	249.503	5.575
136.557	277.802	6.224
153.967	309.140	6.932
171.418	340.552	7.630
190.129	374.232	8.439
211.396	412.514	9.249
233.564	452.415	10.155
256.714	494.085	11.111

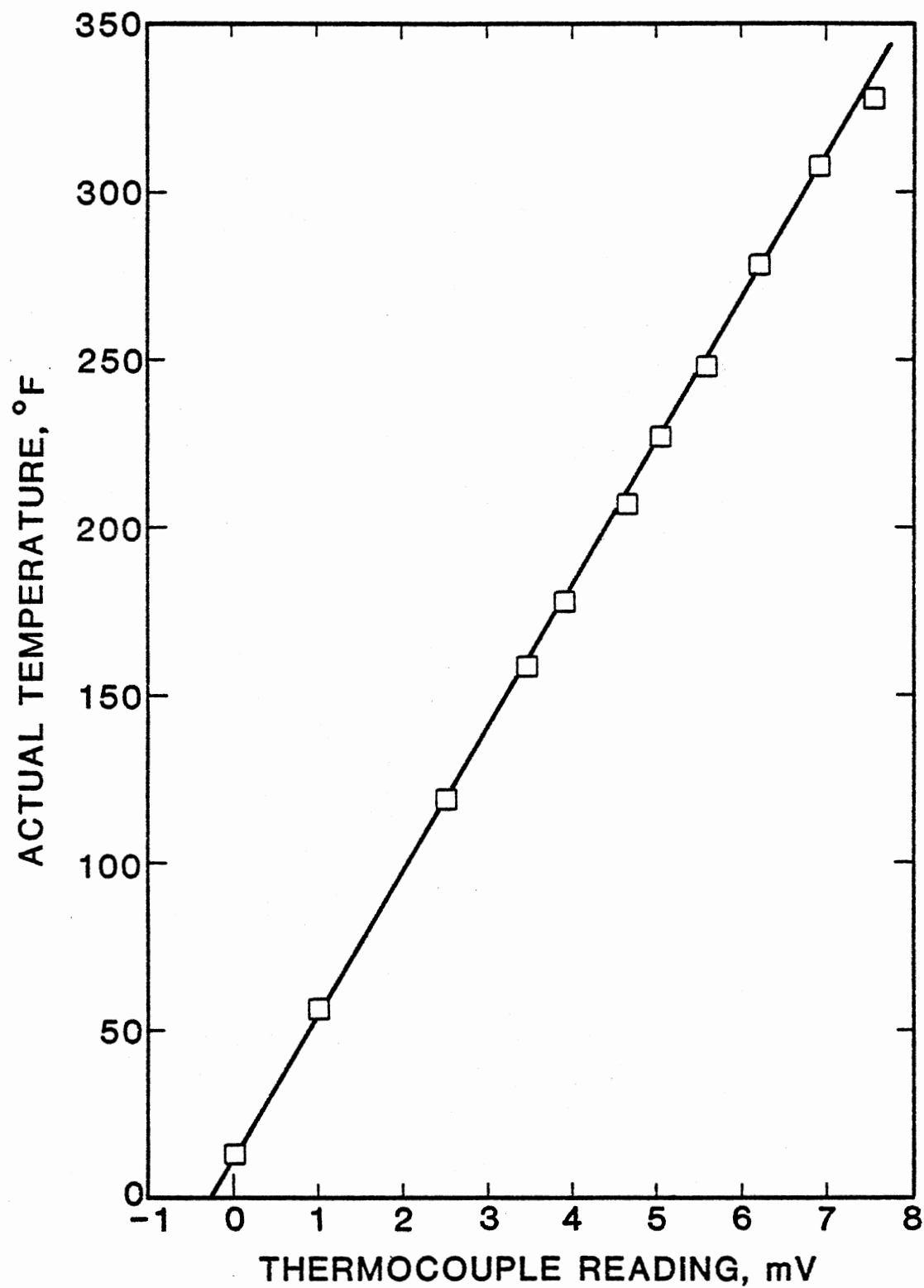


Figure 16. Calibration Curve of the Pressure Cell Thermocouple

J
VITA

Dulaihan Khulaiwi Al-Harbi

Candidate for the Degree of

Doctor of Philosophy

Thesis: VISCOSITY OF SELECTED HYDROCARBONS SATURATED WITH GAS

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Hayel, Saudi Arabia, May 15, 1943, the son of Mr. and Mrs. Khulaiwi Al-Harbi.

Education: Graduated from Hayel Secondary School, Saudi, Arabia, in 1964; attended the college of Petroleum and Minerals, 1964-1976; obtained the Bachelor of Science degree in Chemical Engineering from Pennsylvania State University, University Park, Pennsylvania, March, 1970; received the Master of Science degree from Pennsylvania State University, University Park, Pennsylvania, in August, 1975; completed requirements for the Doctor of Philosophy degree at Oklahoma State University, Stillwater, Oklahoma in May, 1982.

Professional Experience: Graduate assistant in Chemical Engineering at University of Petroleum and Minerals, 1970-1971; as a lecturer in Chemical Engineering at University of Petroleum and Minerals from 1975 to present.

Professional Membership: Associate member, American Institute of Chemical Engineering; member, Oméga Chi Epsilon.