LIQUID DENSITY BEHAVIOR
IN THE CRITICAL
REGION

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PREFACE

Liquid densities in the critical region were measured for five systems; propylene, methanol, octane, methane-propane, and ethylene-propylene. These data were compared with available literature data and predictive correlations.

I would like to express my gratitude to Dr. R.N. Maddox for the advice, guidance and tolerance he has provided as my thesis adviser. The entire Faculty of the School of Chemical Engineering has provided much assistance throughout my long association with them. Particular appreciation is due Dr. K. J. Bell for the financial support from his projects.

I wish to thank all my family for their understanding and encouragement during my years of graduate study. The most special thanks to my wife, Dorothy, for all the time and work she has put into "our" thesis.

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LIST OF SYMBOLS

English Letters

A - Constant in Density Temp. Curve Fits

B - Constant in Density Temp. Curve Fits

C - Constant in Density Temp. Curve Fits

E - Constant in the Yen and Wood Correlation

F - Constant in the Yen and Wood Correlation

G - Constant in the Yen and Wood Correlation

H - Constant in the Yen and Wood Correlation

I - Constant in the Yen and Wood Correlation

J - Constant in the Yen and Wood Correlation

L - Constant in the Yen and Wood Correlation

English Letters

K - Constant in the Alani and Kennedy Correlation

N - An Integer Constant

P - Pressure

R - International Gas Constant

T - Temperature

V - Volume

Z - Compressibility Factor

a - Constant in Van der Waal Equation

b - Constant in Van der Waal Equation

d - Indicates a Total Derivative

a' - Constant in Density Pressure Curve Fits

b' - Constant in Density Pressure Curve Fits

c' - Constant in Density Pressure Curve Fits

Greek Letters

β - Constant in Chueh and Prausnitz Correlation
Δ - Indicates a Differential Quantity
∂ - Indicates a Partial Derivative
ρ - Density
ω - Expansion Factor in Watson Correlation

Subscripts

c - Indicates Critical Property
l - Indicates Liquid Quantity
r - Indicates Reduced Quantity
s - Indicates Saturated Quantity

CHAPTER I

INTRODUCTION

The physical property density is required in many scientific and engineering calculations. In addition, many correlations for other physical properties use density as one of the parameters. Vapor phase densities can often be estimated by equations of state but liquid densities must generally be estimated by empirical correlations derived from experimental data. With the increased pressures and temperatures of current physical processes the need for accurate correlations and data in the critical region is becoming paramount. Although the volume of data and the number of correlations for density in the literature are enormous, reliable data and correlations in the critical region are scarce.

The purposes of this study were three fold:

1) To modify existing density apparatus to be able to measure liquid densities for pure components and mixtures in the critical region.

2) To evaluate the various proposed methods of density determination to find the most appropriate apparatus and procedure for obtaining accurate critical region density.

3) To evaluate the data obtained experimentally and from the literature and compare these data to current available correlations.

Three pure components were studied: propylene, methanol, and octane. Two binary mixtures were studied: methane-propane and ethylene-propylene.

CHAPTER II

REVIEW OF DENSITY APPARATUS

This chapter is not intended to be an exhaustive study of all density apparatus but rather a survey of the more important methods currently in use and their reported limitations. Many researchers have designed apparatus for the determination of density. Many more researchers have used these techniques to measure density. Since density is by definition the mass per unit volume, most techniques entail some method of either measuring the mass and holding the volume constant or measuring the volume and holding the mass constant.

Pycnometer

The pycnometer takes the approach of holding volume constant, varying the weight and measuring directly the weight of the sample. Ordinary pycnometers have been used to obtain density values correct to 1 x 10^{-5} g/ml by the use of large pycnometers and careful work (32).

The standard procedure for obtaining liquid densities by pycnometeric methods is to weigh an evacuated pycnometer, and fill the pycnometer to a specified level with test fluid at constant temperature. The pycnometer is limited ranges of temperature and pressure for a particular pycnometer. Accurate PVT data, including densities up to critical temperatures and pressures, have been obtained by the means of a steel pycnometer and volumeter in the Beattie apparatus (30). However, considerable manipulative skill and experience are required for the operation of this complex equipment. (6)

Disadvantages of the pycnometer are: 1) To obtain accurate densities the weight of sample must be larger than the weight of the pycnometer. The heavy weights required for this usually force the weighing apparatus to operate in its less accurate region. 2) The large volume of the pycnometer is often difficult to maintain at a constant temperature. 3) The pycnometer exterior surface often adsorbs moisture or possibly bath fluid causing inaccurate measurements.

Dilatometers and Other Constant Weight Apparatus

Dilatometers take the other approach to directly measuring density. The weight is maintained constant and the volume varied. The dilatometers suffer from the same disadvantages as the pycnometer when used for absolute measurements of density but can be considerably more accurate in measuring small changes in relative density. Dilatometers have been designed to measure changes in density with an accuracy of ± 2 x 10^{-6} g/ml and an absolute accuracy of ± 1×10^{-5} g/ml (10).

Sage and Lacey (27) presented an apparatus designed to measure densities of hydrocarbons at pressures up to 10,000 PSI and at temperatures between 0 °F and 460 °F. Their apparatus consisted of an enclosed cell in which a weighed amount of sample was contained. The volume of the sample at various temperatures was determined by an electrical probe which determined the height of a mercury level in the bottom of the cell. The mercury was introduced into the cell to change the volume of the sample. Numerous variations on the basic dilatometer have been tried. Typical is the modification used by Gibson and Loeffler (9). Their apparatus was similar to that of Sage and Lacey (27) but instead of determining the height of the mercury electrically, they weighed the mercury forced out of the cell when the temperature was raised and calculated the amount, and thus the volume, of mercury left inside the test cell.

Floatation Methods

Several variations of the Archimedes float method are currently in use. All of these methods use the fact that the buoyancy of an object completely submerged in a fluid is equal to the volume of the object times the density of the fluid in which the object is emerged. From measurement of the buoyancy and a knowledge of the volume of the float the density of the test fluid can be calculated.

Goldman and Scrase (12) used the Archimedes float method. In their apparatus the buoyancy of the float is measured by measuring the extension of a quartz helical coil from which the float is suspended. One problem with this method, and that used by many authors, is that the float is suspended by a wire or other device which must pass through the liquid gas interface and be subject to surface tension phenomena. To eliminate this problem Tereshkovich et al (32) developed a temperature of floatation method. In this method floats of different densities are caused to float in the test liquid by adjusting the temperature of the test liquid. The disadvantage of this procedure is that a large number of very accurate floats must be maintained to be able to determine very many density values for a test liquid.

A method first presented by Lamb and Lee (19) seems to eliminate the problem of most of the other methods presented. This method uses floats as above but the floats have iron cores so that an external magnetic field can exert a force on the floats. The floats are forced to remain at a specified depth in the test fluid by an external electromagnet. The force exerted by this magnet is calculated by measuring the current and voltage of the electromagnet. A force balance around the float gives the buoyancy and finally, the density of the test liquid. The main disadvantage of the magnetic float method is that some method must be used to sense the position of the float in the test liquid. This is often done by the use of photo cells, but sometimes by the of electromagnets. Both methods lend themselves to systematic errors and the need for frequent calibration.

Using the Archimedes float method, Goldman and Scrase (12) claim accuracies of 0.033 per cent. Tereshkovich et al (32) claims an accuracy of 0.5 x 10^{-6} g/ml. Senter (28) used a modification of Lamb and Lee's (19) apparatus to measure salt solutions to an accurancy of 1 x 10^{-7} g/ml. All of the floatation methods, although good accuracies are claimed, are relative density measurements and not absolute density measurements.

These methods could be made to be absolute if the volume of the float was directly measured. However, the sizes of the floats usually preclude accurate volume measurements without sophisticated apparatus. Therefore most investigators find it more practical to calibrate with known densities.

Methods for Predicting Liquid Densities

Numerous methods are available in the literature for predicting liquid densities. Some are extremely accurate, but extremely complex, while the others are extremely simple and correspondingly less accurate.

The correlations of Alani and Kennedy (1), Chueh and Prausnitz (4), Gamson and Watson (7), Harmens (14), Lu (20), Lu-Rea (3), Rackett (25), Ritters et al (26), and Katz (30) and Yen and Wood (37) are some of the most widely accepted methods for predicting densities.

Alani and Kennedy (1) have used an equation similar in form to the Van der Waals equation:

$$RT = (P+a/V^2)(V-b) \tag{1}$$

$$\text{where: } a = Ke^{(n/7)} \tag{2}$$

$$b = mT+c \tag{3}$$

Lykman et al (21) presented a correlation for the determination of saturated liquid densities for pure components as a quadratic function of the acentric factor:

$$V_s/V_c = V_r^o + \omega V_r^{(1)} + \omega^2 V_r^{(2)} \tag{4}$$

Generalized functions for their equation have been calculated from liquid density for argon, nitrogen, ethylene-propane, carbon tetracloride-benzene, and normal heptane.

Chueh and Prausnitz (4) making use of the Wada (35) correlation for compressibility presented a generalized correlation for the density of normal liquids as:

$$\log(\rho_l) = \log(\rho_l^s) + (1/N)\log[1.0+N\beta^s(P-P_s)] \tag{5}$$

$$\text{where: } N = 9 \tag{6}$$

Chueh and Prausnitz (4) suggest that the correlation of Lykeman et al (21) be used to calculate the volume of saturated liquid.

Watson (36) reported a method of estimating the density of a pure compound from its molecular weight, critical temperature, critical pressure, and an expansion factor:

$$\rho = \rho_i \omega / \omega_i \tag{7}$$

$$\text{where:} \quad \omega = P_r / ZRT_r \tag{8}$$

ω is evaluated as a function of reduced temperature and reduced pressure for one compound on which complete data are available. The equation can then be used for predicting the density of any other compound for which one liquid density value is available to establish ρ_i / ω_i. Gamson and Watson (7) developed the correlation of these expansion factors for mixtures:

$$\rho_i / \omega_i = f(\rho_1, \rho_2, \ldots\ldots, \omega_1, \omega_2, \ldots\ldots) \tag{9}$$

Lu (20) has presented a correlation based on the work of Lyderson et al (22). This correlation:

$$K = f(T_r, P_r) \tag{10}$$

is graphical using T_r as an independent variable and P_r as the parameter with K being a function of reduced volume and Z_c.

$$K = (Z_c)^{.77}/V_r \tag{11}$$

Using the Watson (36) approach the liquid densities of substances can be estimated over T_r and P_r ranges covered by the chart provided density is known at one condition.

Rea (3) has regressed the Lu Chart in terms of reduced temperature and pressure. The Lu constant K is correlated with T_r.

$$\ln K = A_o + A_1 T_r + A_2 T_r^2 + A_3 T_r^3 \tag{12}$$

$$\text{where: } A_i = B_o^i + B_1^i P_r + B_2^i P_r^2 + B_3^i P_r^3 + B_4^i P_r^4 \tag{13}$$

Values of the constants are available in his report.

Harmens (14) has reported that orthobaric densities can be calculated with the expression:

$$\rho_l^s = C[f(T_r)] \tag{14}$$

$$\text{where: } C = P_c[.43875-.625Z_c] \tag{15}$$

$f(T_r)$ is called the generalized density function. This method can be applied to hydrocarbon mixtures by using an empirical method for the determination of average values of critical temperature and constant C for the mixture.

Rackett (25) reported a general equation for the saturated liquid volume of pure substances:

$$V_s/V_c = Z_c^{(1.0-T_r)^{(2/7)}} \quad (16)$$

This equation can be extended to hydrocarbon mixtures and hydrocarbon non-hydrocarbon mixtures by using psuedo critical properties. The mixture critical volume and critical compressibility factors are molal average quantities. The actual experimental critical temperature of a mixture of components from a homologous series is greater than the molal average psuedo critical temperature. Rackett (25), therefore, chose to weight the critical temperature of a binary mixture in favor of the heavier component. The weighting factors are expressed graphically as a function of the difference in the pure component critical temperature for the binary systems.

Ritter et al (26) presented nomographs to give specific gravities at bubble points. The nomographs cover hydrocarbon mixtures, petroleum fractions, and some 90 pure components. Three nomographs give specific gravities of liquids at their bubble point. Another gives specific gravities of petroleum fractions up to 1000 ^{o}F and 1500 psia. Charts are also presented for specific gravities of pure liquids and mixtures of liquids by the methods of Gamson and Watson (7).

Standing and Katz (30) reported a method of calculating liquid densities, assuming additive volumes for all compounds less volatile than ethane and using apparent densities for methane and ethane in the liquid at 60 °F at one atmosphere pressure. These apparent densities were given in the form of a graph as a function of weight per cent of ethane and or methane, in the mixture and the density of the remainder of the liquid. This method was used for predicting densities of crude oil saturated with natural gas.

Yen and Wood (37) modified the correlation of Hou and Martin (15) for the determination of saturated liquid densities and presented it as:

$$\rho_{1r} = 1+A(1-T_r)^{1/3}+B(1-T_r)^{2/3}+D(1-T_r)^{4/3} \qquad (17)$$

The constants A, B, and D are correlated with Z_c and can be evaluated for either a pure compound or mixture.

Yen and Wood (37) define the density of a compressed liquid in reduced quantities as:

$$\rho_{1r} = \rho^{S}_{1r}+(\Delta\rho_{1r})_{.27}+ Z_c \qquad (18)$$

The term $(\Delta P_{1r})_{0.27}$ represents the reduced density increase caused by ΔP_r or (P_r-P_{rs}) reduced pressure increase from the vapor pressure to the specified pressure, for compounds with Z_c value of 0.27. The term ΔZ_c which equals 0 for Z_c

equal 0.27 further corrects the isothermal pressure affect on density for compounds with other Z_c values. Based on the Lyderson and other correlation, values of $(\Delta P_{1r})_{.27}$ were evaluated as a function of ΔP_r and T_r and then fitted to the following equation:

$$(\Delta\rho_{1r})_{.27} = E_{.27}+F_{.27}\ln(\Delta P_r)+G_{.27}\exp(H_{.27}\Delta P_r) \qquad (20)$$

Constants E, F, G, and H are correlated with T_r and can be evaluated for pure compounds or mixtures. The subscript .27 designates Z_c up to 0.27. The correlations for E, F, G, and H are valid for T_r from 0.3 to 1 and ΔPr from 0.2 to 60. The ΔZ_c values are computed from the relationship:

$$\Delta Z_c = I+J\ln(\Delta P_r)+\exp(L\Delta P_r) \qquad (21)$$

Several correlations have been proposed for calculating compressed liquid densities for hydrocarbon mixtures with no experimental data available or for extending known data into other ranges of temperature and pressure. Two of the most widely accepted methods include that of Yen and Wood (37) and Lu (20).

The Rackett (25) method initially introduced by Deam et al (5) has now proved to be an accepted method for predicting saturated liquid densities of pure hydrocarbons, hydrocarbon mixtures, and mixtures of hydrocarbon with nonhydrocarbons. Using the saturated liquid volumes calculated by the Rackett (3) equation, a method involving the Tate equation has been developed to calculate liquid densities at any desired pressure (23).

Huggins (16) presented the Tate equation in the form:

$$(V_s-V)/V_s = .2058 \log[(B+P)/(B+P_s)] \qquad (22)$$

Huggins found that for paraffin hydrocarbons with less than 10 carbon atoms, the constant B in equation (22) can be calculated as follows:

$$T' = (T-T_{mp})/(T_c-T_{mp}) \qquad (23)$$

For T' ranging from 0 to .07

$$B/\rho_c = .54.882-146.427T'+151.11(T')^2 \qquad (24)$$

and for T' ranging from .75 to 1

$$B/\rho_c = 38.510-70.912T'+31.532(T')^2 \qquad (25)$$

CHAPTER III

EXPERIMENTAL APPARATUS

Pressure Measurement and Control

The pressure of the system was measured by the use of a Consolidated Electronics Corporation Model #4-317 pressure transducer. The five volt power supply required for excitation of the pressure transducer was provided by the mercury level limit control unit designed for this study. The pressure of the system was controlled by the air pressure on the mercury system as shown in Figure 1. Addition of air to the left air bomb would force the mercury up in the right air bomb, decreasing the overall volume of the test liquid and raising the pressure of the test liquid. To reduce the pressure, air was vented from the left mercury bomb, reversing the procedure. During the raising of the temperature of a sample it often became necessary to remove all the air from the test bomb to reduce the pressure to the value desired. To obtain lower pressures a liquid sample was drawn from the test liquid, reducing the volume of the test liquid and, therefore, the pressure.

Control of the level of the mercury in the two bombs is the most important item in controlling the test system

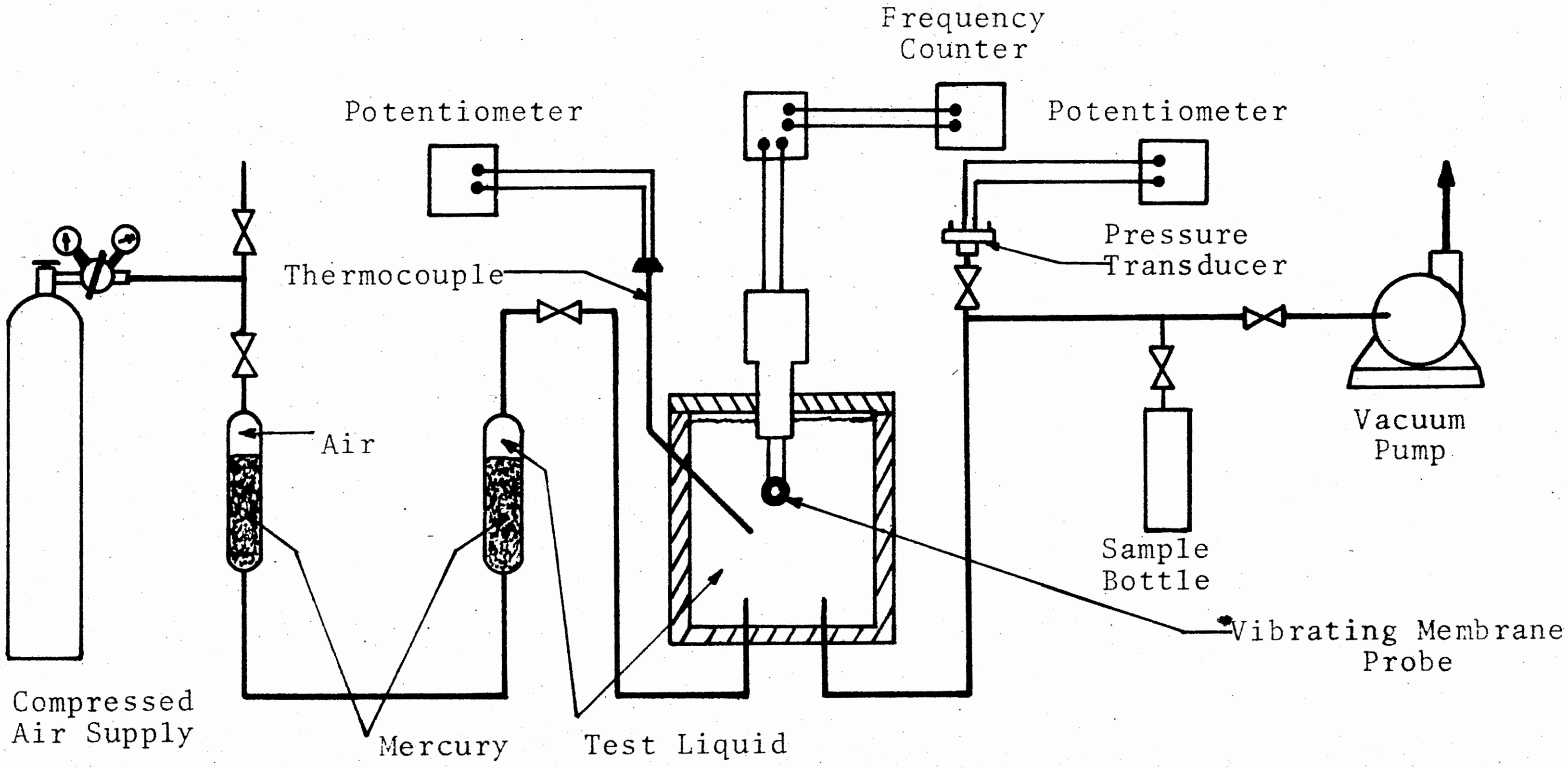

Figure 1. Vibrating Membrane Apparatus

pressure. During the initial phases of the work, frequent problems were encountered from allowing the mercury to move too far to the right and get into the test cell or to lose mercury out the air vent. To overcome this problem, a mercury level limit control unit was constructed.

The mercury level limit control unit is a logic device designed to prevent mercury spills in the density apparatus. By means of contacts at the full and empty levels of the two mercury cells the control unit forms switches. The bombs which contain the mercury are grounded. Whenever the mercury level is such as to cover the lower contacts in both cells but not the upper contacts, a relay is closed opening two solenoid valves installed as in Figure 2. Any condition other than this will cause the relay to open which will close the solenoid valves preventing further mercury flow. If either of the mercury cells tries to overfill, or drain completely, the solenoid valves will close stopping the flow until the operator manually opens the valves and corrects the problem. During the design of the mercury limit level control unit the decision was made to make the unit a master control unit for the density apparatus. Therefore as shown in Figure 3 and detailed in Appendix E, the control unit has a rotary switch to allow the selection of the thermocouples or the pressure transducer for measurement at a potentiometer and provides the power supply for the

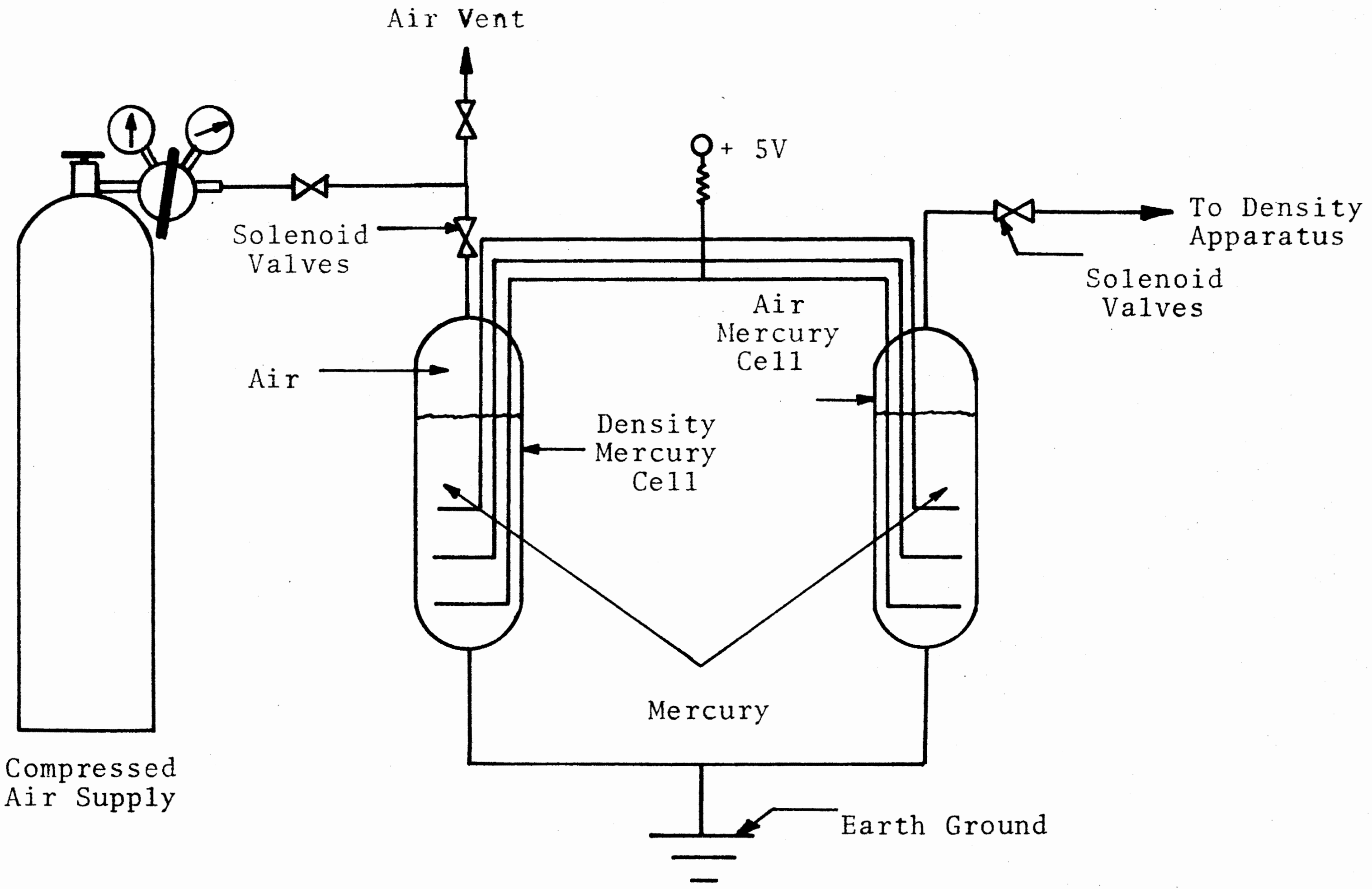

Figure 2. Diagram of Solenoid Valves on Pressure Control Apparatus

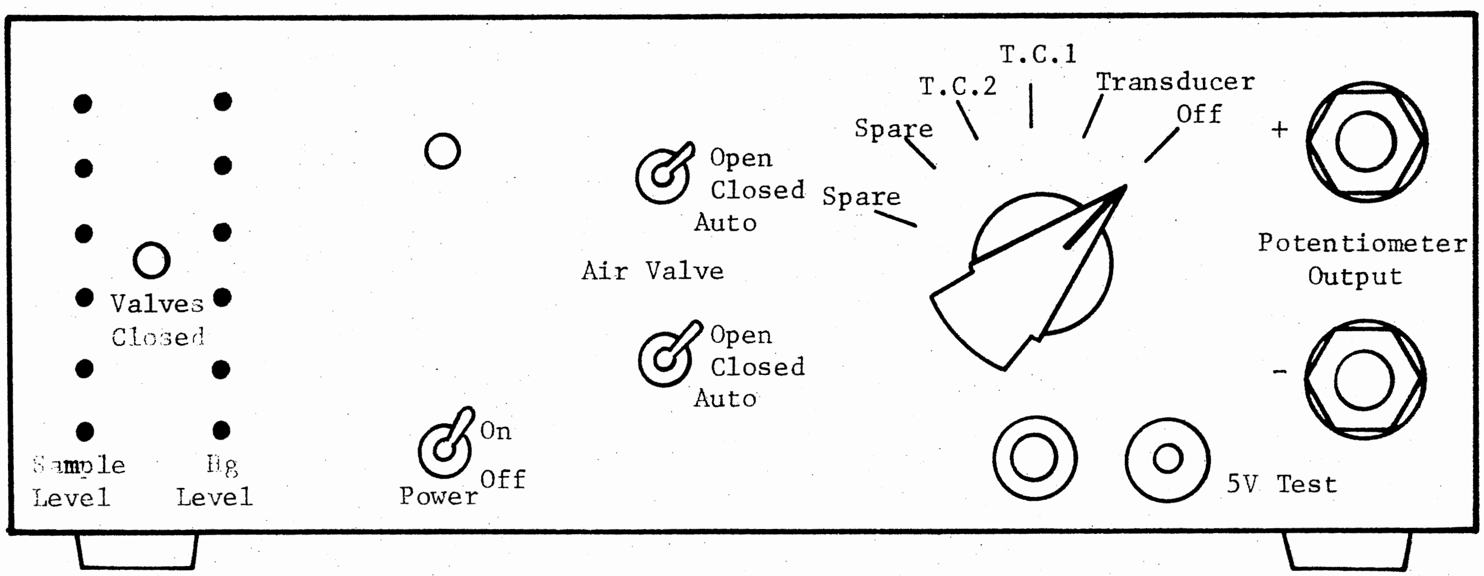

Figure 3. Mercury Limit Level Controller

transducer. The wiring for the potentiometers and thermocouples is shown diagramatically in Figure 4.

Composition Analysis

An F & M Scientific Company Model 500 Serial #1008 Gas Chromatrograph was used to determine the compositions of the mixtures used in this study. The column was a 1/4 inch diameter copper tube 6 feet in length packed with 30/60 mesh silica gel.

Helium was used as a carrier gas at a flow rate of approximately 60 ml/min through both ports of the detector block. The bridge current was set at 175 mA. The column and block temperatures were set at 125 °C for isothermal operation. A Hamilton Company Model #1725 250 gas tight syringe was used to inject gas samples. A Perkin/Elmer Model D2 Serial #GC06053 Integrater was used for the summation of the areas. A Kienzle Model D11-E Serial #1719 printer was used with this equipment. The power was supplied by 150 volt Khunke Serial #17243 isolation transformer. The calibration curves for this equipment are shown in Appendix B.

Temperature, Measurement, and Control

Two temperature baths were used for the control of temperature in this study. Another temperature bath was designed during this study but not used for any of the data included in this study.

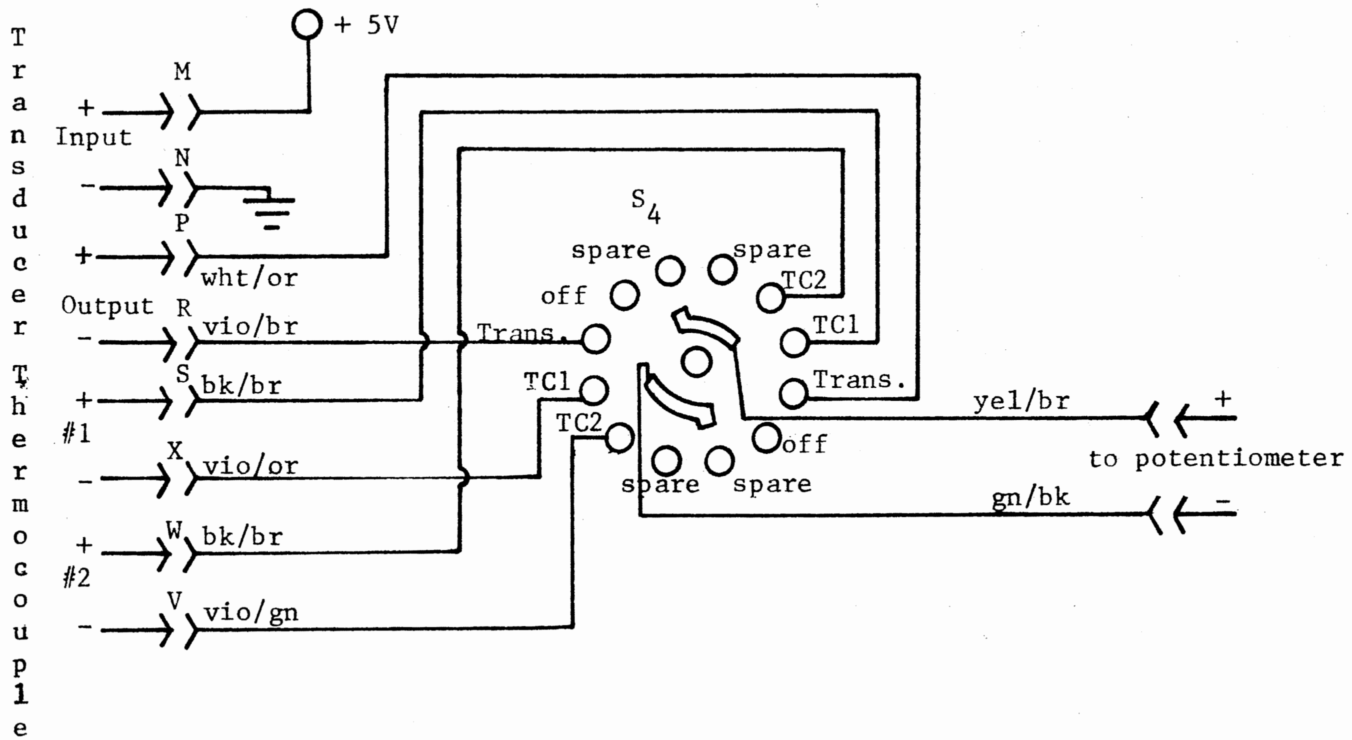

Figure 4. Diagram of Potentiometer and Thermocouple Rotary Switch

Hot Bath

A high temperature bath designed to use silicone oil and to operate between the ranges of ambient temperature and 500 $^{\circ}F$ was used for most of the data. A Fisher, Model #22 Proportional Temperature Controller was used to control the bath fluid temperature. Manufacturer specifications of the temperature controller are for a temperature range of 0 $^{\circ}C$ to 250 $^{\circ}C$ with a sensitivity of ± 0.01 $^{\circ}C$. The electrical controller had two electrical outlets rated at 750 watts each. Two immersion heaters each rated at 500 watts were connected to these outlets.

Cold Bath

The low temperature bath was designed for a temperature range of -100 $^{\circ}F$ to ambient. A Yellow Springs Instrument Co., Inc. temperature controller was used to control the bath fluid temperature. This controller had a manufacturer's specification of ± 0.05 $^{\circ}C$ assuming adequate agitation. A 500 watt immersion heater was used as a trim heater. A cascade refrigeration system was used to cool the bath fluid. The fluid used in the cold bath was normal propanol.

CHAPTER IV

OPERATING PROCEDURE

Vibrating Membrane Operating Procedure

The system as shown in Figure 5 was evacuated and purged three times with the test sample by alternately opening valve H and valve G while the vacuum pump was operating. After this procedure the system was cooled to approximately 0 $^{\circ}$C. Valve G was then opened to allow the vapor pressure at room temperature to force the sample into the test cell. This forced the test cell to be completely filled with subcooled liquid. After the cell had been allowed to fill for some time valve F was closed and valves B, C, D, and E were opened. The cell was checked for liquid fullness by adding mercury to the system and noting whether or not there was a large increase in system pressure with a small decrease in system volume. Mercury was added to the system by adding air to the left mercury container. If the system was not completely filled with liquid valve C was closed, valve F was opened and the system allowed to fill for a longer time.

After the test cell had been filled, the density of the system was monitored by the frequency counter. Equilibrium was assumed after three consecutive sets of

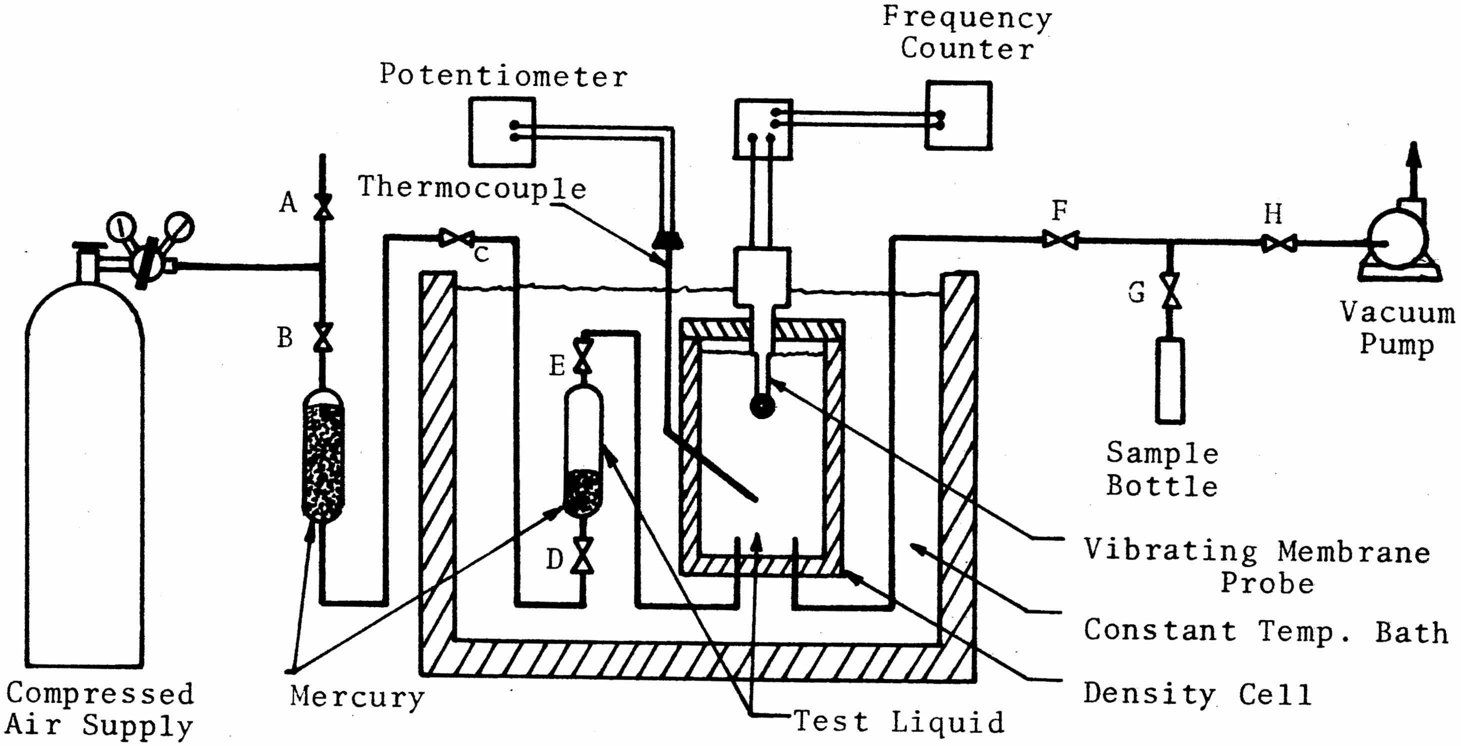

Figure 5. Vibrating Membrane Apparatus with Illustrated Valves

equivalent readings over a one hour period. The pressure, temperature, and density were recorded. The pressure of the system was then decreased by removing mercury through the air system. Density was again monitored until equilibrium was achieved. This procedure was repeated until the pressure could not be lowered by the removal of more mercury from the system. This pressure was assumed to be the saturation pressure at this temperature. The temperature of the system was then raised while the volume was held constant (causing the system to again become subcooled liquid) and the procedure repeated. To keep the mercury from going past valve D, valve F and G were opened occasionally and the mercury level returned to approximately equal levels by allowing air to enter through C. This procedure was necessary to keep from getting mercury into the air pressure system.

Pycnometer Operating Procedure

The pycnometer was connected to the charging apparatus shown in Figure 6. The system was evacuated and purged with the test sample. The pycnometer was then disconnected from the charging apparatus and weighed to give the "empty" weight. The pycnometer was reconnected to the charging apparatus. Since all test samples used with the pycnometer were liquids at room temperature, the pycnometer was allowed to gravity fill. The pycnometer was then attached

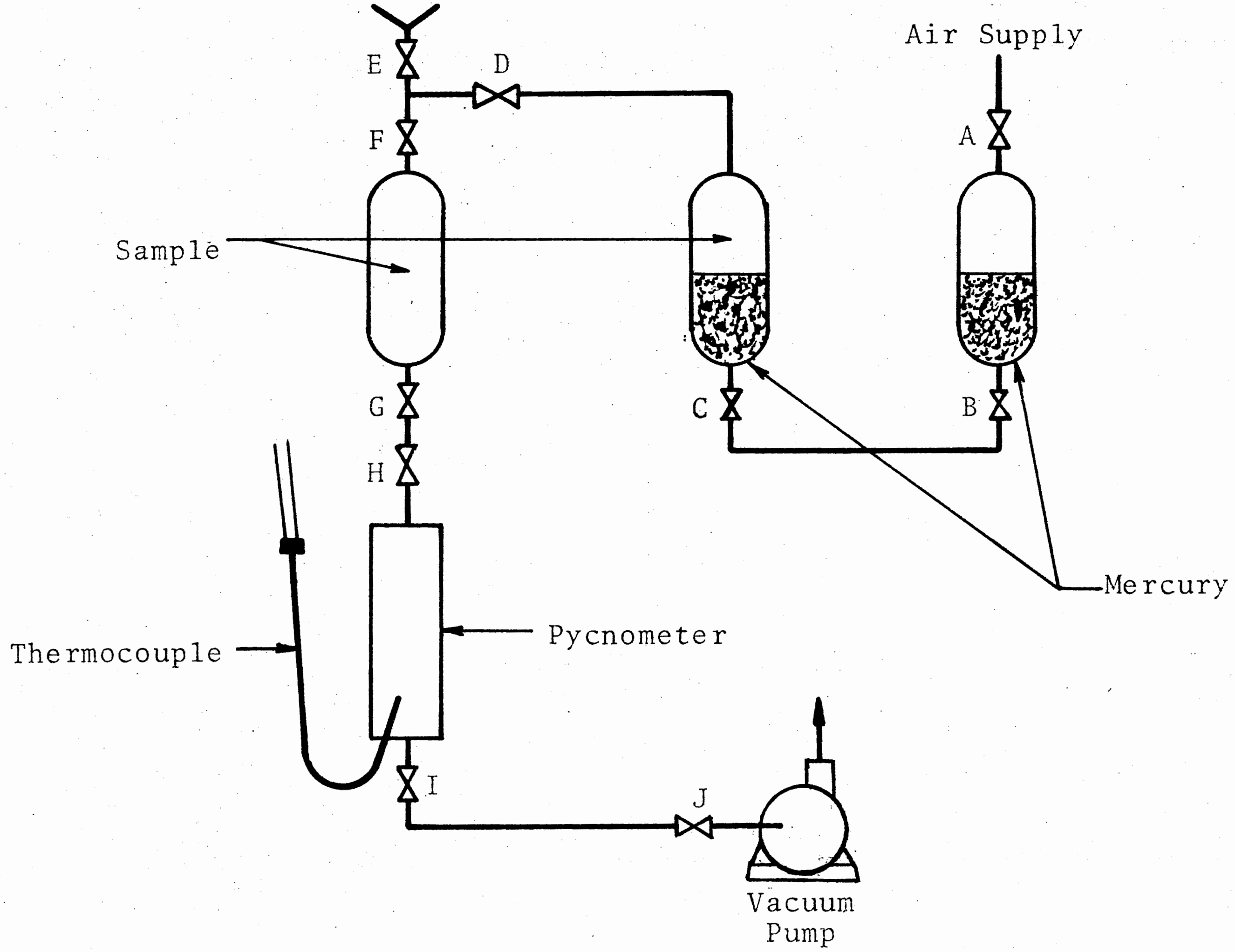

Figure 6. Pycnometer Charging Apparatus

to the pressure control apparatus as shown in Figure 7.

The temperature of the bath was then raised to the desired value. After temperature equilibrium was established the air pressure was adjusted allowing mercury to move in or out to achieve the desired pressure. Once equilibrium was achieved the pycnometer was disconnected from the pressure controlling equipment and weighed. The pycnometer was then reconnected to the pressure controller and the procedure repeated.

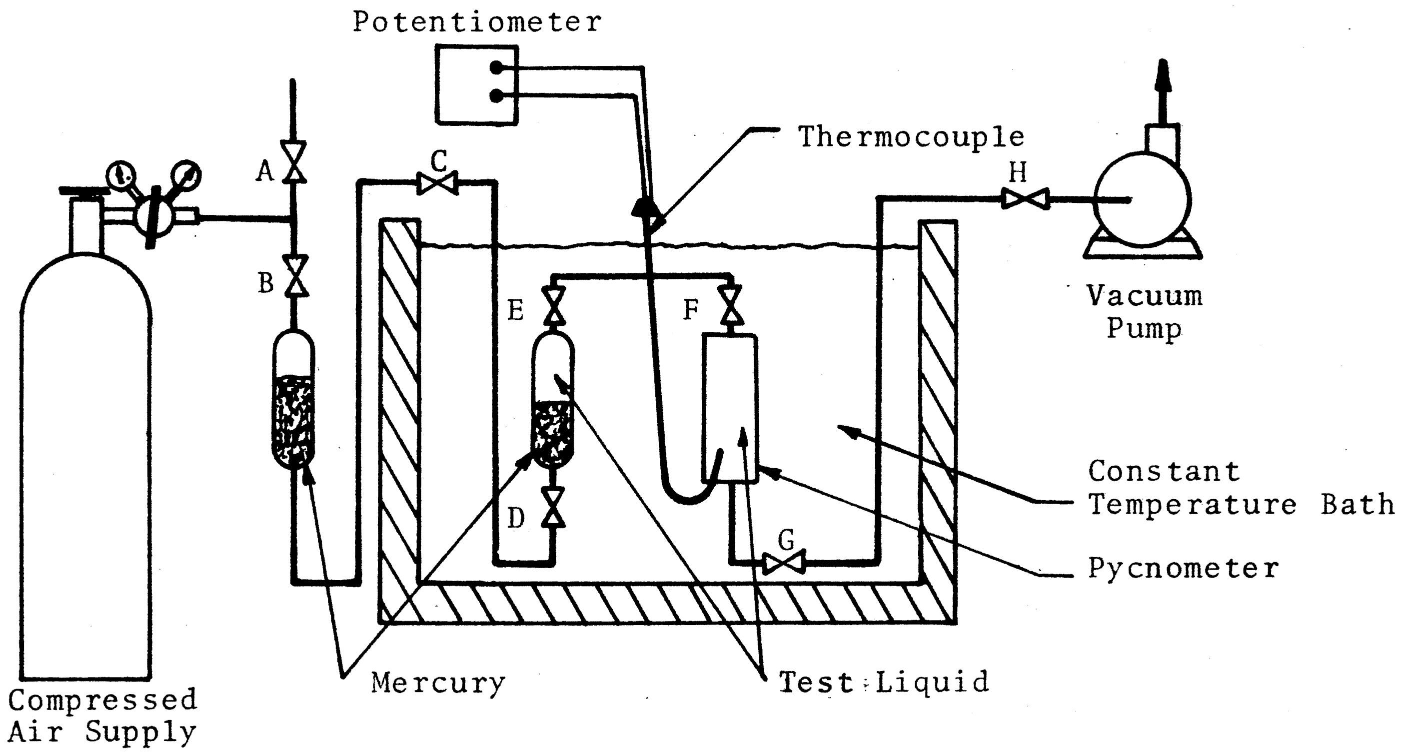

Figure 7. Pressure Controlling Apparatus Connected to Pycnometer

CHAPTER V

EXPERIMENTAL RESULTS

The experimental data for propylene, methane-propane, and ethylene-propylene systems were taken by the vibrating membrane apparatus. These data are presented in Figures 8 thru 12. Figure 8 shows the first data taken for the propylene system. These data are characterized by wide fluctuations as the pressure varies with particularly wide variations around 1000 psia. When the cell was opened for inspection after these data a droplet of mercury was on the membrane. These data were rejected as bad data but are included here for comparison with the data that was used and as a demonstration of the problems associated with the vibrating membrane system.

Figure 9 shows the second set of propylene data taken. These data follow the normal pattern without extreme variations in density. However, the 178 ^{o}F isotherm shows the same peak at approximately 1000 psia. This was still probably due to external loading of the membrane (a mercury droplet) rather than a quirk of nature. The most likely temperature at which a drop of mercury could get on the membrane is at the lowest temperature of a sample.

Figure 10 presents the data taken for the 31 per cent

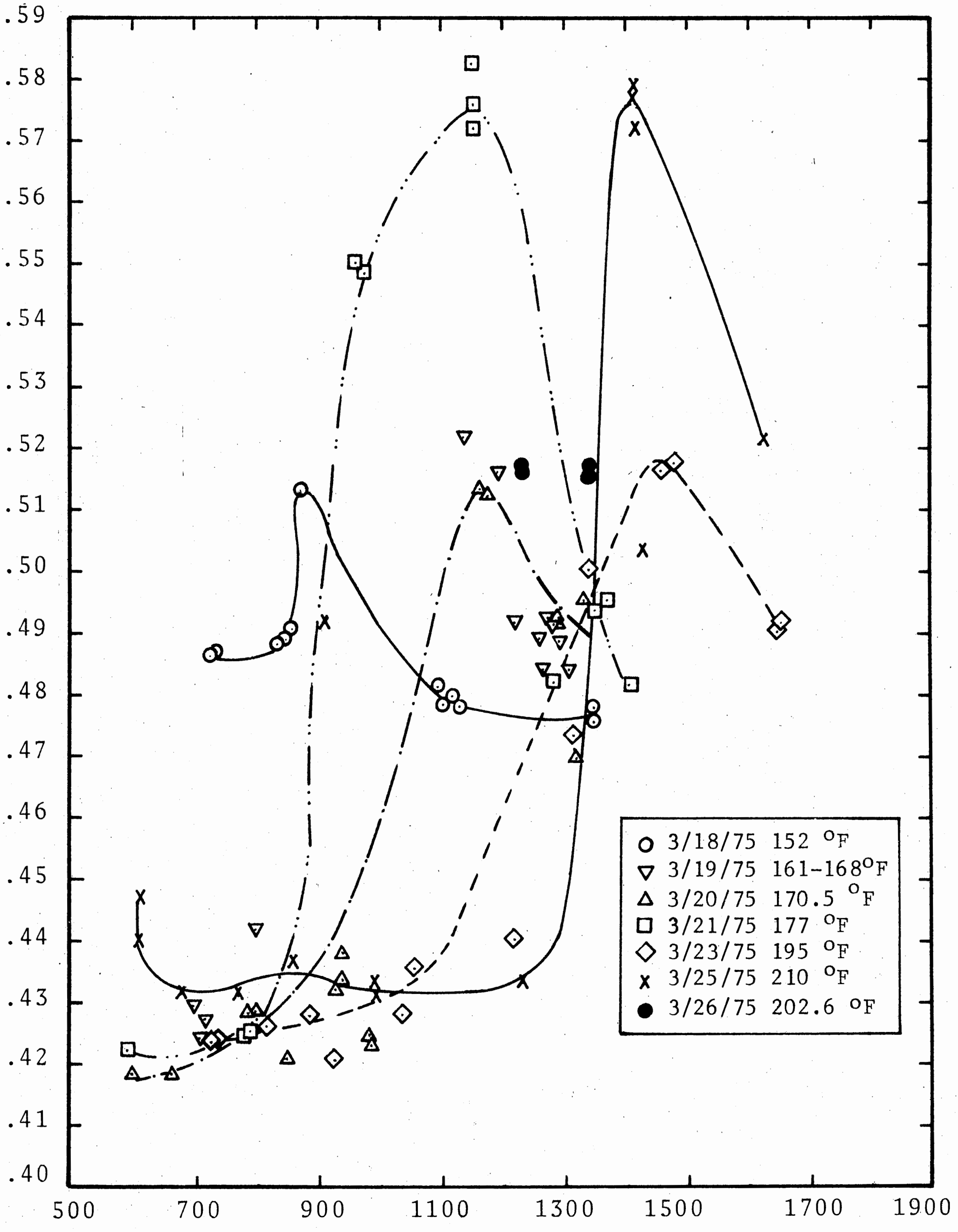

Figure 8. Original Propylene Data

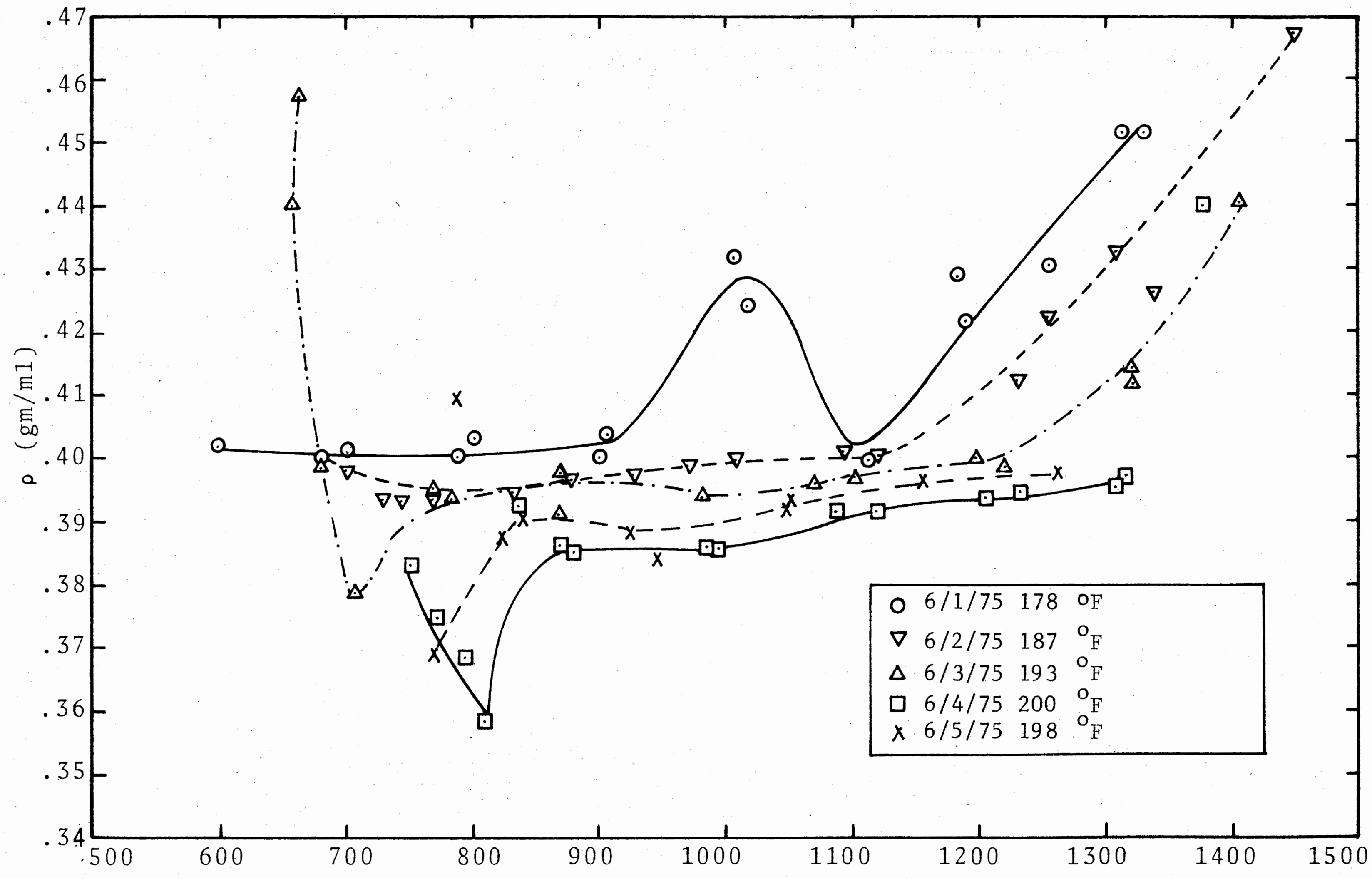

Figure 9. New Propylene Data

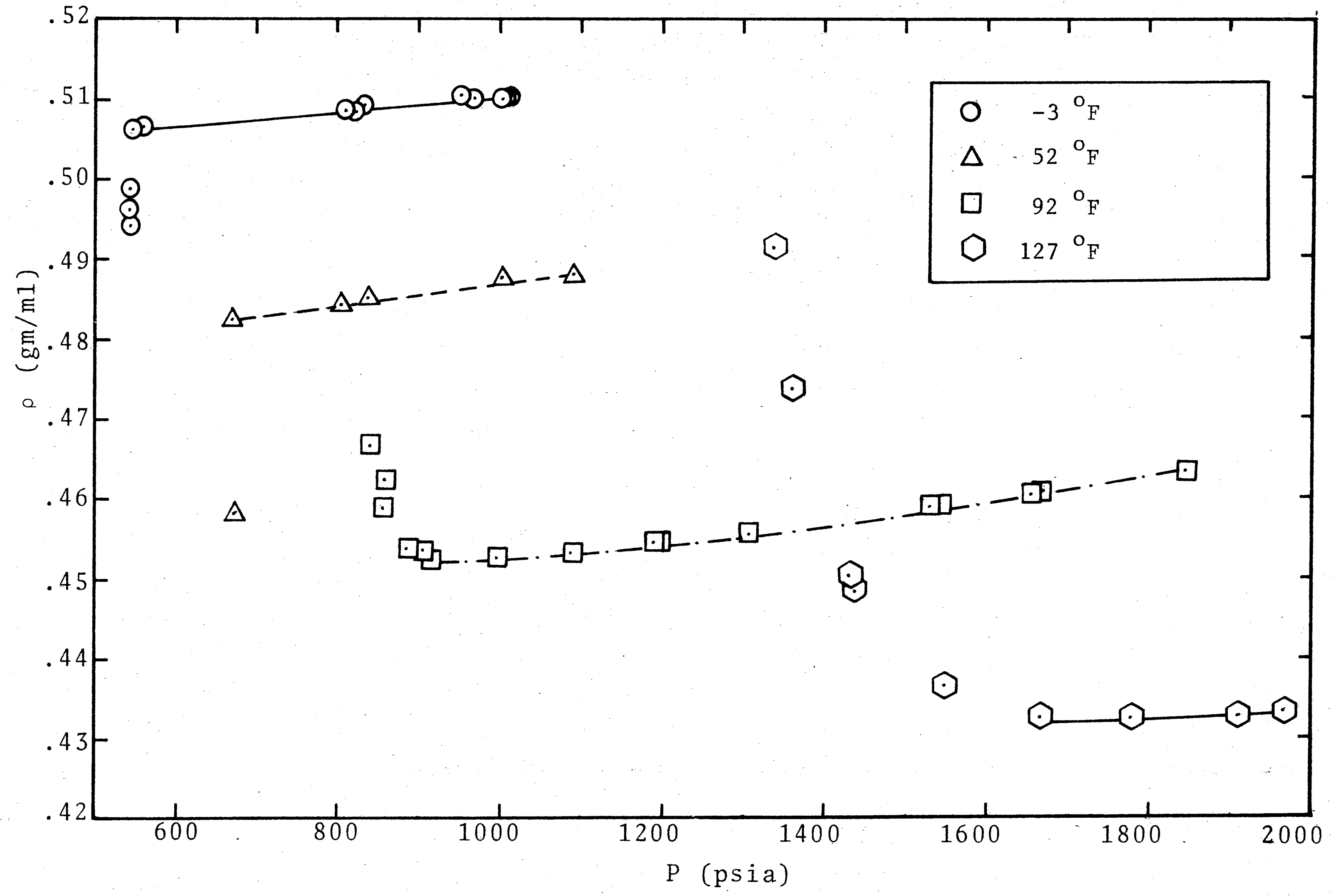

Figure 10. Methane-Propane Data

methane - 69 per cent propane system. The critical temperature of this system was calculated to be approximately 80 ^{o}F. The data appear to follow the predicted shapes for this system.

Figure 11 presents the data taken for the ethylene-propylene system. These data follow the expected pattern and show no anomalies as did the propylene data. In addition Figure 12 presents an isotherm or one data run with the points numbered showing the order in which the data were taken. This gives a good idea as to the reproducibility of the data taken by the vibrating membrane system.

The methanol and octane data were taken by the pycnometric system. Figures 13 and 14 present these data. The data with these systems were taken with a smaller pressure variation than the data taken with the vibrating membrane apparatus. Therefore, these figures are ploted as density versus temperature with pressure as the parameter, rather than as density versus pressure with temperature as the parameter. The data show the expected decreasing density with increasing temperature. The large difference in density between the 465 ^{o}F and 470 ^{o}F points for methanol and between the 375 psia and 360 psia points for octane are to be expected at phase changes and are discused in Chapter VI.

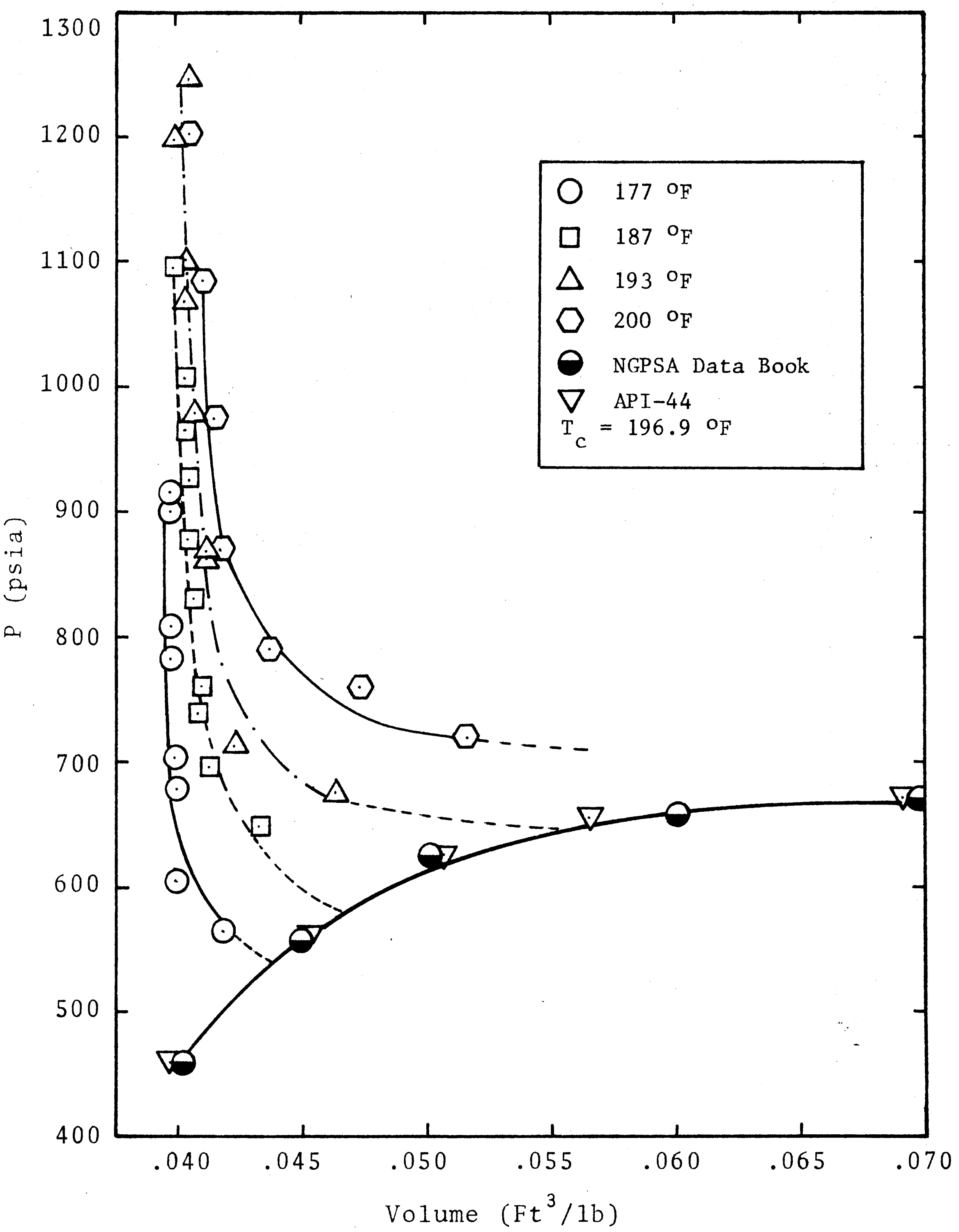

Figure 11. Comparison of Propylene Data with Literature Data

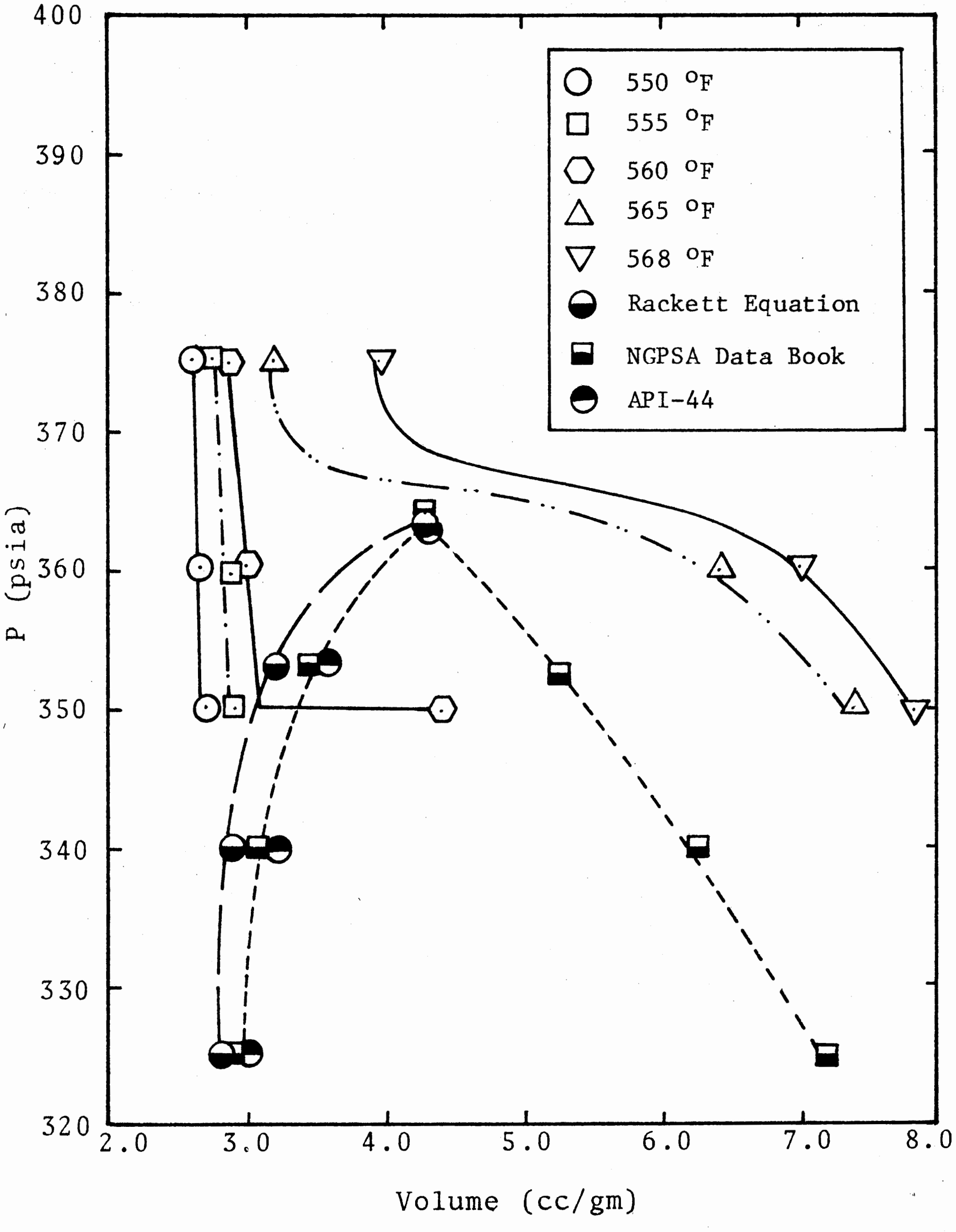

Figure 12. Comparison of Octane Data with Literature Data

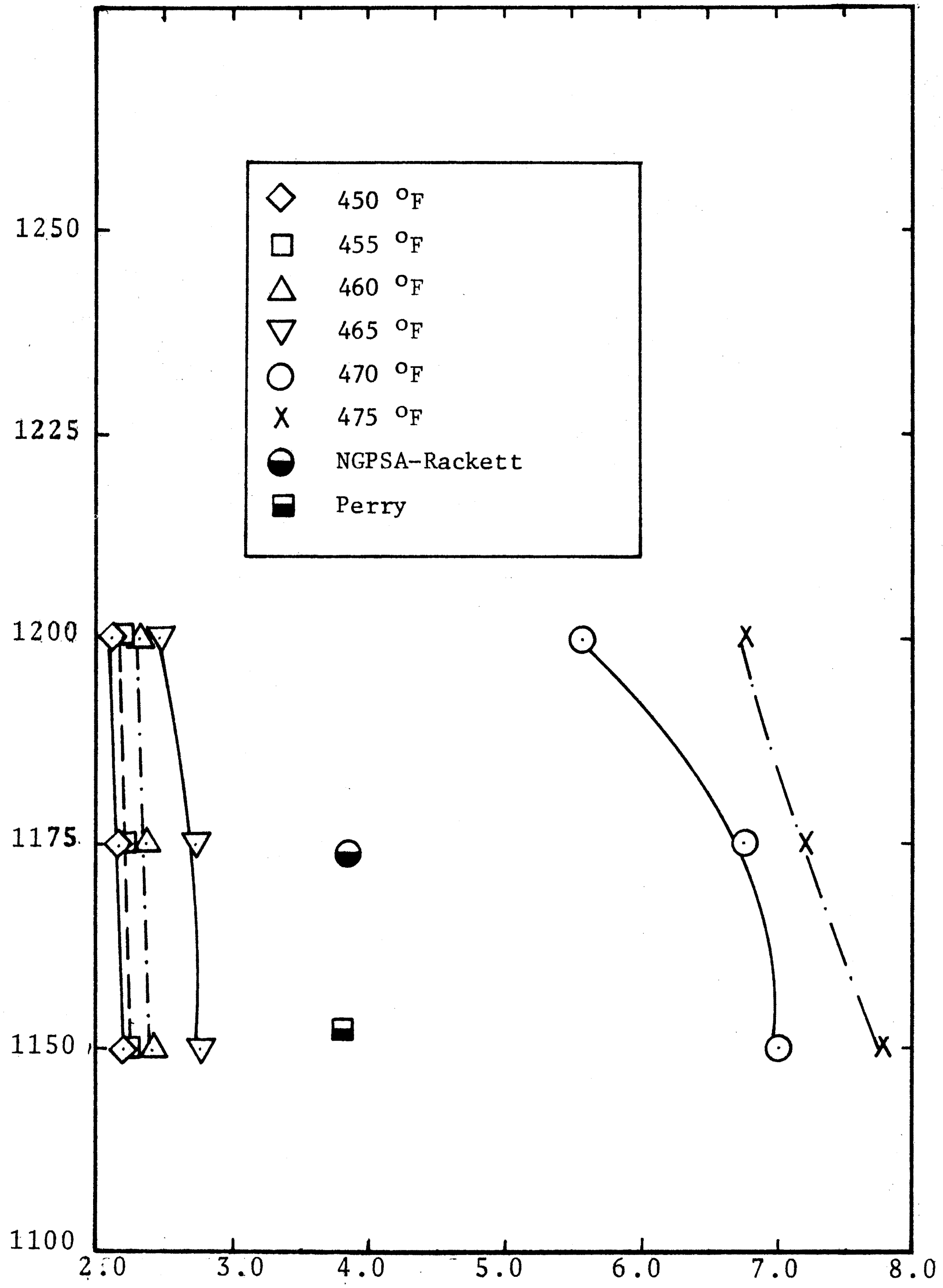

Figure 13. Comparison of Methanol Data with Literature Data

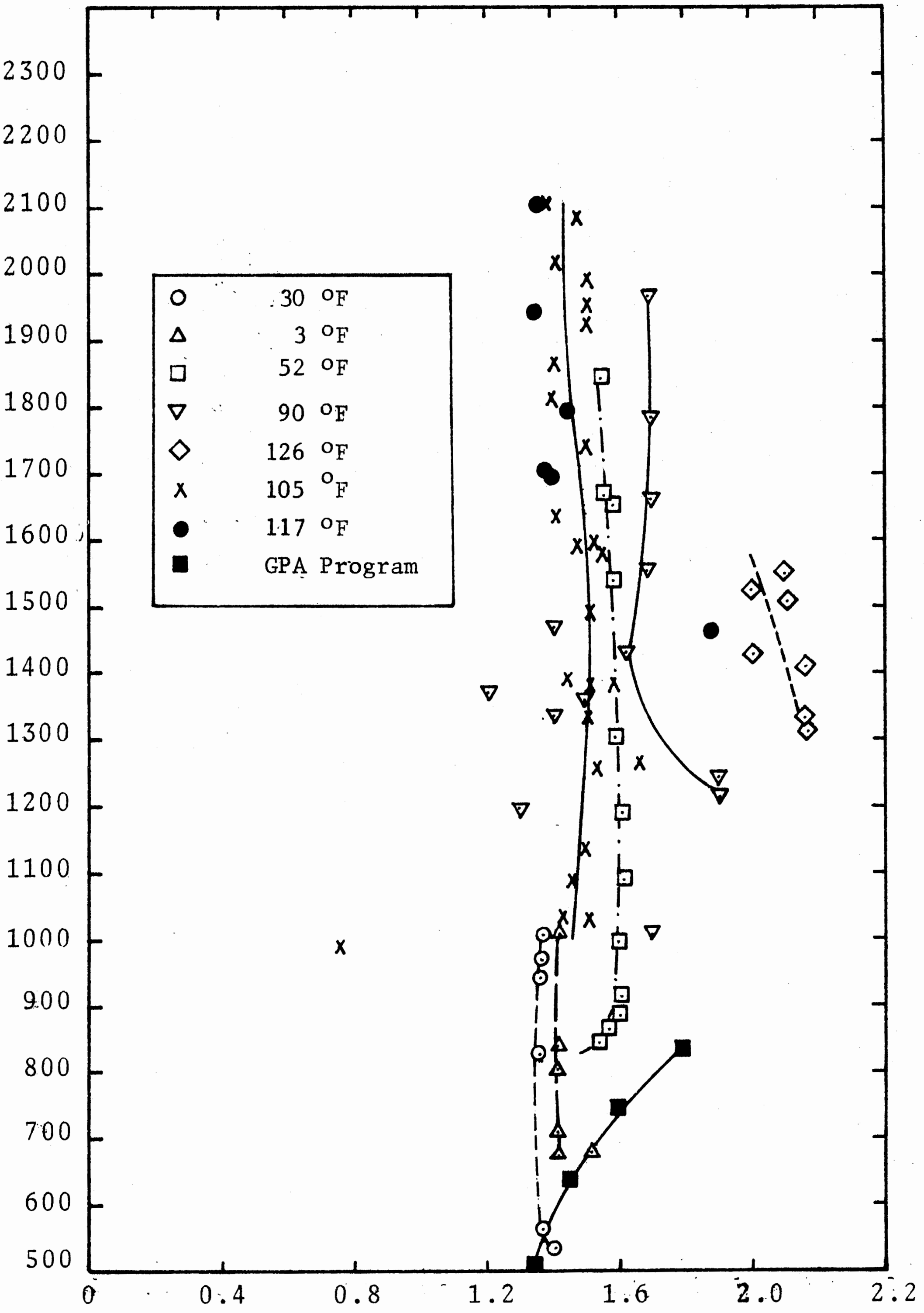

Figure 14. Comparison of Methane-Propane Data in the Critical Region

CHAPTER VI

DISCUSSION OF RESULTS

The systems for which experimental data were obtained were propylene, methanol, octane, methane-propane, and ethylene-propylene.

The pure component propylene is shown in Figure 11. The saturation densities are obtained from the 1972 GPSA engineering data book (8) and API Technical Data Book (2). The data are reasonably well behaved and tend to follow the literature data. These data were taken with the vibrating membrane apparatus and indicate that this system was capable of taking accurate data.

Note that the data for the 177 °F isotherm above 1000 psia are not included. In general, the data from Figure 9 that show a large deviation from a smooth curve are not included. The sharply curved portions of the data in Figure 9 are thought to be equipment malfunctions. However, Kay (18) noted anomalous behavior of ethylene in the critical region such that he suggests ethylene forms a viscous complex in the vicinity of the critical point. This type of behavior could explain the wide variance in density measured by the vibrating membrane, as the vibrating membrane is slightly sensitive to viscosity.

The octane data taken with the pycnometer are shown in Figure 12. Values for the saturated density were calculated by the Rackett (25) equation and read from the GPSA data book (8) and API Technical Data Book (2). These data seem to follow the predicted values. The Rackett values and the GPSA values differ only slightly. However the values of the Rackett equation are perhaps a little better as evidenced by the 560 ^{O}F isotherm. One data point at 560 ^{O}F and 350 psia is in the two phase region. Therefore the vapor pressure at 560 ^{O}F must be 350 psia. Extending the 375 psia and 360 psia points to 350 psia most nearly intercepts the Rackett curve and not the GPSA data.

Figure 13 shows the data for methanol taken by the pycnometer. In addition the critical density is plotted as given by the GPSA data book, with the critical pressure as given by GPSA and by Perry´s (24) data book. The large discrepancy indicates the problems inherent in critical region data. The shape of the data taken is similar to the shape of the octane data and is probably of high quality.

The binary system methane-propane data are presented in Figure 14. These data were taken with the vibrating membrane apparatus during the preliminary stages of this work. The data appear to be fairly precise with the main problem being that the data was not taken close enough to the critical region. Saturation densities obtain from the GPA K&H Mod II (23) computer program are shown. These data agree as closely as can be compared.

Figure 15 presents the ethylene-propylene data taken with the vibrating membrane apparatus. As with the methane-propane system these data were taken at the beginning of the study. No literature data are included in Figure 15 as the experimental data show several discrepancies. For instance the 185 ^{o}F isotherm crosses several isotherms. In addition the 107 ^{o}F isotherm has a larger specific volume than the 129 and 180 ^{o}F isotherms. There is some indication from the raw data that a leak and thus a composition change occured during the taking of this data.

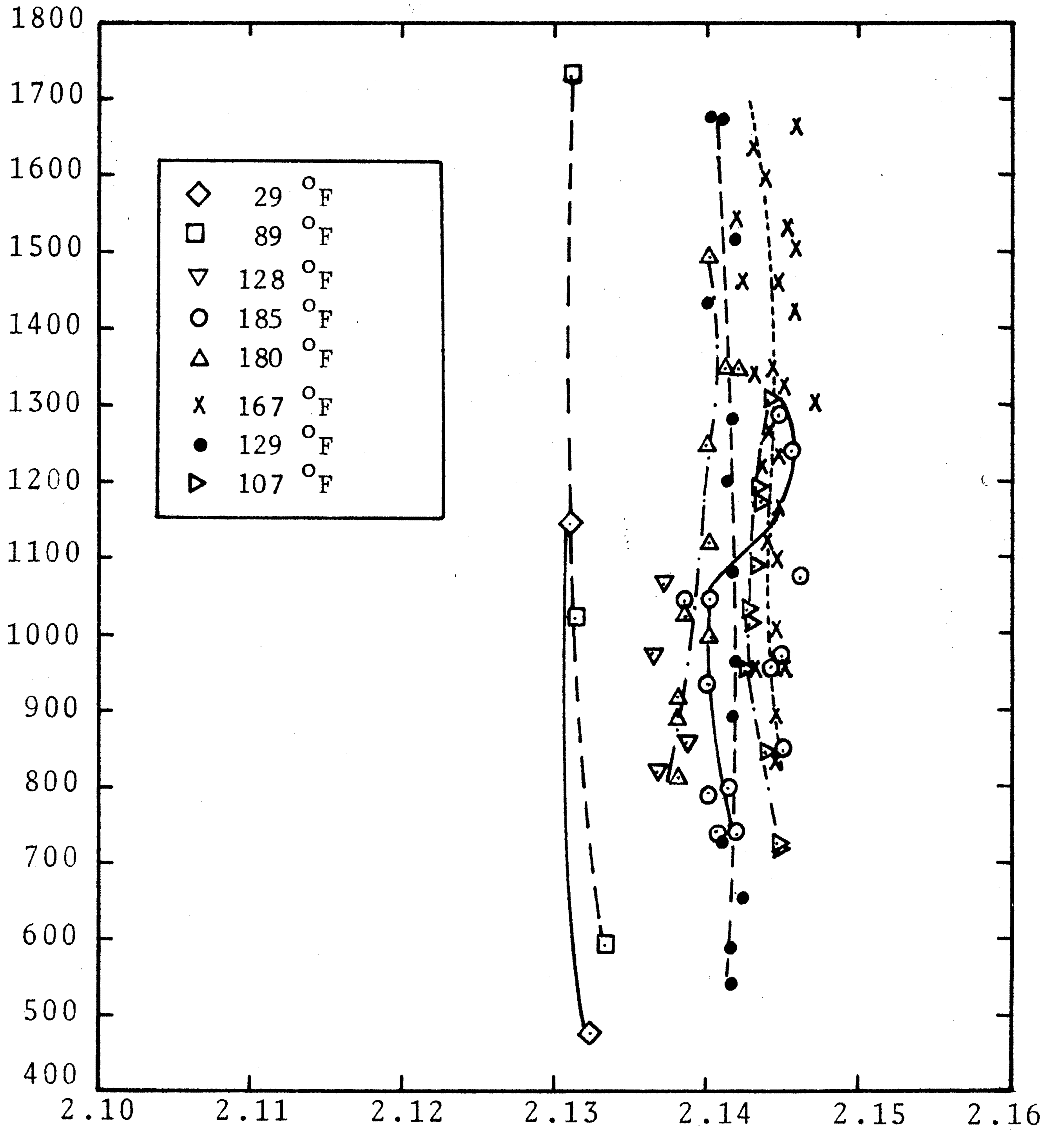

Figure 15. Ethylene-Propylene Volume Meteric Data Near the Critical Region

CHAPTER VII

RECOMMENDATIONS AND CONCLUSIONS

Conclusions

The purposes of this study were:

1) To modify existing density apparatus to be able to measure liquid densities for pure components and mixtures in the critical region.

2) To evaluate the various proposed methods of density determinations to find the most appropriate apparatus and procedure for accurate critical region density.

3) To evaluate the data obtained experimentally and from the literature and compare these data to current available correlations.

Five systems were studied propylene, methanol, octane, methane-propane, and ethylene-propylene. The data for all systems were found to agree well with the available data. The behavior of the data for which there are no literature data to compare does not seem to disagree with any expected behavior in the critical region. The propylene data do seem to undergo some strange behavior in the 1000-1200 psia range as discussed in Chapter V. But this is probably only an equipment problem.

Recommendations

Both sets of equipment used in this study seem to produce reliable results. However the vibrating membrane system is severely limited by the temperature limitation (-50 ^{o}F to 250 ^{o}F). This limitation is a manufacturers limitation and can only be overcome if the manufacturer should produce a different model densitometer.

The pycnometer system is limited by the time required to disconnect the apparatus and weigh the sample. The pycnometer is also limited in the absolute accuracy that can be obtained as shown in Appendix C.

For future density data in the critical region, if the critical temperature is low enough accurate data can be rapidly taken with the vibrating membrane system. For all other data the pycnometer system should provide reasonably accurate data if careful procedures are used.

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APPENDIX A

EXPERIMENTAL DATA

TABLE I

ORIGINAL PROPYLENE DATA

Temperature (^{o}F)	Pressure (psia)	Density (gm/cc)
152.34	1356.66	.47553
152.14	1133.71	.47828
152.34	1128.45	.47864
152.42	1119.10	.47908
152.22	1113.84	.47944
151.53	869.62	.51327
151.53	1354.07	.47802
151.20	1108.80	.47997
151.93	1093.25	.48122
152.22	1087.87	.48176
152.95	1072.92	.48292
152.42	1068.59	.48337
152.22	726.22	.48552
152.22	747.49	.48651
152.42	838.63	.48786
152.26	854.18	.48930
152.10	864.93	.48939
152.18	867.27	.49147
151.85	854.53	.49465
167.17	1258.69	.49274
167.53	1261.61	.49165
166.24	1265.82	.48795
165.36	1294.68	.48750
165.92	1266.64	.48750
163.83	1276.22	.48408
162.62	1281.83	.48337
161.70	1280.66	.48310
162.06	1261.24	.48346
161.82	1266.15	.48364
162.87	1305.52	.48426
165.16	1221.03	.48202
162.95	1037.34	.52163
164.07	1098.66	.51561
164.60	800.92	.44135
162.95	714.10	.42399
162.75	709.54	.42860

TABLE I(Continued)

Temperature (^{o}F)	Pressure (psia)	Density (gm/cc)
162.54	718.31	.42794
170.65	1321.73	.49501
170.73	1322.21	.49520
171.01	927.14	.43274
171.21	927.37	.43332
171.09	938.35	.43465
171.13	945.71	.43783
170.01	662.22	.41803
169.77	601.81	.41803
170.57	846.73	.42080
169.97	796.02	.42761
170.29	788.66	.42736
170.57	984.03	.42333
170.01	981.46	.42407
169.61	981.70	.42440
171.09	1273.01	.49111
170.93	1271.26	.49183
171.01	1271.38	.49202
170.97	1173.57	.51271
171.05	1169.48	.51392
171.09	1166.79	.51392
176.95	1345.81	.49383
175.36	1353.38	.49410
177.30	1136.15	.57189
176.87	1136.04	.57310
177.07	1135.68	.57605
176.71	774.14	.42432
176.95	781.74	.42473
178.06	591.39	.42186
177.82	592.79	.42186
177.94	985.42	.54741
177.11	972.80	.54790
176.75	967.77	.54956
176.95	1405.38	.48122
176.27	1288.30	.48167
175.87	1290.28	.48203
194.72	1640.88	.49084
194.96	1642.40	.49093
194.96	1643.68	.49093
194.88	1462.56	.51645
195.00	1466.42	.51702
195.31	1469.80	.51702
194.80	1284.59	.33321
194.69	1321.87	.47447

TABLE I(Continued)

Temperature (^{o}F)	Pressure (psia)	Density (gm/cc)
194.14	1324.21	.47174
194.72	1331.10	.47121
195.00	1333.32	.47059
195.08	1335.31	.47007
194.84	1336.13	.46980
195.23	1224.18	.44051
194.69	1223.95	.44351
194.41	1030.67	.42719
194.20	1030.78	.42728
194.69	921.64	.42031
194.41	921.41	.42047
194.69	811.78	.42580
195.27	814.70	.42571
195.08	816.22	.42571
194.92	738.05	.42440
194.49	729.40	.42432
194.53	888.32	.42761
194.29	888.90	.42752
193.98	1054.48	.43549
194.26	1052.38	.43582
194.45	1340.54	.50206
194.10	1341.36	.50206
210.41	1625.64	.52182
210.33	1629.50	.52230
209.56	1422.90	.57098
209.41	1419.28	.57523
209.37	1420.10	.57625
209.06	1235.35	.43332
209.76	1235.47	.43437
209.25	1237.10	.43432
209.45	998.03	.43083
209.06	908.14	.43083
209.02	996.39	.43100
207.48	990.90	.43116
208.33	990.90	.43116
202.83	988.79	.43207
210.99	991.48	.43315
210.45	857.80	.43640
210.45	856.17	.43674
210.68	769.11	.43174
210.33	770.75	.43174
210.72	669.79	.43216
210.53	670.02	.43216
208.67	611.24	.43992

TABLE I(Continued)

Temperature (^{o}F)	Pressure (psia)	Density (gm/cc)
209.14	610.54	.43942
209.14	613.46	.44034
211.18	611.95	.44778
211.18	612.18	.44778
210.99	612.18	.44752
210.06	612.30	.44744
211.30	917.86	.49156
210.14	912.61	.48229
209.64	910.50	.47262
209.99	1335.96	.50408
209.91	1338.07	.50417
209.52	1337.01	.50427
202.44	1231.43	.51514
202.40	1231.90	.51533
202.60	1231.90	.51570
202.67	1231.90	.51608
202.60	1230.73	.51683
203.41	1337.65	.51692
202.94	1329.94	.51720
202.63	1328.65	.51758

TABLE II

ETHYLENE-PROPYLENE DATA

Temperature (^{o}F)	Pressure (psia)	Density (gm/cc)
29.16	1146.72	.47147
28.12	475.40	.47112
29.30	488.84	.47112
61.58	1325.27	.47200
88.27	1726.77	.47139
88.79	1016.43	.47130
89.66	586.64	.47103
88.66	585.59	.47086
88.22	585.24	.47095
127.79	857.27	.46980
128.75	977.16	.47024
128.04	818.59	.46998
129.67	1069.83	.47007
128.50	1053.58	.46998
170.73	1766.03	.46930
178.30	1139.00	.46980
179.29	1140.87	.46980
185.42	1205.61	.47007
184.51	1203.62	.47007
182.30	1192.99	.46901
180.40	1126.03	.47007
181.07	1131.99	.46980
179.80	1130.24	.46980
186.33	1040.61	.46989
187.03	1045.76	.46945
186.68	1038.63	.46954
186.13	933.46	.46937
185.85	931.94	.46945
186.05	930.42	.46945
185.42	798.64	.46919
185.38	790.08	.46928
184.51	735.75	.46919
185.06	737.38	.46893
185.10	736.21	.46884
183.84	849.09	.46840
183.72	845.12	.46858

TABLE II(Continued)

Temperature (^{o}F)	Pressure (psia)	Density (gm/cc)
183.25	975.18	.46840
184.08	958.23	.46858
183.72	955.90	.46858
183.64	1077.42	.46814
183.64	1075.20	.46814
184.35	1234.35	.46823
183.84	1286.12	.46849
179.88	1287.69	.46928
180.52	1489.68	.46928
180.44	1345.01	.46901
180.48	1347.70	.46910
180.44	1244.17	.46928
180.32	1244.87	.46919
180.24	1115.40	.46945
180.24	1119.37	46937
180.28	999.24	.46945
180.40	1010.58	.46945
180.40	998.43	.46954
181.03	813.45	.46989
180.64	822.22	.46989
180.24	889.99	.46989
179.45	898.17	.46998
178.89	902.38	.46980
179.37	909.74	.46980
179.01	917.57	.46980
179.49	1020.16	.46980
178.89	1017.13	.46980
168.01	1540.27	.46901
169.49	1552.43	.46901
169.13	1533.26	.46901
169.45	1462.68	.46893
169.45	1452.17	.46875
169.37	1449.48	.46875
169.73	1348.17	.46875
169.77	1341.86	.46849
170.21	1336.60	.46849
170.37	1260.06	.46858
170.29	1115.98	.46858
170.13	1112.95	.46849
170.29	1002.75	.46849
170.21	1000.42	.46849
170.65	885.43	.46849
171.29	885.43	.46858
171.65	835.65	.46849

TABLE II(Continued)

Temperature (^{O}F)	Pressure (psia)	Density (gm/cc)
172.09	833.43	.46840
171.93	830.86	.46849
172.09	950.05	.46875
172.89	949.82	.46884
168.25	1217.18	.46866
168.57	1214.37	.46875
169.53	1635.27	.46875
169.17	1633.87	.46884
167.41	1614.94	.46866
166.36	1591.34	.46866
165.32	1464.67	.46866
166.24	1459.41	.46866
165.76	1348.52	.46858
167.01	1338.94	.46858
166.77	1227.93	.46849
167.01	1218.58	.46849
171.09	1111.66	.46849
171.65	1108.86	.46849
169.17	1099.27	.46849
168.97	1000.65	.46849
168.49	993.29	.46849
167.81	875.97	.46849
167.33	871.41	.46849
171.85	867.44	.46849
173.09	868.96	.46840
168.33	955.55	.46840
168.13	951.57	.46840
175.40	1166.28	.46831
166.48	1165.06	.46840
166.72	1318.14	.46831
166.20	1307.74	.46831
166.12	1302.71	.46823
165.32	1419.57	.46823
163.39	1404.14	.46814
163.03	1524.62	.46831
163.07	1507.79	.46823
164.52	1662.15	.46823
164.80	1664.60	.46823
164.88	1666.12	.46823
132.49	1674.89	.46928
132.24	1670.45	.46919
131.45	1431.13	.46928
131.29	1420.27	.46928
130.66	1194.51	.46910

TABLE II(Continued)

Temperature (^{o}F)	Pressure (psia)	Density (gm/cc)
129.54	1184.11	.46910
129.21	959.63	.46910
129.50	956.13	.46910
128.87	880.53	.46910
128.46	875.50	.46901
129.04	724.18	.46910
128.04	718.92	.46901
127.75	654.53	.46901
127.71	653.95	.46893
128.75	581.97	.46910
129.67	580.68	.46901
131.99	541.65	.46910
129.83	535.69	.46910
130.08	872.46	.46910
130.12	869.07	.46910
129.71	1079.41	.46910
129.54	1074.97	.46901
129.79	1279.34	.46910
129.92	1277.24	.46910
130.12	1516.55	.46910
129.96	1514.80	.46910
107.29	1303.30	.46849
107.12	1302.71	.46849
107.12	1085.02	.46858
107.46	1082.56	.46849
107.50	846.17	.46849
107.80	846.40	.46849
107.80	729.20	.46849
107.89	728.15	.46840
107.93	715.76	.46840
108.01	714.83	.46849
107.93	950.40	.46840
106.82	1029.63	.46831
106.99	1028.93	.46831
107.16	1011.98	.46831
107.20	1189.83	.46823
107.16	1186.33	.46831
106.90	1174.18	.46814

TABLE III

SECOND SET OF PROPYLENE DATA

Temperature (°F)	Pressure (psia)	Density (gm/cc)
177.50	1188.71	.42104
177.82	1323.91	.45213
177.74	1325.31	.45230
177.50	1256.37	.43058
177.86	1132.39	.30937
177.78	1132.62	.39921
177.34	1014.02	.43241
176.91	1014.37	.43249
176.59	901.37	.40420
176.99	903.71	.40420
177.11	783.00	.40333
177.38	784.40	.40341
176.95	679.35	.40079
177.30	603.87	.40151
177.50	703.66	.40127
177.70	807.77	.40389
177.78	809.29	.40381
177.74	919.25	.40381
177.70	917.50	.40389
178.18	1038.21	.42342
178.42	1038.91	.42374
178.69	1178.66	.42893
178.93	1179.13	.42868
179.21	1339.33	.45213
179.09	1337.70	.45221
187.86	1452.24	.46718
187.62	1454.24	.46700
187.55	1340.42	.42580
188.96	1342.17	.42588
187.66	1203.12	.42227
187.62	1204.87	.42186
187.55	1094.56	.40119
187.23	1095.85	.40111
187.15	1006.92	.39977
187.03	925.60	.39772
187.11	834.68	.39473

TABLE III(Continued)

Temperature (^{O}F)	Pressure (psia)	Density (gm/cc)
186.88	784.34	.39317
187.55	697.38	.39819
187.51	740.85	.39340
187.11	739.80	.39340
187.07	730.10	.30371
187.15	734.31	.39379
187.03	876.75	.39614
186.99	967.66	.39898
187.35	1121.21	.40024
182.06	1229.18	.41374
185.85	1316.12	.43349
193.04	1406.51	.44068
193.86	1322.14	.41471
193.71	1222.00	.39827
194.69	1100.12	.39701
193.98	980.70	.39348
192.45	871.44	.39748
192.73	767.44	.39450
192.89	663.79	.45771
192.38	660.52	.44059
192.61	680.04	.39913
193.00	714.16	.37910
191.08	776.56	.39301
195.12	867.12	.39028
195.00	1068.57	.39606
195.23	1198.63	.39929
195.39	1322.96	.41746
200.57	1373.89	.44026
200.34	1313.49	.30575
200.26	1204.70	.39395
200.19	1086.68	.39020
200.19	978.94	.38594
199.56	867.11	.38555
200.30	790.92	.36796
200.73	751.90	.38293
200.15	774.68	.37415
200.81	806.35	.35768
200.92	839.18	.39192
200.30	838.02	.39215
202.48	881.72	.38470
202.48	988.52	.38617
202.60	1120.10	.30121
201.86	1232.16	.39434
201.86	1316.41	.39646

TABLE III(Continued)

Temperature (^{o}F)	Pressure (psia)	Density (gm/cc)
197.85	1264.04	.39732
198.12	1154.31	.39583
198.24	1048.79	.39199
198.28	1049.61	.39293
197.65	927.15	.38849
197.89	825.37	.38772
197.77	757.48	.36826
201.00	946.90	.38486
202.36	840.68	.39137
198.98	788.10	.40923

TABLE IV

METHANE-PROPANE DATA

Temperature (°F)	Pressure (psia)	Density (gm/cc)
-28.78	1001.97	.50945
-28.94	1001.39	.50992
-28.89	1001.62	.51001
-30.07	997.87	.50992
-30.73	530.22	.49805
-30.37	538.87	.49684
-30.27	539.10	.49392
-30.48	556.98	.50658
-30.32	540.50	.50593
-31.09	827.96	.50862
-32.28	810.21	.50815
-31.25	806.12	.50815
-30.99	967.97	.51010
-30.78	951.84	.51010
-30.84	940.73	.51010
2.39	1086.66	.48804
2.93	804.37	.48426
2.73	801.45	.48417
3.03	673.37	.48238
3.03	664.61	.48220
3.22	656.89	.52628
3.17	678.16	.45823
3.32	997.28	.48777
2.50	836.25	.48579
2.78	832.16	.48570
2.00	708.76	.48408
1.90	704.43	.48391
2.29	667.62	.48615
1.75	720.20	.48408
52.14	1845.23	.46369
52.01	1666.10	.46091
51.69	1649.15	.46065
52.60	1536.74	.45892
52.37	1522.36	.45866
52.37	1306.99	.45556
52.24	1192.93	.45427

TABLE IV(Continued)

Temperature (^{o}F)	Pressure (psia)	Density (gm/cc)
52.60	1185.45	.45418
52.97	1085.31	.45315
52.24	1078.41	.45315
52.28	840.96	.46613
52.37	995.91	.45256
52.60	995.32	.45221
52.24	858.13	.46264
52.24	851.23	.45866
52.51	882.90	.45375
52.19	877.98	.45393
53.10	912.81	.45264
52.55	908.83	.45333
91.71	1465.65	.48408
91.23	1370.17	.54477
90.97	1357.89	.47377
90.71	1236.00	.39811
91.10	1008.95	.43265
90.62	1972.18	.43365
90.84	1954.89	.43340
89.57	1777.89	.43265
89.84	1664.19	.43249
90.14	1661.04	.43290
90.18	1547.93	.43607
90.66	1543.85	.43682
90.10	1433.20	.44837
90.27	1430.40	.45033
90.45	1223.38	.39969
90.45	1334.12	.49111
90.40	1195.66	.52135
126.79	1409.89	.36154
126.70	1330.43	.36191
126.41	1306.46	.36161
126.79	1545.16	.38178
126.79	1543.87	.38247
126.45	1527.50	.39028
126.25	1514.64	.39803
126.25	1547.01	.38285
126.96	1546.10	.38324
126.37	1540.35	.38447
126.79	1531.72	.38625
126.62	1522.33	.38772
127.29	1516.41	.38756
126.25	1380.63	.38132
126.71	1513.84	.37872

TABLE IV(Continued)

Temperature (^oF)	Pressure (psia)	Density (gm/cc)
124.07	1462.42	.38432
129.21	2075.89	.42301
128.33	2086.06	.42547
128.33	2069.69	.42563
127.75	1927.12	.42497
105.28	1580.43	.46343
105.07	1470.01	.46160
105.92	1375.58	.46152
105.50	1257.00	.46377
107.46	1987.87	.47350
106.01	2088.15	.47775
105.58	1950.00	.47571
105.97	1031.96	.47553
105.92	1917.54	.47580
105.75	1735.13	.47244
106.05	1596.08	.46980
106.61	1486.95	.46831
106.18	1367.88	.46718
105.67	1250.79	.46656
105.02	1142.71	.47016
106.78	1025.06	.49120
108.95	2078.84	.48346
106.52	1994.75	.48777
104.85	1805.34	.48426
105.37	1589.40	.47962
104.77	1330.69	.47474
106.14	2005.59	.49903
105.67	1858.23	.49720
105.54	1632.24	.49301
105.58	1391.17	.48840
105.11	1387.54	.48876
105.97	1169.95	.48669
105.79	1079.74	.48579
105.11	993.36	.73577
106.05	2105.91	.50381
104.94	2094.23	.50417
116.16	1798.34	.48894
118.86	1460.49	.40401
118.99	2101.66	.50732
117.55	2112.74	.51168
117.01	2109.79	.51168
117.81	1935.66	.51308
116.96	1702.65	.50908
116.96	1691.20	.51405

TABLE V

METHANOL DATA

Temperature (^{O}F)	Pressure (psia)	Density (gm/cc)
450.0	1200	.46576
450.0	1175	.46490
450.0	1150	.45452
455.0	1200	.45498
455.0	1175	.45251
455.0	1150	.44934
460.0	1200	.43073
460.0	1175	.42212
460.0	1150	.41012
465.0	1200	.40467
465.0	1175	.36808
465.0	1150	.35931
470.0	1200	.17875
470.0	1175	.14840
470.0	1150	.14154
475.0	1200	.14709
475.0	1175	.13817
475.0	1150	.12844

TABLE VI

OCTANE DATA

Temperature (^{o}F)	Pressure (psia)	Density (gm/cc)
550.0	375	.37950
550.0	360	.37441
550.0	350	.36650
555.0	375	.36096
555.0	360	.34232
555.0	350	.34090
560.0	375	.34514
560.0	360	.33335
560.0	350	.21076
565.0	375	.31299
565.0	360	.15619
565.0	350	.12883
568.5	375	.25041
568.5	360	.14239
568.5	350	.12158

APPENDIX B

INSTRUMENTATION

INSTRUMENTATION

Thermocouple Calibration

The Copper-Constantan thermocouple used to measure the temperature of the sample and bath were calibrated using a Leeds & Northrup platinum resistance thermometer, a Mueller bridge, and a K-5 potentiometer. The data obtained from this procedure are given in Table VII. A plot such as Figure 16 was used to correct temperature readings.

Transducer Calibration

The Consolidated Electronic Corporation Transducer Model #4-317 (Serial # 8642) was calibrated using a Ruska Model 2400HL dead weight gauge. The manufacturer specified accuracy for this equipment was a minimum of .01 per cent of reading up to 12,000 psia. The data obtained from this procedure are given in Table VIII and ploted in Figure 17. A least squares curve fit was made of this data and was actually used in calculating the pressure. Table IX shows a comparison of the calculated data with the measured data.

The calibration curve for the composition analysis of the ethylene-propylene data is given in Figure 18. These curves were used to evaluate the final composition of the mixtures studied.

TABLE VII

THERMOCOUPLE CALIBRATION

Potential Measured (mv)	Actual Temperature (°F)	Temperature Calculated (°F)	Difference (Act.-Cal.) (°F)
.98988	76.996	76.689	-.307
.99070	77.031	76.689	-.342
1.26771	89.202	88.858	-.344
1.26706	89.175	88.849	-.326
1.64061	105.312	104.985	-.327
1.63953	105.264	104.965	-.299
2.11358	125.290	124.912	-.378
2.11296	125.265	124.930	-.335
2.53879	142.938	142.720	-.218
2.53880	142.938	142.729	-.209
2.98376	161.060	160.889	-.171
2.98316	161.035	160.885	-.150
3.38950	177.300	177.350	.050
3.38899	177.280	177.350	.070
3.81261	193.984	194.572	.588
3.81110	193.926	194.545	.619
4.18645	208.497	210.029	1.532
4.18079	208.274	210.027	1.753

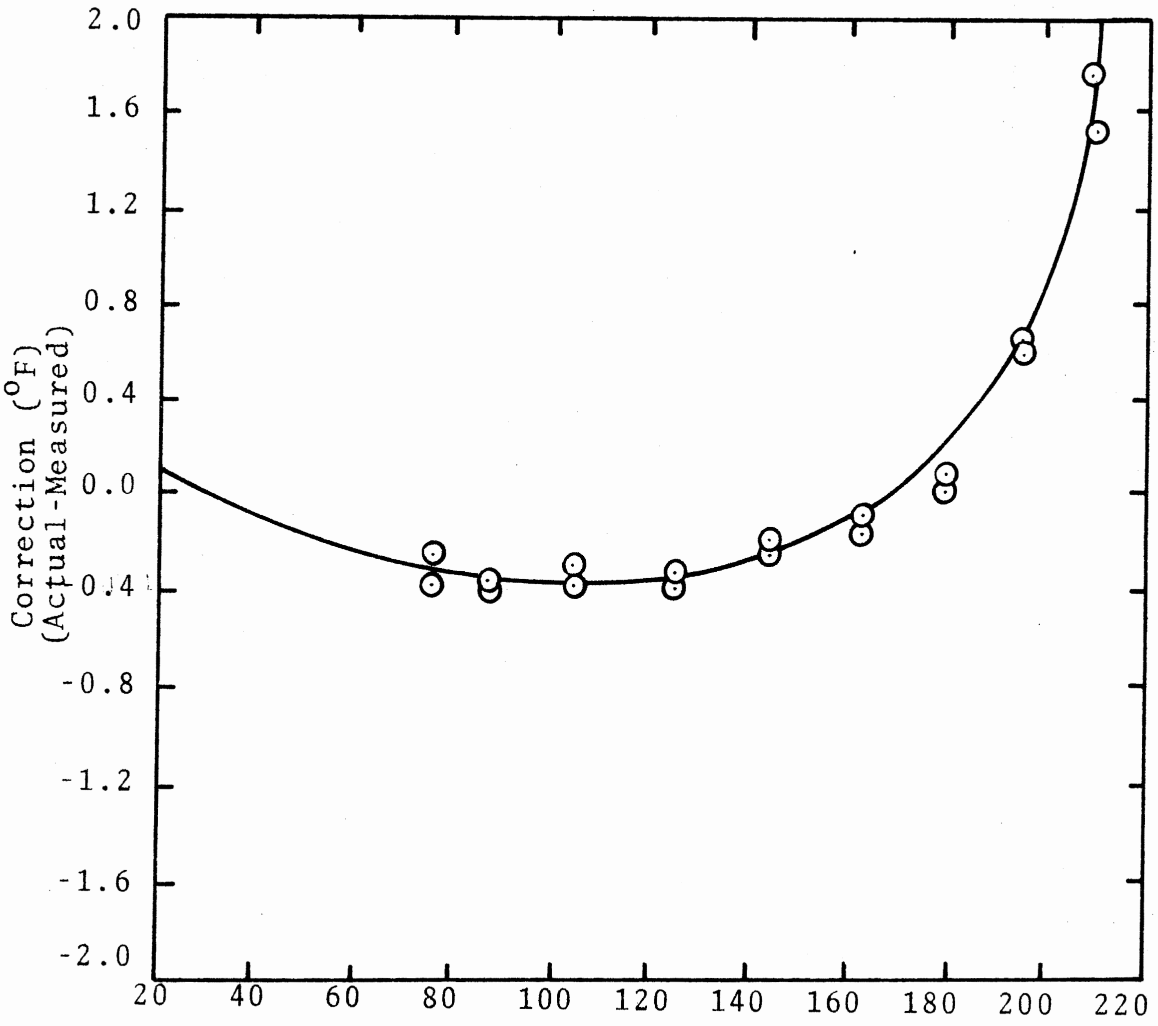

Figure 16. Temperature Correction Curve for Copper-Constantan Thermocouple

TABLE VIII

CALIBRATION OF CEC MODEL 4-317 PRESSURE TRANSDUCER SERIAL NUMBER 8642

Dead Weight Tester (psig)	Null Indicator	Actual Pressure (psig)	Pressure Transducer (mV)
-	-	-	3.86020
26.1+ 3 gm	0	26.612	4.01195
121.7	-20	121.338	4.82184
222.9+ 2 gm	-6	223.154	5.61653
325.5+ 4 gm	-6	326.096	6.42124
430.3	13	430.588	7.24474
528.7	4	528.809	8.01830
629.0	19	629.406	8.80666
730.4	22	730.864	9.60572
833.1	-21	832.716	10.41627
929.3	10	929.529	11.17404
1023.4	-20	1023.038	11.91285
962.5	15	962.828	11.40666
864.4	-4	864.332	10.62285
758.7	4	758.809	9.78004
651.7	-6	651.613	8.94036
553.7	-14	553.454	8.16733
451.4+ 3 gm	-10	1.741	7.36495
355.0+ 2 gm	-1	355.614	6.61412
249.7+ 2 gm	-7	249.934	5.79159
147.1+ 2 gm	-9	147.293	4.98890
47.9	4	48.009	4.21608
-	-	-	3.83925

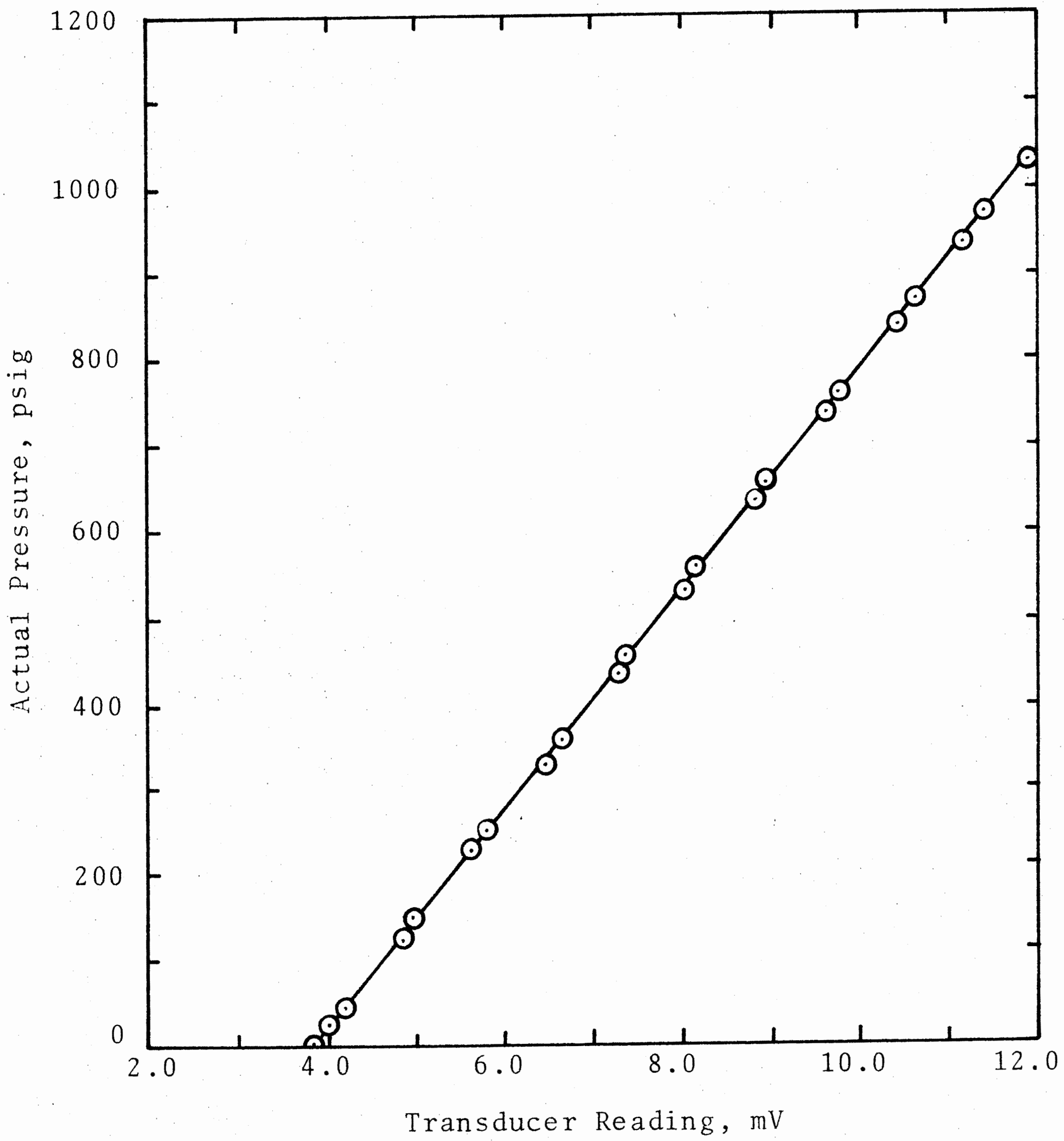

Figure 17. Calibration Curve for CEC Transducer

TABLE IX

COMPARISON OF CALCULATED PRESSURES WITH MEASURED VALUES

Measured Voltage (mv)	Measured Pressure (psig)	Calculated Pressure (psig)	Difference (psig)	Difference (%)
1.06291	0.0	.2	-.2	-100.0
1.29039	23.0	26.7	-3.7	-14.1
2.09794	119.0	121.1	-2.1	-1.7
2.95500	220.0	221.3	-1.3	-.5
3.82398	320.0	322.8	-2.8	-.8
4.71154	421.0	426.5	-5.5	-1.3
5.54654	522.0	524.1	-2.1	-.4
6.39846	621.0	623.6	-2.6	-.4
7.26150	721.0	724.5	-3.5	-.4
8.13460	821.0	826.5	-5.5	-.6
8.95526	920.0	922.4	-2.4	-.2
9.74940	1016.0	1015.2	.7	.0
9.21288	957.0	952.5	4.4	.4
8.37035	856.0	854.1	1.8	.2
7.46672	750.0	748.5	1.4	.1
6.56052	648.0	642.6	53.	.8
5.72674	550.0	545.1	4.8	.8
4.86149	445.0	444.0	.9	.2
4.04871	350.0	349.1	.8	.2
3.16024	249.0	245.2	3.7	1.5
2.29261	148.0	143.9	4.0	2.8
1.45736	49.0	46.3	2.6	5.8
1.05134	0.0	-1.1	1.1	-100.0

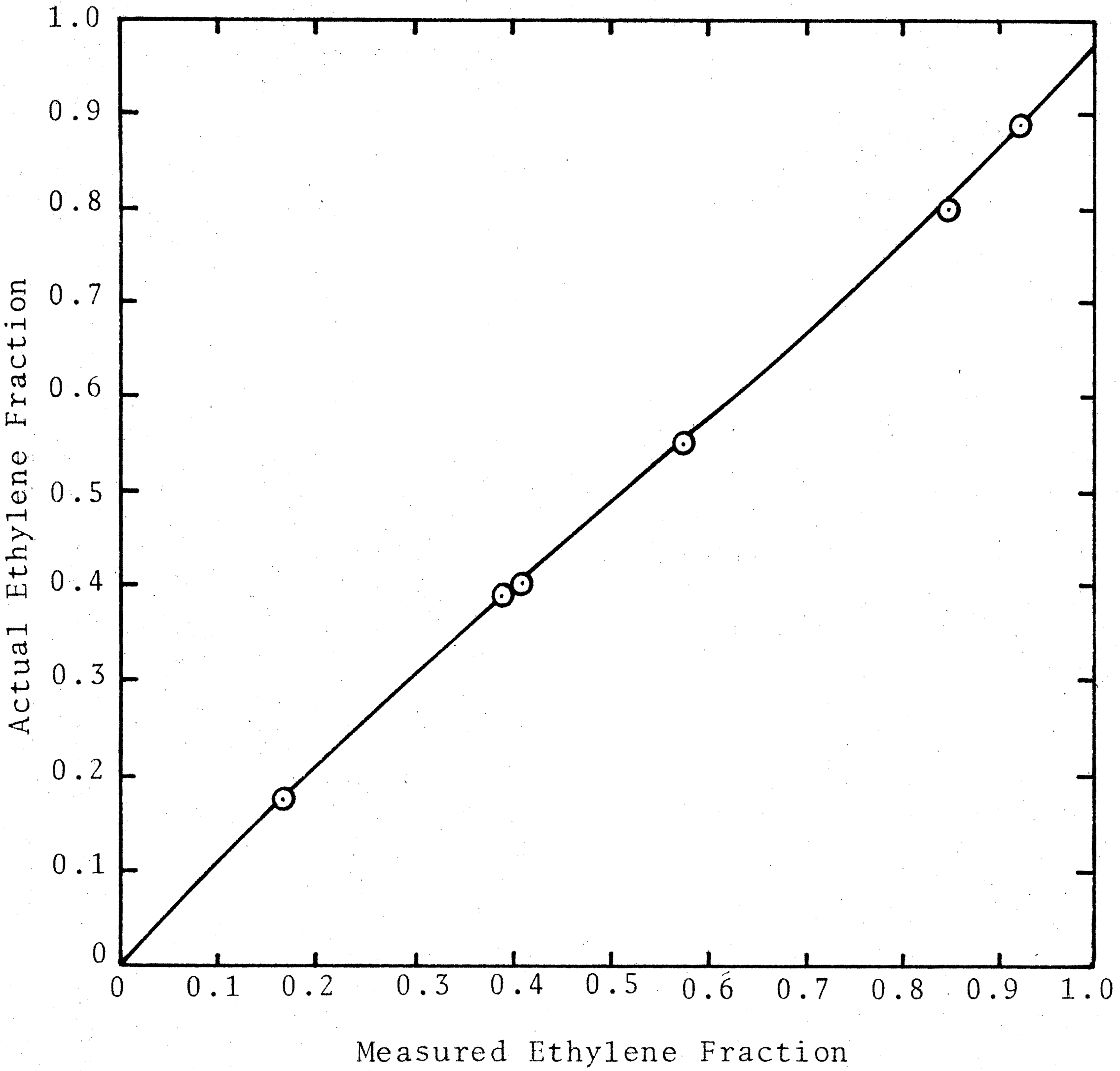

Figure 18. Chromatograph Calibration for Ethylene-Propylene System

APPENDIX C

ERROR ANALYSIS

ERROR ANALYSIS

The limits of the absolute accuracy in the experimental results of the liquid density of the pure components and of the mixtures studied in this work may be established in the following manner. The total error in the density data can be related to the error in each of the variables measured.

The error in the experimental density results from the errors in measuring the variables involved in liquid density determination. For the pycnometer these variables are temperature, mass, volume, pressure and composition. Any error incurred in measuring any of these variables regardless of the accuracy in measuring the others, will cause an error in the density value. If each quantity is measured independently, then the density can be considered to be a function of each of these variables. Mathematically this is represented as shown in equation (25).

$$\rho = \rho\ (t, M, V, P, X) \qquad (25)$$

Differentiation of equation (25) yields:

$$d\rho = (\partial\rho/\partial t)\ dt + (\partial\rho/\partial M)\ dM + (\partial\rho/\partial V)\ dV$$
$$+ (\partial\rho/\partial P)\ dP + (\partial\rho/\partial X)\ dX \qquad (26)$$

The terms held constant in each partial derivative in equation (26) have been omitted for simplicity. All variables are held constant in each partial differentiation except the one that the density is being differentiated with respect to. If the errors in the individual measurements are small then equation (26) can be written as shown in equation (27).

$$\Delta\rho = (\partial\rho/\partial t)\ \Delta t + (\partial\rho/\partial M)\ \Delta M + (\partial\rho/\partial)\ V + (\partial\rho/\partial P)\ \Delta P + (\partial\rho/\partial X)\ \Delta X \qquad (27)$$

Where ΔT, ΔM, ΔP, ΔV, and ΔX are the errors in the individual measurements of temperature, mass, pressure, volume, and composition respectively.

Equation (27) is the general expression which was used to calculate the limits of the absolute accuracy of the experimental liquid density values of the different systems studied in this work. In order to apply this equation, all the terms of the right hand side must be estimated as indicated below.

Estimate of the Partial Derivatives

The Partial Derivative of the Density with Respect to Temperature

This quantity maybe estimated from a knowledge of the liquid density values themselves. Density may be related to temperature for this data by equation (28).

$$\rho = A + Bt + Ct^2 \tag{28}$$

Differentiation of this equation yields:

$$d\rho/dt = B + 2Ct \tag{29}$$

Values B & C for each system maybe obtained by least squares curve fit of the data for a given system.

The Partial Derivative of the Density with Respect to Mass

The density is defined by equation (30):

$$\rho = M/V \tag{30}$$

Differentiation of equation (30) with respect to mass yields:

$$(\partial\rho / \partial M)_{V,P,t,X} = 1/V \tag{31}$$

Because the same pycnometer was used in determining the liquid density of all the systems studied, it is clear from equation (31) that the partial derivative of the density with respect to mass is the same for all the systems.

For this work the volume of the pycnometer was approximately 30 ml. Therefore from equation (31):

$$(\partial\rho/\partial M)_{V,P,t,X} = 1/30 = 0.033 \text{ g/ml-g} \qquad (32)$$

The Partial Derivative of the Density with Respect to Volume

Differentiation of equation (30) with respect to volume yields:

$$(\partial\rho/\partial V)_{M,P,t,X} = -\rho/V \qquad (33)$$

From this equation and for a volume of 30 ml we have:

$$(\partial\rho/\partial V)_{M,P,t,X} = -0.033\rho \qquad (34)$$

The Partial Derivative of the Density with Respect to Pressure

This quantity was also estimated from the knowledge of the liquid density obtained from this work. Density as a function of pressure maybe represented in accordance with equation (35):

$$\rho = a' + b'P + c'P^2 \qquad (35)$$

Differentiation of this equation yields:

$$d\rho/dP = b' + 2c'P \qquad (36)$$

The values for B′ and C′ for each system are shown in Table X.

The Partial Derivative of the Density with Respect to Composition

The effect of impurities on the density of the pure components is assumed to be negligible. Therefore the error in composition, ΔX, for the pure components is considered equal to 0.

Estimate of the Errors in the Individual Measurements

Error in Temperature Measurement, Δt

The accuracy of temperature measurement as shown in Appendix B is approximately ± 0.5% F.

Error in Measuring the Volume, ΔV

The error in measuring the volume is estimated to be $\pm 3 \times 10^{-4}$ ml. This value accounts for 1) the uncertainties in the weights required to determine the volume of the pycnometer at room temperature, 2) the effect of expansion or contraction of the pycnometer, and 3) the uncertainties in the liquid densities used in the calibration in the volume.

TABLE X

CONSTANTS FOR CURVE FITS FOR THE OCTANE AND METHANOL SYSTEMS

Compound	Pres. (psia)	Temp. (^{o}F)	A	B	C	a	b	c
Octane	370	-	-130.90	.4760	$-4.315x10^{-4}$	-	-	-
Octane	360	-	-242.96	.8844	$-8.035x10^{-4}$	-	-	-
Octane	350	-	6.50	-.0070	$-7.555x10^{-6}$	-	-	-
Octane	-	550	-	-	-	-2.187	$1.36x10^{-2}$	$-1.81x10^{-5}$
Octane	-	555	-	-	-	5.838	$-3.11x10^{-2}$	$4.40x10^{-5}$
Octane	-	560	-	-	-	-61.904	$3.38x10^{-1}$	$-4.59x10^{-4}$
Octane	-	565	-	-	-	38.066	$-2.16x10^{-1}$	$3.09x10^{-4}$
Octane	-	568	-	-	-	25.199	$-1.43x10^{-1}$	$2.05x10^{-4}$
Methanol	1200	-	-132.34	.5880	$-6.508x10^{-4}$	-	-	-
Methanol	1175	-	-106.79	.4783	$-5.331x10^{-4}$	-	-	-
Methanol	1150	-	-107.93	.4832	$-5.384x10^{-4}$	-	-	-
Methanol	-	450	-	-	-	-10.314	$1.81x10^{-2}$	$-7.62x10^{-6}$
Methanol	-	455	-	-	-	-0.453	$1.43x10^{-3}$	$-5.60x10^{-7}$
Methanol	-	460	-	-	-	-3.806	$6.78x10^{-3}$	$-2.71x10^{-6}$
Methanol	-	465	-	-	-	30.029	$-5.14x10^{-2}$	$2.23x10^{-5}$
Methanol	-	470	-	-	-	25.219	$-4.34x10^{-2}$	$1.88x10^{-5}$
Methanol	-	475	-	-	-	-1.195	$1.90x10^{-3}$	$-6.48x10^{-7}$

Error in Pressure Measurement, ΔP

The error in measuring the pressure by the CEC transducer was estimated from Appendix B to be ± 0.5 psia.

Error in Measurement Mass, ΔM

The error in measuring the mass of the test liquids is caused by three sources, 1) uncertainties in the weights themselves, 2) the adhesion of liquids to the outside of the pycnometer, and 3) the loss of a minute amount of sample in the valve assembly. The uncertainty from these causes is estimated to be ± 0.05 g.

Calculation of the Limits of the Absolute Accuracy of the Liquid Density Results

Equation (27) was used to calculate the absolute accuracy of the experimental results. For the pure components in the pycnometer the accuracy was calculated to be ± 0.05 to ± 5.0 per cent.

VITA 2

Larry Lee Lilly

Candidate for the Degree of

Doctor of Philosophy

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Biographical:

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Education: Graduated from Memorial High School, Tulsa, Oklahoma, in May, 1967; entered undergraduate engineering program at Oklahoma State University, Stillwater, Oklahoma in September, 1967; received Bachelor of Science Degree in Chemical Engineering from Oklahoma State University in May, 1972; received Master of Science Degree at Oklahoma State University in July, 1973; completed requirements for Doctor of Philosophy Degree, May, 1978.

Membership in Scholarly or Professional Societies: Omega Chi Epsilon, associate member of National A.I.Ch.E.

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