

DEVELOPMENT OF APPARATUS TO
MEASURE DENSITY OF
LIQUID MIXTURES

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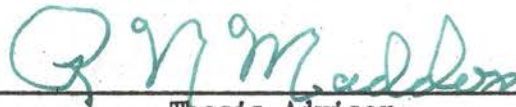
1971

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in Partial fulfillment of the requirements
for the Degree of
MASTER OF SCIENCE
July, 1973

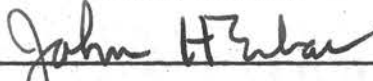
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Thesis Approved:



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PREFACE

Two complete systems for the measurement of saturated and subcooled liquid densities were designed. These two systems were employed to measure the density of three pure component systems; water, ethane, and propane.

I wish to express my gratitude to Dr. R. N. Maddox for the guidance provided by him as my thesis adviser. I would like to thank Drs. John H. Erbar and R. L. Robinson for their words of encouragement. I would especially like to thank Dr. K. J. Bell for the financial support from his projects and my wife, Dorothy, for her understanding and perserverance.

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LIST OF SYMBOLS

Major Symbols

English Letters

A and A'	- constant in density equations 17 and 18
a	- constant in density equation 7
b	- constant in density equation 7
B	- constant in density equation 19
C and C'	- constant in density equation 17 and 18
E	- error in composition
f	- frequency
H	- thickness of probe membrane
L	- length of probe membrane
M	- total mass in System
Mw	- molecular weight
V	- volume
W	- weight
X	- molar concentration liquid phase
Y	- molar concentration vapor phase

Greek Letters

- β - coefficient of thermal expansion
 ρ - density

Subscripts

- a - air
c - recorded by Cahn Electrobalance
L - liquid phase
M - membrane
N - New
P - plummet
X - liquid phase composition
One - Plummet 1
Two - Plummet 2

CHAPTER I

INTRODUCTION

The physical property density, whether for a mixture or pure component, is required in most engineering design calculations and correlations for prediction of physical properties. 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.

The purpose of this study was to design an apparatus that could be used to determine saturated liquid densities accurately over wide conditions of temperature and pressure. To achieve this purpose two density cells were designed. One consisted of a Cahn Electrobalance and used Archimedes principle for the measurements. The second consisted of an ITT Barton densitometer which measures density by a vibrating membrane technique.

Three pure component systems were studied: water, ethane, and propane. Only saturated densities were taken on the water and propane systems but subcooled liquid densities were also taken on the ethane system. The data show that both systems, with slight modifications, give accurate results. However, the vibrating membrane system was much easier to operate and was therefore the system used to take most of the data of this study.

CHAPTER II

REVIEW OF PREVIOUS WORK

Many researchers have designed apparatus for the determination of liquid densities. Many more researchers have used these apparatus to measure liquid densities of varying degrees of accuracy. This chapter is not intended to be an exhaustive study of all density apparatus but a survey of the more important methods currently in use and their reported limitations.

Pycnometers

The pycnometer was the first density measuring device designed and still one of the most popular. Ordinary pycnometers can be used to obtain density values correct to 1×10^{-5} by the use of large pycnometers and careful work (22).

The standard procedure for obtaining liquid densities via pycnometric methods is to weigh the evacuated pycnometer. Then fill the pycnometer to the specified level with test liquid, thus introducing a known volume of test liquid into the pycnometer. The pycnometer is again weighed with the test liquid. The weight of the test liquid and the volume occupied give the density of the test liquid directly. One of the advantages of the pycnometer is that it is a method of measuring absolute density rather than relative density. The temperature of the

pycnometer must be rigidly controlled during the filling of the pycnometer to the specified volume to obtain accurate densities. In addition the pycnometer must be kept as cool as the filling temperature during the weighing step to keep from bursting the pycnometer by the expansion of the test fluid.

Shraiber and Kukolenko (18) used a pycnometer of their own design to obtain densities of several salt solutions of water to a reported accuracy of $\pm 2 \times 10^{-5}$ gm./cm.³. Their pycnometer had a liquid volume of approximately 30 cm.³. Shraiber and Kukolenko used a temperature control system capable of temperature control of ± 0.001 °C.

One disadvantage of the pycnometer method is the large number of time consuming accurate weighings that must be made. Tomlinson (23) partially solved this problem by using what he called the isochor method. This method modifies the standard procedure for pycnometers as follows. The pycnometer is weighed empty and full as before but not at each temperature that a data point is desired. Instead after each loading of the pycnometer several temperatures and pressures are measured all at the same weight and volume of test liquid and thus the same density. The pycnometer is then loaded with a different weight of test liquid and the procedure repeated.

Tomlinson (23) using the above procedure studied mixtures of ethane and propane to include the pure components from 40 °F to 100 °F. The data of Tomlinson agree well with other data (19,20) and has an apparent accuracy of better than 0.1% and a precision of better than 0.01%. Reference should be made to the fact that Tomlinson makes no claim as to the accuracy or precision of his data and the values stated above

are inferred by this author from the data presented by Tomlinson (23).

As indicated pycnometers can be used to determine accurate liquid densities. However, the use of pycnometers is usually restricted to limited ranges of temperature and although accurate PVT data, including densities, up to critical temperatures and pressures, are obtained by means of a steel pycnometer and volumenometer in the Beattie apparatus (4) considerable manipulative skill and experience are required for operation of the complex equipment.

Disadvantages of the pycnometer are: 1) The heavy weights required to be measured usually force the balance used 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 surface often absorbs moisture causing inaccurate measurements. 4) As previously noted the pycnometer is difficult to use at a temperature far from ambient.

Dilatometers and Other Constant Weight Apparatus

Dilatometers, like pycnometers, are usually restricted to limited ranges of temperature (8). Dilatometers have been designed to measure changes in density with an accuracy of $\pm 2 \times 10^{-6}$ gm./ml. and an absolute accuracy of $\pm 1 \times 10^{-5}$ gm./ml. (6). The principle of the dilatometer is essentially the same as the pycnometer. However, the dilatometer maintains a constant weight and varies the volume. The dilatometer suffers from the same disadvantages of the pycnometer when used for absolute measurements of density but can be considerably more accurate in measuring small changes in relative density.

Sage and Lacey (16) presented an apparatus designed to measure densities of hydrocarbons at pressures up to 10,000 psia and at temperatures between 0 ° 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. Using this apparatus on a natural gas-oil mixture Sage and Lacey claim an accuracy of 0.5%.

Numerous variations on the basic dilatometer approach have been tried. Typical is the modification used by Gibson and Loeffler (8). Their apparatus was similar to Sage and Lacey (16) 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 then calculated the amount of mercury and thus the volume of mercury left inside the test cell.

Gildseth et al. (6) developed a dilatometer for the measurement of the density of pure water. This apparatus was capable of measuring the volume of the contents of the dilatometer to about $\pm 1 \times 10^{-4}$ ml. Temperature was controlled and measured to within ± 0.001 °C over the entire range of 5-80 °C. Gildseth claims an accuracy of 5×10^{-6} gm./ml. for all of his recalculated data and a precision for his raw data of 2×10^{-6} gm./ml. The recalculated data merely adjusts his data to the standard water density at 4 °C of 1.0000000 gm./ml. This amounted to a change of approximately 13×10^{-6} gm./ml.

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 immersed. From some type of 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 (7) used the Archimedes' bob method. In their apparatus the buoyancy of the bob is measured by measuring the extension of the quartz helical coil the bob is suspended from. With this apparatus the authors claim an accuracy of .033% for measuring liquid nitrogen and oxygen from 80 °K to the critical temperature.

One problem of the Archimedes' bob method as used above and by many authors is that the bob 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. (22) 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. Using this procedure the authors were able to obtain densities of potassium dichromate solutions to an accuracy of 0.5×10^{-6} gm./ml.

One disadvantage of the temperature of floatation method 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 (9) seems to eliminate the problems 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 height 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. Lamb and Lee calculate this method can be used to measure the density of water to an accuracy of 3×10^{-7} gm./ml. Senter (17) used a modification of Lamb and Lee's apparatus to measure salt solutions to an accuracy of 1×10^{-7} gm./ml. However, most of his measurements were only accurate to 1×10^{-6} gm./ml. since this precision required temperature control of ± 0.005 °C. Beams and Clarke (1) also used a modification of the apparatus of Lamb and Lee to measure protein samples of .2 cm.³ of liquid to an accuracy of ± 0.0001 gm./ml.

Hales (8) has presented a detailed description of the magnetic float method he used. The apparatus he designed can be used to measure densities from 0.7 to 2.9 gm./ml. at temperatures from 20 to 150 °C and pressures up to 700 kN/m². Using this apparatus to measure the density of benzene and hexafluorobenzene an accuracy of $\pm 50 \times 10^{-6}$ gm./ml. was achieved.

The main disadvantage of the magnetic float method is that some method must be used to sense the height of the float in the test liquid. This is often done by the use of photocells, but sometimes magnetically. Both methods lend themselves to systematic errors and the need for calibration frequently.

CHAPTER III

EXPERIMENTAL APPARATUS

Two complete systems were designed for the measurement of densities. One consisted of a Cahn Electrobalance and used Archimedes principle to measure density. The second consisted of an ITT Barton densitometer which used a vibrating membrane to measure density. For ease of presentation the equipment can best be discussed with reference to the four intensive properties which this study is concerned with; temperature, pressure, density, and the composition of the system.

Temperature Measurement and Control

Both systems were equipped with the same equipment for temperature measurement and control. All descriptions in this section apply to both systems unless specifically stated otherwise.

Temperature measurements were made by the use of copper-constantan thermocouples measured by the use of a Leeds and Northrup model K-5 potentiometer or by a Leeds and Northrup model 8686 potentiometer. The potentiometer used for any particular data set is given in Appendix A with the raw data.

The K-5 potentiometer is capable of measuring potentials to within a temperature equivalent of 0.025°F while the 8686 potentiometer is capable of measuring potentials to within a temperature equivalent of 0.08°F for all temperatures of this study.

For the initial data the temperature of the system was controlled by a BLU-M (model number MR-2416A serial number RR-721) constant temperature bath capable of maintaining a temperature constant to within ± 0.5 °F. Due to the large temperature variations of the BLU-M bath, later runs were controlled by a Hallikainen (Model 1053A) temperature controller capable of temperature control to within ± 0.1 °F.

Pressure Measurement and Control

All data taken with the Electrobalance System were at atmospheric pressure, so all comments of this section pertain only to the vibrating membrane system.

Pressure was measured with a Ruska dead weight gauge (catalogue number 2400HL serial number 10381) capable of measurement of pressure to ± 0.1 psi. Due to a lack of care with the system the actual pressure measurements for this study were accurate to approximately ± 2 psi.

Pressure was controlled by using a Ruska hand pump (catalogue number 2426.1 serial number 10509) to remove or add mercury to the system as shown in Figure 1 to change the effective volume and thus the pressure of the subcooled liquid system.

Composition

All data for this study were taken on pure components. The ethane and propane used were Phillips Petroleum Company pure grade 99 mole % minimum purity. The water used was singly distilled obtained locally.

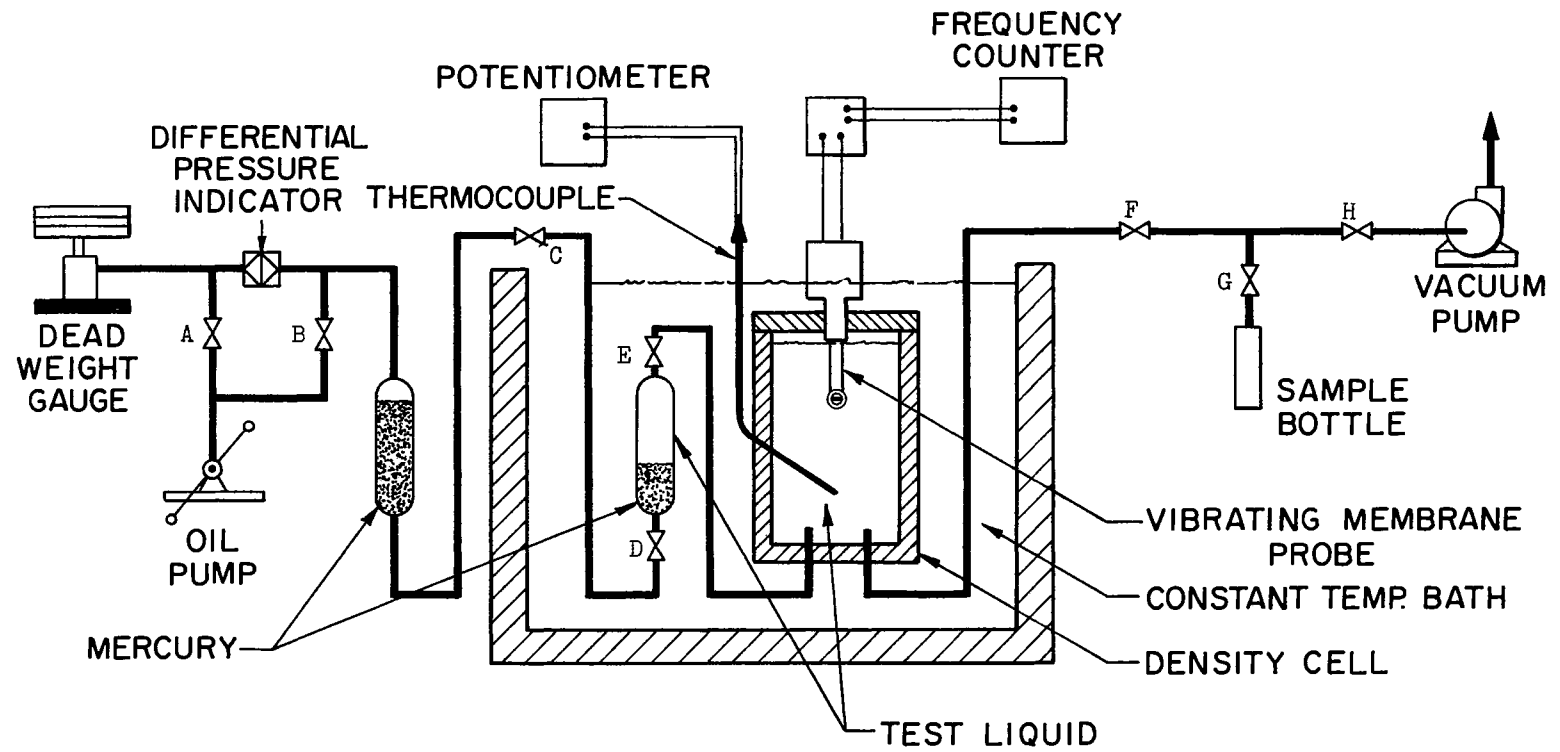


Figure 1. Overall Diagram of Vibrating Membrane Apparatus

Density Measurement by Cahn Electrobalance

The first system constructed consisted of a Cahn Electrobalance model RG with a Cahn Density Cell (model number 2700) attachment. The Electrobalance is based on the null-balance principle. The balance arm of the Electrobalance is connected to a flag that is positioned between a light source and a phototube. The movement of the balance arm changes the amount of light striking the phototube by changing the position of the flag between the light source and phototube. The phototube current is proportional to the amount of light striking it and thus proportional to the weight on the balance arm. However, the procedure of the Electrobalance is to adjust another current applied to a coil attached to the balance beam so that the balance beam will return the flag to the original position and therefore the phototube current to its original value. Thus the restoring force exerted by the electromagnetic coil is exactly equal to the change in weight of the sample and the balance arm is maintained in dynamic equilibrium. This restoring force is directly proportional, by Ampere's law, to the current producing it. This current is the actual signal that is measured by the circuitry of the electrobalance.

The system used for atmospheric measurement is shown in Figure 2. The system designed for high pressure and temperature measurements is shown in Figure 3. Although the system shown in Figure 3 has not been completely tested the principles and feasibility were proven with the system shown in Figure 2.

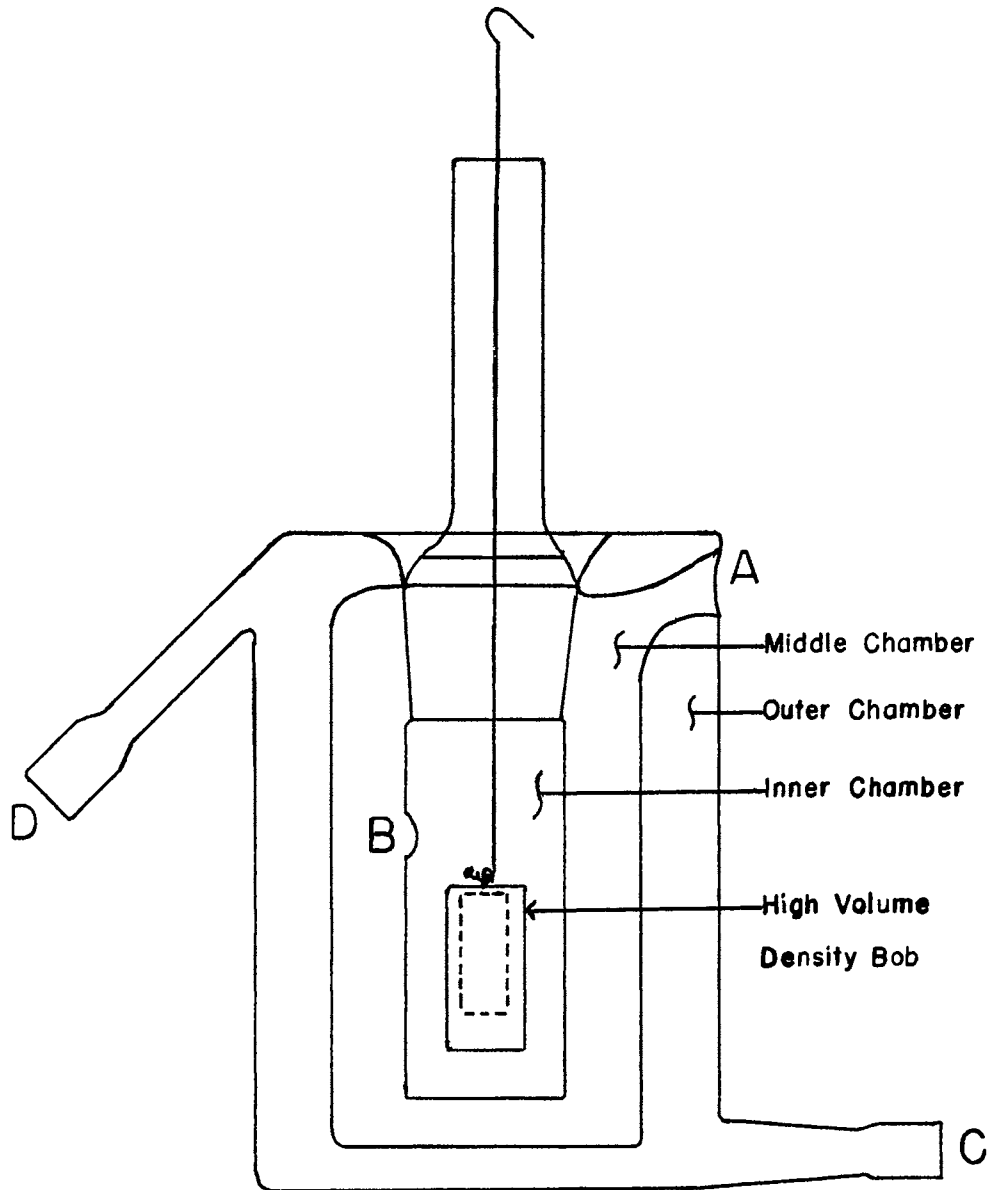


Figure 2. Atmospheric Pressure Cell for Cahn Electrobalance Apparatus

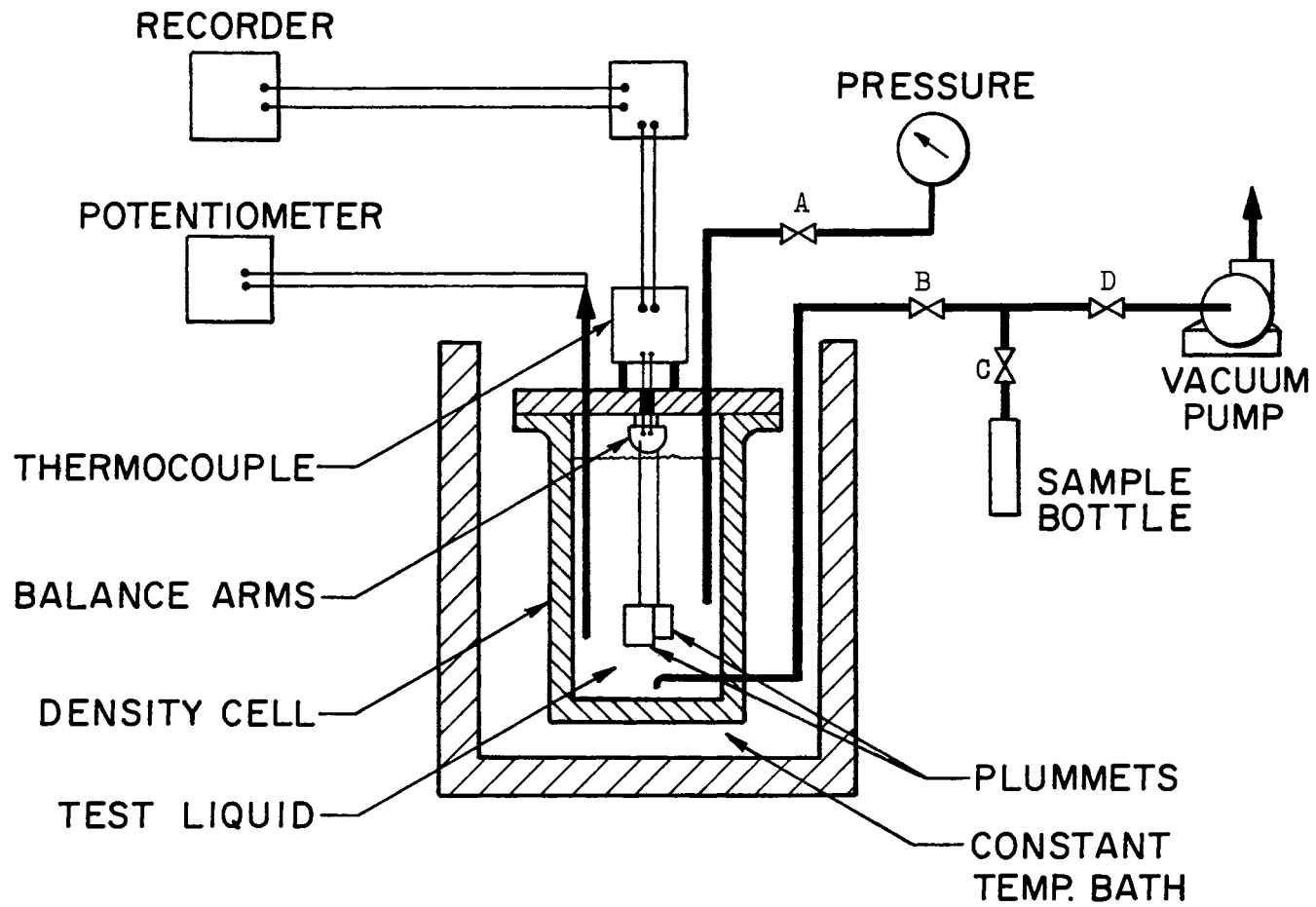


Figure 3. Overall Diagram of High Pressure Cahn Electrobalance Apparatus

The system shown in Figure 2 consisted of a Cahn (model number 2879) high volume Plummets immersed in the test liquid. The test liquid was introduced into the middle chamber by an eyedropper inserted in opening A. The middle chamber was filled with the test sample until the level reached opening B. The inner cell was then filled by continual addition of sample to the middle cell through opening B. Constant temperature water was circulated through the outer cell to maintain a constant temperature in the inner cell filled with the test liquid.

The system shown in Figure 3 consisted of the same Cahn equipment as above with the addition of one number 2879 Plummets. The additional plummet is required since the high pressure operation this system is designed for would forbid the addition of counterweights to the balance arm during operation. As shown in Appendix B, with the addition of this plummet the system can still be used as above with only slight modification of the working equation.

A cell was designed to contain the balance arm of the Cahn Electrobalance as shown in Figure 4. This cell was made from 304 stainless steel and designed for a maximum operating pressure of 3000 psia with a 5 to 1 safety factor. The glass rods are designed to be Welch Allyn fiber optics capable of conducting the light necessary for the operation of the balance arm into and out of the cell. This permits the phototube and light source, which are both designed for only moderate pressures, to be removed from the high pressure region. The windows are fused quartz lenses $\frac{1}{2}$ inch by $1\frac{3}{4}$ inch outside diameter. The cell as shown was designed for a liquid controlled multicomponent system, i.e. the

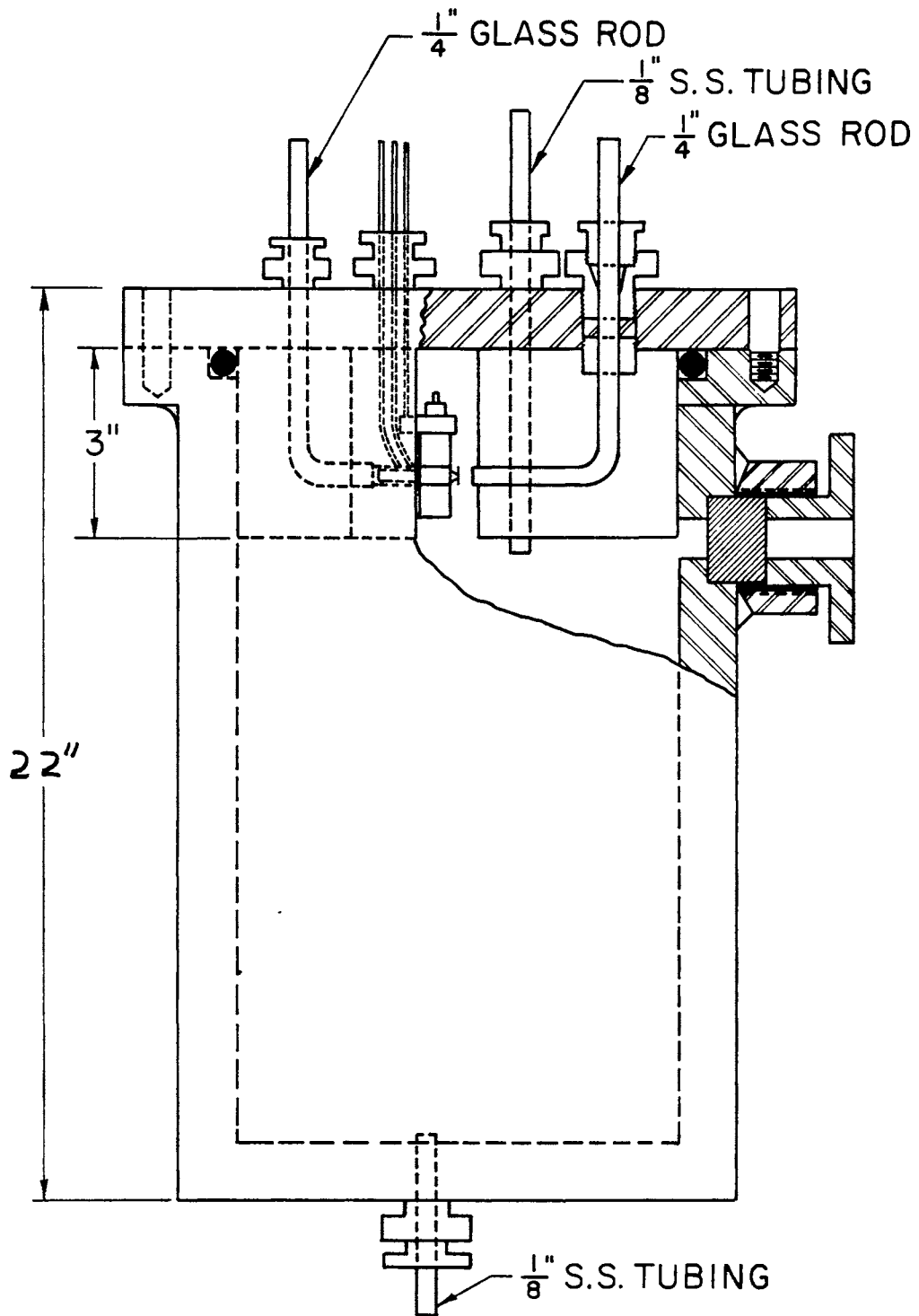


Figure 4. High Pressure Cell for Cahn Electrobalance Apparatus

vapor volume is small enough to keep from changing the composition of the liquid by the vaporization of the light component. The calculations of the liquid to vapor volume ratio required for this condition are shown in Appendix B.

Density Measurement by Vibrating Membrane

The second system consisted of an ITT Barton series 650 densitometer for the measurement of density. The densitometer and transmitter used were model number 662 and model 652 respectively.

A vibrating membrane technique is used to measure the density of the test fluid by this system. This membrane is magnetically vibrated causing an acceleration of the test fluid. The fluid in turn inertially loads the vibrating membrane thus contributing to the effective mass and changing the resonant frequency of the membrane. The transmitter measures the resonant frequencies and produces two outputs; an analog signal that assumes equation 18, developed in Appendix C, is valid and a digital frequency signal nonlinearly related to density which is the resonant frequency at these conditions.

The density probe was inserted into a test cell as shown in Figure 5. The test cell was designed for a maximum of 3000 psi with a 5 to 1 safety factor. The test cell was made from 304 stainless steel. The bolts are $\frac{1}{2}$ inch national fine threads 2 $\frac{1}{2}$ inches long. The probe threads are 1 $\frac{1}{4}$ inch normal pipe threads.

The density probe is capable of application in pressures up to 1200 psig and temperatures from -30°F to $+250^{\circ}\text{F}$. The density probe has a temperature sensitivity of $0.00006 \text{ gm./cc. }^{\circ}\text{F}$ and a maximum

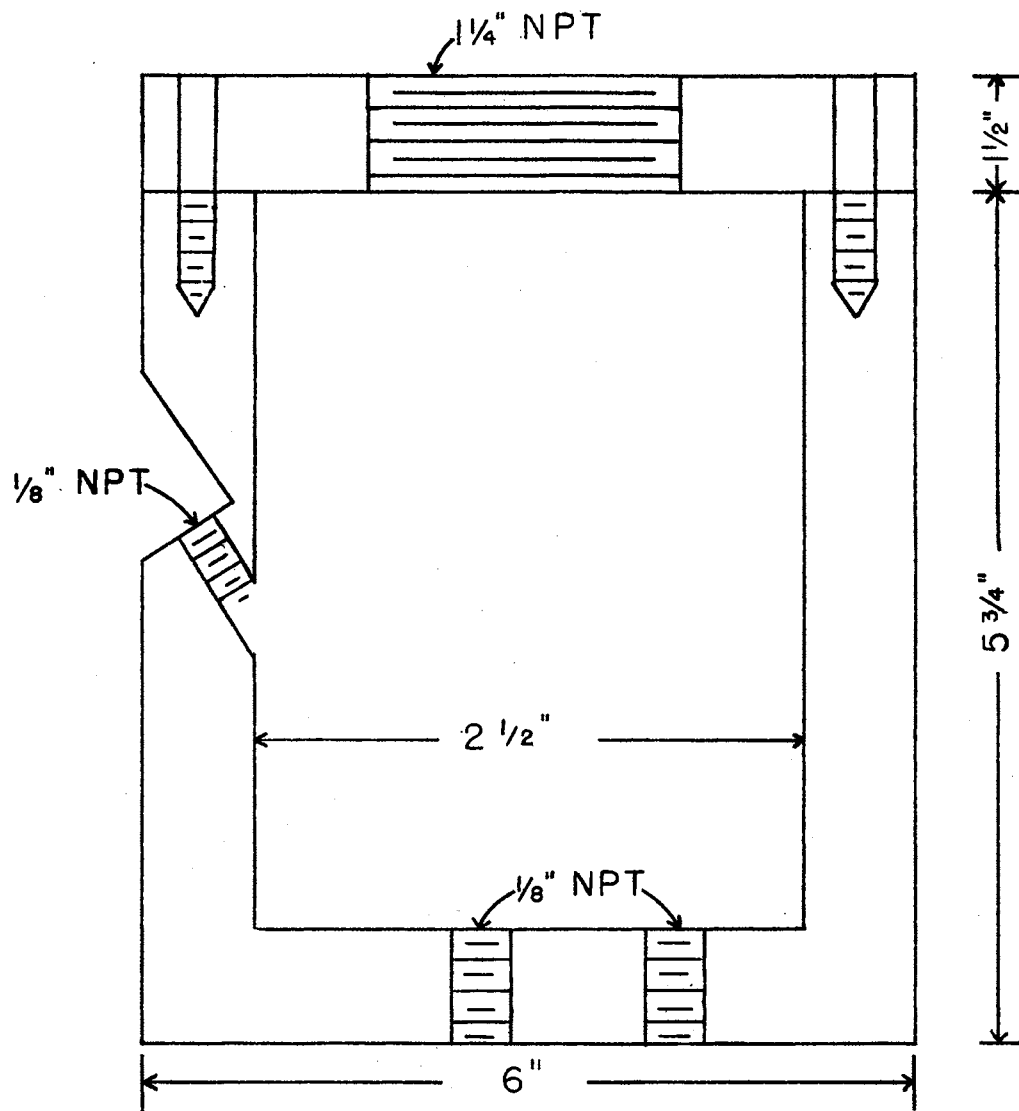


Figure 5. High Pressure Cell for Vibrating Membrane Apparatus

allowable liquid viscosity of 10 centipoise. The analog signal of the densitometer has a reported precision (including hysteresis and repeatability) of $\pm 0.001 \text{ gm./cm.}^3$ and a frequency signal repeatability equal to the densitometer probe. The frequency signal was measured with a Heath-Schlumberger (model SM-110) frequency counter capable of measurements of frequency of $\pm 0.1 \text{ Hz}$ out of 1 to 5 KHz with a temperature stability of $\pm 10 \text{ ppm}$. The analog signal was measured with the same K-5 potentiometer given in the temperature measurement section.

CHAPTER IV

EXPERIMENTAL PROCEDURE

The operating procedures for the Electrobalance system and vibrating membrane system are discussed separately since they are different. However, the Electrobalance system shown in Figure 2 and the proposed system shown in Figure 3 operating procedures will be discussed together.

Electrobalance Operating Procedure

At the first of a data run the cell was evacuated and the controls of the Electrobalance set so that the recorded weight difference (W_c) was somewhere near its maximum value. The cell was then charged with the test sample. The analog output from the electrobalance was then monitored by a Sargent (model DSRG) recorder. When the density signal was constant for a period of ten minutes or more and the rate of change of the density signal as recorded by the Cahn (model 3100) time derivative computer, Mark II, was approximately zero equilibrium was assumed. The temperature, pressure, and density output were recorded, the temperature changed, and the procedure repeated.

Vibrating Membrane Operating Procedure

The system as shown in Figure 1 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 °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 by screwing the oil pump in and noting whether or not there was a large increase in system pressure with a small decrease in system volume. 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 either the frequency counter or the potentiometer. Equilibrium was assumed after three consecutive sets of 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 oil pump 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 valve E by the oil pump. This procedure was necessary to keep from getting the test liquid into the oil pressure system, thus forming an "air" bubble in the oil line. This bubble could lodge in the differential pressure indicator causing erroneous pressure readings.

CHAPTER V

EXPERIMENTAL RESULTS

The systems for which experimental data were obtained were water, ethane, and propane. These systems were examined over the temperature range from 20 °F to 100 °F. The system pressure was the saturation pressure for the ethane and propane systems. The water system was studied at ambient pressure. The raw data are given in Appendix A.

Saturated liquid densities were obtained graphically for the ethane system from a plot similar to Figure 6. A line was drawn through the data points and the saturated density taken to be the intersection of this line and the saturation pressure. The values of the saturated liquid densities are shown in Figures 7, 8, and 9. The values for the saturated liquid ethane, propane, and water densities are given in Tables I, III, and IV, respectively.

Ethane data from Tomlinson (23) and Sliwinsky (19) are included for comparison in Figure 7. Propane data from Tomlinson (23), Sliwinsky (19), and NGAA (20) are included in Figure 8 for comparison. The water data of Gildseth (6) and Chappuis (3) are included in Figure 9 for comparison.

An attempt was made to measure the density of several oil-water emulsions by using the vibrating membrane. However, no constant resonant frequency could be achieved before the emulsions began to separate

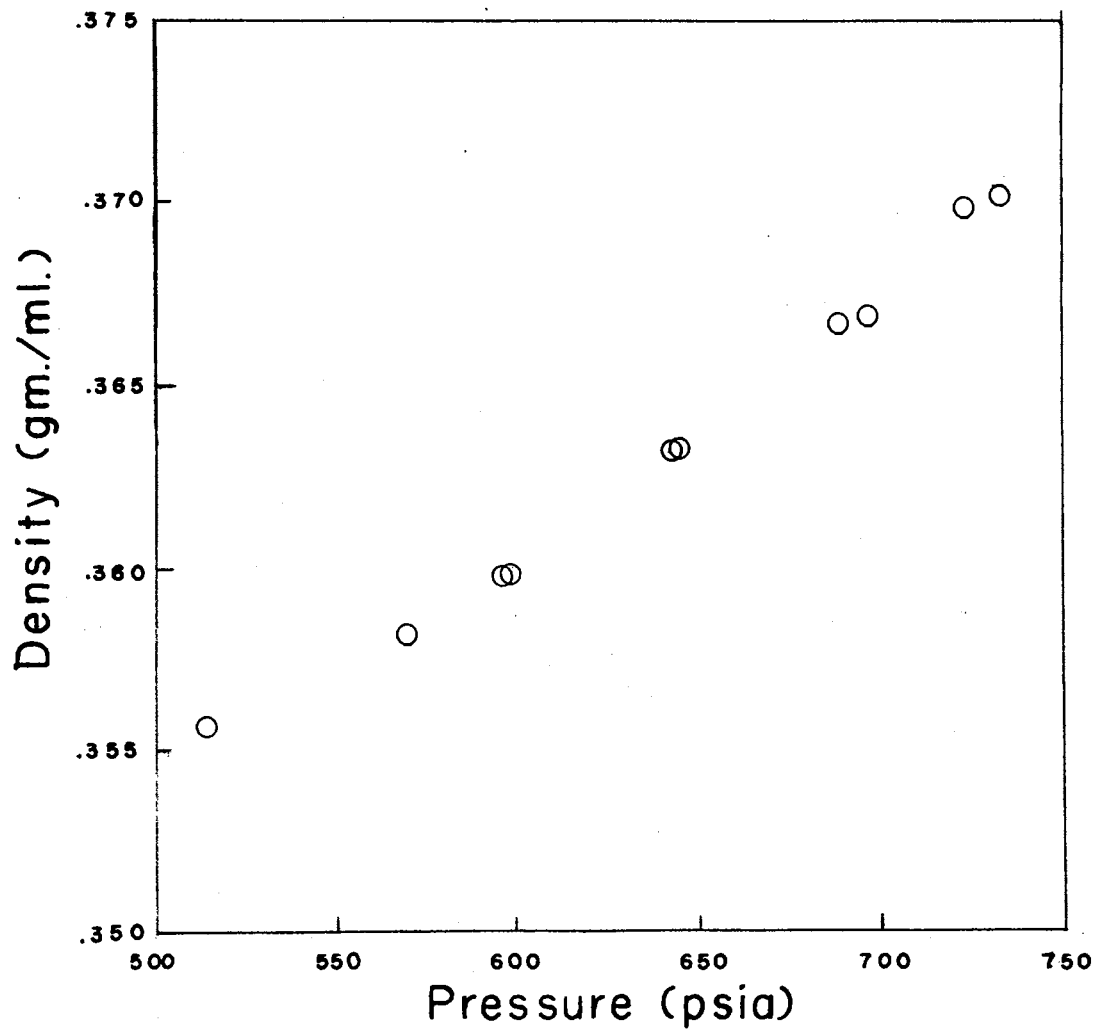


Figure 6. Isothermal (63.5°F) Subcooled Pure Ethane
Data From Vibrating Membrane Apparatus
as a Function of Pressure

TABLE I
SATURATED LIQUID DENSITIES FOR
ETHANE FROM VIBRATING
MEMBRANE SYSTEM

System Temperature (°F)	Saturation Pressure (Psia)	Experimental Density (gm./cm. ³)
23.9	329.7	0.4211
44.5	409.0	0.3863
63.5	514.0	0.3551
79.6	622.0	0.3006

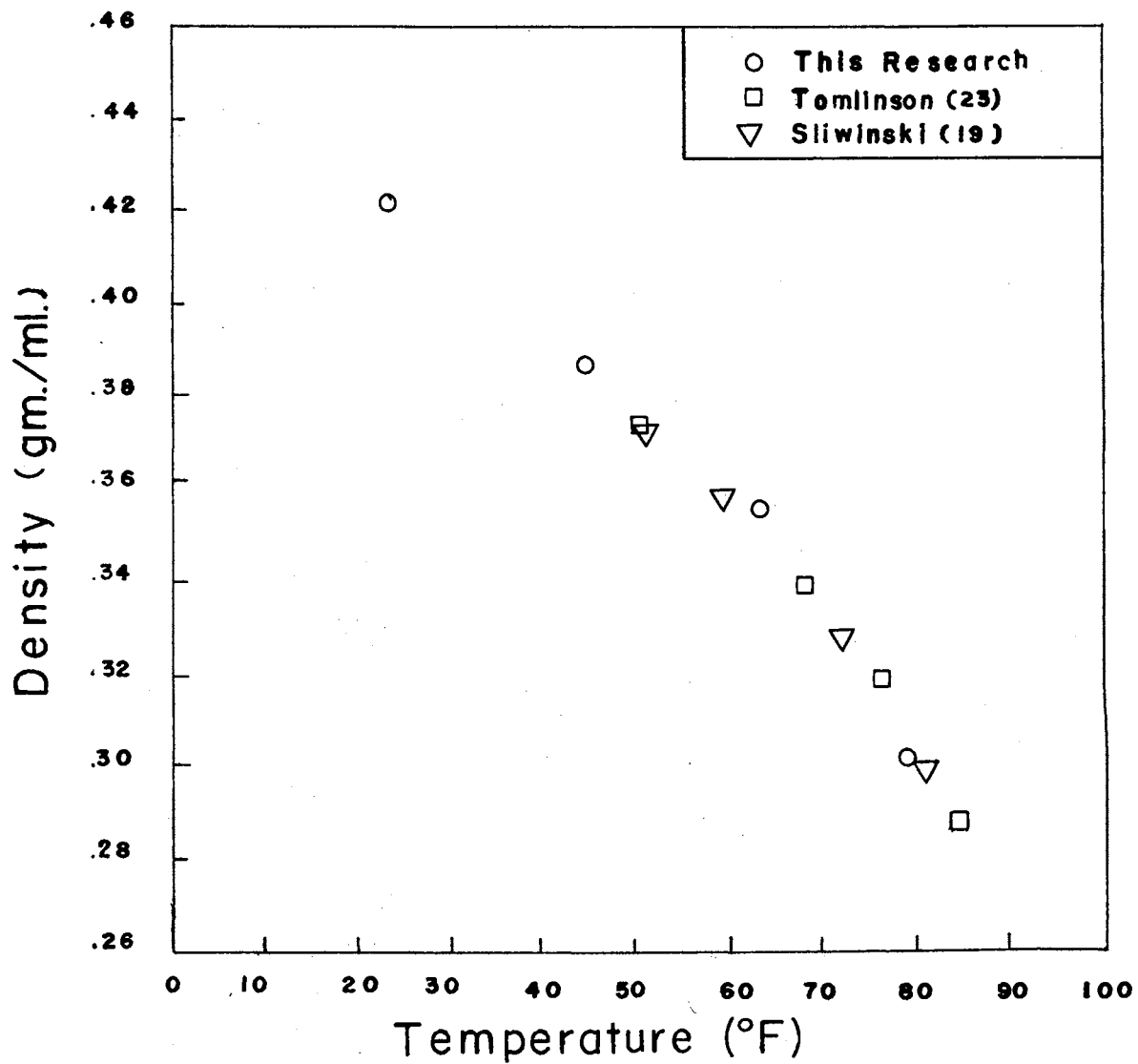


Figure 7. Saturated Liquid Pure Ethane Densities From Vibrating Membrane Apparatus as a Function of Temperature

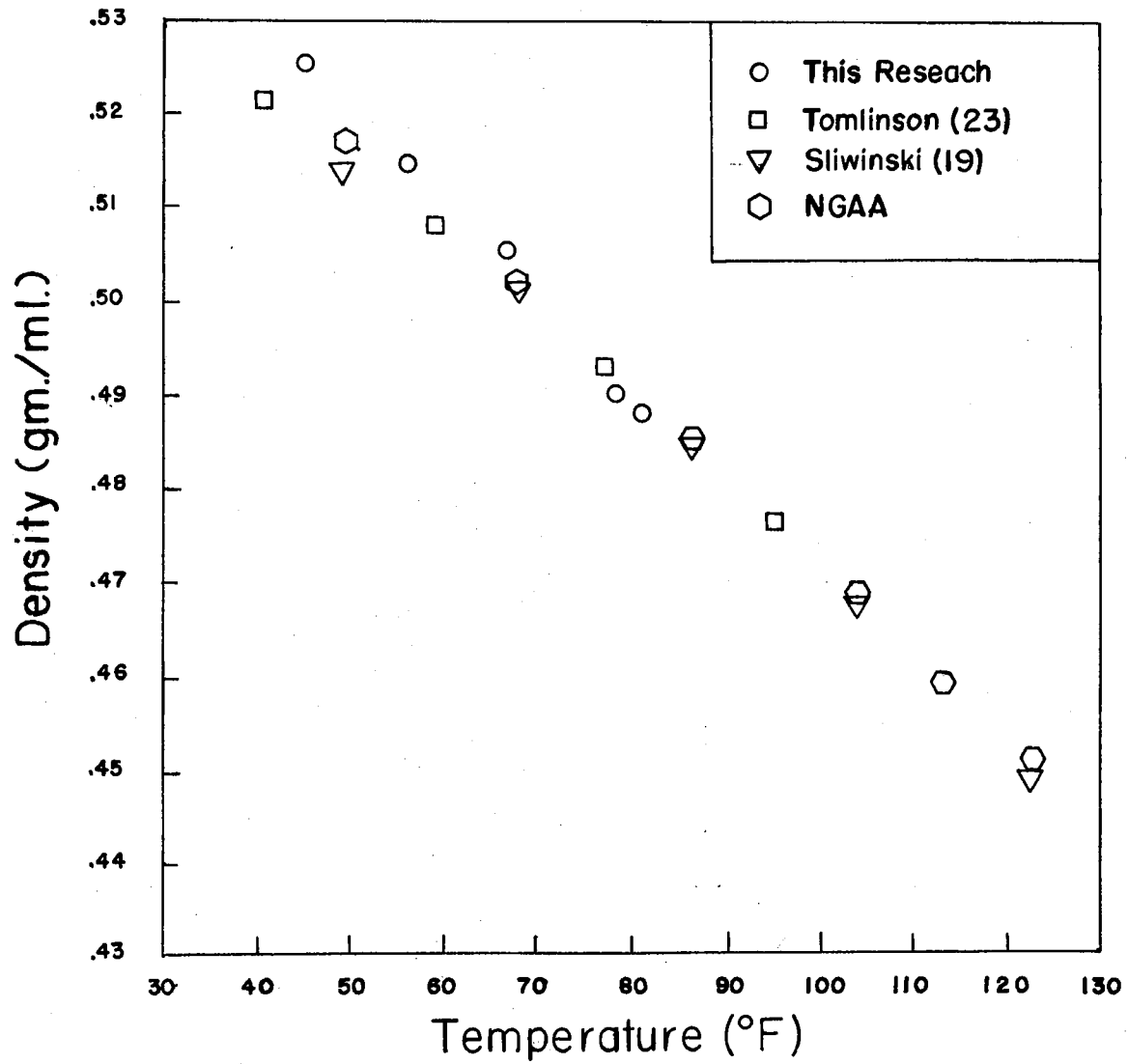


Figure 8. Saturated Liquid Pure Propane Densities From Vibrating Membrane Apparatus as a Function of Temperature

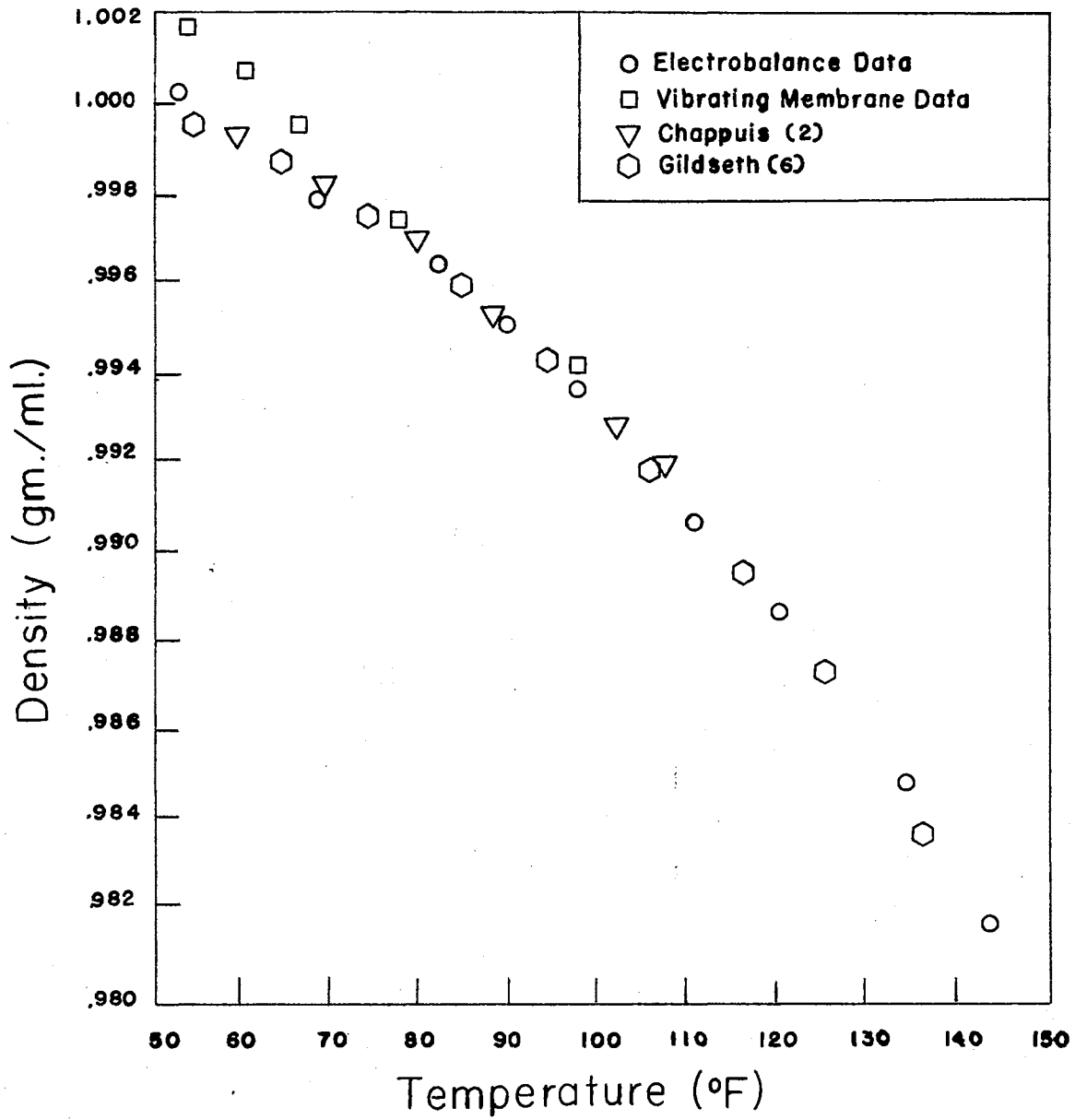


Figure 9. Atmospheric Distilled Water Density Data From Both Experimental Apparatus as a Function of Temperature

into two phases. A semi-stable frequency was achieved when the probe was immersed in milk. The measured density of the milk at room temperature by the probe was $1.026 \text{ gm./cm.}^3 \pm 0.004 \text{ gm./cm.}^3$. The density of the milk at room temperature as measured by a pycnometer was $1.0228 \text{ gm./cm.}^3 \pm 0.0003 \text{ gm./cm.}^3$. A possible explanation for the difficulty of measuring emulsions is that the vibration of the membrane aided in breaking the emulsions.

CHAPTER VI

DISCUSSION OF RESULTS

Comparisons of the saturated liquid densities for ethane and propane as measured by this research and by Tomlinson (23) are given in Tables II and III, respectively. Comparisons of the water data taken by the Electrobalance and vibrating membrane systems as compared to the data taken by Gildseth (6) are given in Tables IV and V, respectively. The data of Tomlinson and Gildseth were chosen for comparison because of the precision of their results, the recentness of their data, and their complete coverage of the temperature ranges and pressures encountered in this study.

A comparison of the water data to the ethane and propane data indicates the difficulties encountered in measuring the liquid densities of substances normally in the gaseous phase at room temperature, as evidenced by the larger average absolute differences in the experimental data of this research and that available in the literature in the ethane and propane systems. A similar comparison between the Electrobalance and vibrating membrane water data indicates the inherent precision and potential accuracy of the Cahn Electrobalance as compared to the vibrating membrane.

TABLE II

COMPARISON OF ETHANE DATA FROM
VIBRATING MEMBRANE APPARATUS
WITH DATA OF TOMLINSON

Density in gm./cm. ³		Temperature (°F)	Difference (Tom.-Exp.)	Difference (Percent)
Experimental	Tomlinson(23)			
.4211	.4038*	23.7	-.0173	-4.28
.3863	.3829*	44.5	-.0034	-.88
.3551	.3509	63.5	-.0042	-1.20
.3006	.3066	79.6	.0060	1.96
		Ave.	% Ave.	
		Abs. Dev. .0077	Abs.Dev. 2.06	

* Extrapolated Graphically

TABLE III

COMPARISON OF PROPANE DATA FROM
VIBRATING MEMBRANE APPARATUS
WITH DATA OF TOMLINSON

Density in gm./cm. ³				
Experimental	Tomlinson(23)	Temperature (°F)	Difference (Tom.-Exp.)	Difference (Percent)
.5269	.5187	45.2	-.0082	-1.58
.5140	.5102	56.3	-.0038	-.74
.5051	.5016	66.5	-.0035	-.70
.4903	.4919	78.6	.0016	.33
.4881	.4901	80.3	.0020	.41
		Ave.	_____	% Ave.
		Abs. Dif.	.0038	Abs. Dif. .75

TABLE IV
 COMPARISON OF WATER DATA FROM CAHN
 ELECTROBALANCE APPARATUS WITH
 DATA OF GILDSETH

Density in gm./cm. ³				
Experimental	Gildseth(6)	Temperature (° F)	Difference (Gil.-Exp.)	Difference (Percent)
.99823	.99823	67.6	.00000	.00
.99742	.99723	73.8	-.00019	-.02
.99624	.99615	82.8	-.00009	-.01
.99492	.99480	90.3	-.00012	-.01
.99339	.99340	98.1	.00001	.00
.99347	.99340	98.1	-.00007	-.01
.99347	.99340	98.1	-.00007	-.01
.99059	.99045	111.4	-.00009	-.01
.98860	.98847	120.2	-.00013	-.01
.98848	.98847	120.2	-.00001	-.00
.98647	.98650	127.8	.00003	.00
.98434	.98435	135.7	.00001	.00
.98186	.98124	144.8	-.00062	-.06
.98466	.98465	134.7	-.00001	-.00
.98432	.98465	134.7	.00033	.03
.99366	.99379	96.1	.00013	.01
.99612	.99624	82.2	.00012	.01
.99803	.99832	67.0	.00029	.03
.99711	.99884	62.3	.00173	.17
.99707	.99882	62.5	.00175	.18
.99513	.99777	71.8	.00264	.26
.99532	.99733	75.2	.00201	.20
.99248	.99307	100.0	.00059	.06
.99235	.99300	100.4	.00065	.07
.99249	.99300	100.4	.00051	.05
.99687	.99827	67.6	.00140	.14
.99737	.99819	68.3	.00082	.08
.99828	.99900	61.0	.00072	.07
.99918	.99941	55.4	.00023	.02
.99936	.99948	54.3	.00012	.01
.99918	.99942	55.7	.00024	.02
.99891	.99954	55.2	.00063	.06
1.00003	.99985	53.4	-.00018	-.02
.99973	.99993	47.2	.00020	.02
.99912	.99938	44.5	.00026	.03
		Ave.	% Ave.	
		Abs. Dif.	.00053	Abs. Dif. .05

TABLE V
 COMPARISON OF WATER DATA FROM VIBRATING
 MEMBRANE APPARATUS WITH DATA
 OF GILDSETH

Density in gm./cm. ³		Temperature (° F)	Difference (Gil.-Exp.)	Difference (Percent)
Experimental	Gildseth(6)			
.9993	.9986	64.6	-.0007	-.07
1.0008	.9986	64.9	-.0022	-.22
.9968	.9971	76.8	.0003	.03
.9973	.9971	77.2	-.0002	-.02
.9983	.9970	77.5	-.0013	-.13
.9952	.9933	98.8	-.0019	-.19
.9948	.9933	98.8	-.0015	-.15
.9945	.9933	98.8	-.0012	-.12
.9940	.9933	98.8	-.0007	-.07
.9995	.9982	68.0	-.0013	-.13
.9997	.9982	68.5	-.0015	-.15
1.0006	.9989	61.6	-.0017	-.17
1.0012	.9989	61.9	-.0023	-.23
1.0016	.9994	54.9	-.0022	-.22
		Ave.	_____	% Ave.
		Abs. Dif. .0014	_____	Abs. Dif..14

Electrobalance Water Data

The apparent high degree of accuracy for this data set as shown in Table IV actually represents a high degree of precision. The reason that the data should be interpreted this way is the fact that the data of Gildseth (6) were used to determine the effective volume of the plummet, as shown in Appendix B.

Between points 18 and 19 the system was disassembled, cleaned and refilled. The large increase in error between these two points is probably due to an error in the zero adjustment for data points 19 through 36. The fact that all of the errors but one for points 19 through 36 are positive would tend to indicate that there was a systematic error, the wrong zero point recorded.

Vibrating Membrane Water Data

As shown in Appendix A the water data were not taken by directly measuring the frequency output from the vibrating membrane but rather by measuring the analog output from the transmitter accompanying the probe. Although the data are very accurate, maximum absolute difference of 0.0023 gm./cm.^3 , water data are easier to take than hydrocarbon densities. An additional aid to the accuracy of this data is the fact that the "true" density only changes approximately 0.006 gm./cm.^3 . A good measure of the experimental reproducibility of the analog output of the vibrating membrane can be obtained by examining the four data points in which the density calculated by Gildseth (6) is 0.9933 gm./cm.^3 . The experimental densities of this research for these data

points vary from 0.9952 to 0.9940 gm./cm.³ giving a experimental reproducibility of ± 0.0006 gm./cm.³.

As all data points obtained by this research except one are higher than those obtained by Gildseth (6), a systematic error seems to be indicated. This error could be a calibration error in the constants used in the density calculations (as shown in Appendix C), a calibration error for the thermocouple used, or some procedure error.

Ethane Data

The first two data points of this system were the first data taken using a direct reading of the resonant frequency from the vibrating membrane probe. The large error of the first data point indicates the difficulties encountered in gaining the "art" of balancing the pressure of the system with the pressure of the dead weight gauge. The smaller error of the second point reflects both the development of skill and the extreme care taken in assuring every point was at equilibrium.

Between the second and third ethane data points the entire set of propane data was taken. The relatively large errors of these points would seem to be counter to the statements above concerning the development of skill in taking data. However these errors can best be explained by realizing these points were taken closer to the critical temperature.

Propane Data

As indicated in Appendix A no subcooled liquid densities were recorded for the propane system. The reason for this is that the

procedure given in Chapter IV was slightly modified. Instead of allowing the system to overpressure during the temperature changing phase, an attempt was made to maintain the system pressure as close as possible to the saturation pressure. The system pressure was then adjusted to the saturation pressure by the procedure outlined in Chapter III. The adjusting to obtain equilibrium at the saturation pressure was quite tedious and often required over a week to accomplish.

The differences between the data of this study and that of Tomlinson (23) are reasonable, even though not quite as good as those desired, and future results can be improved by the recommendations of Chapter VI.

The single most important improvement in the precision of the data seemed to be the use of the Hallikainen temperature controller instead of the BLU-M controller. This can be seen by examining Figure 10, the 44.5 °F isotherm for ethane (before installation of the Hallikainen controller) and Figure 6 the 63.5 °F isotherm of ethane (after installation of the Hallikainen controller).

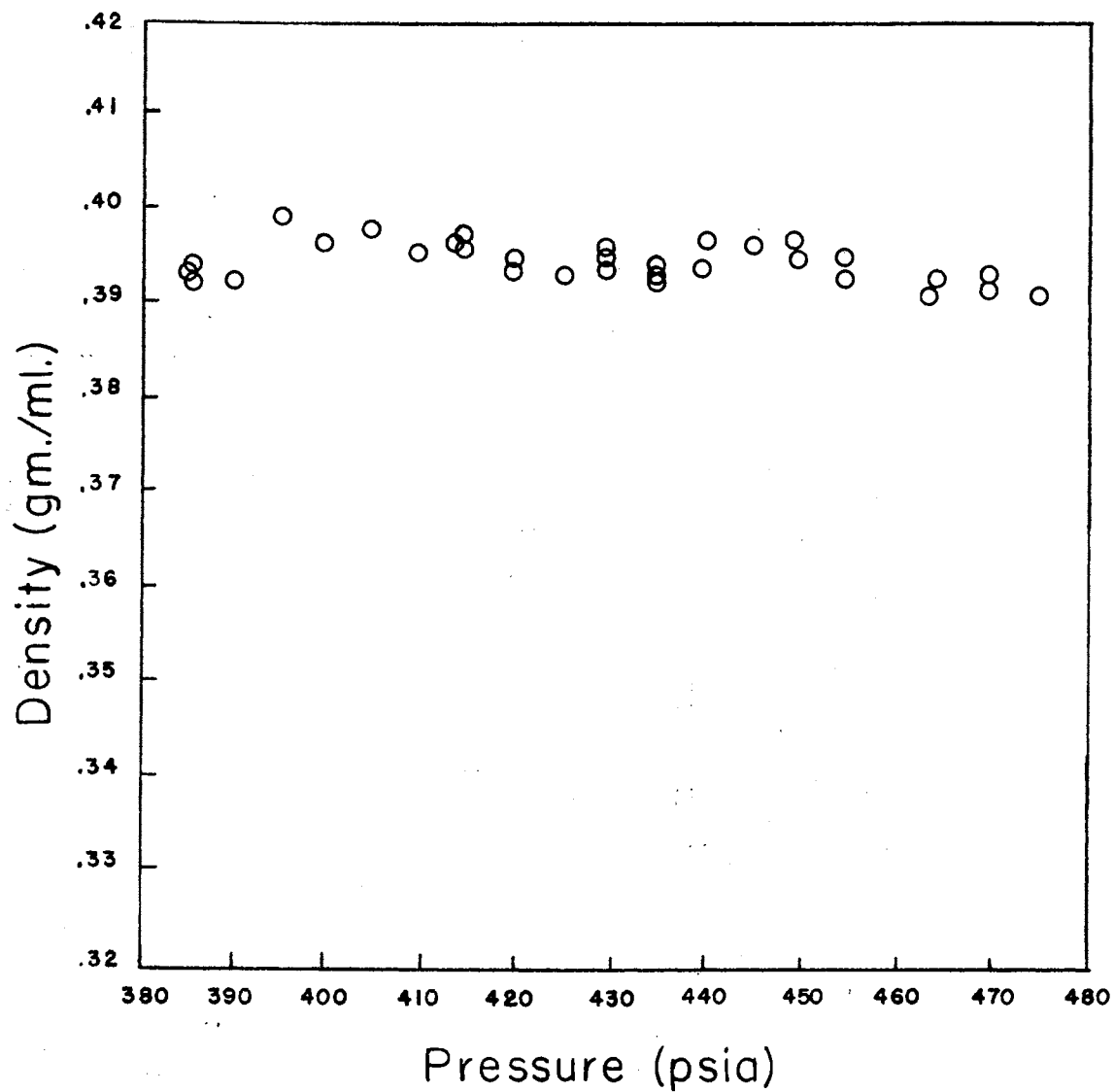


Figure 10. Isothermal ($44.5^{\circ}\text{F} \pm 1^{\circ}\text{F}$) Subcooled Pure Ethane
Data From Vibrating Membrane Apparatus as a
Function of Pressure

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The purpose of this study was to design an apparatus that could be used to determine saturated liquid densities accurately over wide ranges of temperature and pressure. Two systems were constructed to achieve this goal, a vibrating membrane system and a Cahn Electrobalance system.

The second system that was constructed was found to be the easiest to operate and capable of measuring saturated liquid densities to an accuracy of ± 0.005 gm./cm.³ over a wide range of temperatures and pressures. With this system the temperature was measured to ± 0.1 °F and the pressure measured to ± 2 psia.

The second system constructed was used to measure the liquid density of ethane, propane, and water. The first system constructed was used to measure the liquid density of water. Experimental data obtained for these systems were compared with similar data presented by Tomlinson (23) and by Gildseth (6).

Recommendations

Although the vibrating membrane system was found to be much easier to operate than the Electrobalance system, certain changes could improve

the ease of use of the vibrating membrane system. A flow diagram for the recommended changes is given in Figure 11.

The air-mercury system is designed to replace the oil pump-mercury system shown in Figure 1. This change is recommended to increase the speed with which the pressure on a sample can be changed. With the oil pump considerable time was required to remove a significant amount of mercury from the system.

The change from the differential pressure indicator and dead weight gauge to a pressure transducer will reduce the possible accuracy of the pressure measurements. However, the relative insensitivity of liquid densities to pressure and the large amount of time required in balancing the pressures of the differential pressure indicator seem to warrant this change.

Examination of Figure 10 shows the extreme sensitivity of the measured densities to temperature. This is represented by the variation of the data around the probable density at any particular pressure. Therefore a recommendation is made that the temperature of the system be measured as accurately as possible (use of the K-5 potentiometer) and controlled as closely as possible (use of the Hallikainen controller).

Although the data seem to agree quite well with the values available in the literature, careful recalibration over a wide range of frequencies could improve the accuracy of the data. This could be accomplished by connecting the vibrating membrane system and Cahn Electrobalance system in "series" or by the use of data from the literature.

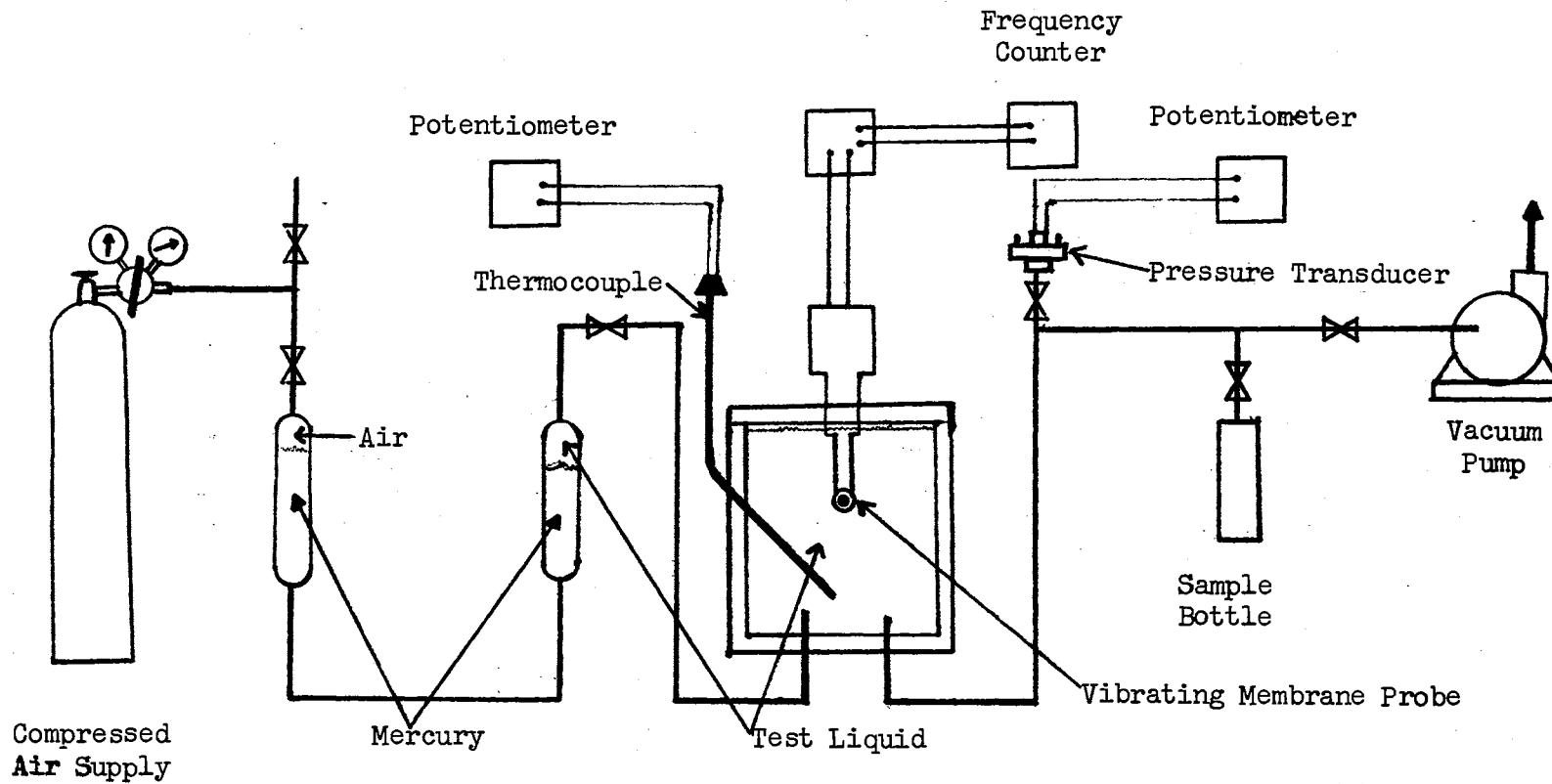


Figure 11. Overall Diagram of Proposed Modifications to Vibrating Membrane Apparatus

Two approaches should be used in trying to improve the accuracy of the vibrating membrane system. One, include more terms in the relation between the measured frequency and calculated density as shown in equation 1. Two, correlate the effect of temperature on the measured frequency.

$$\rho_L = \sum_{i=0}^N \frac{a_i}{f^i} \quad (1)$$

The modifications shown in Figure 11 are recommended to the point of being almost mandatory to make the system operable. The recalibration although not essential would seem to be highly desirable.

SELECTED BIBLIOGRAPHY

- (1) Beams, J. W. and Alexander M. Clarke. "Magnetic Suspension Balance Method for Determining Densities and Partial Specific Volumes." The Review of Scientific Instruments, Vol. 33, No. 7, 750 (1962).
- (2) Bourman, Horace A. and Randall M. Schoonover. "Procedure for High Precision Density Determinations by Hydrostatic Weighing." Journal of Research of the National Bureau of Standards-C. Engineering and Instrumentation, Vol. 71C, No. 3, 179 (1967).
- (3) Chappuis, P. Travel Memoirs de Bureau of International Measurement, Vol. 13, CIO (1907).
- (4) Douslin, D. R., R. H. Harrison and R. T. Moore. Journal of Chemical Thermodynamics, Vol. 1, 305 (1969).
- (5) Erbar, J. H. "K & H Computer Program, I.B.M. Series 360." N.G.P.A. (1966).
- (6) Gildseth, Wayne, Anton Habenschuss, and Frank H. Spedding. "Precision Measurements of Densities and Thermal Dilation of water between 5 ° and 80 ° C." Journal of Chemical and Engineering Data, Vol. 17, No. 4, 402 (1972).
- (7) Goldman, K. and N. G. Scrase. "Density of Saturated Liquid Oxygen and Nitrogen." Physica, Vol. 44, 555 (1969).
- (8) Hales, J. L. "An Apparatus for Accurate Measurement of Liquid Densities Over an Extended Temperature Range." Journal of Physics E: Scientific Instruments, Vol. 3, 855 (1970).
- (9) Lamb, Arthur B. and R. Edwin Lee. "The Densities of Certain Dilute Aqueous Solutions by a New and Precise Method." Journal of the American Chemical Society, Vol. 35, 1667 (1913).
- (10) Maddox, R. N. "Modified Rackett Equation, I.B.M. Series 360." N.G.P.A. (1972).
- (11) Miller, Michael B. "Experimental Determination of the Interfacial Tension of Binary System." (M. S. thesis, Oklahoma State University, 1972).

- (12) Operation and Service Manual. "Frequency Counter Model SM-110 Series." Benton Harbor, Michigan, 1973.
- (13) Orwoll, Robert A. and Paul J. Flory. "Equation of State Parameters for Normal Alkanes. Correlation with Chain Length." Journal of the American Chemical Society, Vol. 89, 6814 (1967).
- (14) Reding, J. N. "Densities and Molal Volumes of Molten Magnesium Chloride, and Barium Chloride Mixtures." Journal of Chemical and Engineering Data, Vol. 10, No. 1, 1 (1965).
- (15) Ruska Dead Weight Gauge Manual. Ruska Instrument Corporation, Houston, Texas, 1966.
- (16) Sage, B. H. and W. N. Lacey. "Apparatus for Determination of Volumetric Behavior of Fluids." Transactions of AIME, 102 (1947).
- (17) Senter, James P. "Magnetic Densimeter Utilizing Optical Sensing." The Review of Scientific Instruments, Vol. 40, No. 2, 334 (1969).
- (18) Shraiber, L. S. and O. V. Kukolenko. "Technique for Precision Measurement of Liquid Density over a Wide Temperature Range." Russian Journal of Physical Chemistry, Vol. 39, 281 (1965).
- (19) Sliwinski, P. Z. Physik. Chem. N. F., Vol. 63, 263 (1969).
- (20) Technical Committee, Natural Gasoline Association of America. Industrial Engineering Chemistry, Vol. 34, No. 10, 1240 (1942).
- (21) Technical Manual. "Gas and Liquid Densitometer." ITT Barton, Monterey Park, California, 1972.
- (22) Tereshkovich, M. O., et al. "Accurate Determination of Dilute Solutions at Different Temperatures." Journal of Applied Chemistry U.S.S.R., Vol. 43, No. 1, 158 (1970).
- (23) Tomlinson, Dr. J. R. "Liquid Densities of Ethane, Propane, and Ethane - Propane Mixtures." Technical Publication TP-1. N.G.P.A. (1971).

APPENDIX A

EXPERIMENTAL DATA

TABLE VI
 EXPERIMENTAL DENSITY FOR ETHANE
 FROM VIBRATING MEMBRANE
 APPARATUS

Temperature (°F)	Pressure (psia)	Frequency (Hz)	Density (gm./cm. ³)
23.7	329.7	2330.4	.39390
23.7	472.5	2295.2	.42230
24.7	500.0	2294.6	.42240
23.4	560.0	2293.4	.42300
24.4	622.0	2292.7	.42280
24.5	700.0	2294.4	.42380
24.3	740.0	2295.1	.42440
43.5	499.0	2335.1	.39016
43.8	494.0	2332.7	.39205
43.8	494.0	2333.8	.39157
43.8	494.0	2332.8	.39197
44.7	489.0	2332.8	.39197
45.1	489.0	2332.3	.39244
45.0	484.0	2331.6	.39291
44.9	479.0	2329.6	.39449
44.9	479.0	2331.8	.39276
45.1	479.0	2331.7	.39283
45.3	474.0	2327.8	.39592
45.1	474.0	2328.4	.39545
45.2	474.0	2328.5	.39537
45.7	474.0	2328.8	.39513
45.6	469.0	2328.2	.39560
45.5	469.0	2328.5	.39537
45.5	464.0	2327.4	.39624
44.6	464.0	2331.2	.39323
44.6	459.0	2330.6	.39370
44.3	459.0	2333.0	.39157
44.3	459.0	2332.6	.39216
44.8	454.0	2329.7	.39445
44.8	454.0	2328.7	.39520
44.3	454.0	2331.4	.39306
43.9	449.0	2332.0	.39257
43.9	449.0	2332.0	.39261
44.4	444.0	2329.8	.39434
44.1	444.0	2330.6	.39368
44.7	439.0	2326.6	.39685
44.1	439.0	2328.4	.39541
44.4	438.0	2327.6	.39608

TABLE VI (Continued)

Temperature (°F)	Pressure (psia)	Frequency (Hz)	Density (gm./cm. ³)
44.3	434.0	2327.8	.39592
44.3	429.0	2325.9	.39745
44.1	424.0	2327.5	.39615
44.4	419.0	2324.1	.39887
44.4	414.0	2332.0	.39258
44.4	414.0	2332.2	.39245
44.4	410.6	2332.6	.39210
44.4	410.0	2331.2	.39324
44.3	409.0	2332.3	.39235
63.5	514.0	2380.6	.35540
63.5	569.0	2376.7	.35820
63.5	593.0	2374.8	.35971
63.5	642.0	2370.0	.36305
63.5	644.0	2370.0	.36320
63.5	687.5	2365.6	.36665
63.5	696.0	2365.5	.36670
63.5	721.5	2361.3	.36989
63.5	732.5	2361.0	.37015
79.6	622.0	2459.0	.30001
79.6	640.0	2444.1	.31013
79.6	676.0	2429.9	.31995
79.6	690.0	2429.5	.32022
79.6	733.0	2421.7	.32569
79.6	821.0	2408.6	.33500
79.6	898.0	2399.2	.34177
79.6	944.0	2395.3	.34461
79.6	1086.0	2382.9	.35371
79.6	1211.0	2374.8	.35973
79.6	1382.0	2364.9	.36717

TABLE VII
EXPERIMENTAL DENSITY FOR PROPANE
FROM VIBRATING MEMBRANE
APPARATUS

Temperature (°F)	Pressure (psia)	Frequency (Hz)	Density (gm./cm. ³)
45.2	86.0	2178.4	.5269
56.3	103.0	2191.9	.5140
66.5	120.0	2201.3	.5051
78.1	142.0	2217.2	.4903
80.3	148.0	2219.6	.4881

TABLE VIII
EXPERIMENTAL DENSITY FOR WATER
FROM VIBRATING MEMBRANE
APPARATUS

Temperature (°F)	Pressure (mm. Hg.)	Analog Output (mV)	Density (gm./cm. ³)
64.6	739.7	19.955	.9993
64.9	739.7	20.050	1.0008
76.8	740.0	19.795	.9968
77.2	739.9	19.825	.9973
77.5	739.7	19.890	.9983
98.8	739.6	19.695	.9952
98.8	740.6	19.670	.9948
98.8	741.6	19.670	.9948
98.8	741.6	19.650	.9945
98.8	743.1	19.620	.9940
68.0	744.6	19.970	.9995
68.5	744.6	19.980	.9997
61.6	744.3	20.040	1.0006
61.9	743.6	20.075	1.0012
54.9	744.6	20.100	1.0016

TABLE IX
 WATER DENSITY DATA FROM
 CAHN ELECTROBALANCE
 APPARATUS

Cahn Electrobalance Readings

Mass Dial Setting	Recorder Range (mg)	Recorder Reading (Percent)	System Temperature (mv.)	Room Pressure (mm. Hg.)	Calibration Weights (mg)	Tare Weights (mg)
.500	1	-1.5	.785	737.2	0	590
.510	1	12.7	.925	739.7	0	590
.520	1	79.2	1.130	739.7	0	590
.540	1	66.3	1.300	740.0	0	590
.565	1	31.5	1.480	740.0	0	590
.565	1	21.0	1.480	739.9	0	590
.565	1	20.8	1.480	739.9	0	590
.600	1	77.5	1.790	379.7	0	590
.630	1	58.5	2.000	739.6	0	590
.630	1	76.6	2.000	739.6	0	590
.660	1	60.5	2.180	740.6	0	590
.690	1	61.2	2.370	741.6	0	590
.730	1	11.3	2.590	743.1	0	590
.685	1	66.6	2.345	744.6	0	590
.690	1	64.1	2.345	744.6	0	590
.560	1	44.1	1.435	743.6	0	590
.525	1	46.0	1.115	744.4	0	590
.500	1	26.5	.770	744.6	0	590
.260	1	84.3	.665	744.5	1150	2045
.270	1	4.3	.670	744.5	1150	2045
.340	1	95.0	.880	740.5	1150	2045
.340	1	20.5	.955	740.3	1150	2045
.340	1	47.0	.965	740.3	1150	2045
.450	1	80.5	1.525	739.0	1150	2045
.450	4	33.1	1.535	739.0	1150	2045
.450	1	75.7	1.535	739.0	1150	2045
.270	1	84.5	.785	742.9	1150	2045
.250	1	53.5	.800	742.8	1150	2045
.220	1	9.5	.635	740.7	1150	2045
.180	1	41.1	.510	739.0	1150	2045
.170	1	65.7	.485	738.8	1150	2045
.180	1	63.1	.515	737.3	1150	2045
.180	1	39.5	.505	737.3	1150	2045
.190	1	50.0	.465	744.4	1150	2045
.140	1	90.1	.325	742.6	1150	2045
.150	1	30.6	.265	742.6	1150	2045

TABLE X
 CALCULATED WATER DENSITIES FROM
 CAHN ELECTROBALANCE
 APPARATUS

Temperature (°F)	Density (gm./cm. ³)
67.6	.99823
73.8	.99742
82.8	.99624
90.3	.99492
98.1	.99339
98.1	.99347
98.1	.99347
111.4	.99059
120.2	.98860
120.2	.98848
127.8	.98647
135.7	.98434
144.8	.98186
134.7	.98466
134.7	.98432
96.1	.99366
82.2	.99612
67.0	.99803
62.3	.99711
62.5	.99707
71.8	.99513
75.2	.99532
75.6	.99532
100.0	.99248
100.4	.99235
100.4	.99248
67.6	.99687
68.3	.99737
61.0	.99828
55.4	.99918
54.3	.99936
55.7	.99912
55.2	.99918
53.4	.99891
47.2	1.00003
44.5	.99973

APPENDIX B
DEVELOPMENT OF EQUATIONS FOR
CAHN ELECTROBALANCE
APPARATUS

DEVELOPMENT OF EQUATIONS FOR
CAHN ELECTROBALANCE
APPARATUS

Density Relations

The mechanism by which the Electrobalance system measures density is commonly referred to as Archimedes' principle. This principle states that the buoyancy, or apparent loss of weight, of an object completely immersed in a fluid is equal to the volume of the object times the density of the fluid in which it is emersed. The equation that would calculate the apparent weight of the plummet of Figure 2 would be:

$$W_L = W_a - \rho_L V_P \quad (2)$$

Rearranging this gives the working equation for the atmospheric data of this system.

$$\rho_L = \frac{W_a - W_L}{V_P} \quad (3)$$

This equation assumes that the weight of the plummet measured in air (W_a) is the "actual" weight of the plummet. This obviously does not take into account the buoyancy of the fluid air. Using the volume of the plummet as 1.5 ml. and the density of air as 1.22×10^{-3} gm./ml. gives the error from the "true" value for the weight of the plummet as

1.8 mg. Since the weight of the plummet in air was approximately 1500 mg. this would give an error of approximately .12%. However, since the buoyancy of air on the counterweights was also not included these two errors tend to cancel each other.

The system designed for high pressure operation as shown in Figure 3 alleviates some of the problems and limitations of the system shown in Figure 2. This system recommends the use of two plummets of identical material as shown in Figure 12. Using Archimedes principle gives equation 4 the difference between the effective weight for plummets one and two.

$$W_c = (W_1 - V_1 \rho_L) - (W_2 - V_2 \rho_L) \quad (4)$$

Or solving for ρ_L .

$$\rho_L = \frac{W_c + W_2 - W_1}{V_2 - V_1} \quad (5)$$

Since plummet one and two are made of the same material they will have the same coefficient of thermal expansion and therefore $V_2 - V_1$ will be a function of temperature as given in equation 6.

$$V_2 - V_1 = (1 + \beta t) (V_2 - V_1)_0 \quad (6)$$

Where $(V_2 - V_1)_0$ is the difference in volume at some reference temperature. Defining a as the reference volume difference and b as the ratio of the weight difference to volume difference at the reference temperature gives equation 7.

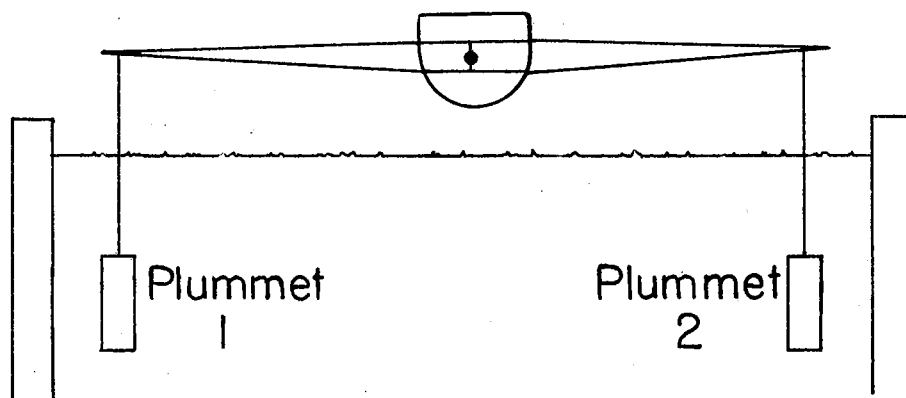


Figure 12. Diagram of Electrobalance Arm and Plummets for Proposed High Pressure Electrobalance System

$$\rho_L = \left(\frac{W_c}{a} + b \right) \left(\frac{1}{1 + \beta t} \right) \quad (7)$$

Constant a can be determined by direct measurement of V_2 and V_1 and a knowledge of the thermal expansion of the material or more accurately by determining the slope of a series of density measurements of two fluids of known density and using equation 8.

$$a = \text{slope} = \frac{W_{c_2} - W_{c_1}}{\rho_{L_2} - \rho_{L_1}} \quad (T = \text{constant}) \quad (8)$$

Constant b could be determined by direct measurement of W_1 and W_2 and a knowledge of a , by the use of one known ρ_L and W_c , or perhaps by the best method of several measurements of known ρ_L and W_c .

Liquid Volume Calculations for Cahn Electrobalance System

The purpose of the large pressure cell shown in Figure 4 was to provide a large enough liquid volume so that the change in composition of liquid caused by the formation of vapor would be negligible. Defining the change in liquid composition of the light component as E_x .

$$E_x = X_1 - X_{1N} \quad (9)$$

An overall mass balance and a mass balance around component 1 give.

$$M = M_L + M_V \quad (10)$$

$$(M)(X_1) = (M_L)(X_{1N}) + (M_V)(Y_1) \quad (11)$$

Combining equations 9, 10, and 11 and rearranging gives:

$$E_x = \frac{M_V}{M_L} (Y_1 - X_1) \quad (12)$$

Noting that

$$M_V = V_V \rho_V M_{wV} \quad (13)$$

$$M_L = V_L \rho_L M_{wL}$$

and substituting into equation 12 gives:

$$E_x = \frac{V_V \rho_V M_{wV}}{V_L \rho_L M_{wL}} (Y_1 - X_1) \quad (14)$$

The vapor volume of the cell shown in Figure 4 is designed to be 34 inches³ and the liquid volume 644 inches³. This gives a vapor to liquid volume ratio of .0528.

From the N.G.P.A. K & H program (5) and the O.S.U. modified Rackett program (10) the following properties were obtained for a binary system of normal-pentane in para-xylene with a liquid phase composition of 10.32 mole percent normal-pentane as reported by Miller (11).

Liquid composition:	10.32 mole % n-pentane 86.68 mole % p-xylene
Temperature:	393 °F
Pressure:	104.4 psia
Vapor density:	.01894 gm./cm. ³
Vapor composition:	46.17 mole % n-pentane 53.83 mole % p-xylene

Molecular weight (vapor): 90.46 gms./gm. mole
Molecular weight (liquid): 102.66 gms./gm. mole
Liquid density: .65439 gm./cm.³

Using these values in equation 14 gives $E_x = .048$ mole percent. In other words the liquid composition of 10.32 mole percent n-pentane would have changed to 10.272 mole percent, well within the limits of the chromatograph intended for use in this study.

APPENDIX C
DEVELOPMENT OF EQUATIONS FOR
VIBRATING MEMBRANE
APPARATUS

DEVELOPMENT OF EQUATIONS FOR
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APPARATUS

Density Relations

Theory (21) shows that the resonant frequency of a vibrating membrane surrounded by an incompressible liquid is given by equation 15.

$$f = \frac{f_o}{\sqrt{1 + \beta}} \quad (15)$$

where

$$\beta = \left(\frac{\rho_L}{\rho_M} \right) \left(\frac{L}{H} \right) \quad (16)$$

Since the ratio of the length of the membrane to thickness of the membrane is constant equation 15 may be written as equation 17.

$$\rho_L = \frac{A' \rho_M}{f^2} + C' \rho_M \quad (17)$$

If the density of the membrane is assumed to be constant equation 17 can be reduced to the equation used in this study.

$$\rho_L = \frac{A}{f^2} + C \quad (18)$$

If the sample is compressible equation 18 becomes equation 19.

$$\rho_L = \frac{A}{f^2} - \frac{B}{f} + C \quad (19)$$

The facts that the density of the membrane is not constant and all fluids are somewhat compressible are the basis of two of the recommendations of Chapter VI.

Calibration of Probe

The constants A and C used in this study were those determined by a factory calibration. The densities of the fluids used and the frequencies recorded are given in Table XI. In addition the value of density calculated using $A = 5.0037$ and $C = -.5275$ are given in Table XI.

TABLE XI

CALIBRATION DATA
FOR PROBE

Density Test Liquid (gm./cm. ³)	Measured Frequency (KHz)	Density Calculated (gm./cm. ³)	Difference (Test-Cal.)
.70	2.0189	.7001	-.0001
.85	1.9058	.8501	-.0001
1.00	1.8099	1.0000	.0000

APPENDIX D
INSTRUMENTATION

INSTRUMENTATION

Thermocouple Calibration

The copper-constantan thermocouple used to measure the temperature of the sample was calibrated using a Leeds and Northrup platinum resistance thermometer, a Mueller bridge, and the K-5 potentiometer used in the temperature measurement. The data obtained from this procedure are given in Table XII. A plot such as Figure 13 was used to correct temperature readings.

Dead Weight Gauge

The dead weight gauge used for the pressure measurements of the vibrating membrane system was factory calibrated and the manual accompanying this instrument contains all equations and curves necessary to convert the weight recorded to actual weight. These equations consist of the basic equation, given below, and equations for series of correction factors (k_1) used to modify equation 20. These corrections are based on the temperature of the room, the pressure of the room, the pressure of the system, the gravity at the systems' location, etc.

$$P = \frac{W}{A} k_1 k_2 k_3 \quad (20)$$

These corrections would seem to bring the calculated value to the exact value of the pressure. However, there is one error that was made during this study that is not accounted for in the corrections factors.

TABLE XII

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

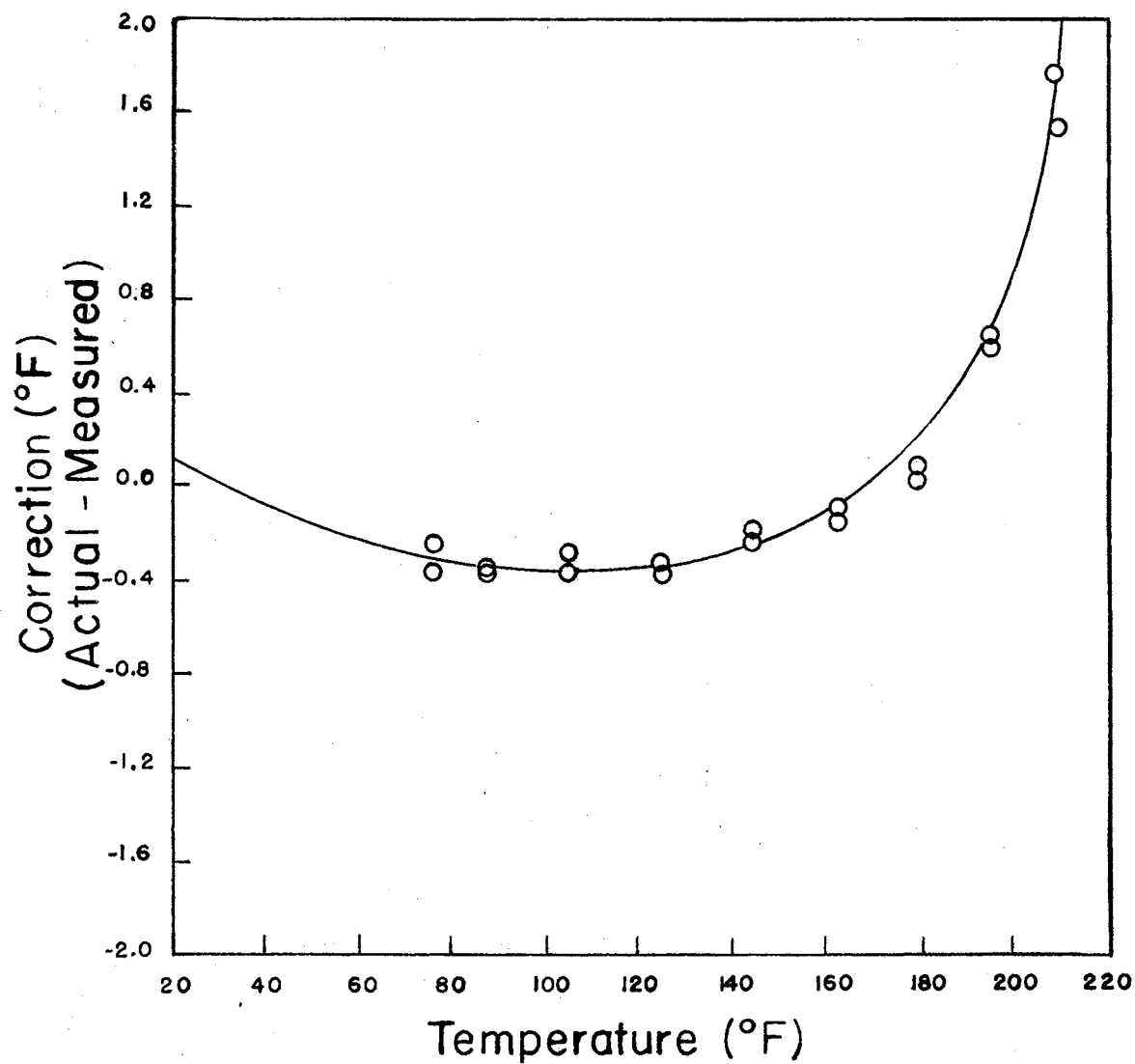


Figure 13. Difference Between Actual and Calculated Temperature as Read by the Copper-Constantan Thermocouple Used in This Study Versus Temperature

As seen in Figure 1 there is the possibility if not probability that the two mercury levels will not be the same height above the bottom of the test cell.

The cylinders shown in Figure 1 are 8 inches tall meaning the maximum unaccounted for static head could be ± 8 inches. This would translate into a pressure error of ± 4 psi. However, the actual range of pressure error is probably less since no more than two complete pumpfuls of oil were ever removed from the system before valve F was opened and the two pumpfuls of oil returned to the system thus returning the mercury levels to approximately the same level.

VITA

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