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RELATIVE VOLATILITY IN THE SYSTEM

1-BUTENE - n-BUTANE

BY

STEVEN LEWIS WALKER, 1950-

A THESIS

Presented to the Faculty of the Graduate School of the

UNIVERSITY OF MISSOURI-ROLLA

In Partial Fulfillment of the Requirements for the Degree

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Approved by

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James F. Roberts

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ABSTRACT

An apparatus suitable for the rapid collection of P-x data at constant T is described. Isothermal P-x data at 40, 70, 100, 130, and 160 degrees Fahrenheit at the extremes of the composition range for the 1-butene - n-butane system are presented as a demonstration of the suitability of the device for its intended purpose. Limiting values of the relative volatility for the binary are presented. The relative volatilities were calculated using limiting forms of the general coexistence equation which are given in the literature. Several recommendations are given for improvements of the equipment and experimental technique.

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I. INTRODUCTION

Industrial process design requires thermodynamic data of high precision over wide ranges of temperature and pressure. Although extensive theoretical procedures are available for the prediction of thermodynamic properties of mixtures from pure component data, the prediction process is highly complicated and requires considerable amounts of computer and engineering time. In addition, for new or different mixtures the predictions may ultimately have to be checked experimentally anyway. The result of these needs and facts is that an attractive alternative to the theoretical prediction of these thermodynamic properties would be easy, accurate experimental measurements of the desired quantities. The experimental alternative might prove considerably more reliable and less expensive if the proper equipment and techniques were available. This thesis deals with the development of the necessary pressure measuring equipment to step toward the realization of the more attractive experimental method.

A. The Problem

Pressure is one of the basic and most important of the thermodynamic properties which needs to be measured in any experiment. Rapid and precise pressure measurement is one of the most important aspects of a satisfactory experimental design. The problem to be attacked in this study was the following:

Develop a differential pressure transducer which has

the following attributes:

1. Mass less than 100 grams
2. Able to withstand 2000 pounds per square inch absolute
3. Sensitive to pressure differences of 0.01 pounds per square inch
4. Useful between -100 and +100 degrees Centigrade
5. Able to withstand 2000 pounds per square inch difference
6. Constructed of corrosion resistant materials

The transducer should be used in conjunction with the Burnett P-V-T apparatus to measure the behavior of propylene at 100 and 160 degrees Fahrenheit.

During the course of the development of the transducer the context of the problem changed with respect to the data to be taken with the transducer in order to demonstrate it. It was decided to make use of the low mass of the device in order to measure vapor pressures of mixtures of butane and 1-butene for the purpose of demonstrating both the transducer and a convenient method for determining the limiting values of relative volatility for a binary mixture.

B. Method of Solution

The problem just presented was approached in a straightforward manner. Construction of the device was begun using hired labor. When the results were somewhat disappointing, the construction task was assumed by the author and his

advisor. A combined high pressure cell and transducer was constructed for the purpose of making up and measuring the vapor pressures of mixtures of hydrocarbons. The resulting device was tested and then used to measure vapor pressures of butane and 1-butene and their dilute solutions in one another at 30 degree intervals between 40 and 160 degrees Fahrenheit. The temperature limits were imposed by the limitations of the temperature bath which was used. In addition, a literature search was conducted to find comparable data and other measuring techniques.

II. DESCRIPTION OF EQUIPMENT

The experimental equipment developed in this study will be described first since it was the primary object of the effort. The unique equipment used in this study consists of a combined cell and transducer which is shown in Figure 1. It is suitable for making up mixtures of hydrocarbons of precisely known composition and for the measurement of their vapor pressures. The unit may be used over a wide range of temperatures, pressures, and compositions. The device is used in conjunction with necessary peripheral equipment during the course of the measurements.

A. Pressure Transducer and Cell

Figure 2 shows a section view of the transducer with the internal details clearly visible. The device consists of two stainless steel discs machined with male and female steps designed to engage and crimp the diaphragm upon assembly. The mating face of the male disc is dished about 0.5 degree from edge to center. The mating face of the female disc is machined flat for 1/16-inch radially and then dished about 0.5 degree to the center. The flat on the female surface provides footing for the edge on the male surface to clamp and seal the diaphragm. A spray on teflon coating is applied during assembly to insure the seal. The diaphragm sandwiched between the dished faces is cut from 0.001 inch 302 stainless steel shim stock. The assembly is secured by 12 6-32 socket head machine screws spaced at equal angles around the perimeter. The holes in the female disc are tapped to accept

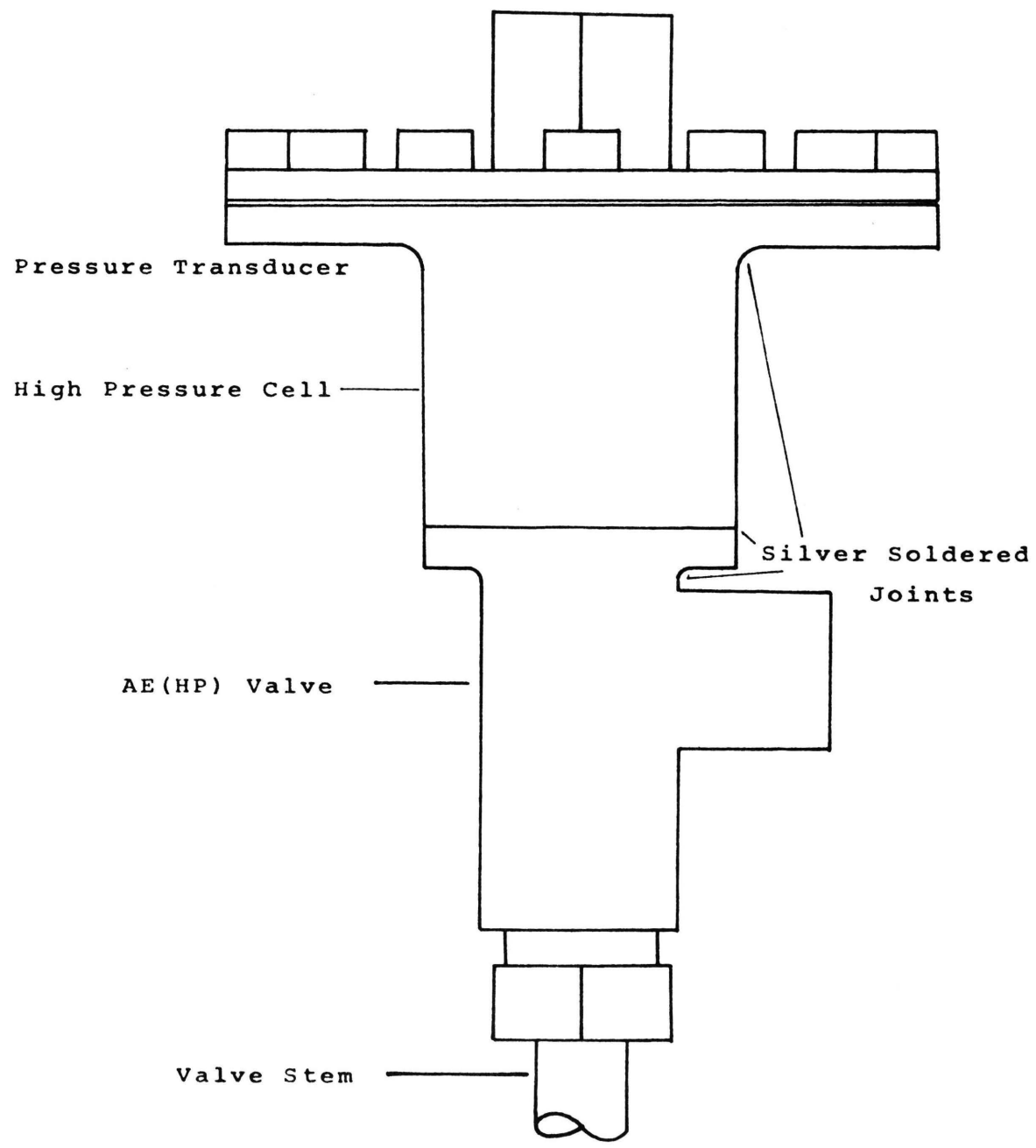


Figure 1. Cell and Transducer for Vapor Pressure Measurement

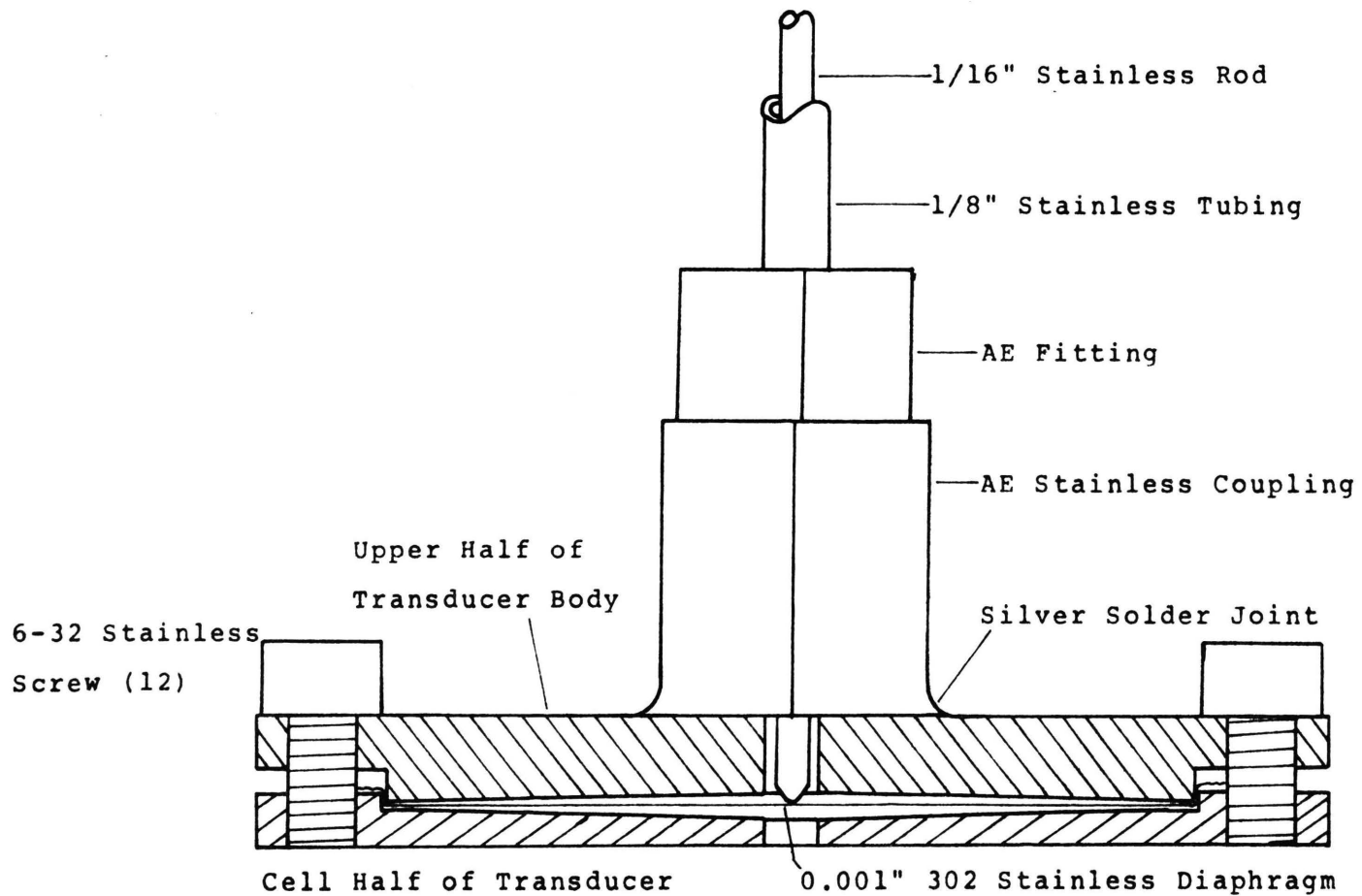
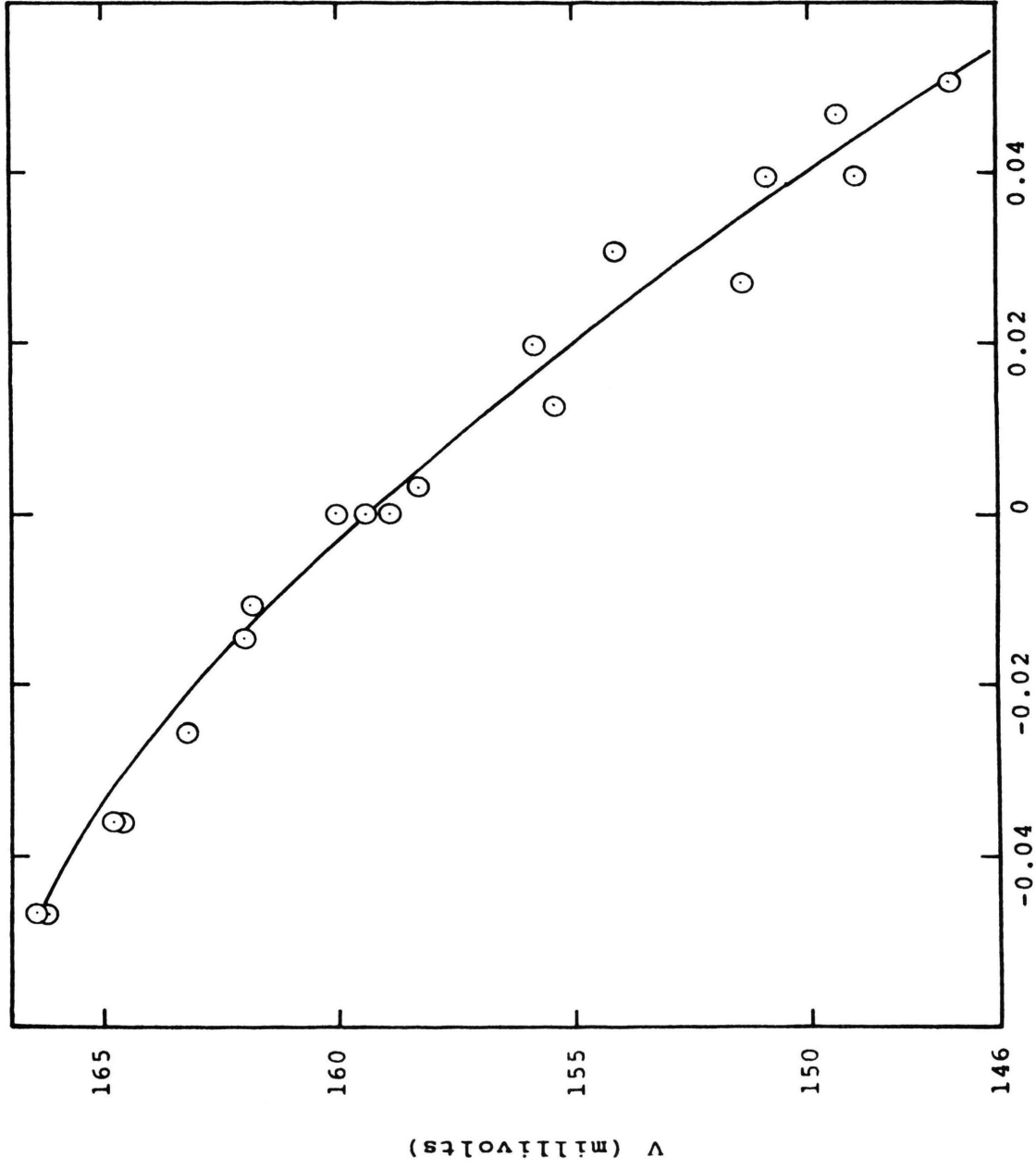


Figure 2. Pressure Transducer Section View

the screws. The entire transducer is 2 inches in diameter with an effective diaphragm cavity of about 1.6-inch diameter. The device is about 3/16 of an inch thick neglecting the height of the screw heads. Holes of 3/32-inch diameter are drilled in the centers of the discs. The hole in the female disc connects directly to the high pressure cell. The hole in the male disc connects to half of an Autoclave Engineers positive bite coupling which is silver soldered to the outer side of the disc. A length of 1/8-inch stainless tubing is connected at the coupling and carries the external pressure and contains the 1/16-inch diameter stainless rod which is part of the null sensing apparatus. All joints in the construction are silver soldered.

The zero pressure differential or null point of the transducer is sensed by way of the stainless rod which follows the movements of the diaphragm within the dished cavity. The stainless rod drives a steel core whose position can be sensed by a Trans Tek differential transformer fixed on the stainless tubing. A nylon spacer maintains a constant distance along the tubing between the transformer and the transducer body. The transformer produces a voltage which is linear with respect to the displacement of the core. In this manner pressure differential is converted to a voltage output to produce Figure 3.

The high sensitivity shown in Figure 3 is one of several important features of the transducer which make it well suited to do the job for which it was constructed. Combined



P (psid)

Figure 3. Transducer Sensitivity Curve

with its sensitivity of about 0.01 pounds per square inch difference are its light weight, strength, relatively low pressure and temperature dependence, convenience of use, and ease of repair. The entire assembly shown in Figure 1 with a valve handle on the stem has a mass of about 226 grams and, therefore, can be weighed on a 240 gram capacity Mettler analytical balance for the purpose of determining the composition of the mixture which is being placed in it. The device is capable of operating at high pressure and can withstand large overpressures due to the support given the diaphragm by the slightly dished cavity at overpressures in excess of about 1 pound per square inch difference. Between temperatures of 40 and 160 degrees Fahrenheit and pressures of 15 and 150 pounds per square inch absolute the drift in the null point of the transducer is significantly less than the desired sensitivity range of 0.01 pound per square inch difference (See Appendix B). The system for use of the transducer is such that the time for determining a vapor pressure at some desired temperature is limited by the slowest step which is the time required to stabilize the temperature controlling medium at the desired temperature. In the event that something should cause the diaphragm to be damaged the transducer can be easily dismantled to replace the injured part.

B. Equipment Configuration

The setup described here is the one which was used for the determination of the data which is presented later in

this thesis. It is presented for the sake of completeness since it is not the ultimate in efficiency or convenience which can be had for the use of the device described above. The equipment is continuously being refined and improved. The setup used consists of a manifold set to which are coupled bottles containing the materials to be studied, a cylinder of nitrogen, a vacuum pump, a dial type Heise pressure gauge, and a Ruska dead weight gauge. There is a Ruska precision metering pump attached to the system also. In addition a connection is provided for connecting the cell to the system. A water manometer can also be attached for the purpose of measuring the sensitivity of the transducer. There were two modes of use for the manifold and its attached equipment - metering and measuring. They are discussed in detail below.

The metering mode shown schematically in Figure 4 was used to meter the sample mixtures into the high pressure cell in such a manner that the amount of material introduced could be controlled. This technique allowed one to roughly predict the composition of the mixture as it was being made up. Exact composition was determined by weighing.

Once a mixture of known composition was made up the transducer was placed in the thermostat of the configuration shown in Figure 5. That setup was the measuring mode. The manifold set was filled with nitrogen and the dead weight gauge was connected for the purpose of determining the precise pressure of the gas in the manifold which was equal to

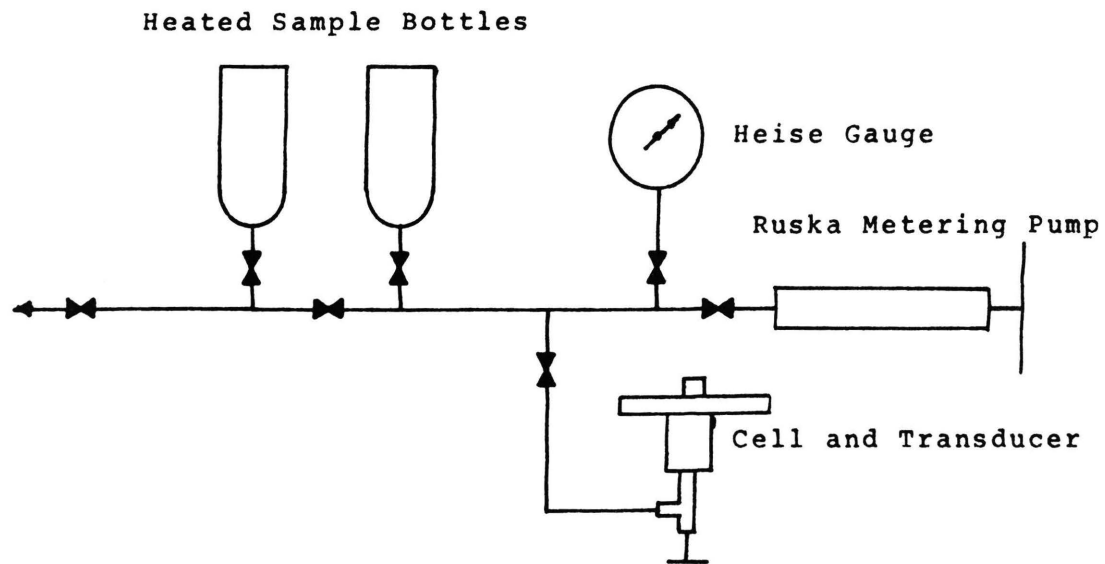


Figure 4. Schematic of System for Making Sample Mixtures

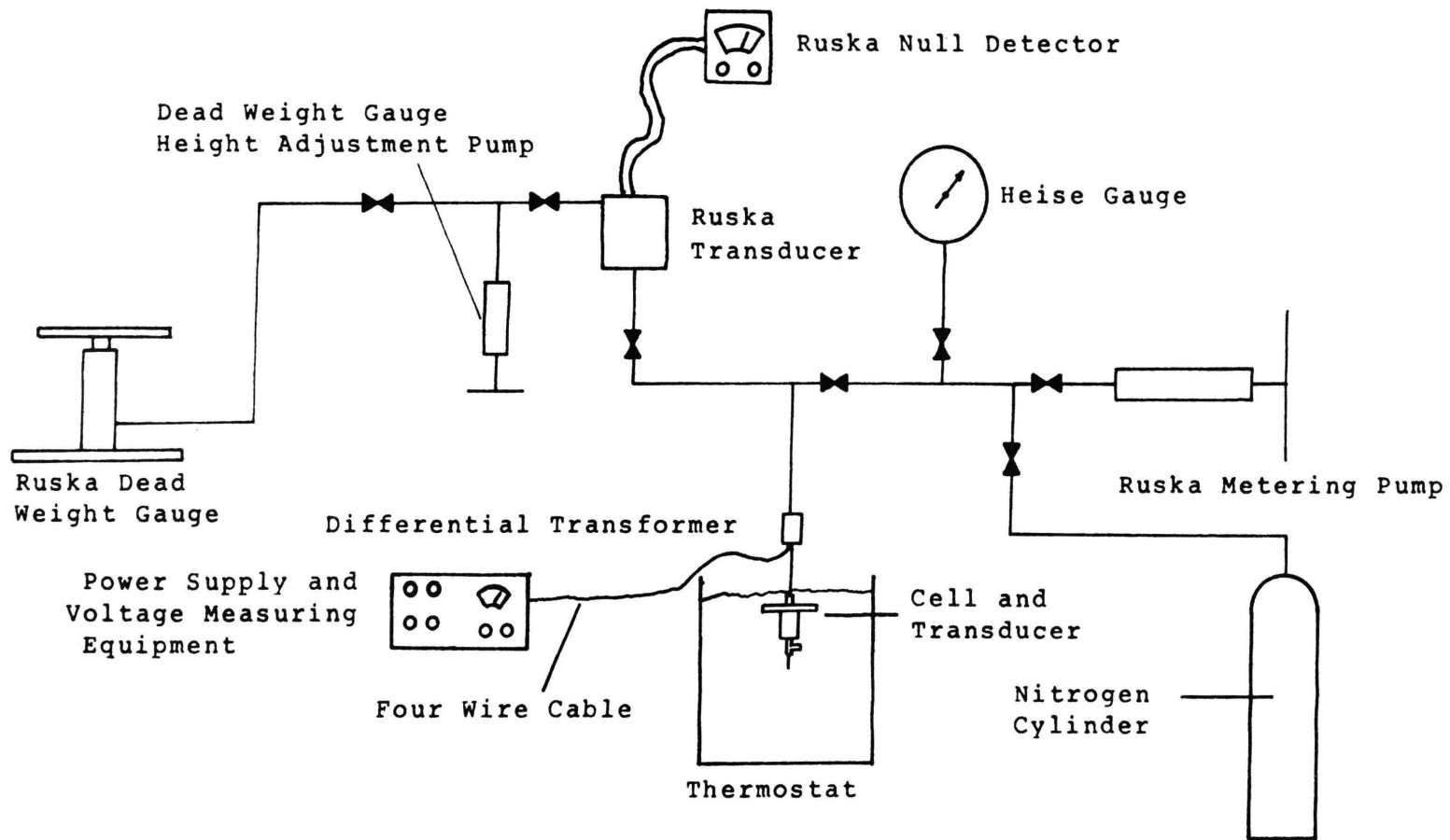


Figure 5. Schematic of System for Measuring Pressure

that in the cell when the transducer was balanced. The measuring mode was the most complex of the two configurations as it required the use of the entire set of electronic equipment used for making the measurements of temperature and pressure. Temperature was maintained by use of a Neslab Instruments RTE 4 circulating temperature bath serial number e04124 and was measured by use of a Leeds & Northrup platinum resistance thermometer serial number 1705472 in conjunction with a Rubicon Instruments Mueller Bridge model 1551 serial number B-1347. The bridge circuit was balanced by use of a Leeds & Northrup DC null detector catalog number 9834. Pressure was measured with a Ruska dead weight gauge serial number 17889 and a dial type Heise gauge CMM 7358. The range used on the dead weight gauge was 6-6000 pounds per square inch in 0.01 pounds per square inch increments and the Heise gauge had a range of 0-100 pounds per square inch with 0.1 pounds per square inch graduations. The dead weight gauge measured to a precision of 0.01 pounds per square inch while the Heise gauge was read to a precision of 0.01 pounds per square inch. The null point of the transducer was detected by means of the output from a Trans-Tek model 240-000 K1 differential transformer which was measured using a Leeds & Northrup model K-3 guarded potentiometer serial number 1704603. The potentiometer bridge circuit was balanced using the DC null detector described above. All manifold valves were high pressure units purchased from

Autoclave Engineers. Vacuum was provided by a Welch unit
serial number 128633.

III. LITERATURE REVIEW

The literature review presented here is designed to serve two purposes - to present the train of investigations and thought which lead to the construction of the equipment described in this work and to indicate the existing data which are comparable to those obtained in this study. In addition to the history, the first of these purposes will be concerned with the presentation of the fundamental mathematical relationships which were used in the reduction of the P-x data taken in this study.

A. The P-x Approach to Vapor-Liquid Equilibrium

The Gibbs Phase Rule makes it obvious that for a binary mixture with two phases in equilibrium the definition of just two of the intensive properties of the system P-x, T-x, P-y, T-y will define the state of the system and make possible the calculation of all other intensive properties of the system. It has been of considerable interest to various investigators to determine how best to make use of these facts to improve the speed and accuracy of experimental determinations of the properties of binary mixtures in liquid-vapor equilibrium. While it is helpful to take data in redundant sets, such techniques are more time consuming and the results are often not consistent. That is, the measured y values in equilibrium with solutions of composition x are not always in mathematical agreement with the P-x data. There then arises the question of which data is "correct" - that is, which data does one use to predict the behavior of the binary in order

to design a distillation process to separate it. The problem of which data to take has been approached by several investigators.

Barker⁽¹⁾ presented a method for determining activity coefficients in binaries which relied upon P-x measurements and produced good agreement with measured y values. While not as direct as the approaches of others, Barker's method does illustrate what others have since found to be true - that P-x measurements are quite often as reliable and convenient as a full set of measurements.

Several investigators have presented methods for calculating liquid-vapor compositions from experimental P-x at constant T or T-x at constant P data. In this discussion P-x means P-x at constant T. Tao⁽²⁾ presents a rigorous method suitable for computer calculation which makes use of the Gibbs-Duhem equation to calculate activity coefficients and then calculates the compositions from the activity coefficients. Ljunglin and Van Ness⁽³⁾ present a method of using the Gibbs-Duhem equation directly to compute the compositions by use of the coexistence equation which must be satisfied by all phases which are in equilibrium. The method given is suitable for computer calculation. Mixon, Gumowski, and Carpenter⁽⁴⁾ present a method which can be applied to systems with more than two components. A later work by Van Ness⁽⁵⁾ discusses the disadvantages of using the coexistence equation which Mixon, et al claim their method does not suffer from. However, the general coexistence equation is

still useful as demonstrated by Manley and Swift⁽⁶⁾ in their study of the Propane-Propene system. There has been a great deal of interest in making better use of existing data and in taking better data at a more rapid pace.

Why all the interest in the use of P-x data in the determination of vapor-liquid equilibrium? The answer is convenience and accuracy. In a recent pair of papers Van Ness, Byer, and Gibbs^(7,8) present an appraisal of data reduction methods which indicates that, since measurements of y are of the greatest uncertainty, P-x data should be used in preference to any combination of variables which includes y. They further conclude that the redundant y values are useful only for consistency tests which are of dubious value. They state that unless a consistency test is considered indispensable, experimental time and effort are better spent on improvement of the P-x measurements than on the measurement of redundant data. The second article of the pair presents correlations of data based on P-x data for 15 systems. The data bears out the conclusions stated above. Gibbs and Van Ness⁽⁹⁾ have constructed an apparatus designed specifically for rapidly taking P-x data in which compositions are determined by volumetric metering and temperature and pressure are precisely measured. In addition to direct calculation of the vapor compositions, other quantities have been shown to be calculable in a straightforward manner from only P-x data. Manley⁽¹⁰⁾ has shown a method whereby the limiting relative volatility of a binary system can be calculated using only P-x data.

Other investigators have examined the problem of experimental error and its effect on the results of using only P-x data and forcing the resulting y values to be consistent. Ulrichson and Stevenson⁽¹¹⁾ concluded that the use of P-x data in such a manner would be questionable unless the equation used represented the original data within the uncertainty of the experimental measurement. They emphasized the need for experimental estimates of the uncertainty of the measurements. Mackay and Salvador⁽¹²⁾ examined the errors in y values computed from vapor pressure data and those measured directly and concluded that for systems of high relative volatility the P-x method is preferable. However, Manley⁽¹³⁾ examined the method from the point of view of the effect of errors on the relative volatility of the two components and concluded the opposite of Mackay and Salvador. Further, he proposed an experimental method whereby one could directly measure a differential property and obtain a value for the relative volatility. A variation of the method which Manley proposed has been used to obtain the data given in this study.

The method which Manley proposed addresses itself mainly to limiting values of relative volatility although it does discuss the methods previously mentioned here with respect to their effect on the value of the relative volatility. The technique makes use of the previous work of Manley and Swift and of Manley^(6,9). The applicable equations given by those works are:

$$\lim_{x \rightarrow 0} \alpha = 1 + \left[\frac{\Delta Z}{P} \frac{dP}{dx} \right]_{x=0} \quad (1)$$

$$\lim_{x \rightarrow 1} \alpha = \frac{1}{1 - \left[\frac{\Delta Z}{P} \frac{dP}{dx} \right]_{x=1}} \quad (2)$$

Where:

α is the relative volatility $\frac{y(1-x)}{x(1-y)}$

ΔZ is the difference between vapor and liquid compressibility factors

P is the vapor pressure at the limit

x, y the mole fraction of the more volatile component in the liquid phase and vapor phase respectively

The terms in brackets in equations (1,2) are to be evaluated experimentally. Manley proposed to do this by placing two high pressure cells containing mixtures of slightly different composition in a temperature bath and directly measuring the difference in the vapor pressures exhibited by the two mixtures. One of the cells would hold a pure component and the other would hold a mixture containing only a trace of the other component. Manley suggests that from his error analysis the relative volatility should be less than about 1.5 or the liquid mole fraction less than about 0.07. Precise temperature control would not be necessary since the two

mixtures would be at the same temperature when the measurement was taken and errors in other quantities such as material purity would tend to cancel. The important variables would be overall composition and its relationship to liquid composition along with the observed pressure difference. The other quantities needed would be available from other sources as they would be the more common pure component data.

B. Thermodynamic Properties of 1-Butene, n-Butane and Their Mixtures

There is, as one might expect, considerable data in the literature on the two pure materials. However, the same cannot be said of their mixtures in the temperature range selected for this study.

Several investigators and handbooks report thermodynamic properties for n-butane which are suitable for comparison to the data of this study^(14, 15, 16, 17, 18). These include all the data necessary for finding the quantities necessary for equations (1,2) to be applied to P-x data for the system given in this study. In addition there are two sources^(17, 19) which report data for 1-butene which are usable in this study.

Equilibrium data for the system studied here are somewhat more difficult to locate than the pure component properties. There have been two pieces of experimental work done with the system 1-butene and n-butane which are in the temperature range of interest here. The more recent one is by Manley⁽²⁰⁾ and yields data at 125 degrees Fahrenheit.

The earlier work is one by Sage and Lacey⁽²¹⁾ which yields data at 100 degrees and 160 degrees Fahrenheit. The data of each is such that relative volatilities can be calculated for mixtures across the composition range.

IV. EXPERIMENTAL PROCEDURE

The procedure used to obtain the data presented in this thesis was dictated by the situation of using a device which was still under development. As a result, the procedure does not reflect the very best obtainable situation for the equipment used. However, it does reflect a strong effort to obtain the best possible data under the circumstances. The technique used is presented here for the sake of completeness and in order to clarify its effect on the experimental results. Better techniques for use in the future will be discussed in the section on results.

A. Sample Makeup

The several steps given below are those which were followed in making up the samples whose vapor pressures were determined in this study. Samples were made up as follows:

1. Cell evacuated and weighed for tare weight.
2. System and cell purged with butene and re-evacuated.
3. Cell filled with butene and weighed.
4. Cell vented to proper mass for desired quantity of butene.
5. System purged with butane and filled with liquid butane.
6. With cell valve slightly open butane metered in to achieve the approximate composition desired.
7. Cell weighed and valve opening plugged.

The list above refers to the system as the metering set up to the point where the cell is attached. A purge includes vacuum, filling with next component, and vacuum again. The valve opening was plugged after the last weighing in order to preclude any possibility of leakage by that avenue during the course of an experimental run. In addition, the handle was removed from the stem before placing the cell in the thermostat.

The sample which has been placed in the thermostat should be one which has a known composition and exhibits a vapor pressure which is dependent solely upon temperature. To insure that these criteria were met the samples were weighed in such a manner that the cell would be about 80 per cent full of liquid at all times. This insured two things - that the overall composition would be essentially the same as the liquid composition and that the effect of any noncondensable in the system would be the same for all cases.

B. Pressure Measurement

Once the cell was placed in the temperature bath it was connected to the manifold system which was filled with nitrogen. The resistance thermometer was placed in the temperature bath near the cell to measure the bath temperature as close to the cell as possible. The temperature controller was set to 40 degrees Fahrenheit. The series of pressure measurements was then made as follows:

1. Measure temperature (resistance) of thermometer.
2. Set zero of transducer on potentiometer.

3. Balance transducer and read Heise gauge and dead weight gauge.
4. Set next temperature on controller and return to step 1.

During the series of measurements the sample was stirred by shaking several times at 3 or 4 minute intervals before the temperature was measured to insure that the system of liquid and vapor contained in the cell was, indeed, at equilibrium. The details of step 2 above are discussed in Appendix B.

It should be noted that two gauges were used in this study. The reason for this technique was to insure that readings could be quickly reached with the dead weight gauge after the Heise gauge had been read. It should also be pointed out that the vapor pressure of pure butane at 40 degrees is less than the least pressure measurable with the dead weight gauge. Hence, it was necessary to rely on the Heise reading alone at the lowest temperature at the butane end.

V. RESULTS AND DISCUSSION

The results presented and discussed in this section are those measurements which were made of the necessary quantities to be used in equations (1,2) to calculate values of limiting relative volatility for the 1-butene - n-butane system. The results are presented and compared with literature data and Raoult's Law results.

A. Results

The results of the data taking effort are presented in Table I. Table II presents the results given in Table I after they have been corrected to the reference temperatures used for this study. A description of the correction method used is given in Appendix A. Table III gives the derived results of the data in Table II. Those results include the calculated values of the limiting relative volatility, α , estimates of the precision of α , $\Delta \alpha$, and the value of the natural logarithm of α . The third quantity is given as a measure of the economic effect of the value of relative volatility as explained by Manley⁽¹³⁾. A description of how the error estimate was arrived at is given in Appendix A.

The results given in Tables II and III are presented in comparison to the available literature data in Figures 6, 7, 8, 9, 10. The results for a system which obeys Raoult's Law is also shown for comparison in Figures 6 and 7.

B. Discussion

The results obtained and presented in Tables I, II, and III must be viewed as the limited data which they are. It

TABLE I
EXPERIMENTALLY OBSERVED DATA

<u>x</u> (mole fraction butene)	<u>T (°F.)</u>	<u>P (psia)</u>
1.0000	39.98	22.13
	69.95	38.36
	100.47	63.21
	129.72	96.30
	159.93	143.05
0.9456	40.03	21.78
	69.96	37.91
	99.88	61.76
	129.74	95.45
	159.76	141.47
0.9032	39.98	21.64
	69.97	37.69
	99.88	61.38
	129.74	94.91
	159.76	140.26
0.0950	40.00	18.57
	69.98	32.28
	99.87	52.96
	129.75	82.44
	159.75	122.91

TABLE I (continued)

<u>x</u> (mole fraction butene)	<u>T (°F.)</u>	<u>P (psia)</u>
0.0432	39.98	18.41
	69.97	31.84
	99.88	52.43
	129.75	81.49
	159.76	121.51
0.0000	40.00	18.13
	70.03	31.56
	99.85	51.82
	129.74	80.71
	159.78	120.57

TABLE II
 TEMPERATURE ADJUSTED RAW DATA

<u>x</u> (mole fraction butene)	<u>T (°F.)</u>	<u>P (psia)</u>
1.0000	40.0	22.13
	70.0	38.39
	100.0	62.76
	130.0	96.67
	160.0	143.18
0.9456	40.0	21.77
	70.0	37.94
	100.0	61.88
	130.0	95.79
	160.0	141.89
0.9032	40.0	21.64
	70.0	37.71
	100.0	61.50
	130.0	95.24
	160.0	140.67
0.0950	40.0	18.57
	70.0	32.29
	100.0	53.07
	130.0	82.73
	160.0	123.29

TABLE II (continued)

<u>x</u> (mole fraction butene)	<u>T (°F.)</u>	<u>P (psia)</u>
0.0432	40.0	18.42
	70.0	31.86
	100.0	52.53
	130.0	81.78
	160.0	121.88
0.0000	40.0	18.13
	70.0	31.54
	100.0	51.94
	130.0	81.01
	160.0	120.90

TABLE III
RESULTS OF RELATIVE VOLATILITY CALCULATIONS
OF EQUATIONS (1,2)

A. Equation (1)

<u>T (°F.)</u>	<u>α</u>	<u>$\Delta\alpha$</u>	<u>$\ln \alpha$</u>
40.0	1.247	0.015	0.2211
	1.359	0.025	0.3066
70.0	1.235	0.012	0.2109
	1.220	0.015	0.1992
100.0	1.205	0.011	0.1862
	1.235	0.013	0.2112
130.0	1.190	0.010	0.1736
	1.187	0.010	0.1712
160.0	1.164	0.008	0.1522
	1.148	0.008	0.1383

B. Equation (2)

<u>T (°F.)</u>	<u>α</u>	<u>$\Delta\alpha$</u>	<u>$\ln \alpha$</u>
40.0	1.279	0.021	0.2460
	1.398	0.036	0.3353
70.0	1.169	0.009	0.1564
	1.199	0.012	0.1817
100.0	1.183	0.009	0.1684
	1.228	0.012	0.2053
130.0	1.128	0.006	0.1210
	1.141	0.007	0.1316
160.0	1.142	0.007	0.1328
	1.130	0.007	0.1221

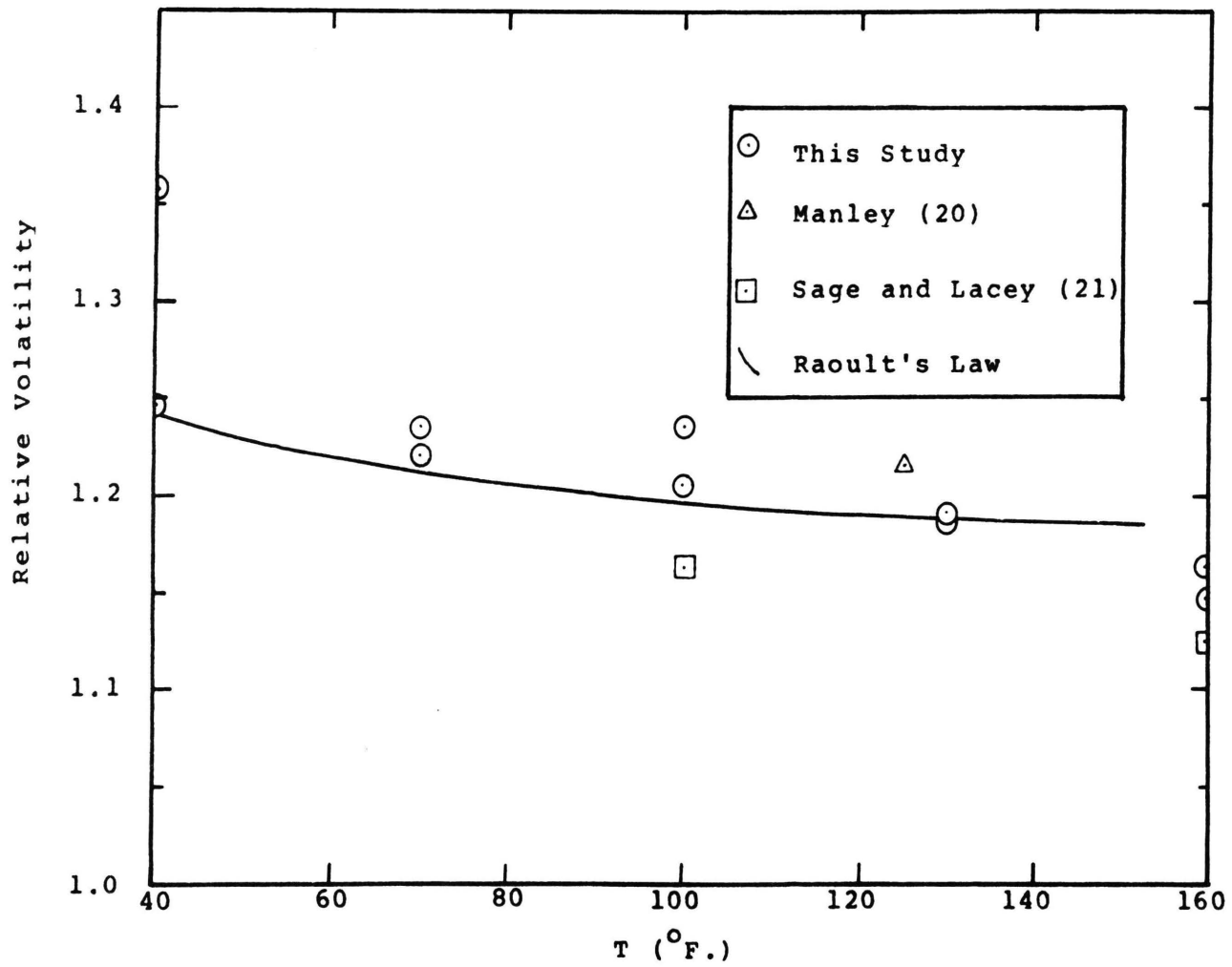


Figure 6. Relative Volatility in Butane Rich System

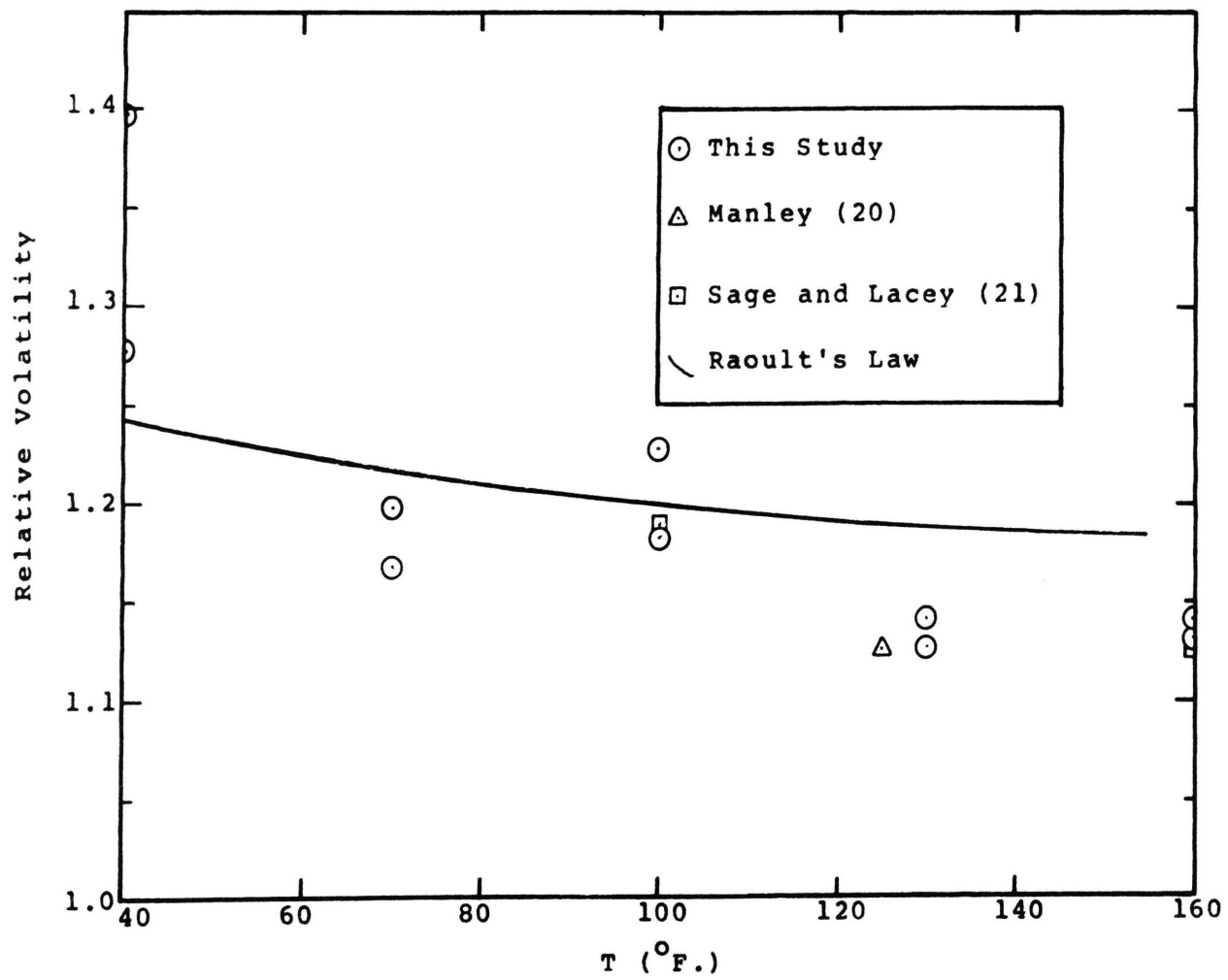


Figure 7. Relative Volatility in Butene Rich System

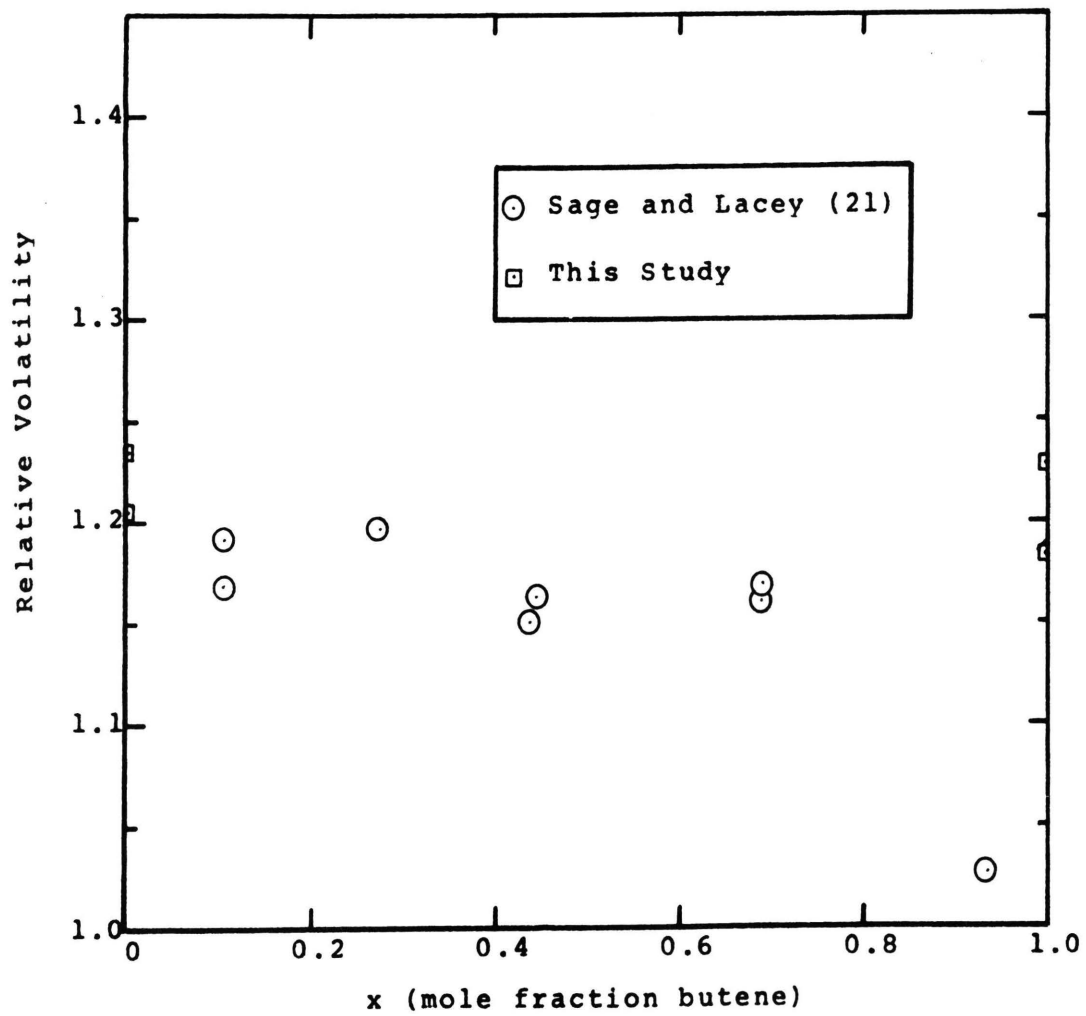


Figure 8. Relative Volatility at 100° F.

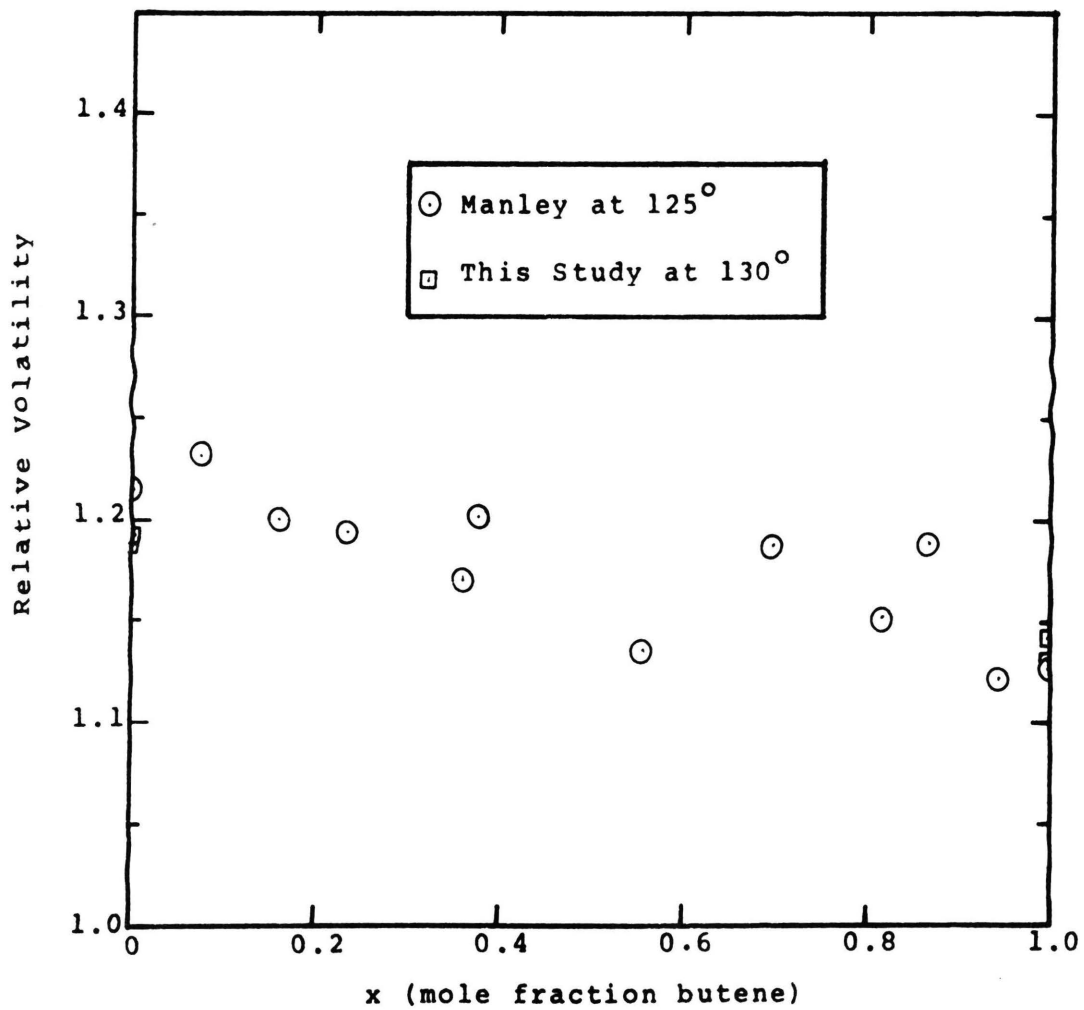


Figure 9. Relative Volatility near 125° F.

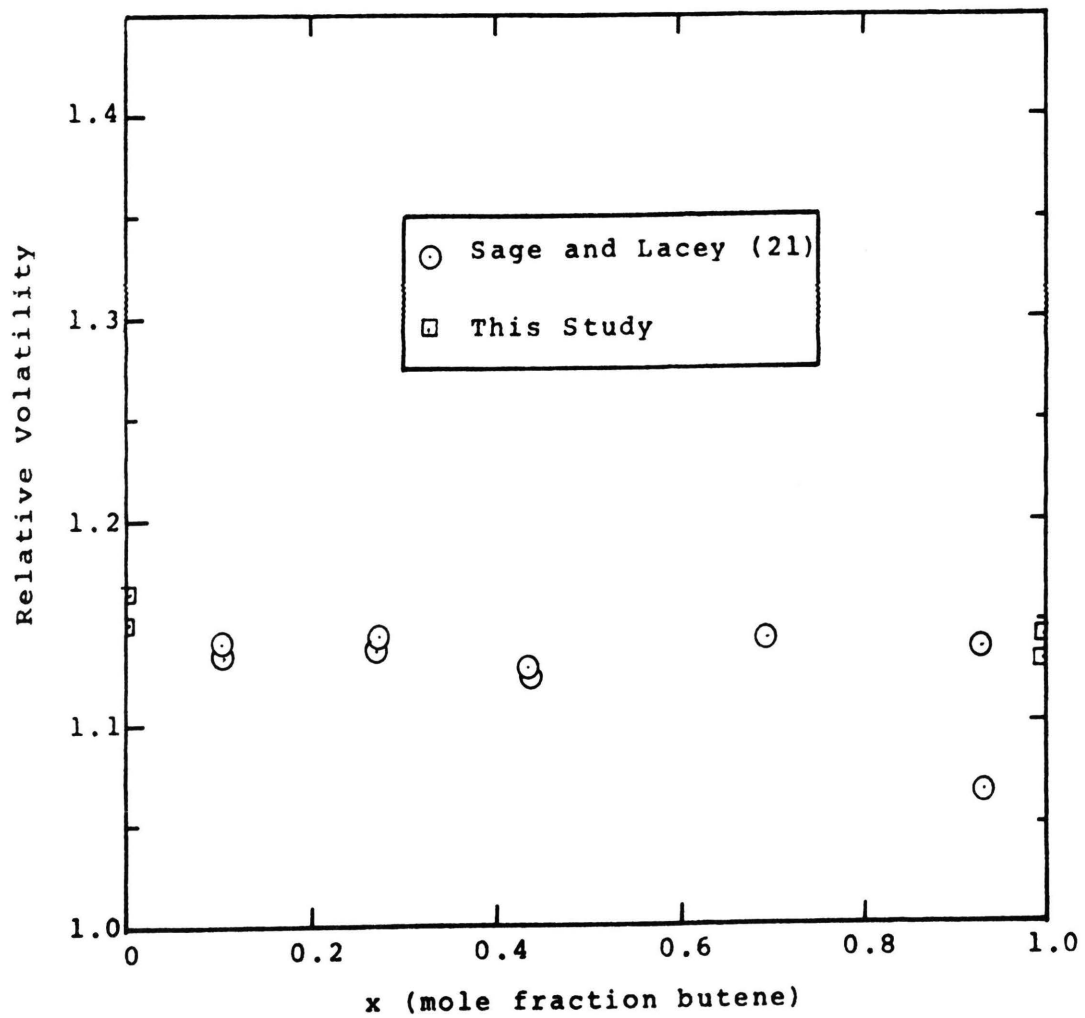


Figure 10. Relative Volatility at 160° F.

should first be noted that they were taken only near the ends of the composition range in order that equations (1,2) might be applied to them. Figures 6 and 7 indicate a considerable amount of scatter in the data which is confirmed by the fact that only four of the ten pairs of points presented agree with one another within the limits of the estimated error for the individual points. This disagreement is a source of some concern since the data were taken in order to demonstrate a new and previously untried experimental apparatus. It is believed, however, that these discrepancies are not the result of defects in the apparatus, but are the result of uncontrolled variations in the experimental parameters, especially temperature. Figures 8, 9, and 10 clearly show the scatter which has previously resulted during vapor-liquid equilibrium studies of the butene-butane system. This scatter might indicate that the error estimates given in this study are overly optimistic or that something was amiss during the measurements. Appendix A will discuss these possibilities further. However, it should be noted that the values determined by this study seem to agree with the literature data within the scatter shown on the graphs, although it must be pointed out that in Figure 9 the data of Manley at 125 degrees are compared with data of this study at 130 degrees. Thus, the apparent agreement in that figure might simply indicate the results of fortuitous scattering of both sets of data or the small difference in the α values at 5 degree temperature intervals.

Although only a few of the data given agree well within the estimated experimental error, the fact that a significant number do show some repeatability is itself an encouragement. Such behavior indicates that refinements in techniques and equipment will bring better results. Indeed, during the course of the experiments stirring was found to improve the results. The need for stirring indicates that more attention must be given to insuring that the system is at equilibrium before a pressure measurement is taken. The results of the experiments where stirring was not used (see Figure 7 and part B of Table III) show consistency for only one pair of data points - those at 160 degrees. The data taken with stirring (see Figure 6 and part A of Table III) show consistency for three of the five pairs of points - those at 70 degrees, 130 degrees, and 160 degrees. Stirring is a good addition to the technique.

VI. CONCLUSIONS

The results of the study conducted for this thesis have led to the following conclusions:

1. An apparatus has been constructed which
 - a. measures pressure differences as small as 0.01 pounds per square inch
 - b. has a temperature independent response over a range of 40-160 degrees Fahrenheit
 - c. has a null point independent of pressure between 15 and 150 pound per square inch absolute
 - d. can withstand pressures as high as 150 pounds per square inch absolute
 - e. can withstand pressure differentials as high as 150 pounds per square inch
 - f. weighs less than 100 grams
 - g. is constructed of corrosion resistant materials
2. The apparatus represents a convenient technique determining P-x data of high precision due to the measurement of composition by gravimetric methods.
3. Preliminary data taken with the apparatus show promising agreement with literature data.
4. The equations given by Manley⁽⁹⁾ can readily be applied to raw experimental data with good results.

5. The technique for using the apparatus and the apparatus itself need refinement.
6. More work of the type outlined in this thesis should be done.

VII. RECOMMENDATIONS

Since preliminary data indicates that the device constructed for this study can produce good results, it is recommended that the equipment and experimental technique be refined in order to improve the data.

One of the primary problems with the apparatus is discussed in Appendix B. The problem is leaks. The seal at the edge of the diaphragm is difficult to make. It is recommended that steps be taken in future designs to improve the surface finish of the female disc at the circle where the seal is made and to insure a more uniform and sharp edge on the male disc. The improvement of the edge seal by such methods would also aid in preventing the diaphragm from slipping at the edge when overpressured. It is further recommended that a method for cutting uniform diaphragms for the assembly be found and used. Great care should be taken to insure uniformity and good finish during construction.

The data from this study have shown more scatter than seems necessary. It is recommended that steps be taken to eliminate the error problems discussed in Appendix A. The technique should be refined by thoroughly degassing all materials to be studied so that vapor volume will not be a critical factor in the measurement. It is further recommended that the two cell technique suggested by Manley⁽¹³⁾ be fully implemented to deal with the problem of temperature variations. Provision for stirring the cell which contains

a mixture should be included in future experimental designs. A metering system should be constructed which has the smallest volume possible in order to minimize wasted materials.

Aside from slight modifications in the present equipment design it is recommended that other designs be considered with greater changes such as smaller diameter and thicker body along with a deeper dish.

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VITA

Steven Lewis Walker was born May 8, 1950 at Morgantown, West Virginia the son of Delmar Lewis and Mary Geneva Walker. He received his secondary education at Glendale High School in Springfield, Missouri from 1964 to 1968. He entered the University of Missouri-Rolla in September 1968 and received his bachelor's degree in Chemical Engineering in May 1972. Since that time he has been enrolled in the graduate school at the University of Missouri-Rolla and is presently a candidate for the degree Master of Science in Chemical Engineering.

APPENDIX A
ERROR ANALYSIS

There were three variables measured in this series of experiments. They were z , the overall composition of the mixture, T , the temperature of the mixture, and P , the vapor pressure exhibited by the mixture. The errors in all of these quantities will be examined.

The overall composition of the mixture was dependent upon the results of three weighings on a precision analytical balance Mettler model H14. The balance weighs to 0.1 milligram and that figure was taken to be the uncertainty of the measurement. Using techniques of analysis for normally distributed variables, the largest expected error in a mass measurement would be 0.00017 gram. The effect of this uncertainty on the value of z calculated from it is so small as to be negligible. In this study the value of z was considered to be certain. However, the overall composition of the mixture is not quite the variable of interest in a study where one hopes to measure P - x data. The quantity really desired is x , the liquid composition. A series of calculations was made for the pair of materials used in this study for each of the temperatures used. A fixed volume was assumed to be 0.8 full of liquid in equilibrium with vapor. The value of relative volatility calculated by assuming that x and z were equal was used along with the liquid and vapor densities of Canjar and Manning⁽¹⁸⁾ at each temperature. The appropriate z was assumed and material balances were made to calculate a value for x . The resulting x was then compared to the z value assumed. The results of those

calculations are presented in Table IV. The largest discrepancy between z and x was 3 in the fourth decimal place. No correction was made for the difference between x and z for this study.

TABLE IV
LIQUID AND OVERALL COMPOSITIONS

<u>T (°F.)</u>	<u>z</u>	<u>x</u>
40.0	0.90000	0.89996
70.0	0.90000	0.89968
100.0	0.90000	0.90008
130.0	0.90000	0.89989
160.0	0.90000	0.89990

The temperature of the cell and mixture was maintained by a water bath which has been identified elsewhere in the thesis. The limits of control claimed by the manufacturer are ± 0.05 degree Centigrade or about 0.09 degree Fahrenheit. Temperature gradients about the cell were found to be negligible and the maximum observed variation in the bath temperature was about as claimed by the manufacturer. However, the controller was difficult to set at a desired temperature within these limits and each mixture was measured at a different time. The result was that, while temperature could be measured to better precision than the bath could control it, the data were taken at temperatures different than those at which they were reported. Had the two cell system

proposed by Manley⁽¹³⁾ been used this temperature discrepancy would not have been a problem. However, each point of data (value of relative volatility) depended on two experimental pressure determinations. One determination was the vapor pressure of the pure component and the other was the pressure of the dilute solution of one component in the other. The difference in pressures and compositions of the two solutions were then used in equations (1,2). Hence, some method had to be used to "normalize" the two separate data points to the same condition before the isothermal relationships could be applied to calculate the relative volatility. The method chosen was a simple interpolation scheme given by Carnahan, Luther, and Wilkes⁽²²⁾. The data were interpolated as $\ln P$ and T in pounds per square inch absolute and degrees Fahrenheit respectively by a second degree Newton's divided difference polynomial in T to yield $\ln P$ and thus P . The interpolation was done on a Data General Corporation Nova 800 computer. It should be noted that the interpolation was not over a great range since the original data were all within about 0.2 degrees Fahrenheit of the desired temperature.

whatever the temperature, the vapor pressures measured are considered to be good to a precision of 0.01 pound per square inch. The vapor pressures measured for the pure components were slightly low for butane when compared to the smoothed literature values as in Figure 11. The values found for butene are somewhat better as shown in Figure 12. The materials used were pure grade furnished by Phillips

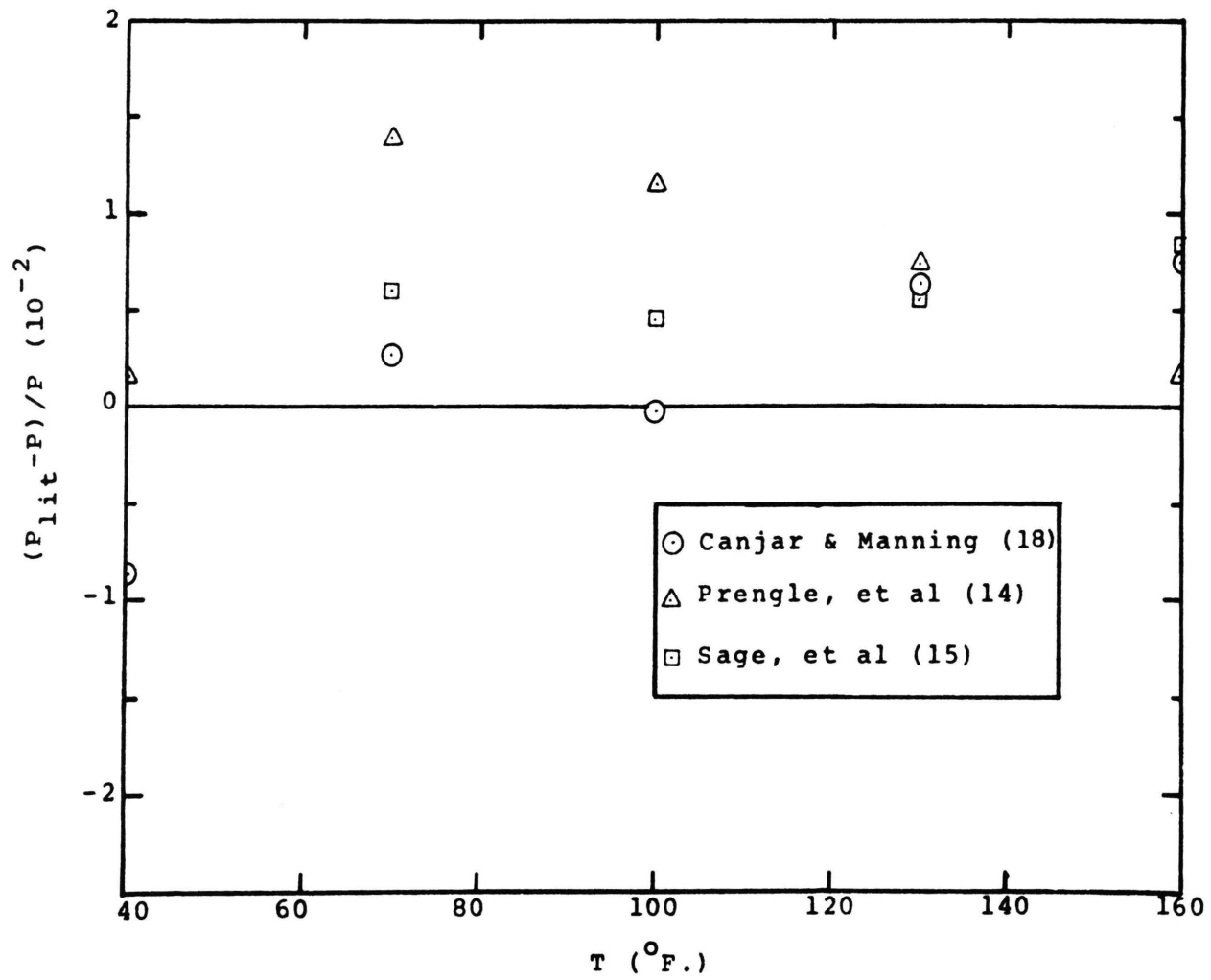


Figure 11. Comparison of Vapor Pressures of Butane

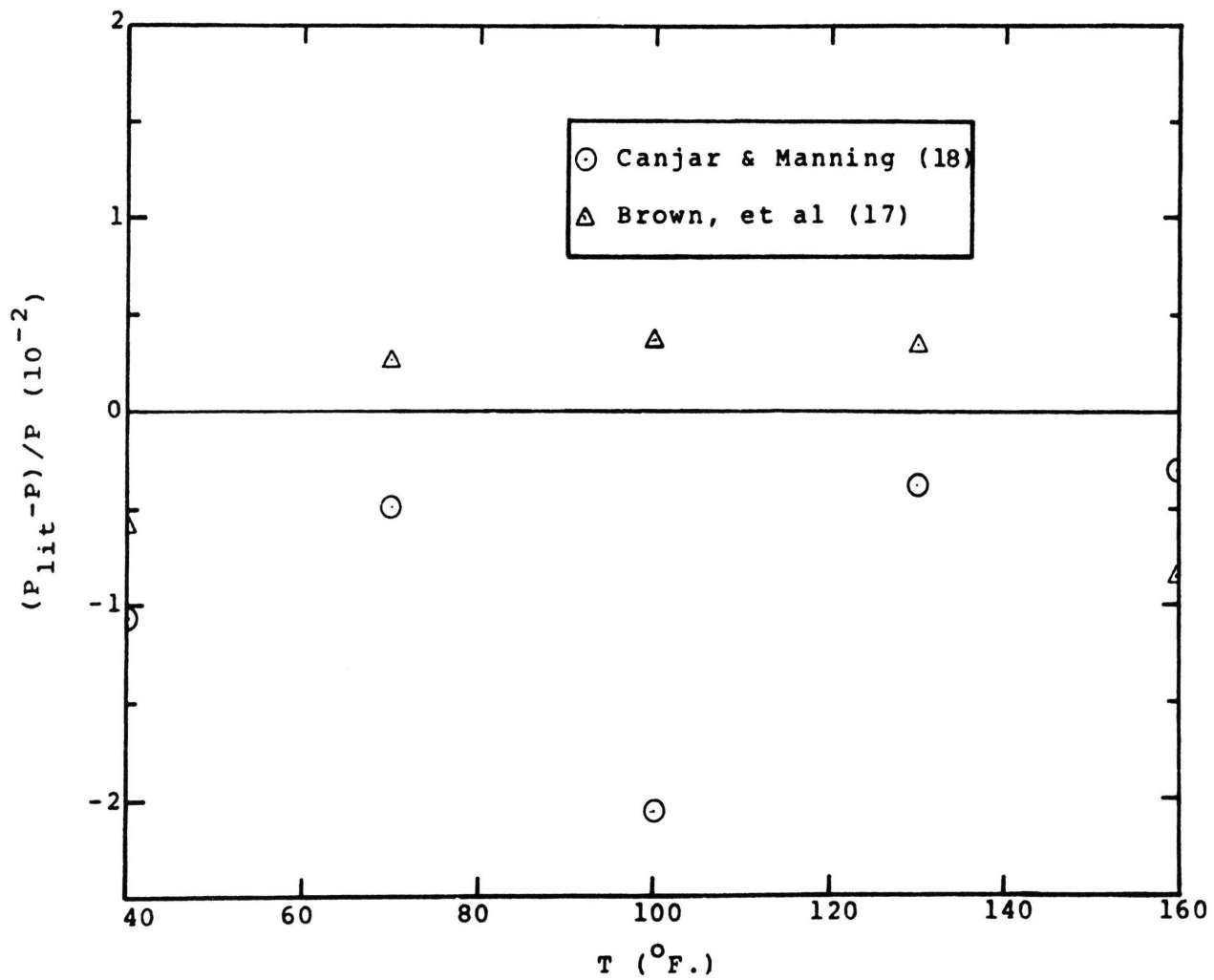


Figure 12. Comparison of Vapor Pressures of Butene

Petroleum Company. No special procedures were used to degas them before use except for venting some of the vapor from the bottles to the atmosphere. The data were taken from two different lots of the two materials since one was used up in early experiments. The first lot gave vapor pressures which agreed with literature values to 1 per cent or less (Figure 12). The second lot gave the poorer results (Figure 11). The second lot of butane was analyzed by gas chromatography and found to contain about 0.4 per cent air while analysis of the second lot of butene revealed about 0.06 per cent air. The presence of air might account for some of the scatter in the data since the volume of liquid in the cell during a particular experiment could not be precisely controlled. It is difficult to estimate the effect of such impurity, however.

The estimation of errors in α was carried out in the same manner as outlined by Manley⁽¹³⁾ save for the fact that the error in α was examined rather than the error in $\ln \alpha$. The following values for precision in the independent variables were assumed:

ΔZ	5 per cent
P	0.01 pound per square inch
ΔP	0.014 pound per square inch
Δx	0.0005 mole fraction

In addition, an estimate of the effect of the curvature of the P-x curve on the value of the derivative and α was made. The effect was estimated by examining the data of Sage and Lacey⁽²¹⁾ in its raw and smoothed forms by the application

of equations (1,2) of this study to them. The results were at $x=0$ a difference of ± 0.017 and at $x=1$ a difference of ± 0.03 in the value of α at 100 degrees Fahrenheit. These differences are of the same size as the errors estimated from the strict analysis of the difference equations which are equations (1,2) in this study. Since the error estimates made on the basis of the equations include some of the factors which are in the derivative it is difficult to separate the effects. The error estimated here is not additive with the error estimates given in Table III and is not included there.

APPENDIX B

EQUIPMENT DESIGN AND CALIBRATION

The device used in this study was constructed somewhat by trial and error with some rough theoretical considerations to guide the process. Several aspects of the design will be discussed here. They are leaks, theoretical response, slippage, null point location, repeatability, and pressure temperature effects.

Leaks are an ever present problem in any device where some sort of mechanical seal is necessary. The pressure transducer built for the study just completed was no exception. When a metal to metal seal is desired it is necessary to finish the mating surfaces to close tolerances in order to insure that a seal can be made. For the device at hand the seal remains somewhat of a problem. At present, the seal around the diaphragm is insured by a spray on teflon coating which forms a gasket of sorts which can meet the temperature requirements of the final design. However, teflon is slippery and is prone to cause other problems which can hamper the performance of the transducer. After discussing the theoretical response of the transducer, these problems will be discussed.

The theoretical response of the transducer can be calculated by using the equations for large deflections of a thin membrane given by Timoshenko and Woinowsky-Krieger⁽²³⁾. The equations are:

$$w_0 = 0.665 a \sqrt[3]{\frac{qa}{Eh}} \quad (3)$$

$$\sigma_o = 0.423 \sqrt[3]{\frac{Eq^2 a^2}{h^2}} \quad (4)$$

Where:

- w_o is the deflection of the diaphragm at its center
- a is the radius of the diaphragm
- E is Young's modulus for the diaphragm material
- h is the thickness of the diaphragm
- σ_o is the tensile stress at the center of the diaphragm
- q is the difference in pressure

In addition, when the diaphragm is stopped against the dished cavity the shear imposed on the membrane where it is unsupported at the 3/32-inch hole can be calculated by

$$\tau = \frac{\Delta Pr}{2h} \quad (5)$$

Where the value of r is 3/32. Equations (3,4,5) were used to make a calculation for the apparatus with the following data:

tensile yield stress	80,000 psi
shear yield stress	40,000 psi
Young's modulus	28×10^6
maximum deflection	0.014 inch
diaphragm radius	0.8 inch
diaphragm thickness	0.001 inch

The results of the calculation were:

ΔP at maximum deflection	0.64 psi
distance moved by 0.01 psi	0.0017 inch
tensile stress at center	8204 psi
shear in center at 200 psi	4688 psi

Since the differential transformer should be able to detect 0.0001 inch movements the sensitivity of the transducer should be what is desired even though the sensitivity of the transformer is dulled somewhat by the intervening metal tubing between it and its core. Further, the device has reserve strength to handle much higher pressures than 200 pounds per square inch as evidenced by the low stresses introduced by the overpressure. It is apparent that a 2000 pound per square inch overpressure is out of reach due to the shear at the center of the diaphragm and strength limitations of the screws used.

The response calculated above is true only as long as the edges of the membrane remain clamped. Should the edges slip the diaphragm might assume a set or become wrinkled and begin to produce spurious responses. Some evidence has appeared to support such a theory.

The theory presented above is supported by the movement of the null position between experimental determinations. The null position was located during an experimental run at each temperature by overpressuring the diaphragm from both sides, measuring the voltage at each stop, and applying a previously determined factor to the range thus determined to

locate the zero between the two extremes of travel. The factor applied to the range was determined by locating the zero point between the extremes as a fraction of the distance from one to the other. The evidence for slippage at the edges was that the factor seemed to change from experiment to experiment. The shift was not unbearable since it was usually only of the order of the instrument's sensitivity. It was checked each time the transducer and cell was emptied and refilled. Even then the behavior was somewhat disturbing.

Repeatability was checked by measuring the vapor pressures of a sample repeatedly at the same temperature. Pressures were found to be within 0.04 pound per square inch at all times. That difference could be attributed to drift in the temperature.

The effects of pressure and temperature variations on the response of the transducer were examined by setting the zero for the device and varying the temperature. At each temperature the pressure was varied from 0 to 100 pounds per square inch gauge. Results are shown in Figure 13 and Figure 14. The factor mentioned above was checked at about 71 degrees Fahrenheit and again at 160 degrees. It was found to shift by about the equivalent of a 1 millivolt rise from the lower to the higher temperature (0.293 at 71 degrees and 0.288 at 160 degrees).

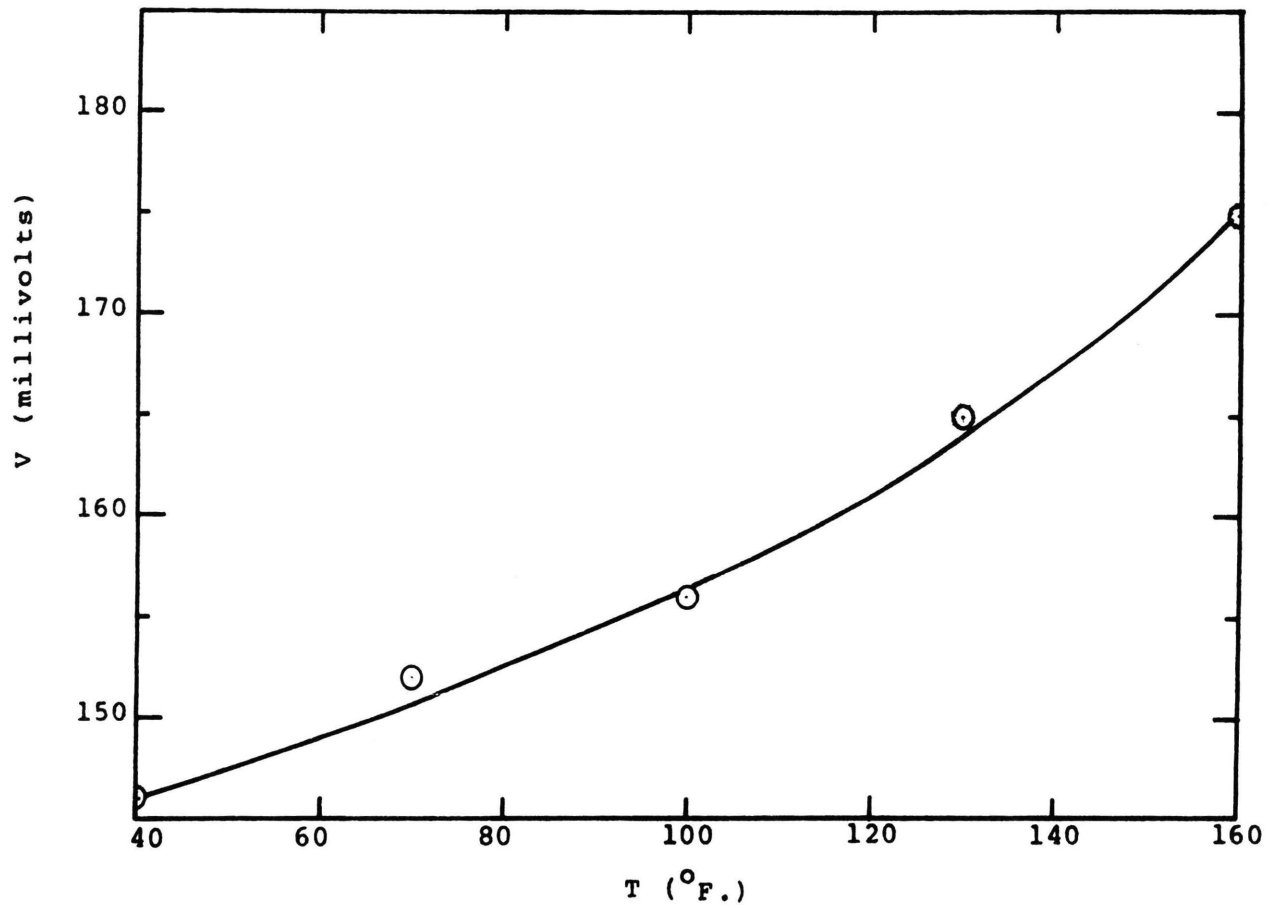


Figure 13. Null Drift with Temperature

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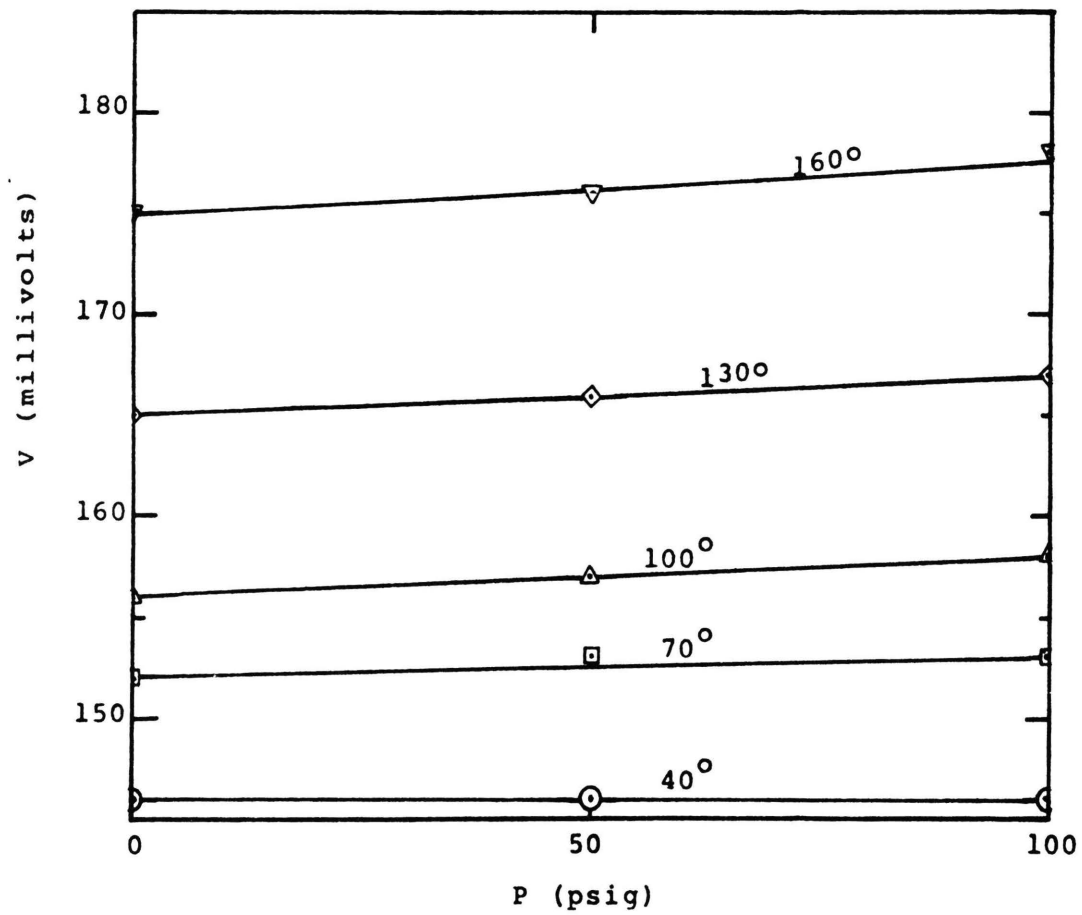


Figure 14. Null Drift with Pressure