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PRESSURE VOLUME TEMPERATURE RELATIONSHIPS AND
PHASE EQUILIBRIA IN THE SYSTEM ETHYLENE-NORMAL BUTANE

by

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Fulfillment of the Requirements for the Degree of
Doctor of Philosophy in The University of Michigan

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SUMMARY

This dissertation presents the results obtained in the experimental investigation of the binary hydrocarbon system, ethylene-normal butane. The pressure-volume-temperature relations at the liquid-vapor phase boundaries and in the single phase regions were determined for four mixtures of this system. The experimental results are reported as such, and in the form of generalized equilibrium constants and densities.

By comparison with other binary systems, it was found that the volatility of ethylene in butane solutions is considerably greater than that of a corresponding, but necessarily hypothetical, paraffin hydrocarbon.

The deviations from the ideal gas law of the mixtures in the gaseous regions were compared with those of pure ethylene and pure butane. Upon the bases of reduced pressures and temperatures, the compressibility factors agreed remarkably well.

The construction and operation of the apparatus, which is suitable without modification for the study of other gaseous mixtures, is described.

* * * * *

ACKNOWLEDGEMENT

The guidance of Dr. George Granger Brown and Dr. Donald L. Katz and the facilities for research provided by the University of Michigan are acknowledged with gratitude.

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INTRODUCTION

The need of modern technology for more extensive and more reliable data than currently exist is much too well known to require repetition here. The petroleum industry, for example, requires more information regarding the equilibrium relationships of vapor and liquid, critical properties and the densities of hydrocarbon mixtures. As a result of many years' effort, the behavior of mixtures of paraffin hydrocarbons has been reasonably well, but yet far from completely, explored. The behavior of mixtures which include unsaturated hydrocarbons is not so familiar. It was the purpose of this study to extend this knowledge by the investigation of the vapor-liquid phase equilibria and the pressure-volume-temperature-composition relationships of the binary system, ethylene-normal butane.

Knowledge of binary systems is frequently directly applicable to an industrial problem, and is always useful in developing empirical or thermodynamic relationships which can be used to predict the behavior of the constituents of a binary system in a more complex mixture. As many of the problems in the petroleum industry involve such complex mixtures that an experimental analysis of the properties is, from a practical standpoint, impossible, it is very desirable to obtain as much information as possible regarding the properties of the various types of hydrocarbons in simple mixtures.

At the start of this investigation, it was known that the results of similar work were soon to be published which would complete the data for the three binary paraffin systems: ethane-n-butane, ethane-n-heptane and n-butane-n-heptane^(18,19,21). The particular

system ethylene-n-butane was chosen as the subject for this investigation to further some integration of the overall problem, and to compare the behavior in butane of ethylene with that of the corresponding paraffin, ethane.

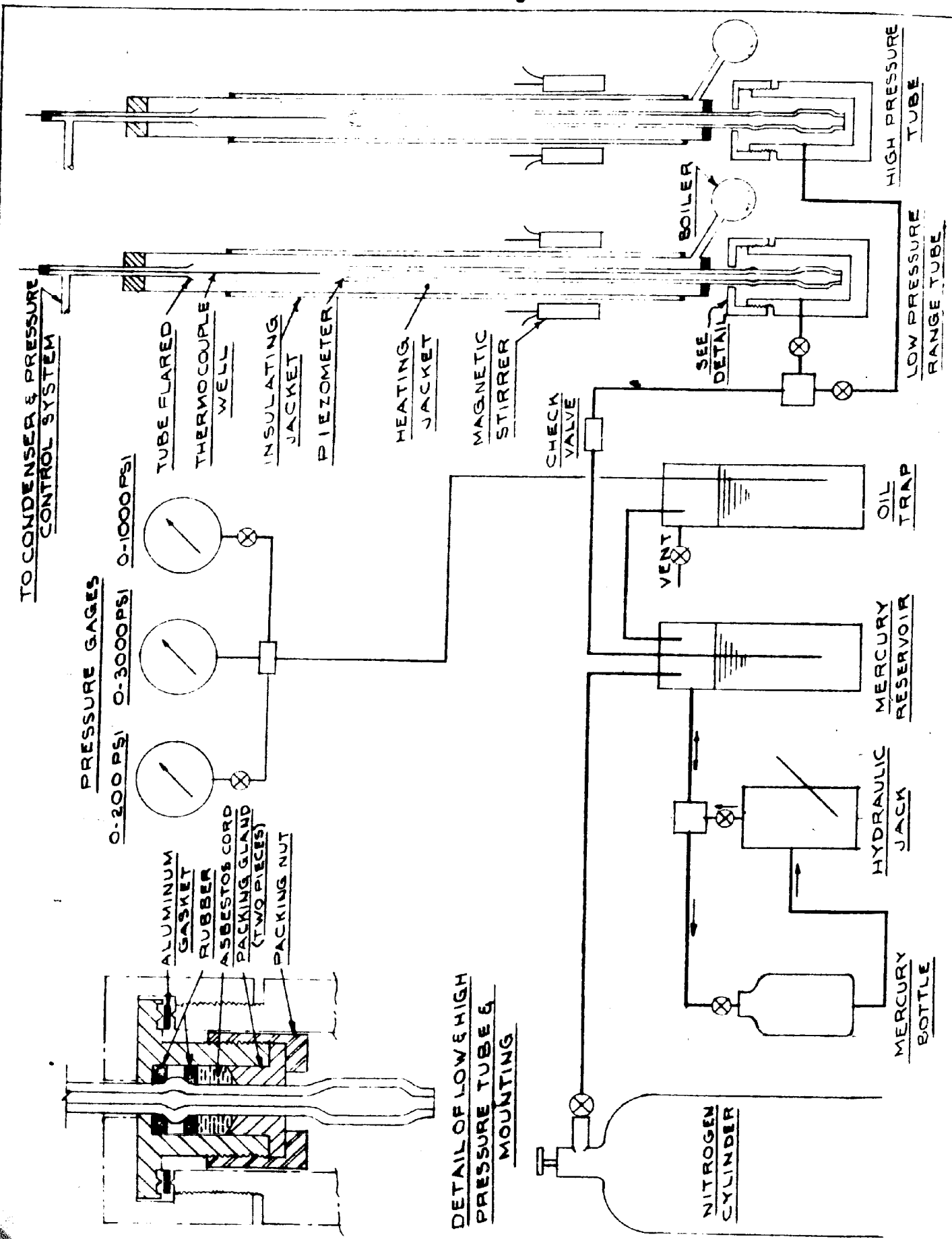


FIGURE 1 - APPARATUS USED FOR MEASURING DENSITIES AND PHASE BOUNDARIES

DESCRIPTION OF THE APPARATUS

The Piezometric Equipment

The sketch, Figure 1, shows the equipment used in observing the dew and bubble points and the densities of the samples. The apparatus is similar to that used by Sydney Young in his classical studies and to that later used by Kay^(1,17-21). A sample of known weight of the hydrocarbon mixture under study is confined over mercury in a Pyrex tube (piezometer). The open end of the tube was fastened tightly in a high pressure bomb and was under a liquid seal. The details of the stuffing box and closure are also shown in Figure 1. Once installed, the tubes were never removed from the stuffing boxes.

In this investigation two glass tubes were used, one for measurements at relatively high pressures, the other used in the lower pressure ranges. The external diameter of each tube was about 15 millimeters and the internal diameters 5.0 and 1.9 millimeters, respectively. A bulb, about 15 cubic centimeters in volume, was blown in the base of each tube so that a gas sample charged at atmospheric pressure might be large enough to result in a volume which could be measured with sufficient accuracy at high pressures. The overall length of the tube was about 70 centimeters. The volume of the sample confined over the mercury was found by measuring with a cathetometer the position of the mercury relative to a reference point on the tube. The volume corresponding to this position was then found by reference to a calibration of the tube, which is described elsewhere in this report.

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The tubes were enclosed, as shown, by glass jackets, forming a vapor bath and insulation. The temperature was maintained wherever desired by the choice of the proper boiling liquid and regulation of the pressure. The compounds used and their atmospheric boiling points are:

Acetone	133.0°F
Benzene	176.15
Toluene	231.1
Mono-chlorobenzene	269.0
Mono-brombenzene	312.6
Acetophenone	396.3
Methylsalicylate	432.1

The temperatures were measured by copper-constantan thermocouples suspended over the top of the tube, and the glass connections were shaped to prevent drops of cold condensate from falling on the thermocouples.

Agitation of the sample in the tube to ensure equilibrium between phases was accomplished by inclusion of a small steel rod in the tube. The rod was moved magnetically by the solenoid surrounding the tube.

The source of pressure which was either a cylinder of compressed nitrogen or a hydraulic jack filled with mercury, was connected to a small pressure vessel filled with mercury. This vessel served as a trap and a reservoir of mercury. The pressure in the system was measured at this point. As the bourdon tubes were filled with oil, an oil-filled trap was placed between the mercury reservoir and the gages. The surge volume of gas contained in these reservoirs was sufficient to prevent changes in pressure as a result of slight deviations in either room or test temperature.

The pressure in the reservoir was transmitted to either of the piezometers by the flow of mercury. A ball check valve was inserted in this line to limit surges and loss of mercury in the event of breakage of the glass tubes. The check valve was installed with a slight tilt so that the buoyancy of the ball would prevent sealing at low rates of flow, and yet would close at high rates.

All tubing was 1/8-inch O.D. steel, and the connections were of the cone and follower type fabricated by the American Instrument Company. All valves were 1/4-inch metric valves.

Pressure Control System

This system was designed to regulate the pressure in the vapor baths so that the desired limit of variation in temperature, $\pm 0.01^{\circ}\text{F}$, might be attained. As, in the usable region, the slope of the vapor pressure curves of the compounds used in the vapor baths was 6 - 10 mm mercury per degree Fahrenheit, it was necessary that the pressure be regulated to about ± 0.1 mm mercury. The system, illustrated by the flow diagram in Figure 2, behaved admirably; with it the galvanometer frequently remained motionless for hours.

In essence, a surge volume of ten gallons was connected to the vapor baths. Air was supplied to or withdrawn from this volume continuously for operation above or below atmospheric pressure, respectively. This tendency toward a change in the pressure was offset by intermittent leakage or venting through an electrically operated flutter valve which was actuated by the pressure in the system.

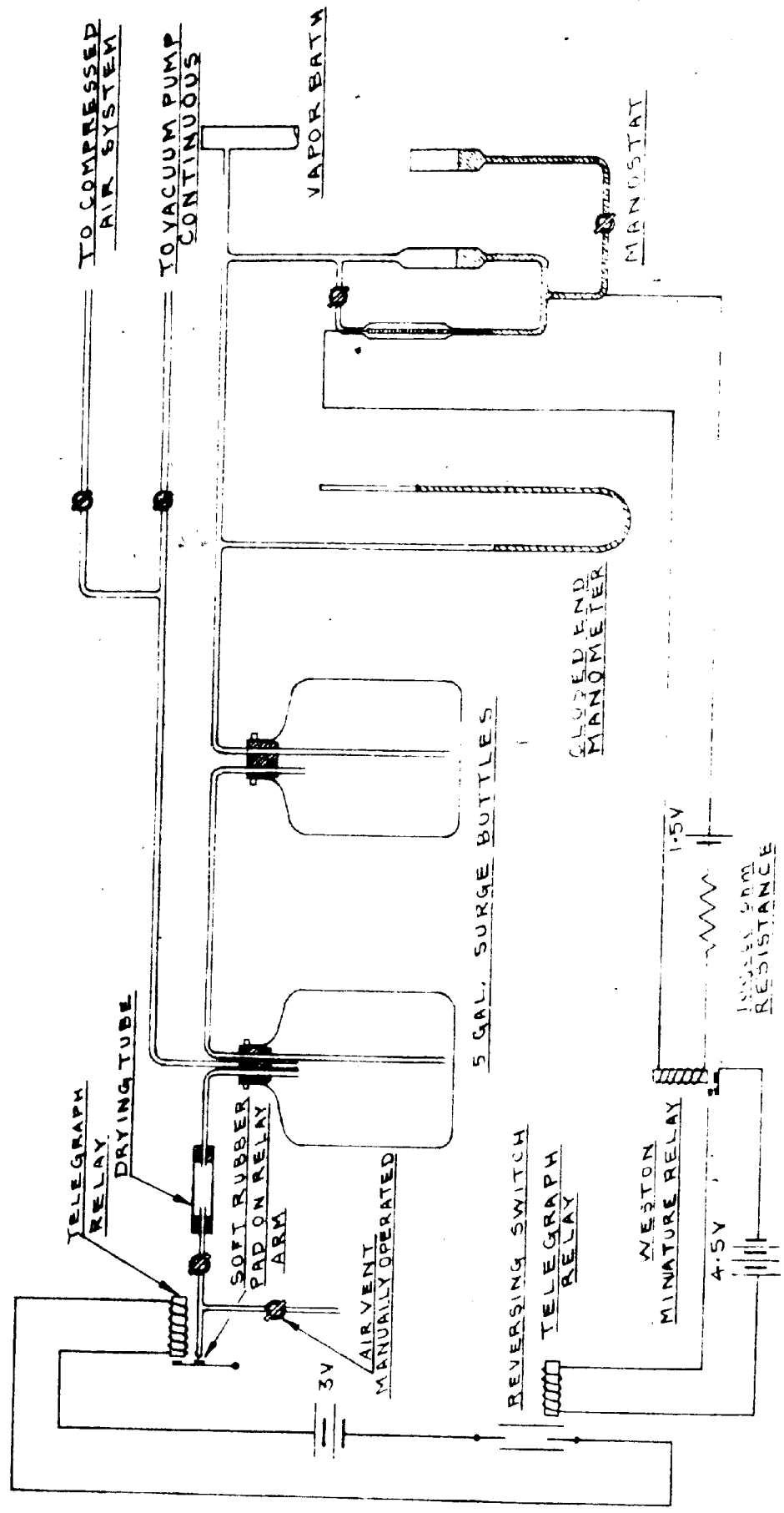


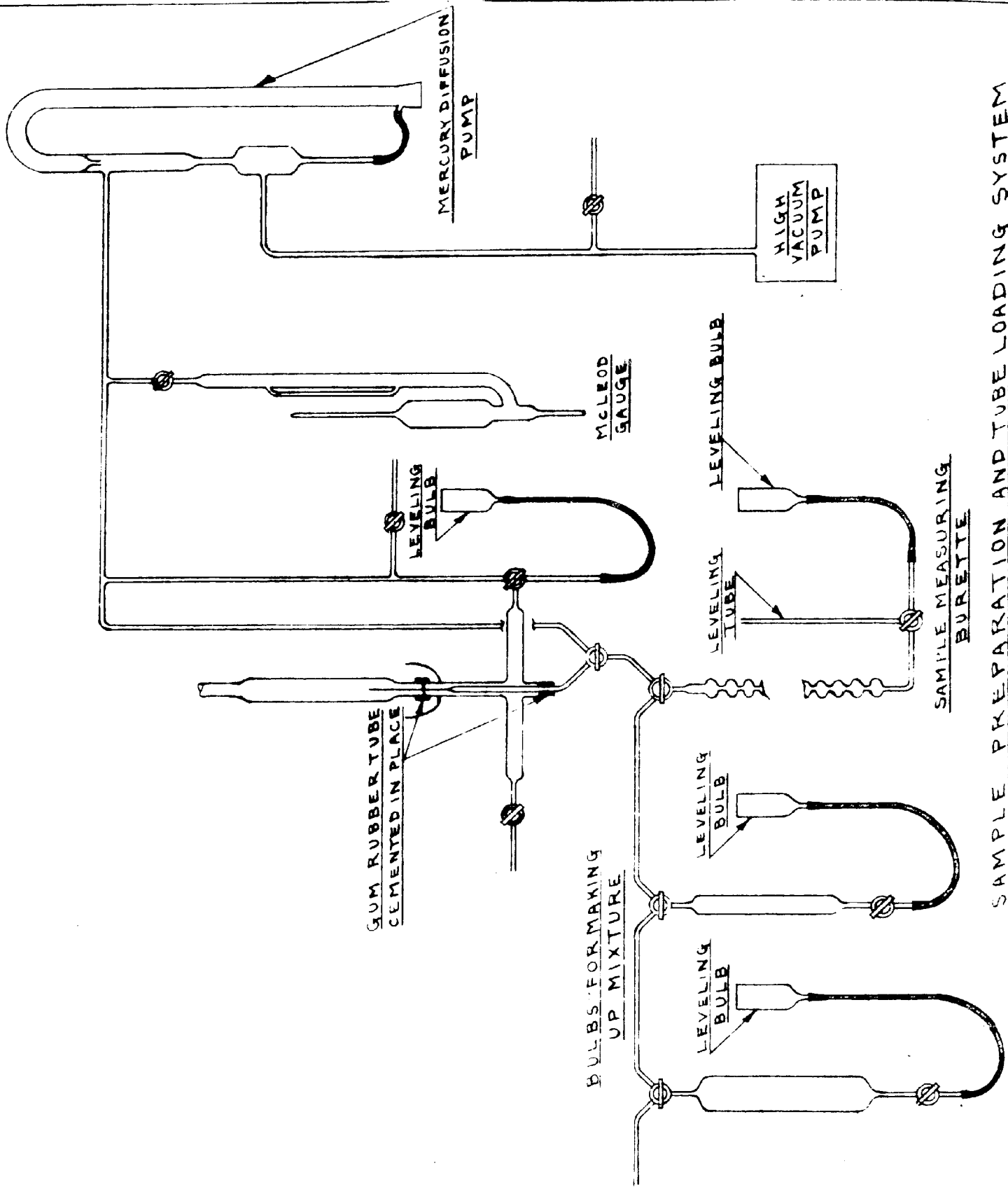
FIGURE 2
PRESSURE REGULATION SYSTEM

To follow the operation, suppose that while the vapor bath is under vacuum, its pressure rises slightly. As a result, the mercury level rises in the small arm of the manostat, and closes the circuit of the miniature relay. This closes, in turn, the second relay and the relay flutter valve. In the latter, a soft rubber pad was attached to the moving arm of the relay, so placed that when the relay circuit was closed the pad sealed the end of the vent tube. To continue the sequence of events, the closure of the vent tube stopped the leakage of air into the system and allowed the vacuum pump to reduce the pressure to the required value.

The absolute pressure of the system was roughly set by manipulation of the throttle valves in the vacuum pump or compressed air lines, and in the vent line. A fine adjustment could be made by use of the extra level of mercury attached to the manostat. Other refinements were the reversing switch which was useful in transferring from vacuum to above atmospheric pressure and the manually operated auxiliary vent valve. The use of the miniature relay, which required only about 15 microamperes, assured rapid response without arcing to small changes in pressure at the manostat. The system operated smoothly and without hunting at all desired pressures.

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SAMPLE PREPARATION AND TUBE LOADING SYSTEM

FIGURE 8

Preparation of the Mixtures

The apparatus used in preparing the mixtures and introducing measured samples in the tubes is shown in Figure 3. Two glass bulbs, connected as shown each with its own mercury leveling bottle, were used to make the gaseous mixtures. The large bulb, with a volume of approximately one and one-half liters, had about seven times the capacity of the smaller bulb.

A mixture was prepared by filling the small bulb a number of times with one gas or the other, and emptying its contents into the large bulb. For instance, one filling of ethylene and four of butane would result in a mixture of approximately 20 mol percent ethylene.

The small bulb was filled to an etched reference mark, and the pressure above or below atmospheric determined by measurement, with a cathetometer, of the difference between the level in the sample bulb and in the leveling bulb. The temperature, which was maintained by immersion in a water bath, was measured to 0.01°F with a thermometer. As the volume of the small bulb was taken as unity, no calibration of the volume was necessary.

The densities and deviations from the ideal gas laws are accurately known for butane and ethylene at and near atmospheric temperatures and pressures (3,4,5,6,8,15,16). With these known densities the relative weights of butane or ethylene in each of the portions of the total mixture were easily calculated. A sample calculation of this sort is included in the appendix.

After preparation, a sample was thoroughly mixed by agitation and by standing before the piezometric tubes were filled.

The method, used in this investigation, of determining the weight of the sample placed in the piezometers required precise knowledge of the densities of the mixtures at room conditions. Therefore, as a prelude to loading the piezometers, the density of each mixture was measured over a range of pressures from 300 to 900 mm mercury at a temperature as close to 68°F (25°C) as possible. The densities were found by weighing the quantity of ethylene in a glass density bulb of known volume. The customary precautions and technique of using a second bulb as a counter balance were followed. The temperature of 68°F was chosen as, at this temperature, the densities of ethylene and butane are most accurately known.

These experimental densities were used to compute the amount of material charged to a piezometer. A tabulation of the dimensionless compressibility factors (PV/NRT) for various pressures at 68°F, and for the four mixtures made, follows:

<u>Pressure</u> <u>mm Hg</u>	<u>Mol Percent Ethylene</u>			
	<u>19.85</u>	<u>40.72</u>	<u>66.18</u>	<u>80.88</u>
950	0.9677	0.9745	0.9827	0.9875
800	0.9716	0.9776	0.9850	0.9892
700	0.9746	0.9800	0.9866	0.9905
500	0.9813	0.9853	0.9902	0.9930
200	0.9925	0.9941	0.9961	0.9972

The measured densities and compressibility factors agree very well with densities obtained by molar interpolation between the densities of the pure compounds. The maximum deviation between the experimental and interpolated densities was 0.044%; the former was the higher density at this point. This is in accord with the reported behavior of butane-pentane mixtures⁽¹⁶⁾.

As a precaution against major errors in the computed compositions, each mixture was analyzed in an absorption gas analysis apparatus over bromine water. Naturally, the accuracy of analysis by absorption is inherently far less than that of a computed analysis, only gross errors in composition would be revealed. The analytical and calculated compositions agreed within one percent.

Filling the Tubes

The apparatus used to fill the tubes, which is also shown in Figure 3, consists of two essential parts, namely, the precision buret in which the sample is measured, and the device for placing this sample in the piezometer without loss or leakage of air.

The weight of a sample was computed from the measured volume of vapor at a known pressure and temperature, by means of the compressibility factors previously cited. In order to combine the properties of sufficient capacity and accuracy, a buret was made by blowing a number of bulbs, as shown, in a relatively small bore glass tube. About two centimeters of straight tube were left between adjacent bulbs. The volume of the buret was calibrated with mercury by the same technique used for the piezometers. The total volume of the buret was about 35 cubic centimeters. As the measurements of height were made in the straight sections, in which the volume was one cubic centimeter per twelve centimeters of length, the accuracy of volume measurement should have been comparable to that of a calibrated tube over 400 centimeters long.

The buret was submerged in a water bath for constancy of temperature. The pressure in the buret was found by measuring, with the cathetometer, the difference in height of the mercury columns in the buret and in the second leg which was open to atmospheric pressure. The internal diameters of the straight portions of the buret and the external leg were the same. This eliminated errors caused by differences in the extent of capillary depression of mercury.

As for any composition, the gaseous density was known as a function of temperature and pressure, the conversion from volume confined in the buret to weight was simple and accurate. In practice, the weight of sample was verified by repeating the volume measurements at two or three pressures. No significant discrepancy was ever noticed.

The known sample was transferred to the pressure tubes through a hypodermic needle in the apparatus sketched in Figure 3. A cross of large bore glass tubing was made with a cup sealed around one of the short arms. This cross was mounted securely upon a frame in the position shown, and one long arm was permanently connected to the vacuum system, i.e., a McLeod gage, a mercury diffusion pump, and a Cenco Hyvac pump.

The pressure tube to be filled was then sealed to the upper arm with a sleeve of rubber tubing and deKhotinsky cement. The buret assembly was installed with the leuc of the hypodermic attachment inserted into the lower arm so that the tip of the needle extended well into the bulge in the piezometer, but was below the rim of the cup. The leuc, which had been chosen with a close clearance in the lower arm, was sealed in place with a rubber sleeve and cement.

The procedure used in filling a tube was as follows:

- 1) The cup surrounding the top arm was filled with mercury, and the entire system was evacuated for 24 - 36 hours at an absolute pressure of less than 0.1 micron of mercury. At intervals the tube was heated to aid the removal of adsorbed gases from the glass surface.
- 2) When evacuation and desorption were considered complete, the tube was flushed with some of the gaseous mixture to be studied and reevacuated.
- 3) After this second evacuation, mercury was admitted through the long arm until the liquid level in the piezometer was just below the top of the needle.
- 4) The gas sample, the weight of which had been determined, was passed from the buret through the needle into the tube.
- 5) By use of the leveling bulb, the pressure in the piezometer was adjusted to very slightly above one atmosphere.
- 6) The rubber-cement joint between the piezometer and the cross was removed. Without breaking the liquid seal, the tube was disengaged from the needle.
- 7) In order to transport the tube to the pressure equipment without breaking the liquid seal, a very small beaker was then fitted under the open end of the tube under the mercury level in the cup. As the small beaker formed a seal, it and the tube could be removed from the cup and placed under the mercury level in the high pressure bomb without air leakage or loss of sample. After this, the small beaker was removed, the bomb closed and made ready for the experiments.
- 8) Owing to certain unavoidable features in the construction, it was possible that small amounts of the gas sample might be trapped

in the stopcocks and connecting tubes. Before the piezometer was removed, a test was made for the presence of trapped vapor by closing the stopcock nearest the leuc and reducing the pressure in the buret by lowering the mercury level. In no case was any of the measured gas sample so lost.

EXPERIMENTAL TECHNIQUE

The operation of the apparatus which has been described was basically simple. It involved the application of pressure, control of the temperature and measurement of a volume. However, various refinements, especially in determining dew and bubble points, and arbitrary conditions of equilibrium and tightness were found necessary. These are described here as a possible aid to further work, and as a clue to the accuracy of the recorded data.

Leakage in the System

In certain portions of the two-phase region the density or quality of the sample was extremely sensitive to small changes in the pressure or temperature. This was especially true near the critical points and in the retrograde region. Owing to this sensitivity, the determination of dew or bubble points, and the volume was frequently very slow. Maintenance of pressure through elimination of leakage was, therefore, absolutely essential. Accordingly, an arbitrary standard for tightness of the system was set: the allowable pressure drop was one percent at 1000 lb./sq.in. in twenty-four hours. This allowed two hours for a single measurement at the maximum pressure with a loss of pressure of but one-tenth of one percent. Actually the leakage was always less than this. The maximum resulted in a loss of about 0.7 percent in twenty-four hours.

Order of the Measurements

In general, measurements were made at successively higher temperatures within the temperature range of any one compound used in the vapor bath, and further, successively higher boiling compounds were used. However, after the range had been explored, measurements were repeated at approximately the medium temperature and at the lowest temperature to test for any chemical or physical changes in the sample. In all cases, there was no apparent deterioration.

Maintenance of Steady State Conditions

No data were recorded until steady state or equilibrium conditions had been maintained for at least two minutes. The indications of stability were no visible change in pressure, no change in the mercury level and agreement to 0.4°F between the temperature indicated by the thermocouples and that corresponding to the pressure of the vapor bath. The limit of 0.4°F was rather high, but it was about the limit of accuracy given by the combination of vapor pressure data, the manometer and the purity of the vapor bath. The stipulation, however, insures uniformity of temperature between the base and the top of the tube, and the attainment of equilibrium after a change in temperature.

Determination of Bubble Points

Bubble points were determined by approaching from the single phase region. After the sample had been thoroughly stirred, and iso-

thermal conditions maintained, the pressure was slowly decreased by venting nitrogen from the system until the merest bubble of vapor appeared in the top of the tube. This was noted as the bubble point pressure, and was repeated at least once as a check. When well removed from the critical region, the compressibility of the liquid is low, and the bubble point density may be measured at pressures slightly above the bubble pressure. However, near the critical region the compressibility is much greater, and much more care was required in measuring the density.

Determination of the Dew Points

As with the bubble points, these were best determined by approach from the single phase region, either by isothermal increase or decrease (in the retrograde region) of pressure. As the volume was relatively large at the dew point, the resulting long, narrow shape of the sample made stirring more difficult. Frequently, it was necessary to augment the magnetic stirring device by alternate expansion and recompression.

When viewed by reflected light, the dew point was characterized by the appearance of small black or dark spots on the glass wall. Other indications of the dew point which were also sensitive, but which usually occurred after further penetration into the two-phase region, were the appearance of the interference colors and the glistening of the meniscus because of the presence of a thin film of liquid. These indications of the dew point were very sensitive. For instance, in the tube filling buret at the ice point, the colored film was observed to appear and disappear with a change in pressure of one millimeter at a total pressure of two atmospheres.

Determination of the Critical Point

The experimental determination of the critical point is best described by its definition, namely, the point of intersection of the dew point and bubble point lines. In determining bubble points the meniscus first appeared at the top, for dew points it first appeared at the bottom of the sample. To fix the critical point, many dew and bubble point determinations were made at slight changes in temperature. The point at which the meniscus seemed suddenly to appear at neither the top nor at the bottom was judged the critical point. It is believed that the critical points were determined within 0.05°F and 1 lb./sq.in. The region of opalescence existed over a temperature range as high as 5°F.

PURIFICATION OF MATERIALS

Ethylene

A cylinder of C.P. ethylene 99% pure, obtained from the Ohio Chemical Company, was used in preparing the pure material for the investigation. The raw gas was dried by phosphorus pentoxide and condensed in the reboiler of a silvered, vacuum jacketed Podbielniak distillation column. The fractionating medium was a wire helix about three feet in length. The liquefied ethylene was degassed by prolonged distillation at essentially total reflux, and then was slowly fractionated at a high reflux ratio. A constant boiling heart cut of about 30% was condensed in a high pressure storage cylinder. The storage cylinder had been previously deaerated by evacuation while warm, and was purged several times with ethylene before the purified sample was collected. Approximately twenty cubic centimeters of liquid were purified. When tested by absorption in bromine water, the absence of any residual gas proved the refining process to be satisfactory.

Butane

The raw material, in this case, was a sample of C.P. n-butane produced by the Philips Petroleum Corporation, and was reported to contain 99.6% n-butane. The pure hydrocarbon was prepared in the same fashion as was the ethylene, that is, by fractionation and collection of the middle, constant boiling fraction. However, before distillation, the raw butane was bubbled through fuming sulfuric acid, then through concentrated

potassium hydroxide and dried by phosphorous pentoxide. As a test of the purity, a portion of the finished butane was condensed in a glass tube immersed in melting ice. As the change in pressure during the condensation process was about 0.25 mm of mercury or less than 0.05% of the total vapor pressure, the purification was considered to be satisfactory.

Calculation of Densities

A sample calculation in the appendix shows the use of the various corrections and calibrations in computing the density of a sample in the tube.

CALIBRATION OF THE EXPERIMENTAL EQUIPMENT

Cathetometer

The measurements of all levels of mercury, either in determining the density of mixtures or in calibrating the piezometer tubes, were made by a cathetometer. With this instrument distances were measured to 0.001 cm by using the vernier scale. To test the accuracy and precision of measurement, the length of a carefully machined and calipered metal bar was determined by use of the cathetometer at several locations along the meter length of the latter. The scale proved to be accurate, as readings were precise and reproducible over the entire range of the instrument. However, the scale bar was rather wavy and it was necessary to level the telescope before each reading and to focus the lens carefully to minimize the effect of parallax. With these simple precautions the measurements were absolutely dependable, and were used directly, without correction. With care, the maximum difference between check readings did not exceed 0.002 cm, and the average difference was less than 0.001 cm.

Thermocouples

The temperatures were measured by the combination of copper-constantan thermocouples and a Leeds and Northrup type K potentiometer. With this arrangement, voltages were read, by interpolation, to 0.0001 millivolts which corresponds approximately to 0.005°F. Temperatures were recorded to the nearest 0.01°F. In fabricating the thermocouples, all the customary precautions were observed, such as testing for homogeneity of

the wires, using all copper leads and switches and maintaining proper cold junction conditions. The instruments were calibrated by comparison with a platinum resistance thermometer and several precision mercury thermometers. All devices used for comparison had been calibrated by the National Bureau of Standards.

The thermocouples were tested during and after the experiments, and the calibrations were found to be unchanged.

Pressure Gages

Three pressure gages were used; the ranges were:

0 - 200 psi	6" dial
0 - 1000 psi	10" dial
0 - 5000 psi	6" dial

Nearly all the pressure readings were made with the first two of these gages. Pressures were estimated and recorded to 0.1 psi but are probably accurate only to 0.3 - 0.4 psi. The gages were calibrated with a dead weight tester before the experiments, and thereafter were rechecked weekly.

Piezometer Tubes

The volume of a tube was determined by incremental filling with small weighed amounts of mercury and by measuring the height of the mercury column after each addition. Table X shows the data obtained by this procedure. The calibrations were used by plotting on a large graph, as a function

of length, the deviations from the volume of a cylinder with a diameter equal to the arithmetic average diameter of the bore. This method is extremely accurate and simple to use. It is interesting to note that the deviations seem to follow a very rough sine curve.

Before use, the mercury was triple-distilled and degassed. The portions were weighed to the nearest 0.00005 gram with calibrated weights. In measuring the length of the mercury column, two reference points were used. These were the top of the sealed end of the tube and the end of the bore. Either one of these points made a convenient and visually clear base mark. In practice four or five readings were taken of the location of each reference, and of the top and of the bottom of the mercury meniscus.

During the calibration the tube was immersed in a water column to maintain a constant temperature; this eliminated fluctuation in the level and assured a uniform temperature, and therefore density, throughout the column of mercury.

To obtain the actual volume of the tube at any point on the length by this method, it is necessary to allow for the volume occupied by the meniscus. There are recorded some empirical relations⁽²⁶⁾ between the meniscus volume, height and diameter but which, when applied to these tubes, were obviously inaccurate. Therefore, the meniscus was assumed to be spherical and its volume calculated as a spherical segment for the given diameter and height. The relative volumes involved and the fact that the height of the meniscus in calibration was so very close to that in the system, density measurements justify this assumption.

Stirring Rods

The small rods used as magnetic stirring devices in the piezometers were short pieces of polished iron wire, as nearly fashioned into a cylinder as possible. The volume of each rod was determined in two separate ways. It was calculated directly from micrometer measurements, and it was computed from the weight of the rod by using the handbook density. The volumes determined by these methods agreed within three parts in one thousand.

After this comparison showed such good agreement between the two methods, the rods were polished to round the ends and remove any sharp edges. The final volume was then obtained from the weight.

In use the volume was corrected for thermal expansion. As an example of the size of the rod and the correction, the following values were given for the rod used in the high pressure piezometer.

<u>Temperatures °F</u>	<u>Volume cm³</u>
70 - 140	0.00483
140 - 240	0.00484
240 - 340	0.00485
340 - 400	0.00486

EXPERIMENTAL RESULTS

In the course of this investigation, four mixtures of ethylene and normal butane were prepared and their behavior studied. The compositions of these four mixtures are given in Table I. The densities, pressures and temperatures at the liquid-vapor phase boundaries were determined by the techniques previously described. The densities in the single phase region were determined at several isotherms for each mixture. The limits of the temperature range explored were about 60°F, the temperature of cooling water, and 400°F. The recorded pressures varied from about 50 to 1100 pounds per square inch.

The experimental data are presented graphically on the succeeding pages by Figures 4 - 10, which show respectively, the pressure-temperature relationships at the phase boundaries, the saturated densities of the mixtures and densities at various isotherms for each of the mixtures. The experimental points from which these plots were constructed are shown in the plots and are also listed in Tables VII - IX, which are to be found in the Appendix. The conditions defining the critical points, and the points of maximum temperature and pressure for each of the mixtures are reported in Table I.

The vapor pressures of pure ethylene and butane are also shown in Figure 4. Data for these two curves were selected from the literature. The references are: ethylene^(14,25) and normal butane^(1,8,11,14,20,23,25). In this figure, the critical locus is the envelope curve which terminates at the critical points of the two pure compounds and is tangent to each of the border curves as it passes through the respective critical point.

T A B L E I

COMPOSITION AND CRITICAL CONSTANTS OF
MIXTURES OF ETHYLENE AND n-BUTANE

Mol % Ethylene	Composition Wt. % Ethylene	Molecular Weight	Critical Point		Maximum Pressure Point		Maximum Temperature Point				
			Temp. °F	Press. psia	Density gms/cc	Temp. °F	Press. psia	Temp. °F	Press. psia	Density gms/cc	
0	0	58.12	306.0	550.1	0.225						
19.85	10.68	52.15	266.51	752.8	0.2564	262.95	756.7	271.5	677	0.2885	0.185
40.78	24.95	45.86	224.47	889.3	0.2617	214.4	909	254.6	762	0.3033	0.175
66.18	48.57	38.22	169.02	973.5	0.2541	170.01	973.5	189.54	823	0.2508	0.145
80.88	67.13	33.80	125.97	945.7	0.2429	132.5	951.5	147.44	823	0.2120	0.135
100	100	28.05	49.1	736.0	0.220						

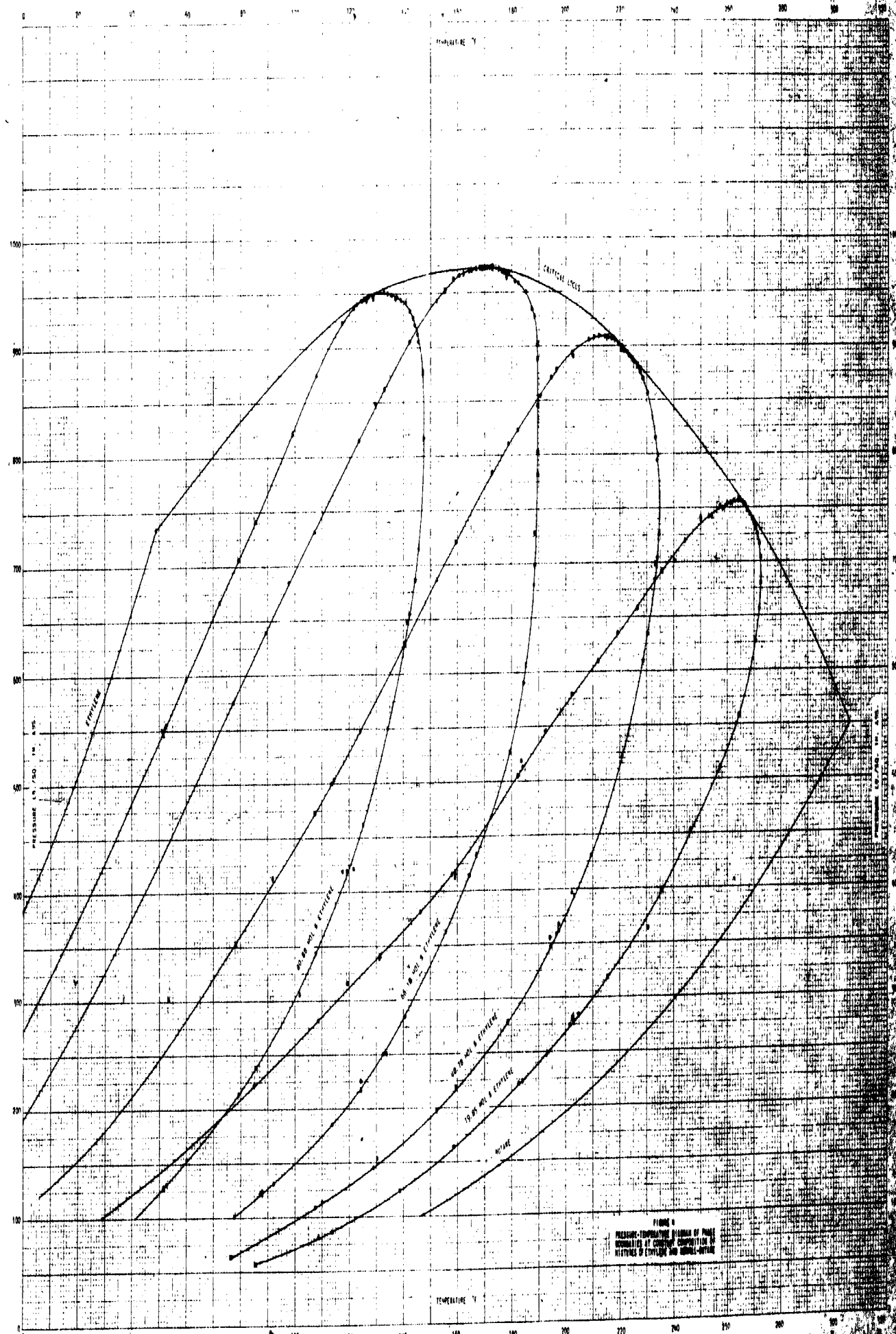


FIGURE 3
PRESSURE-TEMPERATURE DIAGRAM OF PURE
ETHYLENE AT CONSTANT COMPOSITION OF
METHYLENE OXYANE AND Methyl-Oxyane

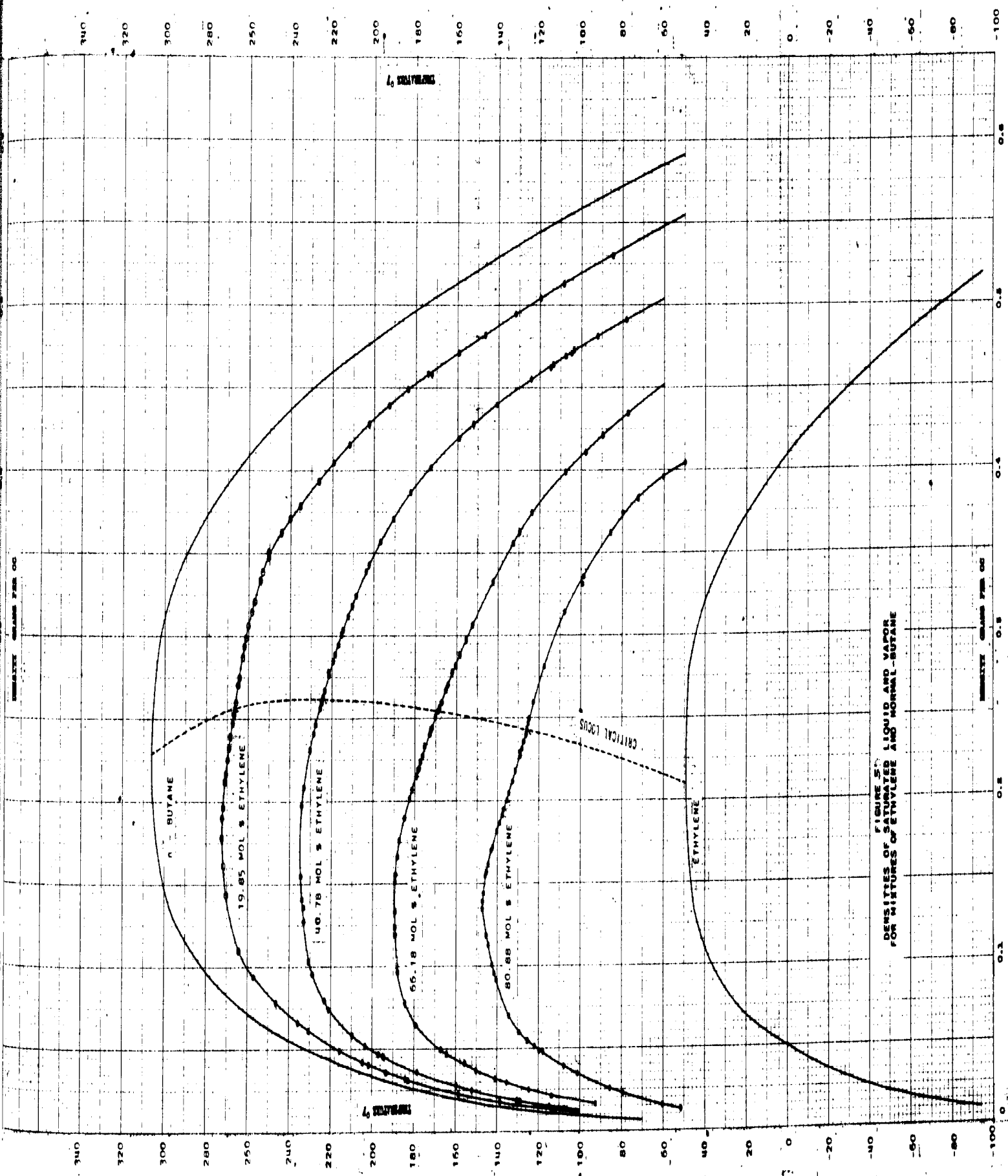


FIGURE 5
DENSITIES OF SATURATED LIQUID AND VAPOR
FOR MIXTURES OF ETHYLENE AND NORMAL-BUTANE

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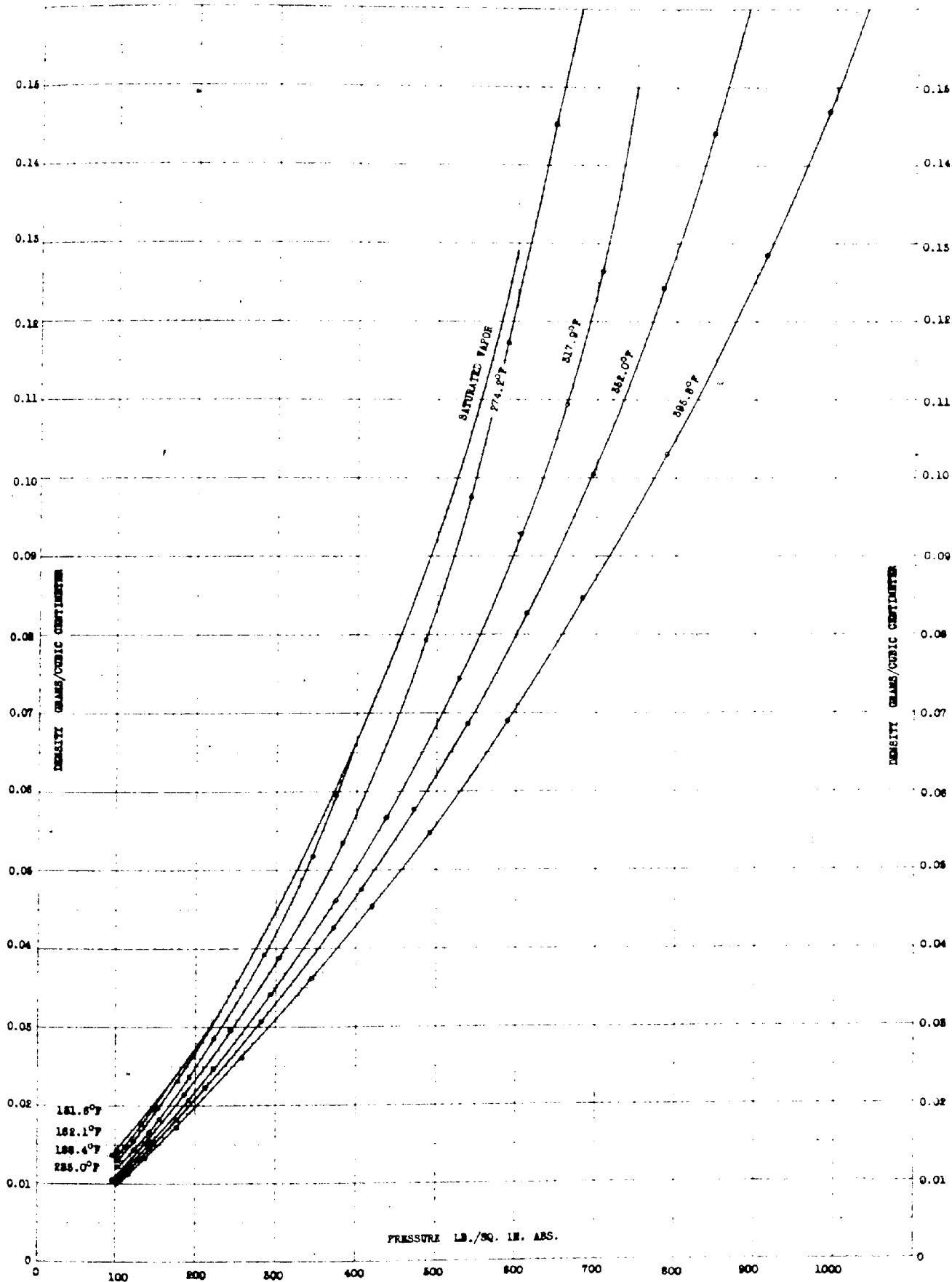
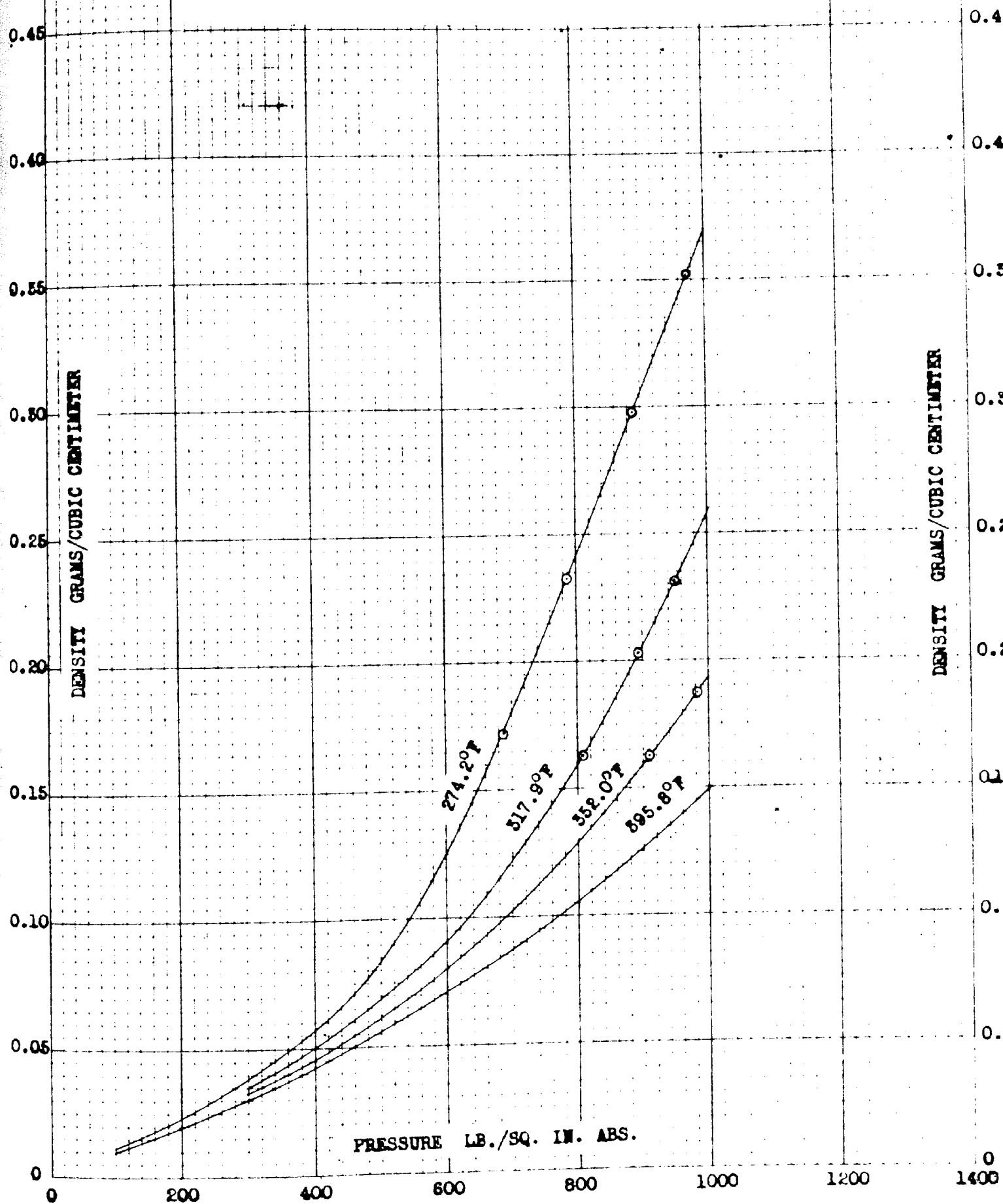


FIGURE 6
EXPERIMENTAL ISOTHERMAL VAPOR DENSITIES FOR A MIXTURE
CONTAINING 19.85 MOL PERCENT ETHYLENE IN n-BUTANE

FIGURE 7
 EXPERIMENTAL ISOTHERMAL VAPOR DENSITIES FOR A MIXTURE
 CONTAINING 19.85 MOL PERCENT ETHYLENE IN n-BUTANE



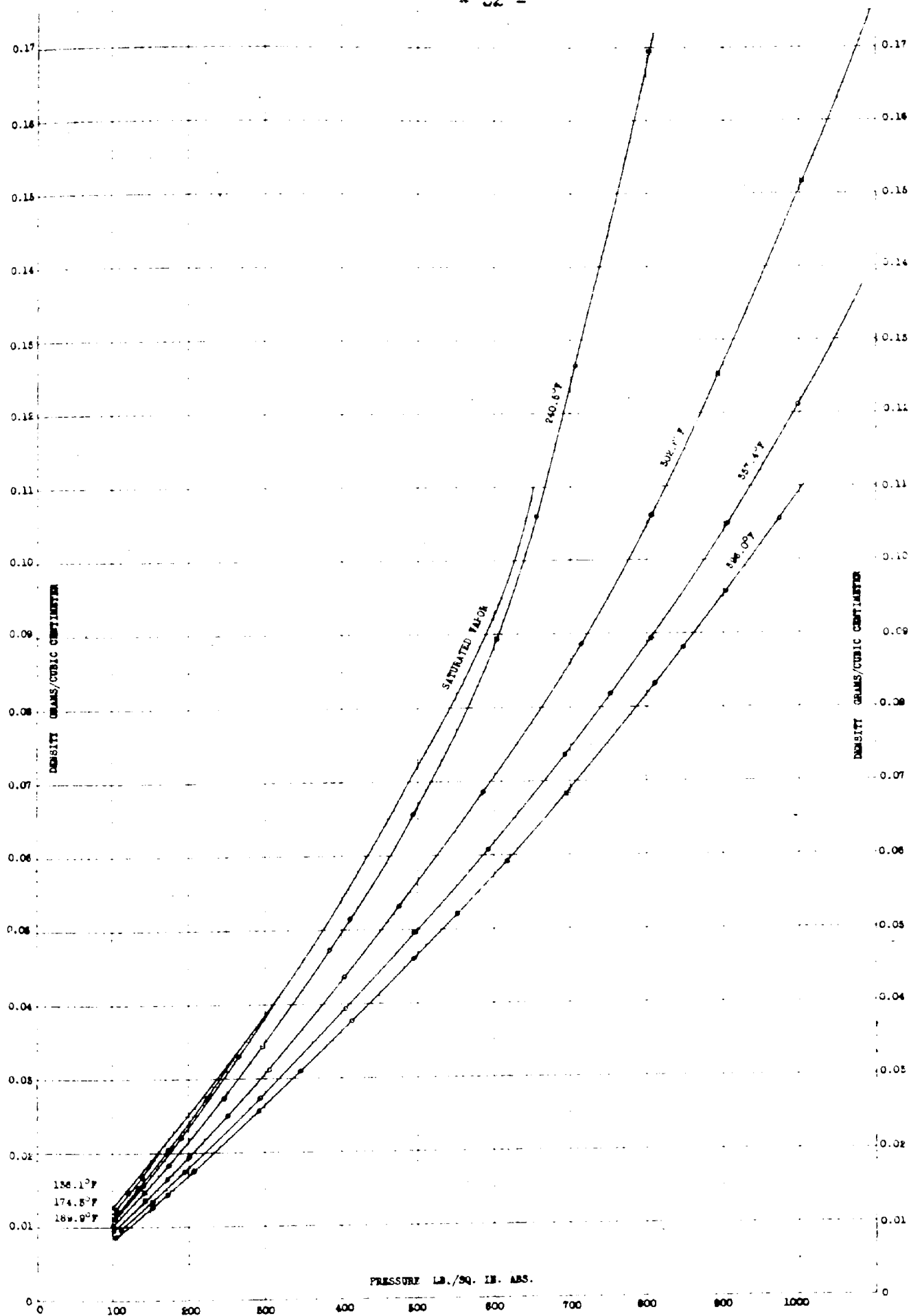


FIGURE 5
EXPERIMENTAL ISOTHERMAL VAPOR DENSITIES FOR A MIXTURE
CONTAINING 40.78 MOL PERCENT ETHYLENE IN n-BUTANE

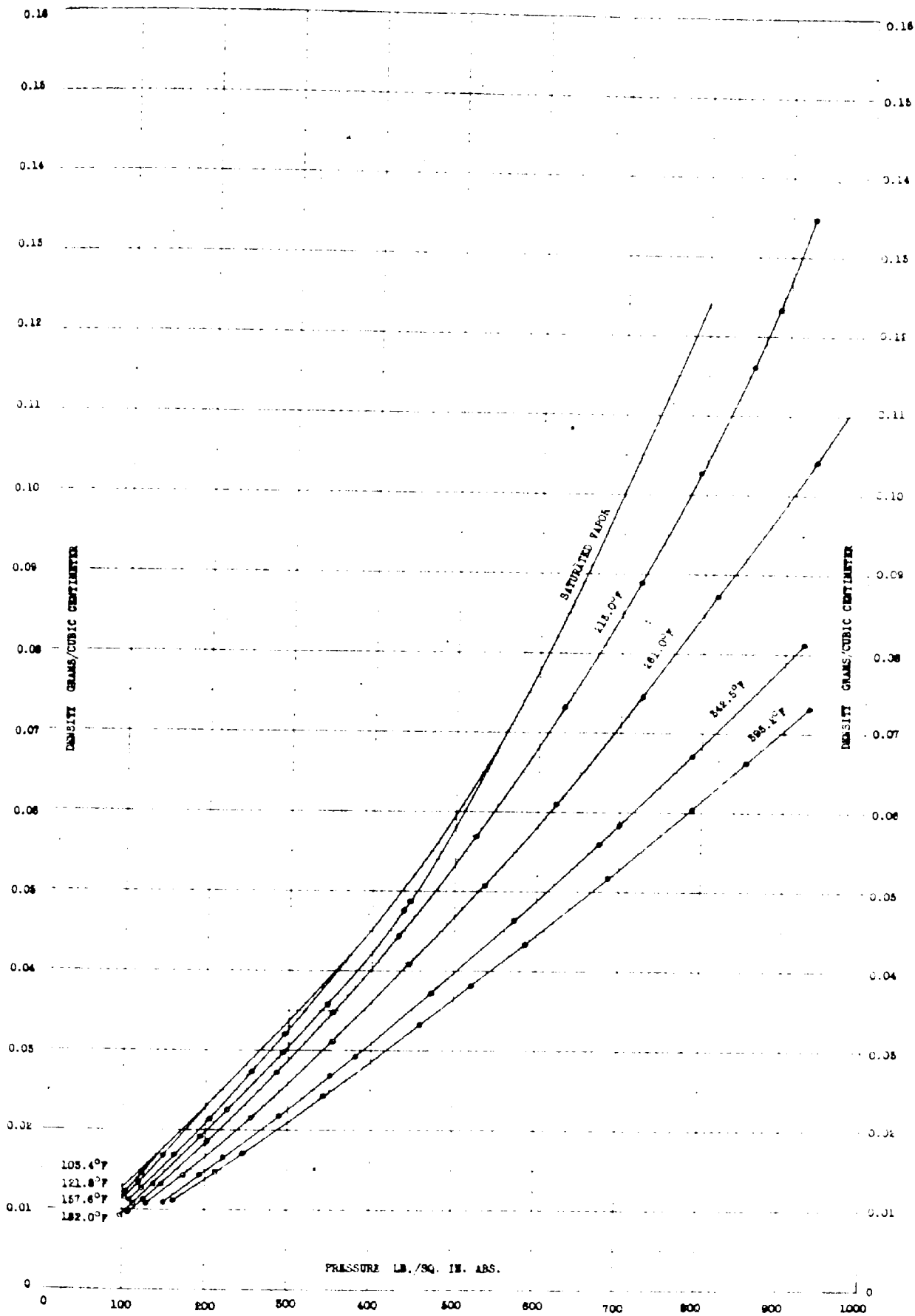


FIGURE 9
EXPERIMENTAL ISOTHERMAL VAPOR DENSITIES FOR A MIXTURE
CONTAINING 66.18 MOL PERCENT ETHYLENE IN n-BUTANE

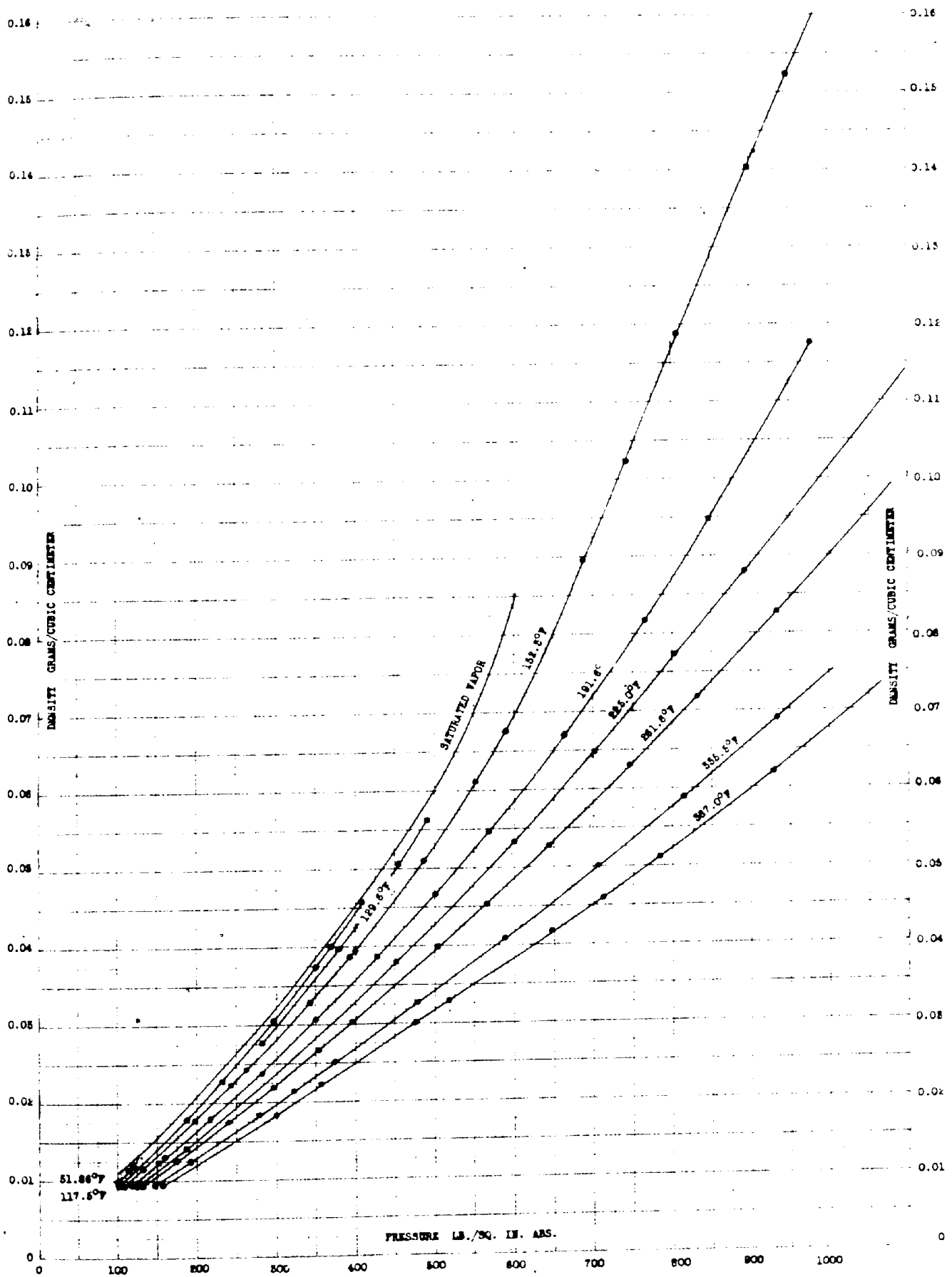


FIGURE 10
EXPERIMENTAL ISOTHERMAL VAPOR DENSITIES FOR A MIXTURE
CONTAINING 80.86 MOL PERCENT ETHYLENE IN n-BUTANE

Calculations and Accuracy of the Reported Data

The possible errors involved in the reported data, and the accuracy of the various measurements are summarized in the following discussion. Two sample calculations which show the methods of computing the analysis of a mixture and the steps involved in converting the original data to the reported values of pressure, temperature and density are given.

Pressure

All pressures are reported as the absolute values. The two most important corrections to be made to the gage reading are the calibration of the dial and the correction for the atmospheric pressure. Only one other correction of any consequence was required. As the level of mercury in the piezometer was frequently higher than the reservoir to which the gages were connected, the pressure in the tube was lower than the gage reading by an amount equivalent to the head of mercury. Accordingly, this correction was always made.

There were two other possible corrections to the gage reading. These were the effect of capillary depression and of the vapor pressure of mercury. The capillary depression of mercury has been measured⁽³⁰⁾ and in tubes as large as those used in this study, the correction was negligible. Also at all temperatures the vapor pressure of mercury was insignificant.

The accuracy of the reported pressure reading is believed to be 0.5 percent at 200 lb./sq.in. and to decrease linearly to 0.1 percent at 1000 lb./sq.in.

Temperature

The accuracy of the reported temperatures is believed to be $\pm 0.025^{\circ}\text{F}$.

Composition

Considering the possible errors in measuring the pressure and temperature in making up a mixture of gas, the analysis given is accurate within 0.0005 mol fraction.

Densities

The accuracy of the reported densities depends upon the magnitudes of the errors in the weight and volume of the sample. A tabulation of the sources and possible magnitudes of error and the effect upon the density follows:

Weight of the Sample

<u>Measurement</u>	<u>Possible Error (\pm)</u>	<u>Effect on Result</u>
Temperature	0.05°F	1×10^{-4}
Pressure	0.02 mm Hg	0.2×10^{-4}
Cathetometer	0.01 mm	0.2×10^{-4}
Analysis	0.0005	-
Possible Total		1.22×10^{-4}

Volume Measurement

Cathetometer	0.01 mm	Maximum	6.5×10^{-4}
		Minimum	0.2×10^{-4}
Calibration		Maximum	2×10^{-4}
		Minimum	0.6×10^{-4}
Possible Total		Maximum	8.5×10^{-4}
		Minimum	0.26×10^{-4}

Since an error in either volume or weight is carried directly to the density, the maximum possible error in the density is very nearly 0.1 percent. The largest source of error lies in the cathetometer readings. The accuracy of this instrument for an average of several readings was taken as ± 0.01 millimeter. As the length of the piezometer occupied by the sample varied between 15 and 350 millimeters, it is obvious that at high densities the accuracy will be far less than at very low densities.

The calibration procedure involves the same source of error. In view of the number of measurements made in calibrating the portion of the tube used at the higher densities and the smoothness of the resulting plot which showed the volumetric deviation from a true cylinder, it is probable that the accuracy of the calibration curve is better by one significant figure than the accuracy of the cathetometer reading. However, to be conservative, it was arbitrarily assumed that the error of the calibration was one-third of the possible error of the cathetometer reading.

Densities are reported to four significant figures. The accuracy increases approximately linearly from about 0.1 percent at a density of 0.5 gram/cc to approximately 0.03 percent at a density of 0.01 gram/cc.

The sample calculation shows the correction in the calibrated volume for thermal expansion of glass; a linear coefficient of $2.0 \times 10^{-6}/^{\circ}\text{F}$ has been reported⁽¹⁰⁾ for Pyrex. As the measuring scale was not a part of the heated system, the volumetric coefficient is only twice the above, or 4.0×10^{-6} .

SAMPLE CALCULATION

COMPOSITION OF A MIXTURE

$$PV = ZMRT$$

Assume $V = 1$ liter

Then Weight per liter = $\frac{PM}{ZRT} =$ grams/liter

Where $P =$ Pressure atmospheres
 $M =$ Molecular weight
 $T =$ Absolute temperature $^{\circ}K$
 $R =$ A constant - 0.08206 liter atm./ $^{\circ}K$ /Mol

Then Illustrating this by application to the first recorded unit volume of ethylene in the data below:

$$\text{grams/liter} = \frac{769.32 \times 28.050}{760 \times 0.9940 \times 0.08206 \times 297.77} = 1.1674$$

<u>Component in Unit Volume</u>	<u>Pressure Mm Hg</u>	<u>Temp. $^{\circ}K$</u>	<u>Z</u>	<u>Grams/Liter</u>
Ethylene	769.32	297.77	0.9940	1.1674
Ethylene	829.02	297.91	0.9936	<u>1.2576</u>
Total				2.4250
Butane	754.50	298.00	0.9665	2.4416
Butane	747.05	298.08	0.9668	2.4161
Butane	752.85	298.10	0.9664	<u>2.4357</u>
Total				7.2934

$$\text{Weight fraction ethylene in mixture} = \frac{2.4250}{2.4250 + 7.2934} = 0.2495$$

$$\text{Corresponding mol fraction} = 0.4078$$

SAMPLE CALCULATION

DENSITY OF SINGLE PHASE FLUID IN THE

HIGH PRESSURE TUBE

Composition of Mixture	80.98 Mol % Ethylene
Weight of Sample in High Pressure Tube	0.10439
Temperature	
E.M.F. Measured	3.730 volts
Corresponding Temperature	191.95 °F
Pressure	
Recorded Pressure Reading on 1000 psi gage	815.5 psi
Less: a) Head of Mercury in Tube above point of Pressure Measurement	12.2 psi
b) Calibration of Gage Reading	<u>51.0</u>
Corrected Gage Pressure in Tube	752.3 psi
Barometric Pressure	14.4 psi
Total - Absolute Pressure	766.7 psi
Negligible corrections to Pressure	
Vapor Pressure of Mercury at 191.95°F ~	0.007 psi
Capillary Depression of Mercury ~	0.02 psi

Volume Measurements

Cathetometer Readings

Reference Point	60.658 cm
Top of Meniscus	50.280
Bottom of Meniscus	50.249
Height of Meniscus	0.031

Volumes

Volume in Tube to Bottom of Meniscus	0.18127 cm ³
Less: a) Volume of Stirring Rod	0.00484
b) Volume of Meniscus	<u>0.00045</u>
Net Volume of Tube at 70°F	0.17598

Thermal Expansion of Tube

Coefficient = $4.0 \times 10^{-6}/^{\circ}\text{F}$	
Temperature Difference from Datum (70°F) = 121.85°F	
Corrected Volume at 191.85°F	
$(1 + 4.0 \times 10^{-6})(121.85)(0.17598) = 0.17606 \text{ cm}^3$	

True Density of Sample = $\frac{0.01439}{0.17606} = 0.081501$

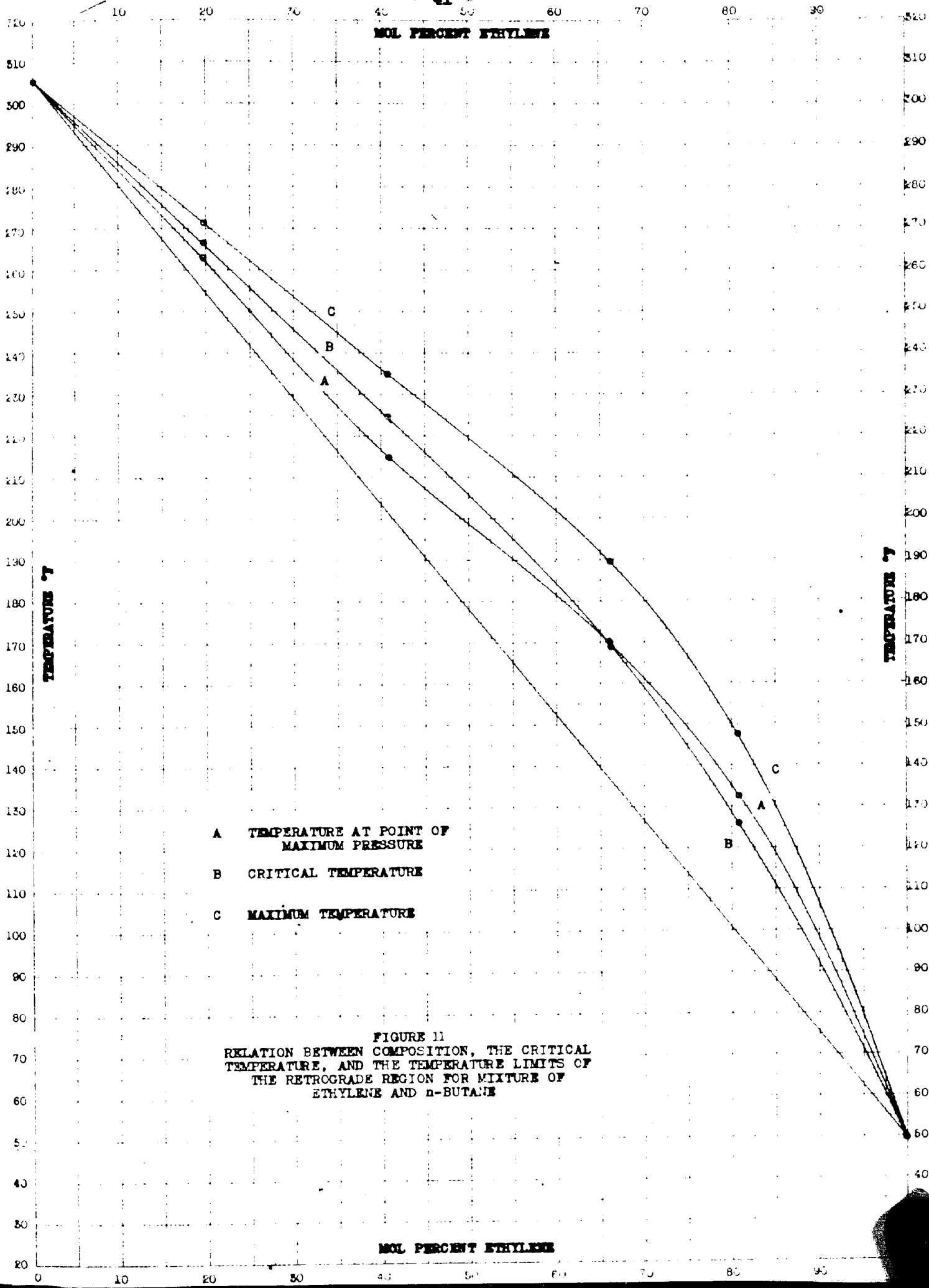
DISCUSSION OF THE EXPERIMENTAL RESULTS

Liquid-Vapor Phase Equilibria

The general shape of the phase diagrams, that is, the pressure-temperature plots shown by Figure 4 is similar to those reported for other binary mixtures of hydrocarbons, and the same increase of critical pressure over those of the pure components is noted. The effect of composition upon the critical constants and the points of maximum temperature and pressure which define the retrograde region are shown in Figures 11 and 12. Upon comparison with the methane-butane system^(24,27) and the ethane-butane system⁽¹⁹⁾ the general relationship of critical properties is verified. That is, in general, the greater the difference between the normal volatilities or between the molecular weights, the larger will be the range of retrograde condensation and the range of critical pressures. The following data may be cited:

	<u>Ethane-Butane</u>	<u>Ethylene-Butane</u>	<u>Methane-Butane</u>
Maximum Pressure lb./sq.in.	843	973	1800
Maximum Range of Re- trograde Region lb./sq.in.	70	150	900
°F	15	22	75

The data for the methane-butane system are not complete as they do not extend far into the methane rich region; the values given, then, may not necessarily be exactly the maximum. It is interesting to note that each of the above respective maxima occurs at about the same concentration of ethylene as ethane.



- A TEMPERATURE AT POINT OF MAXIMUM PRESSURE
- B CRITICAL TEMPERATURE
- C MAXIMUM TEMPERATURE

FIGURE 11
 RELATION BETWEEN COMPOSITION, THE CRITICAL TEMPERATURE, AND THE TEMPERATURE LIMITS OF THE RETROGRADE REGION FOR MIXTURE OF ETHYLENE AND n-BUTANE

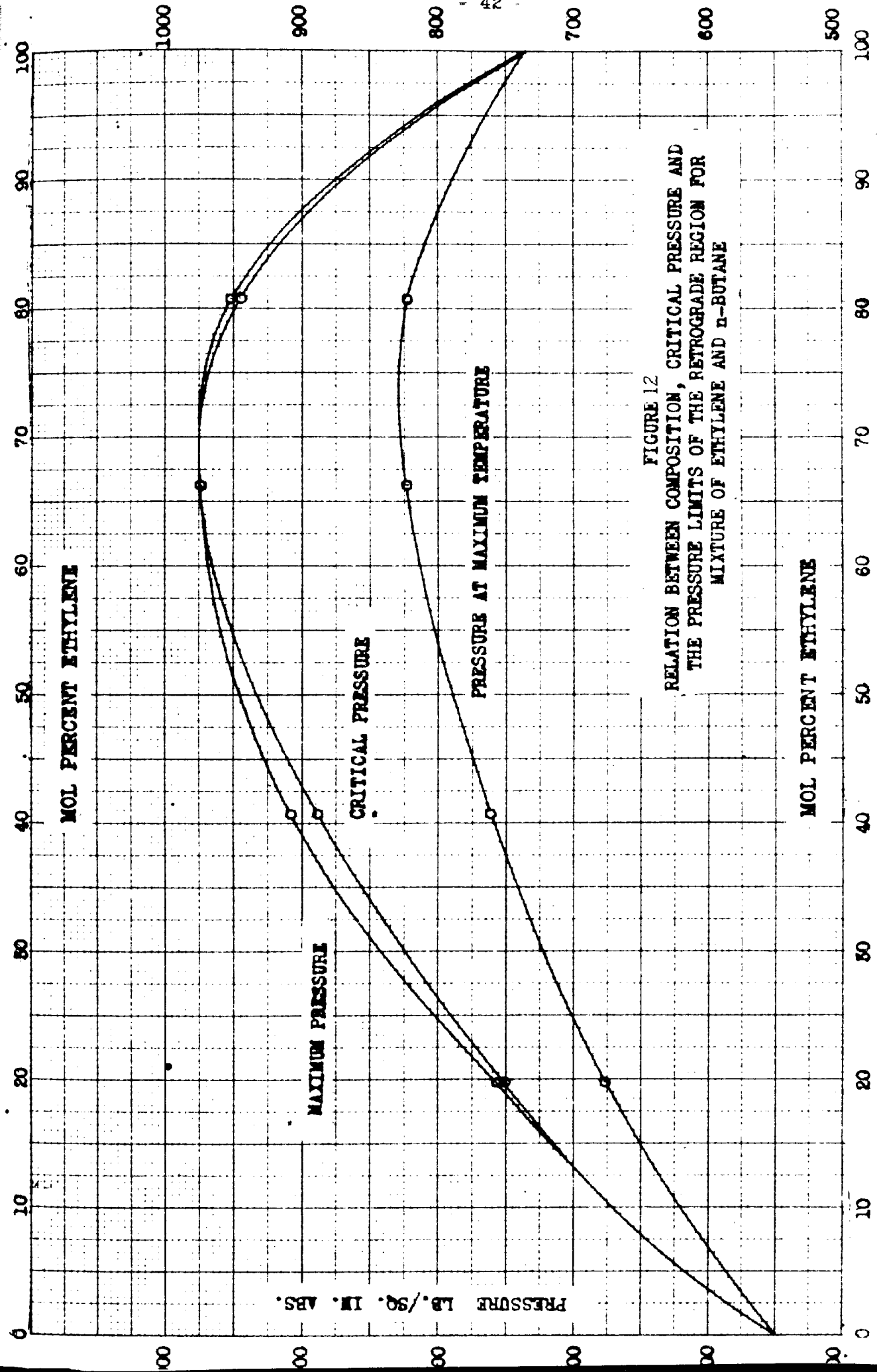


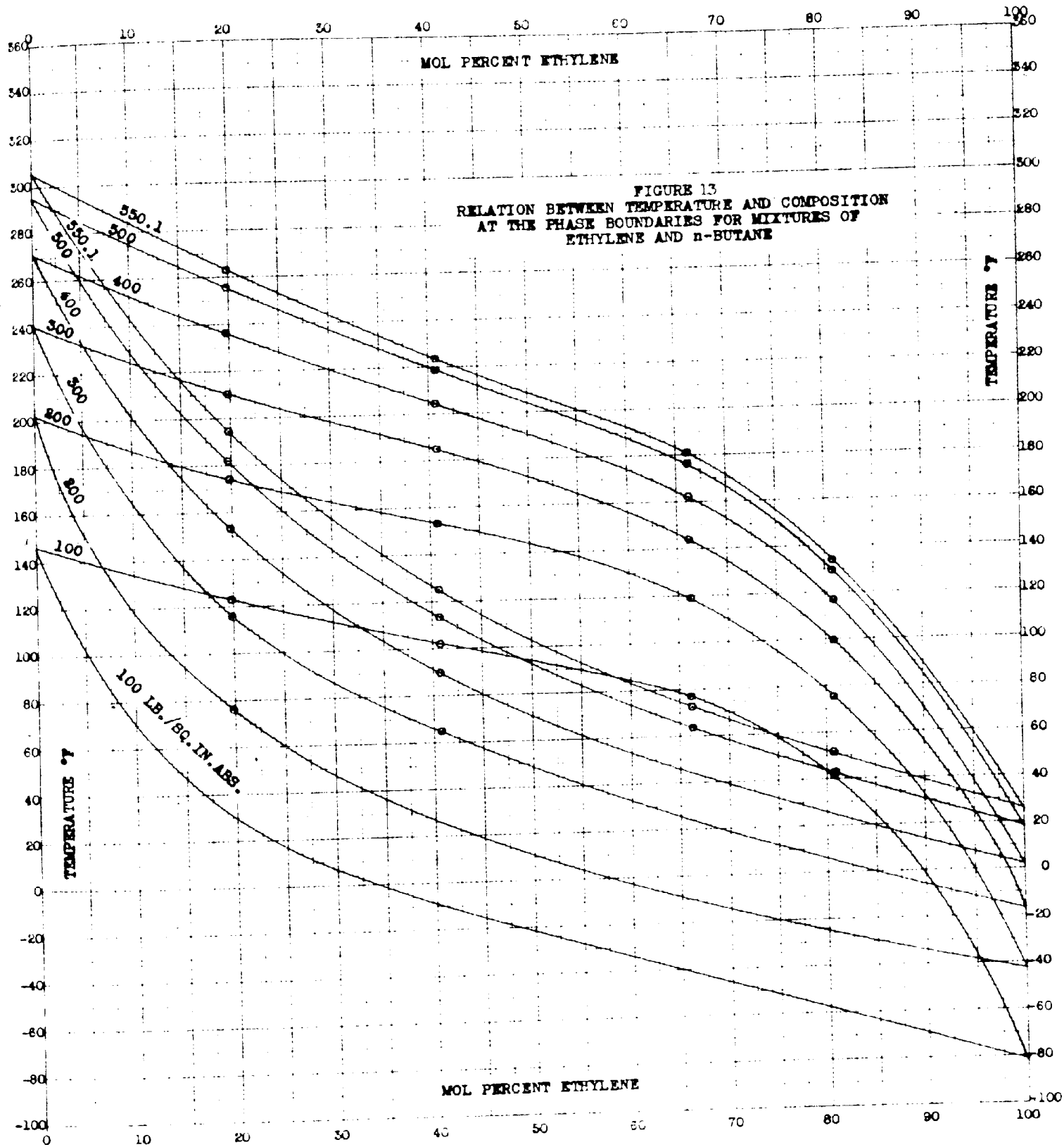
FIGURE 12
 RELATION BETWEEN COMPOSITION, CRITICAL PRESSURE AND
 THE PRESSURE LIMITS OF THE RETROGRADE REGION FOR
 MIXTURE OF ETHYLENE AND n-BUTANE

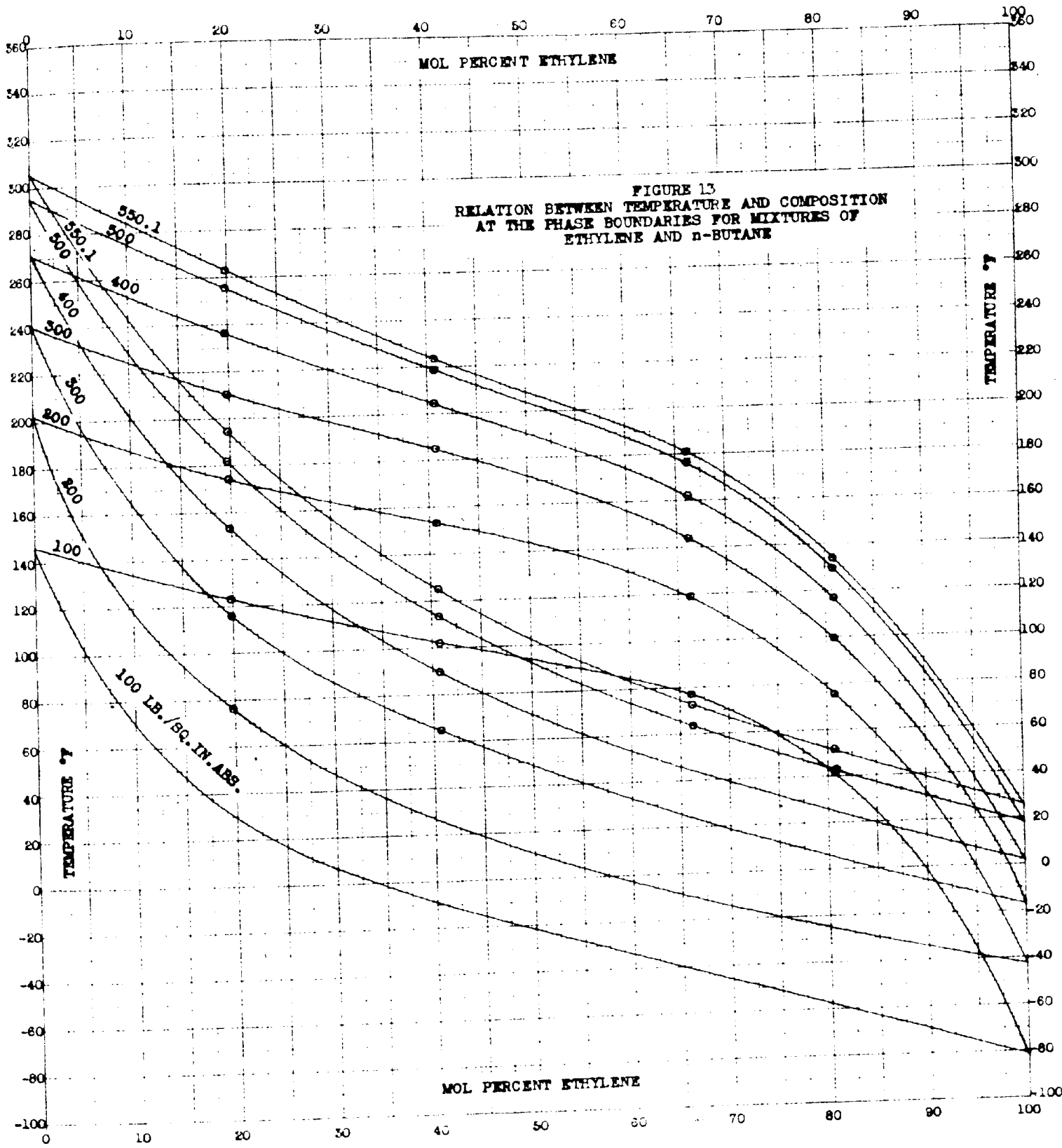
The interpolated temperatures, and densities at uniform intervals of pressure are listed in Tables II and III for the phase boundary curves and the locus of critical points, respectively.

Vapor-Liquid Equilibria

Another two dimensional representation of the three dimensional spacial shape may be obtained by cross plotting the boundary curves of Figure 4 to show the vapor and liquid temperatures as a function of composition at a constant pressure. Such curves, Figures 13 and 14, are also known as boiling point diagrams. These plots are extremely useful for interpolating between the experimental concentrations so that equilibrium data may be obtained at any composition. Interpolated points from these curves are recorded in Table IV.

The curves in Figure 13 represent isobars up to the lowest critical pressure in the system, that of pure butane, while in Figure 14 all the curves are at pressures greater than the critical pressure of butane. The diagrams show the shrinkage of the area of co-existing liquid and vapor as the pressure is increased. That is, at pressures above the critical of one or both pure components, there are limiting compositions as well as limiting temperatures at each isobar. To illustrate, at 500 lb./sq.in. liquid and vapor may co-exist at all concentrations of either component. At 800 lb./sq.in. the composition of the phases must be between the limits of 24.8 and 95.7 mol percent ethylene. The two-phase region vanishes at the point of maximum pressure, 973 lb./sq.in.; the composition at this point is approximately 69 mol percent ethylene.





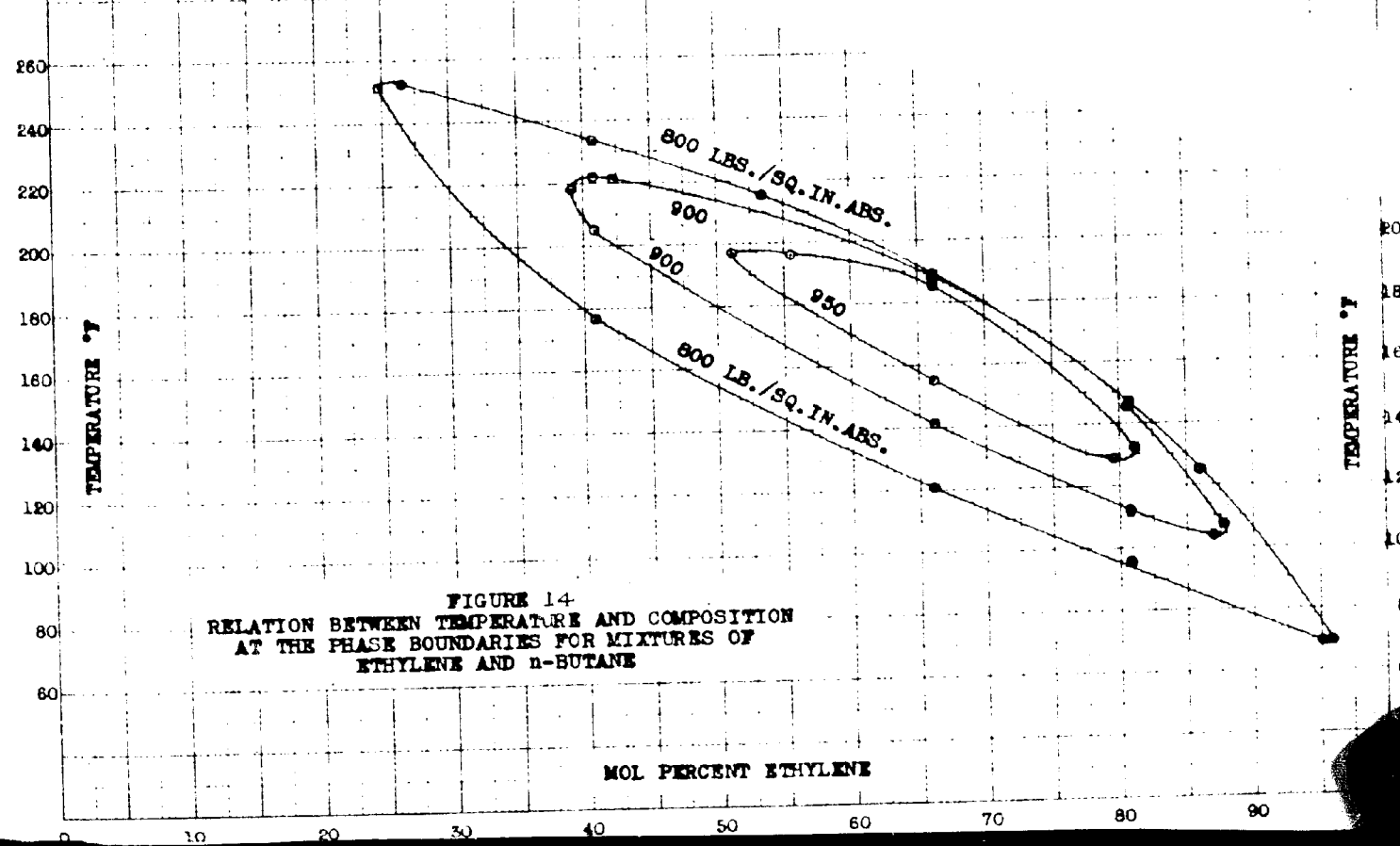
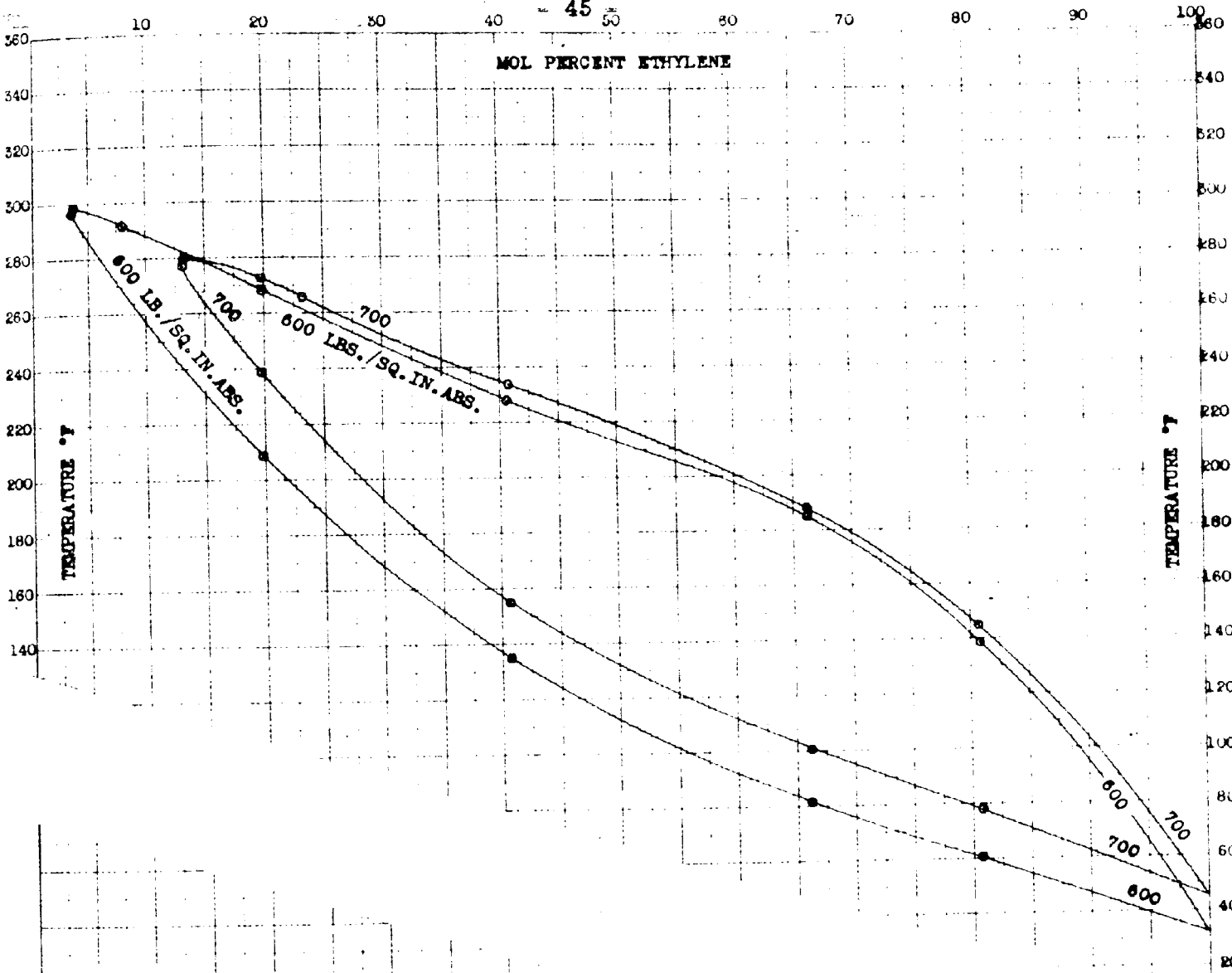


FIGURE 14
 RELATION BETWEEN TEMPERATURE AND COMPOSITION
 AT THE PHASE BOUNDARIES FOR MIXTURES OF
 ETHYLENE AND n-BUTANE

At pressures above the criticals of a pure component more points become available for establishing the curves. Those, which are shown in Figure 8, represent the temperature, pressure and the composition at the criticals and the points of maximum temperature and pressure. The critical pressure of the mixtures, shown as a function of composition in Figure 12, reaches a maximum value at an intermediate composition. Therefore, if the pressure of a two-phase system is greater than the critical pressures of either pure component, there must be for each isobar two critical temperatures and corresponding compositions.

Similarly, for each isobar there are two points at which the pressure is a maximum, each with its corresponding temperature and pressure. A third set may be derived from the other limit of retrograde condensation, the point of maximum temperature, but the pressure range does not extend as far as the two others. At pressures between the criticals of ethylene and butane, there is, of course, only one set of these three points for each isobar and it lies in the butane rich end of the boiling point curves.

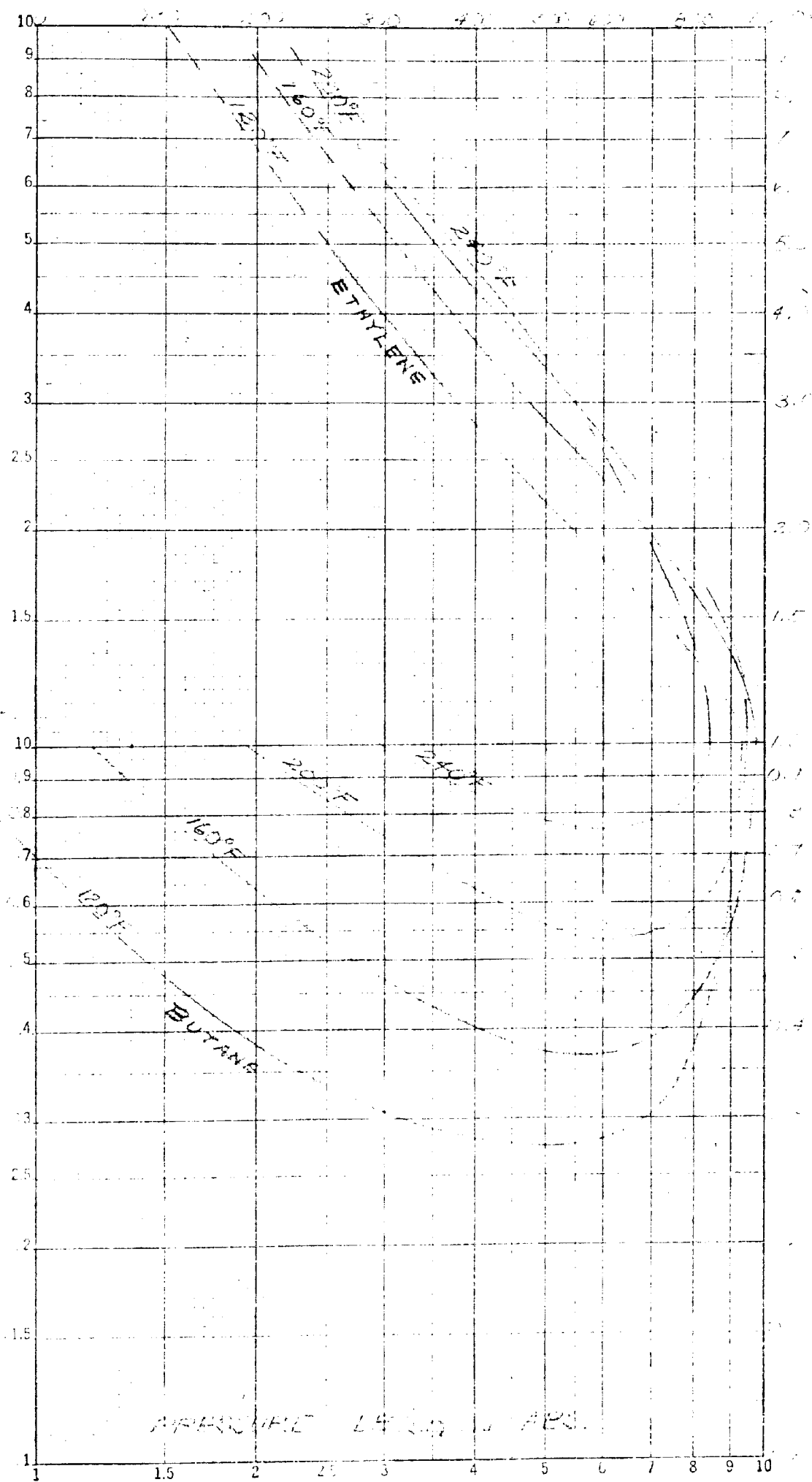
In technical calculations which involve vapor-liquid equilibria, it is customary and convenient to express the relation between the composition of liquid and vapor in terms of the so-called equilibrium constant, $K = y/x$, in which y and x are the mol fractions of a component in vapor and in the liquid, respectively. The composition of vapor and liquid and the corresponding equilibrium constants for various isotherms are listed in Table V; the isothermal equilibrium constants are plotted as a function of pressure in Figure 15.

As is the case for other systems plotted in this manner, the equilibrium constant of the lighter component decreases continuously with increasing pressure to a value of unity at the critical pressure. As the

pressure is increased, the constant for heavier component decreases, passes through a minimum and converges with the constant of the lighter component at the critical pressure and unity.

The construction of these curves demonstrates the difficulty of obtaining, at low pressures, accurate equilibrium constants for the lighter component when it is present in low concentrations. For instance, at concentrations of ethylene less than, say 5 percent, the steep slope of the bubble point curve in Figure 13 can easily cause small errors in the interpolated compositions. Although the absolute value of the error is small, it becomes relatively large at low concentrations and may result in a considerable error in the equilibrium constant. This error of interpolation usually does not appear in the dew point composition as the slope of this curve is low. The relative magnitudes of the error of interpolation and the concentration of butane are such that here the resulting inaccuracy is insignificant. As, in the ethylene rich region, the dew point line is steep and the bubble point line is relatively flat. A similar error is apt to appear in the equilibrium constant of butane. At higher pressures the curves are not so steep and, as mentioned above, there are additional points available for establishing the curves.

When the concept of the equilibrium constant was proposed^(7,29), values of the constants for hydrocarbons were reported and have been widely used. These constants were based upon fugacities computed from deviations from ideal gas laws and the assumption of ideal solutions. The composition of the solution is, therefore, not a variable. As the fugacities were computed from a generalized P-V-T plot derived from ethylene, a comparison between the ideal and the experimental equilibrium constants in the binary



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mixture will indicate the extent to which this binary system deviates from ideality. In the following tabulation, some values of the constants⁽²⁸⁾ computed from fugacities are compared with the experimental constants as listed in Table V. The constants cited from the literature are ideal below the critical pressures; at higher pressures a correction is included to allow for the phenomenon of convergence.

Vapor-Liquid Equilibrium Constants of Ethylene

<u>Pressure</u>	120°F		160°F		200°F		240°F	
	<u>Expt'l.</u>	<u>Ideal</u>	<u>Expt'l.</u>	<u>Ideal</u>	<u>Expt'l.</u>	<u>Ideal</u>	<u>Expt'l.</u>	<u>Ideal</u>
300 lb./sq.in.	4.0	3.32	5.40	4.2	6.15	5.3	6.40	6.55
500	2.18	2.10	2.83	2.68	3.40	3.3	3.48	4.05
700	1.56	1.61	1.956	2.0	2.135	2.5	1.89	3.05
800	1.315	1.47	1.615	1.82	1.79	2.2	1.38	2.7

Vapor-Liquid Equilibrium Constants for Butane

<u>Pressure</u>	120°F		160°F		200°F		240°F	
	<u>Expt'l.</u>	<u>Ideal</u>	<u>Expt'l.</u>	<u>Ideal</u>	<u>Expt'l.</u>	<u>Ideal</u>	<u>Expt'l.</u>	<u>Ideal</u>
300 lb./sq.in.	0.307	0.355	0.47	0.54	0.742	0.74	0.994	0.97
500	0.275	0.3	0.372	0.44	0.560	0.61	0.782	0.76
700	0.304	0.325	0.339	0.45	0.547	0.60	0.734	0.73
800	0.380	0.34	0.442	0.46	0.538	0.60	0.865	0.71

The agreement between the ideal and experimental constants is not good except in a few short sections of the curves. In general, the ideal constants for the lighter component are too high at pressures greater than 500 lb./sq.in. and the deviation increases with increasing temperature or pressure. In other words, the discrepancy of the ideal constants is greatest in the critical region. The differences, of course, are the result of departure of ethylene-butane mixtures from ideal solutions in the two-phase region. That is, assumptions such as no heat of mixing and additivity of volumes must be invalid in this case.

Except for the highest isotherm, the minimum points of the experimental butane constants are appreciably lower than those of the ideal constants. The ideal constants again fail to show the temperatures or pressures at the critical or convergence points.

Another way in which the behavior of a compound may be shown is through comparison with the properties of adjacent hydrocarbons. The vapor-liquid equilibria of methane, of ethane and of heptane in butane have been reported in the literature^(19,21,24,27). Because of the differences in the temperature ranges of the two-phase systems, only the equilibrium constants of the light hydrocarbons in butane can be compared. In figures 16 and 17 the equilibrium constants of methane, ethylene and ethane are plotted at 160°F and 190°F. In order to show the volatility of ethylene relative to the paraffins, the equilibrium constants at constant pressure and temperature are plotted in Figure 18 against the temperatures of the boiling points at atmospheric pressure. Upon this basis, the equilibrium constant, or volatility of ethylene in butane, is as much as 40% greater than would have been predicted by this approximation.

Densities of Hydrocarbon Mixtures

The densities of the saturated liquid and vapor for the four mixtures and the two pure compounds are shown, in relation to the temperature, by Figure 5. As was reported for the ethane-heptane and the ethane-butane systems^(18,19) there is a point of inflection in the density curve at the critical density. Further, this point of inflection becomes more pronounced with increasing ethylene concentrations. A second point of

100 200 300 600 1000 2000

FIGURE 16
VAPOR-LIQUID EQUILIBRIUM CONSTANTS OF METHANE,
ETHYLENE AND ETHANE IN n-BUTANE AT 160°F

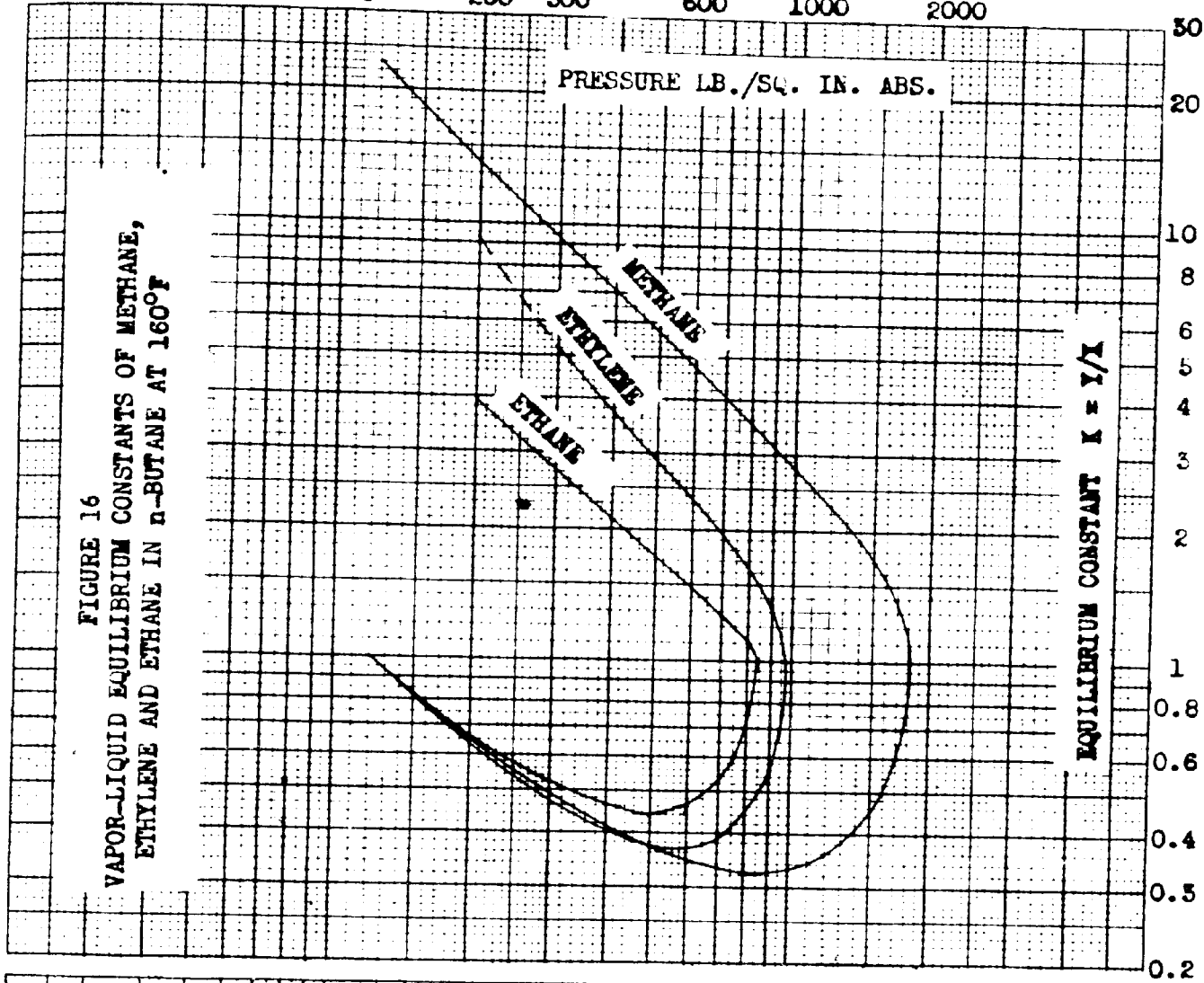
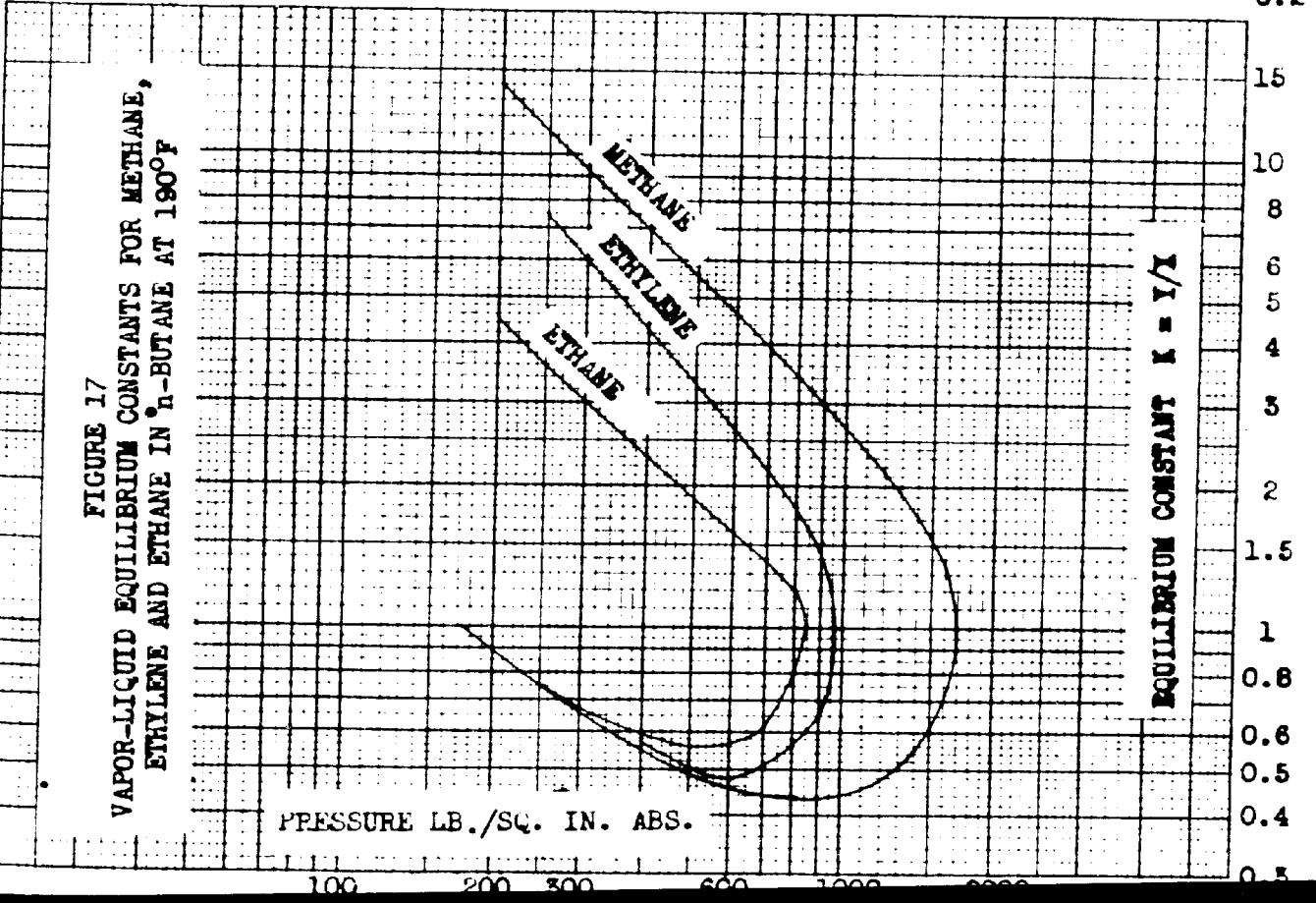


FIGURE 17
VAPOR-LIQUID EQUILIBRIUM CONSTANTS FOR METHANE,
ETHYLENE AND ETHANE IN n-BUTANE AT 190°F



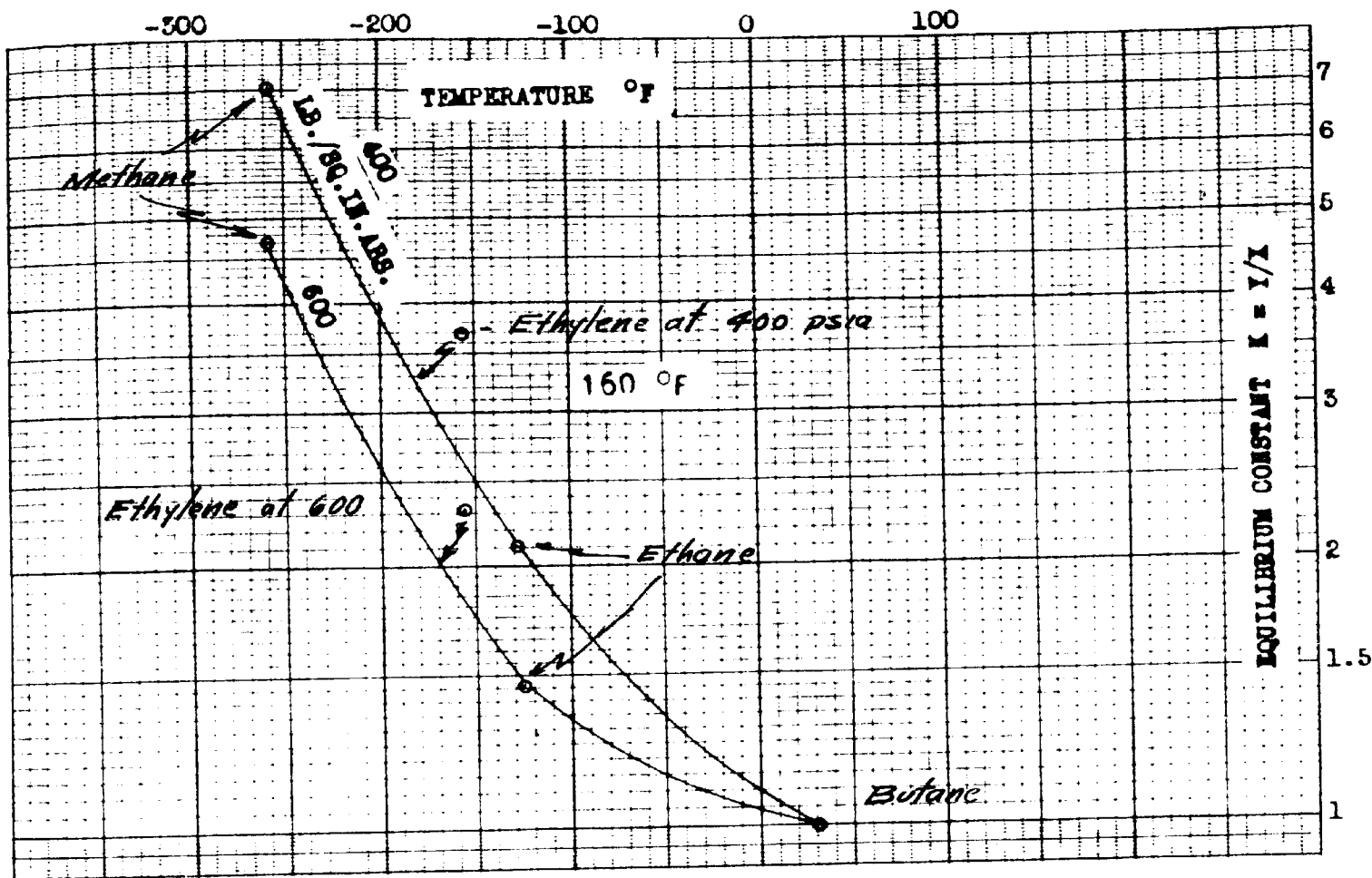
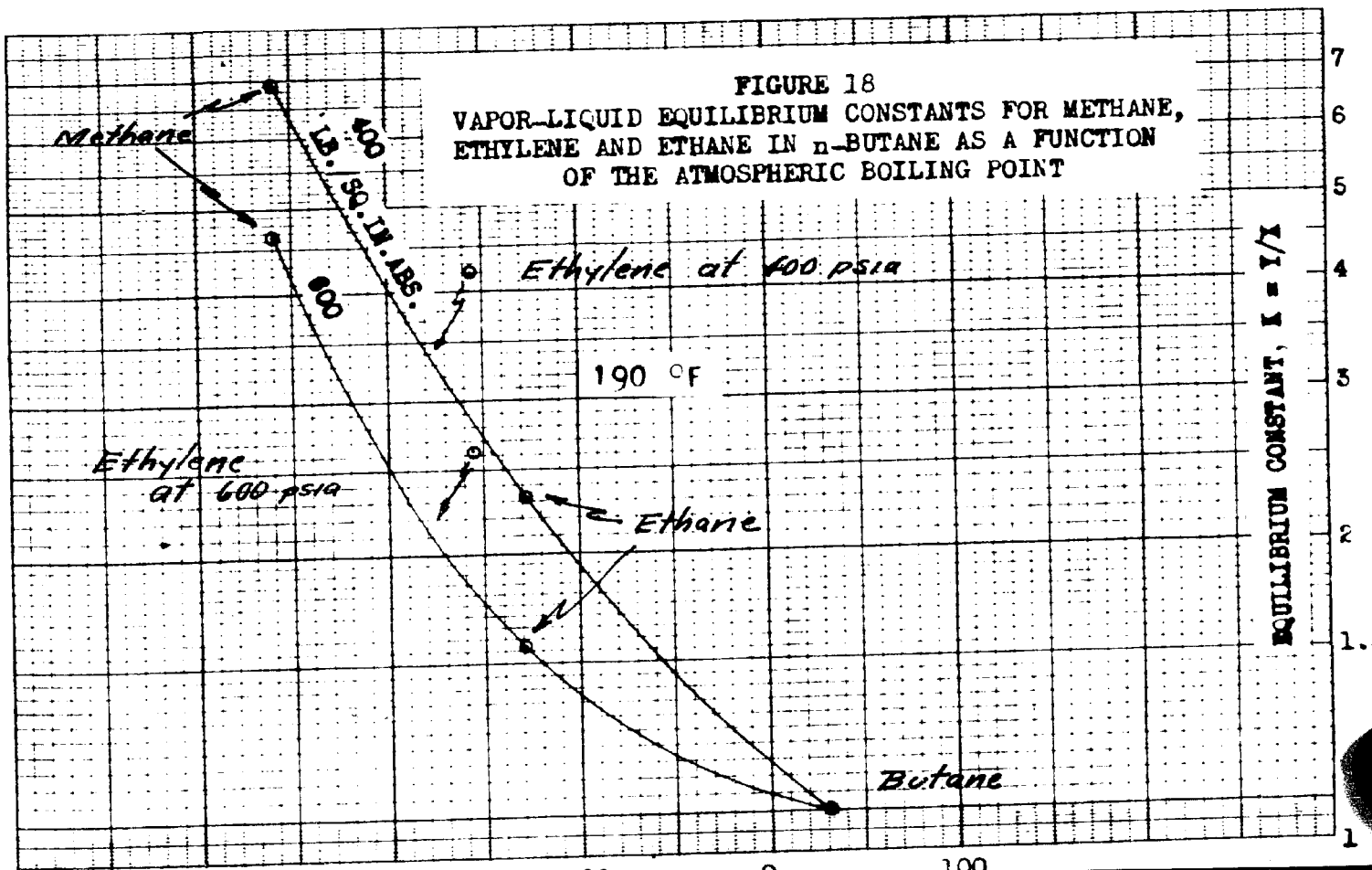


FIGURE 18
VAPOR-LIQUID EQUILIBRIUM CONSTANTS FOR METHANE,
ETHYLENE AND ETHANE IN *n*-BUTANE AS A FUNCTION
OF THE ATMOSPHERIC BOILING POINT



inflection at a lower density was found in the other two systems, but this point is not easily discernible in the phase diagrams of the ethylene-butane mixtures. The density curves show some irregularity at lower concentrations of either component, this indicates, perhaps, the deviation from ideality is greatest in these regions.

In addition to the densities at the phase boundaries, the pressure-volume-temperature relationships were determined in the single phase region. The experimental data are reported in Tables VIII and IX. The former table covers densities of superheated vapor, while in the latter, the reported densities refer to the liquid and the fluid in the vicinity of the critical points. The densities which were determined isothermally, and are shown in Figures 6 - 10, were put in a more usable or customary form by cross plotting to show the density as a function of temperature for several uniformly spaced isobars in Figures 19 - 22.

The method of predicting or correlating densities of gaseous hydrocarbons by the law of corresponding states has been well developed and is highly successful^(7,9,22). As is now well known, according to the theorem of corresponding states, the compressibility factors, PV/NRT , of the pure hydrocarbons are approximately equal at identical values of reduced pressure and reduced temperature. These terms which must be taken in consistent units are identified as:

- P - Pressure
- T - Temperature
- V - Volume
- N - Number of mols considered
- R - Gas law constant

The reduced pressure and temperature are, of course, the ratio of the existing temperature or pressure to the respective critical values.

It has been shown that the compressibility factors of mixtures of hydrocarbons can be correlated with those of the pure compounds on a reduced basis in which a hypothetical point, termed the pseudo-critical, is used rather than the true critical point⁽¹⁷⁾. It has been further shown that for mixtures of light hydrocarbons, the coordinates of the pseudo-critical point may be taken as the molal average of the critical pressures and temperatures of the individual components.

To test the validity of this procedure with mixtures of ethylene and butane, the compressibility factors were computed from the experimental data, are given in Table VI and are plotted on a reduced or pseudo-reduced basis in Figure 23.

The densities of ethylene reported in the literature^(1,12) were used as the basis of the work referred to above^(7,9,22) on the generalized properties of hydrocarbons, and is also used as the basis of Figure 23.

The compressibility factors for ethylene are shown in this figure as the solid line as a function of pressure for two reduced temperatures. The compressibility factors of butane and the four mixtures are shown as points for the same reduced or pseudo-reduced temperatures. The critical or pseudo-critical constants and the temperatures corresponding to the reduced or pseudo-reduced temperatures are given in Table VI. In making the graph, the compressibility factors were computed at pressures in multiples of 100 lb./sq.in. abs.

It is not possible to use a wider range of pseudo-reduced temperatures and show the data for all four mixtures, for if the pseudo-reduced temperature of 1.10 is reduced by as little as 1%, it will lie within the two-phase region of the ethylene rich mixture, and if increased over 1.20, it will fall outside the experimental range of temperature for the butane rich mixture.

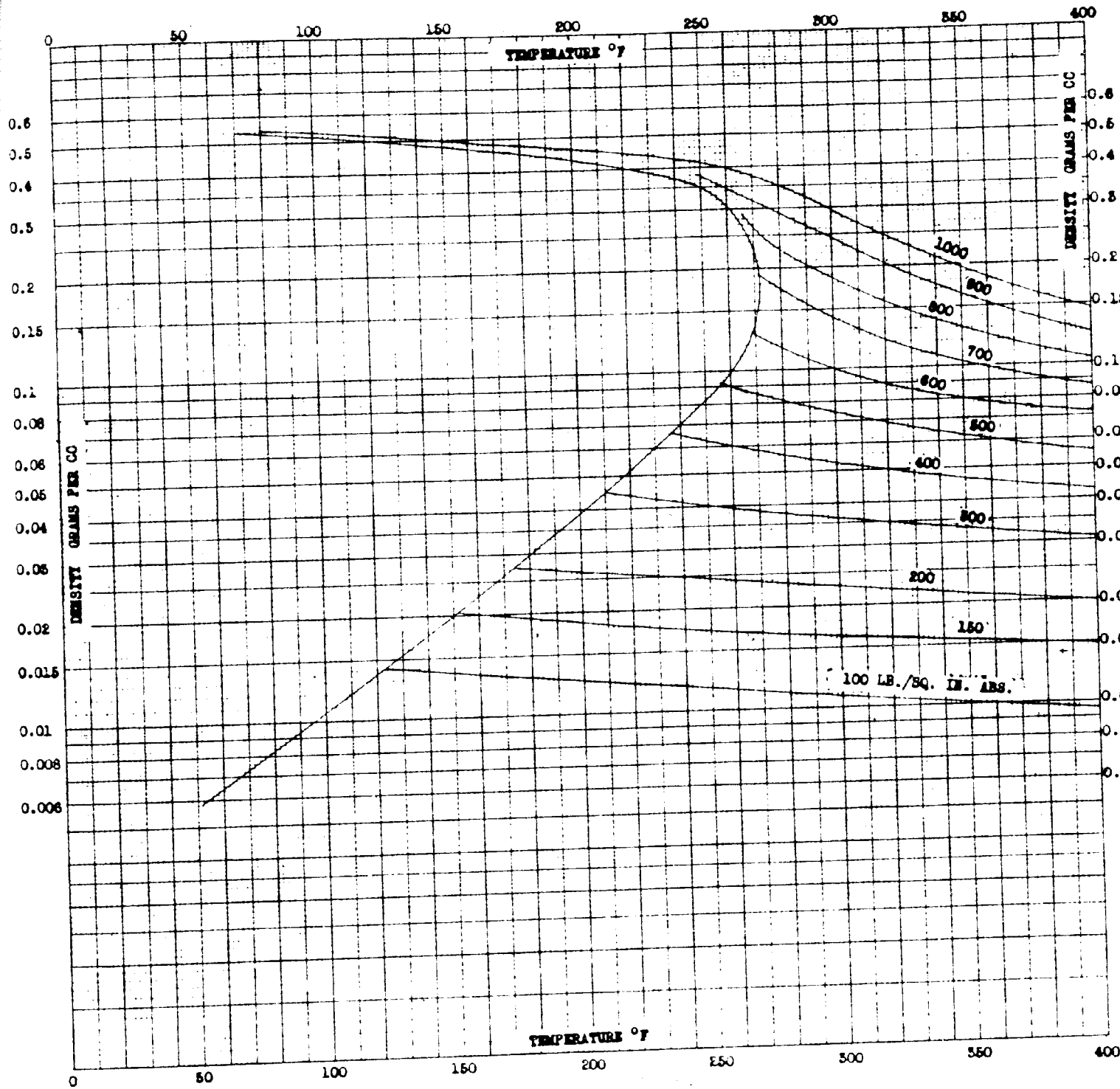


FIGURE 19
DENSITY OF A MIXTURE CONTAINING 19.85 MOL PERCENT
ETHYLENE IN n-BUTANE

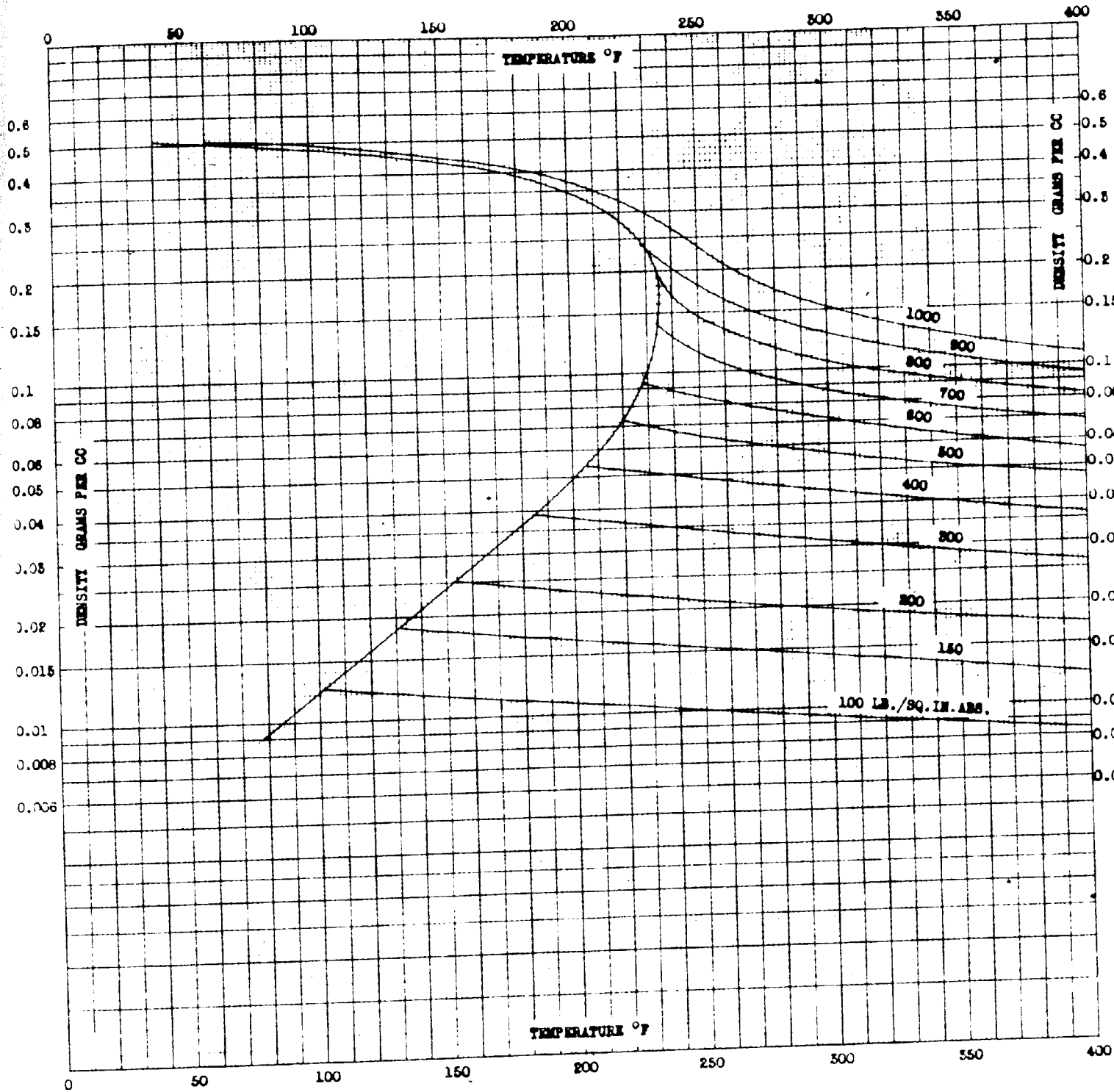


FIGURE 20
 DENSITY OF A MIXTURE CONTAINING 40.78 MOL PERCENT
 ETHYLENE IN n-BUTANE

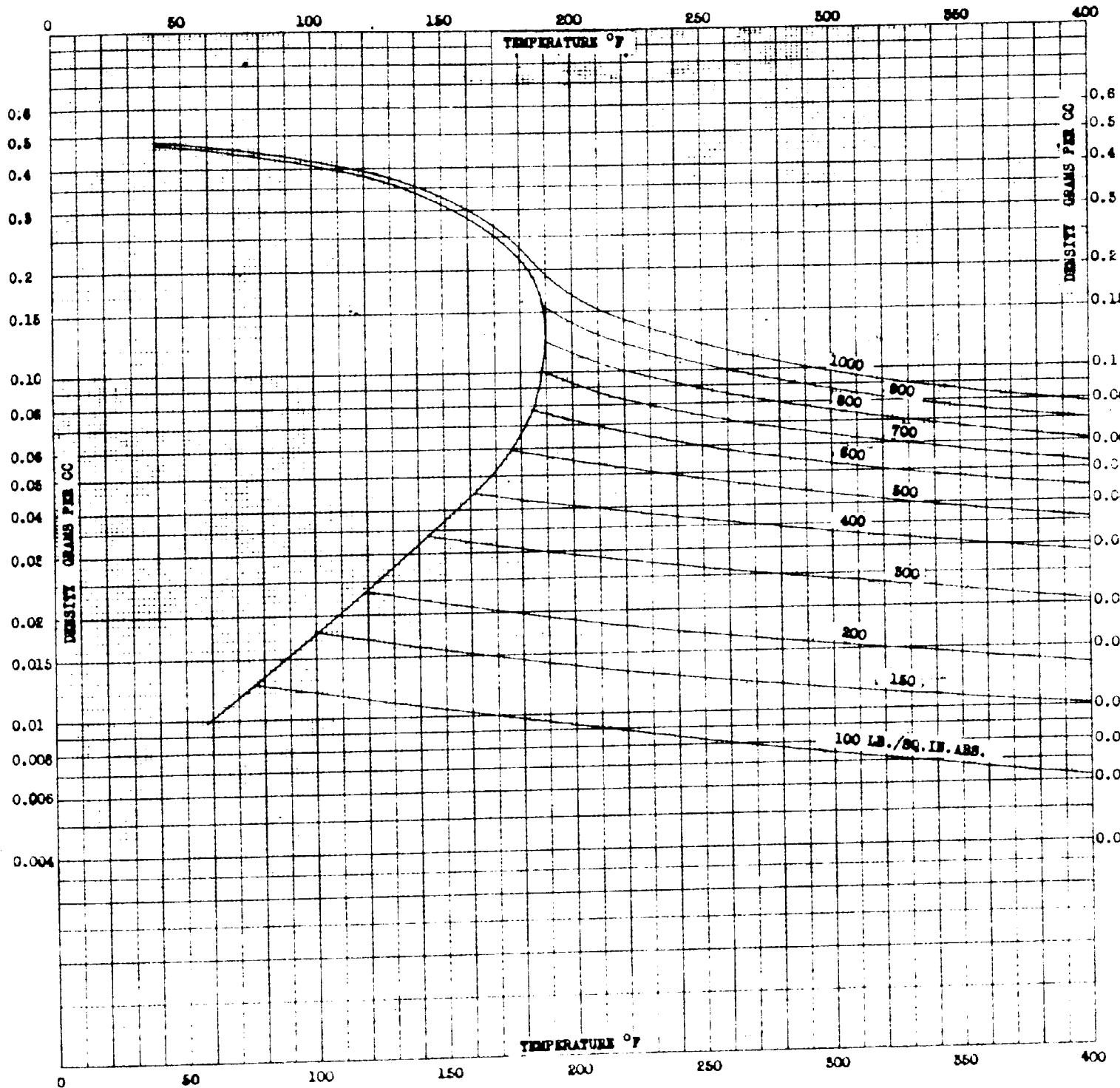


FIGURE 21
DENSITY OF A MIXTURE CONTAINING 66.18 MOL PERCENT
ETHYLENE IN n-BUTANE

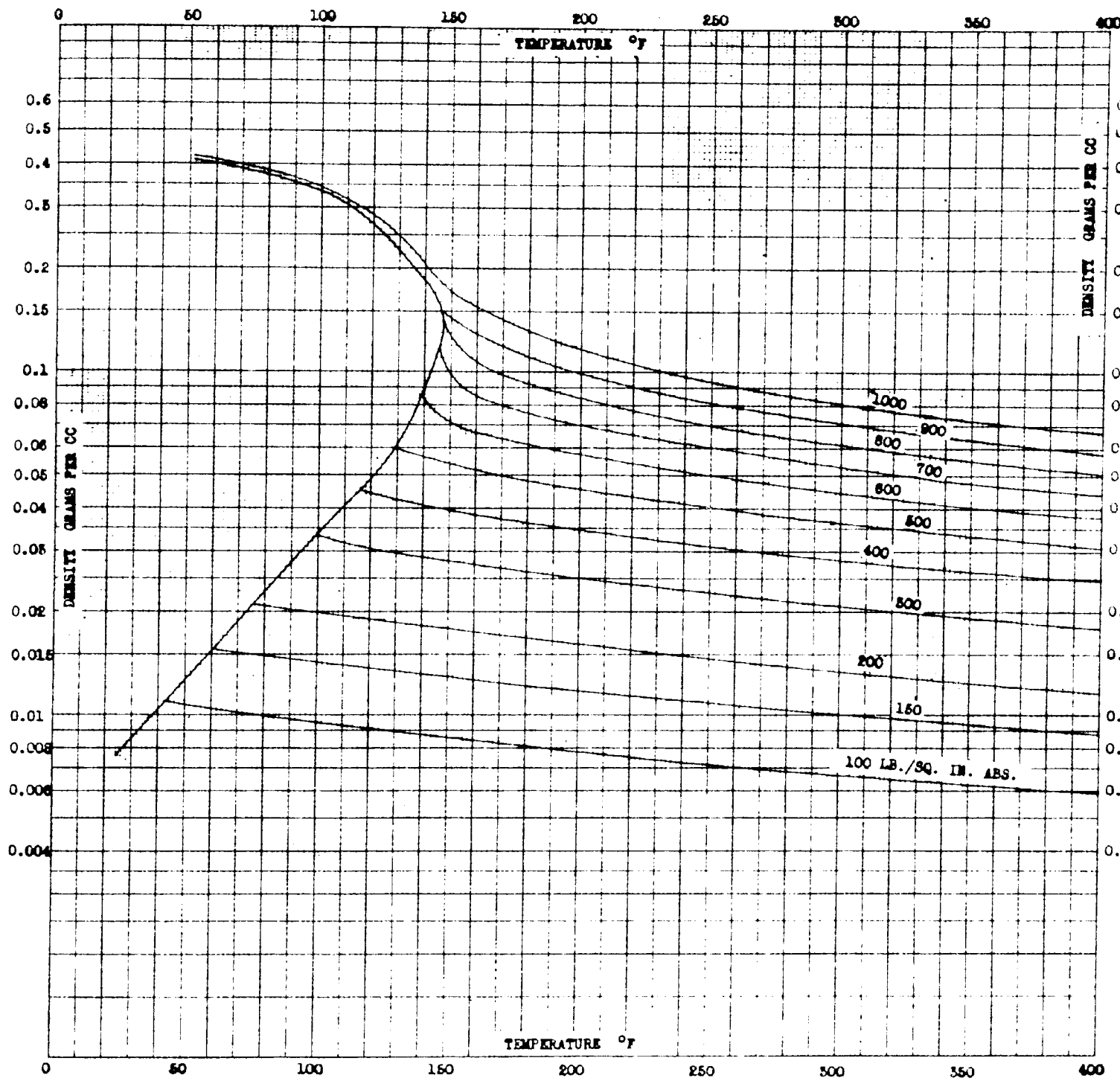


FIGURE 22
DENSITY OF A MIXTURE CONTAINING 80.88 MOL PERCENT
ETHYLENE IN n-BUTANE

However, the data do demonstrate that deviations from the theorem of corresponding states tend to increase as the two-phase region is approached. A visual inspection of Figure 23 readily proves this. At the higher pseudo-reduced temperature the average deviation from the line which represents the compressibility factor of ethylene is about one percent. The similar deviation at the lower pseudo-reduced temperature, which is nearer the liquid region, is almost three percent. Further, the largest such deviation noted, about eight percent, occurs in the mixture richest in ethylene at 800 lb./sq.in.abs. and 154.7°F. At this pressure the temperature is but 8°F higher than the dew point. However, for the same mixture at the same pressure the deviation falls to less than one-half of one percent at 210.3°F which is about 65°F above the dew point.

It is also to be noted that these deviations, relative to pure ethylene, from the theorem of corresponding state increase with increasing pressure. This is part of the same effect, namely, that the discrepancies tend to occur near the phase boundaries.

In general, the data show that on a pseudo-reduced basis mixtures of this type conform to the the rem of corresponding states as well as do the two pure hydrocarbons except when near the liquid region.

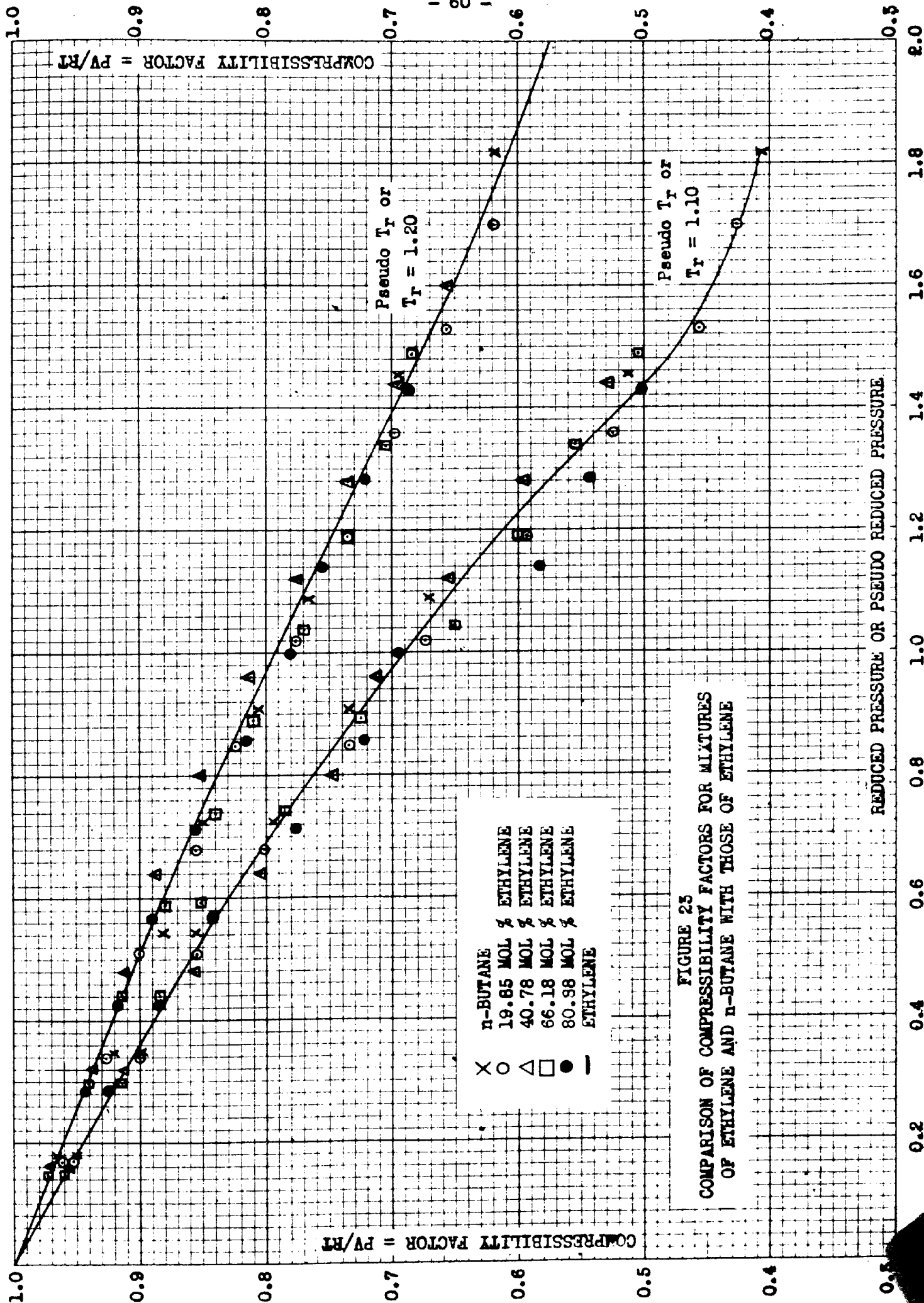


FIGURE 25
 COMPARISON OF COMPRESSIBILITY FACTORS FOR MIXTURES
 OF ETHYLENE AND n-BUTANE WITH THOSE OF ETHYLENE

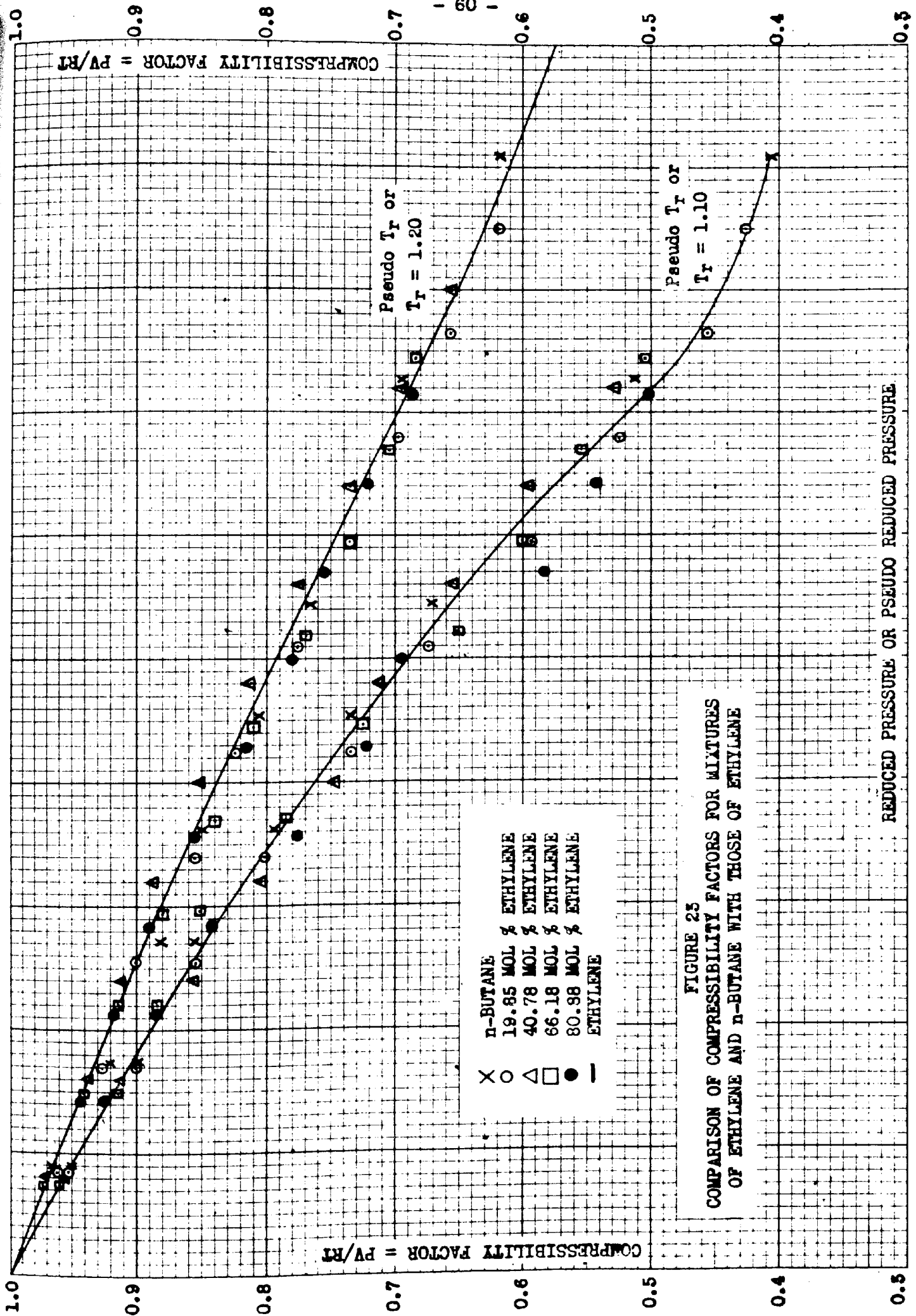


FIGURE 25
 COMPARISON OF COMPRESSION FACTORS FOR MIXTURES
 OF ETHYLENE AND n-BUTANE WITH THOSE OF ETHYLENE

CONCLUSION

Four mixtures, uniformly distributed in the composition range, were prepared. The pressures, temperatures and densities at the liquid-vapor phase boundary were determined experimentally for each of these mixtures in addition to similar measurements in the single phase region. These data, taken with those reputed for pure ethylene and butane, enable the construction of diagrams which show the properties, such as the composition of coexisting liquid and vapor as functions of pressure and temperature throughout the entire composition range. Graphs, presented in this dissertation, show the volatility of ethylene in butane in comparison with reported data for methane and ethane in the same solvent. The experimental data, pressure-volume-temperature relationships at the phase boundary and in the single phase region, are also shown graphically for each of the mixtures studied. The densities of the gaseous mixtures are shown to obey the theorem of corresponding states, but that slight deviations occur near the two-phase boundary.

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A P P E N D I X

T A B L E II

SUMMARY OF PRESSURE, TEMPERATURE AND DENSITY DATA
AT PHASE BOUNDARIES FOR THE ETHYLENE-n-BUTANE SYSTEM

Press. psia	100 Mol % Ethylene		80.88 Mol % Ethylene		66.18 Mol % Ethylene	
	Temp. °F	Density gms/cc	Temp. °F	Density gms/cc	Temp. °F	Density gms/cc
50						
75						
100			41.6		50.7	
125			50.3		64.2	.0106
150			58.9		77.3	.01285
175			67.3	.015	89.5	.01512
200			75.1	.0178	100.4	.0178
225			82.3	.0209	110.1	.02040
250			88.7	.0240	118.7	.02322
275			94.3	.0270	126.1	.02602
300			99.6	.0303	132.4	.0285
325		.4330	104.3	.0334	138.4	.03112
350		.4265	108.7	.0362	143.7	.0359
375		.4188	112.9	.0398	148.7	.0367
400		.412	116.7	.0429	153.4	.0388
425		.4045	120.3	.0465	157.7	.0418
450		.3970	123.7	.0495	161.9	.0449
475		.3900	126.7	.0527	166.0	.0487
500		.3830	129.4	.0565	169.7	.0518
525		.3755	131.9	.0602	173.2	.0559
550		.3622	134.2	.0645	176.4	.0601
575		.3502	136.3	.0695	179.2	.0647
600		.3318	138.4	.0753	181.4	.0695
625		.3148	140.2	.0830	183.3	.0745
650		.2980	142.0	.090	184.8	.0797
675		.2827	143.6	.0988	186.0	.0835
700		.2680	145.0	.1072	186.9	.0885
725		.2540	146.2	.1181	187.6	.0922
750		.2410	147.1	.1270	188.2	.0965
775		.2290	147.3	.137	188.7	.106
800		.2180	147.5	.157	189.2	.1165
825		.2080	147.5	.189	189.5	.1250
850		.1990	147.4	.234	189.7	.130
875		.1910	147.2	.290	189.8	.140
900		.1840	146.3	.360	189.6	.147
925		.1780	145.6	.450	189.5	.152
950		.1730	143.6	.560	189.2	.158
970		.1690	134.6	.695	188.3	.1672
				.870	184.9	.1898
				1.130	176.2	.2272

T A B L E III

CRITICAL PROPERTIES OF ETHYLENE-n-BUTANE MIXTURES

<u>Critical Pressure psia</u>	<u>Critical Composition Mol % Ethylene</u>	<u>Critical Temperature °F</u>	<u>Critical Density gms/cc</u>
550.1	0	306.0	0.228
575	2.0	301.7	0.233
600	4.0	297.5	0.237
625	6.2	293.2	0.240
650	8.5	288.7	0.245
675	10.7	284.1	0.247
700	13.3	279.0	0.250
725	16.1	273.4	0.253
750	19.2	267.2	0.256
775	22.5	260.4	0.258
800	26.2	253.0	0.260
825	30.0	245.4	0.261
850	34.2	237.6	0.262
875	38.2	229.4	0.262
900	42.6	220.5	0.262
925	47.8	210.2	0.261
950	54.4	196.4	0.259
965	59.9	184.2	0.257
973.5	65.3	171	0.255
965	59.8	145.0	0.248
950	79.9	128.9	0.244
925	84.0	114.6	0.239
900	86.9	103.9	0.236
875	89.4	94.3	0.2315
850	91.6	85.6	0.227
825	93.5	77.2	0.223
800	95.3	69.3	0.219
775	97.2	61.3	0.216
750	98.9	53.6	0.212
736	100	49.1	0.210

T A B L E I V

ETHYLENE-n-BUTANE SYSTEM

Temperature - Composition Curves
At Constant Pressures

<u>Mol % Ethylene</u>	100 psia		200 psia		300 psia	
	<u>Liquid Temp. °F</u>	<u>Vapor Temp. °F</u>	<u>Liquid Temp. °F</u>	<u>Vapor Temp. °F</u>	<u>Liquid Temp. °F</u>	<u>Vapor Temp. °F</u>
0	146.0	146.0	202.7	202.7	241.2	241.2
5	101.5	140.3	151.7	194.2	196.6	232.6
10	70.0	134.2	118.2	186.7	164.4	224.5
15	47.0	128.4	94.3	179.9	137.1	217.0
20	29.5	122.6	75.2	173.8	115.3	209.9
30	7.0	112.1	46.8	163.6	86.2	197.8
40	- 9.0	102.8	26.7	154.0	65.8	185.7
50	-21.5	94.1	10.6	143.9	48.3	172.1
60	-34.0	84.7	- 2.9	130.1	32.8	156.2
70	-45.5	70.0	-14.5	109.8	18.7	134.6
80	-57.5	43.5	-25.0	78.4	5.9	102.4
85	-63.5	24.2	-29.7	57.9	- 0.1	80.6
90	-69.0	- 1.5	-34.5	32.1	- 6.0	55.5
95	-75.5	-35.5	-38.5	- 0.3	-11.7	24.4
100	-80.4	-80.4	-42.8	-42.8	-17.1	-17.1

<u>Mol % Ethylene</u>	400 psia		500 psia		550.1 psia	
	<u>Liquid Temp. °F</u>	<u>Vapor Temp. °F</u>	<u>Liquid Temp. °F</u>	<u>Vapor Temp. °F</u>	<u>Liquid Temp. °F</u>	<u>Vapor Temp. °F</u>
0	270.9	270.9	295.0	295.0	306.0	306.0
5	233.6	261.9	259.5	285.0	273.2	294.9
10	201.3	253.8	228.6	275.0	242.8	284.0
15	175.4	244.0	202.4	264.9	216.3	273.3
20	152.4	235.7	180.2	254.9	193.6	262.8
30	117.6	220.1	143.4	236.8	156.3	243.1
40	91.2	205.2	115.3	220.0	126.4	224.7
50	70.3	190.4	92.9	203.9	102.8	208.1
60	53.4	174.3	73.8	187.8	83.4	192.8
70	38.7	152.6	57.9	166.3	66.8	171.4
80	25.8	119.9	43.5	132.4	52.4	137.2
85	19.7	97.2	37.0	110.5	45.3	124.9
90	13.6	70.2	30.8	84.3	39.0	89.1
95	7.5	37.5	24.5	53.1	32.3	59.0
100	2.5	2.5	18.6	18.6	25.7	25.7

T A B L E I V
(Continued)
ETHYLENE-n-BUTANE SYSTEM

Temperature - Composition Curves
At Constant Pressures

<u>Mol % Ethylene</u>	600 psia		<u>Mol % Ethylene</u>	700 psia		<u>Mol % Ethylene</u>	800 psia	
	<u>Liquid Temp. °F</u>	<u>Vapor Temp. °F</u>		<u>Liquid Temp. °F</u>	<u>Vapor Temp. °F</u>		<u>Liquid Temp. °F</u>	<u>Vapor Temp. °F</u>
a) 4.0	297.5	297.5	a) 13.3	279.0		a) 26.2	253.0	253.0
b) 3.6	297.7		b) 13.3	276.8		b) 24.7	242.5	
5	286.8	297.7	15	264.0	279.2	30	219.7	248.1
10	257.2	288.0	20	237.4	272.4	40	179.8	234.9
20	208.1	268.3	30	192.6	252.3	50	154.4	220.7
30	168.3	247.8	40	157.1	234.9	60	132.8	202.8
40	136.9	229.2	50	132.2	218.8	70	113.2	180.0
50	112.2	213.1	60	112.2	200.7	80	95.3	149.4
60	92.3	197.2	70	95.1	179.0	90	78.1	105.8
70	75.4	175.3	80	78.9	146.9	95	69.3	75.2
80	61.5	141.8	90	62.5	103.3	a) 95.3	69.3	69.3
90	46.9	94.7	100	44.8	44.8	b) 96.0		69.3
95	39.6	65.5						
100	32.3	32.3						

	900 psia			<u>Mol % Ethylene</u>	950 psia	
	<u>Mol % Ethylene</u>	<u>Liquid Temp. °F</u>	<u>Vapor Temp. °F</u>		<u>Liquid Temp. °F</u>	<u>Vapor Temp. °F</u>
a)	42.6	220.5	220.5	a) 54.4	196.4	196.4
b)	39.2	218.5		b) 51.2	196.3	
	40	208.7	221.7	55	182.5	196.5
	50	179.8	213.8	60	171.0	194.0
	60	155.1	200.1	70	146.5	175.0
	70	133.0	179.3	80	138.6	139.0
	80	113.8	148.2	a) 79.9	128.9	128.9
	85	105.9	102.9	b) 81.2		131.5
a)	86.9	103.9	103.9			
b)	87.8		107.6			

- a) Critical Point
- b) Temperature and Pressure at Point of Maximum Pressure

T A B L E V

ETHYLENE-n-BUTANE SYSTEM

Vapor-Liquid Compositions and Equilibrium Constants at Constant Temperatures

	Pressure psi	Mol % Ethylene		Vapor-Liquid Equilibrium Constant	
		In Liquid	In Vapor	Ethylene	n-Butane
120°F	94 70.8	0	0	-	-
	200	10.8	65.7	6.8	0.38
	300	18.7	75.0	4.0	0.507
	400	28.7	80.0	2.8	0.28
	500	38.2	83.0	2.18	0.275
	600	46.6	85.1	1.82	0.280
	700	55.8	86.6	1.56	0.504
	800	66.3	87.2	1.315	0.580
	900	76.6	85.5	1.115	0.618
	956	82.5	82.5	1	1
160°F	140 120	0	0	-	1
	200	3.7	33.7	9.05	0.69 0.63
	300	10.7	57.8	5.40	0.47
	400	18.2	67.0	3.66	0.402
	500	25.2	72.2	2.85	0.372
	600	32.5	75.1	2.34	0.369
	700	39.1	76.3	1.956	0.389
	800	47.5	76.8	1.615	0.442
	900	57.9	76.8	1.328	0.556
	950	64.4	74.4	1.15	0.719
972	64.7	64.7	1	1	
200°F	194	0	0	-	1
	200	0.15	1.45	11	0.988
	300	4.6	28.2	6.15	0.742
	400	10.2	43.6	4.28	0.628
	500	15.5	52.7	3.40	0.560
	600	21.8	58.4	2.68	0.532
	700	28.2	60.3	2.155	0.547
	800	34.2	61.3	1.79	0.588
	900	42.4	60.0	1.415	0.694
	944	52.7	52.7	1	1
240°F	296	0	0	6.5	1
	300	0.1	0.65	6.40	0.994
	400	3.8	17.4	4.59	0.860
	500	8.1	28.2	3.48	0.782
	600	13.2	34.1	2.48	0.759
	700	19.5	36.9	1.89	0.784
	800	26.2	36.2	1.38	0.865
	842	32.8	32.8	1	1

T A B L E VI

COMPRESSIBILITY FACTORS (Z) OF THE ETHYLENE-n-BUTANE SYSTEM

Press. psia	0 Mol % Ethylene					19.85 Mol % Ethylene					40.78 Mol % Ethylene				
	Reduc. Press.	Ideal	Density gms/cc	Actual	Z	Pseudo- Reduc. Press.	Ideal	Density gms/cc	Actual	Z	Pseudo- Reduc. Press.	Ideal	Density gms/cc	Actual	Z
100	0.182	0.0105	0.0108	0.0108	0.952	0.170	0.00991	0.0104	0.0104	0.952	0.160	0.0094	0.0098	0.0098	0.957
200	0.364	0.0206	0.0229	0.0229	0.899	0.340	0.0198	0.0220	0.0220	0.900	0.320	0.0188	0.0204	0.0204	0.922
300	0.546	0.0309	0.0361	0.0361	0.855	0.510	0.0297	0.0348	0.0348	0.854	0.480	0.0282	0.0330	0.0330	0.855
400	0.728	0.0412	0.0520	0.0520	0.795	0.680	0.0396	0.0495	0.0495	0.801	0.640	0.0376	0.0468	0.0468	0.805
500	0.910	0.0515	0.070	0.070	0.735	0.850	0.0495	0.0675	0.0675	0.733	0.800	0.0470	0.063	0.063	0.746
600	1.092	0.0618	0.092	0.092	0.671	1.020	0.0594	0.0880	0.0880	0.674	0.960	0.0564	0.079	0.079	0.713
700	1.274	0.0721	0.121	0.121	0.512	1.190	0.0694	0.117	0.117	0.592	1.120	0.0658	0.100	0.100	0.658
800	1.456	0.0824	0.161	0.161	0.406	1.360	0.0793	0.151	0.151	0.525	1.280	0.0752	0.126	0.126	0.596
900	1.638	0.0927	0.213	0.213	0.300	1.530	0.0892	0.196	0.196	0.455	1.440	0.0846	0.1598	0.1598	0.529
1000	1.820	0.105	0.253	0.253	0.200	1.700	0.0991	0.233	0.233	0.426	1.600	0.0940	0.1998	0.1998	0.475
- Tr = 1.10 -															
100	0.182	0.00936	0.0098	0.0098	0.966	0.170	0.00909	0.00946	0.00946	0.960	0.160	0.00675	0.00901	0.00901	0.971
200	0.364	0.0187	0.0205	0.0205	0.920	0.340	0.01818	0.0196	0.0196	0.927	0.320	0.0175	0.0187	0.0187	0.936
300	0.546	0.0281	0.0318	0.0318	0.880	0.510	0.02727	0.0305	0.0305	0.901	0.480	0.02625	0.0288	0.0288	0.912
400	0.728	0.0374	0.0440	0.0440	0.85	0.680	0.03636	0.0425	0.0425	0.855	0.640	0.0350	0.0398	0.0398	0.890
500	0.910	0.0468	0.0580	0.0580	0.807	0.850	0.04545	0.0554	0.0554	0.820	0.800	0.0438	0.0515	0.0515	0.852
600	1.092	0.0561	0.073	0.073	0.768	1.020	0.05454	0.0714	0.0714	0.765	0.960	0.0525	0.0646	0.0646	0.812
700	1.274	0.0655	0.108	0.108	0.695	1.190	0.06363	0.0866	0.0866	0.735	1.120	0.06125	0.0791	0.0791	0.775
800	1.456	0.0749	0.148	0.148	0.619	1.360	0.07272	0.104	0.104	0.698	1.280	0.0700	0.0952	0.0952	0.735
900	1.638	0.0842	0.193	0.193	0.500	1.530	0.08181	0.124	0.124	0.657	1.440	0.07875	0.113	0.113	0.697
1000	1.820	0.0935	0.238	0.238	0.419	1.700	0.0909	0.147	0.147	0.619	1.600	0.0875	0.133	0.133	0.656
- Tr = 1.20 -															

T A B L E VI
(Continued)
COMPRESSIBILITY FACTORS (Z) OF THE ETHYLENE-BUTANE SYSTEM

Press. psia	66.18 Mol % Ethylene				80.88 Mol % Ethylene			
	Pseudo- Reduc. Press.	Density Ideal	Density Actual	Z	Pseudo- Reduc. Press.	Density Ideal	Density Actual	Z
				Tr = 1.10				
100	0.149	0.00870	0.00905	0.96	0.143	0.0082	0.00845	0.970
200	0.298	0.0174	0.0191	0.915	0.286	0.0164	0.0177	0.925
300	0.447	0.0261	0.0294	0.885	0.429	0.0246	0.0278	0.885
400	0.596	0.0348	0.0408	0.852	0.572	0.0328	0.0390	0.842
500	0.745	0.0435	0.0555	0.785	0.715	0.0410	0.0532	0.775
600	0.894	0.0522	0.0720	0.725	0.858	0.0492	0.0682	0.721
700	1.043	0.0609	0.0935	0.651	1.000	0.0574	0.0895	0.645
800	1.192	0.0696	0.116	0.60	1.143	0.0656	0.0113	0.581
900	1.341	0.0783	0.142	0.55	1.286	0.0738	0.136	0.542
1000	1.490	0.0870	0.172	0.505	1.430	0.082	0.163	0.502
				Tr = 1.20				
100	0.149	0.00798	0.0082	0.974	0.143	0.00753	0.00770	0.975
200	0.298	0.0159	0.0169	0.941	0.286	0.01506	0.0160	0.942
300	0.447	0.0239	0.0261	0.815	0.429	0.0226	0.0246	0.919
400	0.596	0.0319	0.0363	0.879	0.572	0.0301	0.0358	0.890
500	0.745	0.0399	0.0475	0.840	0.715	0.03765	0.0440	0.855
600	0.894	0.0479	0.0591	0.81	0.858	0.0452	0.0555	0.814
700	1.043	0.0559	0.0725	0.771	1.00	0.0527	0.0675	0.780
800	1.192	0.0639	0.0870	0.735	1.143	0.0603	0.0801	0.753
900	1.341	0.0718	0.102	0.705	1.286	0.0678	0.094	0.721
1000	1.490	0.0798	0.117	0.684	1.430	0.0753	0.110	0.685

T A B L E VI
PSEUDO-CRITICAL CONSTANTS

<u>Mol % Ethylene</u>	<u>Pseudo- Critical Pressure psia</u>	<u>Pseudo- Critical Temp. °F</u>	<u>Temperature at</u>	
			<u>Tr = 1.10</u>	<u>Tr = 1.20</u>
0	550.1	306.0	382.6	459.2
19.85	587	255.4	326.5	398.1
40.78	625	201.7	268.2	334.4
66.18	673	136.3	196.4	256.0
80.88	700	98.6	154.7	210.5
100	736	49.1	100.0	150.9

T A B L E VII

ETHYLENE-n-BUTANE SYSTEMActual Measurements of Pressures, Temperatures
and Densities at the Phase Boundaries

19.35 Mol % Ethylene

<u>Pressure</u> <u>psia</u>	<u>Temp.</u> <u>°F</u>	<u>Density</u> <u>gms/cc</u>	<u>Pressure</u> <u>psia</u>	<u>Temp.</u> <u>°F</u>	<u>Density</u> <u>gms/cc</u>
57.1	85.22	0.00882	755.5	265.12	0.2707
81.5	108.74	0.01185	756.1	264.24	0.2752
87.3	113.70	0.01251	756.5	262.79	0.2881
124.2	138.57	0.01726	754.6	261.31	0.2994
163.5	158.62	0.02231	754.3	262.06	0.2940
221.0	182.65	0.03079	754.0	260.02	
223.3	184.07	0.03137	753.6	260.04	0.3056
249.5	193.20	0.03526	748.5	258.24	0.3148
274.1	201.73	0.04003	751.4	257.20	0.3207
279.2	202.94		742.2	254.28	0.3339
282.5	202.90		741.5	253.42	0.3392
282.7	204.79	0.04243	741.4	251.02	0.3504
318.1	215.55	0.04936	738.5	250.25	0.3477
363.2	230.63	0.06142	720.1	244.22	0.3632
398.5	235.84	0.06603	701.8	240.26	0.3713
450.7	246.21	0.07795	690.7	235.68	0.3785
510.2	257.20	0.09442	658.3	226.62	0.3937
557.6	264.33	0.1102	635.1	219.27	0.4047
627.3	270.55	0.1437	609.2	212.04	0.4154
657.0	271.95	0.1619	578.8	202.53	0.4278
680.2	272.54	0.1782	545.0	192.78	0.4392
703.5	272.47	0.1905	518.1	183.71	0.4490
716.3	272.10	0.1967	513.2	183.07	0.4586
725.2	271.26	0.2120	505.3	182.26	0.4587
730.5	270.63	0.2168	412.7	159.17	0.4712
735.5	270.01	0.2258	416.2	159.32	
740	269.23	0.2328	414.3	157.05	
744	268.61	0.2392	381.4	146.54	0.4816
748.5	267.59	0.2477	338.7	131.25	0.4947
751.9	267.02	0.2529	340.9	131.18	
*752.8	266.51	0.2564	316.2	119.53	0.5046
752.6	266.52	0.2572	281.0	108.67	0.5132
754.5	266.03	0.2605	220.9	84.80	0.5301

T A B L E V I I
(Continued)
ETHYLENE-n-BUTANE SYSTEM

Actual Measurements of Pressures, Temperatures
and Densities at the Phase Boundaries

40.78 Mol % Ethylene

<u>Pressure</u> <u>psia</u>	<u>Temp.</u> <u>°F</u>	<u>Density</u> <u>gms/cc</u>	<u>Pressure</u> <u>psia</u>	<u>Temp.</u> <u>°F</u>	<u>Density</u> <u>gms/cc</u>
63.4	76.21	0.00885	885.2	225.72	0.2558
108.5	107.61	0.01352	887.2	225.08	0.2597
110.3	114.52	0.01491	* 889.3	224.47	0.2617
144.9	129.05	0.01814	884.2	222.67	
154.1	130.22	0.01856	897.7	221.23	
197.3	152.10	0.02497	881.9	226.39	
217.3	159.67	0.02760	888.7	224.37	0.2675
278.2	178.74	0.03602	891.1	223.49	0.2667
355.0	194.23	0.04490	895.3	221.72	0.2763
347.2	194.55	0.04507	896.5	220.73	0.2758
557.6	196.76	0.04680	898.7	220.71	0.2776
361.2	197.51		900.3	219.74	0.2849
366.1	197.41		906.2	218.52	0.2892
393.4	203.19	0.05213	907.5	217.01	0.2948
396.6	202.27		906.0	215.69	0.3009
431.1	209.48	0.05827	908.4	214.58	0.3042
522.3	220.92	0.07491	909.5	212.24	0.3121
540.5	223.17	0.07945	907.5	210.31	0.3178
609.6	228.7		905.5	208.50	0.3243
601.2	228.72	0.09556	890.2	203.73	0.3345
633.3	230.41	0.1036	893.1	202.19	0.3426
683.5	233.04	0.1279	878.5	196.32	0.3567
699.1	233.27	0.1364	870.7	194.75	
704.5	234.02	0.1408	856.2	190.62	0.3705
726.0	234.66	0.1551	823.4	182.21	0.3869
792.8	233.98		810.1	173.78	
789.9	234.09	0.1982	783.8	172.92	0.4016
683.1	233.04		722.4	159.36	0.4197
698.8	233.31		686.5	152.20	0.4277
704.5	234.03		627.3	140.55	0.4401
792.8	233.95		547.7	124.24	0.4548
798.6	234.17	0.1982	504.5	114.46	0.4622
815.0	233.20	0.2079	500.2	113.61	0.4641
856.2	230.21	0.2315	472.3	107.51	0.4695
868.6	228.68	0.2412	412.5	92.03	0.4811
875.5	227.66	0.2469	353.2	78.19	0.4910

T A B L E V I I
(Continued)
ETHYLENE-n-BUTANE SYSTEM

Actual Measurements of Pressures, Temperatures
and Densities at the Phase Boundaries

66.18 Mol % Ethylene

<u>Pressure</u> <u>psia</u>	<u>Temp.</u> <u>°F</u>	<u>Density</u> <u>gms/cc</u>	<u>Pressure</u> <u>psia</u>	<u>Temp.</u> <u>°F</u>	<u>Density</u> <u>gms/cc</u>
101	77.3	0.01285	968	179.17	0.2152
121	88		968.4	177.24	0.2238
121	87		969.5	176.42	0.2275
124	89.0		971	175.27	0.2328
132	92.2	0.01953	974.5	172.86	0.2402
185	113.8	0.02162	973	172.81	0.2405
225	124.38		973	171.32	0.2446
217	124.38	0.02558	973	170.01	0.2508
251	133.86	0.02901	973	168.24	0.2517
285	140.72	0.0322	973.5	170.55	
363	155.70	0.04081	973.5	169.04	
413	164.35	0.04656	* 973.5	169.02	0.2541
432	167.02	0.04926	973	168.6	
526.3	179.15	0.06453	972	167.03	0.2598
589	184.39	0.07726	970	165.17	0.2672
680	188.12	0.09688	970	164.39	0.2703
699	188.57	0.1006	967.3	162.11	0.2777
728	188.43		965.5	160.72	0.2820
782	189.61	0.1187	963	158.65	0.2885
802.5	189.54	0.1241	952.1	155.60	0.2971
845	189.53	0.1335	941.6	152.48	0.3059
887	189.43	0.1514	909.2	142.31	0.3324
902	189.20	0.1557	862.4	132.73	0.3560
928	188.23	0.1615	849.1	129.47	0.3627
934.5	187.29	0.1764	815.2	123.62	0.3745
950	185.08	0.1890	732.0	107.34	0.3989
958	182.51	0.2011	684.8	97.87	0.4108
960	181.33	0.2063	639.1	89.41	0.4211
964	178.06	0.2197	575.6	77.42	0.4346
967	178.31	0.2185			

T A B L E VII
(Continued)
ETHYLENE-n-BUTANE SYSTEM

Actual Measurements of Pressures, Temperatures
and Densities at the Phase Boundaries

80.88 Mol % Ethylene

<u>Pressure</u> <u>psia</u>	<u>Temp.</u> <u>°F</u>	<u>Density</u> <u>gms/cc</u>	<u>Pressure</u> <u>psia</u>	<u>Temp.</u> <u>°F</u>	<u>Density</u> <u>gms/cc</u>
128.3	51.86	0.01302	947.2	137.58	0.1908
132.2	52.71	-	942.8	137.03	0.19501
153.9	60.27	0.01538	948.7	135.46	0.2001
214.0	79.32	0.02290	950.3	134.34	0.2047
238.1	85.69	0.02516	951.5	132.83	0.2115
305.8	100.81	0.03487	951.5	131.21	0.2179
343.7	107.66	0.03871	949.5	129.01	0.2271
418.5	119.32	0.04827	945	128.88	0.2296
418.9	117.60	0.04743	949.2	128.29	0.2314
421.3	121.86	0.05162	947.5	127.29	0.2359
461.8	125.25	0.05488	944	126.12	0.2396
550.2	134.18	0.06995	* 945.7	125.97	0.2429
626.7	140.62	0.08193	945	125.19	0.2468
648.1	141.37	0.09614	943.5	124.65	0.2492
645.6	142.28	0.1008	940.5	122.80	0.2589
686.7	144.23	0.1123	923.8	117.51	0.2820
714.8	145.09	0.1182	875.5	107.85	0.3146
816.4	147.44	0.1352	822	99.24	0.3325
876.1	147.12	0.1387	741.0	85.71	0.3623
878.7	147.09	0.1443	706.8	79.45	0.3741
905.2	145.69	0.1549	597.3	60.14	0.3913
913.2	145.33	0.1575	553.6	52.75	
920.0	144.16	0.1620	550.2	51.07	
926.6	143.30	0.1701	552.7	52.02	
933.2	142.98	0.1725	545.8	51.95	0.4043
941.1	140.66	0.1814	947	126.52	
944.5	139.02	0.1862	937	121.83	

T A B L E VIII

ETHYLENE-2-BUTANE SYSTEM

Actual Measurements of Pressures and Densities
for Various Isotherms in the Superheated Vapor Region

19.85 Mol % Ethylene

151.6°F				162.1°F				188.4°F				235.0°F			
Temp. °F	Press. psia	Density gms/cc	Temp. °F	Press. psia	Density gms/cc	Temp. °F	Press. psia	Density gms/cc	Temp. °F	Press. psia	Density gms/cc	Temp. °F	Press. psia	Density gms/cc	
151.64	97.5	0.01581	162.12	101.8	0.01355	188.38	103.4	0.01302	234.97	103.5	0.01214	234.97	124.6	0.01436	
151.60	102.1	0.01455	162.10	111.7	0.01476	188.38	123.3	0.01550	234.97	124.6	0.01436	234.97	142.0	0.01668	
			162.10	132.5	0.01772	188.41	154.5	0.01965	234.96	142.0	0.01668				
			162.06	146.0	0.01946	188.40	188.3	0.02315							
						188.40	197.4	0.02622							

274.2°F				352.0°F				395.8°F						
Temp. °F	Press. psia	Density gms/cc	Temp. °F	Press. psia	Density gms/cc	Temp. °F	Press. psia	Density gms/cc	Temp. °F	Press. psia	Density gms/cc	Temp. °F	Press. psia	Density gms/cc
274.17	96.8	0.01056	352.03	103.7	0.01047	395.83	116.8	0.01115	395.83	137.8	0.01328	395.83	177.9	0.01736
274.17	158.5	0.01513	352.01	144.1	0.01443	395.83	157.8	0.01528	395.83	177.9	0.01736	395.83	259.0	0.02607
274.19	187.1	0.02147	352.00	178.1	0.01819	395.83	213.2	0.02257	395.83	259.0	0.02607	395.83	344.5	0.03624
274.19	244.3	0.02951	352.01	223.1	0.02470	395.83	282.4	0.03068	395.82	344.5	0.03624	395.83	420.3	0.04533
274.18	302.6	0.03874	352.00	294.2	0.03407	395.82	372.0	0.04273	395.82	420.3	0.04533	395.83	492.8	0.05461
274.17	382.8	0.05341	352.01	373.2	0.04602	395.81	406.7	0.04759	395.81	589.9	0.06891	395.82	589.9	0.06891
274.17	487.0	0.07935	352.01	437.4	0.05654	395.81	471.6	0.05775	395.83	684.5	0.08462	395.81	684.5	0.08462
274.17	541.7	0.09748	352.00	527.8	0.07448	395.79	539.1	0.06971	395.79	789.0	0.1030	395.79	789.0	0.1030
274.18	588.5	0.1172	352.00	605.6	0.09275	395.82	613.2	0.08281	395.82	913.5	0.1286	395.82	913.5	0.1286
274.18	646.9	0.1452	352.01	661.8	0.1094	395.81	695.3	0.1006	395.81	990.6	0.1469	395.81	990.6	0.1469
274.18	665.2	0.1746	352.01	707.0	0.1265	395.83	783.2	0.1242	395.83			395.83		
274.20	787.2	0.2355	352.02	809.7	0.16651	395.82	847.0	0.1441	395.82			395.82		
274.21	886.0	0.2978	352.01	894.2	0.2028	395.81	906.5	0.1628	395.81			395.81		
274.21	971.3	0.3540	352.03	950.1	0.2309	395.81	982.8	0.1822	395.81			395.81		

T A B L E VIII
(Continued)

ETHYLENE-n-BUTANE SYSTEM

Actual Measurements of Pressures and Densities
for Various Isotherms in the Superheated Vapor Region

40.78 Mol % Ethylene

128.8°F				136.1°F				174.3°F				189.9°F			
Temp. °F	Press. psia	Density gms/cc	Temp. °F	Press. psia	Density gms/cc	Temp. °F	Press. psia	Density gms/cc	Temp. °F	Press. psia	Density gms/cc	Temp. °F	Press. psia	Density gms/cc	
127.95	101.0	0.01198	136.14	105.8	0.01243	174.28	106.0	0.01176	189.92	104.5	0.01118	189.91	141.2	0.01565	
127.99	122.6	0.01465	136.14	139.8	0.01680	174.33	134.7	0.01558	189.91	141.2	0.01565	189.91	190.3	0.02205	
						174.32	224.4	0.02741	189.89	265.6	0.03296				
240.5°F				302.6°F				357.4°F				396.0°F			
Temp. °F	Press. psia	Density gms/cc	Temp. °F	Press. psia	Density gms/cc	Temp. °F	Press. psia	Density gms/cc	Temp. °F	Press. psia	Density gms/cc	Temp. °F	Press. psia	Density gms/cc	
239.48	101.3	0.01015	302.56	101.3	0.00954	357.43	111.3	0.00966	395.97	104.5	0.00871	395.97	153.6	0.01268	
239.48	142.1	0.01473	302.57	142.4	0.01354	357.43	152.7	0.01339	395.97	153.6	0.01268	395.98	174.3	0.01438	
239.47	174.8	0.01844	302.56	173.0	0.01651	357.42	195.6	0.01746	395.98	174.3	0.01438	395.99	207.9	0.01758	
239.47	246.1	0.02751	302.60	200.8	0.01946	357.43	294.1	0.02735	395.98	207.9	0.01758	395.99	292.5	0.02561	
239.46	297.0	0.03436	302.61	250.3	0.02001	357.41	406.0	0.03946	396.02	292.5	0.02561	396.01	347.9	0.03099	
239.44	384.8	0.04728	302.58	306.4	0.03126	357.43	496.8	0.04967	396.01	347.9	0.03099	396.01	413.5	0.03775	
239.47	411.5	0.05148	302.60	404.7	0.04372	357.40	693.7	0.07356	395.98	494.9	0.04608	395.98	494.9	0.04608	
239.48	493.5	0.06551	302.60	475.3	0.05318	357.43	752.6	0.08179	395.99	551.3	0.05204	395.99	551.3	0.05204	
239.49	602.0	0.08941	302.60	586.5	0.06867	357.43	805.5	0.08942	396.02	616.8	0.05923	396.02	616.8	0.05923	
239.47	655.8	0.1060	302.60	714.1	0.08851	357.43	906.0	0.1049	396.00	695.4	0.06847	396.00	695.4	0.06847	
239.46	706.2	0.1265	302.60	807.1	0.1063	357.43	999.1	0.1211	396.02	811.0	0.08332	396.02	811.0	0.08332	
239.48	804.0	0.1694	302.61	891.7	0.1252	357.43			396.02	848.2	0.08816	396.02	848.2	0.08816	
239.48	905.0	0.2038	302.59	1002.5	0.1516				395.97	902.2	0.09577	395.97	902.2	0.09577	
									395.01	973.6	0.1056	395.01	973.6	0.1056	

T A B L E VIII
(Continued)
ETHYLENE-n-BUTANE SYSTEM

Actual Measurements of Pressures and Densities
for Various Isotherms in the Superheated Vapor Region

66.18 Mol % Ethylene

Temp. °F	103.4°F			121.8°F			157.6°F			182.0°F		
	Press. psia	Density gms/cc	Temp. °F	Press. psia	Density gms/cc	Temp. °F	Press. psia	Density gms/cc	Temp. °F	Press. psia	Density gms/cc	
103.38	102.9	0.01224	121.82	101.3	0.01157	157.62	109.0	0.01125	181.96	97.4	0.00936	
103.38	113.5	0.01461	121.83	120.3	0.01342	157.62	122.6	0.01273	181.96	103.6	0.01082	
			121.82	149.8	0.01689	157.63	163.8	0.01683	181.96	158.2	0.01327	
						157.62	104.3	0.02139	181.96	194.9	0.01931	
						157.62	257.3	0.02741	181.95	126.7	0.02248	
						157.62	296.1	0.03197	181.97	194.5	0.02981	
									181.96	348.4	0.03585	
									181.96	439.9	0.04752	
									181.96	446.0	0.04870	

Temp. °F	213.0°F			261.0°F			342.5°F			395.2°F		
	Press. psia	Density gms/cc	Temp. °F	Press. psia	Density gms/cc	Temp. °F	Press. psia	Density gms/cc	Temp. °F	Press. psia	Density gms/cc	
212.97	108.1	0.00978	261.04	129.4	0.01096	342.47	150.3	0.01093	395.20	162.0	0.01108	
212.98	126.5	0.01102	261.04	174.0	0.01432	342.47	194.4	0.01437	395.21	212.3	0.01472	
212.98	148.4	0.01319	261.04	255.9	0.02165	342.44	221.6	0.01643	395.21	247.0	0.01706	
212.98	202.2	0.01855	261.05	353.9	0.03113	342.46	290.2	0.02195	395.23	247.0	0.01709	
212.99	286.7	0.02732	261.03	446.7	0.04081	342.46	352.4	0.02691	395.20	343.6	0.02425	
212.98	354.3	0.03482	261.03	537.0	0.05075	342.47	380.5	0.02920	395.20	460.3	0.03321	
212.98	433.1	0.04445	261.03	622.6	0.06101	352.48	473.2	0.03715	395.22	521.0	0.03811	
212.96	525.3	0.05689	261.03	726.2	0.07448				395.21	587.2	0.04344	
212.96	651.0	0.07309	261.04	817.1	0.08745	342.47	573.7	0.04643	395.22	687.6	0.05178	
	723.6	0.08904	261.02	935.8	0.10418	342.50	676.3	0.05596	395.21			
	792.6	0.10275	261.02			342.51	700.4	0.05843	395.21			
	856.3	0.11609				342.47	788.7	0.06706	395.21	789.1	0.06302	
	888.3	0.12333							395.20	853.5	0.06628	
	928.9	0.1348				342.47	923.0	0.08105	395.21	931.7	0.07314	

T A B L E VIII

(Continued)

ETHYLENE-r-BUTANE SYSTEM

Actual Measurements of Pressures and Densities
for Various Isotherms in the Superheated Vapor Region

80.88 Mol % Ethylene

51.9°F		79.2°F		117.5°F		129.6°F	
Temp. °F	Density gms/cc	Temp. °F	Density gms/cc	Temp. °F	Density gms/cc	Temp. °F	Density gms/cc
51.86	0.00989	79.17	0.00950	117.51	0.00933	129.63	0.02763
51.86	0.01136	79.16	0.01228	117.51	0.01790	129.63	0.03972
51.86	0.01194	79.18	0.01508	117.52	0.02273	129.63	0.05053
		79.15	0.01772	117.52	0.03047	129.63	0.05618
				117.52	0.03742	129.63	0.05924
				117.50	0.04003		
				117.51	0.04568		
				117.50	0.04743		

141.4°F		152.3°F		191.6°F		225.0°F	
Temp. °F	Density gms/cc	Temp. °F	Density gms/cc	Temp. °F	Density gms/cc	Temp. °F	Density gms/cc
141.34	0.00950	152.30	0.00918	191.62	0.00944	225.00	0.00937
141.40	0.01753	152.30	0.01152	191.62	0.01235	225.02	0.01437
141.40	0.02877						
141.40	0.04275	152.31	0.01763	191.62	0.01299	225.01	0.03805
141.39	0.06509	152.31	0.02229				
141.39	0.07449	152.31	0.02415	191.60	0.02366	225.00	0.07722
		152.31	0.03276	191.61	0.02364	225.00	0.08796
		152.29	0.03864	191.62	0.03059		
		152.30	0.03931	191.61	0.03856		
		152.30	0.05084	191.61	0.04650		
		152.30	0.06103				
		152.30	0.06757	191.61	0.05456		
		152.30	0.08952	191.62	0.06698		
		152.30	0.1023				
		152.32	0.1182	191.64	0.08150		
		152.30	0.1402				
		152.32	0.1521				
				191.65	0.09455		
				191.62	0.11056		
				191.62	0.11745		

T A B L E VIII
(Continued)
ETHYLENE-N-BUTANE SYSTEM

Actual Measurements of Pressures and Densities
for Various Isotherms in the Superheated Vapor Region

80.88 Mol % Ethylene

261.6°F				235.5°F				387.20°F			
Temp. OF	Press. psia	Density gms/cc		Temp. OF	Press. psia	Density gms/cc		Temp. OF	Press. psia	Density gms/cc	
261.58	132.1	0.00941		335.55	147.9	0.00942		387.22	157.3	0.00949	
261.57	174.4	0.01255		335.50	192.7	0.01250		387.23	249.3	0.01288	
261.57	239.4	0.01755		335.50	280.3	0.01840		387.24	300.5	0.01844	
261.57	294.9	0.02195		335.50	322.5	0.02152		387.20	357.9	0.02221	
261.57	353.9	0.02668		335.50	375.5	0.02515		387.20	476.9	0.03002	
261.57	396.3	0.03029		335.51	463.6	0.03179		387.20	517.9	0.03295	
261.58	504.7	0.03982		335.51	478.6	0.03267		387.20	647.2	0.04176	
261.60	565.7	0.04537		335.50	478.6	0.0326		387.20	784.9	0.05118	
261.61	644.3	0.05273		335.53	587.5	0.04092		387.20	927.5	0.06201	
261.59	746.9	0.06302		335.52	706.4	0.05001					
261.59	831.7	0.07182		335.49	814.0	0.05818					
261.59	933.2	0.08279		335.50	933.5	0.06890					

T A B L E IX

ETHYLENE-n-BUTANE SYSTEM

Actual Measurements of Temperatures, Pressures
and Densities in the Liquid and Critical Regions

19.65 Mol % Ethylene			40.78 Mol % Ethylene		
<u>Temp.</u> <u>°F</u>	<u>Pressure</u> <u>psia</u>	<u>Density</u> <u>gms/cc</u>	<u>Temp.</u> <u>°F</u>	<u>Pressure</u> <u>psia</u>	<u>Density</u> <u>gms/cc</u>
84.88	431.3	0.5321	72.04	408.2	0.4972
84.88	605.0	0.5357	72.04	624.7	0.5008
84.88	761.5	0.5395	72.04	755.1	0.5029
84.88	864.1	0.5432	72.06	891.9	0.5059
84.88	977	0.5455	72.04	988.4	0.5071
118.92	316.3	0.5056	140.20	695.4	0.4431
118.92	409.2	0.5068	140.21	780.2	0.4465
118.92	486.9	0.5097	140.20	856.3	0.4480
118.92	656.6	0.5122	140.20	981	0.4523
118.92	808.2	0.5145			
118.92	930.3	0.5182	190.64	875.2	0.3744
			190.62	910.7	0.3785
159.38	453.0	0.4728	190.62	963	0.3840
159.38	512.7	0.4796	190.63	1003	0.3921
159.38	625.0	0.4776			
159.37	798.0	0.4823	202.78	895.5	0.3418
159.37	934.1	0.4862	202.78	951	0.3586
			202.79	995	0.3755
202.55	602.4	0.4276	203.11	990	0.3742
202.70	736.0	0.4407			
202.70	840.7	0.4492	208.55	987.5	0.3325
202.70	925.5	0.4563	208.55	963	0.3397
			208.55	1015	0.3595
266.51	775.8	0.2751			
266.51	837.1	0.2965	215.87	945	0.3187
266.51	930.9	0.3348	215.87	967	0.3301
266.50	980	0.3682	215.87	985	0.3324
266.51	1012	0.3774	215.88	991	0.3345

T A B L E IX
(Continued)
ETHYLENE-n-BUTANE SYSTEM

Actual Measurements of Temperatures, Pressures
and Densities in the Liquid and Critical Regions

66.18 Mol % Ethylene			80.88 Mol % Ethylene		
<u>Temp.</u> <u>°F</u>	<u>Pressure</u> <u>psia</u>	<u>Density</u> <u>gms/cc</u>	<u>Temp.</u> <u>°F</u>	<u>Pressure</u> <u>psia</u>	<u>Density</u> <u>gms/cc</u>
71.70	595.9	0.4362	51.86	614.6	0.4142
71.70	660.9	0.4365	51.86	698.5	0.4157
77.68	720.5	0.4386	51.86	870.3	0.4168
77.58	813.8	0.4436	51.86	924.6	0.4193
77.58	874.5	0.4454			
			79.70	753.0	0.3723
123.62	819.3	0.3750	79.66	800.4	0.3781
125.78	942.7	0.3750	79.66	865.3	0.3813
130.86	892.1	0.3643	79.66	930.9	0.3895
			79.67	1007	0.3972
145.07	913.4	0.3251			
145.08	936.7	0.3288	117.51	958	0.2824
145.07	991	0.3385	117.50	965	0.2847
			117.50	981	0.2875
163.21	979	0.2784	117.50	998	0.2926
163.22	994	0.2863			
			122.84	949	0.2625
			122.84	976	0.2702
			122.84	979	0.2751
			122.84	996	0.2794
			134.34	957.5	0.2098
			134.35	969	0.2162
			134.35	983	0.2187
			134.35	996	0.2285

T A B L E X

CALIBRATION OF HIGH PRESSURE TUBE

Distance from End of Tube to Top of Meniscus-cm	Volume of Mercury in Tube-cm ³	Distance from End of Tube to Top of Meniscus-cm	Volume of Mercury in Tube-cm ³	Distance from End of Tube to Top of Meniscus-cm	Volume of Mercury in Tube-cm ³
1.765	0.05497	1.145	0.01636	2.547	0.057854
2.195	.04806	1.964	.04080	5.094	.073668
2.912	.06860	2.681	.06158	4.158	.104257
3.574	.08791	3.641	.08971		
3.858	.09496	4.355	0.10983	2.071	.0437940
4.544	0.10955	5.258	.13647		
5.505	.14388			5.073	0.131382
6.524	.172866	1.474	0.026139		
8.010	.215808	1.770	.034988		
9.001	.244822	1.642	.051174		
11.369	.31476	1.709	.053187		
13.204	.36816				
14.814	.41451	1.577	0.029221		
16.098	.45399	1.938	.039500		
17.835	.50471	2.617	.059692		
18.952	.53691	3.216	.0772625		
20.590	.58476	4.836	0.124615		
22.812	.65010	5.375	.140151		
23.537	.67135	6.205	.164220		
26.717	.76479	7.164	.191889		
29.860	.85568	12.232	.3404111		
32.669	.93885	13.875	0.387461		
35.533	1.02510	15.440	0.435746		
38.484	1.11079	21.582	0.608406		
42.010	1.214200	28.774	0.824692		
45.645	1.32240	36.310	1.046497		
49.539	1.43609	43.664	1.284083		
52.619	1.52709	48.937	1.448168		
		52.107	1.511749		

Volume in tube to point = Volume
of Mercury plus blank volume around
Meniscus

Blank volume = 0.000237 ± 0.00005