

THE PHASE BEHAVIOR OF THE METHANE-PROPANE-PENTANE SYSTEM

Thesis by
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Abstract

The compositions of the coexisting phases in the methane-n-pentane system for a pressure range from atmospheric to 2500 pounds per square inch at temperatures of 100°F., 160°F. and 220°F. were studied. Coupling these determinations with data from other sources, gas-liquid equilibrium constants of methane and pentane as well as dew point specific volumes were calculated.

The composition of coexisting phases in the methane, propane n-pentane system for a temperature of 100°F. and pressures of 200, 500, 1000, 1500, 2000 pounds per square inch in a range of ratios of propane to n-pentane from 0.05 to 1 was studied. From these data, values for the equilibrium constants of methane, propane and pentane were calculated.

Introduction

Since the vaporization of hydrocarbons occurs at all stages of crude oil production, a knowledge of vaporization characteristics of hydrocarbon mixtures is of particular interest in petroleum production and processing. The application of the equilibrium constants proposed by Souders, Selheimer and Brown to vaporization characteristics has been found to be the most suitable. By definition, the gas-liquid equilibrium constant is the ratio of the mole fraction of a component in the gas phase to its mole fraction in the coexisting liquid phase; mathematically expressed as $K = \frac{Y}{X}$ where K is the equilibrium constant, Y is the mole fraction of the component of the gas phase, X is the mole fraction of the component in the liquid phase. It can be seen from the above definition that when given a knowledge of the composition of one phase and the value of K, the composition of the other phase may be calculated directly.

The first consideration of equilibrium constants by Souders, Selheimer and Brown⁽¹⁾ and by Katz and Brown⁽³⁾ was theoretical in nature being based mainly on the assumption of ideal solutions. With the development of accurate methods for the analysis of hydrocarbon mixtures - notably by use of a low-temperature, low-pressure fractionating column devised by Podbielniak⁽²⁾ - a simple procedure for an experimental study of equilibrium constants was available. The first to carry out an investigation of this nature were Katz and Hachmuth⁽⁴⁾. They determined the equilibrium constants for hydrocarbons of the paraffin series through hexane for a crude oil-natural gas mixture at temperatures from 40°F. to 200°F. and at pressures from atmospheric

to above 3000 pounds per square inch. They found that the values of K decreased for all components but methane, as the pressure was increased to about 600 pounds and then rose again as the pressure was further increased. The equilibrium constant for methane decreased continually as pressure increased.

Since then Boomer and associates have published a series of papers on the solubility of methane containing about 67% nitrogen in various hydrocarbons (7,8,9,10). The values for equilibrium constants exhibited in their work are in reasonable agreement with the values determined by Katz and Hachmuth⁽⁴⁾ in the lower pressure regions. Due to the lower critical pressures of the system studied by Boomer and associates, the values of Boomer's equilibrium constants approach unity at a lower pressure

The purpose of the present work was to add to the meager data on equilibrium constants by a systematic study of the following systems:

- 1) The methane-pentane system,
- 2) The methane-propane-pentane system.

The following measurements were completed:

In the methane-pentane system data were obtained at 100°F., 160°F., 220°F. from atmospheric pressure to 2500 pounds per square inch.

In the methane-propane-pentane system, two propane to pentane ratios were studied with varying proportions of methane at 100°F. and 200, 500, 1000, 1500, 2000 pounds per square inch.

Equilibrium Apparatus

The apparatus used to obtain the equilibrium samples of gas and liquid consisted first of the equilibrium cell A shown in Figure 1; second, a high pressure source of mercury B; third, a gas injection chamber K; and finally, a pressure balance D connected to the equilibrium cell through a pressure trap C.

Referring to the figure, the equilibrium cell, whose content was approximately 1 liter, was equipped with a stirrer which was introduced through packing gland and supporting shaft G and was belt-driven by an electric motor. Electrical contacts E and F were connected to two six volt lights and were used to follow approximately the mercury level. Two 2-mil. nickel wires V and W, about two centimeters long were provided to aid in controlling the position of the hydrocarbon liquid level. The wires were connected into a wheatstone bridge circuit. Since the rate of heat dissemination from a wire in the liquid phase is greater than from a wire in the gas phase, the introduction of a small current in the circuit raises the temperature of a wire in a gas phase more than one in the liquid phase. Therefore when the liquid envelopes the lower wire the temperature of the wire drops resulting in a decrease in its resistance. This change in resistance is measured by the wheatstone bridge. The detection of the liquid phase by this means was adequate at low pressures, but ^{of} no value in the neighborhood of the critical region. To be sure that the liquid level was sufficiently high in the high pressure region, the approximate volume of the liquid phase, and the position of the mercury level were used.

The pressure existing in this cell was measured by a fluid pressure balance which had a working range from atmospheric pressure to 3000 pounds per square inch. The absolute probable error in pressure measurements was approximately 1 pound per square inch. It was connected to the cell through the fluid pressure trap C. A correction was added to the balance reading to account for barometric pressure, and the mercury and oil "heads".

The temperature of the cell was maintained at a desired constant value by immersing it in an oil bath, equipped with a mercury regulator used in conjunction with a small heater. To help obtain and maintain temperature the following arrangement was used. A copper coil, through which steam or cold water could be passed, was immersed in the oil. This was provided in order to facilitate rapid heating of the bath. Two exterior heaters of 1800 and 500 watts respectively were used. The bath was insulated by one inch of 85% magnesia. The two heaters could be connected in series or in parallel, or each could be operated alone or in conjunction with internal resistances to obtain the desired energy input. The variation of temperature with time or with position in the cell was not over 0.2°F.

Pressure or volume changes within the portion of the cell occupied by the sample were obtained by injecting or withdrawing mercury through a 3/16 inch steel tube passing into the bottom of the cell.

Gas and liquid samples for analysis were removed through 1/8 inch steel lines R and Q (Figure 1) respectively, which led to the fractionation apparatus.

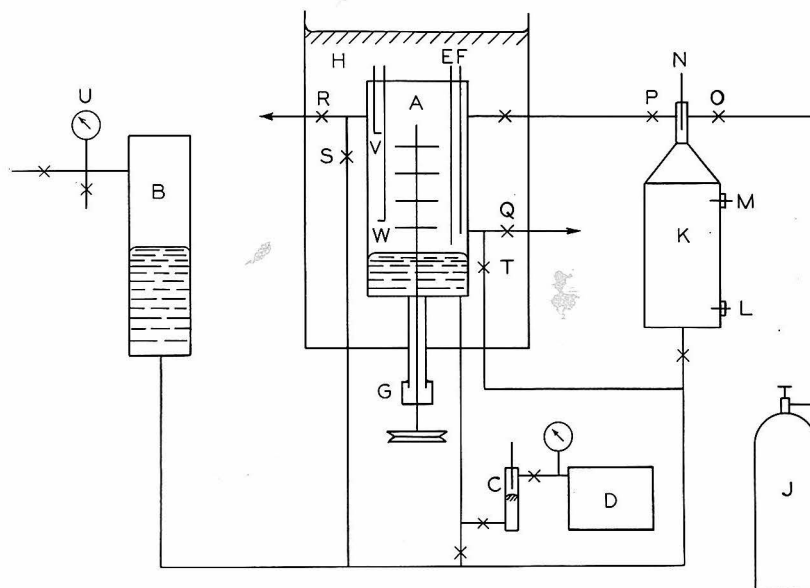


Fig. 1. Equilibrium Apparatus

Operation of the Equilibrium Cell

Liquid pentane was poured into the equilibrium cell directly. Then, after the top of the cell was replaced, a vacuum pump removed pentane vapor for a short time to sweep out all traces of air. Next propane or methane was added by the use of the gas injection chamber K. The material was allowed to enter K from storage cylinder J by withdrawing mercury from the bottom of chamber K, with valves O open and P closed. After closing valve O mercury was forced into the chamber until the pressure exceeded that in the equilibrium cell so that when valve P was opened, the gas flowed from the injection chamber into the equilibrium cell. The position of the mercury in the injection chamber was followed by contacts L, M and N which were connected to 6 volt lights. This process was repeated until the desired quantity of the component had been added.

The oil bath was next brought up to temperature. The temperature was measured by a copper-constantan thermocouple immersed in the oil; the thermocouple was calibrated by comparison with a set of Bureau of Standards thermometers. After adjusting the liquid level to the desired position, the sample was stirred until equilibrium was reached, as ascertained by constancy of pressure. In the three-component study, the final slight variation in pressure from the desired value was adjusted by addition of mercury. Upon the attainment of equilibrium the internal agitation was stopped and the samples withdrawn. During the removal of the samples the pressure in the cell was kept constant by allowing mercury to displace gas and liquid from the cell. The gas sample was throttled into the analytical

apparatus directly from a valve immersed in the oil bath. The liquid was throttled by a valve outside the oil bath but the liquid line was filled with mercury before and after the liquid sample was withdrawn.

Materials Used

The methane used contained 0.1 per cent carbon dioxide. In the analysis of the sample, this percentage of carbon dioxide was deducted in the calculation of composition. At a later period the methane was passed through sodium hydroxide, activated carbon, calcium chloride and ascarite to remove water and carbon dioxide. The pentane contained a small percentage of isopentane.

Analytical Apparatus

The equipment used for the analysis of the samples consisted of two low-pressure, low-temperature fractionating columns as developed by Podbielniak and associates⁽²⁾. The column used for the gas sample analysis was constructed from a 4 mm. pyrex glass tube 50 inches long which was enclosed in a silvered vacuum jacket. This tubing was bowed slightly to take care of differential contraction on cooling in the column. The only break in the silvering was for a small inspection window near the top of the column. To obtain maximum efficiency in column operation and to attain a large capacity with only a small hold-up of liquid, a flat helical strip of nichrome was found to be superior to the standard packings such as wire coils, glass beads, or other designs of glass packing.

Reflux was obtained by injecting liquid air into a small chamber

surrounding the top of the column. This chamber was an extension and enlargement of the vacuum jacket filled with fine copper turnings to promote heat transference from the condenser. The chamber was also equipped with a 50 watt. heater to facilitate the rapid warming of the condenser between the withdrawal of two different components. The top of the column was enlarged and closed with a ground-glass stopper. Passing through the ground-glass just at the top of the column was a sealed glass tube of small diameter which extended just below the condenser. The temperature of the refluxing liquid was ascertained by placing a thermocouple in this glass tube.

The column used for liquid sample analysis differed from the other column in size (the liquid column being a 36 inch length of 6 mm. pyrex tubing) and in the use of an unsilvered strip along the whole length of the column for a window. In order to facilitate the maintenance of reflux throughout the total length of the column, the column kettles were connected to the bottom of the vacuum jacket directly by the use of a ring seal, a part of the kettle being placed in the lower part of the vacuum jacket. The kettles were equipped with a sample inlet near the top and with a capillary tube at the bottom, which served as a means of cleaning the kettle and which would provide a means of removal of residual hydrocarbons in the analysis of more complex mixtures than are considered in this thesis.

Samples were throttled from the equilibrium cell into the analytical apparatus as described above. After passing through a mercury trap, the gas was allowed to flow through tubes of magnesium perchlorate to remove moisture and then into the column. Upon dis-

tillation, the separated gas constituents were collected in any one of a set of three receiving flasks, having capacities of 2000, 500 and 200 milliliters, respectively. These receiving flasks were placed in a water bath, the temperature of which was maintained at a constant value by the use of a mercury regulator and relay system. Mercury manometers were used to measure the pressures in the calibrated receiving flasks and to measure the pressure in the distillation column.

All parts of the apparatus including the column jackets were connected to a vacuum header. The vacua were then obtained by a mercury vapor pump in series with Hyvac pump.

Calibration of the Apparatus

The volume of a calibration flask of about 500 ml. capacity was determined by weighing it empty and filled with water. It was then sealed to the distribution header. By allowing gas to flow from the calibrated flask into various parts of the apparatus, and noting the consequent pressure changes and the temperatures, the volumes of the columns, the collecting flasks and the connecting tubing were calculated on the assumption of perfect gas behavior. The maximum difference in any one such measurement from the mean was only about 0.5%. With the use of four to six measurements the volumes were ascertained with a reasonable degree of accuracy.

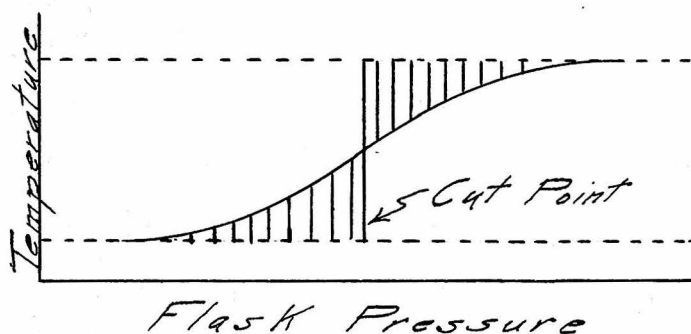
Operation of Fractionating Apparatus

After adequate evacuation of the column jacket, as well as all necessary parts of the apparatus, the sample was introduced into the column kettles. The gases were condensed in the kettle by the

use of liquid air. Samples varying between a minimum of about 10 ml. and a maximum of 50 ml. of condensed gases were used. Smaller samples than 10 ml. reduced the accuracy of the analysis. Larger samples than 50 ml. were inconvenient.

The top of the column was then cooled with liquid air to the reflux temperature of the most volatile constituent. The liquified sample was boiled by lowering the liquid air away from the kettle or, in the case of butane, pentane and higher hydrocarbons, by heating it with a small exterior electrical heater. It was found that the best distillation results could be obtained by the proper manipulation in applying energy to the kettle, cooling the top, and withdrawing gas to keep the reflux just wetting the packing the entire length of the column and giving a drop rate of one drop each 1-10 seconds. The column was operated at 1 atmosphere in distillations up through propane but a pressure of 360 mm. of mercury was used for the propane-pentane "cut". The "cut" is the period of distillation at which a mixture of two components is removed instead of one. The approach to the cut was indicated by a tendency for a decrease in the column pressure and in the reflux temperature as detected by the drop in the electromotive force of the thermocouple as measured by a potentiometer. When these signs appeared the rate of gas removal was decreased from about 40 ml. per minute to from 10 to 20 ml. per minute. When the cut was reached, gas removal was discontinued a short time to allow all traces of the constituent to be removed from the liquid. The last of the gas is removed very slowly. With methane-pentane mixtures this was done by a series of separate

withdrawals while in the propane-pentane separation, and sometimes in the methane-propane cut, a continuous slow withdrawal was found most advantageous. The collecting flask pressure at the cut point was determined by a plot of reflux temperature versus flask pressure, the cut point being that pressure at which the area under the curve equaled that above the curve, as indicated in the sketch.



Experimental Results

The experimental results relating to the methane-pentane system are given in Table I and are graphically depicted in Figure 2. The liquid composition data of Figure 2 were determined by Sage, Webster and Lacey⁽⁶⁾. In a study of Figure 2 several features may be noted.

At low pressures the relative quantity of pentane in the gas phase is large, but decreases rapidly with an increase in pressure. However, a maximum in the methane content occurs at a pressure between 1000 and 1500 pounds per square inch. A further increase in pressure above the maximum results in a rapid increase in the pentane content of the gas. The critical state occurs at the highest pressure at which two phases may coexist at a given tempera-

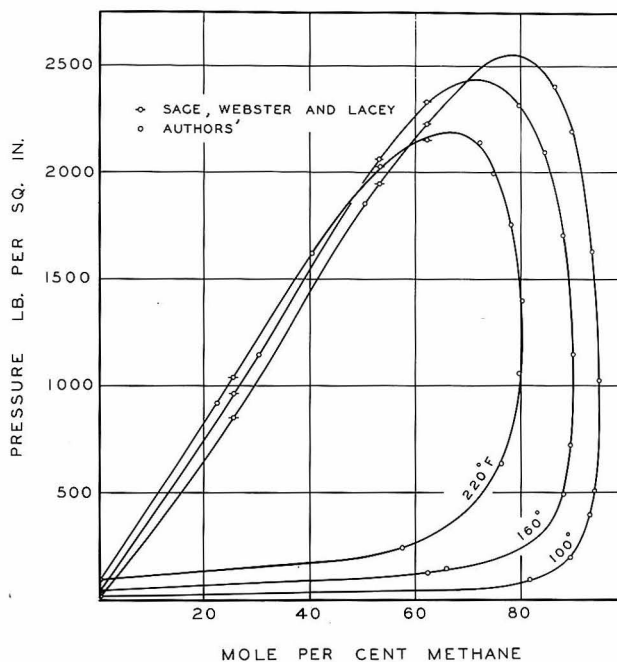


Fig. 2. Effect of pressure upon composition of bubble point liquid and dew point gas for the methane-pentane system at 100°F., 160°F. and 220°F.

ture. Under isobaric conditions an increase in temperature results in a large increase in the pentane content of the gas phase.

In the liquid phase the methane content increases nearly linearly with increase in pressure at constant temperature up to a pressure of 1500 pounds per square inch. From 1500 pounds per square inch to the critical pressure there is a continually more rapid increase in the methane content. Increasing the temperature results in a decrease in the methane content of the liquid phase over the major portion of the pressure range. Near the critical, however, a decrease in temperature results in a decrease in the methane content of the liquid phase.

Of more importance industrially are the data on the gas-liquid equilibrium constant K . Smoothed values of these constants are presented in a part of Table II. A graphical presentation of the variation of the equilibrium constants under isothermal conditions with pressure is shown in Figure 4. The equilibrium constant for methane shows a continual decrease as the pressure increases, with a more rapid decrease as the critical pressure is approached. The minimum in the values of K for pentane shows clearly the region of retrograde condensation - extending from about 700 pounds per square inch to the critical pressure. It is interesting to note the relatively small change in the pressure corresponding to the minimum of K with change in the temperature.

In order to obtain consistent values, the experimental data were interpolated through the use of a plot of equilibrium constants against pressure. The smoothing was supplemented by large scale

plots of the product of the pressure and equilibrium constants versus the pressure; and a large scale plot similar to Figure 2 for the critical range. Further smoothing was accomplished by a temperature correlation.

The smooth values of K as obtained by the author were then compared with equilibrium constants from interpolated data of Boomer et al⁽⁷⁾ on a methane-pentane system containing small percentages of nitrogen, and with some composite values compiled by Sage, Hicks and Lacey from data for a number of binary systems. This information is presented in Table III and a representative curve shown in Figure 3 for pentane equilibrium constants at 160°F. The dashed line curve labelled "correlation" presents the above mentioned composite values. The agreement between the various data is good. The variation exhibited by Boomer's data might well be due to the nitrogen content of his samples. The large deviation of the "correlation" curve from the author's work in the high pressure region is due to the fact that these values were based mainly on Katz and Hachmuth⁽⁴⁾ measurements for a complex system of hydrocarbons. The increase in the critical pressure of their system as a consequence of the presence of heavier components increases the pressure at which the equilibrium constant approaches unity. At the critical state, since the properties of the liquid and gas phases become continuously identical, the equilibrium constant is equal to unity.

The specific volumes of bubble point liquid for varying compositions were known⁽⁸⁾. The specific volume at various pressures and composition were known. With these data and a knowledge of the

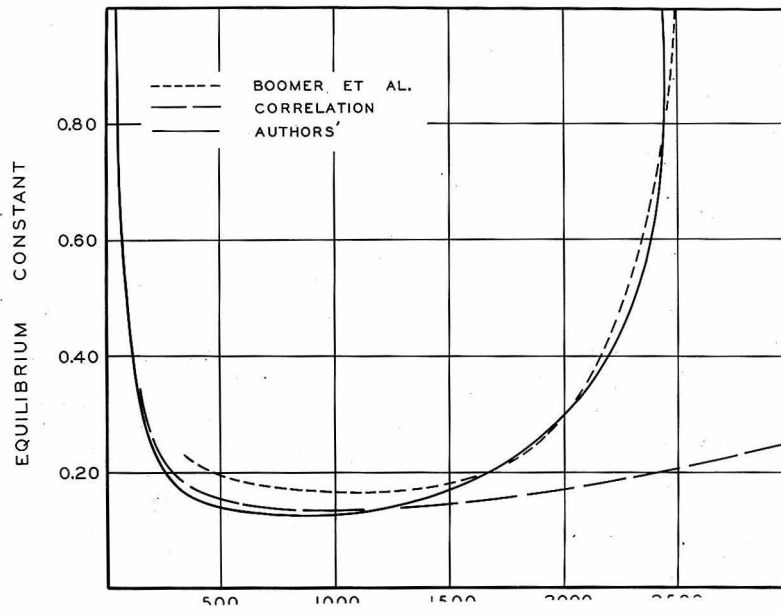


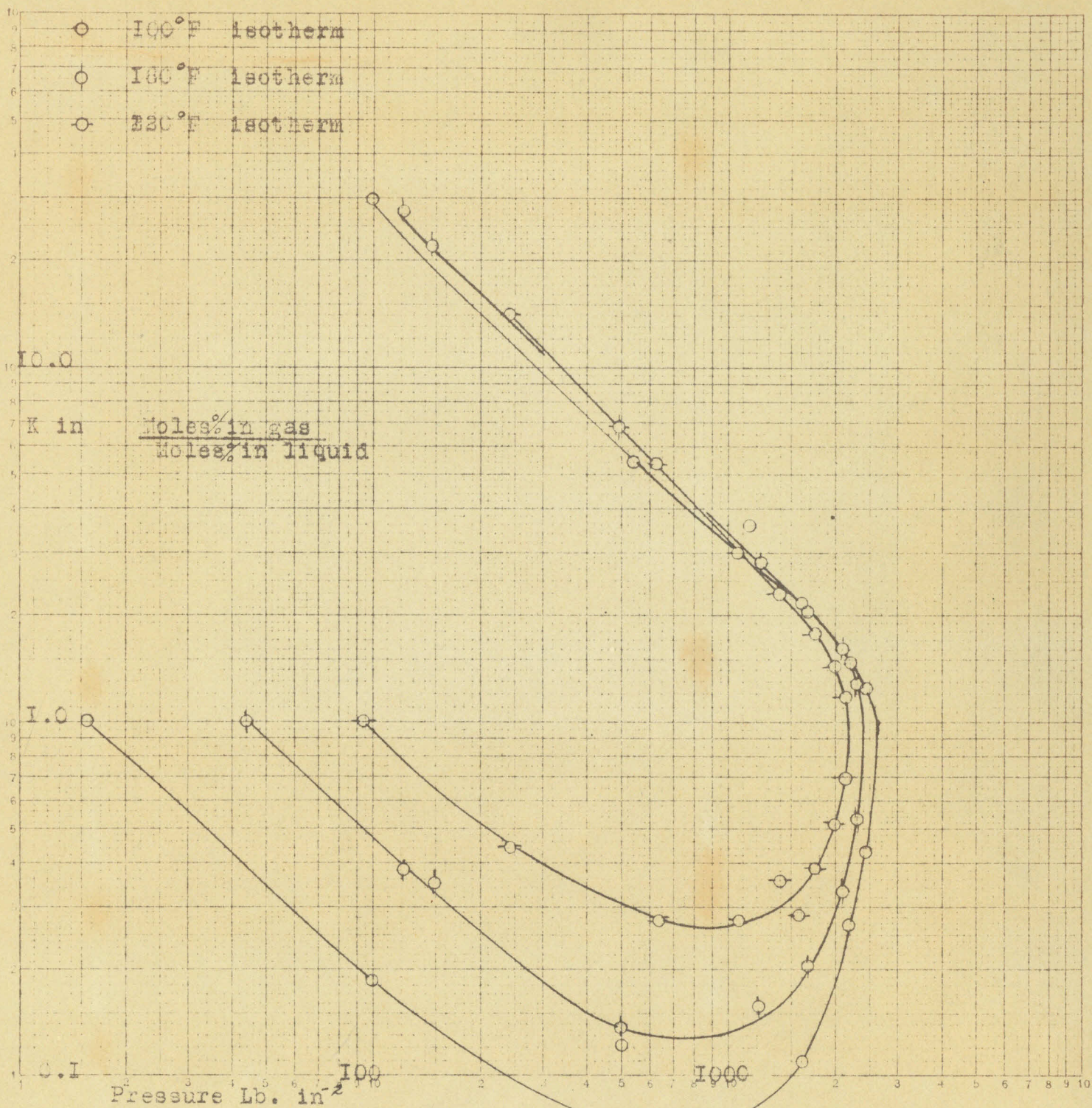
Fig. 3. The agreement of equilibrium constants for pentane in the methane-pentane system at 160°F.

Fig. 4

Equilibrium Constants for Methane and Pentane
plotted at constant tem. vs. pressure

K for methane are plotted above 1.0
K for pentane are plotted below 1.0

10.0



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compositions of the bubble point liquid and dew point gas the specific volumes of the dew point gas were determined as a function of composition. These data are presented in Table 2 and graphically pictured for the 160°F. isotherm in Figure 5. The change in the specific volume of bubble point liquid with exchange in methane content is small. The lower portion of the curve intersects the ordinate axis at a point corresponding to the specific volume of pure liquid pentane. The upper portion of the curve shows the rapid increase in specific volumes of dew point gas. An extension of the dew point curve would intersect the ordinate at a point corresponding to the specific volume of pure saturated pentane gas.

The experimental results relating to the methane-propane-pentane series, are given in Table IV. The composition of coexisting phases are plotted on constant temperature, constant pressure planes in Figures 6 to 10 inclusive. Equilibrium constants calculated from the composition data are also presented in Table IV.

In order to extend the data across the uninvestigated region, advantage was taken of the simplicity of the liquid composition curve. With the interpolated liquid composition curve and values of K as a function of the mole fraction of propane in the liquid phase, the gas phase's composition could be calculated. In the higher pressure range (1500 and 2000 pounds per square inch) where the critical composition is in the three component region, the curves might be extended on the simple postulate that the mole fraction of a component in the gas phase is a straight line function

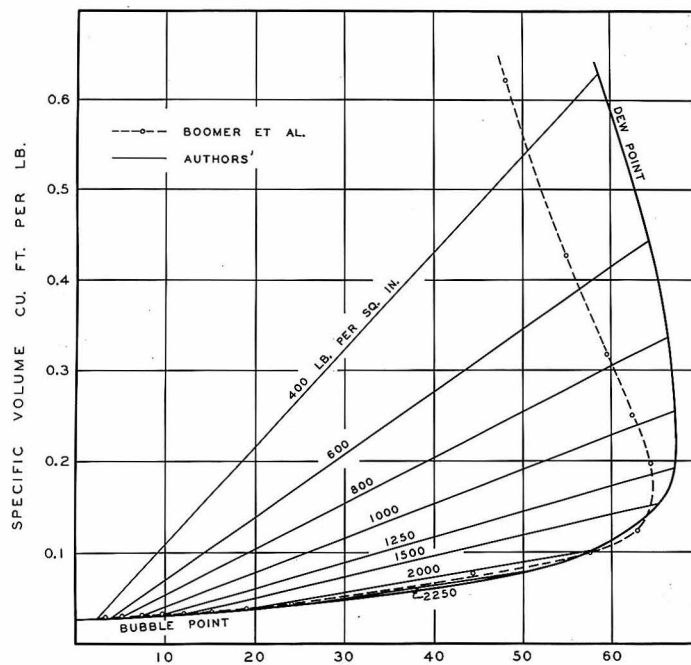


Fig. 5. Effect of weight per cent methane on the specific volume of bubble point liquid and dew point gas for the methane-pentane system at 160°F.

Fig 6

Methane-Propane-Pentane System

Tem. 100°F

Pressure 200 Lb. in⁻²

CH₄

CH₃

CH₃

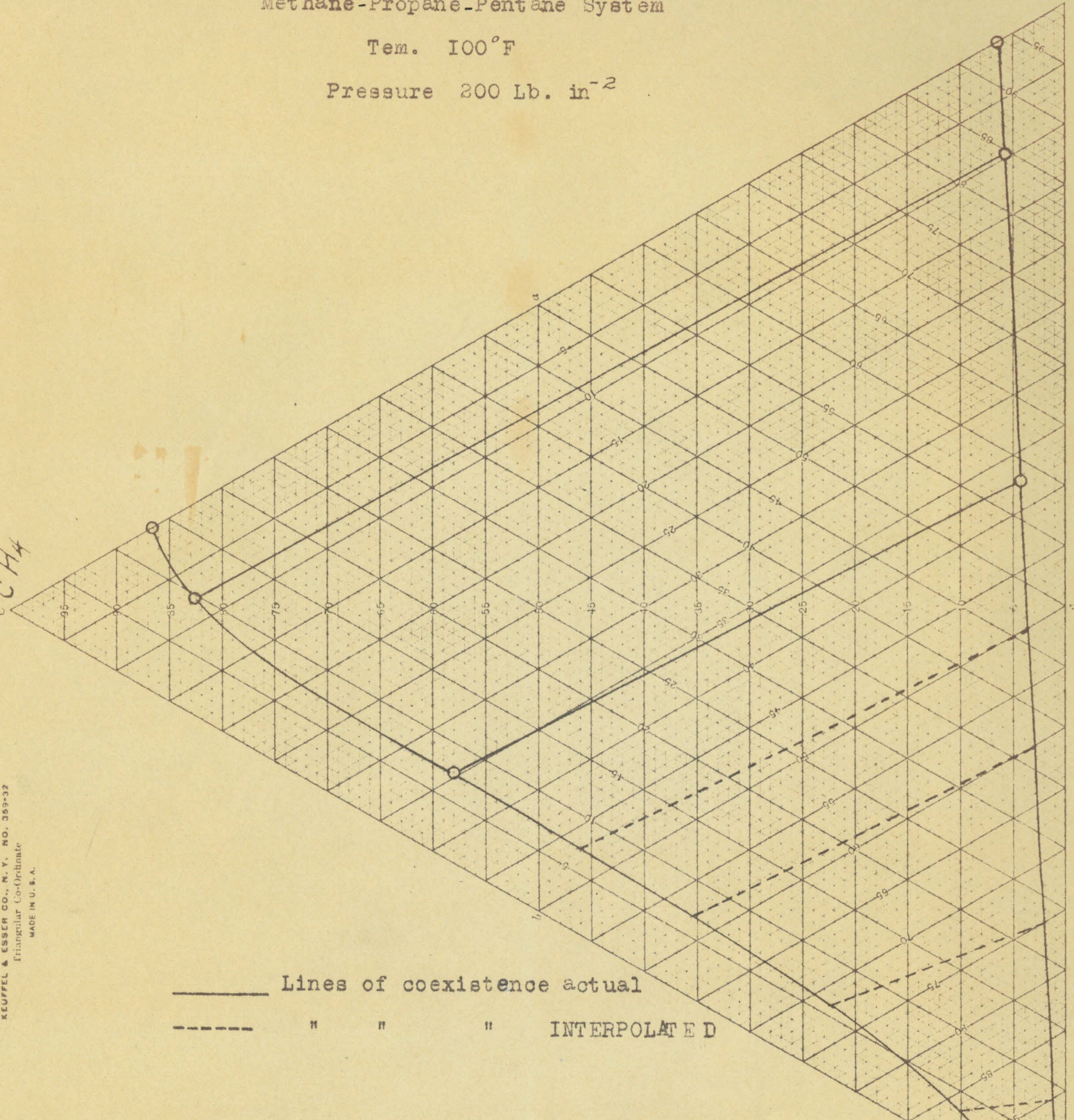


Fig. 7

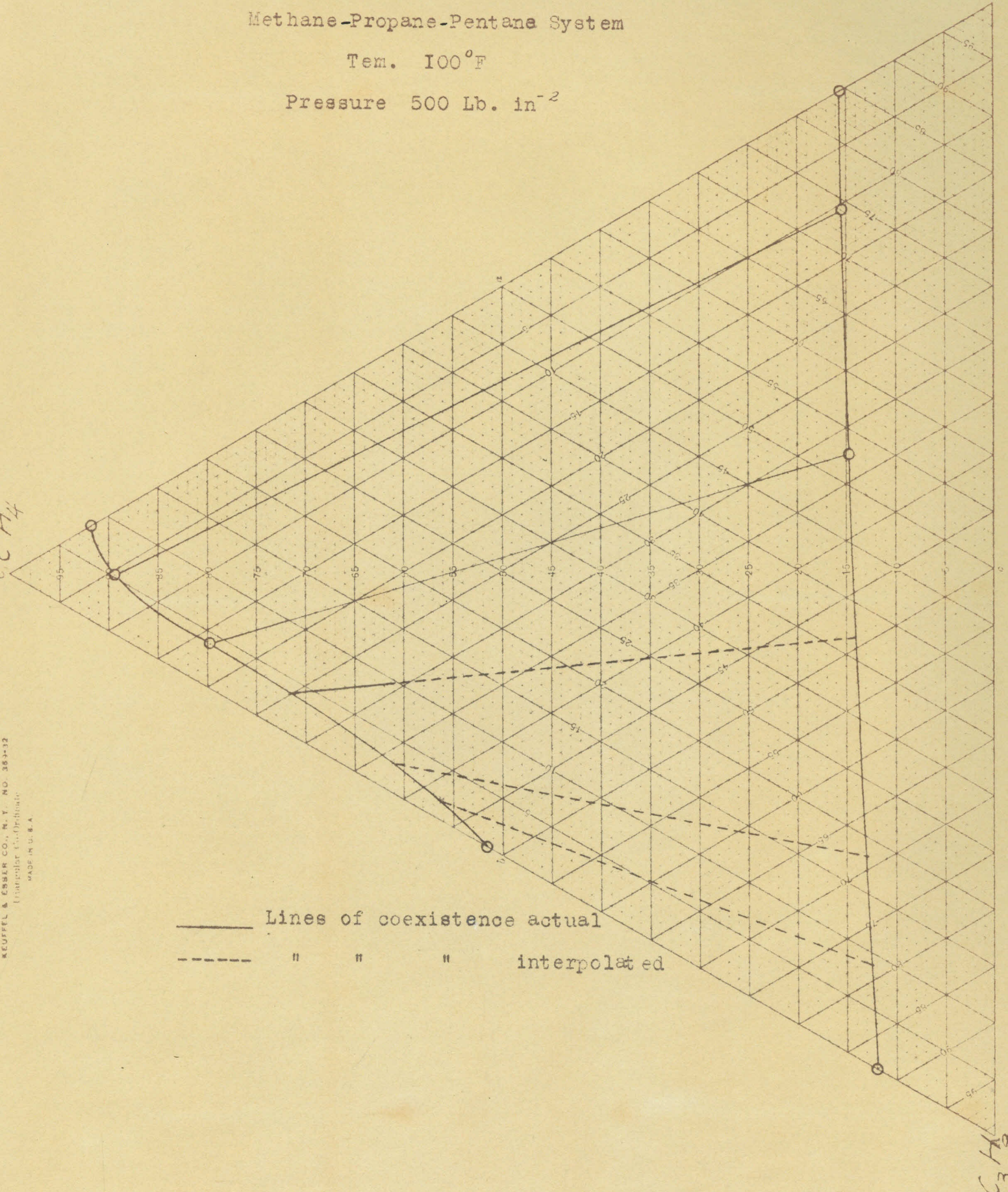
Methane-Propane-Pentane System

Tem. 100°F

Pressure 500 Lb. in⁻²

C₂H₄

C₅H₁₂



— Lines of coexistence actual
- - - " " " interpolated

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C₃H₈

Fig 8

Methane-Propane-Pentane System

Tem. 100°F

Pressure 1000 Lb. in⁻²

C₃H₈

C₅H₁₂

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Triangular Co-Ordinate
MADE IN U.S.A.

— Lines of coexistence actual
- - - " " " interpolated

C₃H₈

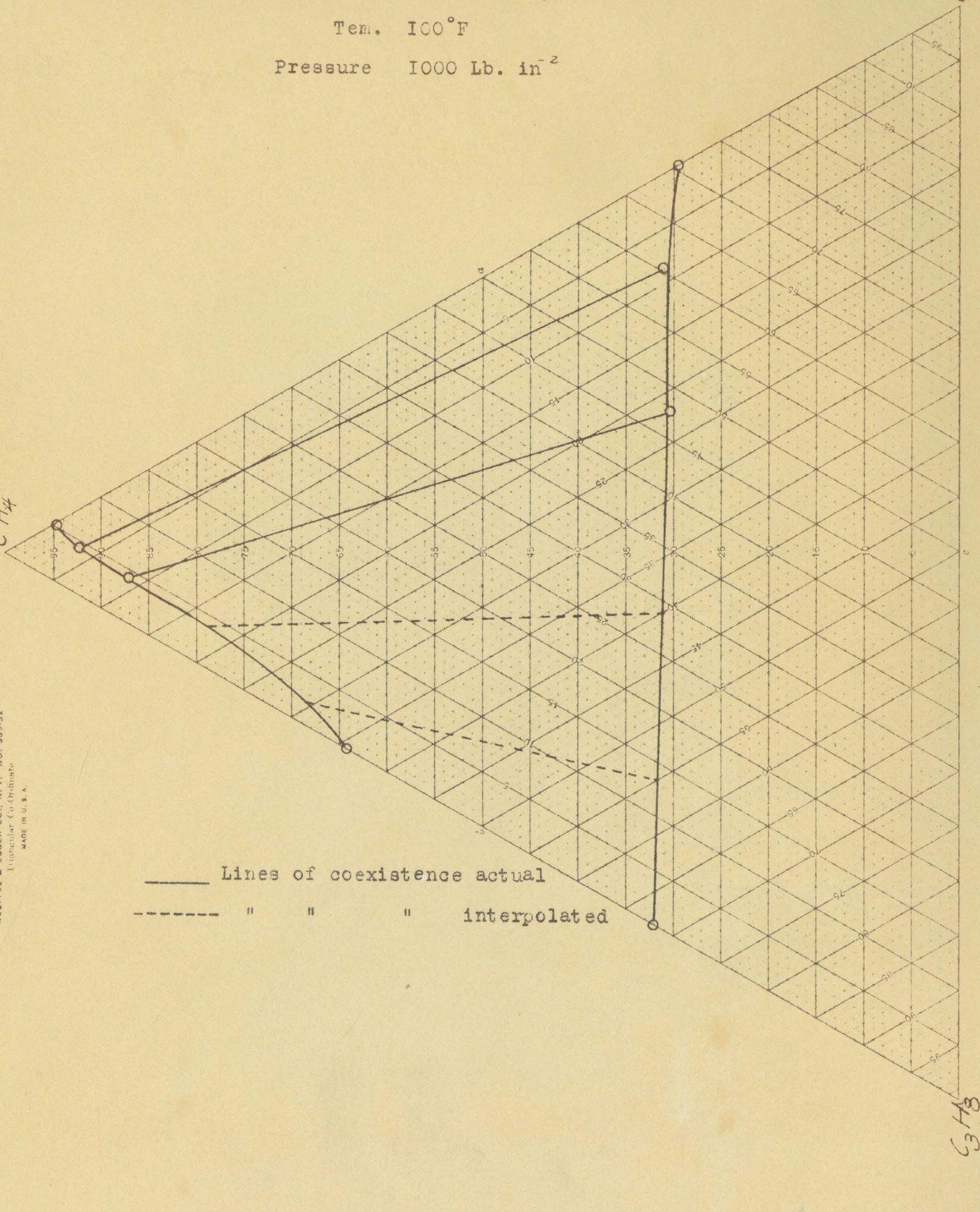
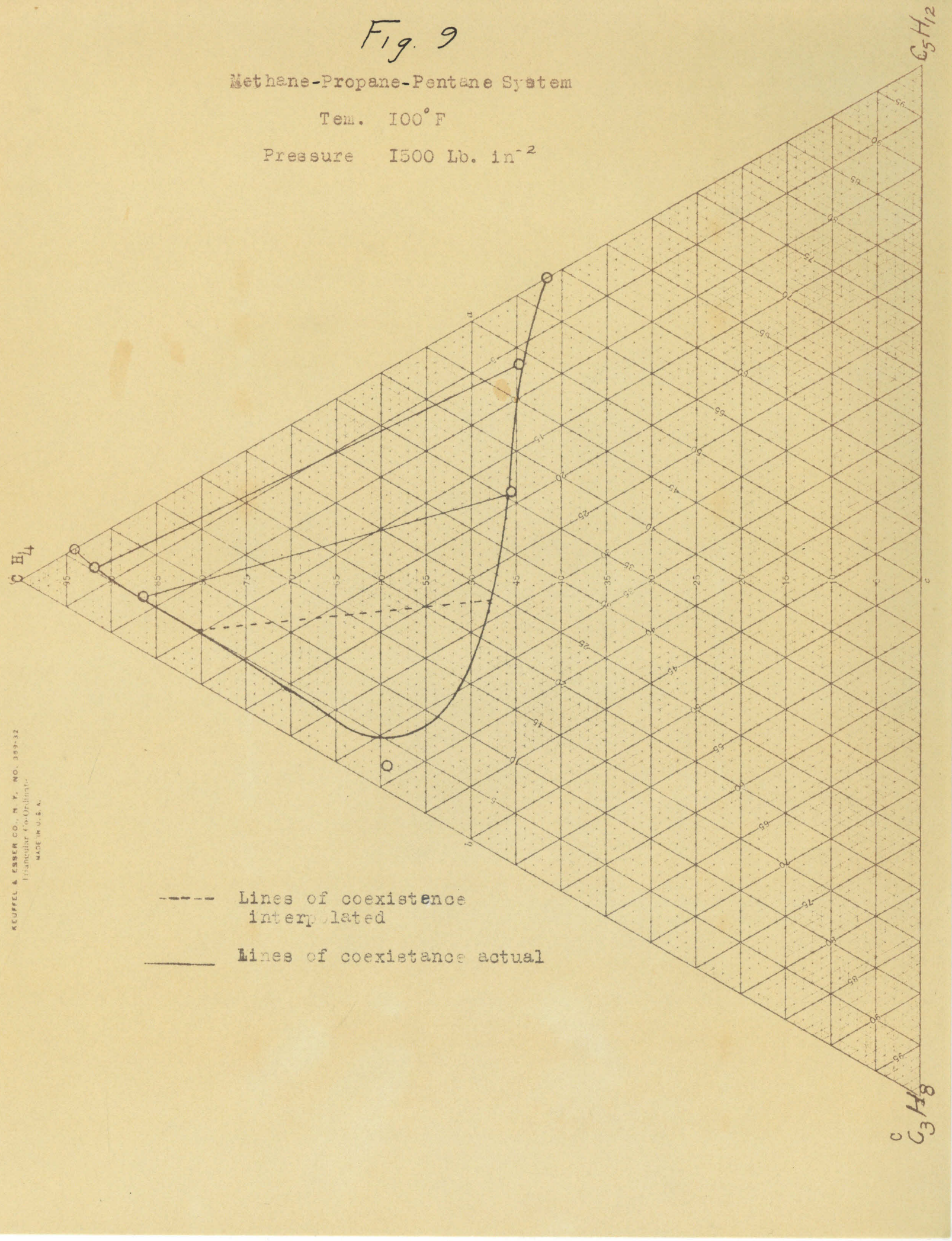


Fig. 9

Methane-Propane-Pentane System

Tem. 100° F

Pressure 1500 Lb. in⁻²



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- Lines of coexistence interpolated
- Lines of coexistence actual

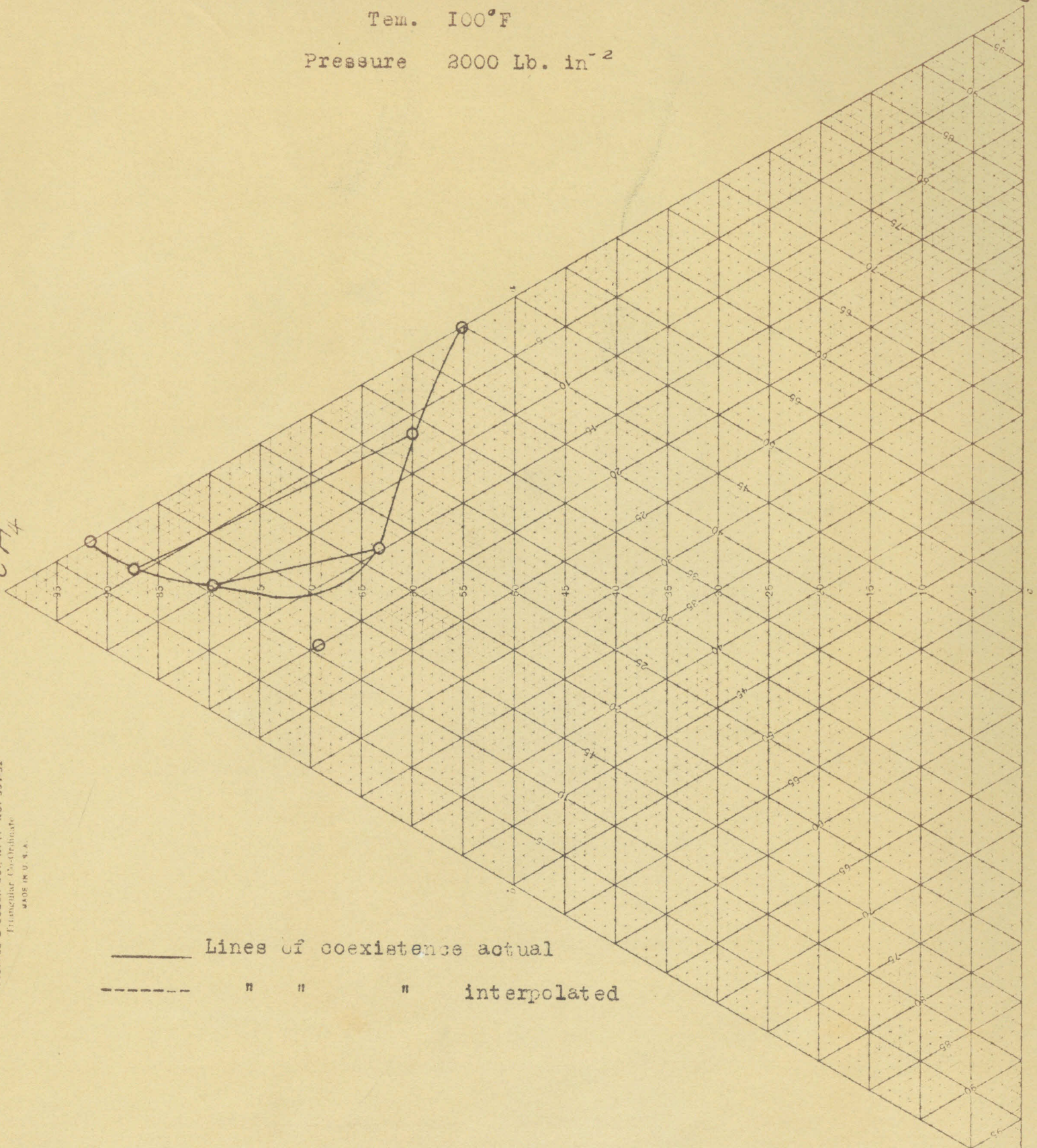
Fig. 10
Methane-Propane-Pentane System

Tem. 100°F

Pressure 3000 Lb. in⁻²

C₃H₈

C₅H₁₂



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Triangular Co-ordinates
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— Lines of coexistence actual
- - - " " " interpolated

C₃H₈

of the pressure. It was in this manner that the two divergent points shown in Figures 9 and 10 were calculated. Since these points did not appear consistent with the experimental curves, they were not utilized. A check on the interpolated points for the gas phase and the smoothed K values is afforded by the fact that with the values of K for the three components, the mole fraction of each component in the gas phase may be calculated. The sum of these fractions must be equal to unity. The interpolated values for coexistent phase compositions and equilibrium constants are given in Table V.

Figures 6 to 10 indicate that except for a slight convexity at low propane-pentane ratios the liquid composition lines below 1500 pounds per square inch are nearly straight. In other words the methane concentration in the liquid phase varies nearly directly as the propane content of the liquid phase. At the lower pressures (200 and 500 pounds per square inch) the methane content of the liquid decreases with increase in propane content, while at pressures above about 700 pounds per square inch, the mole fraction of methane increases with increase in propane content.

In the gas phase, especially at the lower pressures, the pentane fraction undergoes more or less rapid changes at both low and high propane fractions. At the intermediate propane fractions the pentane content of the gas is nearly constant.

With the accumulation of more experimental data, notably for the higher propane-pentane ratios, the more exact nature of composition trends may be noted and a more accurate calculation of equili-

rium constants made. These additional data will also help to establish the critical compositions indicated at 1500 and 2000 pounds per square inch.

Lines were drawn connecting the compositions of coexistent liquid and gas phases. The solid lines were based upon the actual data and the dotted lines were the results of the calculations discussed above.

The phase composition data as related to pressure at 100°F. are presented as a three coordinate picture in Figure 16. The ordinate is pressure, while compositions are plotted in constant pressure planes. The intersections of the gas and liquid composition envelope with the three border planes corresponding to the two-component systems give the pressure-composition diagram for these systems. In the two cases of binary systems involving methane, the two-phase regions are shaded whereas in the propane-pentane system the dotted lines extending from 190 to 42 pounds per square inch near the bottom of the diagram are used to indicate the position of the two-phase region. Solid lines are drawn for gas composition and dotted lines for liquid compositions at pressures of 190, 500, 1000, 1500, 2000 pounds per square inch. In addition the locus of the critical pressures for the methane-propane-n-pentane system has been indicated.

Plots of equilibrium constants for methane, propane and pentane versus percent propane of the propane, pentane content of the liquid phase at constant pressure are shown in Figures 11, 12 and 13, respectively. All points shown in these graphs between 50 and 100% are interpolated

points. As a consequence the curves are dotted in this region, except where additional data at 100% (methane-propane system) gave more accurate information. Critical composition as observed from Figures 9 and 10 gave the positions at which K approached unity for the 1500 and 2000 pounds per square inch isobars.

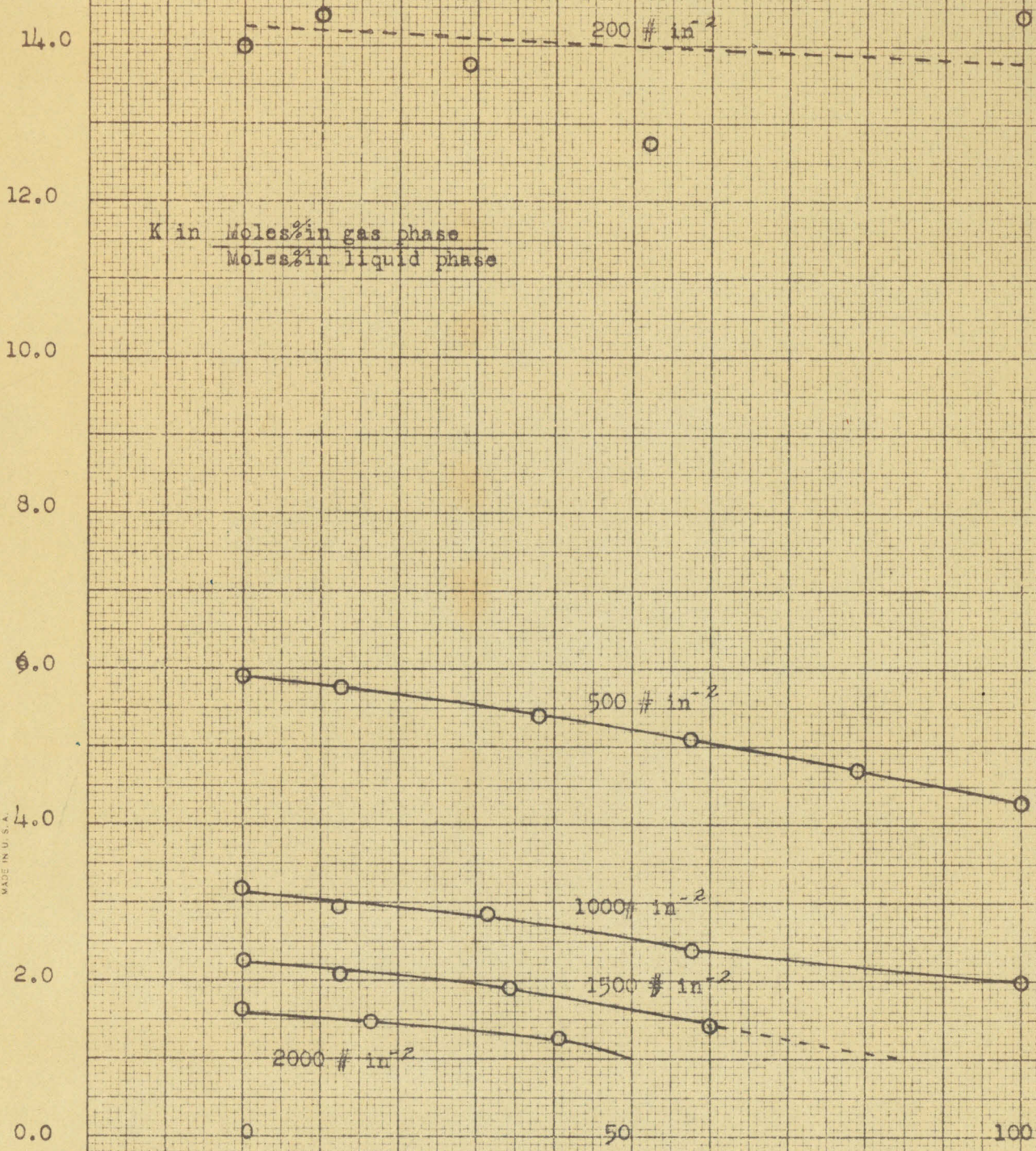
The change in the values of K even under conditions far from the critical region indicates the roughness of the approximations of Souders and associates ⁽¹⁾ in predicting values of K as a function of pressure and temperature alone. In the neighborhood of the critical region the values deviate as much as 200 percent and more from normal values.

From Figures 11, 12 and 13 values of K at constant mole per cent propane of the propane-pentane content of the liquid phase were determined and tabulated in Table VI. Figures 14 and 15 are graphical presentations of the data from Table VI.

The indicated values of critical data - composition and pressure at given temperatures - as afforded by Figures 2, 14 and 15 and by similar curves for the methane-propane system - are presented in Table VII. Critical and cricondothem data furnish interesting subsidiary features of composition analyses.

Fig. 11

Equilibrium constants for methane at 200 500 1000 1500 2000 # in⁻²
 Plotted vs. Mole % propane of the propane and pentane content of
 the liquid phase
 Temperature 100° F

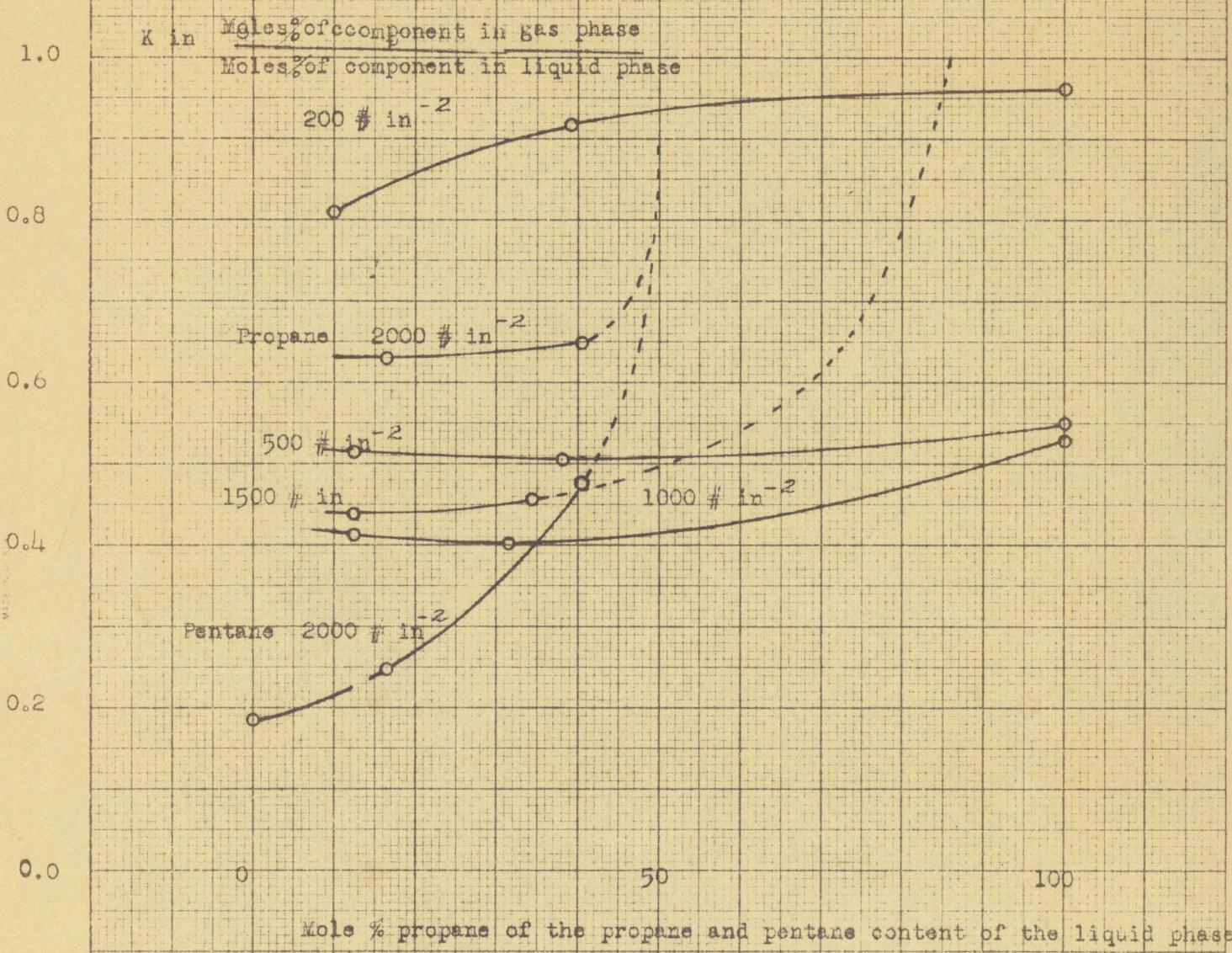


Mole % propane of the propane and pentane content of the liquid phase

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 2 1/2" x 20" to the inch, 10th lines heavy.
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Fig. 12

Equilibrium constants for Propane at 200 500 1000 1500 2000 # in⁻²
" " " " Pentane at 2000 # in⁻²
Plotted vs. % Propane of the propane and pentane content of the
liquid phase (Mole %)
Temperature 100°F



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Fig. 13

0.4

Equilibrium constants for
Plotted vs. Mole % propane
the liquid phase

pentane at 200 500 1000 1500 2000 # in⁻²
of the propane and pentane content of

Temperature 100°F

K in $\frac{\text{Moles}\% \text{ of gas phase}}{\text{Moles}\% \text{ of liquid phase}}$

0.3

0.2

0.1

0.0

2000 # in⁻²

200 # in⁻²

200 # in⁻²

1500 # in⁻²

500 # in⁻²

1000 # in⁻²

500 # in⁻²

Mole % propane of the propane and pentane content of the liquid phase

50

100

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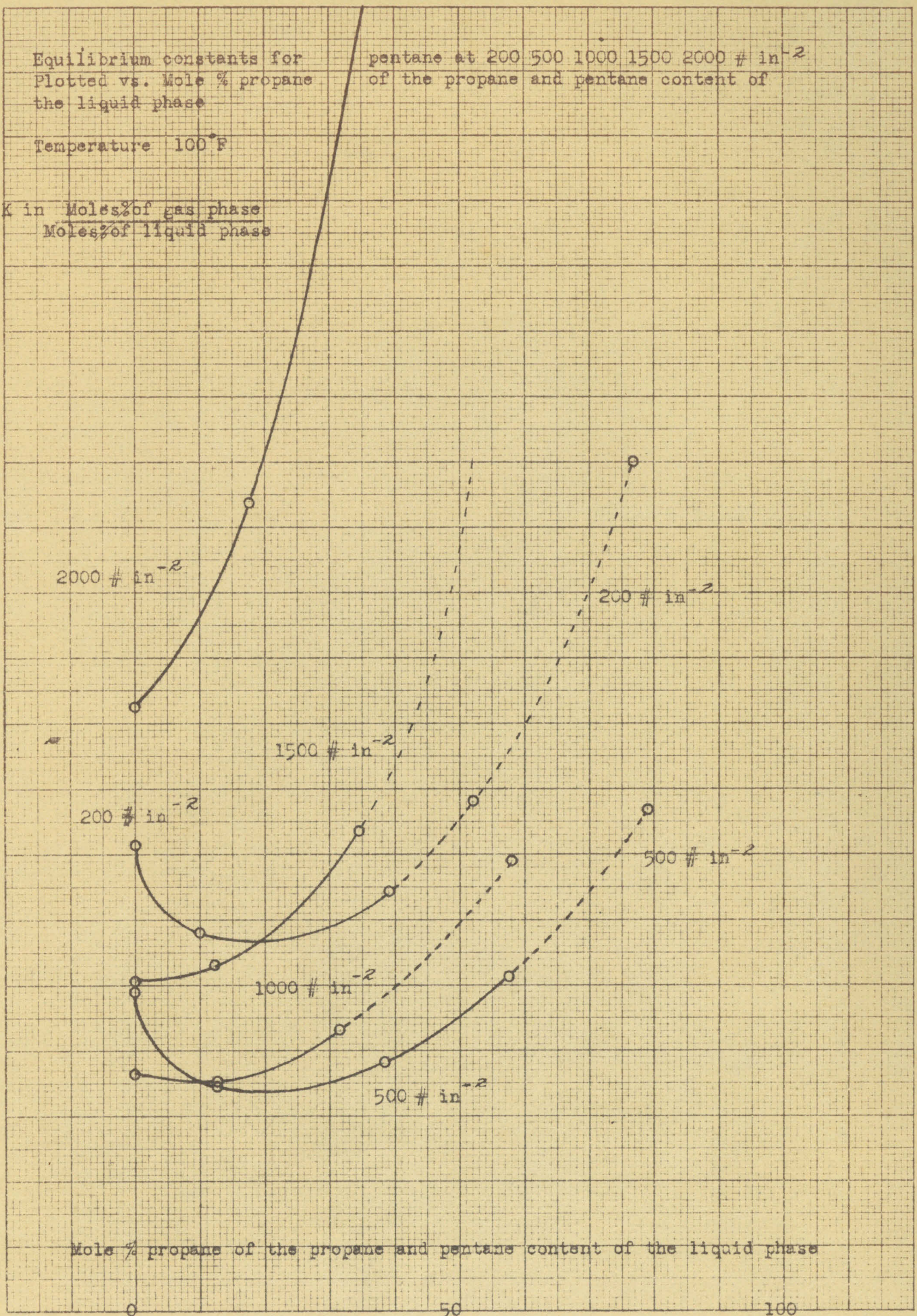
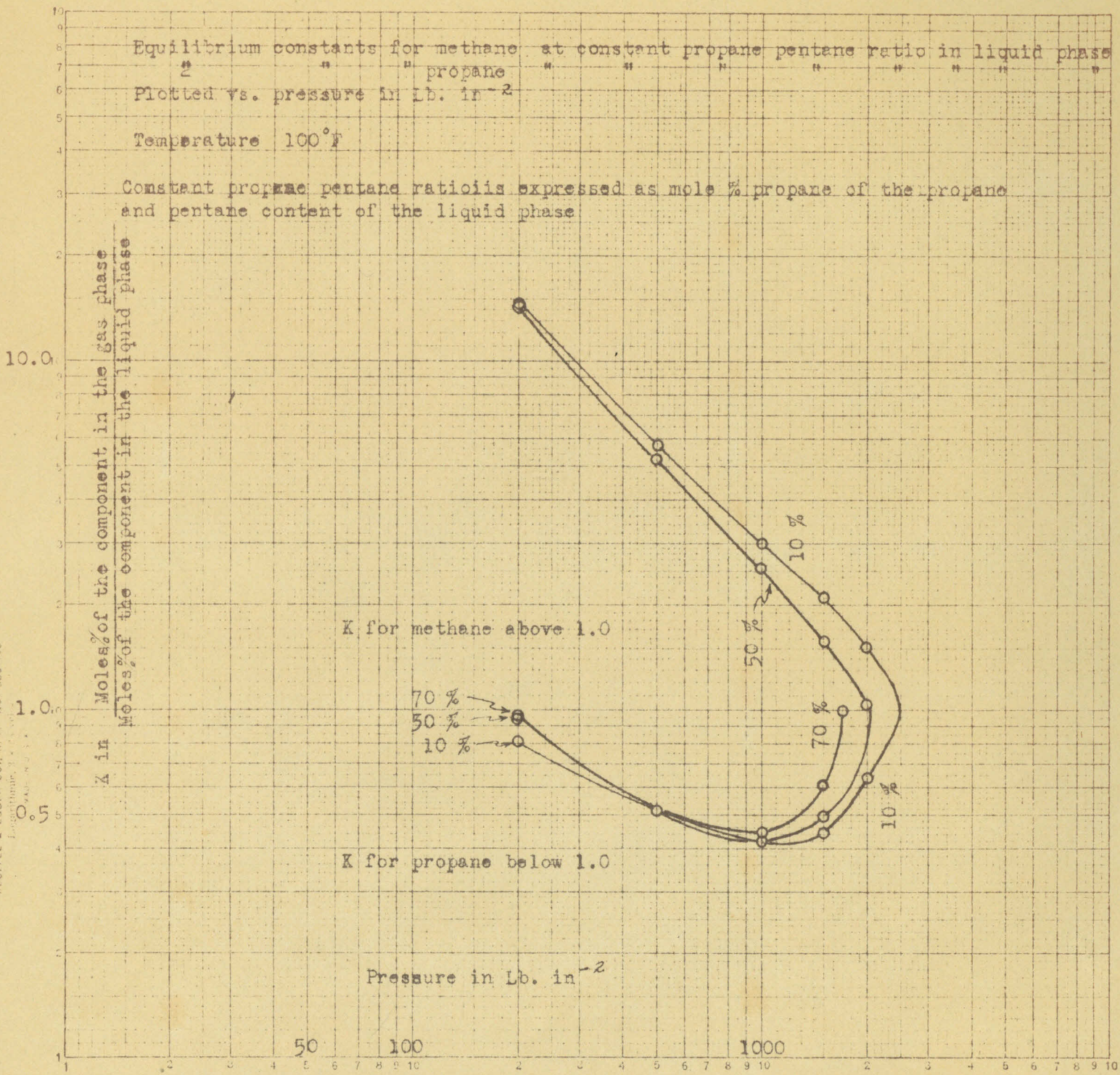


Fig. 14



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Fig. 15

Equilibrium constants for pentane vs. pressure at constant composition ratio between propane and pentane expressed as Mole % propane of the propane and pentane content of the liquid phase

Temperature 100° F

X in Moles% of component in gas phase
 liquid phase

50 % Propane
 30 %
 10 %

Pressure in Lb. in⁻²

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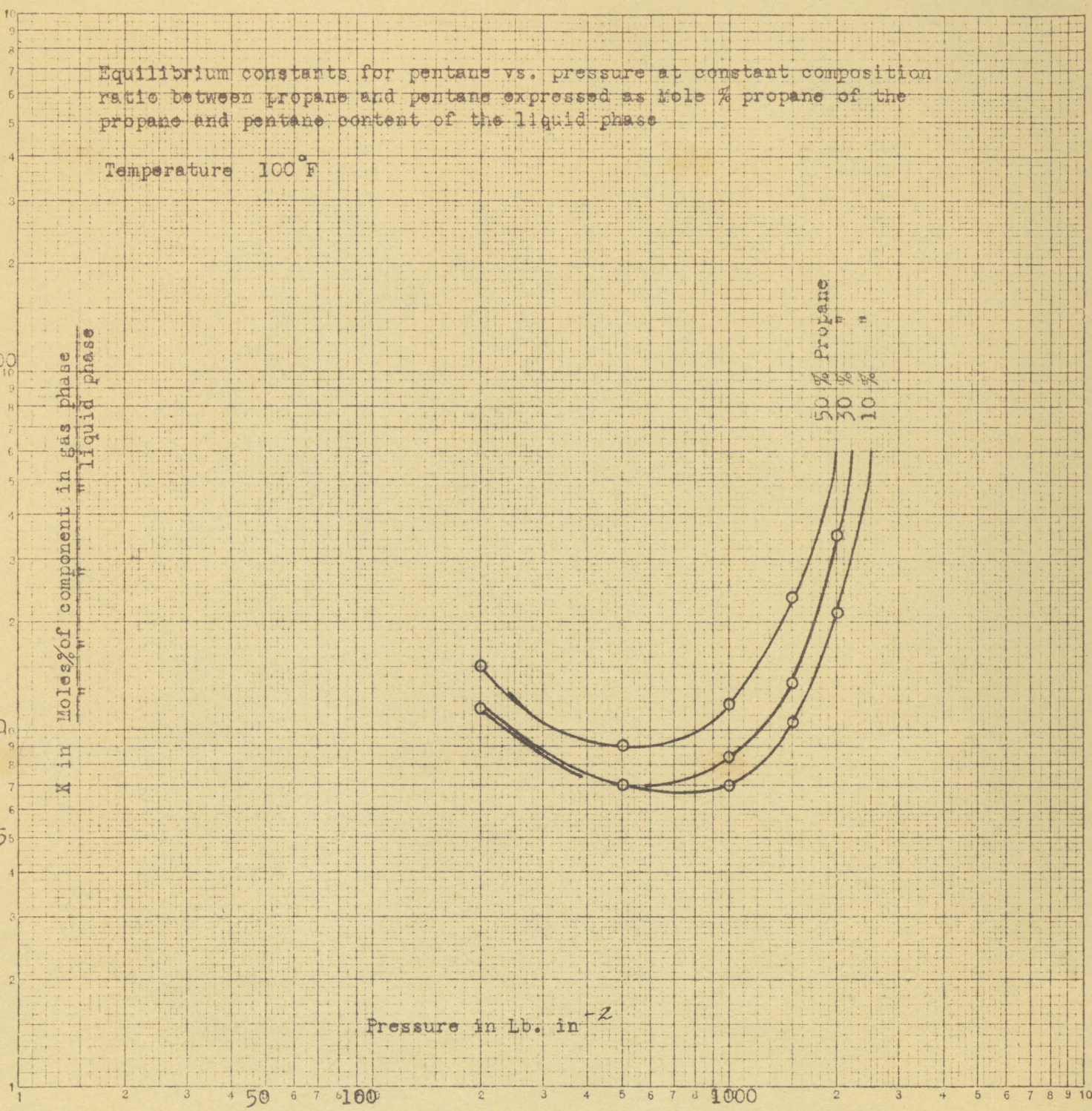
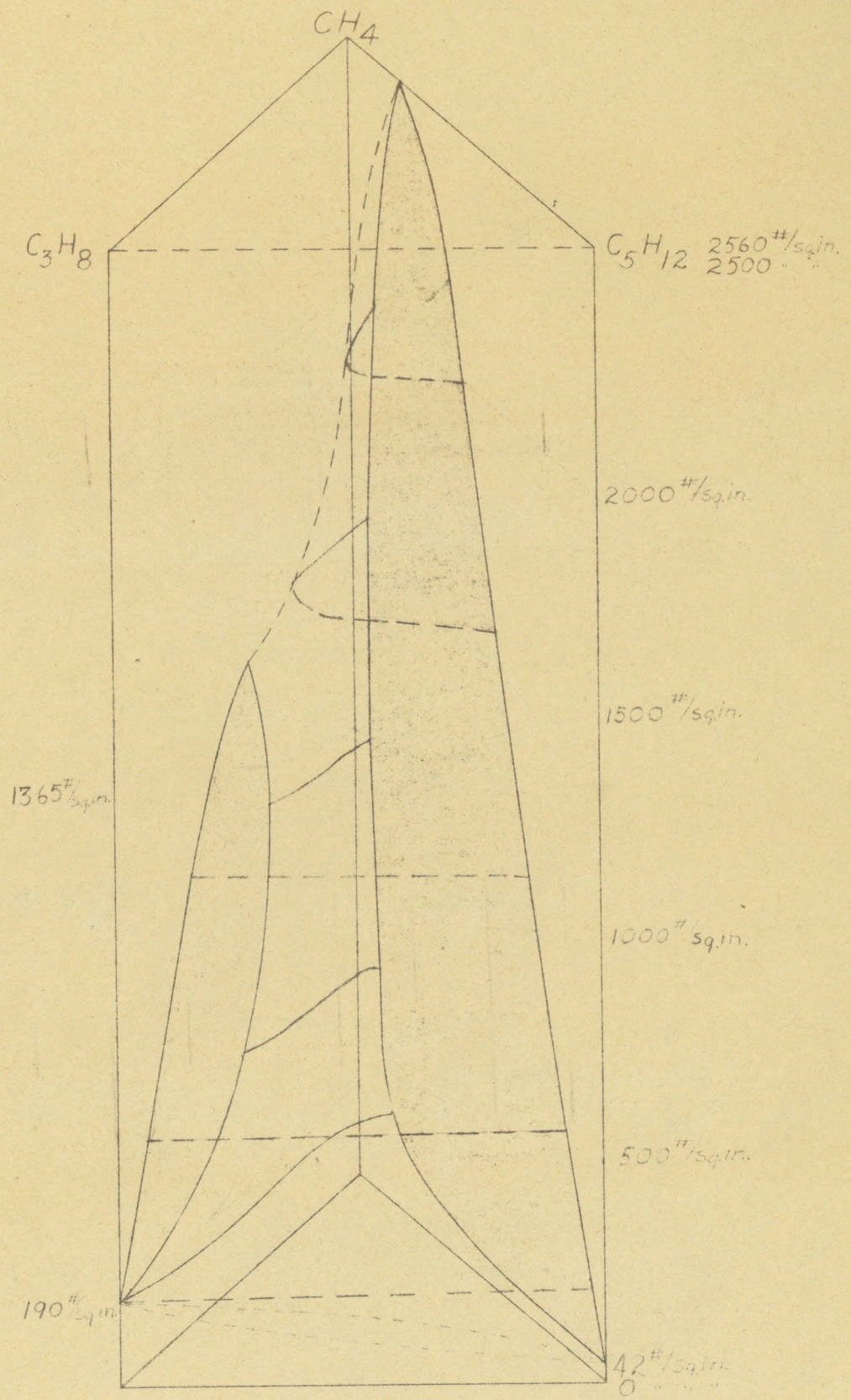


Fig. 16

Methane Propane Pentane System
Tem. 100°F

Composition of the liquid and gas phases vs Pressure



Summary

Values for the equilibrium constants of methane and pentane were experimentally determined for the methane-pentane system at temperatures of 100°F, 160°F., and 220°F. from pressures of 42 to 2500 pounds per square inch.

Values for the equilibrium constants of methane, propane and pentane were experimentally determined for the methane-propane-pentane system at 100°F. for pressures from ^{200 to} 2000 pounds per square inch.

The propane-pentane ratio was varied from zero to about one. Interpolated values of methane were determined over the entire composition range while the values of the equilibrium constants for propane and pentane were interpolated up to a propane-pentane ratio of about 2.3

Composition of coexisting phases were experimentally determined for the methane-pentane system at 100°, 160° and 220°F. over the entire two phase region.

The composition of coexisting phases for the methane-propane-pentane system were experimentally determined for a temperature of 100°F. at pressures of 200, 500, 1000, 1500, 2000 pounds per square inch for ratios of propane to pentane of approximately 0.1 ^{and} to 0.7. By the use of these meager data and compositions of coexisting phases of the methane-propane and the methane-pentane systems interpolated data were accumulated over the entire composition range. This is the first systematic experimental investigation that has ever been made on a ternary hydrocarbon mixture.

An indication of the nature of critical pressures, temperatures and compositions are given for methane-pentane and methane-propane-

pentane systems.

The values of the equilibrium constants are found to be a complex function of temperature, pressure and composition of the system. This fact brings to light the need for a large amount of research to be carried out in this field, if reliable values of equilibrium constants for industrial calculation are to be known.

Table I. Composition of Bubble Point Liquid and Dew Point Gas in the Methane-n-Pentane System

Pressure Lbs/sq.in. Absolute	Composition Mole Per Cent Methane		Pressure Lbs/sq.in. Absolute	Composition Mole Per Cent Methane		Pressure Lbs/sq.in. Absolute	Composition Mole Per Cent Methane	
	Liquid	Gas		Liquid	Gas		Liquid	Gas
15.6	0.0	0.0	42.2	0.0	0.0	94.0	0.0	0.0
98.0	-	81.81	122.4	-	62.74	241.2	-	57.70
199.4	-	89.42	148.3	-	65.93	635	-	76.46
510	-	94.06	496.8	-	88.02	921	22.44	-
1028	-	95.20	1144	30.55	-	1064	-	79.60
1631	-	93.67	1226	-	89.94	1400	-	80.07
1855	50.4	-	1671	-	88.51	1530	-	82.90
2192	-	89.65	2096	-	84.63	1619	40.42	-
2403	-	86.44	2313	-	79.61	1761	-	78.40
						1989	-	74.86
						2152	-	72.15

TABLE II

PROPERTIES OF THE CO-EXISTING PHASES IN THE METHANE-n-PENTANE SYSTEM

Temp. °F.	Pressure Lb/sq. in. Absolute	Composition		Specific Volume		Equilibrium Constants	
		Mole Per Cent Methane		Cu. ft./lb.		Methane	Pentane
		Liquid	Gas	Liquid	Gas		
100	200	6.39	89.46	- -	- -	14.00	0.112
	400	12.75	93.20	0.0275	0.681	7.31	0.078
	600	18.70	94.25	0.0280	0.458	5.04	0.071
	800	24.25	94.86	0.0285	0.343	3.91	0.068
	1000	29.55	94.85	0.0289	0.270	3.21	0.073
	1250	35.45	94.67	0.0294	0.207	2.66	0.081
	1500	41.45	94.34	0.0303	0.162	2.27	0.101
	1750	47.99	92.97	0.0315	0.128	1.94	0.133
	2000	55.1	91.7	0.0337	- -	1.66	0.185
	2250	63.7	89.2	0.0372	- -	1.42	0.292
	2500	78.9	85.3	0.0422	- -	1.13	0.514
160	200	4.66	75.63	- -	- -	16.23	0.256
	400	10.50	86.42	0.0291	0.616	8.27	0.152
	600	15.96	88.90	0.0298	0.427	5.57	0.132
	800	21.20	89.78	0.0304	0.328	4.24	0.130
	1000	26.45	90.19	0.0310	0.264	3.41	0.133
	1250	32.60	90.15	0.0316	0.205	2.77	0.146
	1500	38.45	89.40	0.0325	0.160	2.33	0.172
	1750	44.5	87.9	0.0338	0.126	1.97	0.217
	2000	51.4	85.6	0.0363	0.100	1.67	0.296
	2250	59.1	81.8	0.0406	- -	1.39	0.45
	220	200	2.77	46.51	0.0306	- -	16.82
400		8.20	68.24	0.0314	0.448	8.33	0.346
600		13.69	75.31	0.0321	0.347	5.50	0.286
800		19.24	78.67	0.0329	0.284	4.09	0.264
1000		24.67	80.19	0.0336	0.232	3.25	0.263
1250		31.11	80.57	0.0347	0.179	2.59	0.280
1500		37.27	79.86	0.0364	0.138	2.14	0.321
1750		43.55	77.87	0.0390	0.107	1.79	0.392
2000		52.30	75.06	0.0435	0.084	1.44	0.523

TABLE III.

EQUILIBRIUM CONSTANTS IN THE METHANE-n-PENTANE SYSTEM

Temp. °F.	Pressure Lb/sq. in. Absolute	Methane			n-Pentane		
		Boomer	Correlation	Authors	Boomer	Correlation	Authors
100	400	7.28	7.11	7.31	0.145	0.077	0.078
	600	4.92	4.91	5.04	0.117	- -	0.071
	1000	3.07	3.13	3.21	0.100	0.078	0.073
	1500	2.16	2.19	2.27	0.111	0.091	0.101
	2000	1.66	1.66	1.66	0.347	0.113	0.185
	2500	1.19	1.28	1.13	- -	0.152	0.514
160	400	7.88	7.68	8.27	0.216	0.168	0.152
	600	5.34	5.25	5.57	0.183	- -	0.132
	1000	3.29	3.29	3.41	0.162	0.136	0.133
	1500	2.23	2.26	2.33	0.187	0.149	0.172
	2000	1.63	1.65	1.67	0.299	0.174	0.296
220	400	- -	7.90	8.33	- -	0.293	0.346
	600	- -	5.43	5.50	- -	- -	0.286
	1000	- -	3.40	3.25	- -	0.260	0.263
	1500	- -	2.30	2.14	- -	0.216	0.321
	2000	- -	1.67	1.44	- -	0.246	0.523

Table IV

Composition of Coexisting Phases in the Methane-Propane-n-Pentane System

	Methane*	Propane*	Methane	Propane	Pentane	Methane	Propane	Pentane	Methane	Pentane	
			200 pounds per square inch absolute								
Gas**	4.3	95.7	58.05	54.45	7.50	82.59	7.77	9.84	86.58	13.42	
Liquid**	0.3	99.7	4.23	57.44	58.33	5.71	9.60	84.69	6.18	93.82	
K	14.3	0.96	13.73	0.92	0.128	14.4	0.81	0.116	14.0	0.143	
			500 pounds per square inch absolute								
Gas	51.6	48.4	79.62	16.34	4.04	89.49	5.40	5.10	91.7	8.3	
Liquid	12.0	88.0	14.71	32.43	52.87	15.57	10.48	73.95	15.5	84.5	
K	4.3	0.549	5.40	0.504	0.0765	5.75	0.515	0.069	5.91	0.098	
			1000 pounds per square inch absolute								
Gas	64.1	35.9	87.07	8.79	4.14	92.2	3.57	4.23	94.35	5.15	
Liquid	32.1	67.9	30.21	21.97	47.81	31.07	8.69	60.24	29.54	70.46	
K	1.99	0.529	2.88	0.400	0.0866	2.97	0.411	0.0702	3.21	0.073	
			1500 pounds per square inch absolute								
Gas	86.16	8.54	86.16	8.54	5.30	91.84	2.98	51.77	94.12	5.88	
Liquid	45.37	18.75	45.37	18.75	35.88	44.60	6.80	48.60	41.59	58.41	
K	1.90	0.455	1.90	0.455	0.1476	2.055	0.438	0.1063	2.27	0.101	
			2000 pounds per square inch absolute								
Gas	79.87	9.66	79.87	9.66	10.46	87.55	4.18	8.27	91.67	8.33	
Liquid	63.13	14.90	63.13	14.90	21.97	60.02	6.63	33.35	55.06	44.94	
K	1.262	0.648	1.262	0.648	0.476	1.46	0.631	0.248	1.66	0.185	

K = Equilibrium Constant

* Reference 5

** Gas and Liquid refer to the compositions of the gas and liquid phases in mole per cent.

Table V

Composition of Coexisting phases in the Methane-Propane-i-Pentane System

	Calculated Data					
	Methane	Propane	Pentane	Methane	Propane	Pentane
				200 pounds per square inch absolute		
Gas*	(1) 45.8	(3) 46.9	(5) 7.27	(1) 36.5	(3) 56.9	(5) 6.65
Liquid*	3.6	50.0	46.4	3.1	60	36.9
K*	12.75	0.939	0.156			11.0
Gas	---	86.4	---			
Liquid	1.0	90.0	9.0			
				500 pounds per square inch absolute		
Gas	(1) 71.5	(3) 24.8	(5) 3.7	(1) 61.1	(3) 36.1	(5) 2.8
Liquid	14.0	49.0	36.0	13.0	68.8	18.2
K	5.1	0.506	0.1028	4.7	0.524	0.154
				1000 pounds per square inch absolute		
Gas	(1) 74.0	(3) 17.52	(5) 4.0	(1) ---	(3) 25.9	(5) ---
Liquid	31.1	40	28.9	31.7	55	13.3
K	2.37	0.434	0.133		0.471	
				1500 pounds per square inch absolute		
Gas	(1) 67.8	(3) 14.4	(5) ---	(1) ---	(3) 22	(5) ---
Liquid	47.8	28.0	24.2	51.5	35	13.5
K	1.415	0.614	---			

* Gas refers to composition of the gas phase in mole percent liquid refers to composition of the liquid phase in mole percent.

K = Equilibrium constant.

Table VI

Equilibrium Constants at Constant Ratios of Propane to Pentane

Mole Per cent propane of the propane-pentane content of the liquid phase

Pressure lbs/sq. in. Absolute	K for Methane			
	10 percent	30 percent	50 percent	70 percent
200	14.2	14.1	14.0	
500	5.76	5.48	5.2	
1000	3.0	2.90	2.55	
1500	2.09	1.96	1.60	
2000	1.52	1.38	1.01	
	K for Propane			
200	0.81	0.895	0.935	0.951
500	0.515	0.508	0.509	0.520
1000	0.412	0.401	0.413	0.448
1500	0.439	0.448	0.495	0.61
2000	0.63	0.635	0.95 ?	---
	K for Pentane			
200	0.116	0.118	0.150	
500	0.07	0.070	0.090	
1000	0.07	0.084	0.119	
1500	0.104	0.135	0.235	
2000	0.212	0.350	---	

Table VII

Critical Data for the Methane-n-Pentane System *

Tem. °F.	Pressure	Composition in mole percent Methane
	Lbs/sq. in. Absolute	
100	2560	79.3
160	2430*	72.6*
220	2190*	67.0*

Critical Data for the Methane-Propane System

Tem. °F.	Pressure	Composition in mole percent Methane
	Lbs/sq. in. Absolute	
195.5	766	10
159.5	1018	30
115.3	1290	50
100	1365	57

Critical Data for the Methane-Propane-n-Pentane System

Tem. °F.	Pressure	Composition in mole percent		
	Lbs/sq. in. Absolute	Methane	Propane	Pentane
100	1500	60.5	35.0	4.5
100	2000	71.0	15.0	14.0

* Reference 5

Bibliography

1. Souders, Selheimer and Brown, Ind. Eng. Chem., 24, 517 (1932)
2. Podbielniak, Ibid., 25, 119 (1933)
3. Katz and Brown, Ibid., 25, 1373 (1933)
4. Katz and Hachmuth, Ibid., 29, 1072 (1937)
5. Sage, Lacey, and Schaafsma, Ibid., 26, 214 (1934)
6. Sage, Webster and Lacey, Ibid., 28, 1045 (1936)
7. Boomer, Johnson and Piercey, Canadian Journal of Research, 16,
319, (1938)
8. Boomer and associates, Ibid., 16, 328 (1938)
9. Boomer and associates, Ibid., 15, 363 (1937)
10. Boomer and associates, Ibid., 15, 367 (1937)

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