The Phase Behavior of the Methane-

Propane-n-Pentane System

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Abstract

The composition of the coexisting gas and liquid phases in the ternary system consisting of methane, propane, and normal pentane was determined at 100° F. and at pressures of 200, 500, 1000, 1500, and 2000 pounds per square inch. From these data the values of the equilibrium constants for methane, propane, and pentane were calculated.

The actual phase behavior of the ternary system is compared to the phase behavior predicted from Raoult's Law and to the predictions made from a correlation of previously available data.

Introduction

Knowledge of the phase behavior of hydrocarbon mixtures is of value in the production and refining of petroleum. It is of great importance to be able to predict with engineering accuracy the properties of these hydrocarbon mixtures both in design of new processes and in the operation of existing ones.

The use of gas-liquid equilibrium constants has been found convenient in the prediction of the composition of coexisting phases. The so-called equilibrium constants is defined as the ratio of the mole fraction of a component in the gas phase to the mole fraction of the same component in the liquid phase. Expressed as an equation this definition becomes:

$$K = \frac{y}{x}$$

where K = equilibrium constant

y = mole fraction in gas phase

x = mole fraction in liquid phase

In the absence of experimental data, equilibrium constants have been formulated on the basis of various assumptions. The most common assumption made is that the system follows the law of ideal solutions. "The ideal solution is one in which the fugacity of each component is proportional to the mole fraction of that component at every pressure and temperature." (1) Moreover it should be realized that the fugacity of a component in a mixture is proportional to the fugacity of the pure component at the same temperature and pressure and in the same kind of phase.

The fugacity of a component may be defined as follows:

$$b_k T \ln f_k = \mu_k + B$$

Differentiating with respect to pressure at constant temperature;

$$b_k T \left(\frac{\partial \ln f_k}{\partial P} \right)_T = \left(\frac{\partial \mu_k}{\partial P} \right)_T = \bar{V}_k$$

Integrating

$$b_k T \ln \frac{f_k}{f_{0k}} = \int_0^P \bar{V}_k \, dP$$

But from consideration of kinetics

$$\bar{S}_{0k} = S_{0k}^{\circ} + b_k \ln m_k$$

The above equation applies at infinite attenuation

$$\mu_k = \bar{E}_k + P\bar{V}_k - T\bar{S}_k$$

Hence

$$\mu_{0k} = E_{0k}^{\circ} + P_0 V_{0k}^{\circ} - T S_{0k}^{\circ} + T b_k \ln m_k$$

$$\mu_{0k} = b_k T \ln m_k + \mu_{0k}^{\circ}$$

Hence

$$b_k T \ln f_{0k} = b_k T \ln m_k + b_k T \ln f_{0k}^{\circ}$$

$$f_{0k} = m_k f_{0k}^{\circ}$$

$$b_k T \ln \frac{f_k}{m_k f_{0k}^{\circ}} = \int_0^P \bar{V}_k \, dP$$

$$\bar{V}_k = \frac{b_k T}{P} - \underset{\sim}{\bar{V}}_k$$

$$b_k T \ln \frac{f_k}{m_k f_{0k}^{\circ}} - b_k T \ln \frac{P}{P_0} = - \int_0^P \underset{\sim}{\bar{V}}_k \, dP$$

Since $\quad f_{0_k}^0 = P_0$

$$\ln f_k = \ln n_k P - \frac{1}{6_k T} \int_0^P \tilde{V}_k \, dP$$

For pure substance when $n_k = 1$

$$\ln f_k^0 = \ln P - \frac{1}{6_k T} \int_0^P \tilde{V}_k \, dP$$

Assuming ideal solutions

$$\ln f_k = \ln f_k^0 + \ln n_k$$

$$\ln f_k = \ln f_k^0 + \ln n_k = -\frac{1}{6_k T} \int_0^P \tilde{V}_k \, dP + \ln n_k P$$

$$\ln f_k^0 = \ln P - \frac{1}{6_k T} \int_0^P \tilde{V}_k \, dP$$

Hence if Law of Ideal Solutions applies

$$-\frac{1}{6_k T} \int_0^P \tilde{V} \, dP + \ln P = -\frac{1}{6_k T} \int_0^P \tilde{V}_k \, dP + \ln P$$

Thus if the assumption of Ideal Solutions is to be valid, the partial specific volume must equal the specific volume over the pressure range from infinite attenuation to the pressure in question.

For two phases in equilibrium we may write:

$$d u_{k g} = d u_{k l}$$

Limiting the process to an isothermal one

$$u_k = \phi \left(P, n_i, n_{m-1} \right)$$

Since at infinite attenuation

$$f_{ok} = \underline{m}_k f_{ok}^{\circ}$$

$$b_k T \ln \underline{m}_k + b_k T \ln f_{ok}^{\circ} = \mu_{ok} + \beta$$

$$u_k = b_k T \ln \underline{m}_k + \alpha + \int_0^P \bar{V}_k \, dP$$

$$d u_k = \left(\frac{\partial u_k}{\partial P}\right)_{T,m} dP + \sum_{i=1}^{i=m-1} \left(\frac{\partial u_k}{\partial \underline{m}_i}\right)_{T,P} d\underline{n}_i$$

Where

$$\left(\frac{\partial u_k}{\partial P}\right)_{T,n} = \bar{V}_k$$

$$\sum_{i=1}^{i=m-1} \left(\frac{\partial u_k}{\partial \underline{m}_i}\right)_{T,P} d\underline{n}_i = \sum_{j=1}^{j=m-1} \left(\frac{\partial \bar{V}_k}{\partial \underline{m}_i}\right)_{T,P} d\underline{n}_i + \frac{b_k T}{\underline{m}_k} \sum_{i=1}^{i=m-1} \left(\frac{\partial \underline{m}_k}{\partial \underline{m}_i}\right)_{T,P} d\underline{n}_i$$

But for ideal solutions it has been shown that

$$\left(\frac{\partial \bar{V}_k}{\partial \underline{m}_i}\right)_{T,P} = 0$$

Also

$$\sum_{i=1}^{i=m-1} \left(\frac{\partial \underline{m}_k}{\partial \underline{m}_i}\right)_{T,P} d\underline{n}_i = d\underline{m}_k$$

Hence

$$d u_k = V \, dP + \frac{b_k T}{\underline{m}_k} d\underline{m}_k$$

Since

$$d u_{kg} = d u_{kl}$$

$$V_{kg} \, dP + b_k T \, d \ln Y = V_{kl} \, dP + b_k T \, d \ln X$$

$$\frac{d \ln k}{dP} = \frac{1}{b_k T} (V_{kl} - V_{kg})$$

When P is the vapor pressure of the pure component K = 1

$$\ln K_k = 1 + \frac{1}{b_k T} \int_{p=}^{p} (V_{kl} - V_{kg}) dP$$

Thus it is seen that for ideal solutions, the equilibrium constant is independent of the nature and amount of the other components of the system.

When volumetric data are lacking the still more simplifying assumption of Raoult's Law can be made.

Considering an isothermal process for two phases in equilibrium we may write as before

$$d u_{kg} = d u_{kl}$$

$$u_k = \phi(P, \underline{n_i}, \underline{n}_{n-1})$$

Since at infinite attenuation

$$f_{ok} = \underline{n}_k f^{\circ}_{ok}$$

$$b_k T \ln \underline{n}_k + b_k T \ln f^{\circ}_{ok} = u_{ok} + \beta$$

$$u_{ok} = b_k T \ln \underline{n}_k + \alpha$$

$$u_k = b_k T \ln \underline{n}_k + \alpha + \int_0^p \bar{V}_k dP$$

$$\left(\frac{\partial u_k}{\partial \underline{m_i}}\right)_{T,P,n_i} = b_k T \left(\frac{\partial \ln \underline{n}_k}{\partial \underline{m_i}}\right)_{T,P} + \int_0^p \left(\frac{\partial \bar{V}_k}{\partial \underline{m_i}}\right)_{T,P,n_i} dP$$

Assuming additive volumes

$$\int_0^p \left(\frac{\partial \bar{V}_k}{\partial \underline{m_i}}\right)_{T,P,n_i} dP = 0$$

Hence

$$d\mu_k = \bar{V}_k \, dP + \frac{b_k T}{n_k} \sum_{i=1}^{i=n-1} \left(\frac{\partial n_k}{\partial n_i}\right)_{T,P,n_j} dn_i$$

$$\sum_{i=1}^{i=n-1} \left(\frac{\partial n_k}{\partial n_i}\right)_{T,P,n_j} dn_i = dn_k$$

$$d\mu_k = \bar{V}_k \, dP + \frac{b_k T}{n_k} \, dn_k = \bar{V}_k \, dP + b_k T \, d\ln n_k$$

since $\quad d\mu_{kg} = d\mu_{kl}$

$$\bar{V}_{kg} \, dP + b_k T \, d\ln Y = \bar{V}_{kl} \, dP + b_k T \, d\ln X$$

Neglecting volume of the liquid

$$\bar{V}_{kl} \, dP = 0$$

Assuming the gas phase obeys the laws of perfect gases

$$d\ln k_k = -d\ln P$$

When the pressure is equal to the vapor pressure of component K, the equilibrium constant is unity

Thus

$$\ln k_k = \ln \frac{P^\circ}{P}$$

$$K = \frac{P^\circ}{P}$$

Assuming Raoult's Law involves the assumption of additive volumes, neglects the volume of the component in the liquid phase, and assumes the gas phase behaves as a perfect gas.

Souders, Selheimer, and Brown (2) in the absence of adequate data, predicted the phase behavior of hydrocarbon mixtures on the assumption of ideal solutions. More recently investigations have been made to determine experimentally the compositions of coexisting phases. Katz and Hachmuth (3) determined experimentally the equilibrium constants for the paraffinic hydrocarbons from hexane through methane for a crude oil-natural gas mixture throughout a pressure range from atmospheric pressure to above 3000 pounds per square inch for temperatures of from 40° F. to 200° F. They found that as the pressure increased the equilibrium constants of all components except methane decreased until a minimum value less than unity was reached. With further increase in pressure the equilibrium constants increased. The equilibrium constants for methane decreased continuously with increasing pressure.

W. B. Kay (4) has published data on the Ethane-n-Butane system and on the Ethane-n-Heptane system. He found that at pressures less than 200 pounds per square inch and at temperatures less than 200° F. the experimental results were in fair agreement with the predictions made from the assumption of ideal solutions. However, as the critical state was approached the deviations from ideal solutions became large.

Boomer and his associates (5) have published a series of papers on the solubility of methane in various hydrocarbons. The values obtained are in fair agreement with the values determined by Katz and Hachmuth at lower pressures.

The present work is a study of the phase behavior of the ternary system consisting of methane, propane, and n-pentane at pressures of 200, 500, 1000, 1500, 2000 pounds per square inch at a temperature of 100° F. Equilibrium constants were calculated for the coexisting phases over the possible ranges in composition.

Equilibrium Apparatus

The methods and apparatus employed in this study are similar to those used by Taylor, Wald, Sage, and Lacey (6) in their study of the methane-n-pentane system. Since they are described in some detail in their publication only a brief resume will be given here.

In principle the method is to bring to equilibrium in a suitable chamber various proportions of methane, propane, and pentane so that two phases exist, and then remove samples of the gas and liquid phases for analysis without disturbing the equilibrium.

Referring to figure 1, the equilibrium cell (A) was maintained at a constant temperature by use of an agitated oil bath (H). Equilibrium was obtained by means of a mechanically driven agitator which entered the cell through a packing gland (G). The mercury pump (K) was used to pump the gaseous hydrocarbons from the storage tank (J) into the equilibrium cell. Cylinder (B) was connected to a source of high pressure air to force mercury to the various parts of the system. A fluid pressure balance (D) connected to the equilibrium cell through a mercury-oil trap (C) measured the pressure within the cell.

The approximate levels of the mercury in the cell and pump were determined by the use of electrical contacts (E, F, L, M, N). Two nickel resistances (V, W) served to determine the position of the interface between the gas and liquid phases. Advantage was taken of the fact that the rate of heat dissemination from a wire to a liquid phase is greater than from a wire to a gas phase. The potential across each was determined when a small current was passed through the two

wires in series. The ratio of these potentials, as determined by means of a potentiometer, was nearly independent of pressure and temperature as long as both were in the same phase. However, when they were in different phases, the ratio was changed because of the difference in temperature of the two wires. These two stationary indicators gave a sufficient indication of the location of the gas-liquid interface.

Operation of Equilibrium Cell

After the liquid pentane was poured into the cell and the top was replaced, the cell was connected to the vacuum system and pentane vapor removed to sweep out all traces of air. The propane and methane were then added through the gas injection chamber.

After the desired amounts of hydrocarbons were added, the liquid level was adjusted to the desired position and the oil bath and cell were brought up to temperature. The agitator was then set in motion until the pressure remained constant at the desired value. Small adjustments in pressure were made by the addition or withdrawal of mercury through valve (S). After the two phases were in equilibrium, ascertained by the pressure remaining constant, the gas and liquid samples were throttled directly into the analytical apparatus by means of valves (R, T).

The one change in the apparatus and operation thereof, as described by Taylor, Wald, Sage, and Lacey (6), is the replacement of the needle valves on the gas and liquid sample lines by specially designed throttle valves built directly into the wall of the equilibrium cell. Previously the valve on the liquid sample line had been placed outside of the oilbath.

The line connecting the valve and the cell was filled with mercury before and after the withdrawal of the liquid sample. Also the steel tubing of the liquid sample line was steam jacketed to insure complete vaporization and complete recovery of the liquid sample.
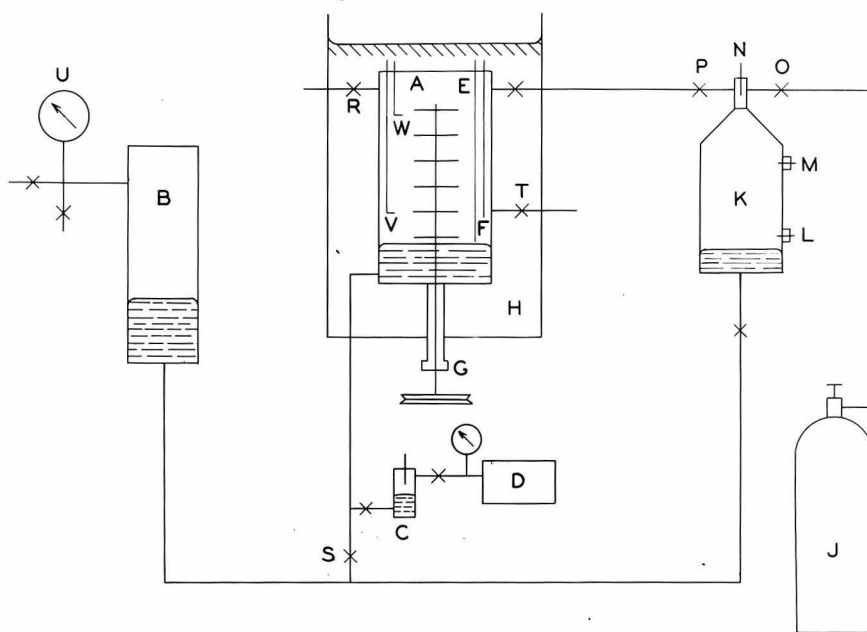
Figure 1. Equilibrium Apparatus

Materials Used

The methane used was obtained from the Buttonwillow Field in California and originally contained one tenth of one per cent ethane and heavier hydrocarbons and three tenths of one per cent carbon dioxide. That the amount of nitrogen and other non-condensable gases present was negligible has been indicated by combustion analysis on similar samples.

The methane was then passed through calcium chloride, activated charcoal, ascarite, and sodium hydroxide at pressures of two hundred to five hundred pounds per square inch. The methane was then believed to contain less than two tenths of one per cent impurities.

The propane and normal pentane used were recovered from mid-continent crudes by the Phillips Petroleum Company. Their analysis of the propane showed less than two tenths of one per cent impurities.

Their analysis of the n-pentane showed it to contain from two to five tenths of one per cent iso-pentane.

Analytical Apparatus

For the analysis of the hydrocarbon samples, two low-pressure, low-temperature fractionating columns of the type developed by Podbielniak and associates (7) were used. The column used for the analysis of the gas sample was constructed from a pyrex glass tube six millimeters outside diameter and 50 inches long, which was enclosed in a silvered vacuum jacket. To obtain maximum efficiency with large capacity and small hold-up of liquid, a flat strip of nichrome formed

into a helicalcoil was found to be superior to the standard wire packings.

Reflux in the column was obtained by injecting liquid air into a small chamber at the top of the column. This chamber was an extension of the vacuum jacket and was filled with copper turnings to promote heat transference from the condenser. This chamber also contained a 50 watt heater to facilitate the heating of the chamber during the removal of pentane.

The column used for the analysis of the liquid sample was shorter than the gas sample column and was constructed from a 36-inch length of eight millimeter outside diameter pyrex tubing. The temperature of the reflux in each column was measured by a thermocouple contained in a narrow glass tube. This tube was sealed into the column by a ground glass stopper at the top and extended down the column to a point just below the condenser.

The glass kettles were connected directly to the columns by the use of ring seals. The kettles were equipped with a sample inlet near the top and with a capillary inlet at the bottom for the introduction of samples not readily volatilized. Samples were throttled directly from the equilibrium cell into the columns through the above described sample inlets.

During fractionation of the samples, the separated constituents were collected in receiving flasks having capacities of 2000, 500, and 200 milliliters. These receiving flasks were immersed in an oil bath, the temperature of which was maintained at a fixed point by the use of a mercury regulator.

All parts of the apparatus including the equilibrium cell and column jackets were connected to a vacuum header. The vacuum was produced by a mercury vapor pump in series with a Hyvac pump.

Calibration of Apparatus

The volumes of the columns, collecting flasks, and connecting lines, were determined by allowing air to flow from a calibrated flask to various parts of the apparatus and then noting consequent changes in pressure and temperature. From four to six measurements were made on each volume. Assuming perfect gas behavior for the air it was found that the maximum deviation of any one measurement from the mean was five tenths of one per cent.

Operation of Fractionating Apparatus

After adequate evacuation of all necessary parts of the apparatus was attained, the samples were throttled into the kettles of the apparatus. The gases were condensed in the kettles by having the latter immersed in liquid air. The average size of the sample withdrawn was 25 milliliters. Somewhat larger amounts were withdrawn when the sample contained only a small amount of any one constituent.

The top of the column was then cooled to the reflux temperature of the most volatile component, which was methane in this case. When the reflux just wetted the packing in the entire length of the column, gas was withdrawn at the rate of 40 milliliters per minute.

The pressure in the column was maintained at one atmosphere for propane and methane and reduced to one half atmosphere when pentane was being withdrawn. When the separation, or "cut", between two components was reached the column was closed in and operated at infinite reflux for short periods to insure complete separation of the lighter component.

The collecting-flask pressure at the cut point was determined by plotting flask pressure against reflux temperature and selecting the pressure such that the area under the curve was equal to that above.

Experimental Results

The experimental results obtained in this study are given in Table I. These results and those obtained by Wald (8) in his study of the methane-propane-pentane system are presented in figures 2-6. The compositions of coexisting phases are plotted on constant temperature, constant pressure planes. The equilibrium constants calculated from these data are shown in Table II.

An examination of figures 2-6 shows that at pressures less than 1000 pounds per square inch the liquid composition lines are nearly straight while the gas phase composition lines have slightly more curvature. At pressures lower than about 500 pounds per square inch the methane content of the liquid phase decreases with increasing propane content while at higher pressures the reverse is true.

As a measure of the variation of the equilibrium constants with composition, the equilibrium constants for methane, propane, and pentane at the various pressures investigated are plotted versus the per cent propane in the propane-pentane content of the liquid phase, figures 7-9.

The erratic variation in the equilibrium constants for methane at the pressure of 200 pounds per square inch is to be attributed to the errors involved in determining small amounts of methane in the liquid phase.

The plots for methane show that as the average molecular weight of the system increases, the equilibrium constant for methane increases. The reverse is true for pentane. The equilibrium constant increases rapidly as the composition approaches the critical composition for the

temperature and pressure in question. The variation of the equilibrium constant for propane is less decided. On those pressure-temperature planes where a critical state exists, the equilibrium constants change rapidly and reach unity at the critical state.

Figure 11 is a plot of the product of the equilibrium constant and pressure versus pressure at 100° F. for various percentages of propane in the propane-pentane content of the liquid phase. This plot shows graphically the variation in the equilibrium constant with composition at constant temperature and pressure. The curves are extrapolated to the vapor pressure of the less volatile components at low pressures and to equilibrium constants of unity corresponding to critical state at high pressures.

As an indication of the variation of the experimentally determined equilibrium constants from those predicted from a correlation of published data, Figure 10 is a plot of the ratio of the experimental values of the equilibrium constants to those predicted by Sage, Hicks, and Lacey (9). The correlated values of K for methane were chosen for a less volatile component of molecular weight of 60 and a viscosity-gravity factor of 0.82. These values are compared to the equilibrium constants of methane for a constant composition of 40 per cent propane in the propane-pentane content of the liquid phase. Examination of the plot shows the predicted values for methane are consistently high. This disagreement is due to the effect of the difference in the viscosity-gravity factor between the system considered by Sage, Hicks, and Lacey and the system under consideration in this paper. The values predicted for propane are low and the deviation increases with increasing pressure. The deviation at high pressures is due to the fact that the methane-propane-pentane is

approaching the critical state and the equilibrium constants are approaching unity. The constants for pentane show large deviations probably because the correlated values were for mixtures of higher average molecular weight.

Figure 12 is a comparison of the experimental values to those predicted by Raoult's Law. The exceedingly large deviations at high pressures are seen to become as much as 1000 per cent for pentane at pressures near the critical pressure.

Summary

The compositions of the coexisting phases for the methane-propane-pentane system were determined for a temperature of 100° F. and for pressures of 200, 500, 1000, 1500, 2000 pounds per square inch. The equilibrium constants for each of the components were calculated from these data and were found to be a function of the total composition of the system as well as a function of the temperature and pressure.

The experimental values were found to deviate considerably from the values predicted from correlated data at the temperature and pressure at which a critical state existed. Deviations from Raoult's Law were found to be large and increased with increasing pressure.

Acknowledgment

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Nomenclature

P pressure in pounds per square inch

T temperature, degrees Rankine

V volume, specific volume, cubic feet per pound

$\overline{V}$ partial volume, partial specific volume, cubic feet per pound

$\underset{\sim}{V}$ residual volume, cubic feet

$\underset{\sim}{\overline{V}}$ residual partial volume, cubic feet per pound

E internal energy, specific internal energy, B.t.u. per pound

$\overline{E}$ partial specific internal energy, B.t.u. per pound

S entropy, specific entropy, B.t.u. per pound per degree Rankine

$\overline{S}$ partial specific entropy, B.t.u. per pound per degree Rankine

F free energy, specific free energy, B.t.u. per pound

$\overline{F}$ partial specific energy, B.t.u. per pound

u_K chemical potential of component K in a phase

X_K mole fraction of component K in a liquid phase

Y_K mole fraction of component K in a gas phase

$\underline{n}_K$ mole fraction of a given constituent in a system as a whole

b gas constant, per pound, $b = \dfrac{R}{M}$

K_K equilibrium constant of component K, $K_K = \dfrac{Y_K}{X_K}$

Subscripts

  0 infinite attenuation

  K component K

  i any component

  j all components except components i, K, n

Superscripts

  0 pure substance

Table I

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

200 pounds per square inch absolute

	Methane	Propane	Pentane	Methane	Propane	Pentane
Gas	31.32	63.39	5.28	20.18	75.78	4.04
Liquid	2.77	63.32	33.91	1.53	78.38	20.10
K	11.3	1.00	.156	13.2	.967	.201
Gas	66.57	25.16	8.27	86.96	3.60	9.44
Liquid	4.57	25.26	69.17	5.89	3.79	90.32
K	14.6	.958	.120	14.8	.950	.105

500 pounds per square inch absolute

	Methane	Propane	Pentane	Methane	Propane	Pentane
Gas	60.70	37.35	1.95	75.46	21.83	2.71
Liquid	13.55	74.34	12.11	13.93	44.57	41.50
K	4.48	.502	.161	5.42	.490	.065

1000 pounds per square inch absolute

	Methane	Propane	Pentane	Methane	Propane	Pentane
Gas	71.56	26.15	2.26	72.33	25.66	2.01
Liquid	30.63	58.92	10.45	31.11	54.79	14.10
K	2.34	.444	.216	2.32	.468	.144

1500 pounds per square inch absolute

	Methane	Propane	Pentane	Methane	Propane	Pentane
Gas	53.31	40.62	6.06	81.15	14.51	4.34
Liquid	53.31	40.62	6.06	46.89	28.88	24.23
K	1.00	1.00	1.00	1.73	.520	.172
Gas	81.05	14.53	4.42			
Liquid	46.82	29.87	23.30			
K	1.73	.502	.179			

Table II

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	53.05	34.45	7.50	82.39	7.77	9.84	89.46	10.54
Liquid	0.3	99.7	4.23	37.44	58.33	5.71	9.60	84.69	6.39	93.61
K	14.3	0.96	13.73	0.92	0.128	14.4	0.81	0.116	14.0	0.113
500 pounds per square inch absolute										
Gas	51.6	46.4	79.62	16.34	4.04	89.49	5.40	5.10	93.91	6.09
Liquid	12.0	88.0	14.71	32.43	52.87	15.57	10.48	73.95	15.69	84.31
K	4.3	0.549	5.40	0.504	0.0765	5.75	0.515	0.069	5.98	0.072
1000 pounds per square inch absolute										
Gas	64.1	35.9	87.07	8.79	4.14	92.2	3.57	4.23	94.85	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			56.16	8.54	5.30	91.84	2.98	51.77	94.12	5.88
Liquid			45.37	18.75	35.88	44.60	6.80	48.60	41.59	58.41
K			1.90	0.455	0.1476	2.055	0.438	0.106	2.27	.101
2000 pounds per square inch absolute										
Gas			79.88	9.66	10.46	87.55	4.18	8.27	91.67	8.35
Liquid			63.13	14.90	21.97	60.02	6.63	33.35	56.06	44.94
K			1.26	0.648	0.476	1.46	0.631	0.248	1.66	0.185

* Reference No. 6

** Reference No. 8

Table III

Equilibrium Constants at Constant Ratios

of Propane to Pentane

Mole percent propane of the propane-pentane content of the liquid phase

K for methane

Pressure Lbs./sq.in. Absolute	20%	40%	60%	80%
200	14.3	14.3	14.3	14.3
500	5.63	5.30	4.97	4.28
1000	2.92	2.73	2.60	1.99
1500	1.97	1.90	1.67	
2000	1.40	1.20	1.00	

K for propane

	20%	40%	60%	80%
200	.950	.955	.961	.966
500	.509	.495	.488	.497
1000	.407	.402	.408	.437
1500	.431	.447	.564	
2000	.628	.650	.822	

K for pentane

	20%	40%	60%	80%
200	.119	.128	.148	.246
500	.068	.070	.086	.178
1000	.077	.090	.113	.233
1500	.144	.138	.196	
2000	.263	.462		

Figure 2

Methane–Propane–Pentane System

Temperature 100 °F

Pressure 200 Lb. In^{-2}
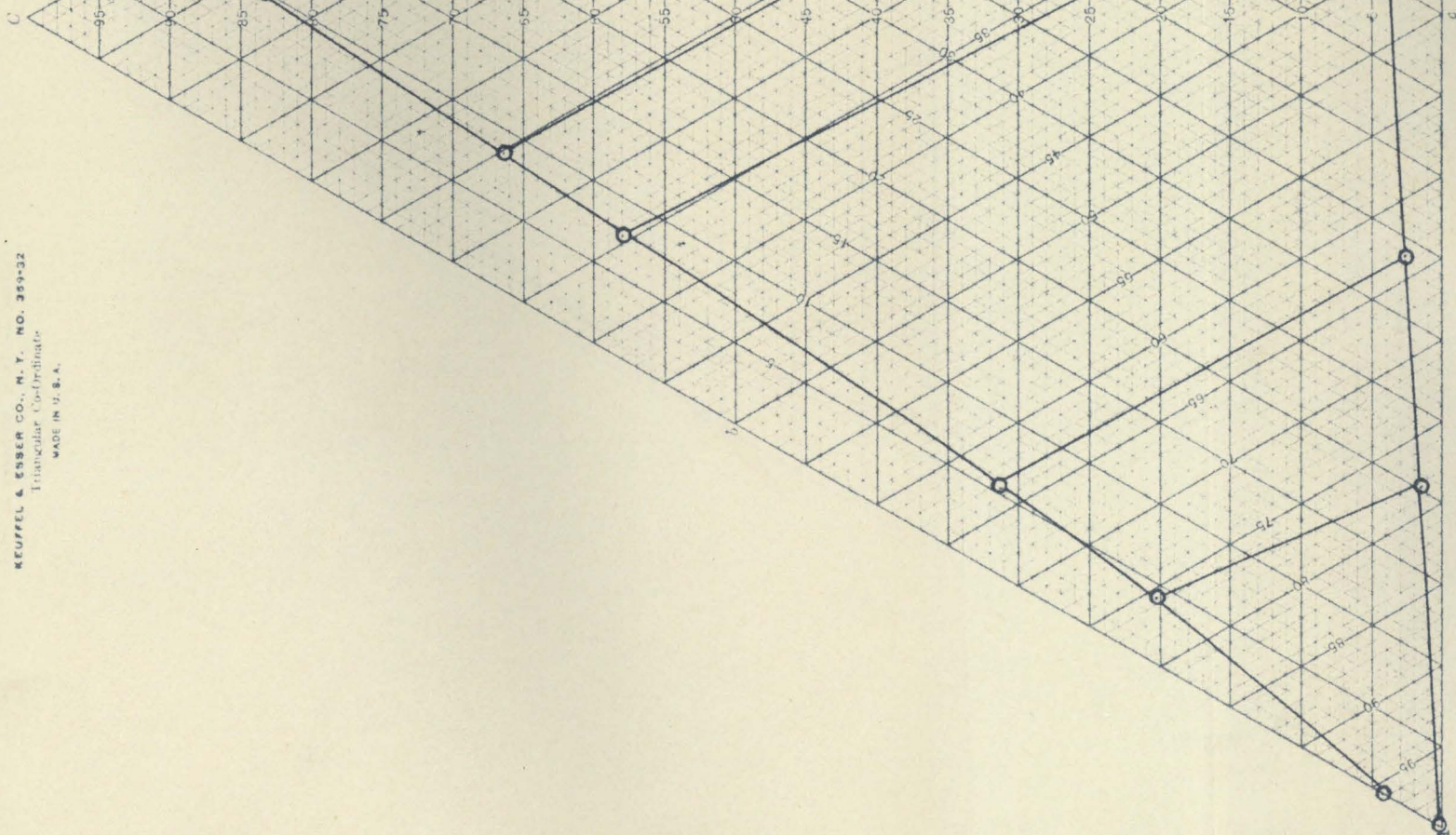
Figure 3

Methane–Propane–Pentane System

Temperature 100° F

Pressure   500 Lb. In.$^{-2}$
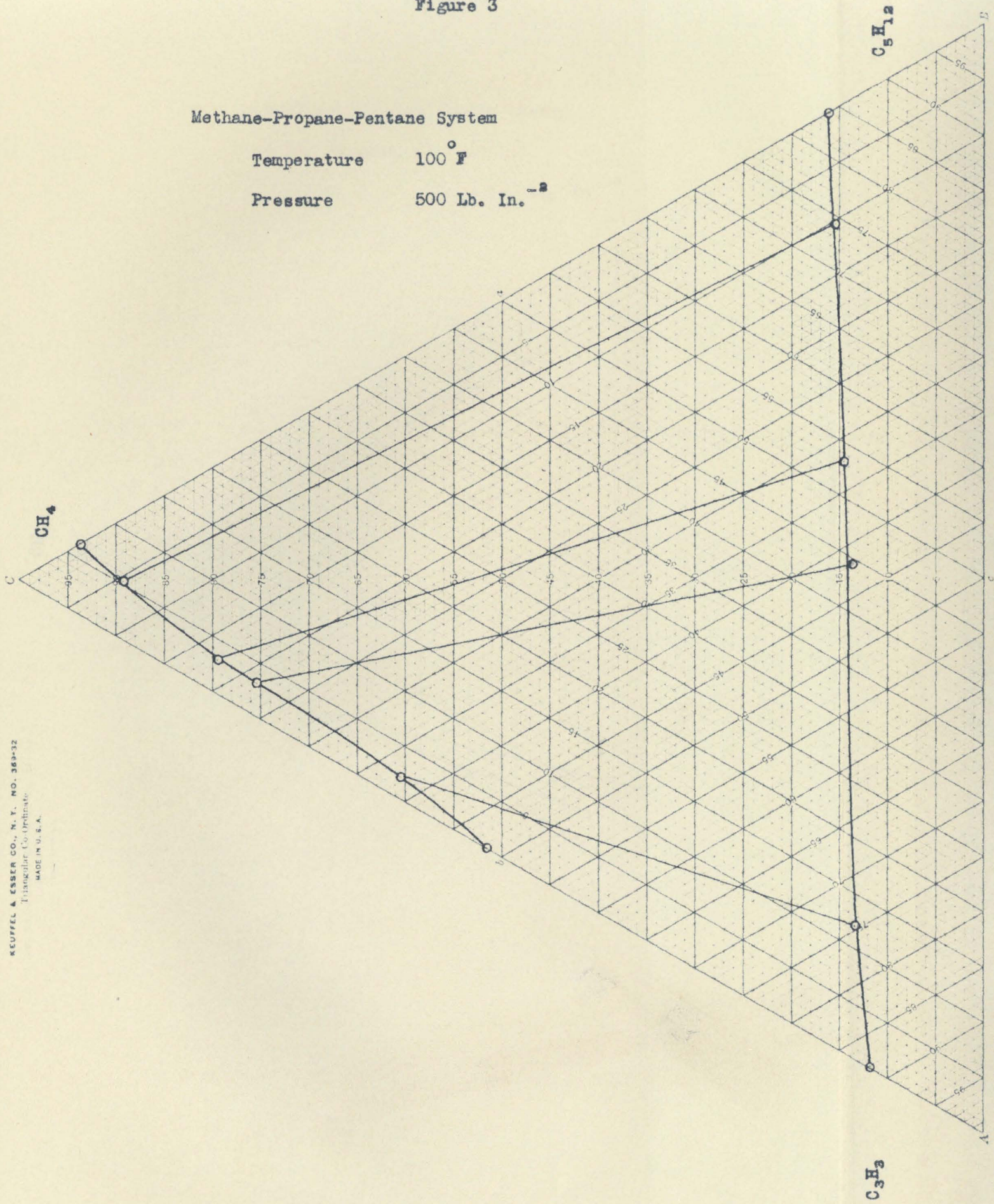
Figure 4

Methane–Propane–Pentane System

Temperature   100 $^{\circ}$F

Pressure   1000 Lb. In.$^{-2}$
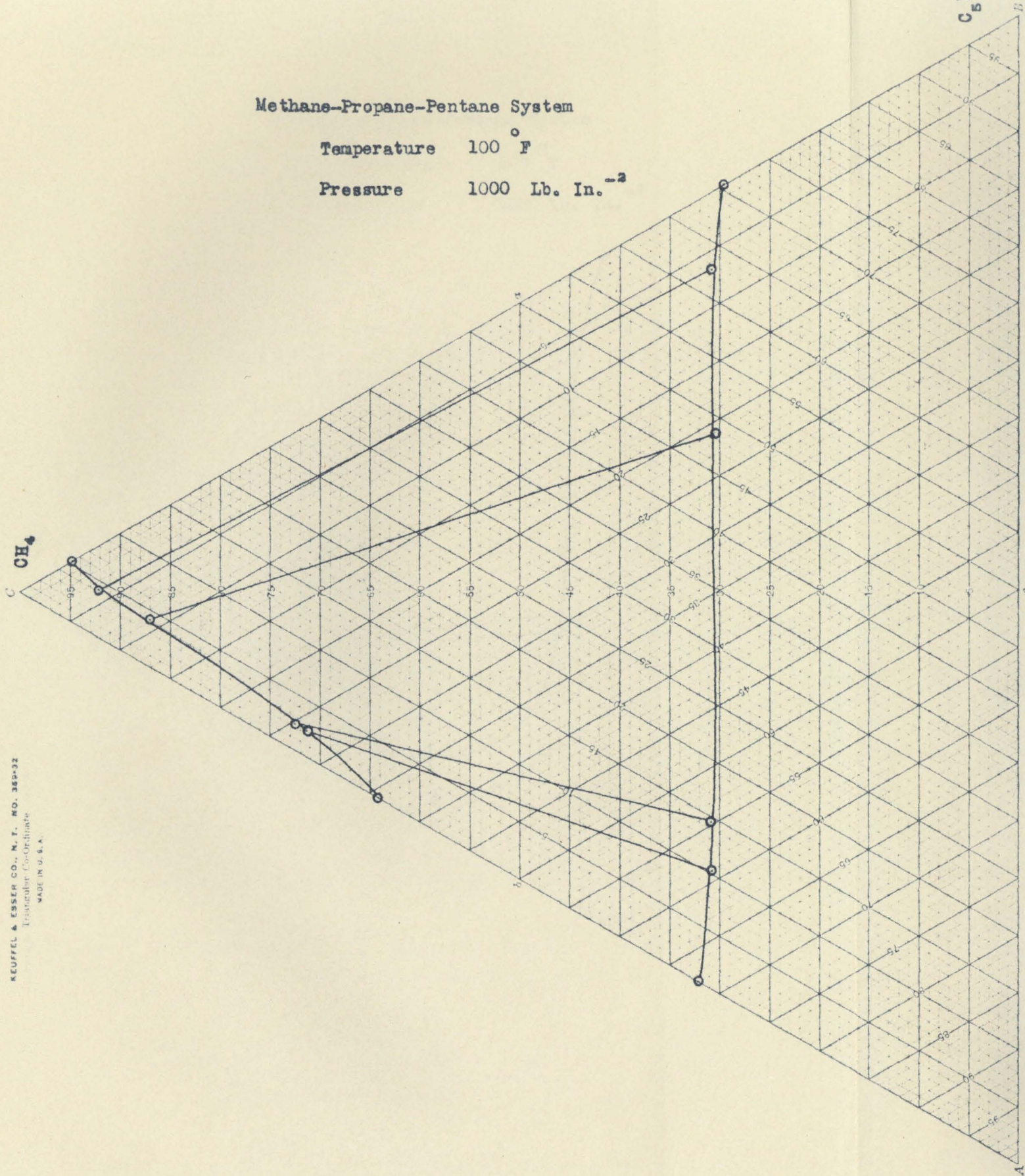
Figure 5

Methane-Propane-Pentane System

Temperature 100 °F

Pressure 1500 Lb. In.⁻²
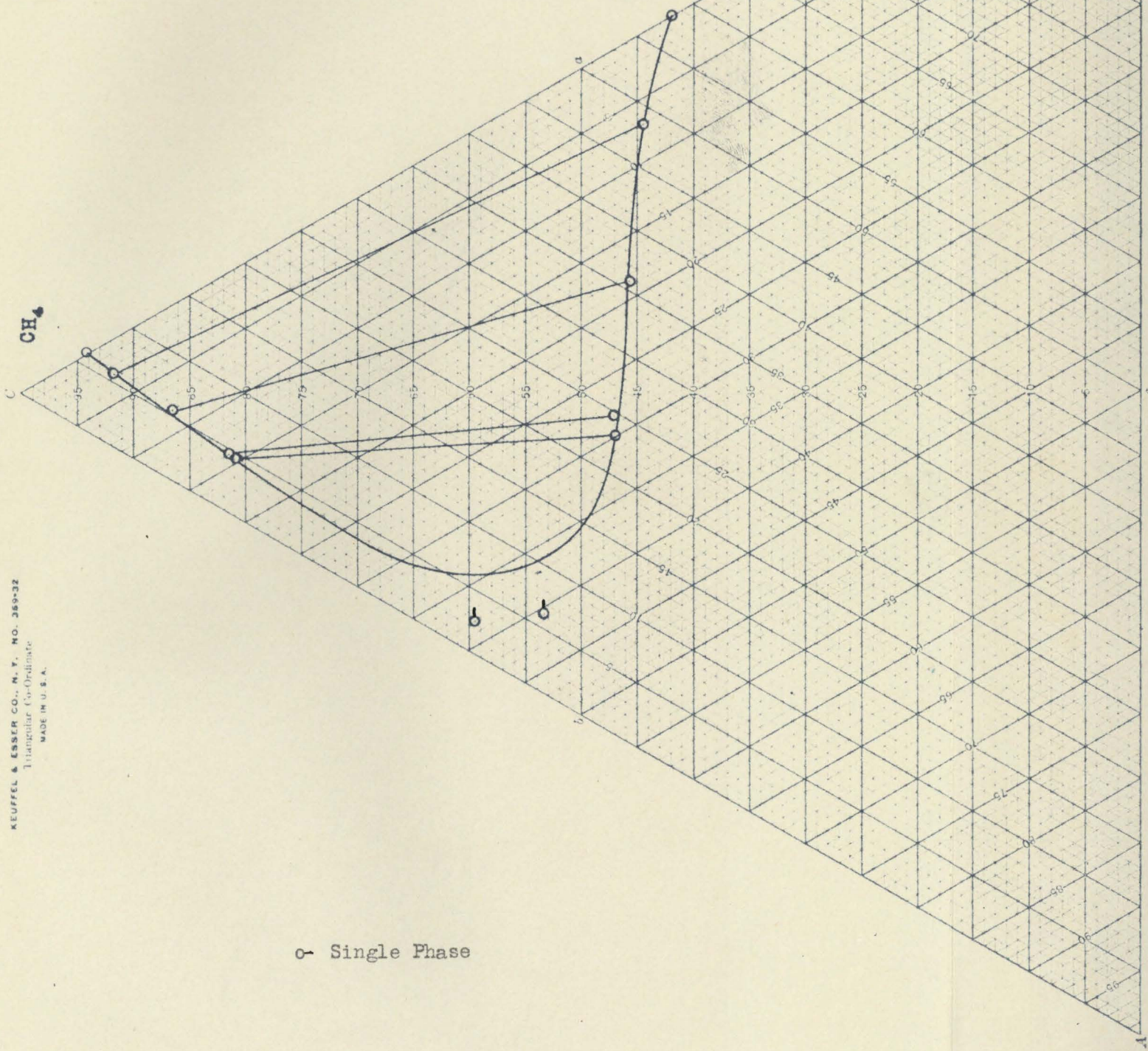
o— Single Phase

Figure 6

Methane-Propane-Pentane System

Temperature 100 °F

Pressure 2000 Lb. In.$^{-2}$
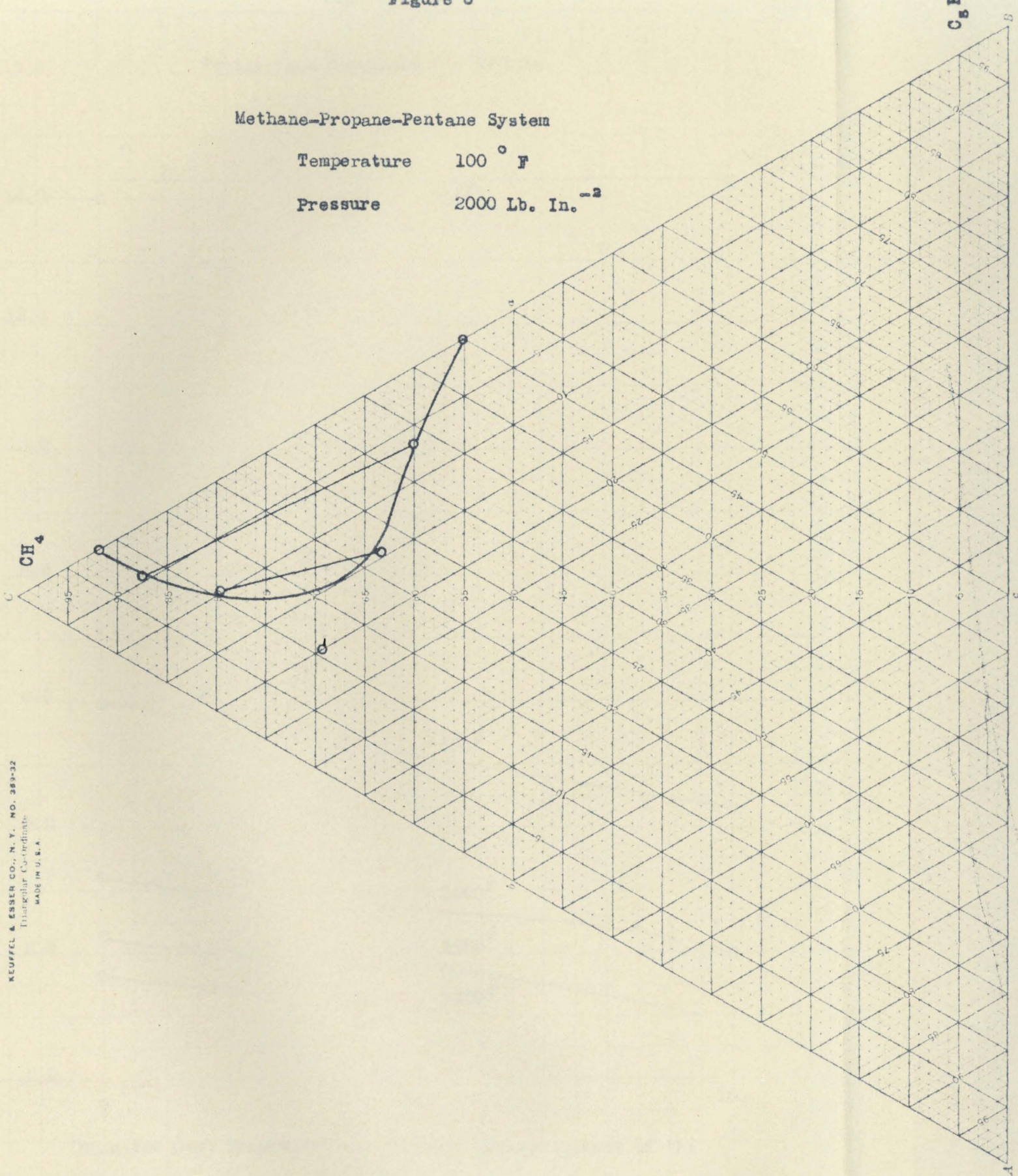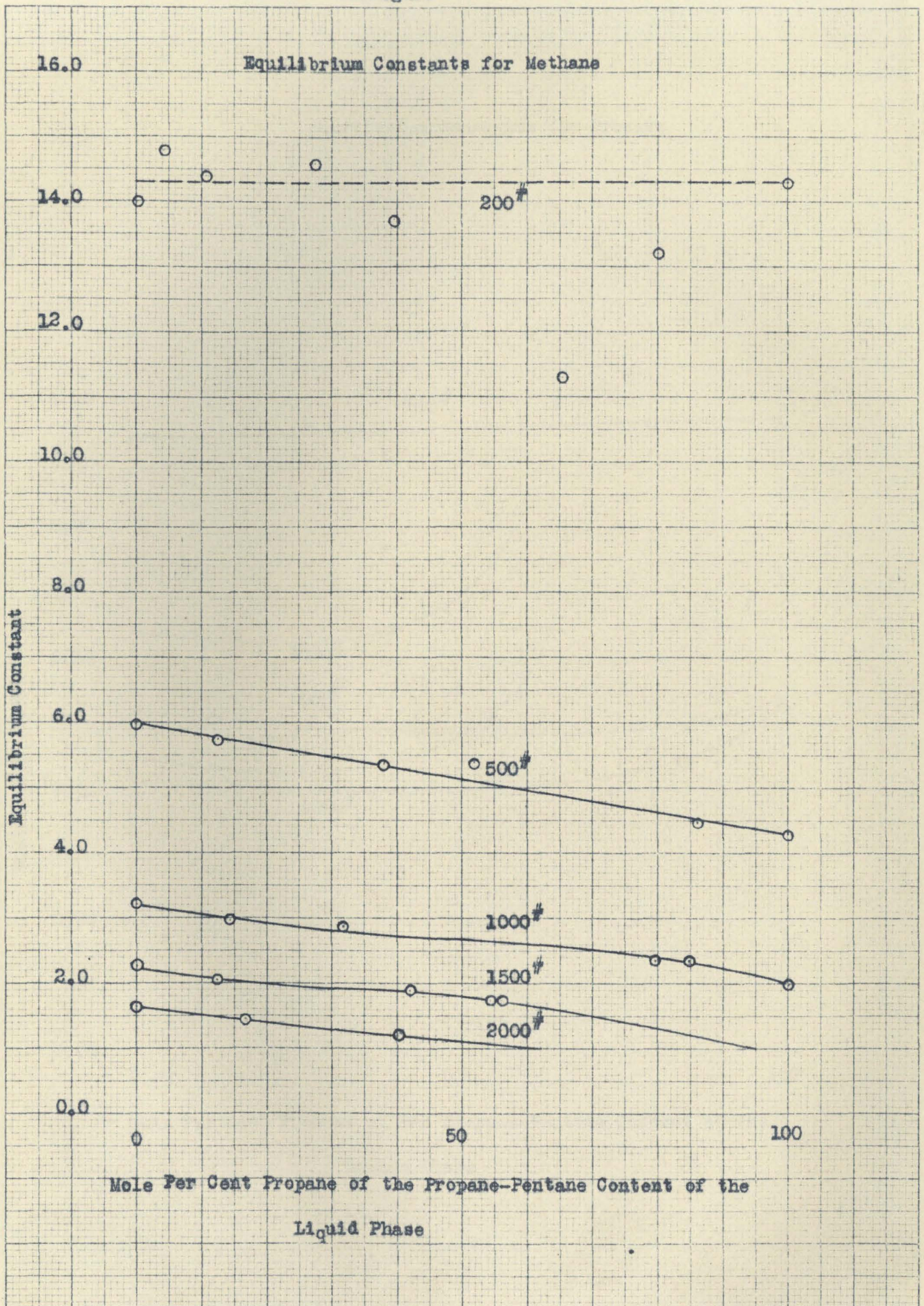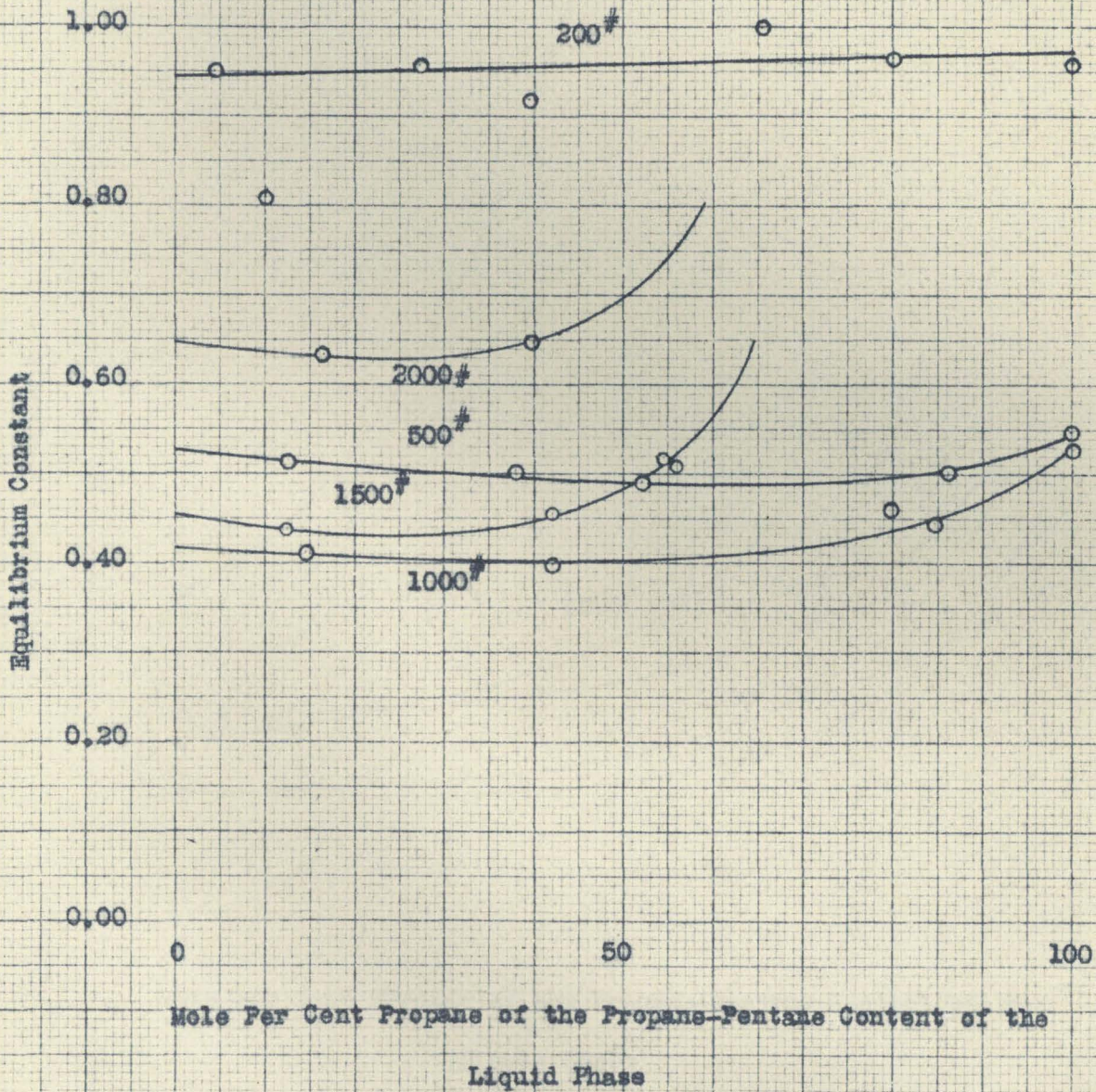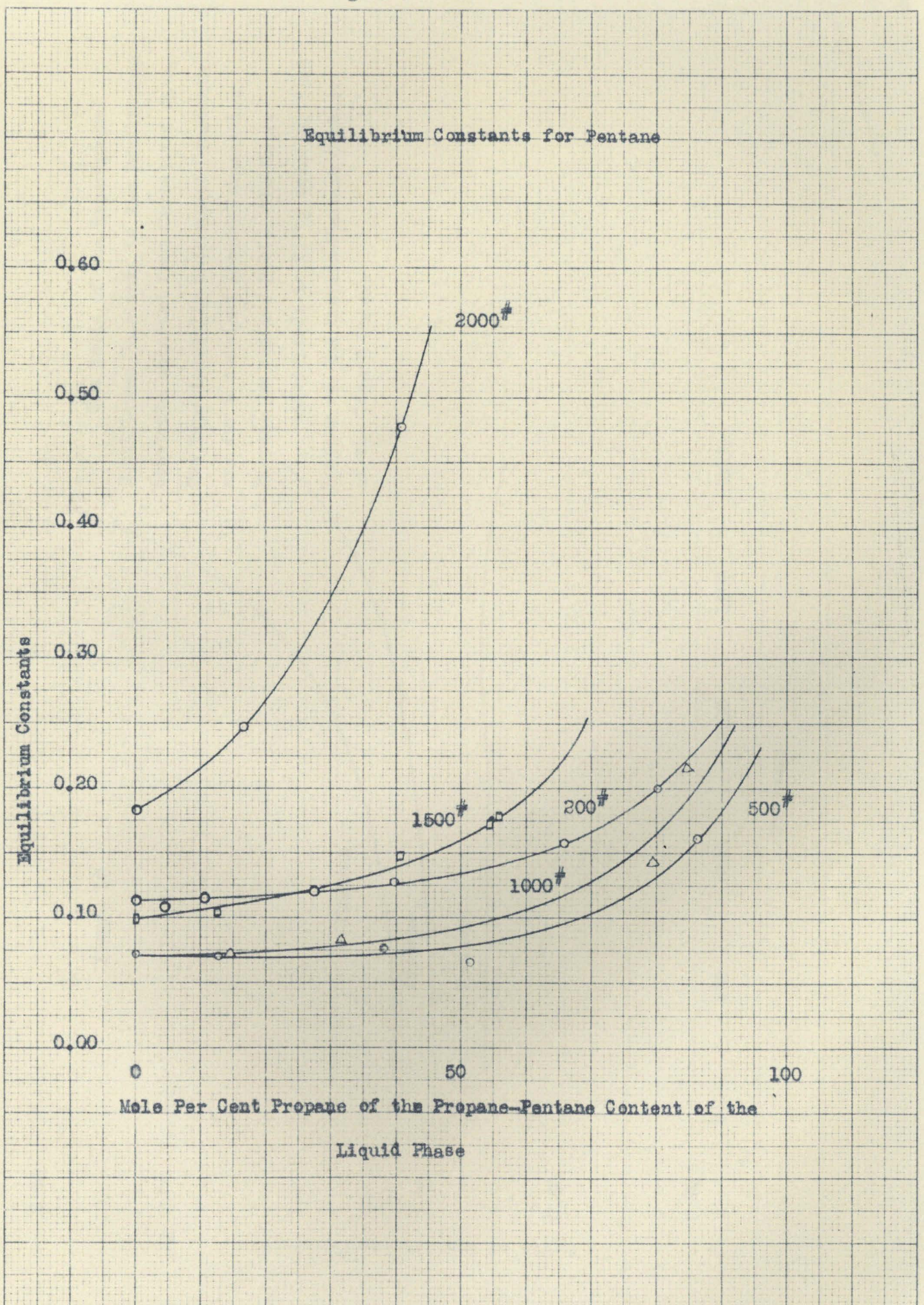
Figure 7

Figure 8

Figure 9

Figure 10

The Ratio of the Experimental
Equilibrium Constants to the Equilibrium
Constants obtained from Correlated data.
The Experimentally determined Constants
are for a constant Liquid Composition
Propane to Pentane Ratio. The Ratio
corresponds to fifty mole per cent
Propane of the Propane-Pentane Content
of the Liquid Phase.

Pentane

Propane

Methane

Pressure

Ratio of Equilibrium Constants

2.50

2.00

1.50

1.00

0.50

0.00

0   400   800   1200   1600   2000

Figure 11

The Ratio of the Experimental Equilibrium
Constants to the Equilibrium Constants
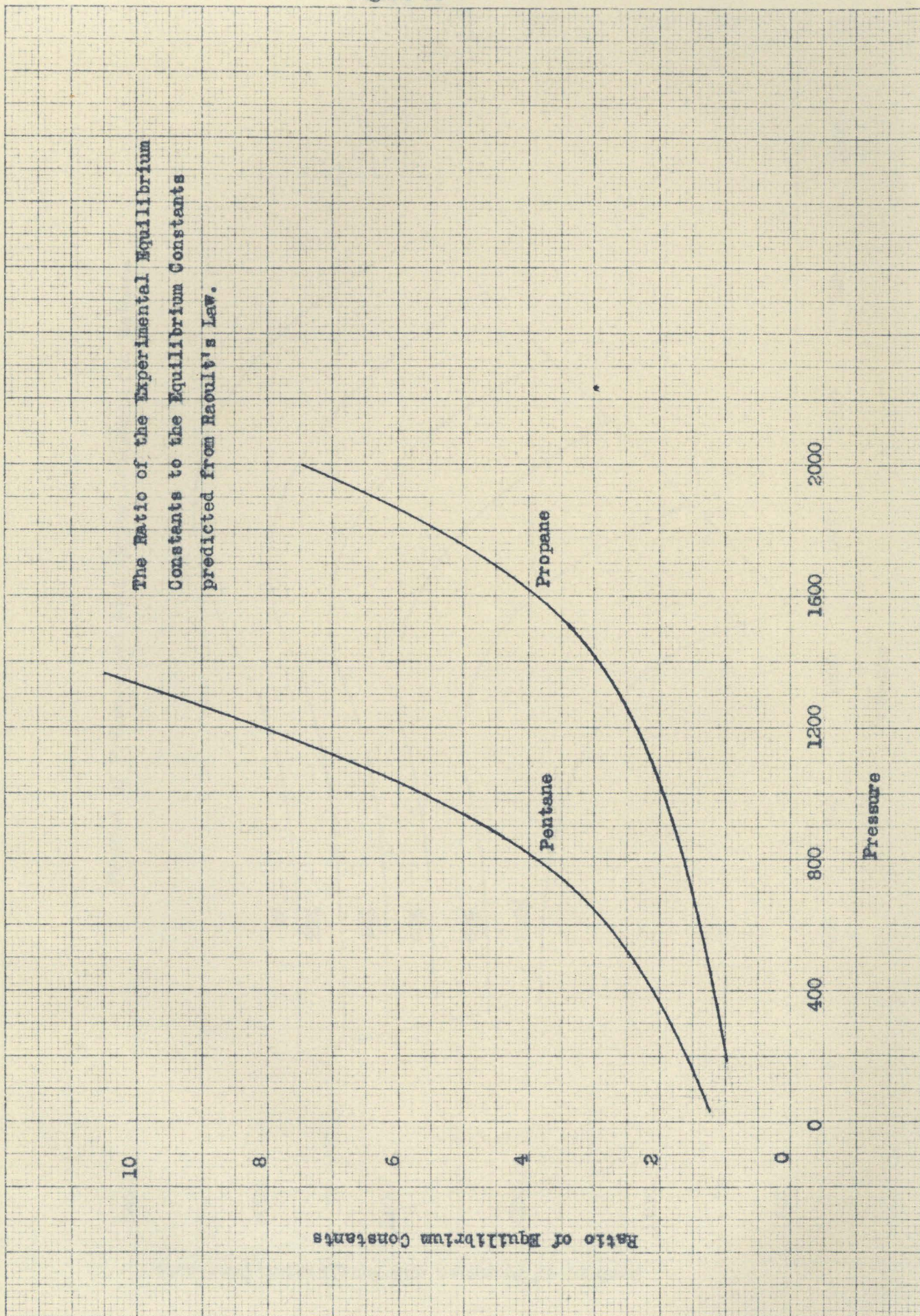predicted from Raoult's Law.

Figure 12

Product of Pressure and Equilibrium Constants for Methane