

ADSORPTION EQUILIBRIA OF GASES ON ACTIVATED CHARCOAL
OVER A WIDE RANGE OF TEMPERATURE AND PRESSURE

By

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Bachelor of Arts

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Austin, Texas

1934

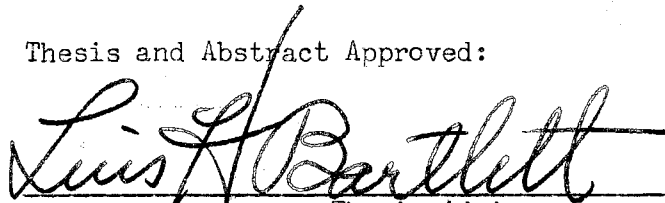
Submitted to the School of Chemical Engineering
Oklahoma A & M College
In Partial Fulfillment of the Requirements
For the Degree of
MASTER OF SCIENCE
1952

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Thesis and Abstract Approved:



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ACKNOWLEDGEMENT

I wish to express my appreciation to Dr. L. H. Bartlett and to other members of the faculty of the School of Chemical Engineering without whose guidance and advise this work would not have been possible. Thanks are also extended to Dr. G. C. Ray for his cooperation and assistance in conducting a portion of the experimental work, and to the Phillips Petroleum Company for permission to publish experimental data obtained in its Research Laboratory.

Dwarfing all others in magnitude, I am indebted to Velma, Elgene, and Diane for their inspiration and very enthusiastic endurance.

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STRATHMORE BOND
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ABSTRACT

The adsorption equilibria for eleven gases, including the hydrocarbon gases methane, acetylene, ethylene, ethane, propylene, propane, and n-butane, on a single sample of commercially available charcoal were studied. The range of fundamental information was extended to 600 psig and 400°F. Adsorption equilibria for several gases on silica gel and on three types of activated charcoal were also studied. A general correlation of quantity of gas adsorbed with the surface area of the adsorbent was obtained. In all cases the single gas adsorption followed the Langmuir equation. Only in the instance of acetylene was there a deviation from the predicted volatilities of the adsorbates.

The vapor-adsorbate equilibria for binary mixtures of low molecular weight hydrocarbon gases were studied at pressures of 0 psig and 200 psig and at a temperature of 100°F. In all instances the volume of each component to be adsorbed from the mixture was less than it would have been if only the single pure gas were at equilibrium at a pressure equal to its partial pressure in the mixture. Several methods of correlating binary mixture adsorption data were applied. An approximate method was developed based upon an empirical curve expressing the fraction of the total adsorbent surface covered with a monomolecular layer. The Langmuir equations for binary mixtures were found to be applicable in many instances although no universal relationship could be stated.

INTRODUCTION

When a gas or a vapor is brought in contact with an evacuated solid a part of it is taken up by the solid. This phenomenon of adsorption was discovered more than a century and a half ago by Scheele in 1773. The solid that takes up the gas or vapor is called the adsorbent, the gas or vapor attached to the surface of the solid is called the adsorbate.

Most adsorbents are highly porous bodies with tremendously large internal surfaces while the external surface constitutes only a small fraction of the total surface. So long as the gas adsorbed does not penetrate into the field of force that exists between the atoms or molecules inside the solid, it is considered to be on the outside even though it is adsorbed on the internal surfaces of the adsorbent.

The atoms or molecules constituting a solid are held together by several forces: valence forces, electrostatic forces, van der Waal forces, etc. Whatever the nature of these forces, an atom located inside the body of the solid is subjected to equal forces in all directions while an atom in the plane of the solid surface is subjected to unbalanced forces. The greater inward pull tends to decrease the surface thus resulting in a definite surface tension of the solid. An atom or a molecule of the gas adsorbed by the solid saturates some of these unbalanced forces and thereby reduces the surface tension. Thus all adsorption is spontaneous and results in a decrease of the free energy of the system. Since prior to adsorption, the gas molecule was free to move in three dimensions, the adsorption process is accompanied by a decrease in entropy. The change in heat content of the system is

$$\Delta H = \Delta F + T\Delta S$$

and since both ΔF and $T\Delta S$ are negative, ΔH is also negative. This means that

all adsorption processes are exothermic.¹

The amount of a gas adsorbed on the surface of an adsorbent at equilibrium is a function of the nature of the adsorbent and the adsorbate as well as a function of the temperature and pressure. The earliest attempt to correlate adsorption with certain physical properties of the adsorbed gas was made in 1814 by Saussure (23) who found that the most easily condensed gases are adsorbed in the largest quantities by a given adsorbent.

For a given gas and weight of a given adsorbent the amount of gas adsorbed at equilibrium is a function of the final pressure and temperature,

$$(1) \quad a = f(p, T)$$

Where a is the amount of gas adsorbed per gram of the adsorbent. When the pressure of the gas is varied and the temperature is kept constant, a plot of the amount adsorbed vs. the pressure is called the adsorption isotherm, expressed by

$$a = f(p) \quad T = \text{constant.}$$

Similarly, the adsorption isobar is expressed by

$$a = f(T) \quad P = \text{constant.}$$

And finally the adsorption isostere is expressed by the relation

$$p = f(T) \quad a = \text{constant.}$$

The adsorption isostere resembles the vapor pressure curves of liquids. On the vapor pressure curve every point represents a pressure and temperature at which the liquid and vapor are in equilibrium with each other. On the adsorption isostere every point represents a pressure and temperature at which the adsorbate-adsorbent is in equilibrium with the vapor or gas. For equilibrium systems the Clausius-Clapeyron equation permits the evaluation of the heat exchange in the

¹G. N. Lewis and M. Randall, Thermodynamics, New York 1923, p. 162.

transition from one phase to the other,

$$\frac{d \ln p}{d (1/T)} = - \frac{q}{R} \quad \text{where } q = \text{change in heat content of the system.}$$

R = gas constant

If $\ln p$ is plotted against $1/T$ obtained from the isostere one may obtain the heat of adsorption. According to the theory of multimolecular adsorption the physical adsorption of gases and vapors in the first layer is determined by two factors, the heat of adsorption and the surface area of the adsorbent. The surface area of the adsorbent may be obtained from calculations based upon the adsorption of nitrogen or some other inert gas.

Most of the technical applications of adsorption processes involve mixtures of gases rather than single pure gases. Solid adsorption has been employed for many years for the separation of hydrocarbon mixtures yet it has not gained wide acceptance due to mechanical difficulties involved in the intermittent cyclical fixed bed processes in use. Several recent publications (1) (2) (5) have discussed commercial and pilot plant scale separation of gas mixtures with activated charcoal using a moving bed of adsorbent. In this "Hypersorption" process (13) (14) a bed of activated charcoal moves downward through a tower equipped with a cooling section at the top and a heating section at the bottom, with an adsorption section intermediate between the two. When a low boiling gaseous feed mixture is charged to the central section of the tower, the heavier components are carried downward by the carbon while the lighter components pass out of the tower overhead. The carbon carrying the heavier components is heated in the lower section and the desorbed material thus removed is recovered as a bottom product. Side cutting as in a fractionating tower is feasible and frequently desirable. Design of such a process requires that a large volume of fundamental information be available on the adsorption characteristics of individual gases, multicomponent mixtures, and

on the probable adsorbents.

Until recently there was no information in the literature which would permit an evaluation of a charcoal over a wide range of conditions as might be commercially required. Ray and Box (15) and Lewis, Gilliland, Chertow and Cadogan (7) have published data on the adsorption of all light hydrocarbons and many other gases on single samples of charcoal and silica gel. Very little is yet available on the adsorption of mixtures of gases of low molecular weights on activated charcoal. The vapor-adsorbate equilibria for binary mixtures of the lower gaseous hydrocarbons on silica gel and on a single sample of charcoal have been studied by Lewis, and co-workers (8).

The theoretical handling of mixed adsorption is somewhat more difficult than that of simple adsorption. In considering the adsorption of binary mixtures, perhaps the simplest case is one in which the adsorption of one gas is so much smaller than the adsorption of the other that it can be completely neglected, and the adsorption of the heavier gas can be treated as a simple operation. If the adsorption of one component is not negligible in comparison with that of the other, there are three obvious possibilities: the adsorption is not influenced, it is decreased, or it is increased. Examples of all three cases are described and discussed by Brunauer (4).

From the available data, and this is further verified from the experimental work described herein, it appears that mixed adsorption is a complex process in which both gases in a binary mixture compete for the surface of the adsorbent. The normally more strongly adsorbed gas is a better competitor but each gas is ordinarily displaced to some extent by the other. The degree of this mutual displacement varies with temperature, pressure, feed composition, and the relative adsorbabilities of the components of the mixture.

Attempts have been made to develop a theory of unimolecular adsorption

which would quantitatively explain the adsorption of all binary gas mixtures. None of these have been adequate in a general sense. However, over limited conditions some adsorption data have been readily correlated with the theory of Langmuir. It is based upon the assumption that the adsorption is unimolecular, and the heat of adsorption is constant. The latter implies both uniformity of surface of the adsorbent and absence of interaction between adsorbed molecules. In a rigorous sense neither of these two assumptions is valid for if these two conditions are fulfilled, the only effect that one adsorbate can have upon the adsorption of the other is to cut down the available surface.

EXPERIMENTAL MATERIALS AND EQUIPMENT

1. Charccals:

- (a) In most of the experimental work a sample of Columbia Grade L activated charcoal of 20/48 mesh size was used. A sample of this charcoal had a surface area of 1152 sq. meters per gram. This value was obtained by the adsorption of nitrogen using the Brunauer-Emmett-Teller method. This is a hard coconut charcoal and manufactured by the Carbide and Carbon Co., Fostoria, Ohio.
 - (b) A soft charcoal of 20/50 mesh and a surface area of 816 sq. meters per gram manufactured by the Pittsburgh Coke and Chemical Co.
 - (c) Darco charcoal with a surface area of 506 sq. meters per gram. This charcoal is recommended by the manufacturer primarily for liquid adsorption and is quite soft.
2. Silica Gel - A sample of Davison Refrigeration Grade silica gel of 20/48 mesh and having a surface area of 816 sq. meters per gram was used.
3. The compressed gases used in the experimental work were of the highest purity obtainable in most instances. The source and purity of each gas is listed below:
- (a) Hydrogen. Cylinder gas was treated to remove traces of oxygen by passing over copper turnings heated to 250°- 300°C followed by drying over Drierite.
 - (b) Methane. 99.7 mole per cent purity, Phillips Petroleum Co.
 - (c) Carbon monoxide. 98 mole per cent purity, Mathieson Co.
 - (d) Ethylene. Research grade, 100.0 mole per cent purity, Phillips Petroleum Company.

- (e) Ethane. 99.7 mole per cent purity, Phillips Petroleum Co.
 - (f) Nitrogen. National Cylinder Gas Co. treated to remove oxygen by passage over copper turnings at 250° - 300°C followed by drying over Drierite.
 - (g) Helium. 99.5 mole per cent purity, Ohio Chemical Company.
 - (h) Propane. Pure grade, 99 mole per cent minimum, Phillips Petroleum Company.
 - (i) Propylene. Pure grade, 99 mole per cent minimum, Phillips Petroleum Company.
 - (j) n-Butane. Pure grade, 99 mole per cent minimum, Phillips Petroleum Company.
 - (k) Carbon dioxide. 99.5 mole per cent, Pure Carbonic Company.
 - (l) Acetylene. Prestolite Company. This gas was washed in gas scrubbers with (1) aqueous sodium bisulphite, (2) aqueous sodium hydroxide, (3) and finally dried over indicating Drierite. Purity about 99 mole per cent.
 - (m) Methyl mercaptan. Pure grade, Eastman Kodak Co.
4. All stopcocks used in the glass apparatus were precision ground by the Eck and Krebs Company.
 5. Only Apiezon N high vacuum lubricant obtained from the James G. Biddle Co. was used for stopcock lubrication.
 6. The oil diffusion pump was a single stage model G4-928 pump employing Amoil-S for the pumping fluid. It was manufactured by the Distillation Products Company.
 7. The oil diffusion pump was backed by a single stage Welch Duo-Seal vacuum pump.
 8. Temperature control was maintained by a Cenco-DeKhotinsky control unit

number 99500. This unit controlled to $\pm 0.2^{\circ}\text{C}$.

9. A McLeod gauge obtained from the Eck and Krebs Company was used for measurement of the vacuum obtained in the system. It was backed by a Cenco Hyvac pump.
10. In the oil bath mineral oil was used at temperatures to 300°F and a hydrogenated vegetable oil was used at those temperatures higher than 300°F .
11. In the superatmospheric pressure adsorption apparatus all valves were Hoke type 431 packless diaphragm valves.
12. The charcoal adsorption tube used in the superatmospheric pressure experiments was made from two sections drilled from SAE 1020 hot rolled steel bar stock welded together. The internal diameter of this tube was $13/16$ inches and the outside diameter $1\ 1/16$ inches. The tube was $4\ 1/2$ inches in length and was swaged down at each end and threaded for $1/8$ inch NPT fittings. The threaded sections carried a $5/32$ inch hole at each end through which the gas and the charcoal could be admitted. Stainless steel $1/16$ inch tubing was used throughout the pressure system.
13. In the glass apparatus for studying mixtures of gases an automatic Toepler pump was used. This pump was of all glass fabrication with mercury check valves and was controlled by relay operated solenoid valves for automatic operation. The Toepler pump was obtained from the Eck and Krebs Company. The solenoid valves were standard 110 volt Minneapolis-Honeywell units.

EXPERIMENTAL PROCEDURES

In obtaining the experimental data reported in this thesis there were three different arrangements of equipment. The adsorption of single gases at pressures up to 15 psia was conducted in the all glass system shown in Fig. 1. This apparatus was fabricated in fixed position on a 1/2 inch steel rod latice. No ground glass joints were used thus reducing the sources of leakage in the high vacuum system. To conduct the adsorption experiments at pressures from atmospheric to 600 psia the all metal system shown in Fig. 2 was set up. Modification of the all glass apparatus for the study of adsorption characteristics of mixtures of gases is illustrated in Figure 3. A detailed description of each assembly follows in discussing the procedures during each experiment.

Adsorption of Single Gases at Sub-atmospheric Pressures

The equipment used in this work is schematically diagrammed in figure 1 with its legend attached. The weight of dry degassed charcoal used in the adsorption tube was determined prior to sealing the Pyrex adsorbent tube to the manifold of the apparatus. The adsorption tube was fitted with short lengths of rubber tubing and glass stopcocks. This was tared on an analytical balance and then filled with the desired adsorbent. The charcoal filled tube was then connected to a Welch vacuum pump through the glass stopcock. The charcoal was degassed by heating for 4 hours at 230°C under a pressure of less than 1 mm. absolute. The stopcock was then closed, and after cooling, the charcoal sample was weighed in vacuo. Rubber connections were then removed and the tube was sealed to the pyrex manifold of the adsorption system.

The free space in the apparatus (the volume bounded by the mercury level

in manometer 6 and stopcocks 5, 13, and 21 of figure 1) was next determined. This was accomplished by bleeding a measured volume of pure helium into the previously evacuated system and measuring the pressure produced on the manometer. Helium is not adsorbed on the surface of the charcoal hence the free space can be calculated from the gas laws. Details of the free space determinations are given in the appendix.

Since in the determination of most isotherms a part of the free space is at the temperature of the constant temperature oil bath while the remainder is at room temperature, it is necessary to break down the total free space into two component volumes. This was done by making the free space determinations at two different temperatures. From the gas laws, the amount of free space below and above the oil level was then calculated.

A fixed level of oil was maintained in the constant temperature bath. A fixed level of mercury was maintained in the mercury manometer leg open to the manifold. This was accomplished by means of a mercury filled leveling bulb. The charcoal was degassed at 250°C for 24 hours at a pressure of 1×10^{-3} mm. An electric furnace not shown in the drawing was used in this operation.

Between isotherms and when changing to a different gas to be adsorbed, the charcoal was degassed to 1×10^{-5} mm.

The adsorption measurements were made by introducing a known volume of gas from burette 4 into the evacuated system bounded by the mercury level in the manometer and stopcocks 5, 13, and 21. After successive readings on the manometer had indicated that equilibrium between the charcoal and the gas had been reached, the manometer reading was noted, and a second known volume of the gas was admitted to determine a second point on the adsorption isotherm. This was continued up to a maximum pressure of approximately one atmosphere absolute. The time required to reach equilibrium

varied from several minutes to 36 hours depending upon the temperature of the charcoal and the adsorbate gas being studied.

The quantity of gas introduced from the burette less the quantity of gas occupying free space at equilibrium conditions represents the quantity of gas adsorbed. No corrections for deviation from ideal behavior of gases was made. These corrections would be of the order of 0.5 per cent for 1.5 ethane, 1.5 per cent for propane, and 2.5 per cent for butane at 100°F and a pressure of one atmosphere. This correction would be considerably less under the conditions of most of the experimental data.

When a different sample of adsorbent was to be used a new adsorption tube, filled with the properly degassed, dried and weighed adsorbent, was sealed into place on the manifold. It was necessary to make new free space determinations when such changes were made. Each adsorbent was heated prior to this operation while being evacuated with the oil diffusion pump.

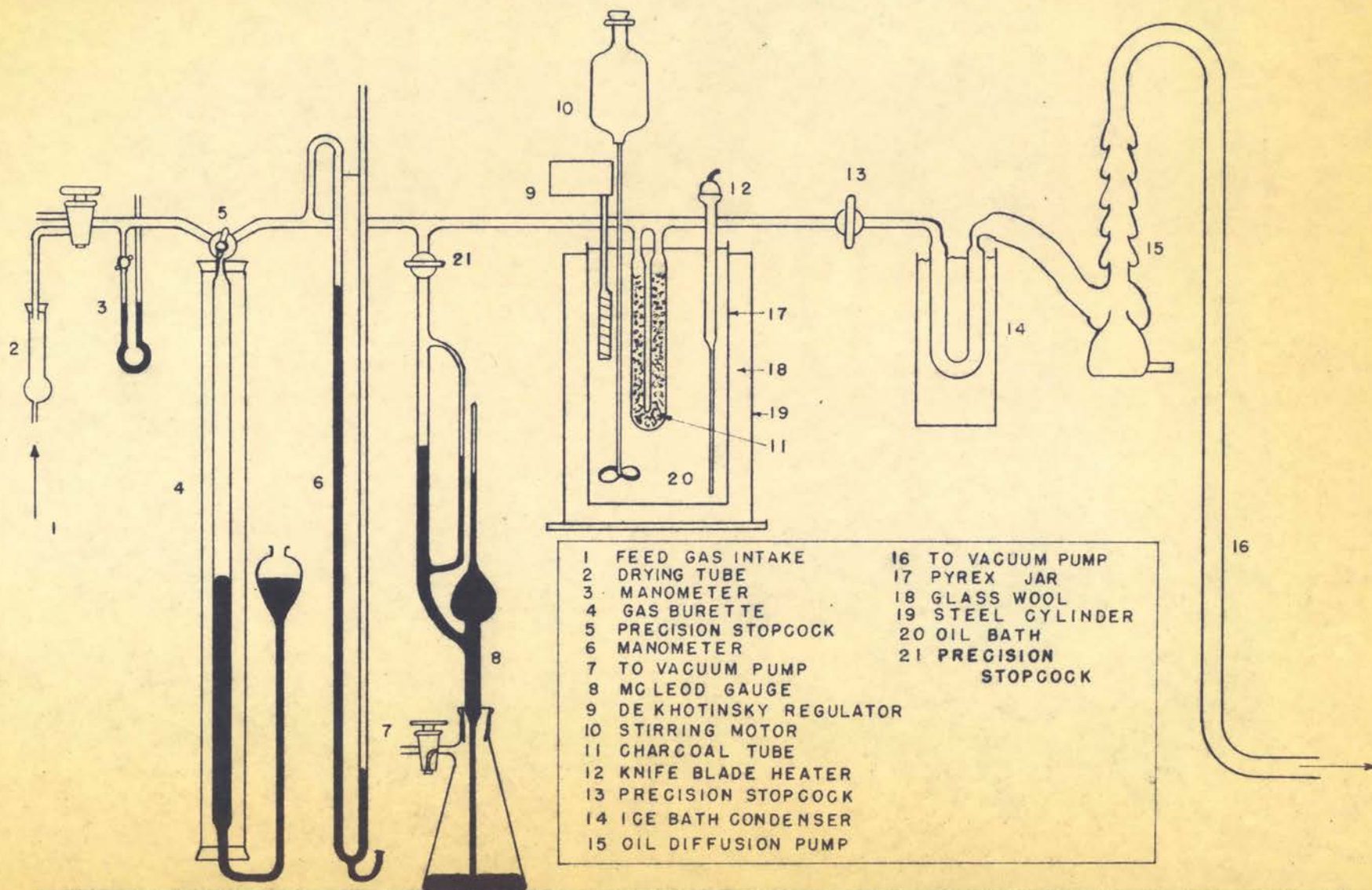


FIG. I APPARATUS FOR MEASURING THE ADSORPTION OF GASES ON CHARCOAL

Adsorption of Single Gases at Pressures up to
600 PSIA on Activated Charcoal

The equipment used in this investigation is schematically diagrammed in figure 2 and the attached legend makes it largely self-explanatory.

The sample of Columbia Grade L activated charcoal used in these experiments was initially prepared for use by heating in a pyrex tube while under the vacuum of a Cenco Hyvac pump. Heating was continued for 15 hrs. at 200°C followed by heating for two hours at 265°C. The charcoal was weighed and then transferred to the steel bomb. In these experiments 7.983 grams of charcoal were used. Between isotherms or when changing from one gas to another the charcoal was evacuated with the vacuum pump at the temperature of the experiment to be started. In order to prevent evacuating against the pressure gauge it was filled to one atmosphere with the gas to be used prior to evacuating the remainder of the system. The total free space in the pressure adsorption system bounded by valves 2, 11, and 12 was determined with helium by a method similar to that described for the sub-atmospheric adsorption system. Free space determinations were made at two different temperatures and from the gas laws the two component volumes were calculated. These calculations are recorded in the Appendix. The free space in the pressure gauge and the steel manifold above valve 11 was determined by filling with mercury and weighing the mercury as it was withdrawn.

The adsorption measurements were made by first introducing an indefinite quantity of gas from a pressured feed cylinder into the evacuated charcoal tube and manifold through line 1 and controlled by valve 2. After super-atmospheric pressure was reached in the system, valve 11 was opened and more gas bled in until the desired upper limit registered on the pressure gauge. Valve 12 was closed during this operation. Valve 2 was then closed and the

gas was allowed to equilibrate with the charcoal at the temperature controlled by the oil bath. Equilibrium was considered to have been reached when no further change in pressure was registered on the pressure gauge after two hours. After equilibrium was established, valve 12 was opened cautiously and a quantity of the gas was bled off into the gas measuring burette.

While bleeding gas out through valve 12 approximately atmospheric pressure was maintained on the manometer 13 by lowering the leveling bulb on the burette 16. Final leveling was accomplished after closing valve 12 with the manometer. After noting the volume of gas in the burette the gas was dispelled to the atmosphere through a vent tube to the roof of the building. Subsequent to the withdrawal of several burettes of gas in this manner the system was again allowed to reach equilibrium at a new and lower pressure. Again after several hours gas was withdrawn through valve 12 into the gas measuring system and this sequence was continued until the entire system was at room atmospheric pressure.

The amount of gas adsorbed on the charcoal at a given temperature and at one atmosphere absolute pressure was determined for a given gas by reference to the curves obtained for that gas on the sub-atmospheric pressure adsorption apparatus. Isotherms for all gases studied at the lower pressures are found in the Appendix. These data were obtained by Ray and Box (15) on the same apparatus described in a portion of this work.

Corrections were applied for the quantity of gas present in the free space in the system. The compressibility of the gas was taken into account when making these free space corrections for methane, ethylene, ethane, and propane. The deviations of hydrogen, nitrogen, and carbon monoxide from the ideal gas laws introduces an error of less than 1 per cent at the lowest temperature and highest pressure for which data are recorded. Compressibility

factors for the hydrocarbon gases are well known and are found in several publications by Sage and Lacey (18) (19) (20) (21) (22) and Brown (11).

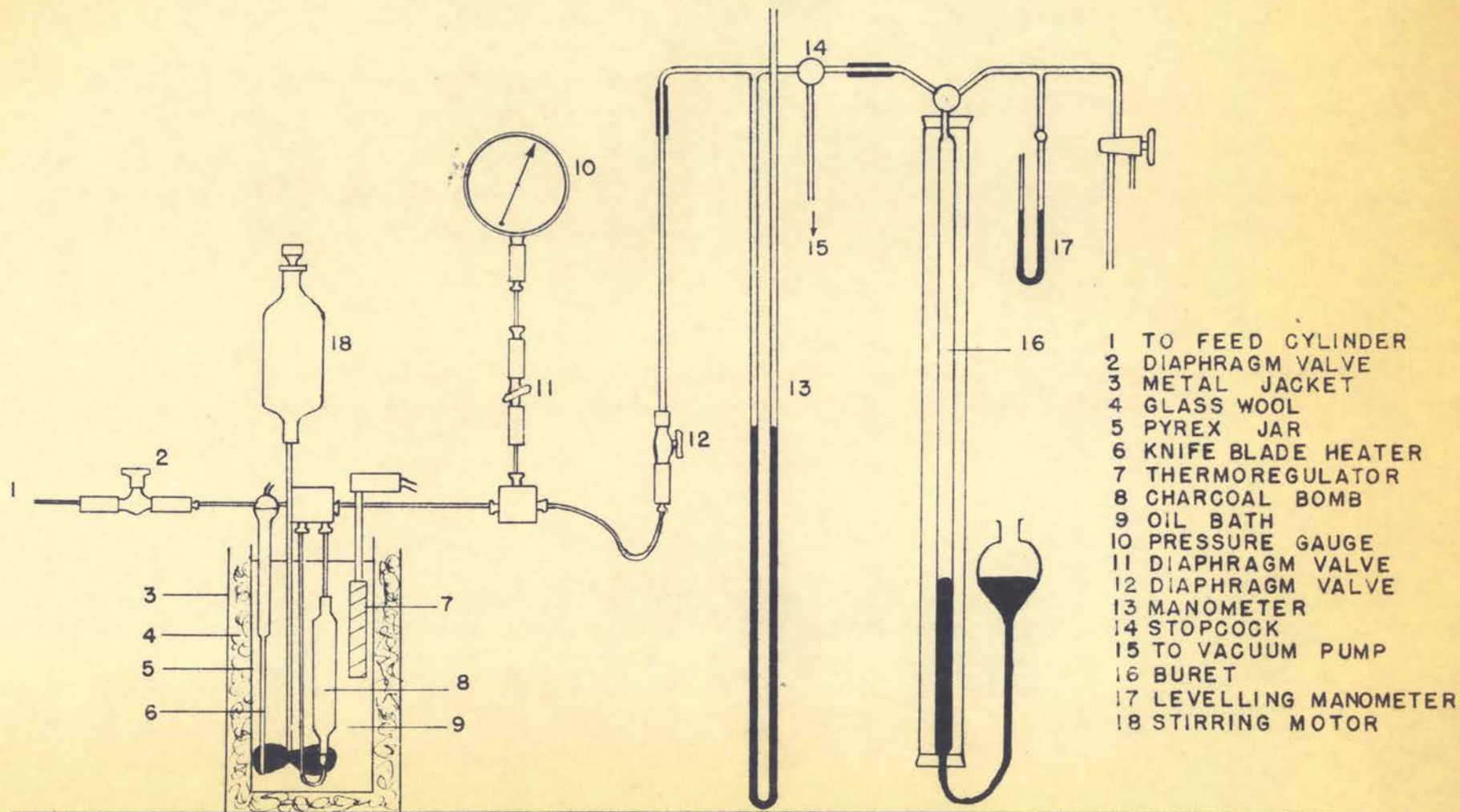


FIG.2 APPARATUS FOR DETERMINING ADSORPTION ISOTHERMS AT ELEVATED PRESSURE

Adsorption of Binary Gas Mixtures on A Sample
of Activated Charcoal

The equipment used in the sub-atmospheric pressure experiments with single gases was modified for this work and is shown in figure 3. The oil diffusion pump, temperature control unit, McLeod gauge, manometer, stirrer, and oil bath remained unchanged. The manifold was modified to permit a flow system and to permit the use of an automatic Toepler pump for pumping the gas off the surface of the charcoal.

Before each adsorption experiment, a mixture of the two gases was prepared by blending in a 5 gallon liquefied petroleum gas cylinder. This mixture was then analyzed by Orsat procedure. Since in each binary mixture one component was an olefin this was a simple procedure using a concentrated sulphuric acid absorbent in the Orsat apparatus.

The charcoal system bounded by stopcocks 4, 5, 6, and 7 was evacuated to about 1×10^{-4} mm with the diffusion pump. After reading the pressure on the McLeod gauge, stopcock 5 was closed. The feed mixture was introduced slowly through the mercury safety trap 1, drying tube 2, and rotameter 3, by carefully opening stopcock 4. This was continued until atmospheric pressure was registered on manometer 15. At this time stopcock 7 was opened so as to vent the effluent from the charcoal tube. The feed rate from the charge cylinder was adjusted so that the rotameter indicated a flow rate of about 30 ml/minute. About 8 hours was allowed for the feed mixture and the charcoal to reach equilibrium. At the end of this time stopcocks 4 and 7 were simultaneously closed, stopcock 7 being given a quarter turn clockwise. Gas bottles 25 and 26 and Toepler pump 23 were evacuated with a vacuum pump not shown in figure 3, to less than 1 mm pressure as indicated by manometer 24. This vacuum pump was usually connected to stopcock 11. All other stopcocks

were appropriately adjusted during this evacuation procedure. Stopcock 7 was turned a quarter turn clockwise to the position which permits flow of gas from the charcoal system into the Toepler pump and then into the appropriate pressure bottle. After equalization of pressure in this manner the automatic Toepler pump was put into operation, pumping gas from the charcoal surface into the selected calibrated gas bottle. The Toepler pump continued to pump at the rate of about two strokes per minute until the pressure in the charcoal tube had been reduced below 1 mm absolute. This procedure required 2-8 hours. At the end of the pumping period the pressure in the gas storage bottle was recorded and the total gas volume was then calculated. The quantity of gas which had been adsorbed on the surface of the charcoal was then determined by subtracting the free space volume from the total gas volume in the storage bottle. It was necessary to make a correction for the volume of gas present in the glass tubing between the gas storage bottle and the exit mercury loaded check valve at the top of the Toepler pump. The volumes of the gas storage bottles were obtained by filling with distilled water and weighing. Standard density tables were used for computation of volume.

Analysis of the gas in the storage bottle was made by first transferring a sample of the gas to a mercury filled gas sampling bulb via line 28. The Toepler pump was used in this operation also. Standard sulphuric acid Orsat analysis was used for determining the olefin content of the gas. In the case of the nitrogen-methane binary mixture, a vapor pressure method was used for analysis of the gas. In making calculations for a volume of each component adsorbed on the charcoal, it was assumed that the free space volume was occupied by gas of the same composition as the feed mixture.

The accuracy of these data will vary somewhat with the binary mixture studied and the conditions for the equilibrium. Therefore no general state-

ment of accuracy is adequate. For example, in studying ethylene-methane mixtures, in one experiment an error of 0.5 per cent in determining ethylene in the Orsat on a total of 414 ml gas adsorbed equals to about 2.1 ml. Since methane was determined by difference, the error in methane adsorption introduced by the Orsat error is about 1.8 per cent. However, in a run where the methane adsorption was very low, this error is greatly magnified.

In studying ethylene-propane mixtures an error of 0.5 per cent on the Orsat introduces less error in the determination of propane adsorption than it did on the methane due to the much greater adsorptivity of propane.

The accuracy of free space determinations is believed to be better than ± 1 ml. In most of the experiments this error would be a maximum error of 0.3 per cent of the total gas adsorbed. In most instances the error made in determining the total volume of gas adsorbed was of the order of 1-2 ml based upon an error in reading the manometer of 0.5 mm.

In those experiments where the adsorption was conducted at super-atmospheric pressures the experimental errors are probably slightly higher due to magnification of the free space errors. In runs at 215 psia the free space error made at atmospheric pressure is magnified 14 times. Determination of the total gas adsorbed at this higher pressure is probably just as accurate as was the case at one atmosphere.

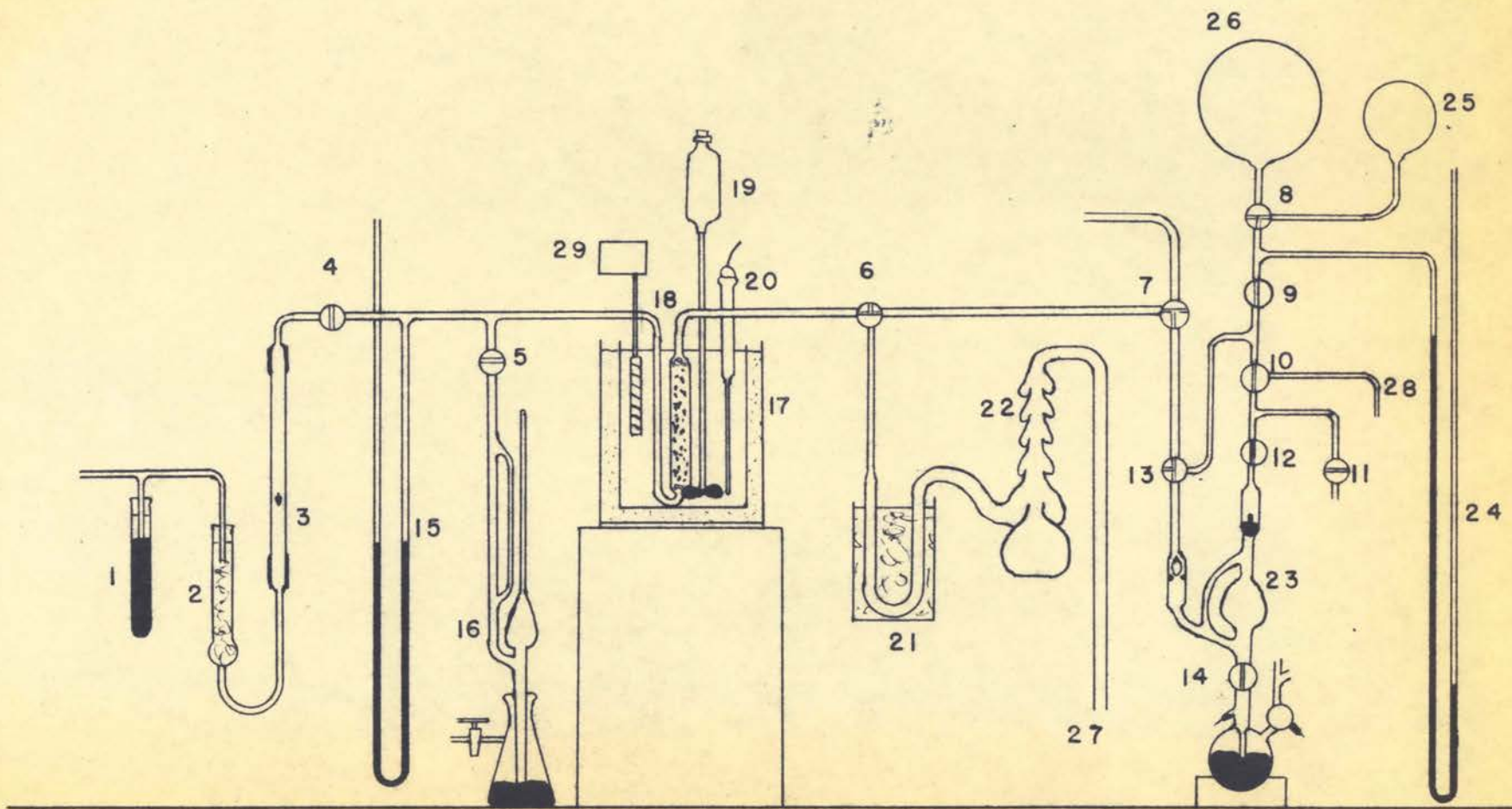


FIG.3 APPARATUS FOR MEASURING ADSORPTION OF GAS MIXTURES ON CHARCOAL (0 PSIG)

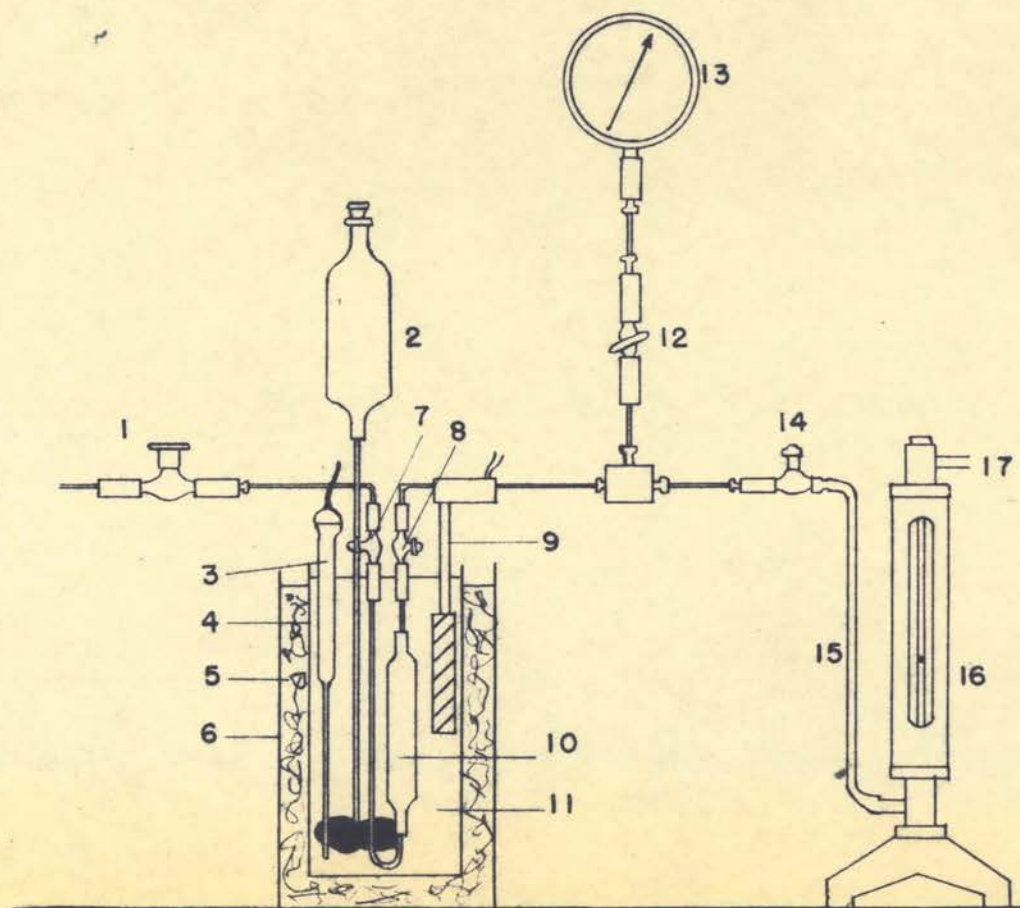
Legend for Figure 3

1. Mercury safety trap
2. Drying tube
3. Flowrator
- 4-13. Precision ground stopcocks
14. Rate controlling stopcock
15. Manometer
16. McLeod gauge
17. Insulated oil bath
18. Charcoal filled tube
19. Stirring motor
20. Knife-blade heater
21. Ice trap
22. Oil diffusion pump
23. Automatic Toepler pump
24. Manometer
25. Gas bottle (1 liter)
26. Gas bottle (2 liters)
27. To Hyvac pump
28. To sampling bottle
29. DeKhotinsky thermoregulator

ADSORPTION OF BINARY GAS MIXTURES
ON COLUMBIA GRADE L CHARCOAL AT 200 PSIG

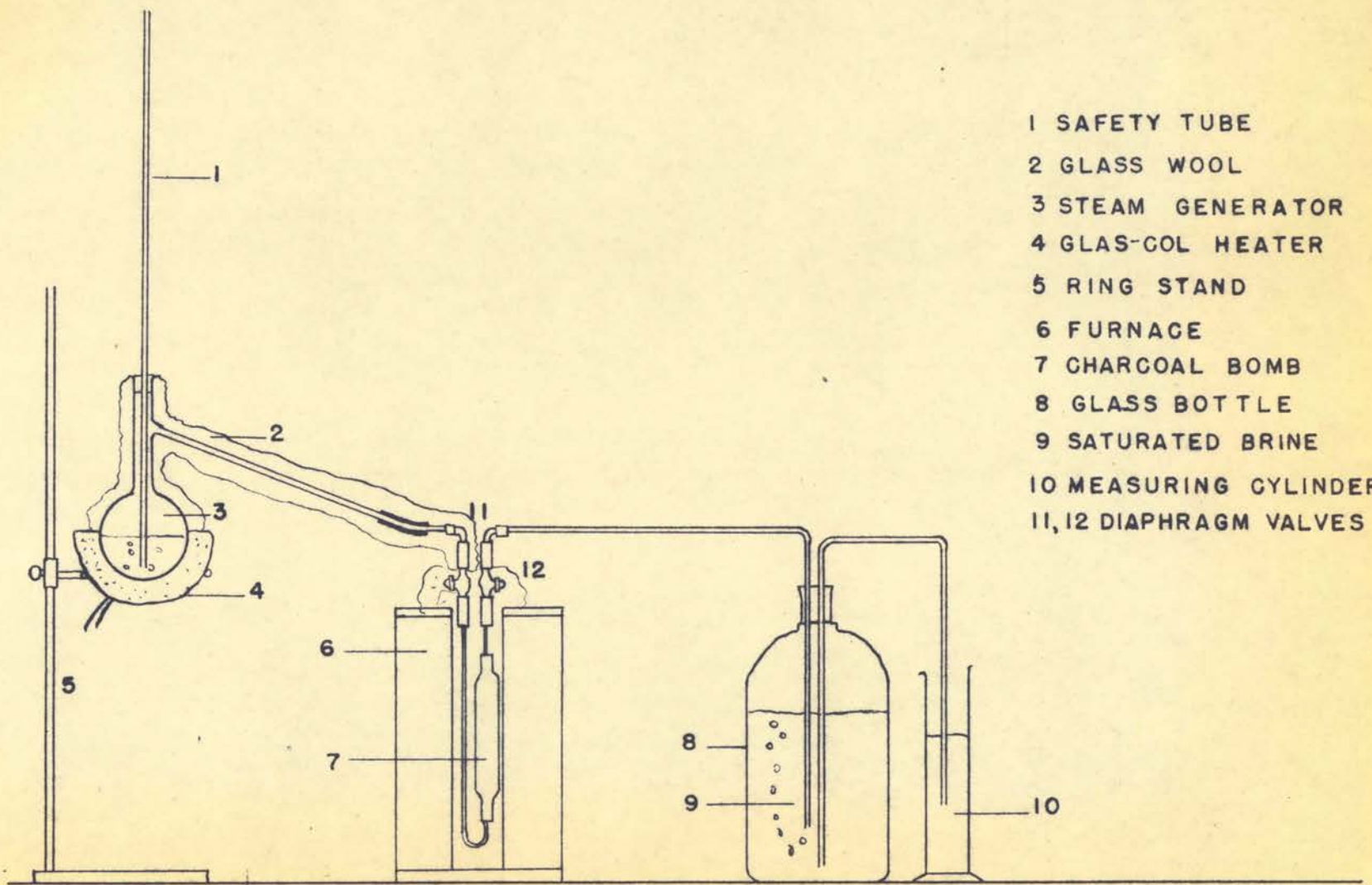
The equipment used for the study of adsorption of gas mixtures on charcoal is shown in Fig. 4 and is a modification of that used in the study of single gas adsorption at elevated pressures. In order that a flow system could be employed valves 7 and 8 replaced the T-block shown in Fig. 2. A compressed gas cylinder containing the binary gas mixture of known composition was fitted with a suitable regulator and attached to the system at valve 1. The regulator was set to feed gas from the cylinder at the pressure condition desired for the experiment. Accurate measure of the system pressure was made by the steel tube pressure gauge 13. Valve 14 was then opened slightly and the gas passed to atmospheric pressure through the flowrator. Valve 14 was set so that a constant rate of flow registered on the flowrator and a constant pressure of about 200 psig. registered on the gauge. This flow was continued for 2-3 hours after which time valves 7 and 8 were simultaneously closed and the adsorption tube disconnected just above these valves.

In order to completely desorb gas from the charcoal a system as shown in Fig. 5 was employed. The adsorption tube was placed in a small electric furnace heated to 250-300°F and steam was passed through the charcoal bed. All gases were collected over saturated brine by displacement. The volume of the gas was determined from a knowledge of the volume of brine displaced. Suitable corrections were made for vapor pressure of the brine solution, temperature, atmospheric pressure and hydrostatic head. After thorough mixing of the gas in the receiving bottle an Orsat analysis was made to determine the quantity of olefinic gas present, the other component being determined by difference.



- 1,7,8,12,14 DIAPHRAGM VALVES
- 2 STIRRING MOTOR
- 3 KNIFE-BLADE HEATER
- 4 PYREX JAR
- 5 GLASS WOOL
- 6 METAL CYLINDER
- 9 THERMOREGULATOR
- 10 CHARCOAL BOMB
- 11 MINERAL OIL
- 13 DURAGAGE (0-600PSIG)
- 15 RUBBER TUBING
- 16 FLOWRATOR
- 17 TO VENT

FIG. 4 APPARATUS FOR MEASURING ADSORPTION OF GAS MIXTURES ON CHARCOAL (600PSIG)



- 1 SAFETY TUBE
- 2 GLASS WOOL
- 3 STEAM GENERATOR
- 4 GLAS-COL HEATER
- 5 RING STAND
- 6 FURNACE
- 7 CHARCOAL BOMB
- 8 GLASS BOTTLE
- 9 SATURATED BRINE
- 10 MEASURING CYLINDER
- 11,12 DIAPHRAGM VALVES

FIG. 5 APPARATUS FOR STEAM DESORPTION OF GAS MIXTURES FROM CHARCOAL

METHODS OF CALCULATIONS

The data of Ray and Box (15) have been incorporated into the appendix of this report and have been plotted into a system of isotherms for each gas studied. These isotherms are shown in Figs. 6-16. Frequent reference to these plots must be made in evaluating the data on adsorption of gases from binary mixtures. Further, the data obtained at pressures above atmospheric pressure required a knowledge of the capacity of the adsorbent for the particular gas at the pressure and temperature of the room at the time of the experiments.

The Freundlich empirical equation is still widely used by investigators, particularly in industrial practice. In general a large number of the experimental results in the field of van der Waals adsorption can be expressed by means of the Freundlich equation (4). In its simplest form it is frequently expressed as

$$v = kp^{1/n} \quad (1)$$

However, if expressed in a logarithmic form,

$$\log v = \log k + \frac{1}{n} \log p \quad (2)$$

this linear equation affords a graphical evaluation of $\log k$ as the intercept and $1/n$ as the slope of the line. Application of this equation to single gas adsorption has been made in this study and the results are shown in Fig. 32. Obviously the Freundlich equation is not satisfactory for correlation of adsorption at any but very low pressures since a plot of experimental data shows a large deviation from the straight line as the pressure approaches one atmosphere.

The Langmuir equation (6) is perhaps the most important single equation in the field of adsorption. Langmuir assumed that adsorption is a chemical

process and that the adsorbed layer was unimolecular. The equation may be stated

$$v = \frac{v_m bp}{1 + bp} \quad (3)$$

However, like the Freundlich equation, this equation may also be expressed in the form of a straight line:

$$\frac{1}{v} = \frac{1}{v_m b} \cdot \frac{1}{p} + \frac{1}{v_m} \quad (4)$$

A plot of $1/v$ against $1/p$ gives a straight line and the value of v_m is given by the reciprocal of the intercept. The value of the adsorption coefficient, b , can be obtained from the slope of the line.

Figs. 33-37 are plots of Langmuir isotherms for methane, ethylene, ethane, propane and n-butane, on Columbia Grade L charcoal. The values of v_m and b were obtained graphically as described.

The values of v_m and b can also be obtained by a procedure described by Russell and Stokes (17). If the surface area of a given adsorbent is known and the actual area occupied by a single molecule on the surface can be calculated, then the volume of a gas required to lay down a monomolecular layer can readily be calculated. Such an equation for the area occupied by a single molecule is given by

$$\text{Area } (\text{\AA})^2 = 1.53 \left(\frac{M}{d}\right)^{2/3} \quad (5)$$

Values of the liquid density, d , are given in Table I and were obtained from the values of Russell and Stokes and from the data of Morrison (11) in a more recent work. Thus in the case of methane adsorbed on Columbia Grade L charcoal of 1152 sq. meters/gram surface area it is computed that 6.37×10^{21} molecules are required to form a molecular layer. From this value and the Avogadro number we can arrive at a value of $v_m = 235$ ml/gram.

TABLE I

LIQUID DENSITIES AND MOLECULAR AREAS OF GASES

<u>Gas</u>	<u>Liquid Density</u> g/ml	<u>Molecular Area, sq. Angstroms</u>	
		<u>Russell & Stokes</u>	<u>Morrison</u>
O ₂	1.14	14.1	-
CO	0.763	16.8	-
CO ₂	1.179	17.0	-
CH ₄	0.392	18.1	19.4
C ₂ H ₂	-	-	19.8
C ₂ H ₄	-	26.0	23.1
C ₂ H ₆	-	-	25.9
C ₃ H ₆	-	-	36.0
C ₃ H ₈	-	30.3	37.8
n-C ₄ H ₁₀	0.601	37.2	42.1
N ₂	0.751	16.2	16.2

TABLE II

MOLECULES REQUIRED TO FORM A MONOMOLECULAR LAYER

<u>Gas</u>	<u>Russell & Stokes</u> x 10 ²¹	<u>Morrison</u> x 10 ²¹
N ₂	7.13	7.13
CH ₄	6.37	5.94
C ₂ H ₄	4.43	4.98
C ₂ H ₆	-	4.45
C ₃ H ₈	3.81	3.05
n-C ₄ H ₁₀	3.10	2.74

The Langmuir equation can be applied to mixtures of gases with some degree of correlation. Using the values of v_m and b calculated from the pure gas isotherms, and applying the basic equation we may express the volume of each gas adsorbed from a binary mixture as

$$v_1 = \frac{v_m^{(1)} b_1 p_1}{1 + b_1 p_1 + b_2 p_2} \quad (6)$$

$$v_2 = \frac{v_m^{(2)} b_2 p_2}{1 + b_1 p_1 + b_2 p_2} \quad (7)$$

Gas 2 decreases the adsorption of gas 1 as p_2 and b_2 (its partial pressure and adsorption coefficient) become greater. If the factors $b_1 p_1$ and $b_2 p_2$ are negligible as compared to 1, the equations reduce to

$$v_1 = v_m^{(1)} b_1 p_1 \quad (8)$$

$$v_2 = v_m^{(2)} b_2 p_2 \quad (9)$$

in which case each gas is adsorbed as though the other were not present at all. This occurs only when both components of the mixture are weakly adsorbed.

Equations (6) and (7) have been applied to some of the experimental data reported herein. These expressions did not quantitatively correlate the data except in certain instances. As was the case with the mathematical expression of Freundlich, the Langmuir equations do not adequately explain adsorption phenomena except over limited ranges of temperature and pressure.

TABLE III
CALCULATED CONSTANTS FOR LANGMUIR EQUATION
FOR BINARY MIXTURES

Gas	Data of Morrison		Langmuir Plot	
	v_m	b	v_m	b
CH ₄	219	.00136	173	.00019
C ₂ H ₄	184	.00114	102	.00206
C ₂ H ₆	165	.00204	127	.00307
C ₃ H ₈	113	.0161	131	.0067
n-C ₄ H ₁₀	101	.0458	105	.0328

In a recent publication by Lewis and co-workers (8) a method of correlating binary mixture adsorption was proposed which is not concerned with the mechanism of adsorption. Rather it attempts to provide a means of predicting the quantity of a gas adsorbed under a set of conditions. Let N_1 and N_2 represent the moles of components 1 and 2 respectively, which are adsorbed from a binary mixture of the two at a given temperature and pressure. Also let N_1' and N_2' represent the number of moles of pure gas 1 and pure gas 2 adsorbed on the same quantity of charcoal, the same temperature, and at a total pressure equal to the total pressure of the mixture. Lewis et al, found in studying the adsorption of mixtures of light hydrocarbons on charcoal that a plot of N_1 vs N_2 yielded a straight line with terminal points of N_1' and N_2' . If the ratio $\frac{N_1}{N_1'}$ is plotted against the ratio $\frac{N_2}{N_2'}$ a straight line results, the equation for which is

$$\frac{N_1}{N_1'} + \frac{N_2}{N_2'} = 1 \quad (10)$$

It has been found that this correlation fits fairly well the data obtained on the adsorption of a number of binary mixtures on charcoal between 0-200 psig and 100-200°F. Figure 44 shows a plot of N_1/N_1' vs N_2/N_2' for these data. Since N_1' and N_2' are known from isotherms of the pure gases, N_1 and N_2 can be evaluated if another expression relating N_1 and N_2 is available. This relation is made available from the empirical plot of Fig. 43. In this figure the mole fraction of the least adsorbed component in the gas phase is plotted against the mole fraction of the same component in the gas phase. A single curve roughly defines the points for the methane-ethylene, ethylene-propane, and propylene-n-butane systems. The ratio of N_1 to N_2 in the adsorbed phases can be read from this curve if the composition of the feed gas is known. It is assumed that the composition of the feed gas and the gas phase above the adsorbent at equilibrium are identical. By substituting the value of this ratio into the expression of equation (10) along with the values of N_1' and N_2' obtained from the pure gas isotherms, the values for N_1 and N_2 can be calculated. Thus the adsorptive behavior of a given gas at equilibrium with the adsorbent is predicted from the pure gas isotherms.

Table 4 quantitatively compares the adsorption of the individual gases in binary mixtures calculated in this manner with those found experimentally.

TABLE IV
COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES FOR THE
ADSORPTION OF THE INDIVIDUAL COMPONENTS OF BINARY MIXTURES
 (Method of Lewis and Co-workers)

Run No.	Components		Calculated Vol. (ml) Adsorbed		Experimental Vol. (ml) Adsorbed		% Deviation from Experiments	
	A	B	A	B	A	B	A	B
96	Methane	Ethylene	32	453	75	462	-57	-2
3	Methane	Ethylene	69	440	56	442	+22	-0.5
7	Methane	Ethylene	64	446	47	489	+36	-8
41	Methane	Ethylene	111	242	112	302	-1	-19
51	Methane	Ethylene	96	341	42	533	+22	-36
66*	Methane	Ethylene	48	951	88	958	-47	-0.5
70*	Methane	Ethylene	298	675	328	620	-9	+1
29	Ethylene	Propane	267	590	189	643	+41	-8
14	Ethylene	Propane	130	786	112	791	+16	-0.5
47	Ethylene	Propane	48	910	61	906	-21	+0.2
49	Ethylene	Propane	33	933	56	968	-41	-4.0
53**	Ethylene	Propane	81	555	63	513	+27	+8
55	Ethylene	Propane	99	840	76	816	+28	+3
59*	Ethylene	Propane	324	737	404	700	-19	+5
62*	Ethylene	Propane	324	737	371	723	-12	+2
72	Ethylene	Ethane	294	457	279	435	+5	+4
80*	Ethylene	n-Butane	604	483	445	592	+35	-18
83	Ethylene	n-Butane	752	600	120	609	+500	-1
78	Propylene	n-Butane	1030	1093	423	512	+250	+200
85	Propylene	n-Butane	160	875	198	746	-19	+17

* Experiment at 215 PSIA

**Experiment at 200 F

DISCUSSION OF RESULTS

The adsorption isotherms of pure light hydrocarbons and other low molecular weight gases on a single sample of Columbia Grade L charcoal were smooth and typical isotherm plots. They are shown in Figs. 6-16 for pressures below atmospheric. It is significant to note the completeness of evacuation of the charcoal when changing condition or when changing gases. Some 60 separate isotherms for 12 different gases were obtained on the same sample of charcoal. Check determinations shown in Figs. 10 and 12 indicate 100 per cent reproducibility of results. As a precaution, however, the single isotherm of methyl mercaptan was not determined until after all other experiments had been completed for the sample of charcoal being used. It should also be mentioned that butylenes were not studied because of their greater tendency toward polymerization on the surface of the adsorbent.

Adsorption isosteres for each gas can be plotted and the heats of adsorption can be obtained. Such plots were made, but since a detailed study of heat of adsorption is not within the scope of this paper only two "typical" sets of isosteres are included. Figs. 18 and 19 are sets of isosteres for methane and propylene on the sample of Columbia Grade L charcoal used by Ray and Box (15).

In order to expand the information on adsorption of the hydrocarbon gases on charcoal into a range of temperature feasible in commercial operation, data were obtained to approximately 600 psig and to 400°F. From these data extrapolations can be made for most gases to 1000 psig and at intermediate temperatures. In the regions of the critical conditions and the dew point much deviation from normal adsorptive behavior was observed. In the cases of propane and propylene any pressure above 100 psia gave sharp breaks in

the isotherms. Obviously, at or near the normal dew point for the gas, the apparent adsorption was actually accompanied by some liquefaction. This was also observed in the case of ethylene above 600 psig although its dew point should have been of the order of 650 psig under the conditions. Similarly the data for ethane is somewhat erratic above 450 psig.

A brief series of experiments was made using several other adsorbents. The purpose was to determine if a correlation could be found between the surface area of the adsorbent and the quantity of gas adsorbed. The adsorbents being compared were:

Columbia Grade L Charcoal	1152 sq. meters/gm.
Davidson Silica Gel	630
Darco Charcoal	506
Pittsburgh Chemical Co.	816

Isotherms were plotted for pressures up to one atmosphere and at a temperature of 100°F for the adsorption of several gases on each adsorbent. Fig. 28 illustrates the point that for non-polar gases charcoal is a better adsorbent both in its total capacity and the capacity based upon the volume adsorbed per unit of surface area.

Choosing ethane as the common adsorbate and then comparing the three charcoals of different surface areas it was possible to show that the volume of a gas adsorbed is directly proportional to the surface area of the adsorbents. This is illustrated in Fig. 30 in the case of ethane. Similarly, a comparison of the relation between surface area and volume of gas adsorbed is shown for propane and for ethylene in Fig. 31.

The empirical Freundlich equation did not prove satisfactory for correlation of the data obtained on single gases at pressures in excess of one atmosphere. Selected hydrocarbon gas isotherms are plotted according to the linear logarithmic form of the Freundlich equation and included in

Fig. 32. Since the actual data are not linear in these plots no attempt was made to evaluate the adsorption constant k or the exponent $1/n$.

When the data obtained for methane, ethylene, ethane, propane, and n-butane were plotted according to the Langmuir equation in its linear form, equation (4), an excellent correlation was found. Figures 33-37 are plots of $1/v$ against $1/p$ for these gases at temperatures of 100°F, 200°F, and 300°F. The straight lines obtained at the several temperatures do not, however, give the same intercept. Thus, if accepting Langmuir's assumptions, the volume of a gas required for laying down a mono-molecular layer of molecules on the surface is dependent upon the temperature. Since the size of the molecules remains unchanged and since v_m from the plots becomes smaller with temperature elevation, one would be forced to consider that the adsorbed molecules have some freedom of motion on the surface. As the temperature is increased that freedom of motion is also increased because of the greater energy of the molecule. It may be stated that when the adsorption takes place in a mono-molecular layer, or a portion thereof, the data obtained in this work can be fitted satisfactorily by means of the simple Langmuir equations (3) and (4).

Still another means of obtaining a value for v_m and therefore b , to be substituted into equation (4), is that of determining the area actually occupied by molecules and assuming a certain packing density. Table 3 shows a comparison of the values obtained from the Langmuir isotherms by the graphical method and those obtained by the method of Russell and Stokes using equation (5).

In all these calculations it is assumed that the surface area of the adsorbent is known without error. This is far from being true. Surface areas determined by the gas adsorption method are reproducible within about 5 per

cent on the same adsorbent, while relative surface areas can be obtained to better than 10 per cent. As far as an absolute value of surface area is concerned probably 20 per cent is a more realistic figure. Consequently, absolute values of all adsorption correlations are apt to be very difficult to arrive at. Yet on a relative basis the data and correlations are quite valid and useful.

The study of mixed adsorption is of far more practical importance. This study has dealt with binary gas mixtures adsorbed on a single homogeneous adsorbent, namely, Columbia Grade L charcoal. Markham and Benton (9) have derived equations for the adsorption of binary mixtures of gases based upon the Langmuir equation for single gases. Those equations, (6) and (7), have been applied in this investigation.

Before attempting any explanation of binary mixture behavior the data obtained in this study can be graphically presented. Four binary pairs were studied in some detail. They were methane-ethylene, ethylene-propane, propylene-n-butane, and ethylene-n-butane. Figs. 38, 39, 40, and 41 show the composition of adsorbed gases plotted against the composition of the feed mixture. In all instances it is readily apparent that the more strongly adsorbed gas suppresses the adsorption of the less strongly adsorbed component. This effect becomes greater as the composition of the feed mixture is increased in the heavier component. It is further observed that each component actually decreases the adsorption of the other. Using the values of v_m and b calculated, equations (6) and (7) were applied with varying success. Table 5 shows the results of several such determinations.

Another attempt at correlating the data was made on the basis of surface area covered by the adsorbate. From the pure gas isotherms for the components a predicted adsorption value for v_1 and v_2 was obtained at the proper tempera-

ture and at a pressure equal to the partial pressure of the component in the feed gas. The ratio of the experimental volume adsorbed from the binary mixture to the predicted adsorption was expressed as the fraction of predicted adsorption. Assuming the theory of mono-molecular adsorption, from the volume of gas actually adsorbed from the mixture can be calculated the fraction of the surface area covered by the heavier component. A plot of the fraction of predicted adsorption of the lighter component against the fraction of surface covered with a mono-molecular layer of the heavier component was made for all experimental data obtained for binary mixtures. This plot, Fig. 42, while being a highly empirical curve, gave a surprising degree of correlation. The points on the curve are numbered for reference back to the source of the data for the particular point in Tables 30, 31, and 32.

From the plot of Fig. 42 an approximation of the behavior of any of the binary mixtures at any temperature and pressure can be made as follows:

- (1) Assume the adsorption of the more strongly adsorbed component to be uninfluenced by the presence of the other component.
- (2) Use the pure gas curve for the more strongly adsorbed component to determine its adsorption at a total pressure equal to its partial pressure in the binary mixture.
- (3) Calculate the fraction of adsorbent surface covered by this component using the equation (5) and a knowledge of the total surface area of the adsorbent.
- (4) Use Figure 42 to determine the amount of displacement of the less strongly adsorbed component.
- (5) Use the pure gas curve to determine the adsorptivity of the less strongly adsorbed gas at a total pressure equal to its partial

partial pressure in the mixture.

- (6) Multiply the value obtained in step (5) by the value obtained in step (4) to determine the amount of adsorption of the less strongly adsorbed component of the binary mixture at the total pressure of the binary mixture.

Calculations of the behavior of a binary mixture by this method would be rough, usually of the order of 20 per cent deviation from experimental values.

Following the correlation suggested by Lewis (8), a plot was made of the vapor adsorbate equilibria for the binary mixtures studied. In this plot the mole fraction of the lighter component in the adsorbate is plotted against the mole fraction of the same component in the gas phase. If each component were adsorbed according to its partial pressure in the vapor phase such a plot would be a straight line, i.e., each gas would be adsorbed without effect upon the adsorption of the other component. However, no binary mixtures studied indicated this to be true. Rather it was observed in all instances that some mutual decrease in adsorption occurs. The curve representing the data obtained is shown in Fig. 43. Considering that the pressures were either 14.5 psia or 214.5 psia and that the composition of the gas mixtures varied greatly this correlation is significant. It will be noted from the plot that a separate line was drawn for the one experimental point on an ethylene-ethane equilibria plot. Because of the very close similarity between the two gases and their individual pure gas isotherms being very much alike, this binary pair would be expected to approach the ideal straight line. Further data would be necessary to substantiate this point.

A plot of N_1/N_1^0 (ratio of moles adsorbed from the binary mixture to

TABLE V

APPLICATION OF LANGMUIR EQUATIONS TO ADSORPTION OF BINARY MIXTURES

Experiment No.	Vol. Gas Adsorbed		Morrison Data		Langmuir Plot		% Deviation			
	<u>CH₄</u>	<u>C₂H₄</u>	<u>CH₄</u>	<u>C₂H₄</u>	<u>CH₄</u>	<u>C₂H₄</u>	Morrison		Langmuir	
	<u>CH₄</u>	<u>C₂H₄</u>	<u>CH₄</u>	<u>C₂H₄</u>	<u>CH₄</u>	<u>C₂H₄</u>	<u>CH₄</u>	<u>C₂H₄</u>	<u>CH₄</u>	<u>C₂H₄</u>
3615-96	8.03	49.3	6.05	38.9	6.92	40.6	-25	-21	-13	-17
3735-3	5.95	47.2	4.23	41.6	7.48	40.9	-28	-12	+25	-13
3735-7	4.97	52.2	6.02	38.0	5.48	41.9	+21	-27	+10	-19
3735-41	11.90	32.2	8.70	18.1	12.9	24.5	-27	-43	+8	-23
3735-51	4.47	56.8	3.14	60.7	26.2	45.8	-30	+7	+400	-19
3735-66	11.1	120.	45.7	83.1	5.74	94.5	+300	-30	-49	-21
3735-70	41.2	84.0	164.0	37.6	35.0	72.6	+300	-15	-53	-13
	<u>C₂H₄</u>	<u>C₃H₈</u>	<u>C₂H₄</u>	<u>C₃H₈</u>	<u>C₂H₄</u>	<u>C₃H₈</u>	<u>C₂H₄</u>	<u>C₃H₈</u>	<u>C₂H₄</u>	<u>C₃H₈</u>
3735-29	20.2	68.6	28.6	79.2	35.6	46.7	+31	+17	+76	+36
3735-14	11.95	84.5	12.6	88.8	21.2	71.5	+5	+5	+77	-15
3735-47	6.52	96.7	4.75	98.5	9.3	92.8	+27	+2	+42	-4
3735-49	5.97	103.	2.98	101.	6.07	98.5	-50	-2	+2	-4
3735-55	8.11	87.1	9.6	92.6	17.2	78.8	+18	+6	+110	-9
3735-59	50.6	87.6	32.3	93.3	48.2	66.8	-36	+6	-5	-23
3735-62	46.5	90.5	32.3	93.3	48.2	66.2	-30	+3	+4	+26
	<u>C₂H₄</u>	<u>C₄H₁₀</u>	<u>C₂H₄</u>	<u>C₄H₁₀</u>	<u>C₂H₄</u>	<u>C₄H₁₀</u>	<u>C₂H₄</u>	<u>C₄H₁₀</u>	<u>C₂H₄</u>	<u>C₄H₁₀</u>
3735-80	55.7	74.1	30.2	83.5	33.7	79.3	-45	+12	-39	-6
3735-83	12.8	65.0	24.8	69.2	27.2	56.5	+94	+6	+101	-13
	<u>C₂H₄</u>	<u>C₂H₆</u>	<u>C₂H₄</u>	<u>C₂H₆</u>	<u>C₂H₄</u>	<u>C₂H₆</u>	<u>C₂H₄</u>	<u>C₂H₆</u>	<u>C₂H₄</u>	<u>C₂H₆</u>
3735-72	29.8	46.5	34.0	60.0	25.5	43.2	+14	+28	-14	-7

moles of the same adsorbed component at the same temperature and at a total pressure equal to the pressure of the mixture) against N_2/N_1' (similar ratio for the less volatile component) is represented by the straight line of Fig. 44. This line satisfies the equation

$$\frac{N_1}{N_1'} + \frac{N_2}{N_2'} = 1 \quad (10)$$

From a knowledge of the pure gas isotherms one can obtain N_1' and N_2' but another expression is needed to determine N_1 and N_2 . If the composition of the feed gas is known then the mole fraction of the lighter component in the adsorbate can be read from Fig. 43, thus the composition of the adsorbate is known.

SUMMARY AND CONCLUSIONS

The data on adsorption of hydrocarbon gases on activated charcoal have been extended to a temperature of 400°C and a pressure of 600 psig. Such data, all obtained on a single sample of charcoal, permits a critical study of the adsorption characteristics of mixtures. Design of commercial gas adsorption equipment requires a knowledge of gas mixture behavior.

Adsorption of selected gases on three charcoals ranging from 506 to 1152 sq. meters/gram, showed that the quantity of a gas adsorbed was proportional to the surface area. However, when the nature of the surface was altered, as in the case of silica gel, this proportionality did not hold.

The Langmuir equation was applied to the data on single gases. In each instance a plot of $1/v$ vs $1/p$ gave straight lines from which slope and intercept constants were readily obtained.

In the study of binary mixture adsorption an empirical correlation was developed based upon the fraction of the total adsorbent surface area covered by a monomolecular layer of the less volatile component. While the correlation gives values in error by about 10-20 per cent, it is based upon the assumption that no mutual reduction in adsorption exists. Where the volatilities of the two components are nearly equal this method is fairly accurate.

Application of the Langmuir equations as modified by Markham and Benton for binary mixtures, and assuming some mutual reduction in adsorption of each component, gave results in fair agreement with experimental data. However, application of these equations is dependent upon a satisfactory determination of the constants b and v_m . If the intercept and slope of

Langmuir plots for single gases are used somewhat better agreement is obtained than if these constants are calculated from the molecular areas.

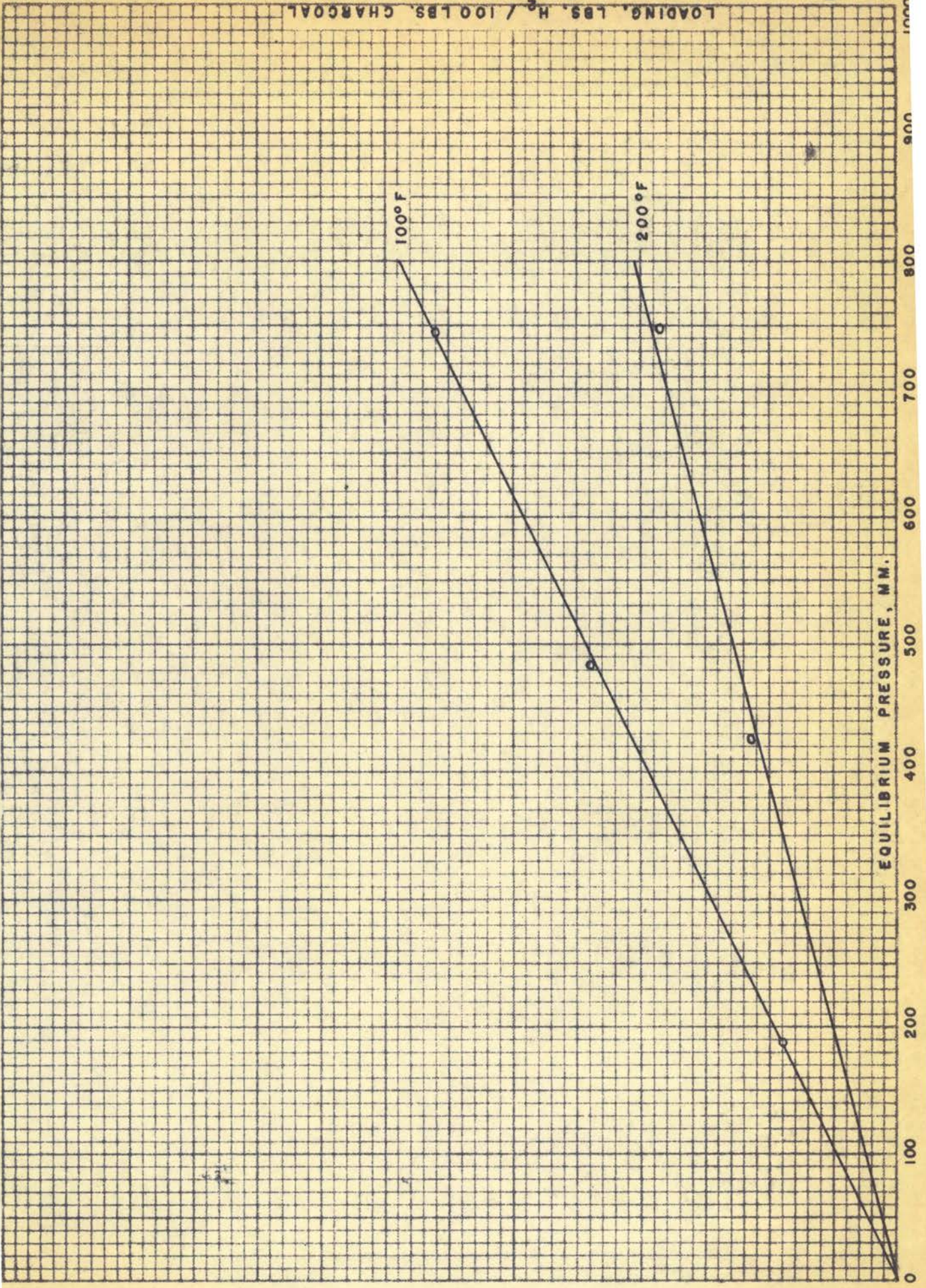
For a specified temperature and total pressure, the behavior of a binary mixture is conveniently expressed in a plot of feed composition vs gas adsorption. Such a plot (Figs. 38, 39, 40, 41) can be consulted and the adsorbate concentration can be readily determined.

In another correlation attempt it was found that a plot of vapor-adsorbate equilibria gave a smooth curve somewhat resembling a vapor-liquid equilibrium curve. From this and a knowledge of the mole fraction of the lighter component in the gas phase, one can readily determine the mole fraction of that component in the adsorbate.

It is apparent that no adsorption equation studied is capable of giving absolute correlation of data. While the adsorption behavior of single pure gases can be observed with a high degree of accuracy, application of any system of correlating with mixed adsorption phenomena introduces some approximation. For design purposes the degree of approximation is not excessive.

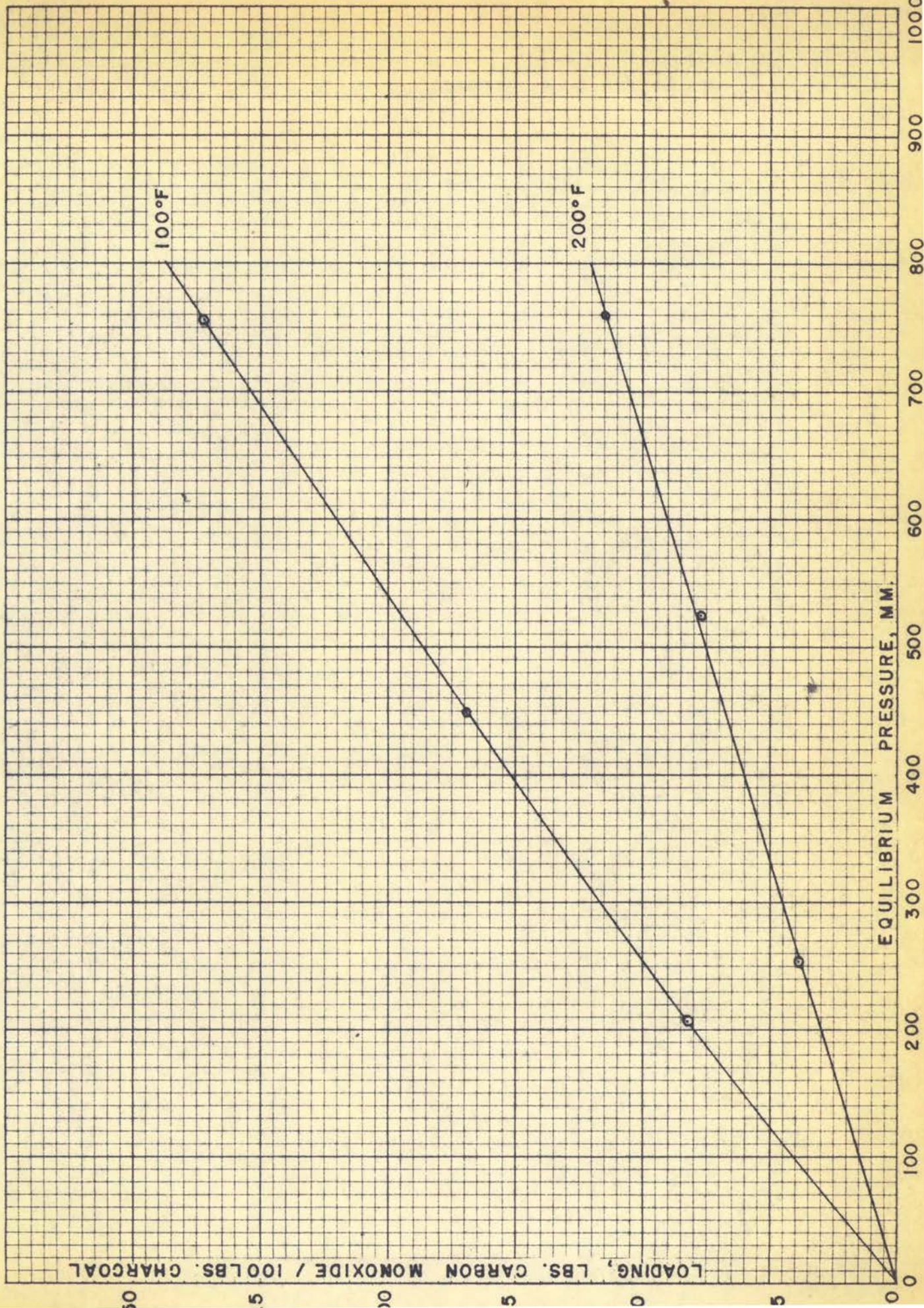
LOADING, LBS. H₂O / 100 LBS. CHARCOAL

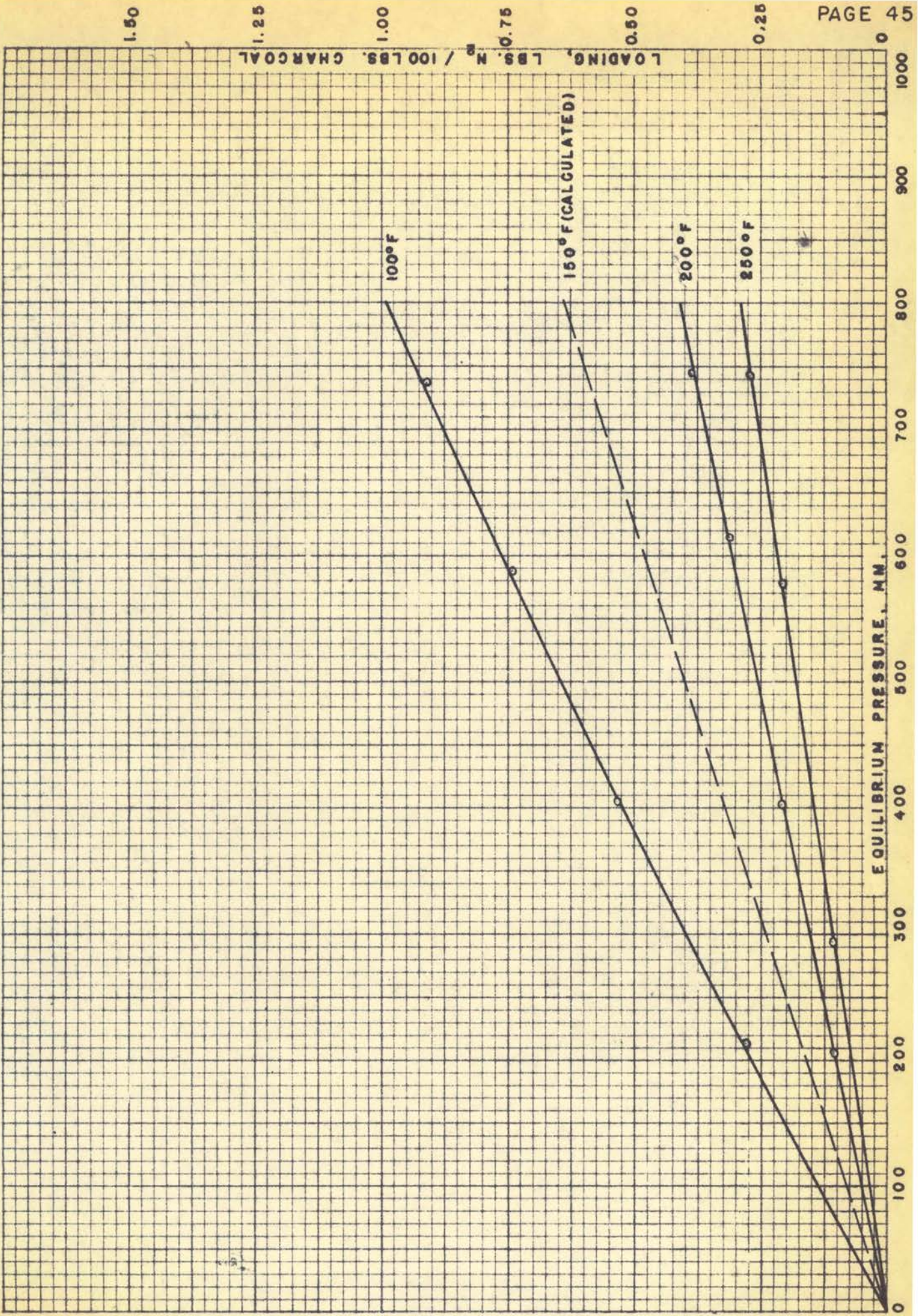
EQUILIBRIUM PRESSURE, MM.

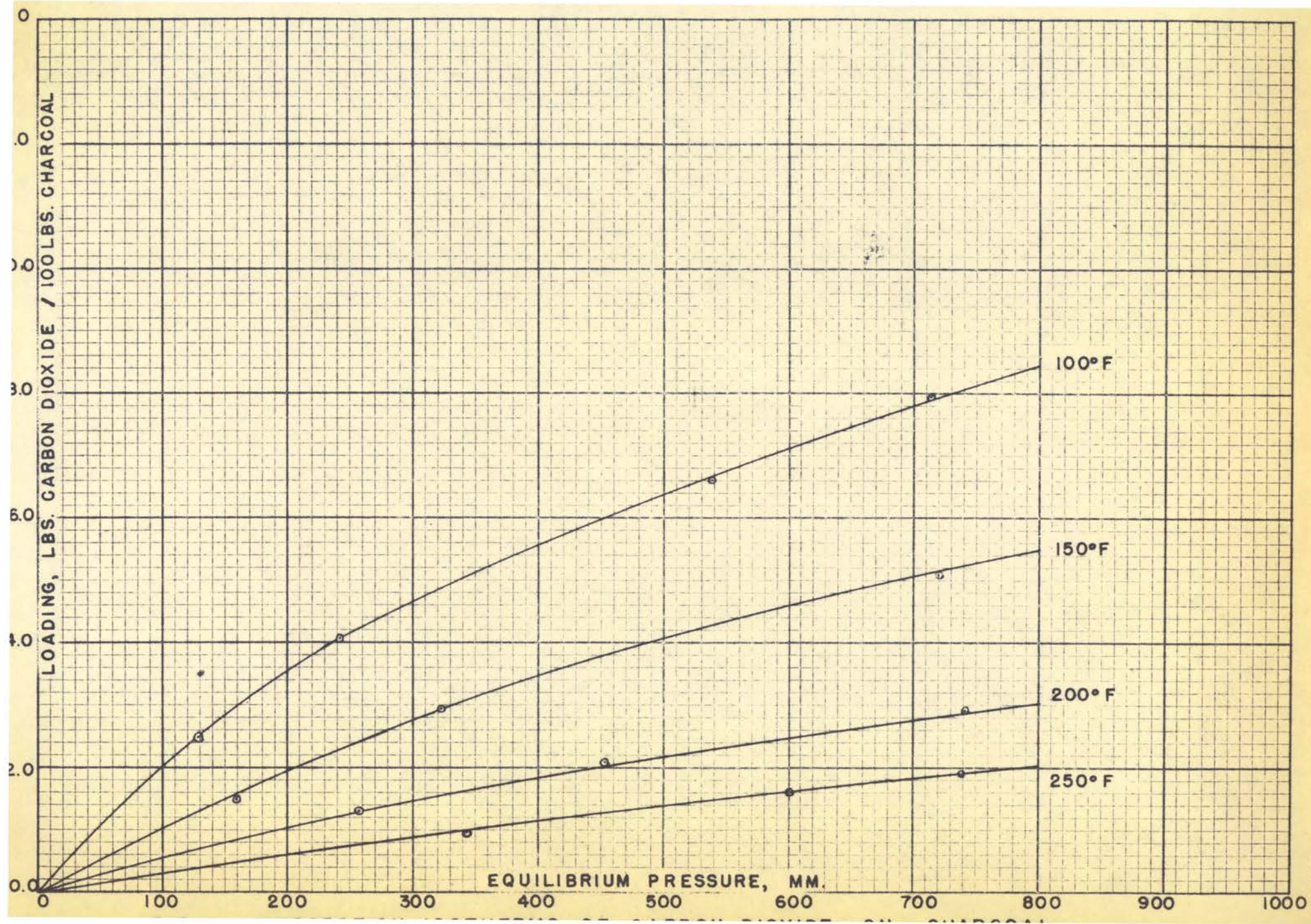


1 X 10⁻²
9
8
7
6
5 X 10⁻¹
4
3
2
1 X 10⁰

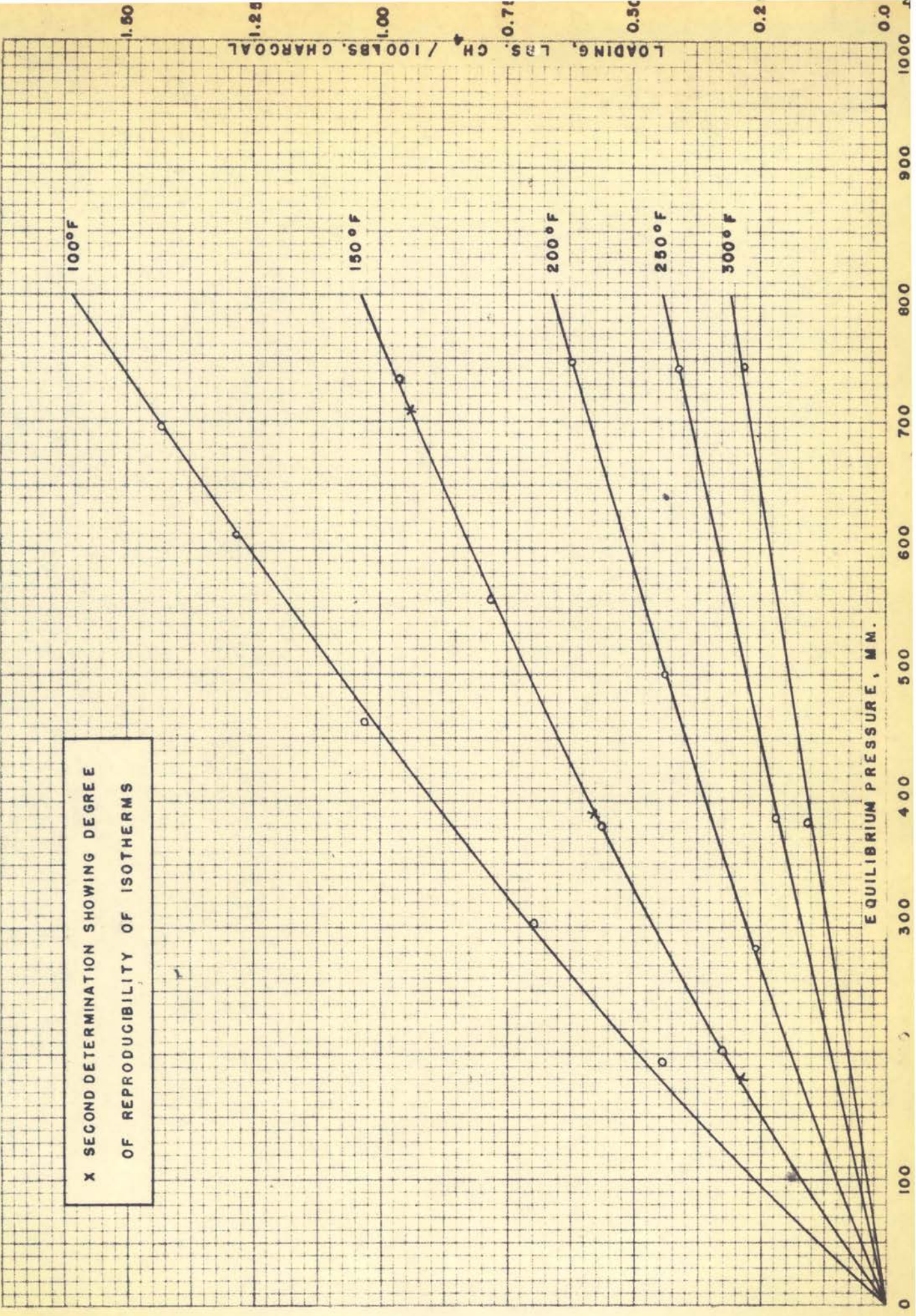
1000
900
800
700
600
500
400
300
200
100
0

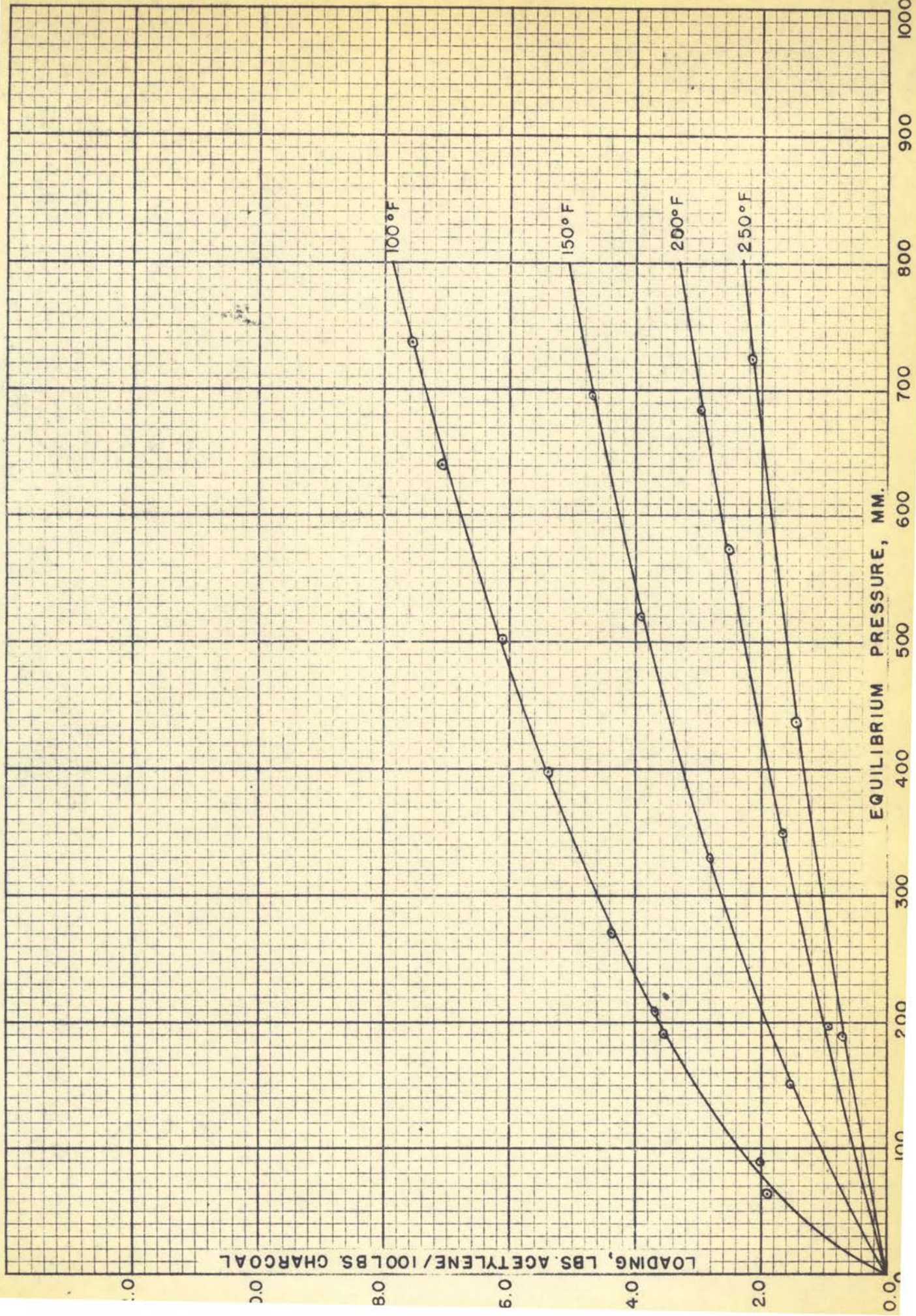




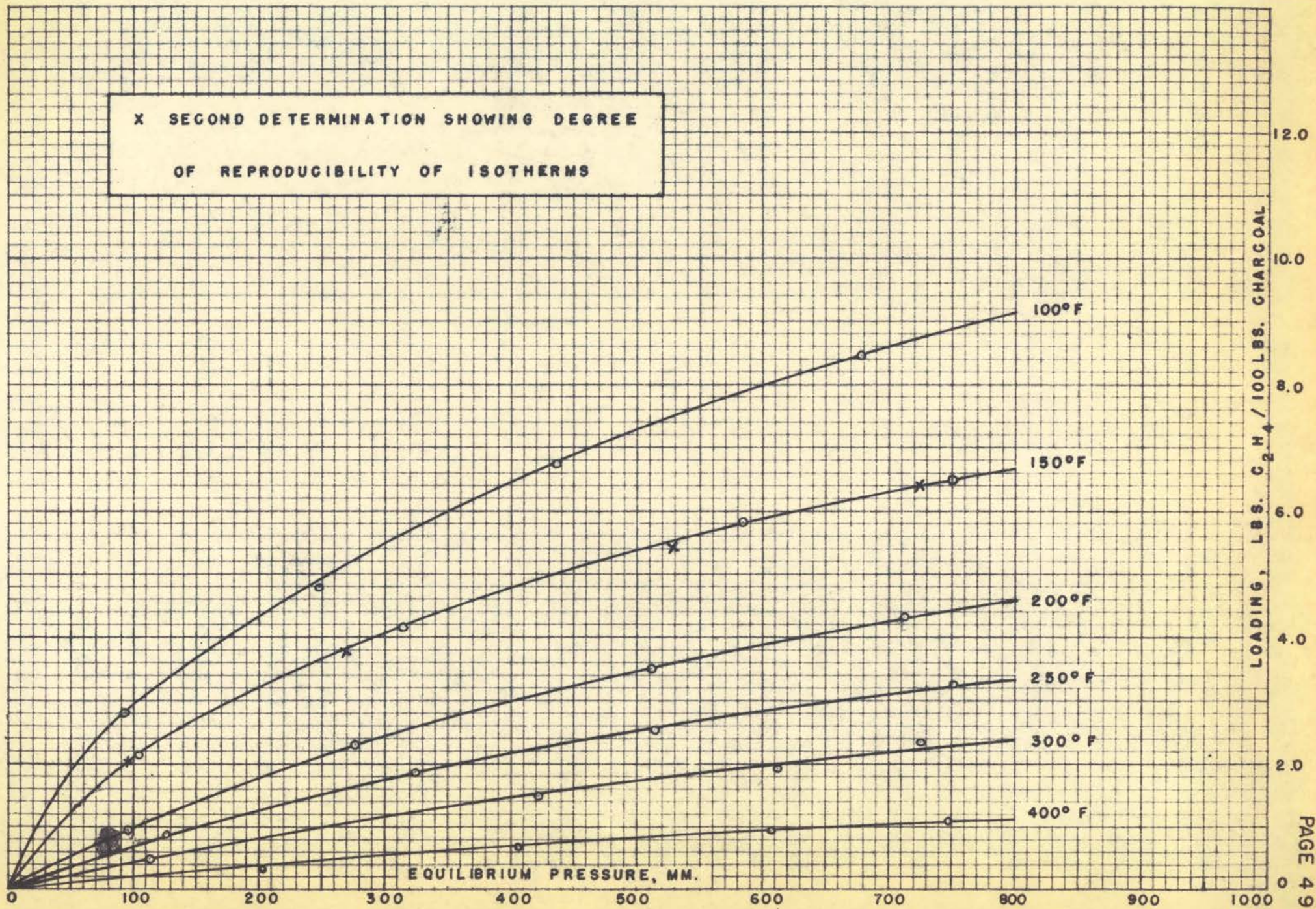


X SECOND DETERMINATION SHOWING DEGREE OF REPRODUCIBILITY OF ISOTHERMS





X SECOND DETERMINATION SHOWING DEGREE
OF REPRODUCIBILITY OF ISOTHERMS



LOADING, LBS. C_2H_4 / 100 LBS. CHARCOAL

EQUILIBRIUM PRESSURE, MM.

LOADING, LBS. ETHANE / 100 LBS. CHARCOAL

12.0

10.0

8.0

6.0

4.0

2.0

0

EQUILIBRIUM PRESSURE, MM.

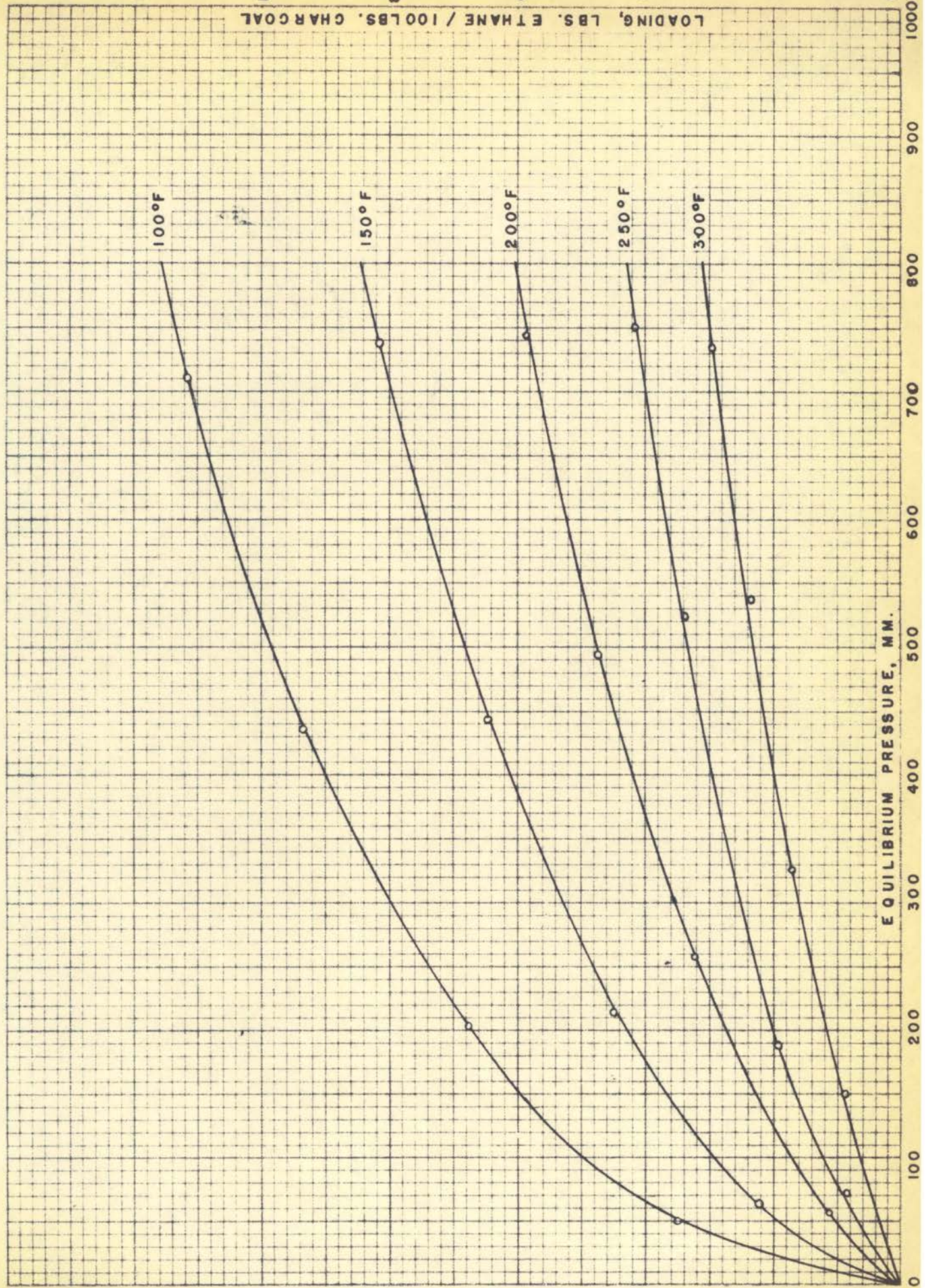
100°F

150°F

200°F

250°F

300°F



LOADING, LBS. PROPYLENE / 100 LBS. CHARCOAL

24.0

20.0

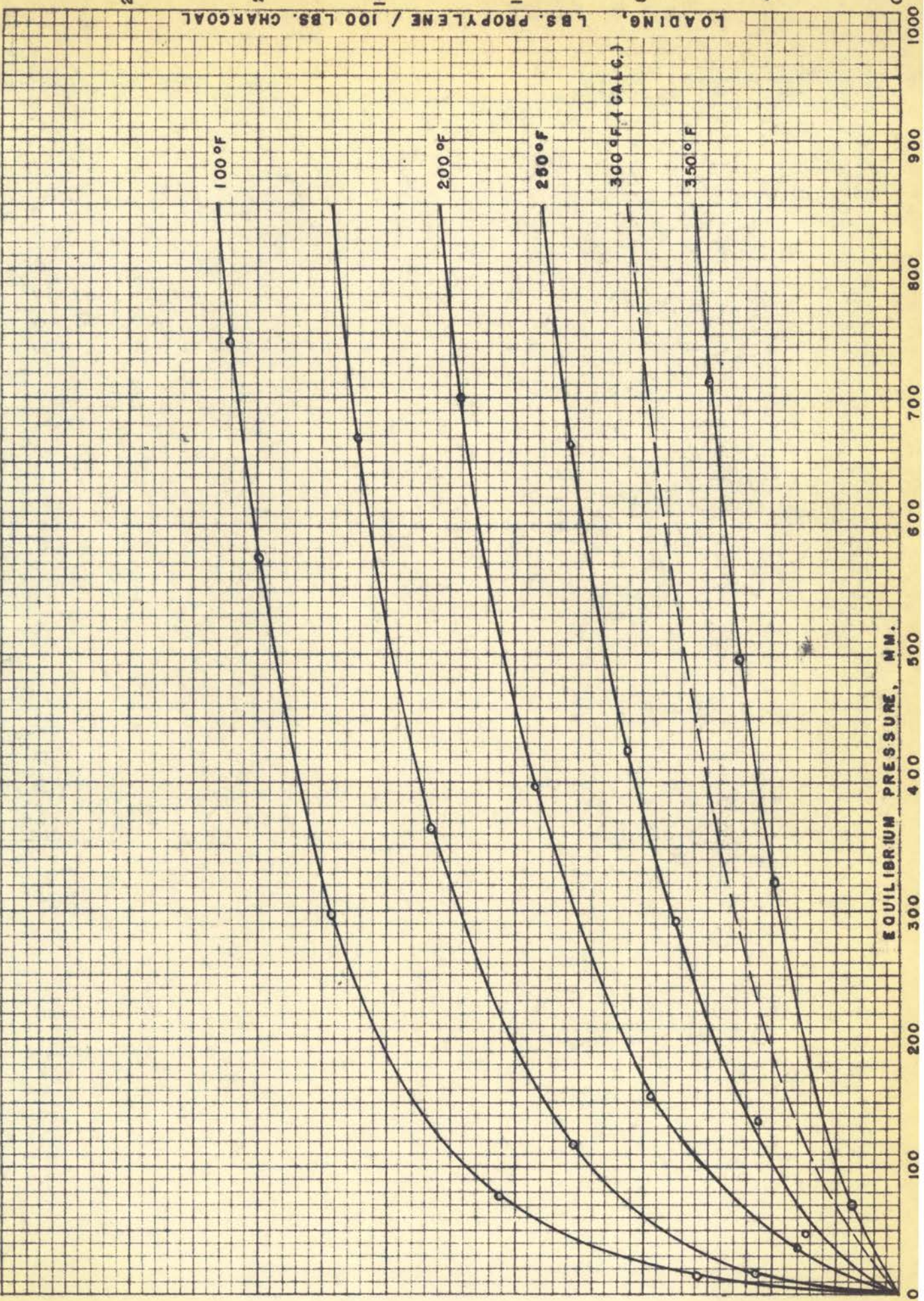
16.0

12.0

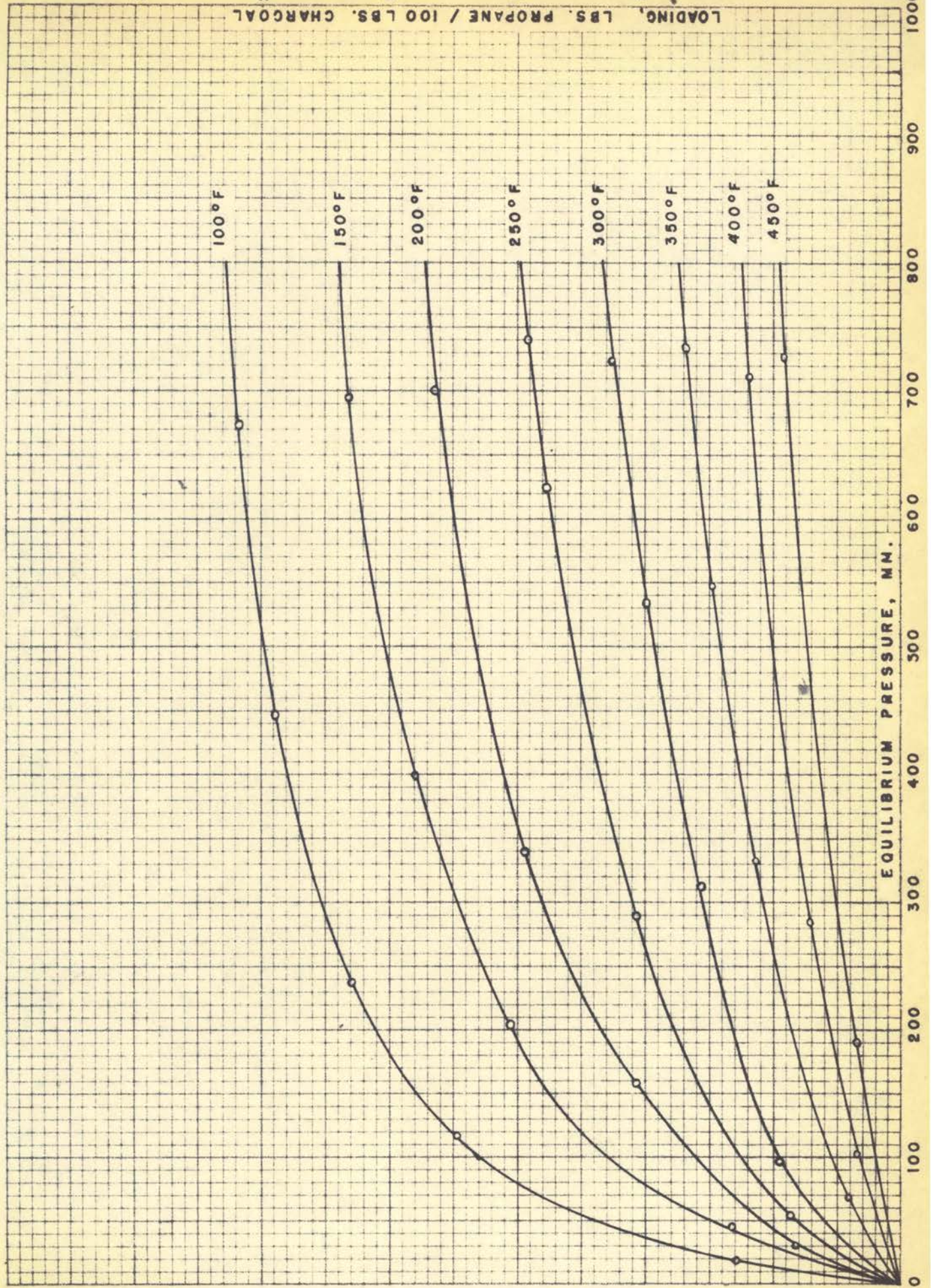
8.0

4.0

EQUILIBRIUM PRESSURE, MM.



LOADING, LBS. PROPANE / 100 LBS. CHARCOAL



24.0

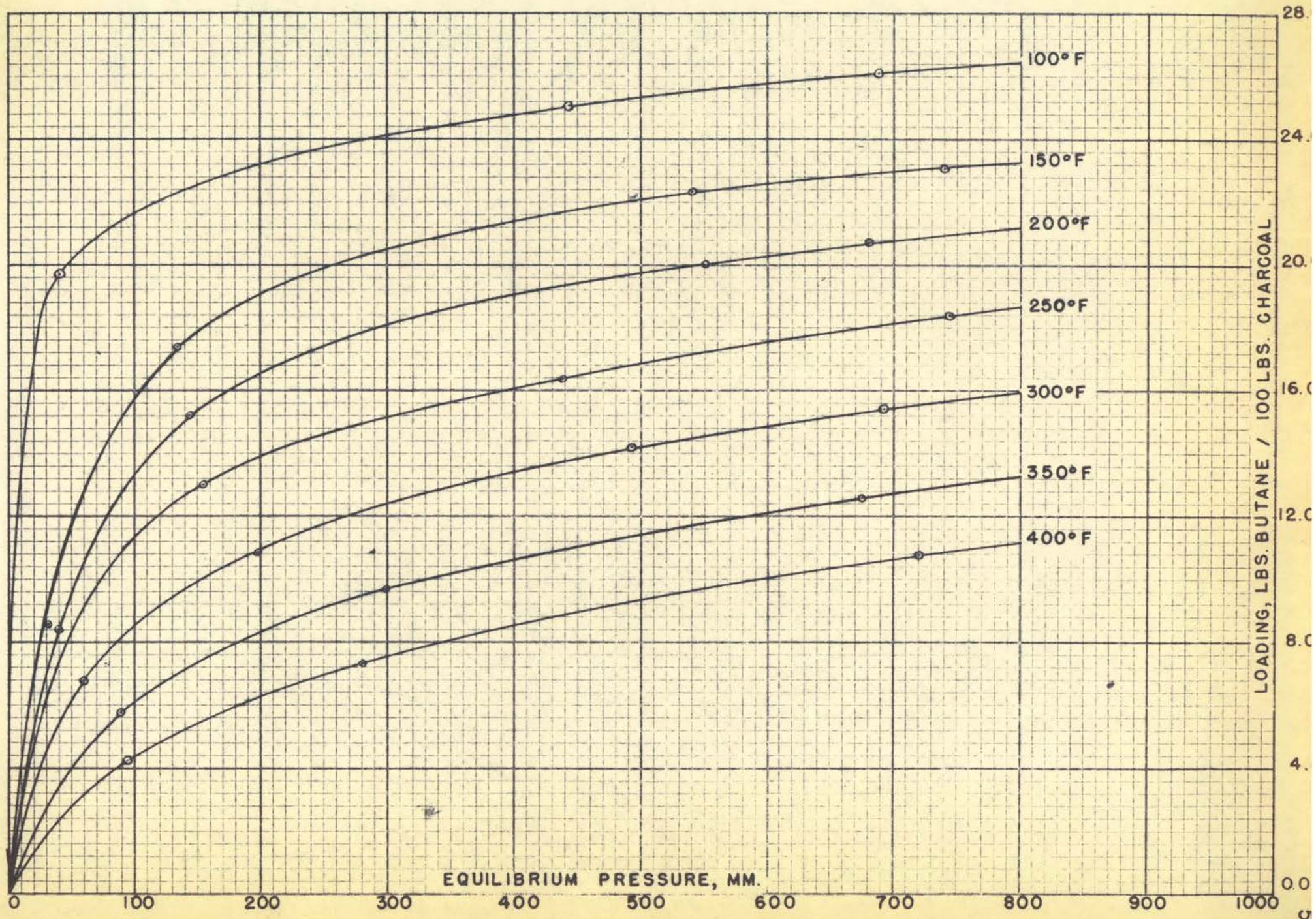
20.0

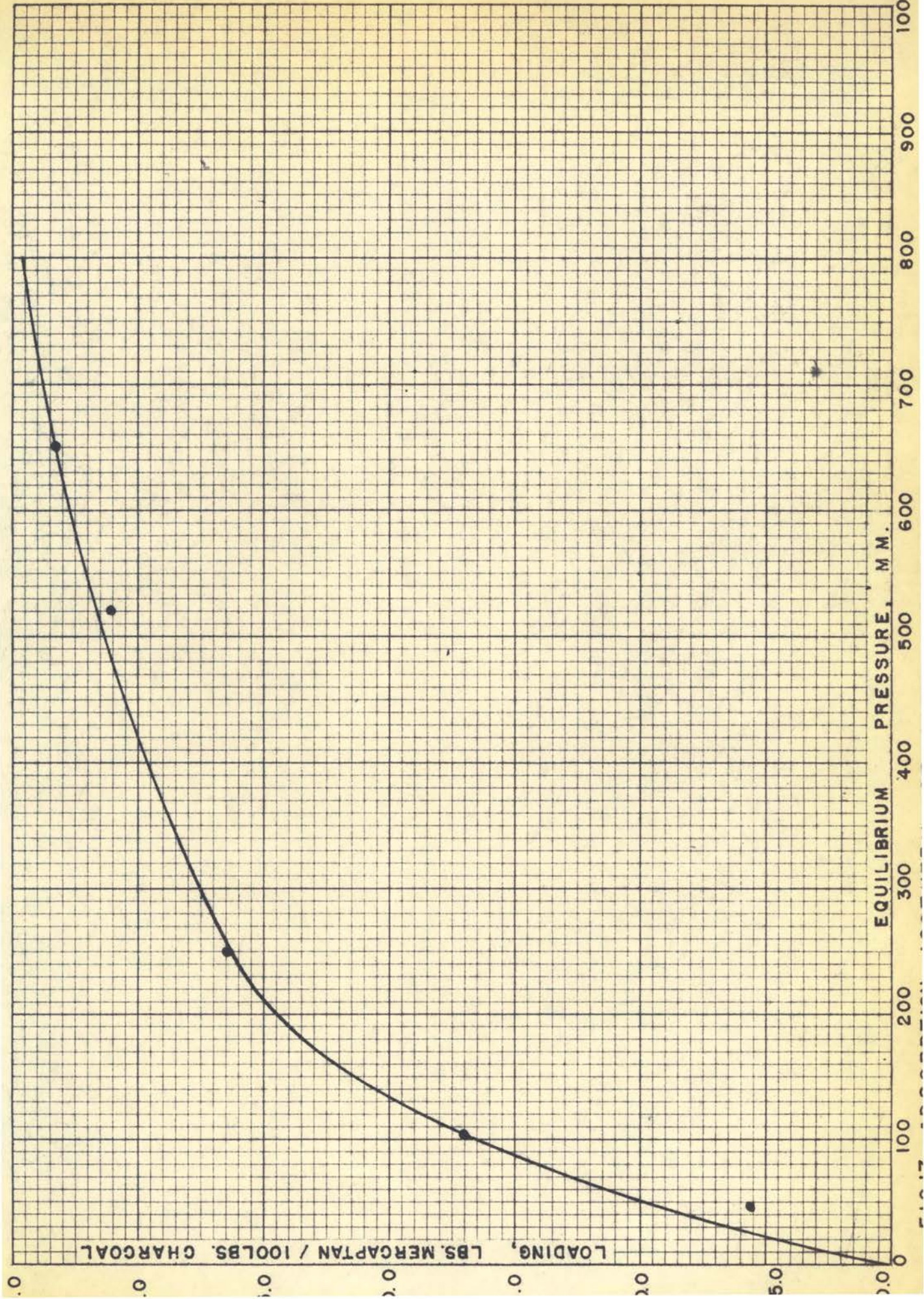
16.0

12.0

8.0

4.0





700

600

500

400

300

200

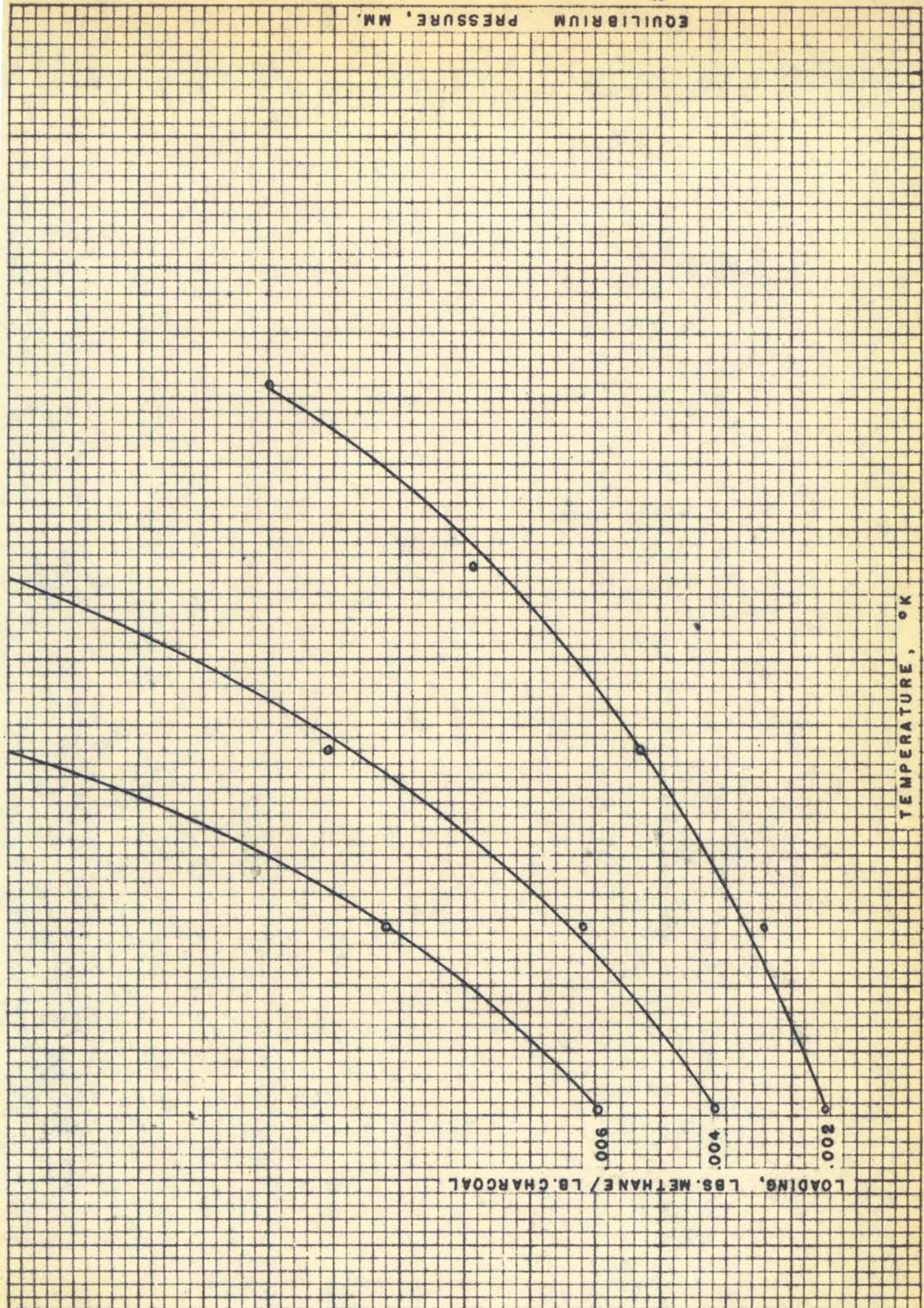
100

0

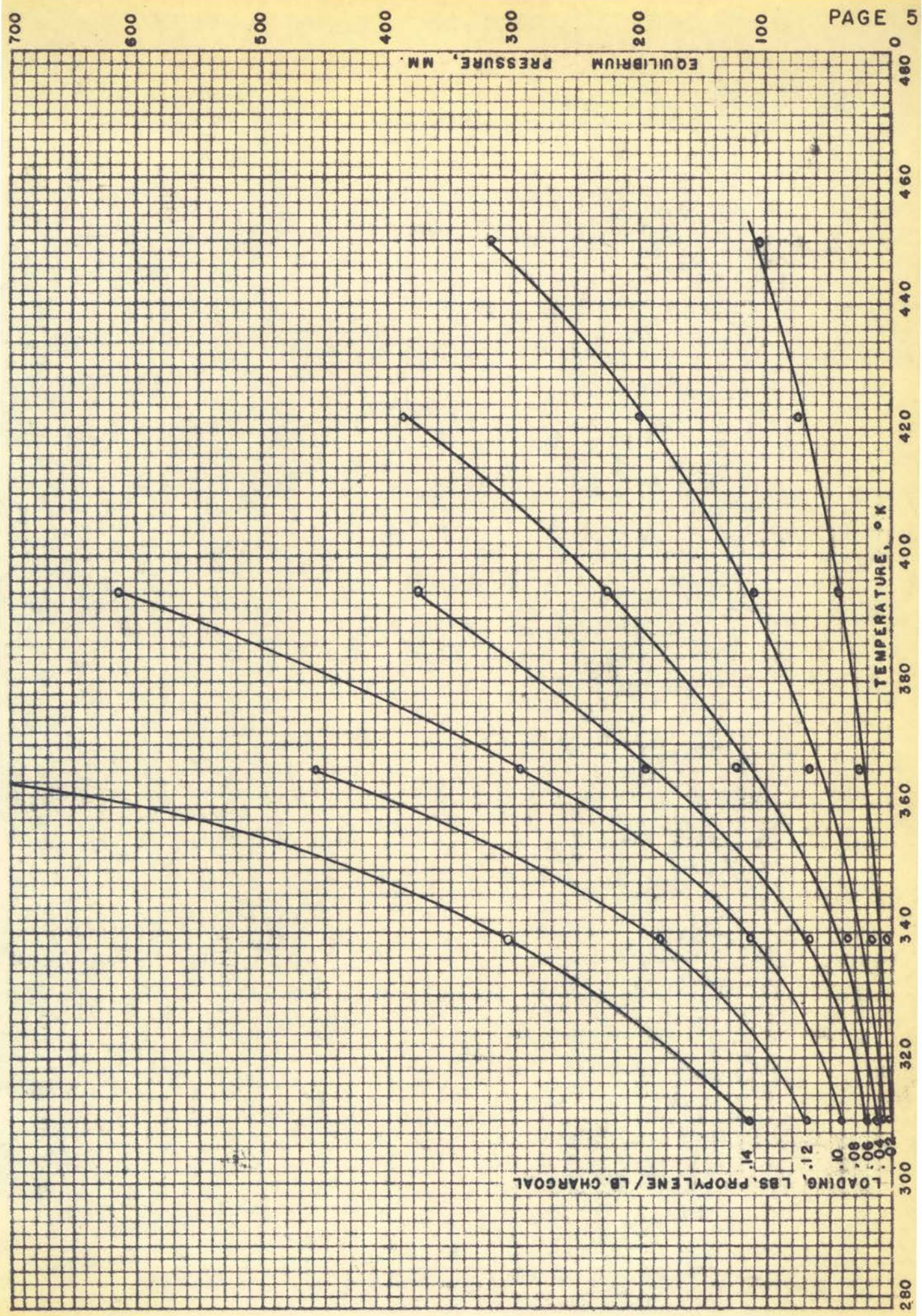
EQUILIBRIUM PRESSURE, MM.

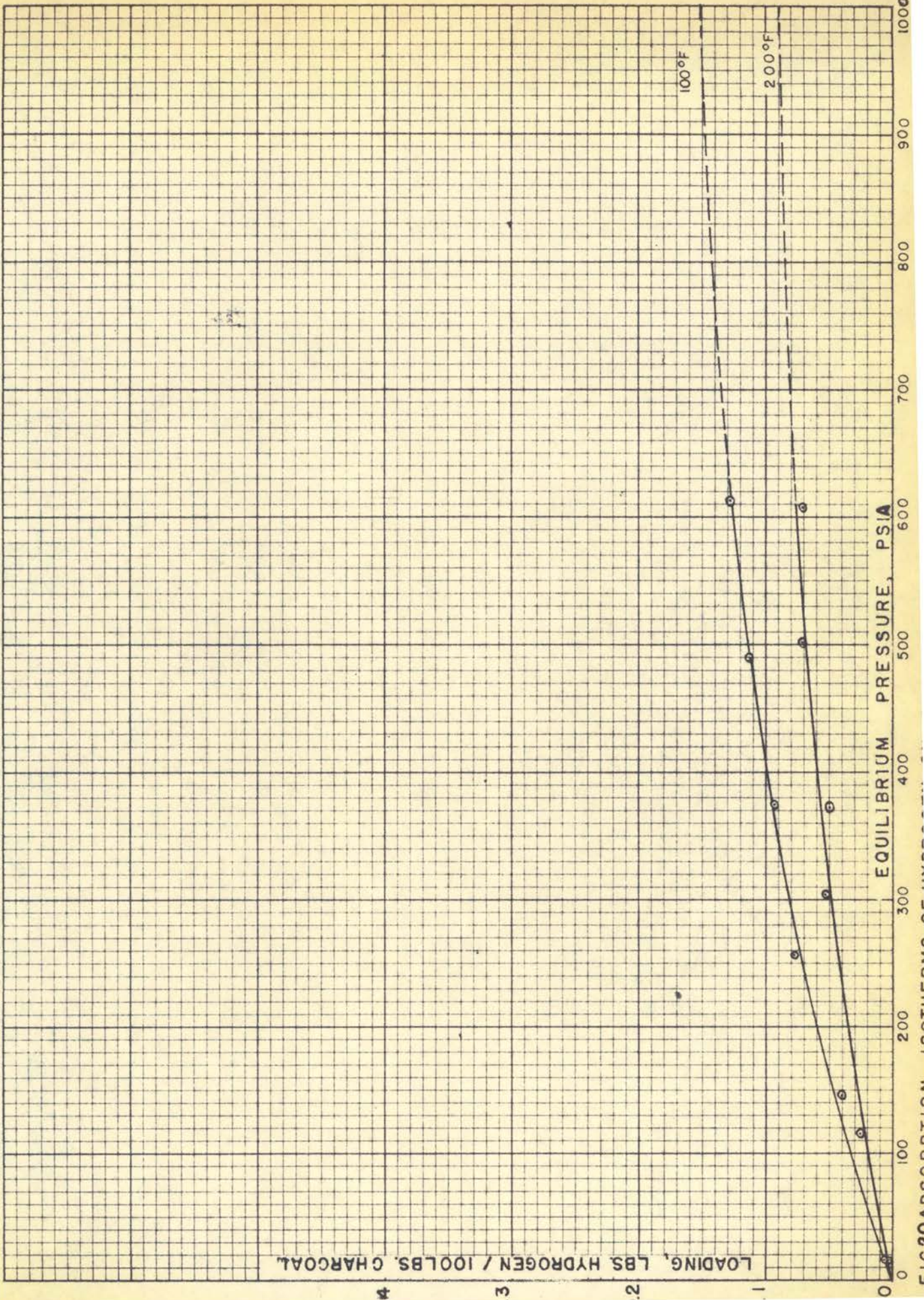
TEMPERATURE, °K

LOADING, LBS. METHANE / LB. CHARCOAL



480 460 440 420 400 380 360 340 320 300

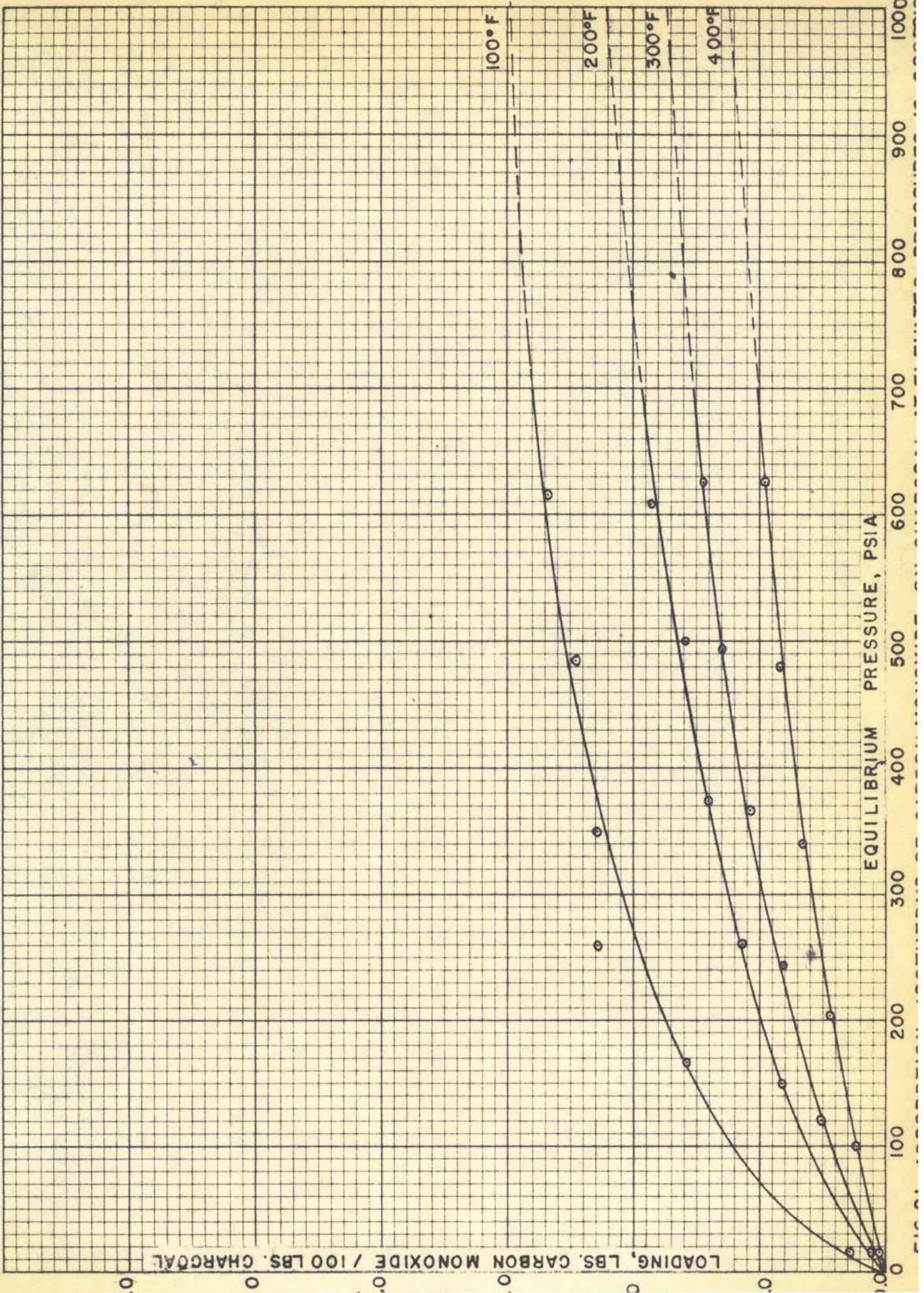


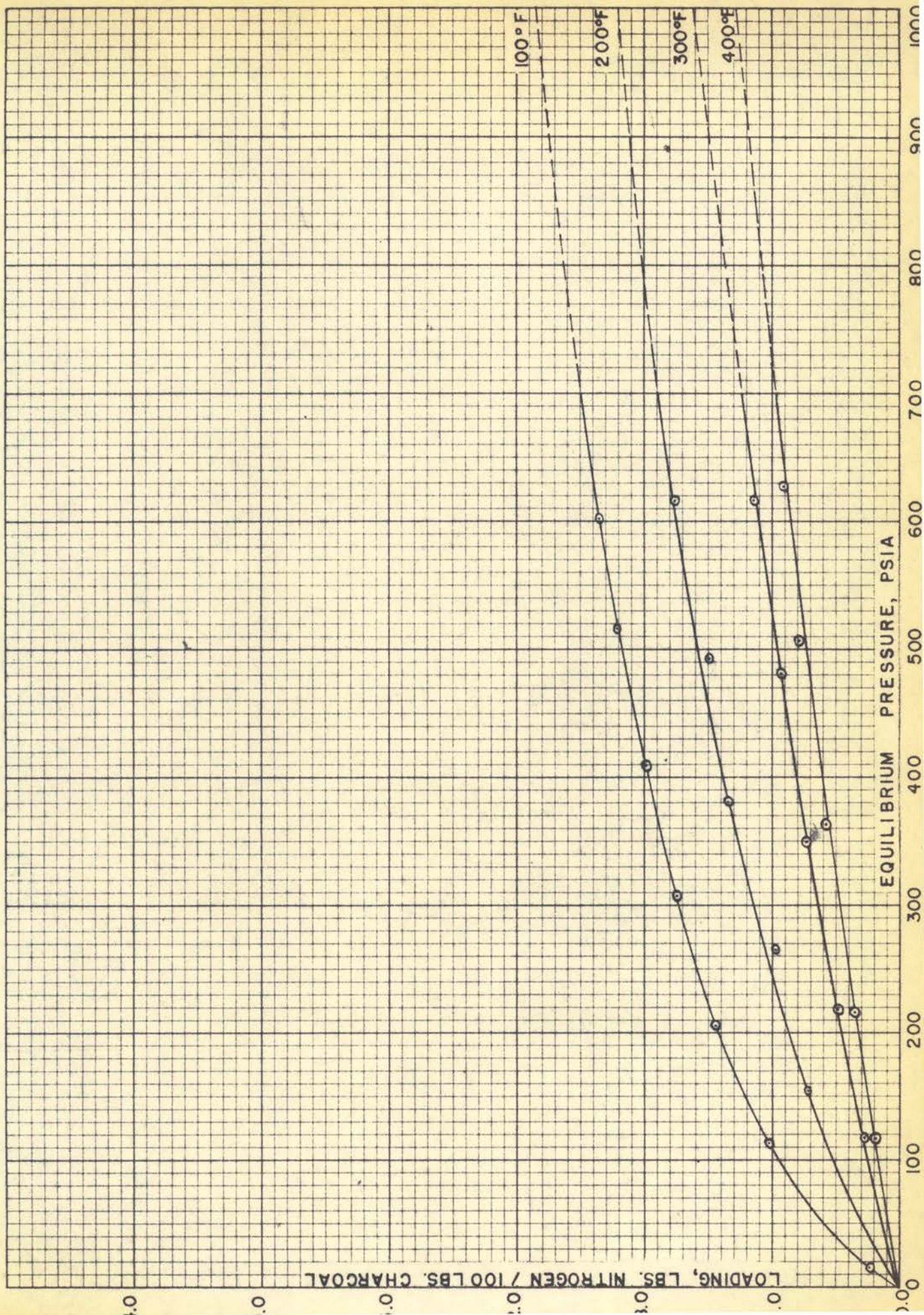


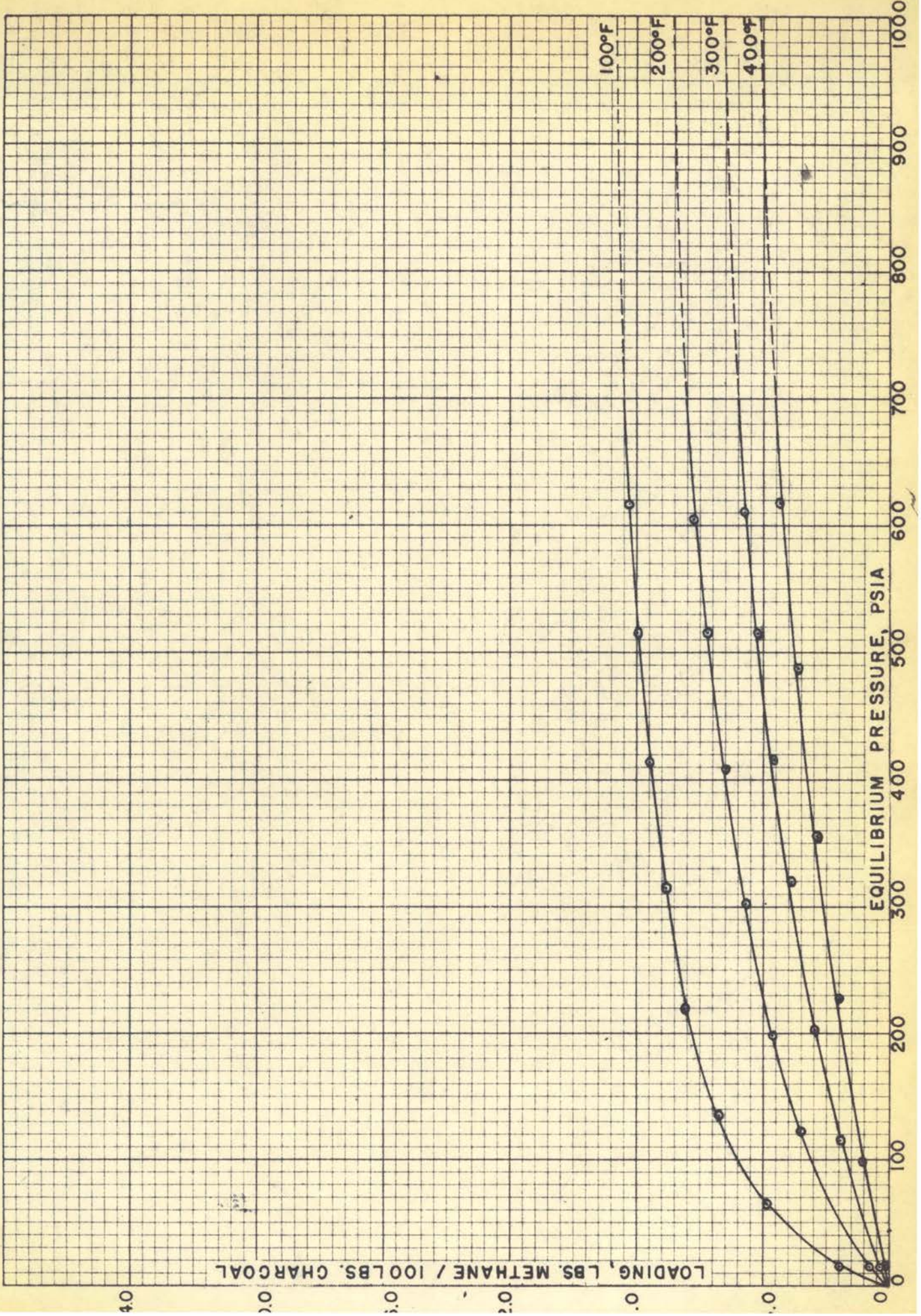
LOADING, LBS. HYDROGEN / 100 LBS. CHARCOAL

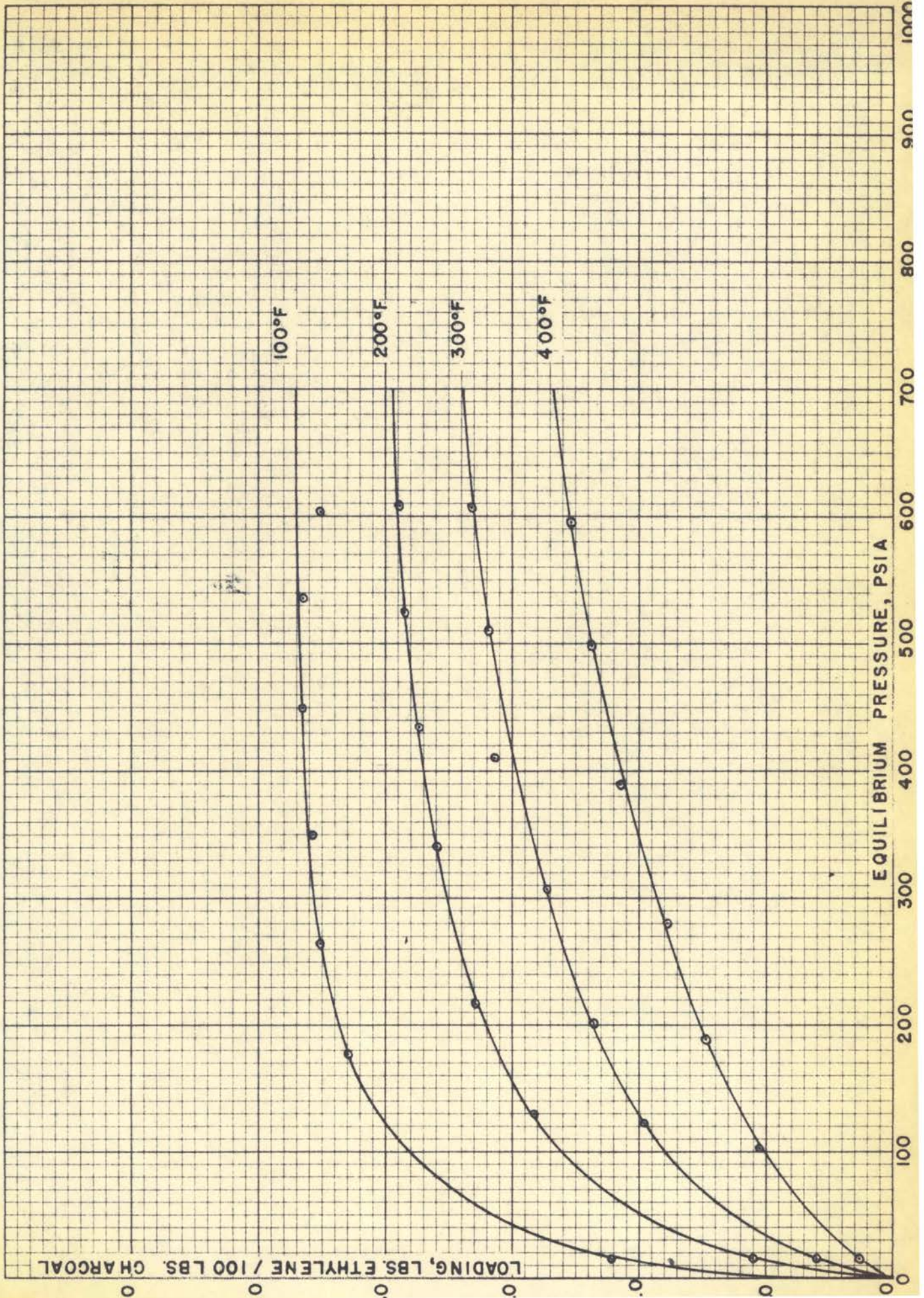
EQUILIBRIUM PRESSURE, PSIA

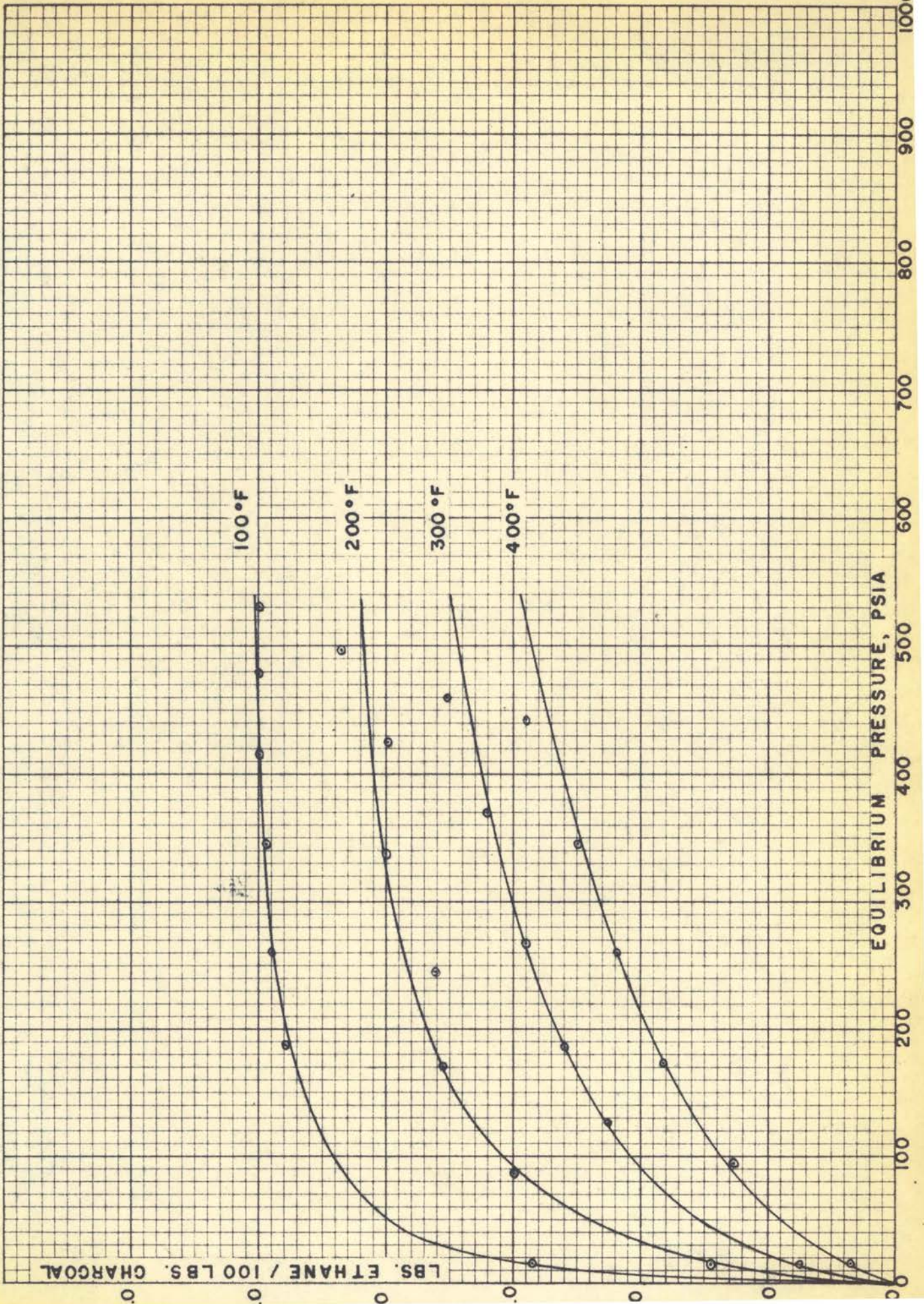
FIG 20 ADSORPTION ISOTHERMS OF HYDROGEN ON CHARCOAL

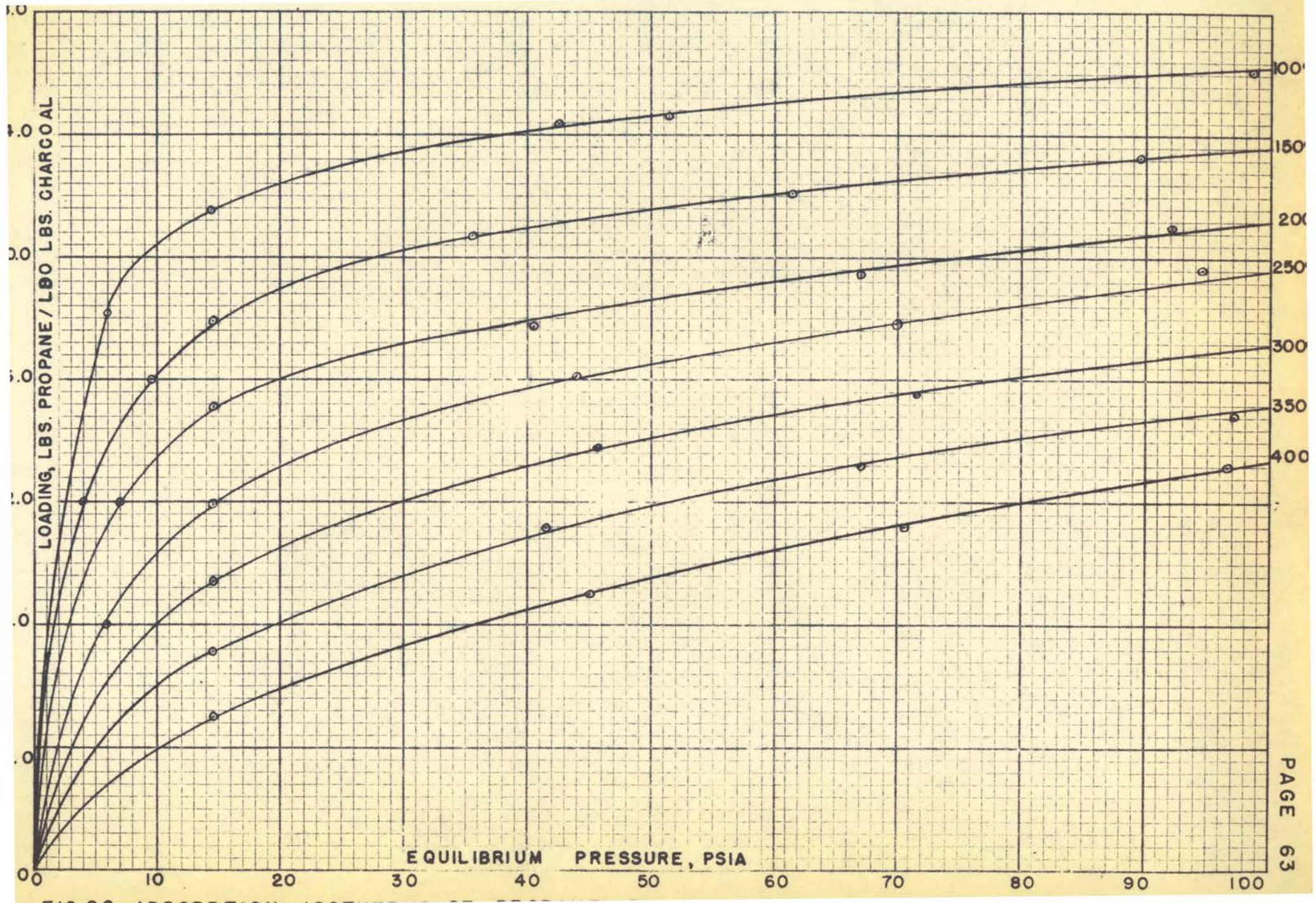


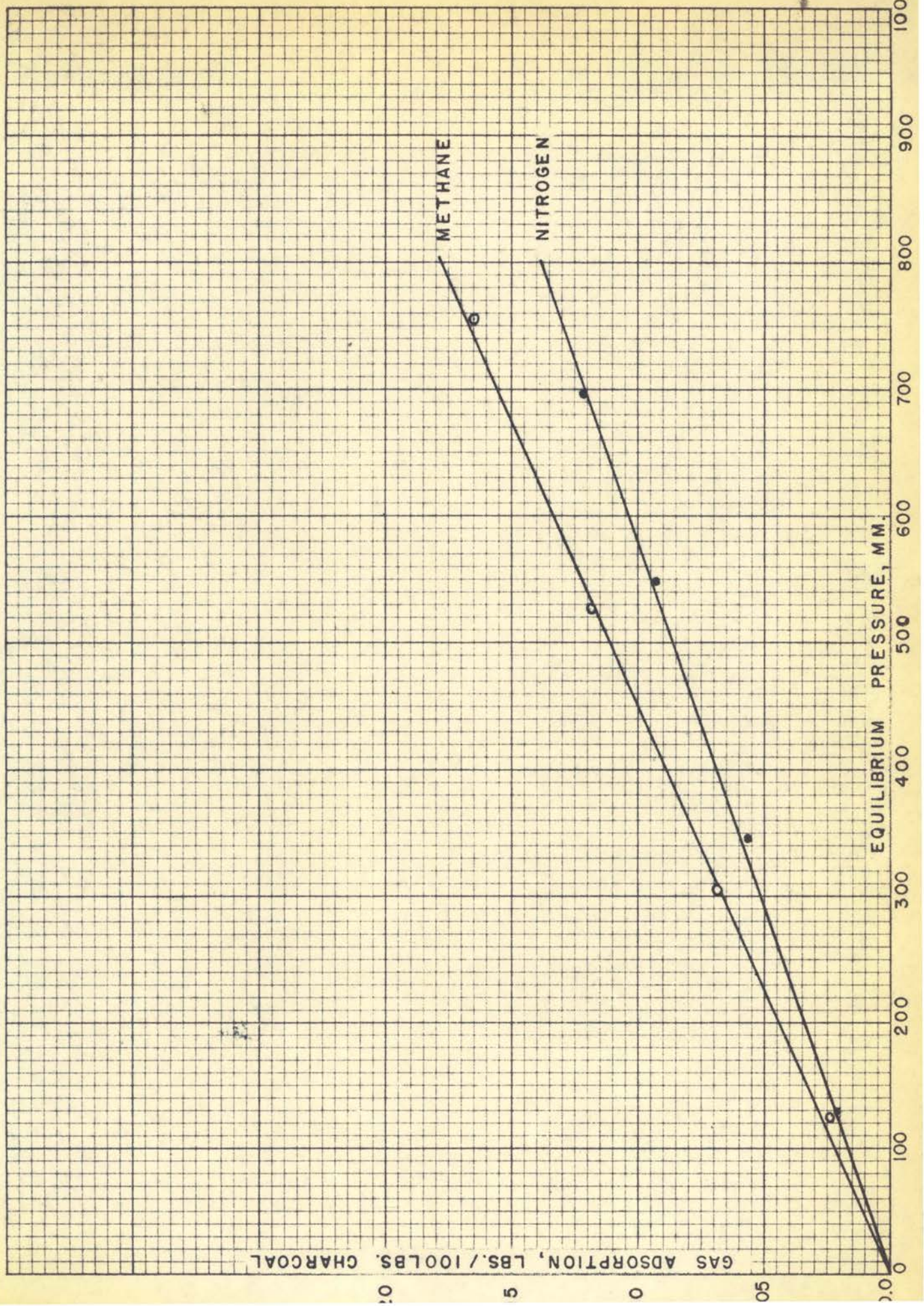


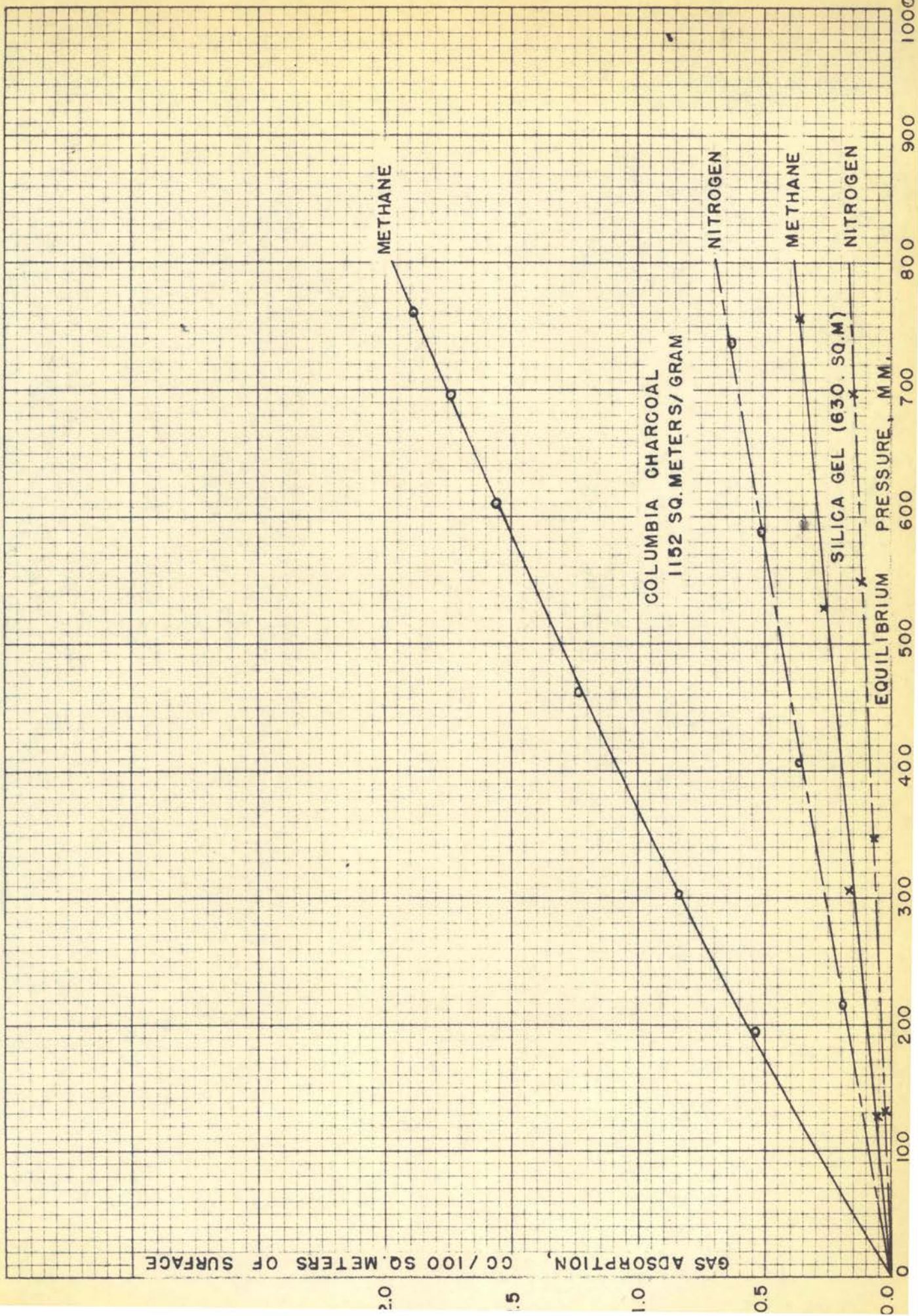


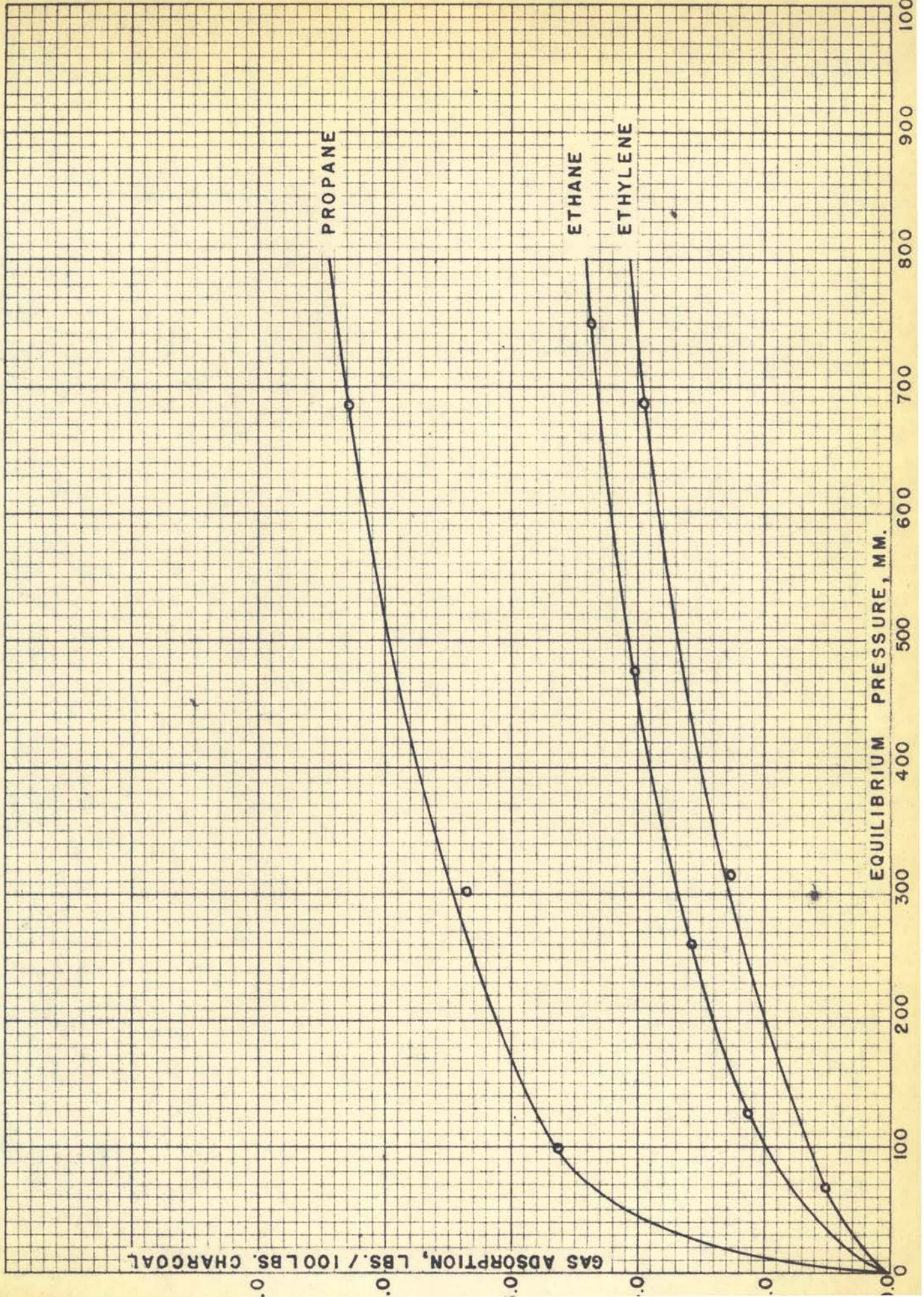


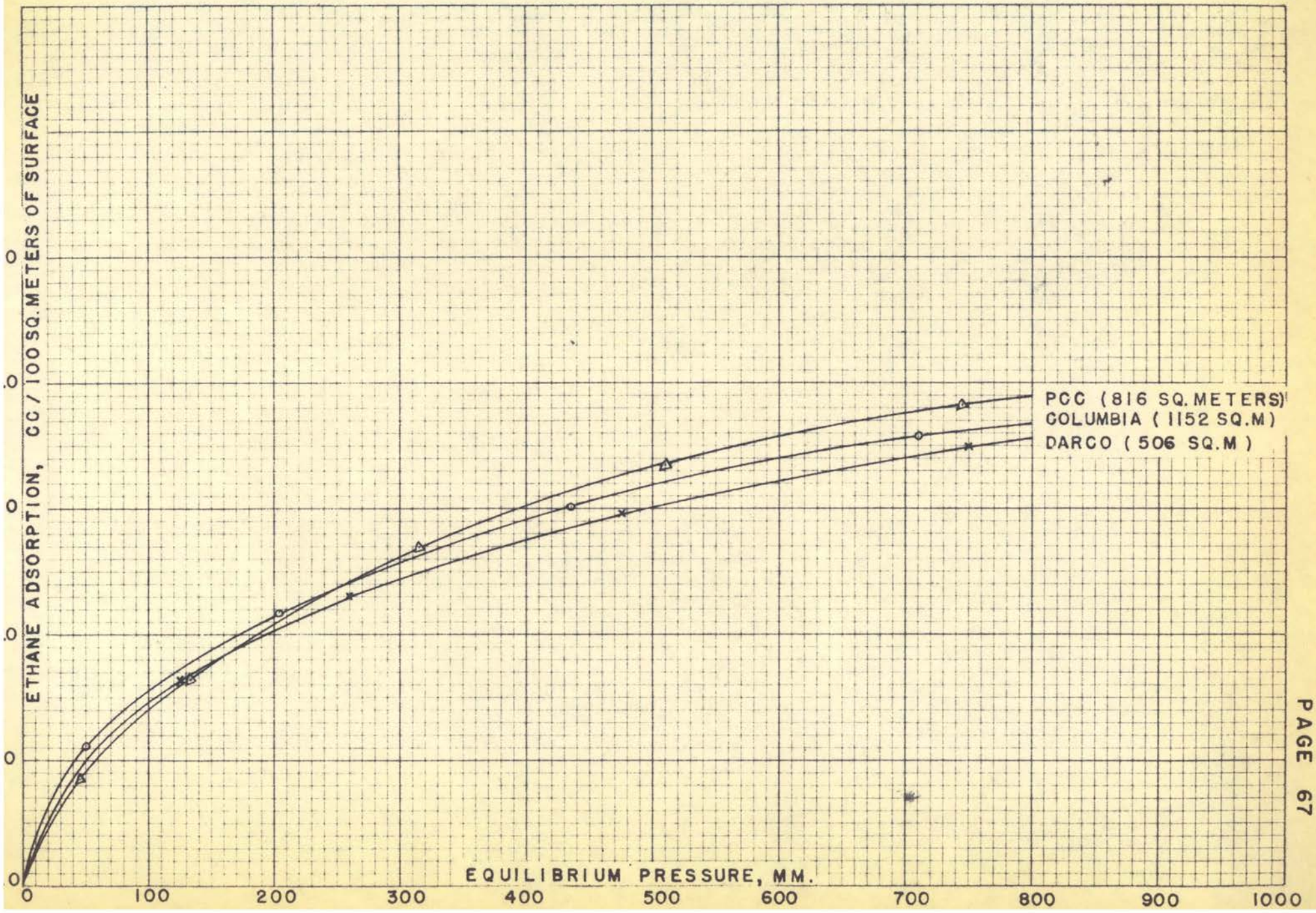


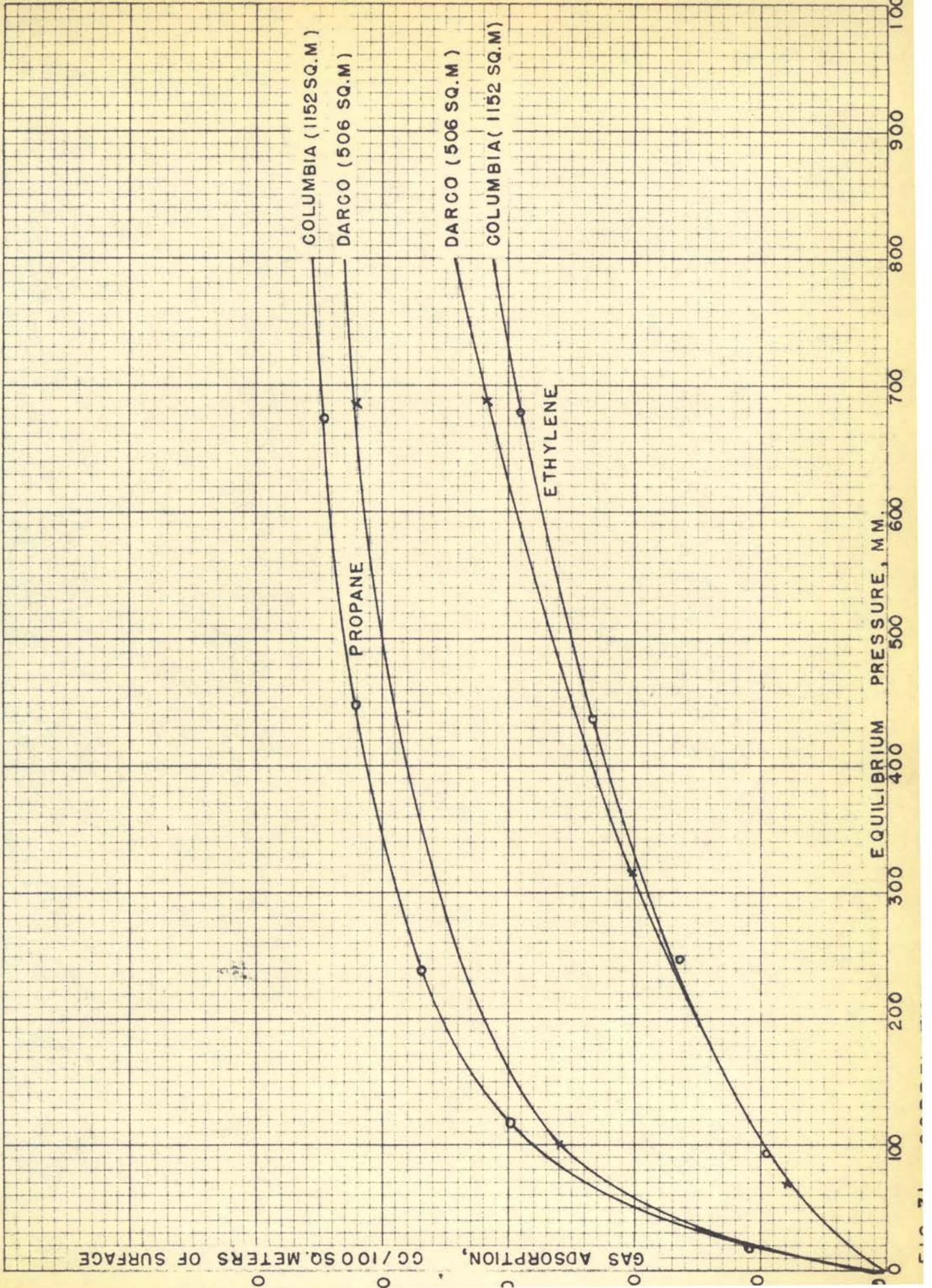












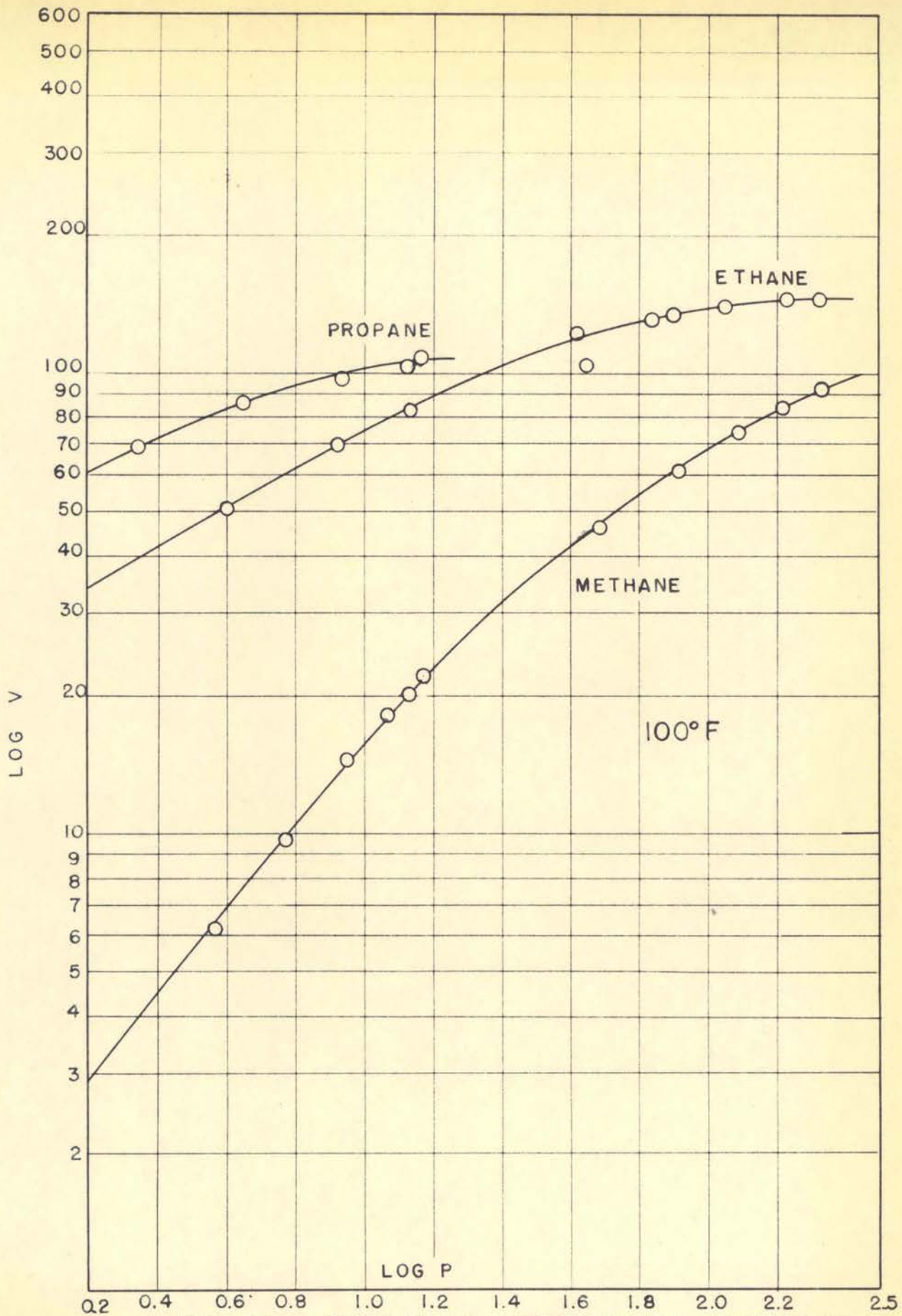


FIG. 32 SELECTED FREUNDLICH ISOTHERMS

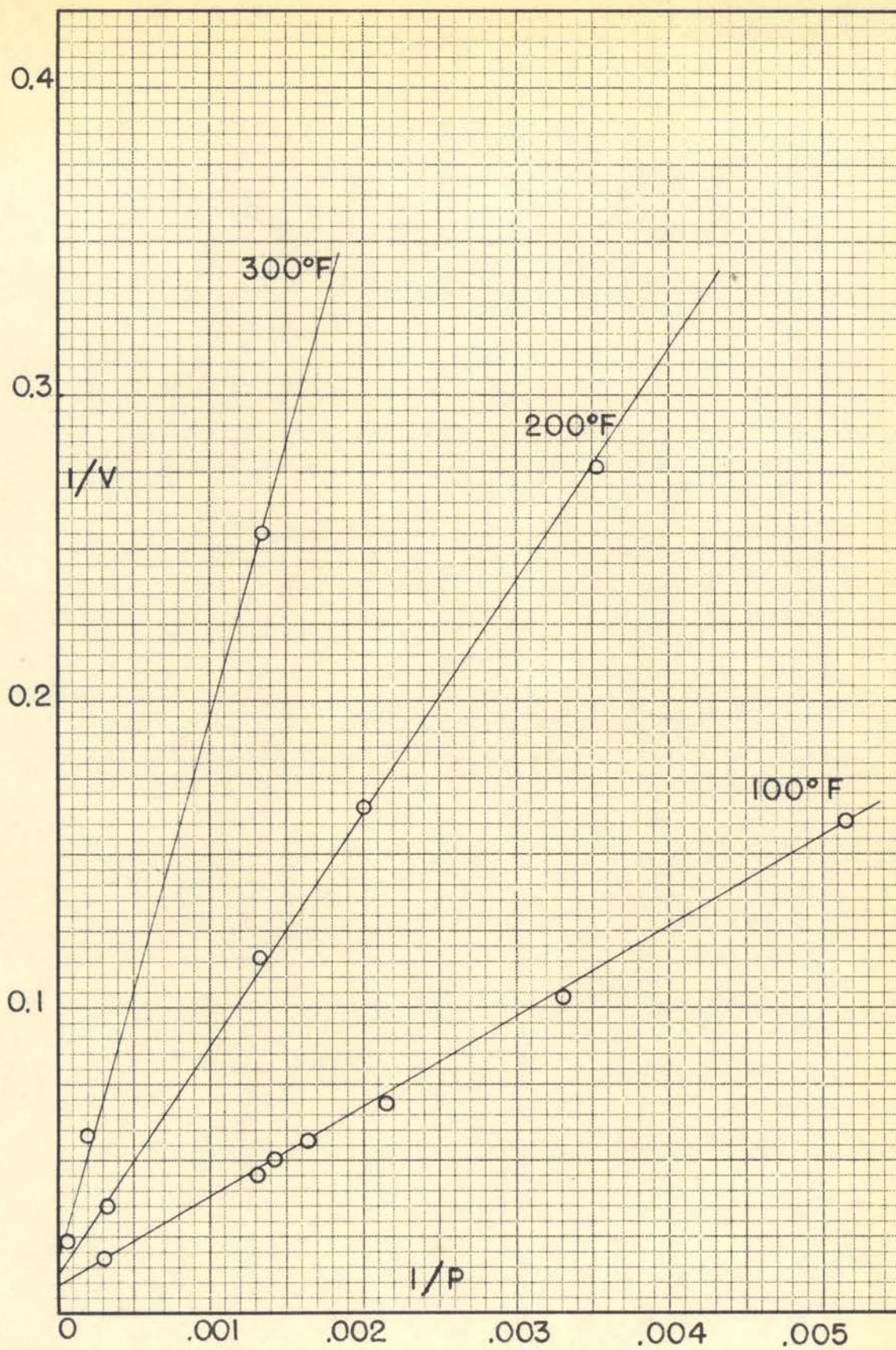


FIG. 33 LANGMUIR ISOTHERMS FOR METHANE

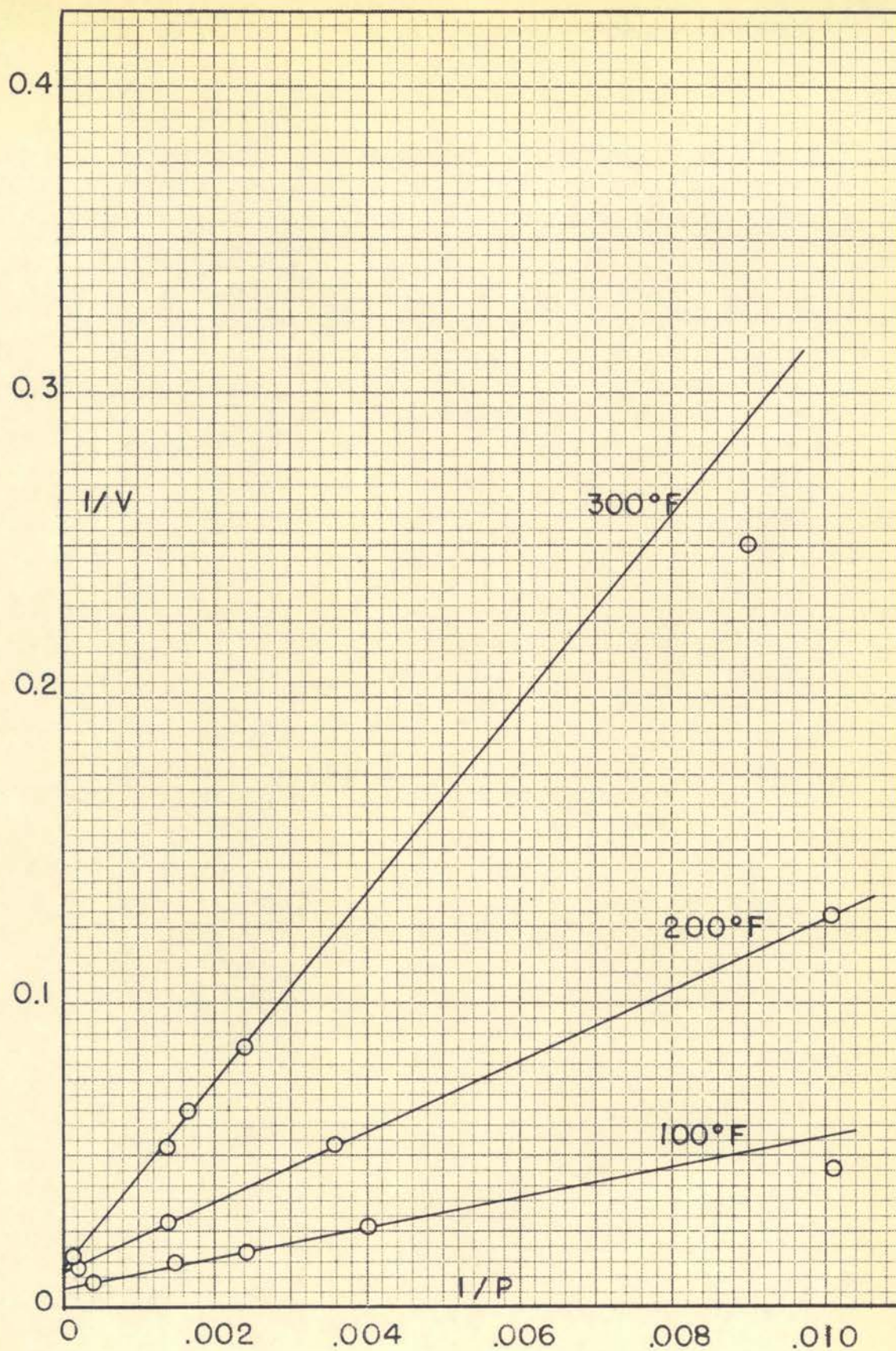


FIG. 34 LANGMUIR ISOTHERMS FOR ETHYLENE

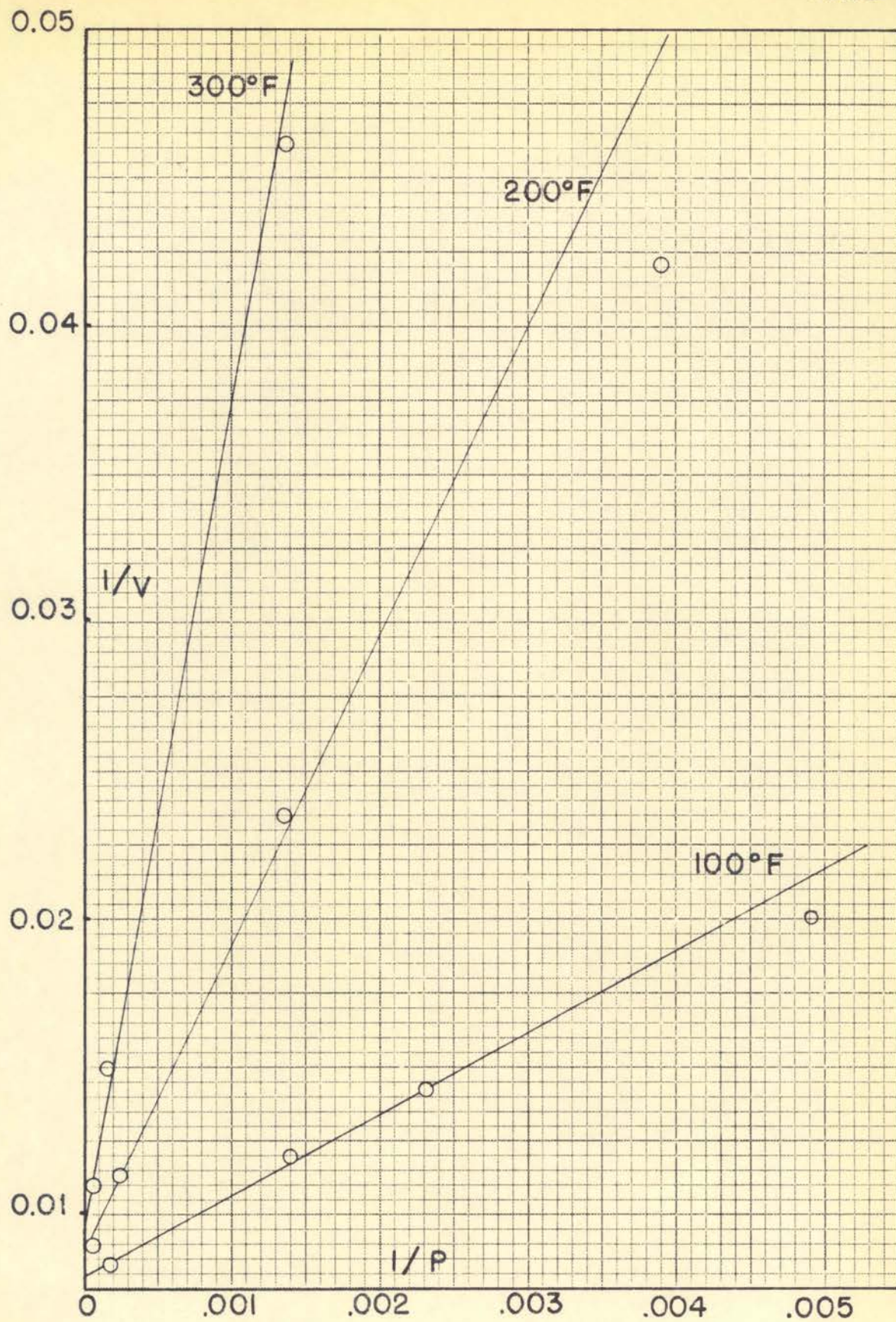


FIG. 35 LANGMUIR ISOTHERMS FOR ETHANE

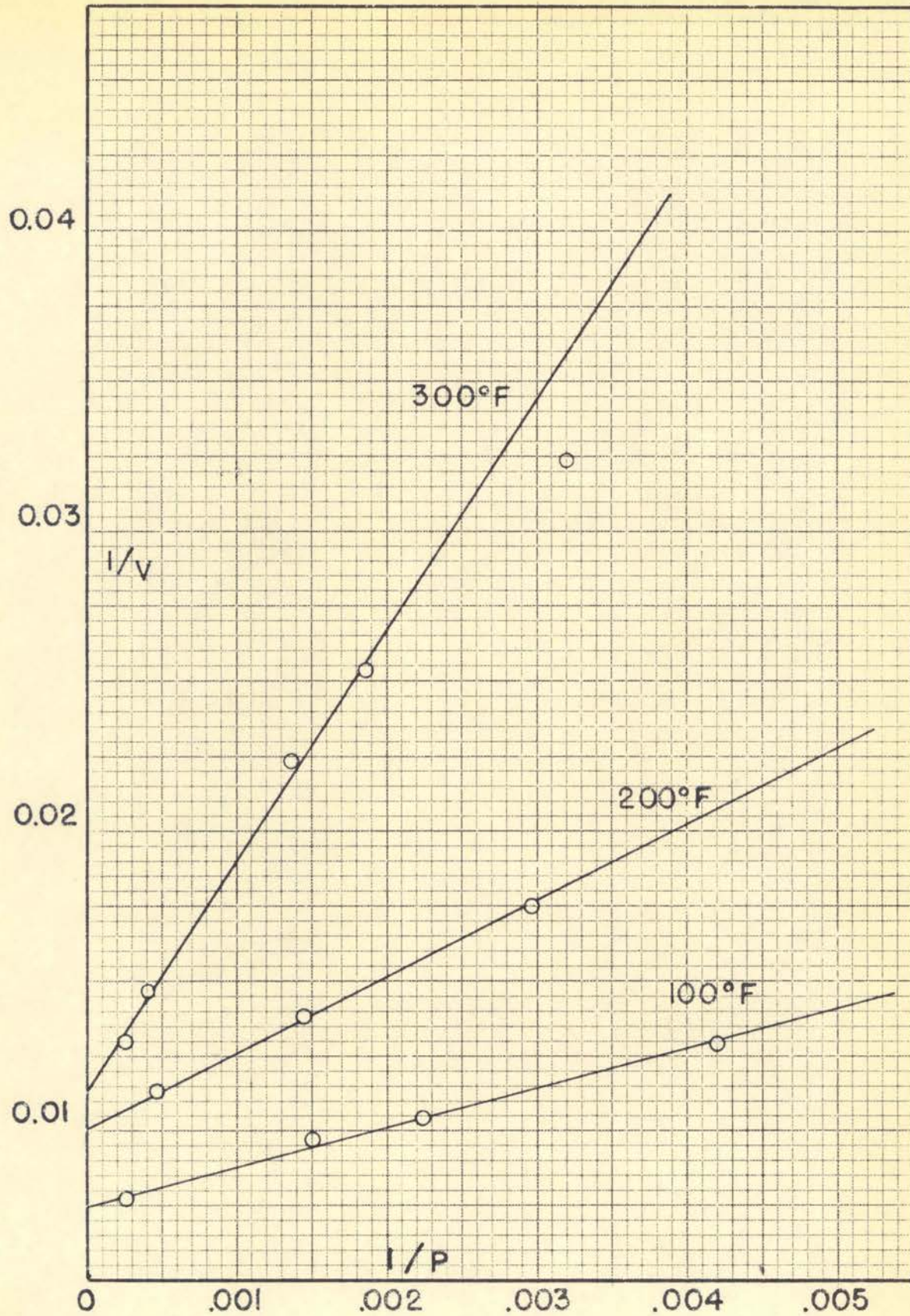


FIG. 36 LANGMUIR ISOTHERMS FOR PROPANE

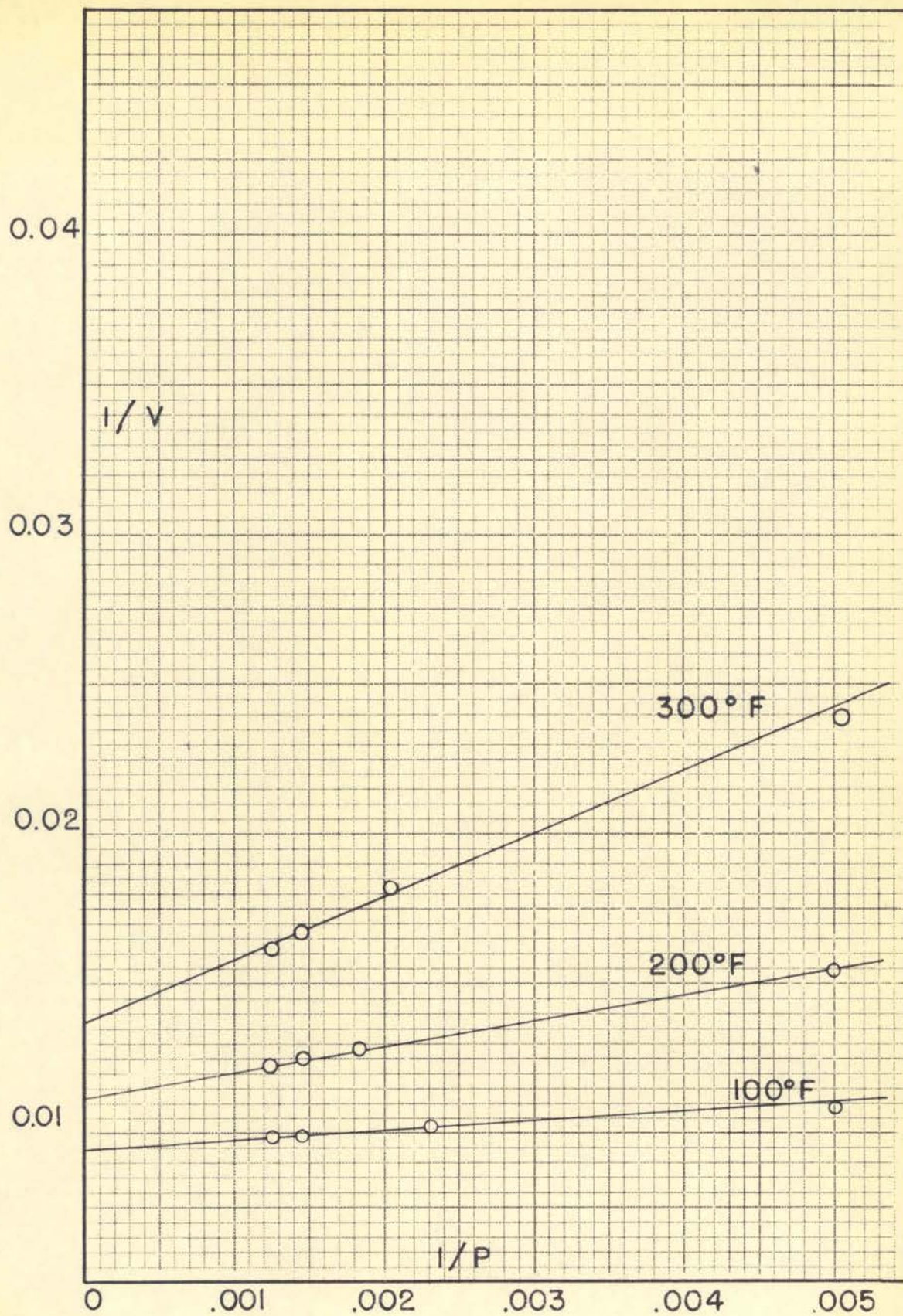
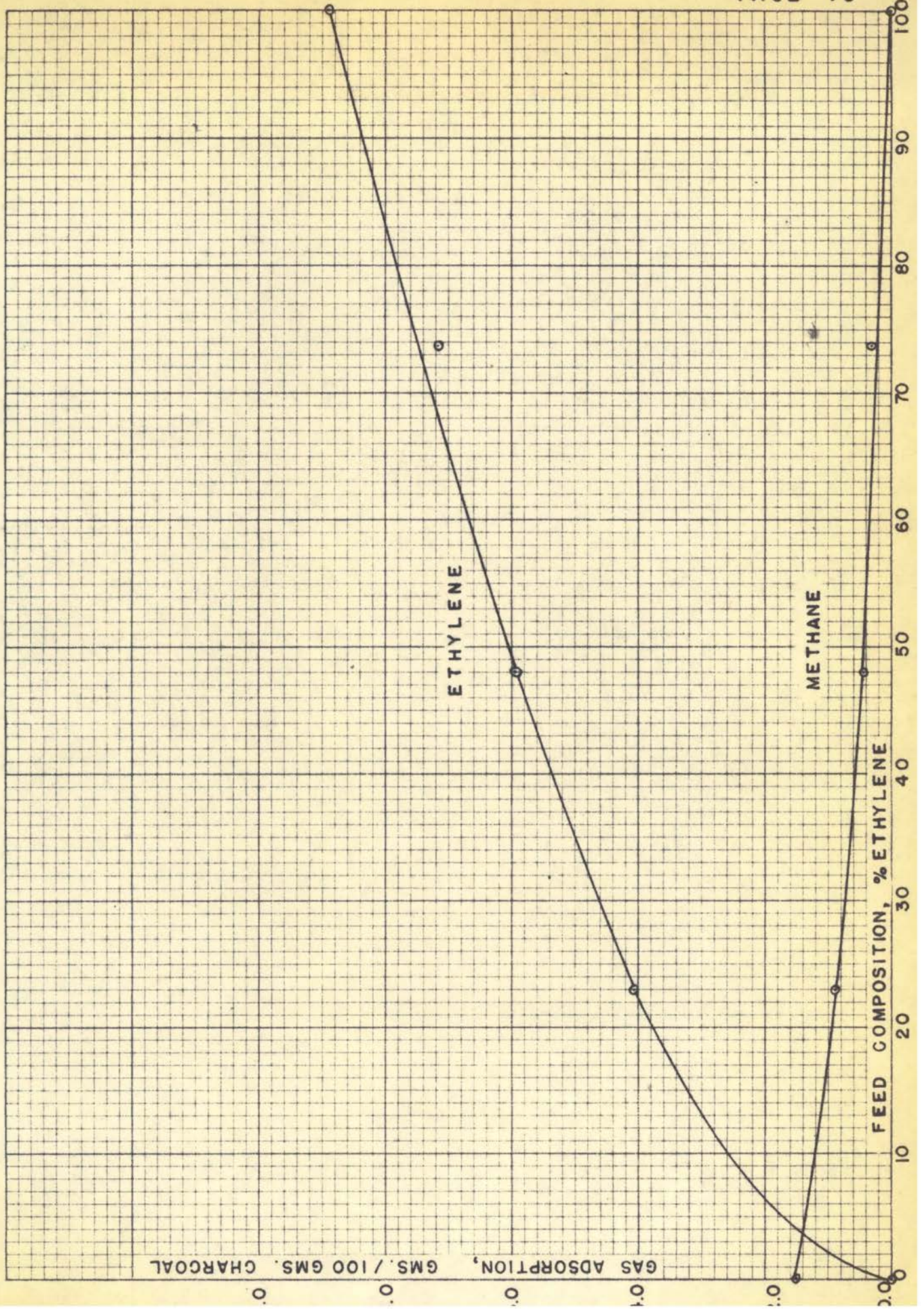
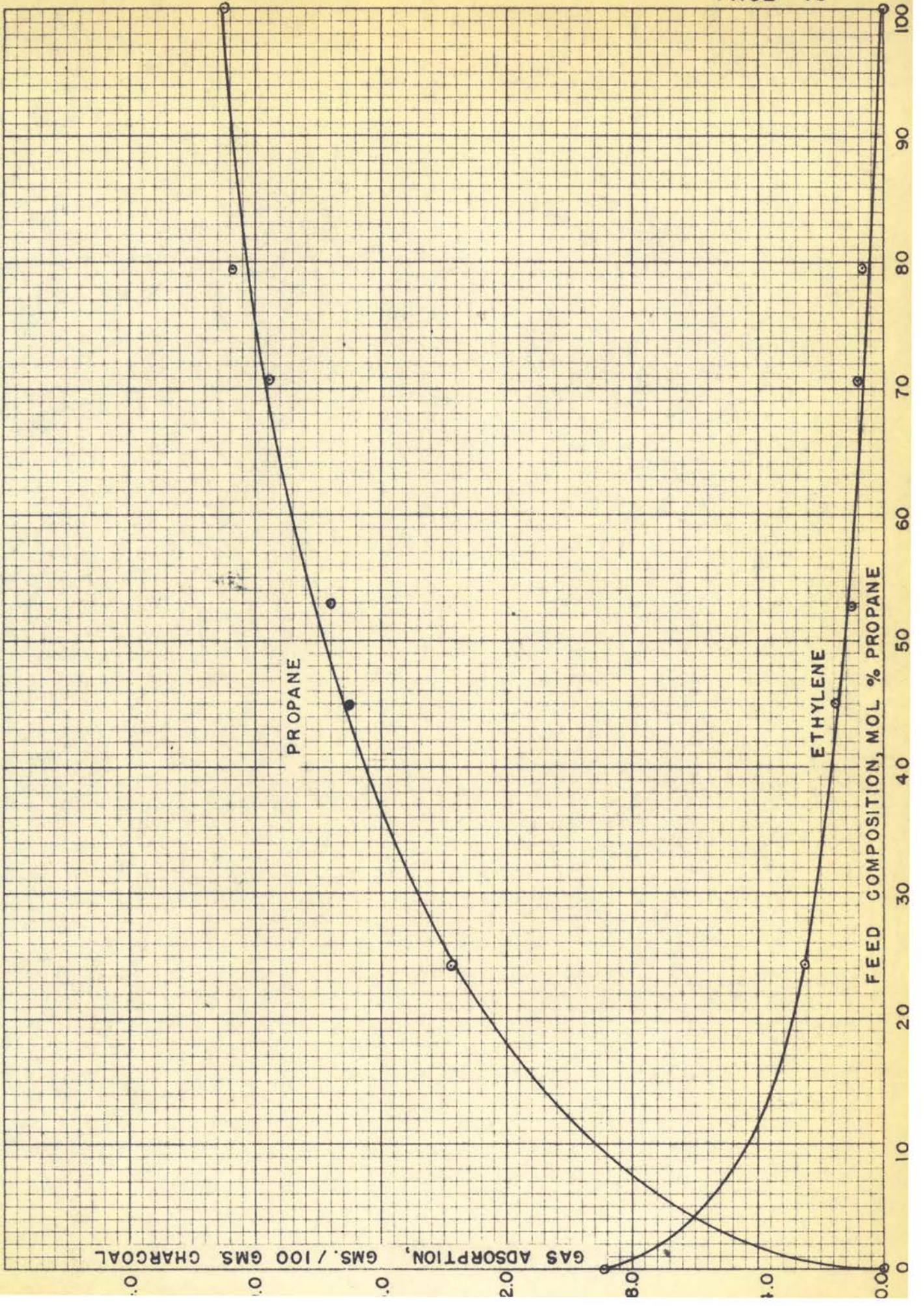
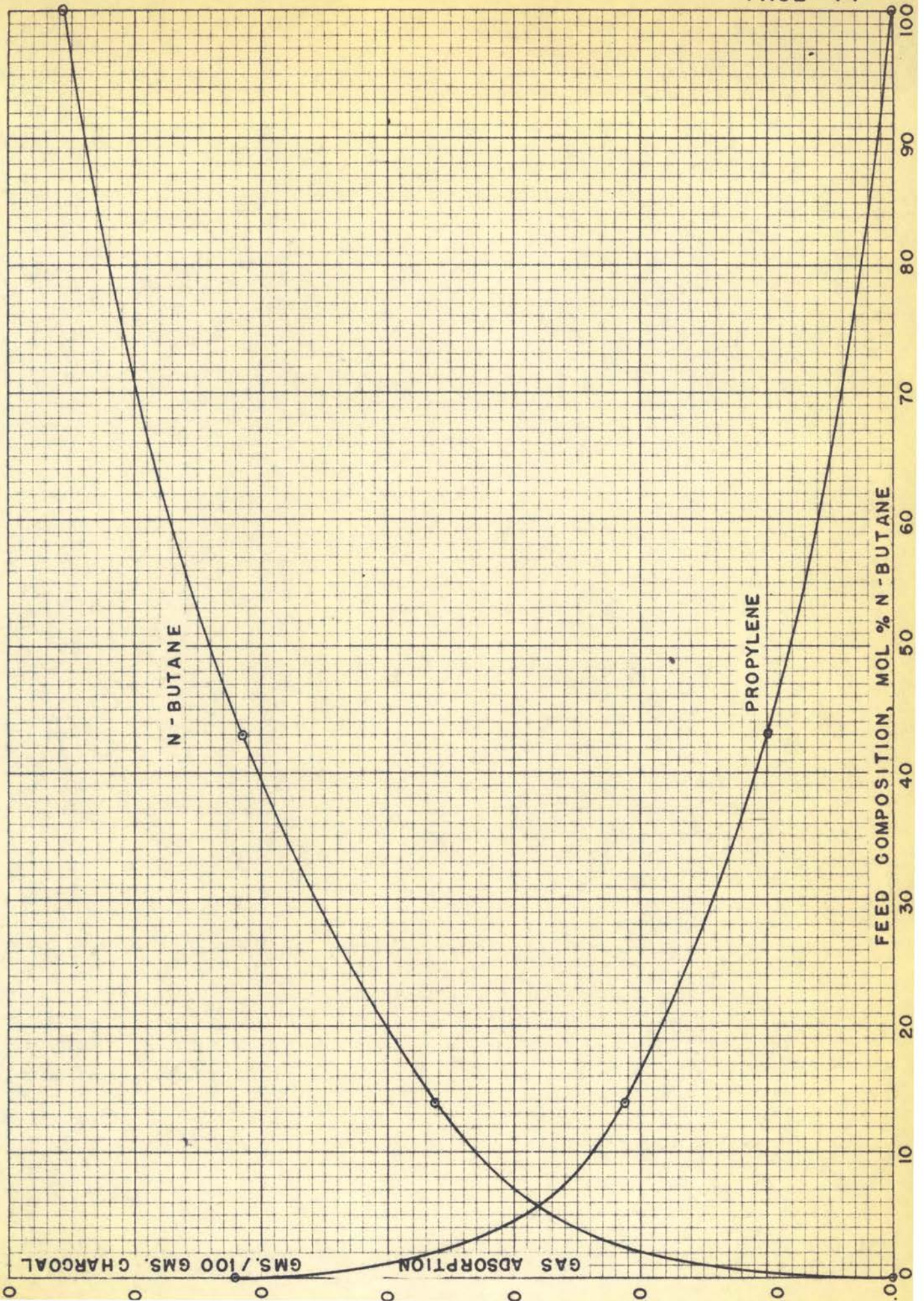
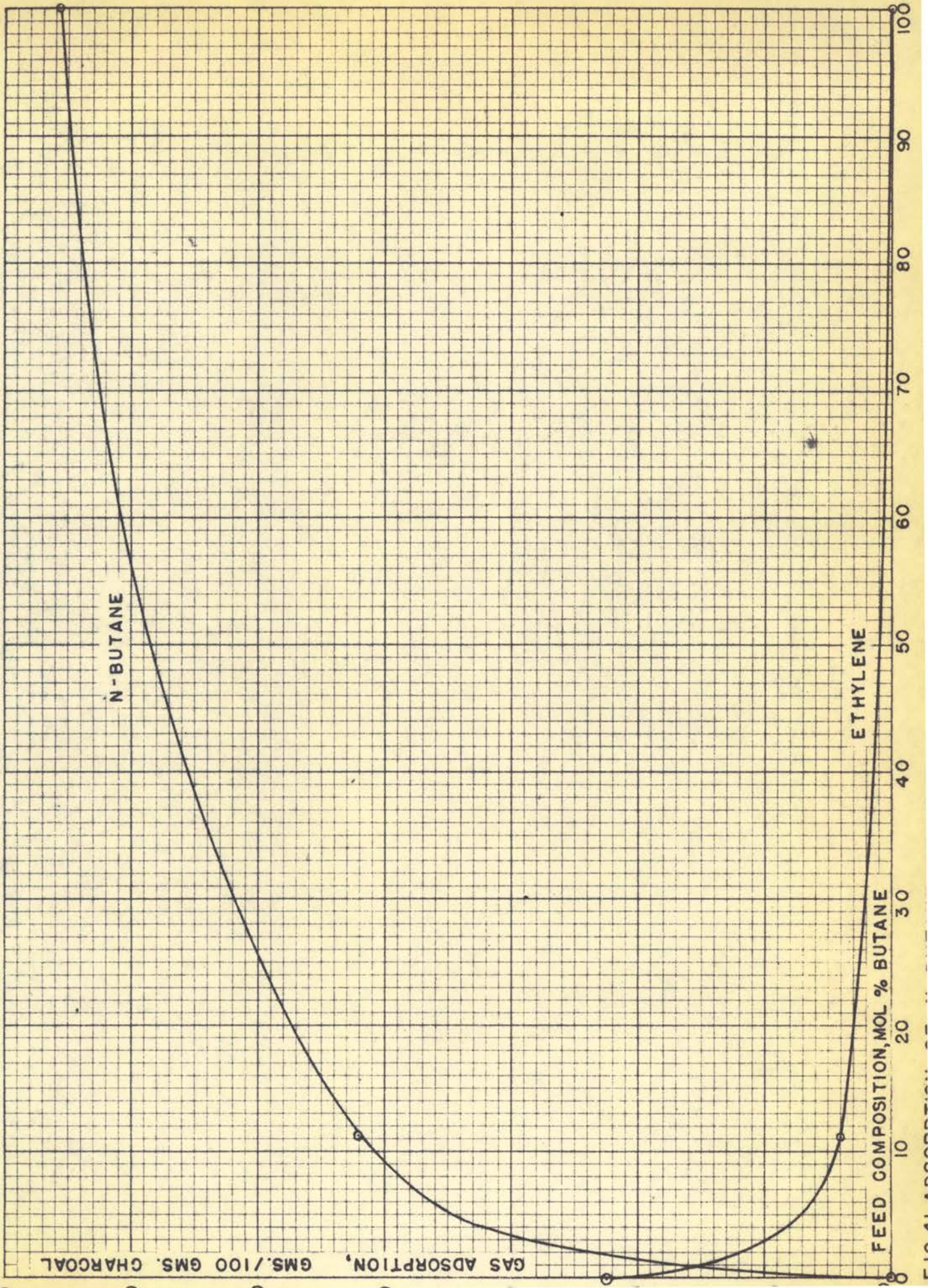


FIG. 37 LANGMUIR ISOTHERMS FOR n-BUTANE







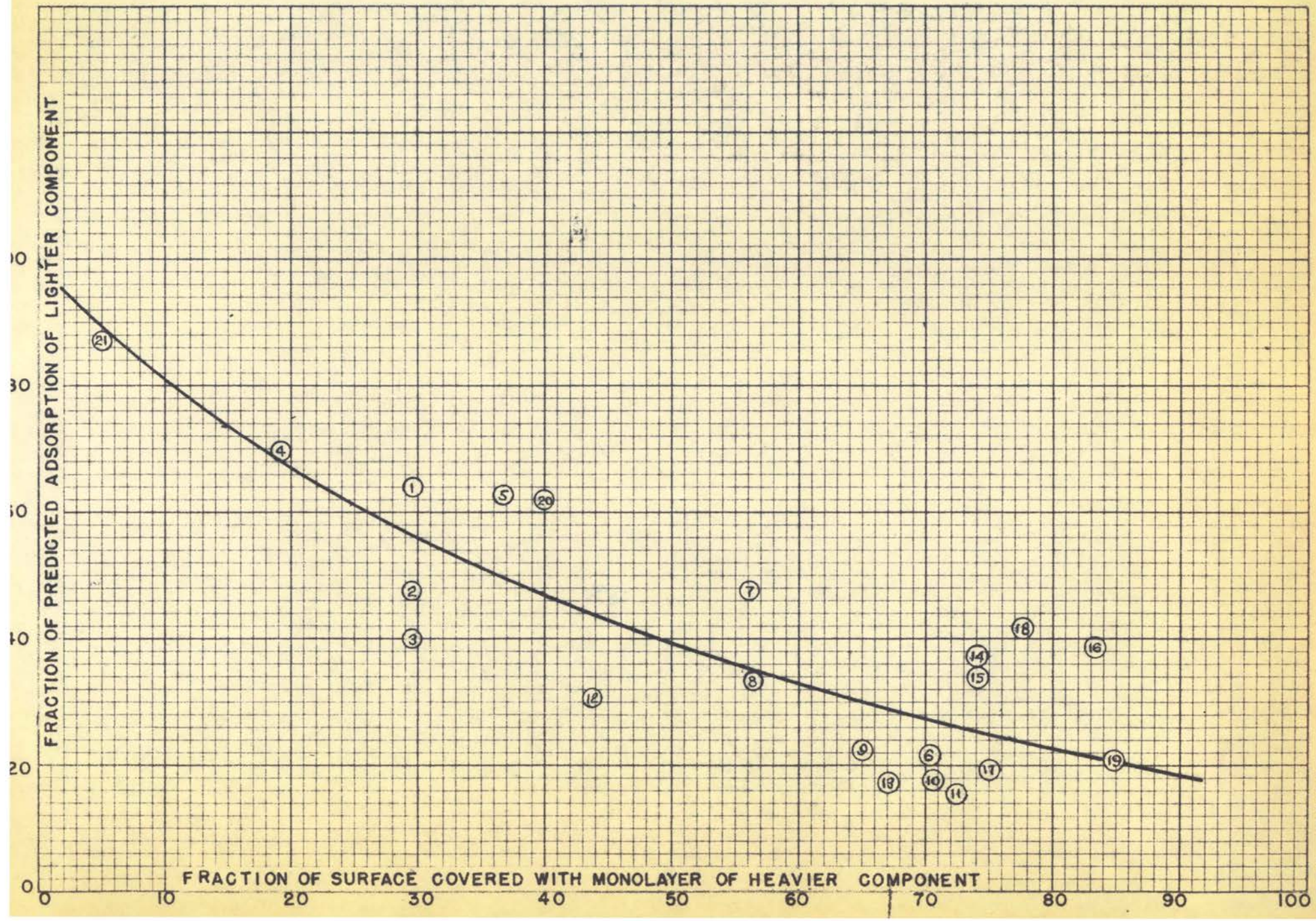


GAS ADSORPTION, GMS./100 GMS. CHARCOAL

N-BUTANE

ETHYLENE

FEED COMPOSITION, MOL % BUTANE



LEGEND

- △ METHANE - ETHYLENE
- ETHYLENE - PROPANE
- × PROPYLENE - N-BUTANE
- ETHYLENE - ETHANE

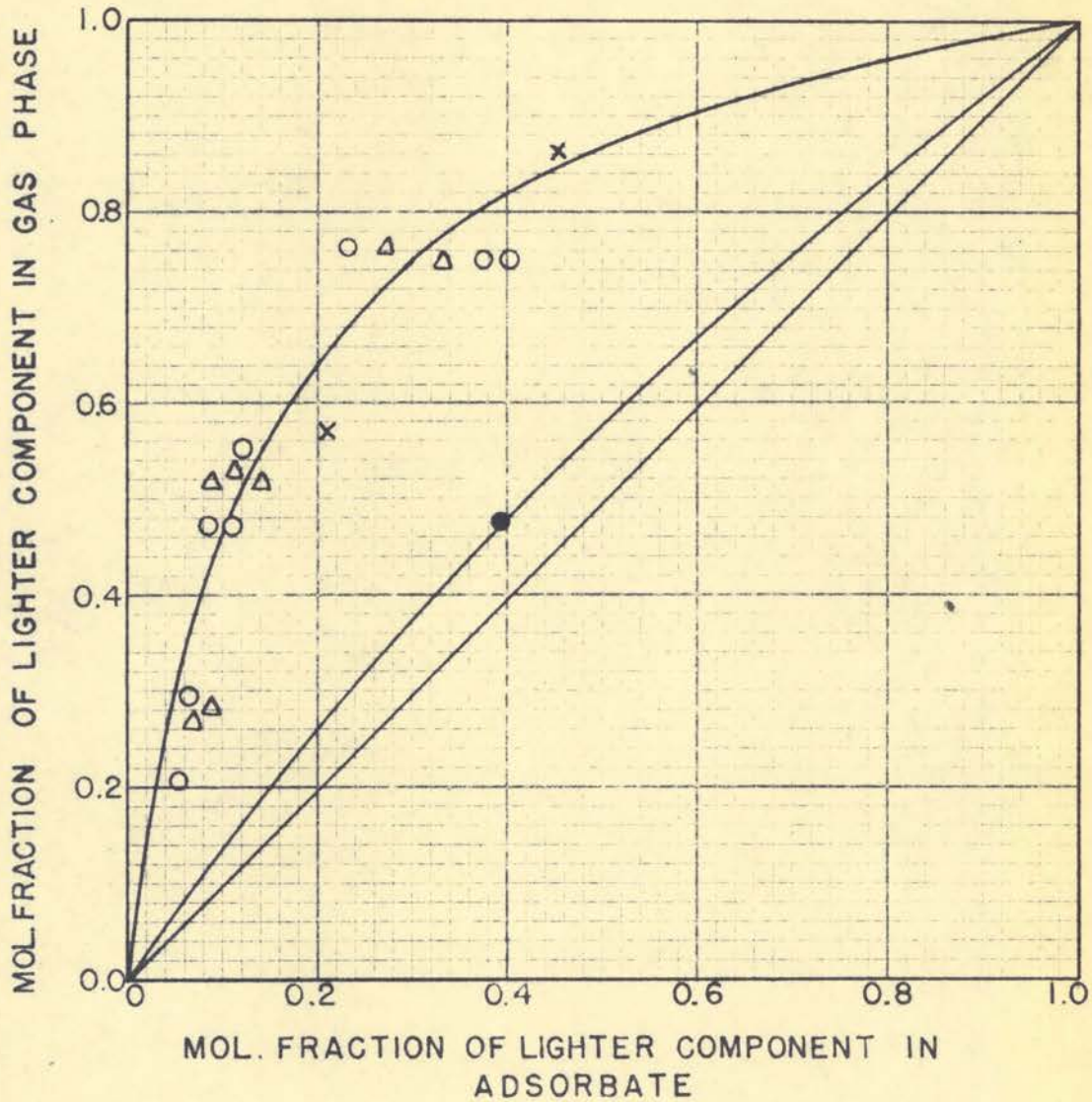


FIG. 43 VAPOR - ADSORBATE EQUILIBRIA

LEGEND:

- METHANE - ETHYLENE
- ETHYLENE - PROPANE
- × ETHYLENE - N-BUTANE
- △ PROPYLENE - N-BUTANE
- ▼ ETHYLENE - ETHANE
- ⊙ NITROGEN - METHANE

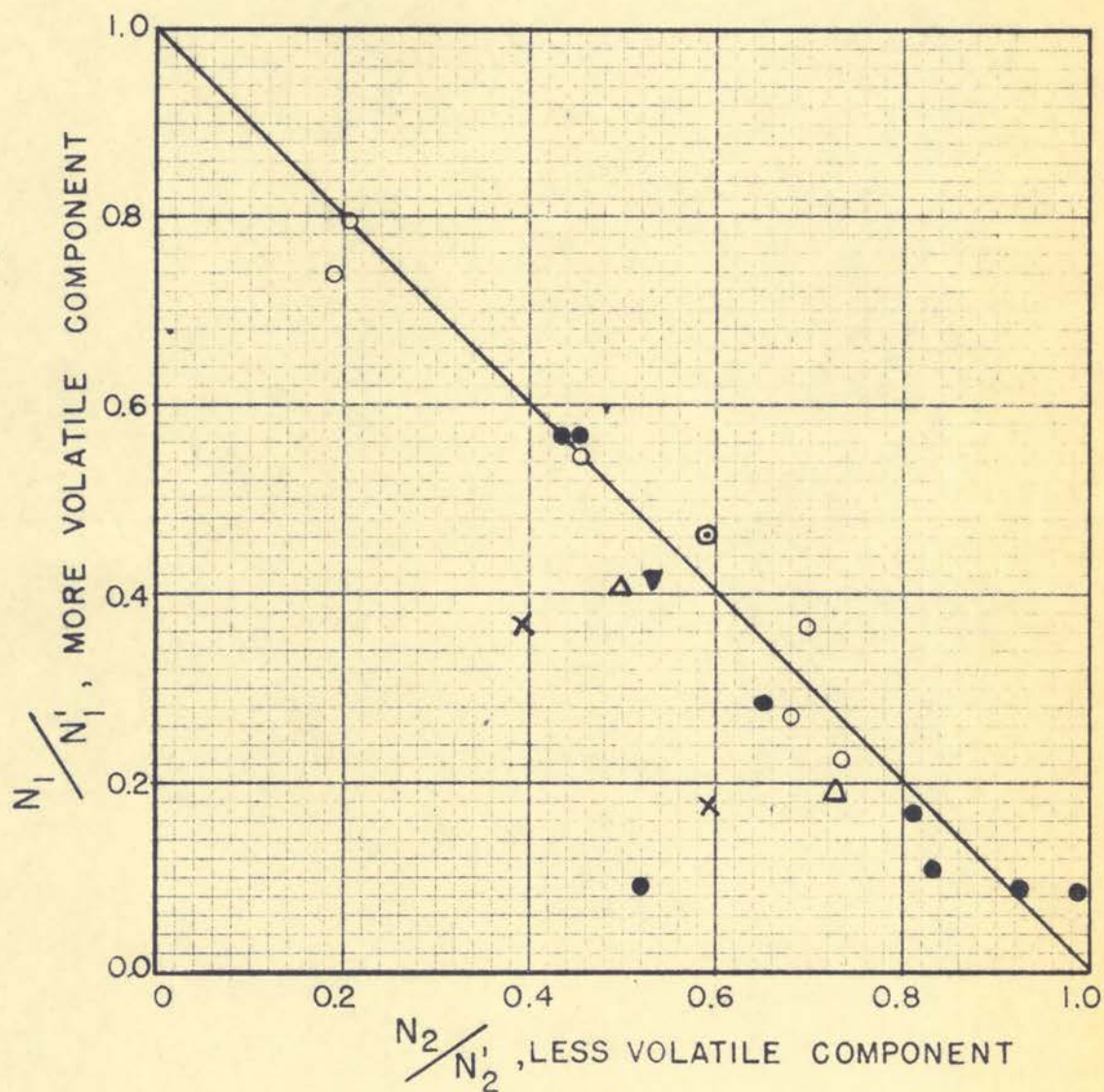


FIG.44 CORRELATION OF QUANTITY OF GAS ADSORBED
FROM BINARY MIXTURES

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NOMENCLATURE

A	Area, square meters per gram.
\AA	Angstroms
$(\text{\AA})^2$	Area of a single molecule of gas, square Angstroms
a	Amount of gas adsorbed per unit weight of an adsorbent
b	Adsorption coefficient
d	Liquid density of a gas, gms/ml.
k, k'	Constants characteristic of a gas and having a bearing on the relative adsorbability of each gas on an adsorbent. Sub-script 1 and 2 refer to gas components of a binary mixture.
N_1, N_2	Moles of gaseous components 1 and 2, respectively, which are adsorbed from a binary mixture of the two at a given temperature and pressure.
N_1', N_2'	Moles of pure gases 1 and 2 respectively, which are adsorbed on the same quantity of charcoal, at the same temperature and at a total pressure equal to the total pressure of the mixture.
n	Moles of a gas (in gas law equation)
P	Absolute pressure, lbs./sq.in.abs.
p	Partial pressure of the gas, lbs./sq.in. or mm of Mercury.
R	Gas law constant, Consistent Units.
T	Absolute temperature, K.
V	Volume of a gas at 0°C and 760 mm.
V_1	Free space volume in adsorption system normally at room temperature, ml.
V_2	Free space volume in adsorption system normally at temperature of the adsorbent, ml.
V_m	Molecular volume, ml./mole.
v	Volume of a gas adsorbed. Subscript 1 and 2 respectively, refer to volumes of components adsorbed from a binary mixture, ml.

- v_m Volume of a gas necessary to cover the entire surface of the adsorbent with a unimolecular layer of adsorbed gas. Subscript 1 and 2 refer to components in a binary gas mixture, ml.
- Z Compressibility factor for deviation of gas from ideal gas law behavior.

APPENDIX

APPENDIX

For each adsorbent used in the experimental work all weighings were made on the analytical balance and extreme care was taken in making the weight determinations. Free space determinations were also made with much care since the ultimate accuracy of the adsorption data depended upon these factors. It was necessary to repeat these two procedures each time there was a change in the adsorbent and the glass tube containing same. The data and detailed procedure for only one case is described herein in the interest of brevity.

Weight Determinations on Charcoal Used in Single
Gas Adsorption Isotherms

Wt. of Charcoal, glass tube, connections, etc.	80.5980
Wt. of glass tube, connections, etc.	<u>71.2308</u>
Wt. of dry and degassed Grade L Charcoal	9.3672 gms.

Helium Free Space Determinations on Apparatus
Used for Low Pressure Single Gas Adsorption

After evacuating the system between stopcocks 5, 13, and 21 of fig. 1, helium was bled into the system with both manifold and charcoal tube at 29°C (302°K). A total of 59.8 ml. of helium measured at 29°C and 748 mm pressure produced a pressure of 748 mm in the system. Hence the total free space was taken to be 59.8 ml.

With the manifold at 29°C and the oil in the constant temperature bath at 132°C (405°K), 50.7 ml of helium measured at 29°C and 748 mm produced a pressure of 748 mm in the system. From the gas contained in the free space at two different temperatures it is possible to evaluate the free space in that portion of the system at each condition.

Let V_1 = Free space volume above the oil level

V_2 = Free space volume below the oil level

$$\text{Then, } V_1 + V_2 = 59.8$$

$$V_1 = 59.8 - V_2$$

$$(59.8 - V_2) + (V_2 \times \frac{302}{405}) = 50.7$$

$$V_2 = 35.6 \text{ ml}$$

$$V_1 = 59.8 - 35.6 = 24.2 \text{ ml}$$

The level of mercury was maintained constant in the manometer at the 136 mm mark on the left leg for the final measurements in the free space determinations. This level was used as a free space mark for all subsequently determined points on adsorption isotherms. This was readily accomplished by means of a mercury leveling bulb mounted on a vernier raising and lowering device.

Weight Determinations on Charcoal Used in Single
Gas High Pressure Adsorption Apparatus

Since it was not feasible to weigh the steel adsorption tube on the analytical balance it was necessary to degas and dry the charcoal in glass and weigh it by difference into the steel tube. The weights are given here for the sample of Columbia Grade L charcoal used in most of the high pressure studies.

Wt. of Charcoal and glass tube (evacuated and before heating)	84.079
Wt. of evacuated glass tube	<u>74.404</u>
Wt. of rough charge of charcoal in glass tube	9.675 gms.
Wt. of Charcoal and glass tube (evacuated and before heating)	84.079
Wt. of Charcoal and glass tube (evacuated and after heating)	<u>83.954</u>
Loss in weight upon heating (weighed cool)	0.125 gms.

Wt. of charcoal and glass tube (evacuated and after heating)	83.954
Wt. of charcoal and tube after transferring sample to steel tube	<u>75.971</u>
Wt. of dry and degassed charcoal charged	7.983 gms.

Helium Free Space Determinations on Apparatus
Used For High Pressure Single Gas Adsorption

After evacuation of the system bounded by stopcocks 2 and 11, and the gas burette stopcock shown in fig. 2, helium was bled into the glass manifold system up to valve 12 at atmospheric pressure. The temperature of the steel manifold above the oil level of the bath and the bath proper was 24°C (297°K). Valve 12 was then opened and helium bled into the adsorption tube to atmospheric pressure. The difference between the two burette readings represents the free space volume. The right leg of the mercury manometer was maintained constant with the leveling bulb. Two determinations were made:

	(1)	(2)
Volume of helium	46.9 ml	45.9 ml

Another point was determined with the bath at 127°C (400°K) and the manifold at 24°C (297°K). The volume of helium required was 35.4 ml to bring the system to atmospheric pressure. Following the same procedure as before, let,

V_1 = volume in the system below the oil level

V_2 = volume in the system above the oil level

Then,

$$V_1 + \frac{\text{Trial (1)}}{V_2} = 46.9$$

$$V_1 + \frac{\text{Trial (2)}}{V_2} = 45.9$$

$$V_1 = (V_2 \times \frac{297}{400}) - 35.4$$

$$V_1 + (V_2 \times \quad) - 35.4$$

$$V_2 = 44.8$$

$$V_2 = 40.9$$

$$V_1 = 2.1$$

$$V_1 = 5.0$$

Average values: $V_1 = 3.6$ ml

$$V_2 = 42.7$$
 ml

The temperature gradient caused by the conductivity of steel was a probable cause for the discrepancy on the two free space determination trials.

Determination of Free Space in Pressure Guages

The free space in the Bourdon tube pressure guage was found by filling the tube with mercury and weighing the mercury as it was later removed from the tube.

0 - 600 PSI Duraguage

Guage volume	16.8 ml
Steel tubing	<u>1.6</u>
Total	18.4 ml

TABLE VI
IDEAL SEPARATION FACTORS FOR GASES ADSORBED ON
COLUMBIA GRADE L CHARCOAL AT 100°F AND 750 MM PRESSURE

Gas A	Gas B	Grams of Gas Adsorbed per 100 gms Charcoal		Ideal Separation Factor $\frac{\text{Grams A Adsorbed}}{\text{Grams B Adsorbed}}$
		A	B	
CH ₄	H ₂	1.52	0.0072	211
N ₂	H ₂	0.92	0.0072	128
CH ₄	N ₂	1.52	0.92	1.66
C ₂ H ₆	CH ₄	11.4	1.52	7.5
C ₂ H ₄	CH ₄	8.9	1.52	5.9
C ₂ H ₆	C ₂ H ₄	11.4	8.9	1.3
C ₃ H ₈	CH ₄	21.0	1.52	13.8
C ₃ H ₈	C ₂ H ₆	21.0	11.4	1.8
C ₃ H ₈	C ₂ H ₄	21.0	8.9	2.4
C ₃ H ₈	C ₃ H ₆	21.0	20.8	1.0

TABLE VII

ADSORPTION OF HYDROGEN ON 9.367 GRAMS OF GRADE LCOLUMBIA ACTIVATED CHARCOAL*

<u>°F</u>	<u>Equilibrium Pressure mm.</u>	<u>Volume Hydrogen Adsorbed ml.</u>	<u>Vol. Hydrogen per Gram Charcoal, ml/gm.</u>	<u>Wt. Per Cent of Hydrogen on Charcoal</u>
100°F	187	1.9	0.20	0.0018
	483	5.0	0.53	0.0048
	745	7.5	0.80	0.0072
200°F	426	2.4	0.26	0.0023
	748	3.9	0.42	0.0037

* Ray, G. C. and Box, E. O., Jr., Ind. and Eng. Chem. 42, 1315-1318 (1950)

TABLE VIII
ADSORPTION OF CARBON MONOXIDE ON 9.367 GRAMS
OF COLUMBIA GRADE L ACTIVATED COCONUT CHARCOAL

<u>Temp.</u> <u>°F</u>	<u>Equilibrium</u> <u>Pressure,mm</u>	<u>Vol. Carbon</u> <u>Monoxide adsorbed</u> <u>ml</u>	<u>Vol. CO</u> <u>per gram</u> <u>Charcoal</u>	<u>Wt. Per cent</u> <u>of CO on</u> <u>Charcoal</u>
100°F	206	26.3	2.8	0.413
	448	53.9	5.7	0.845
	755	86.8	9.3	1.360
200°F	253	12.5	1.3	0.196
	524	24.7	2.6	0.388
	761	35.4	3.8	0.555

*Ray, G. C. and Box, E. O., Jr., Ind. Eng. Chem. 42, 1315 (1950)

TABLE IX
ADSORPTION OF NITROGEN ON 9.367 GRAMS OF
GRADE L COLUMBIA ACTIVATED CHARCOAL*

<u>Temp.</u> <u>°F</u>	<u>Equilibrium</u> <u>Pressure, mm</u>	<u>Vol. Nitrogen</u> <u>Adsorbed</u> <u>ml</u>	<u>Vol. N₂</u> <u>per gram</u> <u>Charcoal</u>	<u>Wt. Per cent</u> <u>of N₂ on</u> <u>Charcoal</u>
100	214	20.9	2.23	0.28
	405	39.9	4.26	0.53
	589	55.4	5.91	0.74
	737	68.0	7.26	0.91
200	207	8.1	8.64	0.11
	401	15.4	1.64	0.21
	615	23.4	2.50	0.31
	744	29.0	3.10	0.39
250	294	8.3	8.85	0.11
	578	15.6	1.67	0.21
	742	20.3	2.16	0.27

*Ray and Box, Ind. Eng. Chem., 42, 1315 (1950)

TABLE X
ADSORPTION OF CARBON DIOXIDE ON 9.367 GRAMS
OF COLUMBIA GRADE L ACTIVATED CHARCOAL*

<u>Temp.</u> <u>°F</u>	<u>Equilibrium</u> <u>Pressure</u> <u>mm.</u>	<u>Vol. Carbon</u> <u>Dioxide Ads.</u> <u>ml.</u>	<u>Vol. CO₂ Per</u> <u>Gram of</u> <u>Charcoal</u>	<u>Wt. Per cent</u> <u>of CO₂ on</u> <u>Charcoal</u>
100	127	118.7	12.6	2.50
	241	192.2	20.5	4.06
	539	314.4	33.5	6.63
	713	376.8	40.2	7.95
150	159	71.0	7.56	1.50
	321	139.3	14.8	2.94
	513	184.1	19.7	3.89
	719	240.1	25.6	5.08
200	257	62.1	6.67	1.31
	452	100.7	10.7	2.13
	742	139.7	14.9	2.94
250	343	45.0	4.8	0.95
	600	76.1	8.12	1.61
	737	89.0	9.5	1.88

*Ray and Box, Ind. Eng. Chem., 42, 1315 (1950)

TABLE XI
ADSORPTION OF METHANE ON 9.367 GRAMS
OF COLUMBIA GRADE L ACTIVATED CHARCOAL*

<u>Temp.</u> <u>°F.</u>	<u>Equilibrium</u> <u>Pressure</u> <u>mm.</u>	<u>Vol. Methane</u> <u>Adsorbed</u> <u>ml.</u>	<u>Vol. CH₄ Per</u> <u>Gram of</u> <u>Charcoal</u>	<u>Wt. Per Cent</u> <u>of Methane</u> <u>on Charcoal</u>
100	194	58.1	6.20	0.44
	302	91.0	9.71	0.70
	462	134.5	14.34	1.03
	610	167.9	17.90	1.28
	697	186.9	19.92	1.43
	760	204.0	21.78	1.56
150	202	42.5	4.54	0.32
	380	73.4	7.83	0.56
	559	101.9	10.86	0.78
	732	126.8	13.52	0.97
200	283	34.0	3.63	0.26
	500	57.3	6.08	0.44
	747	81.1	8.65	0.62
250	387	28.8	3.07	0.22
	741	53.9	5.75	0.41
300	381	20.0	2.13	0.15
	744	36.8	3.92	0.28

*Ray and Box, Ind. Eng Chem., 42, 1315 (1950)

TABLE XII
ADSORPTION OF ACETYLENE ON 9.367 GRAMS
OF COLUMBIA GRADE L ACTIVATED CHARCOAL*

Temp. °F	Equilibrium Pressure mm.	Vol. Acetylene Adsorbed ml.	Vol. C ₂ H ₂ Per Gram Charcoal	Wt. Per cent Acetylene on Charcoal
100	63	146.7	15.6	1.82
	189	284.7	30.4	3.53
	267	353.7	37.8	4.38
	503	490.8	52.4	6.09
	734	611.9	65.3	7.59
150	149	122.8	13.1	1.52
	328	224.5	23.9	2.78
	516	313.1	33.4	3.88
	694	380.0	40.6	4.72
200	196	67.3	7.2	0.83
	347	132.9	14.2	1.65
	572	203.4	21.7	2.52
	683	204.2	25.6	2.98
250	187	59.0	6.31	0.73
	438	116.8	12.5	1.45
	721	172.0	18.4	2.13

*Ray and Box, Ind. Eng. Chem., 42, 1315 (1950)

TABLE XIII

ADSORPTION OF ETHYLENE ON 9.367 GRAMS
OF COLUMBIA GRADE L ACTIVATED CHARCOAL*

Temp. °F	Equilibrium Pressure mm.	Vol. Ethylene Adsorbed ml.	Vol. C ₂ H ₄ Per Gram of Charcoal	Wt. Per Cent Ethylene on Charcoal
100	93	208.9	22.3	2.81
	247	356.4	38.2	4.79
	437	502.3	53.6	6.75
	678	628.9	67.1	8.45
150	104	160.9	17.15	2.16
	314	311.6	33.2	4.18
	584	432.4	46.1	5.81
	750	483.5	51.6	6.50
200	95	72.1	7.71	0.97
	277	172.4	18.4	2.32
	511	261.3	27.8	3.51
	712	322.4	34.2	4.33
250	126	67.6	7.21	0.91
	324	137.3	14.63	1.85
	513	189.0	20.15	2.54
	751	214.5	22.9	3.25
300	112	37.4	3.99	0.50
	421	109.5	11.68	1.47
	611	144.7	15.42	1.94
	726	174.5	18.62	2.35
400	202	25.4	2.69	0.34
	406	49.9	5.32	0.67
	608	69.7	7.43	0.94
	752	81.4	8.68	1.10

*Ray and Box, Ind. Eng. Chem., 42, 1315 (1950)

TABLE XIV
ADSORPTION OF ETHANE ON 9.367 GRAMS
OF COLUMBIA GRADE L ACTIVATED CHARCOAL*

<u>Temp.</u> <u>°F</u>	<u>Equilibrium</u> <u>Pressure</u> <u>mm.</u>	<u>Vol. Ethane</u> <u>Adsorbed</u> <u>ml.</u>	<u>Vol. C₂H₆ per</u> <u>gram of</u> <u>Charcoal</u>	<u>Wt. Per Cent</u> <u>Ethane on</u> <u>Charcoal</u>
100	50	242.1	25.8	3.52
	204	469.1	50.1	6.78
	435	648.5	69.2	9.37
	710	772.6	83.4	11.17
150	63	153.5	16.4	2.23
	214	309.5	33.0	4.48
	443	445.5	47.6	6.45
	739	561.5	59.7	8.14
200	57	78.8	8.40	1.14
	259	223.3	23.8	2.23
	493	327.6	34.9	4.74
	743	401.4	42.8	5.81
250	71	58.0	6.19	0.84
	188	133.3	14.2	1.93
	524	235.3	25.1	3.41
	750	289.2	30.8	4.18
300	150	62.9	6.71	0.91
	326	118.0	12.6	1.71
	538	163.8	17.5	2.37
	734	202.7	21.6	2.94

*Ray and Box, Ind. Eng. Chem., 42, 1315 (1950)

TABLE XV
ADSORPTION OF PROPYLENE ON 9.367 GRAMS
OF COLUMBIA GRADE L ACTIVATED CHARCOAL*

Temp. °F	Equilibrium Pressure mm.	Vol. Propylene Adsorbed ml.	Vol. C ₃ H ₆ Per Gram Charcoal	Wt. Per Cent of Propylene on Charcoal
100	14	316.0	33.7	6.32
	77	625.3	66.6	12.51
	298	886.1	94.5	17.72
	574	1000.0	106.7	20.00
	741	1042.6	111.2	20.85
150	16	223.0	23.8	-
	117	510.0	54.4	-
	361	730.9	78.0	-
	669	847.1	90.5	-
200	36	161.8	17.3	3.24
	154	388.3	41.4	7.76
	396	568.4	60.6	11.37
	699	684.2	72.4	13.68
250	44	151.3	16.1	3.03
	135	219.6	23.4	4.40
	290	351.6	37.4	7.03
	424	423.4	45.2	8.47
	663	516.9	55.1	10.34
350	70	74.5	7.89	1.48
	321	197.4	21.5	3.95
	495	251.0	26.8	5.02
	712	296.8	31.7	5.94

*Ray and Box, Ind. Eng. Chem., 42, 1315 (1950)

TABLE XVI
ADSORPTION OF PROPANE ON 9.367 GRAMS
OF COLUMBIA GRADE L ACTIVATED CHARCOAL*

Temp. °F	Equilibrium Pressure mm.	Vol. Propane Adsorbed ml.	Vol. Propane per gram Charcoal	Wt. Per Cent Propane on Charcoal
100	17	239.3	25.6	5.15
	117	646.1	69.0	13.91
	238	797.5	85.1	17.18
	447	909.4	97.1	19.56
	673	964.1	103.0	20.68
150	45	245.0	26.2	5.28
	204	565.8	60.4	12.20
	399	705.4	75.3	15.21
	695	804.5	85.9	17.35
200	30	159.1	17.0	3.44
	158	384.3	41.1	8.28
	340	546.7	57.3	11.79
	700	676.9	72.3	14.60
250	53	162.7	17.4	3.51
	290	384.3	41.1	8.28
	624	512.9	54.7	11.08
	739	543.1	58.0	11.72
300	98	155.8	16.6	3.36
	313	289.8	30.9	6.25
	533	369.3	39.4	7.97
	722	419.6	44.7	9.05
350	68	75.5	8.05	1.63
	334	209.8	22.4	4.52
	548	275.5	29.4	5.93
	734	314.1	33.6	6.76
400	102	65.9	7.03	1.42
	285	134.0	14.3	2.89
	711	220.1	23.5	4.75
450	189	67.8	7.24	1.46
	726	171.1	18.3	3.69

*Ray and Box, Ind. Eng. Chem. 42, 1315 (1950)

TABLE XVII
ADSORPTION OF n-BUTANE ON 9.367 GRAMS
OF COLUMBIA GRADE L ACTIVATED CHARCOAL

<u>Temp.</u> <u>°F</u>	<u>Equilibrium</u> <u>Pressure</u> <u>mm.</u>	<u>Vol. n-Butane</u> <u>Adsorbed</u> <u>ml.</u>	<u>Vol. n-C₄H₁₀</u> <u>per Gram of</u> <u>Charcoal</u>	<u>Wt. Per Cent</u> <u>of n-Butane</u> <u>on Charcoal</u>
100	40	713.1	76.1	19.71
	443	908.6	96.8	25.10
	687	943.7	100.5	26.10
150	32	310.7	33.2	8.60
	133	629.6	67.2	17.42
	540	808.0	86.3	22.34
	739	835.6	89.2	23.12
200	24	240.4	25.6	6.65
	143	549.7	58.7	15.20
	550	723.8	77.2	20.00
	680	748.6	79.8	20.70
250	27	243.3	26.0	6.73
	155	465.9	49.7	12.98
	437	606.0	64.7	16.75
	743	663.6	70.7	18.42
300	60	245.7	26.2	6.79
	198	392.3	41.8	10.85
	492	514.6	54.9	14.23
	691	558.8	59.6	15.45
350	89	208.8	22.3	5.77
	299	348.6	37.2	9.65
	676	456.4	48.7	12.61
400	94	150.5	16.1	4.16
	279	263.7	28.1	7.29
	719	390.1	41.6	10.78

*Ray and Box, Ind. Eng. Chem., 42, 1315 (1950)

TABLE XVIIIADSORPTION OF METHYL MERCAPTAN ON 9.367 GRAMSOF COLUMBIA GRADE L ACTIVATED CHARCOAL

<u>Time</u> <u>Hrs.</u>	<u>Temp.</u> <u>°F</u>	<u>Equilibrium</u> <u>Pressure</u> <u>mm.</u>	<u>Vol. Mercaptan</u> <u>Adsorbed</u> <u>ml.</u>	<u>Vol. CH₃SH</u> <u>per Gram</u> <u>Charcoal</u>	<u>Wt. Per Cent</u> <u>Mercaptan on</u> <u>Charcoal</u>
1.1	100	50	243.5	25.9	5.6
1.6	100	103	744.0	79.4	17.0
15.6	100	249	1158.7	123.6	26.5
4.3	100	423	1229.8	131.2	28.2
17.3	100	522	1353.5	144.5	31.0
16.2	100	650	1451.9	155.1	33.3

TABLE XIX
ADSORPTION OF HYDROGEN ON 7.983 GRAMS
OF COLUMBIA GRADE L CHARCOAL AT 0-600 PSIG

<u>Temp.</u> <u>°F</u>	<u>Equilibrium</u> <u>Pressure</u> <u>PSIA</u>	<u>Total Gas</u> <u>on Charcoal</u> <u>and in Free</u> <u>Space, ml.</u>	<u>Total Free</u> <u>Space Vol.</u> <u>Corrected</u> <u>ml. (1)</u>	<u>Vol. Gas</u> <u>Adsorbed</u> <u>ml.</u>	<u>Wt. Per Cent</u> <u>Hydrogen</u> <u>on Charcoal</u>
100 F	611	2282	2169	113	0.13
	490	1838	1739	99	0.11
	374	1410	1328	82	0.09
	257	982	912	70	0.08
	147	558	524	34	0.04
	14.5	58	52	6	0.007
200 F	608	1985	1923	62	0.07
	501	1645	1582	63	0.07
	373	1222	1178	44	0.05
	303	806	958	48	0.05
	198	753	715	38	0.04
	131	498	466	32	0.36
	113	382	357	25	0.03
	65	248	231	15	0.0172
	14.5	49	46	3	0.003

- (1) The compressibility of hydrogen at the conditions of the experiment is so small that no correction was made.

TABLE XX

ADSORPTION OF CARBON MONOXIDE ON 7.983 GRAMS
OF COLUMBIA GRADE L CHARCOAL AT 0-600 PSIG

<u>Temp.</u> <u>°F</u>	<u>Equilibrium</u> <u>Pressure</u> <u>PSIA</u>	<u>Total Gas</u> <u>on Charcoal</u> <u>and in Free</u> <u>Space, ml.</u>	<u>Total Free</u> <u>Space Vol.</u> <u>Corrected</u> <u>ml. (1)</u>	<u>Vol. Gas</u> <u>Adsorbed</u> <u>ml.</u>	<u>Wt. Per Cent</u> <u>CO on the</u> <u>Charcoal</u>
100	615	2867	2183	684	10.70
	485	2347	1721	626	9.82
	351	1835	1246	589	9.24
	260	1410	923	587	9.23
	166	988	589	399	6.26
	14.5	123	50	73	1.15
200	609	2399	1927	472	7.40
	500	1977	1572	405	6.36
	375	1546	1187	359	5.63
	259	1113	820	293	4.59
	150	686	474	212	3.32
	14.5	80	50	30	0.47
300	625	2171	1799	372	5.83
	492	1748	1416	332	5.21
	366	1323	1052	271	4.25
	243	909	698	211	3.31
	120	482	347	135	2.12
	14.5	56	43	13	0.20
400	625	1908	1663	245	3.84
	479	1486	1273	213	3.34
	340	1073	905	168	2.64
	203	653	539	114	1.79
	98	322	260	62	0.97
	14.5	47	38	9	0.14

- (1) The compressibility of carbon monoxide at the conditions of the experiments is so small that no corrections were applied.

TABLE XXI
ADSORPTION OF NITROGEN ON 7.983 GRAMS OF
COLUMBIA GRADE L CHARCOAL AT 0-600 PSIG

<u>Temp.</u> <u>°F.</u>	<u>Equilibrium</u> <u>Pressure</u> <u>PSIA</u>	<u>Total Gas</u> <u>on Charcoal</u> <u>and in Free</u> <u>Space, ml</u>	<u>Total Free</u> <u>Space Vol.</u> <u>Corrected</u> <u>ml. (1)</u>	<u>Vol. Gas</u> <u>Adsorbed</u> <u>ml.</u>	<u>Wt. Per Cent</u> <u>Nitrogen on</u> <u>Charcoal</u>	
100	603	2744	2140	604	9.46	
	516	2396	1831	565	8.85	
	410	1964	1454	510	8.00	
	306	1534	1086	448	7.03	
	206	1100	731	369	5.78	
	164	994	647	347	5.42	
	114	668	404	264	4.14	
	74	497	291	206	3.22	
	14.5	111	52	59	0.93	
	200	615	2390	1944	446	7.00
493		1963	1572	371	5.83	
379		1540	1199	341	5.35	
263		1070	832	238	3.75	
152		646	480	186	2.92	
105		513	374	139	2.18	
55		274	195	79	1.24	
14.5		72	46	26	0.41	
300		617	2046	1775	291	4.56
		481	1617	1384	233	3.66
	348	1185	1002	183	2.87	
	218	754	627	127	1.99	
	116	408	334	74	1.16	
	49	208	162	46	0.72	
	14.5	52	42	10	0.16	
	400	625	1895	1663	232	3.64
505		1548	1343	205	3.22	
362		1116	963	153	2.40	
216		677	574	97	1.52	
104		329	276	53	0.83	
14.5		42	39	3	0.04	

(1) The compressibility of nitrogen under the conditions of the experiments is so small that no corrections were applied.

TABLE XXII

ADSORPTION OF METHANE ON 7.983 GRAMS OF COLUMBIAGRADE L CHARCOAL AT 0-600 PSIG

<u>Temp.</u> <u>°F</u>	<u>Equilibrium</u> <u>Pressure</u> <u>PSIA</u>	<u>Total Gas</u> <u>on Charcoal</u> <u>and in Free</u> <u>Space, ml.</u>	<u>Total Free</u> <u>Space Vol.</u> <u>Corrected</u> <u>ml. (1)</u>	<u>Vol. Gas</u> <u>Adsorbed</u> <u>ml.</u>	<u>Wt. Per Cent</u> <u>Methane on</u> <u>Charcoal</u>
100	617	3287	2369	918	8.24
	515	2847	1958	889	7.98
	414	2399	1554	845	7.59
	316	1961	1172	789	7.09
	221	1529	808	721	6.48
	166	1351	676	675	6.06
	136	1094	490	604	5.42
	64	659	227	432	3.88
	14.5	225	52	173	1.56
	200	605	2690	2000	690
516		2346	1701	645	5.80
409		1920	1336	584	5.24
303		1490	984	506	4.55
198		1052	637	415	3.73
121		699	383	316	2.84
59		440	212	228	2.06
14.5		116	46	70	0.63
300		612	2342	1829	513
	514	1992	1529	463	4.17
	416	1639	1231	408	3.68
	320	1287	943	344	3.09
	203	856	593	263	2.37
	116	515	333	182	1.63
	14.5	74	42	32	0.29
	400	618	2091	1705	386
487		1659	1334	325	2.92
355		1223	966	257	2.31
226		792	611	181	1.63
99		360	264	96	0.86
14.5		54	39	15	0.14

(1) Compressibility corrections were made for deviation from the ideal gas laws.

TABLE XXIII

ADSORPTION OF ETHYLENE ON 7.983 GRAMS
OF COLUMBIA GRADE L CHARCOAL AT 0-600 PSIG

<u>Temp.</u> <u>°F</u>	<u>Equilibrium</u> <u>Pressure</u> <u>PSIA</u>	<u>Total Gas</u> <u>on Charcoal</u> <u>and in Free</u> <u>Space, ml.</u>	<u>Total Free</u> <u>Space Vol.</u> <u>Corrected</u> <u>ml. (1)</u>	<u>Vol. Gas</u> <u>Adsorbed</u> <u>ml.</u>	<u>Wt. Per Cent</u> <u>Ethylene on</u> <u>Charcoal</u>
100	603	4034	2900	1134	17.9
	536	3617	2443	1174	18.5
	449	3116	1938	1178	18.6
	351	2605	1445	1160	18.3
	264	2179	1034	1145	18.1
	176	1755	668	1087	17.2
	97	1167	348	819	12.9
	48	1034	185	849	13.4
	14.5	614	51	563	8.87
	200	607	3365	2385	980
524		2939	1965	974	15.4
434		2514	1569	945	14.9
340		2097	1185	912	14.4
216		1552	718	834	13.2
130		1142	428	714	11.3
73		873	270	603	9.52
14.5		327	46	281	4.4
300		603	2927	2060	867
	510	2497	1682	815	12.8
	410	2067	1262	805	12.7
	306	1636	947	689	10.9
	201	1202	607	595	9.4
	122	855	364	491	7.75
	14.5	193	42	151	2.38
	400	597	2546	1900	646
498		2122	1515	607	9.52
390		1685	1139	546	8.52
279		1253	802	451	7.08
188		902	525	377	5.92
103		553	287	266	4.18
14.5		103	39	64	1.01

(1) Compressibility corrections were made for deviation from the ideal gas law.

TABLE XXIV

ADSORPTION OF ETHANE ON 7.983 GRAMS
OF COLUMBIA GRADE L CHARCOAL AT 0-600 PSIG

Temp. °F	Equilibrium Pressure PSIA	Total Gas on Charcoal and in Free Space, ml.	Total Free Space Vol. Corrected ml. (1)	Vol. Gas Adsorbed ml.	Wt. Per Cent Ethane on Charcoal
100	530	3965	2972	1172	19.9
	477	3531	2355	1176	19.95
	414	3089	1909	1180	20.05
	344	2664	1501	1163	19.75
	259	2218	1062	1156	19.62
	187	1862	732	1130	19.20
	102	1422	480	942	16.00
	14.5	727	53	674	11.43
200	556	3439	2358	1081	18.40
	497	3022	1995	1027	17.45
	424	2597	1659	938	15.92
	338	2169	1226	943	16.01
	246	1746	875	871	14.8
	170	1407	572	835	14.2
	86	985	281	704	11.96
	14.5	388	46	342	5.82
300	520	2737	1832	905	15.4
	459	2389	1560	829	14.1
	369	1957	1203	754	12.8
	266	1518	833	685	11.6
	185	1176	563	613	10.4
	127	911	381	530	9.02
	14.5	219	42	177	3.01
400	525	2486	1695	791	13.45
	442	2042	1360	682	11.60
	345	1604	1017	587	9.97
	260	1254	743	511	8.70
	173	908	481	427	7.26
	94	558	256	302	5.13
	14.5	121	39	82	1.40

(1) Compressibility corrections were made for deviation from the ideal gas law.

TABLE XXV

ADSORPTION OF PROPANE ON 7.983 GRAMS
ON COLUMBIA GRADE L CHARCOAL AT ELEVATED PRESSURE

Temp. °F	Equilibrium Pressure PSIA	Total Gas on Charcoal and in Free Space, ml.	Total Free Space Vol. Corrected ml. (1)	Vol. Gas Adsorbed ml.	Wt. Per Cent Propane on Charcoal
100	98.5	1472	436	1036	26.1
	69.5	1330	296	1034	26.1
	42.5	1140	175	965	24.4
	14.5	906	58	848	21.5
150	116.5	1520	487	1033	26.2
	89.5	1282	362	920	23.3
	61.5	1116	242	874	22.1
	35.5	954	136	818	20.7
	14.5	763	53	710	17.9
200	92.0	1180	351	829	21.0
	67.0	1016	250	766	19.4
	40.5	850	150	700	17.7
	14.5	645	51	594	15.1
250	94.5	1120	343	777	19.7
	70.0	953	250	703	17.8
	44.0	789	154	635	16.1
	14.5	519	49	470	11.9
300	100.5	1098	352	746	18.9
	71.5	856	244	614	15.5
	45.5	696	152	544	13.8
	14.5	417	47	370	9.4
350	97.0	910	326	584	14.8
	67.0	742	219	523	13.2
	41.5	576	134	442	11.2
	14.5	328	46	282	7.14
400	96.5	833	312	521	13.2
	70.5	664	224	440	11.2
	45.0	495	141	354	8.97
	14.5	240	44	196	4.96

(1) Compressibility corrections were made for deviation from the ideal gas law.

TABLE XXVI

ADSORPTION OF METHANE AND NITROGEN ON 20.352 GRAMS
OF DAVIDSON REFRIGERATION GRADE SILICA GEL AT 100°

<u>Methane</u>			
<u>Equilibrium</u> <u>Pressure</u> <u>mm.</u>	<u>Vol. Methane</u> <u>Adsorbed</u> <u>ml.</u>	<u>Vol. Methane Per</u> <u>Gram of Silica</u> <u>ml./Gm.</u>	<u>Wt. Per Cent</u> <u>of Methane on</u> <u>Silica Gel</u>
125	6.6	0.32	0.023
305	19.2	0.96	0.069
527	33.7	1.66	0.118
755	46.7	2.29	0.165
<u>Nitrogen</u>			
130	3.4	0.17	0.021
344	9.3	0.46	0.057
547	15.1	0.74	0.093
696	19.8	0.97	0.122

TABLE XXVII

ADSORPTION OF ETHYLENE, ETHANE, AND PROPANE ON
9.175 GRAMS OF DARCO ACTIVATED CHARCOAL AT 100° F

<u>Ethylene</u>			
<u>Equilibrium Pressure</u> <u>mm.</u>	<u>Vol. Gas Adsorbed</u> <u>ml.</u>	<u>Vol. Gas Per Gram of Darco</u> <u>Charcoal</u>	<u>Wt. Per Cent of Gas Adsorbed on</u> <u>Charcoal</u>
66	74.6	8.2	1.03
314	187.4	20.4	2.57
687	284.8	31.1	3.92
<u>Ethane</u>			
125	153.3	16.7	2.26
260	213.6	23.3	3.16
476	273.7	29.8	4.04
751	323.3	35.2	4.78
<u>Propane</u>			
99	240.0	26.2	5.28
302	305.3	33.2	6.72
685	389.9	42.5	8.60

TABLE XXVIII

ADSORPTION OF ETHANE ON 11.783 GRAMS
OF PITTSBURGH CHEMICAL COMPANY CHARCOAL

<u>Equilibrium Pressure</u> <u>mm.</u>	<u>Vol. Ethane Adsorbed</u> <u>ml.</u>	<u>Vol. Ethane per Gram of Charcoal</u> <u>ml./Gram</u>	<u>Wt. Per Cent of Gas Adsorbed on Charcoal</u>
45	162.4	13.8	1.86
129	316.6	26.9	3.63
315	521.6	44.2	5.06
508	656.3	55.7	7.51
744	735.4	62.5	8.43

TABLE XXIX

ADSORPTION OF A BINARY MIXTURE OF
ETHYLENE AND PROPANE ON DARCO CHARCOAL AT 100°F IN A
FLOW SYSTEM AT ATMOSPHERIC PRESSURE

	<u>Ethylene</u>	<u>Propane</u>
Feed Composition, mol. %	57.4	42.6
Adsorbate Composition, mol. %	17.7	82.3
Volume adsorbed on 9.175 gsm.	67 ml.	312 ml.
Adsorbate Composition, mol. %	13.0	87.0
Obtained using same feed mixture on Columbia Grade L charcoal		

ADSORPTION OF METHANE-ETHYLENE MIXTURES ON

COLUMBIA GRADE L CHARCOAL AT 100°F

Experiment No.	Length of Experiment Hrs.	Pressure mm or PSIA	Feed Composition Mol %		Composition of Adsorbate Mol. %		Vol. of Gas Adsorbed ml.		Predicted (3) Adsorption ml		Fraction of (1) Predicted Adsorption		Fraction of Surface (2) Covered by Heavier Component	Point No. on Figure 4
			CH ₄	C ₂ H ₄	CH ₄	C ₂ H ₄	CH ₄	C ₂ H ₄	CH ₄	C ₂ H ₄	CH ₄	C ₂ H ₄		
3615-96	2.2	759	52.2	47.8	14.0	86.0	75.2	462	117	453	0.64	1.02	0.295	1
3735-3	2.1	758	53.8	46.2	11.2	88.8	55.7	442	117	453	0.475	0.978	0.295	2
3735-7	3.4	748	52.2	47.8	8.7	91.3	46.7	489	117	435	0.396	1.082	0.295	3
3735-41	7.8	747	77.2	22.8	27.0	73.0	112.0	302	161	293	0.695	1.030	0.191	4
3735-51	8.6	749	26.7	73.3	7.3	92.7	42.9	533	67	564	0.627	0.945	0.368	5
3735-66	7.9	214.5psia	27.9	72.1	8.4	91.6	88.0	958	413	1082	0.213	0.885	0.703	6
3735-70	7.2	214.5psia	75.5	24.5	33.0	67.0	328	670	693	861	0.473	0.778	0.561	7

(1) Volume of component gas adsorbed from mixture
 Volume of pure gas adsorbed at same total as its partial pressure in the binary mixture

(2) Number of molecules of ethylene calculated from its predicted adsorption
 Number of molecules of ethylene required to cover the total charcoal surface with a monomolecular layer of gas.

(3) Volume of pure gas adsorbed at same total pressure as its partial pressure in the binary mixture.

ADSORPTION OF ETHYLENE-PROPANE MIXTURES ON

COLUMBIA GRADE L CHARCOAL AT 100 F

Experiment No.	Length of Experiment Hrs.	Pressure mm or PSIA	Feed Composition		Composition of Adsorbate		Vol. of Gas Adsorbed		Predicted (3) Adsorption		Fraction of (1) Predicted Adsorption		Fraction of Surface (2) Covered by Heavier Component	Point No. on Figure 42
			Mol. %		Mol. %		ml.		ml		C ₂ H ₄ C ₃ H ₈			
			C ₂ H ₄	C ₃ H ₈	C ₂ H ₄	C ₃ H ₈	C ₂ H ₄	C ₃ H ₈	C ₂ H ₄	C ₃ H ₈	C ₂ H ₄	C ₃ H ₈		
3735-29	7.7	756	75.8	24.2	22.8	77.2	189	643	578	745	0.330	0.870	0.565	8
3735-14	3.1	745	55.1	44.9	12.3	87.7	112	791	485	860	0.220	0.921	0.652	9
3735-47	7.7	752	29.4	70.6	6.5	93.5	61	906	342	932	0.178	0.975	0.706	10
3735-49	8.5	756	20.4	79.6	5.5	94.5	56	968	275	951	0.156	1.015	0.722	11
3735-53**	7.5	757	47.3	52.7	11.2	88.8	63	513	209	575	0.303	0.890	0.436	12
3735-55	23.9	748	47.3	52.7	8.3	91.7	76	816	445	887	0.170	0.921	0.673	13
3735-59	7.8	214.5psia	75.0	25.0	36.7	63.3	404	700	1090	976	0.370	0.718	0.741	14
3735-62	7.9	214.5psia	75.0	25.0	40.0	60.0	371	723	1090	976	0.340	0.742	0.741	15

**This experiment was at a temperature of 200 F.

- (1) $\frac{\text{Volume of component gas adsorbed from the mixture}}{\text{Volume of pure gas adsorbed at the same total pressure as its partial pressure in the binary mixture.}}$
- (2) $\frac{\text{Number of molecules of propane calculated from its predicted adsorption}}{\text{Number of molecules of propane required to cover the surface of the charcoal with a monomolecular layer of gas.}}$
- (3) $\frac{\text{Volume of pure gas adsorbed at the same total pressure as its partial pressure in the binary mixture.}}$

TABLE XXXII

ADSORPTION OF VARIOUS BINARY GAS MIXTURES ON

COLUMBIA GRADE L CHARCOAL AT 100 F

Experiment No.	Length of Experiment Hrs.	Pressure mm or PSIA	Feed Composition Mol. %		Composition of Adsorbate Mol. %		Vol. of Gas Adsorbed ml		Predicted (3) Adsorption ml		Fraction of (1) Predicted Adsorption		Fraction of Surface Covered by Heavier Component	Point No. on Figure 42
			C_2H_4	C_4H_{10}	C_2H_4	C_4H_{10}	C_2H_4	C_4H_{10}	C_2H_4	C_4H_{10}	C_2H_4	C_4H_{10}		
3735-80	8.0	214.5psia	88.8	11.2	42.8	57.2	445	592	1160	862	0.383	0.687	0.833	16
3735-83	7.6	748	88.8	11.2	13.4	86.6	120	609	623	775	0.192	0.786	0.749	17
3735-78	6.1	752	86.1	13.9	45.2	54.8	423	512	1020	804	0.415	0.636	0.775	18
3735-85	8.6	748	57.0	43.0	20.9	79.1	198	746	950	876	0.208	0.853	0.847	19
3735-72	7.3	752	47.6	52.4	39.1	60.9	279	435	449	621	0.622	0.700	0.404	20
3735-24	8.1	755	52.5	47.5	21.7	78.3	33.3	120	38	115	0.87	1.04	0.052	21

(1) Volume of component gas adsorbed from the mixture

Volume of pure gas adsorbed at the same total pressure as its partial pressure in the binary mixture.

(2) Number of molecules of heavier component calculated from its predicted adsorption

Number of molecules of heavier component required to cover the surface of the charcoal with a monomolecular layer of gas.

(3) Volume of pure gas adsorbed at the same total pressure as its partial pressure in the binary mixture

TABLE XXXIII

TABULATION OF COORDINATES FOR VAPOR-ADSORBATE EQUILIBRIA CURVES
(Figures 43 and 44)

Exp. No.	Feed Composition		Adsorbate Composition		Quantity of Gas adsorbed, Milligram Moles/Gram Charcoal					
	Mol Fraction		Mol fraction		N ₁	N ₂	N ₁ '	N ₂ '	N ₁ /N ₁ '	N ₂ /N ₂ '
	Gas 1	Gas 2	Gas 1	Gas 2						
	<u>CH₄</u>	<u>C₂H₄</u>								
3615-96	.522	.478	.140	.860	.358	2.20	.972	3.16	.368	.697
3735-3	.538	.462	.112	.888	.265	2.15	.972	3.16	.273	.680
3735-7	.522	.478	.087	.913	.223	2.33	.972	3.16	.229	.738
3735-41	.772	.228	.270	.730	.534	1.44	.972	3.16	.550	.456
3735-51	.267	.733	.073	.927	.199	2.54	.972	3.16	.205	.804
3735-66	.279	.721	.084	.916	.314	3.42	.263	4.60	.195	.743
3735-70	.755	.245	.330	.670	1.170	2.39	.263	4.60	.446	.520
	<u>C₂H₄</u>	<u>C₃H₈</u>								
3735-29	.758	.242	.228	.772	.900	3.06	3.16	4.68	.285	.654
3635-14	.551	.449	.123	.877	.534	3.78	3.16	4.68	.169	.809
3735-47	.294	.706	.065	.935	.291	4.32	3.16	4.68	.092	.925
3735-49	.204	.796	.055	.945	.267	4.62	3.16	4.68	.084	.990
3735-55	.473	.527	.083	.917	.362	3.89	3.16	4.68	.104	.832
3735-59	.750	.250	.367	.633	1.44	2.50	4.03	5.75	.357	.435
3735-62	.750	.250	.400	.600	1.33	2.58	4.03	5.75	.330	.450
	<u>C₂H₄</u>	<u>n-C₄H₁₀</u>								
3735-80	.888	.112	.428	.572	1.59	2.11	4.03	5.75	.394	.368
3735-83	.888	.112	.134	.866	.572	2.91	3.14	4.91	.182	.593
	<u>C₃H₆</u>	<u>n-C₄H₁₀</u>								
3735-78	.861	.139	.452	.548	2.02	2.44	4.97	4.91	.407	.497
3735-85	.570	.430	.209	.791	.945	3.56	4.97	4.91	.190	.725
	<u>C₂H₄</u>	<u>C₂H₆</u>								
3735-72	.476	.524	.391	.609	1.33	2.08	3.14	3.89	.424	.535
	<u>N₂</u>	<u>CH₄</u>								
3735-24	.525	.475	.217	.783	.158	.572	.334	.968	.473	.591

SAMPLE CALCULATIONS

1. Adsorption of methane on 7.983 grams of charcoal at 0-600 psig and 100°F. Room at 757 mm, 22°C.

<u>Equilibrium, psig</u>	<u>Vol. Bled from system after each equilibrium point, ml.</u>
602	440
500	448
399	438
301	432
206	435
121	435
49	434
0	-
	<u>3062 ml (ntp)</u>

Total methane in system at room pressure:

$$(a) \quad 42.7 \times \frac{757}{760} \times \frac{273}{311} = 37.3$$

$$(b) \quad 16.0 \times \frac{757}{760} \times \frac{273}{295} = 14.7$$

52.0 ml in free space

- (c) Adsorbed (from Fig. 10)

$$\frac{203}{9.367} \times 7.983 = 173 \text{ ml.}$$

- (d) $3062 + 173 + 52 = 3287 \text{ ml. total}$

Free space corrections reduced to a factor x PSIA

$$(a) \quad 42.7 \times \frac{\text{PSIA}}{14.7} \times \frac{273}{311} = 2.55 \times \text{PSIA}$$

$$(b) \quad 16.0 \times \frac{\text{PSIA}}{14.7} \times \frac{273}{295} = 1.007 \times \text{PSIA}$$

Calculations for 602 psig equilibrium point

$$(a) \quad 602 \text{ psig} = 617 \text{ psia} \quad (Z = 0.929 @ 100F, 0.920 @ 22 C)$$

$$(b) \quad 2.55 \times 617 \times \frac{1}{.929} = 1694$$

$$(c) \quad 1.007 \times 617 \times \frac{1}{.920} = 675$$

2369 ml. Free space total methane at 617 psia

(d) $3287 - 2369 = 918$ ml. methane adsorbed.

(e) $\frac{918}{7.983} \times .0007168 \times 100 = 8.24$ gms/100 gms of charcoal

Calculations for 500 psig equilibrium point

(a) 500 psig = 515 psia (Z = .988 @ 100F, .929 @ 22 C)

(b) $2.55 \times 515 \times \frac{1}{.938} = 1400$

(c) $1.007 \times 515 \times \frac{1}{.929} = \frac{558}{1958}$ ml. total in free space

(d) $3287 - 440 = 2847$ ml. total in system at the
515 psia equilibrium

(e) $2847 - 1958 = 889$ ml adsorbed
= 7.98 gms./100 gms of charcoal

Repeat stepwise to room pressure

2. Molecular area (methane)

$$\begin{aligned} (R)^2 &= 1.53 \left(\frac{M}{d}\right)^{2/3} = 1.53 \left(\frac{16}{.3916}\right)^{2/3} \\ &= 18.1 \text{ square Angstroms} \end{aligned}$$

3. Monomolecular layer on Columbia Grade L charcoal

$$\frac{1152 \times (10^{10})^2}{18.1} = 6.37 \times 10^{21} \text{ molecules of methane}$$

4. Calculation of v_m for methane

$$\frac{6.37 \times 10^{21} \times 22.4 \times 10^3}{6.06 \times 10^{23}} = 235 \text{ ml./gm.}$$

5. Calculation of adsorption coefficient, Langmuir equation

$$1/v = .08$$

$$1/p = .00244 \text{ selected point on methane isotherm}$$

$$.08 = 1/235 b (.00244) \cdot 1/235$$

$$b = .000137$$

VITA

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MASTER OF SCIENCE

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The content and form have been checked and approved by the author and thesis adviser. Changes or corrections in the thesis are not made by the Graduate School office or by any committee. The copies are sent to the bindery just as they are approved by the author and faculty adviser.

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