

THE RATE OF DIFFUSION OF METHANE IN LIQUID HYDROCARBONS

Thesis by  
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## DIFFUSION OF NATURAL GAS THRU OIL AND OIL-SATURATED SANDS

The use of gas for repressuring has rapidly increased in the petroleum industry during recent years. The "repressuring" of oil-bearing sands by forcing natural gas into the formation thru surrounding wells has been undertaken with the view of increasing the yield of oil from the formation. The great uncertainty as to the true value of this procedure and the nature of the change taking place during a repressuring operation, makes a study of the rates and mechanism of the diffusion of gases into oils of considerable importance. Beecher and Parkhurst<sup>1</sup> have shown in their work on the decrease of the viscosity of crude oil, due to the presence of dissolved gas, that it is of great value to keep gas dissolved in oil or replace it if it has been removed. Although the subjecting of a liquid to high pressures generally increases its viscosity these investigators have shown that a solution of methane in a crude oil in equilibrium with the gas at 500 lbs/sq.in. pressure exhibits a viscosity of about half that of the pure oil. This pronounced lowering of the viscosity would tend to make the oil flow more easily in a given formation and would have a direct bearing on the yield from the sand. If oil field conditions are such that the gas used in repressuring will be dissolved in the oil held in the pores of the sand, the repressuring is a valuable aid in increasing the yields of oil. A study of the rates of diffusion for this case (of a natural gas and various oils) based upon a suitable mechanism of the process involved will enable a fairly accurate estimate of the effectiveness of repressuring a formation. A consideration of the diffusion law for such cases is essential in the determination of the mechanism.

There are essentially two phases to the problem: The study of the diffusion process thru liquid oil and thru oil-saturated sands. The latter is the one of practical application to the oil field problem of "repressuring", but the former is essential as a basis for the oil-sand study.

The previous work upon solubilities of gas in oil and the effect of dissolved gas upon properties of oil as carried out by Beecher and Parkhurst,<sup>2</sup> Dow and Calkin,<sup>3</sup> has been chiefly with various crude oils and natural gases. Since both of these substances are highly complicated in nature they are unsuitable for basic or fundamental measurements. It appeared desirable to first make a study of the diffusion process with pure hydrocarbons as liquids and with a gas of practically only one constituent. By the use of simple substances the number of variable factors is greatly reduced and it becomes possible to accurately measure the effect of changing one condition at a time, such as temperature or pressure. The variation in the rate of diffusion with a change of the liquid, with other factors remaining constant, can be determined. Furthermore, by the selection of a group of pure or nearly pure hydrocarbons occurring to a large extent in crude oil and belonging to one series, i.e., paraffins, it is possible to observe any relationship existing between the diffusion processes in the case of different hydrocarbons and their physical properties such as viscosity, density, and molecular weight, which in turn largely determine the nature of a crude oil.

The following consideration of the diffusion process, as well as the complete development of the process as given in the appendix, is due to Mr. Scudder.

The mechanism of the diffusion of various solutes thru aqueous solutions has been investigated and is fairly well known; this phenomenon having first been considered by Parrot in 1815.

Graham<sup>4</sup> made the first real investigation of the subject in 1850 and Fick in <sup>5</sup>1855 proposed that "the quantity of salt which diffuses thru a given area is proportional to the difference between the concentrations of two areas infinitely near one another," or

$$\frac{dQ}{dt} = -k A \frac{dc}{dx} \quad (1)$$

where: Q = quantity of solute passing a given section  
 A = area  
 c = concentration  
 x = distance in direction of flow  
 t = time  
 k = diffusion constant

This proposition of Fick has been experimentally verified by Barus<sup>6</sup> and others. There have been discovered in the literature no reports on work involving a case of the nature of this problem, in which the diffusing gas is so similar chemically to the solvent and in which small concentrations of solute cause pronounced changes in the physical properties of the solution. Although it is evident that Fick's assumption, made for a different situation, will not hold exactly in this case, it has been taken as sufficiently accurate for practical purposes. Subsequent development of the equations for diffusion on this basis and their complete experimental verification have justified this basic assumption. The general experimental method adopted after a careful consideration of several possibilities consisted of measuring the quantity of gas, as a function of time, which diffused into a body of oil or oil-saturated sand of known dimensions and weight when the pressure of the gas on its

surface was held constant. A saturation value for the particular sample was determined at the specified temperature and pressure.

Assuming the proposition of Fick, the relationship between the diffusion constant  $k$  and the quantity of gas absorbed  $Q$  is:

$$\frac{dQ}{dt} = -k A \frac{dc}{dx} \quad (1)$$

from which (see appendix)

$$\frac{dc}{dt} = k \left( \frac{\partial^2 c}{\partial x^2} \right) \quad (2)$$

The conditions of the experiment require that the following conditions be satisfied.

$$\frac{\partial c}{\partial x} = 0, \text{ at the bottom of the cell, where } x = 0.$$

(no flow, hence no gradient)

At the surface of the liquid  $c = c_s$  (saturation)

When  $t = 0$ ,  $c = 0$

As shown in the appendix Scudder has obtained the desired relation between the quantity of gas absorbed, the time, the saturation value and the length of the liquid column thru a development of the diffusion equations by application of the equations for the flow of heat thru solid bodies to the case at hand.

The general equation is:

$$\frac{Q}{Als} = \frac{Q}{Q_s} = \left[ 1 - \frac{8}{\pi} \sum_{m=1}^{m=\infty} \frac{1}{(2m-1)^2} \cdot e^{-k \left( \frac{2m-1}{2l} \right)^2 \pi^2 t} \right] \quad (3)$$

where:  $A$  = area  
 $S$  = solubility of gas at saturation  
 $l$  = length of liquid column  
 $k$  = diffusion constant  
 $t$  = time  
 $Q$  = quantity of gas dissolved at time  $t$

It was found by mathematical operations later to be verified by experimental measurements that for values up to 30% saturation the curve of the rate of absorption (  $\frac{Q}{A l S}$  vs  $t$  ) approximates a parabola with an error not exceeding 0.02% and that the general equation simplifies to the form:

$$\frac{Q}{A l S} = 1.1284 \sqrt{\frac{K t}{l}} \quad (4)$$

Above the value of 70% saturation the curve approximates a simple exponential (with an error not exceeding 0.02%) and the general equation simplifies to:

$$\frac{Q}{A l S} = 1 - 0.8106 \times 10^{(-1.07159 \frac{K t}{l})} \quad (5)$$

Between the values of  $Q/A l S = 30\%$  and  $Q/A l S = 70\%$  the equation (4) can be used to a value of  $Q/A l S$  of 50% with an error of only 0.25% at 50% saturation, and from this point to 70% saturation the exponential equation (5) can be used with a maximum error of 0.2% (at  $Q/A l S = 50\%$ ). It is evident that for all practical purposes cases covering the entire range from zero concentration to saturation these simplified equations may be used with sufficient accuracy.

Equation (4) is the one of greatest interest in this present study as few absorption rate runs have been carried beyond 50% saturation due to the length of time necessary for such measurements. The results of the various runs made with methane and a group of nearly pure hydrocarbons have been shown graphically by plotting the gas dissolved by the liquid/unit of surface area against the  $\sqrt{t}$ .

$$\frac{Q}{A} = S(1.1284)k_1\sqrt{t} = S k_2\sqrt{t}$$

For a given oil at a specified temperature and pressure  $S$  is a constant value; therefore:

$$\frac{Q}{A} = k'''\sqrt{t}$$

where  $k'''$  is an empirical constant and is the slope of the straight line obtained by plotting  $Q/A$  against the  $\sqrt{t}$ ,  $t$  is expressed in minutes.

#### EXPERIMENTAL METHOD

The accurate measurement of the absorption rate of gases by hydrocarbons or oils and the determination of the solubility of the gas in the oil at saturation, presented a number of experimental difficulties. The use of pure or nearly pure hydrocarbons limited the quantities of materials to be used because of the difficulty and expense entailed in their preparation. A suitable method for determination of amount of gas diffusing into a given volume had to be devised. Since it was the purpose of this investigation to ascertain the factors determining the rate and amount of absorption of gases by oils on account of its bearing upon the repressuring operations of the petroleum industry, it was advisable to conduct the experimental work under conditions approaching (as nearly as possible) to those encountered in oil formations. By this is meant the measurement of absorption rates at high pressures and reasonably warm temperatures. It was necessary to construct an apparatus capable of withstanding the pressures to be used and entirely leak proof. Preliminary surveys had shown the impossibility of determining the amount of gas dissolved by any analytical method because of the inertness of the substances used, their tendency to form super-

saturated solutions and the high pressures at which absorption was to take place. The discussion of the experimental work will be taken up under three divisions: the preparation of the materials, the details of the apparatus, and the methods used in the laboratory measurements of diffusion rates and solubilities.

#### Materials Used in Experimental Measurements.

In the study of the mechanism and rate of diffusion of natural gases in crude oils, it seemed advisable to first work with simple substances. Previous work on the absorption of gases by oils has involved the use of crude oils and natural gases. Because of the highly complex nature of petroleum and the varied composition of typical natural gases it becomes extremely difficult to show the true effect of a change of a certain variable or to formulate any general relationships as to absorption rate and the viscosity, molecular weight and density of the liquid substance. It was decided to employ methane as the gas and a group of pure paraffin hydrocarbons and narrow boiling range fractions as the liquids. This necessitated the preparation of relatively pure materials. Of the two methods of preparation, synthesis and a fractional distillation from gasoline or petroleum, the latter method was selected.<sup>7</sup>

#### Preparation of Paraffin Hydrocarbons.

The following pure hydrocarbons were used in the absorption rate measurements: n-hexane, n-heptane, iso-octane, n-decane (narrow boiling range fraction) and benzene. In addition to these, preliminary measurements were made on a commercial water-white kerosene and a high boiling kerosene fraction.



The hydrocarbons were prepared from 9 gallons of commercial gasoline. The first distillations were made with a three liter glass still heated by an immersed resistance coil heater, and equipped with a 3-foot by 1-inch glass fractionating column packed with cut glass rings and thoroughly lagged. The column was equipped with a reflux through which tap water was circulated. No attempt was made to condense the lighter fractions with ice. The initial sample was cut into 23 fractions as shown in Table I.

A second distillation of the fractions obtained in the first distillation was made. The fractions are shown in Table II.

Two smaller stills consisting of one-liter balloon flasks and 40 cm. glass columns packed with glass rungs were employed for additional fractionations. Stills were heated by gas burners. Various fractions of distillation 2 (Table II) were redistilled and two degree cuts removed. The distillations showed only slight evidence of cracking. Since all of the pure paraffin hydrocarbons were prepared in a similar manner, the preparation of one substance, n-heptane, will be described in some detail.

TABLE I

## First Fractionation Commercial Gasoline

Temperature	Vol. of Fraction	Total Volume	Temperature	Vol. of Fraction	Total Volume
To 33°C	455	455	89 - 91	575	9840
33 - 41	1185	1640	91 - 94	1045	10885
41 - 47	1290	2930	94 - 104	2810	13695
47-- 53	1130	4060	104 - 117	2695	16390
53 - 57	760	4820	117 - 130	2850	19240
57 - 61	500	5320	130 - 140	1875	21115
61 - 65	515	5835	140 - 150	2005	23120
65 - 70	790	6625	150 - 160	1830	24950
70 - 77	850	7475	160 - 170	1645	26595
77 - 80	310	7785	170 - 180	1700	28295
80 - 85	540	8325	Above 180	4000	32300
85 - 89	940	9265			

TABLE II

## Second Fractionation

Fraction No.	Temperature	Fraction No.	Temperature
1	To 31	16	100 - 105.8
2	31 - 34	17	105.8 - 110
3	34 - 41	18	110 - 115
4	41 - 47	19	115 - 120
5	47 - 53	20	120 - 126
6	53 - 57	21	126 - 130
7	57 - 62	22	130 - 135
8	62 - 66	23	135 - 142.6
9	66 - 71	24	142.6 - 146.6
10	71 - 77	25	146.6 - 152
11	77 - 80	26	152 - 162
12	80 - 85	27	162 - 167
13	85 - 92	28	167 - 173
14	92 - 95	29	173 - 180
15	15 - 100	30	Above 180

Preparation of Normal Heptane.

The normal heptane was prepared from the following fractions of the second preliminary distillation:

	<u>Boiling Range</u>	<u>Volume</u>
(1)	95 - 100°C	1150 cc.
(2)	98.2 - 102°C	58 cc.

The fractions were first distilled in an apparatus consisting of a 2-liter flask (burner heated), a 40-cm. fractionating column packed with glass rings and well lagged to prevent heat loss, and a reflux through which tap water was run. All thermometer readings were corrected for stem exposure. The fractions between 70.4°C and 95.8°C were discarded and the remaining liquid was placed in the acid treating apparatus.

A second fraction of liquid for treatment was obtained by fractionating the (92-95°) fraction (1150 cc.) of the second preliminary distillation and discarding all distillate boiling below 93.8°C. The total volume of heptane fraction to be treated was about 1540 cc.

The hydrocarbon fractions were treated with fuming nitric acid, <sup>8.9</sup> nitrosulphuric acid and concentrated H<sub>2</sub>SO<sub>4</sub> in the order named.

The apparatus in which the fractions were treated with acid consisted of the following: a three-liter pyrex balloon flask fitted with a 70-cm. water jacketed condenser cooled by ice water and having a ground glass joint on account of the extremely corrosive effect of acid vapors. The flask was heated by a steam bath and agitated by hand.

The heptane fractions were first treated with small quantities, 5 - 10 cc., of fuming nitric acid and the liquid kept at a temperature just below boiling. The addition of the fuming nitric acid caused a large evolution of heat accompanied by a violent cracking noise (probably

due to the action of the oxides of nitrogen upon the  $H_2O$  in the hydrocarbon fraction). A considerable quantity of brown fumes poured from the top of the reflux condenser. Fuming  $HNO_3$  was added over a period of several days at intervals of several hours. The charge in the flask was permitted to boil gently between additions of the acid. The hydrocarbon fractions turned to dark brown color upon addition of the acid and a viscous black layer separated at the bottom of the flask. The hydrocarbon fraction separated from the acid layer was a brilliant orange color. The hydrocarbon layer was again treated with fuming  $HNO_3$  and gently boiled for several days, the hydrocarbon layer turning a brilliant green. The dark viscous acid layer was separated from the hydrocarbon fraction. Treatment with fuming nitric acid was continued until no marked reaction occurred upon the addition of the acid. The hydrocarbon fraction was next treated with 50 to 100 cc. of nitro-sulphuric acid ( $SO_2 \begin{matrix} \text{OH} \\ \diagdown \\ \text{O}-NO_2 \end{matrix}$ ), a one-to-one mixture of nitric acid and  $H_2SO_4$ . The mixture was gently boiled for 48 hours on the steam bath, nitro-sulphuric acid being added at intervals of several hours. The dark brown acid layer was separated from the hydrocarbon layer. The latter was again returned to the treater and 100 cc. of concentrated  $H_2SO_4$  added. The mixture was put on the steam bath and thoroughly agitated at intervals for 8 - 12 hours. The acid layer was separated and the fractions again treated with  $H_2SO_4$  until there was very little evolution of heat and only a slight darkening of the acid layer upon addition of fresh  $H_2SO_4$ . After the final separation of the  $H_2SO_4$  layer the fraction was thoroughly washed several times with water and then treated with three 100-cc. portions of 2 normal sodium hydroxide by vigorous agitation in a separatory funnel. The hydrocarbon was then thoroughly washed with water several

times, being allowed to stand in contact with the water between washings. As a final step in the refining process, the hydrocarbon fraction was dried for 3 days over anhydrous calcium chloride. It was now ready for the final fractionations.

The final fractionations were carried out in a glass distilling apparatus equipped with a 60-cm. glass rung packed column well lagged but not fitted with a reflux and a water jacketed condenser. The following cuts were made: (With the exception of cuts 1 and 2 the distillations were made using a 50°C range thermometer having total immersion and accurate to 0.5°C.)

#### First Distillation

Cut Number	Boiling Range	Pressure
1	(89.7 - 95.7)	744.6 mm.
2	(95.7 - 98.2)	741.6
3	(98.2 - 99.1)	741.6

Volume of distillate obtained = 596.0 cc.

#### Second Distillation

Volume of fractions distilled = 596.0 cc.

Cut Number	Boiling Range	Pressure	Volume
1	(75 - 95.0)	747.0 mm.	158.0 cc.
2	(95.0 - 96.5)	747.0	94.0
3	(96.5 - 99.1)	747.0	--

Third Distillation (Final Fraction)

The cut number 2 (95.0-96.5) from distillation 2 (about 92.0 cc) was placed in the flask and distillate taken off up to 96.5°C. To the fraction remaining in the flask Cut number 3 of distillation 2 was added and the distillation continued.

Cut Number	Boiling Range	Pressure	Volume
1	(92.0 - 96.5)	748.7 at 18°C	discarded
2	(94.5 - 97.0)		"
3	(97.0 - 98.5)	747.0 mm.	

N.Heptane (nearly pure) Boiling range (97.0 - 98.5°C) at 747 mm.

Vol. = 159.0 cc.

Boiling range - Brooks "Non Benzenoid Hydrocarbons - 98.2-98.5 at 760 mm.

Hexane.

The normal hexane was prepared in an identical manner. The sources of the hydrocarbon were the fractions of boiling range (67 - 71°C) from the distillation of commercial gasoline. Total volume of material = 1480 cc. The Nor. Hexane prepared, had a boiling range of (67.4 - 68.7)°C at 740 mm. and a volume of 104 cc.

Iso-Octane.

The iso-octane was prepared by the method outlined, from fractions of (112 - 122°C) boiling range, obtained from the commercial gasoline.

Boiling Range (116.1 - 117.2)°C at 747 mm.

Volume 110 cc.

Decane Fraction.

Although this fraction was not pure decane it possessed a boiling range of narrow limits and was largely free of unsaturated and cyclic compounds. It was considered advisable to make measurements on the decane as it represented a rather high molecular weight liquid paraffin.

The decane was prepared from the (170 - 180°) fraction of the gasoline distillation. Its refining treatment followed that outlined for the heptane but all distillations were carried out at reduced pressure, in order to prevent cracking of the hydrocarbon.

Boiling Range (79.4 - 88.5) at 38 mm.

Volume 143.0 cc.

The greater part of the decane distilled over between the temperature of 83°C and 88.5°C.

Benzene.

The benzene used was obtained from Kahlbaum and was thiophene free. Boiling point, 79°C at 743 mm.

Table IIQ summarizes the materials used and their boiling ranges.



TABLE IIA

## Hydrocarbons Used in Absorption Rate Measurements

Hydrocarbon	Boiling Range °C	Pressure mm.	Accepted Boiling Point of pure HC at 760 mm. 68.95°C
n-Hexane	67.4 - 68.7	740.0	
n-Heptane	97.0 - 98.5	747	(98.2-98.5)
Iso octane	116.1 - 117.2	745	(117.9-118.1)
Decane fract.	79.4 - 88.5	38	173
Benzene (Thiophene-free)	79.0	743	80.36

### Preparation of Methane.

The gas used in the absorption rate measurements was methane, selected because it constituted the greater part of practically all natural gases and it could readily be obtained in a fairly pure condition. The source of the methane was natural gas from the Seal Beach Field, California, obtained from high pressure deep wells. The gas was collected in steel tanks under pressures of 900 - 1200 lbs. The natural gas was of high methane content having approximately 92% methane and 8% of ethane and heavier constituents. The process of removing the ethane and heavier constituents from the natural gas consisted in passing the gas at high pressure thru activated charcoal. This method proved quite effective and had the advantage of simplicity. The gas, after passage thru the charcoal, gave an average analysis of 2.5 to 3.0% ethane. This analysis and the one of the natural gas were obtained in the following manner.

An airtight apparatus was evacuated by means of a hyvac pump. The gas, after passage through the charcoal, was run into the system until atmospheric pressure was reached. Liquid air was applied to a trap in the system. After a constant pressure was recorded on the manometer for some time, the pump was again connected and the methane was pumped off, leaving the solidified ethane in the trap. The system was again shut off from the pump and the tube containing the ethane warmed up. The resulting pressure was taken as that of the ethane and heavier constituents. Knowing the barometric pressure, the percentages of the ethane and heavier could be readily calculated and that of the methane obtained by difference between the ethane pressure and the total pressure.

The activated charcoal was placed in a heavy 9 mm. brass cylinder, very similar in appearance to the oil absorption cell. The cell had a capacity of approximately 220 cc. The top of the cell was fitted with a large lead washer and fastened to the cell proper by means of 8 bolts. Gas was admitted to the top through a short 1/8-inch copper tube fitted with a union for connection with the cylinder of natural gas, and left the bottom of the cell by means of 1/8-inch flexible copper tubing which connected to the control needle valve of the reservoir gauge. After each filling of the reservoir the charcoal cell was placed in an electric oven, heated to about 110°C for 3 hours and exhausted. Although this reactivation was quite effective, frequent changes of charcoal were made.

#### Description of Apparatus.

The method for obtaining diffusion rates and solubilities consists in measuring the quantity of gas absorbed by a known volume of liquid of a definite surface area, the gas being maintained at a specified pressure over the liquid. This is accomplished by a measurement of the volume of gas passing from a reservoir into a cell containing the liquid. This is a direct measure of the amount of gas that has diffused into the liquid from the saturated surface layer. The above is briefly the general method used in all the measurements. For a determination of the solubility of the gas in the liquid it would only be necessary to continue the rate measurements until the oil became saturated at the operating pressure. Practically this was never carried out because of the excessively long time interval necessary due to the rapid decrease of the absorption rate, as saturation was approached. The solubilities are

obtained by completely saturating the oil with gas by means of violent agitation of the oil.

The essential pieces of the apparatus are: an absorption cell in which the liquid is placed, an indicating pressure gauge for determining the pressure of the gas above the surface of the liquid, a large calibrated reservoir gauge from which gas is lead under the desired pressure to the surface of the hydrocarbon, a means of accurately controlling the amount of gas introduced into the absorption cell and a thermostat enclosing the entire equipment in order that constant temperature may be maintained thruout a diffusion rate measurement.

The absorption cell is constructed of heavy brass and was built for operating pressures up to 600 lbs/sq.in. The dimensions and details of the cell are shown in Figures 1 and 2. The problem of preventing leakage of either the hydrocarbon or gas during the runs which frequently lasted 48 hours or more is a rather difficult one, but has been satisfactorily solved with the following arrangements. The top of the cell is securely fastened to the cell proper by means of 6 bolts, leakage being prevented by a lead gasket which is squeezed into the grooves D of the flange and the cell cover. These gaskets are made from a mold and are of such a size that they can gradually be squeezed down over a period of time covering a number of runs before being discarded. No leakage has occurred at any time from this point on the cell. As originally constructed, the absorption cell was equipped with a stirrer mounted on a steel shaft passing thru the hole B in the bottom of the chamber and the compartment C in which the shaft was packed with a number of rawhide washers forced tightly around the shaft by means of a follower and large nut

which screwed into position. The end of the shaft extending below the threaded portion of the cell was equipped with a small base having two holes which fitted over two short uprights on a vertical revolving shaft. This arrangement comprised the motor driven stirring mechanism and was used for agitation in the determination of solubilities for approximately half of the runs. Considerable heating due to friction of the shaft and the length of time needed for saturation caused this method to be replaced by another. In the present arrangement the stirrer has been discarded and the hole B sealed with solder. Agitation of the hydrocarbon is accomplished by vigorously shaking the cell by hand, keeping it in the thermostat during this procedure. The cell top is fitted with a small blow-off needle valve N (Fig. 1) an outlet, O, to take a pressure gauge and the gas inlet P. All parts are sweated into place. The blow-off valve was used in the early runs in the displacing of the air above the liquid by the gas. The brass structure O has a fine capillary communicating with the cell. The space Q is packed with rawhide washers fitting around the brass tube communicating with the cell pressure gauge G. This space can be filled with solder, thus eliminating the necessity of the packing gland. The gas enters the cell from the reservoir gauge by means of the brass elbow P, having a very small bore. A small copper disk has been placed a short distance below the inlet in order to deflect the high pressure gas stream and prevent the churning up of the liquid surface. It was found that the extremely erratic pressure readings obtained during the first part of some of the early runs were in a large measure due to the churning up of the hydrocarbon by the entering gas thus causing a variable rate of solution. The gauge is also fitted with an electric buzzer which

vibrates the gauge and prevents sticking of the pointer when a reading is to be made. When completely assembled the cell is clamped into position directly in front of the large gauge as shown in Figure 4.

The gas reservoir is a large (9 inch) Ashton pressure gauge with a pressure range from 300 lbs. to 600 lbs. and graduated in 2-lb. intervals. The Bourdon tube of the gauge is of sufficient size to serve as a gas reservoir, holding, when filled to a pressure of 600 lbs., a volume of gas equivalent to approximately 2500 cc. at atmospheric pressure. By means of a series of calibrations the gauge readings in pounds per square inch pressure are converted into cc. of gas discharged and thus serve as a measure of the gas going into the oil. As shown in Figure 3 the gauge is securely mounted on a heavy wooden framework in a vertical position.

To the bottom of the large gauge and also mounted on the wooden frame is fastened a specially constructed, extremely sensitive needle valve packed on the low pressure side by a large number of rawhide washers which make it gas tight. This valve in turn is connected to the cell by means of a coiled flexible  $1/8$ " copper tube fitted on both ends with unions made gas tight by small lead gaskets similar to the large one used on the absorption cell. Due to the difficulty of turning the valve because of tight packing and due to the necessity of obtaining extremely fine adjustment in the opening and closing of the valve, the shaft is equipped with heavy brass disk to which is fastened a lever arm. The swing of the arm is adjusted by means of a chain.

The entire set-up, mounted on a heavy wooden base, is enclosed within an air thermostat measuring  $4 \times 2\frac{1}{2} \times 21$  feet. (Figure 3)

The thermostat is constructed of celotex insulating building board lined with asbestos board. A fan mounted at one end of the thermostat provides air circulation. Heat is furnished by means of a small resistance wire coil mounted directly in front of the fan and controlled by the thermostat regulator. The heater is connected in parallel with a lamp bank which serves as an additional means of control. A second heater on a separate circuit is used to bring the thermostat up to operating temperature. The thermostatic regulator, which has proved very satisfactory, consists of an inch bimetallic strip (invar-brass) one end of which is securely fastened and the other end carries a small brass cup filled with mercury which makes contact with an adjustable platinum wire contact. The regulator, shunted by a condenser, actuates a relay which controls the small heater. At 30° Centigrade (86°F), the temperature used in the measurements, a control of one tenth of one degree Centigrade is obtained. Temperatures are measured by a thermometer graduated to 0.1°C. The front of the thermostat is removable and is fitted with a glass window through which gauge readings are made. The needle valve is operated through a small door in the front of the thermostat. The room in which the work is conducted is rather small and can be thermostated in a very rough manner.

A closer temperature control, especially during warm weather when the room temperature is nearly 30°C was obtained by a 1/4" copper coil cooler through which tap water or ice water is circulated. This coil is mounted directly in front of the fan about a foot from it. The water entering the coil is circulated through a large copper coil condenser surrounded with ice.

## METHOD OF MEASUREMENTS

The procedure outlined in the following discussion of the methods employed in making the diffusion rate measurements is the result of several years of experimental work.

Calibration of Gauge.

The large reservoir gauge which indicates pressure in pounds per square inch is calibrated in order to give values in cc. (30°C and 760 mm. of mercury) of the gas discharged from the gauge starting at a full position, i.e., gauge reading of 600 lbs. per square inch. The calibration of the gauge is effected by means of a specially constructed gas burette of about 53 cc. capacity. The burette is made entirely of glass and consists of two bulbs whose volume is accurately known connected by means of a length of glass tubing part of which is capillary tubing. One of the bulbs is filled with mercury, displacing the air in it. Gas from the large gauge is passed into this bulb displacing the mercury into the second bulb until atmospheric pressure is reached as indicated by a small differential manometer. Correction is made for any small deviation of the pressure from barometric. In this manner the gauge is calibrated from the 600 lb. division to the lower end of the scale. The volumes of gas admitted each time are corrected to 760 mm. and the temperature used in the rate measurements (30°C). These volumes are then progressively added giving at any time the total volume of gas corresponding to a given pressure reading which the gauge has delivered. Calibrations of the gauge are made at intervals of several months. It is found that the calibrations have a small but distinct drift upward, i.e., increased volume for a definite pressure interval, which indicates that the gauge characteristics are changing. Small irregularities in



the individual calibrations are ironed out by composite curves made up of a number of calibrations properly weighting the individual ones in determining the composite. A very complete calibration table giving the volume equivalent for every two pounds on the gauge dial has been compiled, using the 600 lb. mark as zero volume of gas delivered from the gauge. Interpolation tables were also worked out for readings lying between those given in the table. A system was devised whereby the large reservoir gauge could be accurately read to  $1/6$  of a pound, which corresponds to approximately 1.2 cc. In the calculation of the runs the relative times between the date of the run and the dates of the calibration preceding and the one following the run are employed in weighting the volume equivalents of the two calibrations.

#### Absorption Rate Measurements.

The absorption rate measurements may be divided into three parts: the preparation for the run, the actual rate measurements, and the determination of solubilities.

The first step is to fill the large reservoir gauge with methane. The charcoal cell is connected to the large gauge with the needle valve on the gauge closed. The cell is evacuated and then fitted with residual methane from the reservoir gauge. The gauge is then filled with methane obtained by passing the high methane content natural gas through the charcoal cell. A sample of the hydrocarbon used is weighed out and the distance from the surface of the liquid to the top of the cell measured.

The absorption cell and gauge are connected up, the thermostat brought up to temperature and the apparatus kept for several hours at operating temperature before starting the run. In most of the measurements a gas pressure of 300 lbs. per square inch was maintained on the

cell. An initial reading of the large gauge, defined as the Initial Gauge Reading in the report of the measurements is made. The needle valve connecting the cell and reservoir is opened, the exact time being noted, and the gas run into the cell until the desired pressure is obtained, the time being noted again at this point. During the admission of the gas, the time when the cell pressure reaches half the operating pressure is also recorded. This time, recorded to the nearest second is termed the Initial Time in the reports on the runs. The time interval of letting in the gas to the oil chamber is very short, the average value being from 5 to 12 seconds. The large gauge is read and the time noted, when the pressure indicated on the cell gauge is exactly the specified pressure of the run. Immediately pressure on the cell is raised to 1 lb. or  $1\frac{1}{2}$  lbs. above run pressure and then is permitted to drop a corresponding amount below before more gas is let in. The gas is run into the cell to exactly specified pressure and the large gauge read again. The time interval existing between successive readings (called  $\Delta t$  in the run reports) is quite small at the beginning of a run and then increases according to the equation

$$\Delta t = k_3 \sqrt{t}$$

$t$  = time in hours from start of run.

$\Delta t$  = time interval between successive readings in minutes.

This equation is obtained from equation (4) in the following manner.

$$\frac{Q}{A l S} = \frac{1.1284 \sqrt{k' T}}{l} \quad (4)$$

Since for any hydrocarbon under specified conditions  $S$  and  $A$  are constant:

$$Q = k_2 \sqrt{t}$$

$$Q^2 = k_2^2 t$$

Differentiating:

$$2 Q dQ = k_2^2 dt$$

Substituting:

$$Q = k_2 \sqrt{t}$$

$$2k_2 \sqrt{t} \Delta Q = k_2^2 \Delta t$$

$$\Delta t = \frac{2 k_2 \sqrt{t} \cdot \Delta Q}{k_2^2}$$

$\Delta Q$  is a constant being about 1.0 to 2.0 lbs. on the big gauge or 7 - 14 cc.

$$\Delta t = k_3 \sqrt{t}$$

$k_3$  is an empirical constant determined for each run.

In general the measurements of diffusion rate are continued until 35 - 45% saturation has been obtained. The time required for this varies from approximately  $3\frac{1}{2}$  hours in the case of normal hexane to approximately 34 hours in the case of the normal decane fraction.

At the conclusion of the rate measurements the gas is let into the cell to a pressure several pounds above that used during the run and the cell shaken thoroughly by hand, keeping it in the thermostat all the time. This agitation is continued until no reduction of pressure is noted on the cell gauge after several periods of shaking. The large gauge reading is recorded and designated as the saturation volume equivalent ( $V_s$ ). In the runs made on the lighter materials, such as hexane and heptane, a part of the cell volume is filled up by a brass plug. The great solubility of the gas in the hydrocarbon necessitates this. A detailed and complete report of a typical absorption rate run, that of methane in normal hexane, Run No. 27, is given under the heading of report of measurements. The method outlined above may be more fully understood by reference to this data.

## EXPERIMENTAL RESULTS

The following report covers a total of 20 runs, 16 of which were made using various liquid hydrocarbons; the remaining four were made with sands saturated with the hydrocarbons. The results are given in table form, Tables III and IV, supplemented with a few notes on the runs. Run No. 27 (methane and hexane) is given in full detail to show the entire method used including the various steps in the calculations. All the measurements were made and results calculated as shown in this sample run with but few minor changes. During the development of the technique and methods kerosene was used as the liquid, because of its abundance.

Definition of Terms

Volume Equivalent ( $V$ ). This is the volume of gas in cc. (obtained from the pressure reading in lbs. in the reservoir gauge) that has been let out of the reservoir gauge in reducing the pressure reading from 600 lbs. (corresponding to zero vol. Eq.) to the reading in question. The Volume Equivalents are obtained from the calibration tables.

Initial Volume ( $V_i$ ). The volume equivalent corresponding to the reading of the large gauge before any gas has been released from it.

( $V_0$ ) The volume equivalent at the instant when the gas has reached operating pressure in the cell and is starting to diffuse into the liquid. This value is obtained by extrapolation of the straight line curve of volume equivalent vs.  $\sqrt{t}$  to zero time.

Saturation Volume Equivalent ( $V_s$ ). The volume equivalent corresponding to the reservoir gauge reading when the sample of liquid has been saturated at the specified pressure.

$V_s - V_0 = V_a$  The volume of gas absorbed by the hydrocarbon.

TABLE III

## Absorption Rate Runs - Methane and Hydrocarbons

Run Number	16	17	18	25	26	27	28(a)	28(b)
Date	5/15/29	6/6/29	7/10/29	9/25/29	10/9/29	10/14/29	10/15/29	10/18/29
Liquid	Kerosene	Kerosene	iso-Octane	n-Hexane	n-Hexane	n-Hexane	n-Decane	n-Decane
Temperature	30°C	30°	30°	30°	30°	30°	30°	30°
Pressure (lbs/sq.in.gauge)	289	289	289	287.5	287.5	287.5	143.5	287.5
Method of Agitation (for sat'n)	Stirrer	Stirrer	Stirrer	Stirrer	Stirrer	Stirrer	Stirrer	Stirrer
Air Displacement	Yes	Yes	Yes	Yes	Yes	No	No	No
Deflector	No	No	No	No	No	Yes	Yes	Yes
Weight of liquid	61.00	61.20	56.89	22.08	21.05	21.40	60.77	60.77
Distance from liquid surface to cell top	23.0	21.5	19.0	20.0	20.0	21.0	22.6	22.6
Initial Volume in cc. (Reservoir Gauge)	11.1	68.3	22.3	203.8	1.2	--	3.5	752.2
V <sub>0</sub> , cc.	669.3	698.6	616.7	819.7	629.5	451.5	294.0	1060.0
Saturation Vol. Equivalent, V <sub>s</sub> , cc.	1511.3	1550.4	1710.5	1391.3	--	985.1	752.2	1519.1
Total Volume Absorbed, cc.	842.0	851.8	1093.7	571.6	--	533.6	460.3	459.0
Solubility in cc/gm	13.80	13.92	19.22	25.90	--	24.93	7.58	7.56
Length of rate measurements, hrs.	10.28	128.0	20.5	10.	7.25	.66	46.	39.

TABLE III (cont)

## Absorption Rate Runs - Methane and Hydrocarbons

Run Number	29	30	32	33	34	35	36
Date	10/23/29	11/7/29	12/12/29	12/20/29	1/30/30	2/6/30	2/8/30
Liquid	n-Decane	n-Decane	Benzene	Benzene	n-Heptane	n-Heptane	n-Heptane
Temperature (°C)	30°	30	30	30	30	30	30
Pressure (lbs/sq.in.gauge)	287.5	287.5	287.5	287.5	300	300	300
Method of Agitation (for sat'n)	Stirrer	Stirrer	Shaken	Shaken	Shaken	Shaken	Shaken
Air Displacement	No	No	No	No	No	No	No
Deflector	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Weight of Liquid	61.35	62.38	68.10	68.83	23.52	28.43	29.60
Distance from liquid surface to cell top, mm.	20.0	20.0	23.0	22.0	21.0	14.0	12.5
Initial Volume in cc. (Reservoir Gauge)	--	--	66.9	--	--	--	--
V <sub>0</sub> (cc.)	564.5	544.7	792.5	647.0	845.0	685.0	457.2
Saturation Vol. Equivalent, V <sub>s</sub> (cc)	1462.5	1424.4	1567.7	1455.9	1391.0	1267.5	1103.4
Total Volume Absorbed (cc)	898.0	879.7	775.2	808.9	546.0	582.5	646.2
Solubility in cc/gm	14.62	14.10	11.38	11.74	23.25	20.5	21.85
Length of rate measurements (hrs.)	13.0	41.0	26.5	46.2	22.5	11.3	2.5

TABLE III (cont)

## Absorption Rate Runs - Methane and Hydrocarbons

Run Number	37 (a)	37 (b)	37 (c)
Date	3/3/30	3/7/30	3/7/30
Liquid	n-Heptane n-Heptane n-Heptane		
Temperature (°C)	30	30	30
Pressure (lbs/sq.in.gauge)	135.0	250.0	380.0
Method of Agitation (for sat'n)	Shaken	Shaken	Shaken
Air Displacement	No	No	No
Deflector	Yes	Yes	Yes
Weight of Liquid	17.53	17.53	17.53
Distance from liquid surface to cell top, mm.	12	12	12
Initial Volume in cc. (Reservoir Gauge)	--	298.7	657.9
V <sub>0</sub> (cc)	158.0	536.0	927.0
Saturation Vol. Equivalent, V <sub>s</sub> (cc)	297.3	657.9	1062.1
Total Volume Absorbed (cc)	139.3	121.9	135.1
Solubility in cc/gm	7.95	6.95	7.70
Length of rate measurements (hrs)	11.8	8.0	11.5

All measurements were made at a temperature of 30°C. Pressures given are gauge pressures. Barometric pressure was 14.5 lbs/sq.in. As the experimental work proceeded minor changes and improvements were made in the apparatus and method. In the earlier runs - up to Run 27, no deflector was used over the gas inlet to the cell and the air in the cell was displaced at the start of the run by methane. This latter procedure was discontinued because of the danger of vaporizing some of the light hydrocarbons used. In the later runs saturation was obtained through agitation by means of shaking in place of motor driven stirrer. Curves of  $Q/A$ , the volume of gas absorbed in cc. per square centimeter of area plotted against the square root of the time in minutes, are given for most of the runs, Figs. 5 to 15. Where several measurements have been made using the same liquid and at the same temperature and pressure, results are plotted on the same graph in order to indicate the reproducibility of the method. Figs. 17 to 20 show the absorption rates of methane in a uniform grain sand saturated with various hydrocarbons.

Results of Measurements with Liquids. Methane and Kerosene.

Since the runs previous to Run 16 were of questionable reliability due to poor temperature control and the fact that the experimental technique was being developed, they have been omitted from this consideration. The rate curve is shown in Fig. 5, for Run 16 (methane and water-white commercial kerosene). The solubility given in Table III shows that at a pressure of 289.0 lbs/sq.in. gauge 13.80 cc. of methane dissolved per gram of kerosene. Run 17 (fig. 6 ) a check run on No. 16 appears to have a smaller slope. This means that the absorption rate was somewhat less as determined by this measurement. The solubility (Table III)



of 13.92 cc. of  $\text{CH}_4$ /gm. kerosene shows excellent agreement with that of No. 16. The deviation from the average, 13.86 cc/gm, is only 0.86%. A third run, No. 18, with methane and kerosene (not shown) was calculated and showed an extremely irregular rate curve, due to poor temperature control. This run clearly indicated the effect of even small variations of temperature upon absorption rate. Temperature variation in this run was a maximum of approximately one degree centigrade.

#### Methane and Iso Octane.

The absorption rate curve for iso octane at 280 lbs gauge pressure is shown in Fig. 7. It will be noted that the first 4 points lie somewhat above the line. This is due to the unsettled conditions existing at the start of the run. In this case, since no deflector over the gas inlet was used, the churning of the liquid no doubt partially accounted for the deviation. The solubility of methane in iso octane at 289 lbs. gauge is 19.22 cc/gm of the hydrocarbon (Table III). This is considerably higher than that of kerosene, as might be expected from the difference in absorption rates.

#### Methane and Hexane.

Three absorption rate measurements were made for hexane, the curves of which are given in Figures 8 and 9. Figure 8 shows the results of runs No. 25 and No. 26, both made at 287.5 lbs gauge pressure. The decided deviation of the experimental points from the straight line, where the value of  $\sqrt{t}$  is 21, for Run 25 is due to the effect of the bottom of the cell. The saturation has reached the value of 50 percent and the rate curve deviates from a straight line as would be expected from a consideration of the diffusion equations.

The significance of this change in diffusion rate may be easily seen by considering the following facts. At the beginning of the diffusion process only the surface film will contain dissolved gas, being rapidly saturated. The ensuing process consists of diffusion of dissolved gas from this saturated film ~~into~~ the main body of liquid. Up to the time when the entire body of liquid contains 50% of the gas required to saturate it, the diffusion proceeds as though into an infinite volume, there being no dissolved gas in the liquid furthest removed from the surface. After the 50% point has been reached the concentration gradually builds up throughout the liquid and the gas which has reached the furthest portion of liquid can move no further. This second stage would be expected to show a different rate from the first stage. Run 26 very closely checked the values obtained for 25. The third measurement (No. 27) was a very short run of about 0.7 hours made for a solubility determination. The solubilities (Table III) are 25.90 and 24.92 cc. of methane per gram of hexane for runs 25 and 27 respectively. No saturation value was obtained for No. 26.

#### Methane and Normal Decane.

The liquid was a narrow boiling range decane fraction. The results of the runs Nos. 28, 29 and 30 shown in figures 10, 11 and 12, respectively. Run 28 was divided into two parts. In part (a) the absorption rate was measured at a pressure of 143.5 lbs per sq.in. gauge. The run was made for 46 hours. At the end of this period the decane was saturated at 143.5 lbs. The result was a volume of liquid saturated at a given pressure and with a concentration gradient of zero. The gas pressure was then suddenly raised to 287.5 lbs (approximately twice the

first value) and the absorption rate measured (part b) for about 39 hours. The concentration gradient being zero, at the start of the second part and the hydrocarbon saturated at 143.5 lbs, the actual pressure gradient from the gas to the liquid was 144 lbs or approximately equal to that in the first case. It would be expected that the absorption rates would be the same for the two stages. Experimental data completely verified this assumption, as seen by the curve for the runs (Figure 10).

Run No. 29 (Figure 11) was a measurement of the absorption rate at 287.5 lbs/sq in gauge. Run 30, (Figure 12) was made at the same pressure as No. 29 but the length of the run was 41 hours as compared to the 13 hours for 29. In all three decane runs a deflector was used and air was not displaced by methane. The solubility of methane in decane was for (28a) 7.58 cc of methane per gm. Decane at 143.5 lbs gauge or 158.0 lbs absolute. In 28b, the solubility is 7.56 cc of methane per gm decane or a total of 15.14 cc/gm decane at 287.5 lbs pressure. The solubility in (b) is twice that in (a), a further experimental proof of the assumption that the quantity of gas dissolved in an oil is directly proportional to the absolute pressure. The solubility of 14.62 cc of methane per gm of decane for Run 29 and 14.10 cc/gm for 30 are in reasonably good agreement.

#### Methane and Benzene.

Two absorption rate runs were made with C.P. benzene as the liquid in order to obtain information as to the absorption rates of aromatic hydrocarbons in comparison with those of the paraffins. A comparison between absorption rates and solubilities of methane in hexane and benzene, both hydrocarbons having the same number of carbon atoms in the molecule, may be made. Figure 13 shows the results of Runs

No. 32 and 33, in which the rates of absorption of methane in benzene at 287.5 lbs gauge and 30°C were measured. The agreement between the two curves is excellent. Run 33 lasted about 46 hours while 32 was made for 26½ hours. The solubilities (Table III) of 11.38 cc of methane per gm of benzene for No. 32 and 11.74 cc/gm for No. 33 are not in as close agreement as the rates. This deviation may be due to the fact that in run 32 saturation was attained for the first time by shaking the cell instead of using the stirrer and due to unfamiliarity with this method the benzene was not quite completely saturated. The value of 11.74 cc/gm would therefore appear the more reliable.

#### Methane and Normal Heptane.

The normal heptane was one of the purest of the hydrocarbons used and gave very satisfactory results. Figure 14 shows the absorption rate curves for two heptane runs No. 34 and No. 35 made at 300 lbs gauge and 30°C. The rates, as the plot shows, check perfectly. It will be noted that the curve for run 34 (a 22½ hour run) begins to deviate from a straight line where  $\sqrt{t}$  is 27. This is due to effect of the bottom of the cell on pressure gradient as was pointed out in the discussion of the hexane measurements. At this point, the liquid has absorbed an amount of gas equal to 50% of the amount necessary for saturation. Run No. 36 was extremely short since it was made for a solubility determination only. The values of the solubility of 22.5, 20.3 and 21.85 cc of methane per gm of normal heptane for Runs 34, 35 and 36 respectively do not check as closely as results of other measurements. An average value of the three results, 21.9 cc/gm, may be taken as the solubility of methane in heptane at 300 lbs. pressure. The heptane measurements and those following them

were made at a pressure of 300 lbs per sq.in. gauge because a new and more accurate (0 to 500 lb) pressure gauge whose dial readings checked with a standard hydraulic gauge tester, was installed on the cell. The gauge used on the cell up to these runs had given high readings and consequently it was necessary to correct them by a calibration curve. Run No. 37 shown in Figure 15 was divided into three parts: a, b and c. In part (a) the absorption rate of methane in heptane was measured at 135 lbs gauge and the hydrocarbon was then saturated at that pressure. Actually a little too much gas was let into the cell so a saturation value at 135.5 lbs was obtained and this was corrected to 135 lbs. In part (b), the heptane saturated at 135.5 lbs in (a) had the gas pressure on its surface suddenly raised to 250 lbs and a rate measurement was made at this pressure. As shown in Figure 15, the curve for (b) lies below that for (a). This is exactly what would be expected, for in part (a) the pressure gradient is 135 lbs gauge, but in part (b) it is only 114.5 lbs/sq in. At the conclusion of the rate measurement in part (b) the heptane was saturated at 251 lbs per sq.in. (this was corrected to 250 lbs). The pressure of the gas on the heptane, saturated at 251 lbs, was suddenly raised to 380 lbs per sq.in. and the absorption rate measured, part (c), Figure 15. The pressure gradient was in this case, 129 lbs, hence the rate curve lies slightly below that for part (a) where the pressure gradient was 130 lbs and above that for (b) where the gradient was 114.5 lbs. The heptane (c) was next saturated at 380 lbs per sq.in., the highest pressure used in any of the measurements. The solubilities of methane in decane in cc per gram of liquid are 7.95 at 135 lbs, 14.90 at 250 lbs and 22.60 at 380 lbs are very nearly in the ratios of the absolute pressures which is to be expected.

Typical Absorption Rate Run

Rate of Absorption and Solubility of Methane in Normal Hexane  
 Run Number 27  
 Boiling Point Range of Hexane, 67.4 - 68.7°C  
 Jet Deflector and Brass Plug in Cell

Time	Reservoir Gauge Reading	Volume August Calibration	Volume Equivalent November Calibration	Corrected Volume Equivalent	$\Delta T$ (Minutes)	Volume Absorbed Q	Q/A
8:53,05		451.5					
8:53,27	538 $\frac{1}{3}$	457.5	463.9	455.4	.366	0.605	0.386
8:54,10	536 $\frac{5}{6}$	468.0	464.5	466.0	1.083	1.042	1.433
8:55,40	535 $\frac{1}{2}$	477.6	474.1	475.6	2.583	1.609	2.383
8:56,52	534 $\frac{1}{2}$	485.0	481.3	482.8	3.783	1.945	2.997
8:58,22	533 $\frac{5}{6}$	489.9	486.2	487.7	5.283	2.30	3.580
9:01,40	532 $\frac{2}{3}$	478.6	494.8	496.4	8.583	2.93	4.440
9:10,35	530 $\frac{1}{3}$	514.3	510.0	511.8	17.50	4.18	5.970
9:15,05	529 $\frac{1}{2}$	523.6	519.0	520.9	22.00	4.69	6.865
9:20,32	528 $\frac{2}{3}$	530.3	525.4	527.4	27.45	5.24	7.510
9:26,48	527 $\frac{1}{3}$	540.3	535.2	537.3	33.72	5.81	8.490
9:32,45	526 $\frac{1}{2}$	546.1	541.0	543.1	39.67	6.30	9.060
Saturation	464 $\frac{2}{3}$	991.8	980.4	985.1			

at 295 lbs. per sq.in. and 30°C

$V_s = 985.1$  cc. (extrapolated from curve)

$V_o = 451.5$  cc.

$V_s - V_o = 985.1 - 451.5 = 533.6$  cc. Total volume absorbed

$\frac{533.6}{21.40} = 24.92$  cc. of  $CH_4$ /gm. of normal hexane at 295 lbs. per sq.in.

Typical Absorption Rate Determination.

Run No. 27, made with methane and normal hexane has been given in detail in order to show the method of taking data on a run and its calculation. This run was quite short but will serve to illustrate the methods used in the longer ones. The initial time given as 8:53, 05 was determined by taking the time when the gas was first let into the cell from the reservoir gauge and the time when the pressure reached 295 lbs (287.5 lbs corrected) on the cell gauge. The average value, i.e., the time at which the pressure was 150 lbs is taken as the initial time (zero time). The value of  $V_0$  as determined from curve of volume equivalent vs.  $\sqrt{t}$  corresponds to this initial time. The second column gives the values of the reservoir gauge readings in lbs per sq.in. taken when the cell gauge read 295 lbs. Corresponding to the times in column 1. The next two columns contain the volume of gas in cc. discharged from gauge which is equivalent to the pressure reading of the gauge. In one column the volume equivalent as determined by the previous calibration, that of Aug. 23 is given and in the next column that of the Nov. 20 calibration are given. The values given in the column headed corrected volume equivalent are calculated by subtracting the volume equivalents as determined by the November calibration from those determined from the August calibration and multiplying the difference by a factor. This factor is the time interval in days between the date of the run and the date of the preceding calibration (Aug. 23 in this case) over the time interval in days between the two calibrations. For Run 27 this equals 52/89. Column 6 gives the time interval ( $\Delta t$ ) in minutes from the start of the run (initial time of 8:53,05). In the next column the  $\sqrt{T}$  (time in minutes) is given.

At the end of the columns the reservoir gauge reading, volume equivalents from August and November calibrations and the corrected volume equivalents are given for the point of saturation of the hexane at 287.5 lbs. The value of  $V_0$ , the volume equivalent corresponding to the reservoir gauge reading at the instant when the gas starts to diffuse into the liquid is determined by plotting the values of corrected volume equivalent against the  $\sqrt{t}$  and extrapolating the straight line to zero time.  $V_0$  equals 451.5 for this run. The calculation of the total volume absorbed by the weight of liquid used is shown. This volume absorbed divided by the weight of oil used gave the solubility in cc of gas/gm of liquid at the specified pressure. Column 8 gives the volume absorbed at the various times calculated by subtracting  $V_0$  from the corrected volume equivalent. The values of  $Q/A$  were obtained by dividing  $Q$  by the surface area of the liquid (10.11 cm<sup>2</sup>, the cell area). These values were then plotted against the  $\sqrt{T}$  in minutes as shown in Figure 9.

#### Measurements with Hydrocarbon-soaked Sands.

After having measured the diffusion rates and solubilities of methane in various liquid hydrocarbons only, investigations were carried to the measurement of the rates of absorption of methane by hydrocarbon-saturated sands. This condition more nearly approached those actually existing in oil formations. A series of four measurements were made upon the rates of absorption of methane by a uniform grain sand saturated with various liquid hydrocarbons. The sand used in all of these determinations was a very pure, white Ottawa sand of uniform grain size and designated as sand 1. It was treated by washing with water then washing with dilute hydrochloric acid three times and again washing with water



the wash water no longer gave an acid test. The sand was then dried thoroughly. The sand was weighed out and placed in the cell with packing caused only by gently tapping the cell. The liquid was then poured in slowly until its level was exactly that of the sand. Table 4 gives the results of the four runs. No saturation values were determined. It was assumed that the solubilities of methane in the various hydrocarbons (determined for liquid only) were correct for the case when the liquid was in the pore spaces of the sand.

#### Methane and Normal Heptane in Sand 1.

The absorption rate for this run No. 39 is given in Figure 18. The rate of diffusion into the hydrocarbon-sand mixture was very slow compared to that for the liquid only. The measurement lasted approximately 30.2 hours. Assuming the solubility of methane in heptane to be the same in this case as that in the case of the liquid only it is found that at 30.2 hours the percentage of saturation at 300 lbs pressure in the case of the sand is only 35%, while it is 33% for pure liquid (only) heptane at 4.2 hours. The results of a previous determination (Run 38) with the same materials are shown in Figure 17. The sudden jump in this curve is accounted for by the fact that between the points on the curve where  $\sqrt{t}$  equals 13 and  $\sqrt{t}$  equals 17 the pressure of the gas in the cell which had been at 300 lbs per square inch gauge gradually built up to 305 lbs due to a slight leaking of gas thru the needle valve into the cell. The run was continued at 305 lbs. This curve shows the effect of pressure on absorption rate in a very striking manner.

Methane and Iso Octane and Sand 1.

An absorption rate determination was made for methane at 300 lbs. in a sand saturated with iso octane. The curve for this run (No. 40) is shown in Figure 19. It also, like the heptane runs shows a much lower absorption rate than that for the pure liquid.

Methane and Normal Decane Fraction and Sand 1.

The results of Run 31, in which the rate of absorption of methane by sand 1 saturated with normal decane was measured, are given in Figure 20. The sudden break in the curve between  $\sqrt{t}$  equals 38 and  $\sqrt{t}$  equals 42 is very difficult to account for. It is very likely that poor temperature control (the temperature was from 0.2 to 1.50 high) for some time before this point caused the four points below the break to be low and hence the dotted line is the true rate curve.

TABLE IV

Absorption Rate Runs Methane  
and Hydrocarbons with Sand

Run Number	31	38	39	40
Date	11/14/29	4/26/30	4/29/30	5/2/30
Liquid	n-Decane	n-Heptane	n-Heptane	iso-Octane
Sand	Sand 1	Sand 1	Sand 1	Sand 1
Temperature	30°C	30°C	30°C	30°C
Pressure (lbs/sq.in.gauge)	287.5	300*	300	300
Air Displacement	No	No	No	No
Deflector	Yes	Yes	Yes	Yes
Distance of Oil-Sand Surface to Cell Top (mm)	29.0	16.82	17.61	17.51
V <sub>0</sub> (cc)	781.5	903.2	891.0	935.5
Length of Run (in hours)	80	20	16.2	17.5

\*Pressure built up to 305 lbs. and measurement continued at this value

## SUMMARY

The study of the rate of absorption of methane by various nearly pure hydrocarbons has revealed a number of interesting facts. In Figure 16 is shown a group of curves giving the relative absorption rates for the hydrocarbons studied. These curves have been constructed by plotting the volume of gas in cubic feet absorbed per square foot of surface area per 100 pounds absolute pressure differential against the square root of the time in hours. These straight line curves hold with good accuracy only up to the time when the liquid is 50% saturated. As seen in the chart, the rate of absorption of methane by kerosene is the lowest of any of those studied. Normal decane, the heaviest of the paraffins used, shows a rate somewhat higher than that for kerosene. Benzene has a rate only slightly higher than that of normal decane. Comparing the benzene curve with that for the hexane it is seen that the absorption rate for benzene is only slightly more than half that for the hexane. This marked difference for two compounds of the same number of carbon atoms in the molecule, one belonging to the paraffin series and the other to the aromatic, shows what variation in absorption rates exists between the hydrocarbons of the two series. It is evident that the presence of considerable quantities of aromatics in a crude oil would have a pronounced effect in slowing down the absorption of a natural gas by the oil during "repressuring." The curve for iso octane shows a considerably higher absorption rate than the one for benzene. Normal heptane, the next lower compound in the paraffin series, exhibits a higher rate than the iso octane. Hexane, the lightest hydrocarbon, displays the highest rate of absorption of methane. The increase in rate between normal hexane and normal heptane is considerably greater

than that between normal heptane and iso octane. This may indicate that the absorption rate of the isomeric paraffins is higher than that of the corresponding normal compounds.

The absorption rate measurements made at two different pressures on normal decane (Run No. 28, Figure 10) show some very interesting results. From the curves it is seen that the absorption rate is the same for (a) and (b), as would be expected since the pressure gradient is substantially the same in the two cases, being 143.5 lbs in (a), where the pressure of the gas in the oil is initially zero, and 144 lbs in (b) where the liquid has been saturated with the gas at 143.5 lbs/sq.in. gauge. This means that provided the concentration gradient of the gas in the liquid is initially at zero, the rate of absorption of the gas is dependent only upon the pressure differential, the other factors such as temperature, surface area, etc. remaining fixed. It is evident that results of measurements of the absorption rate of natural gas by crude oils made at a given pressure gradient with the oil containing no dissolved gas may be applied to actual petroleum formation conditions where the oil may be uniformly saturated with gas at a certain pressure.

The measurements with the hydrocarbons and sand show a very much lower rate of absorption than in the case of the corresponding liquids alone. Since in the determination of  $Q/A$  for a sand run the surface area of the entire mixture is used and the actual surface of the liquid exposed is relatively small, the greatly decreased rate may be due to the small area of liquid.

## ACKNOWLEDGMENT

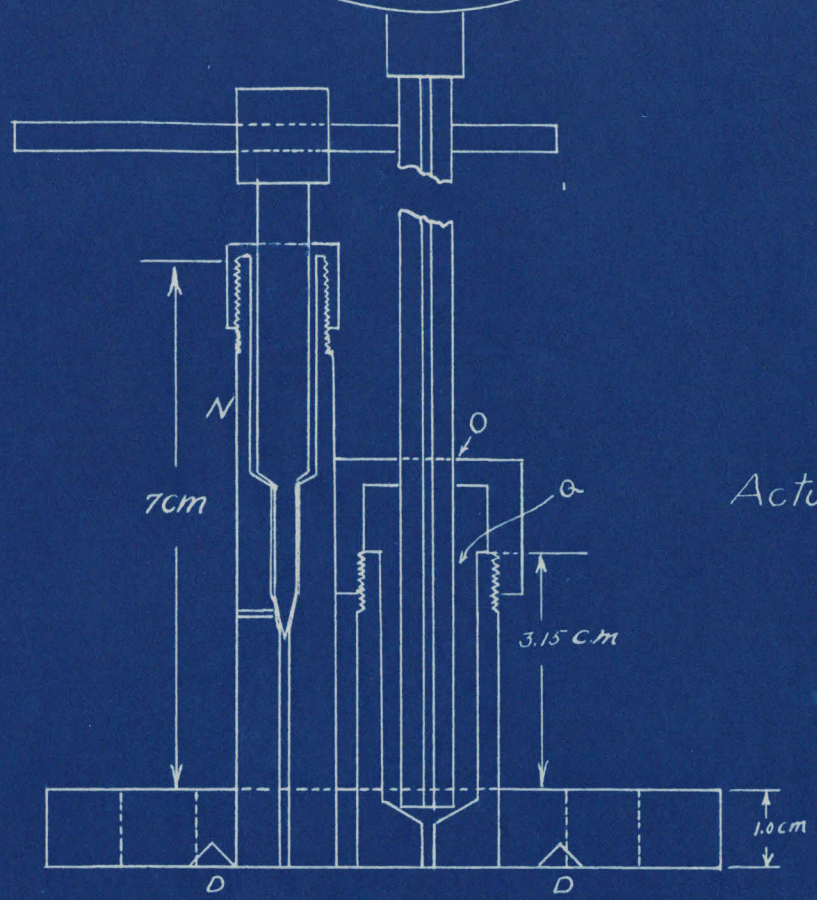
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Fig. 1.



Actual Size

TOP OF ABSORPTION CELL

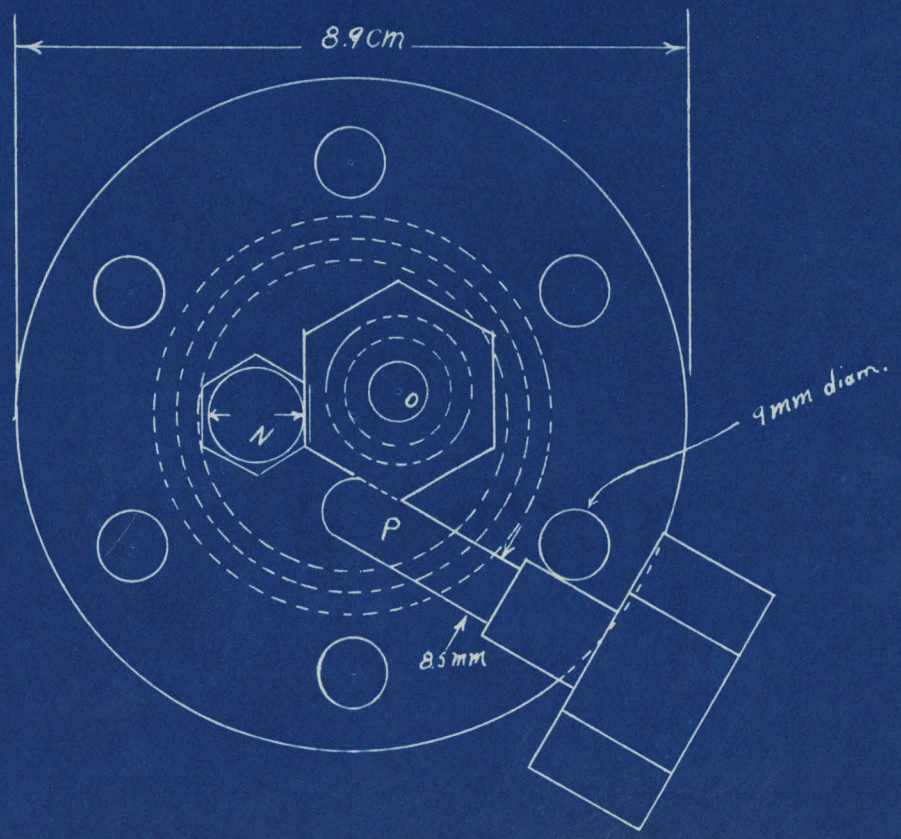
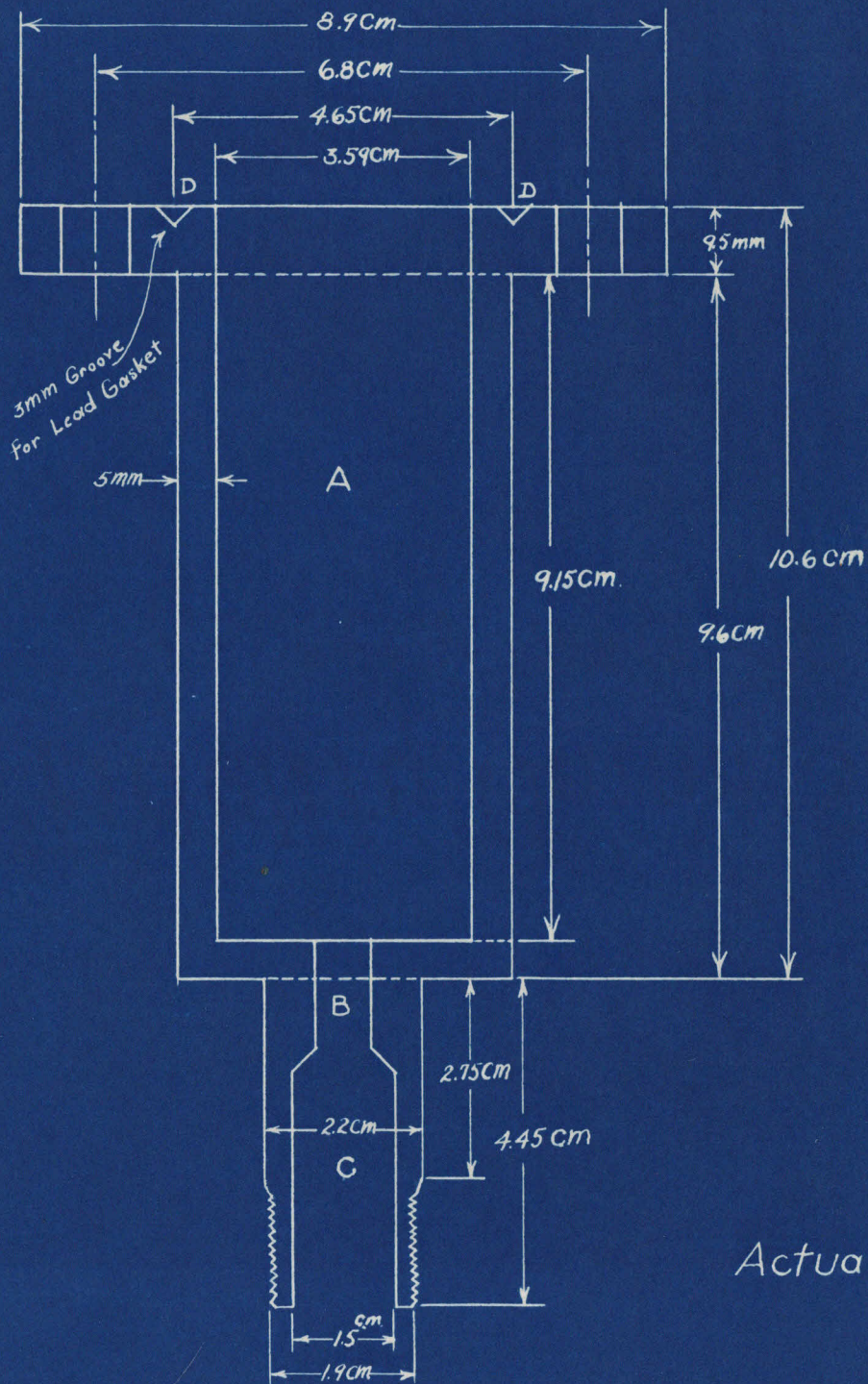




Fig. 2.



ABSORPTION CELL

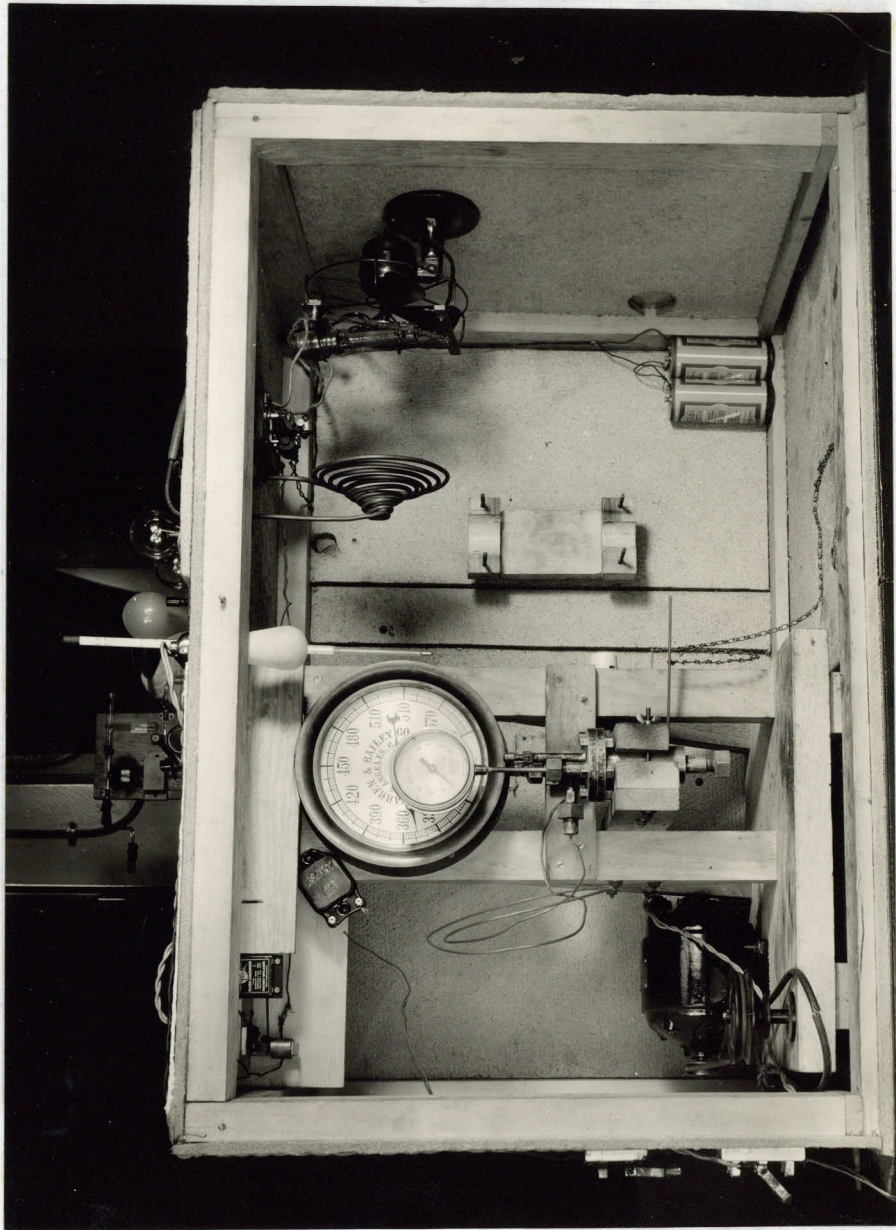


Fig. 3.

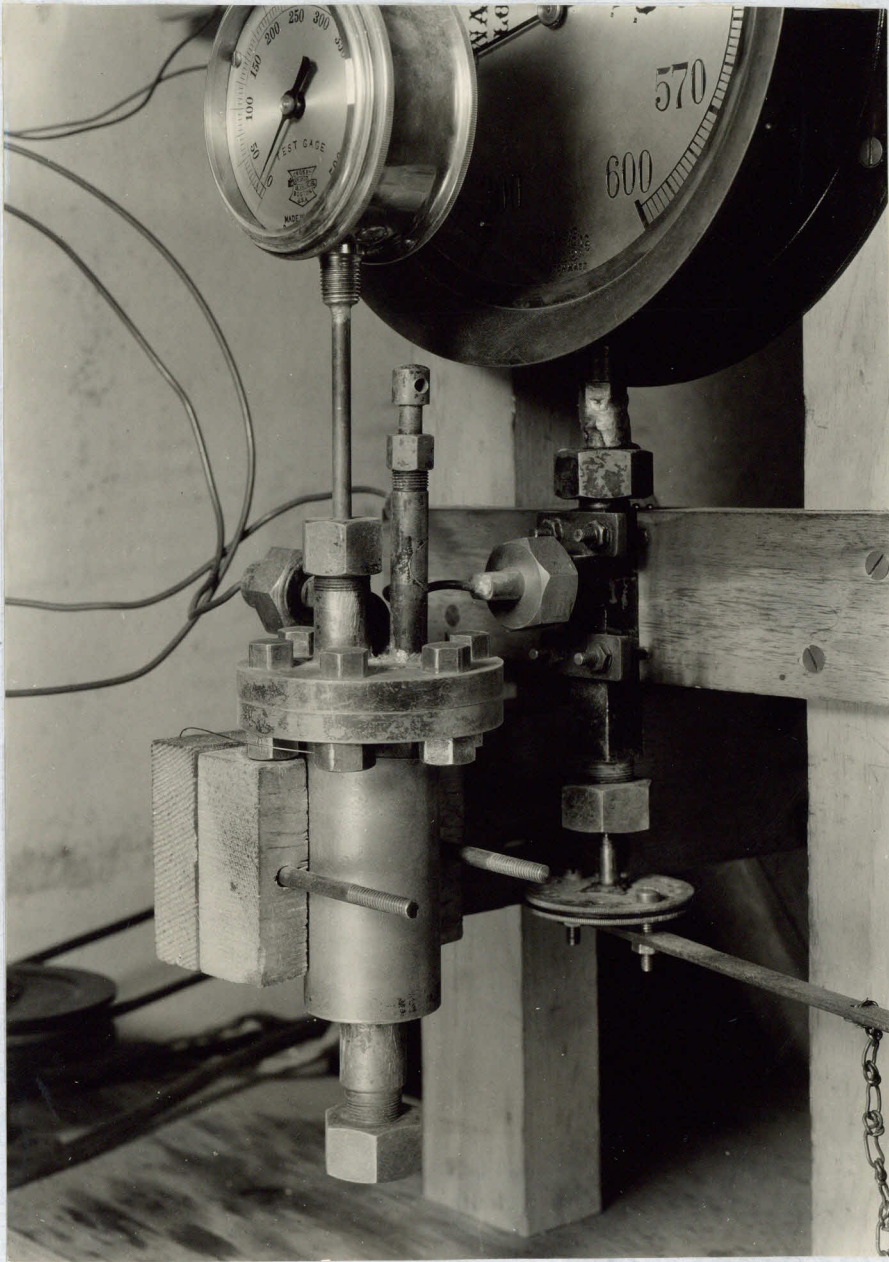


Fig. 4.

Fig. 5

Rate of Absorption of Methane  
by Kerosene at 289 #/sq in

Temp = 30°C

Run No. 16

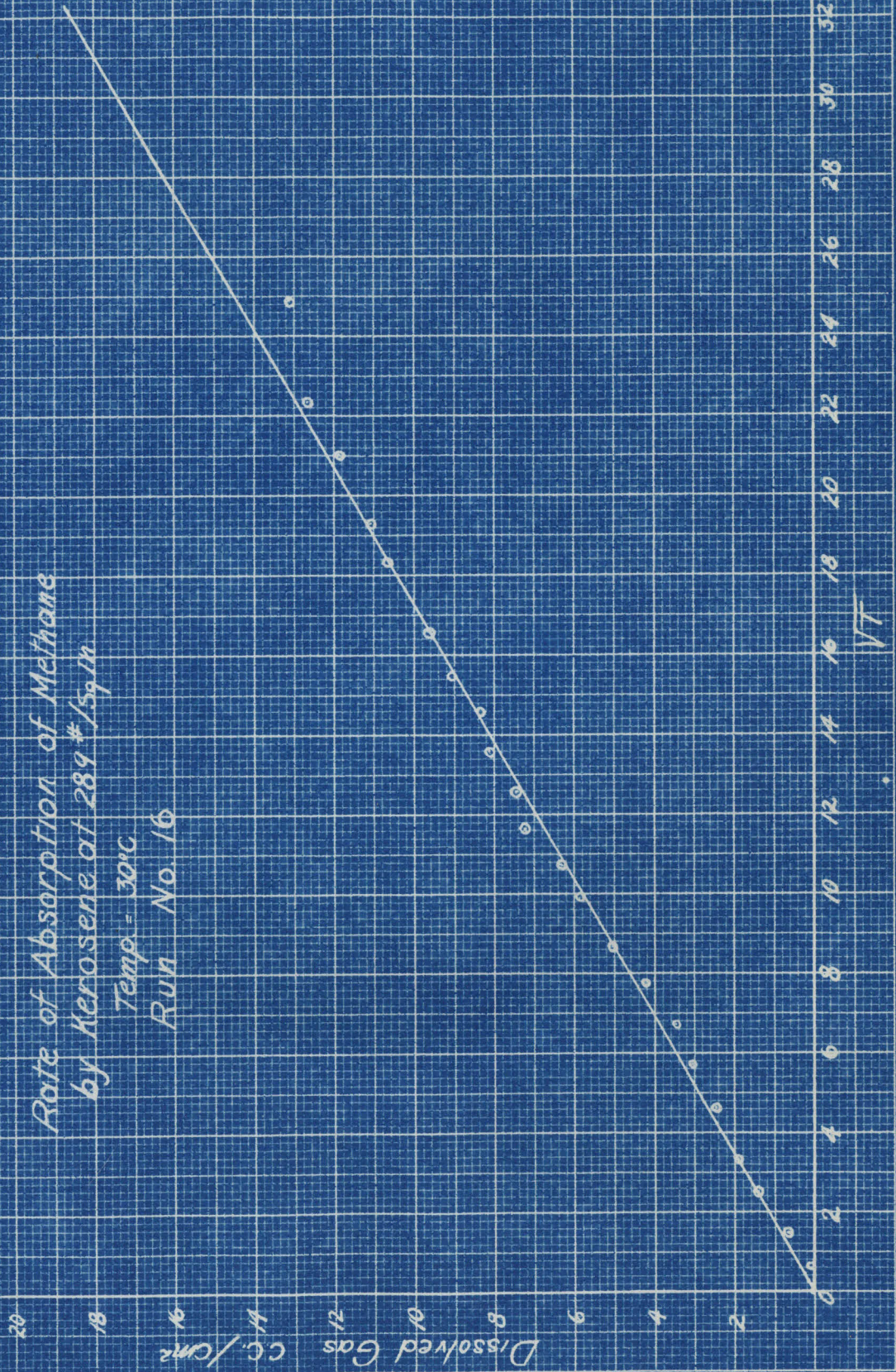


Fig. 6.

Rate of Absorption of Methane  
by Kerosene at 289 #/Sq. In.  
Temp 30°C  
Run No 17

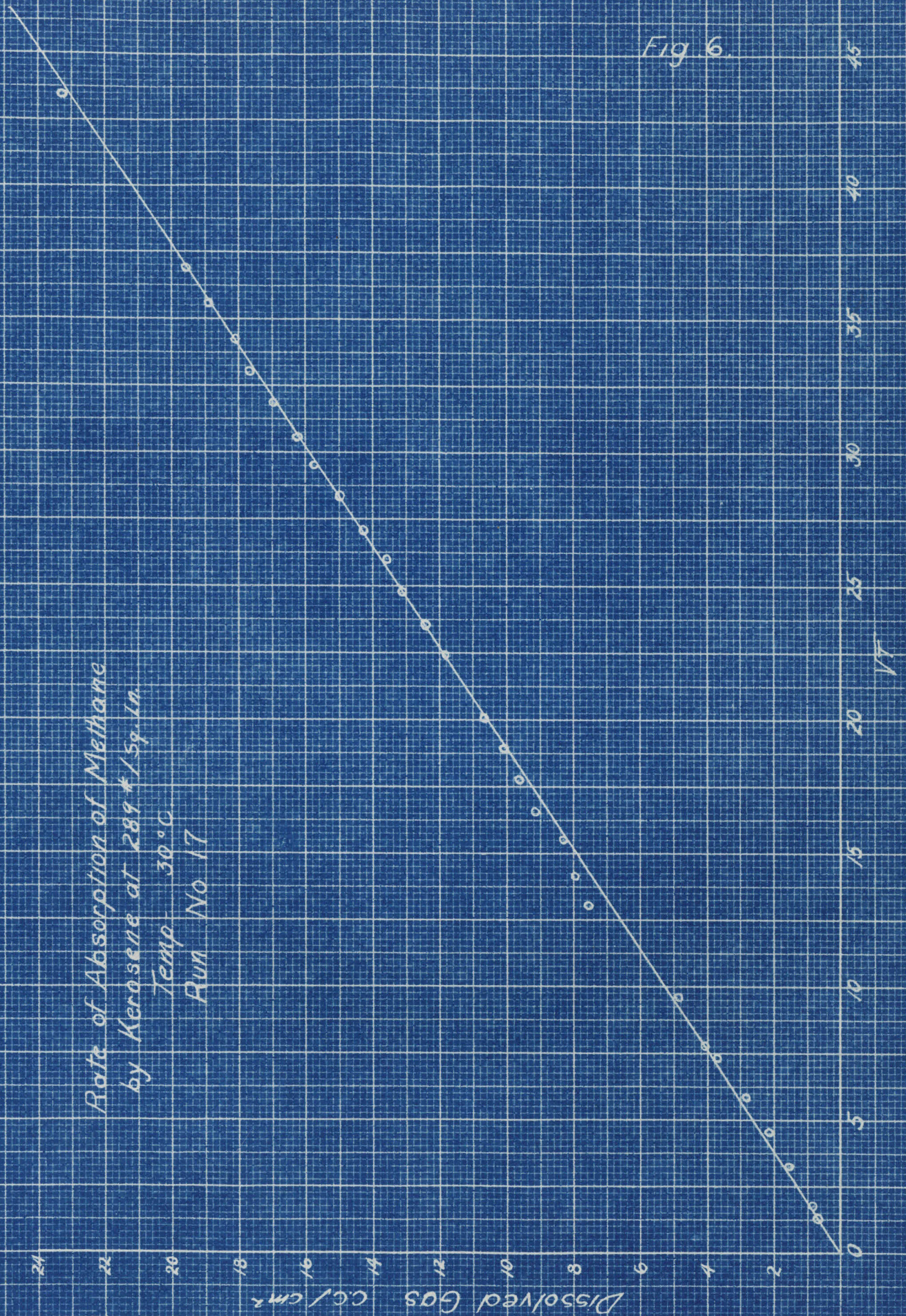


Fig 7

Rate of Absorption of Methane  
by Iso-Octane at 28.9\*/sq.in.  
Temp. 30°C  
Run No. 19

Dissolved Gas cc/cm<sup>3</sup>

$\sqrt{T}$

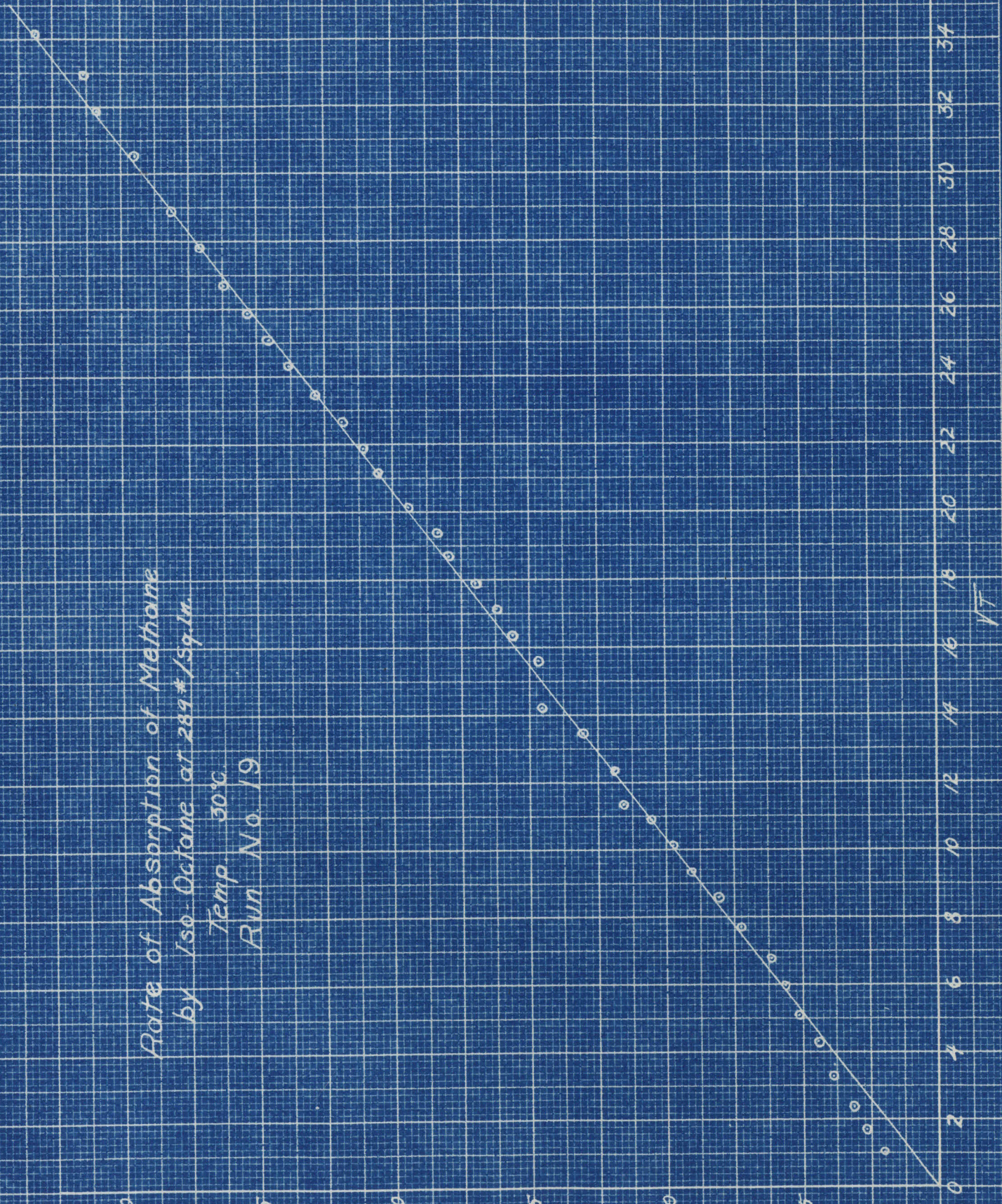


Fig 8

Absorption Rate of Methane  
by *nor*-Hexane at 287.5#/59 In.  
Temp. 30°C

○ Run #25 Sept. 25, 1929  
△ Run #26 Oct. 9, 1929

Dissolved Gas cc./cm<sup>2</sup>

36  
34  
32  
30  
28  
26  
24  
22  
20  
18  
16  
14  
12  
10  
8  
6  
4  
2  
0

0 2 4 6 8 10 12 14 16 18 20 22 24

$\sqrt{t}$

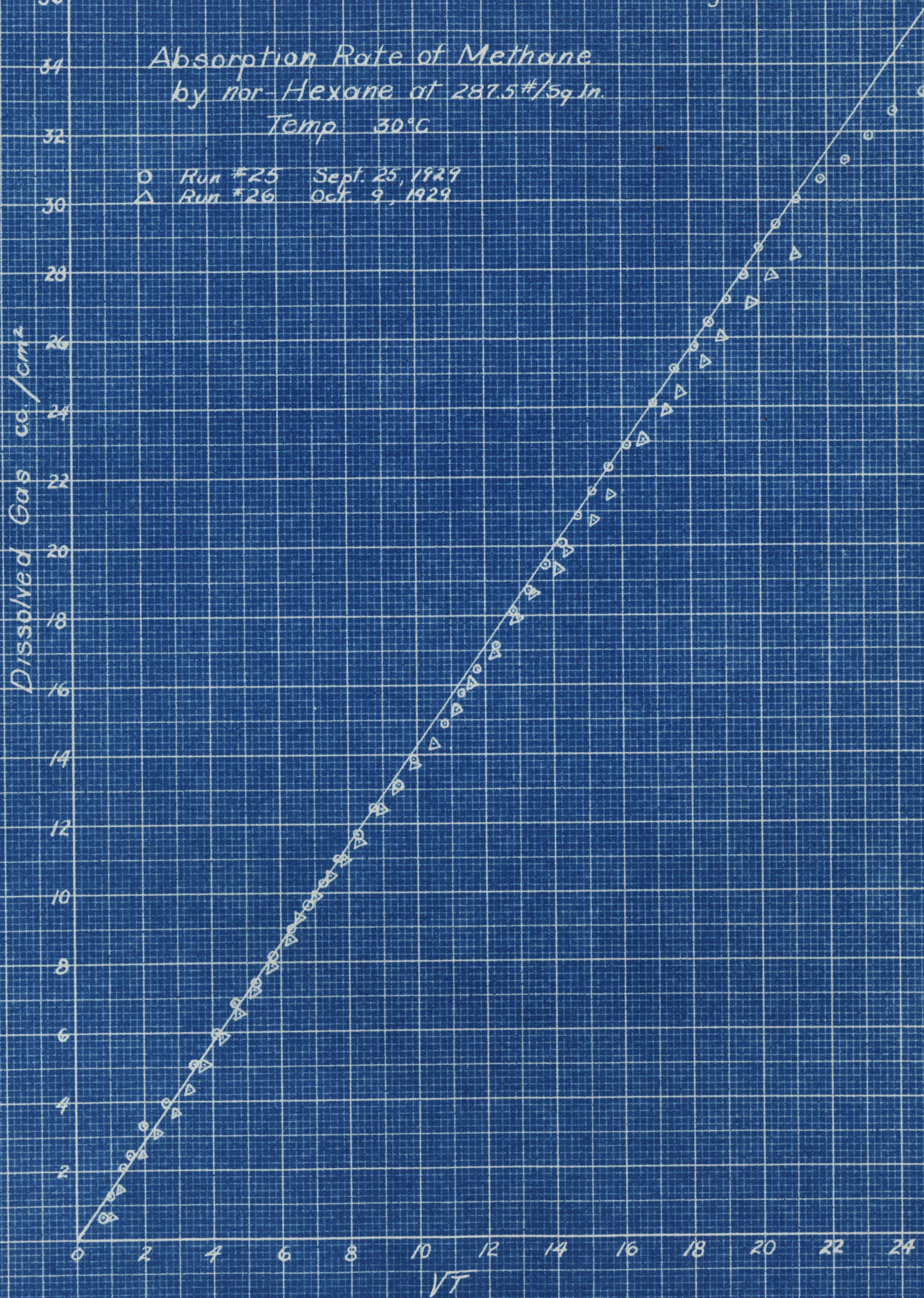
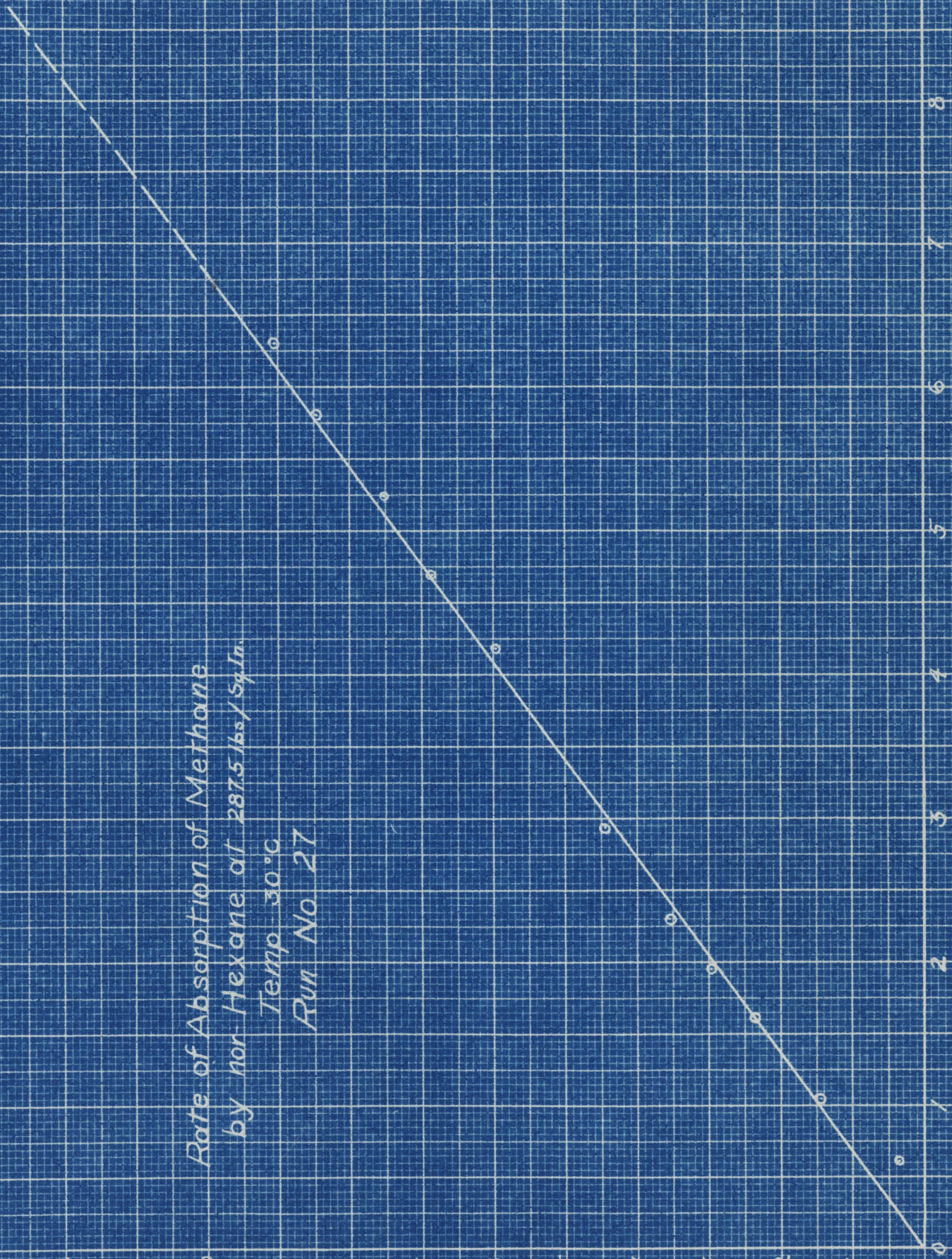


Fig 9

Rate of Absorption of Methane  
by non Hexane at 287.5 lbs / Sq In.  
Temp 30°C  
Run No 27

Dissolved Gas cc/cm<sup>2</sup>

$\sqrt{T}$





Rate of Absorption of Methane  
by nor-Decane Fraction

Temp 30°C

○ Run 28 a Press 143.5 lbs/Sq In.

△ Run 28 b Press 287.5 lbs/Sq In. Decane previously sat'd at 143.5 #/Sq In.

Fig 10.

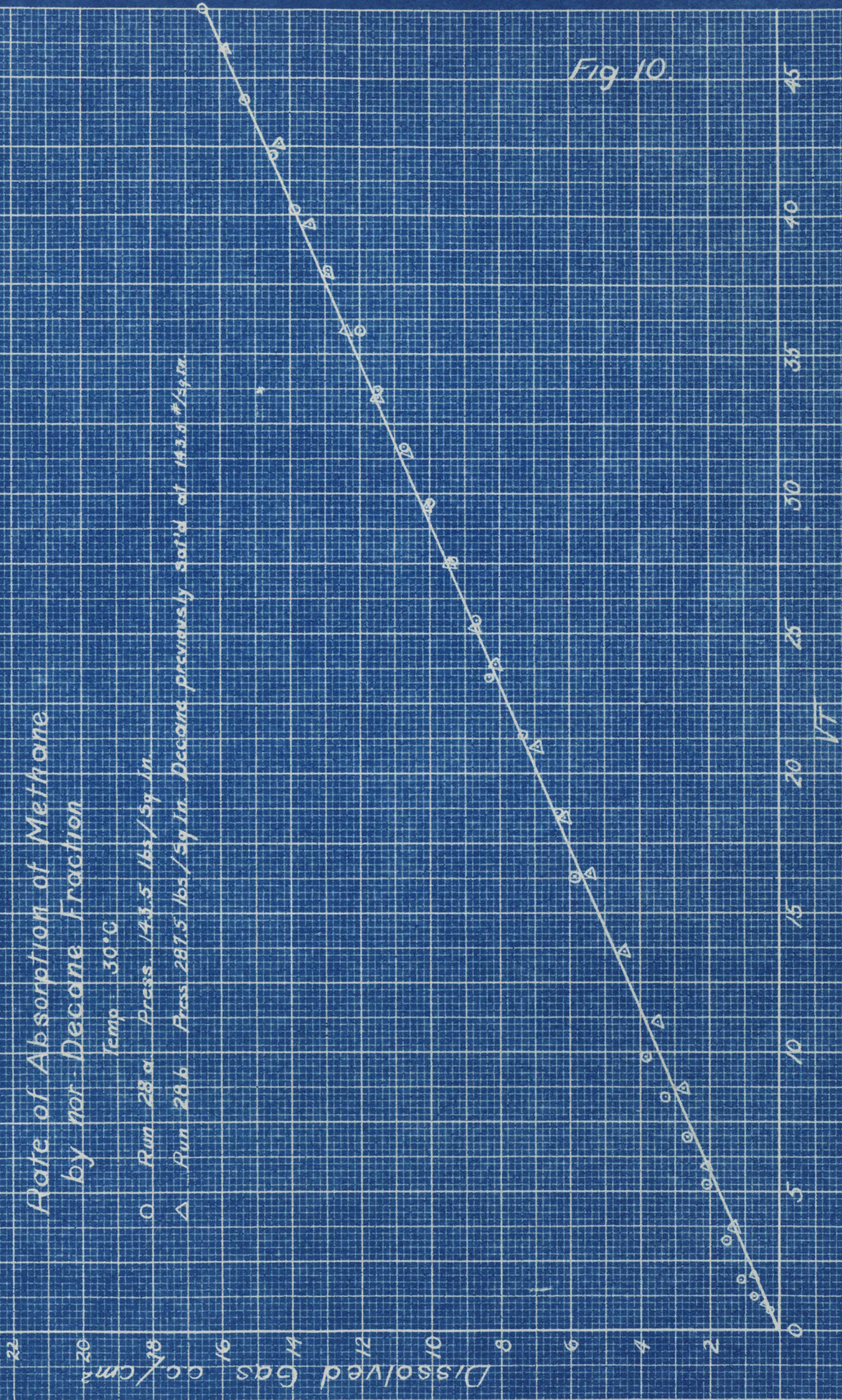


Fig. II

Rate of Absorption of Methane  
by nor Decane Fraction  
Press 2875 lbs/sq In Temp 30°C  
Run No 29

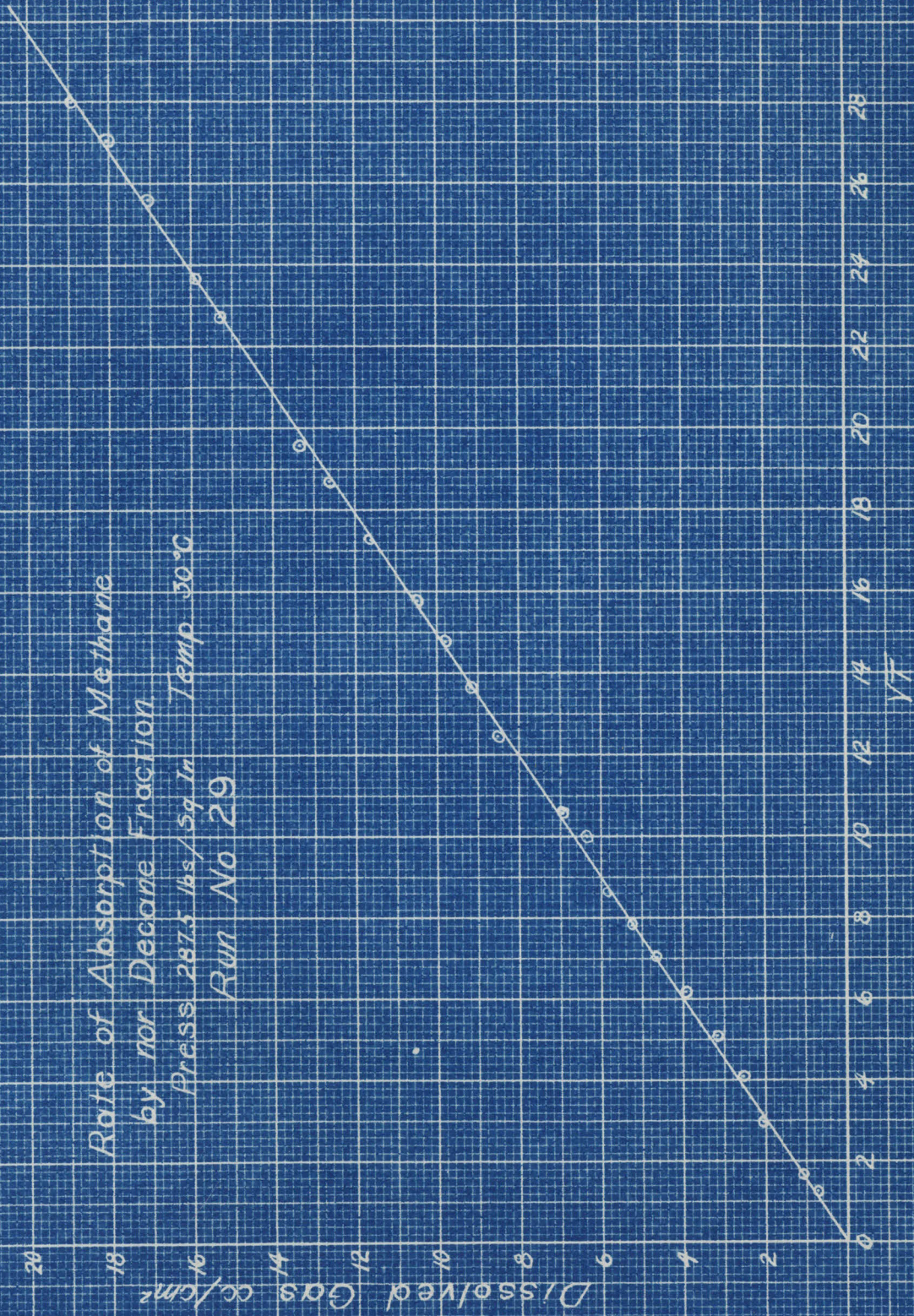


Fig 12

Rate of Absorption of Methane  
by 100. Decane Fraction  
Press 287.5 lbs/sq.in. Temp 30°C  
Run No. 30

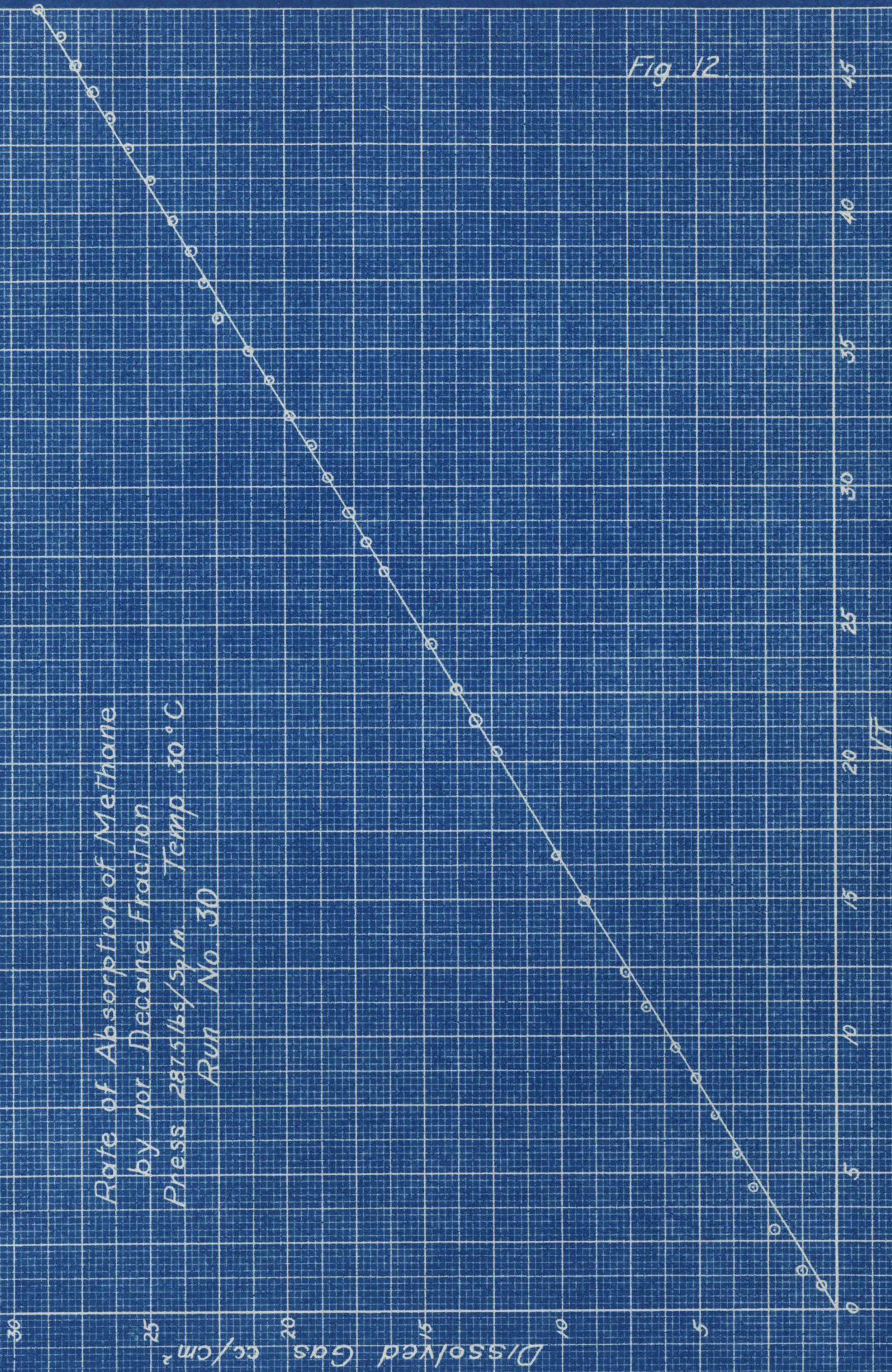
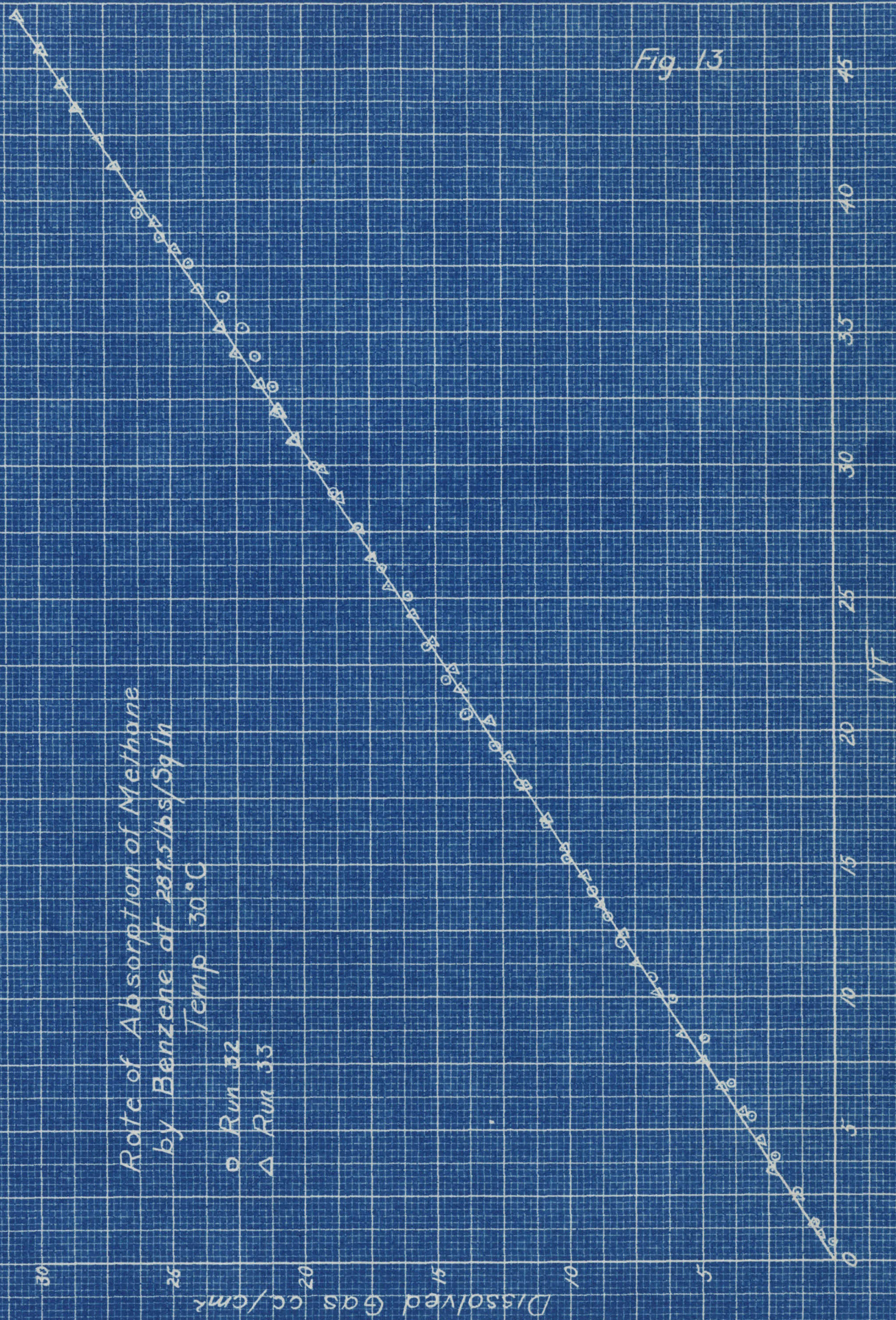


Fig. 13

Rate of Absorption of Methane  
by Benzene at 281.5 lbs/Sq In  
Temp 30°C

○ Run 32  
△ Run 33



Rate of Absorption of Methane  
 by nor-Heptane at 300 lbs/Sq.In

o Run 34 22 1/2 Hrs  
 Δ Run 35 12 Hrs

Fig. 14

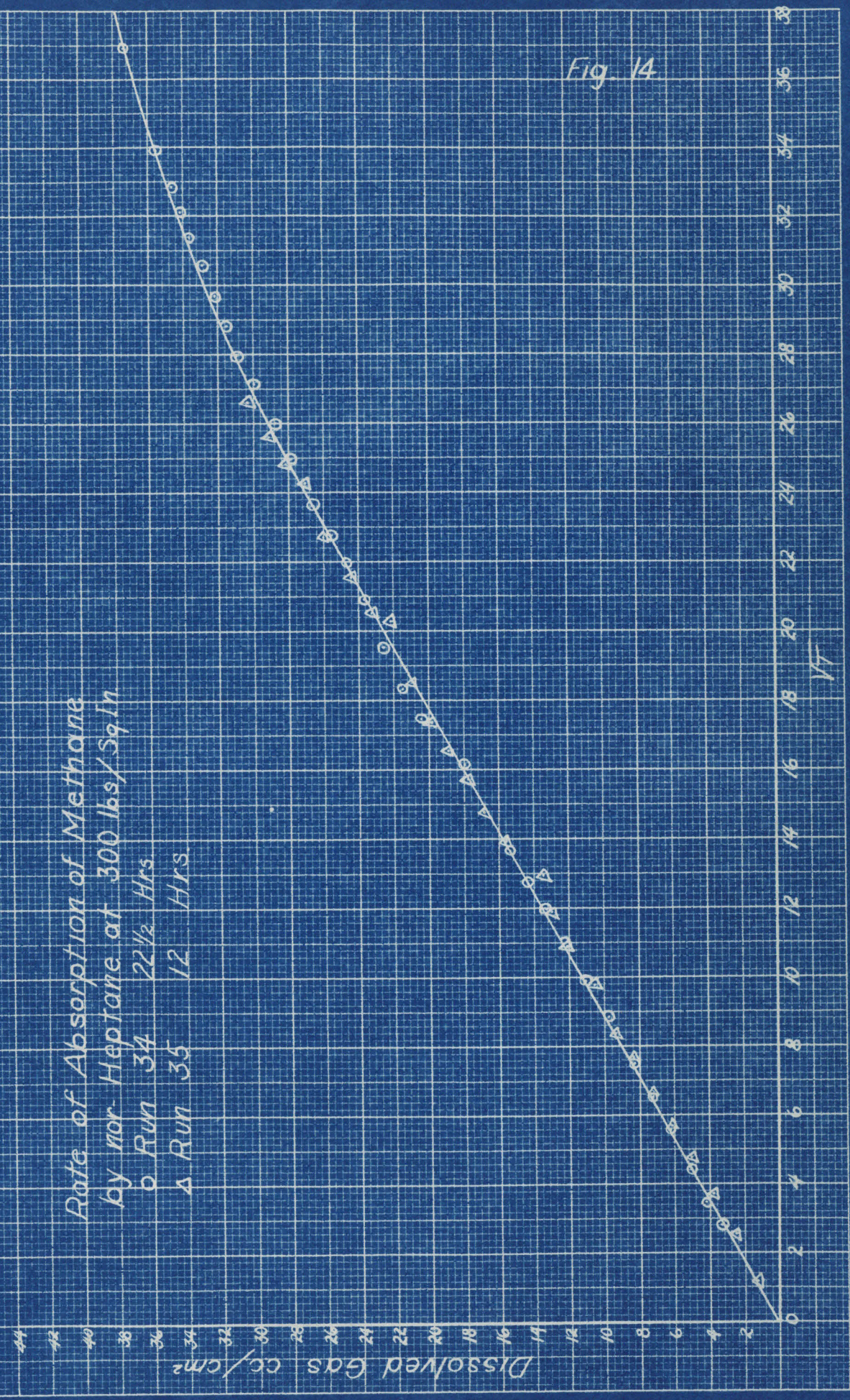


Fig. 15.

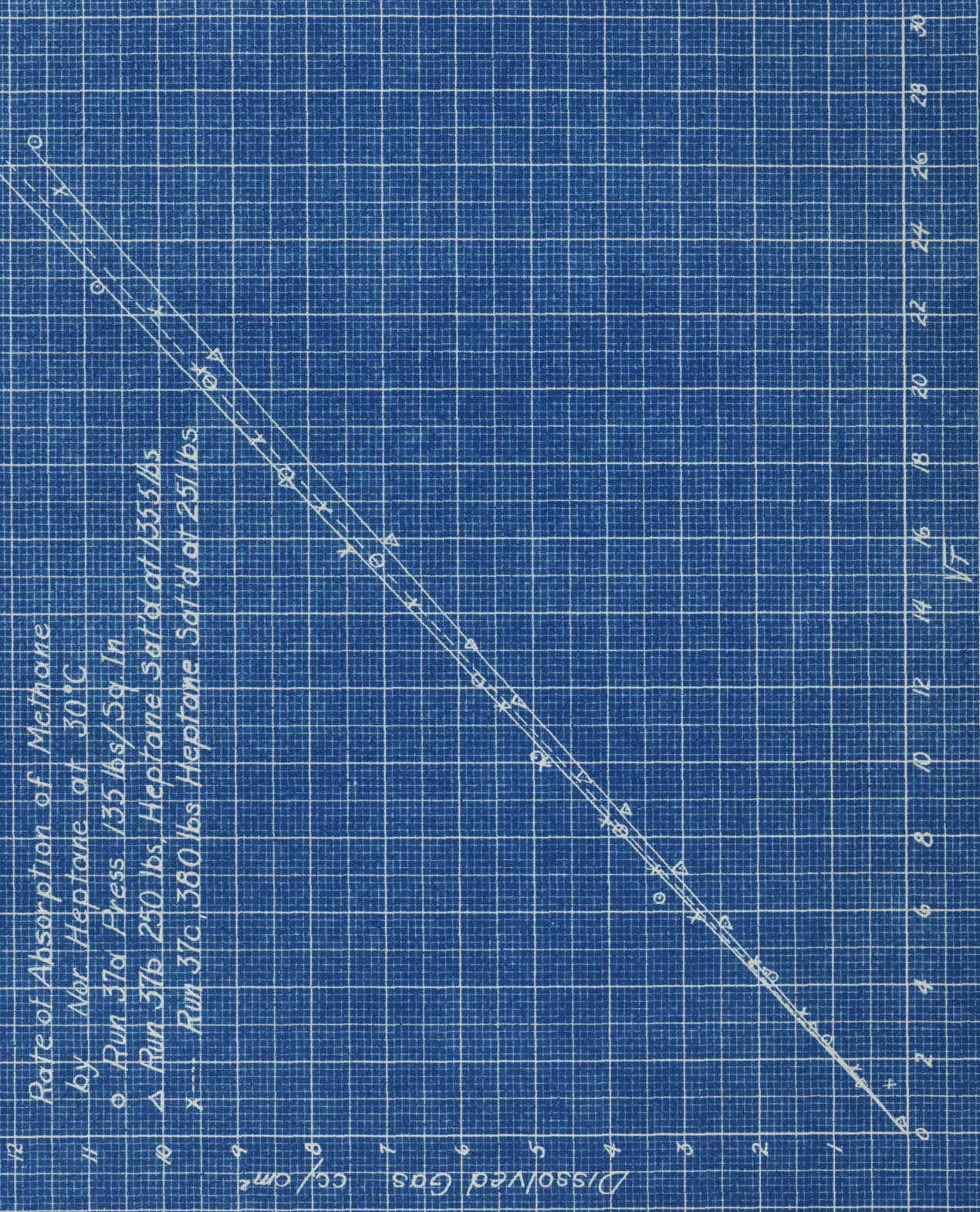


Fig. 16

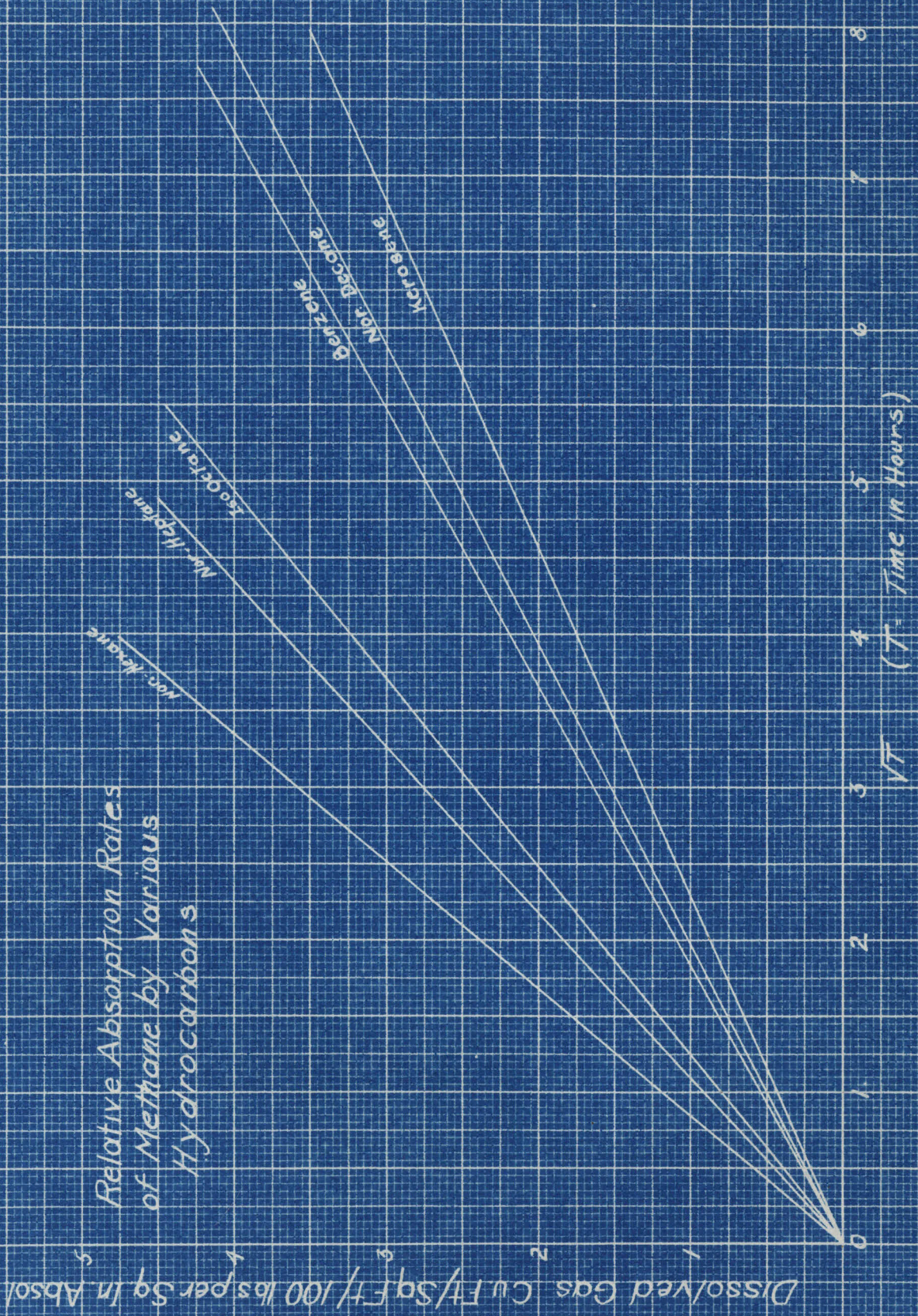
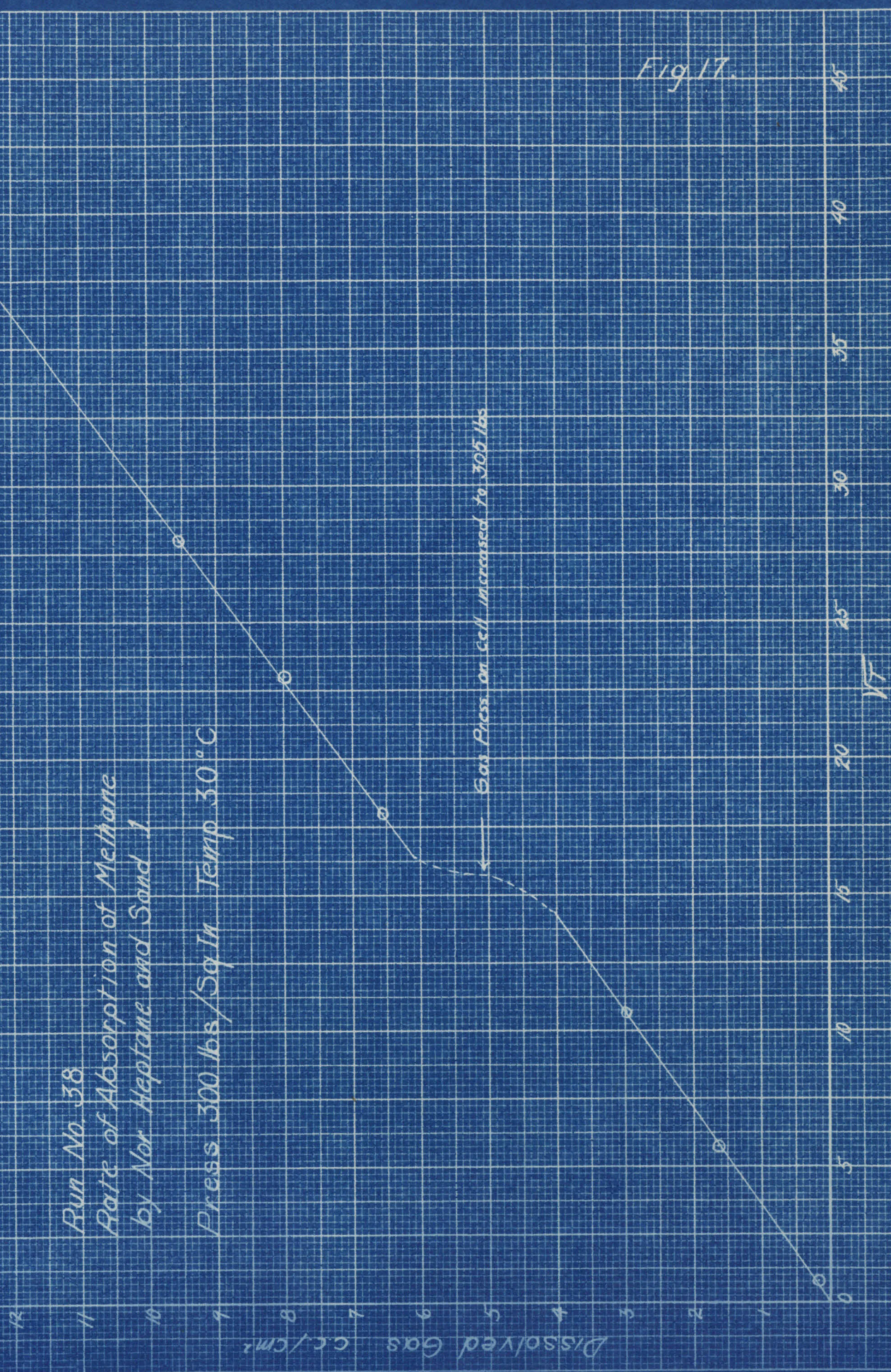


Fig. 17.

Run No. 38  
Rate of Absorption of Methane  
by Nor Heptane and Sand 1  
Press 300 lbs/Sq In Temp 30°C

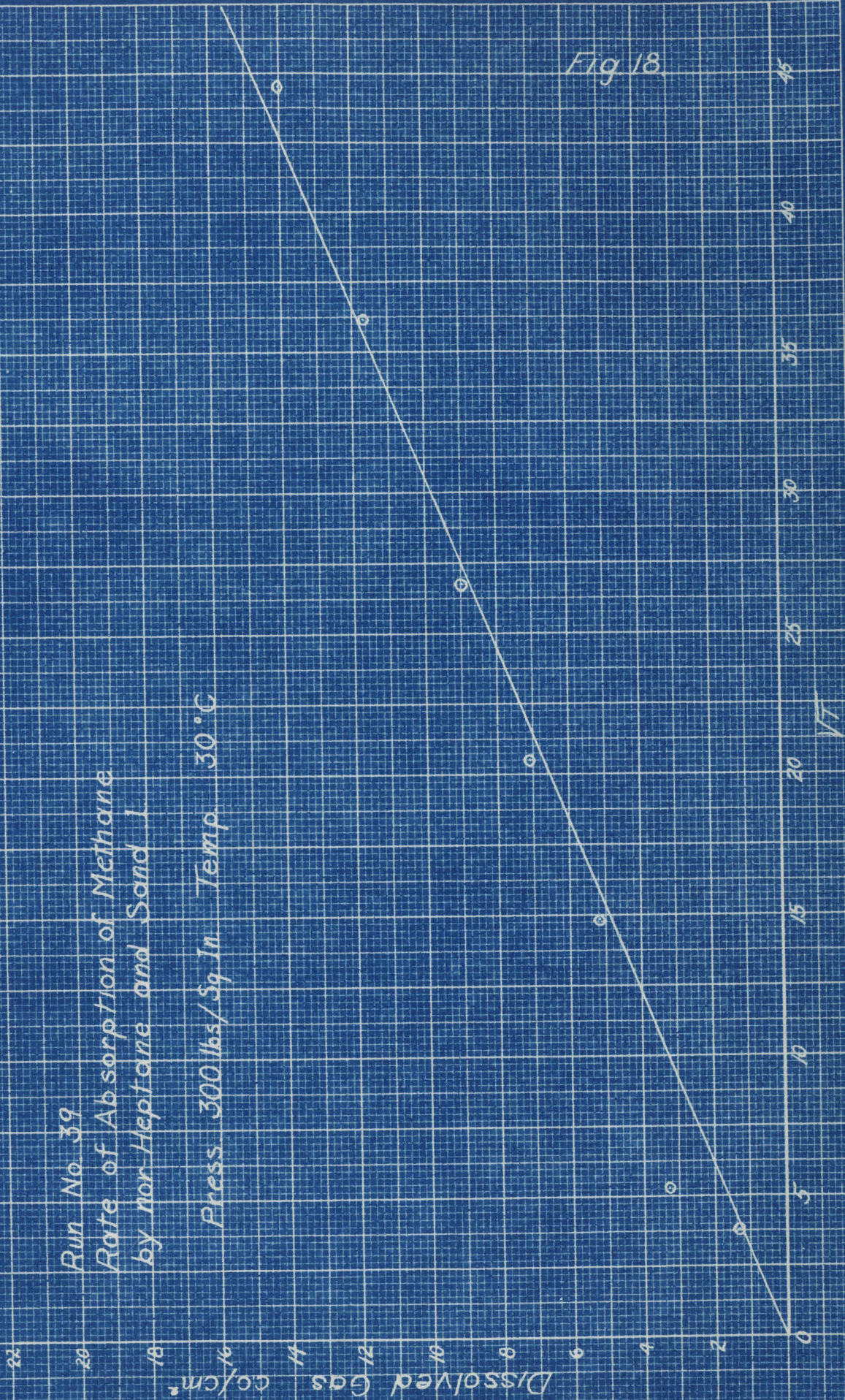




Run No. 39  
Rate of Absorption of Methane  
by non-Heptane and Sand I

Press 300 lbs/Sq In Temp 30°C

Fig 18



Run No 40  
Rate of Absorption of Methane  
by Iso-Octane and Sand 1  
Press. 300 lbs/Sq In Temp 30°C

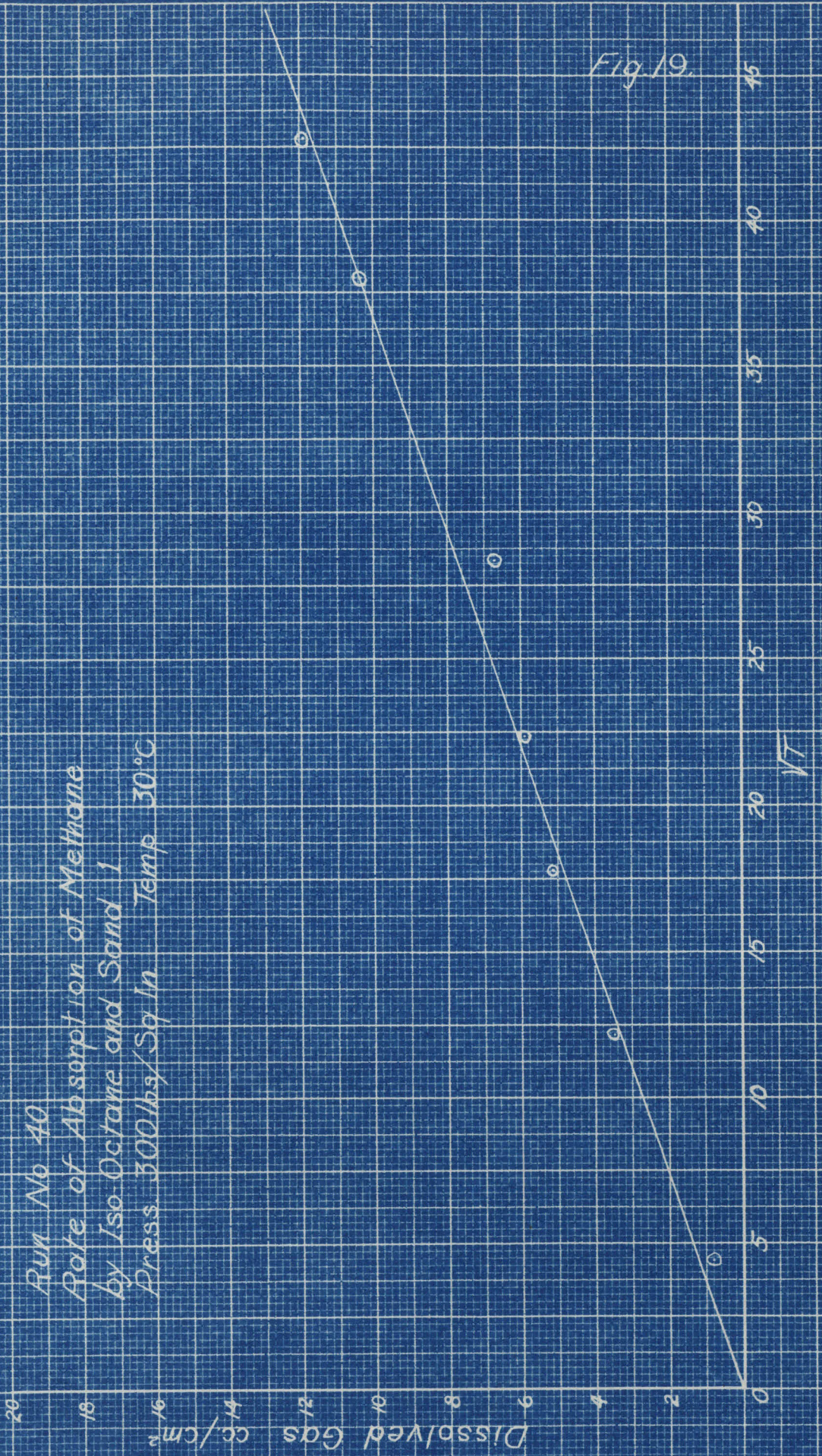


Fig 20.

Rate of Absorption of Methane  
by nor Decane and Sand 1  
Run No. 31 Press 2875 lbs/Sq In.  
Temp 30°C

