

Diffusion of Hydrocarbon Gases  
into Oils and Oil Sands

Thesis by

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## Diffusion of Hydrocarbon Gases into

### Oils and Oil Sands

#### Introduction

The increasing use of repressuring operations as a means of increasing the recovery of petroleum from oil fields, and the practice of storing oil and gas in formations of known limited extent make it extremely important to know as accurately as possible how long it will take for the gas to diffuse into the formation.

The equations for the diffusion of a gas into a liquid hydrocarbon have been developed by Nathan F. Scudder (1) and extended and simplified by Richard D. Pomeroy (2). The simplified forms used in the calculations are, for a column of liquid of infinite length,

$$Q = 2 C_s A \sqrt{\frac{Dt}{\pi}}$$

where  $Q$  = quantity of gas diffusing through the surface

$C_s$  = solubility of the gas in the oil

$A$  = area of the surface

$t$  = time

$D$  = absolute diffusion constant. For

For a column of finite length after 50% saturation the simplified equation is

$$\frac{Q}{Q_s} = 1 - \frac{8}{\pi^2} \cdot e^{-\frac{\pi^2 Dt}{4l}}$$

where  $Q_s$  = quantity of gas required to saturate the body of oil

$l$  = final length of the column of oil.

### Description of Materials

Liquid hydrocarbons representing a wide range of densities and composition were prepared or purchased. The high gasoline fraction with a B.P. of 79.4 - 88.5°C at 38 mm., and the heptane fraction, B.P. 97.5 - 99°C. were prepared by F. P. Stapp (3). Pure cyclohexane, B.P. 80.8°C, and hexane, B.P. 68.5°C were purchased from the Eastman Kodak Co. Isopentane, B.P. 27.3 - 28.2°C, was prepared by redistilling a 5 gallon lot of casing head gasoline from Santa Fe Springs No. 4, Standard Gasoline Co. This distillation was carried out with a 9 ft. glass ring packed column jacketed with asbestos to prevent heat loss. Ice water was circulated thru the reflux condenser and the final condenser with an air lift. The distillation was repeated 7 times giving isopentane that should be nearly as pure as the other pure hydrocarbons used. A purified oil with a high density, used for medicinal purposes, called liquid petrolatum, was purchased. The density of this oil is above that of any paraffins that are liquid at ordinary temperatures. Hence, it probably has been prepared from a naphthene base crude and contains a high percentage of naphthenes.

The crude oil samples were from widely scattered fields as follows:

Lima, Ohio, from Ohio Oil Co., 38.4° A.P.I. 60°F.

Santa Fe Springs, Cal., from Shell Oil Co., Sample No. 9x94, tank farm, tank No. 502, 33.0° A.P.I. 60°F.

Bartlesville, Okla. from U. S. Bur. of Mines, 32.6° A.P.I. 60°F.

Bradford, Pa. from Forest Oil Co. 44.5° A.P.I. 60°F.

The Lima, Ohio and Bradford, Pa. crudes probably have a paraffin base while the Bartlesville, Okla. crude has an intermediate base and the Santa Fe Springs crude has a naphthene base.

TABLE I  
GAS ANALYSIS

METHANE

	July 26, 1930	Dec. 29, 1930
Methane -----	98.64 %	98.13 %
Ethane -----	1.36 %	1.87 %

ETHANE

	May 15, 1931
Methane -----	2.87%
Ethane -----	96.48 %
Propane -----	0.65 %



The sand used in the measurements of the diffusion of methane into oil sand mixtures was practically pure quartz. The grain size in run P-6 and P-7 was approximately 20 mesh and minus 200 mesh respectively.

The methane was prepared in the same way that F. P. Stapp prepared it by absorption of the ethane and heavier constituents of natural gas on charcoal. Two analyses show that the ethane content (Table I) was about 1.4% to 1.9%.

The ethane used in run E-52 was prepared and analyzed (Table I) by the Standard Gasoline Co. at their Santa Fe Springs Laboratory, by condensing the ethane and heavier constituents from natural gas and separating the ethane by fractional distillation.

#### Methods of Measurement

The operation of the apparatus has been described by Richard D. Pomeroy (2). This operation varied only in the case of the measurement on the rate of diffusion of ethane. In this run the charcoal cell used for preparation of the methane was replaced by the steel cell used by Bruce H. Sage (5) for measuring solubilities of natural gases in crude oils at high pressures. This cell was connected to the low pressure ethane supply tank and to the refill valve on the reservoir of the apparatus used for measuring the rate of diffusion. The steel cell was placed in a bath of low boiling gasoline and several pounds of solid carbon dioxide added. Sufficient ethane was liquified to supply the run and the higher pressure required was obtained when the cell was warmed up to room temperature.

#### Definition of Terms.

W = weight of oil used;

d = density of oil at 30°C;

$V$  = volume of oil used;

$P$  = pounds per square inch;

$V_i$  = initial volume equivalent of gas let out of reservoir gage  
in cc. measured at 86<sup>o</sup>F and 760 mm., representing the  
volume of gas over the oil at the beginning of the run  
obtained by extrapolating the rate curve to zero time;

$V_s$  = total amount of gas admitted to cell at time of saturation;

$m$  = slope of the experimental diffusion rate curve corrected for  
increase in volume of the liquid phase due to solution  
of gas;

$m'$  = uncorrected slope;

$\epsilon'$  = Increase in volume of liquid phase determined by using the  
uncorrected saturation, in cc. increase in volume of oil  
per cc. of gas dissolved;

$\epsilon$  = Increase in volume of liquid phase expressed in cc. increase  
in volume of oil per cc. of gas dissolved, using the cor-  
rected saturation value;

$C_s$  = solubility of the gas in a cc. of solution at the given pres-  
sure and temperature, expressed in cc. gas at 30<sup>o</sup>C and 760 mm.;

$S$  = solubility of the gas in one cc. of initial oil, expressed in  
cc. of gas at 30<sup>o</sup>C and 760 mm.;

$D$  = absolute diffusion constant in square centimeters per second  
or in square feet per hour.

#### Increase in Volume of Liquid Phase

The method of determining and calculating this value per cc. of  
gas dissolved has been described by Richard D. Pomeroy (2). It is in-  
teresting to apply this calculation to the data reported by Mills and  
Heithecker (4).

Bartlesville crude oil, 33.3° A.P.I. at 70°F

Pressure in lbs. per sq. in	Solubility in cc. of gas per cc. of oil	Percentage increase in volume	cc. increase per cc. gas dissolved
200	6.9	1.49	0.00216
400	13.9	2.88	0.00208
600	21.0	4.38	0.00208
800	27.7	5.82	0.00210
1000	34.9	7.30	0.00209

Inglewood, California crude, 21.1° A.P.I. at 70°F

200	5.0	1.10	0.00220
400	9.9	2.15	0.00217
600	14.9	3.23	0.00216
800	19.5	4.30	0.00220
1000	24.5	5.40	0.00221

Seminole, Okla. crude 41.4° A. P. I. at 70° F

200	10.2	1.72	0.00169
400	20.5	3.47	0.00169
600	31.2	5.20	0.00167
800	41.8	6.97	0.00167
1000	51.8	8.70	0.00168

Analysis of gas used by Mills and Heithecker,

	per cent
Methane	76.77
Ethane	12.38
Carbondioxide	0.98
Illuminants	0.90
Oxygen	0.65
Nitrogen	8.32

This shows that the increase in volume of the oil per cc. of gas dissolved is, within experimental error, a constant up to 1000 lb. per sq. in. and may be extrapolated to somewhat higher pressures without any serious error.

### Experimental Results

The slope of the curves showing the quantity of gas absorbed plotted against the  $\sqrt{t}$  gives the value of  $m'$  which must be corrected for change in volume of the oil before using it in the final calculation of  $D$ . The values for the initial volume and  $m'$  were determined on plots 3 times as large as the experimental curves given here. In some cases it was found necessary to add or subtract a constant value before plotting the experimental data in order to retain the same scale. This can be determined easily by consulting the data table (Table II) for the values of  $V_1$ .

Check runs on the rate of absorption of methane in kerosene (Fig. 1) and in cyclohexane (Fig. 2) show very good agreement for the value of  $m$ . In the case of liquid petrolatum (Fig. 3), the runs were made at different pressures and the slope of the curves have the right order of magnitude but the diffusion constant deviates 17% from the average value. However, at such a slow rate of absorption the volumes of gas were so small that the chances for experimental error were relatively large; although actually not much greater in magnitude than in the runs where good agreement was obtained. The rate of absorption of methane in the high gasoline fraction (Fig. 4) is different from the values reported by F. P. Stapp (3). It is likely that this fraction was given further treatment after being used in earlier runs and no longer had quite the same composition. The rate of absorption of methane in pure hexane (Fig. 5) was determined to fill in the homo-

TABLE II

EXPERIMENTAL RESULTS at 30°C.

with Methane (Ethane in E-52)

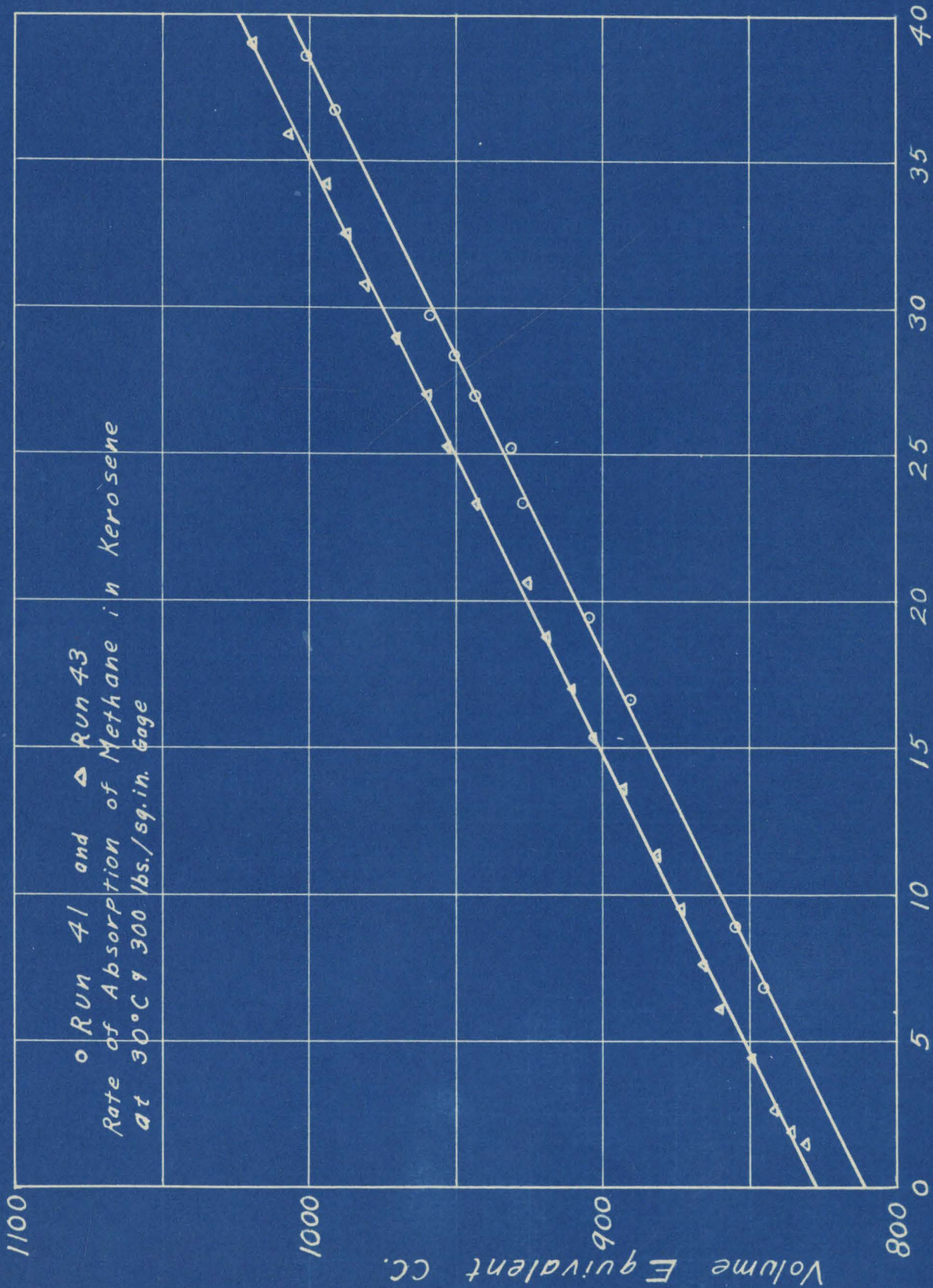
Run No.	Oil	W gm.	Density 30°C	°A.P.I. 60°F.	P lb./sq. in.	m'	m	V <sub>i</sub>
41	Kerosene	62.34	0.7963	43.8	300	4.84	5.03	811.2
43	"	60.90	0.7963	43.8	300	4.88	5.07	978.2
44	High Gasoline Fraction	35.18	0.772	45.3	350	7.84	8.28	742.4
45	Cyclohexane	70.75	0.7689	49.8	249	7.117	7.373	474.8
46	"	68.84	0.7689	49.8	249	7.113	7.369	446.0
47	Liquid Petrolateum	71.32	0.8771	29.4	350	1.62	1.70	789.1
48	"	71.64	0.8771	29.4	302.5	1.16	1.21	672.8
50	Isopentane	28.69	0.6102	95.1	192.5	D calc. for each point		374.5
51	Hexane	35.82	0.653	81.8	298.5	14.30	15.09	176.5
E-52	Cyclohexane with Ethane	37.61	0.7689	49.8	249	37.8	40.0	128
C-2	Lima, Ohio	70.07	0.822	38.4	298.5	3.78	3.94	565.7
C-3	Santa Fe Springs, Cal.	76.41	0.850	33.0	298.5	3.65	3.82	549.9
C-4	Bartlesville, Okla.	73.85	0.852	32.6	298.5	3.03	3.16	571.4
C-5	Bradford, Pa.	69.09	0.793	44.5	298.5	5.48	5.75	735.5
P-6	Heptane Fraction	22.13	0.7095	64.4	350.	4.26	4.50	700.0
	20 mesh sand	130.3	2.644					
	38.8% porosity							
P-7	Same oil	22.98	0.7095	64.4	350	4.99	5.28	943.4
	-200 mesh sand	106.6	2.644					
	44.6% porosity							

Cross-section Area of Cell = 9.9203 cm.<sup>2</sup>  
 in Runs 50, 51, 52 = 9.8788 "

TABLE II (continued)

Run No.	$V_s$	$V_s - V_i$	Length of run hours			$C_s$	S	$D \times 10^5$
41	1607.2	796.0	30.2	0.00183	0.00179	10.52	10.72	3.02
43	1760.7	782.5	35.8	0.00183	0.00179	10.59	10.79	3.07
44			32.0	0.00224	0.00218	11.31		4.85
45			32.0	0.00197	0.00191			5.08
46	1502.6	1056.6	27.0	0.00197	0.00191	11.93	12.21	5.08
47	1416.3	627.2	16.5	0.0019	0.0018	7.96	8.01	0.62
48	1209.0	536.2	107.6	0.0019	0.0018	16.76	6.85	0.43
50	880.8	505.8	104.5	0.00278	0.00270	10.50	11.15	14.00
51	1127.4	950.9	12.5	0.00266	0.00250	17.54	18.34	9.93
E-52	2484.5	2356.5 at 197 lb.	70.4 lb.	0.00367	0.00355	52.6 at 249 lb.	64.6	7.75
C-2	1336.9	771.2	34.0	0.0020	0.0019	9.27	9.44	2.40
C-3	1320.9	771.1	30.6	0.00218	0.00210	8.83	9.00	2.49
C-4	1286.0	714.6	32.2	0.00190	0.00180	8.45	8.85	1.86
C-5	1662.8	927.3	29.8	0.00224	0.00218	10.88	11.15	3.72
P-6			33.0		0.00237	8.25		5.37
P-7			31.5		0.00237	8.25		5.58





E.S.H.

Fig. 1



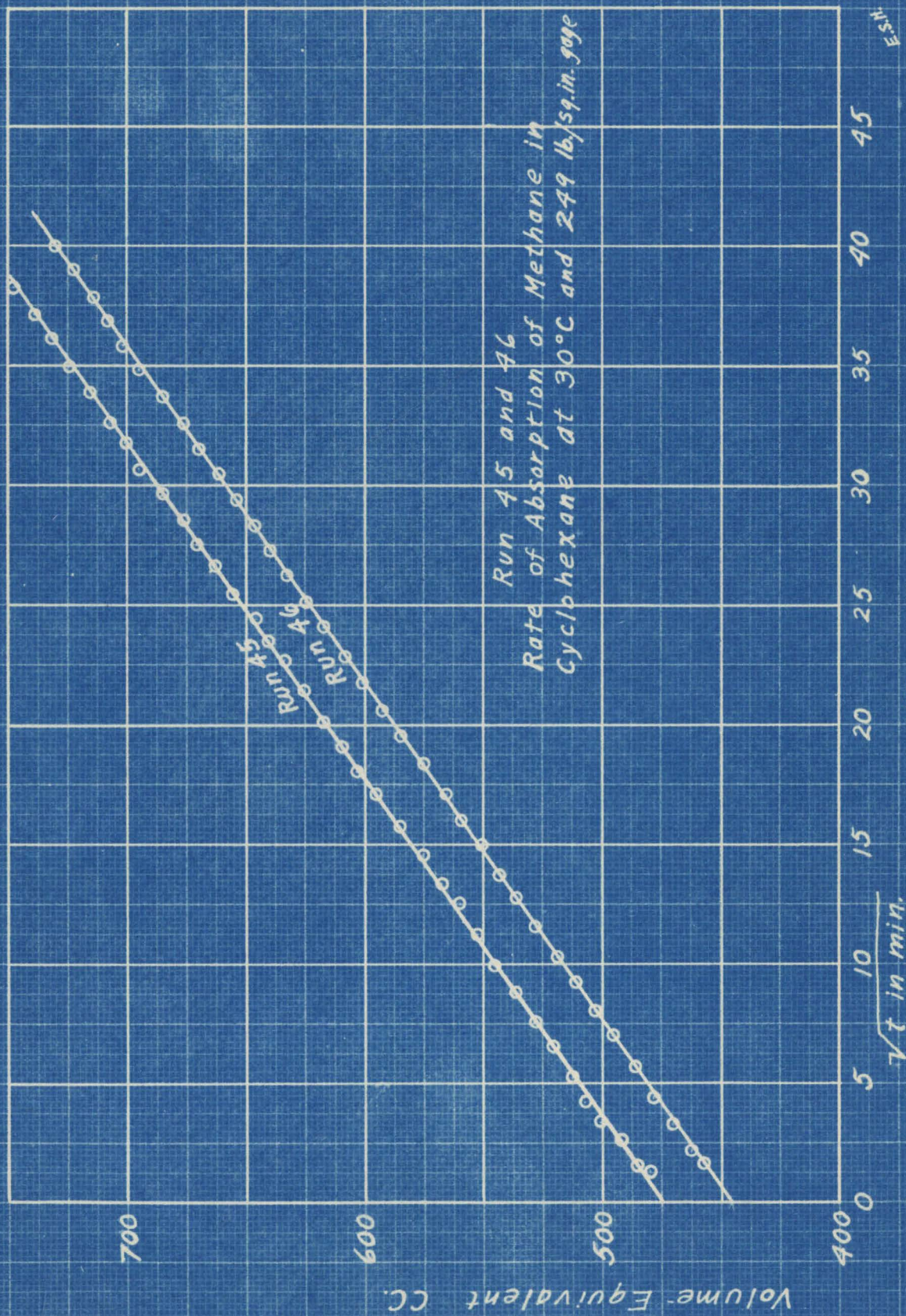
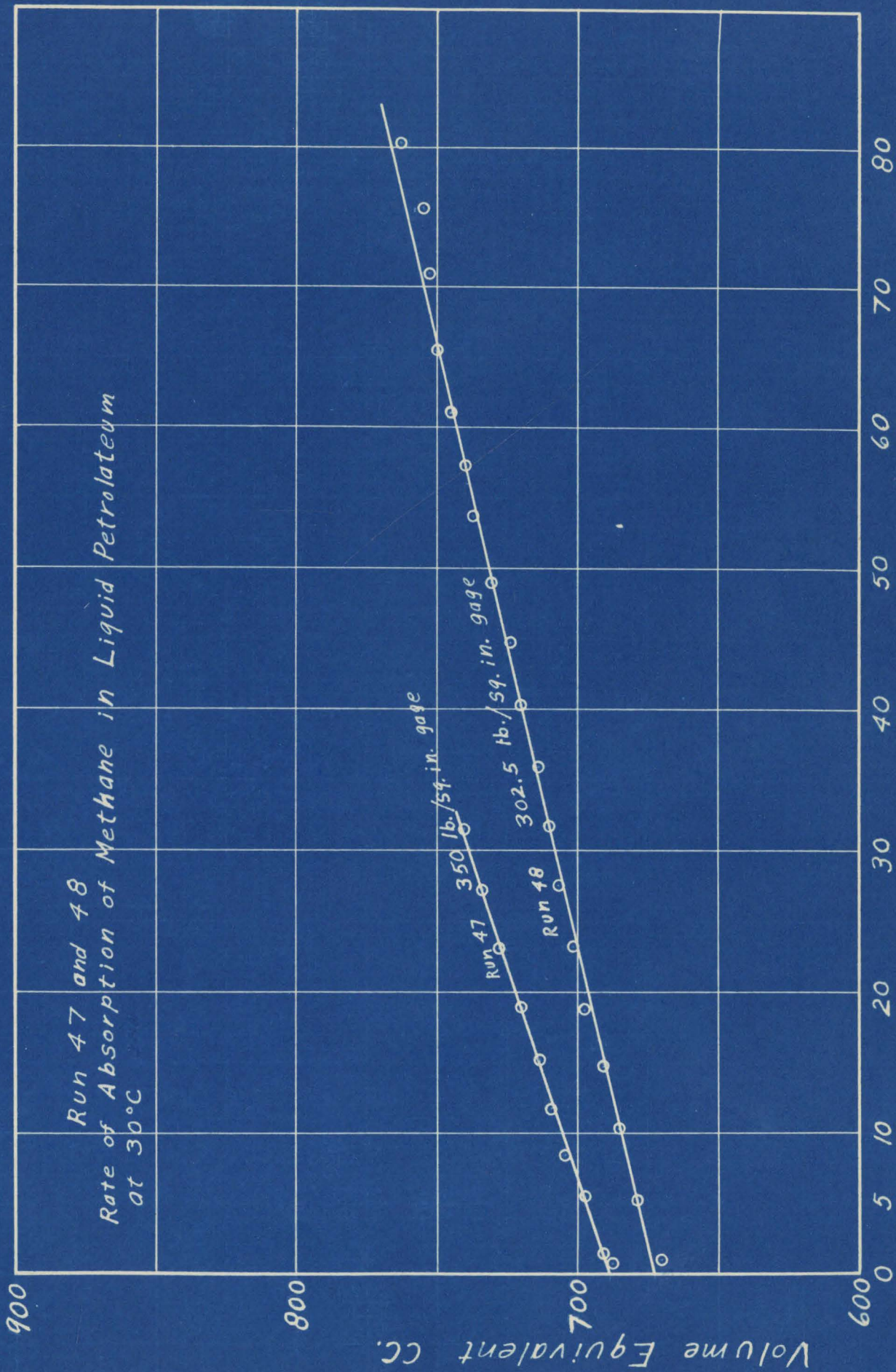


Fig. 2





E.S.H.

Fig. 3



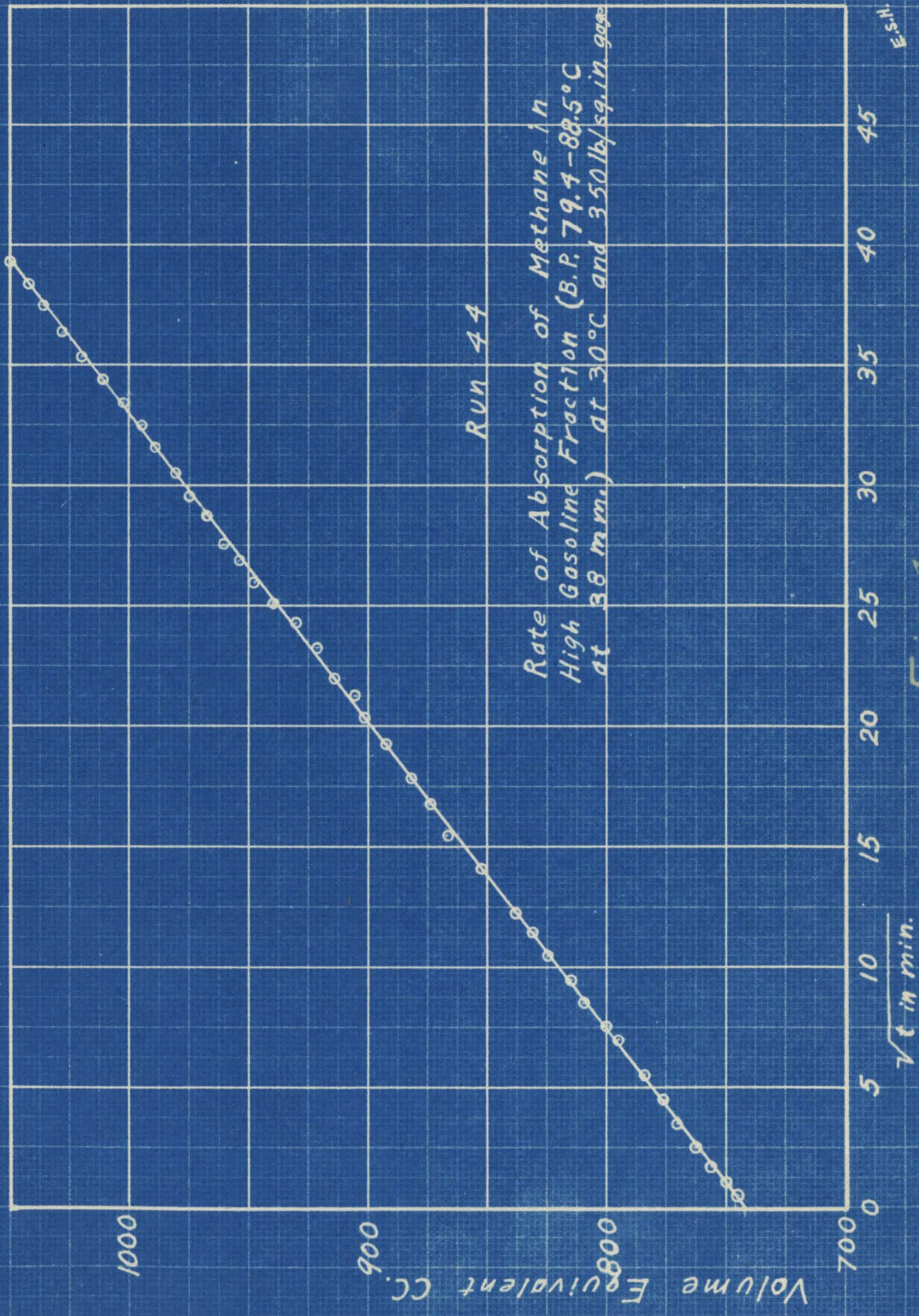
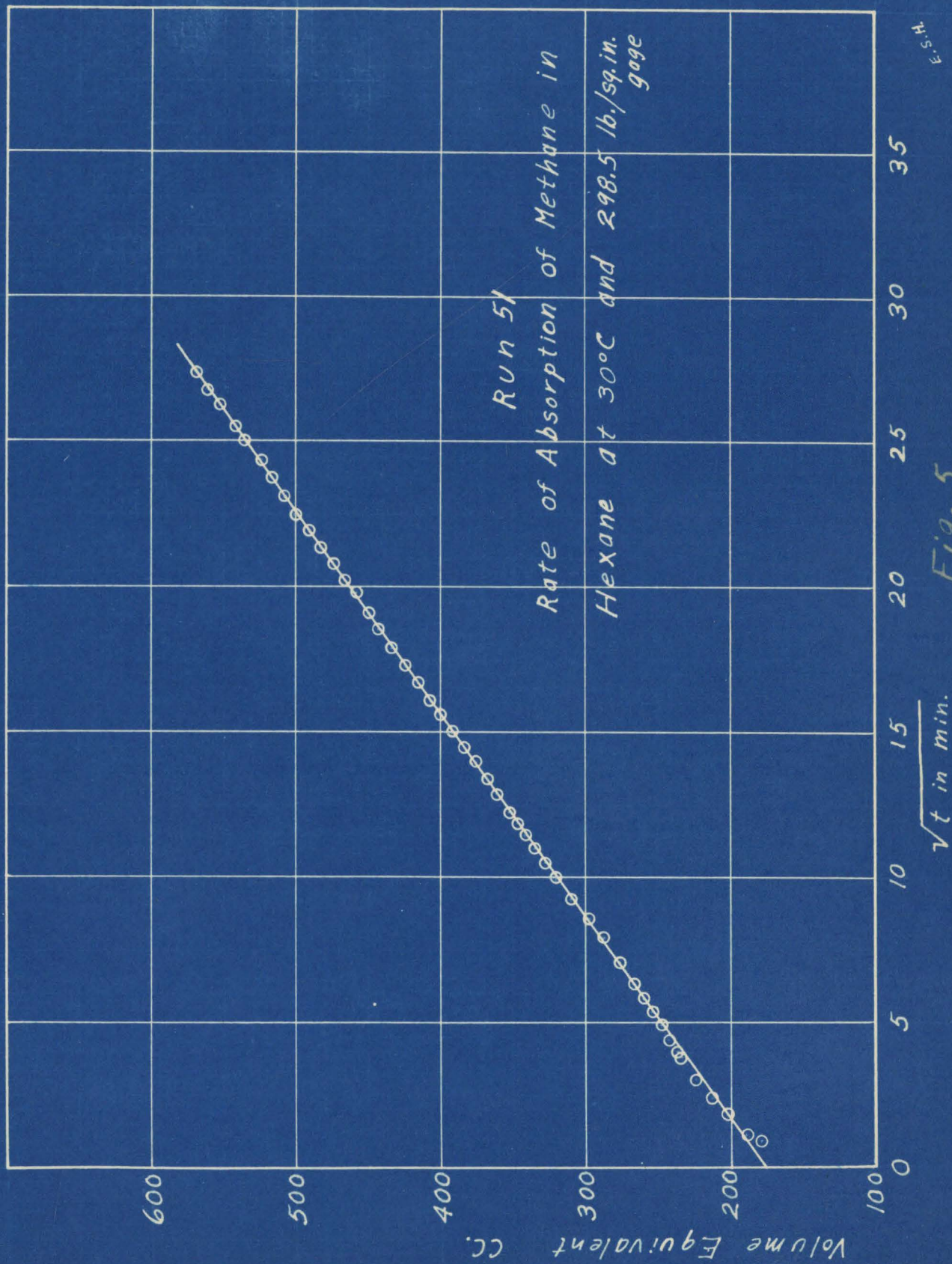


FIG. 4





E.S.H.

Fig. 5

logus paraffin series as much as possible.

The rate of diffusion of methane into isopentane (Fig. 6) was measured and the run carried out to nearly complete saturation requiring 105 hours. The agreement of this run with the theoretical equations is given by Richard D. Pomeroy and is very good. It shows how the rate deviates from the square root of the time relation after 50% saturation. However, the deviation does not become marked for practical purposes until after 80% saturation when the logarithmic rate begins to have an appreciable effect. The increasing time in the latter part of the run shows that a run giving such a high degree of saturation with an oil into which methane diffuses slowly, would require several weeks.

The rate of absorption of ethane by cyclohexane (Fig. 7) was measured at the same pressure and temperature as the rate of absorption of methane in the same oil. It was found (Fig. 12) that it required about  $5\frac{1}{2}$  times longer for a given quantity of methane to diffuse into cyclohexane as for the same quantity of ethane to diffuse under the same conditions into the same oil. In this run, a slug was supported in the top of the cell to reduce the total volume of the system. The 2 points on the curve following the square root of the time in minutes equal to 60 are off the curve, because the volume of the liquid phase had increased so much that the surface of the liquid reached the bottom of the slug and the surface area for gas to diffuse into was reduced to a small fraction of its value earlier in the run. Due to this difficulty, the saturation value was determined at 197 lb. per sq. in. gauge, in order that the final volume of the liquid would not be greater than the total volume of the absorption cell. The saturation value at 249 lb. per sq. in. was calculated by assuming the solubility directly proportional to pressure which is a reasonable assumption since all data on natural gas solubilities show that this is true at these low pres-

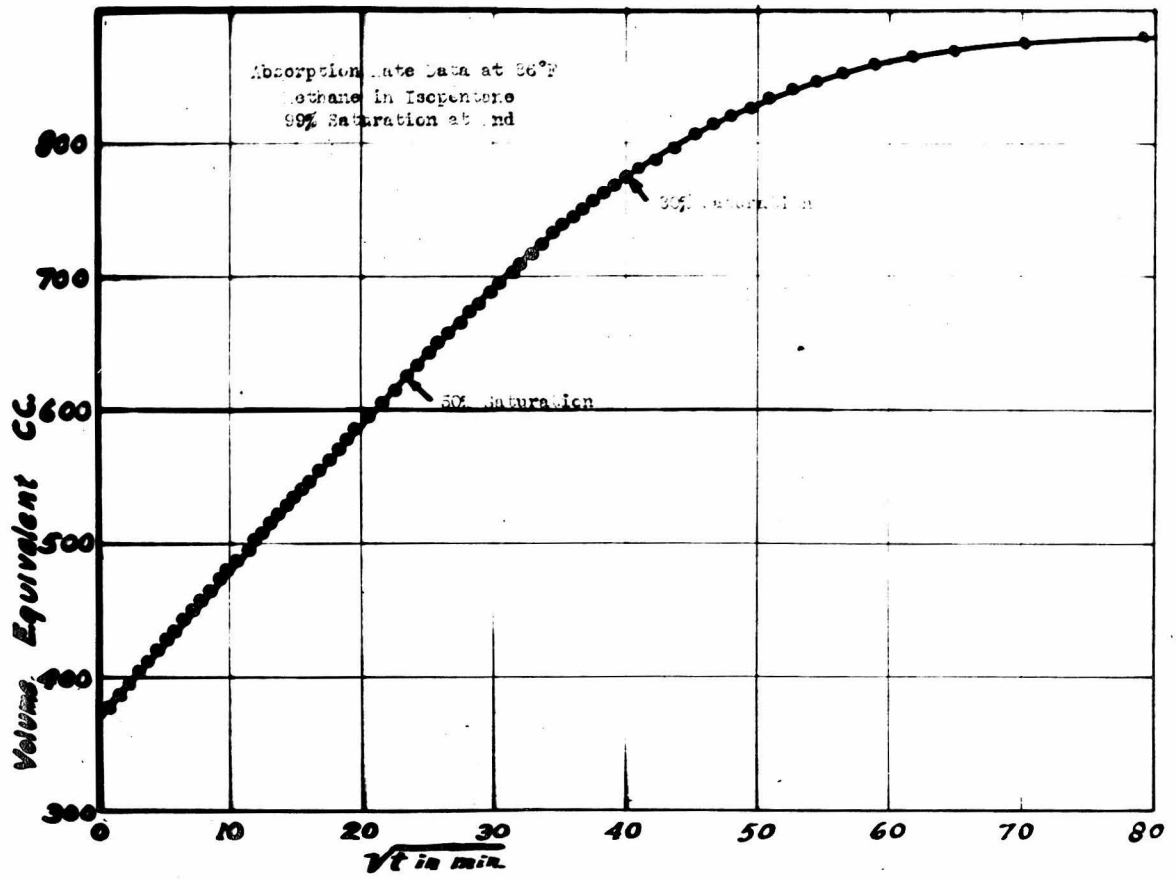
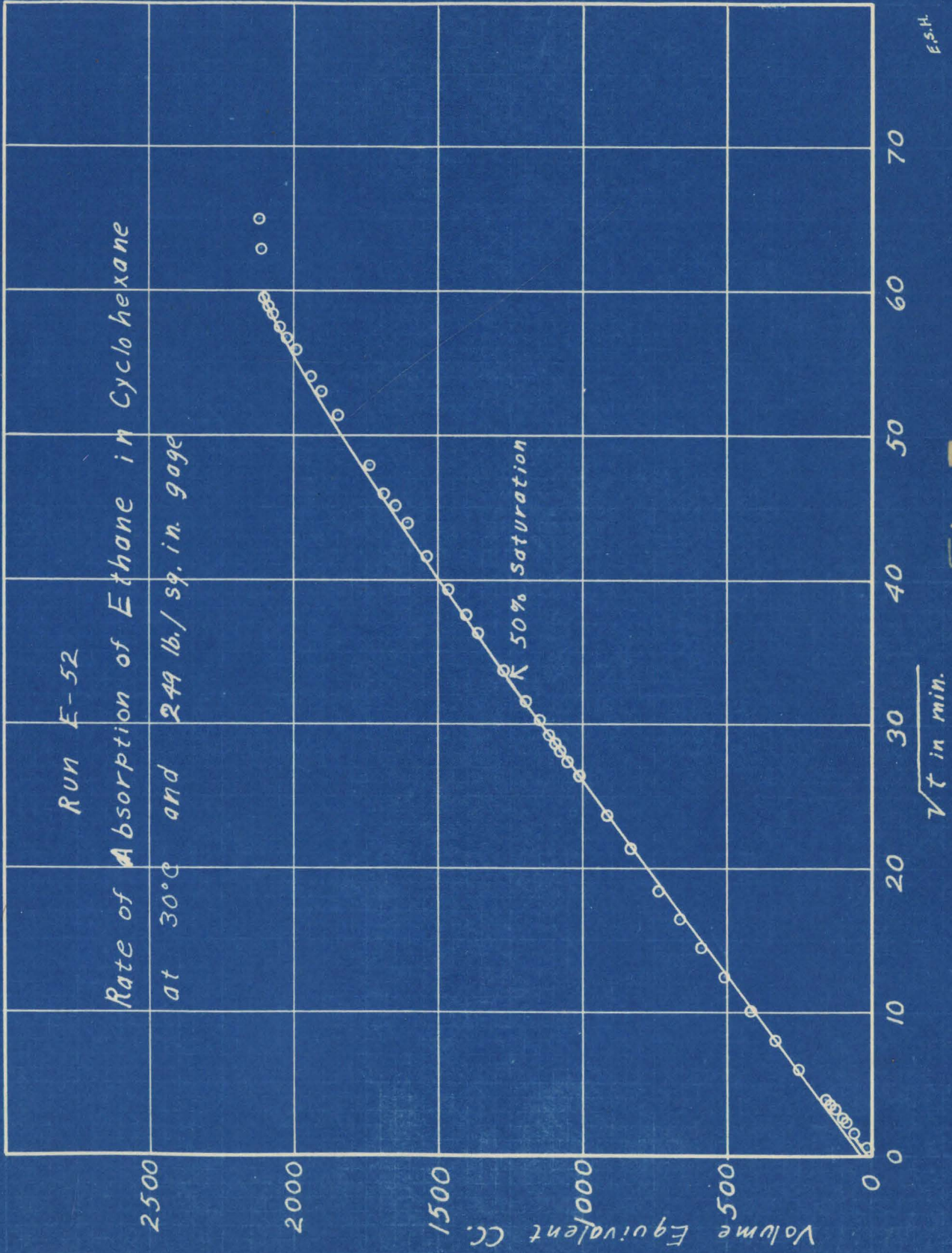


Fig. 6





E.S.H.

Fig. 7



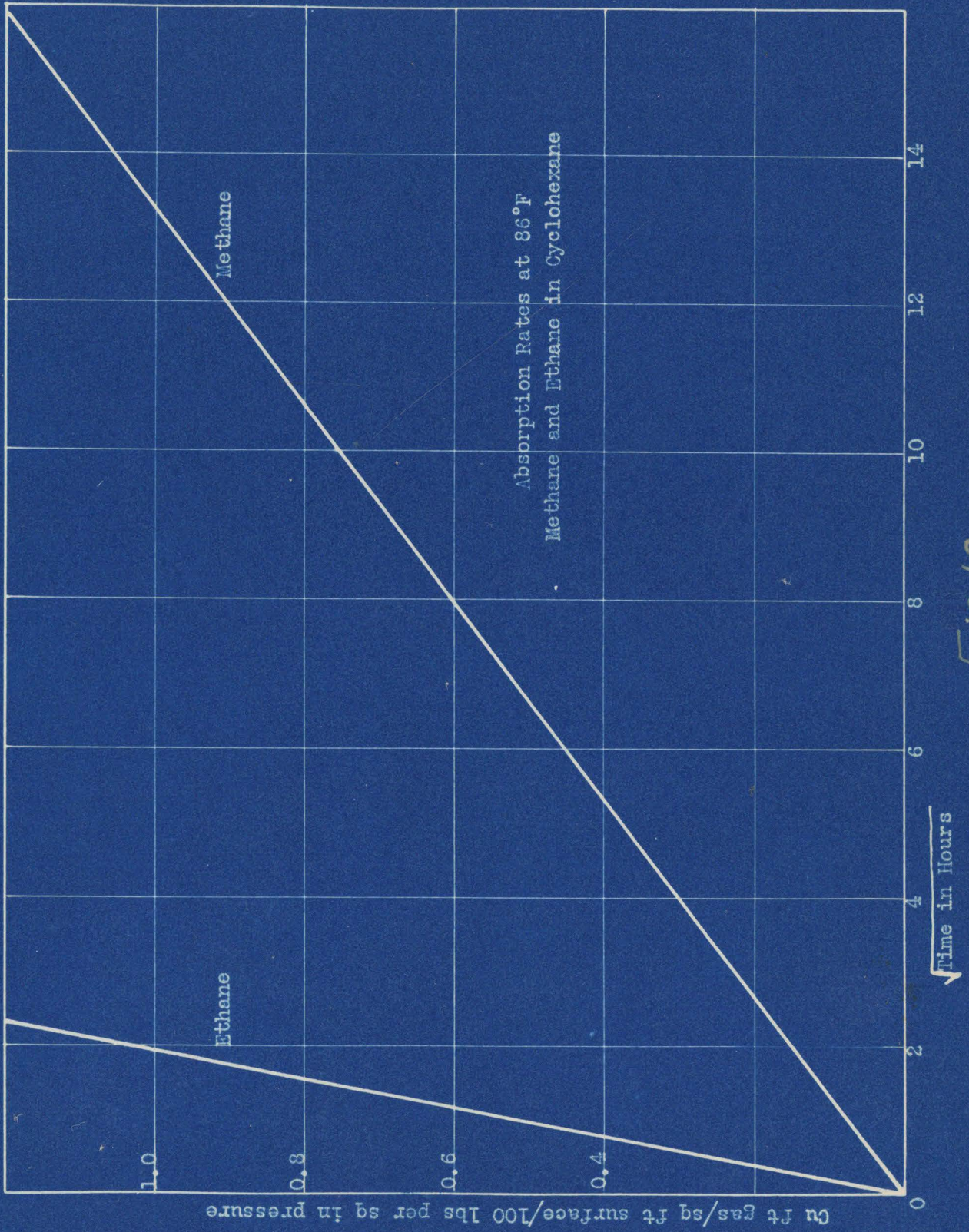


Fig. 12



tures. This value was found to be about  $4\frac{1}{2}$  times as great as the solubility of methane in this oil. Since the diffusion constant is the ratio of the squares of  $m$  and  $C_s$ , the diffusion constant is greater than for methane. The line obtained is not quite straight below 50% saturation because the partial pressure of ethane is not constant, but decreasing due to the increasing concentration of methane in the gas over the oil. This increasing concentration is due to the fact that a constant ratio of ethane to methane is admitted to the cell at each reading, while the rate of solution of ethane is  $5\frac{1}{2}$  times as great as for the methane. This concentration of methane is probably 2 or 3 times as great at 50% saturation as at the beginning of the run; therefore, the curve should not be a straight line in the first half of the run, because the partial pressure of ethane is decreasing.

Measurements of the rate of diffusion of methane into the crudes at  $30^{\circ}\text{C}$  and  $298\frac{1}{2}$  lb. per sq. in. gauge (Fig. 8) shows that the same relation holds for a mixture of petroleum hydrocarbons as for a single hydrocarbon. The variation in the rate between the different crudes seems to have no relation to the crude base, because the Lima, Ohio and Santa Fe Springs crude have practically the same rate, while the example of a mid-continent crude is lower and another paraffin crude, Bradford, Pa., shows a higher rate. No definite conclusions can be drawn from such a small number of examples other than that the rate of diffusion of methane into crudes has the same order of magnitude as the rate of diffusion into purified oils with the same density and origin.

The rate of diffusion of methane was made with one oil using 2 porosities and 2 grain sizes (Fig. 9). The variation in grain size from 20 to 200 mesh apparently has little effect on the rate. Since the



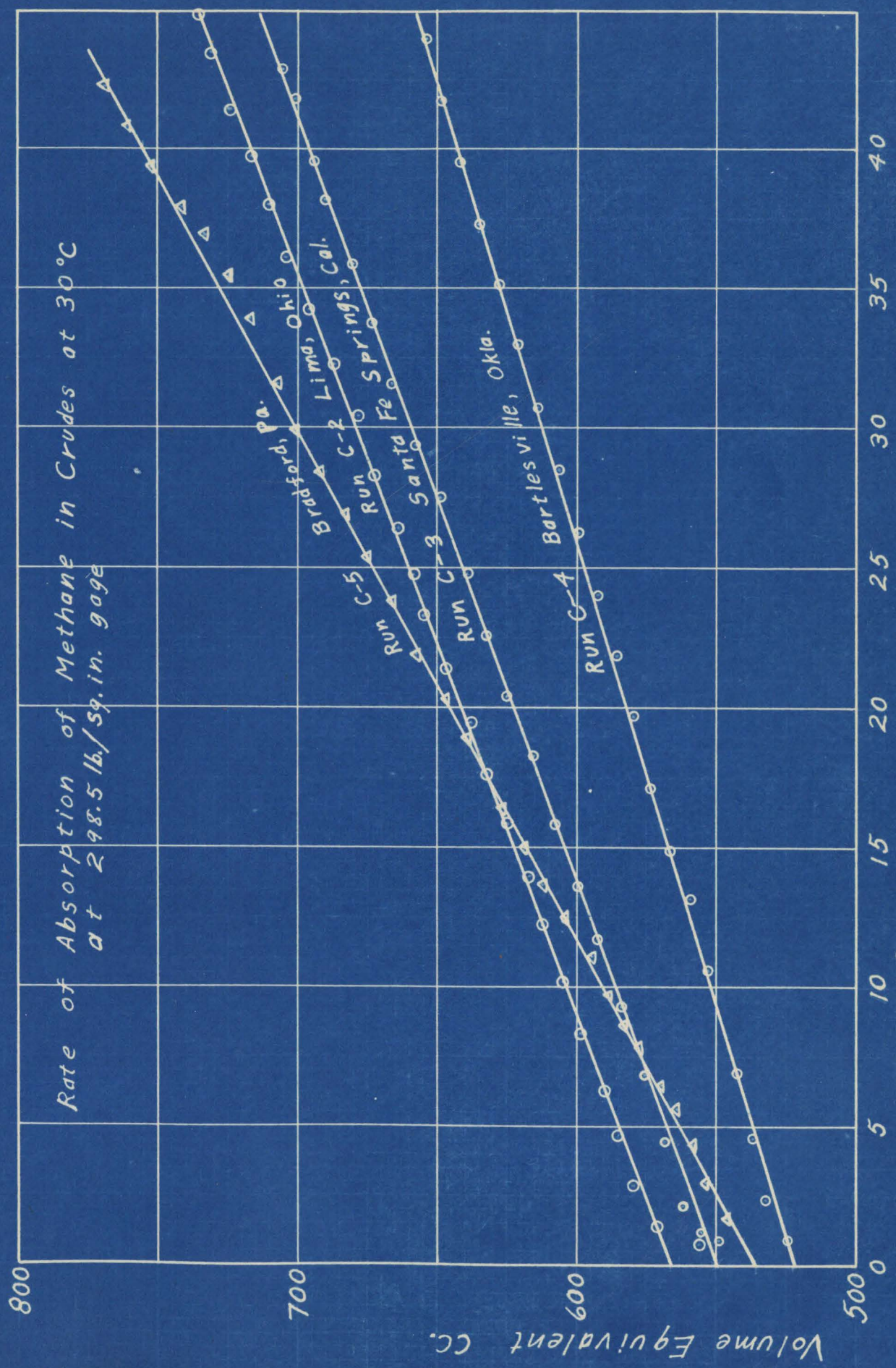


Fig. 8



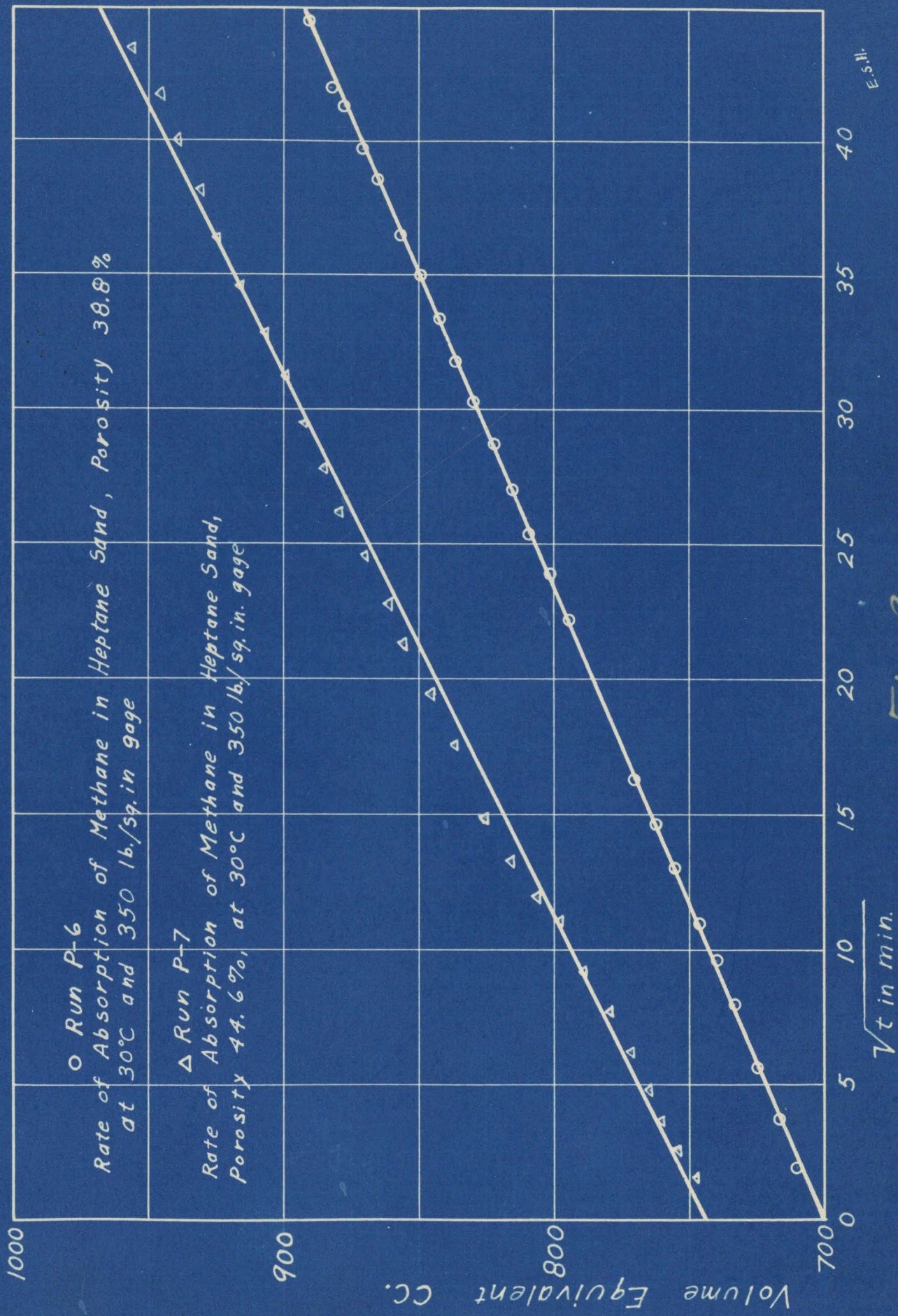


Fig. 9

E.S.H.



rate of diffusion into a unit surface of oil is less when the oil is in a sand than when it is not, as shown by the smaller diffusion constant (reduced from 8.20 to 5.37 in P-6 and to 5.58 in P-7), there is some relation between porosity and the diffusion constant.

### Conclusions

It is interesting for the purpose of comparison to plot all the rates of diffusion on the same scale for a 100 **lb.** per sq. in. pressure differential (Fig. 10). This has been done on the curves showing the rate of diffusion in cu. ft. per sq. ft. per 100 **lb.** pressure differential against the square root of the time in hours. It is to be observed on the plot that the rate is 32 times as fast for isopentane as for the liquid petrolatum. This is the maximum variation of rates studied. In the paraffin series the rate of diffusion of methane decreases as the number of carbon atoms increases. The solubilities show also that the total amount of gas that will be dissolved is less in the heavier liquids (Table III). On another curve (Fig. 11) the rate of absorption of methane by the crudes is illustrated on the **same** basis. It is observed that the low A.P.I. gravity crudes, that are usually found in depleted fields, will require a longer time for diffusion of the same quantity of gas into the oil.

The rate of diffusion of methane into a sand filled with oil is shown to be less (Fig. 14) than into the oil, even if the cross-section area is corrected for the presence of the sand. This is shown with 2 porosities by the heptane sand runs and with one porosity by the high gasoline fraction sand. The best explanation is that the gas must travel in a horizontal as well as in a vertical direction in diffusing through the oil and sand. The rate measurement on the oil was made under such conditions that the diffusion took place

Absorption Rates at 86°F Methane in Prepared Liquids

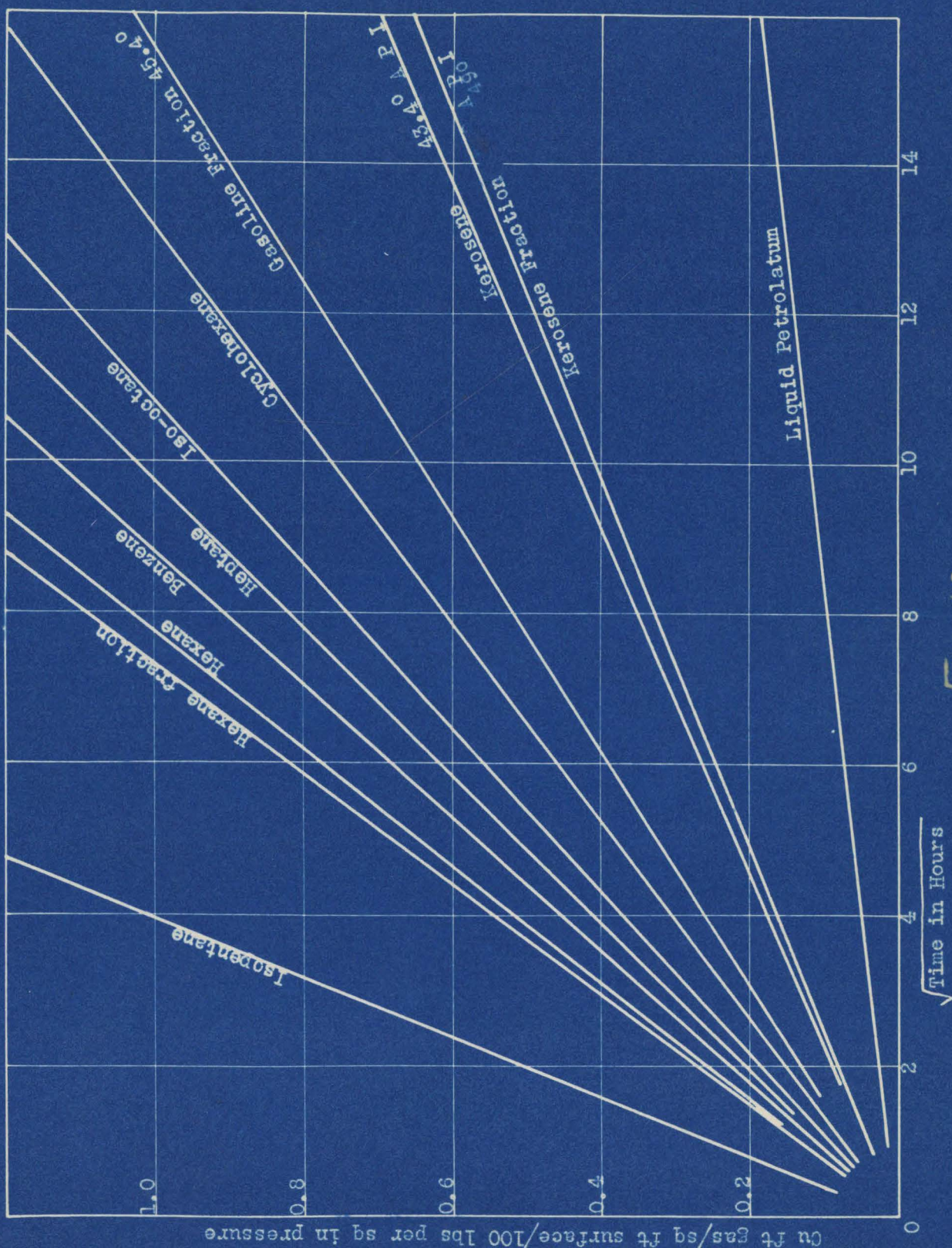


Fig. 10



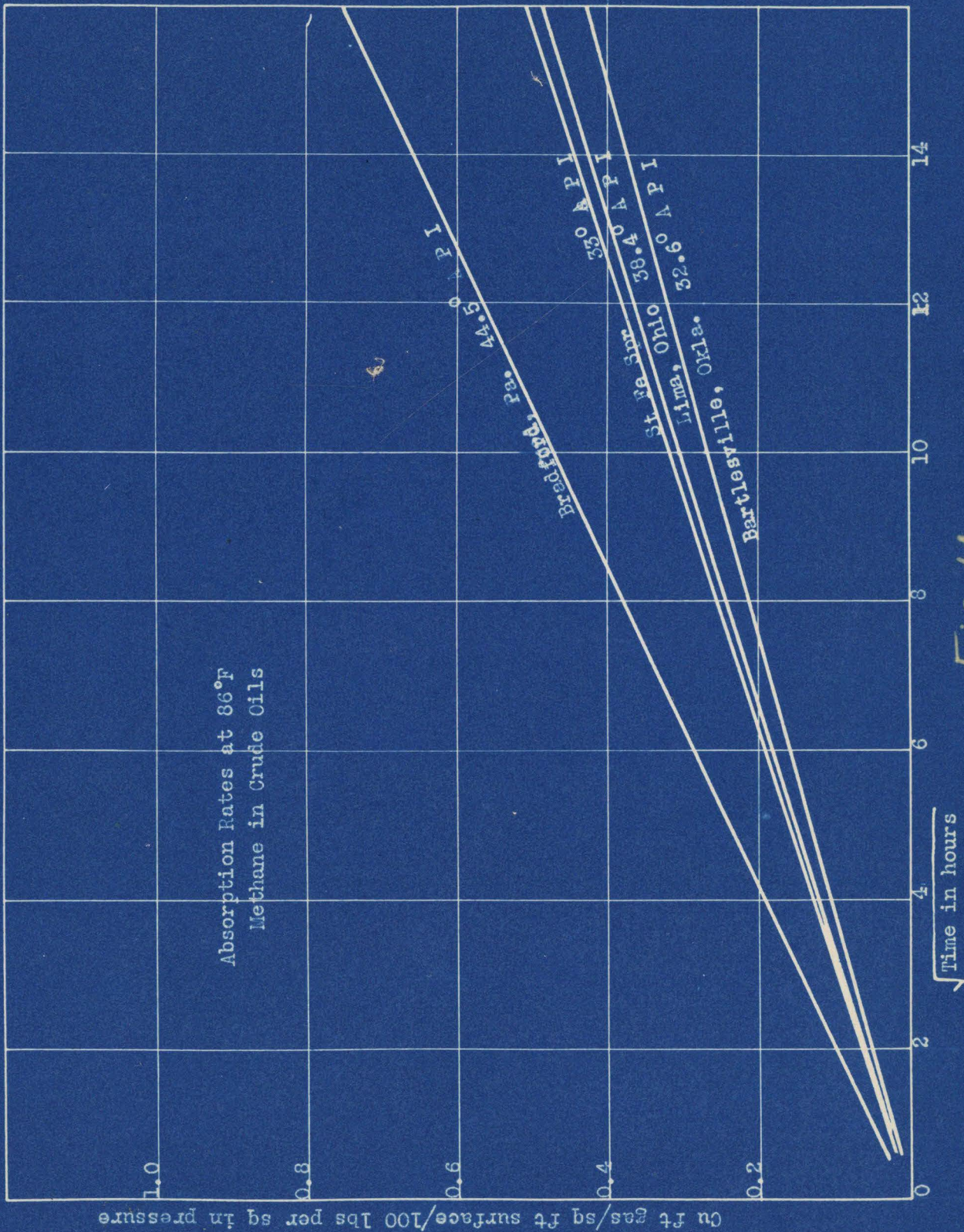


Fig. 11



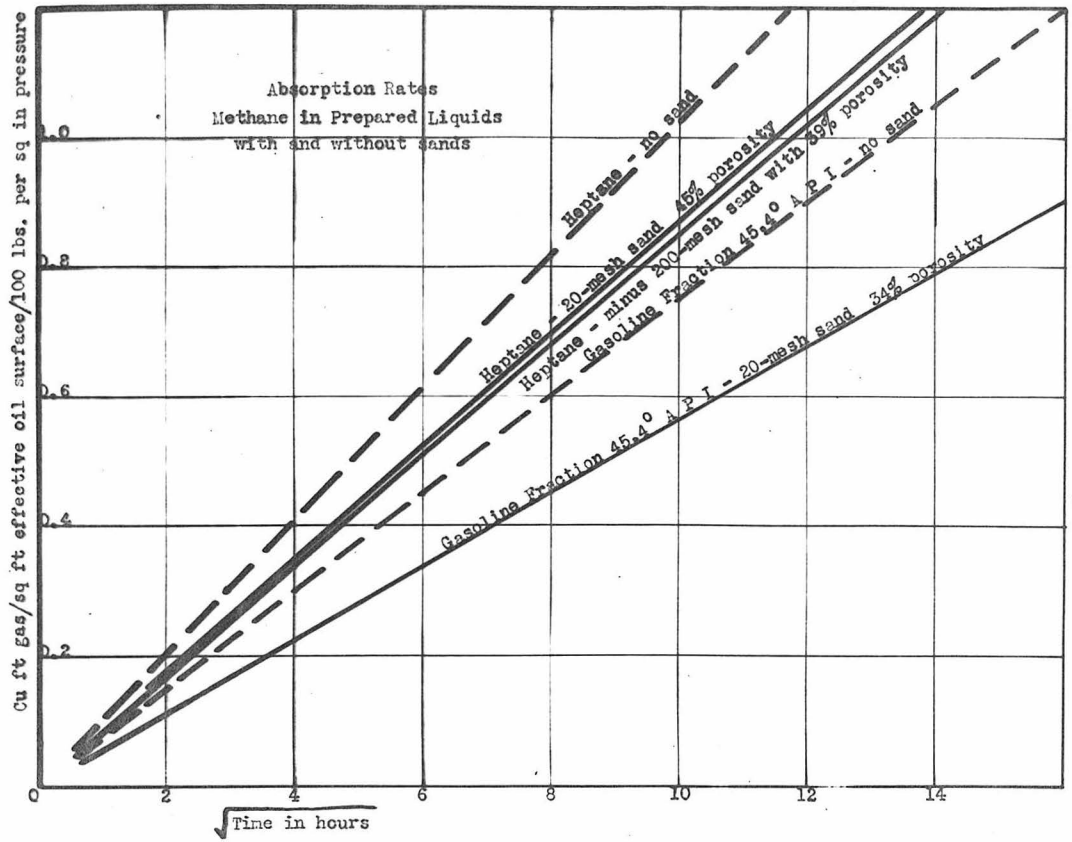


Fig. 14

only in a vertical direction. When the sand is present, the gas must travel in a horizontal direction to get around the sand grains. Therefore, if the rate of diffusion through the oil is the same, it should require a longer time for the gas to diffuse through the surface of a unit area of oil when the sand is present than when it is not.

When the temperature of the oil and gas is increased, the run with the high gasoline fraction at 30°C and 45°C shows that the rate of diffusion is higher at the higher temperature (Fig. 13). The increase in this case is over 25%. However, no quantitative conclusions can be drawn from a single run, except as to order of magnitude.

In order to illustrate the time required to repressure a formation, a plot (Fig. 14) has been made with the crudes and oil sands of the time required to 50% saturate a liquid, or sand full of oil, 10 ft. deep with methane at 30°C and 100 lb. per sq. in. differential pressure with gas diffusing through one surface of the oil. The chart shows that this requires a comparatively long time. The plot of Santa Fe Springs crude sand has been made assuming the same percentage reduction in the diffusion constant for the same porosity as in the case of the prepared liquids. This shows that it requires longer to 50% saturate a given depth of oil sand than it does to saturate the same depth of oil. These comparatively long times required for the diffusional process are an important consideration in repressuring oil sands and also in the storing of gas in formations of known limited extent.

The plot of the diffusion constants against A.P.I. gravity is interesting (Fig. 15). It looks as if a straight line might be drawn through these points. However, if this is done, the diffusion constant becomes zero at about an A.P.I. gravity of 25° which is false, because

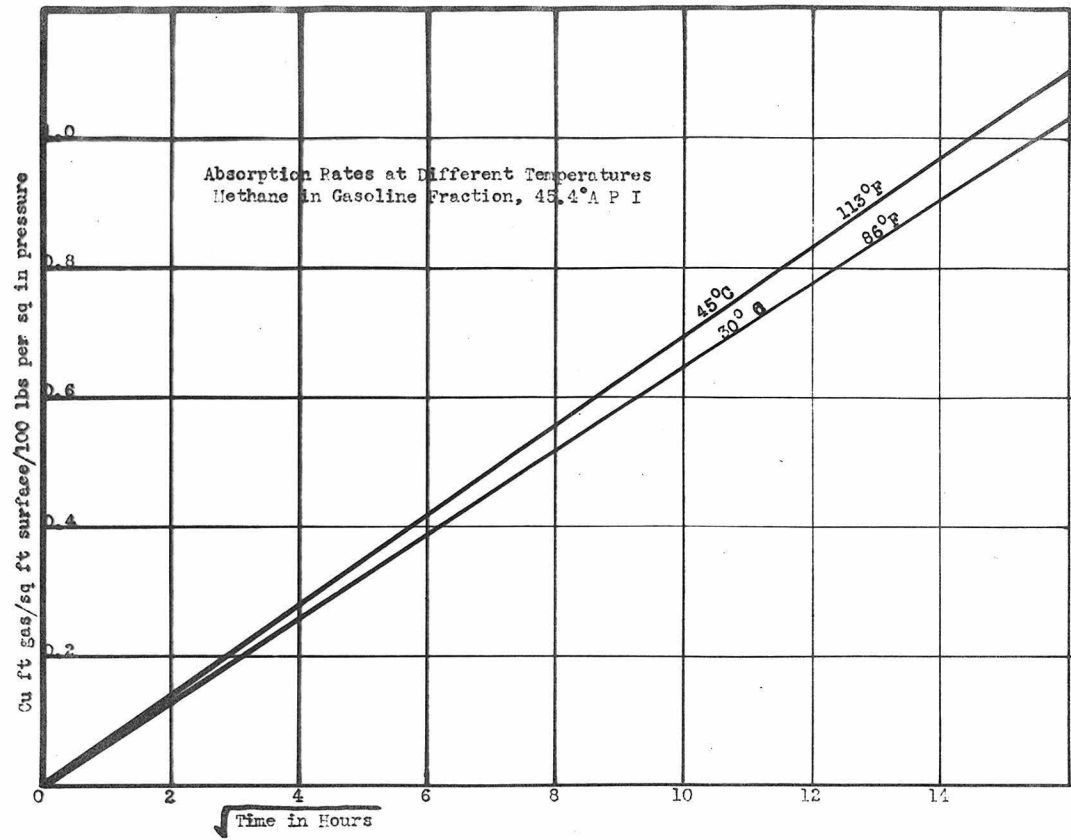


Fig. 13



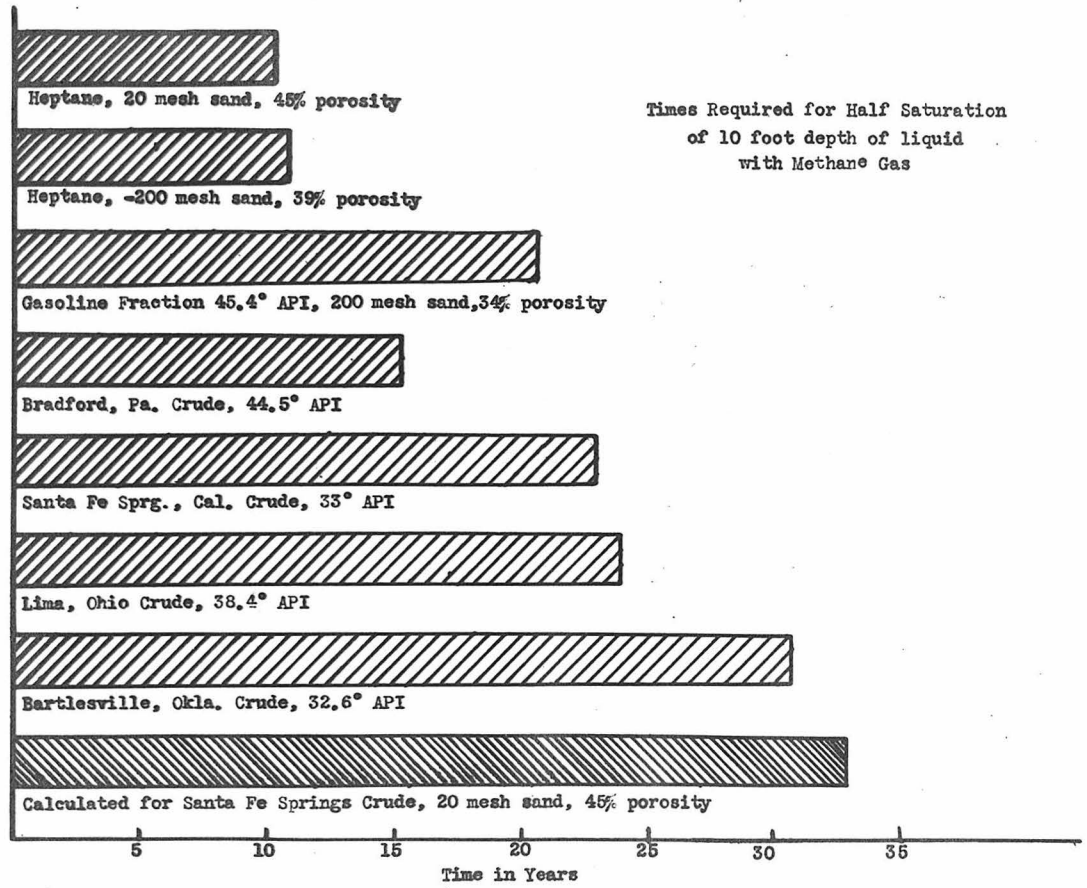


Fig. 15.

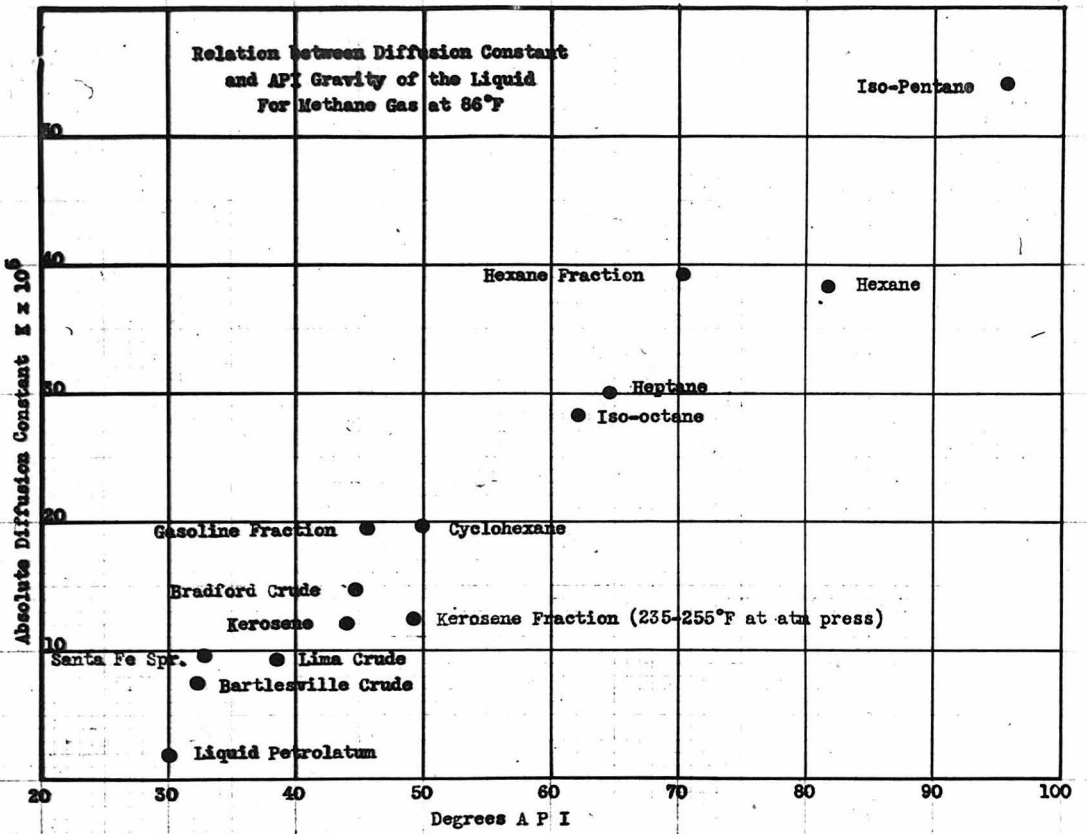


Fig. 16



there would be some diffusion; although, it would be small. Therefore, the lower part of the curve should not be a straight line but should slowly approach zero, never quite reaching it. One reason these points tend to give a straight line is the fact that a majority of them are for paraffins for which the constant would be very small at low A.P.I. gravities, because the oils are solid at 30°C. However, benzene lies far above the other points showing that the class of compounds has a large influence on the rate, and such a curve could not be applied in general for all types of crudes. It might, however, be applied to determinations of the diffusion constants on oils from a single district having the same base. The fact that the two paraffin crudes lie near a line drawn through the paraffin compounds plotted, substantiates this conclusion. Furthermore, the naphthene base crude lies off the line as would be expected. However, it must be pointed out that this is only for diffusion of methane at 30°C and cannot be used for a mixture of gases or at other temperatures. It is likely that some other factor, or factors, which are indirectly related to the density of the hydrocarbon liquid is the variable that effects the diffusion constant most profoundly, because this plot only shows a general trend of values and not a smooth curve.

Table III is a tabulation of the results obtained by Stapp, Pomeroy, and the writer.

### Acknowledgements

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TABLE III

SUMMARY OF RUNS by Stapp, Pomeroy, and Hill  
with Methane at 30° C.

No.	Oil	$C_g$ /100 lb.	Accepted $C_g$ /100 lb.	$D \times 10^5$	Average $D \times 10^5$ c.g.s.	$D \times 10^5$ in Eng. units
28a	High Gasoline Fraction # 1	4.18	4.13	4.97	4.98	19.3
28b	"	4.15		5.00		
29	"	4.09		4.98		
30	Same # 2		3.94		4.85	18.80
34	Heptane Fraction			7.69		
35	"			8.31		
36	"	5.21	5.21	8.26	8.30	31.78
37a	"			6.56		
37b	"			8.58		
37c	"			8.20		
23	High Gasoline Fraction # 1 at 45° C.		4.08		6.40	24.82
19	Iso-octane		4.84		7.37	28.5
21	Kero Fraction		3.24		3.19	12.35
24	Hexane Fraction			10.45		
25	"	6.22	6.13	9.97	10.10	39.10
26	"			9.51		
27	"	6.05				
51	Hexane		5.88		9.93	38.4
32	Benzene	3.63	6.58	6.02	6.05	23.38
33	"	3.53		6.07		
41	Kerosene	3.57	3.52	3.02	3.06	11.90
43	"	3.53		3.07		

TABLE III (continued)

No.	Oil	$C_s$ /100 lb.	Accepted $C_s$ /100 lb.	$D \times 10^5$	Average $D \times 10^5$ c.g.s.	$D \times 10^5$ in Eng. units
45	Cyclohexane			5.08		
46	"		4.78	5.08	5.08	19.65
47	Liquid Petrolateum	2.27	2.25	0.62	0.52	1.97
48	"	2.23		0.42		
50	Isopentane		5.65		14.00	54.23
E-52	Cyclohexane with Ethane at 30°C.		21.12		7.75	30.0
C-2	Lima, Ohio		3.11		2.40	9.30
C-3	Santa Fe Springs, Cal.		2.91		2.49	9.64
C-4	Bartlesville, Okla.		2.83		1.86	7.21
C-5	Bradford, Pa.		3.64		3.72	14.40
P-31	High Gasoline Fraction #2 20 mesh sand 34.2% porosity		3.94		2.76	10.70
P-6	Heptane Fraction 20 mesh sand 38.8% porosity		5.21		5.37	20.78
P-7	Same oil -200 mesh sand 44.6% porosity		5.21		5.58	21.58



TABLE III (continued)

No.	Oil or Oil Sand	Time in <u>Years</u> to 50 % Saturate a 10 ft. Layer with Methane at 30°C and 100 lb./sq, in. pressure differential.
C-2	Lima, Ohio	24.1
C-3	Santa Fe Springs, Cal.	23.3
C-4	Bartlesville, Okla.	31.1
C-5	Bradford, Pa.	15.5
P-31	High Gasoline Fraction # 2 20 mesh sand, 34.8% porosity	21.0
P-6	Heptane Fraction 38.8 % porosity 20 mesh sand	10.78
P-7	Same oil -200 mesh sand, 44.6% porosity	10.36
	Assumed crude sand with Santa Fe Springs Crude	33.38