The Rate of Solution of Methane and Propane in Hydrocarbon Oils

Thesis by

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THE RATE OF SOLUTION OF METHANE AND PROPANE IN HYDROCARBON OILS

For many years after its first commercial success in 1912 repressuring of oil formations with natural gas has been considered and used. At first its use was confined to stripper wells in fields from which the gas pressure had reached an advanced stage of depletion. In more recent years repressuring has been applied early in the lives of some fields to maintain the pressure. Instead of allowing the gas to waste, the pressure to fall off, and the production to decline rapidly with increasing unit production costs, it has been found that the surplus gas in the flush stages of a field can be returned to the ground with manifold advantages. The Sugarland, Texas, field, operated by the Humble Oil and Refining Company, is a notable example of this kind of repressuring, or pressure maintenance. Repressuring begun several years after discovery has made the drilling of many wells unnecessary, has conserved gas and gas pressure, has kept the wells flowing, and has made the recovery costs notably cheap. Storage of natural gas in depleted formations has become a factor in natural gas distribution from producing fields because it provides a cheap storage space, produces a wet gas from a dry gas, and increases the oil recovery from the formation.

An investigation of the literature shows very little data which can be used to calculate the quantities of gas, pressure, and the number of wells required to develop a field with gas repressuring methods. Much of the development has been that of pumping the gas into the formation and finding out what happened in the formation by taking data on the quantities of gas pumped in, the pressures in the input and in surrounding wells, and the effect on production. This is an unsatisfactory method as shown by the fact that the process has been unsuccessful in a number of applications. These uncertain conditions indicate that an investigation of the fundamentals involved is necessary. For this purpose an investigation of the time required for natural gas to dissolve in petroleum oils in formations was begun as a part of American Petroleum Institute Research Project Number 37 in 1927. This investigation has progressed continuously since that time to the present in the hands of several investigators. The problem has resolved itself into several sections which can be classified into two principal divisions; fundamental laws of diffusion of natural gas in oil and oil-filled sands, and the determination and application of the physical constants for these laws.

The fundamental diffusion equation explaining the rate of solution process has been investigated by the previous investigators, Pomeroy, Scudder, and Stapp(1,2,3) and a satisfactory equation found to fit the cases for which their assumptions apply. Reference should be made to their paper and to Pomeroy's and Stapp's theses(1,2) for a derivation of the equations described below and for a description of the general methods of making the determinations. It has been shown that the Fick proposition is valid with certain limiting assumptions for this work. This proposition may be stated in the following equation:

$$\frac{\partial q}{\partial t} = - D A \frac{\partial c}{\partial x}$$

where q = quantity of solute which has passed a given point

A = area at right angles to the direction of flow

c = concentration

x = distance in direction of flow

t = time

D = diffusion constant in sq.cm./sec. or sq.ft./hr.

C_s = concentration at infinite time

Solution of this equation for the case of a liquid column of infinite depth gave the following result for the quantity of das dissolved:

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

It has been shown (2,3) that for most practical purposes this is the only solution that will need to be considered in the determination of the physical constants involved.

The limiting assumptions in obtaining this equation for the rate of solution are as follows: (a) the diffusion constant does not change with the concentration of the solution; (b) the layer immediately under the surface film does not retard the passage of gas into the liquid; (c) the gas moves through the liquid only by diffusion.

The determination of the physical constants for the rate of solution equation involves the determination for each gas present in natural gas in appreciable quantities in a series of oils covering the range that may be met in the fields. This study should cover the effect of temperature, pressure, gas composition, and sand on these constants, and if sufficient field data can be obtained from some of the numerous field tests some calculations should be made to determine how well these fundamental equations cover the field conditions. This thesis is confined chiefly to the determination of the physical constants; namely, the diffusion constant and the final concentration value, together with other required data such as viscosity of the oils, gas compressibilities, and expansion of the liquid upon solution of gas, for methane and propane. In these determinations it was found that at least two of the limiting assumptions involved in the original equation were not fully complied with in the case of propane; namely, that the diffusion constant is not independent of the concentration, and that expansion of the liquid on dissolving the more soluble gases causes movement of gas other than that by diffusion. An attempt has been made to devise means of evaluating the results of these effects.

Materials

The methane used for the studies that were made to determine the effect of temperature on the diffusion constant of methane was prepared by the same method as that used by Pomeroy, Scudder, and Stapp with some modifications of the apparatus to give more reproducible results. However, the purity of this methane was not exceptionally good. The ethane content was approximately 1.5% but the nitrogen content was unknown and not negligible as supposed at the time. The natural gas used for the preparation of this methane was obtained in the Santa Fe Springs field from a gas-lift compressor plant on the Walker lease of the Standard Gasoline Company. All ethane content analyses were run by the liquid air trap method used by Stapp and Pomeroy.(1,2,3)

The methane used for the runs at high pressures was prepared from city gas in the same way as that used for the temperature measurements but in a larger setup described by Kircher.(4) This gas contained 0.98% ethane and the air content was calculated to be 3.2% from the gas density obtained with an Edwards gas density balance.

The methane used for all the final determinations at 30°C was prepared from city gas by a process which removed most of the air as well as the ethane and heavier. The ethane and heavier constituents were removed by activated charcoal as before but with better results. The final ethane present being 0.36%. After treatment with charcoal the gas was passed thru a steel bomb surrounded by liquid air; the pressure inside the bomb was maintained at 40 mm. or less. At this temperature and pressure methane is a solid and drops out of the gas stream. At higher pressures the apparatus freezes up, and at lower pressures the capacity of the vacuum pumps is reduced and the loss of methane is greater. Methane solidifies at 89°C absolute. The vapor pressure of the solid is about 20 mm. at liquid air temperatures, depending somewhat on the composition of the cooling medium. By this method the solid methane is condensed in a gas space where the nitrogen present is small and the degree of separation ought to be good. Unfortunately the laboratory assistant responsible for analysis of the methane for air content has not yet been able to get reproducible results on methane of this purity. This methane certainly contains only a small fraction of the impurities that were in the methane used at the beginning of this work.

No additional work has been done with ethane because the experience with propane indicates that the quantity of impurities present in the 96.5% ethane available would cause a large divergence of the final concentration value from that for pure ethane.

The propane was obtained in a sufficiently large quantity from the Standard Gasoline Company. It was supposed to be 99% propane but after a number of runs were made it was suspected that the quantity of impurities present was larger. A fractionation analysis showed 4.03% ethane, 93.20% propane, and 2.77% isobutane. Figure 33 showing the curve of experimental data for the rate of solution of commercial propane in kerosene shows the effect of changing composition of gas in the gas phase in the tank. The gas for these two runs came from the same tank with possibly a twentieth of the total quantity present being removed between the two runs, which were made at the same temperature and pressure with the same oil. This divergence due to changing gas composition is too large to permit even approximate determinations. If the tank had been inverted and the propane withdrawn from the liquid phase, this change in composition would not have been apparent until a large amount of the material had been used and possibly all of the data on propane would have been erroneous.

The commercial propane was redistilled in a glass still at dry ice temperatures. The still consisted of a kettle, a column one inch in diameter and ten feet long packed with glass rings, and a steel condenser bomb. Acetone cooled with solid carbon dioxide was used to obtain the low temperatures for the distillation, to obtain reflux at the top of the column, and to condense the final product. Two and one-half liter Dewar tubes were used as containers for the cooling medium. It was found that materially higher rates of condensation could be obtained in the final condenser, with resulting lower pressure on the column, by using acetone, as compared with natural gasoline. This was due to the lower viscosity of the cold acetone mixture with less foaming when carbon dioxide gas was evolved. Commercial acetone was found too corrosive and unpleasant to handle since the frothing frequently caused it to get on the hands and clothing of the operator. Distillation in a glass still having a packed column two feet long, with sodium hydroxide, reduced the corrosive action on the steel parts of the apparatus.

The kettle of the propane still had an 800 cc. capacity, an inlet tube sealed to the bottom, and an internal electric heater. It was cooled by the cooling fluid in a Dewar tube. The inlet tube was brought up the outside of the kettle within the Dewar tube and out to a stop-cock. Since the propane was condensed into the kettle from the steel tanks in which it was stored as a liquid at room temperatures, it was desirable to have this type of a connection to fill the kettle in a reasonable length of time without running up the pressure in the glass apparatus.

The column was heat insulated with ordinary steam pipe lagging. This lagging is none too satisfactory to use for any length of time, unless the covering is made air-tight, because moisture from the atmosphere condenses on it next to the cold column and eventually wets the lagging so that it loses its heat insulating properties. The reflux condenser was a jacket on the upper end of the column, thru which cold acetone was circulated. Since the column was vertical, the circulation, after once being started, was automatic due to the evolution of dissolved carbon dioxide gas when the fluid was warmed in the reflux condenser, producing a gas-lift pumping action. This method of circulating the condenser fluid at a rate dependent on the amount of heat to be removed is not entirely satisfactory unless precautions are taken to carefully heat-insulate the tube connecting the container, where the solid carbon dioxide is added, with the bottom of the reflux condenser.

The progress of the distillation was followed by means of a mercury manometer; thermocouples placed in the head of the column, in the inlet and outlet of the reflux condenser, in the kettle, and in the final condenser bath; and an illuminated window near each end of the column. The distillation was carried out in 800-cc. batches. The first portion of the gas coming over was blown off, consisting of ethane and propane. Since ethane cannot be refluxed with solid carbon dioxide at the pressures that can be used in glass apparatus, this loss of propane could not be prevented. After the ethane was removed, the pressure could be lowered to 350 to 400 mm. where the distillation was continued. The rate of condensation in the steel bomb used for the final condenser was the controlling factor in the rate of distillation except at the beginning. When the column began to prime at the bottom, the rate of distillation was slowed down until the reflux drained down to the kettle. This occurred only during the beginning of the distillation when the rate of condensation in the final condenser was highest. After the final condenser was filled to the level of the cooling liquid, the valve connecting it to the column was closed and another opened to a steel storage tank. The cold acetone on the condenser bomb was then removed and replaced by hot water and the propane distilled into the storage tank.

The final analysis of the product by fractionation showed 99.2% propane and 0.8% isobutane. This method of analysis tends to give high values for a heavier gas present in quite small amounts in a lighter gas, so the purity was believed to be satisfactory.

The gas used in the two natural gas runs was obtained in September, 1931, from the Standard Gasoline Company property in the Santa Fe Springs field. The fractionation analysis gave the following results: 87.28% methane, 7.96% ethane, and 4.76% propane. However, since the gas was drawn at 20°C thru a 40-foot line from the tank at a pressure of 700 lbs. per sq.in., it may have been somewhat dryer when it reached the reservoir of the rate of solution apparatus. The exact composition of this gas was immaterial since the runs were only preliminary in order to find out how a mixed gas would behave in the apparatus. The oils used for the determinations consisted of pure individual liquids, refined oils, and crudes. The physical constants are given in Table I. Isopentane and pentane were obtained from the Philgas Company. The isopentane analysis was: n-butane 0.20%, isopentane 99.73%, and n-pentane 0.07%. The pentane was specified as C.P. and its purity probably approaches that of the isopentane. n-Hexane, cyclohexane, benzene, n-pentane, and 2,2,4-trimethylpentane were obtainfrom the Eastman Kodak Company, and all had a satisfactory purity except the n-hexane which was considerably below specifications. The impurity was a heavier oil. Nine-tenths of the liquid distilled between 67.8 and 70.3°C and the end point was 77.2°C. The oil should have had a 1°C boiling range. The benzene was thiophene free. The cyclohexane had been purified by fractional crystallization. The n-heptane and 2,2,4-trimethylpentane had 0.3°C boiling ranges. The kerosene was purchased from the Shell Oil Company; it was water white when received but after two years it had precipitated some solid and changed color. The spray oil supplied by the Union Oil Company was stable and did not change its physical appearance. The petrolatum was a water white medicinal oil sold by the Sterling Laboratories. The crudes came from the following sources:

Bradford, Pa.	from	Forest Oil Co.
Smackover, Ark.	"	Standard Oil Co. of Louisiana
Bartlesville, Okla	"	U.S.Bureau of Mines, Bartlesville.
Lima, Ohio	"	Ohio Oil Co.
Sugarland, Texas	"	Humble Oil and Refining Company.
Ventura, Calif.	"	Gosnell Lease of Shell Oil Co.
Rosecrans, Calif.	"	Union Oil Company's Chandler No. 3 in the Rosecrans District from the lower Hoge zone.

Apparatus and Methods

Altho the general method of making the determinations has been described before, a number of changes have been made since the description was made by Stapp.(1) The flow sheet (Figure 1) shows the connections used. A gauge equipped with a stainless steel tube was used for the reservoir instead of the old multi-tube bronze gauge. A refill valve was added so that the reservoir could be refilled during a determination. A special, fine-lined, uniformly graduated scale was placed on the reservoir gauge instead of the original test gauge scale. This materially improved the accuracy of the reservoir readings. The reservoir tube was found to check between successive calibrations within about 1/4%. The test gauge used to measure the pressure of the determination was removed from the absorption cell head and placed on the gas inlet line between the control valve and the flexible coil. A 10x magnifier was supported from a hole in the center of the test gauge glass making it possible to reproduce a setting to ±0.1 lb./sq.in. as read on the gauge. A valve was added to the inlet line so that the absorption cell system could be evacuated when desired, and the test gauge calibrated at the end of a determination without removing it from the apparatus. The line leading to the gauge tester was approximately 40 feet long and 23 feet in elevation above the tester, and consisted of 3/16 inch copper tubing with a small boiler water-column near the tester. Connections were made directly to the gauge glass holders on this boiler water-column and the valves at the top and bottom closed so that gas and oil were admitted to the gauge glass section only. This gauge glass served as an oil trap since an oil line from its bottom was connected to a gauge tester and a gas line from the apparatus to the top. In order to check the gauge, the gas line was filled up to as nearly as possible the same pressure as the determination with gas from a nitrogen tank before the valve to the apparatus was opened. A 5-foot mercury manometer attached to this line was used to give the zero reading of the tester and for calibration up to 25 pounds gauge. Correction for the weights of the gas column to the gauge tester was made on the readings.

A low pressure regulator was placed in the vacuum line to control the low pressure required in evacuating the air from the oil. The system was developed on another American Petroleum Institute project for vacuum distillation control and found quite satisfactory.(5) In connection with this a trap was designed so that the cooled part could be easily removed and weighed to determine the loss of oil from the cell during the long evacuation. S.A.E. brass flared fittings were used with copper tubing for the connections to the trap and found to be superior to any known ground glass or rubber tubing method of connection. The quantity of oil pumped over into this trap was seldom more than 0.1% of the total in any of the cases where the method was used.

The change in volume tube was substantially the same as formerly except that the use of slightly heavier glass and longer annealing times (8 to 10 hours) permitted pressures twice as great to be used so that the expansion in liquid volume could be determined at the same pressure as that used in the determination up to about 305 lbs./sq.in. This tube was surrounded by a suitable guard and attached to the apparatus as shown on the right in Figure 7 when it was desired to make a determination.

The accuracy was materially improved by better technic and the substitution of 1/8" O.D. copper tubing for the rubber hose formerly used to connect it to the apparatus.

A new calibrating burette was designed and built (Figure 5). It had two bulbs, 5 cc. and 25 cc., so that any irregular portion of the reservoir calibration could be followed closely. A gravity return of the mercury to the upper position by setting the leveling bottle on a stand and allowing the mercury to flow into the burette was substituted for the former method of blowing it back with air pressure. Sliders with a fine wire indicator were placed on the meter stick between the burette and its manometer so that the mercury level could be easily read to 0.1 mm. This burette requires one-half the time for a reading of equivalent accuracy compared with the former burette. It was operated so that readings were taken at constant pressure making it unnecessary to correct for the 1/8" O.D. copper tubing used to connect it to the apparatus.

The absorption cell was removed from the former rigid support and placed in a weighted, triangular support mounted on rubber stoppers four high (Figure 6). This was found desirable due to vibration of the building and the former support. The weight of this system was about 30 lbs. for the brass cell and 50 lbs. for the steel cell. In determining the final concentration value the absorption cell was placed in a shaker operated from outside the thermostat, instead of using the hand to hold the cell and shake it inside the thermostat as formerly. This eliminated temperature disturbance due to heating or cooling the cell with the hand. The steel cell (Figure 2) was built with approximately three times the area of the old brass cell to give sufficiently high rates of flow for accurate measurements on oils with a low diffusion constant and for oil sands. This cell was designed to operate at pressures up to 3000 lbs. per sq.in. so that it could be used with the other high pressure apparatus of the project. Also it will enable the use of high pressures in obtaining uniform sand porosities in an unconsolidated sand when pressing a sample into the cell. The drawing of the steel cell shows the construction features. The head was designed to avoid dead gas space with the blowoff plug having an extension that nearly fills up the hole that leads up to it. The size of the gasket on this cell was cut down to a fraction of the size used in the older cells. For very high rates of solution the accuracy of the reservoir system is impaired and larger quantities of materials are used than are necessary. Hence, two brass slugs were made with different sized stems to place in the brass cell to cut down the cross section area and the total volume (Figure 3). The small end of one of the slugs shown in Figure 3 was placed in the bottom of the cell and the liquid level maintained as near the bottom of the large portion of the slugs as feasible. By this combination of cells and slugs, and a slug in the bottom of the reservoir, the reservoir was operated over a far more accurate range than was formerly possible in many cases. The liquid level was placed as close to the top of the cell as possible without seriously interfering with the determination of a final concentration value.

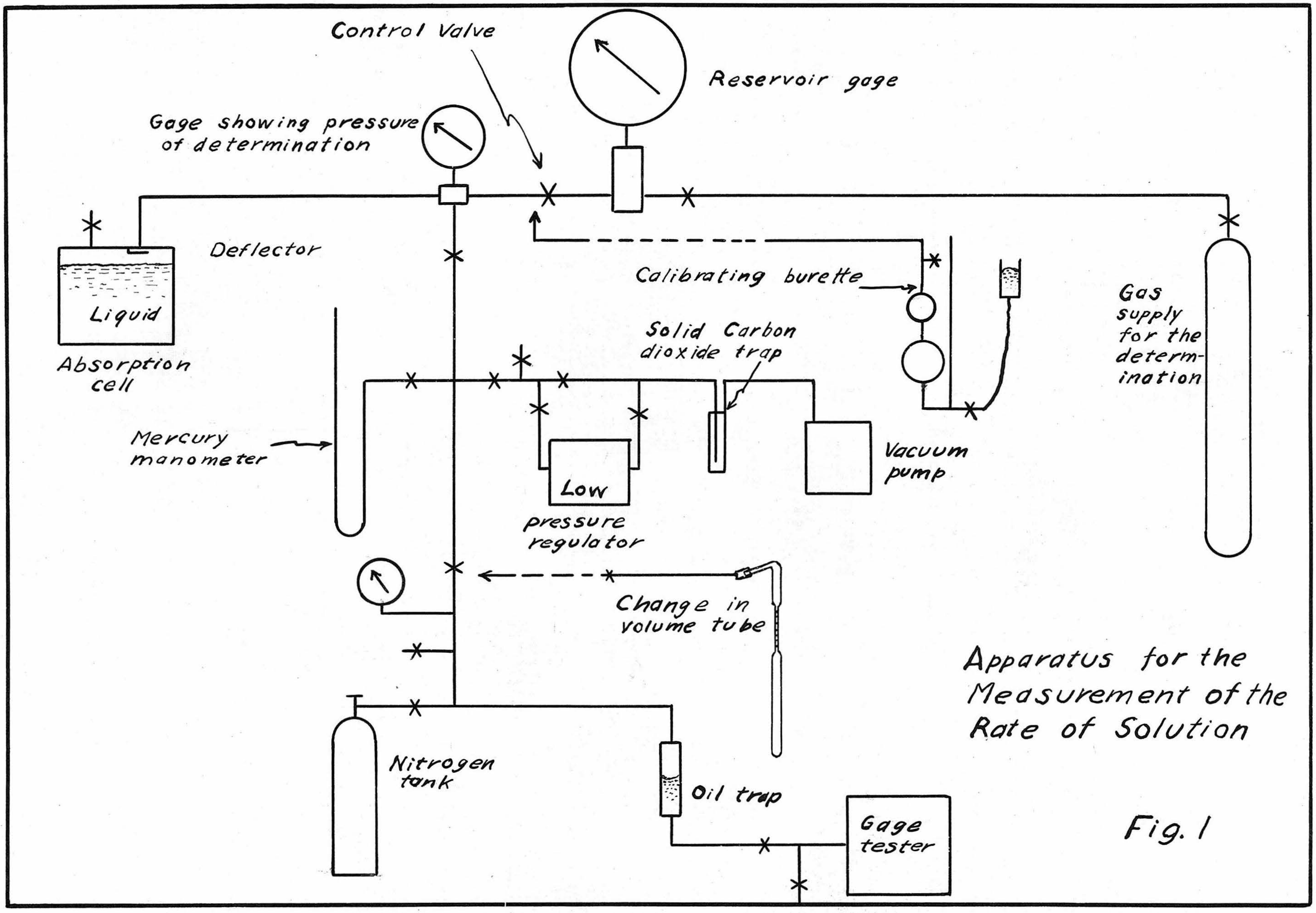
The photographs show the apparatus setup for various determinings. Figure 4 shows the front of the thermostat in place with the location of the gauges inside. A chart used to enable the operator to read the reservoir accurately to 0.1° on the scale is shown just to the right of the window. Figure 5 shows the front removed and the calibrating burette in place. The calibration is, of course, done with the front on the thermostat as is the case for all the other determinations. Figure 6 shows how the apparatus is connected up for a rate of solution determination with the cell and its support in the left end of the thermostat. The fourth view (Figure 7) shows the change in volume tube in place for a determination. The connection for the absorption cell is blanked off during this operation and the same gauge used to determine the equilibrium pressure. In this photograph the absorption cell has been placed in the shaker for an equilibrium determination.

Figure 8 shows the supporting frame and one of the Ostwald type of viscometers used to measure the viscosity of the original oils. A quartz instrument having a water time of 580 seconds at 30°C was used as a calibrating standard and for the determination of the viscosities of the lighter oils where it was thought desirable to make the determinations. A pyrex instrument with a water time of 94.3 sec. at 45°C was used for measuring the viscosity of the heavier oils. This instrument was calibrated with kerosene measured in the quartz instrument because the water time was too short to avoid turbulence. Such a combination of different sized capillaries gave viscosity measurements accurate to 0.5%. The small bottles on the right side of the viscometer were partially filled with liquid of the same composition as that in the viscometer to cut down evaporation losses. Air pressure was used to force the oil up into the small bulb on the left arm of the instrument from which it flowed thru the submerged capillary into the large bulb on the right arm at a rate depending on the viscosity. Short times were measured with a chronograph driven by a synchronous motor. This chronograph was used to calibrate a stop-watch for the longer times beyond the range of the chronograph.

The thermostat itself was completely rewired and all necessary controls designed and placed in position so that the temperature control and other electrical parts of the apparatus were operated with very little trouble and few changes over a period of more than two years.

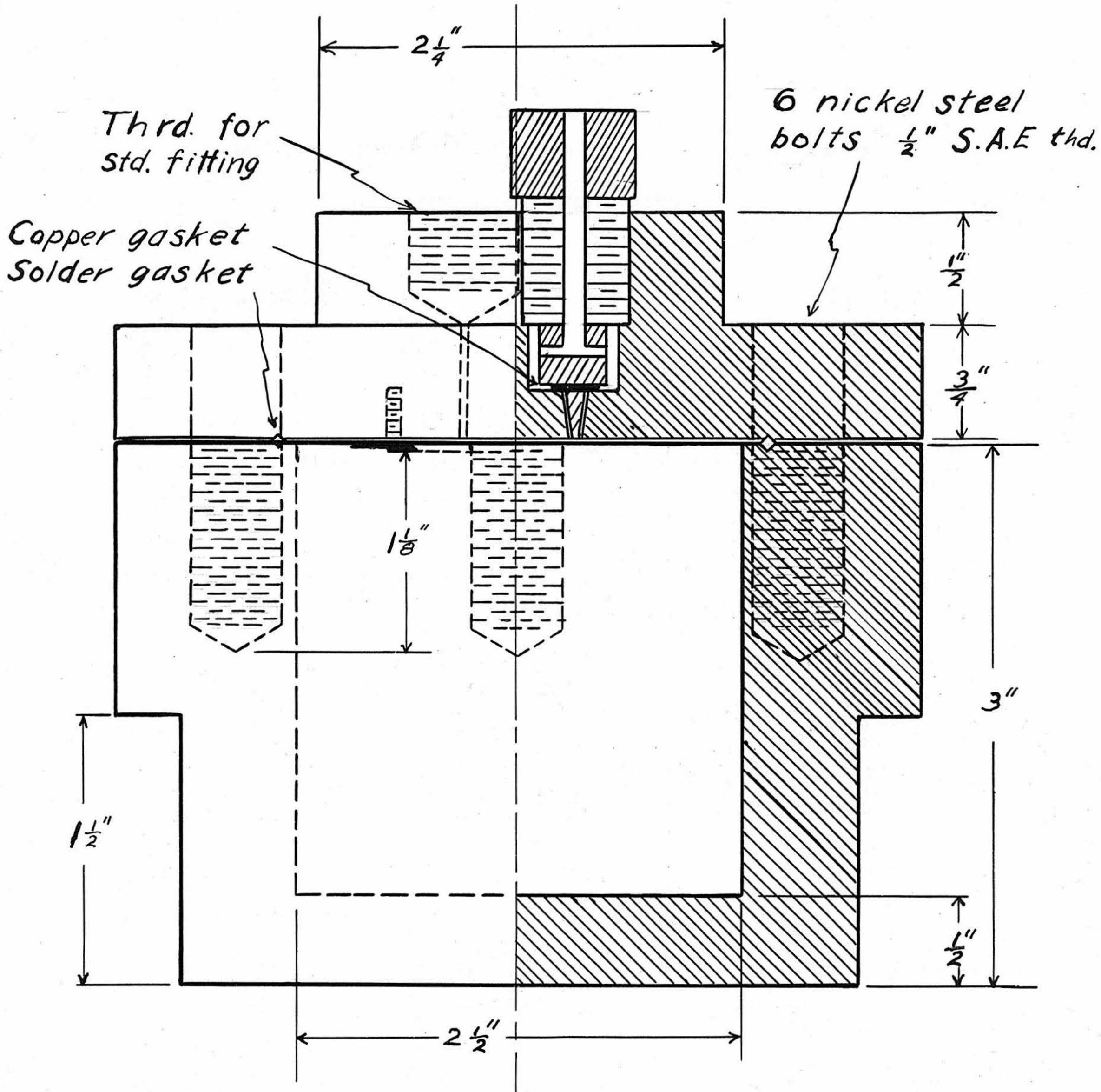
The density of the oils was determined by weighing the oil in a calibrated pycnometer.

The average molecular weights of the crudes, kerosene, spray oil, and petrolatum were determined by the freezing-point lowering of benzene.



Apparatus for the Measurement of the Rate of Solution

Fig. 1



Steel Cell

E.S.H.

Fig. 2

Cell Slugs

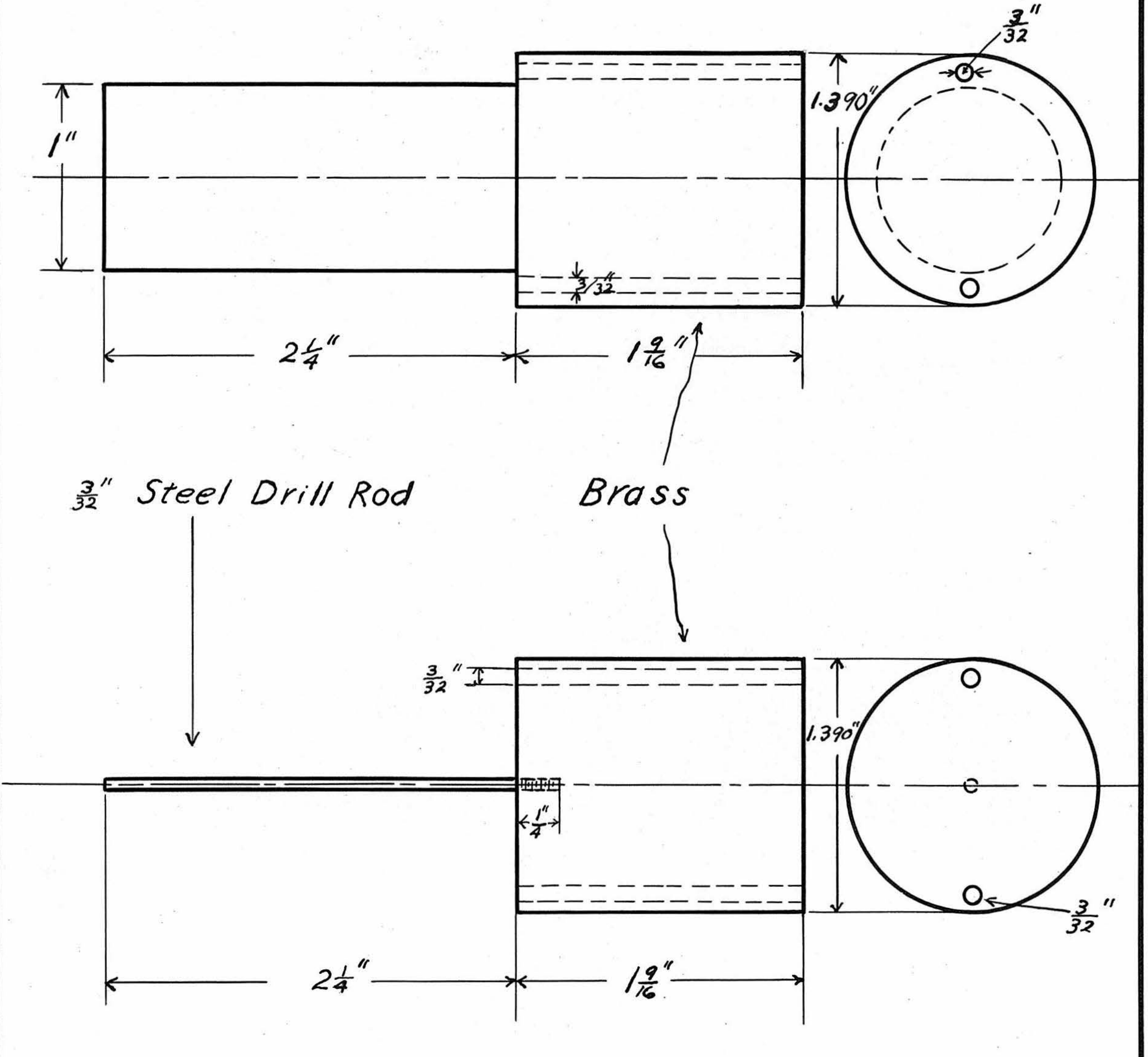


Fig. 3

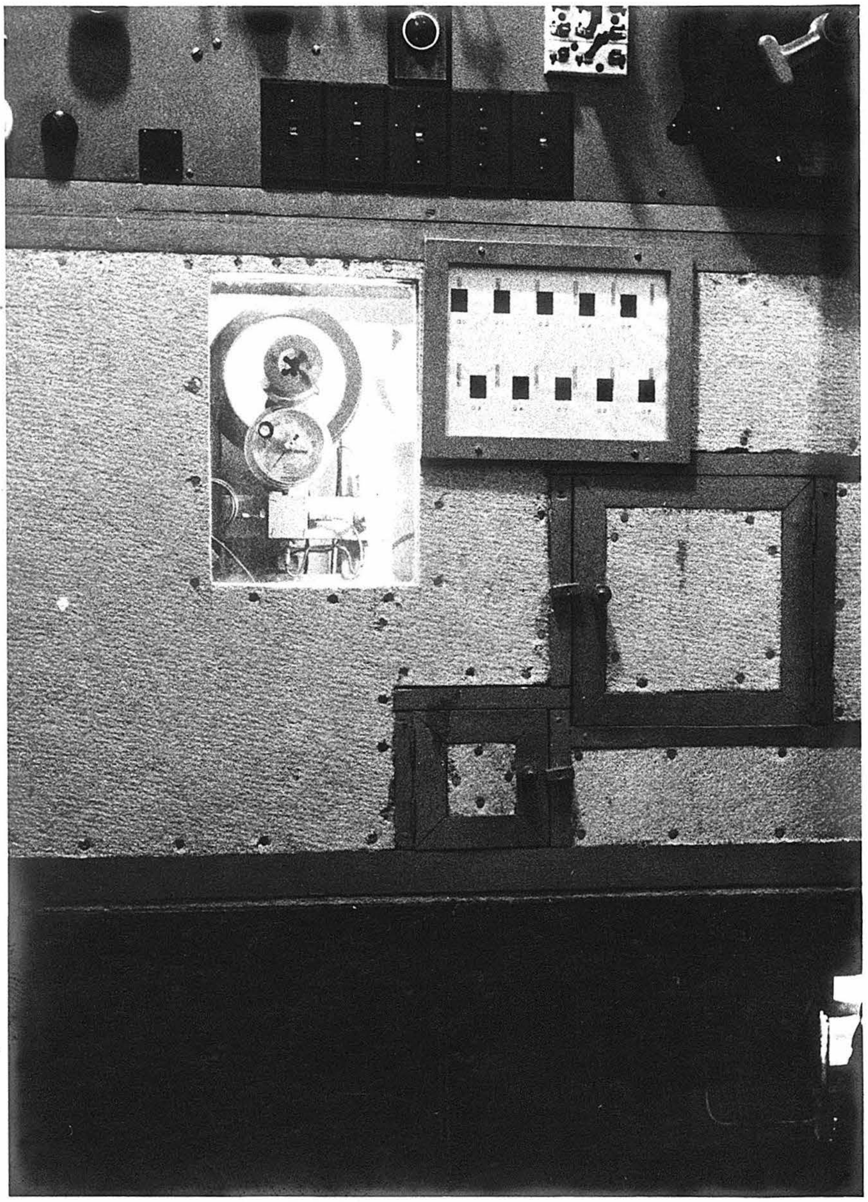


FIGURE 4

Front of Thermostat

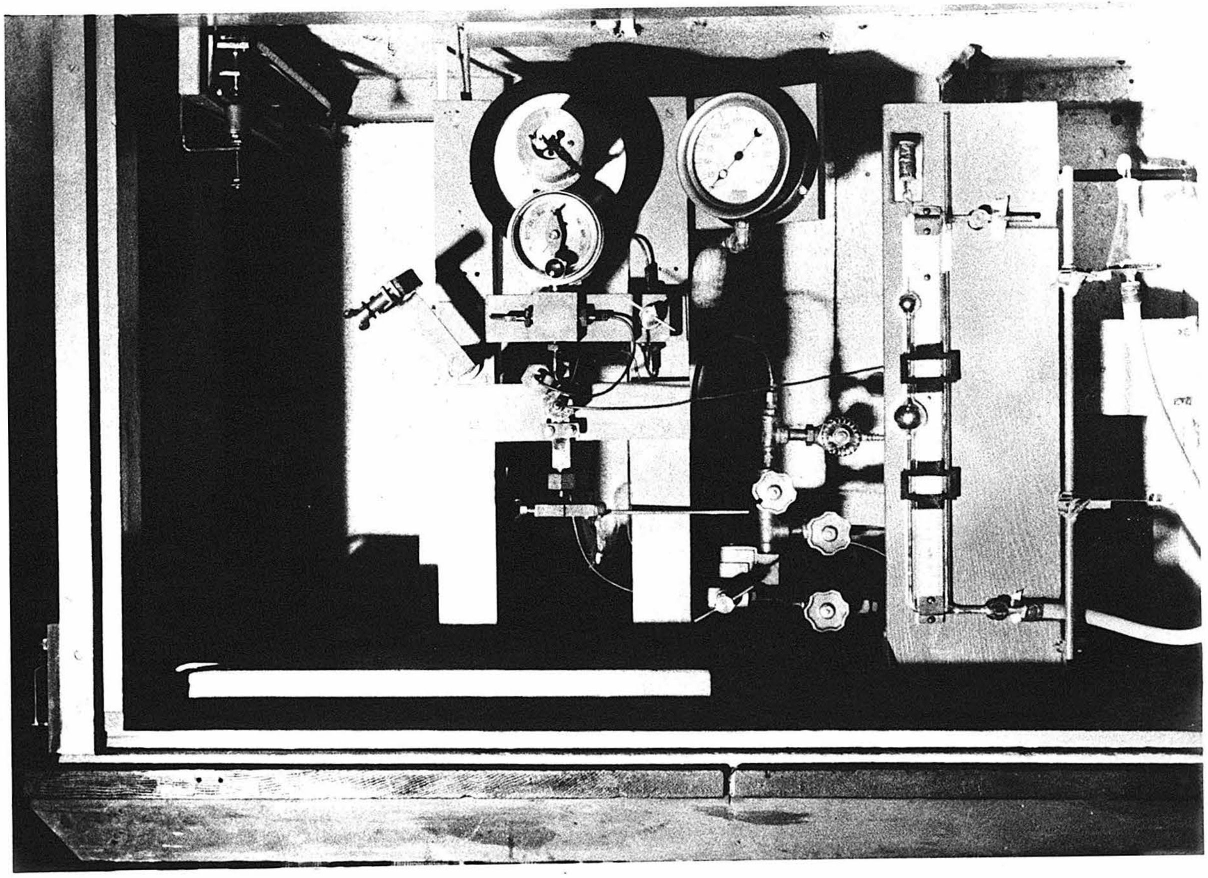


FIGURE 5

Calibrating Burette

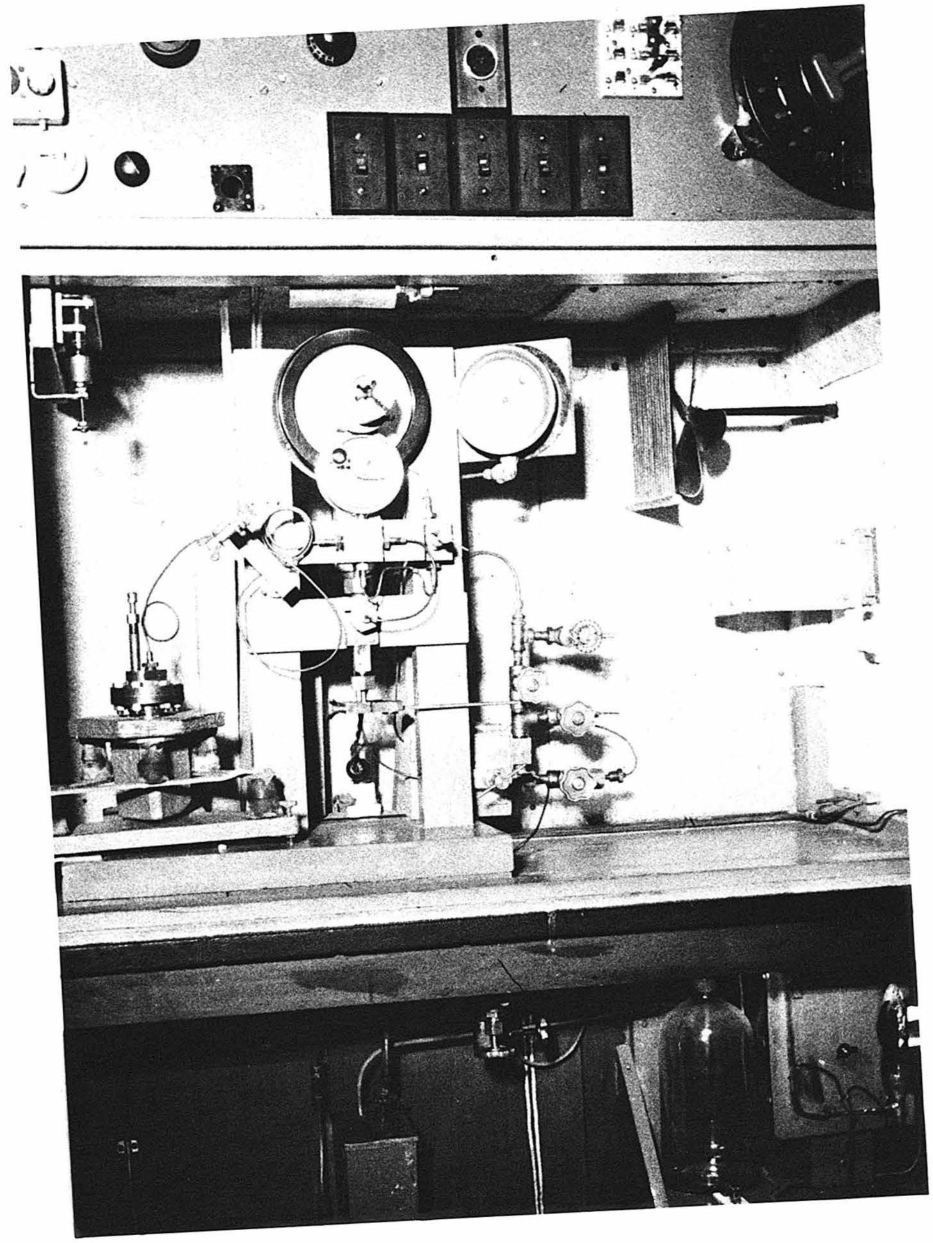


FIGURE 6

Absorption Cell

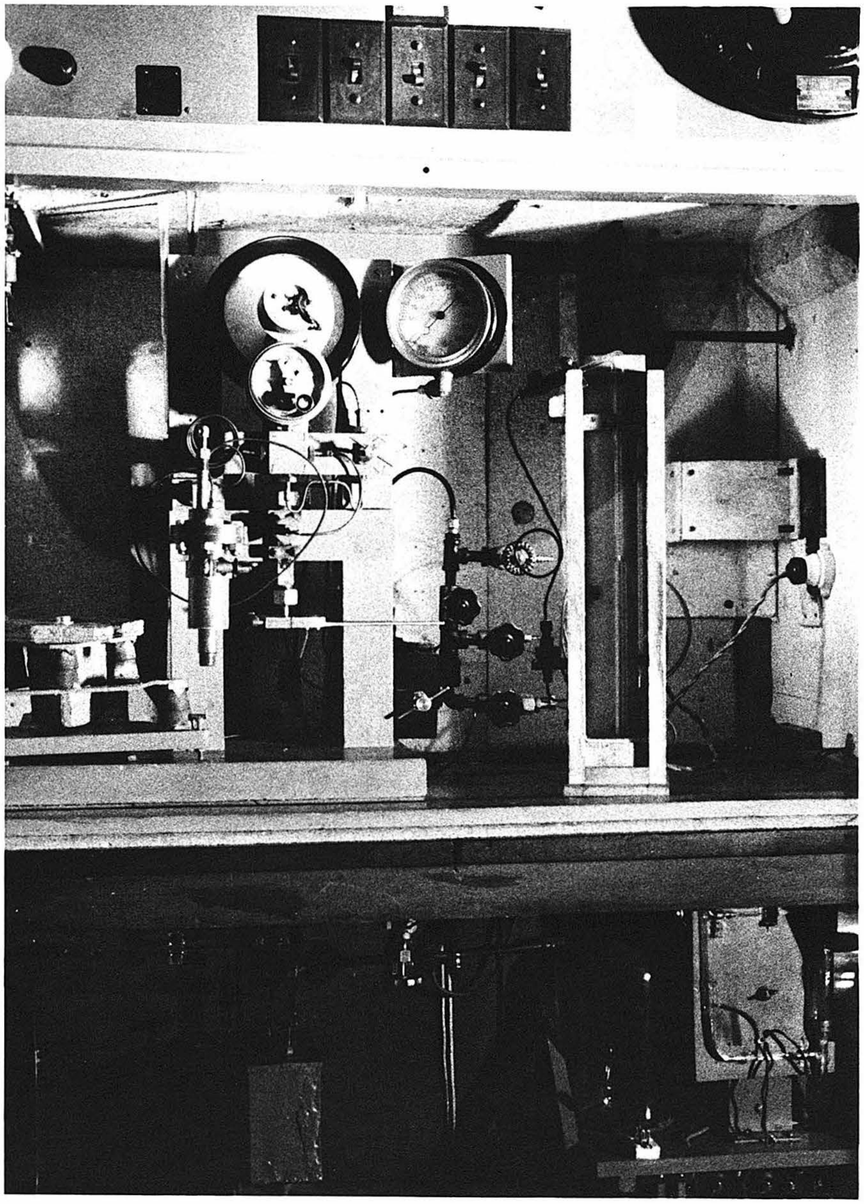


FIGURE 7

Change in Volume Tube

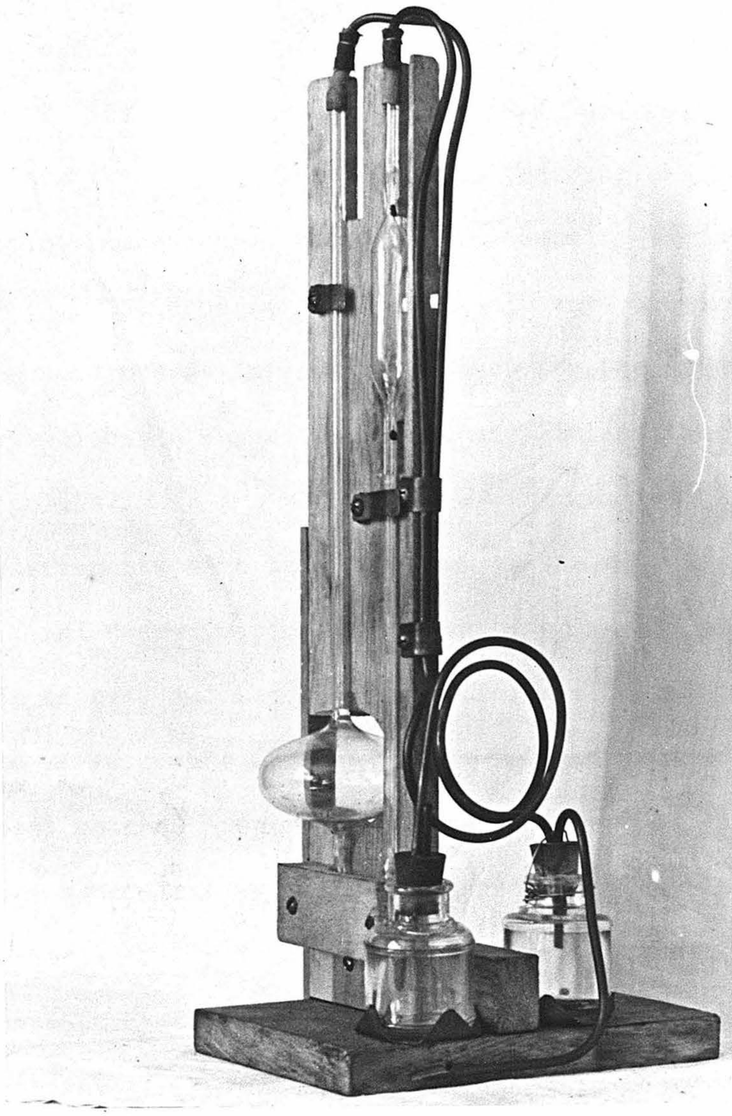


FIGURE 8

Viscometer

Methane

The rates of solution of methane in seventeen oils were measured at 30°C (86°F) and at two or three higher temperatures for four of these oils. This data is given in Tables I and II and the plots of the volume of gas admitted to the cell versus the square root of the time are given in Figures 9 - 30. The run numbers given in the table are the same as those used in the original notes, while the oil or point numbers have been used to identify the points on Figures 27 - 32. The data for Figures 9 - 30 were originally plotted on a scale three times as large as that used for the figures. This was necessary to obtain a reasonable accuracy in locating the lines through the points.

Measurements were made not only of the rate of solution, but also of the final concentration value, the increase in liquid volume upon solution of gas, and the viscosity of the original oil.

The measurements for runs 136 - 160 and C-20 to 25 were made with the purest methane prepared. The plots of experimental data showing the volume equivalent versus the square root of the time will not be discussed individually as in previous theses because the methods of operating the apparatus were standardized to such an extent that there was little variation. An occasional variation is found such as the peculiar curvature at the beginnings of Runs 138 and 144. This is probably due to faulty control valve opening at the beginning of the run, permitting the gas to be admitted too rapidly. However, this is of small importance because the points before the end of the first half hour are seldom given any weight in drawing the line. Missing points such as in 137, 144, 152 are due again to irregular opening of the control valve, or missing a reading, causing a greater pressure variation than that used for the other parts of the run. Check runs have consistently shown this variation to have no appreciable effect on the slope, altho it is undesirable. A column in the table is designated "cell" because the cross-section area used in all the runs is not the same. The area of cell B was 9.935 cm^2 at 30°C. For cell B with ss slug, the area was 9.891 cm^2 In cell S the area was 31.467 cm^2 The determinations made on the same oil with different cell areas gave the same diffusion constant as shown by 148, 157, and by 155, 156. Several runs with spray oil in B did not check 158, 159, but the slope was so low that it could not be determined very accurately. Furthermore, the reservoir gauge was erratic during these runs, and failed at the soldered point where the cap is screwed on the end of the tube during the last of this group of runs not reported. Run 133 was made with a gas whose nitrogen content is uncertain; altho reported as 2%, it was probably considerably less. This run and 139 were made with the air evacuated from the cell and the oil. The variation from the determinations made with one atmosphere of air in the cell and oil is within the experimental error. This is quite fortunate because the removal of the dissolved air from the crudes without changing their composition would have required an extensive setup. The fact that the air is not removed from the system introduces an error which could not be neglected if the apparatus were designed to give a high degree of accuracy.

The expansion of the liquid due to the solution of gas was determined with the change in volume tube and shown in the column as percent increase in volume. From this data and the final equilibrium concentration the value ϵ' was calculated for the apparent increase in volume of the oil for each unit volume of gas dissolved. Following this the true value of ϵ was calculated. The apparent value is used to correct the apparent concentration to obtain the value of S which is the equilibrium quantity of gas dissolved in a unit volume of original oil. Dividing this by the final solution volume gives C_s which is the equilibrium quantity of gas dissolved in a unit volume of solution. The gas volumes were calculated for 30°C and one atmosphere in the experimental work and corrected to 60°F and 30 inches of mercury for the final values.

From the corrected slope of the line of the quantity of gas admitted to the cell versus the square root of the time and the equilibrium concentration C_s the diffusion constant was calculated as follows:

$$D = k\left(\frac{m}{C_s}\right)^2$$

where k contains the area of the oil surface and other constants. At 30°C it has the following values: for the B cell, 1.3262×10^{-4}; for B_{ss}, 1.3380×10^{-4}; for B_{ls}, 5.392×10^{-4}; and for S, 0.13220×10^{-4}. This method of calculating and correcting the various factors has been completely described by Pomeroy$^{(2,3)}$. A sample of the calculation of an isopentane run is given in the Appendix.

The experimental data for runs 57 - 62 and C-7 to C-17 (see Figures 18 - 23) were obtained with the older methane which contained a higher nitrogen content. These data are, of course, not as good for this reason and also because the apparatus was not as reliable as it was at a later date when the 30°C determinations were made. However, as will be brought out later, this data should be included to show the effect of increased temperature on the diffusion constant of methane up to 60°C.

Figure 24 shows runs 87 and 88 made at 2000 lbs. per sq.in. with the assistance of the solubility apparatus described by B.H.Sage.(6) This work was preliminary in order to find out whether any large variation in diffusion constant would be found with the use of high pressures. The results indicate some increase in the diffusion constant with pressure, but the change is small compared to that in the case of propane, as will be shown later.

Figure 25 is a plot of two runs made with Santa Fe Springs dry natural gas. These curves have a definite curvature at the beginning that extends well beyond the usual disturbances at the beginning of a run. After a time the rate settles down to the straight line relation. The curvature is due to the higher rate of solution of the ethane and propane in the gas causing them to be depleted in the gas space. During this depletion the composition of the gas in the space over the oil is changing to a different composition from that being admitted to the cell. This change continues to take place until an equilibrium is reached, so that the gas going into solution has the same composition as that of the gas being admitted to the cell. The diffusion constant for this dry natural gas after the rate had settled down to a regular square root relation is about 10% greater than that for pure methane. Some preliminary calculations on the probable rates of solution of a methane-propane mixture showed that the composition of the gas over the oil will be different from that admitted to the cell, except for one particular composition of the gas over the oil at each pressure. The composition of the gas over the oil will be very low in propane. This is due to the widely different solubilities of methane and propane.

Figure 26 is the plot of temperature versus viscosity used to obtain the 60°C values for Rosecrans and Bradford crudes. This was necessary because the change in composition of the crudes at this temperature was so rapid, in spite of the vapor bottles, that a value could not be obtained and extrapolation had to be resorted to.

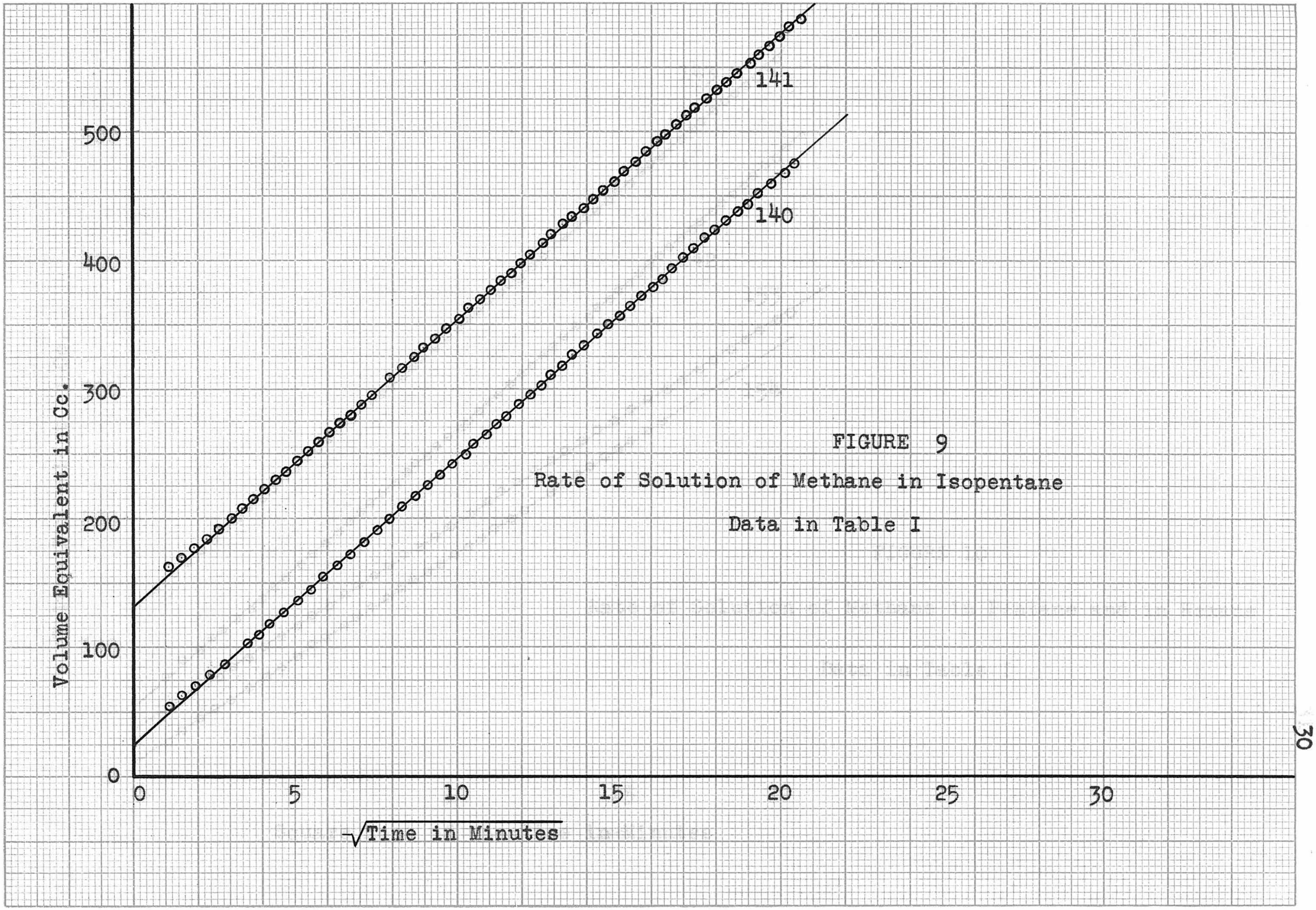


FIGURE 9

Rate of Solution of Methane in Isopentane

Data in Table I

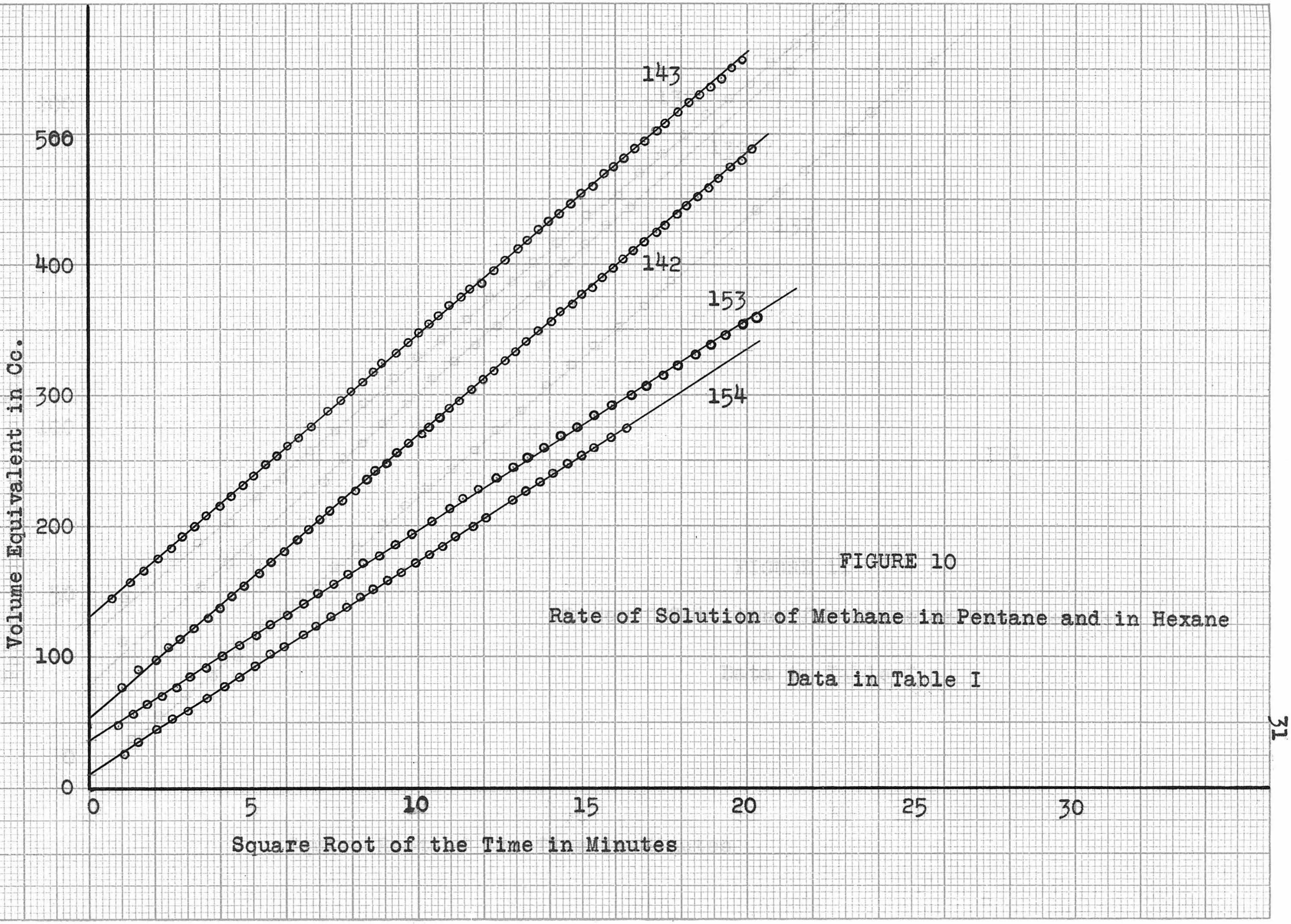


FIGURE 10

Rate of Solution of Methane in Pentane and in Hexane

Data in Table I

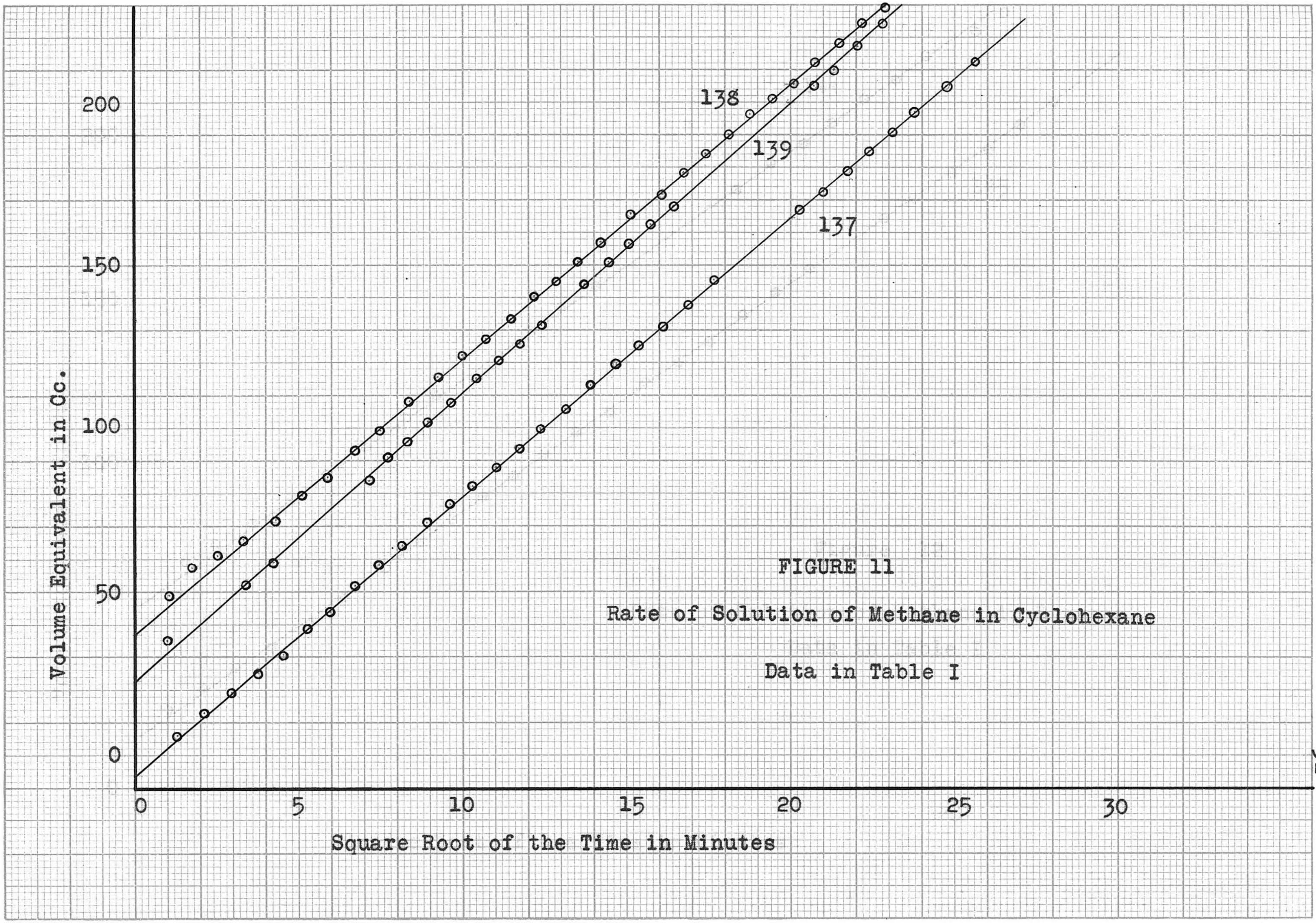


FIGURE 11

Rate of Solution of Methane in Cyclohexane

Data in Table I

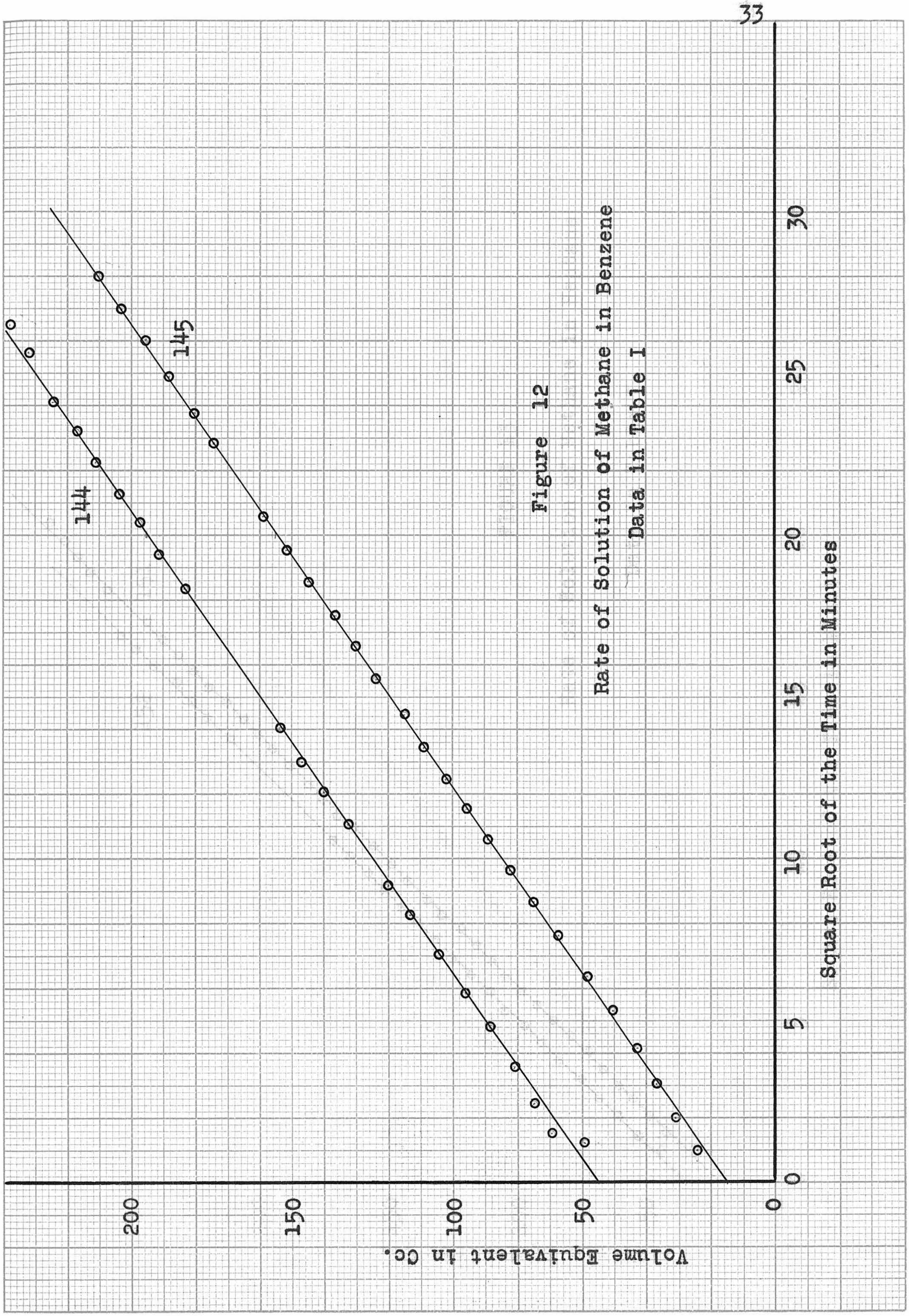


Figure 12

Rate of Solution of Methane in Benzene

Data in Table I

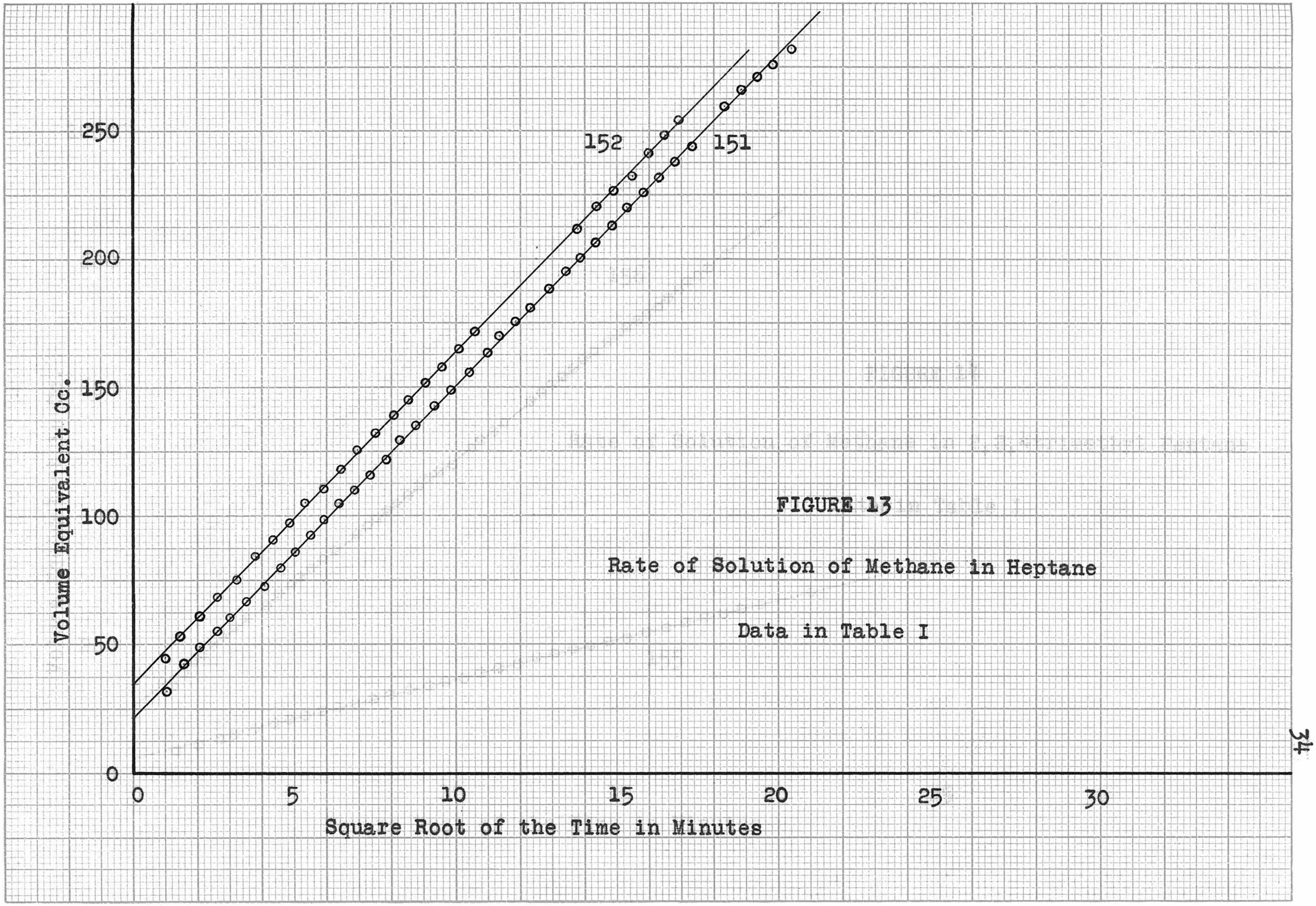


FIGURE 13

Rate of Solution of Methane in Heptane

Data in Table I

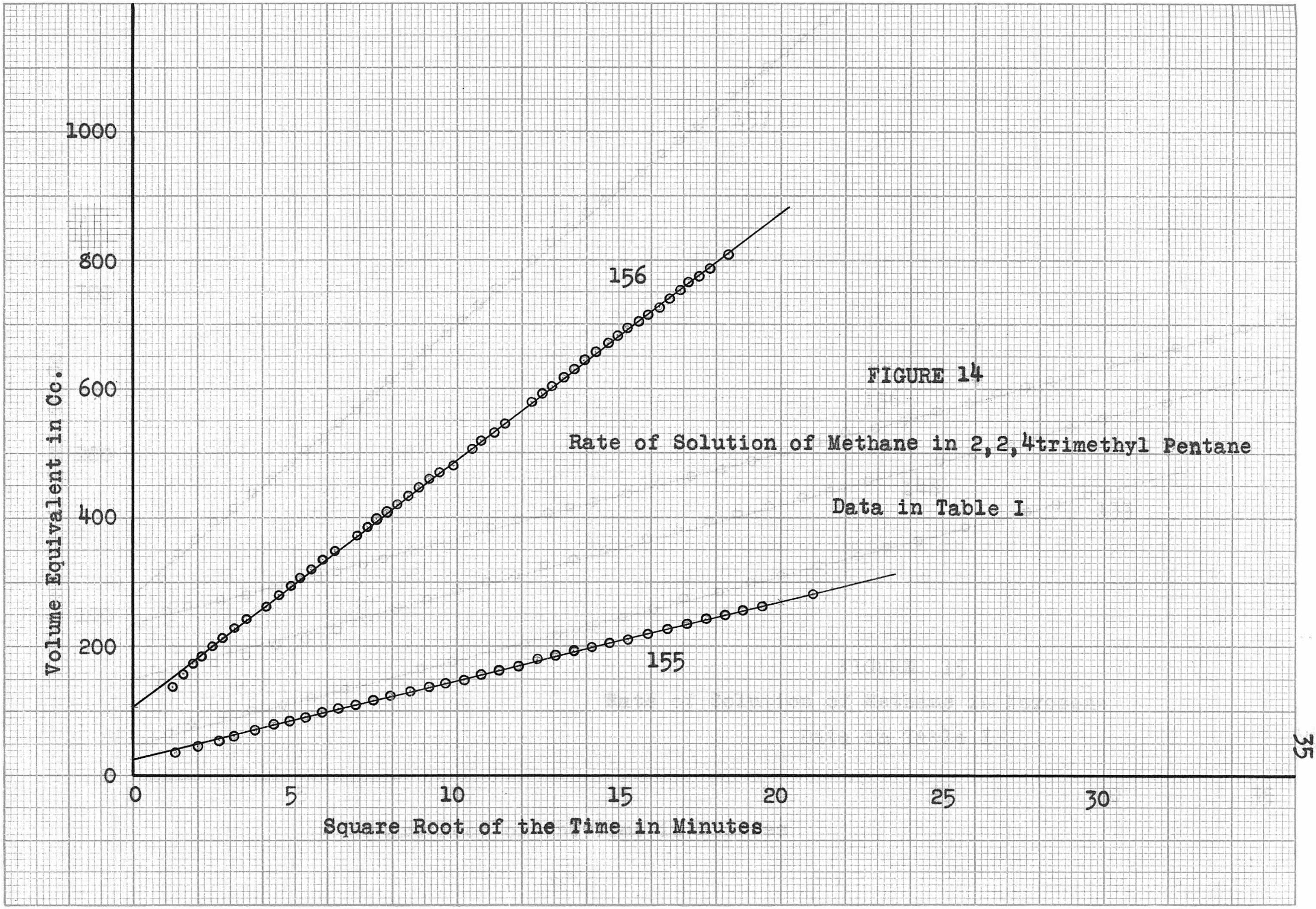


FIGURE 14

Rate of Solution of Methane in 2,2,4trimethyl Pentane

Data in Table I

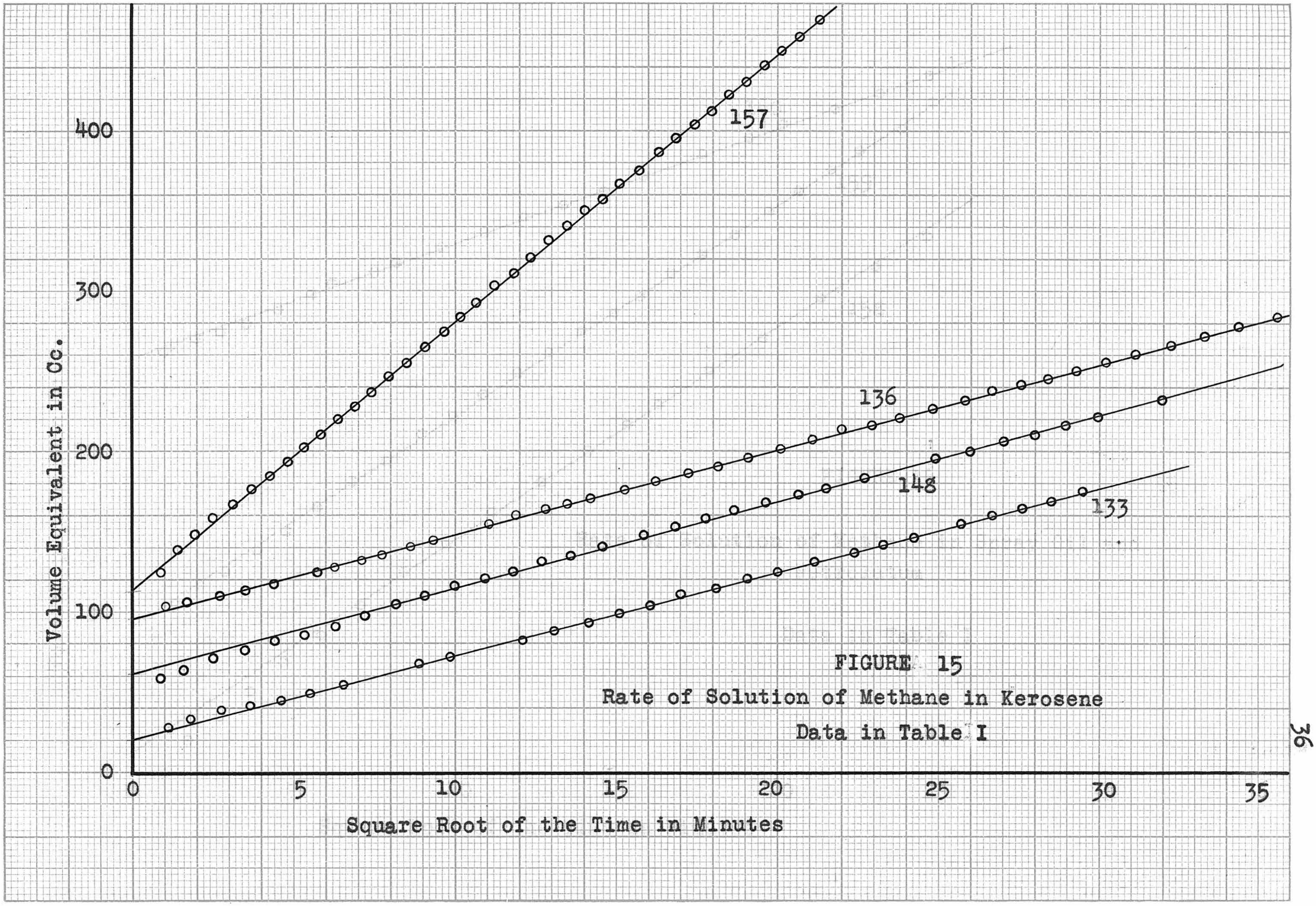


FIGURE 15

Rate of Solution of Methane in Kerosene

Data in Table I

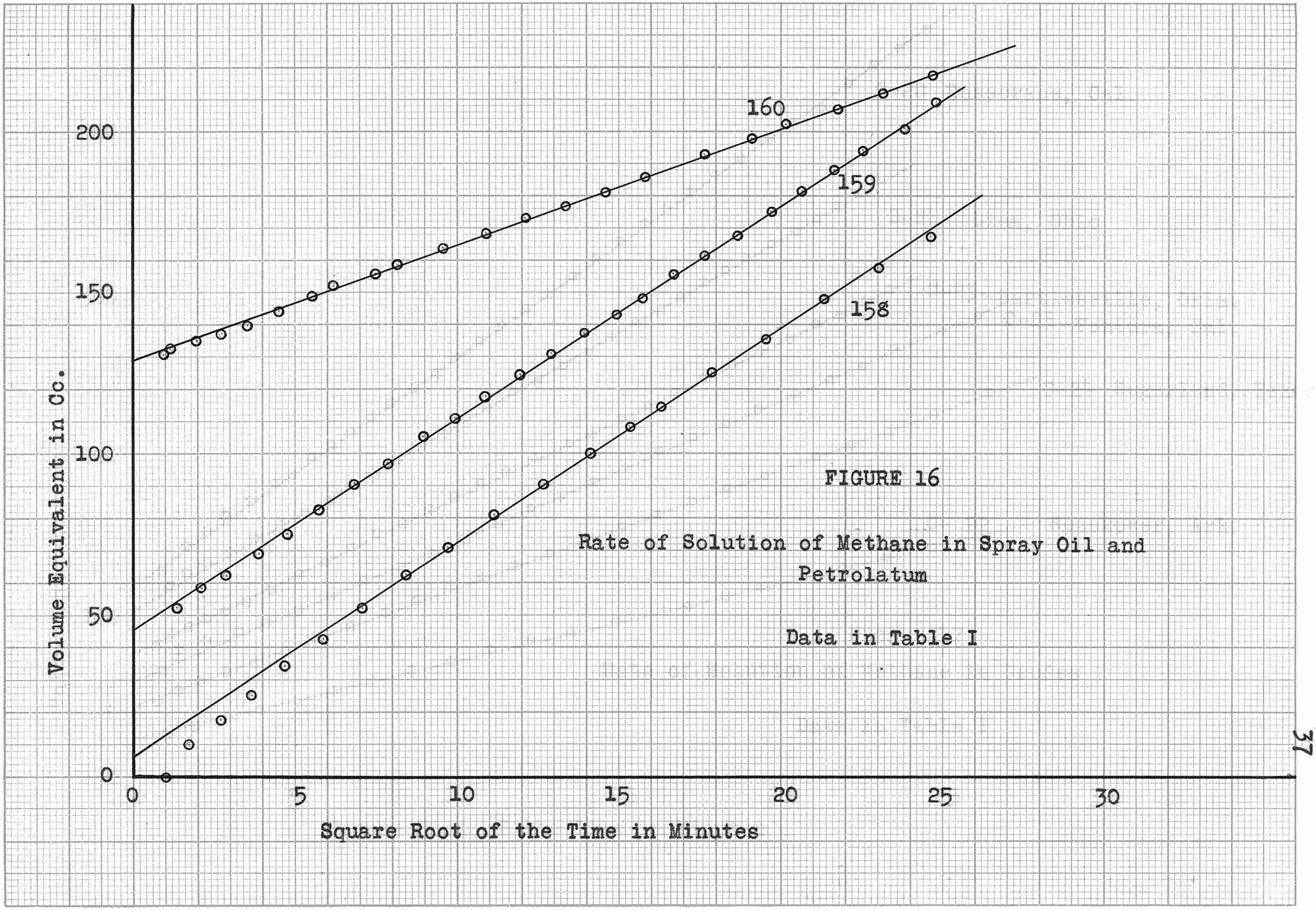


FIGURE 16

Rate of Solution of Methane in Spray Oil and Petrolatum

Data in Table I

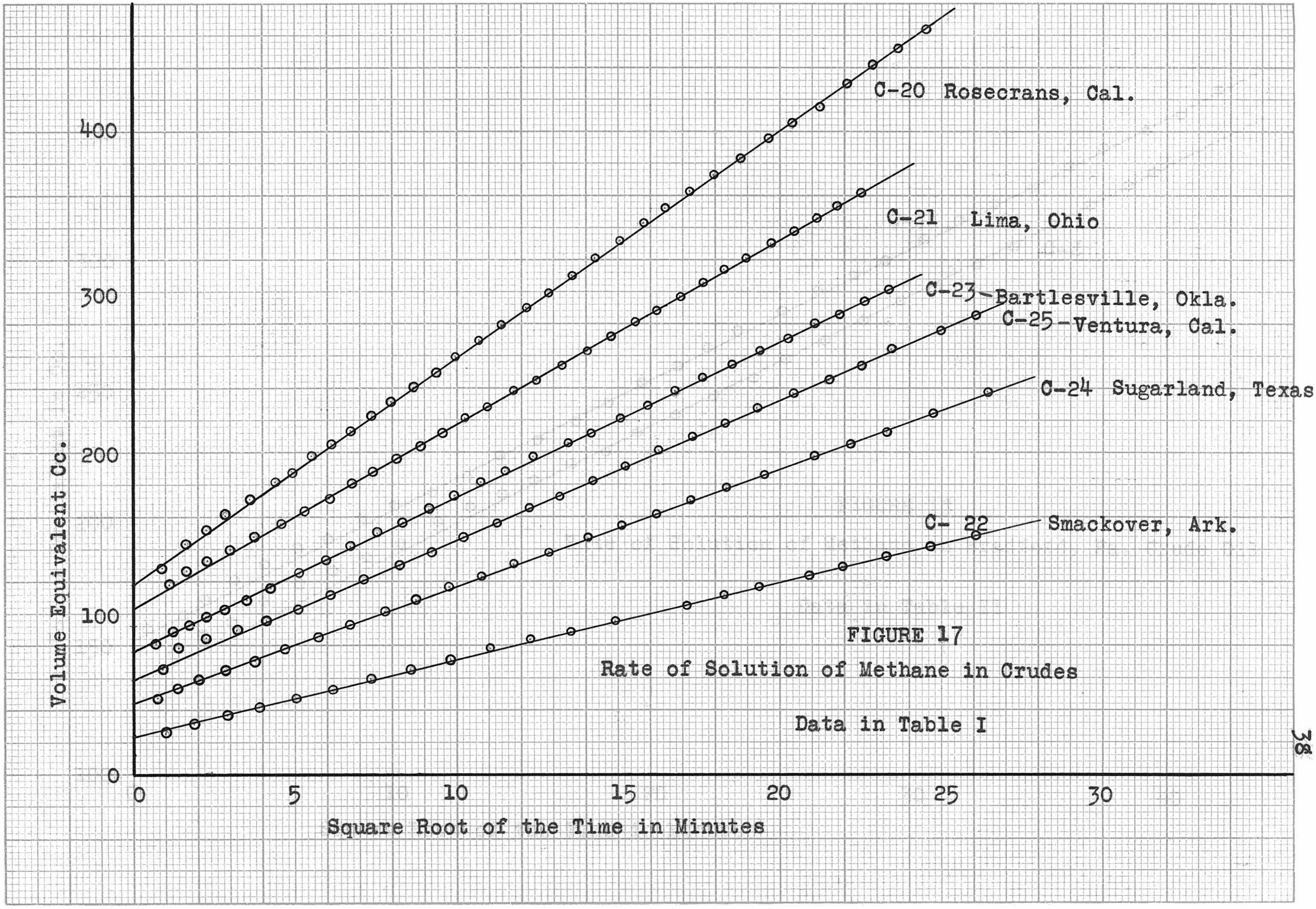


FIGURE 17

Rate of Solution of Methane in Crudes

Data in Table I

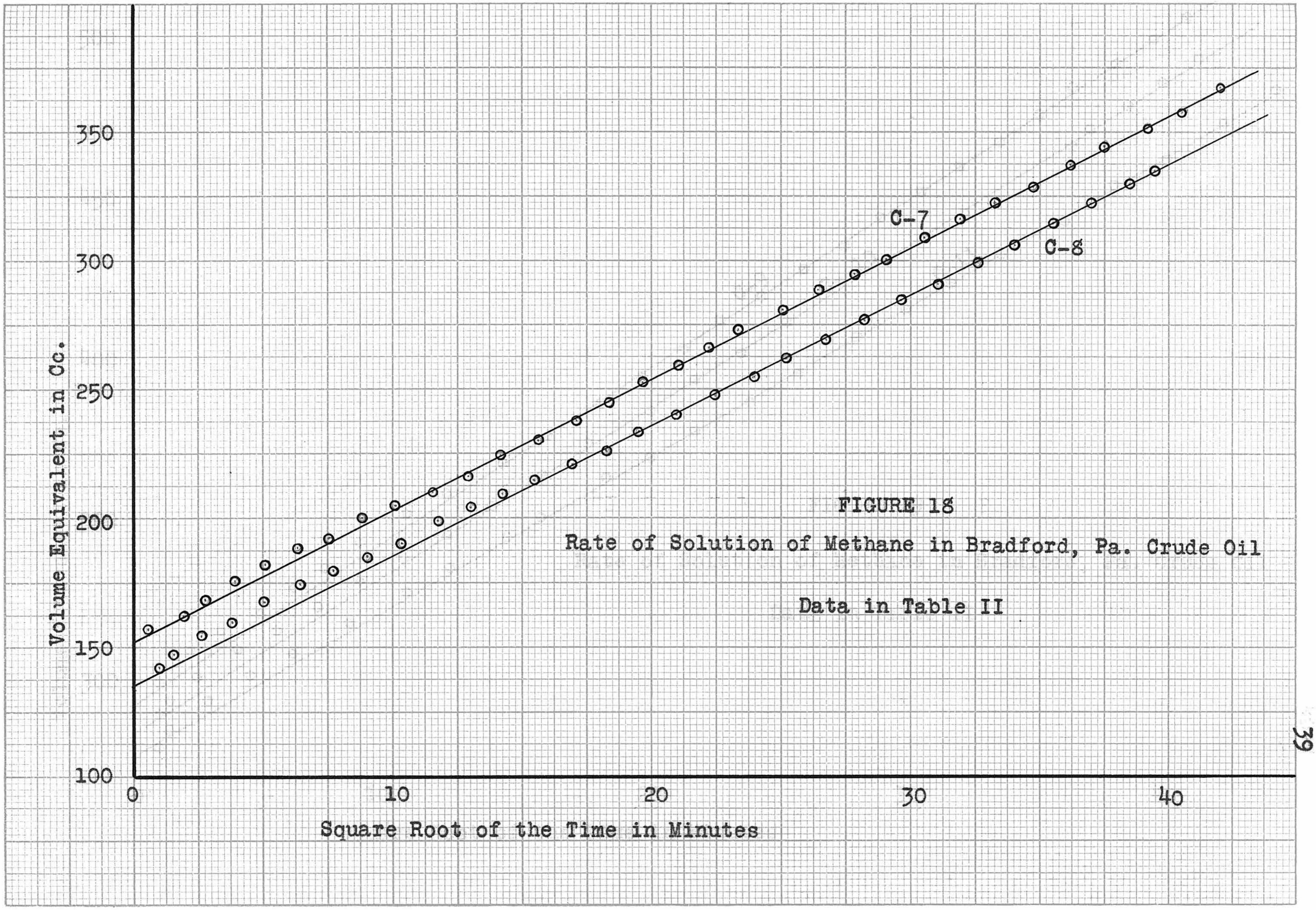


FIGURE 18

Rate of Solution of Methane in Bradford, Pa. Crude Oil

Data in Table II

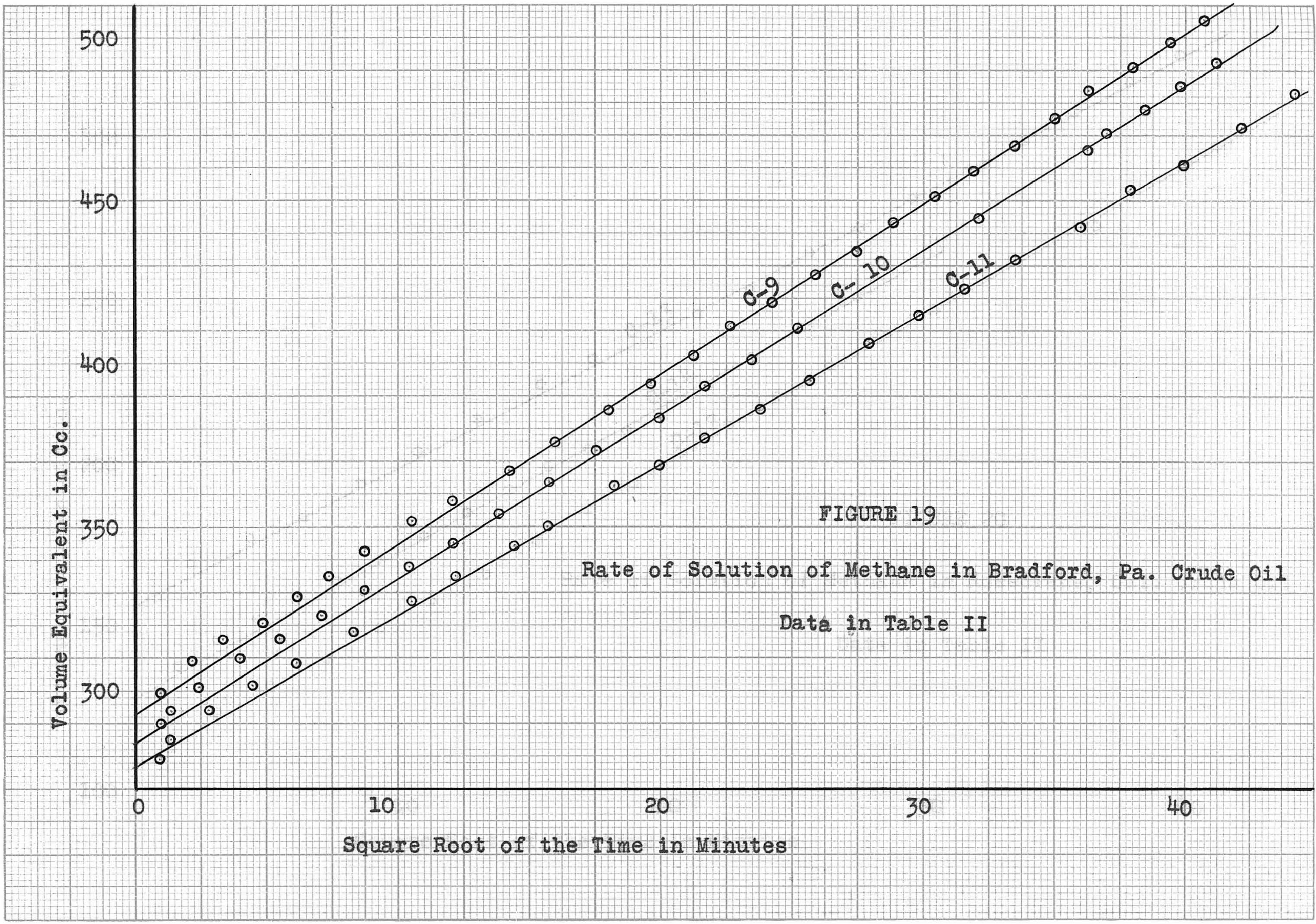


FIGURE 19

Rate of Solution of Methane in Bradford, Pa. Crude Oil

Data in Table II

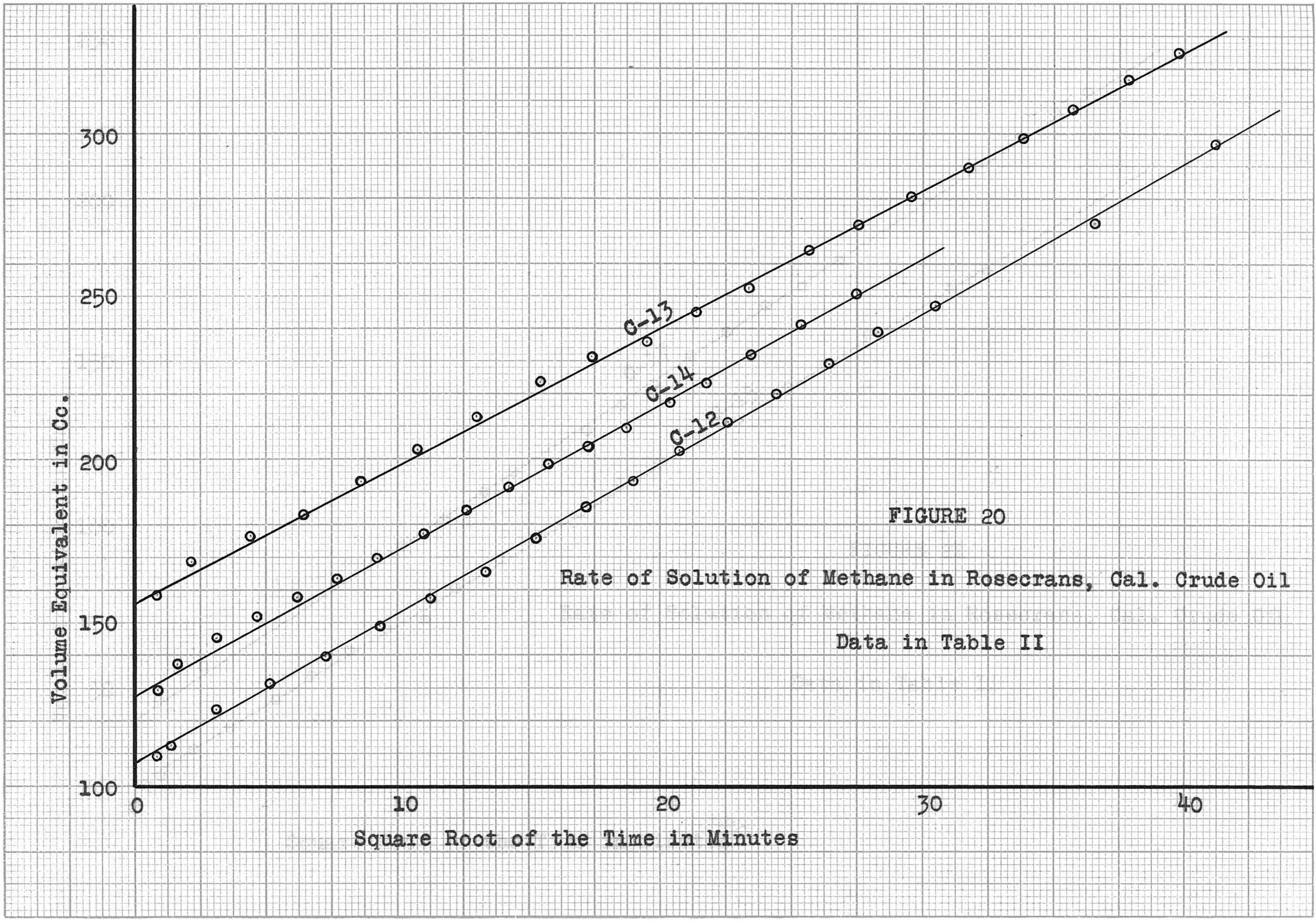


FIGURE 20

Rate of Solution of Methane in Rosecrans, Cal. Crude Oil

Data in Table II

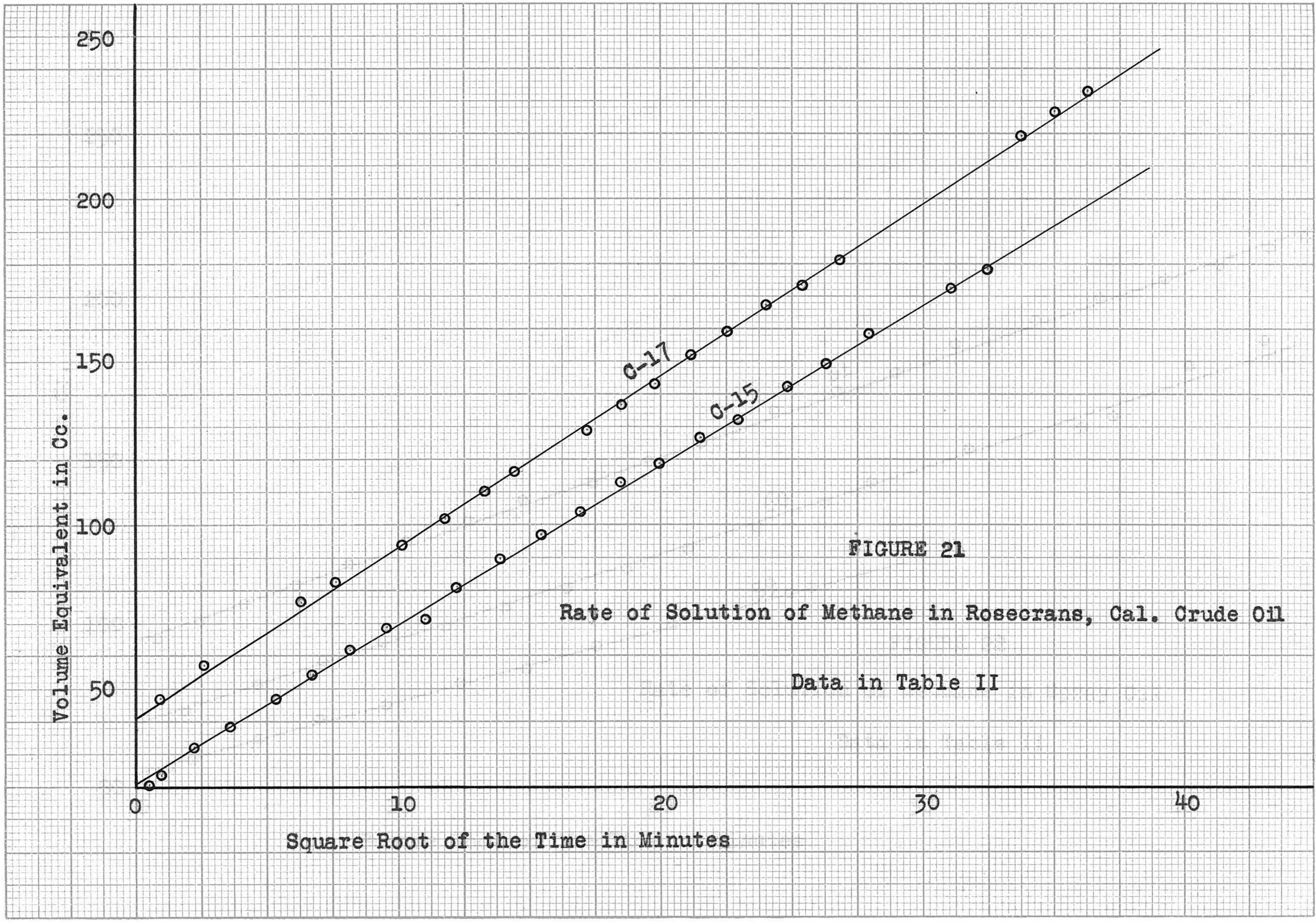


FIGURE 21

Rate of Solution of Methane in Rosecrans, Cal. Crude Oil

Data in Table II

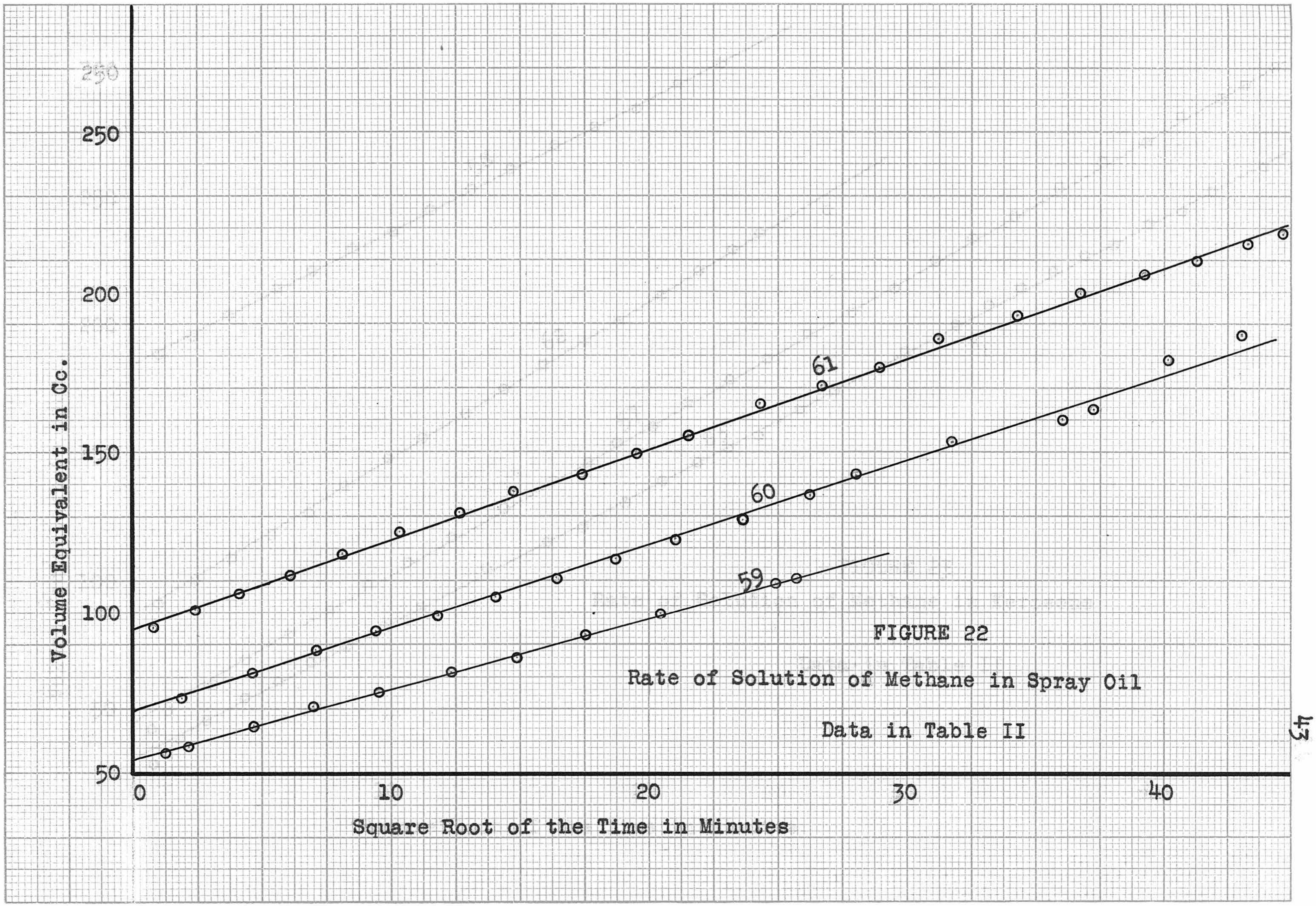


FIGURE 22

Rate of Solution of Methane in Spray Oil

Data in Table II

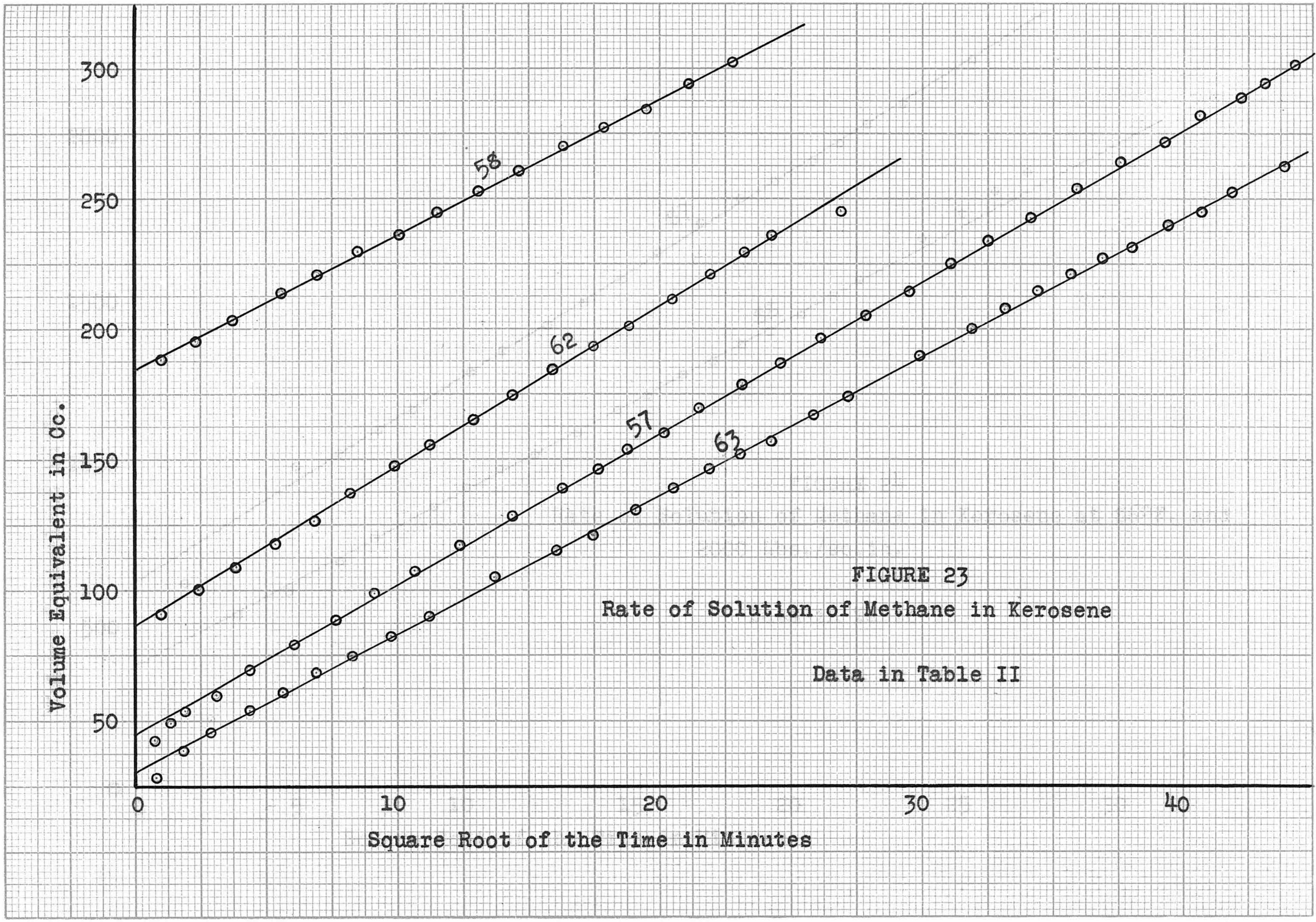


FIGURE 23
Rate of Solution of Methane in Kerosene

Data in Table II

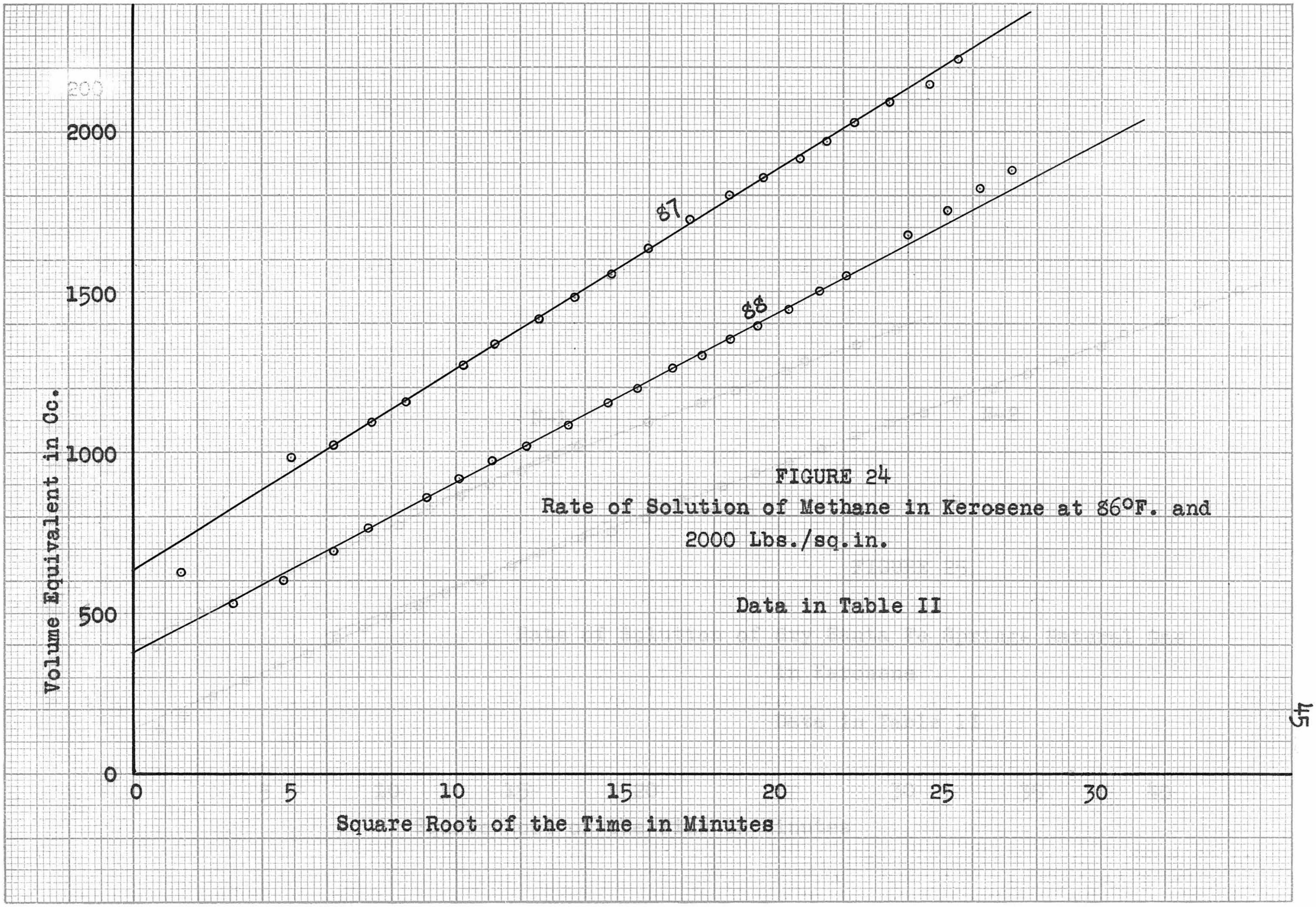


FIGURE 24

Rate of Solution of Methane in Kerosene at 86°F. and 2000 Lbs./sq.in.

Data in Table II

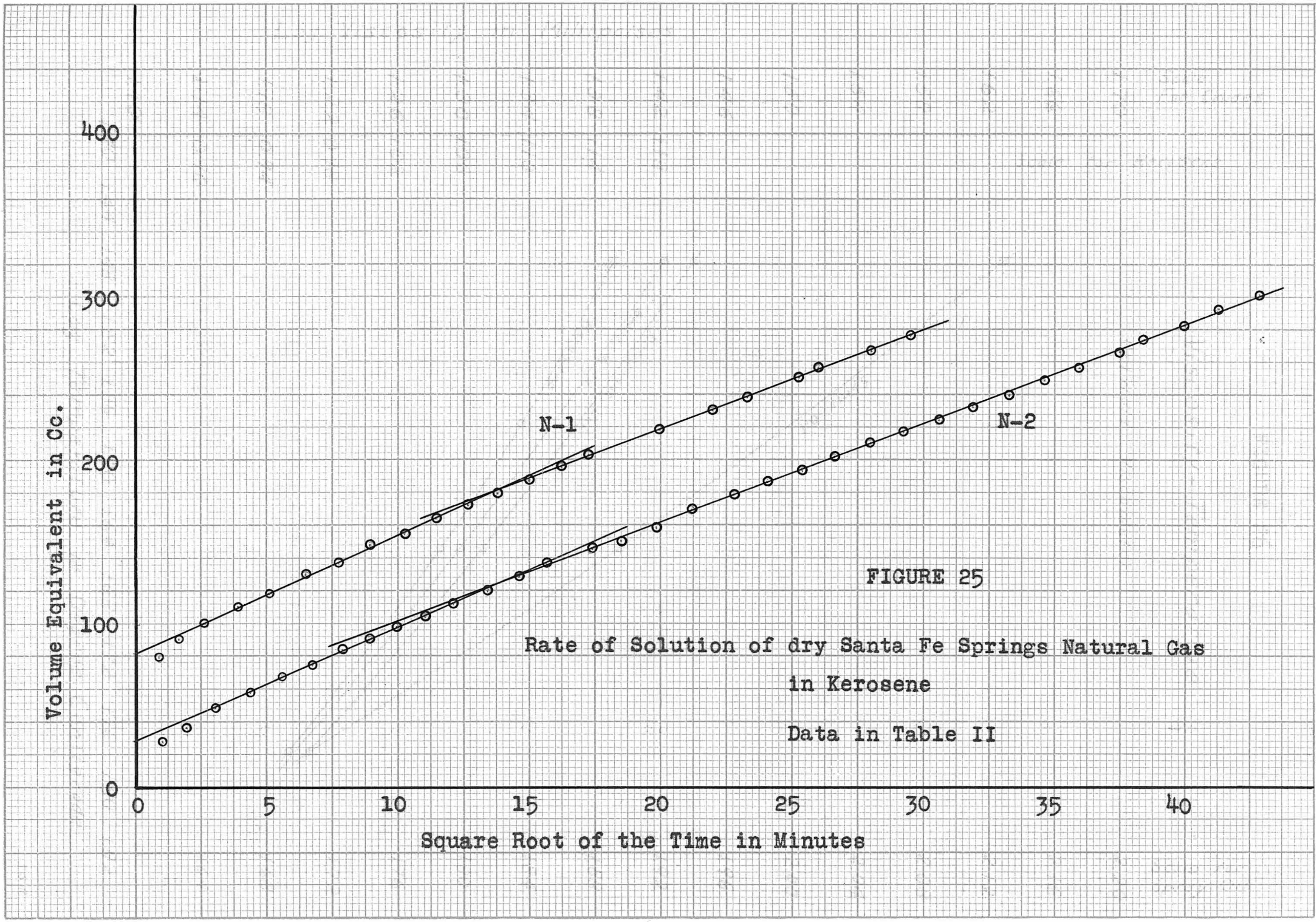
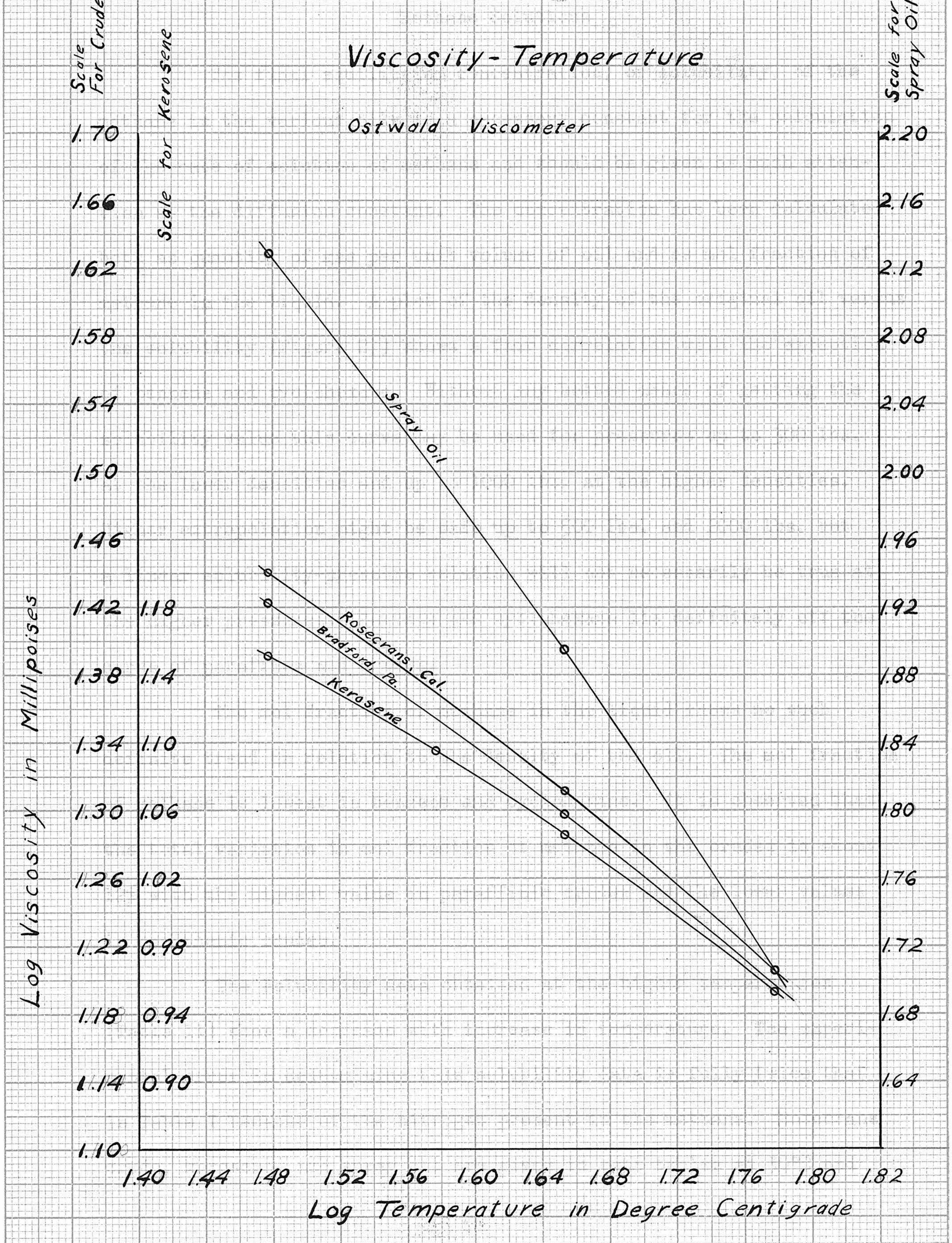


FIGURE 25

Rate of Solution of dry Santa Fe Springs Natural Gas in Kerosene

Data in Table II

FIGURE 26



Viscosity - Temperature

Ostwald Viscometer

Methane Solutions

The final equilibrium concentration, or solubility, of the methane in the various oils is a necessary constant for the calculation of the rate of solution of methane and should be given as much attention as the diffusion constant. The concentration has been calculated both as quantity of gas per unit volume of oil and as mol fraction of methane in the liquid. A plot of the density of the original oil versus the solubility (Figure 27) shows a fair correlation with the exception of benzene and cyclohexane. Without any better means of getting the solubility value this curve may be used for pressures up to 300 lbs. at the lower densities and up to 1000 lbs. at the higher densities. Higher extrapolation might be safe up to 500 lbs. and 2000 lbs. but a linear solubility-pressure relation will not necessarily be true at the higher pressures. Benzene and cyclohexane lie definitely off the curve of paraffins and crudes.

The mol fraction of methane in the liquid shows no such definite trend in relation to the density of the oil. The mol fraction of methane is lowest in benzene and cyclohexane. It is observed that the total variation in mol fraction of methane in the crudes is about 12% with the highest value in paraffinic crudes and the lower values in naphthenic crudes.

The solubility data obtained at the higher temperatures (Table II) show a decrease with increase in temperature. The experimental error in determining this solubility data is fully twice that in Table I because of the nitrogen present in the methane. Rosecrans crude, kerosene, and spray oil are given in both tables at 30°C and show deviations of 5.5%, 6.0%, and 5.4%, respectively. These regular low values show that the work with the impure methane is consistent and these solubilities may be corrected by adding 5.5 to 6.0%. However, if such a correction is made, the corrected solubility should not be applied to the experimental data and diffusion constants calculated, because the nitrogen also affected the slope of the rate lines.

At this point comparison will be made with some other solubility data reported. The solubility of methane in isopentane reported by Pomeroy is 28% below that obtained with a purer methane. His low value was due to the high nitrogen content of the gas. It is observed, however, that the effect on the diffusion coefficient is only 5.4% higher which is in the direction expected. Frolich(7) reports data on the solubilities of pentane, hexane, cyclohexane, and benzene from which comparative values were calculated as shown by Table III. The difference is not consistent and is greater than the supposed experimental error of either investigation. Frolich neglects to say how he analyzed his methane for nitrogen. The difference in the case of hexane is partially due to impurity in the oil. Frolich's measurements were made by the method of measuring the gas evolved from a given sample of solution which is the opposite of the method used in obtaining the data for this thesis. Failure to obtain proper separation of the gas from the liquid would have given Frolich this sort of a difference because the most volatile oil, pentane, would have tended to vaporize and be measured as methane, giving a high value for his solubility. The least volatile oil would have tended to retain the most methane in solution at the end of the process and given Frolich low solubility values. This is apparently substantiated by the differences shown, altho Frolich reports having corrected for the solvent vapor pressures, the solubility at one atmosphere, and that he had no trouble in obtaining equilibrium.

In order to check the reproducibility of the solubility results B.H.Sage ran a check with the same methane and pentane in the compression cell described by him(8) giving results that agreed within 2% at 300 lbs. per sq.in. The compression cell value was higher than that obtained in the rate of solution apparatus. However, the check is quite good, considering how widely different the two methods are from each other. This was the first time that a check has been made on the solubility values obtained in the rate of solution apparatus to test the reliability of obtaining the volume of gas in the space over the oil by extrapolating the square root of time versus volume equivalent to zero time.

The increase in the volume of the liquid phase plotted against solubility in Figure 28 was used to obtain the values for petrolatum and the crudes, (Sugarland, Ventura, and Smackover) which could not be run satisfactorily in the change in volume tube due to their high viscosity. In Figure 29 the values of ϵ (cu.ft. increase in volume of liquid per cu.ft. of gas dissolved) have been plotted against the solubility. The value of ϵ does not change with pressure but changes with the oil used as the solvent. For a given oil, it does not change with solubility.(9) From Figure 29 it is to be seen that the same quantity of methane dissolved in different oils gives a different apparent volume for the dissolved methane. This gives a variation in the apparent density of the dissolved gas plotted in Figure 30 as a function of the density of the original oil. Benzene and cyclohexane again do not agree with a line thru the other points. The apparent density of the dissolved gas is seen to increase as the density and molecular weight of the solvent increases.

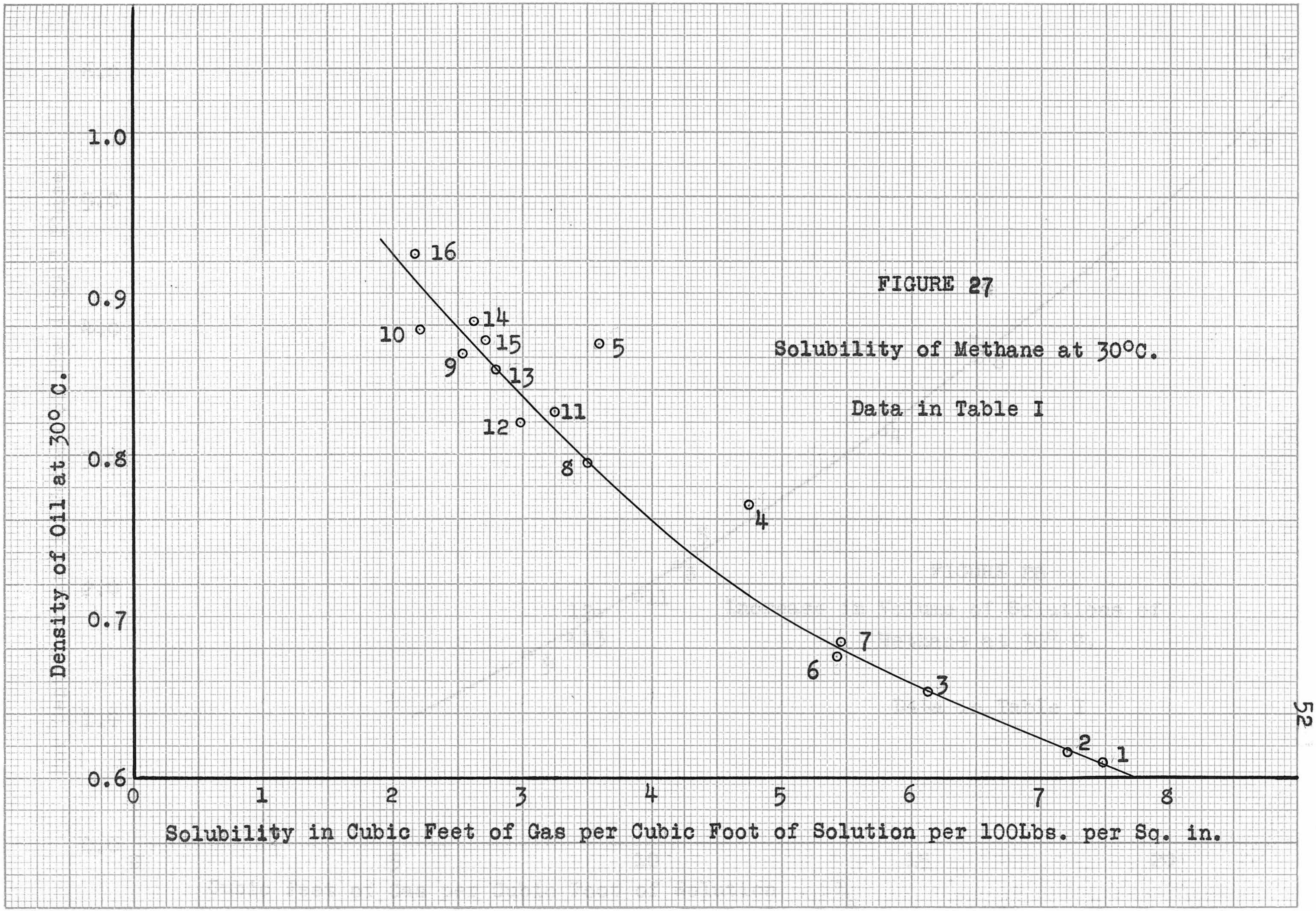


FIGURE 27

Solubility of Methane at 30°C.

Data in Table I

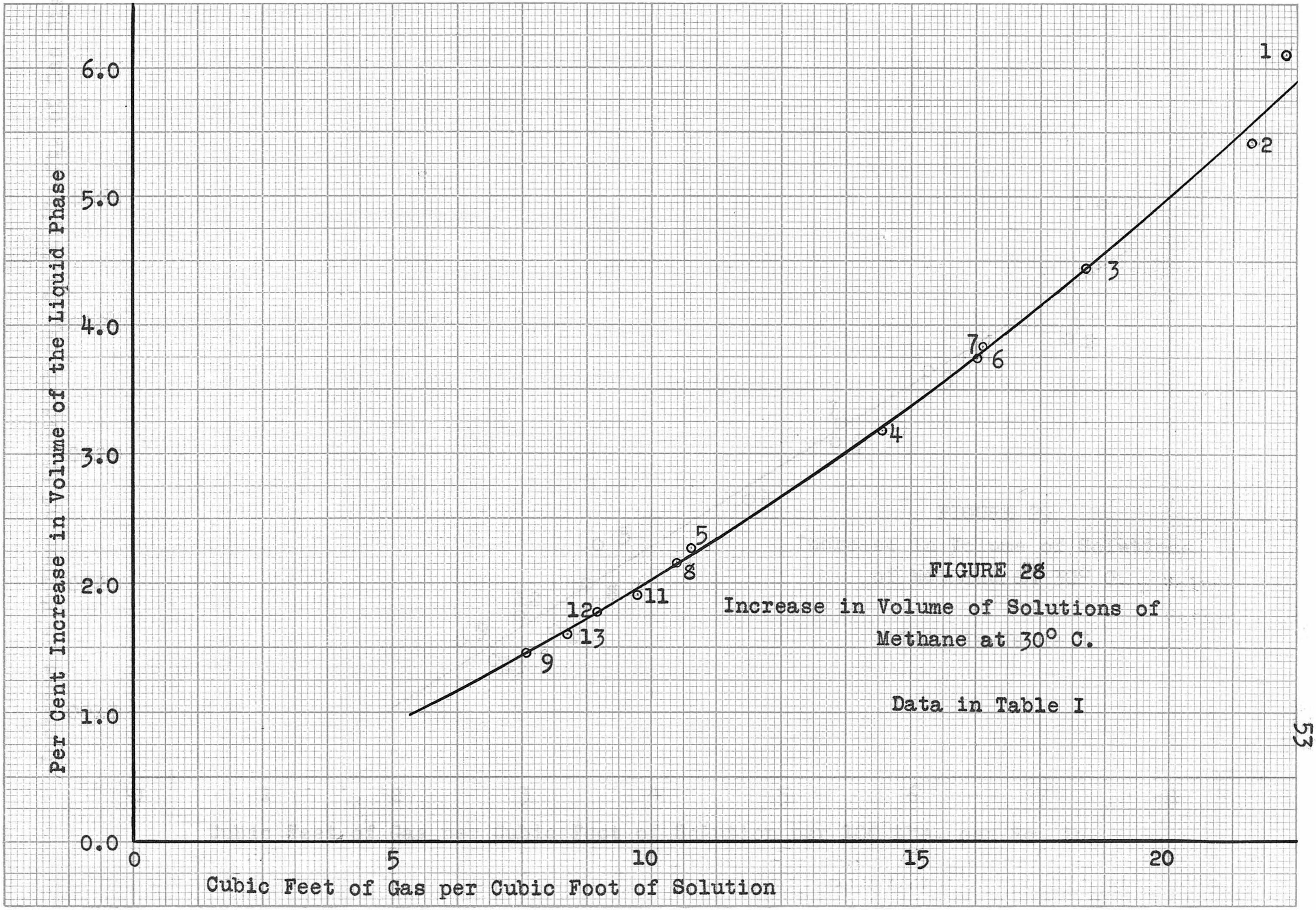


FIGURE 28

Increase in Volume of Solutions of Methane at 30° C.

Data in Table I

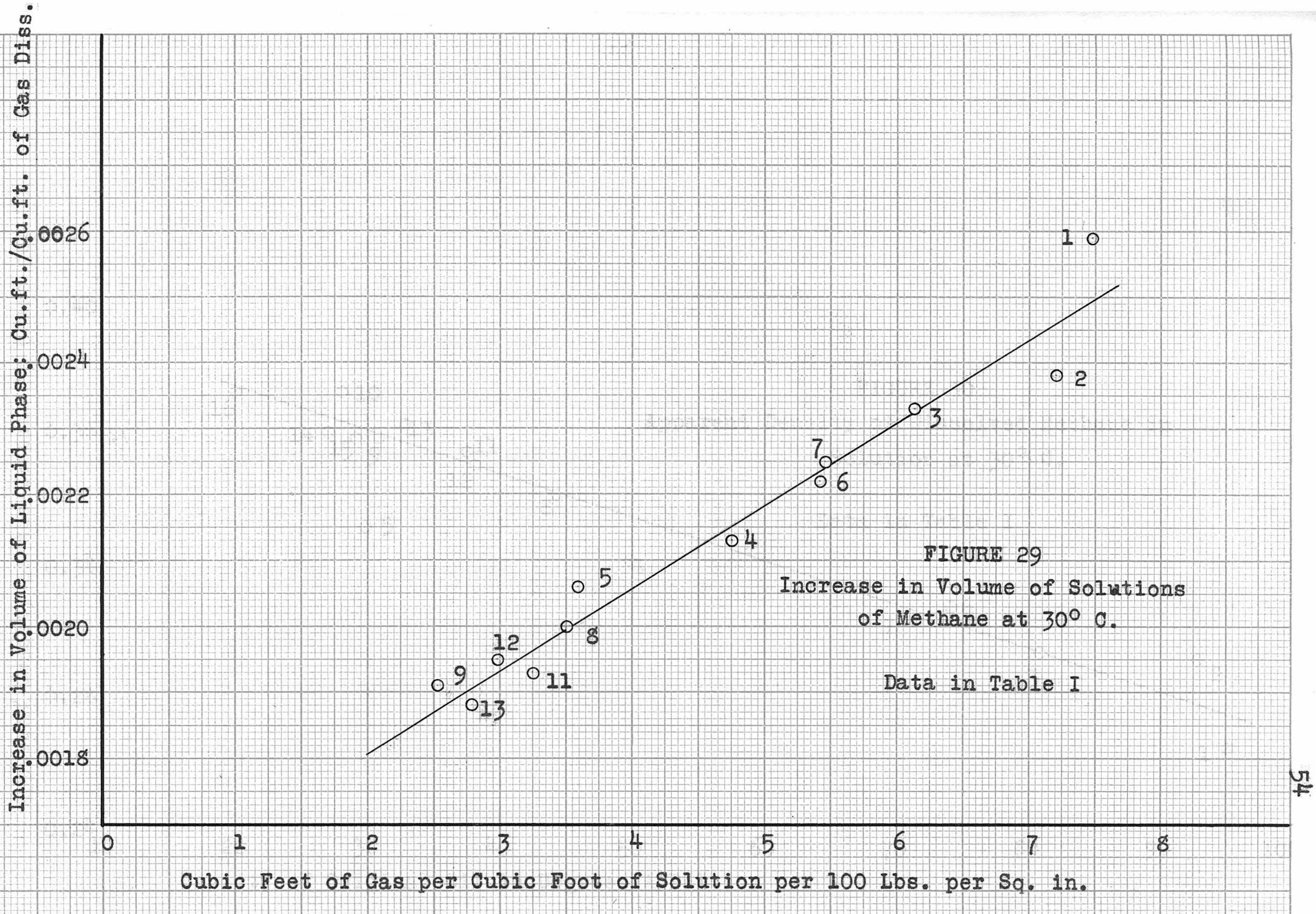


FIGURE 29

Increase in Volume of Solutions of Methane at 30° C.

Data in Table I

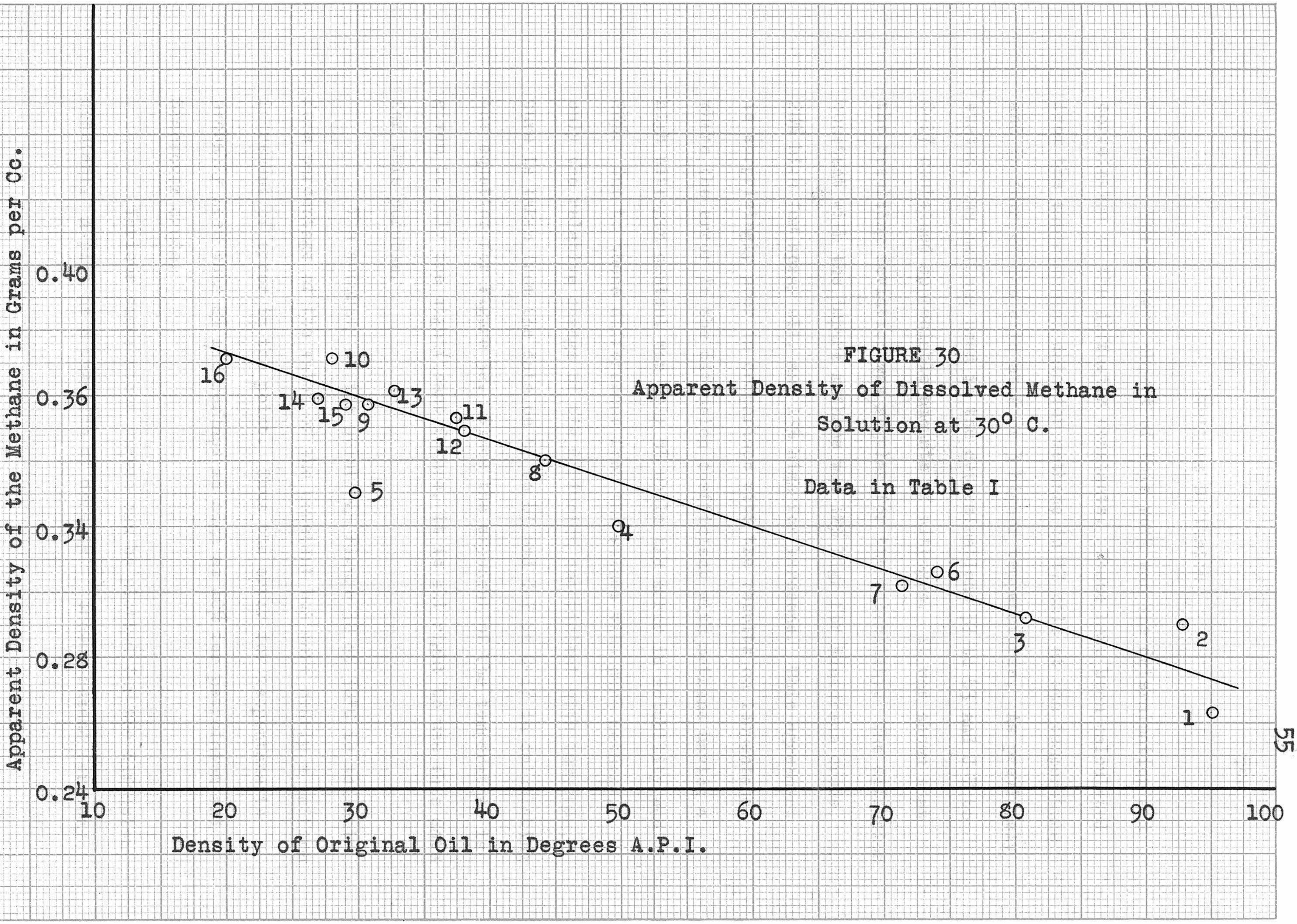


FIGURE 30

Apparent Density of Dissolved Methane in Solution at 30° C.

Data in Table I

Methane Diffusion

The primary object of this work was the determination and correlation of the diffusion constants. These have been calculated from the experimental data for methane in 17 oils at one temperature and in four of the oils at 2 or 3 higher temperatures. As previously stated, the methane used in the determinations 57 to 63 and C-7 to C-17 contained appreciable amounts of nitrogen. It was shown that the resulting deviation was regular for the solubility. The diffusion constant with the impure methane was 12% high for Rosecrans crude, 28% high for spray oil, and 13% high for kerosene. This agreement is surprisingly poor in comparison with the results on isopentane where the error in the diffusion coefficient with methane having a high nitrogen content was only 5% while the error in solubility was 28%. Due to these differences from the values with pure methane, only the relative change of the diffusion coefficient with temperature is taken from the data on 57 to 63 and C-7 to C-17 in calculating the equation for Figure 32. Since the exponent of the temperature is given to only one significant figure, it is all right to use this data for this purpose.

The accuracy of the points in Figure 32 at 30°C is not uniform percentage of the value of the constant but more nearly a uniform increment of error in the point. Thus the error for isopentane is probably less than 2% and perhaps as high as 10% for petrolatum and Smackover crude.

Various correlation curves can be plotted for the diffusion constant. A plot as a function of density(9) shows benzene far away from the other points. A plot as a function of viscosity gives a curve following the axis of the plot (Figure 31). However, when this is plotted on log-log paper the points lie in a reasonably straight line for a constant temperature with the slope of the line greater with higher temperatures. An empirical equation has been calculated for this data which brings the slope of allthe lines at different temperatures down to the same value (Figure 32). This relation is as follows:

$$D = \frac{0.000184}{\eta^{0.528}(t^\circ - 60^\circ)^{0.3}}$$

where D is the diffusion constant in square feet per hour, η is the viscosity in centipoises at the temperature t, and t is in degrees Fahrenheit. This relation is a straight line on log-log paper and should not be extrapolated beyond the region for which it has been calculated. It is at best only a close approximation, but in view of the variety of oils that it covers, it should be quite useful for obtaining values of D if the viscosity of the oil and the temperature are known. The location of the point for Smackover crude above the line is probably not due to experimental error but rather due to the fact that there is another unknown variable not taken into account by the temperature-viscosity relation.

The Stokes-Einstein law for diffusion gives the following relation for the diffusion constant:

$$D = \frac{RT}{N} \frac{1}{6\pi\eta r}$$

where R = the gas constant
T = the absolute temperature
N = Avogadro's number
η = viscosity
r = effective radius of the solute molecule.

The assumption was made in the derivation of this relation that the spherical particles of solute were large compared with the molecules of the solvent. This assumption is sufficient to prevent its application to the diffusion of methane. However, if $D\eta$ = a constant value for one temperature it would hold. As already seen in Figure 32, $D\eta$ is not constant and the law does not hold in this form for the diffusion of methane. Another relation would be true if the law held, namely Dr = a constant. Figure 30 shows that the apparent density of the dissolved gas does not remain constant, consequently its effective molecular radius would not be expected to be a constant in the different solutions.

It is to be observed, however, that the two variables used in the empirical equation for Figure 32 are both present in the Stokes-Einstein diffusion law. Viscosity appears to the -0.528 power instead of the -1. power. The temperature appears to the -0.3 power instead of +1.

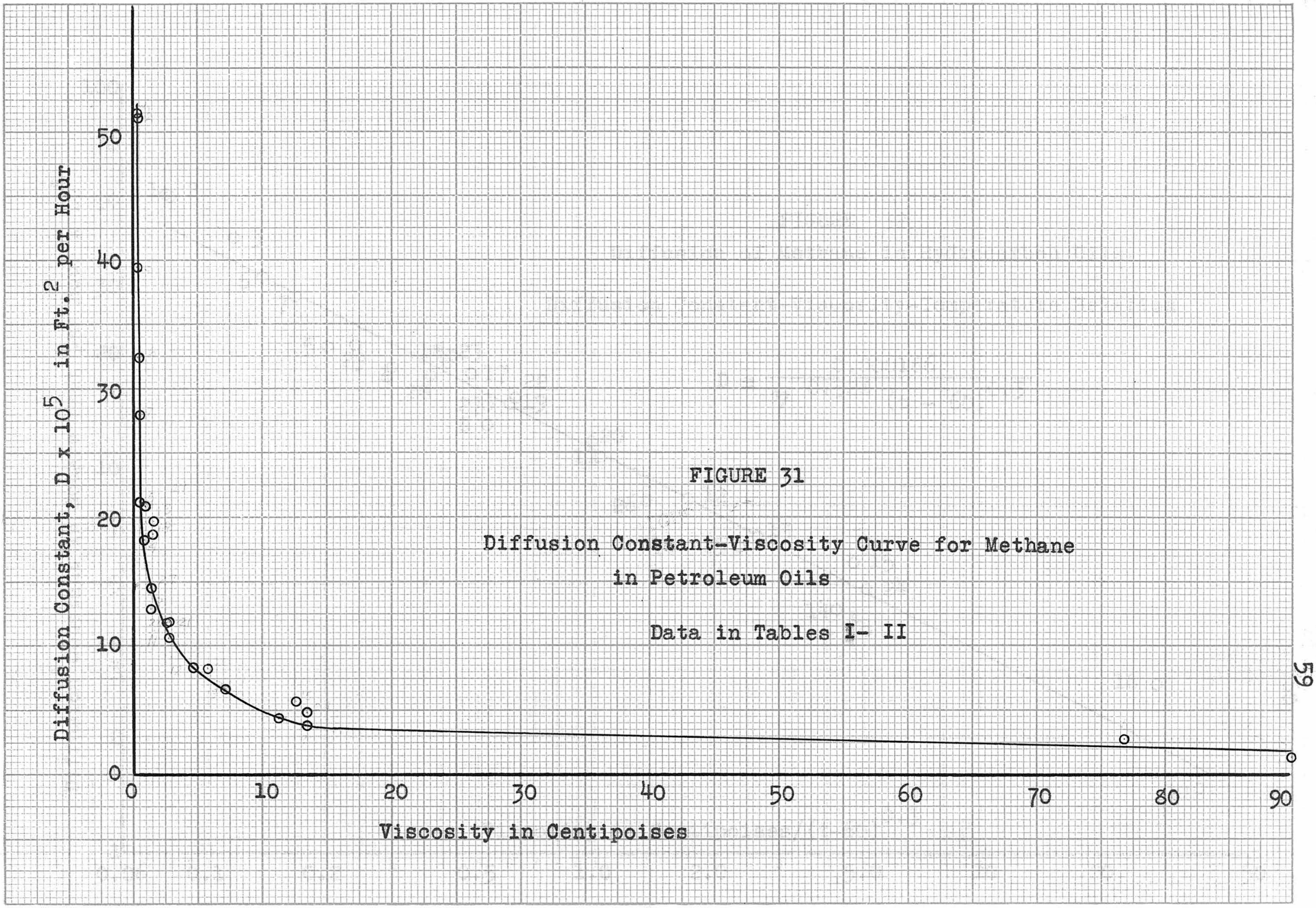


FIGURE 31

Diffusion Constant-Viscosity Curve for Methane in Petroleum Oils

Data in Tables I- II

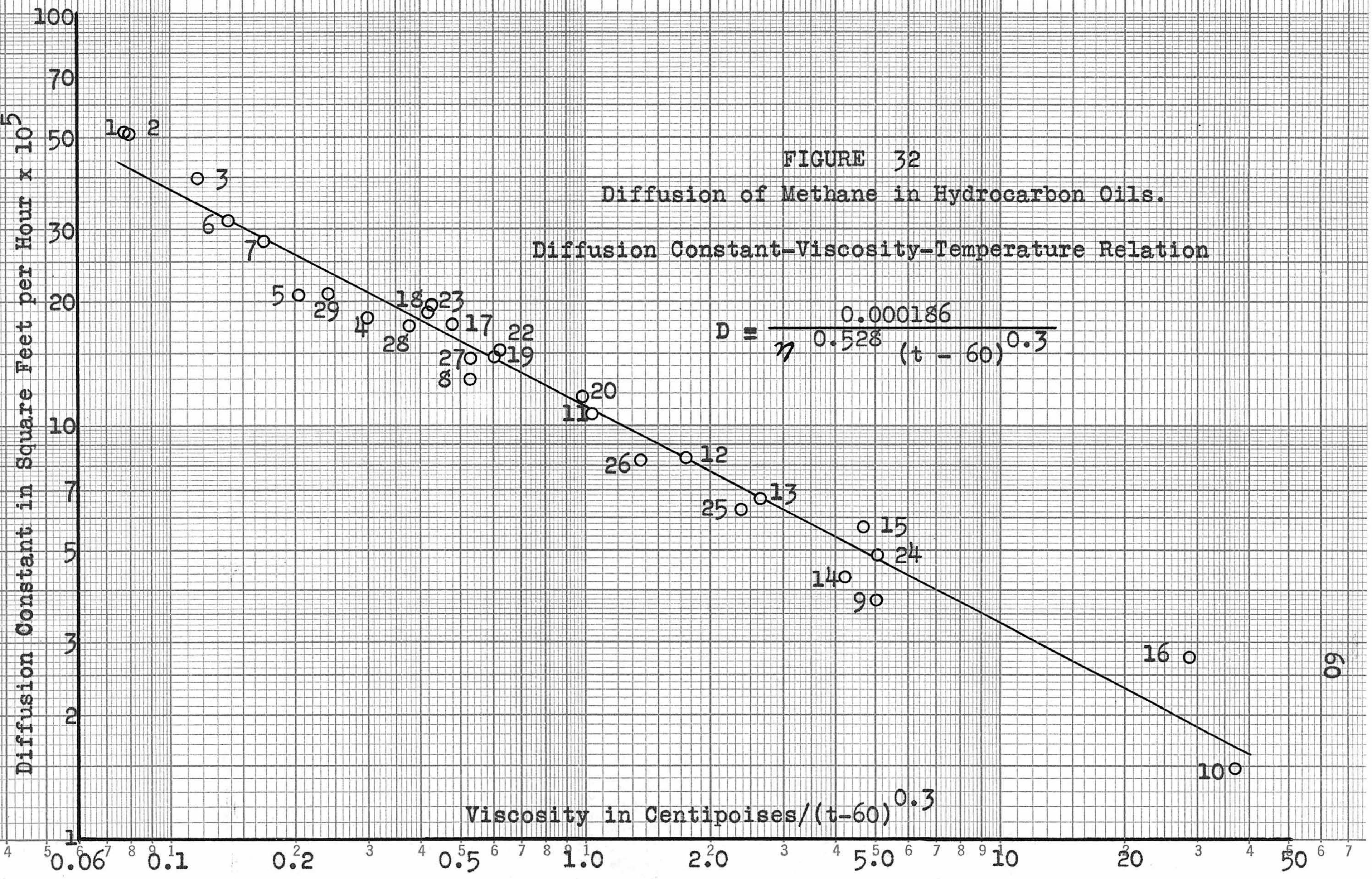


FIGURE 32

Diffusion of Methane in Hydrocarbon Oils.

Diffusion Constant-Viscosity-Temperature Relation

$$D = \frac{0.000186}{\eta^{0.528}\,(t-60)^{0.3}}$$

TABLE I

Rate of Solution of Methane (0.36% C_2H_6, low N_2) at 30°C (86°F)

Run No.	Point No.	Oil	Density of Oil	Degrees A.P.I.	Viscosity in Centipoises	Mol.Wt. of Oil	Cell	Lbs/in²	Atm.
140	1	Isopentane	0.6098	95.0	0.2076	72.09	B	297.7	20.26
141	1	"					B	298.2	20.29
142	2	Pentane	.6164	92.8	0.2103	72.09	B	300.3	20.43
143	2	"					B	300.1	20.42
153	3	n-Hexane	.6526	80.8	0.3074	86.11	B	299.7	20.39
154	3	"					B	300.0	20.42
137	4	Cyclohexane	.7689	49.8	0.797	84.09	B_{ss}	300.2	20.43
138	4	"					B_{ss}	300.2	20.43
139	4	"					B_{ss}	312.2	21.24
144	5	Benzene	.8681	29.6	0.561	78.05	B	300.7	20.46
145	5	"					B	300.6	20.45
151	6	n-Heptane	.6751	74.0	0.3683	100.12	B	299.8	20.40
152	6	"					B	300.6	20.45
155	7	2,2,4-tri-methyl pentane	.6841	71.4	0.4479	114.14	B	300.0	20.41
156	7						S	300.2	20.43
133	8	Kerosene	.7944	44.2	1.417	167	B	297.7	20.26
136	8	"					B	300.2	20.43
148	8	"					B	300.3	20.43
157	8	"					S	299.7	20.39
158	9	Spray Oil	.8617	30.7	13.45	287	S	299.5	20.38
159	9	"					S	300.2	20.43
160	10	Petrolatum	.8771	28.0	98.99	449	S	299.5	20.38
C-20	11	Rosecrans	.8274	37.4	2.753	181	S	300.0	20.41
C-21	12	Lima	.8238	38.1	4.679	228	S	299.9	20.41
C-23	13	Bartlesville	.8515	32.7	7.060	232	S	299.5	20.38
C-24	14	Sugarland	.8829	26.9	11.281	244	S	299.5	20.38
C-25	15	Ventura	.8710	29.1	12.56	236	S	301.2	20.50
C-22	16	Smackover	.9241	20.0	76.82	322	S	299.5	20.38

Table I-B

Run No.	Point No.	% Increase in Volume	m corr.	ϵ * cc/cc	S 100 lbs/in^2	C_s 100 lbs/in^2	S** at run pressure	C_s* at run pressure
140	1	6.11	23.43					
141	1	6.11	23.53	0.00259	8.359	2.877	24.22	22.30
142	2	5.43	22.74					
143	2	5.43	22.69	.00238	7.998	7.585	23.34	21.63
153	3	4.45	16.88					
154	3	4.45	16.97	.00233	6.735	6.449	19.58	18.37
137	4	3.09	8.93					
138	4	3.09	8.83					
139	4	3.37	9.28	.00213	5.159	5.000	15.12	14.45
144	5	2.27	7.32					
145	5	2.27	7.29	.00206	3.869	3.783	11.17	10.80
151	6	3.74	13.58					
152	6	3.74	13.62	.00222	5.920	5.706	17.20	16.27
155	7	3.84	12.75					
156	7	3.84	40.19	.00225	5.966	5.746	17.32	16.38
133	8	2.22	5.43					
136	8	2.15	5.52					
148	8	2.15	5.57					
157	8	2.15	17.48	.00200	3.761	3.681	10.86	10.49
158	9	1.46	6.88					
159	9	1.46	6.88	.00191	2.702	2.665	7.78	7.59
160	10	1.23‡	3.75	.00183	2.353	2.325	6.77	6.61
C-20	11	1.91	14.73	.00193	3.486	3.420	10.05	9.74
C-21	12	1.77	12.04	.00195	3.198	3.141	9.22	8.95
C-23	13	1.60	10.01	.00188	2.985	2.938	8.59	8.36
C-24	14	1.51‡	7.56	.00190	2.801	2.758	8.05	7.45
C-25	15	1.58‡	9.07	.00191	2.902	2.855	8.39	8.17
C-22	16	1.20‡	5.01	.00182	2.311	2.284	6.64	6.50

* Gas volume measured at 60°F and 30 inches of mercury

** Gas and oil volume measured at 60°F and 30 inches of mercury

‡ Extrapolated from Figure 28

TABLE I-C

Run No.	Point No.	D x 10^5 cm^2/sec	D x 10^5 ft^2/hr Ave	Mols CH$_4$ per cc. orig. oil	Mol-frac. CH$_4$ in liquid	Apparent density dis. gas	Density of Solution
140	1	13.18					
141	1	13.37	51.46	1.0039	0.1061	0.263	0.5878
142	2	13.19					
143	2	13.20	51.15	0.9676	.1017	.286	.5976
153	3	10.15					
154	3	10.18	39.41	.9348	.1098	.292	.6361
137	4	4.75					
138	4	4.65					
139	4	4.70	18.21	.6324	.06469	.320	.7542
144	5	5.52					
145	5	5.42	21.20	.4688	.04044	.330	.8566
151	6	8.36					
152	6	8.36	32.40	.7162	.09602	.306	.6610
155	7	7.17					
156	7	7.27	27.98	.7215	.1074	.302	.6690
133	8	3.22					
136	8	3.33					
148	8	3.36					
157	8	3.30	12.90	.4549	.09563	.340	.7845
158	9	0.97					
159	9	0.99	3.80	.3266	.09811	.357	.8543
160	10	0.38	1.47	.2841	.1152	.371	.8708
C-20	11	2.72	10.54	.4215	.08296	.353	.8182
C-21	12	2.16	8.37	.3865	.09663	.349	.8154
C-23	13	1.71	6.63	.3603	.08939	.361	.8436
C-24	14	1.11	4.30	.3381	.08545	.359	.8749
C-25	15	1.47	5.70	.3522	.08712	.357	.8628
C-22	16	0.71	2.75	.2789	.08857	.373	.9174

TABLE II-A

Variation of the Rate of Solution of Methane with Temperature and Pressure

Run No.	Point No.	Oil	Density of oil	Degrees A.P.I.	Viscosity of oil at run temp.	Mol.Wt. of oil	Temp. °C	Cell
C-7	17	Bradford	0.777	44.5	1.722‡	186	54	B
C-8	17	"	.777		1.722‡		54	B
C-9	18	"	.773		1.563‡		60	B
C-10	19	"	.783		1.987		45	B
C-11	20	"	.793		2.645		30	B
C-12	21	Rosecrans	.828	37.4	2.753	181	30	B
C-13	21	"	.828		2.753		30	B
C-14	21	"	.828		2.753		30	B
C-15	22	"	.818		2.050		45	B
C-17	23	"	.808		1.603‡		60	B
59	24	Spray Oil	.8617	30.7	13.45	287	30	B
60	25	"	.8519		7.847		45	B
61	26	"	.8418		5.086		60	B
58	27	Kerosene	.7944	44.2	1.417	167	30	B
63	27	"	.7944		1.417		30	B
57	28	"	.7837		1.245		45	B
62	29	"	.7730		0.897		16	B
87		"	.7944	44.2	1.417	167	30	
88		"	.7944		1.417		30	
Santa Fe Springs, Calif., natural gas in kerosene.								
N-1		Kerosene	.7944	44.2	1.417	167	30	B
N-2		"	.7944		1.417		30	B

‡ Extrapolated from Figure 26

TABLE II-B

Run No.	Point No.	Lbs/in^2	Atm.	% Increase in volume	m corr.	ϵ * cc/cc	Av.S** at Av.run pressure	Av.C_s* at Av.run pressure
C-7	17	288½	19.63	1.82	4.98			
C-8	17	288½	19.63	1.82	4.86	0.00224	8.40	7.96
C-9	18	286½	19.50	1.60	4.98	.00226	8.28	7.85
C-10	19	291½	19.84	1.79	5.00	.00198	9.30	8.89
C-11	20	295½	20.21	2.08	4.84	.00212	9.96	9.60
C-12	21	296	20.14	1.89	4.81			
C-13	21	296	20.14	1.89	4.39			
C-14	21	302	20.55	1.93	4.65	.00195	9.42	9.15
C-15	22	303	20.62	1.75	4.85	.00206	8.88	8.51
C-17	23	297	20.21	1.72	5.14	.00215	8.32	7.87
59	24	296½	20.18	1.43	2.29	.00197	7.29	7.09
60	25	293½	19.97	1.38	2.46	.00203	6.96	6.72
61	26	291½	19.84	1.33	2.66	.00208	6.62	6.33
58	27	296½	20.18	2.09	5.47			
63	27	301	20.48	2.12	5.56	.00210	10.20	9.87
57	28	294	20.01	1.92	5.78	.00210	9.88	9.41
62	29	291½	19.84	1.86	5.83	.00211	9.24	8.69
87		2000	136.1	10.41	66.55	.00150		
88		2000	136.1	10.00	64.19		69.49	62.09
N-1		296	20.14	2.90	6.30	.00245	12.00	11.51
N-2		296	20.14	2.90	6.45	.00244	12.02	11.53

* Gas volume measured at 60°F and 30 inches of mercury

** Gas and oil volume measured at 60°F and 30 inches of mercury

TABLE II-C

Run No.	Point No.	D x 10 cm^2/sec	D x 10 ft^2/hr Ave	Mols CH_4 per cc. orig. oil	Mol-frac. CH_4 in liquid	Apparent density dis. gas	Density of Solution
C-7	17	4.60					
C-8	17	4.50	17.63	0.344	0.0749	0.303	0.769
C-9	18	4.83	18.72	.337	.0742	.300	.766
C-10	19	3.79	14.69	.384	.0822	.344	.775
C-11	20	3.03	11.74	.417	.0870	.321	.783
C-12	21	3.07					
C-13	21	3.04					
C-14	21	3.03	11.82	.395	.0782	.349	.819
C-15	22	3.88	15.04	.368	.0741	.330	.810
C-17	23	5.07	19.65	.340	.0696	.317	.800
59	24	1.25	4.84	.306	.0939	.346	.854
60	25	1.61	6.24	.289	.0876	.335	.845
61	26	2.12	8.22	.271	.0837	.326	.835
58	27	3.68					
63	27	3.84	14.57	.427	.0808	.325	.785
57	28	4.50	17.44	.408	.0785	.325	.775
62	29	5.38	20.85	.376	.0738	.323	.765
87		4.70					
88		3.62	16.12				
N-1		3.58					
N-2		3.76	14.22				

TABLE III

Comparison of Methane Solubilities with Frohlich's Data

	Mol Fraction CH_4 in liquid Calculated from Frohlich's data	Value from Table I at the same pressure	% Difference from Table I
Pentane	0.111	0.102	+ 9
Hexane	0.121	0.110	+10
Cyclohexane	0.601	0.647	- 7
Benzene	0.358	0.404	-11

Propane

Before a mixture of gases can be studied advantageously it is necessary to know how each of the individual gases will behave under the test conditions. Since natural gas is composed of methane, ethane, propane, butanes, and heavier, it will be necessary to determine the diffusion coefficients for each of these gases before reliable predictions can be obtained for the diffusion of any natural gas of known composition; unless, after the determination of the coefficients for two or three of the gases, laws can be found to predict the values for the other gases. Since a satisfactory supply of ethane was not available, propane was obtained as already described.

The same apparatus, with some necessary changes, was used for this work as for methane. Since propane is a highly soluble gas, the reservoir had to be enlarged to measure the larger quantities. This was accomplished by removing the slugs used when methane was measured. The 1000 lb. tube in the gauge was replaced by a 300 lb. stainless steel tube to give a full scale deflection at lower pressures. The linkage, altho apparently the same and made by the same manufacturer, had quite different characteristics from that connected to the 1000 lb. tube. Due to irregularities of the gear teeth, the gauge had to be calibrated with the small bulb on the calibrating burette giving very many points for a reservoir calibration curve.

After several measurements of the rate of solution without removing the air from the cell, it was apparent that erroneous results were being obtained. It was found necessary to remove not only the air from the gas space but also the dissolved air from the oil.

This was accomplished by evacuating the sample, after weighing it into the cell, for approximately 9 hours at a low pressure slightly greater than the vapor pressure of the oil. The low pressure was maintained constant by the law pressure regulator previously described. Losses of oil from the sample were trapped in a tube surrounded by solid carbon dioxide, and kept down to less than 0.1% of the sample without much difficulty.

Only two oils were used in these determinations, namely, the kerosene and spray oil used for methane. Rosecrans, California, crude was used in several of the determinations with the impure propane and with air in the system, but due to lack of time necessary for designing and setting up apparatus for removing the air without changing the oil composition, the crude was not rerun. At the present stage of development, the use of the time required to prepare crude samples is not warranted because nothing widely different was found between diffusion in refined oils and in crudes for methane. Furthermore, the preliminary runs on the refined oils and crudes showed nothing widely different or new to be learned from determinations of the rate of solution of propane in crudes other than the determination of physical constants for the process.

Expansion of the liquid volume due to solution of the propane was determined in the same glass change in volume tube used for methane. The air was removed from the oil as in the rate of solution determinations and the pressure measured on the same gauge. Due to the large increase in volume, smaller oil samples were weighed into the tube, instead of filling the tube up so that the initial oil level could be read on the bottom of the calibrated scale as was done in the determinations when methane was used.

In determining the constants for the rate of solution of propane, it was necessary to go back and check experimentally the accuracy of all assumptions made for methane diffusion. A plot of the amount of gas admitted to the cell as a function of the square root of the time was found to give a straight line as before. It is not necessary to make any further remarks about these lines which have not already been made for similar plots of methane data. (Figures 33 to 43.)

All original plotting of the data was done on a scale 3 times that used in the figures shown. This was necessary to obtain a reasonable accuracy in locating the lines thru the points without calculating its position.

Determinations of the rate of solution and the equilibrium concentration value for propane in kerosene and spray oil at three temperatures were made up to 67% of the vapor pressure of propane at each temperature. In the case of methane, the slope of the rate line on a given oil was proportional to the pressure. In the case of propane, as shown by runs 99 (Figure 34) and 101 (Figure 37), the slope of the rate line is not proportional to the pressure, because doubling the pressure increased the rate nearly 3 times. Again in the case of split-runs best shown by 111 a,b,c, the rate was not the same when the initial concentration was different. In Figure 36 the runs were made by determining the rate at the lowest pressure, 31.4 lbs./sq.in., saturating the oil at this pressure, and then determining the rate with the pressure raised 30.3 lbs./sq.in. to a total of 61.7 lbs./sq.in. After saturating at 61.7 lbs./sq.in. the pressure was raised 29.2 lbs./sq.in. to a total of 90.9 lbs./sq.in. If the rate were independent of the initial concentration, the lines should have all had nearly the same slope. Instead, the last is 2½ times that of the first. Later discussion will show that the rate is definitely a function of the concentration.

The determinations at higher temperatures show smaller amounts of gas dissolved and higher rate constants than at lower temperatures similar to the behavior of methane. The increase in the diffusion coefficient is larger at the higher temperatures as the vapor pressure of the propane is approached. It should be pointed out here that all of these determinations with propane have been made below the critical temperature of the gas, so that if the pressure is high enough the gas will condense in the cell without any other liquid being present. Hence, if the full pressure range were covered from near zero to the vapor pressure of propane at the temperature of the determination, the process would change from one of simple diffusion into the liquid to one of condensation of the gas followed by diffusion of liquid propane into the heavier oil from a layer of liquid propane.

Determination of the slope of the rate line and the apparent amount of gas dissolved at equilibrium is only a part of the data required for propane. It was necessary to obtain values for the gas compressibility, vapor pressure of the propane, and the expansion of the liquid upon solution of propane.

The deviation of the compressibility of propane from that of a perfect gas was required in the correction of the apparent solubility and rates to the true values. This determination was made by measuring the pressure and volume of gas admitted to the cell with two different sized slugs in the cell. The difference in volume of the slugs was known quite accurately, and the difference in the two gas volumes gave the corresponding gas volume for this differential slug volume. The deviation from a perfect gas was calculated directly from this data and plotted in Fig. 44 as a function of the percent of the vapor pressure of propane at the temperature of the determination. This data is not particularly good, but since the size of the correction applied to the apparent diffusion is only a fraction of the total, it is accurate enough for the purpose. Plotting the data as a function of the percent of vapor pressure was found to furnish a convenient means for arranging the data so that interpolations for intermediate temperatures could be made. No further calculation of this data beyond the immediate requirements has been made and is not recommended.

Vapor pressure data for propane plotted in Figure 45 were obtained from the recent work by B.H.Sage(8). This vapor pressure curve is used in all the calculations involving the percent of the vapor pressure of propane.

The expansion of the liquid is plotted for kerosene in Figure 46 and for spray oil in Figure 47, at three different temperatures as a function of the partial pressure of propane. In the case of methane there was very little curvature of this line, but for propane the expansion increases very rapidly as the pressure approaches the vapor pressure of liquid propane. The apparent density of dissolved propane shown in Table IV is seen to decrease as the pressure increases while all values are higher than the saturated liquid propane densities. A plot of these apparent densities indicated nothing except poor expansion values, although Figures 46 and 47 appear to be all right with the points on smooth curves. These expansion values were never intended to be better than 4 or 5% since the correction is only a small fraction except for very high solubilities where the solubility is corrected nearly 50%, of the values measured for diffusion. Due to this and the small number of temperatures covered it is not desirable to use this data to calculate heats of solution with any degree of accuracy. The cubic foot increase in liquid volume per cubic foot of gas dissolved is no longer a constant for a single oil as it was for methane, but it increases as the pressure increases.

The final equilibrium concentration values calculated as cubic foot of gas per cubic foot of solution and as mol fraction of propane in the liquid are found to obey Henry's law as shown by the nearly straight lines obtained in Figure 48. The upper line is for both kerosene and spray oil as the solvent at 30°C. The next line below this is for the same oils at 45°C. It is curved more, but the agreement is not bad. The two lower lines have a different slope for kerosene and spray oil at 60°C. It follows from these curves that the Henry's law constants vary with the temperature, and with the oil at higher temperatures. The solubilities shown in the table for runs 111 b,c are for the oil with an initial concentration shown by the preceding part of the split-run.

A better correlation is obtained in Figure 49, where the mol fraction of propane in the liquid is plotted as a function of the percent of the vapor pressure of liquid propane. The values for both oils at all three temperatures are seen to lie on a nearly straight line. This line must of course pass thru zero and the point: vapor pressure = 100%, mol fraction = 1. From this curve the equilibrium concentration of the propane in a fair range of oils can be predicted at temperatures not too close to the critical temperature of propane. By use of this curve to determine the equilibrium concentration it may be possible to determine the rates of solution of propane in crudes without the use of special apparatus to remove the air from the oil. The air could be rapidly evacuated from the gas space over the crude and the rate run started as soon as possible. This is feasible because the presence of air in the system does not appreciably change the properties of the oil but lowers the partial pressure of propane an unknown amount in a given total pressure. Since the rate of diffusion of air in oil is quite low, the air will remain in the oil to such an extent that it will have little effect on the slope of the rate lines. This of course is not true if the density of the air-saturated oil is less than that of the air-free oil. However, until some data have been obtained on this point there is good reason to believe that the more desirable case is true, because air in water solutions, and carbon dioxide in oil solutions are more dense than the gas-free liquids.

Since the diffusion coefficient for methane was a function of the viscosity of the oil, it was expected for propane also. An insufficient number of oils have been run to determine whether or not the diffusion coefficient of propane is a function of the viscosity of the original oil. Figure 50 shows the density and viscosity of spray oil saturated with propane at 30°C as a function of the partial pressure of propane. Figure 51 shows the apparent diffusion coefficient plotted as a function of this viscosity on a semi-log graph. The straight line obtained is good for interpolation. If sufficient data were available, it is probable that a relation could be found for predicting the diffusion coefficient for propane as a function of viscosity of the final solution. The variation of the viscosity of the solution with equilibrium pressure was plotted on this curve to find out how much of the line would be straight.

The absolute accuracy of the determinations of the coefficient for the rate of solution has not been checked, but the experimental results are reproducible within 3% as shown by the series of runs at a single pressure and temperature (105, 106 a, 111 a). Due to the use of slugs in the cell and frequent reservoir refills during the runs, the variation in the percentage error between low rates of solution and high rates of solution was not as marked as in the case of methane. The gauge calibration arrangement shown on the flow sheet was in place before the propane measurements were made so that the propane partial pressures are reliable to ±0.2 lb./sq.in. The odd pressure readings were due to the fact that the cell gauge was always operated with a reading on a graduation line.

It has already been pointed out in the split runs that the rate of solution of propane is a function of the initial concentration of the solution. From this one might expect the diffusion coefficient to be a function of solubility. This is shown by Figure 52 where the diffusion coefficient is seen to increase more than 100% as the solubility is increased in a given oil. The values of the diffusion coefficient for the second and third parts of the split runs 106, 111 are considerably higher than those for the corresponding original oil, temperature, and pressure shown in Figure 52. It is evident that at least two of the assumptions made in the integration of Fick's proposition must be reconsidered: (a) the diffusion coefficient is independent of concentration of the solution; (b) the gas moves thru the liquid only by diffusion. The second of these assumptions will be considered first at this point because it is a purely mechanical effect for which a calculated correction ought to be feasible. Following this, the determination of the relation between the diffusion coefficient corrected for expansion and the concentration can be evaluated by itself.

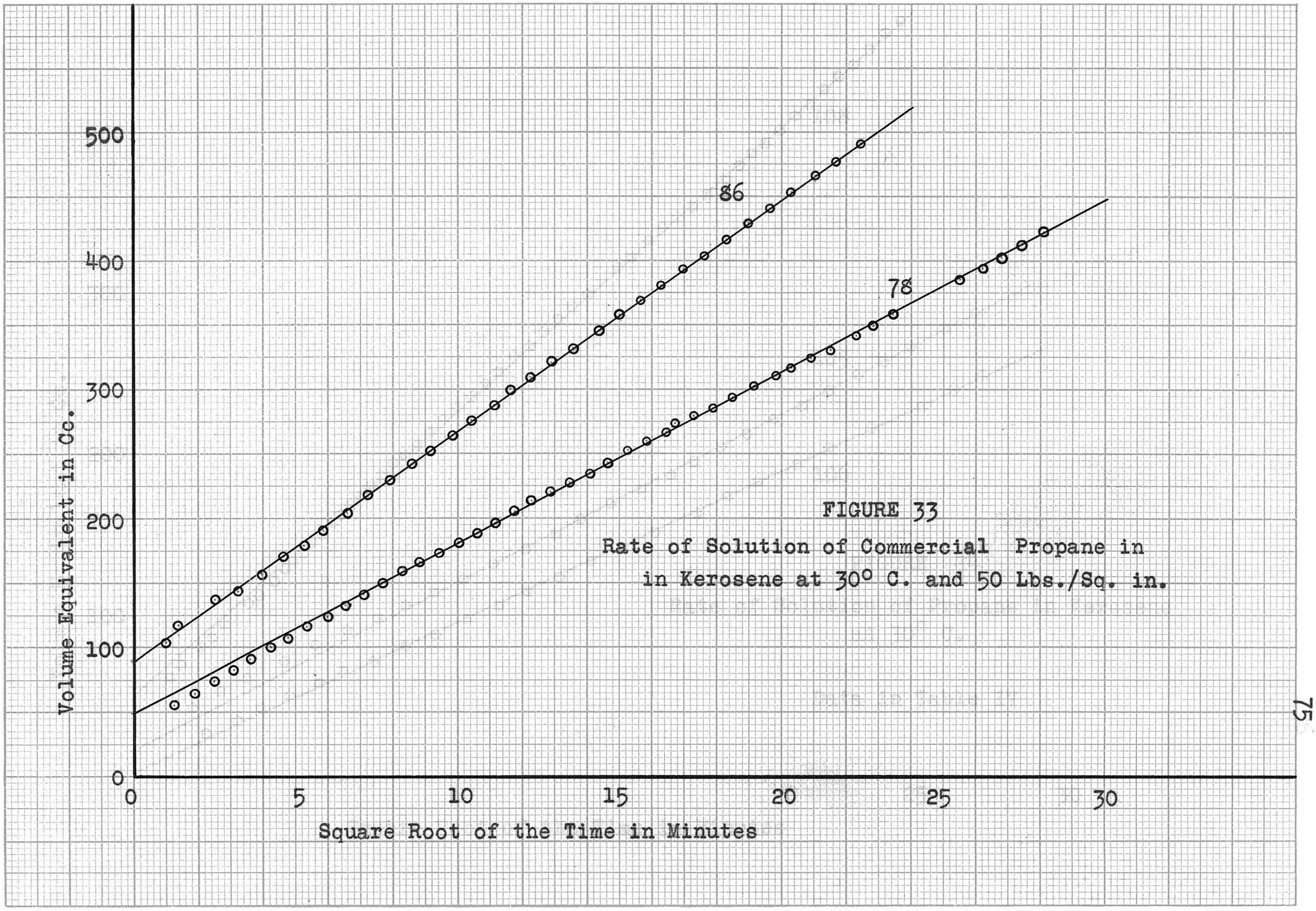


FIGURE 33

Rate of Solution of Commercial Propane in
in Kerosene at 30° C. and 50 Lbs./Sq. in.

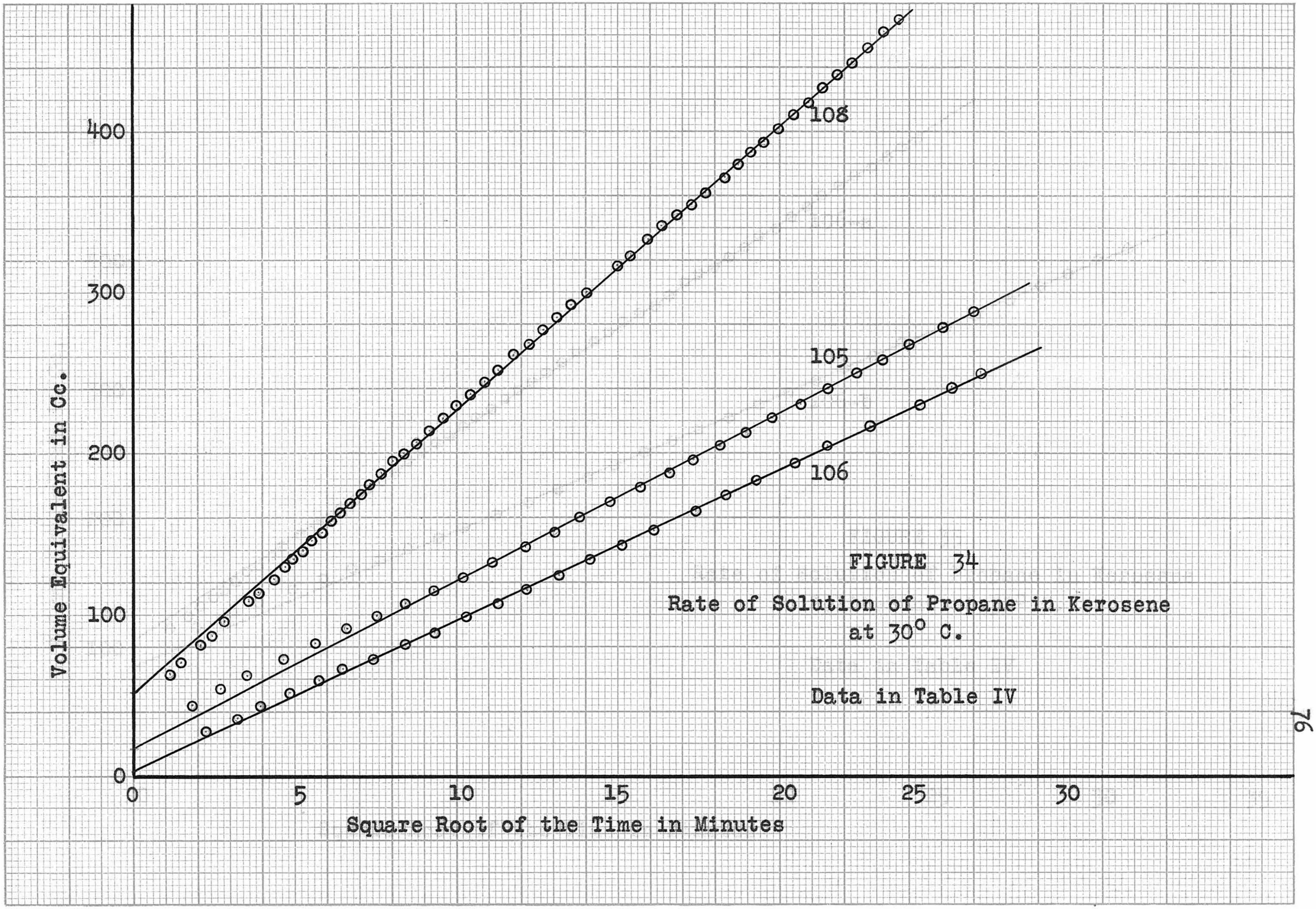


FIGURE 34

Rate of Solution of Propane in Kerosene
at 30° C.

Data in Table IV

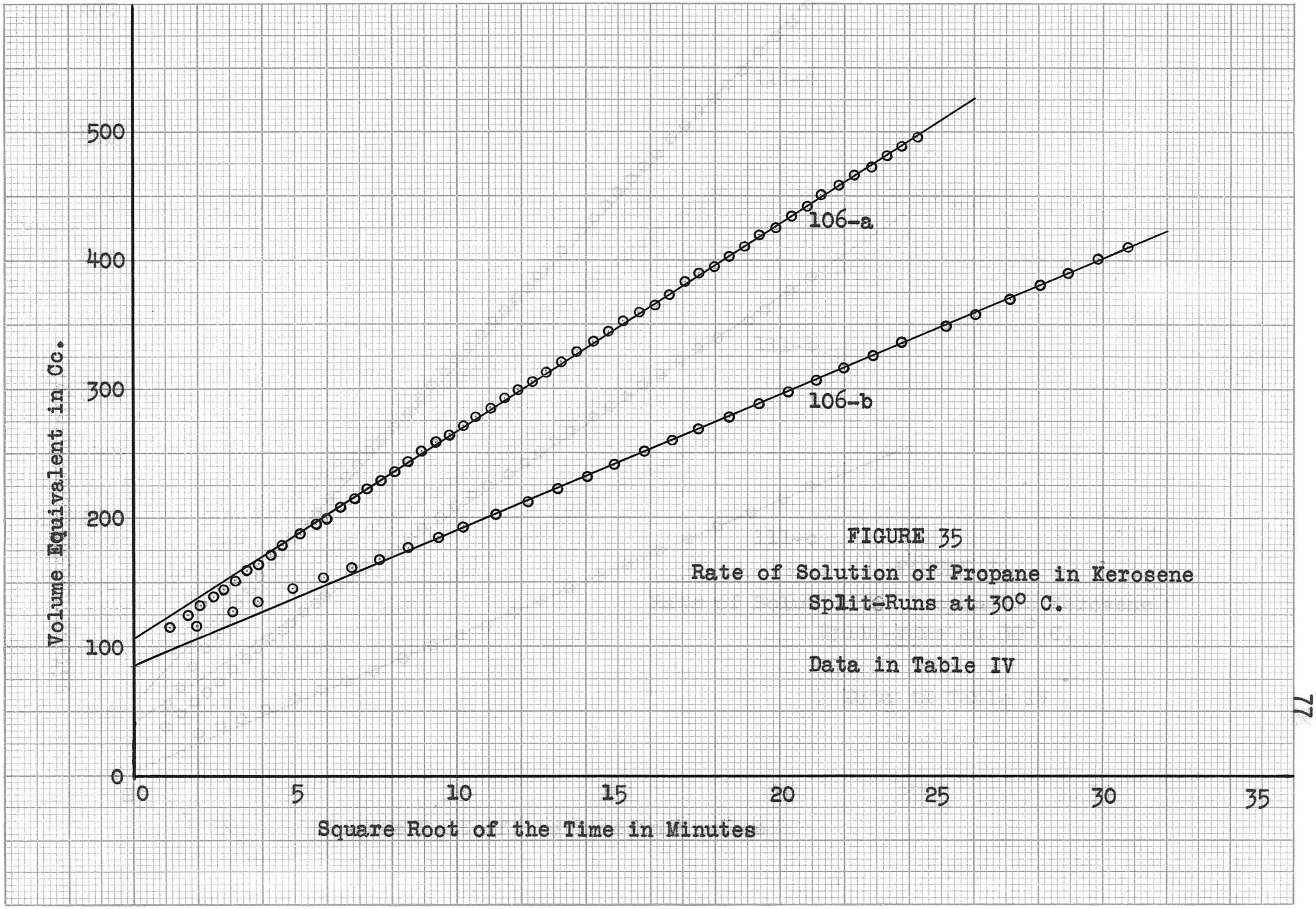


FIGURE 35

Rate of Solution of Propane in Kerosene

Split-Runs at 30° C.

Data in Table IV

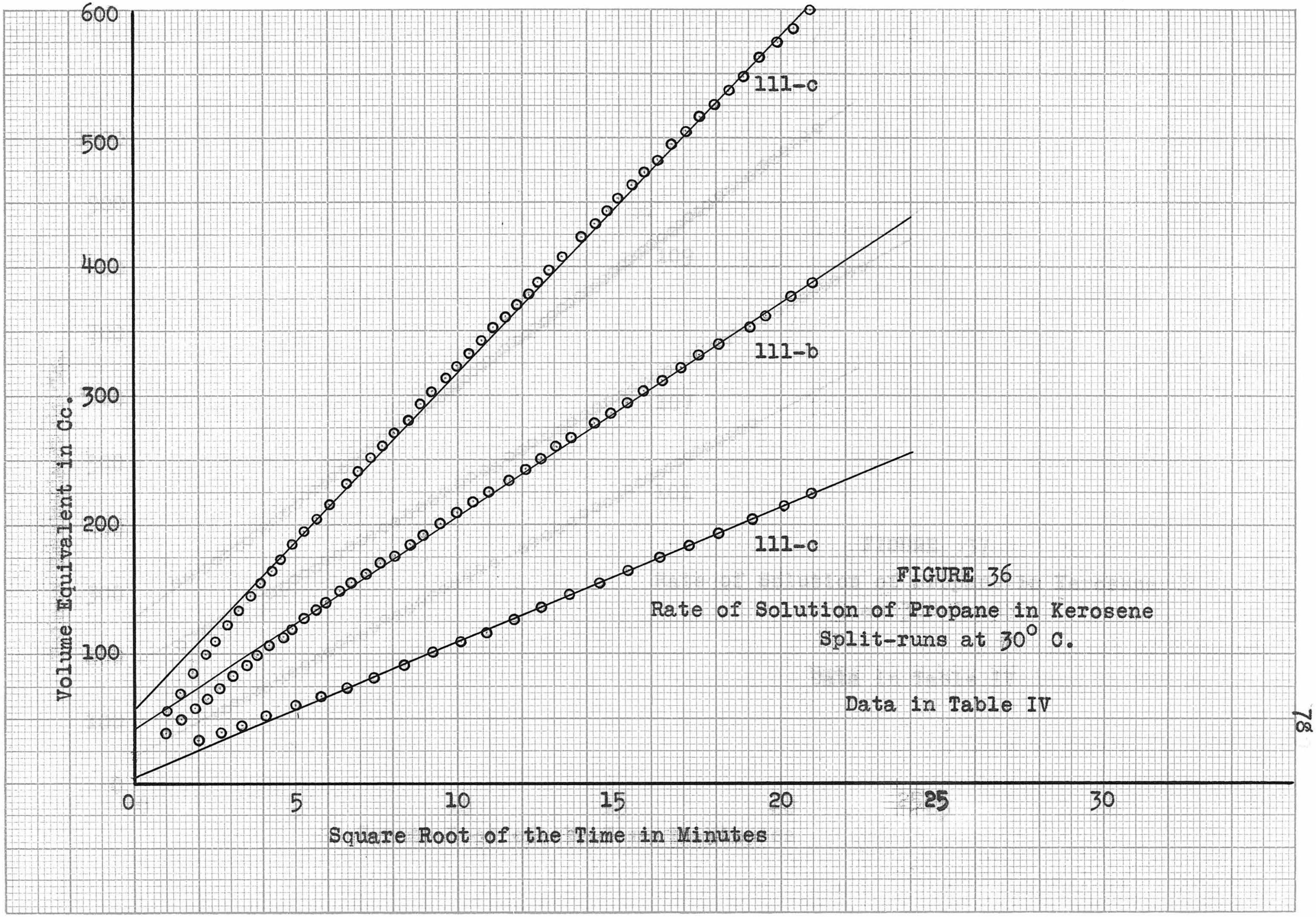


FIGURE 36

Rate of Solution of Propane in Kerosene
Split-runs at 30° C.

Data in Table IV

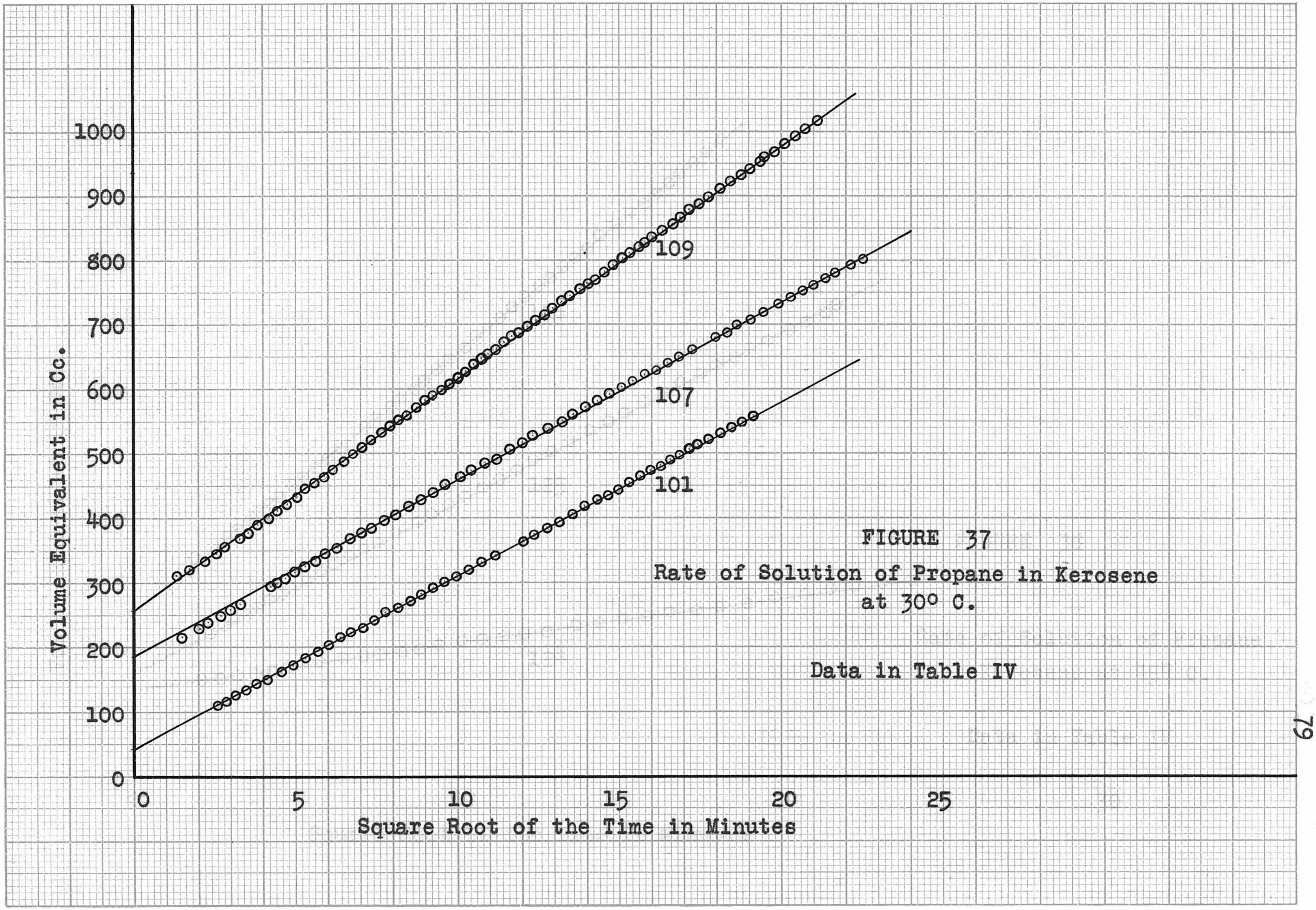


FIGURE 37
Rate of Solution of Propane in Kerosene
at 30° C.

Data in Table IV

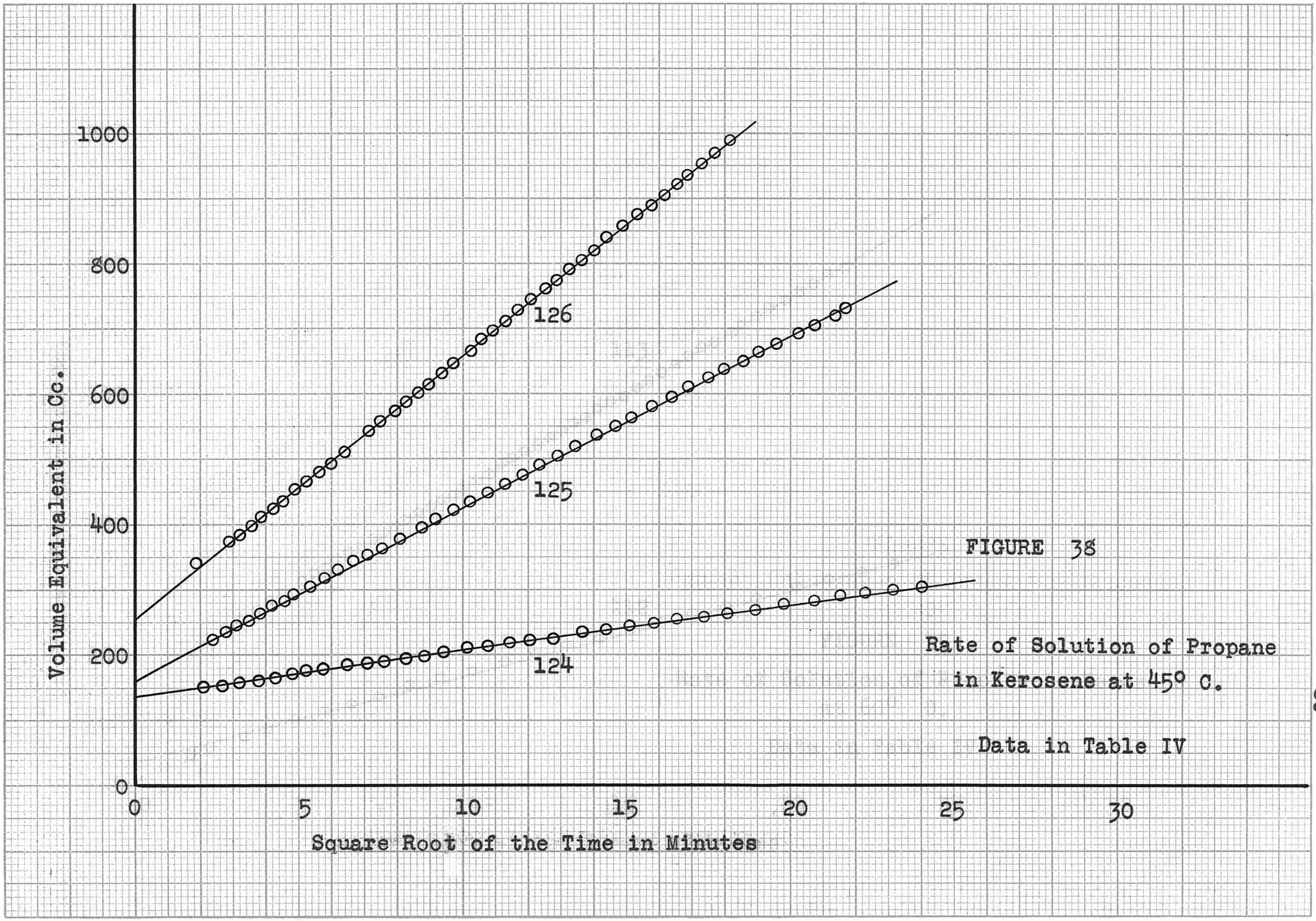


FIGURE 38

Rate of Solution of Propane
in Kerosene at 45° C.

Data in Table IV

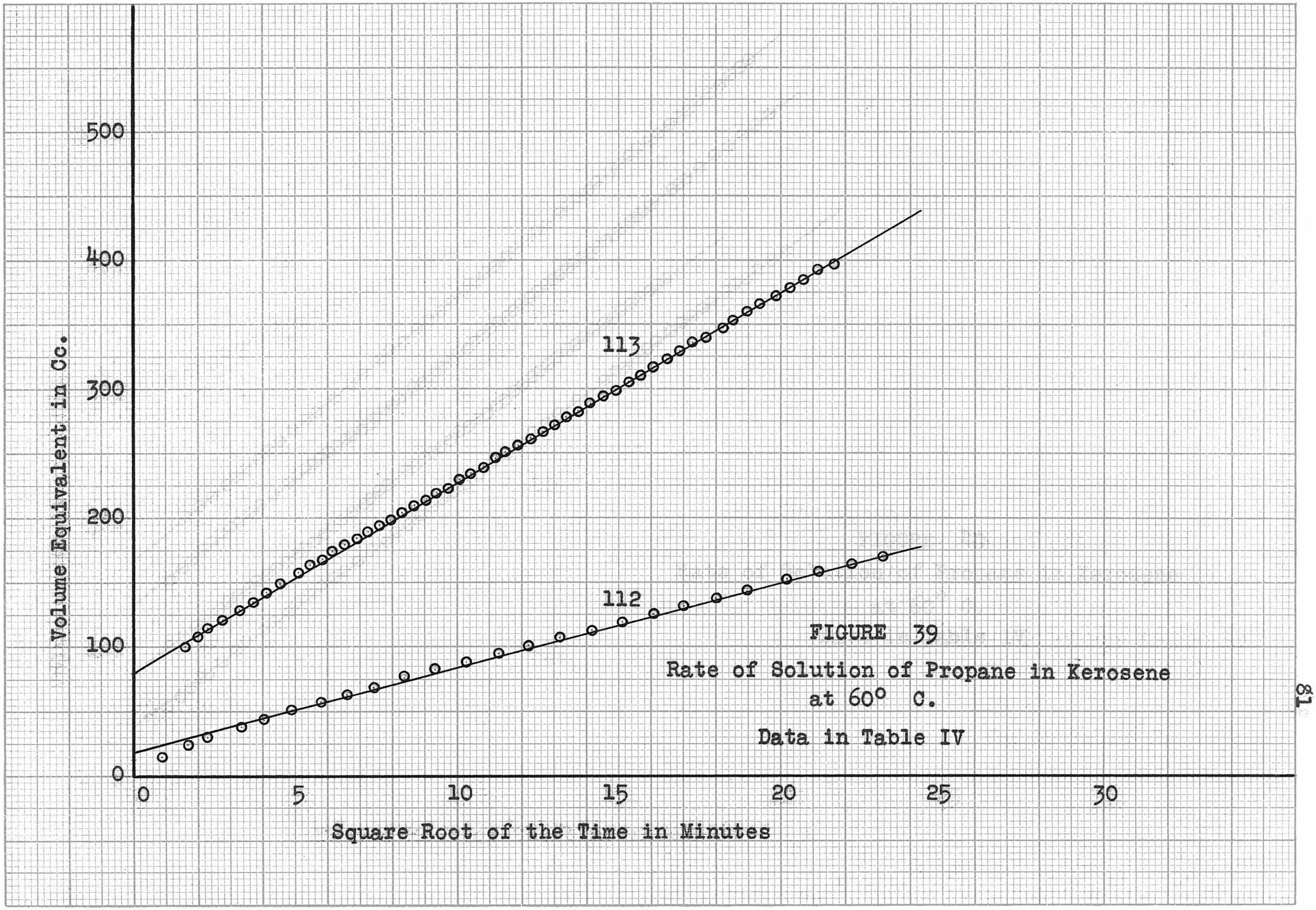


FIGURE 39

Rate of Solution of Propane in Kerosene
at 60° C.

Data in Table IV

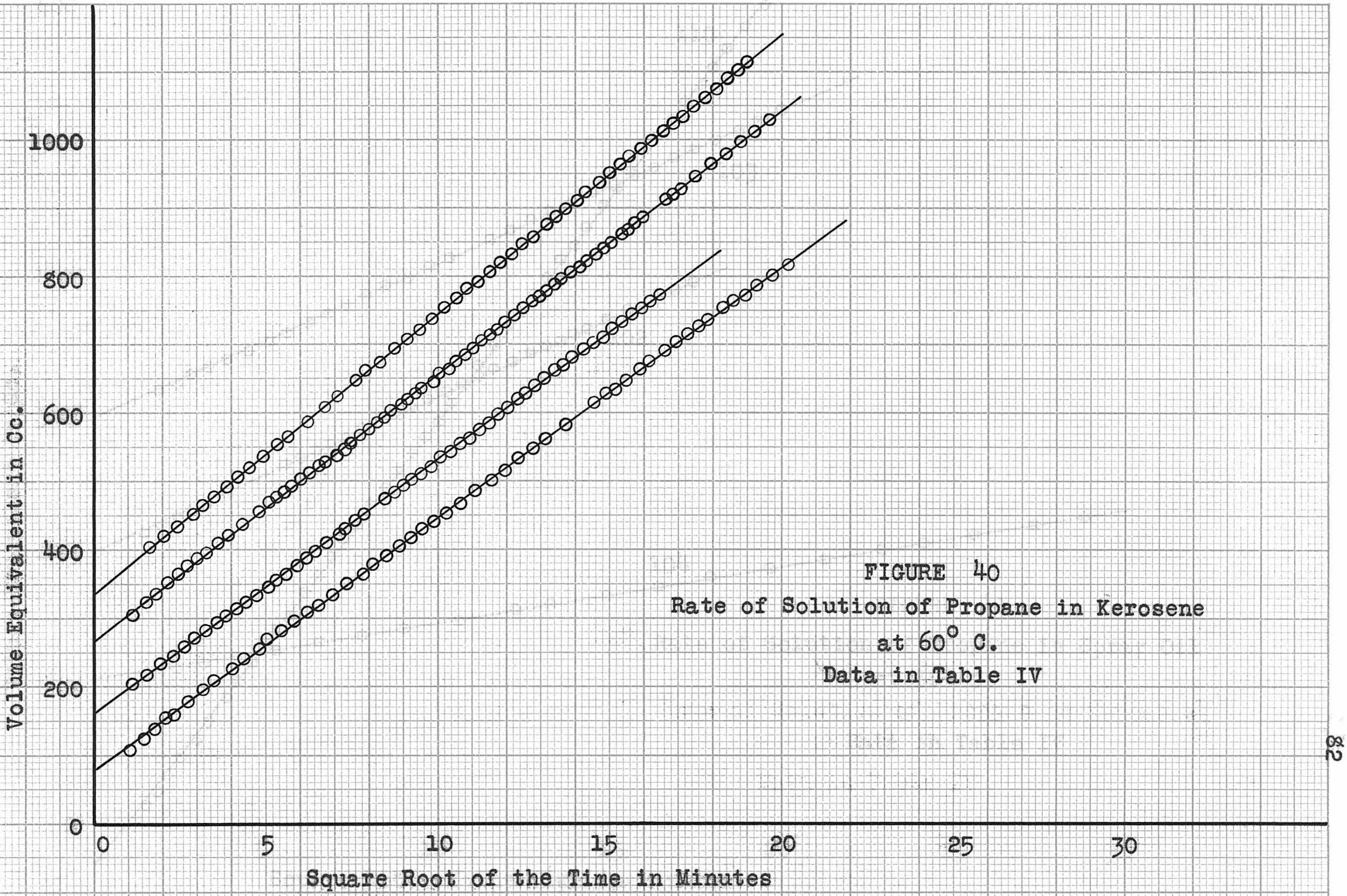


FIGURE 40
Rate of Solution of Propane in Kerosene
at 60° C.
Data in Table IV

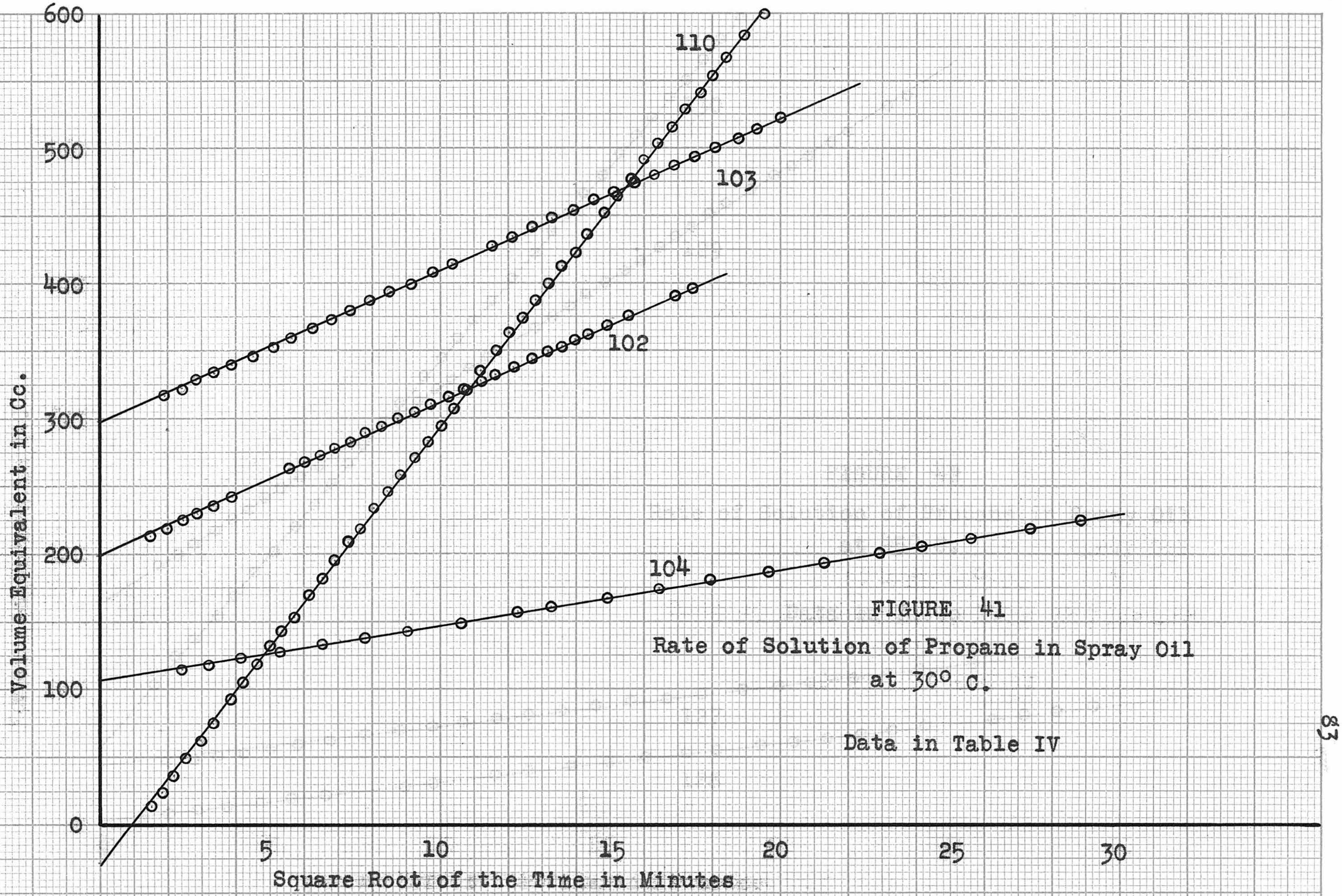


FIGURE 41

Rate of Solution of Propane in Spray Oil at 30° C.

Data in Table IV

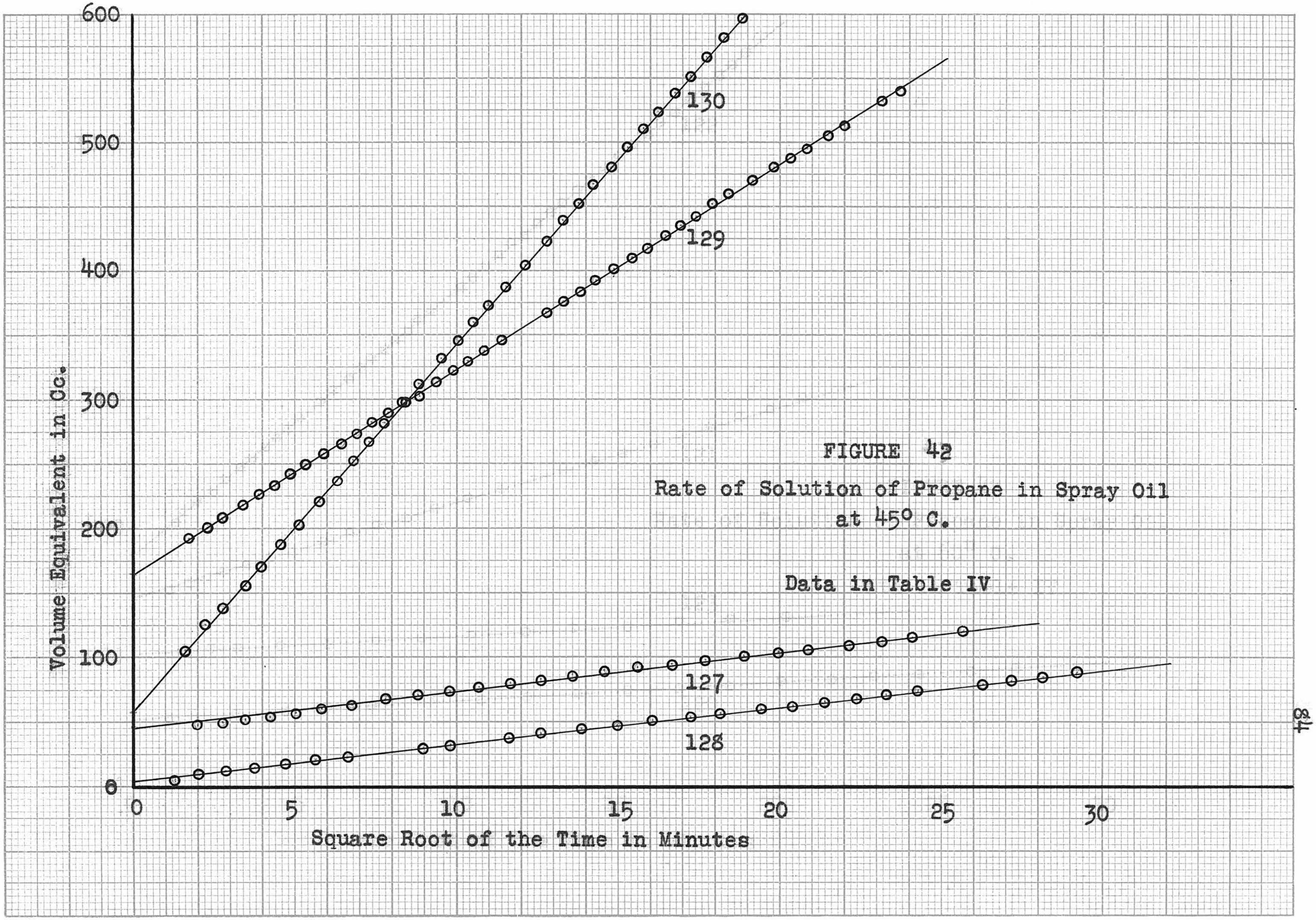


FIGURE 42

Rate of Solution of Propane in Spray Oil at 45° C.

Data in Table IV

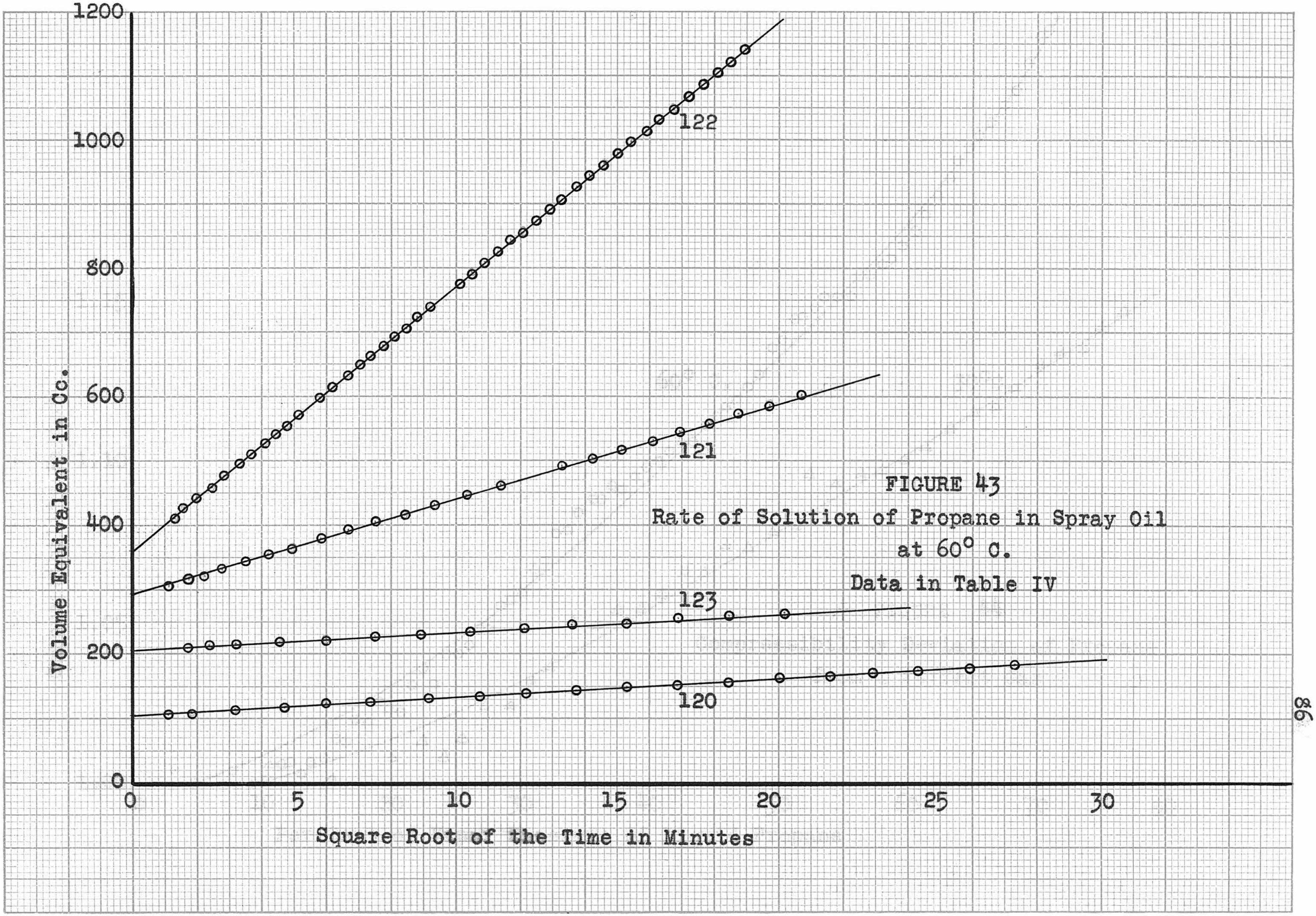


FIGURE 43
Rate of Solution of Propane in Spray Oil
at 60° C.
Data in Table IV

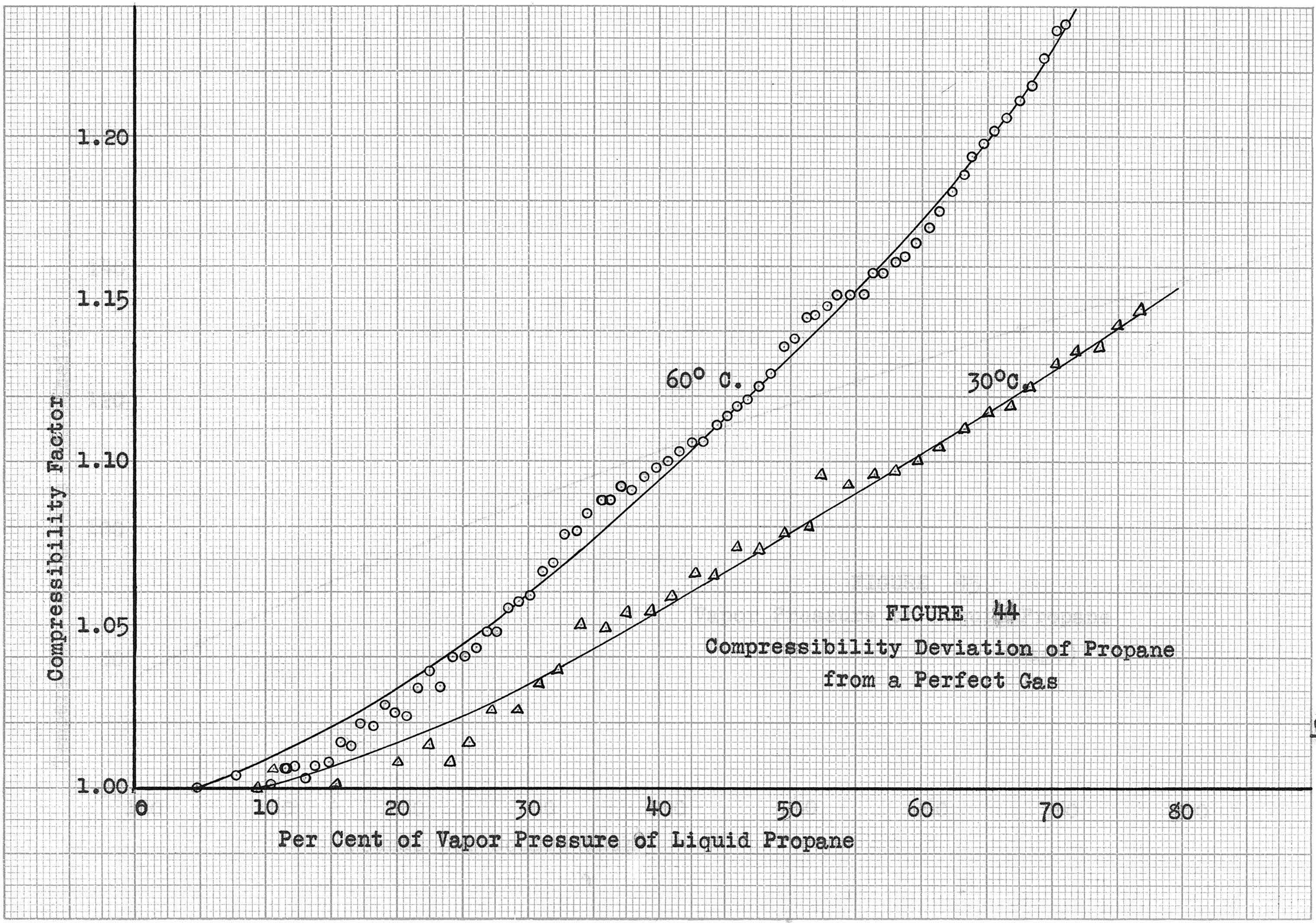


FIGURE 44
Compressibility Deviation of Propane
from a Perfect Gas

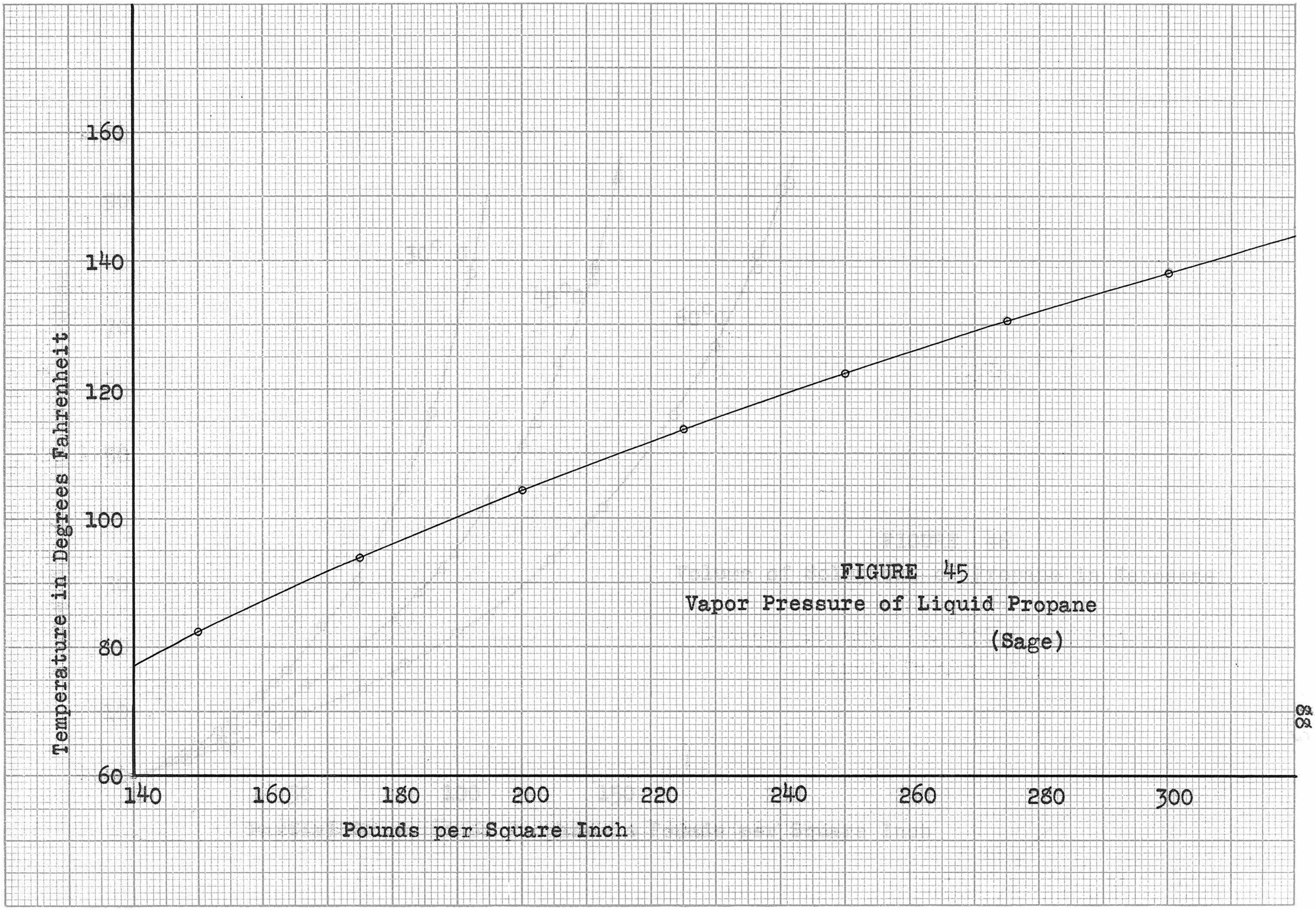


FIGURE 45
Vapor Pressure of Liquid Propane
(Sage)

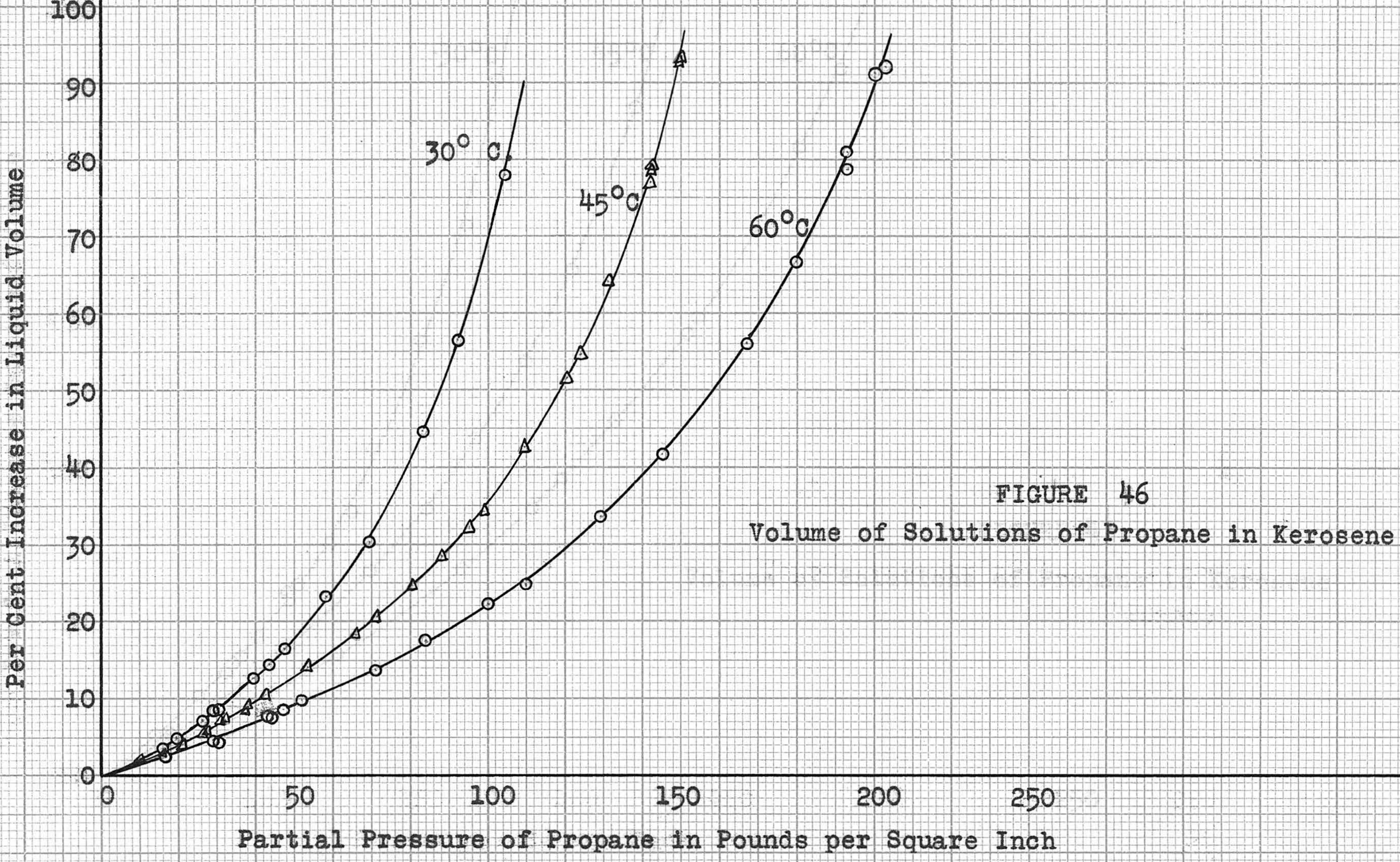


FIGURE 46

Volume of Solutions of Propane in Kerosene

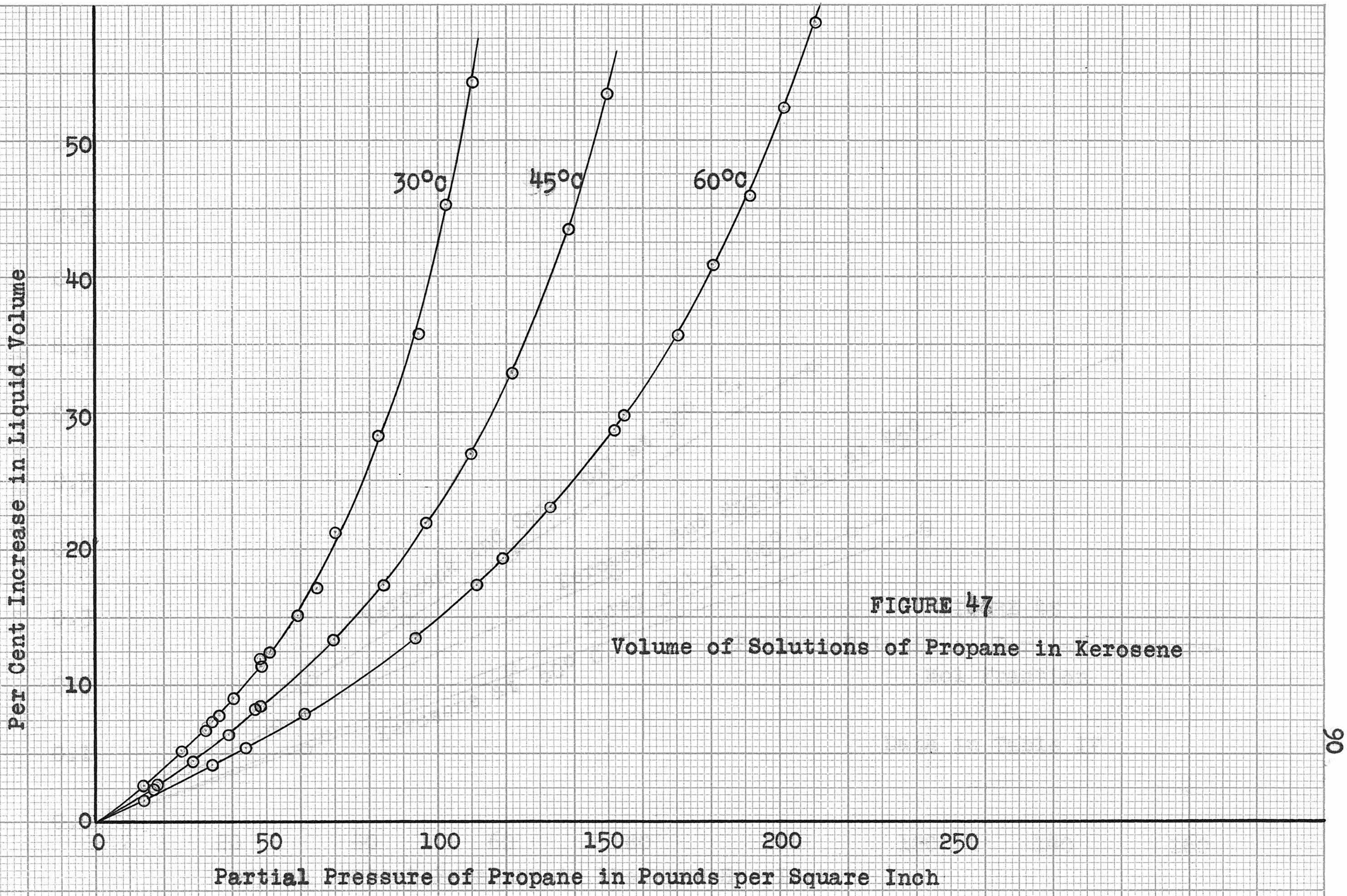


FIGURE 47

Volume of Solutions of Propane in Kerosene

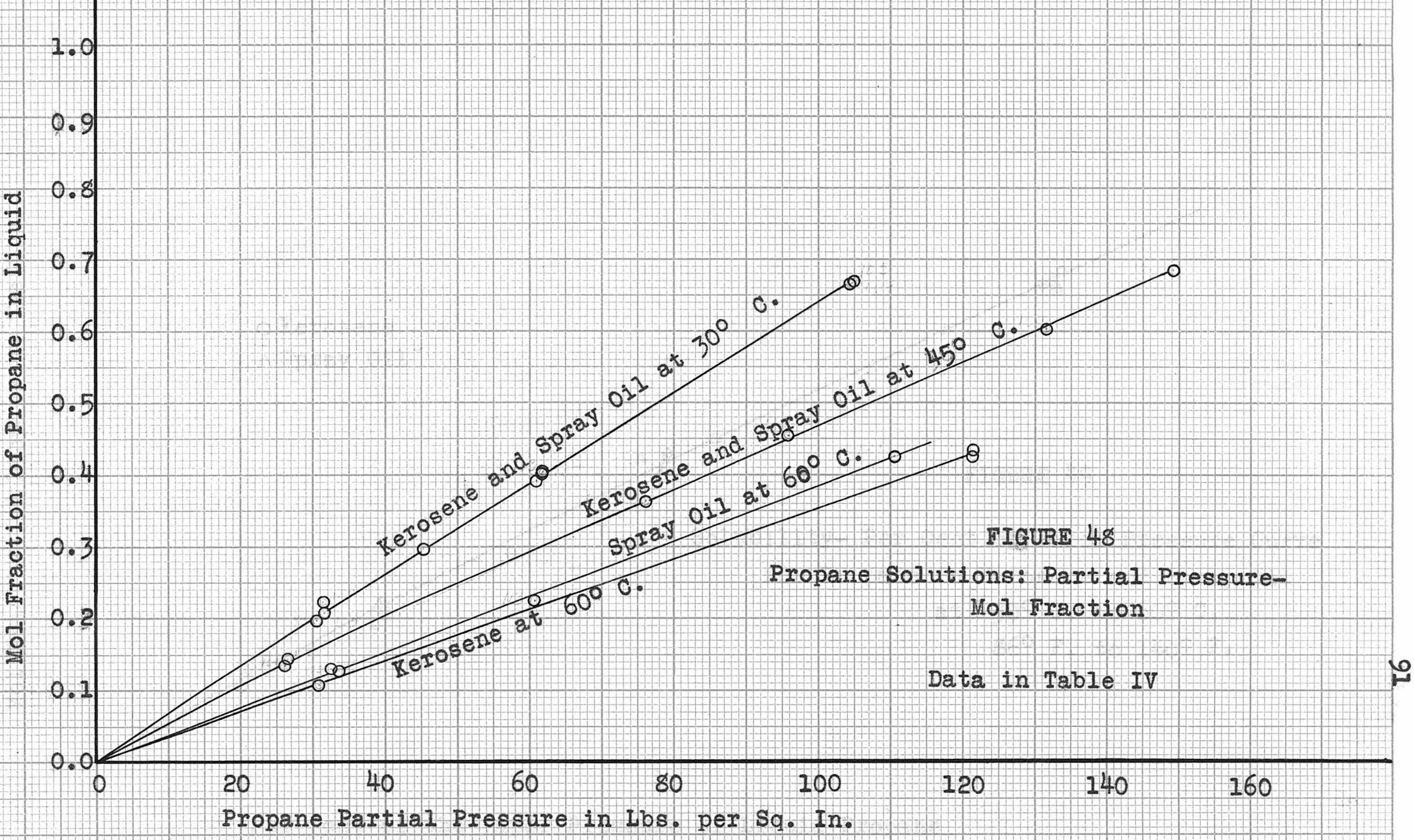


FIGURE 48

Propane Solutions: Partial Pressure-
Mol Fraction

Data in Table IV

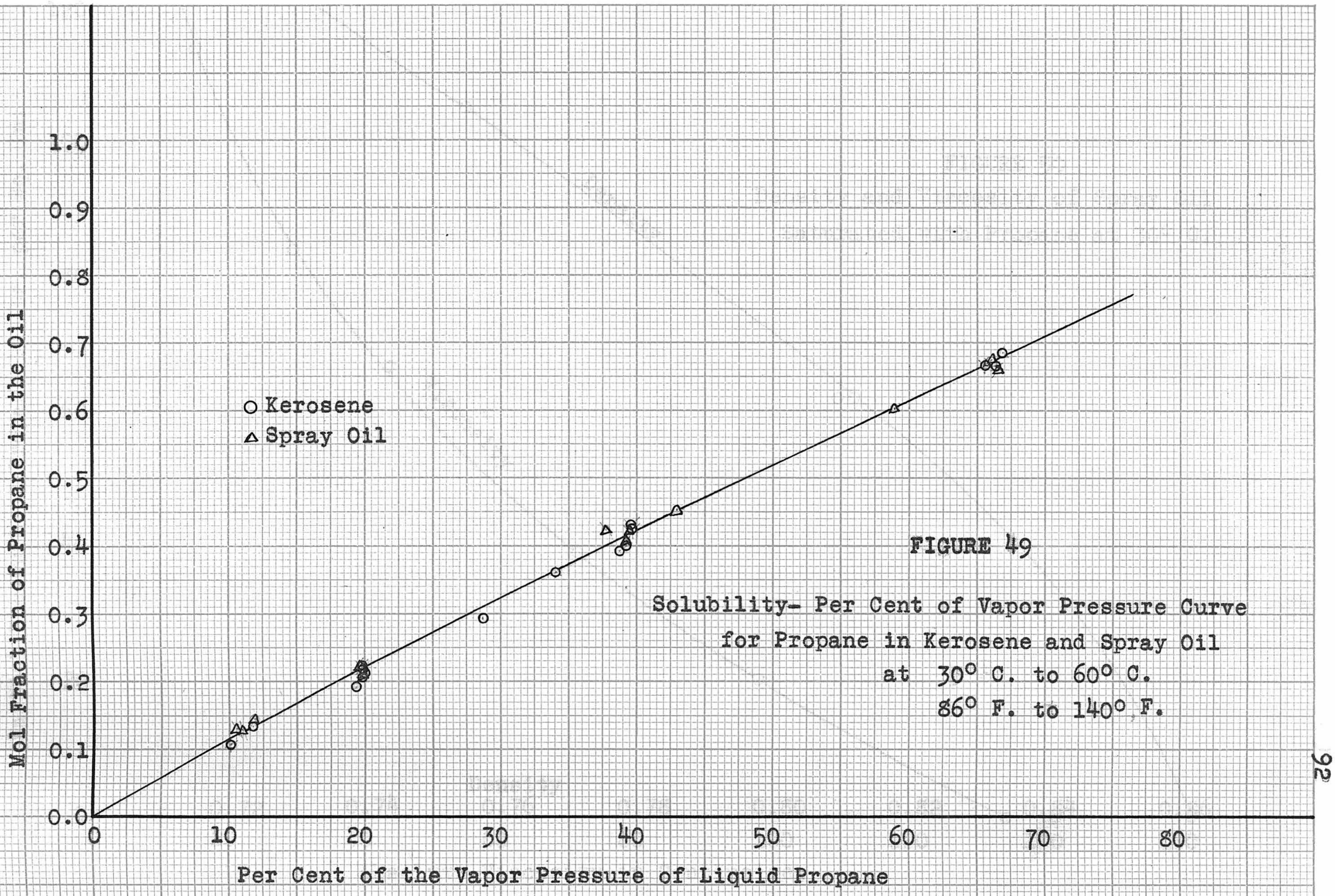


FIGURE 49

Solubility- Per Cent of Vapor Pressure Curve
for Propane in Kerosene and Spray Oil
at 30° C. to 60° C.
86° F. to 140° F.

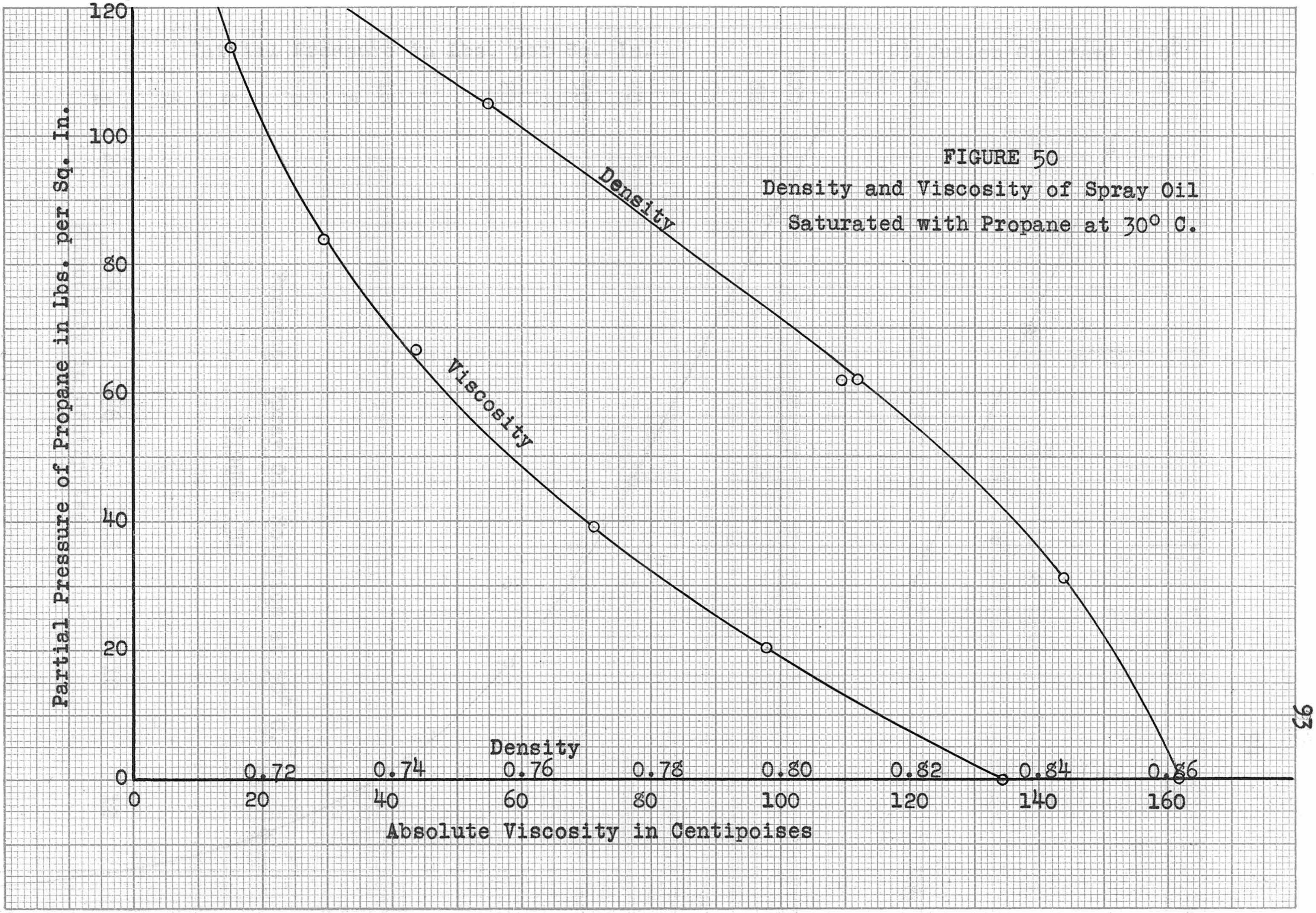
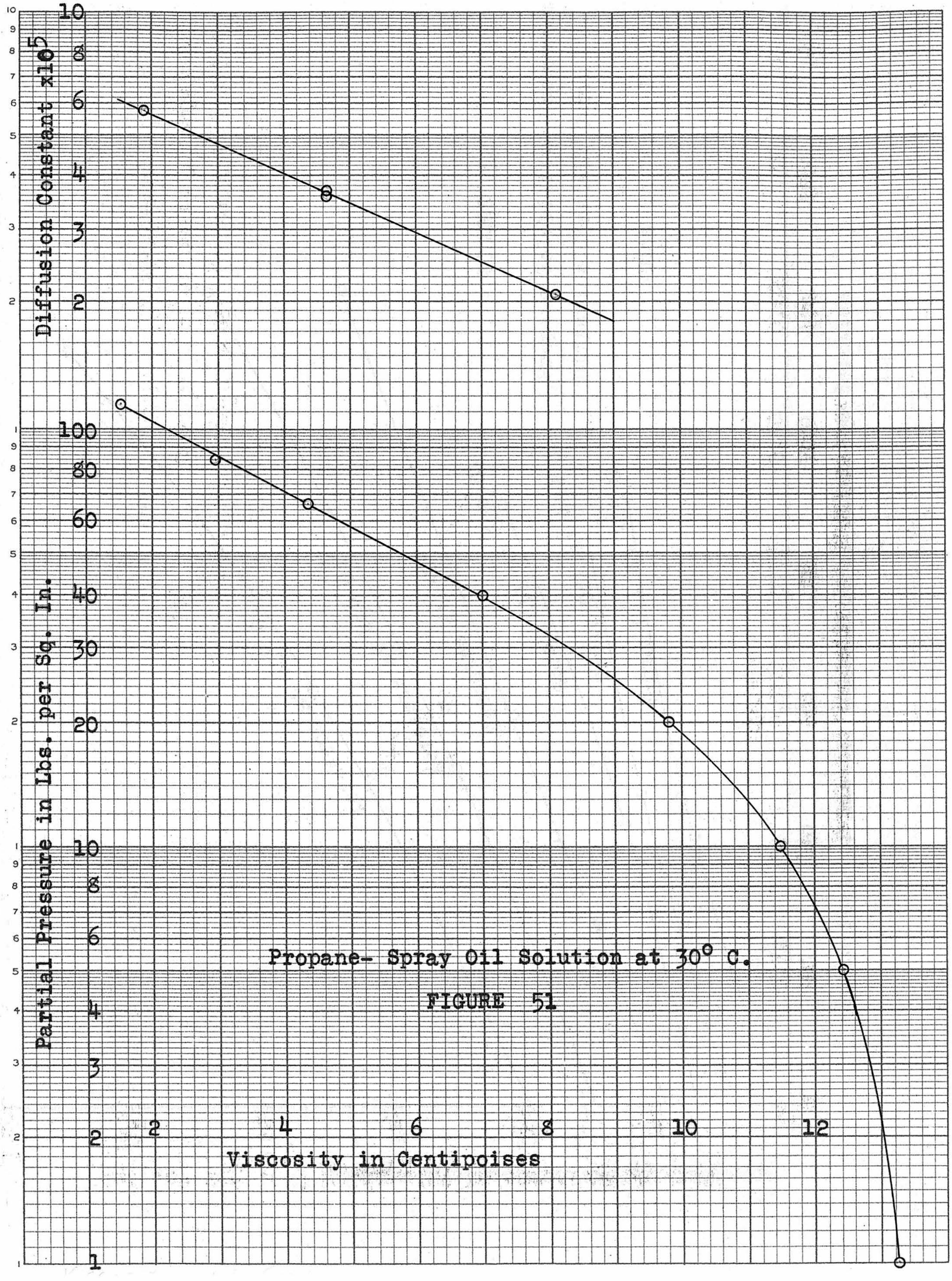


FIGURE 50
Density and Viscosity of Spray Oil
Saturated with Propane at 30° C.



Propane- Spray Oil Solution at 30° C.

FIGURE 51

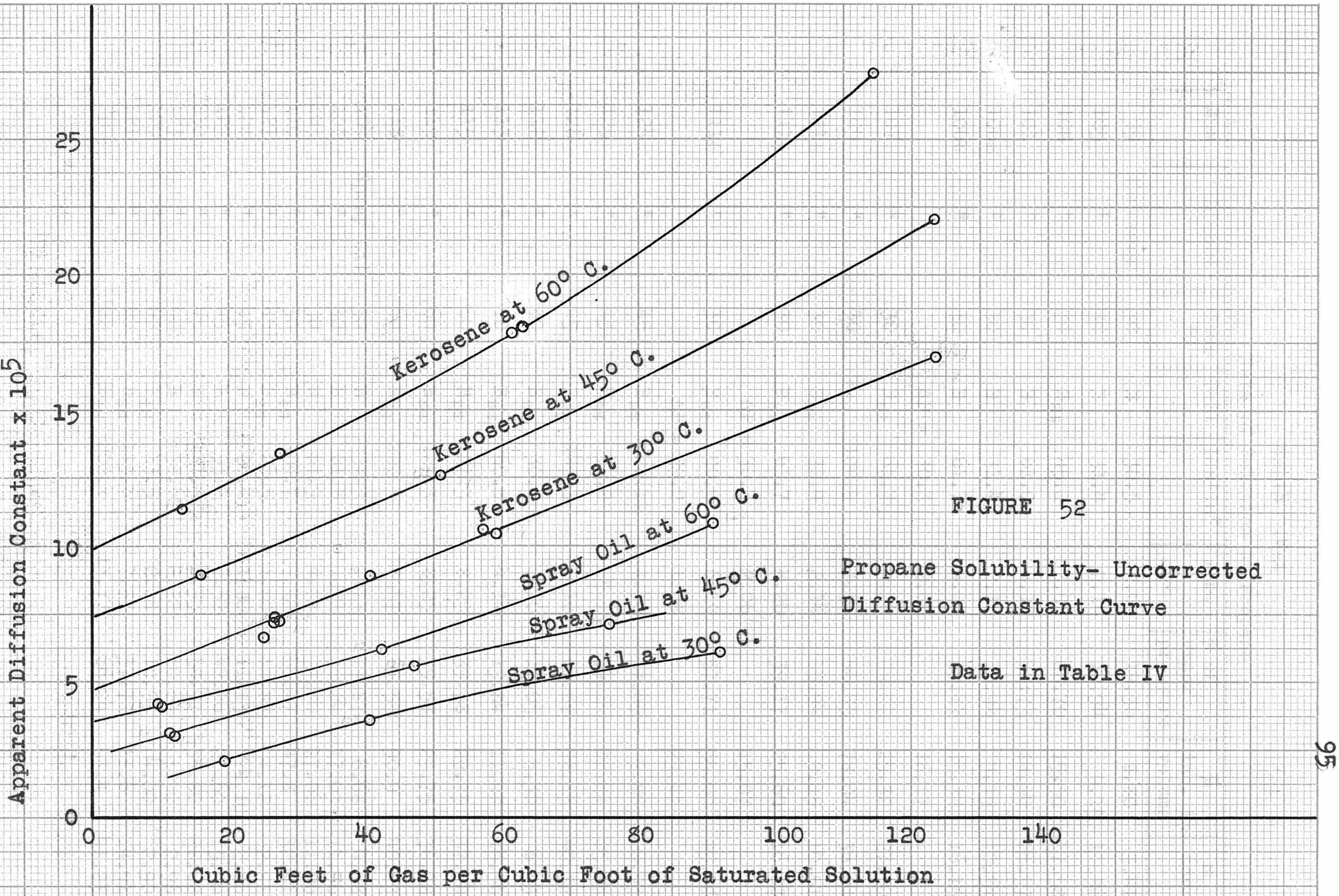


FIGURE 52

Propane Solubility- Uncorrected
Diffusion Constant Curve

Data in Table IV

TABLE IV-A

Rate of Solution of Propane

Run	Liquid	Temp °C	Cell	Lbs/in²	Atm.	% of vapor pressure	% inc. in volume	m corr.
99	Kerosene	30	B	30.5	2.08	19.36	8.80	9.41
105	"	30	B	31.4	2.14	19.94	9.15	10.36
108	"	30	B_{ss}	45.2	3.08	28.70	15.50	17.58
101	"	30	B	61.0	4.15	38.73	24.90	26.97
106a	"	30	B	31.4	2.14	19.94	9.15	10.54
106b	"	30	B	61.7	4.20	39.17	25.32	16.15
			$\Delta P =$	30.3	2.06		16.17	
107	"	30	B_{ss}	61.7	4.20	39.17	25.32	27.50
109	"	30	$B_{\ell s}$	104.5	7.11	66.35	78.04	36.04
111a	"	30	B_{ss}	31.4	2.14	19.94	9.15	10.51
111b	"	30	B_{ss}	61.7	4.20	39.17	25.60	16.28
			$\Delta P =$	30.3	2.06		15.07	
111c	"	30	B_{ss}	90.9	6.19	57.71	55.00	25.70
			$\Delta P =$	29.2	1.98		23.41	
124	"	45	B_{ss}	26.11	1.78	11.69	5.82	6.93
125	"	45	B_{ss}	76.2	5.19	34.14	22.81	25.89
126	"	45	$B_{\ell s}$	149.3	10.16	66.89	93.15	40.32
112	"	60	B_{ss}	30.8	2.10	10.05	5.30	6.43
113	"	60	B_{ss}	60.8	4.14	19.84	11.68	14.56
115	"	60	B_{ss}	121.3	8.25	39.58	29.75	37.94
119	"	60	B_{ss}	121.3	8.25	39.58	29.75	36.78
118	"	60	$B_{\ell s}$	200.9	13.67	65.55	90.9	40.83
104	Spray Oil	30	B	31.3	2.13	19.87	6.68	4.08
102	"	30	B	61.8	4.21	39.24	17.03	11.36
103	"	30	B	61.9	4.21	39.30	17.06	11.26
110	"	30	B_{ss}	104.7	7.12	66.47	47.8	32.41
127	"	45	B_{ss}	26.5	1.80	11.87	4.12	2.91
128	"	45	B	26.4	1.80	11.83	4.10	2.86
129	"	45	B	95.9	6.52	42.96	21.60	15.90
130	"	45	B	131.5	8.95	58.91	38.80	28.68
123	"	60	B	32.6	2.22	10.64	3.90	2.96
120	"	60	B_{ss}	33.5	2.28	10.93	4.00	2.90
121	"	60	B_{ss}	115.6	7.87	37.72	18.6	14.91
122	"	60	B_{ss}	202.4	13.77	66.04	53.4	41.23

TABLE IV-B

Run No.	ϵ * cc./cc.	S**	C_s**	Mols C_3H_8 per cc orig. oil	Mol-frac C_3H_8 in liquid	Apparent density dis. gas
99	0.00324	27.49	24.98	0.00115	0.1967	0.583
105	.00316	29.25	26.51	.001240	.2068	.598
108	.00331	47.49	40.66	.002013	.2973	.566
101	.00348	72.32	57.27	.003066	.3919	.543
106a	.00315	29.40	26.63	.001246	.2076	.600
106b	.					
107	.00342	74.94	59.14	.003177	.4004	.552
109	.00355	222.24	123.43	.009422	.6645	.532
111a	.00312	29.78	26.99	.001263	.2098	.605
111b	.00364	41.82	35.94	.001773	.2715	.519
111c	.00371	63.85	40.73	.002707	.3627	.509
124	.00345	17.25	15.94	.000723	.1335	.548
125	.00365	63.89	50.85	.002677	.3632	.518
126	.00392	243.56	123.25	.010206	.6850	.482
112	.00385	14.36	13.17	.00959	.1072	.491
113	.00378	31.95	27.63	.001323	.2223	.500
115	.00364	84.65	62.98	.003504	.4309	.519
119	.00373	82.64	61.55	.003423	.4251	.506
118	.00417	225.86	114.27	.009354	.6690	.453
104	.00324	20.80	19.28	.000882	.2271	.583
102						
103	.00359	48.08	40.62	.002039	.4045	.526
110	.00352	136.41	92.01	.005830	.6601	.537
127	.00351	12.04	11.30	.000505	.1451	.538
128	.00354	11.86	11.13	.000497	.1434	.534
129	.00377	58.70	47.18	.002460	.4532	.501
130	.00370	107.54	75.72	.004506	.6029	.511
123	.00374	10.80	10.04	.000447	.1332	.505
120	.00395	10.50	9.75	.000435	.1292	.478
121	.00372	51.85	42.23	.002148	.4227	.508
122	.00382	144.50	91.00	.005985	.6711	.495

* Gas volume measured at 60°F and 30 inches of mercury

** Gas and oil volume measured at 60°F and 30 inches of mercury

TABLE IV-C

Run No.	Density of Solution	D x 10^5 cm^2/ sec	D x 10^5 ft^2/hr	D x 10^5 Corr.for liquid expansion ft^2/hr
99	0.7773	1.70	6.59	6.52
105	.7779	1.85	7.17	7.03
108	.7646	2.30	8.91	8.73
101	.7442	2.73	10.58	10.24
106a	.7781	1.90	7.36	7.27
106b		3.16	12.25	12.00
107	.7456	2.69	10.42	10.09
109	.6794	4.38	16.97	15.32
111a	.7788	1.86	7.21	7.12
111b	.7447	2.57	9.96	9.76
111c	.7001	5.04	19.53	18.95
124	.7707	2.31	8.95	8.88
125	.7342	3.25	12.59	12.23
126	.6441	5.69	22.05	19.50
112	.7590	2.92	11.32	11.25
113	.7444	3.45	13.37	13.17
115	.7147	4.66	18.06	17.38
119	.7120	4.59	17.79	17.12
118	.6208	7.09	27.47	25.87
104	.8442	0.54	2.09	2.07
102		0.97	3.76	3.68
103	.8128	0.95	3.68	3.60
110	.7568	1.58	6.12	5.75
127	.8395	0.81	3.14	3.12
128	.8394	0.80	3.10	3.08
129	.7897	1.43	5.54	5.49
130	.7568	1.84	7.13	6.78
123	.8292	1.05	4.07	4.05
120	.8278	1.08	4.19	4.17
121	.7896	1.60	6.20	6.05
122	.7207	2.80	10.85	10.12

Effect of Liquid Expansion on Diffusion

The ordinary processes of diffusion of gases in liquids and diffusion of heat in the unsteady state have been explained by integration of Fick's proposition for a slab of material whose volume does not change as its gas content or heat content increases. This assumption is valid for most cases including the diffusion of methane within the limits of the experimental error of the determinations that have been made. However, in the case of propane diffusion the volume of the slab increases quite markedly. Figures 46 and 47 show that the volume of the saturated solution is nearly double that of the original oil at the higher partial pressures of propane.

As far as the determination of the diffusion coefficient is concerned, this difficulty could be avoided if suitable membranes could be produced that would permit the free passage of propane gas and hold back the oil at the same time. The membranes would have to be able to withstand several hundred pounds per square inch differential pressure. By supporting the oil on a membrane, the gas diffusing thru the oil layer could be measured in the steady state condition. However, the problem of preparing a suitable membrane would require considerable research. The results obtained by McBain and Kistler with cellophane membranes for ultrafiltration indicate that the problem is probably not impossible to solve experimentally.(10)

However, the problem in an oil formation is similar to the unsteady state diffusion rather than the steady state, so it is better to evaluate the effect in the unsteady state condition for the determinations which have been made. In the absorption cell, after a run has progressed for some time, the propane down in the liquid has not had to pass thru as long a liquid column as the propane just entering the liquid surface will have to pass thru before it gets down to the same place. The result is that at any given time, before equilibrium is reached, after the beginning of a run there is more propane in the liquid phase than there would have been if expansion of the liquid had not taken place.

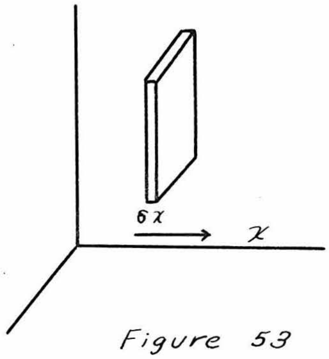


Figure 53

The analysis will be started from the beginning using previously derived steps (2) whenever convenient without repetition of the derivation. Imagine a slab of liquid perpendicular to the direction of flow and of one square cm. - or any other unit - cross section. Let the concentration at the center of the slab be C. The symbols have been defined on page 2 . Then the concentration at the left-hand face is $C - \frac{1}{2}\frac{\partial c}{\partial x}\delta x$ and at a right-hand face is $C + \frac{1}{2}\frac{\partial c}{\partial x}\delta x$ ($\frac{\partial c}{\partial x}$ is assumed negative so that flow of solute will be in the positive direction.) From Fick's proposition $\frac{\partial Q}{\partial t} = -D\frac{\partial c}{\partial x}$ the diffusion of solute thru the left-hand face is:

$$\left(\frac{\partial Q}{\partial t}\right)_1 = -D\frac{\partial}{\partial x}\left(c - \frac{1}{2}\frac{\partial c}{\partial x}\delta x\right)$$

but in addition to this liquid is carried across that boundary by the motion of the liquid away from the surface, which results from the expansion of the solution between this slab and the surface when solute accumulates in that region. The rate of increase in volume of the solution between the slab and the surface is

$$\epsilon\left[\left(\frac{\partial Q}{\partial t}\right)_0 - \left(\frac{\partial Q}{\partial t}\right)_1\right]$$

where ϵ is the increase in liquid volume per unit of gas dissolved, and since a column of liquid of unit cross-section is being considered, this is the rate at which solution passes the boundary of the slab. The rate at which solute is carried across the boundary is:

$$\epsilon\left[\left(\frac{\partial Q}{\partial t}\right)_0 - \left(\frac{\partial Q}{\partial t}\right)_1\right]\left(C - \frac{1}{2}\frac{\partial C}{\partial x}\delta x\right)$$

The total rate of flow of solute across the left-hand boundary is:

$$\left(\frac{\partial Q}{\partial t}\right)_1 = -D\frac{\partial}{\partial x}\left(C - \frac{1}{2}\frac{\partial C}{\partial x}\delta x\right) + \epsilon\left[\left(\frac{\partial Q}{\partial t}\right)_0 - \left(\frac{\partial Q}{\partial t}\right)_1\right]\left(C - \frac{1}{2}\frac{\partial C}{\partial x}\delta x\right) \quad (1)$$

Similar considerations of the rate of flow across the right-hand boundary give:

$$\left(\frac{\partial Q}{\partial t}\right)_2 = -D\frac{\partial}{\partial x}\left(C + \frac{1}{2}\frac{\partial C}{\partial x}\delta x\right) + \epsilon\left[\left(\frac{\partial Q}{\partial t}\right)_0 - \left(\frac{\partial Q}{\partial t}\right)_2\right]\left(C + \frac{1}{2}\frac{\partial C}{\partial x}\delta x\right) \quad (2)$$

Subtracting (2) from (1) to obtain the amount of solute accumulated by the slab,

$$\left(\frac{\partial Q}{\partial t}\right)_1 - \left(\frac{\partial Q}{\partial t}\right)_2 = D\frac{\partial^2 C}{\partial x^2}\delta x + \epsilon\left\{-\left(\frac{\partial Q}{\partial t}\right)\frac{\partial C}{\partial x}\delta x - \left[\left(\frac{\partial Q}{\partial t}\right)_1 - \left(\frac{\partial Q}{\partial t}\right)_2\right]C\right.$$
$$\left. + \frac{1}{2}\left[\left(\frac{\partial Q}{\partial t}\right)_1 + \left(\frac{\partial Q}{\partial t}\right)_2\right]\frac{\partial C}{\partial x}\delta x\right] \quad (3)$$

Note: ϵ is the increase in liquid volume for each unit volume of gas dissolved. Q is the total gas in solution. C is the concentration.

Since $\delta\chi$ may be taken as small as desired relative to χ, the expression $\frac{1}{2}\left[\left(\frac{\partial Q}{\partial t}\right)_1 + \left(\frac{\partial Q}{\partial t}\right)_2\right]$ May be considered to be the average rate of flow thru the slab, and the expression $\left(\frac{\partial Q}{\partial t}\right)_d$ may be substituted in (3) giving:

$$\left[\left(\frac{\partial Q}{\partial t}\right)_1 - \left(\frac{\partial Q}{\partial t}\right)_2\right](1+\epsilon C) = D\frac{\partial^2 C}{\partial \chi^2}\delta\chi - \left[\left(\frac{\partial Q}{\partial t}\right)_0 - \left(\frac{\partial Q}{\partial t}\right)_d\right]\epsilon\frac{\partial C}{\partial \chi}\delta\chi \quad (4)$$

The volume of the slab with unit area is $\delta\chi$, and its increase in concentration can be stated as follows:

$$\left(\frac{\partial Q}{\partial t}\right)_1 - \left(\frac{\partial Q}{\partial t}\right)_2 = \frac{\partial C}{\partial t}\delta\chi \quad (5)$$

Substituting in (4):

$$\frac{\partial C}{\partial t}(1+\epsilon C) = D\frac{\partial^2 C}{\partial \chi^2} - \left[\left(\frac{\partial Q}{\partial t}\right)_0 - \left(\frac{\partial Q}{\partial t}\right)_d\right]\epsilon\frac{\partial C}{\partial \chi} \quad (6)$$

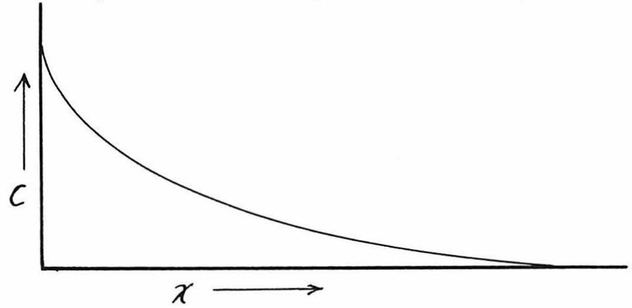


Figure 60

For the case that ϵ is 0, the solution is(2)

$$C = C_s - \frac{2C_s}{\pi}\int_0^{\frac{\chi}{2\sqrt{Dt}}} e^{-\beta^2}\,d\beta \quad (7)$$

This is a curve of the form shown in Figure 60. It always has the same shape, in the sense that it only expands in the x-direction with increasing time, the rate of movement of the curve toward the right being at every point proportional to the value of χ at that point. The area under this curve is $\int_0^\infty \chi\,dc$ and is equal to the total

Note: C_s is concentration value when solution is saturated.

quantity Q of gas in solution. For a small increment of time the increase in the quantity of solute in solution is:

$$\delta Q = \int_0^\infty \delta x \, dc \tag{8}$$

From ref. (2) it was found that the solution of (7) for a unit area is:

$$Q = 2 C_s \sqrt{\frac{Dt}{\pi}} \tag{9}$$

Differentiating

$$\frac{\partial Q}{\partial t} = C_s \sqrt{\frac{D}{\pi t}}$$

Multiply (9) by $\frac{1}{t}$

$$C_s \sqrt{\frac{D}{\pi t}} = \frac{Q}{2t}$$

$$\delta Q = \frac{Q}{2t} \delta t \tag{10}$$

Substituting for Q in

$$Q = \int_0^\infty x \, dc$$

from (8) gives $\delta Q = \frac{\delta t}{2t} \int_0^\infty x \, dc = \int_0^\infty \delta x \, dc$

at one value of t.

$$\frac{x \, \delta t}{2t} = \delta x$$

$$\frac{\delta x}{\delta t} = \frac{x}{2t} = \frac{\partial x}{\partial t} \tag{11}$$

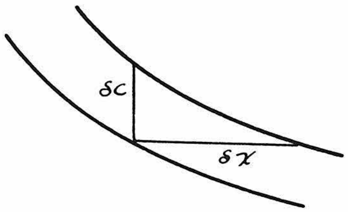


Figure 61

Let the lower curve in Figure 61 represent the concentration-curve at the time t, and the upper curve at a time t + δ t. Then for the time δ t:

$$\delta c = -\delta x \frac{\partial c}{\partial x}$$

or

$$\frac{\partial c}{\partial t} = -\frac{\partial x}{\partial t}\frac{\partial c}{\partial x}$$

Substituting from (11)

$$\frac{\partial c}{\partial t} = -\frac{x}{2t}\frac{\partial c}{\partial x} \qquad (12)$$

The effect of the expansion on the absorption of gas tends to increase the rate, since the expansion helps to carry the solute away from the surface. Therefore, at a given time, the quantity of gas in solution is greater. But the rate of absoprtion is determined solely by the concentration gradient at the surface, in the case being considered, and the gradient must be steeper than it would be if there were no expansion. In order for this condition to be satisfied, the distribution curve in the case of expansion must be related to the simple case in the manner shown by the dotted line in Figure

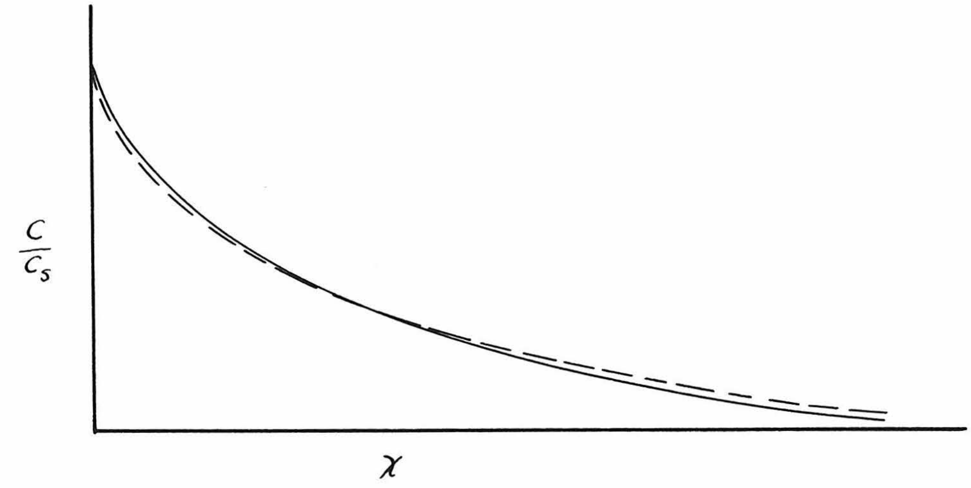


Figure 62

But whatever the relation of these two curves, that relationship must alwyas be the same for it can be shown (2) that at any point the ratio of solute moved by motion of the liquid, to solute moved by diffusion is constant. In other words, both of these curves will expand in the same manner with increasing time. Therefore the rate of increase of the abscissae of the dotted curve will also be $\frac{\partial x}{\partial t} = \frac{x}{2t}$

Then the general equation (6) may be written, after substituting (12):

$$-\frac{x}{2t}(1+\epsilon c)\frac{\partial c}{\partial x} = D\frac{\partial^2 c}{\partial x^2} - \epsilon\frac{\partial c}{\partial x}\left[\left(\frac{\partial Q}{\partial t}\right)_0 - \left(\frac{\partial Q}{\partial t}\right)_d\right] \tag{13}$$

In the last term,

$$\left(\frac{\partial Q}{\partial t}\right)_0 = -D\left(\frac{\partial c}{\partial x}\right)_0 \tag{14}$$

In order to make a substitution for $\left(\frac{\partial Q}{\partial t}\right)_d$ it is necessary to take into account not only the diffusion, but also the transference of the solute by motion of the liquid. The expression becomes:

$$\left(\frac{\partial Q}{\partial t}\right)_d = -D\left(\frac{\partial c}{\partial x}\right)_d + \epsilon c\left[\left(\frac{\partial Q}{\partial t}\right)_0 - \left(\frac{\partial Q}{\partial t}\right)_d\right] \tag{15}$$

Subtracting (15) from (14)

$$\left(\frac{\partial Q}{\partial t}\right)_0 - \left(\frac{\partial Q}{\partial t}\right)_d = -D\left[\left(\frac{\partial c}{\partial x}\right)_0 - \left(\frac{\partial c}{\partial x}\right)_d\right] - \epsilon c\left[\left(\frac{\partial Q}{\partial t}\right)_0 - \left(\frac{\partial Q}{\partial t}\right)_d\right]$$

$$\left(\frac{\partial Q}{\partial t}\right)_0 - \left(\frac{\partial Q}{\partial t}\right)_d = \frac{-D}{1+\epsilon c}\left[\left(\frac{\partial c}{\partial x}\right)_0 - \left(\frac{\partial c}{\partial x}\right)_d\right]$$

the general differential equation is now:

$$-\frac{x}{2t}\frac{\partial c}{\partial x}(1+\epsilon c) = D\frac{\partial^2 c}{\partial x^2} + \frac{\epsilon D}{(1+\epsilon c)}\frac{\partial c}{\partial x}\left[\left(\frac{\partial c}{\partial x}\right)_0 - \left(\frac{\partial c}{\partial x}\right)_d\right] \tag{16}$$

The general form of solution for this diffusion process is as seen in (7):

$$\frac{C}{C_s} = 1 - m \int_0^{\frac{nx}{\sqrt{Dt}}} e^{f(x)}\, dx \qquad (17)$$

Let $q = \frac{x}{2\sqrt{Dt}}$. Equation (17) can be approximated quite closely in the simple case by the expression

$$C = \frac{C_s}{a}\left(\sqrt{a^2 - bq + q^2} - q\right) \qquad (18)$$

except for large values of q which are of small importance here (Figure 54). Upon evaluating the constants, it happens, conveniently, that the best solution is obtained when a and b both have the same value of 1.3.

Substitute $\zeta = \epsilon C_s$, $Q = a^2 - aq + q^2$, $u = \sqrt{Q} - q$ and integrating (16):

$$f\left(\frac{nx}{\sqrt{Dt}}\right) = -q^2 + \frac{2}{3}\,\frac{\zeta q^3}{a} - \frac{2\zeta}{a}\int q\sqrt{Q}\,dq - \frac{\zeta}{2}\int \frac{(a - 2q - \sqrt{Q})\,dq}{a\sqrt{Q} + \zeta Q - \zeta q\sqrt{Q}} + I$$

(Complete steps are shown in Appendix II.)

$$\begin{aligned} f\left(\frac{nx}{\sqrt{Dt}}\right) = & -q^2 + \frac{2}{3}\,\frac{\zeta q^3}{a} - 2\,\frac{\zeta Q\sqrt{Q}}{3a} - \frac{a\zeta(2q-a)\sqrt{Q}}{4} \\ & - \frac{3a^2\zeta}{8}\log\left(\sqrt{Q} + q - \frac{a}{2}\right) + \frac{9a\zeta}{4(\zeta-2)(a+2u)} \\ & + \frac{9\zeta^2}{4(\zeta-2)^2}\log(a+2u) + \frac{1-\zeta-2\zeta^2}{(\zeta-2)^2}\log(a+\zeta u) \end{aligned}$$

(19)

By use of (19), a numerical evaluation of (17) was made for two cases of expansion; namely, δ = 0.1 and 0.5 or 10% and 50% increase in volume of liquid phase. These curves are plotted in Figure 55. The original plot was on a scale three times as large. These corrected curves fulfill the conditions necessary in regard to their relative slope, which was that they be steeper near the surface and displaced more to the right at considerable depth. The curves are displaced uniformly in Figure 55 to prevent overlapping. The value of the amount of gas in solution was obtained from these curves by measuring the area beneath them with a calibrated planimeter. The difference between the area with expansion and the case without expansion is the amount of gas transferred by expansion of the liquid. This effect is plotted in Figure 56. Since in most of the work the total value of this correction is not far from the experimental error of 3%, it was not considered necessary to calculate additional points for this curve which is practically a straight line within the limit of error of the calculations, which was about 0.1%.

This correction is small compared with the total divergence of the diffusion constant from a true constant due to failure of the original assumptions to hold rigorously for this case. The apparent diffusion coefficient and slope of the rate line, after correction for gas volume displaced by the expansion, may be expressed as follows:

$$K = A\left(\frac{m}{c_s}\right)^2$$

where K is the observed diffusion coefficient, A is a constant including the area and the other fixed factors not depending on diffusion, and m is the observed corrected slope of the rate of solution line. If δ

is the fraction of the transference due to expansion of the liquid, then

$$m'' = m(1 - \delta)$$

where m" is the true slope of the rate of solution line for the amount of gas transferred by diffusion alone. Substituting

$$D = A\left(\frac{m''}{C_s}\right)^2$$

$$D = A\,\frac{m(1 - \delta)}{c_s}{}^{2}$$

$$\frac{D}{(1 - \delta)^2} = \left(\frac{m}{c_s}\right)^2 = K$$

$$D = K(1 - \delta)^2$$

The corrected D is calculated and plotted in Figure 57, as a function of the equilibrium concentration value. It is observed that the points lie on straight lines within the experimental error except possibly a small deviation above values corresponding to 50% of the vapor pressure of liquid propane. This is fortunate because a function of the equilibrium concentration can be added directly to the diffusion coefficient at an infinitely small propane partial pressure to give the diffusion coefficient at any higher partial pressure. At partial pressures of propane at the vapor pressure of liquid propane this relation will of course not hold because the process is no longer one of diffusion, but that of simple condensation depending on the rate at which gas is supplied to the apparatus. It is surprising that the relation for a linear increase in the diffusion coefficient holds as well as it does up to nearly 70% of the vapor pressure of pure liquid propane. It is possible that there is very little deviation from this relation before the vapor pressure of liquid propane is reached, because the gas must diffuse into the liquid before more can be absorbed at any pressure below the liquid propane vapor pressure.

The lines in Figure 57 were extrapolated to zero solubility which corresponds to the solubility of propane at zero partial pressure. These extrapolated values are plotted as a function of temperature in Figure 58 with remarkably good results. This curve represents the diffusion constant for propane at very low partial pressures approaching zero and is the true diffusion constant for propane. The value of this diffusion constant for propane is approximately one-third of that for methane in the two oils studied.

The lines in Figure 54 are not parallel but the slope increases with increasing temperature as shown by Figure 59. The increase in slope for spray oil is a linear function of the temperature, while the slope increases more rapidly as the temperature increases for diffusion of propane in kerosene.

A general equation can be written to fit the diffusion coefficients of each of these two oils with suitable constants for each oil. This would not be difficult due to the fact that the variable temperature and solubility known to be involved can be assumed to be nearly straight line functions of the diffusion coefficient. However, the constants for each oil are different and nothing can be obtained from such equations which cannot be read directly from Figures 56, 57, and 58. In order to determine the diffusion coefficient for a particular condition for the rate of solution of propane in one of these oils or in one with similar properties, it is necessary to determine the average molecular weight of the oil. From this and the temperature and pressure of the propane, the equilibrium concentration can be obtained from Figure 49. Proceeding to Figure 58, the value of the diffusion coefficient for propane at nearly zero pressure and the desired temperature can be read. Plot this value from Figure 58 on the ordinate for zero solubility in Figure 57, then draw a line thru this point with a slope obtained from Figure 59. The intersection of this line and the solubility value gives the diffusion coefficient without expansion of the liquid. If the conditions required that a correction be made for the expansion, a value of δ can be calculated from the product of values of ϵ from Table IV and the solubility value from Figure 49. Following this, the fraction of diffusion due to expansion can be obtained from Figure 56. Since this correction is small it does not need to be determined with a high degree of accuracy. This method of estimating a diffusion coefficient from the data given is somewhat more reliable than by use of Figure 52 which gives the experimental values of the diffusion coefficient for the rate of solution of propane in kerosent and in spray oil.

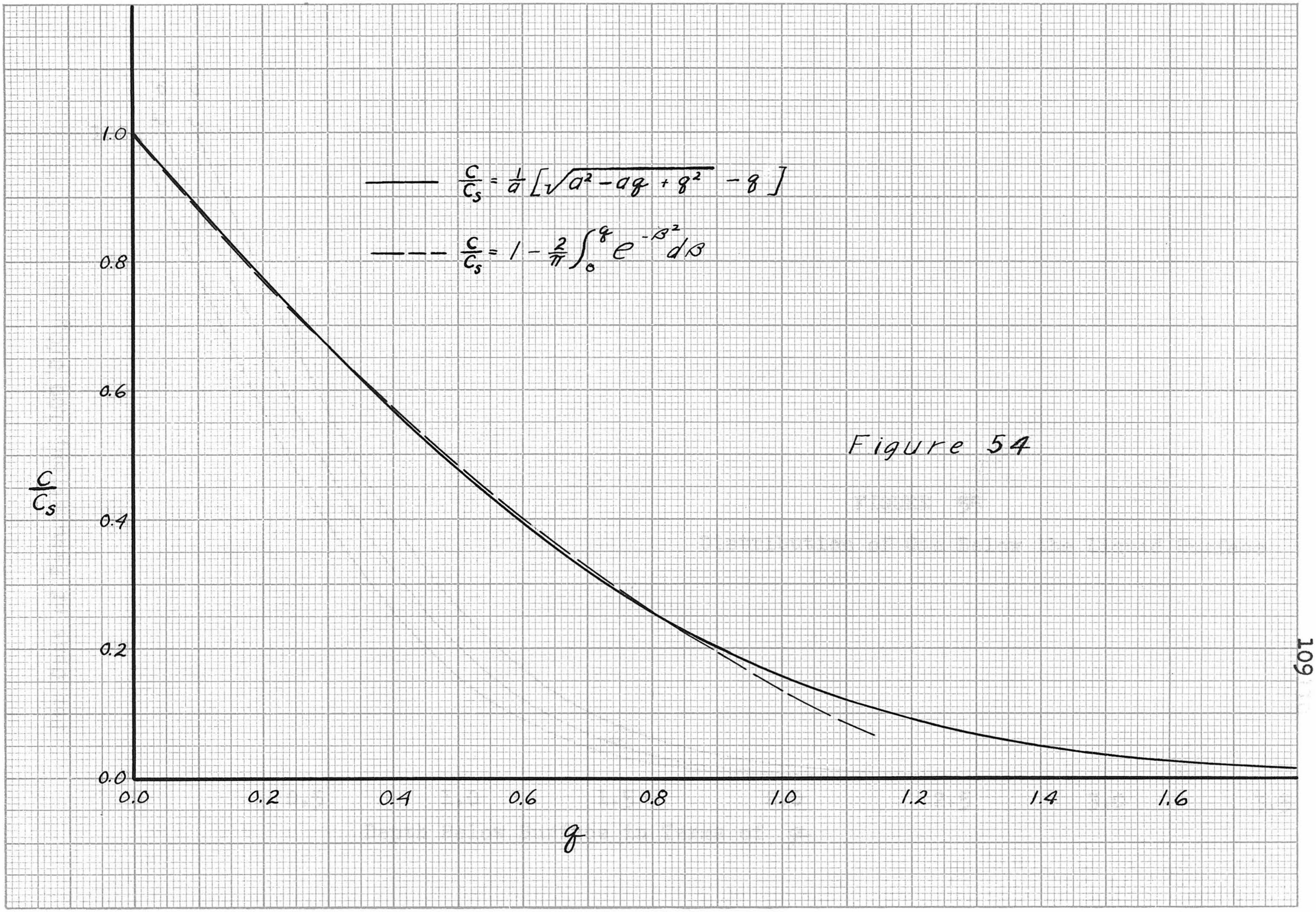

$\frac{C}{C_s} = \frac{1}{a}\left[\sqrt{a^2 - aq + q^2} - q\right]$
$\frac{C}{C_s} = 1 - \frac{2}{\pi}\int_0^q e^{-\beta^2} d\beta$
$\frac{C}{C_s}$
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
q

Figure 54

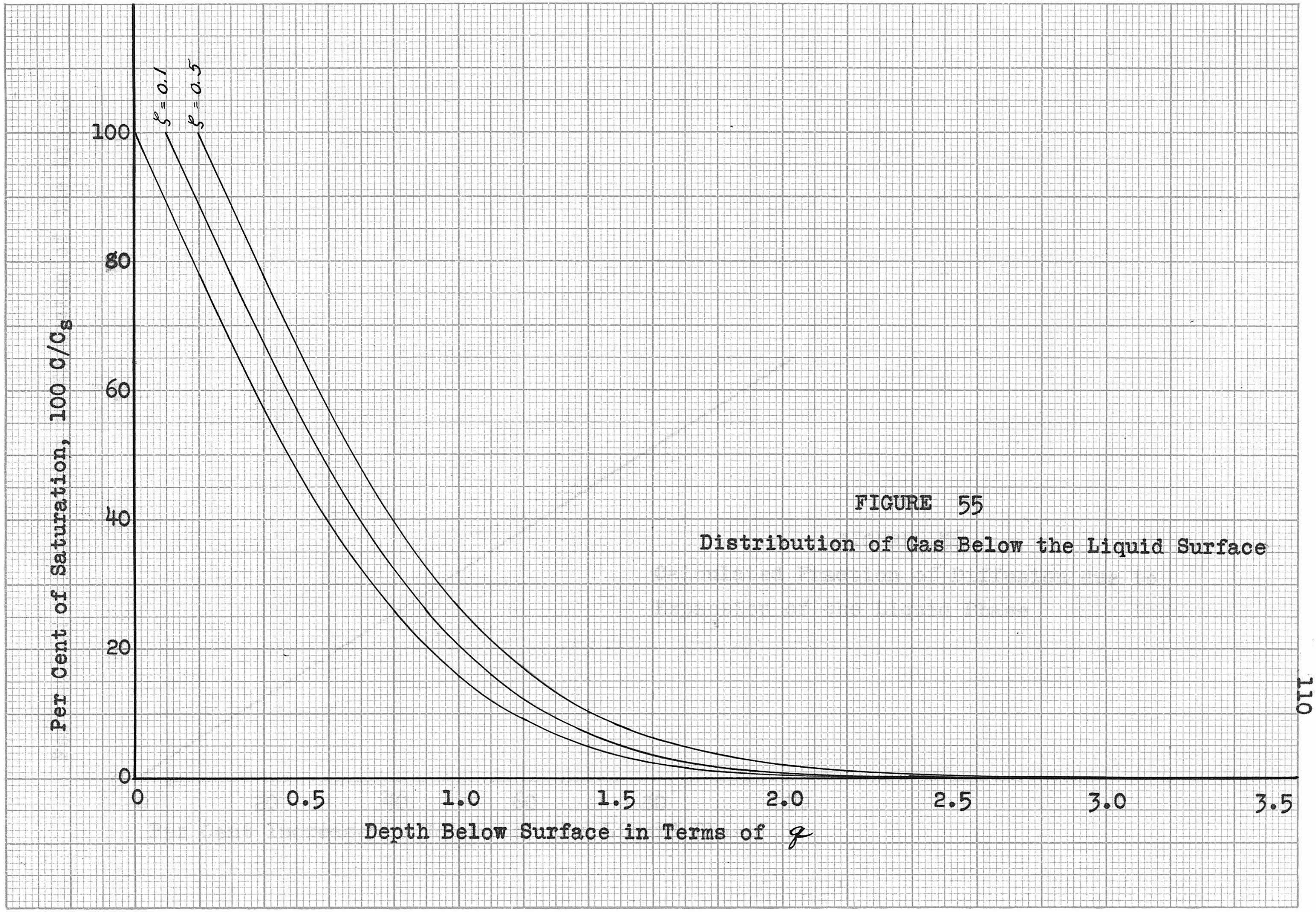


FIGURE 55

Distribution of Gas Below the Liquid Surface

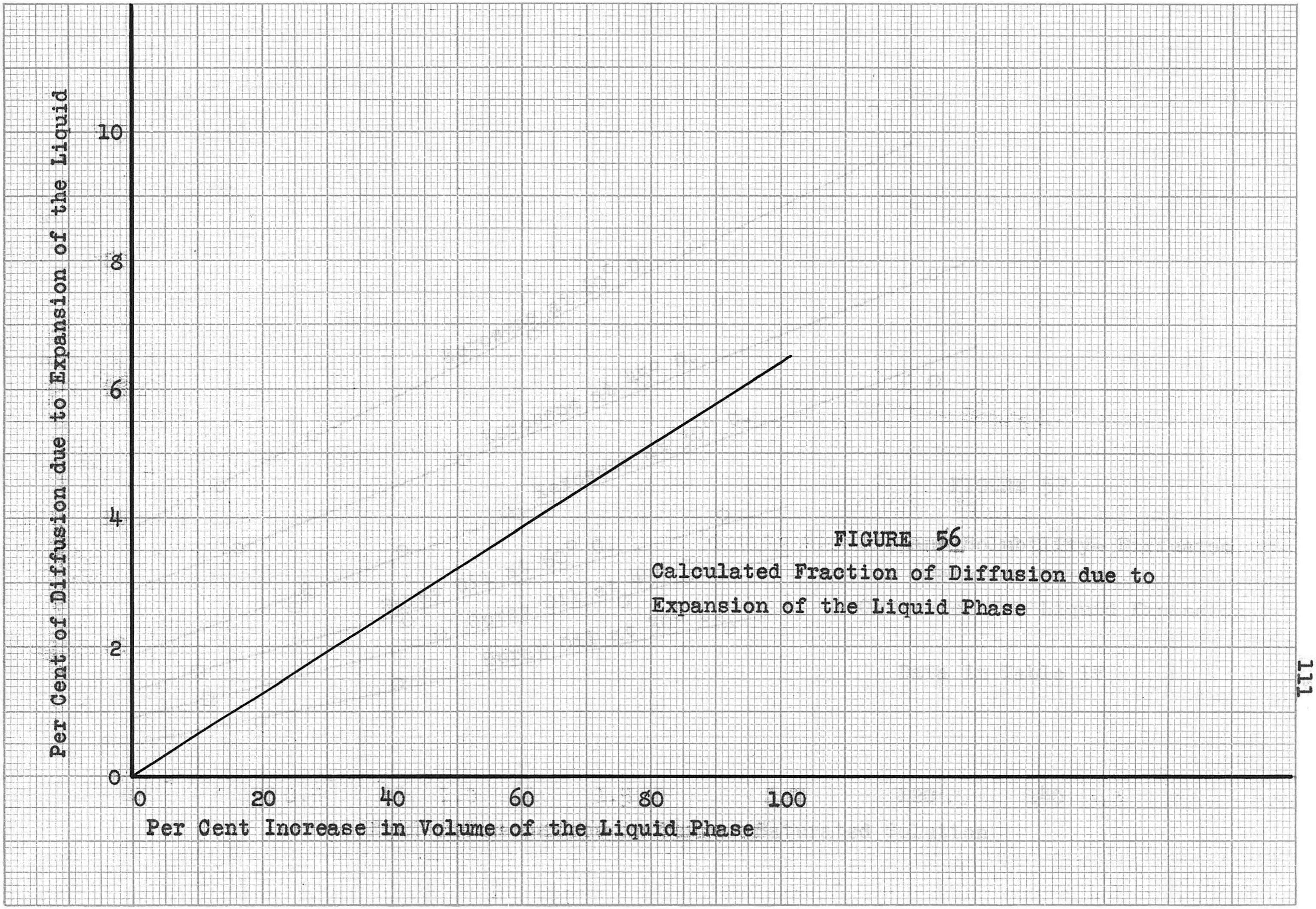


FIGURE 56

Calculated Fraction of Diffusion due to Expansion of the Liquid Phase

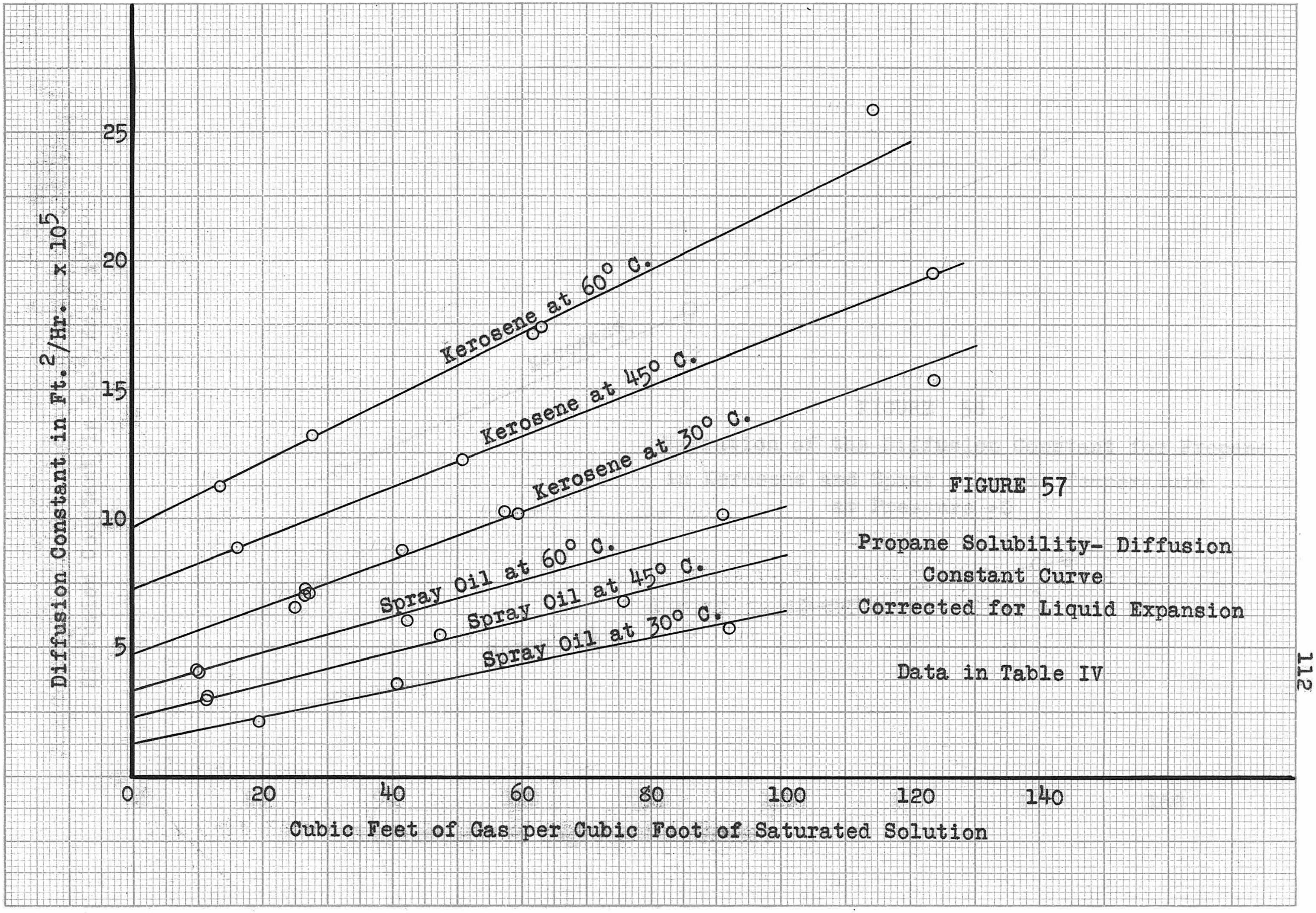


FIGURE 57

Propane Solubility- Diffusion
Constant Curve
Corrected for Liquid Expansion

Data in Table IV

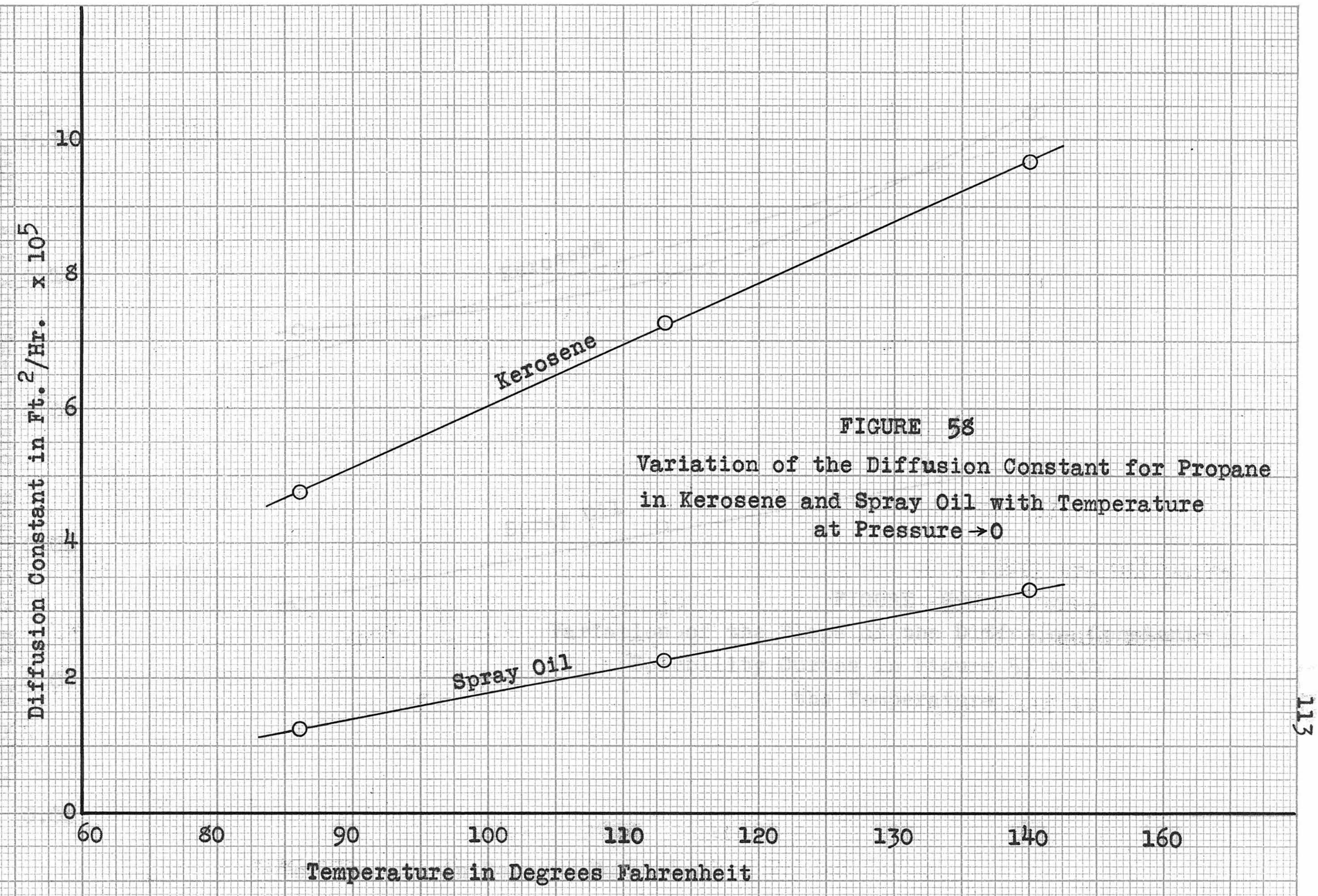


FIGURE 58

Variation of the Diffusion Constant for Propane in Kerosene and Spray Oil with Temperature at Pressure → 0

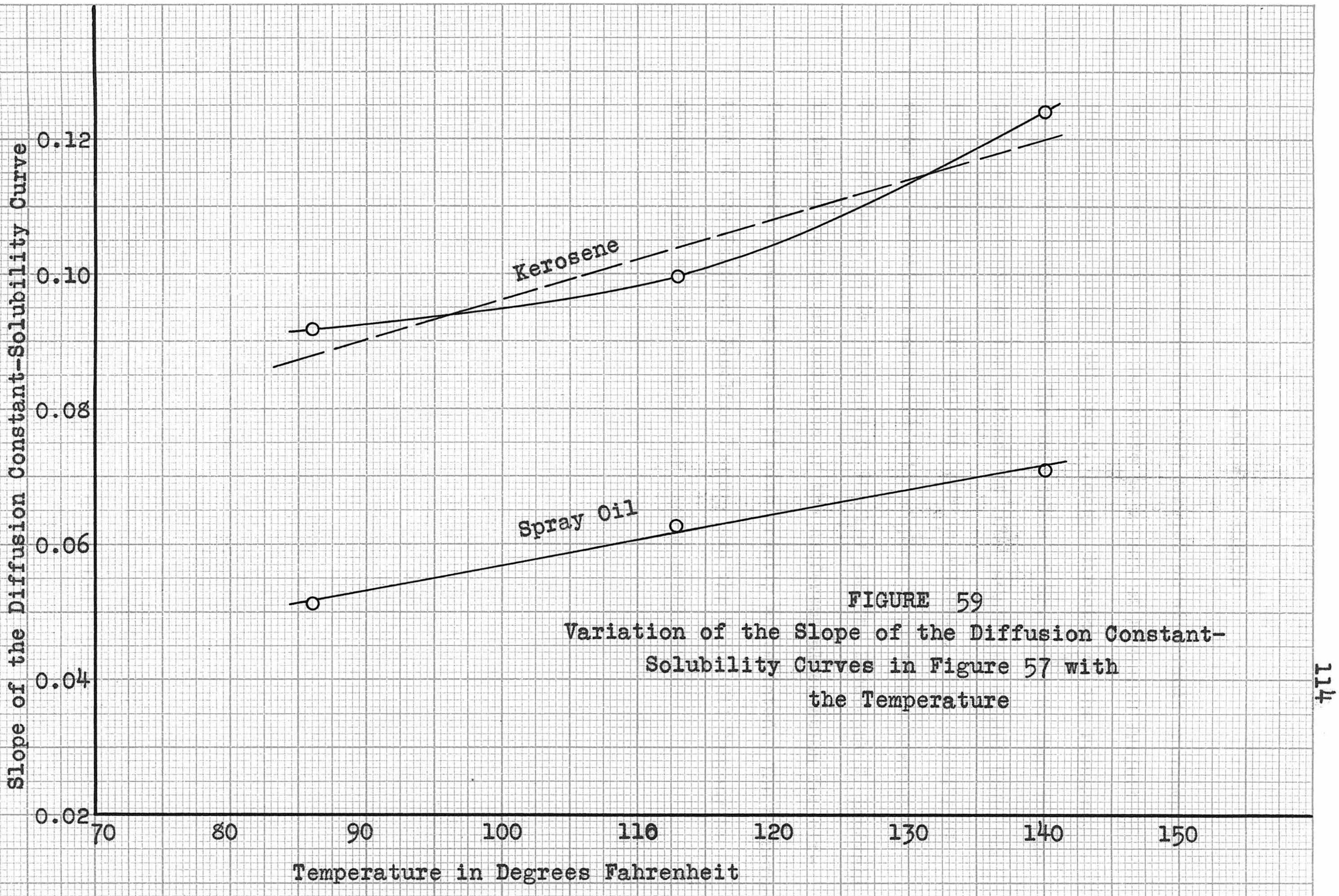


FIGURE 59
Variation of the Slope of the Diffusion Constant-Solubility Curves in Figure 57 with the Temperature

ACKNOWLEDGEMENTS

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SUMMARY

The apparatus used for the determination of the rate of solution of hydrocarbon gases in hydrocarbon oils by Pomeroy, Scudder, and Stapp has been improved so that consistent results reproducible within 3% can be obtained. Methane and propane gases with over 99% purity have been prepared. The coefficients for the rate of solution of methane in 16 oils, varying in viscosity from 0.21 to 99 centipoises, including 6 crude oils, at 86°F (30°C) and 300 lbs./sq.in. (20 atm.) were measured. The equilibrium concentration of methane in the oil has been correlated with the density of the original oil. The effect of temperature on the diffusion coefficient for methane was studied with 2 crudes and 2 refined oils over the range from 86°F to 140°F (60°C). A logarithmic correlation of the diffusion constant for methane over this temperature range has been made with the viscosity of the original oil and the temperature.

The rate of solution of propane in kerosene, and in spray oil over a temperature range of 96°F to 140°F was determined up to 67% of the vapor pressure of liquid propane. The equilibrium concentration in mol fraction of propane in the liquid was found to be a linear function of the percent of the vapor pressure of liquid propane. The effect on the diffusion coefficient of the expansion of the liquid due to solution of gas was calculated and found to be small. The diffusion coefficient for the highly soluble gas, propane, was found to be a linear function of the concentration of propane in the liquid and the temperature, with a variation in the diffusion coefficient of about five-fold.

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APPENDIX I

Sample of Notes and Calculations

Calculation of the data for Isopentane.

Run No. 141.

Liquid: Isopentane

Gas: Methane (0.36% C_2H_6)

Partial pressure methane = 298.2 lbs./sq.in.

Partial pressure isopentane and air = 2.5 lbs./sq.in. gauge

Temperature: 30°C

Weight of oil: 54.221 gm. Volume = 54.221 ÷ 0.6098 = 88.92 cc.

Brass cell; no evacuation; no slugs.

m' = uncorrected slope of rate line = 22.27.

Length of run: 7 hours.

$V_s - V_i$ = Apparent amount of gas dissolved in oil = 2092.5 cc.

C_s' = Apparent solubility per cc. oil = 2092.5/88.92 = 23.53 cc.

Change in volume = 6.11%

88.92 x 0.0611 = 5.433 cc. increase in volume of liquid.

5.433 ÷ 2092.5 = 0.00260 cc. increase / cc. gas dissolved.

Correction factor for liquid expansion:

$$1 + 0.00260 \, \frac{298.2 + 14.3}{14.7} \times \frac{1}{0.968} = 1.0570$$

Compressibility deviation from perfect gas for methane at this pressure = 0.968.

S = solubility of gas in original oil = 23.53 x 1.0570 = 24.87 cc.

C_s = equilibrium concentration in cc. of gas per cc. of solution

= 24.87 ÷ 1.0611 = 23.44 cc.

$m = m' \times 1.0570 = 22.27 \times 1.0570 = 23.53$

$$D = 1.3262 \times 10^{-4} \left(\frac{23.53}{23.44}\right)^2 = 13.37 \times 10^{-5}.$$

$$\epsilon = \frac{0.0611}{24.87} = 0.00245 \text{ cc/cc gas dissolved.}$$

APPENDIX II

Solution of the Differential Equation for Diffusion with Expansion of the Liquid

The differential equation (16) has been set up for the diffusion of a gas into a liquid when the volume of the liquid is increased by the dissolving gas:

$$-\frac{x}{2t}\frac{\partial c}{\partial x}(1+\epsilon c) = D\frac{\partial^2 c}{\partial x^2} + \frac{\epsilon D}{(1+\epsilon c)}\frac{\partial c}{\partial x}\left[\left(\frac{\partial c}{\partial x}\right)_0 - \left(\frac{\partial c}{\partial x}\right)_d\right] \qquad (16)$$

The solution of this equation is not apparent at once, so substitutions for c, $\left(\frac{\partial c}{\partial x}\right)_0$ and $\left(\frac{\partial c}{\partial x}\right)_d$ will be made. For this an approximate algebraic expression for the values of c in the case for no expansion will be used so that substitutions can be recognized. Write (7)

$$c = c_s - \frac{2c_s}{\pi}\int_0^q e^{-\beta^2}\,d\beta$$

where $q = \frac{x}{2\sqrt{Dt}}$. This can be approximated quite closely by an expression of the form:

$$c = \frac{c_s}{a}\left(\sqrt{a^2 - bq + q^2} - q\right) \qquad (17')$$

except for large values of q which are of small importance here (Fig. 54). Upon evaluating the constants, it happens, conveniently, that the best solution is given when a and b both have the same value of 1.3. Therefore (17') can be written:

$$c = \frac{c_s}{a}\left(\sqrt{a^2 - aq + q^2} - q\right) \qquad (18')$$

also

$$\frac{\partial q}{\partial x} = \frac{1}{2\sqrt{Dt}} \qquad (19')$$

$$\frac{\partial c}{\partial x} = \frac{\partial q}{\partial x}\cdot\frac{\partial c}{\partial q} = \frac{\partial c}{\partial q}\cdot\frac{1}{2\sqrt{Dt}} \qquad (20)$$

Differentiating (18) and substituting (19):

$$\left(\frac{\partial C}{\partial x}\right)_a = \frac{C_s}{2a\sqrt{Dt}}\left(\frac{-a+2q}{2\sqrt{a^2-aq+q^2}} - 1\right) \qquad (21)$$

At x = 0, q = 0

$$\left(\frac{\partial c}{\partial x}\right)_0 = \frac{C_s}{2a\sqrt{Dt}}\left(\frac{-a}{2\cdot a} - 1\right) = -\frac{3\,C_s}{4a\sqrt{Dt}} \qquad (22)$$

These approximations affect only the correction terms in (16).

Substituting the values from (18), (21) and (22):

$$-\frac{x}{2t}\,\frac{\partial C}{\partial x}\left[1+\frac{\epsilon C_s}{a}\left(\sqrt{a^2-aq-q^2}-q\right)\right] - D\,\frac{\partial^2 C}{\partial x^2} + \frac{\epsilon D C_s \frac{\partial c}{\partial x}\left[\frac{a-2q}{2\sqrt{a^2-aq+q^2}} - \frac{1}{2}\right]}{2a\sqrt{Dt}\left[1+\frac{\epsilon C_s}{a}\left(\sqrt{a^2-aq+q^2}-q\right)\right]}$$

(23)

Substitute $\zeta = \epsilon C_s$ and $Q = a^2 - a\,q + q^2$ in (23):

$$-\frac{x}{2t}\,\frac{\partial c}{\partial x}\left[1+\frac{\zeta\sqrt{Q}}{a}-\frac{\zeta q}{a}\right] = D\,\frac{\partial c^2}{\partial x^2} + \frac{D\zeta\frac{\partial c}{\partial x}\left(\frac{a-2q}{\sqrt{Q}}-1\right)}{4a\sqrt{Dt}\left[1+\frac{\zeta}{a}\left(\sqrt{Q}-q\right)\right]}$$

$$-\frac{x}{2t}\,\frac{\partial c}{\partial x}\left(a+\zeta\sqrt{Q}-\zeta q\right) - \frac{\zeta\sqrt{D}\,\frac{\partial c}{\partial x}\left(a-2q-\sqrt{Q}\right)}{4\sqrt{t}\left(a\sqrt{Q}+\zeta Q-\zeta q\sqrt{Q}\right)} = D\,\frac{\partial^2 c}{\partial x^2}$$

(24)

Assume that this equation has a solution similar to that of the general case, namely:

$$\frac{C}{C_s} = 1 - m \int_0^{\frac{nx}{\sqrt{Dt}}} e^{f(x)} dx \tag{25}$$

Differentiating:

$$\frac{\partial C}{\partial x} = - \frac{m n C_s}{\sqrt{Dt}} e^{f\left(\frac{nx}{\sqrt{Dt}}\right)}$$

$$\frac{\partial^2 C}{\partial x^2} = - \frac{m n C_s}{\sqrt{Dt}} e^{f\left(\frac{nx}{\sqrt{Dt}}\right)} \left(\frac{d\left[f\left(\frac{nx}{\sqrt{Dt}}\right)\right]}{dx} \right)$$

$$= \frac{\partial C}{\partial x} \frac{d\left[f\left(\frac{nx}{\sqrt{Dt}}\right)\right]}{dx}$$

Substituting in (24)

$$- \frac{x\,dx}{2at}(a + \zeta\sqrt{Q} - \zeta q) - \frac{\zeta\sqrt{\frac{D}{t}}[a - 2q - \sqrt{Q})dx}{4(a\sqrt{Q} + \zeta Q - \zeta q\sqrt{Q})} = D\,d\left[f\left(\frac{nx}{\sqrt{Dt}}\right)\right] \tag{26}$$

Since $x = 2q\sqrt{Dt}$ and $dx = 2\sqrt{Dt}\ dq$

Substituting in (26)

$$- \frac{2q}{a} dq\,(a + \zeta\sqrt{Q} - \zeta q) - \frac{\zeta\,dq\,(a - 2q - \sqrt{Q}}{2(a\sqrt{Q} - \zeta Q - \zeta q\sqrt{Q})} = d\left[f\left(\frac{nx}{\sqrt{Dt}}\right)\right] \tag{27}$$

Integrating (27):

$$f\left(\frac{nx}{\sqrt{Dt}}\right) = -q^2 + \frac{2}{3}\,\frac{\zeta q^3}{a} - \frac{2\zeta}{a}\int q\sqrt{Q}\,dq - \frac{\zeta}{2}\int \frac{(a - 2q - \sqrt{Q})dq}{a\sqrt{Q} + \zeta Q - \zeta q\sqrt{Q}} + I \tag{28}$$

In Pierce's "Table of Integrals" the following formulas are given: (where $X = a + bx + cx^2$)

176. $$\int x\sqrt{X}\,dx = \frac{X\sqrt{X}}{3c} - \frac{b}{2c}\int\sqrt{X}\,dx$$

165. $$\int\sqrt{X}\,dx = \frac{(2cx+b)}{4c} + \frac{(4ac-b^2)}{8c}\int\frac{dx}{\sqrt{X}}$$

160. $$\int\frac{dx}{\sqrt{X}} = \frac{1}{\sqrt{c}}\log\left(\sqrt{X} + x\sqrt{c} + \frac{b}{2\sqrt{c}}\right)$$

$$\int x\sqrt{X}\,dx = \frac{X\sqrt{X}}{3c} - \frac{b(2cx+b)}{8c}\sqrt{X} - \frac{b(4ac-b^2)}{16c^2\sqrt{c}}\log\left(\sqrt{X} + x\sqrt{c} + \frac{b}{2\sqrt{c}}\right) \tag{29}$$

Integration of the 3rd term of (28) by (29)

$$Q = a^2 - aq + q^2$$

$$-\frac{25}{a}\int q\sqrt{Q}\,dq = -\frac{25}{a}\left\{\frac{Q\sqrt{Q}}{3} + \frac{a(2q-a)}{8}\sqrt{Q} + \frac{3}{16}a^3\log\left(\sqrt{Q} + q - \frac{a}{2}\right)\right\} \tag{30}$$

Pierce, 235:

$$\int f\left(x, \sqrt{a+bx+x^2}\right)dx = 2\int f\left(\frac{u^2-a}{b-2u}, \frac{u^2-bu+a}{2u-b}\right)\frac{2(bu-a-u^2)}{(b-2u)^2}\,du \tag{31}$$

where $u = \sqrt{a + bx + x^2} - x$.

When $Q = a^2 - aq + q^2$, $u = \sqrt{Q} - q$.

Substitution in (31)

$$\int f(q, \sqrt{Q})\,dq = -2\int f\left(\frac{a^2-u^2}{a+2u}, \frac{u^2+au+a^2}{2u+a}\right)\frac{(u^2+au+a^2)}{(a+2u)^2}\,du \tag{32}$$

Integration of the last term of (28) by (32):

$$-\frac{\zeta}{2}\int \frac{(a-2q-\sqrt{Q})\,dq}{a\sqrt{Q}+\zeta Q-\zeta q\sqrt{Q}} =$$

$$= \zeta\int \frac{\left[a-\frac{2a^2-2u^2}{a+2u}-\frac{u^2+au+a^2}{a+2u}\right]\frac{u^2+au+a^2}{(a+2u)^2}\,du}{a\left(\frac{u^2-au+a^2}{a+2u}\right)+\zeta\left(\frac{u^2+au+a^2}{a+2u}\right)^2-\zeta\frac{(a^2-u^2)(u^2+au+a^2)}{(a+2u)^2}}$$

$$= \zeta\int \frac{(u^2-au-2a^2)\,du}{(a+2u)^2(a+\zeta u)} \tag{33}$$

Let

$$\frac{A}{(a+2u)^2}+\frac{B}{(a+2u}+\frac{C}{(a+\zeta u)}=\frac{u^2+au-2a^2}{(a+2u)^2(a+\zeta u)}$$

$$A(a+\zeta u)+B(a+2u)(a+\zeta u)+C(a+2u)^2=u^2+au-2a^2$$

Let $u=-\frac{a}{2}$

$$A=\left(a-\frac{a\zeta}{2}\right)=\frac{a^2}{4}-\frac{a^2}{2}-2a^2=-\frac{9a^2}{4}$$

$$A=\frac{9a}{2(\zeta-2)}$$

Let $u=-\frac{a}{\zeta}$

$$C=\left(a-\frac{2a}{\zeta}\right)^2=\frac{a^2}{\zeta^2}-\frac{a^2}{\zeta}-2a^2$$

$$C=\frac{1-\zeta-2\zeta^2}{(\zeta-2)^2}$$

Let $u = 0$

$$aA + Ba^2 + Ca^2 = -2a^2$$

$$B = -\frac{A}{a} - C - 2$$

$$= \frac{9a}{2a(\zeta-2)} - \frac{1-\zeta-2\zeta^2}{(\zeta-2)^2} - 2$$

$$= \frac{9\zeta}{2(\zeta-2)^2}$$

Adding terms:

$$\int(33) = \frac{9a\zeta}{2(\zeta-2)}\int\frac{du}{(a+2u)^2} + \frac{9\zeta^2}{2(\zeta-2)^2}\int\frac{du}{a+2u} + \frac{\zeta(1-\zeta-2\zeta^2)}{(\zeta-2)^2}\int\frac{du}{a+\zeta u}$$

$$= \frac{-9a\zeta}{4(\zeta-2)(a+2u)} + \frac{9\zeta^2}{4(\zeta-2)^2}\log(a+2u) + \frac{(1-\zeta-2\zeta^2)}{(\zeta-2)^2}\log(a+\zeta u) \qquad (33')$$

Integration of (28); adding (32) and (33)

$$f\left(\frac{nx}{\sqrt{Dt}}\right) = -q^2 + \frac{2}{3}\frac{\zeta q^3}{a} - \frac{2\zeta Q\sqrt{Q}}{3a} - \frac{a\zeta(2q-a)}{4}\sqrt{Q}$$

$$- \frac{3}{8}a^2\zeta\log\left(\sqrt{Q}+q-\frac{a}{2}\right) + \frac{9a\zeta}{4(\zeta-2)(a+2u)}$$

$$+ \frac{9\zeta^2}{4(\zeta-2)^2}\log(a+2u) + \frac{1-\zeta-2\zeta^2}{(\zeta-2)^2}\log(a+\zeta u) \qquad (34)$$

Equation (7) may be written:

$$\frac{C}{C_s} = 1 - m\int_0^{\frac{nx}{\sqrt{Dt}}} e^{f(\beta)}\,d\beta \qquad (35)$$

When $\zeta = 0$, the f(x) in (25) can be evaluated from (34) and (35) written:

$$\frac{C}{C_s} = 1 - m\int_0^{\frac{nx}{\sqrt{Dt}}} e^{-\beta^2 + \frac{\log a}{4}}\, d\beta$$

$$= 1 - m\, a^{\frac{1}{4}}\int_0^{\frac{nx}{\sqrt{Dt}}} e^{-\beta^2}\, d\beta \tag{36}$$

but when $\zeta = 0$ there is no expansion and (36) must be the same as the simple case (7). then

$$m\, a^{\frac{1}{4}} = \frac{2}{\sqrt{\pi}} \qquad \text{and} \qquad n = \frac{1}{2}$$

The numerical evaluation of the effect of expansion was accomplished by calculating the distribution curve for two additional cases: $\zeta = 0.1$ and 0.5. The difference between the area under these curves and the area under the distribution curve for $\zeta = 0$ is the amount of gas transferred by liquid expansion.

The evaluation of m was made from the following:

when $\frac{nx}{\sqrt{Dt}} = \infty$, $\frac{C}{C_s} = 0$

$$0 = 1 - m\int_0^{\infty} e^{f(x)}\, dx \qquad \text{from (25)}$$

$$\frac{1}{m} = \int_0^{\infty} e^{f(x)}\, dx \tag{37}$$

Differentiating (25):

$$\frac{dc}{dx} = -\frac{mn}{\sqrt{Dt}}\, e^{f\left(\frac{nx}{\sqrt{Dt}}\right)}$$

$$\left(\frac{dc}{dx}\right)_{x=0} = \frac{mn}{\sqrt{Dt}}\, e^{f(0)}$$

The value of $e^{f(0)}$ at $q = 0$ is 1.09640 calculated from (34)

$$\left(\frac{dc}{dx}\right)_{x=0} = -\frac{1.09640\, mn}{\sqrt{Dt}}$$

$$\left(\frac{\partial Q}{\partial t}\right)_{x=0} = -D\left(\frac{\partial c}{\partial x}\right)_{x=0} = 1.09640\, mn\sqrt{\frac{D}{t}} \tag{38}$$

The area under the concentration distribution curve of $c/c_s \sim q$ is, for a unit area of oil surface:

$$\int_0^\infty \frac{c}{c_s}\, dq = \frac{1}{2\sqrt{Dt}} \int \frac{c}{c_s}\, dx = \frac{1}{2\sqrt{Dt}}\, \frac{Q}{Q_s}$$

$$\frac{Q}{Q_s} = 2\sqrt{Dt} \int_0^\infty \frac{c}{c_s}\, dq \tag{39}$$

Integrate (38) for Q/Q_s value from 0 to t:

$$\frac{Q}{Q_s} = \int_0^t \left(\frac{\partial Q}{\partial t}\right) dt = 1.09640\, mn\sqrt{D} \int_0^t \frac{dt}{\sqrt{t}}$$

$$= 2 \times 1.09640\, mn\sqrt{Dt} \tag{40}$$

$$2\sqrt{Dt}\int_0^\infty \frac{C}{C_s}\,dq = 2 \times 1.09640\, m n \sqrt{Dt}$$

$$n = \frac{1}{1.09640\, m}\int_0^\infty \frac{C}{C_s}\, q \tag{41}$$

The concentration distribution curve plotted in Figure 55 on the left for the case of $\varsigma = 0$ was calculated directly from a table of values of the probability integral. This curve satisfies the conditions when there is no expansion and all curves corrected for expansion will have the same shape with a slightly greater slope at the beginning and a lower slope at considerable depth.

The middle curve in Figure 55 was calculated for $\varsigma = 0.1$ The first step in the calculation was the evaluation of $f\left(\frac{nx}{\sqrt{Dt}}\right)$ from equation (34) for values of q down to 3.50. These were calculated for each 0.01 down to where the slope had decreased sufficiently to make this no longer necessary. Then the value of $e^{f(x)}$ was calculated for each interval. The summation of these values from 0 to ∞ gave a value of m = 1.03271 for this case for equation (37). In order to obtain n, equation (41) was calculated for each value of q above, by taking $(1 - m \sum e^{f(x)})$ at each interval. The summation of the resulting values of $\frac{C}{C_s}\,dq$ was not found sufficiently accurate so it was necessary to plot them accurately on a graph 20" by 30" and determine the area under the curve with a planimeter calibrated with the coordinate lines on the graph paper. The same plot has been made in Figure 55. The value for the simple case was 0.56467. The value for $\varsigma = 0.1$ is 0.56803 or an increase of 0.68%. The value for $\varsigma = 0.5$ was 0.58223 or an increase of 3.20%. The latter has been plotted on the right in Figure 59. From (39) it is evident that $\int_0^\infty \frac{c}{c_s} d\beta$ is proportional to the quantity of gas in solution and since the object of this calculation was to find out the difference between the diffusion with and without liquid expansion, it is not necessary to proceed further with the evaluation of constants. It is to be noted that m is less and n greater than for the case without expansion. A plot of ς versus this correction has been plotted in Figure 56.