RATES OF ABSORPTION AND DESORPTION
OF BUTANE IN CRYSTAL OIL
and
SOME CONSIDERATIONS IN THE CALCULATION
OF DIFFUSION CONSTANTS

Thesis by

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Introduction

The fundamental problem of non-equilibrium behavior is of the utmost practical importance, but while industry has developed a vast literature of empirical data with which to attack the problems of design and control of processes involving such phenomena as absorption, extraction, and the like, the prediction of the behavior of even a simple two phase system is not possible without considerable knowledge of the system itself. The work described here was performed at the direction of Dr. B. H. Sage as a preliminary study of what might be a more fundamental approach to the problems concerned.

A simple system of technical importance to the Petroleum industry might be represented by a hydrocarbon gas dissolved in a non-volatile liquid, so a study of the rates of absorption and evolution of the gas for the system n-butane - crystal oil was begun. After considerable data had been accumulated and roughly interpreted a detailed mathematical analysis of the method used for determining the diffusion constant for this system was finally undertaken. The work is described in two more or less independent sections, since there was no time available for any further experiments designed to check the mathematical treatment of the diffusion problem and possibly recalculate the experimental results on this basis. Part I of this thesis is devoted to a consideration of the rate measurements, and Part II to the mathematical treatment.

PART I

Apparatus

The essential features of the apparatus designed by Dr. Sage for the rate measurements are shown in Fig. 1. The Pyrex glass cell 1, which contains the oil 2 under investigation is 2" in diameter for some 10" of the upper portion, narrowing to 3/8" in diameter at the lower portion 3, and it rests in a narrow ring cut out of the steel block 4 which is mounted in the piece of steel tubing 5 rigidly mounted on the vacuum bench. The connection between the glass tubing 3 and the steel block 4 is made vacuum tight with sealing wax. The block 4 carries on its lower side a packing gland, consisting of the oil-soaked leather washers 6, the steel follower 7, and the steel cap 8, which may be tightened through radial slots in the tubing 5. At the lower end of the tubing 5 is mounted the ball bearing 9,

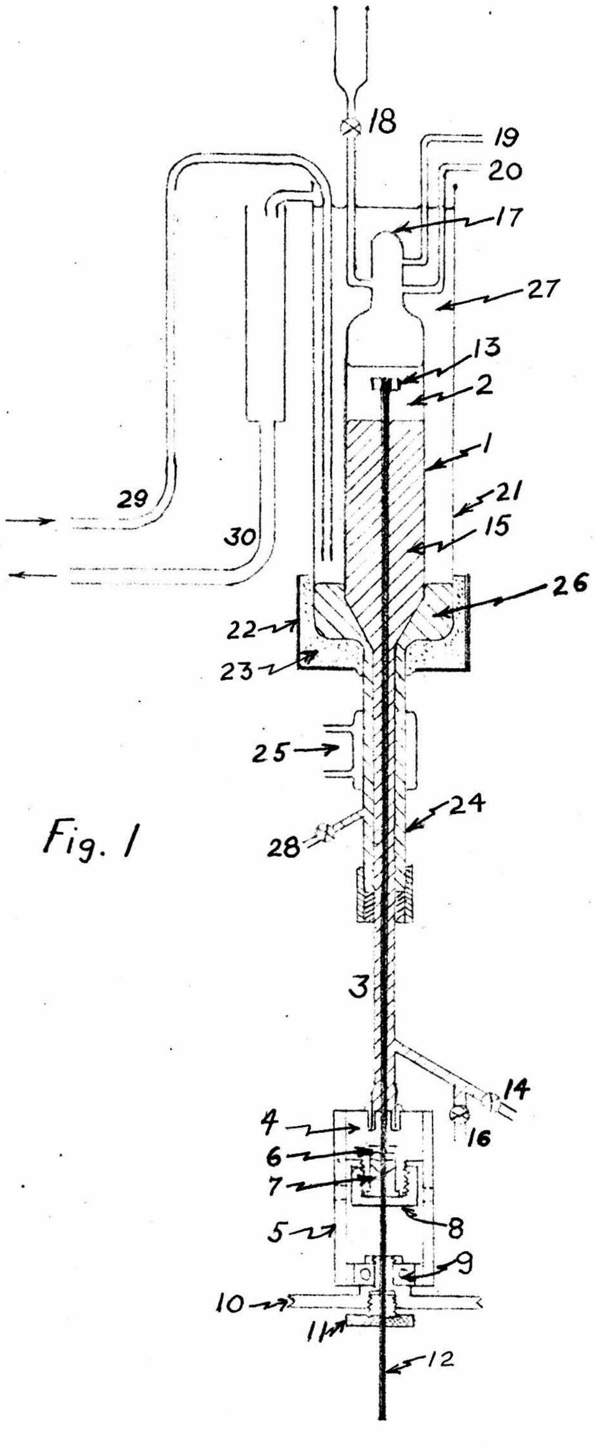
18
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Fig. 1

which is attached to the pulley 10; the split thread thumb screw 11 holds the 1/8" steel drill rod 12 tightly in the pulley. On loosening the thumb screw the drill rod is free to move up or down, bringing the stirring blades 13 to any desired position in the cell.

The cell 1 is connected through the stopcock 14 to a mercury reservoir (not shown) from which the mercury 15 may be forced by air pressure into the cell to any desired height, the stopcock 16 serving to drain the cell. In construction of the apparatus the drill rod 12 with the attached stirring blades 13 was put in place through the narrow top portion of the cell before it was sealed at 17, where the diameter is about 7/8". Oil may be added to the cell through the stopcock 18, and the 4 mm. Pyrex tubing at 19 and 20 leads to the gas measuring and regulating system.

The entire cell is surrounded by a glass thermostat jacket 21 open at the top, which is supported in the brass shell 22 filled with plaster of Paris 23, the lower portion 24 of the jacket being narrowed to fit closely to the lower portion of the cell 3. The water condenser 25 serves to prevent an undue amount of heat from being transmitted down to the wax joint at the block 4; the block 4 is also water cooled with a cooling coil soldered to it (not shown), since the friction in the packing gland during prolonged stirring sometimes produced sufficient heat to soften the wax joint. The connection between 24 and 3 is made with two pieces of rubber tubing, and the length of 3 (the lower portion of the cell 1) between this connection and the side arm leading to the stopcocks 14 and 16 is so adjusted that the thermostat jacket 21 can be lowered to permit opening or sealing the top of the cell at 17. The lower portion of the thermostat jacket is filled with mercury 26, and the mercury and thermostat oil 27 can be drained through the stopcock 28. In maintaining constant temperature the thermostat oil is pumped from a large constant temperature reservoir through the copper tubing 29, the oil discharging from the jacket and flowing by gravity back to the reservoir through the copper tubing 30. The temperature of the thermostat jacket was measured to .1° with a thermometer (not shown), and in order to smooth out fluctuations in temperature due to variations in room temperature and rate of flow of the oil from the reservoir, a small 100 watt heater (not shown) was also placed inside the jacket, the current to it being controlled through the ususl relay circuit from a three-leg mercury thermo-regulator also in the thermostat (but not shown). The oil in the thermostat jacket was vigorously stirred with a stream of air from a copper tube (not shown) reaching almost to the surface of the mercury in the jacket.

The gas measuring and regulating system is illustrated diagramatically in Fig. 2. The two open end U-type manometers A and B of 6 mm. Pyrex tubing serving to measure pressures, the stopcocks in the bend of the U permitting the "locking" of the manometer so that the pressure at a particular time might be recorded subsequently. The measuring bulbs 31, 32, and 33, of 500, 1000, and 1000 cc. capacity respectively, are submerged in a tank of water to determine their temperature. The butane used was stored as a liquid under its own vapor pressure in the steel bomb 34.

In addition to the apparatus illustrated a mercury diffusion pump backed by a Cenco Hyvac served to exhaust various portions of the apparatus

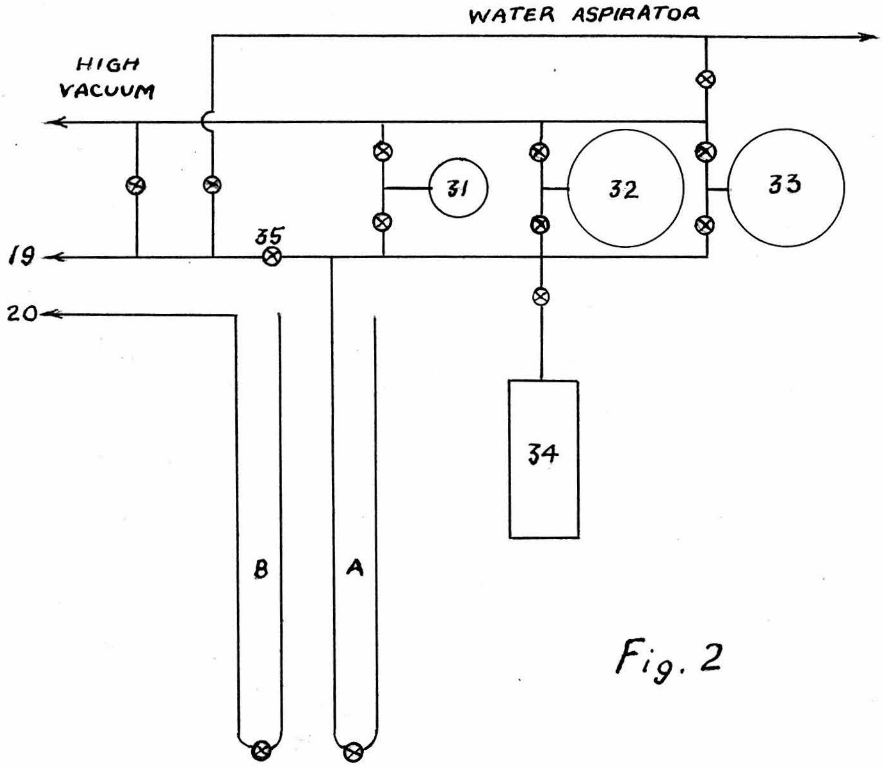


Fig. 2

low pressures being determined with a calibrated McLeod gauge. A water aspirator was provided to avoid the necessity of evacuating large quantities of gas through this high vacuum system.

A small synchronous motor driving a counter served to measure time intervals. Through some error a 50 cycle motor was supplied for use on 60 cycle current, and consequently time is later frequently referred to in terms of "time units" = t_u, where 1 time unit = 5/6 second; in presenting the experimental data convenient use of this unit may be made.

Calibration

The volumes of the connecting tubing and the measuring bulbs 31, 32, and 33 were all determined by observations of the pressure-temperature relations of air, a 1000 cc. glass bulb which had been calibrated by determining the weight of water it contained being sealed to the apparatus for this purpose.

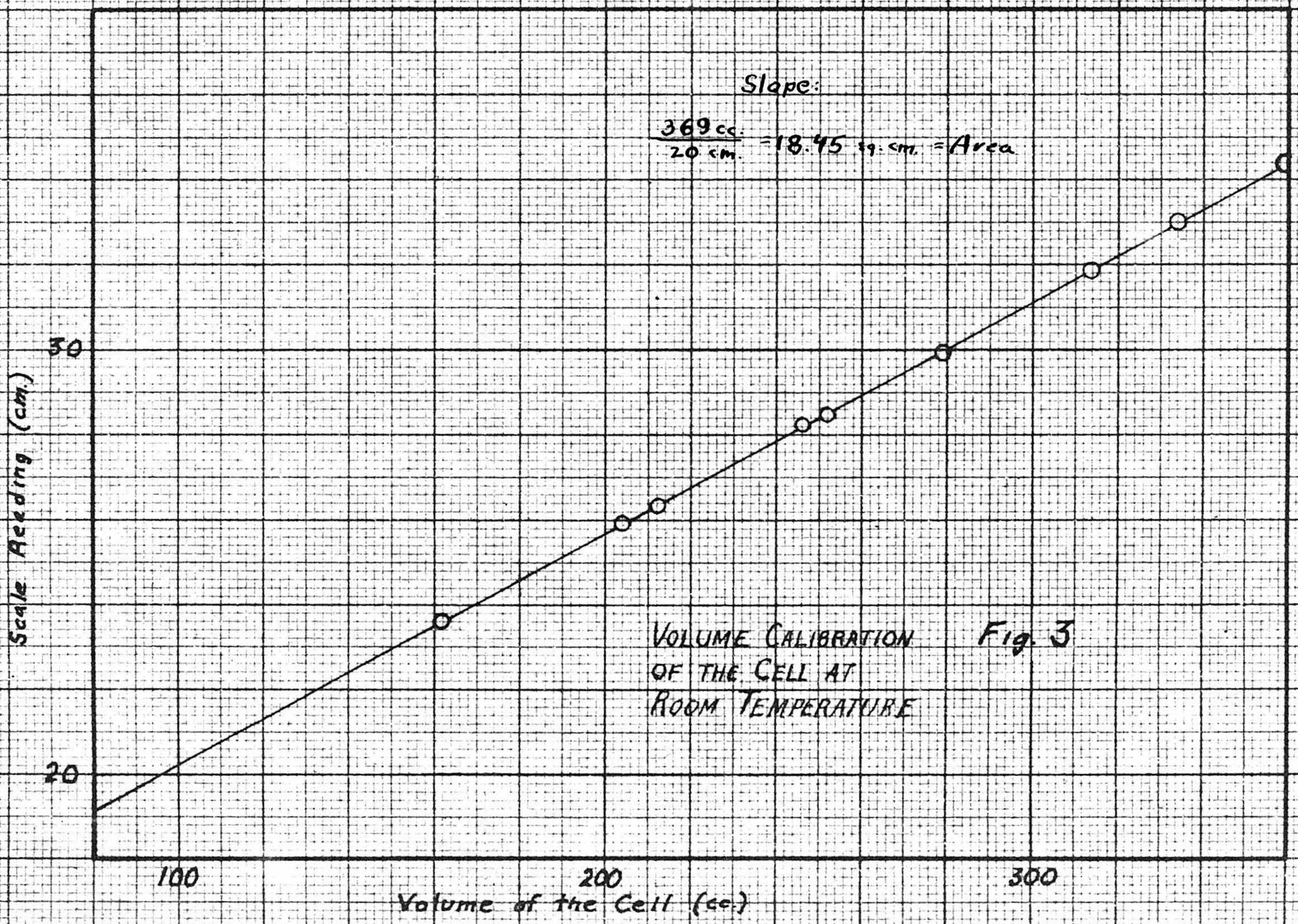
The volume of the cell 1 as a function of its length was similiarly determined, the cell length being measured against a millimeter scale measuring the height of the lower end of the drill rod 12 above the base of the vacuum bench when the lowest point of the stirrer 13 touched the surface of the mercury 15.

The volume of the measuring bulbs, which are designated in the experimental work by the numbers 1, 2, 3, and C (the calibrating bulb) were 1020, 509, 1013, and 1051 cc., respectively. The volume of the manifold or connecting tubing between the bulbs and the "throttle" stopcock 35, which was 13 cc., as well as the volumes of the manometers A and B, which were estimated at 0.12 cc. per cm., are included in the calculations throughout, though they are rarely significant since none of the measurements were considered more accurate than ±0.5%.

The volume-length calibration of the cell is presented in Fig. 3. From the average slope the cross-sectional area of the cell was calculated to be 18.45 sq. cm.

Experimental Procedure

Rate measurements were made on the system normal butane-crystal oil for a variety of experimental conditions, which included different amounts of oil either stirred at different positions in the oil (absorption and desorption) or quiescent (desorption only) with the stirrer at different positions in the oil or beneath the mercury, between the saturation



VOLUME CALIBRATION OF THE CELL AT ROOM TEMPERATURE Fig. 3

pressures of 430, 790, and 1025 mm. at a temperature of 37.8° C. (100° F.).

The quantity of oil sample was determined both from the volume of oil before it was introduced into the cell through 18, and from the volume of the cell it occupied as found from the volume-length calibration of the cell. In any particular run the oil sample was completely de-gassed to a pressure of 10^{-4} mm. as measured on the McLeod gauge, or saturated to the desired initial pressure as measured by the manometer B.

In measuring absorption, a quantity of butane from the bomb 34 was admitted to the previously evacuated measuring bulbs, the temperature of the water bath noted, and the initial amount of gas determined from the pressure as read on manometer A. The stirrer being adjusted to the proper position, the counter was started, and when it passed some convenient number the stopcock 35 was opened until the pressure of gas above the oil (as read on manometer B) reached the desired final pressure. Throughout the run the "throttle" stopcock 35 was adjusted as necessary to maintain as closely as possible this constant final "saturation" pressure above the oil. While the pressure would be somewhat erratic for the first minute, it was found possible to control this pressure to within ±10 mm. for the first few minutes, the variation decreasing during the run to ±3 mm., it being possible to maintain this regulation in the later portions of the run for as long as desired with only occasional adjustment of the stopcock.

As soon as possible after the proper "saturation" pressure, as indicated on manometer B, was reached, the time would be noted and the"locking" stopcock at the bottom of the U of manometer A closed simultaneously, the time and pressure of the gas remaining in the measuring bulbs then being recorded. Measurements of the quantity of gas would be repeated as often as practicable with reasonably careful control of the pressure of gas above the oil during the early part of the run, or as often as observable differences in pressure could be detected on the manometer in the later portions of a run. In measuring the rate of evolution of gas the process was, of course, reversed; the measuring bulbs being evacuated initially and the gas being permitted to flow in the opposite direction past the throttle stopcock and measured in the bulbs. Care was always exercised to assure that any reading of the quantity of gas coincided with the "saturation" pressure of gas above the oil being exactly the desired final value as indicated by the reading of manometer B.

To insure a more uniform accuracy throughout a run, whenever possible the gas was measured in one bulb at a time, the gas being led into (or out of) a second bulb when the pressures in the first bulb approached the constant pressure being maintained above the oil. The "switching" from one bulb to another was accomplished by closing the throttle stopcock momentarily, measuring the pressure of gas in the bulb being used, closing the stopcock leading to this bulb, opening the stopcock leading to the next bulb, again reading the pressure, and then opening the throttle stopcock to continue the flow. This double measuring process could usually be accomplished without any serious deviation from the desired pressure above the oil in the cell, and it provided an additional check on the quantity of gas remaining in the manifold, which was actually, of course, measured twice and had to be subtracted from the subsequent calculated amounts of gas.

Materials

The normal butane used in this investigation was that obtained for an earlier investigation[1] from the Phillips Petroleum Company, who submitted a special analysis of 99.7 mol per cent n-butane and 0.3 mol percent iso-butane, and it was used without further purification. The crystal oil was also that used in an earlier investigation[2] and was a water-white parrafin-base oil refined from Pennsylvania crude stock. Its specific gravity at 100° F. relative to water at its maximum density was .8244, and its viscosity-gravity factor[3] was found to be .7979. For further details of the materials and their properties the references cited may be consulted.

Incidental Measurements and Data

In addition to the rate measurements themselves, considerable data concerning the n-butane - crystal oil system studied were necessary; the measurements and data will be described here.

The density of the crystal oil used, as a

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[1] Sage, Webster, and Lacey, *Ind. Eng. Chem., 29,* 1188 (1937).
[2] Sage, Inman, and Lacey, *ibid., 29,* 288 (1937).
[3] Hill and Coats, *ibid., 20,* 641 (1928).

function of temperature, was determined by R. C. Nellis and his data are presented in Fig. 4. The average molecular weight of the crystal oil, as determined by J. Sherbourne from its freezing point lowering in benzene, was 342, and its vapor pressure was of the order of 10^{-4} mm. of mercury.

The deviations of n-butane from the perfect gas laws is appreciable even at the low pressures used, and the measured pressure values were always corrected with the z factor, defined by $z = PV/NRT$, and measured by Sage[1] which are shown in Fig. 5. For use in calculating, a table of the z values at various temperatures and pressures was constructed from this data.

The volume change of solutions of butane in this crystal oil was calculated from the average of the many measurements of the volume of solutions in the cell when saturated at different pressures of butane. The final values used are shown in Fig. 6, where the molal volume of solutions of butane in crystal oil has been plotted as a function of the mol fraction of butane. The circles indicate the averages of observed values, and the function was assumed to be the straight line given by the

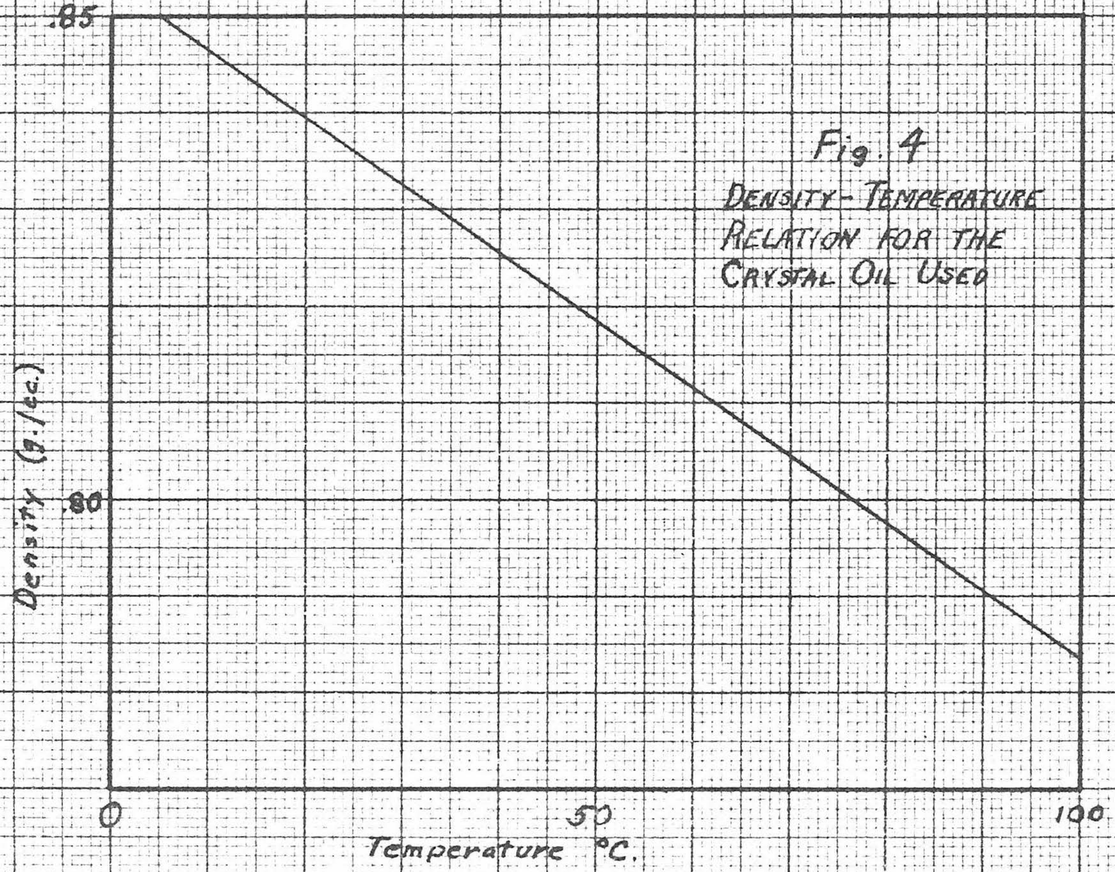

Fig. 4

DENSITY-TEMPERATURE RELATION FOR THE CRYSTAL OIL USED

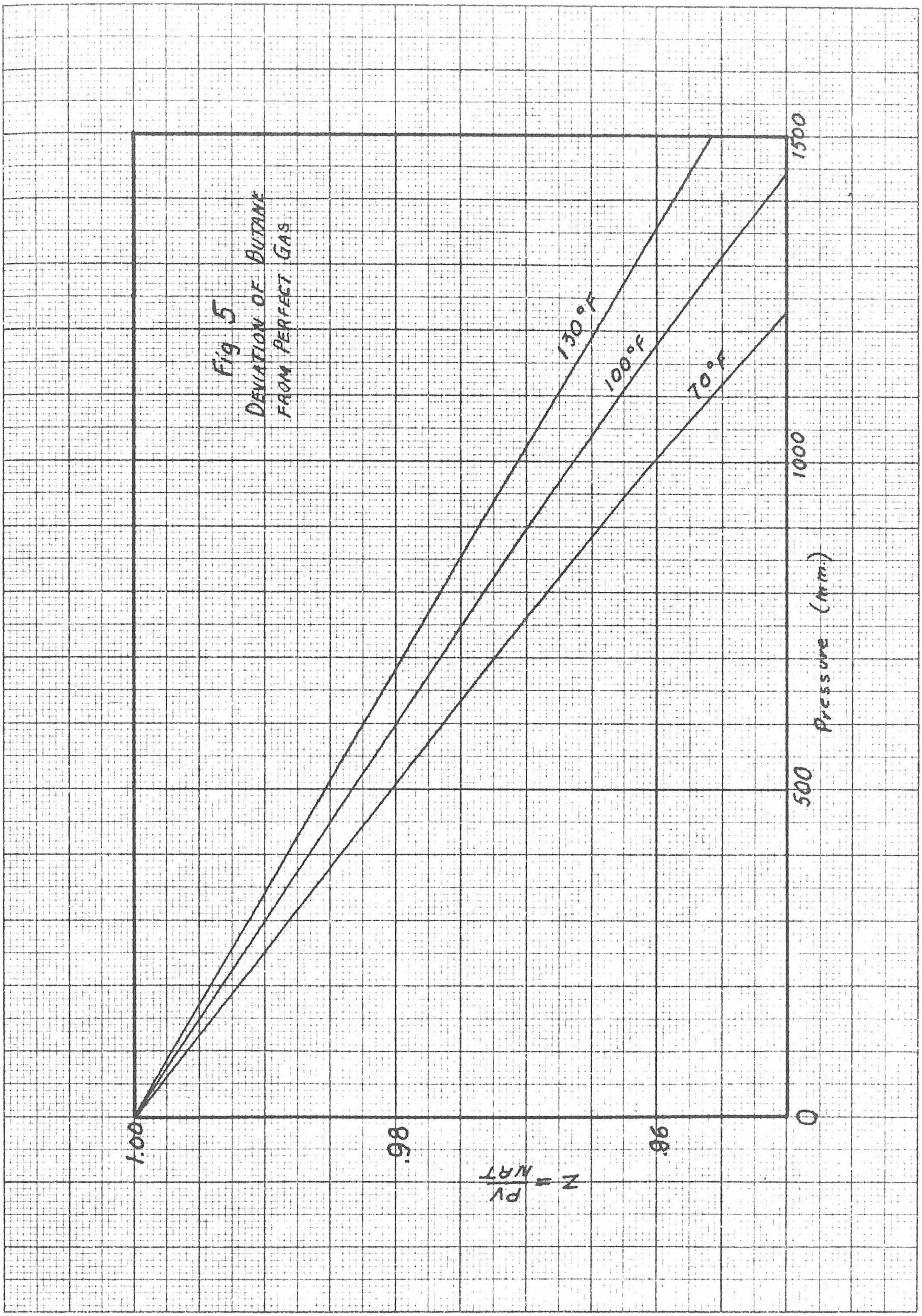

Fig 5
DEVIATION OF BUTANE FROM PERFECT GAS

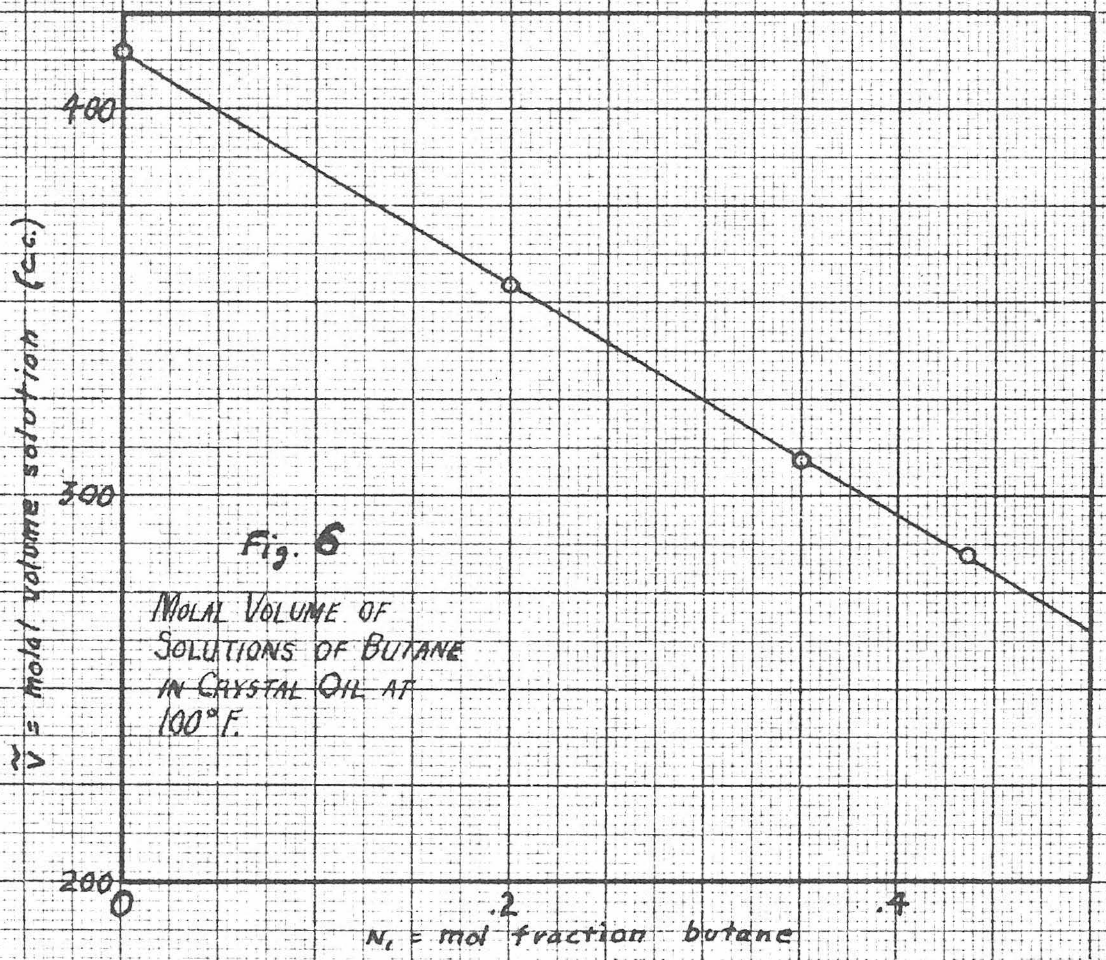

Fig. 6

MOLAL VOLUME OF SOLUTIONS OF BUTANE IN CRYSTAL OIL AT 100° F.

equation $\tilde{v} = 414.84 - 299.74\, N_1$, where $\tilde{v}$ is the molal volume in cc. of the solution, and N_1 is the mol fraction of butane. This equation may be transformed for later use to the form

$$v = .0019817\ m + 1.2134\ g \qquad (1)$$

where v is the volume in cc. of solution containing g grams of oil in which m milligrams of butane are dissolved. From this analytical expression the values of Table I were calculated.

Table I

Volume of Solution

Normal Butane in Crystal Oil at 100° F.

Pressure butane (millimeters Hg.)	Volume (cc./gram)
0	1.2134
430	1.2994
790	1.3946
1025	1.4756

The solubility of butane in this crystal oil was determined from those runs which were carried to completion together with a special series of measurements in which a definite quantity of gas was run into the cell, the throttle valve closed, and the final equilibrium pressure determined after continuous stirring for at least an hour indicated no further change in pressure. Since the later calculation of various quantities is dependent directly on these values, every effort was made to push the accuracy of the determination to the limit of the apparatus, but at the highest pressure (1025)mm.) the reproducibility of the measurements was rather poor. This is principally due to the large percentage error involved in measuring small differences in pressure at high pressures, the difficulty of preventing slow leakage out through the stopcocks, and the fact that at these pressures small temperature variations have a very great effect on saturation pressures; Sage[4] found for a similar crystal oil-butane system that the saturation pressure varied by nearly 25 mm. per °C at pressures around 1000 mm.

The data obtained experimentally are indicated by the points in Fig. 7, where the saturation pressure is plotted against the mol fraction of butane. Data for the solubility from the smooth curve, and concentrations calculated using the data of Table I are presented in Table II.

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[4] Sage and Lacey, Ind. Eng. Chem., 28, 106 (1936).

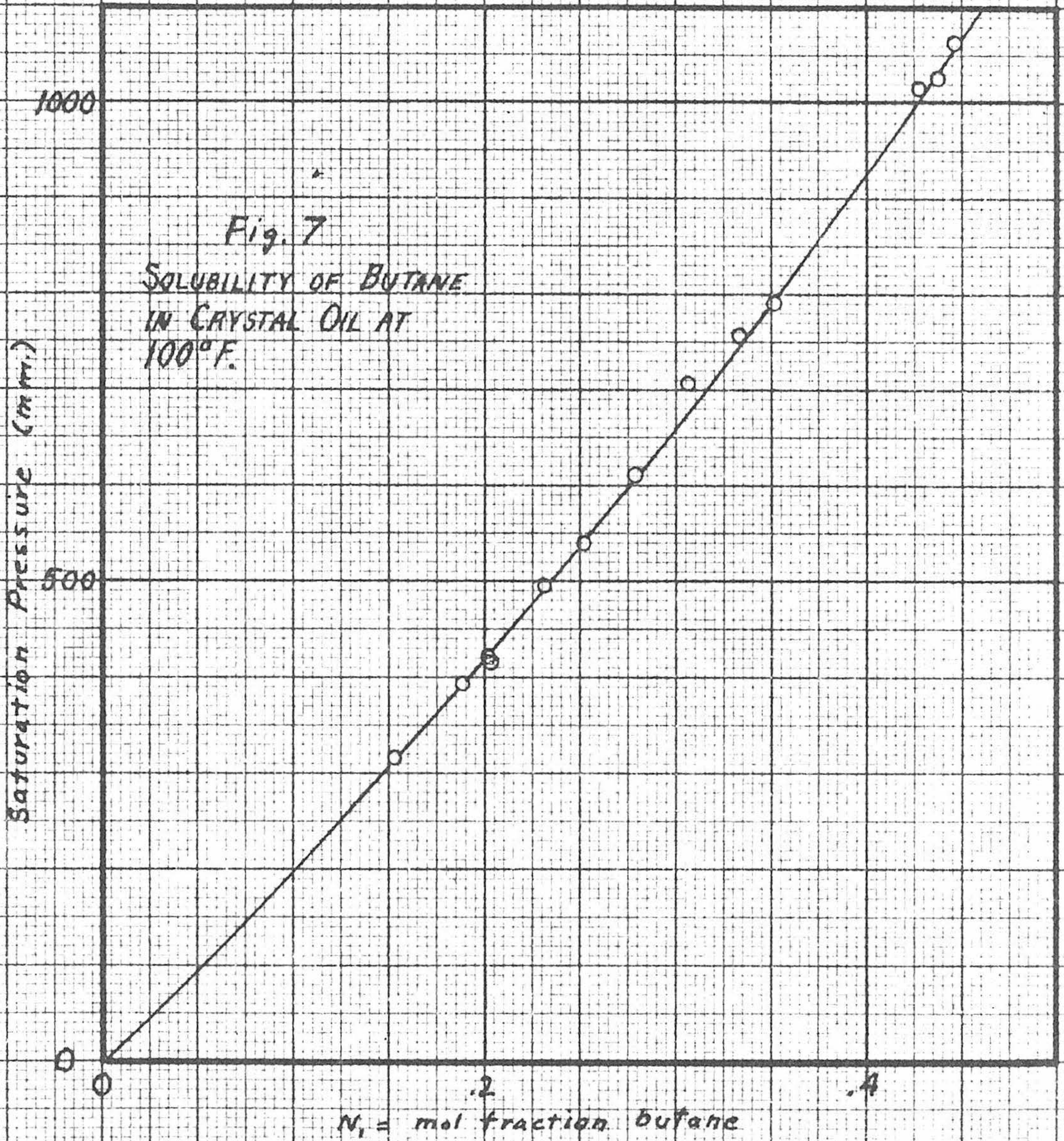
Fig. 7
Solubility of Butane in Crystal Oil at 100°F.
1000
500
0
Saturation Pressure (mm.)
0
.2
.4
N_1 = mol fraction butane

Table II

Solubility of Butane in Crystal Oil at 100° F.

Butane Pressure (mm.)	Solubility (milligrams / gram of oil)	Concentration of saturated solution (milligrams / cc. solution)
430	43.39	33.39
790	91.44	65.57
1025	132.30	89.66

The value of the diffusion constant for butane in this crystal oil was also measured a 100° F. at various pressures of butane by simply measuring the rate of absorption of the gas into quiescent oil by the method used by Pomeroy[5]. In using this method the differential equation for diffusion based on Fick's hypothesis (and assuming no volume change takes place and that the diffusion constant is independent of the concentration) is integrated. The value of the concentration gradient at the surface is then obtained by differentiation, and the diffusion constant calculated from the rate at which the gas dissolves. The details and assumptions inherent in this method are discussed in the paper referred

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[5] Pomeroy, Lacey, Scudder, and Stapp, Ind. Eng. Chem., 25, 1014 (1933).

and in other papers and theses from this laboratory which will be discussed more fully in Part II of this thesis. The experimental values obtained by the simple treatment of Pomeroy will be given here, since these values were used in treating the experimental rate values.

To calculate the diffusion constant Pomeroy used the equation

$$D = \frac{\pi \ m^2}{4A^2(c_s - c_o)^2} \qquad (2)$$

where D = diffusion constant (in sq. cm./sec.)

A = surface area of the oil (in sq. cm.)

c_s = concentration of the solution corresponding to the pressure of gas maintained above the solution

c_o = initial concentration of the solution

and $m = \frac{dQ}{d\sqrt{t}}$ is defined as the slope of the straight line which is obtained when Q, the total quantity of gas absorbed at any time after the beginning of diffusion, is plotted against $\sqrt{t}$, the square root of the time (in seconds) after the beginning of diffusion. Since Q and $(c_s - c_o)$ appear as a ratio, any convenient unit may be used to designate both the quantity of gas absorbed and the quantity in a cc. of solution.

Four measurements gave the values of m and D in Table III.

Table III

Diffusion Constant

Butane in Crystal Oil at 100° F.

Pressure (mm.)		Concentration (mg./cc.)		Slope (mg./sec.)	Diffusion Constant (cm²/sec.)	Mean Conc. (mg./cc.)
init.	sat'n	init. c_o	sat'n c_s	m	$D \times 10^5$	c
0	430	0	33.39	1.666	.574	16.69
430	790	33.39	65.57	1.990	.823	48.48
430	1025	33.39	89.66	3.859	1.085	61.52
790	1025	65.57	89.66	1.871	1.392	77.61

It is obvious that the diffusion constant varies almost threefold over the concentration range evolved, contrary to the assumption made in Pomeroy's treatment, but any error thus introduced was originally to be ignored and the value of the diffusion constant at the mean concentration of the range over which the diffusion constant was measured.

The values were thus plotted against the mean concentration as in Fig. 8, and the value of the diffusion constant over the range was taken as being represented by a linear equation indicated by the solid line

$$D \times 10^5 = .440 + .0097\,c \qquad (3)$$

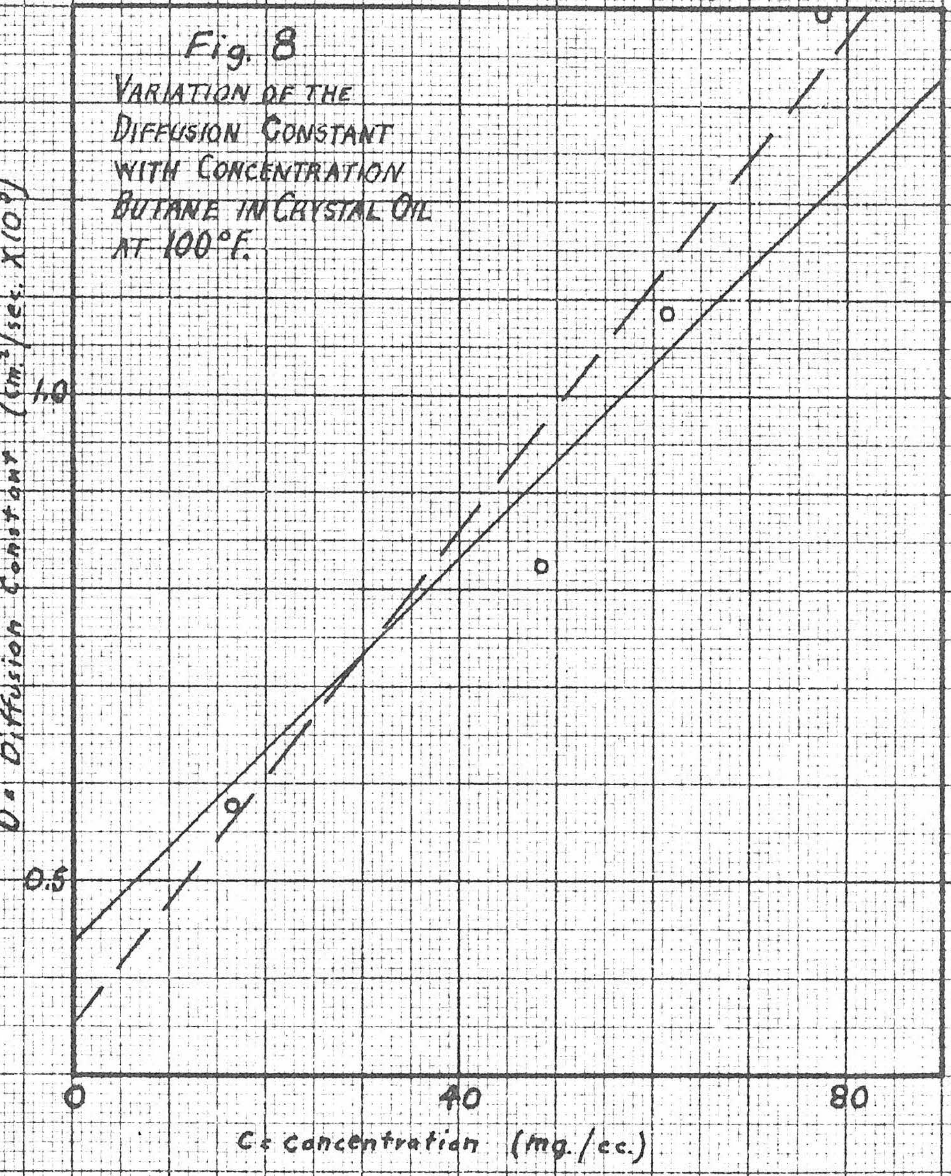

Fig. 8
VARIATION OF THE DIFFUSION CONSTANT WITH CONCENTRATION BUTANE IN CRYSTAL OIL AT 100°F.

where c is the concentration of the solution in milligrams of gas per cc. of solution.

Since this equation is to be used throughout the treatment of the experimental results it might be well to indicate here that a closer approximation such as the dashed line of Fig. 8 might better have been used, but that it would not materially affect the nature of the conclusions regarding the rate measurements. Equation (3) was originally found for slightly different values of the diffusion constants as calculated using incomplete incidental data of the saturation concentration values, etc., and under the pressure of getting some sort of information as to the meaning of the rate measurements (which were nearly completed before the final dterminations of various incidental measurements), the equation (3) was used throughout. It was expected that the final values of the diffusion constant as calculated in this way would be used to recalculate all of the experimental data, but at this time the plan of the investigation was finally reoriented to include a detailed investigation of just this point, the variation of the diffusion constant with concentration, and consequently the recalculation on this empirical basis would have been but a waste of time. Unfortunately time did not permit any verification and application of the considerations, developed in Part II of this thesis, to the diffusion measurements used in the treatment of the rate measurements.

Experimental Data

29 complete and acceptable rate measurements were made under the various experimental conditions; in 13 of which the oil was stirred continuously throughout the run, while in the remainder the stirrer was stationary either beneath the mercury in the cell or at some fixed point in the crystal oil. In the stirred runs the stirrer speed was approximately constant at 300 revolutions per minute; a study of the effects of different stirrer speeds was proposed but not made. Considering the enormous number of individual observations, no attempt will be made to give the complete experimental data for all runs, and course of the runs will be presented in the forms of graphs; however, to illustrate clearly the details of the experiments, the complete set of observed data and calculations for one typical run is presented in Table IV.

Table IV

Complete Data for a Typical Run.

Run 54 Stirred Pressure change 790-430 mm.

Barometer 867.1
126.8
740.3 mm.

Initial pressure 525.2
474.8
50.4
740.3
790.7 mm.

Rod Reading:
Top of oil 21.80 = 128 cc.
Top of Hg. 25.00
3.20

Throttle pressure
740.3
desired 430.0
310.3

650.3
430.5
observed 309.8

Stirrer at 23.80

Initial Conditions:

mg. = .00299 PV/z = .00299 x 790 x 128/.974 = 310
= .00299 x 430 x 128/.986 = 165
145 mg.

1	2	3	4		5	6	7	8
Time units	Man. A	Bulb	Pressure		z	V	△mg.	≤mg.
			Gauge	Abs.				
0		1+3 24°	740.3	0				-145
70	840.3 144.2		696.1	44.2	.998	2046	284	139
125	829.0 166.0	"	663.0	77.3	.997	"	496	351
200	815.0 181.0	"	634.0	106.3	.996	"	683	538
265	805.0 191.2	"	613.8	126.5	.995	"	814	669

Table IV (cont'd)

1	2	3	4		5	6	7	8
Time units	Man. A	Bulb	Pressure Gauge	Abs.	z	V	Δ mg.	Σ mg.
400	786.5 211.0	1+3 24°	575.5	164.8	.994	2047	1062	917
450	780.5 217.6	"	562.9	177.4	.993	"	1145	1000
500	774.9 223.8	"	551.1	189.2	"	"	1221	1076
630	762.5 236.8	"	525.7	214.6	.992	"	1386	1241
700	756.5 243.6	"	512.9	227.4	"	"	1469	1351
750	752.8 247.3	"	505.5	234.8	.991	"	1518	1373
800	749.0 251.5	"	497.5	242.8	"	"	1570	1425
850	745.1 255.3	"	489.8	250.5	"	"	1620	1475
920	741.0 260.0	"	481.0	259.3	.990	"	1678	1533
1000	736.1 264.8	"	471.3	269.0	"	"	1741	1596
1110	730.9 270.5	"	460.4	279.9	"	"	1811	1666
1200	726.5 274.9	"	451.6	288.7	.989	"	1870	1725
1300	722.6 279.2	"	443.4	296.9	"	"	1923	1778
1400	719.0 283.0	"	436.0	304.3	"	"	1971	1826
1630	712.5 289.6	"	422.9	317.4	.988	"	2058	1913

Table IV (cont'd)

1	2	3	4		5	6	7	8
Time units	Man.A	Bulb	Pressure Gauge	Abs.	z	V	Δmg.	Σmg.
1800	708.9 293.8	1+3 24°	415.1	325.2	.988	2048	2110	1965
2020	705.0 297.2	" "	407.8	332.5	"	"	2157	2012
2200	702.5 300.1	"	402.4	337.9	.987	"	2194	2040
2400	700.8 301.9	"	398.9	341.4	"	"	2217	2072
2600	698.9 303.9	"	395.0	345.3	.987	"	2243	2098
2800	697.5 305.0	"	392.5	347.8	"	"	2259	2114
3000	696.8 306.1	"	390.7	349.6	"	"	2270	2125
3225	696.0	"	389.2	351.1	"	"	2280	2135

Referring to Table IV, which is the data calculated and recorded in the notebooks, we see that Run 54 was stirred, the pressure drop of from 790 to 430 mm. indicating that gas was evolved. The barometric pressure just before the beginning of the run (as observed by evacuating manometer A to a vacuum of 10^{-3} or better) was 740.3 millimeters, and thus the actual initial saturation pressure over the oil as observed on manometer B was 790.7. The desired "throttle" pressure as calculated to the value of 310.3 is the desired mean reading of the differences of the heights of the mercury in manometer B after the beginning of the run; it is thus calculated for convenience, since during the early part of th a run considerable agility is required to maintain anywhere near the proper value and still make readings of the amount of gas coming out or going into solution. The value of "observed" as 309.8 mm. indicates that at some time later in the run, when the rate of flow of gas was slower, both sides of the manometer B were actually read to check that the mean pressure being maintained was actually somewhere near the desired value and that no gross error in estimating the desired reading had been made. The scale reading of the top of the oil before starting the run was 21.80, which from Fig. 3 indicates a free gas volume in the cell of 128 cc. The scale reading of the top of the mercury was 25.00, indicating the oil occupied a depth of 3.20 cm. in the cell (it was from the averages of these observed values from all runs that gave the three points on the volume change of solution curve, Fig.6). For this run the scale reading for the position of the stirrer during the run was 23.80. The "Initial Conditions" are simply the calculations based on the free gas volume of the cell, which determine the amount of gas above the oil which will flow out of the cell when the throttle valve is opened to reduce the pressure above the oil to 430. mm. This gas will of course be measured, but must be subtracted from the calculated amounts of gas coming out of the cell at any time to give the actual amount of gas evolved from the oil.

In the tabular recording we find in Column 1 the time (actually the counter reading and therefore in t_u = 6/5 seconds), in Column 2 the readings of manomter A, and in Column 3 the bulb or bulbs in which the gas is being measured and the temperature (°C) of the water bath around the bulbs. Columns 4 gives the calculation of the manometer readings to absolute pressure. In this, before opening the throttle valve the pressure in bulbs 1 and 2 was 0; at 70 t_u after opening the throttle valve, 44.2 mm.; after 125 t_u 77.3 mm., and so on. In Column 5 are given the z values of butane for the temperature of the bulbs and the pressure of gas, in Column 6 the volume of the entire system in which gas is being measured (in this case 1020 + 1013 + 13 cc., the volume of the two bulbs and the connecting manifold), and in Column 7 the milligrams of butane as calculated from the relation $\text{mg.} = \frac{P\ V\ W}{760\ RTz}$

P being the pressure in mm., V the volume in cc., W the molecular weight of butane (58.08), R the gas constant (82.07), T the absolute temperature ($^{\circ}$K), and z the factor for the deviation of butane from the perfect gas laws (Cf. Fig. 5). This calculation, which had to be made for each individual measurement, was simplified by constructing a table of factors for the group of quantities W/760RT. In Column 7 are found the final values of the total amount of gas evolved from the oil, obtained by subtracting from the values in Column 6 the quantity of gas initially over the oil which expands on lowering the pressure, in this case 245 milligrams.

The six different samples of oil which were used are described in Table V. In the table are given Roman numerals which were used to refer to these samples; the weights indicated are derived from the observed volumes using the data of Fig. 4, and will later be used in the calculations; the volume given is the approximate volume of the dry oil at room temperature.

Table V

Oil Samples Used

Oil Sample	Run Nos.	Weight (grams)	Volume (cc.)
Ia	10-17	20.85	25
Ib	18-25	20.85	25
II	26-27	62.95	75
III	28-40	62.45	75
IV	41-48	42.08	50
V	49-63	44.65	50

In Figures 9-21 are presented the graphs of the time (in t_u) against the milligrams of gas absorbed or evolved for the stirred runs. Each figure has included on it the pertinent data for the run; including the pressure change (i.e., the drop or increase in pressure above the oil); the approximate volume of oil; and the scale readings for the top of the oil, the mercury surface, and the position of the stirrer.

In Runs 33 and 36, (Figs. 11 and 14) the actual values of the amount of gas evolved indicated by the points and dotted lines have been corrected to the solid curve. The gross experimental error was due to leakage; the runs are absorption runs, measuring

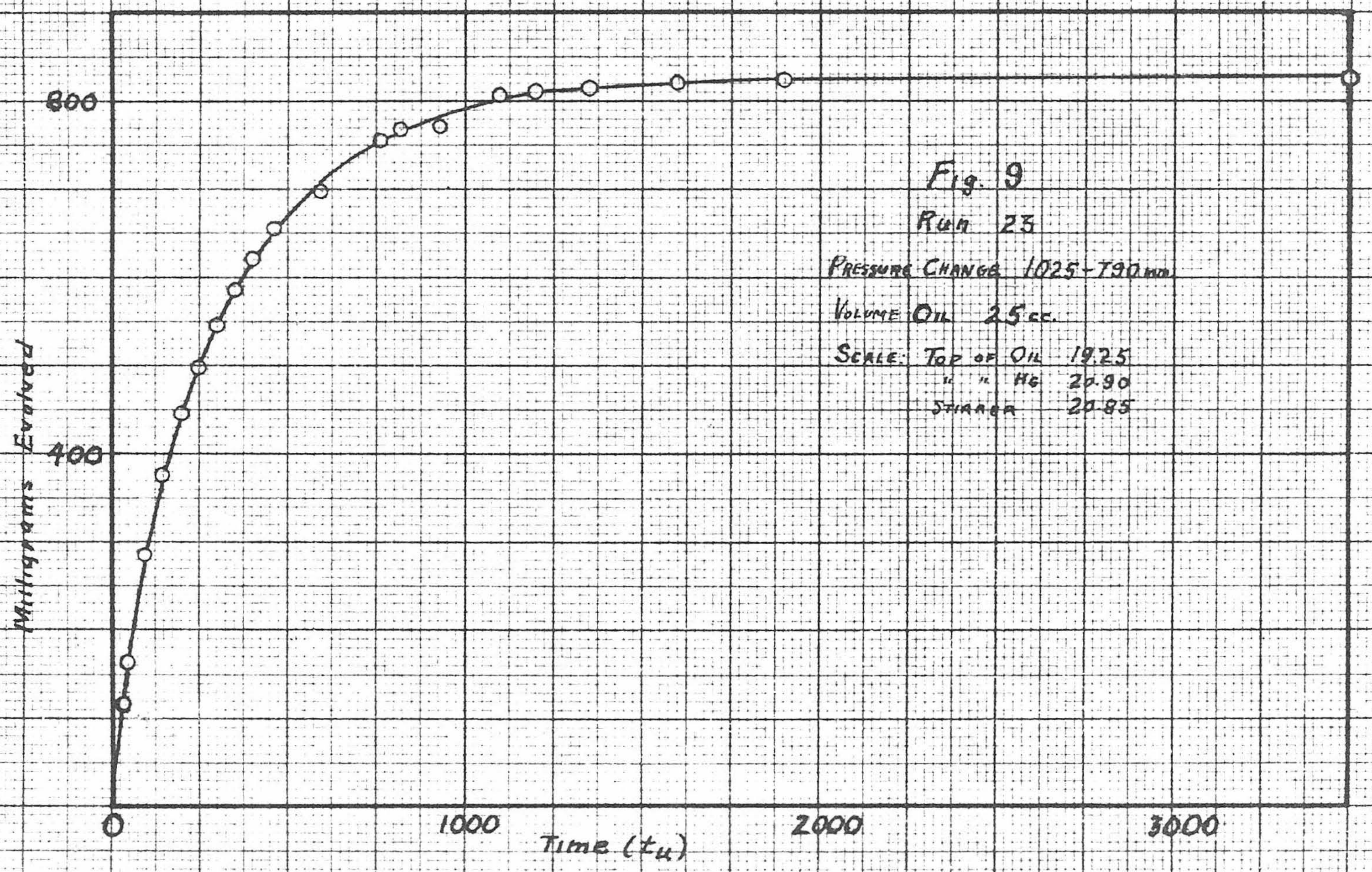

Fig. 9

Run 23

Pressure Change 1025-790 mm

Volume Oil 25 cc.

Scale: Top of Oil 19.25

" " Hg 20.90

Stirrer 20.85

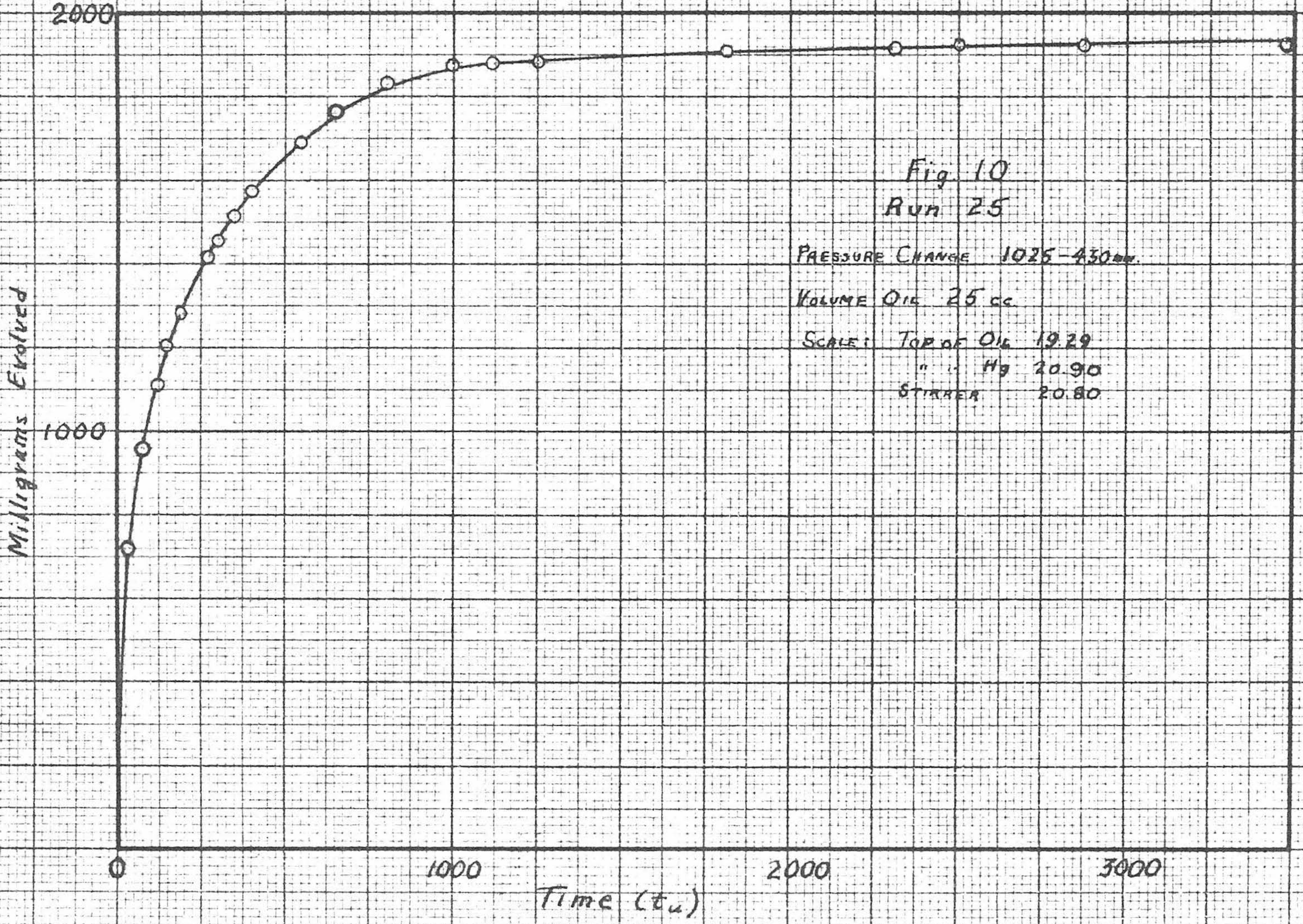

Fig 10
Run 25

PRESSURE CHANGE 1025-430 mm.

VOLUME OIL 25 cc

SCALE: TOP OF OIL 19.29
" " Hg 20.90
STIRRER 20.80

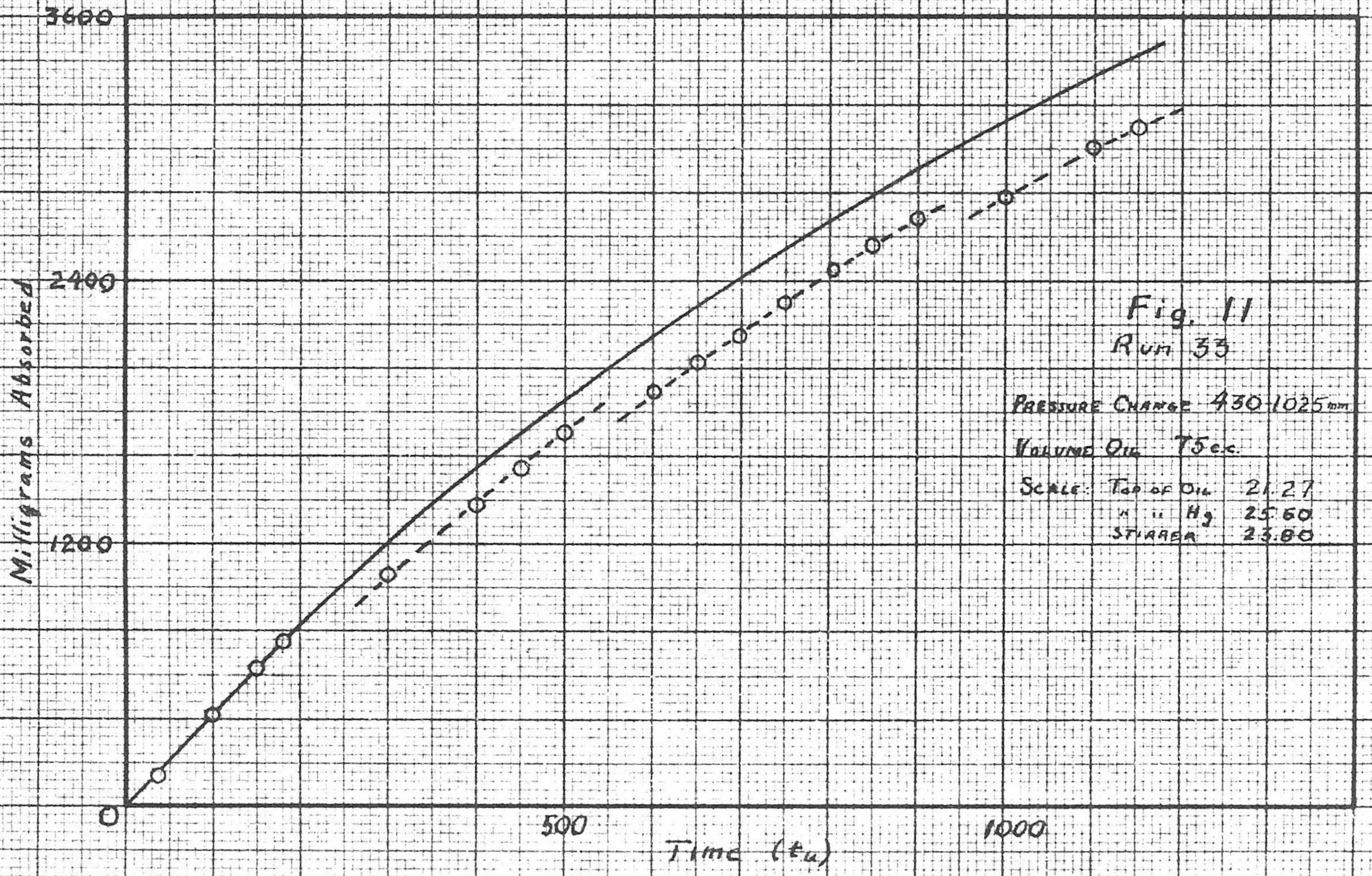

Fig. 11
Run 33

Pressure Change 430-1025mm

Volume Oil 75cc.

Scale: Top of Oil 21.27
" " Hg 25.60
Stirrer 23.80

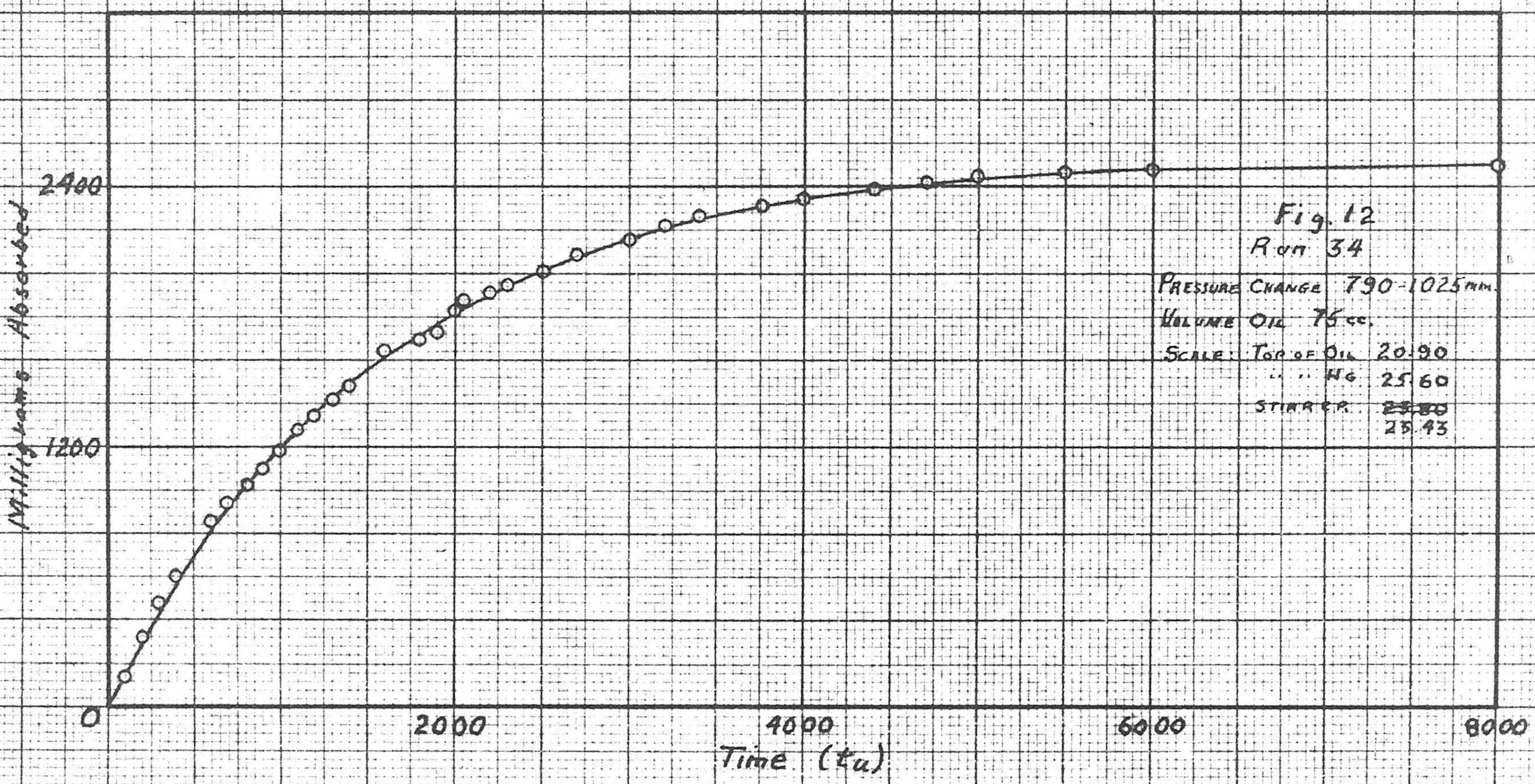

Fig. 12
Run 34

PRESSURE CHANGE 790-1025 mm.
VOLUME OIL 75 cc.
SCALE: TOP OF OIL 20.90
" " HG 25.60
STIRRER ~~25.80~~
25.43

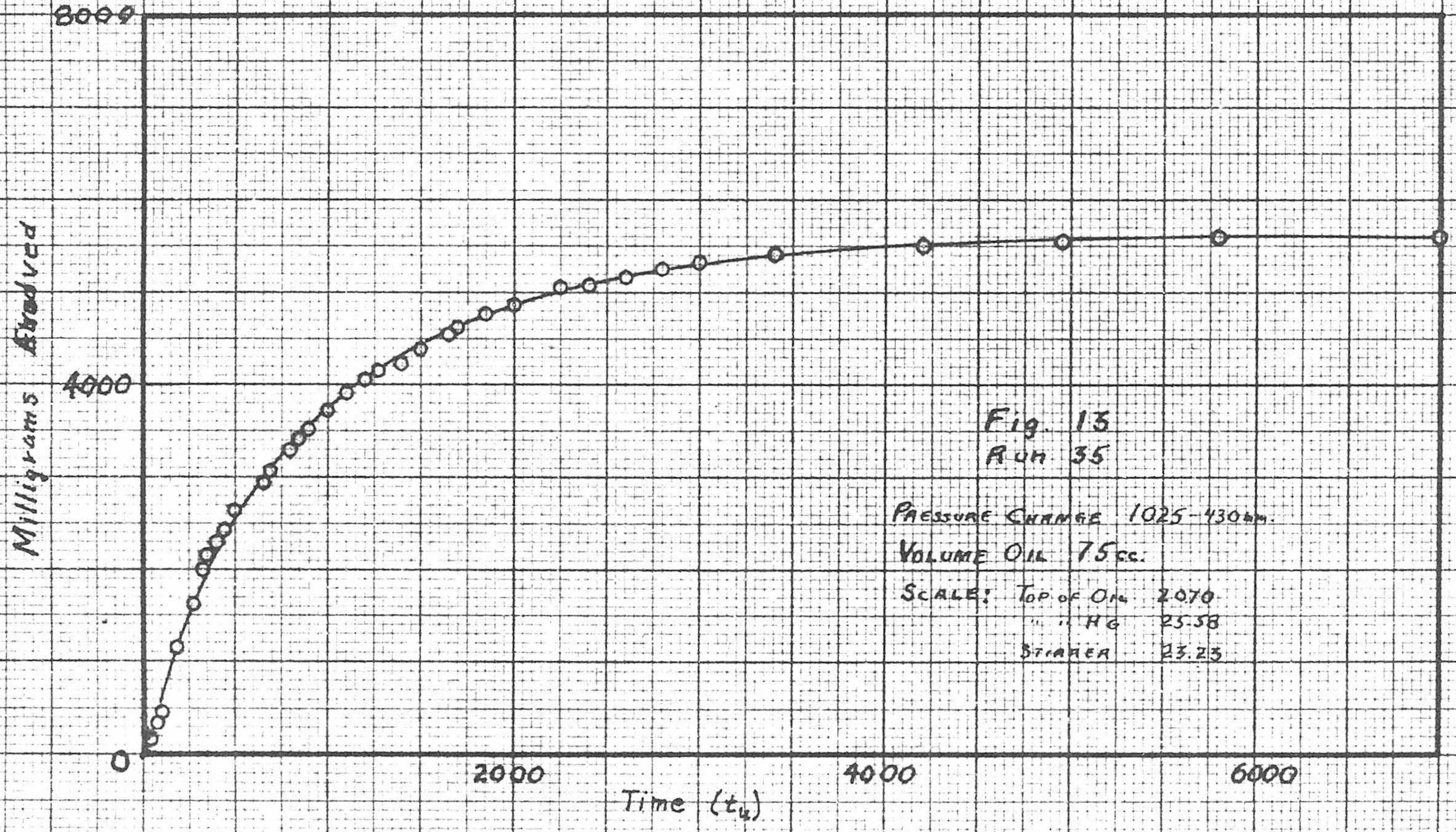

Fig. 13
Run 35

PRESSURE CHANGE 1025-430mm.
VOLUME OIL 75cc.
SCALE: TOP OF OIL 2070
" " HG 25.58
STIRRER 23.23

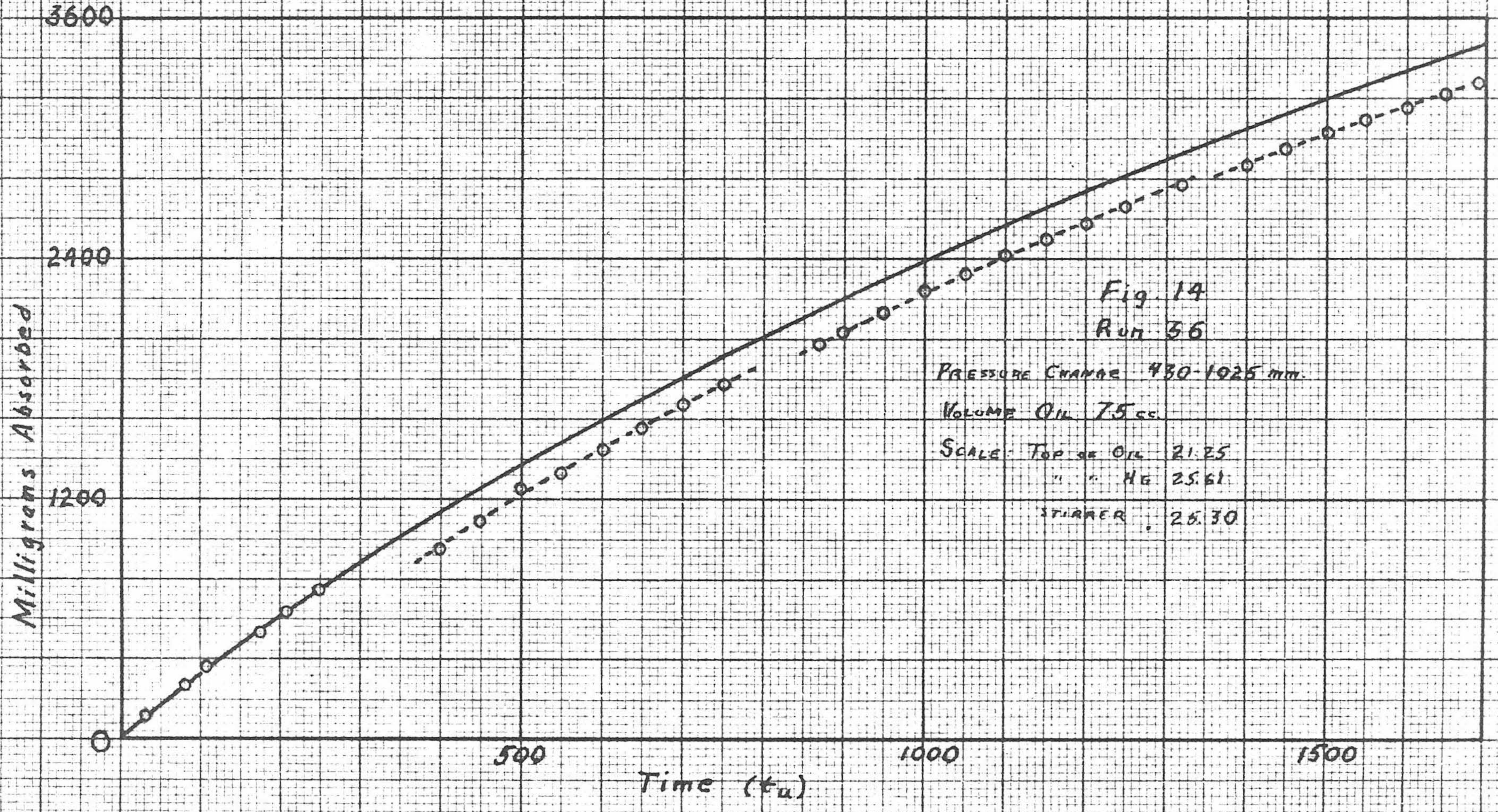

Fig. 14
Run 36

PRESSURE CHANGE 430-1025 mm.
VOLUME OIL 7.5 cc.
SCALE: TOP OF OIL 21.25
" " HG 25.61
STIRRER " 25.30

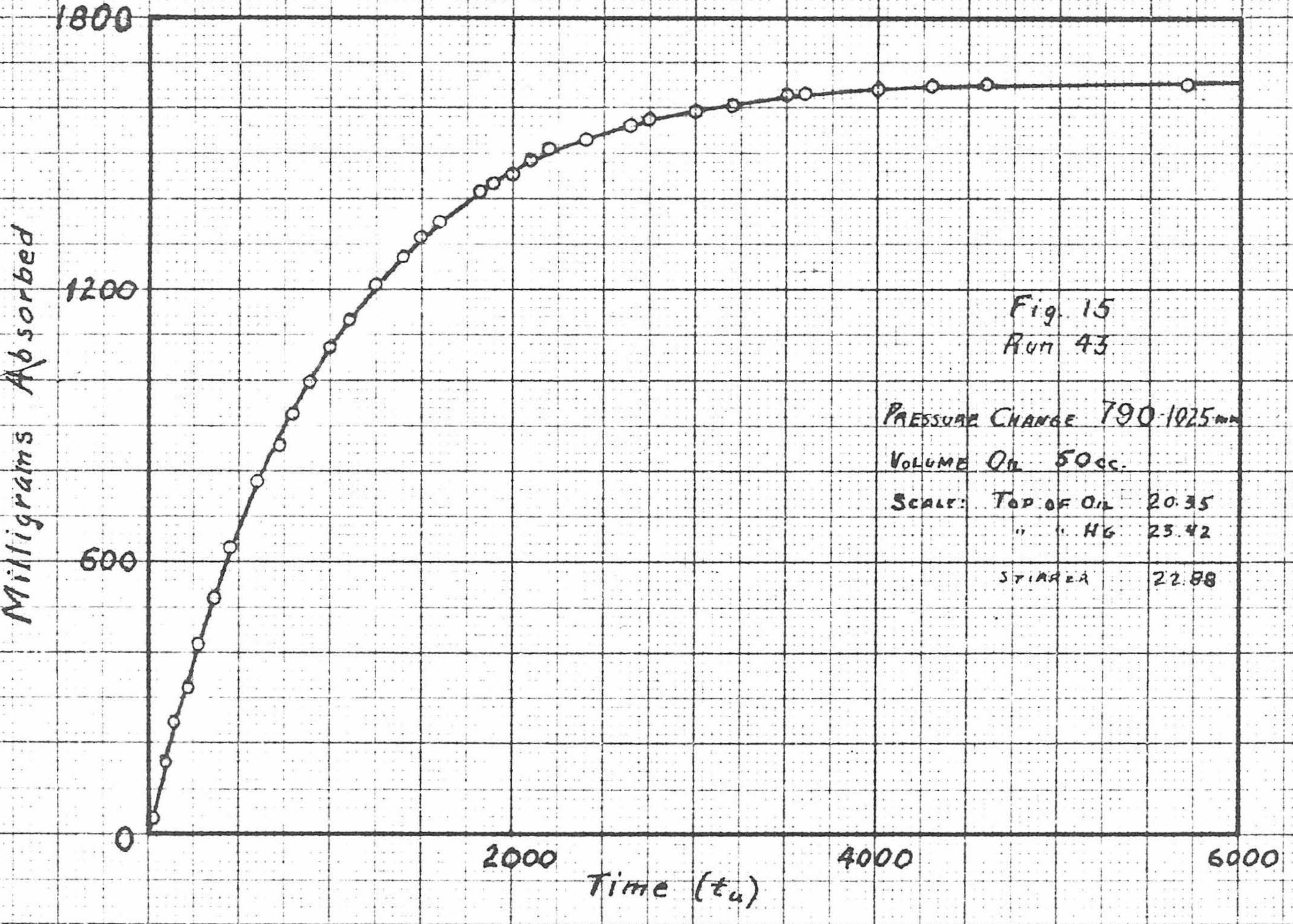

Fig. 15
Run 43

Pressure Change 790-1025 mm
Volume Oil 50 cc.
Scale: Top of Oil 20.35
" " Hg 23.42
Stirrer 22.88

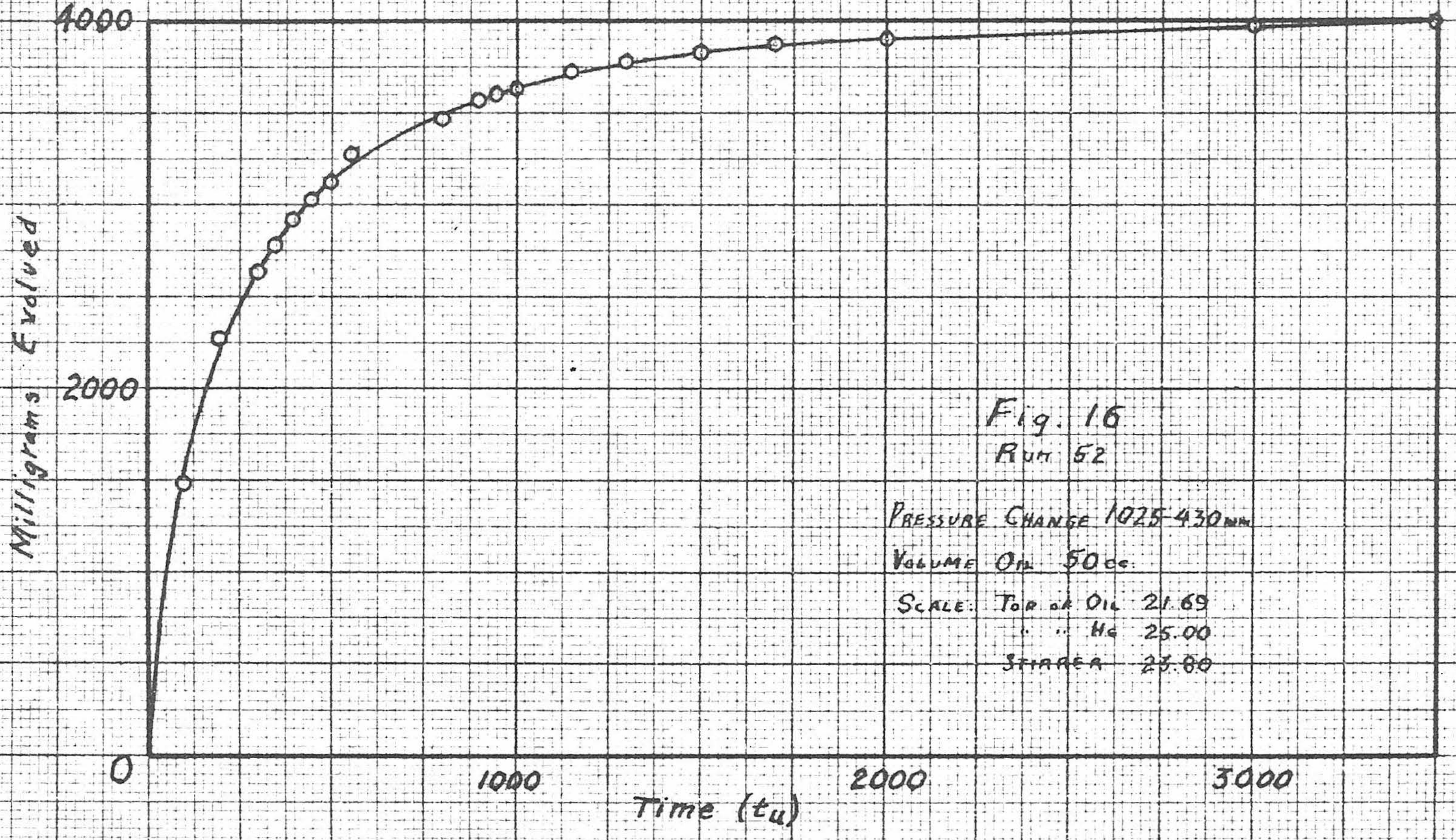

Fig. 16

Run 52

Pressure Change 1025-430mm

Volume Oil 50cc

Scale: Top of Oil 21.69
" " Hg 25.00
Stirrer 23.80

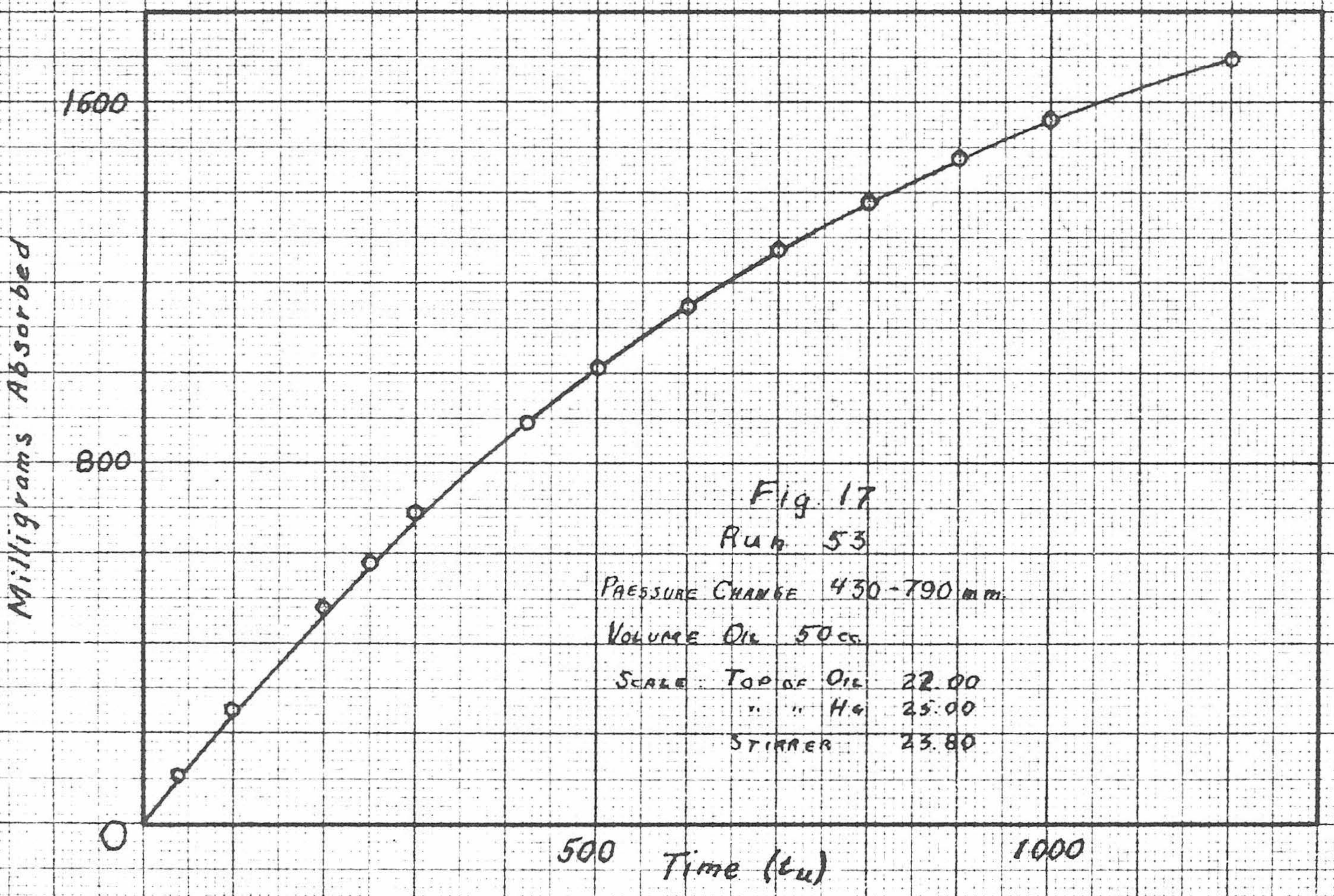

Fig. 17

Run 53

Pressure Change 430-790 mm.

Volume Oil 50 cc.

Scale Top of Oil 22.00
" " Hg 25.00
Stirrer 23.80

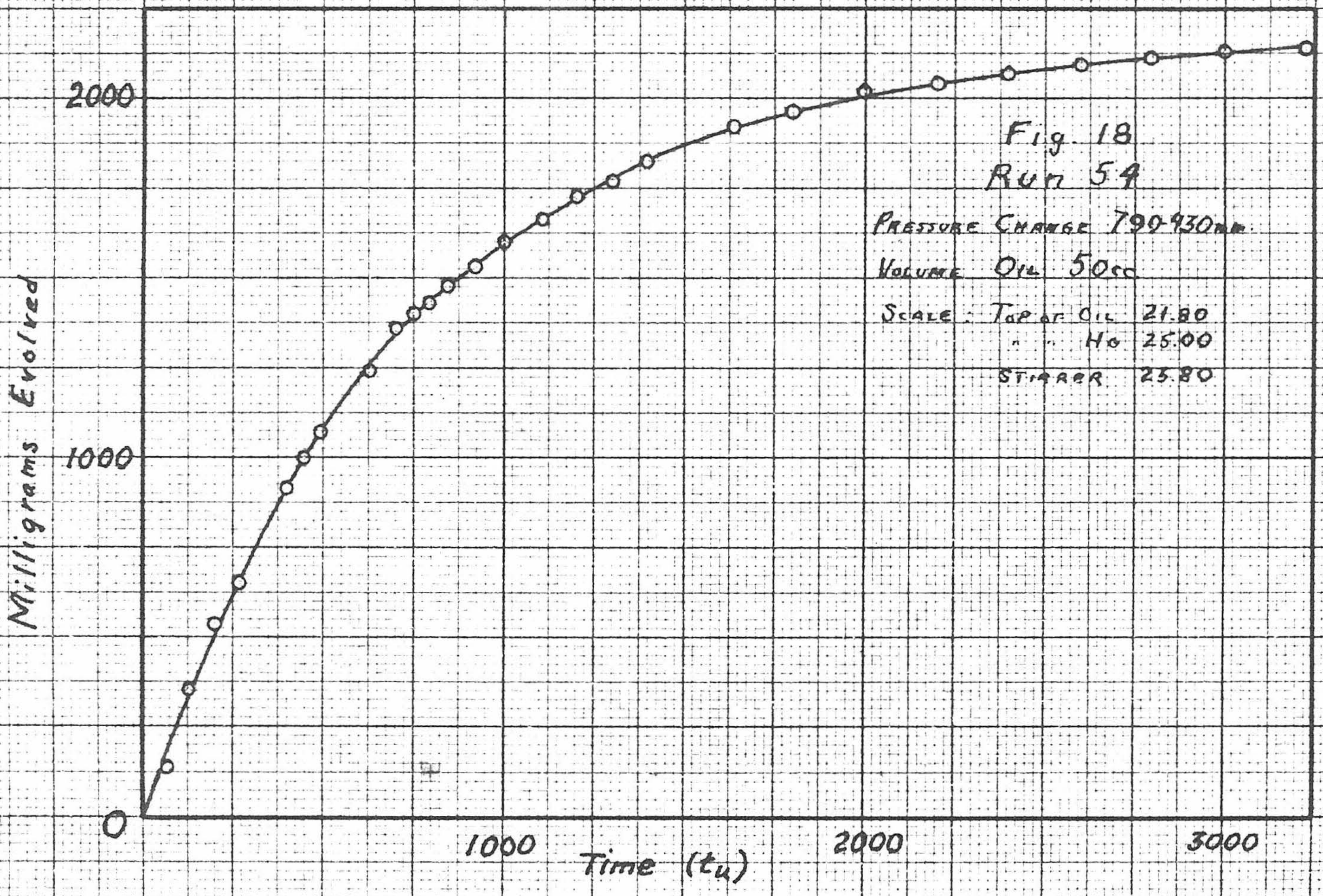

Fig. 18
Run 54

Pressure Change 790-930 mm.
Volume Oil 50 cc
Scale: Top of Oil 21.80
" " Hg 25.00
Stirrer 25.80

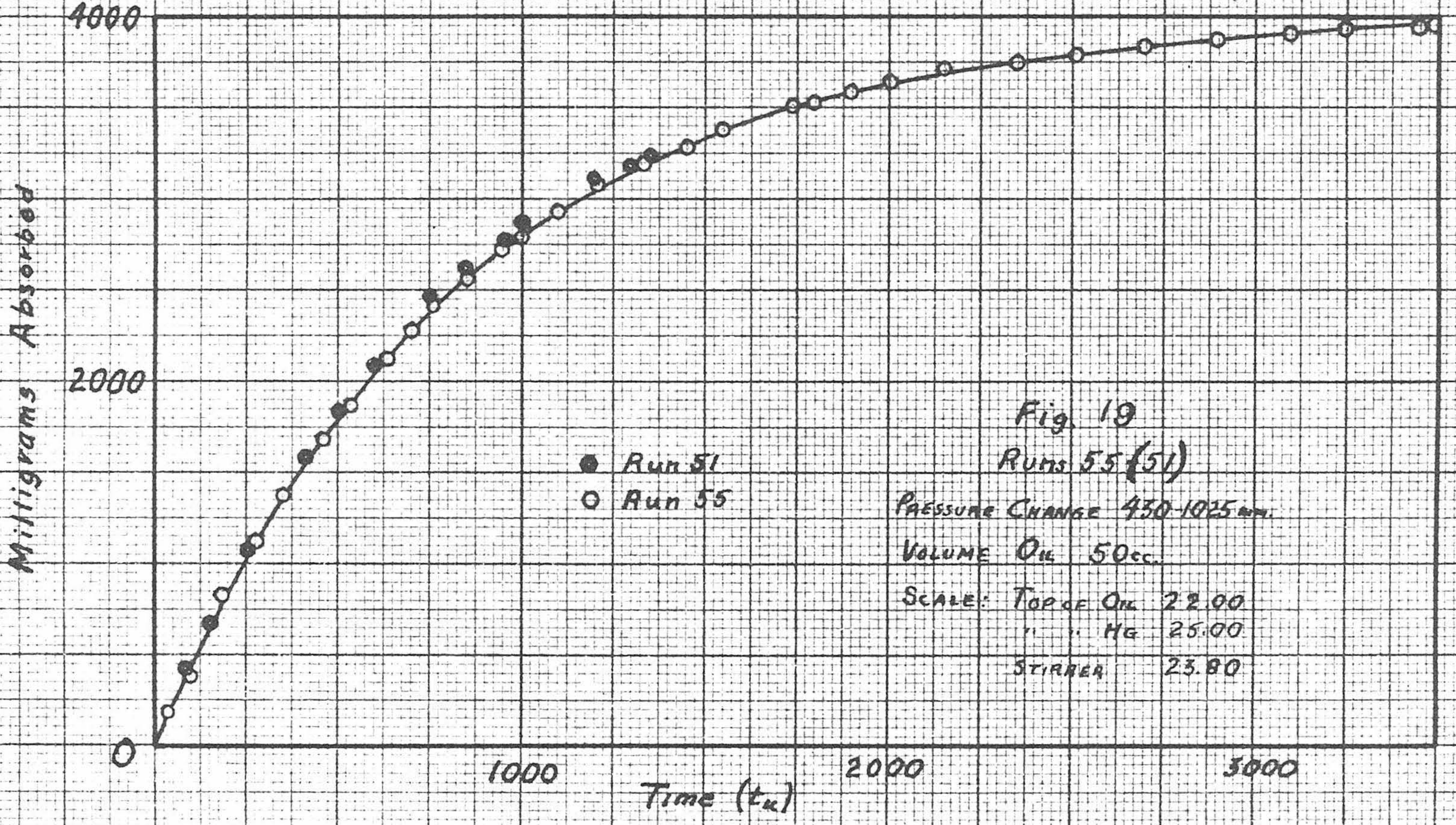

Fig. 19

Runs 55 (51)

Pressure Change 430-1025 mm.

Volume Oil 50cc.

Scale: Top of Oil 22.00
" " Hg 25.00
Stirrer 23.80

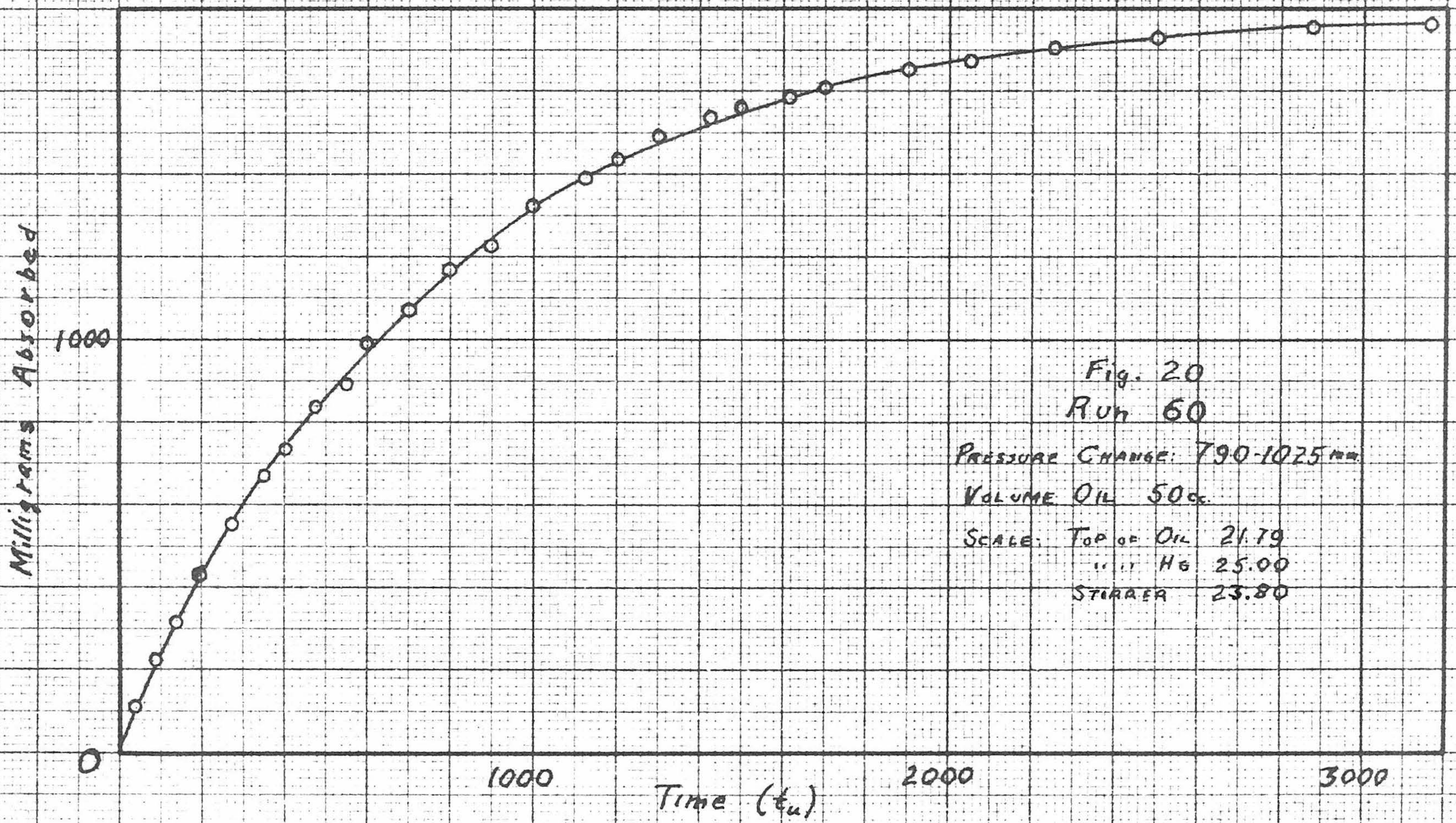

Fig. 20

Run 60

Pressure Change: 790-1025 mm

Volume Oil 50 cc.

Scale: Top of Oil 21.79

" " Hg 25.00

Stirrer 23.80

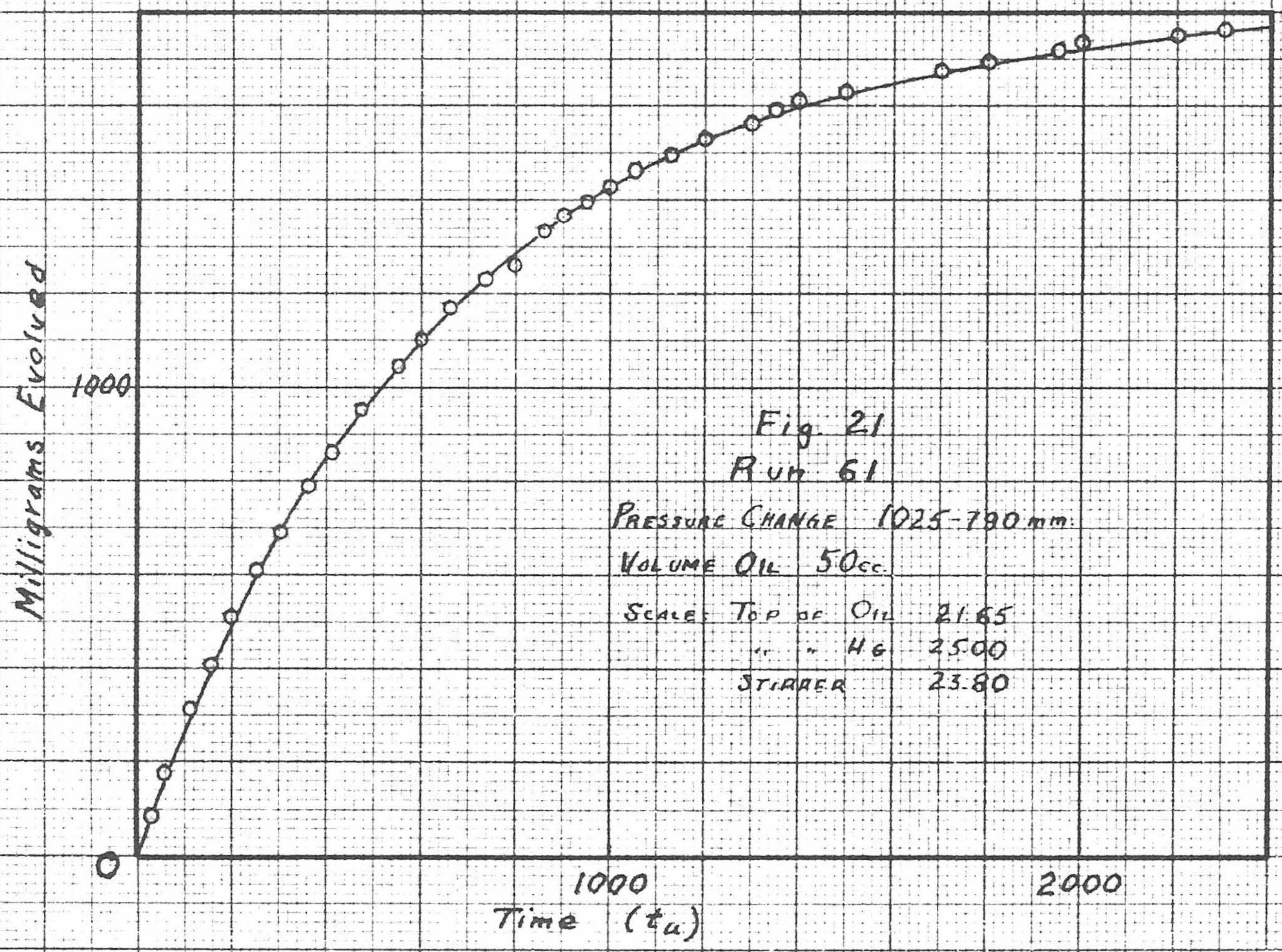

Fig. 21
Run 61
Pressure Change 1025-790 mm
Volume Oil 50cc.
Scale: Top of Oil 21.65
" " Hg 25.00
Stirrer 23.80

the gas absorbed between a lower pressure and the high pressure of 1025 mm. for 75 cc. of oil. This necessitated storing gas in the measuring bulbs at a pressure much greater than 1025 mm., and in each switch of the flow from one bulb to another a definite quantity of gas apparently leaked out through the stopcock. Since the breaks in the curves appeared only at the points that these switches were made, and the points for any particular bulb fell on a smooth curve, it was felt that the correction made by extrapolating the curves through the sets of points and measuring the displacement was justifiable.

In Fig. 22 is presented a graphical illustration which may be found convenient for reference, showing for all of these stirred runs the relative position of the stirrer in the oil, and the height of the oil at the initial and final pressures drawn accurately to the vertical scale. The stirrer, indicated by the shaded portions of the figure, is shown as tapering off at the top to indicate the fact that the nut holding the blades and the threaded portion of the drill rod projected some distande above the actual top of the blades themselves.

In Figs. 23 - 34 the unstirred runs are also

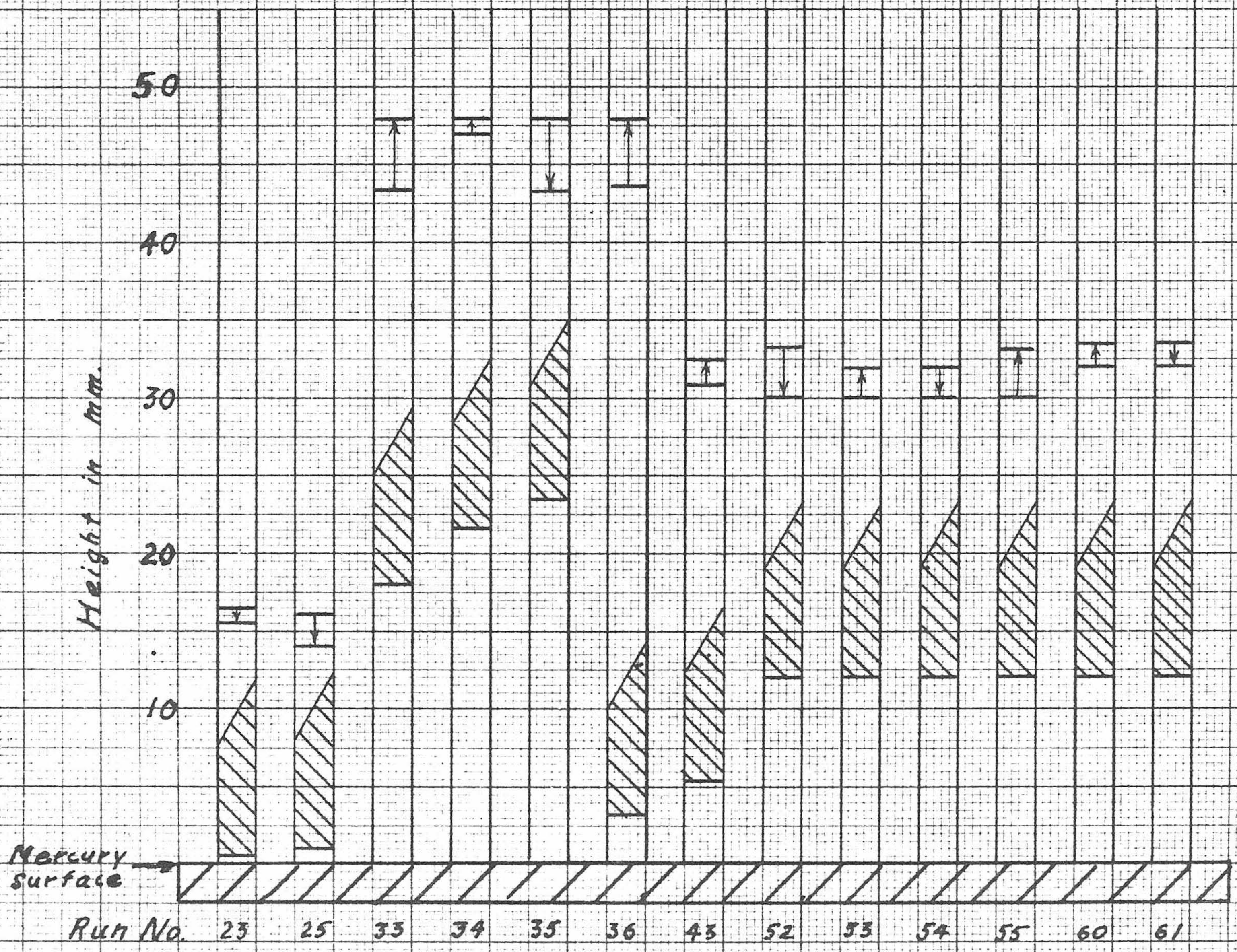

Fig. 22. Height of Stirrer and Oil Surface in Various Runs

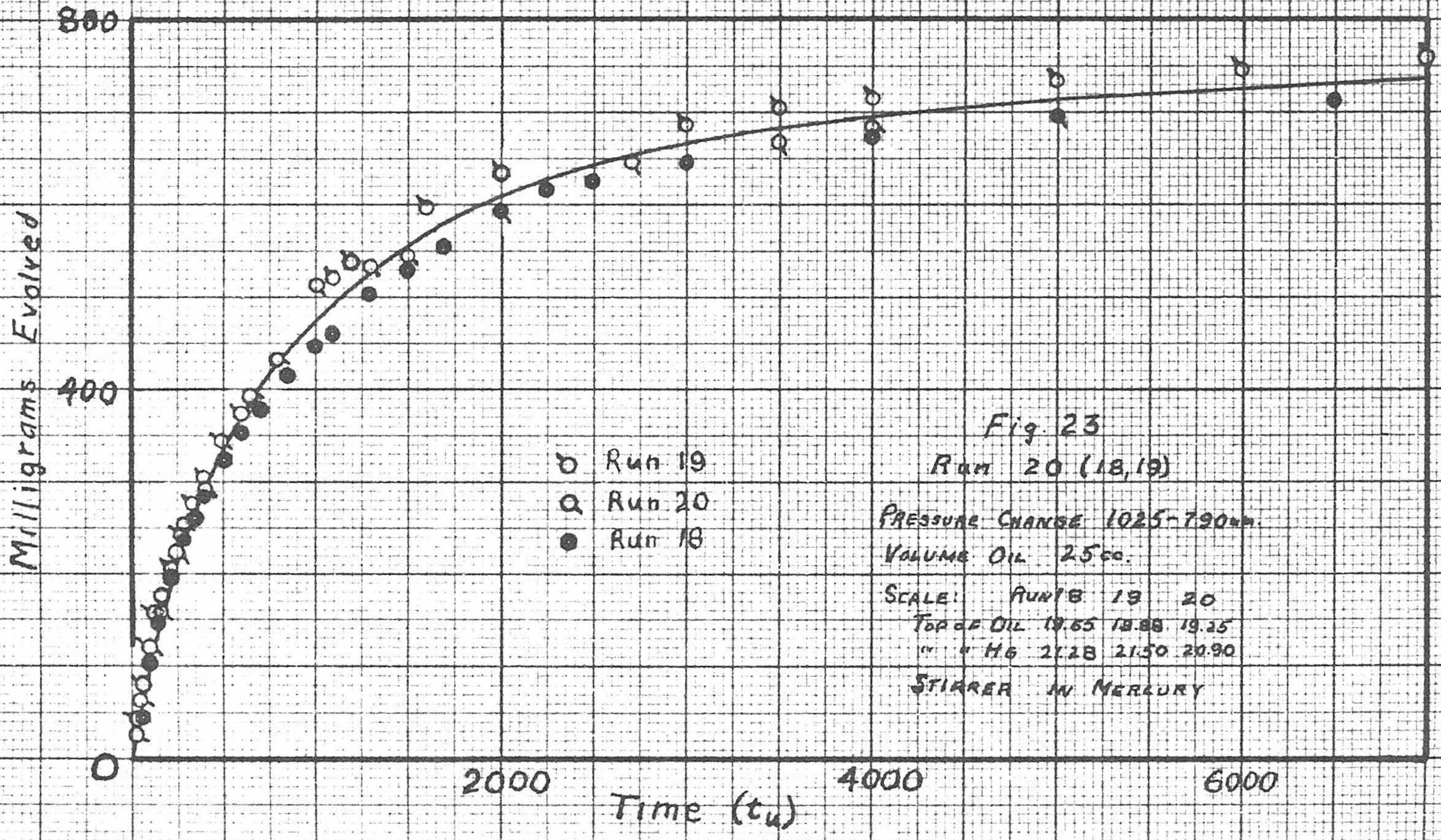

Fig. 23

Run 20 (18,19)

PRESSURE CHANGE 1025-790mm.

VOLUME OIL 25cc.

SCALE: RUN 18 19 20
TOP OF OIL 19.65 19.88 19.25
" " HG 21.28 21.50 20.90

STIRRER IN MERCURY

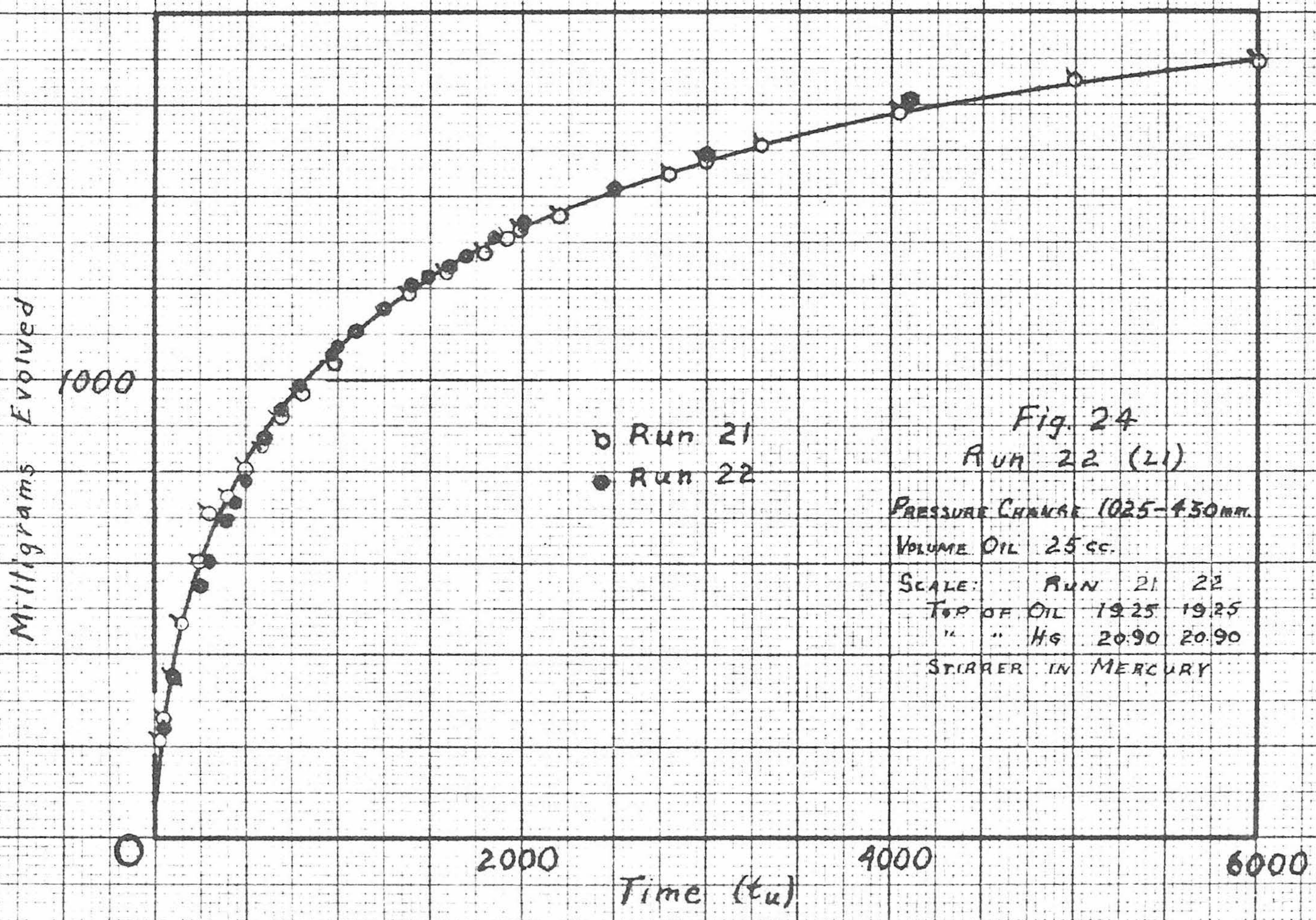

Fig. 24
Run 22 (21)

Pressure Change 1025-430mm.
Volume Oil 25cc.

Scale:	Run	21	22
Top of Oil		19.25	19.25
" " Hg		20.90	20.90

Stirrer in Mercury

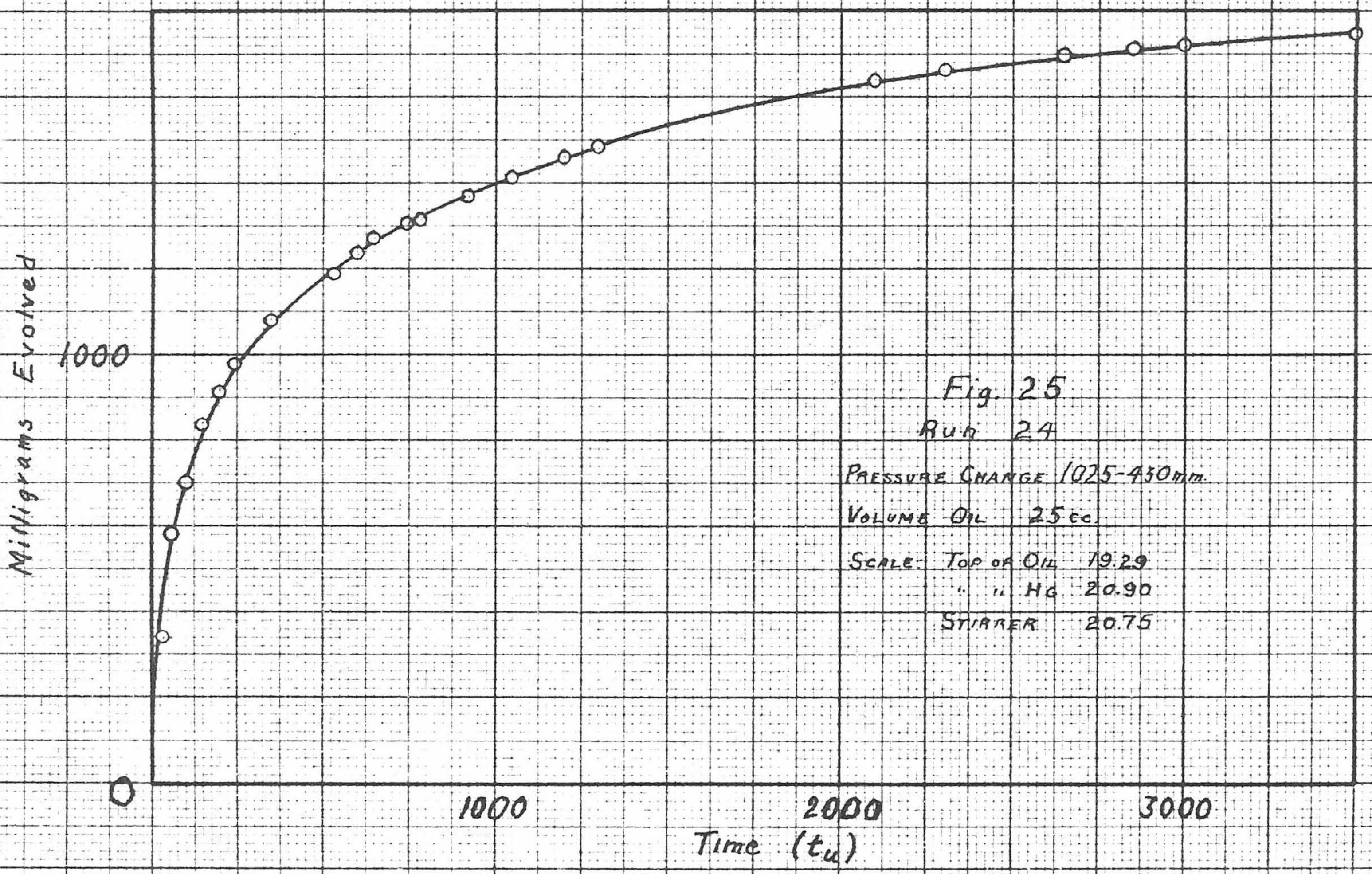

Fig. 25

Run 24

Pressure Change 1025-430mm.

Volume Oil 25cc.

Scale: Top of Oil 19.29
" " Hg 20.90
Stirrer 20.75

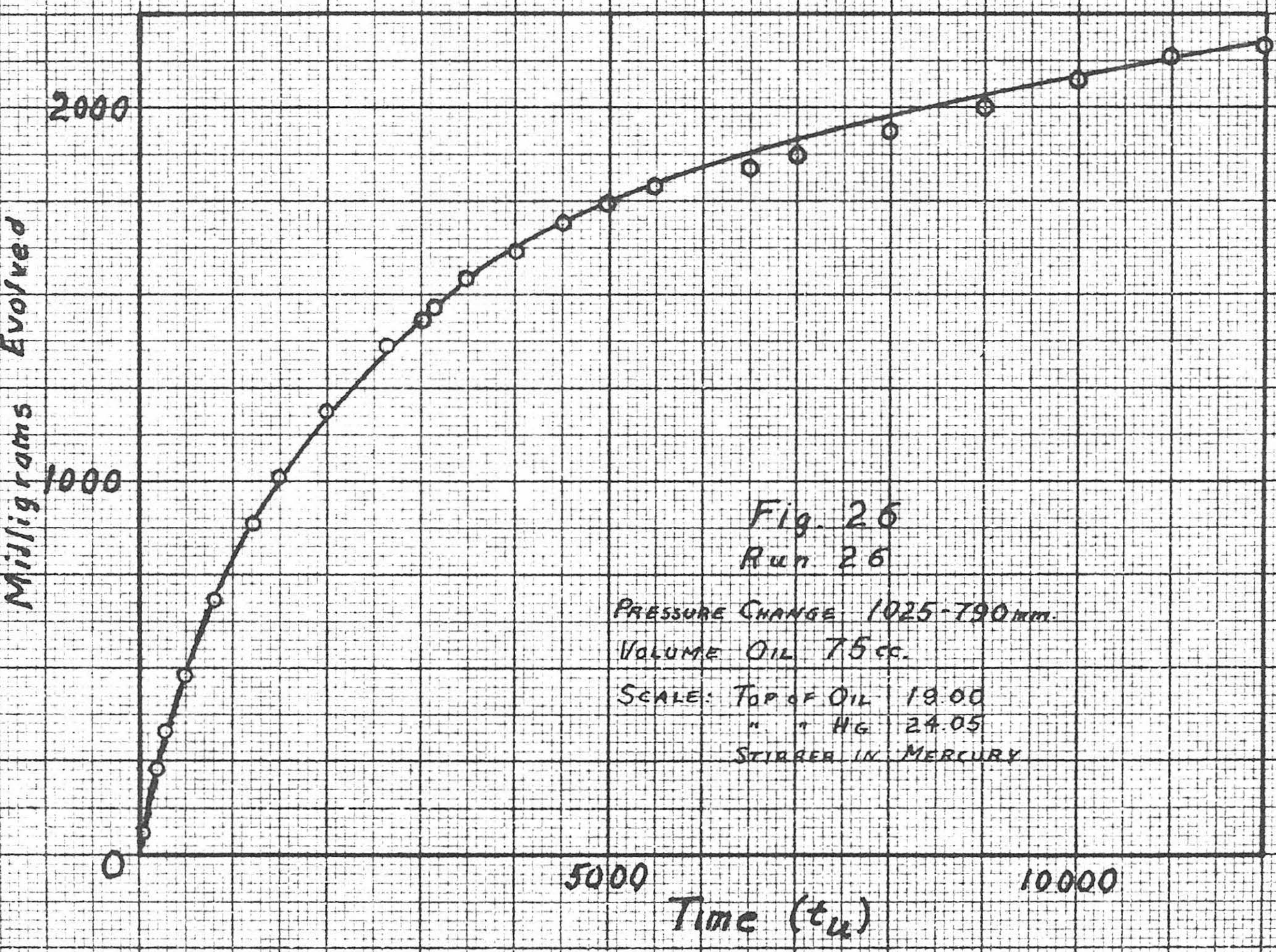

Fig. 26

Run 26
Pressure Change 1025-790 mm.
Volume Oil 75 cc.
Scale: Top of Oil 19.00
" " Hg 24.05
Stirrer in Mercury
Milligrams Evolved
2000
1000
0
5000
10000
Time (t_u)

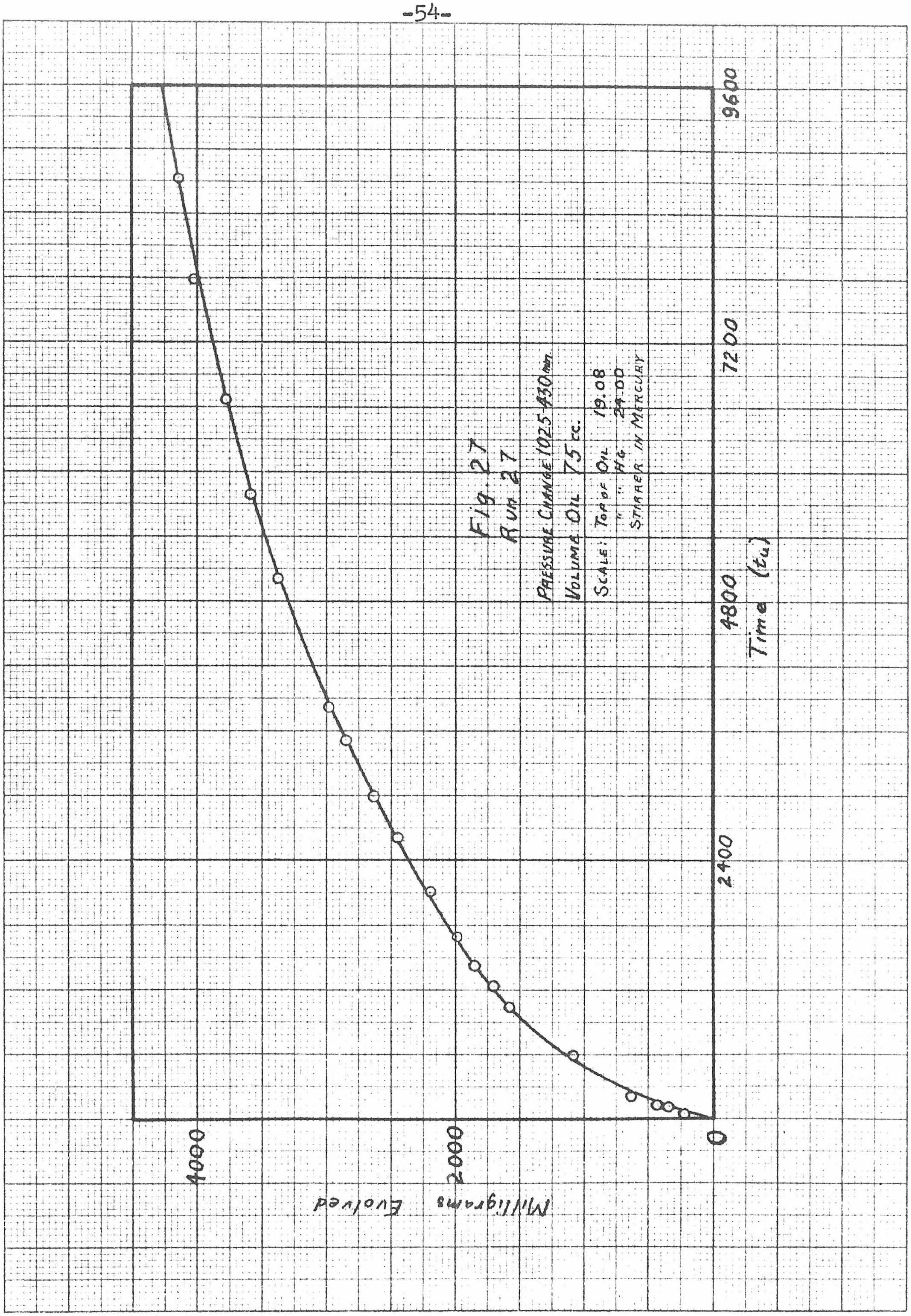

Fig. 27
Run 27

Pressure Change 1025-430 mm.
Volume Oil 75 cc.
Scale: Top of Oil 19.08
" " Hg 24.00
Stirrer in Mercury

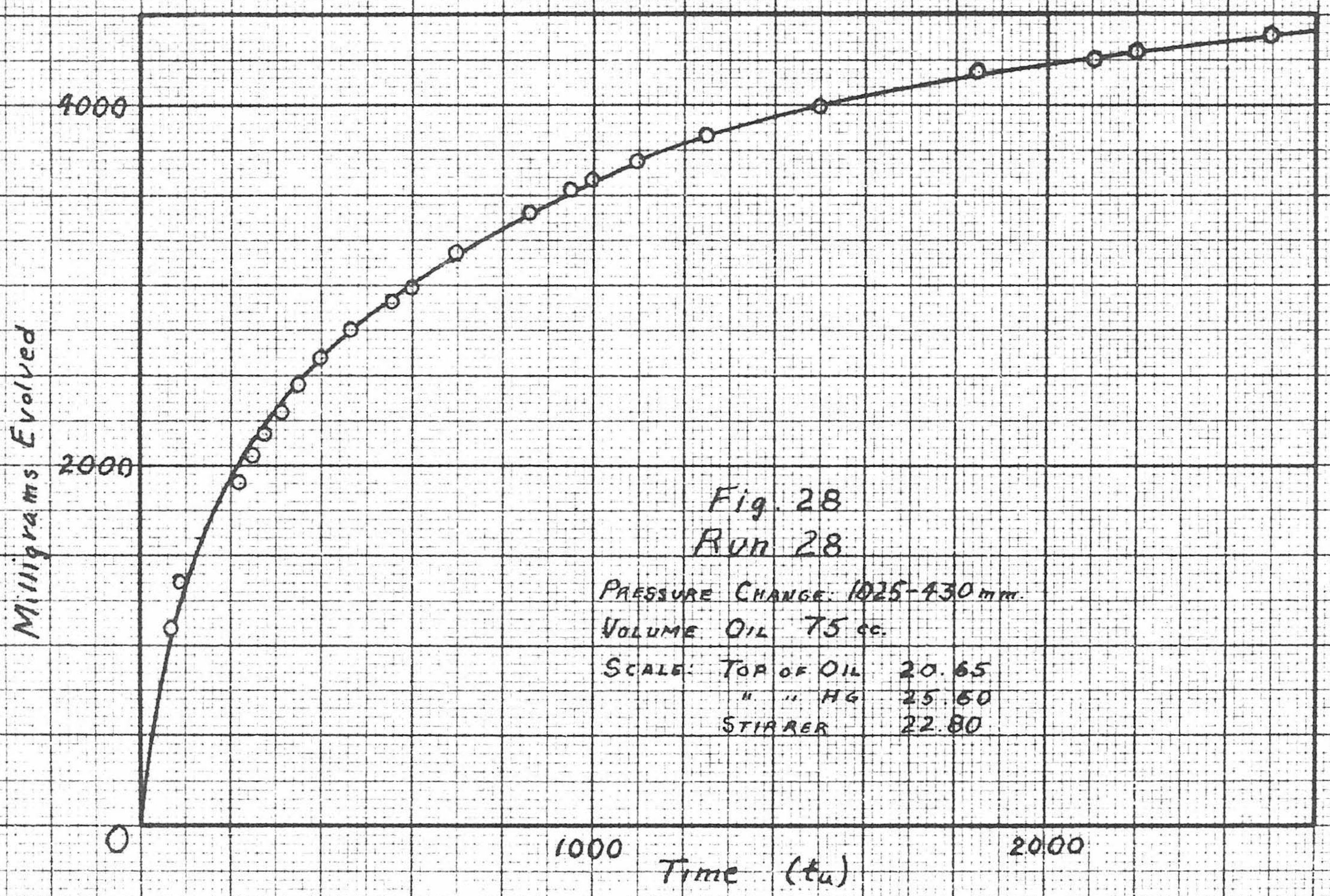

Fig. 28
Run 28

Pressure Change 1025-430 mm.
Volume Oil 75 cc.
Scale: Top of Oil 20.65
" " Hg 25.60
Stirrer 22.80
Milligrams Evolved
4000
2000
0
1000
2000
Time (tu)

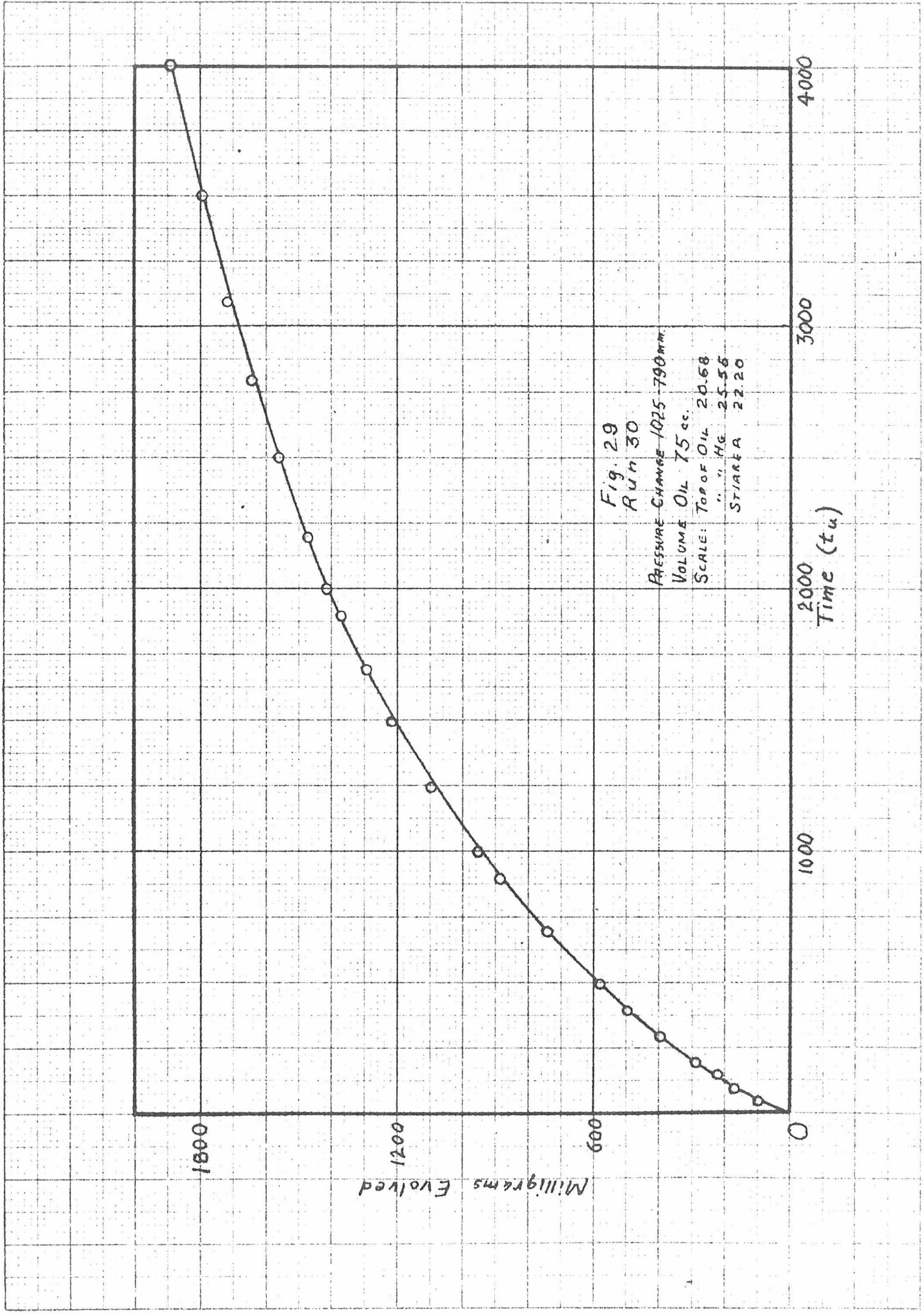

Fig. 29
Run 30

Pressure Change 1025-790 mm.
Volume Oil 75 cc.
Scale: Top of Oil 20.68
" " Hg 25.56
Stiarea 22.20

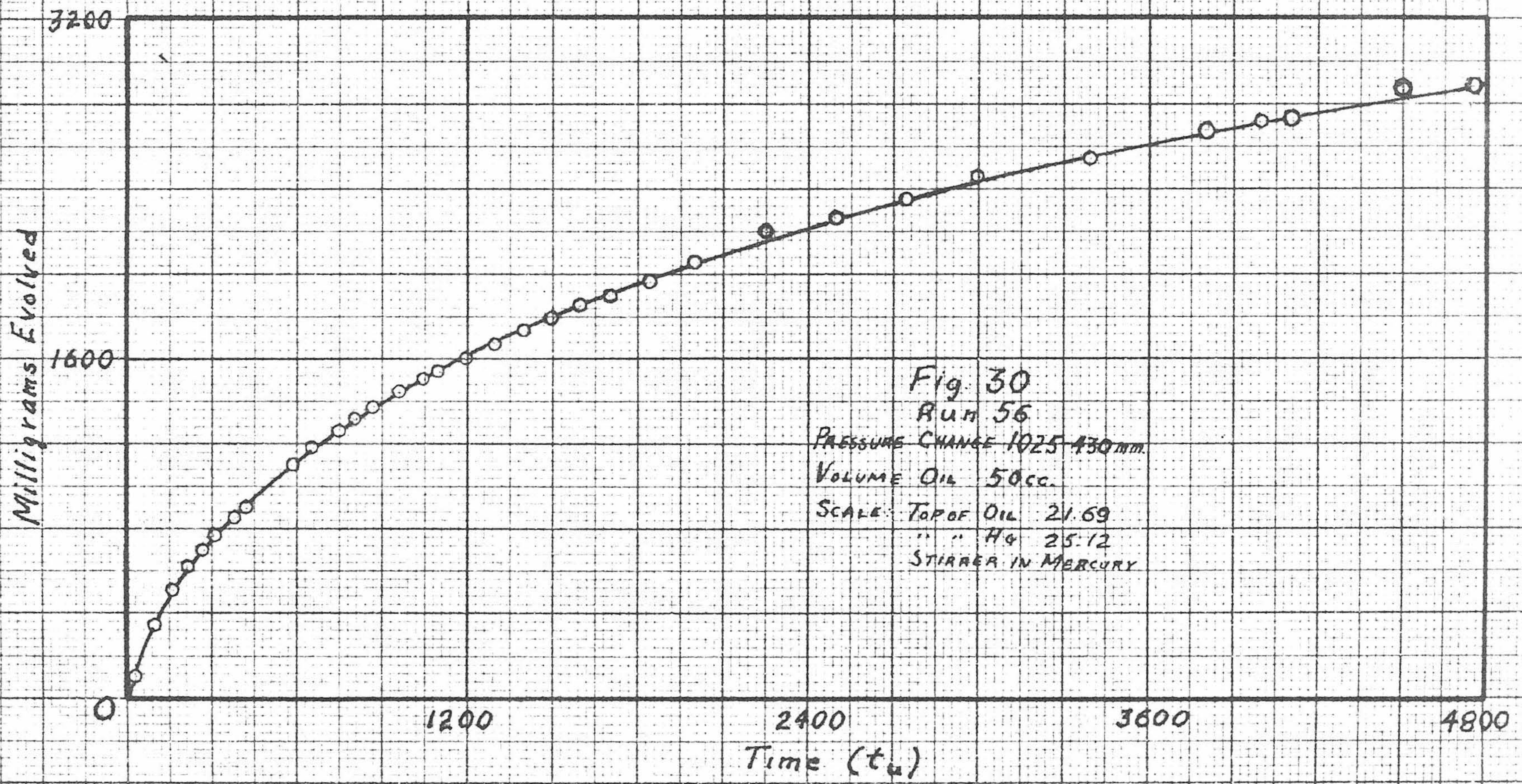

Fig. 30
Run 56
Pressure Change 1025-430mm.
Volume Oil 50cc.
Scale: Top of Oil 21.69
" " Hg 25.12
Stirrer in Mercury

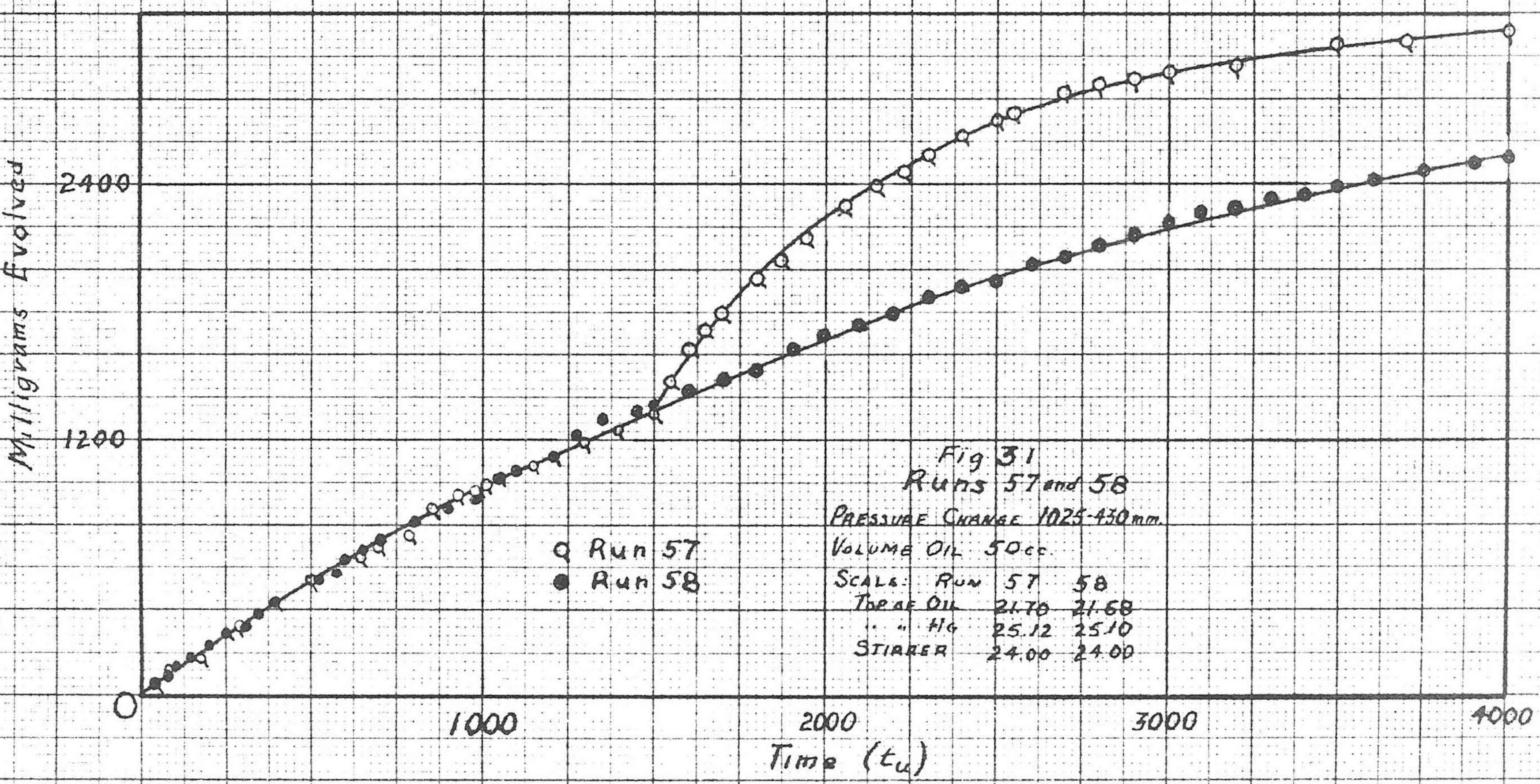

Fig 31
Runs 57 and 58

Pressure Change 1025-430 mm.

Volume Oil 50 cc.

Scale: Run	57	58
Top of Oil	21.70	21.68
" " Hg	25.12	25.10
Stirrer	24.00	24.00

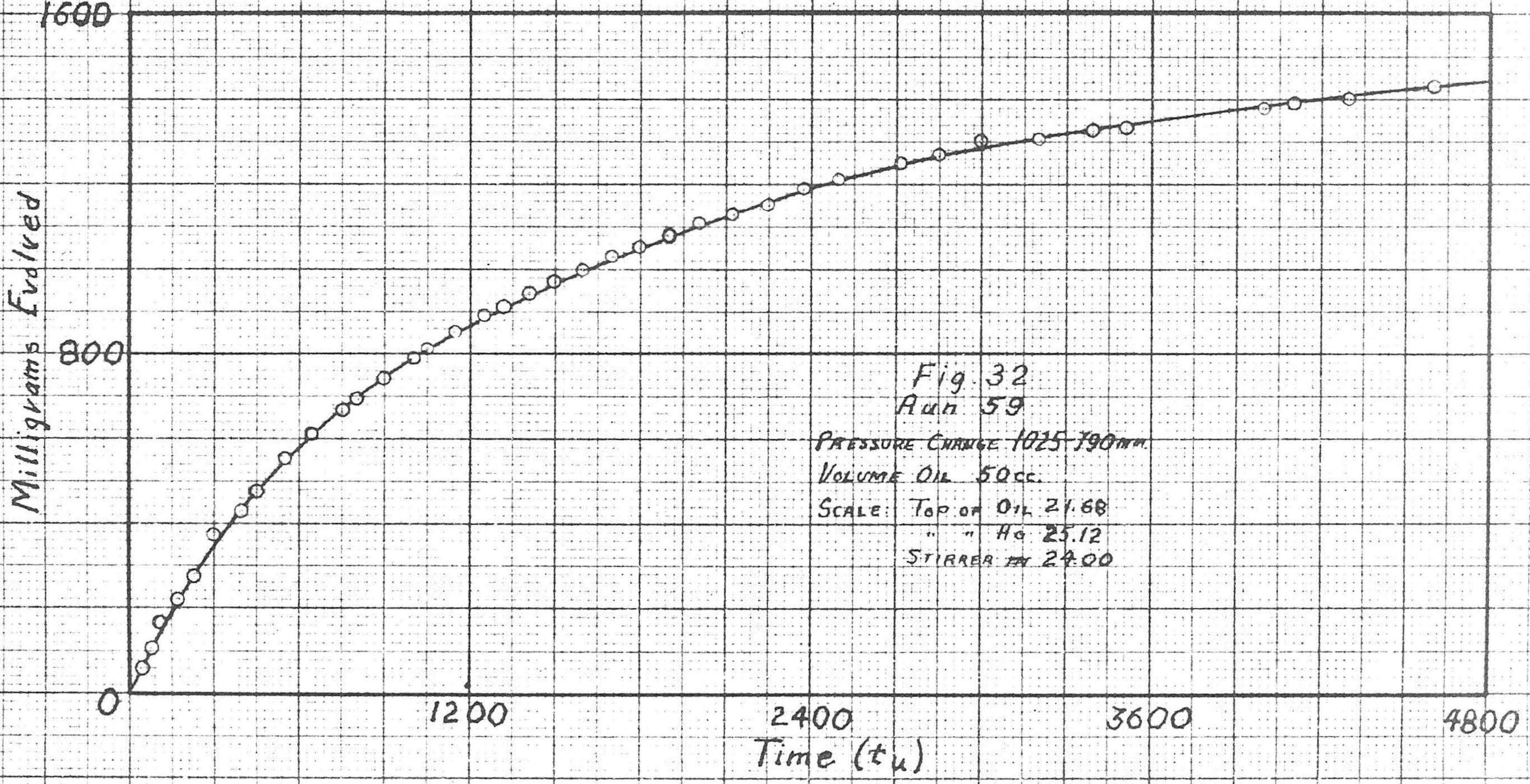

Fig 32
Run 59

PRESSURE CHANGE 1025-790mm.
VOLUME OIL 50cc.
SCALE: TOP OF OIL 21.68
" " Hg 25.12
STIRRER AT 24.00

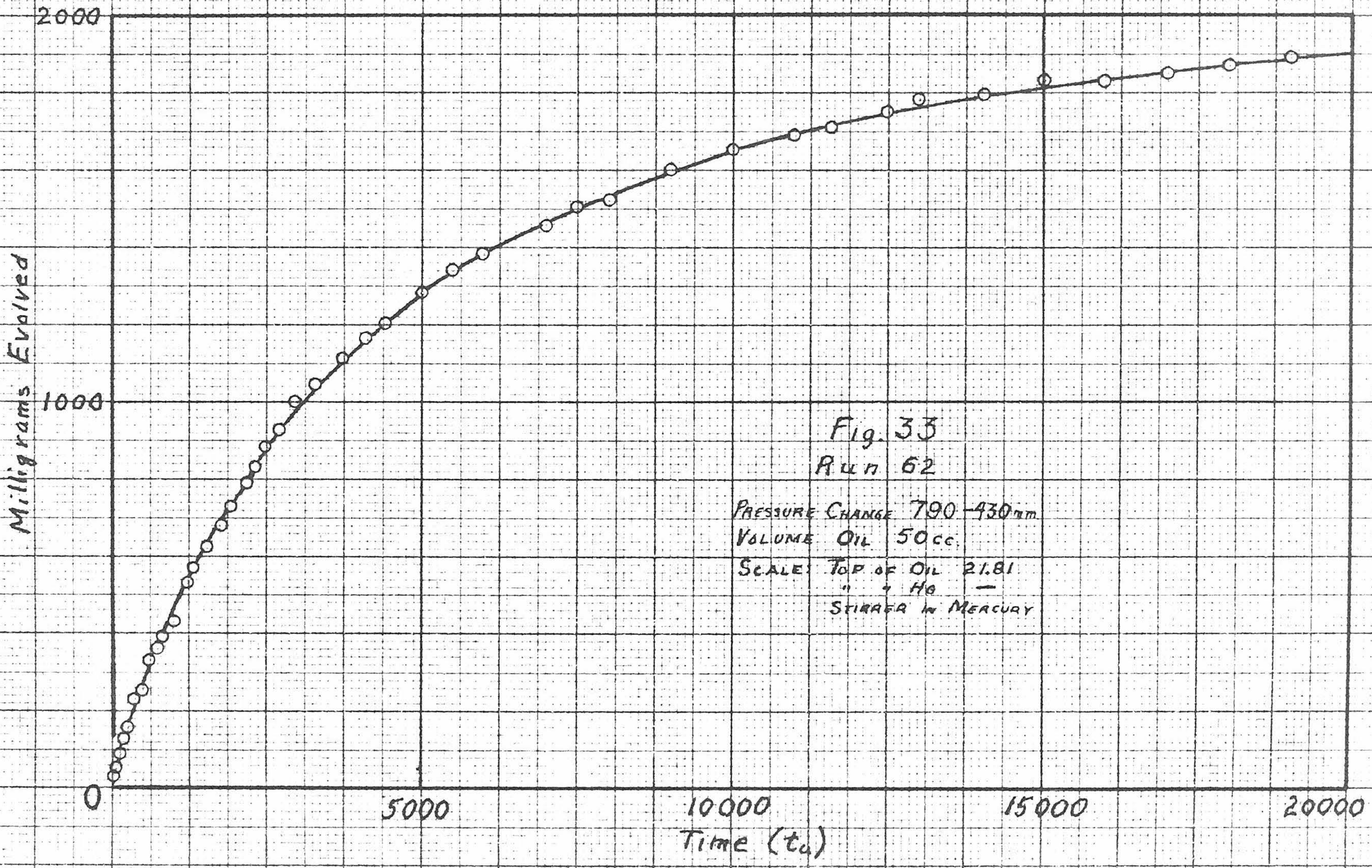

Fig. 33

Run 62

PRESSURE CHANGE 790 - 430mm
VOLUME OIL 50cc.
SCALE: TOP OF OIL 21.81
" " HG —
STIRRER IN MERCURY

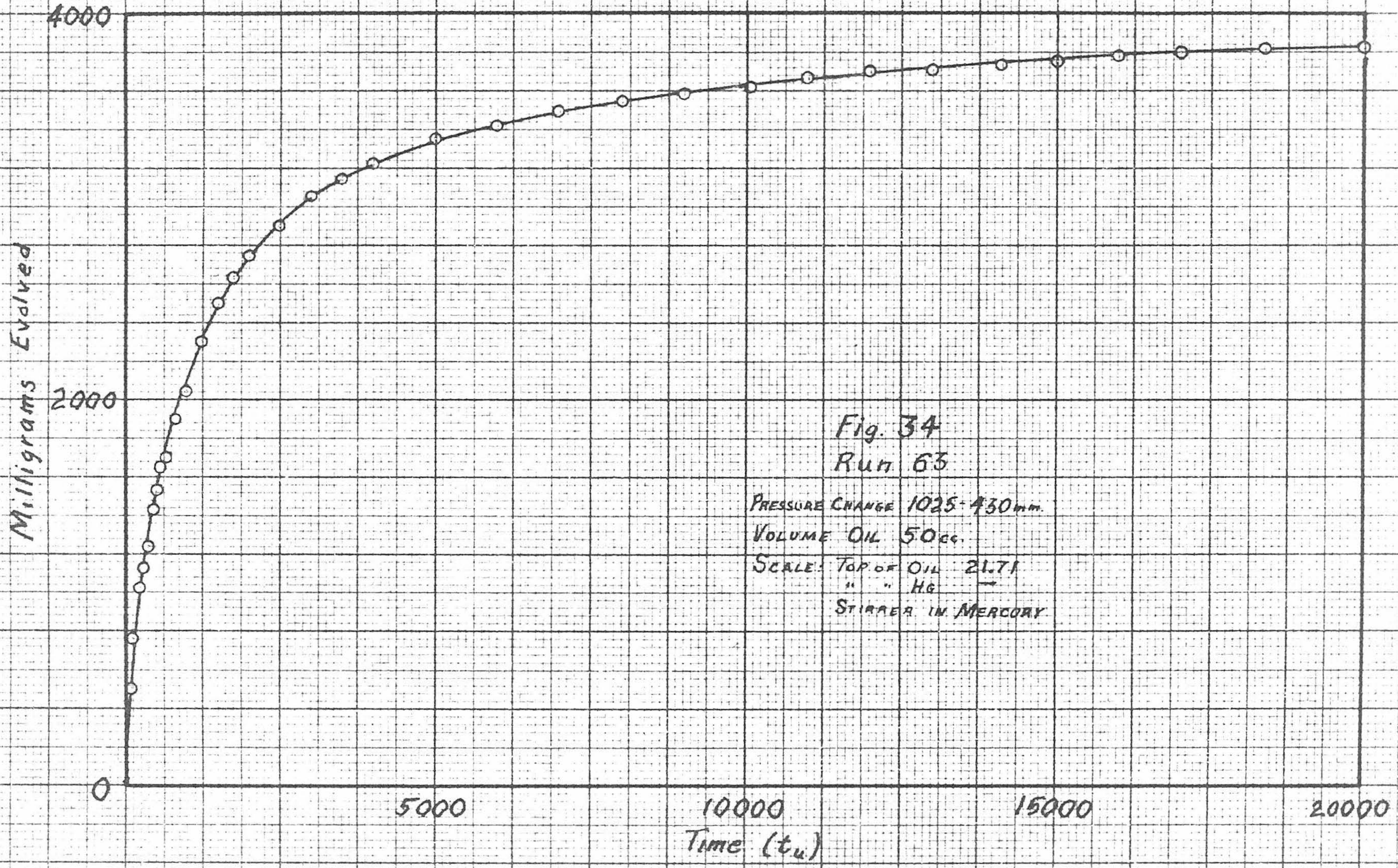

Fig. 34

Run 63

PRESSURE CHANGE 1025-430 mm.

VOLUME OIL 50 cc.

SCALE: TOP OF OIL 21.71

" " HG —

STIRRER IN MERCURY

presented graphically. In these runs the stirrer may be below the surface of the mercury in the cell, or at some point in the oil as indicated.

With the exception of Runs 57 and 58, in all of the runs involving evolution of gas there was observed a formation of foam or bubbles on the surface or in the body of the oil immediately upon decreasing the initial pressure of gas over the oil, the quantity of foam and formation of bubbles decreasing during the course of the run. Runs 57 and 58, made under identical conditions with the stirrer beneath the oil, are plotted together in Fig. 31. In Run 57 there was observed only one bubble at the beginning of the run as the throttle stopcock was opened, one bubble some 700 time units later, and no further bubbles until 1500 t_u, when there was a sudden formation of foam similiar to that usually observed at the beginning of runs. In Run 58 no bubbles at all were observed until 400 t_u, when one or two bubbles were noted at the edge of the surface of the oil, and no further bubbles were observed until approximately 900 t_u, when there began a peculiar surface boiling phenomena, one or more bubbles forming very slowly at the surface, increasing in size, and then bursting, the process being repeated throughout the rest of the run. Run 57, after the burst of foam at 1500 t_u, was more or less normal though this suface boiling phenomena occurred to some extent. It must be remarked in this regard that the constant attention required by the manual control of the throttle valve permitted only rare observations of the behavior in the cell. A simple device for automatically controlling the throttle valve was suggested early in the experimental program, but it was decided that the ten or twelve hours necessary for its construction should be utilized in making more runs. Runs 57 and 58, when plotted on the large scale which was used in plotting all of the runs for later use, which was three to five times the scale of the figures reproduced here, showed quite definite evidences of inflections corresponding to the evolution of the bubbles observed, while the curves for all other unstirred runs seemed quite smooth, and within the experimental accuracy lacked any sudden changes of curvature.

The density of a solution of butane in crystal oil decreases with the amount of butane dissolved, so the less concentrated solution near the surface during runs involving evolution of gas is denser than the main body of the solution. Since the index of refraction is also a function of the concentration it was possible to clearly observe the streaming of this heavier oil to the bottom of the solution in all the unstirred runs.

Reproducibility of Data.

In Figs. 19, 23, and 24, several runs, made under identical conditions and during which no differences in behavior were noted, were plotted together, and serve to indicate the reproducibility of the measurements. In these runs the points fall quite closely together, and in the three figures shown the best curve through all of the points was used in later calculations, and in referring to the combined data the highest run number in the group will be used. Runs 56 and 63 (Figs. 30 and 34) should also show the same behavior but the rates are considerably different; the rate curves are quite smooth, however, so the discrepancy may be due to some difference in behavior which escaped observation.

Theoretical

A simple way of considering the process of the absorption or evolution of a gas from agitated solutions is to assume that the main body of the solutions is of uniform composition and that the sole rate limiting process is the diffusion of the gas through very thin layers of liquid and gas at the surface of the solution. It is a well recognized fact of hydrodynamics that there do exist thin boundary regions in turbulent fluids where the flow is laminar in nature (i.e., regions where there is no component of velocity normal to the surface) and it is thus clear that through this portion of the fluids any transfer of material across the layers must take place by diffusion. Such a layer is not, of course, a definite layer separated from the turbulent portion of the fluid by a sharp boundary, but it is convenient to consider that it is, and then define an "effective film thickness" as the thickness such a layer would have if it did have a sharp boundary.

In applying this concept to a gas liquid system it is possible that two films may be present, a gas film and a liquid film, but it is frequently possible to assume that only one of these is effective in any particular case. Thus in the experiments which have been described there was no inert gas present above the oil, and the vapor pressure of the oil used was of the order of 10^{-4} mm., which may be taken to indicate that any effect of a gas film may be ignored, and only a liquid film need be considered in this interpretation of the process.

It has been established that the thickness of a laminar layer is a function of the velocity of the main body of fluid adjacent to it, but it is not easy to calculate from a knowledge of hydrodynamic behavior the effective thickness of the laminar layer for a suitable experimental apparatus, and so in these experiments this value, together with the diffusion constant, cannot be used to predict the rate of solution or evolution of the gas. However, it is possible to calculate quite readily the "effective thickness" of the film from a knowledge of the rate of solution or evolution and the diffusion constant, and this has been done for all of the experimental rate measurements made. The method of calculation and the assumptions involved are described in detail below.

Calculation of Effective Film Thickness.

Since, as was shown, the diffusion constant D is a function of the concentration, it might be best to write it D(c), so that the usual equation which defines the diffusion constant after Fick reads

$$\left(\frac{dq}{dt}\right)_a = - A\, D(c_a) \left(\frac{\partial c}{\partial x}\right)_a \qquad (4)$$

when q = quantity of diffusing material passing across the particular plane $x = a$ of area A perpendicular to the direction of diffusion.

t = time

c = concentration of diffusing material

$D(c_a)$ = value of the diffusion constant for concentration at $x = a$

x = distance in the direction of flow

so $\left(\frac{dq}{dt}\right)_a$ = rate at which diffusing material crosses the plane $x = a$

and $\left(\frac{\partial c}{\partial x}\right)_a$ = concentration gradient at the plane $x = a$

If x is measured in cm., A in sq. cm., t in seconds, and c is concentration per cc., D has the units of sq. cm. per second, providing q and c are measured in identical mass units.

Considering the particular experiments described we may assume (a) that there exists at the surface of the solution a very thin layer of thickness l through which the gas moves by diffusion, this diffusion determining the rate of absorption or evolution of the gas, and (b) that the concentration gradient across this layer is a linear function of the thickness.

We may then write $\frac{\Delta c}{l}$ for $\left(\frac{\partial c}{\partial x}\right)_a$, but since Δc may have a very wide range of values, we must assume, (c), that the concentration for which the diffusion constant applies is c_m, the mean concentration of the layer l, and so for (4) write

$$\frac{dq}{dt} = - A\ D(c_m)\frac{\Delta c}{l} \qquad (5)$$

where $\frac{dq}{dt}$ is now the rate of absorption of evolution and A the surface area of the oil solution.

If now we assume (d) that the concentration in the main body of the solution at any time, c_b, is uniform up to the inner edge of the boundary layer, and define c_s as the concentration of the gas at the liquid surface, we may write $\Delta c = (c_s - c_b)$. We may further quite readily assume (e) that c_s is the equilibrium concentration corresponding to the pressure of gas maintained above the solution, which in these experimental measurements was maintained at a constant value during a run.

Using the value of the diffusion constant found in equation (3) and noting that $c_m = (c_s + c_b)/2$, we may now write for (5)

$$l = \frac{A\left[.440 + (.00485)(c_b + c_s)\right](c_b - c_s) \times 10^{-5}}{dq/dt}$$

which simplifies to

$$1 = A \frac{-c_s(.440 + .00485\ c_s) + c_b(.440 + .00485\ c_b)}{dq/dt \times 10^5} . \qquad (6)$$

c_b may, of course, be calculated from the amount of gas that has been absorbed or evolved, for

$$c_b = \frac{Q - qt - r}{v_t - v_s} \quad \text{and} \quad c_b = \frac{Q + qt - r}{v_t - v_s} \qquad (7)$$

for evolution and absorption, respectively,

where Q = total quantity of gas originally in solution,

r = the quantity of gas in the surface layer,

q_t = quantity of gas evolved or absorbed at a particular time,

v_t = total volume of solution at the same time,

and v_s = volume of the surface layer at that time.

We may assume (f) that r is very much smaller than $Q \pm q_t$, and v_s is very much smaller than v_t and obtain

$$c_b = \frac{Q - q_t}{v_t}, \quad \text{or} \quad c_b = \frac{Q + q_t}{v_t}. \qquad (8)$$

We have in equation (1) an expression for the volume of the solution which may likewise be included in this expression, so that again neglecting the quantity of gas dissolved in the surface layer;

$$c_b = \frac{Q \pm q_t}{.0019817\ (Q \pm q_t) + 1.2134\ g} \qquad (9)$$

the plus sign being used for absorption, the minus sign for evolution of gas. Substituting in (6)

$$1 = A\left\{\frac{-c_s(.440 + .00485c_s) + \dfrac{.440\ (Q\pm q_t)}{.0019817\ (Q\pm q_t) + 1.2134g}}{dq/dt \times 10^5} + \frac{\dfrac{.00485(Q\pm q_t)^2}{[.0019817(Q\pm q_t) + 1.2134g]^2}}{dq/dt \times 10^5}\right\} \qquad (10)$$

The computation of a very large number of individual values with this equation was simplified by writing S for part of the numerator of equation (10) to obtain the form

$$1 = \frac{A\ S}{dq/dt} \qquad (11)$$

and calculating the factor S for a series of values of $(Q\pm q_t)$ and for each set of values of c_s and g that were used. S was then plotted on a large scale against q_t (the curves were very close to straight lines), and values of S for a long series of values of q_t could be found readily by interpolation along the proper curve.

The film thickness 1 may now be determined from the value of q_t, the amount of gas absorbed or evolved at a particular time, and dq/dt, the slope of the rate curve at that point. It is now apparent why the values of time as recorded in t_u were not recalculated to seconds, since we may write

$$l = \frac{5\ A\ S}{6\ dq/dt_u} \qquad (12)$$

and take the slopes directly from the rate curves as shown in the figures previously reproduced. In using all these equations only the absolute value of l need be considered since the concentration gradient will change sign depending on whether the run is absorption or evolution, while l has been considered as positive in direction <u>into</u> the solution, it will consequently as calculated by (12) have a negative value for absorption runs, unless $-\Delta c$ is used in (5) and the equations thereafter.

The Assumptions Involved.

To a considerable extent any examination of the validity of the assumptions made in this treatment must await the results obtained. Assumption (a) is the fundamental hypothesis we are endeavoring to establish more clearly, and since l cannot be readily calculated by any other means, it is hoped that the quantitive behavior of the film thickness may to some extent indicate its validity. Assumptions (b) and (c) would appear to be the only way to avoid extensive mathematical treatment and calculations and there has been no opportunity for any closer examination of these points. Assumption (d) is very closely approximated in the stirred runs, and the observation of the convection currents in the unstirred runs indicated that there was appreciable stirring. With regard to assumption (e), the assumption in this form may be avoided by merely defining the liquid interface as that point at which the concentration does correspond to the equilibrium pressures. Since the oil has such a low vapor pressure, and only butane gas is present above the solution, the surface as defined in this manner will only differ from the actual surface as identified in some other manner by an amount of the order of molecular sizes, introducing an error in l which may certainly be neglected any treatment such as this. Assumption (f) may be examined very simply by considering equation (7) numerically. The thickest calculated film was 0.2 mm., and in the cell this would occupy a volume of 0.37 cc. in comparison to the total volume of about 25 cc., and would contain at the highest concentration of gas used, 34 milligrams, in comparison to the smallest total quantity of gas possible in the solution $(Q - q_t)$ of some 800 milligrams, giving a maximum error of 5%. Since the total quantity of gas in solution under these conditions (absorption; surface at high concentration , body of liquid at low concentration) would be increased to at least twice this value within 100 seconds, the maximum possible error due to this assumption for any calculated thickness would be about 2%, and in the majority of runs, where larger quantities of oil were used and where the calculated film thicknesses are much smaller, the error is certainly less than 0.5%

To indicate more fully the way in which the calculations of the film thickness were made the complete numerical calculations for one point of Run 55 are given below in Table VI. The values indicated in the table as taken from figures which are shown are actually those obtained from the large scale plots of the data which were actually used in making the calculations of film thickness.

It is difficult to fix the accuracy of these calculations of l exactly, but as may be seen from equation (12) they directly depend on dq/dt_u. Since this is determined graphically from the slope of the rate curves the values both at the very beginning of the runs and when approaching the final saturation pressure are not to be relied upon, since

Table VI

Sample Calculation of Effective Film Thickness for Run 55, at t_u = 625

From	Data obtained
Fig. 3	$A = 18.45$ sq.cm.
Table V	$g = 44.65$ g. oil
Fig. 19, pressure change: 430 to 1025 mm.	
and Table II at 1025 mm.	$c_s = 89.66$ mg./cc.
" " " " 430 mm.	$Q = (43.39)(44.65)$ $= 1937$ mg.
Fig. 19, at $t_u = 625$	$q_t = 2100$ mg.
	therefore $Q + q_t = 4037$ mg.
" " "	$dq/dt = 2.334$
	therefore $dq/dt_u = 2.801$

Equation (9)

$$c_b = \frac{4037}{(.0019817)(4037) + (1.2134)(44.65)}$$

$$= 4037/61.96 = 65.17$$

Equation (6)

$$S \times 10^5 = - 89.66(.440 + .00485 \times 89.66) + 65.17(.440 + .00485 \times 65.17)$$

$$= - 29.26$$

(Value of S from the curves used in the calculations = - 29.35)

Equation (11)

$$l = \frac{- 29.26 \times 18.45}{2.801 \times 10^5} = -.001924 \text{ cm.}$$

the experimental accuracy is very poor at the beginning of a run and the slope is changing rapidly, and near the saturation pressure a very small experimental error may make a very large change in the slope. For these reasons no values of the film thickness are given in these regions.

Interpretation of the Results.

To assist in the interpretation of the calculated values of the film thickness, the values for each run were plotted against the concentration of the main body of the solution as shown in Figs. 35 - 38. In all these figures if the curve for a run does not cross the line at 790 mm. pressure the run was made between thatpressure and 430 or 1025 mm.; when the curve crosses this line it was made between the pressures of 430 and 1025 mm..

In Fig, 35 the arrows on each curve indicate the direction of the run (i.e., whether the gas was going into or out of solution; obviously the concentration decreases for "out" runs and increases for "in" runs) and the other different experimental conditions are indicated as shown. Examination of the figure suggests several interesting

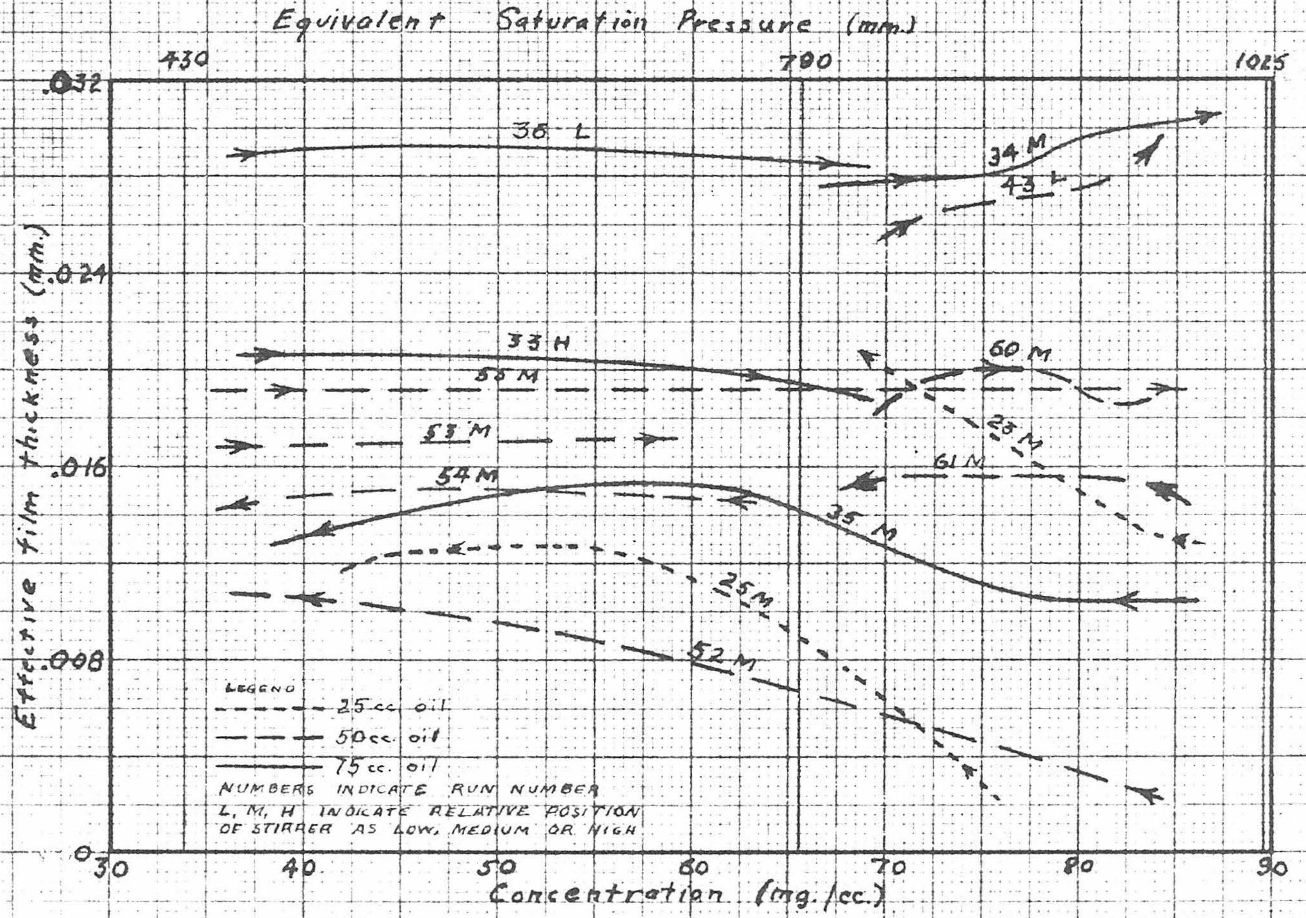

Fig. 35

CALCULATED EFFECTIVE FILM THICKNESS PLOTTED AGAINST THE CONCENTRATION OF MAIN BODY OF THE SOLUTION FOR THE STIRRED RUNS correlations, which tend to indicate the validity of the basic assumption. The fact that anywhere near constant values for the film thickness are obtained (especially the remarkably constant set for run 55, where the values from which the curve was drawn differ from the average by less than 1%) indicates that film thickness is not a function of the concentration, so that the observed rate could be attributed to the diffusion process through this constant thin film. An additional indication that the film thickness is solely a function of the configuration conditions is found in Runs 61 and54, which indicate that the film thickness is not a function of the concentration gradient across the film; for the later portion of 61 and the early portion of 54 are at nearly the same concentration, but the concentration gradients are very different.

The various differences of film thickness with differing configurations are explainable on the basis of hydrodynamic laminar layers. Thus, increasing the effective velocity of the main body of the liquid by raising the height of the stirrer in the solution decreases the film thickness as in Runs 36 and 33, and Runs 43 and 60. However, Runs 25 and 52, and Runs 23 and 61 do not exhibit the proper behavior in this regard.

The fact that the film thickness is always smaller in the "out" runs (where gas is being evolved) than in the "in" runs may be attributed to the additional convection set up both in the body of the solution and in the film as a result of the greater density of the solution at the surface than in the main body of the liquid. In the early portions of the runs, this difference could also be attributed to the formation of foam, which, increasing the effective area of surface (A in equation (5)) would make the value of the calculated film too small, possibly by a factor of several fold, or to convection set up by bubbles rising through the main body of the oil. However, it was noted that the foam and bubbles had usually disappeared long before the calculated film thickness begins to increase, and it is hardly possible that Runs 23 and 25 could be brought into agreement by these assumptions. If we are to consider that the additional convection due to the density difference is a factor as was suggested above, it can then be said that in Run 25, where the difference is much greater than in 23, a smaller film would be expected. But on this basis the later portion of 61, where the density difference is very small, and the early part of 54, where it is large, would be expected to differ, which they do not, and the only alternative is to say that convection due to density difference can only be appreciable when a small quantity of oil is present in these stirred runs. This explanation is further justified if Runs 53 and 54 are considered, since here, where 50 cc. of oil was used, the film thickness is very nearly the same, the convection existing in Run 54 being only enough to lower the film thickness slightly.

The situation in regard to the unstirred runs in which the stirrer was beneath the mercury is shown in Fig. 36, and of course all of these runs are for the evolution of gas. Runs 62 and 56 indicate roughly a lack of dependence on the concentration gradient, but 56 and 63 were made under exactly similiar conditions, and should agree closely. As mentioned before insufficient opportunity for observation of the cell itself during the course of a run makes it impossible to determine whether there was any difference in bubble or foam formation in these two runs. Disregarding

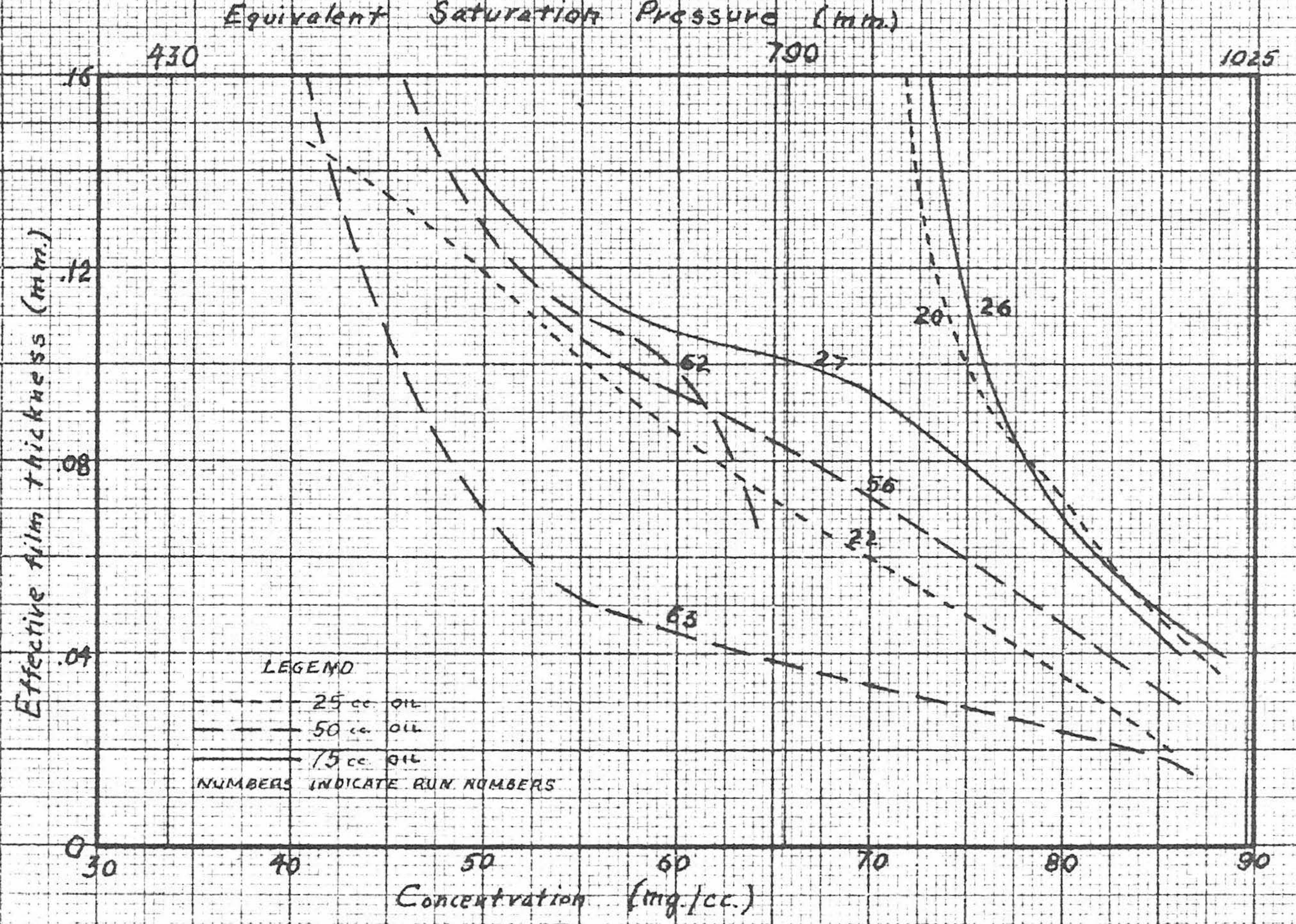

Fig. 36

CALCULATED EFFECTIVE FILM THICKNESS PLOTTED AGAINST THE CONCENTRATION OF THE MAIN BODY OF THE SOLUTION FOR THE RUNS WITH THE STIRRER BENEATH THE MERCURY

Run 63 a consideration of the convection currents in the solution suggests an explanation for the behavior between the different runs. In these runs the only stirring of the solution is by the convection currents, which may be due to bubbles of gas rising through the oil, or to the observed downward "streaming" of the denser liquid. Since bubbles were observed only in the early portions of the runs, convection due to them would rapidly disappear (though it might account for the initial low values of Run 62), but the gradual increase of the film thickness during the whole course of a run may be considered as naturally resulting from the decrease in convection due to the decrease of the density difference as the body of the solution becomes less concentrated. The increase in film thickness with increase in volume of oil as observed would be expected, since a large volume of oil would be less effectively stirred than a small volume by identical amounts of displaced liquid.

In Fig. 37 are four unstirred runs in which the stirrer was at the position in the oil indicated. In both cases the run with the larger volume of oil has a smaller film thickness; this might be explained

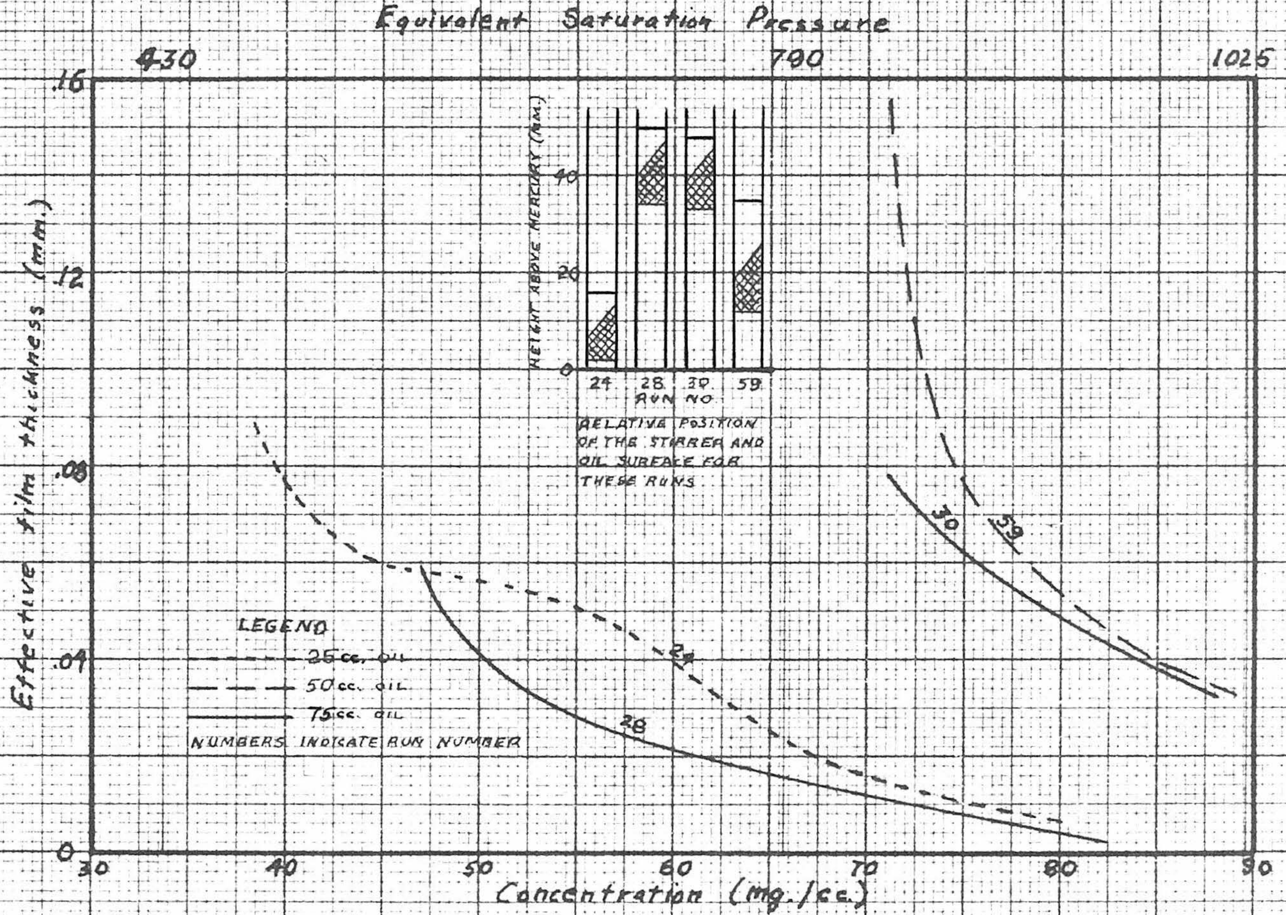

Fig. 37

CALCULATED EFFECTIVE FILM THICKNESS PLOTTED AGAINST THE CONCENTRATION OF THE MAIN BODY OF THE SOLUTION FOR THE RUNS WITH THE STIRRER IN THE OIL by a consideration of the stirrer heights, as in Runs 30 and 59. In 30 the stirrer is much closer to the surface, and it might then be expected that the convection currents set up by the density-difference considered previously would be deflected horizontally by the stirrer blades, resulting in a larger proportionate amount of stirring near the surface and consequently a smaller film thickness than in Run 59. However, it was noted that in Run 24 and Run 59 the bubbles always seemed to be forming on the surface of the oil, while in Run 28 and Run 30 the bubbles formed either on the stirrer or the mercury surface; in the latter case this would naturally result in additional convection and consequently lower the film thickness while bubbles were being formed in the early part of the runs. The fact that the initial film thicknesses are widely different for the two pressure drops is a consequence of either the larger quantity of foam which would be found in the runs with the large initial pressure drop (Runs 24 and 28) or more probably a greater convection throughout due to greater density difference. As was the case with the runs in Fig.36, the increase in film thickness throughout the course of these runs is to be attributed to the gradual decrease in convection as the density difference decreases.

In Fig. 38 the film thicknesses for the anomalous Runs 57,58 are shown. The sudden drop of film thickness in Run 57 at the point when vigorous evolution of gas began is clearly to be expected, but actually it was observed that only 1/8 of the surface of the oil was still covered with foam at the time when the concentration was about 60 mg./cc., yet the film thickness does not increase correspondingly until much later, again leading to the possibility suggested earlier that foam formation itself does not appreciably affect the film, and that the sole factor is the turbulence of the main body of liquid.

Summary

A study of the rates of absorption and desopption of butane in crystal oil has indicated considerable evidence for assuming that the rate limiting process is solely the diffusion of gas through a thin layer of solution at the surface of the oil which is affected only by the velocity of the adjacent liquid. Some details might be better established if further

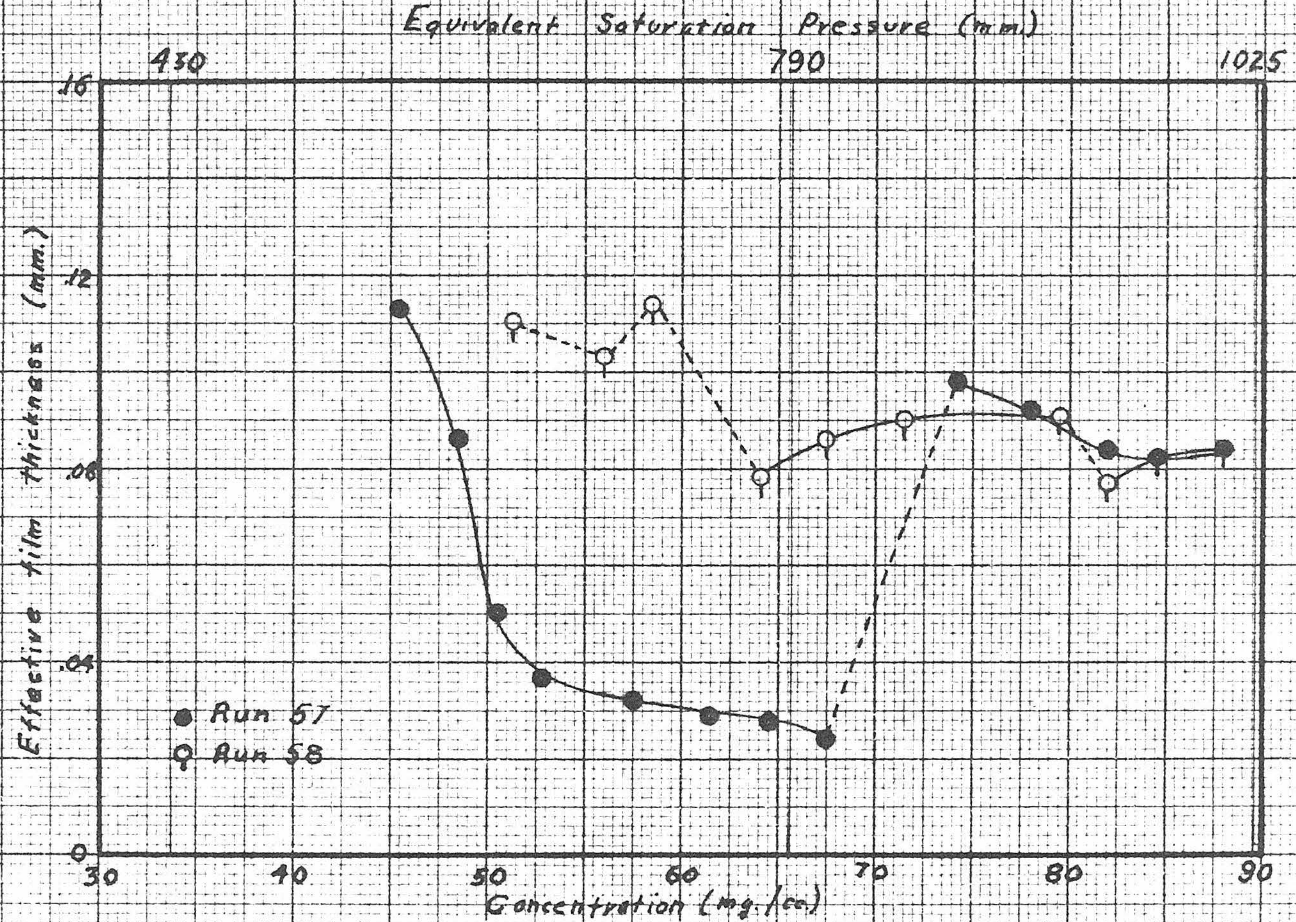

Fig. 38

CALCULATED EFFECTIVE FILM THICKNESS PLOTTED AGAINST THE CONCENTRATION OF THE MAIN BODY OF THE SOLUTION FOR RUNS 57 AND 58 experiments of this type were desirable, but tentatively it appears that the thickness of the layer required by the observed rates is not affected by the concentration of the solution of the concentration gradient across it, and further it is affected only as would be predicted for the laminar layer known to exist at the boundaries of moving fluids.

PART II

The Measurement of the Diffusion Constants.

The method of measuring the diffusion constants by the procedure used by Pomeroy,[5,6] which was briefly described in Part I, has been used by other investigators[7,8,9,10] in this laboratory. In their treatment the assumption is made that the diffusion constant as defined by the Fick equation was not a function of the concentration of the solution, and, neglecting any changes in volume, there results the differential equation

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad (13)$$

which is solved for the boundary conditions

$$\begin{aligned} c &= o, \quad x > o, \quad t = o \\ c &= c_s, \quad x = o, \quad t > o \end{aligned} \qquad (14)$$

where c_s is the concentration corresponding to the

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[6] Pomeroy, Ph.D. Thesis, California Institute, 1931. Both Mc Bain, Zeit. phys. Chem., 68, 471 (1909) and Friedman and Kraemer, J.A.C.S., 52, 1298 (1930) made treatments similar to that of Pomeroy.

[7] Hill, Ph.D. Thesis, California Institute, 1934.

[8] Hill and Lacey, Ind. Eng. Chem., 26, 1324 (1934).

[9] Hill and Lacey, ibid., 26, 1327, (1934).

[10] Bertram and Lacey, ibid., 28, 316, (1936).

saturation pressure maintained above the oil. By making a change of variable,

$$z = \frac{x}{2\sqrt{Dt}} \tag{15}$$

The equation and boundary conditions may be transformed and the solution written

$$c = c_s\left(1 - \frac{2}{\sqrt{\pi}}\int_o^z e^{-\lambda^2}\,d\lambda\right) \tag{16}$$

This solution is then differentiated, and since

$$\frac{dc}{dx} = \frac{dc}{dz}\cdot\frac{dz}{dx} = \frac{1}{2\sqrt{Dt}}\cdot\frac{dz}{dx} \tag{17}$$

$$\left(\frac{dc}{dx}\right)_o = \frac{1}{2\sqrt{Dt}}\left(\frac{dz}{dx}\right)_o = \frac{-2c_s}{2\sqrt{\pi Dt}} \tag{18}$$

and substituting in the Fick equation (4) (but considering D a constant, of course) we obtain

$$\left(\frac{dq}{dt}\right)_o = \frac{A\ c_s\sqrt{D}}{\sqrt{\pi t}}\ , \tag{19}$$

an expression for the rate at which gas crosses the surface. Integrating from t = o to t = t we obtain

$$Q = \frac{2\ A\ c_s\sqrt{D}}{\sqrt{\pi}}\sqrt{t} \tag{20}$$

where Q is the total quantity of gas that has dissolved since the beginning of the process, and this is the equation that was used in the references cited. If the initial conditions had been

$$\begin{aligned} c &= c_o, & x &> o, & t &= o \\ c &= c_s, & x &= o, & t &> o \end{aligned} \tag{21}$$

where c_o is the initial concentration of the solution, the various equations could easily be transformed by putting

$$\begin{aligned} c' &= c - c_o \\ c_s' &= c_s - c_o \end{aligned} \tag{22}$$

and equation (13) conditions (14) would be obtained with c' and c_s' instead of c and c_s. (20) would then be obtained as

$$Q = \frac{2\ A(c_s - c_o)\sqrt{D}}{\sqrt{\pi}}\sqrt{t} \tag{23}$$

which was also used when the oil is initially at concentration c_o and is transformed to equation (2) merely by writing m for the slope $dQ/d\sqrt{t}$.

The Effect of Concentration on the Diffusion Constant.

Although the variation of the diffusion constant with concentration was not appreciable for many of the systems previously studied using this method, Hill[9] showed a threefold change of the value of D for the systems propane-kerosene and propane-spray oil as calculated from the simple solution of (13), and he did not discuss any alternatives. If the diffusion constant is a function of the concentration, equation (13) should be written

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial c}{\partial x}\right) \tag{24}$$

as may be found in textbooks. No general solution of this type of equation is known, but similar equations have been extensively treated for specific problems in various ways. Hidaka[11] has carried the solution of the equation occuring in heat transfer problems

$$c_o\rho_o(1 + \beta\theta)\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x}\left(k_o(1 + \alpha\theta)\frac{\partial \theta}{\partial x}\right) \tag{25}$$

with the boundary conditions

$$\theta = 0, \quad x > 0, \quad t = 0,$$
$$\theta = \Theta, \quad x = 0, \quad t > 0,$$

and where α and β are small constants, to a third approximation. After putting $z = \frac{x}{2}\sqrt{\frac{c_o\rho_o}{k_o t}}$ he assumed a solution of the form,

$$\begin{aligned}\theta = \Theta\,\big[1 - \Phi(z) &+ \alpha\Theta\Psi_1(z) + \beta\Theta\Psi_2(z) + \alpha^2\Theta^2\chi_1(z) \\ &+ \alpha\beta\Theta^2\chi_2(z) + \beta^2\Theta^2\chi_3(z) + \cdots\big]\end{aligned} \tag{26}$$

and found the values of the functions Φ, Ψ, χ which appear.

If we transform (25) to the form of (24) we have

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[k_o(1 + \alpha c)\frac{\partial c}{\partial x}\right] \tag{27}$$

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[11] Hidaka, <u>Geophysical Magazine,</u> Tokio, <u>5,</u> 361 (1932).

and we are representing D by a linear function of the concentration, $D = k_o(1 + \alpha c)$. This may not be even a rough approximation for all diffusion processes, since in the case of electrolytes diffusing in water, and for various organic liquids diffusing among themselves and in water, the variation is by no means linear. However, in the case of such non-polar substances as hydrocarbons the approximation may be fairly close. In addition the constant α must be small if the solution by successive approximations is to be valid, and the rough approximation of (3) indicates this condition will be moderately well satisfied.

Transforming (26) to correspond to the form of (27) and its boundary conditions we obtain

$$c = c_s\left[1 - \Phi(z) + \alpha c_s \Psi_1(z) + \alpha^2 c_s^2 \chi_1(z)\right] \qquad (28)$$

where $z = x/2\sqrt{k_o t}$ and which we may now treat in exactly the same manner as in (16)-(20). Then

$$\left(\frac{dc}{dx}\right)_o = \frac{1}{2\sqrt{k_o t}}\, c_s\left[-\left(\frac{d\Phi}{dz}\right)_o + \alpha c_s\left(\frac{d\Psi_1}{dz}\right)_o + \alpha^2 c_s^2\left(\frac{d\chi_1}{dz}\right)_o\right] \qquad (29)$$

And from Hidaka's paper we find:

$$\Phi(z) = \frac{2}{\sqrt{\pi}}\int_0^z e^{-\lambda^2}\, d\lambda \qquad (30)$$

$$\Psi_1(z) = \left[\frac{ze^{-z^2}}{\sqrt{\pi}} + \frac{1}{\pi} + \frac{1}{2}\Phi(z)\right]\left[1 - \Phi(z)\right] - \frac{e^{-2z^2}}{\pi} \qquad (31)$$

$$
\begin{aligned}
\text{and } \chi_1(z) = &- \left[1 - \Phi(z)\right] \Psi_1(z) + 2\int_0^z \lambda\left[1 - \Phi(\lambda)\right] \Psi_1(\lambda)\,d\lambda \\
&-2\int_0^z e^{-\lambda^2} d\lambda \int_0^\lambda e^{s^2}\left[1 - \Phi(s)\right] \Psi_1(s)\,ds \\
&-4\int_0^z e^{-\lambda^2} d\lambda \int_0^\lambda s^2 e^{s^2}\left[1 - \Phi(s)\right] \Psi_1(s)\,ds \\
&-\Big[2\int_0^\infty \lambda\left[1 - \Phi(\lambda)\right] \Psi_1(\lambda)\,d\lambda \qquad\qquad (32) \\
&-2\int_0^\infty e^{-\lambda^2} d\lambda \int_0^\lambda e^{s^2}\left[1 - \Phi(s)\right] \Psi_1(s)\,ds \\
&-4\int_0^\infty e^{-\lambda^2} d\lambda \int_0^\lambda s^2 e^{s^2}\left[1 - \Phi(s)\right] \Psi_1(s)\,ds\Big]
\end{aligned}
$$

The differentiation of (30) and (31) is obvious, giving

$$\left(\frac{d\Phi}{dz}\right)_0 = \frac{2}{\sqrt{\pi}} \quad \text{and} \quad \left(\frac{d\Psi_1}{dz}\right)_0 = \frac{2\pi - 2}{\pi\sqrt{\pi}} \qquad (33)$$

but it appears that (32) as it is given here from Hidaka's paper contains at least one typographical error, in that $\Phi(z)$ should appear outside the last group of terms in the square bracket. To avoid the arduous labor of carrying out the evaluation of the integrals which is necessary if this is so, as well as to save the trouble of completely checking the full solution, a graphical differentiation was used. Hidaka gives numerical values for all of the functions in his solution for values of $0 < z < 3.0$, which he determined using Simpson's rule, and by plotting the values of χ_1 against z and determining the slope it was found that

$$\left(\frac{d\chi_1}{dz}\right)_0 = -0.59 \pm 0.02 \qquad (34)$$

For convenience -0.59 was written as $\frac{3-2\pi}{\pi\sqrt{\pi}}$, which value is within the limits of error of the determination of the slope, and then putting (33) and (34) in (29) we obtain

$$\left(\frac{dc}{dx}\right)_o = \frac{c_s}{2\sqrt{k_o t}}\left[\frac{-2\pi + 2\alpha c_s(\pi - 1) + \alpha^2 c_s^2(3-2\pi)}{\pi\sqrt{\pi}}\right] \quad (37)$$

which of course reduces to the form (18) when $\alpha = 0$. Proceeding as before we now substitute in the Fick defining equation, which should now be written

$$\left(\frac{dq}{dt}\right)_o = -Ak_o(1 + \alpha c_s)\left(\frac{\partial c}{\partial x}\right)_o \quad (38)$$

the value of c_s appearing since this is the value of c at the point x = 0, and we obtain after integration from t = 0 to t = t,

$$Q = \frac{2c_s A\sqrt{k_o}(1 + \alpha c_s)\left[\pi - \alpha c_s(\pi - 1) - \alpha^2 c_s^2(3/2 - \pi)\right]}{\pi\sqrt{\pi}}\sqrt{t}$$

and finally

$$\frac{dQ}{d\sqrt{t}} = \frac{2c_s A\sqrt{k_o}}{\sqrt{\pi}}\left[1 - \alpha c_s(1 - 1/\pi) + \alpha^2 c_s^2(1 - 3/2\pi)\right]\left[1 + \alpha c_s\right] \quad (40)$$

This is similiar to the equation used previously, and $dQ/d\sqrt{t}$ is the m in equation (2) if $c_o = 0$, so the diffusion constant may be readily calculated.

If the initial conditions are as in (21), a transformation similiar to the one indicated there may be made, or:

$$c' = c - c_o, \qquad c_s' = c_s - c_o ,$$
$$k_o' = k_o(1 + \alpha c_o) \qquad \alpha' = \alpha/(1 + \alpha c_o) \tag{41}$$

to transform to the form of (27) with primes throughout, but the reduction of (40) then leads to a complicated form.

Application of the New Solution

Since the simplest form (40) is applicable to the case where the initial concentration of the solution is zero, and since only four runs had been made in determining the diffusion constant for the system studied in Part I, an immediate application of this solution to Hill's data for propane in kerosene was made. His data for zero initial concentration was of course calculated from the equation

$$D = \frac{\pi m^2}{4A^2 c_s^2} \qquad \text{or} \qquad m = \frac{2Ac_s\sqrt{D}}{\sqrt{\pi}}$$

and writing (40) in equivalent form, with numerical values for some of the expressions involving π we have

$$k_o = \frac{\pi \quad m^2}{4A^2 c_s^2 \ (1-.6817\alpha c_s + .5225\alpha^2 c_s)^2 (1+\alpha c_s)^2}$$

It takes, of course, two measurements of the diffusion constant at different saturation concentrations to determine both α and k_o experimentally, but instead of using the values of m, A, etc., found by Hill it is more convenient to use his final values of D and write for (42) (replacing c_s by s and α by x for convenience in writing)

$$k_o = \frac{D_i}{(1+.3183xs_i-.1592x^2s_i^2+.5225x^3s_i^3)^2} \tag{43}$$

which should hold for each value of D and s (s = his 6_s) which he determined. From Table II of Hill's paper[9] five different values of s and D for his measurements on the propane-kerosene system at 86° F. have been selected, and these values, together with some of the coefficients in equation (43) are presented in Table VII. There is some sort of discrepancy in the data he has presented, since he gives more than one value of C_s, the saturation concentration, corresponding to the same saturation pressure; in these cases the values were averaged.

We may now take the runs which we have numbered 1 and 5 and substitute in (43)

$$\frac{\sqrt{D_5}}{\sqrt{D_1}} = \frac{1+39.35x-2408.5x^2+.9723\times10^{-6}x^3}{1+8.00x-100.9x^2-.826\times10^{-4}x^3} = \pm1.5314$$

which reduces to the equations:

$$x^3-2.3325x^2+28.036x-549.767=0 \tag{45}$$

and

$$x^3-2.5996x^2+52.03x+2552.6=0 \tag{46}$$

Table VII

Averaged Data from Hill[9] Table II

Run	s	$.3183s$	$.1592s^2$	$.5225s^3$ $\times 10^4$	$D\times 10^5$	$D\times 10^{2.5}$
1	25.1	8.00	100.9	.826	1.68	1.2961
2	26.9	8.56	115.2	1.017	1.84	1.3569
3	40.7	12.96	259.0	3.523	2.25	1.5000
4	58.0	18.48	535.5	10.194	2.60	1.6125
5	123.0	39.35	2408.5	97.230	3.94	1.9849

Inspection discloses that for $x \rightarrow -1$ $k_0 \rightarrow \infty$, so we omit any values of x which are negative. (46) has two imaginary and one negative root and is consequently discarded. (45) has two imaginary and one real root $x = +.007791$, which is the value of α, from which k_0 is found to be 1.495, giving

$$\text{True Diffusion Constant} = 1.495(1 + .007791\, c) \qquad (47)$$

To see how well this corresponds to the experimental measurement, these values of k_0 and α were used to calculate a value of D for the remaining three measure-selected, to obtain the values in Table VIII.

Table VIII

Run	$D_{obs.}$	$D_{calc.}$	Difference
2	1.84	1.69	8.1%
3	2.25	1.81	19.5%
4	2.60	2.01	22.7%

It is now obvious that the treatment is not wholly applicable. While the discrepancy is large, it must be noted that these values of $D_{calc.}$ are very sensitive to slight changes of α; thus if α = .00778 the value of $D_{calc.}$ for Run 4 changes by 10%, while the values for Runs 1 and 5 differ from the values used to determine α by only 1%.

The Effect of Change of Volume.

It is possible that these discrepancies may be completely resolved, and by introducing the effect of the volume change of solution into the differential equation in some manner the method of determining the diffusion constant by this method may be made more exact. Unfortunately there has not been time to carry the analysis of this problem further, but it may be pointed out here that in a simple treatment where the velocity of expansion of the liquid solution is denoted by u, which is considered as a function of c alone, the differential equation (24) takes the form

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D - u\ f'(u)\ \frac{\partial c}{\partial x}\right) \qquad (48)$$

and consequently the value of k_o and α as calculated above have also to some extent adjusted for this effect.

A rough attempt to include the volume change effect in the differential equation was made in which it was assumed that within a particular fixed volume of solution each component was diffusing through the other, and obtaining (24) for each component:

$$\frac{\partial n_1}{\partial t} = \frac{\partial}{\partial x}\left(D_1 \frac{\partial n_1}{\partial x}\right) \quad \text{and} \quad \frac{\partial n_2}{\partial t} = \frac{\partial}{\partial x}\left(D_2 \frac{\partial n_2}{\partial x}\right) \tag{49}$$

where the concentration of the two components are are expressed in terms of mols/cc., and the two diffusion constants D_1 and D_2 are for the diffusion of component 1 through 2, and 2 through 1, respectively. Within any fixed volume of solution a relation may be obtained between the quantities of components 1 and 2 which must be present from the volume change of the solution, and in the case of propane in kerosene the relation was given quite closely by

$$n_2 = .00471 - .3044 n_1 - 20.33 n_1^2. \tag{50}$$

If the two equations (49) are subtracted from each other, and equation (50) differentiated with respect to x and t, $\frac{\partial n_2}{\partial x}$ and $\frac{\partial n_2}{\partial t}$ may be replaced by values from (50) and there is obtained the equation

$$(1-A)\left[1-\frac{B}{(1-A)}n_1\right]\frac{\partial n_1}{\partial t} = \frac{\partial}{\partial x}\left\{(D_1-D_2A)\left[1-\frac{{}_1D_2B}{D_1-D_2A}\right]\frac{\partial m_1}{\partial x}\right\} \tag{51}$$

where $A = -.3044$ and $B = -40.66$. This is similar to the equation solved by Hidaka, with β having a known value, and the complete approximation with β may be used. The complete treatment was carried out as above, and the discrepancy between the $D_{obs.}$ and $D_{calc.}$ reduced slightly to 7.6%, 15%, and 16% for the three runs 2, 3, and 4, but it is doubtful if this simple approach is justifiable. At present it appears that some analysis following that of Hill[7] would be the most fruitful in obtaining a form for the differential equation similiar to that treated by Hidaka and in which the constant β is known from the volume change of the solution, but the lack of time has prevented any further treatment of this phase of the problem.

Summary

The correct form of the diffusion equation where the diffusion constant is a linear function of the concentration has been applied to the work of other investigators, and it has been shown that the proper mathematical treatment in this case may be readily utilized in determining a much better value of the true diffusion constant by the method in which the rate at which gas is dissolved in a quiescent liquid is determined. It is suggested that the differential equation wich was used in this treatment may also be used to include consideration of the effect of the volume change of solution.

Acknowledgements

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