

The Rate of Solution of Methane in a Hydrocarbon
Oil Held in the Pores of Sand

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Introduction

The problem of repressuring oil formations with natural gas is an important one to the petroleum industry, for repressuring prolongs the life of wells, reduces the number of wells required, decreases the cost of pumping, and provides a cheap method of storing natural gas. The importance of repressuring of oil formations has prompted the investigation of the rates of solution of natural gas in petroleum oils, and this investigation was begun as a part of the American Petroleum Institute Research Project # 37 in 1927. It has been found desirable to study the rates of solution of the pure constituents of natural gas, rather than to investigate the more complex rate of the natural gas itself, and numerous data have been gathered on the rates of solution of methane, ethane, and propane in various crude oils and pure hydrocarbons by previous investigators working on this project.

Pomeroy and his co-workers (1,2) have shown that the Fick proposition is valid, with certain limiting assumptions, for the diffusion of methane in liquid hydrocarbons. The proposition may be written as follows:

$$\frac{dq}{dt} = -DA \frac{dc}{dx}$$

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

A = area at right angles to the direction of flow.

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where C = concentration.

x = distance in direction of flow.

t = time.

D = diffusion constant.

On integrating the proposition for the case of a liquid column of infinite length, an equation was obtained from which the diffusion constant of the rate of solution of methane in hydrocarbons could be calculated. The equation is:

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

where C_s = final equilibrium concentration of gas in solution.

The limiting assumptions made in obtaining this equation are (a) the diffusion constant does not change with changing concentration of solution; (b) the layer of liquid immediately under the surface is always saturated; that is, that a surface film does not retard the passage of gas into the liquid; (c) the gas moves through the liquid by diffusion only. It was found by Pomeroy and his co-workers that these assumptions are valid for the rate of solution of methane up to partial pressure of 300 lbs./sq. in., and Hill (3,4) found that there was only a small increase in the diffusion constant for the rate of solution of methane in kerosene at a pressure of 2000 lbs./sq. in. Thus it can be seen that the above equation can be used for calculating the diffusion constant in any case where the gas has not reached the bottom of the cylinder, and this is the condition under which all of the runs in the studies discussed in this paper were made.

These previous investigations have dealt with the rate of solution of hydrocarbon gases in liquid alone, but since nearly all petroleum oil is found in sand formations it is desirable to know the effect of the presence of sand on the rate of solution of natural gas in the oil. Some preliminary work on the subject was done by R.D. Pomeroy and E.S. Hill, but no data or results have been published. As in the past investigations on the rate of solution, it was decided that it would be better to work with one pure constituent of natural gas than with the natural gas itself, so methane was chosen for these studies. Also it was deemed better to use one liquid throughout the series, and kerosene was used for reasons which will be discussed later.

It was considered desirable to compare the effects of the presence of sand on the rate of solution of methane in kerosene, to the effect of sand on some other flow process. Langmuir (5) used electrical conductivity experiments to determine the effect of the shape of a body on the transfer of heat, and was able to calculate shape factors which are very useful. It was thought that the conductivity of electricity might be affected by the presence of sand in a similar manner to the effect of sand on the rate of solution of hydrocarbons, and determinations were made on the conductivity of electricity through a CuSO_4 solution with and without sand being present.

Materials

The methane used in these studies was prepared from natural gas. Crude methane was first obtained by removing the ethane and higher hydrocarbons. This was done by throttling compressed ^{gas}, which, due to the Joule-Thomson effect, resulted in a temperature low enough to liquify ethane and the heavier constituents which were caught in a trap and drawn off. The crude methane was then subjected to further compression and throttling until the temperature became low enough to liquify methane, thus separating it from nitrogen. The liquid methane was caught in the trap, from which it was bled into a heated coil and vaporized. This methane vapor was passed through activated charcoal to remove any ethane which remained, and was further purified by passing it at low pressure through a trap that was submerged in liquid air. Solid methane was frozen out, while any remaining nitrogen passed on as a vapor. An analysis of the methane obtained by this method showed it to contain only .01% ethane, and less than .25% nitrogen.

The kerosene which was used in all of the runs was the same as was used by Hill (3), and was purchased from the Shell Oil Company three years earlier.

The (20-30) mesh sand which was used was Ottawa Standard Sand. The (30-40), (40-50), and (50-70) mesh sands were obtained from molding sands which were mined in Nevada. The (100-140) mesh sand was a sand used in the manufacture of glass, and also came from a mine in Nevada. All of these

sands were silica sands, and had densities which were within 1.0% of each other.

Technical copper sulfate was used in making up the solutions which were used in the conductivity runs.

Apparatus and Methods

The apparatus and method of conducting the methane diffusion runs was practically the same as described by Hill (3,4), with the exception that sand was packed with the kerosene in these determinations. Kerosene was chosen for these studies, because methane has a fairly high rate of solution in kerosene with only a small increase in volume of liquid, and also kerosene has a fairly low vapor pressure at 30°C., the temperature at which all runs were made.

The density of the kerosene was determined by weighing the oil in a calibrated pycnometer. The density of the sands was determined by placing a known weight of sand in a weighted calibrated volumetric flask, and then filling the flask with water and weighing again. The volume of water could be calculated since its weight and temperature are known, and hence the volume and density of the sand could be readily determined.

Several methods of packing the sand and oil in the diffusion cell (Fig. 1) were tried, but the one which gave the best experimental results, and the most dependable porosity percentages was as follows. Ten or fifteen cc. of kerosene was placed in the cell, and enough sand was added

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to take up almost all of the kerosene in its void spaces. The oil was then swirled around to get rid of any trapped air, and then the cell was vigorously tapped on a heavy wooden block for several minutes. The rest of the kerosene and sand was packed in a similar manner by adding about five or ten cc. of kerosene each time. When all of the sand had been packed by this method, a level surface was obtained by placing the cell in its wooden vise, which was perfectly level, and then tapping the bottom of the cell with a hammer.

The porosity or percentage of void spaces between the sand particles was determined for each type of sand by taking the mean value of several determinations which were made as follows. After a known weight of sand was packed with kerosene, a steel slug, whose diameter was slightly less than that of the cell, was placed on top of the sand in the cell. The length of the slug which was protruding from the cell was measured by the use of a cathetometer, and in each case readings were taken at several points around the cell. From the height of sand thus obtained, the volume of the sand plus the void space between particles could be calculated; and knowing the volume of the sand, the porosity could readily be determined. Values which were never more than 1.5% apart were obtained, thus giving an average value which was within .75% of the actual porosity, an accuracy that was more satisfactory than could be obtained by other methods which were tried.

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Since it was impossible to avoid trapping a small amount of air in packing the sand and kerosene, two or three cc. of kerosene were added to keep the oil level from dropping below the sand level when the pressure was increased to 20 atmospheres, thus causing the volume of trapped air to shrink nearly twenty fold. The actual amount of air which was trapped was known to be somewhat less than the oil which was added to take up its shrinkage on compression, but it was found that better experimental results were obtained when the oil was carried slightly above the sand level than when carried below it. This difference was probably due to capillary action of the oil in the case of the lower level, thus giving a larger exposed surface area which resulted in an exceedingly high rate of solution for the first few minutes of the run. On the other hand, in carrying the liquid level above the sand a higher rate would result until the methane had reached the sand level, but it was estimated that the methane would reach the sand within a minute or two, and from then on the rate of solution would be related to the rate of diffusion through the oil-filled pores in the sand body.

The diffusion cell packed with kerosene and sand was placed in the weighted, triangular support mounted on rubber stoppers. This support can be seen in Figure 4, and its purpose was to hold the cell in a level position and eliminate outside vibrations. The cell was then connected to the pressure gauge and the methane reservoir gauge by a

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flexible copper coil. The methane reservoir gauge had a finely divided scale which allowed very accurate measurements of the outgoing methane to be made. This gauge was calibrated against a burette (Fig.5) which had two bulbs, 5 cc. and 25 cc. respectively, so that any irregular portion of the reservoir calibration could be followed more closely. Readings were taken at constant pressure, and thus it was unnecessary to make corrections for the line connecting the burette to the reservoir. Slides with fine wire indicators were placed on the meter stick between the burette and its manometer, and thus readings to 0.1 mm. could be made. Successive calibrations of the reservoir showed little or no variations.

The pressure gauge was calibrated against a Crosby fluid pressure scale before each run. These gauges were read with a cathetometer telescope whose end was held flat against the glass window of the thermostatically controlled air bath (Fig. 6) which enclosed the apparatus. A slightly different method of taking readings was used than was followed by Hill (3,4). Instead of allowing the pressure gauge to drop from 2 lb./sq. in. above the run pressure to 2 lb./sq. in. below the run pressure, the author found it more desirable to allow the gauge to drop from one graduated mark to the next graduated mark on the scale, which were 5 lb./sq. in. apart; and assuming the average pressure to be the pressure of the run. On admitting methane to bring the

pressure up to the higher value, the mark was slightly passed each time; and the reading was taken when the pointer passed the mark going down. This was done because it was found that there was a slight increase in pressure due to the heat effect of compression, and it took a few minutes for the gas to reach its original temperature. The amount of methane which was required each time to bring the pressure up to its original value was taken as the amount which had gone into solution, correction being made for the change in volume of the liquid.

The diffusion cell was not evacuated during these runs, because it was found that it caused buckling and cracking of the sand packing, which was probably due to the expansion of trapped air. This cracking of the sand packing caused channeling of the methane, which resulted in an apparent rate of solution that was much greater than if there were no sand present, and the kerosene became nearly saturated in 10 or 12 hours. Since the cell was not evacuated, it was necessary to make corrections to obtain the partial pressure of methane.

Although the time of all the readings was referred to the time when the methane was first admitted to the cell to bring the pressure up to run pressure, reservoir gauge readings were not taken till somewhat later because of the following reasons. The heat effect of compression would introduce a large error in any early readings. Since there was a small amount of kerosene above the level of the sand,

the rate of solution would be high until this layer became saturated. The absorption of methane by kerosene on the side walls of the cell due to capillary action would also invalidate any early readings.

A few runs were also made to determine the absolute diffusion constant of methane in kerosene without sand packing, and to determine the value of the saturation concentration (C_s). These runs were conducted in a similar manner to the method followed by Hill (3,4) in working with the same materials. A known weight of kerosene was placed in the diffusion cell which was connected to the rest of the diffusion apparatus and the system was brought up to run temperature (30°C). Methane was then admitted to the cell from the reservoir gauge so as to bring the partial pressure of methane up to $2\frac{1}{2}$ lbs./sq. in. above the run pressure. When the pressure had fallen to $2\frac{1}{2}$ lbs./sq. in. below the run pressure, methane was admitted until the pressure was slightly above the original pressure, and the time reading was taken when the pressure had fallen to the original pressure. When enough readings had been taken to assure suitable accuracy for the determination of the diffusion constant, the cell was placed in a shaker which could be operated from the outside of the air bath, and methane was added until the kerosene became saturated at run pressure.

The cell used in the electrical conductivity runs (Fig. 2) consisted of a 2 inch glass cylinder which was

cemented into a groove in the copper base, and a piston-like copper disc and rod. The copper base and piston served as electrodes for the alternating current which was passed through the CuSO_4 solution. The base was supported on a wooden shelf and the piston was held in place by an insulated clamp. An A.C. galvanometer and a Wheatstone Bridge were used to measure the resistance of the solution between the electrodes. A transformer was used to reduce the voltage to 6 volts. The distance between the electrodes was measured by the use of a cathetometer, with readings taken at several points around the cell. Figure 7 shows the apparatus set up for a run.

The method of packing the sand in the cell was as follows. The cell was about half-filled with CuSO_4 solution, and a small portion of the sand was added. The solution was swirled around, and then the cell was placed on its wooden holder. The wooden holder was then tapped with a hammer for several minutes, which caused the cell to jiggle up and down. This was repeated until all of the sand had been added, and then the piston was placed in the cell and was held tightly against the sand while further tapping smoothed the surface of the sand.

After the sand had been packed, the distance between the electrodes was measured, and then the resistance of the solution between the electrodes was determined. The specific conductivity of the solution with no sand present was determined by measuring the resistance of the solution with the electrodes at various distances apart.

Experimental Results

The diffusion constant and the final equilibrium concentration of methane in kerosene were determined, the results being practically the same as those obtained by Hill (3,4) on the same kerosene. In calculating these constants, the values of ϵ (increase in volume of liquid per cc. of gas dissolved), and the percentage change in volume of liquid at saturation, which were determined by Hill were used.

Numerous diffusion runs in the presence of sand were made before the methods and technique used became accurate enough to give reproducible results, but duplicate runs were made on each of the five sands of different particle size, and gave results within 1% of each other.

The quantity of gas which had gone into solution at a given time was plotted against the square root of the time, and such a plot for one run for each sand is shown in Figure 3, in which the curves were extrapolated to zero time. The points of these runs fall in nearly straight lines, and their slopes are used in the calculations as has been done by the past experimenters in this work. There is a slight downward bend in most of the curves, and this is probably due to the fact that the liquid is carried slightly above the level of the sand. Since it takes a minute or two for the methane to reach the level of the sand, it can be seen that the time used as the starting time is slightly in error; but because the actual time at which the advancing methane reaches the

level of the sand cannot be determined, the slight difference was neglected. It was calculated that the error introduced by this difference in time was less than .25% and is therefore almost negligible. This slight bend might also be explained by the fact that the sand is probably packed a little closer at the bottom of the cell than it is at the top, and thus the rate would be slightly faster when the foremost gas molecules were penetrating the upper layer of oil.

From the data obtained, a factor for determining an effective area of the liquid for the calculation of the rate of solution of the methane was determined for each run, and the results are shown in Table 1. The values found were practically the same for each run, with the values for the runs in which coarser sand was packed in the oil being slightly larger. This can probably be explained by the fact that the effect of the walls and the upper surface is greater for the larger sand particles. The slight difference in the values for this factor are well within experimental accuracy, and since the range of the particlesizes and of the percentage of void spaces between particles are each almost wide enough to include any condition which may be met in the field, it is the author's opinion that this value is a constant, and that it may be used in the calculation of the rate of solution of natural gases in various oils. Although the values for the constant which were obtained for the cases where the fine sand was used are probably nearest to being correct, an

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average value can be used without introducing any great error because all of the values were within 3% of each other.

The calculation of these constants was made in the following manner.

Run # 32 --- Kerosene packed with (100-140) mesh sand.

Temperature of run = 30 C.

Absolute pressure in cell = 314.3 lbs per sq. in.

Partial pressure of $\text{CH}_4 = 299.5$ lbs. per sq. in.

Percentage of void spaces = $V = 37.28\%$

Diffusion constant of methane into kerosene = $D = 3.30 \times 10^{-5}$.

Equilibrium concentration of methane in kerosene = $C_s = 10.33$ cc./cc.

Horizontal area of cell $A = 31.467$ sq. cm.

Uncorrected slope of curve $(Q/\sqrt{t}) = m'' = 4.74$

Correcting to 300 lbs. per sq. in.

$$m' = 4.74 \times 300/299.5 = 4.748$$

Correcting for expansion of liquid.

$Q =$ cc. of methane dissolved.

$Q' =$ cc. of methane admitted to cell.

$\epsilon =$ increase in volume of oil per cc. of methane dissolved.

$p =$ total pressure in atmospheres.

$f = .968$ compressibility factor of methane at 300 lbs. per sq. in.

$Q\epsilon =$ increase in volume of oil.

$\frac{Q\epsilon p}{f} =$ volume of gas displaced by liquid (at 1 atm. and 30°C)

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$$Q' = Q - \frac{Q \epsilon p}{f} = Q \left(1 - \frac{\epsilon p}{f}\right)$$

$$Q = Q' \times \frac{1}{\left(1 - \frac{\epsilon p}{f}\right)}$$

and since $m = \frac{Q}{\sqrt{t}}$ and $m' = \frac{Q'}{\sqrt{t}}$ where t is in minutes

$$\text{therefore } m = m' \times \frac{1}{\left(1 - \frac{\epsilon p}{f}\right)}$$

$$= 4.748 \times \left[\frac{1}{1 - \left(.002 \times \frac{314.3}{14.7} \times \frac{1}{.968} \right)} \right] = 4.96$$

The effective area of liquid A' = AVB

where B = constant.

substituting A' for A in the general equation

$$Q = 2C_s A' \sqrt{\frac{Dt}{\pi}} = 2C_s (AVB) \sqrt{\frac{Dt}{\pi}}$$

substituting m for Q/\sqrt{t} , changing units to seconds, and expanding.

$$B = \frac{m \times \sqrt{\pi}}{2AVC_s \sqrt{60} \times \sqrt{3.30 \times 10^{-5}}} = \frac{4.96 \times 1.772}{2 \times 31.467 \times .3728 \times 10.33 \times 7.75 \times 5.735 \times 10^{-3}}$$

$$B = .819$$

The electrical conductivity runs gave results which showed that it was affected by the presence of sand in the same way as was the rate of solution. Several determinations were made for each different sand packed in the CuSO_4 solution, and from the data obtained it was possible to calculate a constant which could be used in the calculation of an effective area of the solution. As in the case of the rate of solution, the constant was practically the same for the various sands, and the value for the coarser sands was greater than that for the finer sands. The average value of the constant (.795) was slightly smaller than that obtained in the rate of solution runs (.825), but this difference was probably due to the fact that different apparatus was used for the two determinations. The results were within experimental error of each other, and thus it can be said that the sand affects the two processes in a similar manner.

The method of calculating the constant is as follows.

Conductivity Run # 13.

CuSO_4 solution packed in (20-30) mesh sand.

For solutions without sand present the specific conductivity

$$K = L/RA$$

where L = distance between electrodes.

R = resistance between electrodes

A = area of electrodes.

However in the case where sand is packed in the solution, the area of the solution parallel to the electrodes

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and the mean length of path of solution between the electrodes are changed.

Letting A = horizontal area of cell

$AxV=A'$ = mean horizontal area of solution.

Since the void spaces between the particles of sand are not always perpendicular to the electrodes the effective area for conduction is different from the **horizontal** area, and a constant (**B**) can be introduced to calculate the effective area (A'') of the solution.

Thus $A'' = AxVxB$

Also since the volume of solution in a given volume of sand is equal to $AxVxL$, and the effective area of the solution is equal to $AxVxB$; the effective length of path will be equal to AVL/AVB which is L/B .

$$\text{Thus } KR = \frac{L/B}{AVB} = \frac{L}{AVB^2}$$

$$B = \sqrt{\frac{L}{KRAV}}$$

$$B = \sqrt{\frac{6.03}{.01260 \times 121.4 \times 19.308 \times .3178}} = .803$$

TABLE 1

Effect of sand on rate of solution of methane in kerosene.

Run No.	Mesh size range of sand	Uncorrected Slope	Corrected Slope	% Void Space	Effective Area Constant B
36	20-30	4.01	4.22	.3097	.835
37	20-30	4.01	4.23	.3097	.837
39	30-40	4.24	4.40	.3231	.834
40	30-40	4.20	4.39	.3231	.833
41	40-50	4.24	4.26	.3325	.821
42	40-50	4.275	4.49	.3325	.826
33	50-70	4.37	4.59	.3455	.813
35	50-70	4.39	4.61	.3455	.817
32	100-140	4.74	4.96	.3728	.819
34	100-140	4.81	4.99	.3728	.820
38	100-140	4.82	4.99	.3728	.820

Average B = .825

TABLE 2

Effect of sand on electrical conductivity of CuSO_4 solution.

Run No.	Mesh size range of sand	% Void Space	Conductivity of Solution K	Resistance of Solution R	Height of Sand L	Effective Area Constant B
13	20-30	.3178	.01260	124.6	6.03	.803
14	20-30	.3182	.01242	129.4	6.31	.800
15	20-30	.3193	.01251	116.1	5.70	.798
16	20-30	.3239	.01278	105.4	5.43	.804
21	30-40	.3280	.01450	101.2	5.85	.794
22	30-40	.3337	.01450	100.2	5.90	.795
23	30-40	.3315	.01450	100.0	5.88	.797
26	40-50	.3436	.01450	88.2	5.39	.798
27	40-50	.3387	.01460	88.7	5.35	.796
17	50-70	.3488	.01301	115.8	6.33	.790
18	50-70	.3484	.01310	111.7	6.15	.791
19	50-70	.3507	.01292	114.3	6.22	.790
20	50-70	.3489	.01301	111.6	6.13	.792
24	100-140	.3808	.01450	86.5	5.69	.786
25	100-140	.3808	.01450	86.1	5.59	.787

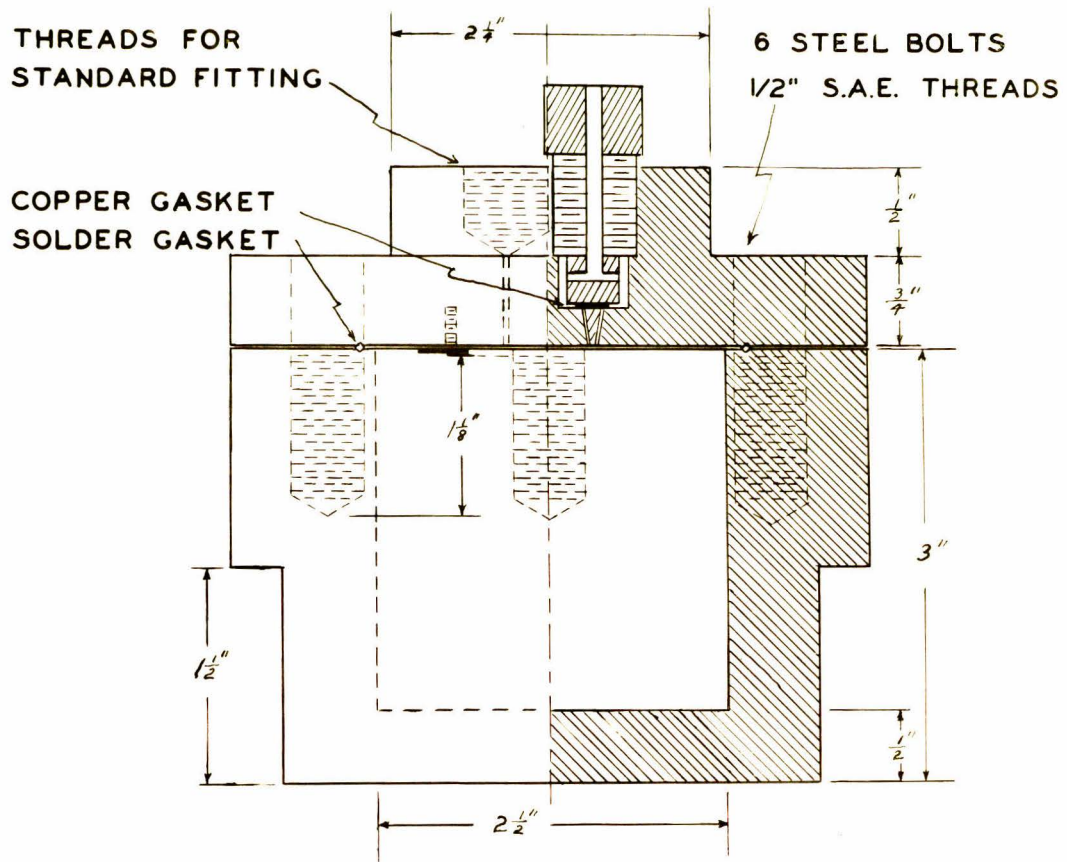
Average B = .795

Summary

The effect of the presence of sand on the rate of solution of methane in kerosene, and on the electrical conductivity of aqueous CuSO_4 solutions has been studied. It was found that the presence of sand had a similar effect in the two cases, and that the effect was practically the same for all sands of the various particle sizes studied. Since each different size of sand gave a different percentage of void space between the particles, and the range was fairly wide (31% to 37%), the constant found should be useful in calculating the rate of solution of methane and other gaseous hydrocarbons in liquid hydrocarbons in the presence of sand.

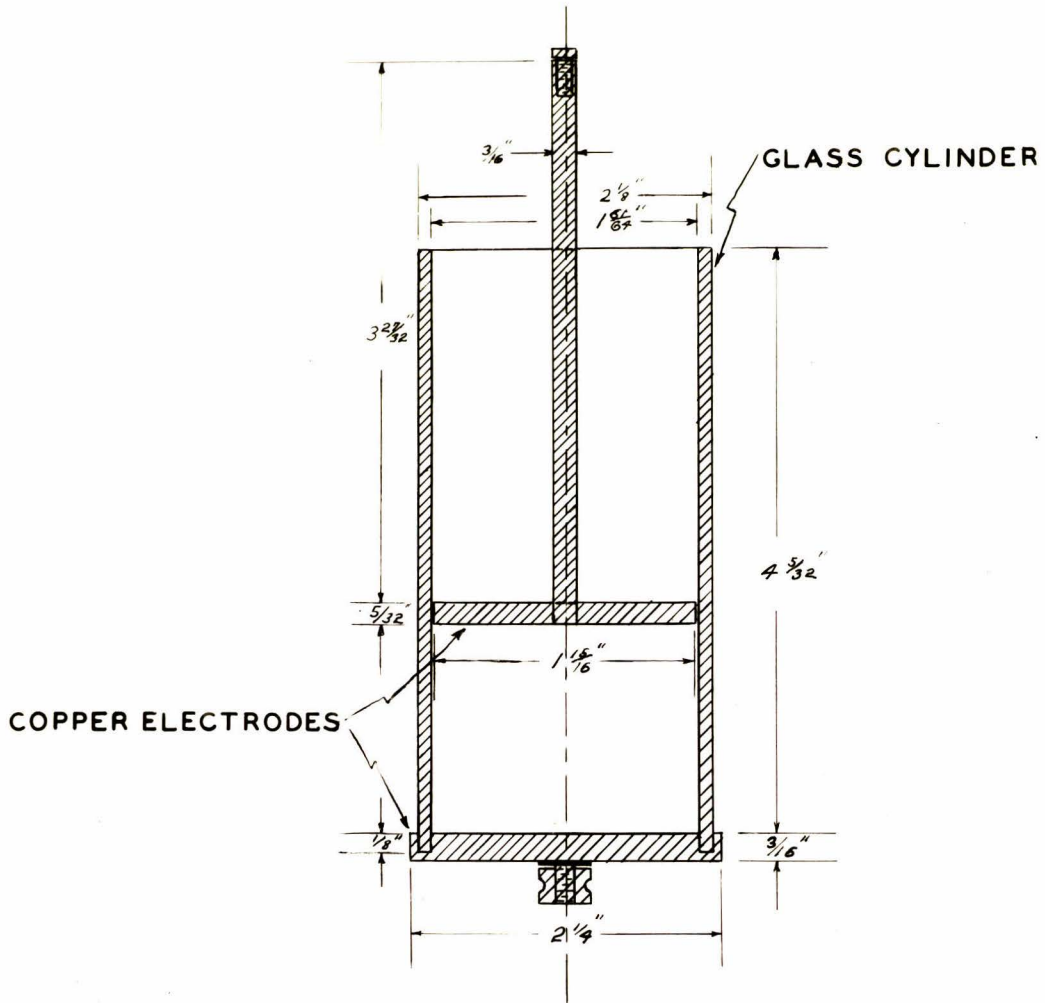
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STEEL DIFFUSION CELL

FIGURE 1



CONDUCTIVITY CELL

FIGURE 2

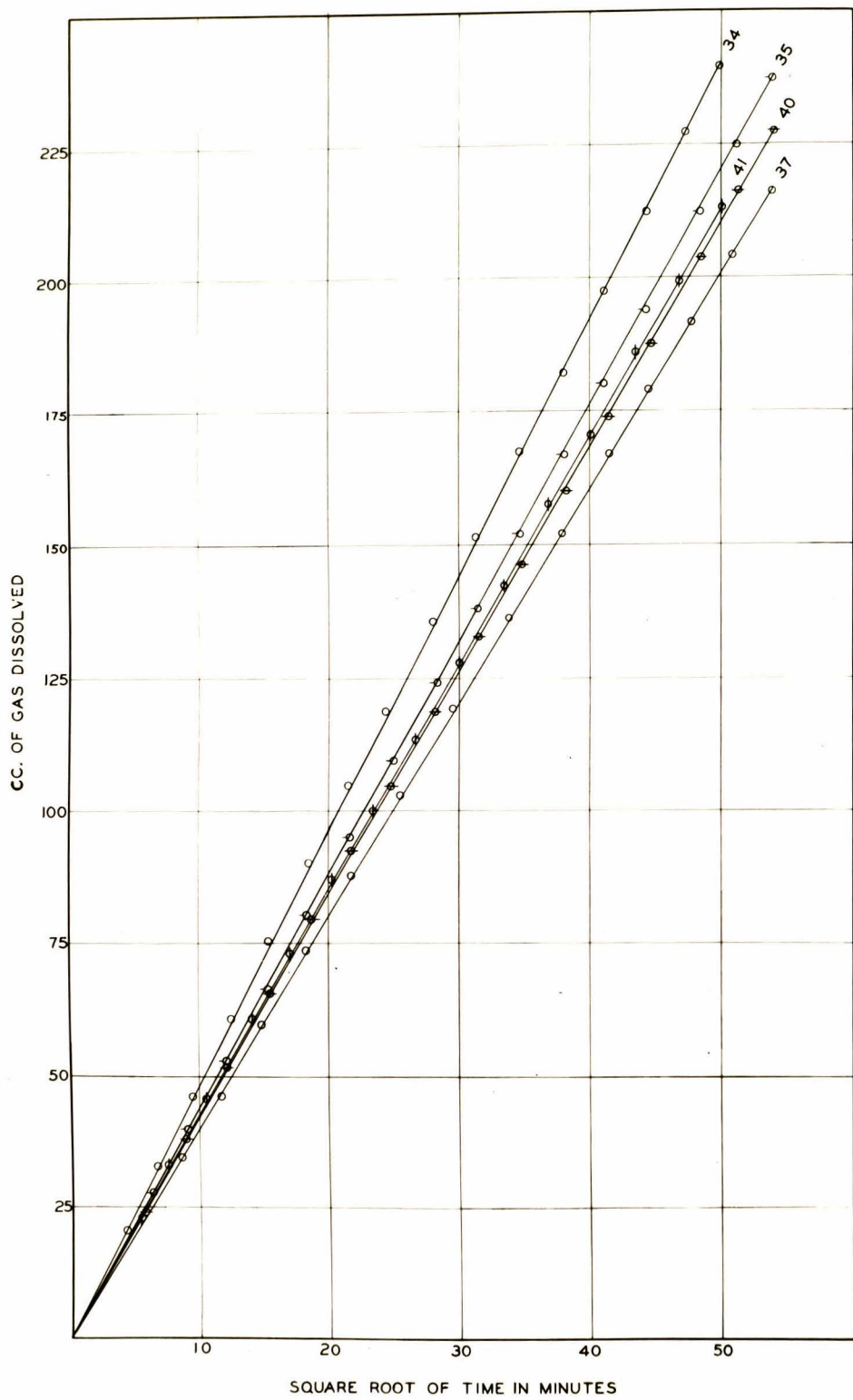
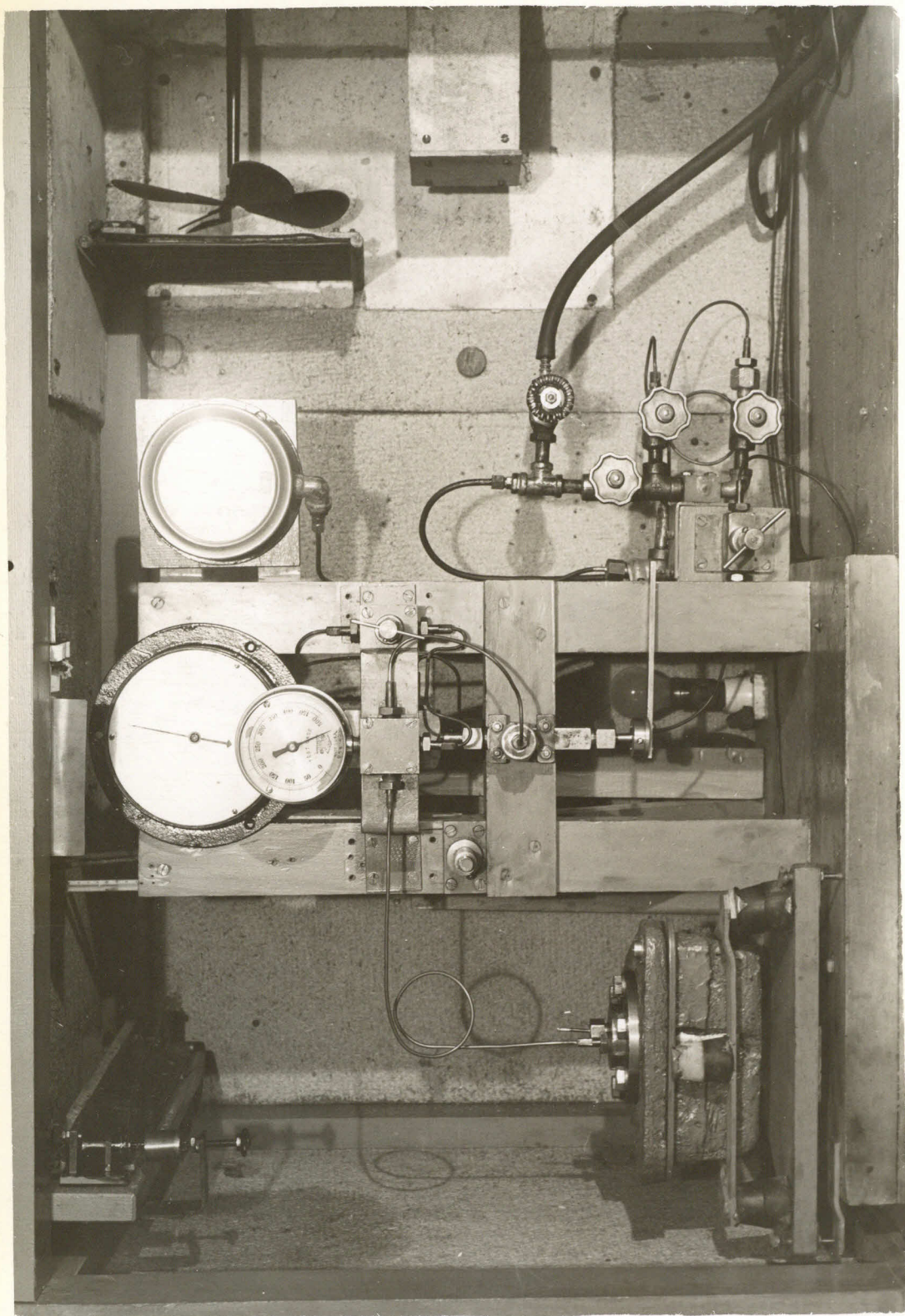
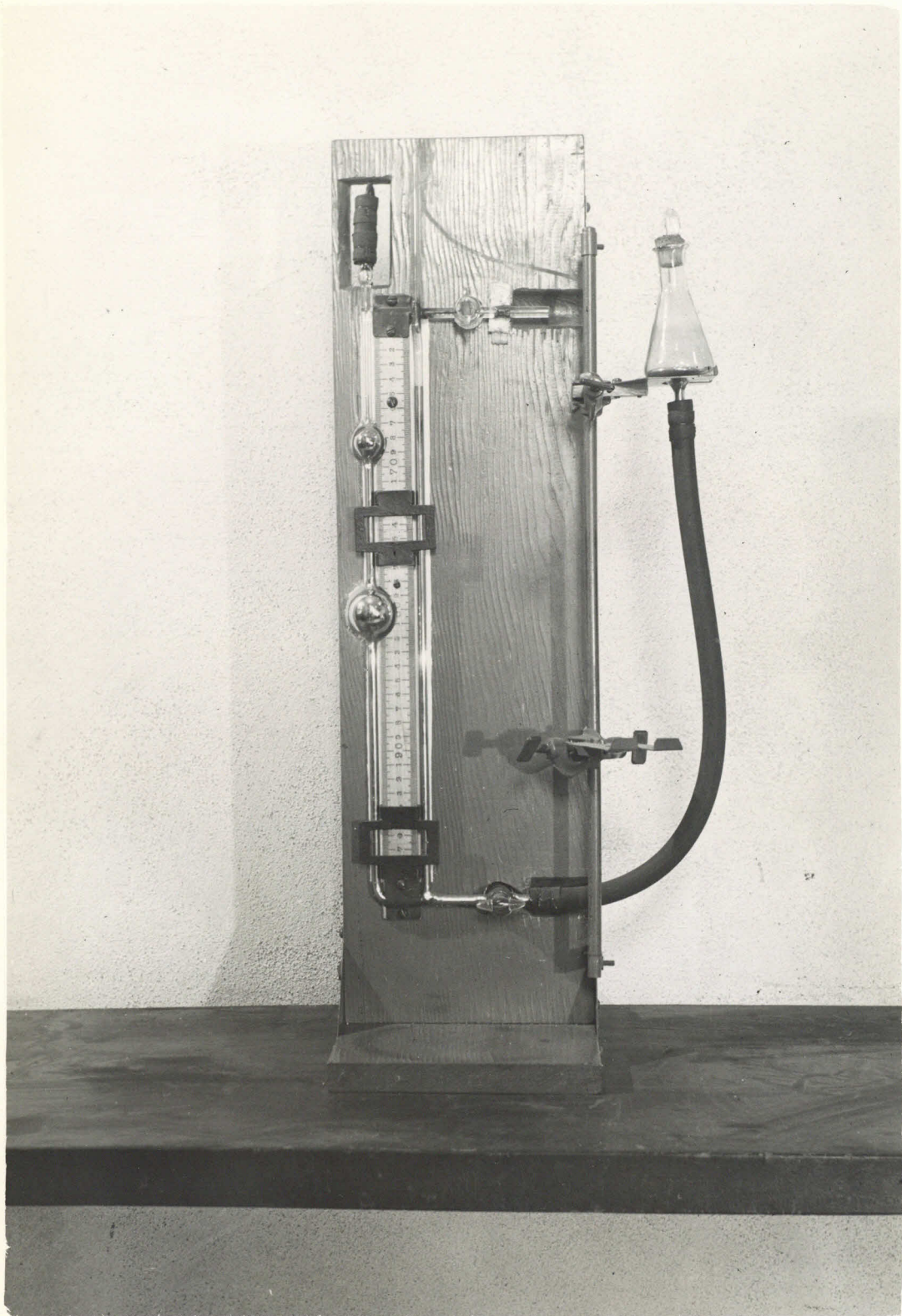


FIGURE 3



DIFFUSION APPARATUS

FIGURE 4



BURETTE
FIGURE 5

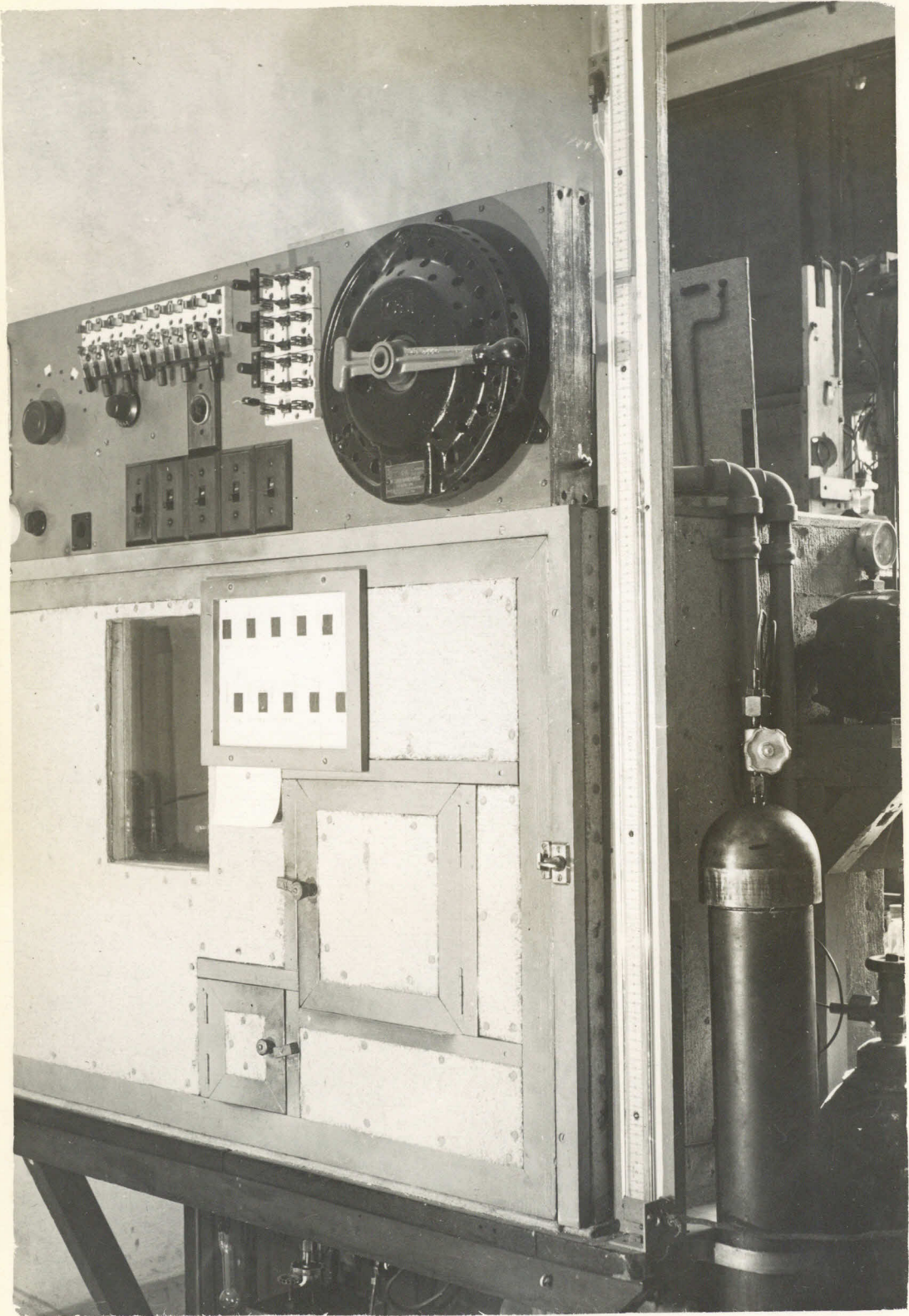
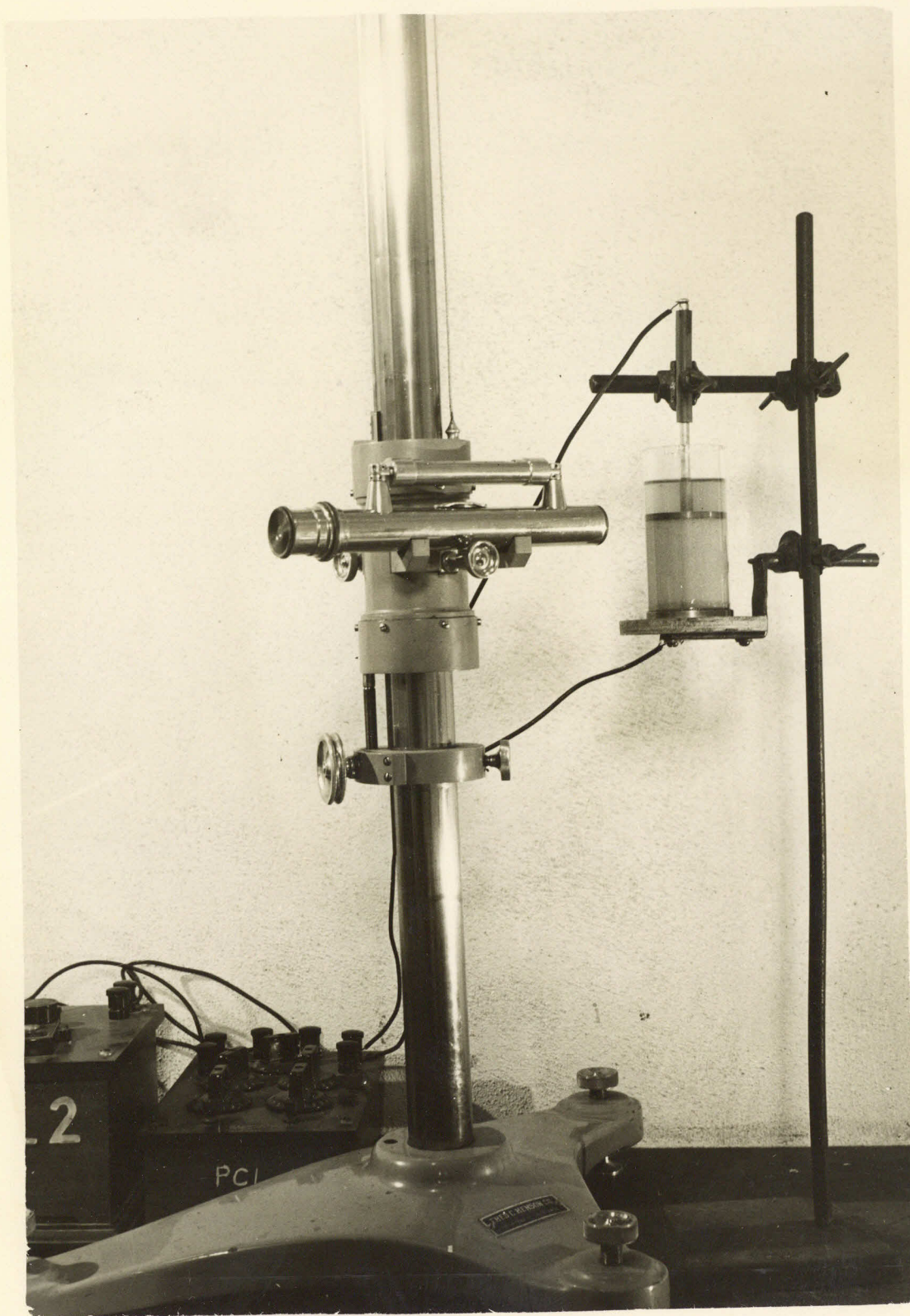


FIGURE 6



CONDUCTIVITY APPARATUS

FIGURE 7