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POLAROGRAPHY WITH SOLID ELECTRODES

L. B. Rogers, H. H. Miller, R. B. Goodrich and A. F. Stehney

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November 13, 1947

Date Received: 12/11/47 Date Issued: 1/2/48

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POLAROGRAPHY WITH SOLID ELECTRODES

I. Investigation of Certain Variables Encountered in Using Automatic Recording with Stationary Platinum Electrodes*

By

L. B. Rogers, H. H. Miller, R. B. Goodrich and A. F. Stehney**

Abstract

Mixtures of ions which react rapidly with mercury usually cannot be analyzed polarographically with the dropping mercury electrode. However, on the basis of experiments with silver ion these polarographic analyses appear to be feasible using a platinum micro-electrode and the usual automatic recording technique. The effect on the half-wave potential and the diffusion current of using different rates of polarization, larger electrode areas and stirring have been examined. Under controlled conditions, the precision of the measurements is somewhat lower than for the dropping mercury electrode.

Introduction

The dropping mercury electrode is used extensively by polarographers because mercury has a high hydrogen-overvoltage which allows a wide range of reduction potentials to be studied. Another advantage of a dropping mercury electrode is its reproducibly fresh surface. However, one is limited in using this electrode because mercury readily dissolves when it is made an anode. In a neutral solution of potassium chloride one can operate only in the range of 0.0 to -1.5 V. versus a saturated calomel electrode. On the other hand, a smooth platinum electrode has a much lower hydrogen-overvoltage, the hydrogen coming off at approximately -0.8 V. but, the electrode can be used as an anode to + 1.0 V. before oxygen is discharged. Thus, the platinum electrode makes available to polarography a new region of potential.

Platinum electrodes have been used for obtaining polarographic data by Laitinen and Kolthoff (1) who determined the reproducibility of diffusion currents and checked the linearity of the relation between diffusion currents and concentration. They used a manually operated instrument and measured the current by determining the potential drop across a standard 9999 ohm resistance in series with the cell. The electrodes were platinum wire (2), 4 mm. long and 0.5 mm. in diameter, sealed in the end of a glass tube. The experiments were carried out at a constant temperature to avoid thermal effects and conditions were such that no mechanical disturbances could interfere. They obtained the points by increasing the emf slowly to the desired value and then waiting two to three minutes for the electrolysis to

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*Presented in part before the East Tennessee Section of the American Chemical Society, May 24, 1947.

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reach a constant current. By proceeding slowly they created a minimum of disturbance in the diffusion state near the electrode and prevented a discharge of gas on the electrode surface. It is apparent that this method of obtaining a curve point by point is very time-consuming even if one substitutes a rotating electrode, which reaches equilibrium immediately, for the stationary electrode.

The application of the usual polarographic procedure involving a continuously changing potential would decrease quite considerably the length of time required to obtain a curve. Zlotowski (3) and Valen and Haissinski (4) used automatic recording with solid electrodes to obtain current-voltage information about electrolytic reactions but these authors were not primarily concerned with the analytical phases of the technique. They did, however, illustrate the usefulness of solid electrodes for anodic as well as cathodic reactions.

The present study was designed to examine the possibility of using the automatic recording technique with solid electrodes for analytical purposes. A study was made of variables such as the effect of changing the size of the electrode, the effect of stirring the solution, and the effect of applying voltage continuously at different rates of change. The criteria used to check the reliability of the data were the reproducibility of half-wave potentials and of diffusion currents. The final consideration for quantitative analysis was the linearity of the relationship between the concentration of reducible ion and the diffusion current.

After the present investigation had been started, Müller (5) reported automatically recorded polarographic studies in which solutions of electrolytes flowed past a stationary platinum electrode in a glass capillary. He showed that the wave heights were a function of the concentration of the reducible material and the rate of flow, and that better agreement of half-wave potentials were obtained with slower rates of flow. According to Matheson (6) polarographic studies with stationary electrodes have also been carried out by H. A. Robinson of the Dow Chemical Company using an oscillographic technique (7) and Matheson reported similarities between Robinson's results and those described in the present paper.*

Silver was selected for study because it has a simple redox reaction which is thermodynamically reversible, because knowledge of such a system is necessary if more complex systems are to be understood, and because the reaction illustrates an application of the platinum electrode to the analysis of an ion which is reduced in the anodic region. After preliminary experiments indicated that copper ion (II) did not interfere with the silver wave, a mixed silver-copper solution was used so that other experiments involving the reduction of cupric ion in the presence of silver could be carried out later on the same solution. Solutions containing other ions have been examined in a preliminary way to test the general applicability of the method, and these experiments will be reported in another paper.

Experimental Details

Reagents and Solutions

All chemicals used in the investigation were reagent grade, and all

*See also a paper published after our work was completed: Randles, J.E.B., Analyst 72, 301 (1947).

solutions were prepared with distilled water. The concentrations of standard stock solutions were known to better than 1%.

The composition of the standard polarographic solution was 5.00×10^{-4}M in silver ion, 1.00×10^{-4}M in cupric ion and 0.100M in potassium nitrate. The pH, adjusted by the addition of about two drops of 6N nitric acid, was 4.00 ± 0.01. This solution was used throughout the experiments described in this report with the exception of the studies concerning changes resulting from differences in the concentration of silver ion. In these studies the copper (II) was omitted.

Tank nitrogen, used for removing oxygen from the polarographic cell, was freed from oxygen by passing the gas through a series of four wash bottles. The first three contained an ammoniacal cuprous chloride solution and strips of copper foil. The fourth wash bottle contained 6N sulfuric acid which removed ammonia from the nitrogen stream. The acid was renewed from time to time to insure complete collection of ammonia. The use of a fifth bottle containing water for the purpose of introducing water vapor into the nitrogen stream and thereby decreasing evaporation losses in the polarographic solutions was unnecessary because large volumes of solution were employed.

Apparatus

About 300 ml. of the polarographic solution was held in a 500 ml. bottle in which was suspended the platinum electrode and an agar bridge. The platinum electrodes were made by fusing platinum wire into a soft glass tube and making electrical contact in the usual way by filling the tube with mercury. The agar bridge, saturated with potassium nitrate, connected the solution to a 60 ml. bottle containing saturated solution of potassium chloride, and another bridge saturated with potassium chloride connected this bottle with the reference electrode, a saturated calomel electrode. In order to be able to make the correction for IR drop, the resistance of the cell was measured before each run with a conductivity bridge, Model RC-1B, made by Industrial Instruments, Inc.

For certain portions of this study it was necessary to stir the polarographic solution during a run. Mild stirring was obtained by bubbling nitrogen through the solution. For faster rates of stirring, a motor-driven glass rod with a 60° bend an inch above the end was used. Its speed was adjusted to 365 r.p.m. by means of a variac.

Polarograph Models XII and XX, manufactured by E. H. Sargent & Company were used for continuous recording. Although it was possible to use these instruments to obtain "manual" current-voltage curves, such curves were usually obtained with a set-up consisting of a Leeds and Northrup potentiometer, a Rubicon galvonometer with a sensitivity of 0.0013 uA per millimeter, and an Ayrton shunt.

A thermostat was felt to be unnecessary for most of this work. The experiments were carried out at room temperature which was usually $26° \pm 2°$ C. Each of the series of studies concerning the relationship between diffusion current and concentration was completed in quick succession during which time the temperature of the room (and the solution) did not change noticeably, i.e. ($\pm 0.1°$ C.). However, a bath maintained at $25.0 \pm 0.1°$ C. was employed whenever critical experiments, such as the study of changes in the half-wave

potential with changes in the concentration of reducible ion, were made.

Procedures

1. Cleaning electrodes.

Preliminary tests showed that the electrode could be cleaned by imposing upon it a sufficiently positive potential to dissolve the silver. However, the electrode could also be cleaned by dipping it into 6N nitric acid for two minutes or more, and then washing it with distilled water. The electrode was then dried with kleenex before using. Because the acid treatment was faster, it was employed throughout this study.

It should be pointed out that unless the platinum-glass seal was very tight, the electrode sooner or later produced erratic results. This appeared to be caused by reaction between the nitric acid and the mercury inside the glass tube.

2. Deaeration of polarographic solutions.

Oxygen-free nitrogen was bubbled through the solution for fifteen minutes immediately before each run and was passed over it during each run. This deaeration was not necessary in that the silver ion was reduced before dissolved oxygen, but the step was desirable in that a possible uncertainty in behavior was removed.

3. Polarography.

The manual technique of Laitinen and Kolthoff (1) was employed to establish standard curves. A closely related procedure in which the potential was changed from one value to another by means of a motor-driven slidewire was later substituted. At a predetermined potential, the motor was stopped, a minute allowed for the current to become constant, the current recorded, and the motor started again. The use of the motor simplified the operation of approaching each potential slowly and reproducibly.

Curves were also recorded in the usual continuous way with the polarograph. The rate of change of potential was calculated in each case after determining by means of a stop watch, the time required for the slidewire to change the applied potential by a volt or more.

Results

Comparison of manual and continuous methods using a micro-electrode.

Figure 1 shows the type of curve obtained with a motor-driven slidewire. Continuously recorded curves usually had round maxima, whereas maxima were rarely observed in manual curves. While the presence of maxima seemed to be the rule in continuous recording, some runs, which were duplicates of others for which a maxima had been found showed no signs of a maximum.

Maxima were expected from experience with the Laitinen and Kolthoff technique. There one finds that current usually increases while the potential is being changed and that as soon as the potential is held constant, the current

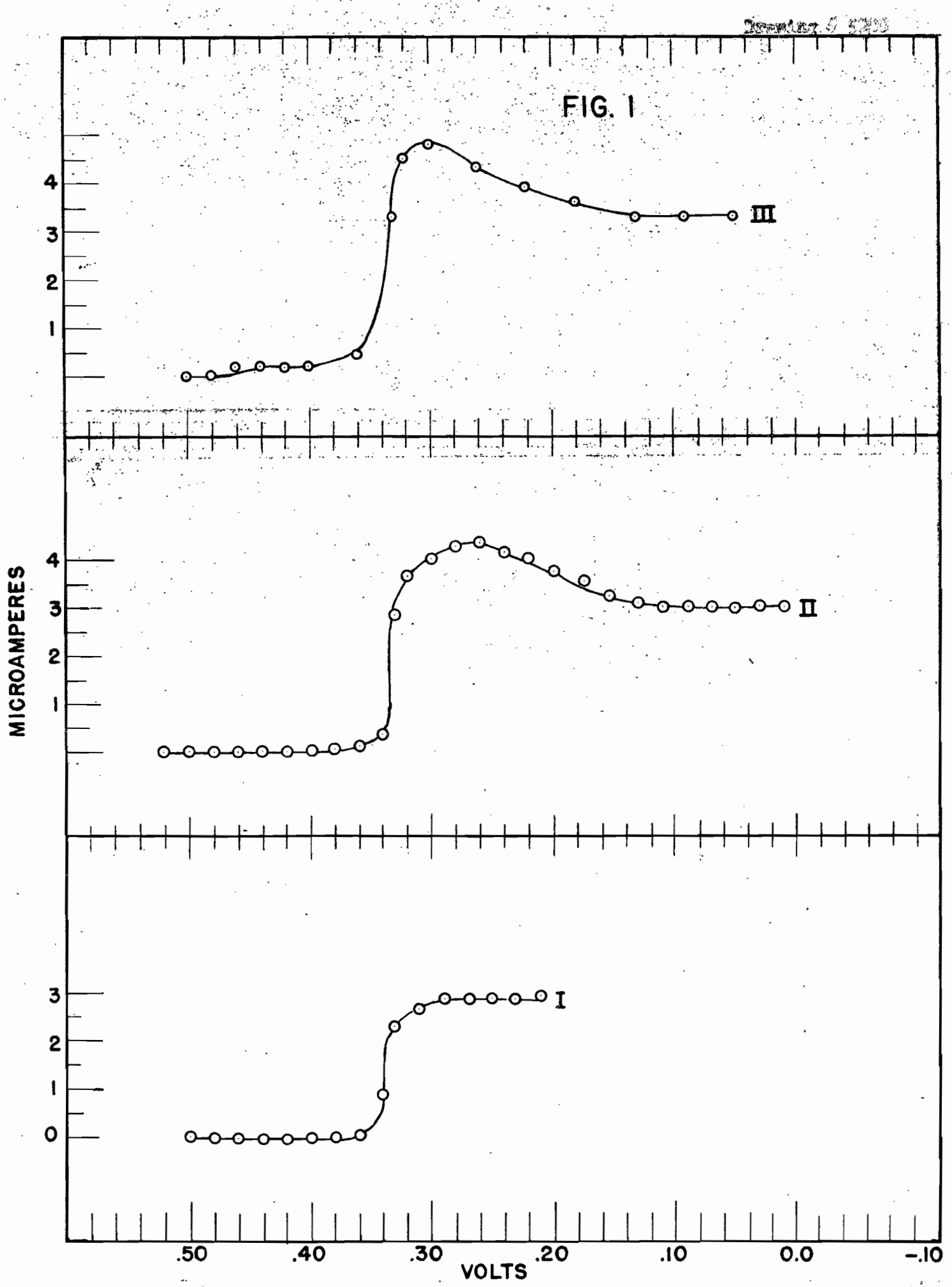


FIG. 1
MICROAMPERES
VOLTS
III
II
I
4
3
2
1
0
.50
.40
.30
.20
.10
0.0
-.10

decreases with time. The decrease is rapid at first but becomes very slow within about a minute after which the current is essentially constant. The changes in current, both positive and negative, are particularly noticeable in the region of voltage where the polarographic wave occurs, and they indicate that the rate at which the system reaches "diffusion equilibrium" is slower than the rate at which the voltage changes. Evidence for such an explanation is found in the fact that these maxima are not of the same type as those encountered with the dropping mercury electrode in so far as the presence of gelatin exerts no repressive effect on them. Thus one would expect slower rates of polarization to produce curves with smaller maxima. However, the irregular occurrence of maxima prevented the authors from reaching a definite conclusion concerning the effect of the rate of polarization on the height of the maximum.

In Table I are listed the average values for the half-wave potential and the diffusion current obtained with three sizes of electrodes. Values listed in this table have been corrected for IR drop and residual current and represent the average of six or more runs. The instrumental limit of accuracy in determining the half-wave potential is considered to be within ± 0.01 volts, and the limit for the diffusion current within ± 0.1 microampere. However, the reproducibility limits of the experimental measurements were wider. Thus, the half-wave potentials for a quiet solution were usually duplicable within ± 0.02 V. although most of the values fell within ± 0.01 V. of the average. Variations in the values for diffusion currents were much more marked, and the magnitude of the variation increased with the size of the average diffusion current.

One may conclude from the table that the half-wave potential is independent of the rate of polarization. The slightly positive shift observed with a 6 mm. electrode is within the limits of experimental error. The half-wave potential for a continuously recorded curve obtained by using the opposite direction of polarization also agreed within the limits of error with the values listed in Table I. It is interesting to note that although the rate of polarization did not affect the half-wave potential, faster rates of polarization did produce larger diffusion currents.

Effect of size of electrode

It has just been pointed out that the size of the electrode does not effect the half-wave potential. Furthermore, an increase in the electrode area appeared to produce no important change in the shape of the corrected polarographic wave as shown in Figure 2. Thus, a large electrode gave a curve very similar to one obtained with a smaller electrode in contact with a higher concentration of reducible ion (Figure 3). However, until the current-voltage curves involving larger currents had been corrected for IR drop, they were much flatter than the curves for which IR corrections were negligible. Figure 4 illustrates this effect which is met in all polarographic work. As an illustration of an exceptional case, Figure 5 shows an uncorrected curve for a foil electrode where the IR drop was so large that no diffusion current plateau appeared before the maximum voltage of the slidewire had been reached.

Despite excessive care in cleaning the electrode and in measuring its area, difficulty was experienced in obtaining a good curve showing the relation between diffusion current and electrode area. Therefore, Figure 6 served only to substantiate the expected trend. One might point out that this figure

Table I

Half-Wave Potentials and Diffusion Currents of Silver in Quiet Solutions.

Rate of Applied Voltage	Manual		1.46 mv/sec.		2.92 mv/sec.		4.38 mv/sec.	
	$E_{\frac{1}{2}}$ V.	id μA.	$E_{\frac{1}{2}}$ V.	id μA.	$E_{\frac{1}{2}}$ V.	id μA.	$E_{\frac{1}{2}}$ V.	id μA.
1. One mm. Electrode (0.02 cm^2)	0.34	0.8	0.33	0.8	0.34	1.0	--	--
2. Six mm. Electrode (0.10 cm^2)	0.33	3.2	0.33	3.0	0.35	3.9	0.35	4.1
3. Foil Electrode (2.14 cm^2)	0.34	29.4	0.34	32.7	---	---	0.33	32.7

Figure 2

Effect of electrode size on current produced in a quiet solution. Rate of polarization - 1.46 mv/sec.

I. One mm. platinum electrode ($0.02\ cm^2$ in area)
II. Six mm. platinum electrode ($0.10\ cm^2$ in area)
III. Foil platinum electrode ($2.14\ cm^2$ in area)

FIG. 2

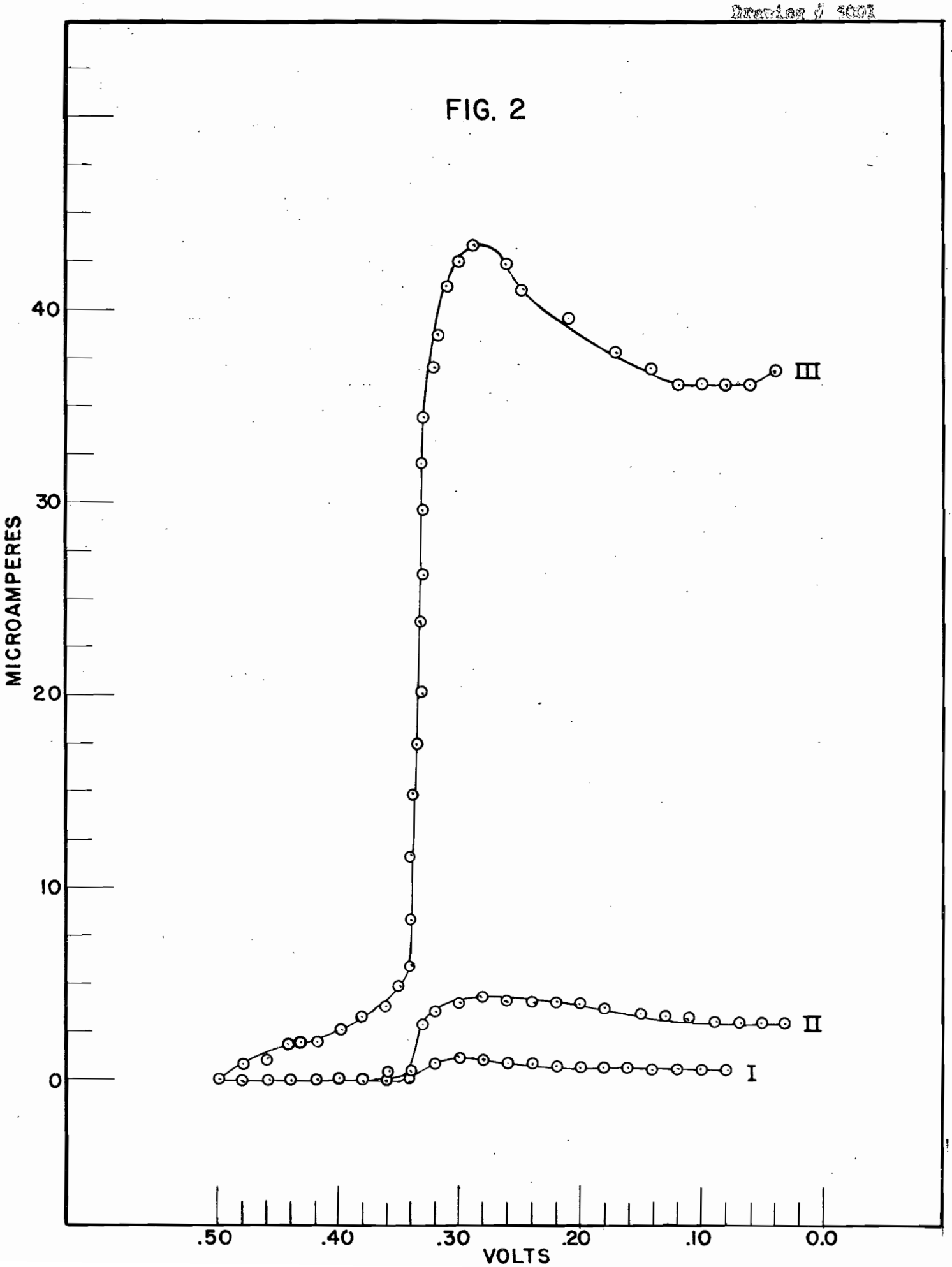


Figure 3

Effect of varying concentration on the maximum from a foil electrode (2.14 cm^2) in a quiet solution. Rate of polarization = 1.46 mv/sec.

I. 5.0×10^{-4} M Ag^+
II. 2.50×10^{-4} M Ag^+
III. 6.25×10^{-5} M Ag^+

FIG. 3

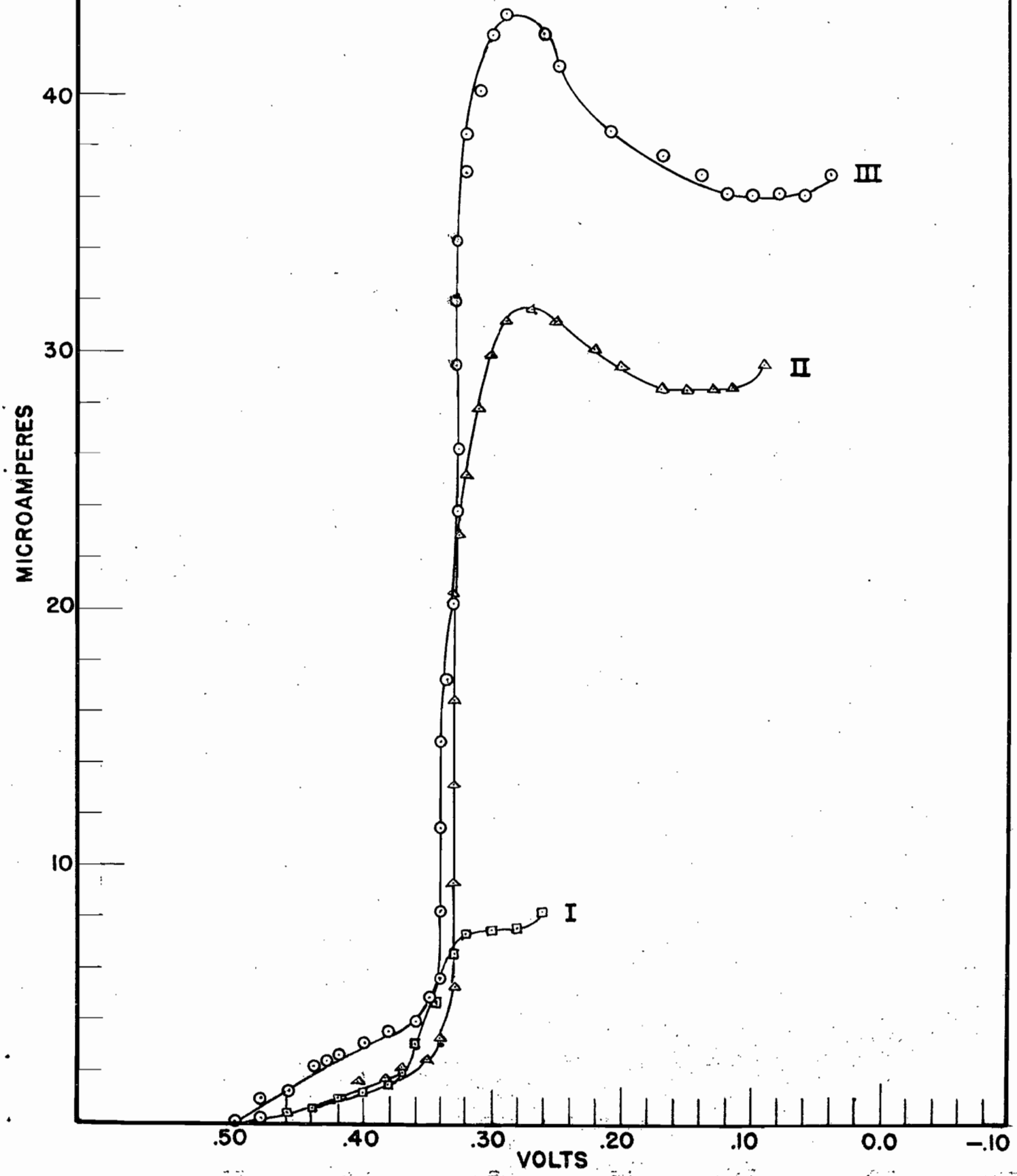


Figure 4

Current-voltage curves showing correction for IR drop across the cell using an electrode in a quiet solution. Rate of polarization = 1.46 mv/sec.

I. Uncorrected curve
II. Corrected curve

Drawing # 5003

FIG. 4

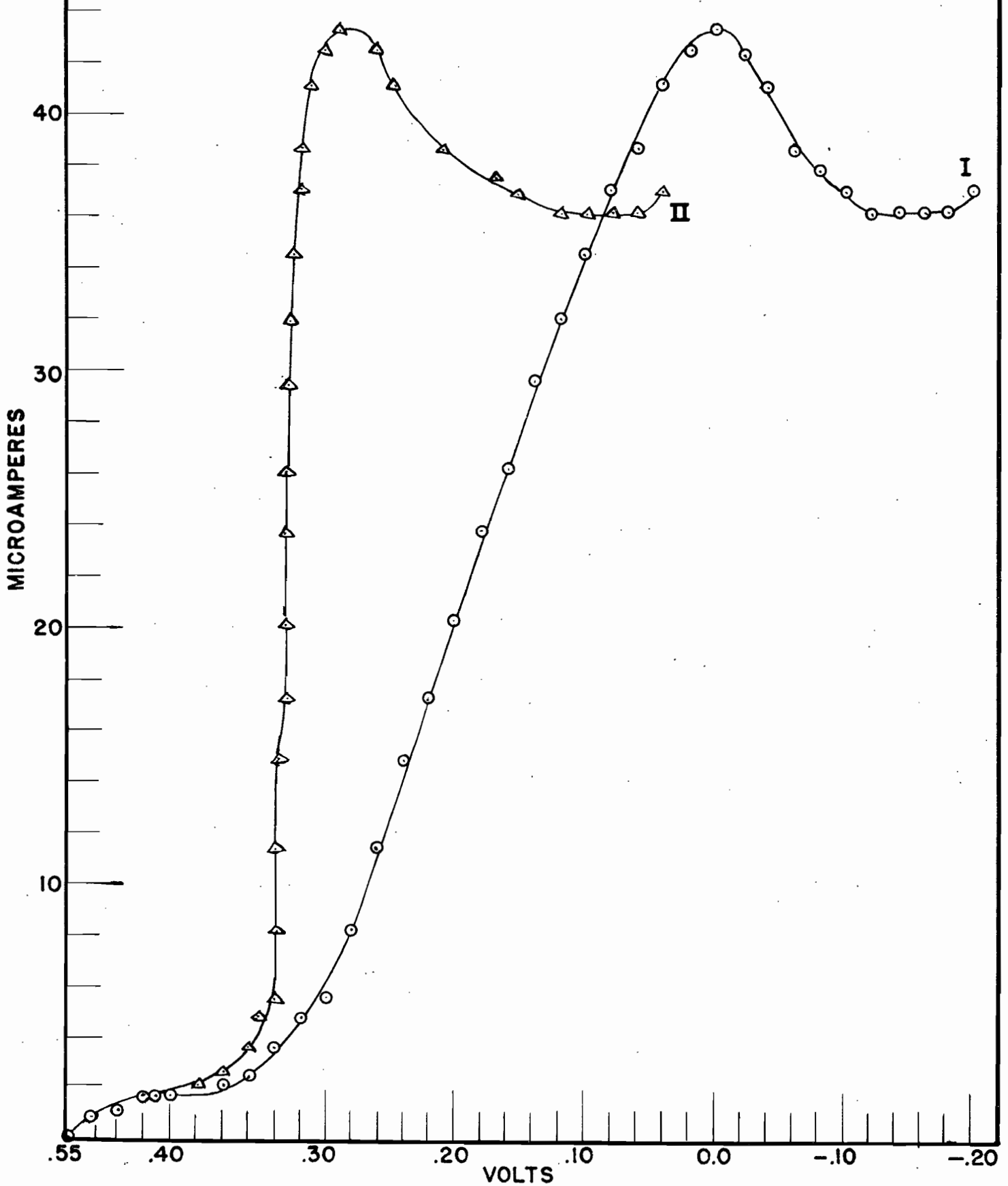


Figure 5

Effect of stirring on the diffusion current using a 2.14 cm^2 foil electrode. Rate of polarization = 1.46 mv/sec.

Drawing # 5024

FIG. 5

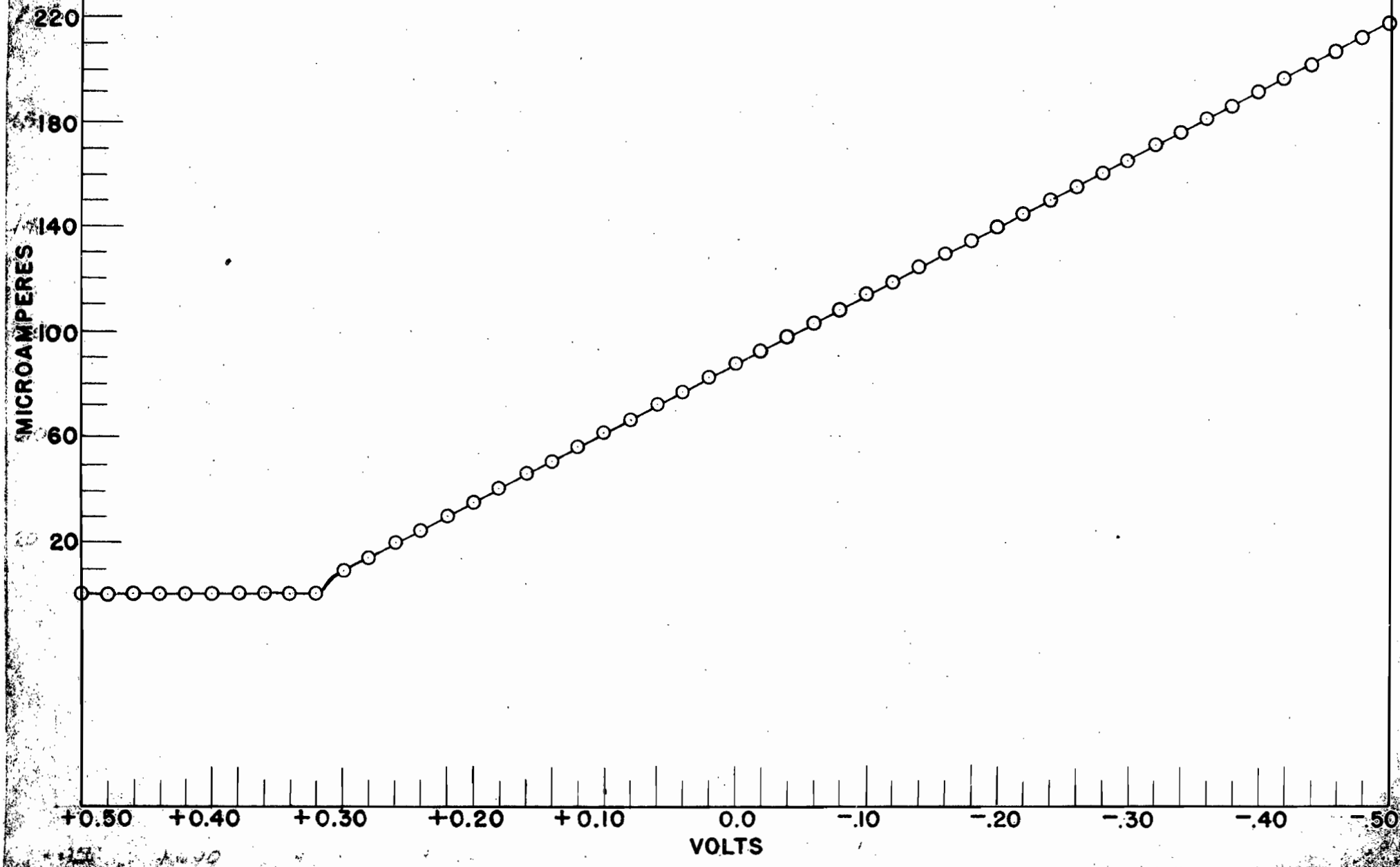
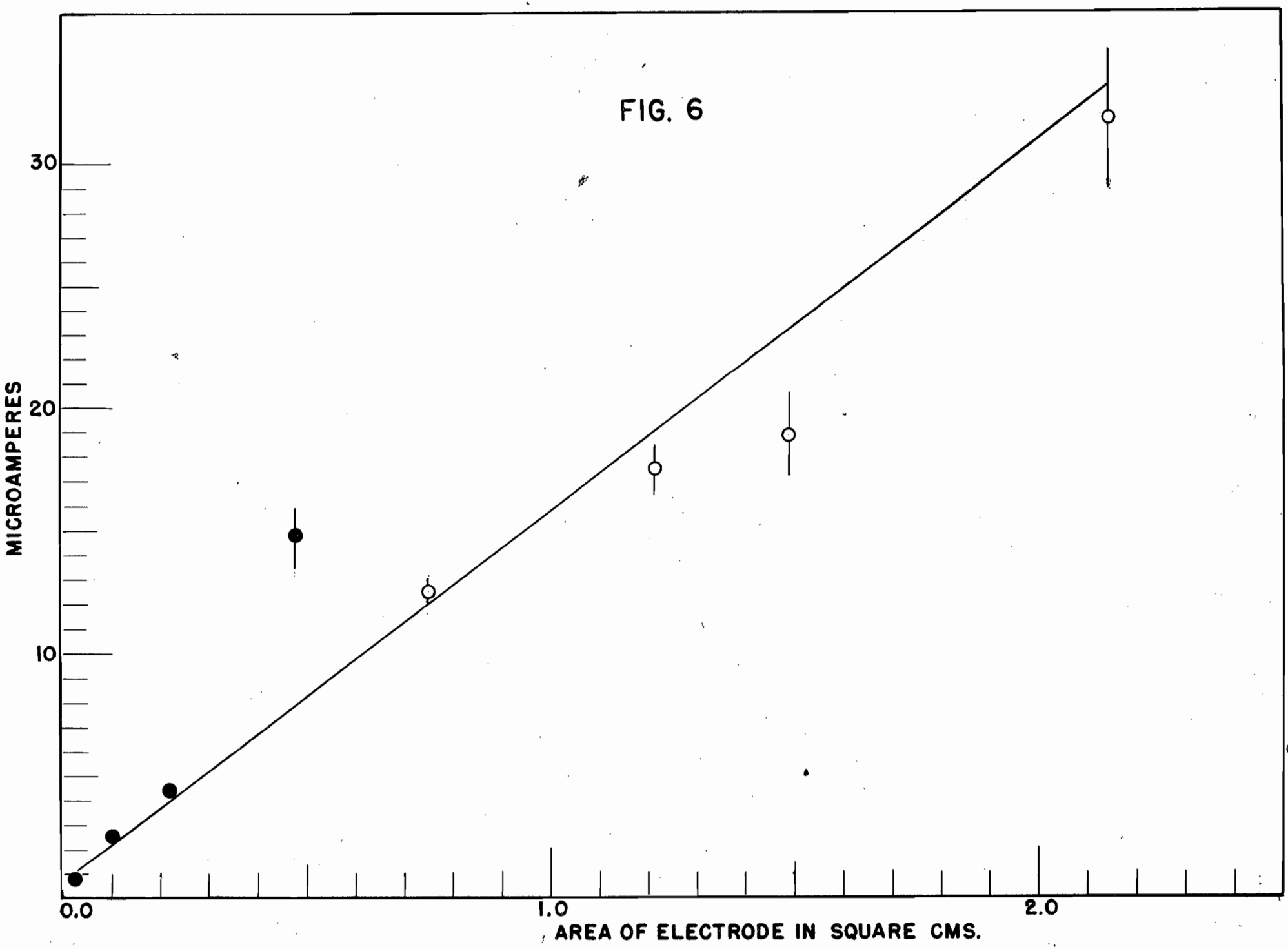


Figure 6

Relation between electrode size and diffusion current in a quiet solution. Rate of polarization = 1.46 mv/sec.

○ = Foil electrodes

● = Wire electrodes



Drawing # 5005

illustrates the better precision which is obtainable with smaller electrodes, and also the magnitude of the error which might be introduced in trying to predict the size of a diffusion current for an electrode by comparing its plane area to the area of a second electrode. It emphasizes the need for calibrating every electrode with a standard solution.

A comparison of Figures 8 and 10 emphasizes the desirability of selecting an electrode area according to the region of concentration that is being examined. That is to say, smaller electrodes are more suitable for higher concentrations and larger electrodes for more dilute concentrations of reducible ions.

Effect of stirring.

One would expect the results from stirred solutions to be similar to those obtained with a rotating electrode or by flowing a solution past the stationary electrode because, in all cases, there is a movement of the solution past the surface of the electrode. The diffusion current for a given concentration of reducible ions should be greater the faster the stirring because of the larger number of ions which are accessible to the electrode surface for reduction within a given time interval. Likewise, there should be no maximum because of the faster rate of reaching equilibrium. These expectations were verified. See Figure 7.

The deposition process is not as simple in a stirred solution as in a quiet one. Laitinen and Kolthoff (8) found in using a rotating platinum electrode that the current-voltage curves had abnormal slopes compared with curves in which concentration polarization was assumed to be the only effective type of polarization. Mention was made earlier of Müller's report that, when the solution flowed past a micro-electrode, a better half-wave potential could be obtained with slower rates of flow. The experiments reported in Table II confirm the above observations and allow several related generalizations to be made.

In the first place, stirring markedly decreased the reproducibility of both the half-wave potential and the diffusion current. In many cases, no half-wave potential could be calculated because of failure to obtain a diffusion current plateau. A similar behavior had been noted in some cases for rotating electrodes (2). Furthermore, when half-wave potentials could be calculated, the values were often spread over a range of 0.06 V. and the average value appeared to be somewhat lower than that for unstirred solutions.

In the second place, although faster rates of stirring resulted in a much smaller probability of finding a diffusion current plateau for a curve, whenever the plateau was found, the expected increase in the magnitude of the diffusion current had occurred. For a given rate of polarization the probability of reaching a diffusion current plateau bore a rough inverse relation to the size of the electrode. The probability of reaching a diffusion current plateau for a particular electrode and a fixed rate of stirring was increased somewhat by using a faster rate of polarization.

Effect of concentration of reducible ion on the half-wave potential.

The deposition of an element at a solid electrode is analogous to the deposition of an element insoluble in mercury at the usual dropping mercury

Table II

Half-Wave Potentials and Diffusion Currents of Silver in Stirred Solutions.

Rate of Applied Voltage	Manual		1.46 mv/sec		2.92 mv/sec		4.38 mv/sec	
	$E_{\frac{1}{2}}$ V.	id μA.	$E_{\frac{1}{2}}$ V.	id μA.	$E_{\frac{1}{2}}$ V.	id μA.	$E_{\frac{1}{2}}$ V.	id μA.
1. One Millimeter Electrode ($0.02\ cm^2$)	0.30	7.8*	0.32	14.4*			0.32	17.2*
	N.D.P.*		0.33	14.4*			0.31	17.2*
	N.D.P.*		0.33	8.2*			0.28	16.8*
	N.D.P.*		0.34	8.0*			0.34	17.4*
	N.D.P.*		0.33	8.4*			0.32	16.9*
			0.34	7.4*			0.34	17.4*
			0.33	7.8*			0.30	17.6*
			0.32	7.8*				
			N.D.P.*					
			N.D.P.*					
2. Six Millimeter Electrode ($0.10\ cm^2$)	0.35	24.6**	0.33	43.0*	0.31	22.5**	0.31	75.9*
	0.34	16.0**	0.33	39.7*	0.34	16.4**	0.31	87.1*
	0.35	18.0**	0.34	36.9*	0.28	30.0**	0.29	82.0*
	0.35	22.9**	0.31	51.3*	0.27	32.8**	0.33	78.9*
	N.D.P.*		0.33	41.0*	0.30	47.2*	0.28	75.4*
	N.D.P.*		N.D.P.*		0.30	69.7*	0.34	82.0*
			N.D.P.*		N.D.P.*			
			N.D.P.*		N.D.P.*			
			N.D.P.*					
3. Foil Electrode ($2.14\ cm^2$)	N.D.P.*		N.D.P.*				N.D.P.*	
	N.D.P.*		N.D.P.*				N.D.P.*	
	N.D.P.*							

N.D.P. means no diffusion current plateau was reached.
*Motor stirred
**Nitrogen stirred; conditions extremely difficult to control.

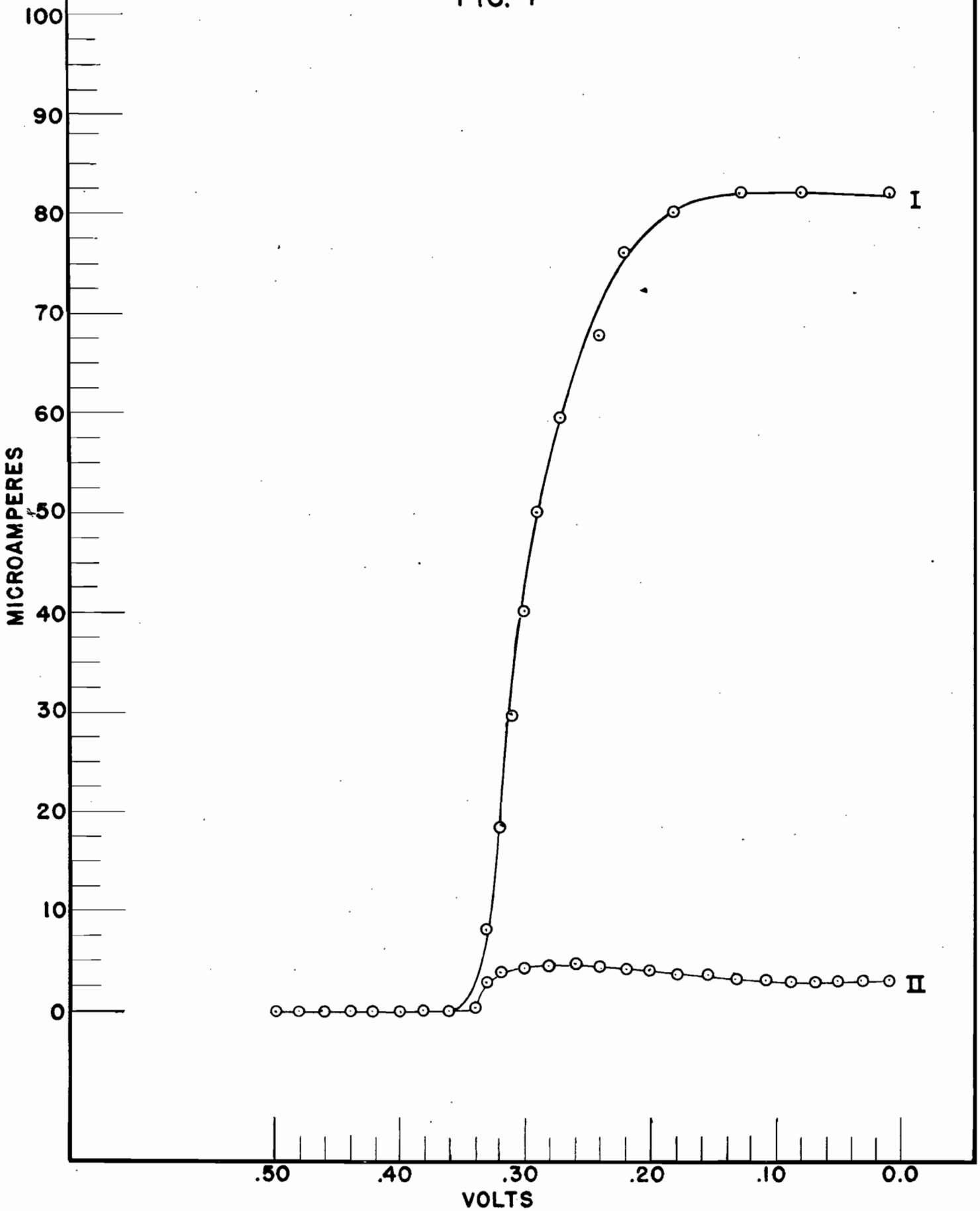
Figure 7

Effect of stirring on the diffusion current for a 6 mm. electrode (0.10 cm^2). Rate of polarization = 4.38 mv/sec.

I. Unstirred solution
II. Motor-stirred solution

Drawing # 5006

FIG. 7



electrode. Therefore, a shift of the half-wave potential to more negative potentials with dilution of the reducible ion should be found (9) in accordance with the equation*

$$E_{\frac{1}{2}} = E^{o} + \frac{RT}{nF} \ln f_s + \frac{RT}{nF} \ln \frac{C}{2} \qquad (1)$$

where f_s is the activity coefficient of the reducible ion. This equation assumes that the activity of the deposit is unity.

In actual practice, there are other factors which must be considered such as overvoltage, variations in the reference electrode potential, and junction potentials. Ordinarily, the current densities encountered in polarography are so small that overvoltage is not a source of large errors, particularly when one is dealing with a readily reversible reaction. Errors in the calomel reference electrode arising from the presence of oxygen are of the order of a millivolt and can be neglected. By using a large reference electrode, errors in the reference potential arising from polarization can be maintained at negligibly small values. Junction potentials, however, may be 0.05 V. or larger. While all of these factors would have to be considered in calculating E^{o} from $E_{\frac{1}{2}}$, they are usually of little concern in polarography where one is concerned simply with keeping them constant.

In polarography, where the activity of the reducible ion is almost always less than one percent of the total activity, f_s is essentially unaffected by differences in the concentration of the reducible ion in two otherwise identical solutions. Thus, the polarographer is usually more concerned with a "practical E^{o}" or "formal potential" which includes E^{o} and the factors discussed above as constants.

$$E_{\frac{1}{2}} = E_f^{o} - \frac{RT}{nF} \ln \frac{C}{2} \qquad (2)$$

E_f^{o} is the formal potential. Providing the assumptions in equation (2) are correct, the $E_{\frac{1}{2}}$ for silver should shift -0.059 V. for each tenfold dilution.

Before testing equation (2) by performing the experiments reported in Table III, the slidewire of the Sargent Model XX was carefully recalibrated. All of the determinations were made with this instrument and with the same micro electrode (0.02 cm). The initial and final potentials of each run were checked with a potentiometer. The solutions were analyzed at 25.0 ± 0.1° C.

Table III shows that the change in the half-wave potential agrees very well with the value of -0.059 V. predicted by equation (2) for the reduction of silver ion on a silver electrode. Therefore, it is essential for reactions of this type, to specify the concentration of the ion whenever the half-wave potential is reported.

It will be noted that the average half-wave potential (0.33 V.) listed in Table I does not agree with the value (0.29 V.) calculated for a 5.0×10^{-4} M.

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*The sign of the potential is reversed from the convention in Latimer's "Oxidation Potentials" to agree with the sign of the polarographic electrode.

Table III

Effect of Changes in Concentration of Silver Ion on its Half-Wave Potential in 0.1 M Potassium Nitrate at pH 4.00

Concentration M.	$E_{\frac{1}{2}}$ Trial 1	Trial 2	Average	$\Delta E_{\frac{1}{2}}$
1.000×10^{-2}	+0.372	+0.375	+0.374	
				-0.055
1.000×10^{-3}	+0.316	+0.322	+0.319	
				-0.057
1.000×10^{-4}	+0.275	+0.259	+0.262	

solution from Table III. It is felt that the latter is a better value because the analyses were obtained under better conditions.

Equation (1) may be tested by calculating f_s after substituting values for E^o (10) with its sign changed and referred to the saturated calomel electrode, $E_{\frac{1}{2}}$ and C. For a 1.00×10^{-3} M. solution one finds:

$$0.059 \log f_s = -(0.80 - 0.25) + 0.32 - 0.059\ (-3.30) \qquad (3)$$

$$f_s = 0.3 \qquad (4)$$

It is readily apparent that this value is not logical and that is is probably about 0.8. Junction potentials and overvoltage are probably the sources of this difference and these effects need total only 0.02 V. to eliminate the discrepancy. An additional consideration which may not be negligible is the formation of a nitrate complex which undoubtedly exists to some extent although no data concerning its stability have been found.

A shift in the $E_{\frac{1}{2}}$ with dilution would not be expected if a soluble ion were produced because $E_{\frac{1}{2}}$ is described by:

$$E_{\frac{1}{2}} = E^o + \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}} \qquad (5)$$

or by

$$E_{\frac{1}{2}} = E_f^{\ o} + \frac{RT}{nF} \ln \frac{c_{ox}}{c_{red}} \qquad (6)$$

At $E_{\frac{1}{2}}$, C_{ox} is essentially equal to C_{red} making $E_{\frac{1}{2}}$ independent of the initial concentration of ferric ion. In order to check this point, the experiments reported in Table IV were carried out.

Attempts to obtain values for 1.00×10^{-5} M. solutions were unsuccessful because the diffusion current was too small. The slight drift of the $E_{\frac{1}{2}}$ toward positive potentials may be real although it is within the reproducibility limits of the experiment.

Effect of concentration of reducible ion on the diffusion current - application to quantitative analysis:

It is obvious that any study designed to test the accuracy of a quantitative method should be carried out under conditions favoring high precision. From the previous discussion, one can see that a quiet solution, a small electrode area, and a moderate rate of change in the polarizing voltage represent such a set of conditions.

A great deal of care was exercised to minimize errors that might result from slight changes in the procedure. For example, the solution was allowed to stand for an interval of several minutes following the deaeration in order to make certain that the polarographic solution was not in motion. In order to avoid the need for thermostating the solutions, they were allowed to stand in the room for several hours after they had been prepared. Then, after they had reached room temperature, each series was run in quick succession.

Table IV

Effect of Concentration on the Half-Wave Potential for the Ferric to Ferrous Reduction in 0.1 M. Hydrochloric Acid.

Concentration M.	$E_{\frac{1}{2}}$ Trial 1	Trial 2	Average	$\Delta E_{\frac{1}{2}}$
1.00×10^{-2}	+0.514	+0.505	+0.510	
				+0.003
1.00×10^{-3}	+0.520	+0.506	+0.513	
				+0.006
1.00×10^{-4}	+0.527	+0.511	+0.519	

Note:

The E^{o}, or more exactly, the E_f^{o} for the reaction

$$Cl^{-} + Fe^{+++} \rightleftharpoons FeCl^{++} + e$$

under the conditions of this experiment is -0.76 V. Agreement with the E^{o} value of -0.77 V. given in Latimer's book for the reaction

$$Fe^{++} \rightleftharpoons Fe^{+++} + e$$

is coincidental.

temperature of the room and the solutions did not appear to change noticeably ($\pm$ 0.1° C.) during the interval of time required to make the analyses. As a result, the precision of the analyses appeared to be higher than that found in the results reported in Table I.

The relation between the diffusion current and the concentration was shown to be linear (Figures 8, 9, and 10) with the three sizes of electrodes that were examined. The values plotted on the graphs represent single determinations rather than averages of two or more determinations. Attempts to duplicate these curves were very successful. For currents greater than 3 uA, differences between two values for a given solution were usually less than 10%, often 5%. For currents less than 3 μA agreement was in the order of 10 to 20% (i.e. $\pm$ 0.1 μA)*.

Other applications.

The recording of curves for other ions, singly and in simple mixtures, has been tested and found to be as satisfactory as for silver. Thus it is possible to use the usual polarographic recording techniques to make qualitative and semi-quantitative analyses for ions such as Ce^{4+}, MnO_4^-, and $Cr_2O_7^{--}$ more easily than when a dropping mercury electrode is used. Analyses for these ions have heretofor been complicated by the spontaneity of their reactions with mercury. Similarly, oxidations of $N_2H_5^+$, Cr^{3+} and other ions which were impossible because of the anodic dissolution of the dropping mercury electrode have been examined with a platinum electrode. These studies will be reported later.

Solid electrodes offer other advantages. It has been possible to make analyses in solutions containing hydrofluoric acid by using a plastic cell and by coating, with wax, the glass in which the platinum electrode is embedded. It appears plausible to expect a solid electrode to be used for studies in liquid ammonia and similar solvents at temperatures below the freezing point of mercury.

Acknowledgment

The authors are indebted to D. B. Ehrlinger for making some of the measurements reported in this paper.

Summary

1. Contrary to what one might have predicted from the work of Laitinen and Kolthoff, well-defined and reproducible current-voltage curves can be obtained for silver ion using a stationary platinum micro-electrode and a continuously changing potential.

2. The half-wave potential of silver in a 0.1 N KNO_3 nitrate solution

*It appears that the precision, particularly in the case of the larger diffusion currents, might be improved appreciably. For example, studies that were made after the work reported above had been completed indicate that more elaborate precautions in the cleaning of the electrode resulted in a slightly more reproducible diffusion current. These experiments will be reported in a separate paper in connection with other studies.

Figure 8

Relation between concentration and diffusion current for a one mm. electrode (0.02 cm^2) in quiet solutions. Rate of polarization - 1.46 mv/sec.

Drawing # 5037

FIG. 8

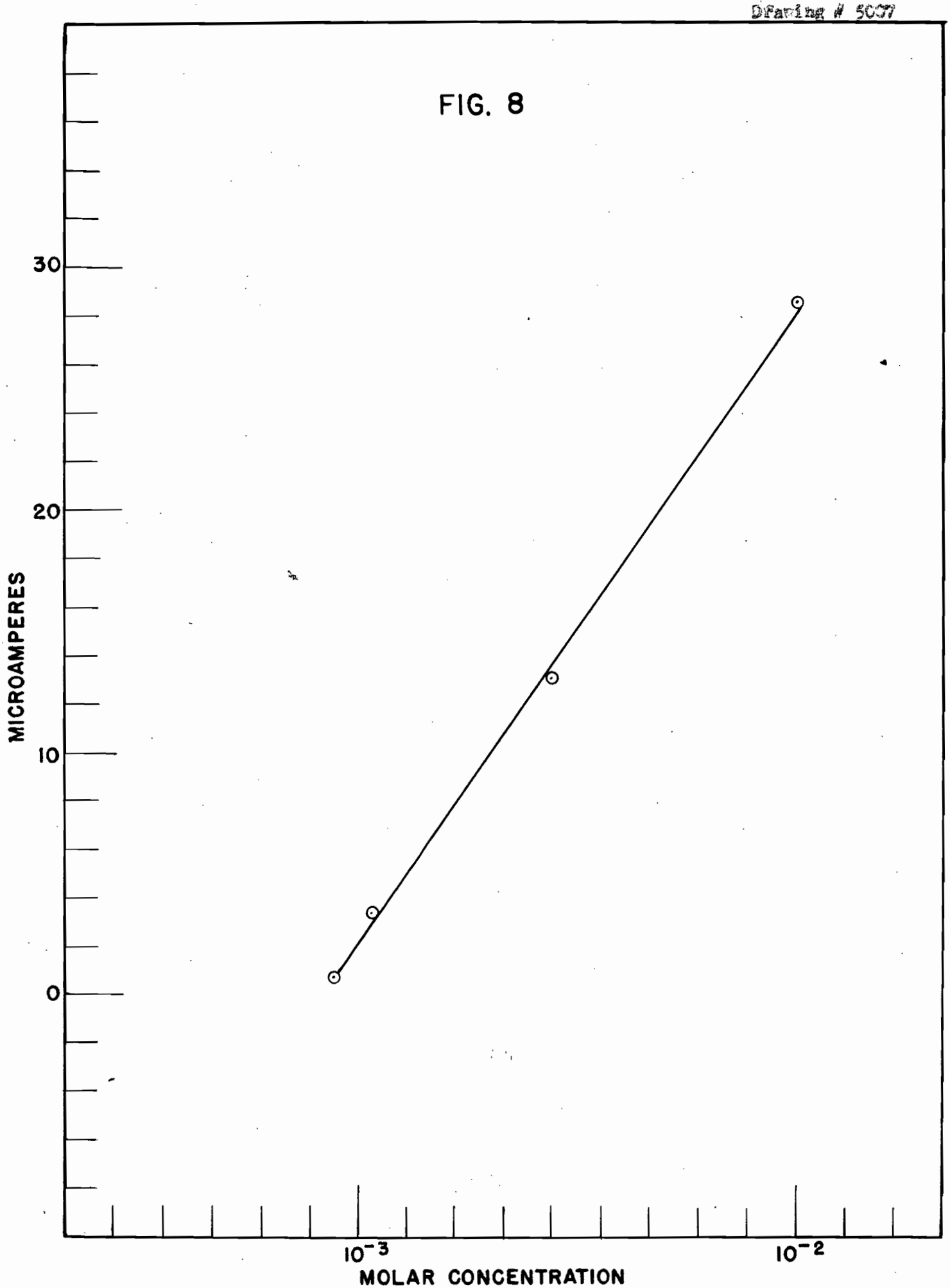


Figure 9

Relation between concentration and diffusion current for a six mm. electrode (0.10 cm^2) in quiet solutions. Rate of polarization = 1.46 mv/sec.

Drawing # 5002

FIG. 9

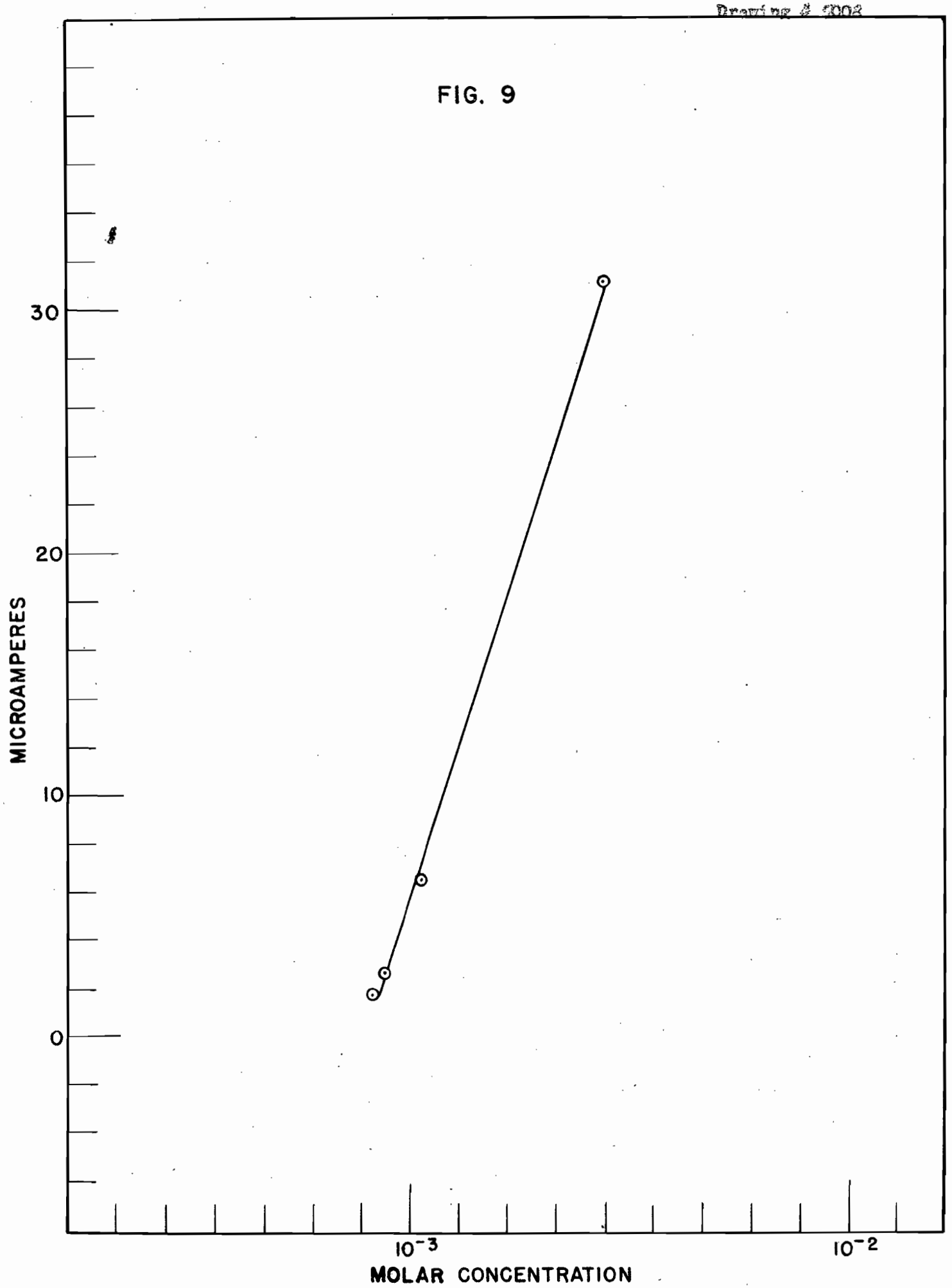
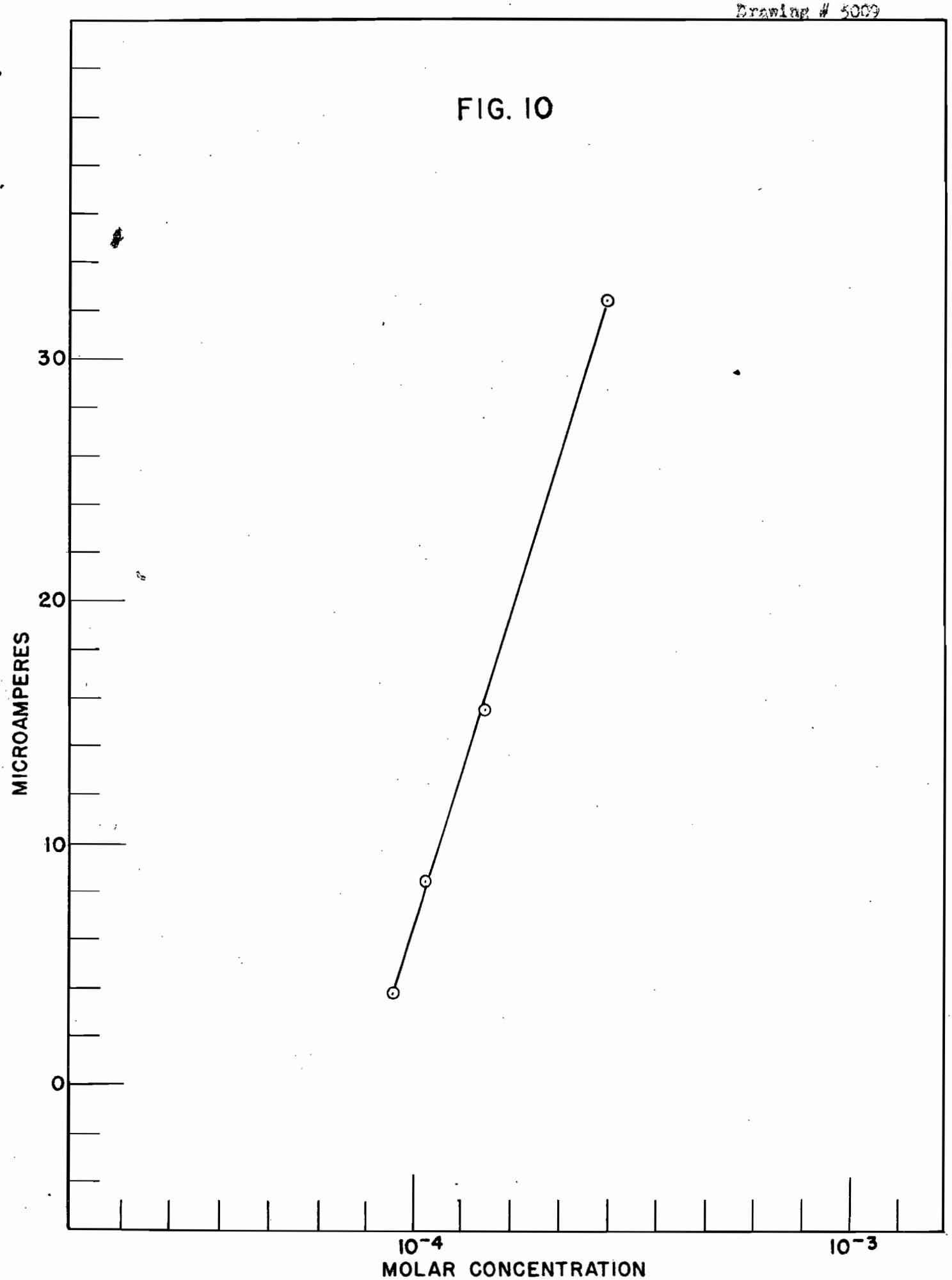


Figure 10

Relation between concentration and diffusion current for a foil electrode (2.14 cm^2) in quiet solutions. Rate of polarization - 1.46 mv/sec.

Drawing # 5009

FIG. 10



of pH 4.00 is independent of the direction of polarization, the rate changing the voltage, and the size of the electrode. It does, however, depend upon the concentration of silver ion according to predictions based upon the Nernst equation.

3. Stirring decreases the reproducibility of both the half-wave potential and the diffusion current. Stirring appears to produce a slight shift of the half-wave potential toward more negative potentials but the extent of the shift is barely larger than the experimental limits of error.

4. The diffusion current increases with the size of the electrode, the rate of polarization, and the speed of stirring. These observations can be used to extend the range of the method to more dilute solutions.

5. Stationary platinum electrodes give a linear relationship between diffusion current and concentration with an accuracy which allows the method to be used for semi-quantitative determinations.

6. A round maximum is usually obtained in quiet solutions, the size of the maximum appearing to increase with electrode area and concentration of reproducible ion. The maximum may result from the time lag in reaching a state of diffusion equilibrium. No maxima were observed in stirred solutions.

7. Solid electrodes offer advantages over the dropping mercury electrode for analyses in the region of positive potentials (vs. S.C.E.), in solutions of hydrofluoric acid, and in solutions at low temperatures.

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Y-12 OPERATIONS DIVISION
Received: JAN 9 1948
Entered: JAN 9 1948