INVESTIGATIONS OF

POLAROGRAPHIC ELECTRODES

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By

ROY F. MANESS

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APPROVED BY:

Paul Arthur

Chairman, Thesis Committee

Tom E. Moore

Member of the Thesis Committee

O C Dermer

Head of the Department

H. G. McIntosh

Dean of the Graduate School

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Historical

The type of dropping electrode that is now commonly employed in
polarographic analysis was originally designed by Professor G. Kucera
at the Charles University about fifty years ago for a quite different
purpose, namely, for investigations of the electrocapillary curve of
mercury in various solutions.[1] During the course of his investigations
Kucera observed certain peculiar inflections in the electrocapillary
curve when the solutions contained reducible substances, and further
investigations by Heyrovsky ultimately led to the development of the
polarographic method of analysis.[2]

The polarographic method of analysis was invented in 1922 by
Professor Jaroslav Heyrovsky of Prague, and its development during the
first fifteen years was largely due to the efforts of this investigator
and his collaborators. The method is based on the interpretation of
the current-voltage curves that are obtained when solutions of electro-
reducible or electrooxidizable substances are electrolyzed in a cell
in which one electrode is a dropping mercury or other microelectrode
and the other a non-polarizable electrode. From the unique character-
istics of such current-voltage curves both the species and concentration
of the electroreducible or electrooxidizable substances present in the
solution can be determined. Originally, Heyrovsky worked with a

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[1] G. Kucera, Ann. Physik, 11, 529 (1903).

[2] J. Heyrovsky, Chem. Listy, 16, 256 (1922).

manual apparatus, and he introduced the term polaromentry (polarized electrodes) for voltammetry carried out with the dropping electrode. Later, when Heyrovsky and Shikata (1925) constructed the self-registering apparatus for the determination of current-voltage curves, the word polarography was introduced. The apparatus was called the polarograph, and the current-voltage curve obtained with it a polarogram. The steep part of the current-voltage curve is called a wave.

As many as five or six different substances may be simultaneously detected and determined from a single polarogram under favorable conditions. The method is especially suitable for small concentrations (10^{-6} to 10^{-2} molar), and since the analysis can be performed with a small volume of solution, mere traces of substances can be determined. A large number of substances, both organic and inorganic, which are reducible, and a smaller number which are oxidizable at the dropping mercury electrode give characteristic polarographic waves. The development of the rotating platinum microelectrode by Laitinen and Kolthoff[3] in 1940 considerably increased the number capable of being oxidized with the self-registering apparatus. These facts, coupled with the advantage of obtaining a simultaneous qualitative and quantitative analysis in a single operation, make the polarographic method a valuable new addition to present analytical methods. Under ordinary conditions the accuracy of the polarographic method is of the order of $\pm$ 2 per cent in the concentration range from about 10^{-4} to 10^{-2} molar, and about $\pm$ 5 per cent

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[3] H. A. Laitinen and I. M. Kolthoff, J. Phys. Chem., 45, 1061 (1941).

between 10^{-5} and 10^{-4} molar. By taking special precautions it is possible to obtain greater accuracy in some cases. Considering the small concentrations that are involved, this degree of accuracy is quite satisfactory and compares favorably with the accuracy of other methods.

Publications on polarographic analysis did not begin to appear in American journals until 1937, at which time the subject had already enjoyed fifteen years of active growth in Europe and about three hundred papers pertaining to it had been published in foreign periodicals. In addition the well known monographs by Semerano[4], Heyrovsky[5], and Hohn[6] had appeared. The first monograph on polarography in English did not make its appearance until 1941[7], and by that time the publications in the field numbered nearly nine hundred. During the last eight years the bibliography of the subject has increased to more than fifteen hundred works. The task of keeping abreast of these has been lightened in no small measure by the excellent bibliographies which Heyrovsky is continuing to publish[8], and the bibliographies being distributed by the Leeds and Northrup Co. (literature up to 1941) and the E. H. Sargent Co. (literature up to 1945). The present well established status of

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[4] G. Semerano, Il Polarografo, Padova, A. Draghi, 1933.

[5] J. Heyrovsky, Polarographic Method. Theory and Practical Applications, (in Russian), Leningrad, 1937.

[6] H. Hohn, Chemische Analyse mit dem Polarographen, Berlin, Julius Springer, 1937.

[7] I. M. Kolthoff and J. J. Lingane, Polarography, New York, Interscience Publishers, 1941.

[8] J. Heyrovsky, Collection Czechoslov. Chem. Commun., 10, 153 (1938); 11, 98 (1939); 12, 156 (1947).

polarography in modern analytical practice is demonstrated by Strong's recent statistical survey[9] of all research papers published in the field of analytical chemistry during 1946 which places polarographic analysis among the five most popular instrumental methods.

[9] F. C. Strong, Ind. Eng. Chem., Anal. Ed., 19, 968 (1947).

Introduction

Dropping Mercury Electrode: A capillary suitable for use as a dropping mercury electrode may be prepared by drawing out a piece of 0.5mm. pyrex capillary tubing. The tubing should be allowed to thicken somewhat in the flame so that the drawn-out capillary will not be too slender and fragile. The tip should have a uniform internal diameter of about 0.03mm. for at least 2 cm. of its length. Capillary tubing such as marine barometer tubing produced by the Corning Glass company is commercially available, and suitable pieces may be used directly as electrode capillaries.

In order to obtain reproducible results, the capillary must be kept immaculately clean. The drop time should be from three to six seconds and should be exactly reproducible for a given capillary. In order to maintain a constant rate of flow through the capillary it is necessary to have a constant head of mercury.

On the basis of diffusion theory, Ilkovic[10] derived the following equation for the diffusion current at the dropping mercury electrode:

$$i_d = 0.63 \ nFCD^{1/2}M^{2/3}t^{1/6}$$

in which the numerical factor 0.63 arises theoretically from the geometric characteristics of the dropping electrode, nF is the number of coulombs involved per mole of electron reaction, C is the concentration, D is the diffusion coefficient of the diffusing material, M is the mass of mercury flowing through the capillary per second, and t is the drop time. In the equation i_d is expressed in amperes, C in moles per

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[10] D. Ilkovic, Collection Czechoslav. Chem. Commun., 6, 498 (1934); J. Chem. Phys., 35, 129 (1938).

milliliter, $\underline{D}$ in square cm. per second, $\underline{M}$ in grams per second and $\underline{t}$ in seconds. The measured diffusion currents for various substances have been found to be in essential agreement with those calculated from the Ilkovic equation.[11]

The quantity $M^{2/3}t^{1/6}$, which is determined by the characteristics of the capillary and the head of mercury used, may be used to establish a relationship by means of which diffusion currents measured with different capillaries may be compared. It is necessary only to determine the mass of mercury flowing per second through each capillary, and the drop time at the diffusion-current region.

Lingane and Loveridge[12] tested the predicted linear relation between i_d and $M^{2/3}t^{1/6}$ with capillaries covering a range of M-values from 0.9 to 16 mg. per second and a range of drop time from 0.5 to 9 seconds. Measurements were made with lead ion in 1 $\underline{M}$ potassium chloride and with zinc ion in 1 $\underline{M}$ ammonium chloride with 0.01 per cent gelatin as a maximum suppressor. All known precautions were taken to prevent experimental errors, and a percision of $\pm$ 0.5 per cent was attained. The results showed that the equation holds quite well at drop times above 3 seconds, but that it fails seriously at drop times of 1.5 seconds or less.

The surface tension of mercury, and therefore the drop time of the capillary, varies according to the charge on the mercury. It has been reported[13] that the quantity $M^{2/3}t^{1/6}$ is practically constant from 0 to

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[11] J. J. Lingane and I. M. Kolthoff, J. Am. Chem. Soc., 61, 825 (1939).

[12] J. J. Lingane and B. A. Loveridge, J. Am. Chem. Soc., 66, 1425 (1944); 68, 395 (1946).

[13] I. M. Kolthoff and J. J. Lingane, Chem. Rev., 24, 1 (1939).

-0.8 volts vs. the saturated calomel electrode, but is 10 per cent lower at a potential of -1.9 volts. In the analysis of mixtures this variation of $M^{2/3} t^{1/6}$ with voltage may be quite important.

Whenever a solution of an indifferent electrolyte is electrolyzed with the dropping mercury electrode, a small residual current flows before the decomposition of the solution begins. It arises from the fact that, as each electrically charged mercury drop grows, it is necessary to build up a charge on the mercury corresponding to the applied potential. This residual current must in each case by subtracted from the observed current in order to obtain the true diffusion current.

The advantages and disadvantages of the dropping mercury electrode are summarized below.

Advantages:

1. The surface is reproducible.
2. The electrode is continually renewed, which tends to prevent contamination and crystal growth.
3. The value of the overvoltage of hydrogen is high on mercury so that work can be done at high negative potentials and in acid solutions without interference from the evolution of hydrogen.
4. The current assumes a steady value immediately and is reproducible.

Disadvantages:

1. The electrode is limited in the direction of positive potentials by the anodic dissolution of mercury. This occurs at about +0.35 volts vs. the S.C.E.

2. The residual current is relatively large owing to the condenser
effect produced by the mercury drops.

3. Oscillations occur in the current-voltage curve due to the
growth of the mercury drops, these oscillations making it
difficult to obtain accurate readings.

4. The electrode requires fairly large quantities of highly pure
mercury.

5. Maxima frequently distort the current-voltage curves produced
with the dropping mercury electrode unless measures are taken
to prevent their occurrence. The use of a dilute solution of
gelatin, 0.01 per cent, is generally sufficient to suppress
their appearance.

Special Mercury Electrodes: In order to increase the size of the mercury
drops Riches[14] suggested the use of a dropping electrode capillary with
the radius at the orifice greater than the radius higher in the tube.
The electrode is constructed by sealing a short length of relatively
large capillary tubing to the bottom of a conventional dropping
electrode capillary, and by proper choice of dimensions an electrode is
obtained with a normal drop time but with a large flow of mercury.
Because of the large $M^{2/3}t^{1/6}$ factor the diffusion current measured with
this type of electrode is much larger than with the conventional type.
Unfortunately, however, the residual current, which also depends on the
rate of flow of mercury, is increased correspondingly and consequently
there is little, if any, net gain in accuracy.

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14 J. P. R. Riches, Nature, 157, 520 (1946).

The use of a multiple-tip electrode, four tips joined to a common tube, has been reported by De Vries and Barnhart[15] as a means of increasing the diffusion current. Here again the residual current increases as the diffusion current increases so that no real gain in accuracy is produced.

Heyrovsky and Forejt[16] invented the streaming mercury electrode for use in oscillographic studies. It consists of a jet of mercury issuing upward from a capillary tube into the test solution. It constitutes a cylindrical electrode whose surface is continuously renewed but which retains a constant area defined by the size of the capillary tip, which is about 0.1 mm. in diameter, and the distance between the capillary tip and the surface of the solution (4 to 8 mm.). The jet electrode is supplied with mercury at about 50 cm. pressure from the usual type of leveling bulb reservoir. The reported reproducibility of the electrode leaves much to be desired.

Solid Microelectrodes: The stationary platinum microelectrode consists of a platinum wire about 4 mm. long and 0.5 mm. in diameter sealed into a piece of glass tubing into which mercury is introduced for electrical contact.

Although the stationary platinum microelectrode is simple in principle, it has certain disadvantages in practical work which has led to the development of other types of microelectrodes in polarography.

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15 T. De Vries and W. S. Barnhart, Ind. Eng. Chem., Anal. Ed., 19 934 (1947).

16 J. Heyrovsky and J. Forejt, Z. physik. Chem., 193, 77 (1943).

The current does not immediately become constant after applying a given potential to the microelectrode and it is necessary to wait approximately two minutes before a steady current state is reached at each applied voltage. The attainment of a steady current state depends on reaching a state of uniform and reproducible diffusion in the solution so it is necessary to perform the experiments in a solution maintained at constant temperature to avoid thermal convection. Also any mechanical disturbances, such as vibrations from the thermostat stirring motor, must be avoided.

In contrast to the dropping mercury electrode, when a steady state of diffusion is attained at solid microelectrodes, the actual diffusion current is given by the following expression which is derived from Fick's first law of diffusion: $i_d = \frac{AD}{l} nFC$ where $\underline{C}$ is the concentration of the electroactive material with a diffusion coefficient $\underline{D}$, diffusing through a diffusion layer of effective thickness $\underline{l}$, to an electrode of area $\underline{A}$. $\underline{n}$ is the number of electrons involved in the electrode reaction, and $\underline{F}$ is the faraday.

The influence of temperature on the diffusion current may be expected to be quite significant, because the equivalent conductances of most ions increase about 2 per cent per degree. With a stationary platinum micro-electrode the temperature coefficient of the diffusion current is larger, being about 4 per cent per degree. In order to measure diffusion currents with an accuracy of $\pm$ 1 per cent, the temperature should be controlled to at least $\pm$ 0.5° with a dropping mercury electrode, and to $\pm$ 0.25° with stationary microelectrodes.

Workers at the Oak Ridge National Laboratory[17] have recently reported attempts to employ the usual polarographic procedure with stationary solid microelectrodes. Time maxima were found to occur whose magnitude seemed to depend on the rate of increase of the polarizing voltage. Reproducibility was poor in comparison with that of the dropping mercury electrode.

The disadvantage of having to wait two minutes at each value of the applied voltage for a steady current state is eliminated by the use of the rotating electrode. Nernst and Merriam[18] were the first to describe current-voltage curves obtained with a rotating platinum electrode. They reported constant regions of diffusion current, which were found to be proportional to the concentration in the electroreduction of iodine, bromine, chlorine, silver ions, and permanganate ions in an excess of indifferent electrolyte. In other cases, such as the electroreduction of dichromate, chlorate, ferricyanide, and persulfate ions, and the electrooxidation of ferrocyanide, ferrous, and stannous ions, a much smaller current was observed than was expected and no well defined diffusion-current regions were observed.

A similar type of investigation was carried out by Rosenthall, Lorch and Hammett[19] on the kinetics of the electrode reaction of the system quinone-hydroquinone, using very rapidly rotating electrodes. It was reported that a speed of rotation could be reached beyond which an

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[17] L. B. Rogers, H. H. Miller, R. B. Goodrich, and A. F. Stehney, Anal. Chem. 21, 777 (1949).

[18] W. Nernst and E. S. Merriam, Z. physik. Chem., 52, 235 (1905).

[19] R. Rosenthall, A. E. Lorch, and L. P. Hammett, J. Am. Chem. Soc., 59, 1795 (1937).

increased rate of rotation no longer influenced the current. Under these conditions the current was determined only by the rate of the electrode reaction itself, which was strongly influenced by the catalytic properties of the electrode surface.

A rotating platinum microelectrode to be used at a constant speed of rotation is described by Laitinen and Kolthoff[20]. The electrode consists of a platinum wire 3.2 mm. long and 0.5 mm. in diameter on one side of an iron shaft. Two flanges on each side of the electrode protect it from mechanical damage or bending when the electrode is inserted into a rubber stopper. A mercury-seal device is used to prevent the entrance of air, and also serves to make electrical contact to the electrode. The entire iron shaft is coated with several layers of ceresin wax for electrical insulation, and the wax carefully scraped away from the platinum wire. The bearing surface of the shaft consists of two 1/2 inch portions of the brass cover section, with a one-inch portion in the middle machined away from the shaft to decrease friction. This electrode was rotated by means of a synchronous motor operating at exactly 1800 rpm. A small pair of gears served to reduce the speed to 600 rpm.

The advantages to be sought in applying the rotating platinum microelectrode rather than the dropping mercury electrode are increased sensitivity and greater simplicity and convenience. Increased sensitivity is brought about by increasing the rate of diffusion by stirring. The absence of a condenser current decreases very markedly the residual current. The fact that the diffusion current is steady rather than fluctuating is an obvious advantage in simplifying measurements.

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[20] H. A. Laitinen and I. M. Kolthoff, J. Phys. Chem., 45, 1061 (1941).

However, the scope of the rotating electrode is much narrower than that of the dropping mercury electrode. First, many systems yield highly irreversible current-voltage curves at rotating microelectrodes. For example, dichromate does not yield a cathodic diffusion current. Secondly, the low hydrogen overvoltage of platinum is a limitation in the range of negative electrode potentials. Thirdly, the electrode surface is not renewed continually during operation; hence the behavior of a solid microelectrode may depend somewhat upon its previous history.

In spite of these limitations, it may be said that in general if a given analysis may be performed with both the dropping mercury electrode and the rotating platinum microelectrode, the latter is preferable for routine work. This is especially true of amperometric titrations.

Muller[21] devised a new technique of polarographic measurements with a platinum microelectrode which involves flowing the solution past the electrode in a constricted glass tube. Under optimum conditions the limiting currents were found to be a linear function of the concentration of the electroactive substance and the logarithm of the rate of flow.

[21] O. H. Muller, J. Am. Chem. Soc., 69, 2992 (1947).

Scope of Research

The purpose of the following experimental work was to devise and test
new forms of electrodes which might be applicable to polarographic analysis
as the indicator electrode. There was an attempt to retain as many as
possible of the advantages of existing electrodes while removing their
disadvantages. The principal characteristics sought were:

1. Reproducibility.

2. Wide range.

3. Smooth current-voltage curves when used with the automatic
   polarograph.

4. Minimum residual current.

5. Simple sturdy design which would require a minimum of manipulation.

6. Renewable surface.

7. Elimination of the use of relatively large quantities of mercury.

Experimental Details

Reagents and Solutions: All chemicals used in the investigation were reagent grade, and all solutions were prepared with distilled water. The concentration of all solutions were known within one per cent.

Tank nitrogen, when used for removing oxygen from the polarographic cell, was freed of oxygen by passing it successively through two gas-washing bottles of alkaline pyrogallol followed by one of concentrated sulfuric acid. Whenever possible sodium sulfite was added to the solution to remove oxygen.

Apparatus: Polarograph Model XII, manufactured by the E. H. Sargent Co. was used as the continuous-recording instrument. The basic circuit for the polarograph is shown in Fig. 1. Essentially it consists of a uniform slide wire around a drum, connected by a set of gears to a cylinder housed in a light-tight compartment and carrying a sheet of photographic paper. The potential drop across the slide wire is adjusted to any desired value by means of a battery, a series resistance, and a voltmeter. The drum carrying the slide wire is rotated either manually or by means of an electric motor, and as it revolves continually increasing voltage is applied to the electrolysis cell. The meter is a sensitive d'Arsonval galvanometer, which possesses a long period. A line of light from a galvanometer lamp is reflected by the moving mirror of the galvanometer on to both the photographic paper and a visual scale on the front of the instrument case. The housing of the photographic cylinder is provided with a narrow slit, which can be opened or closed by a shutter on the revolving drum assembly and through which the light beam of the galvano-meter enters.
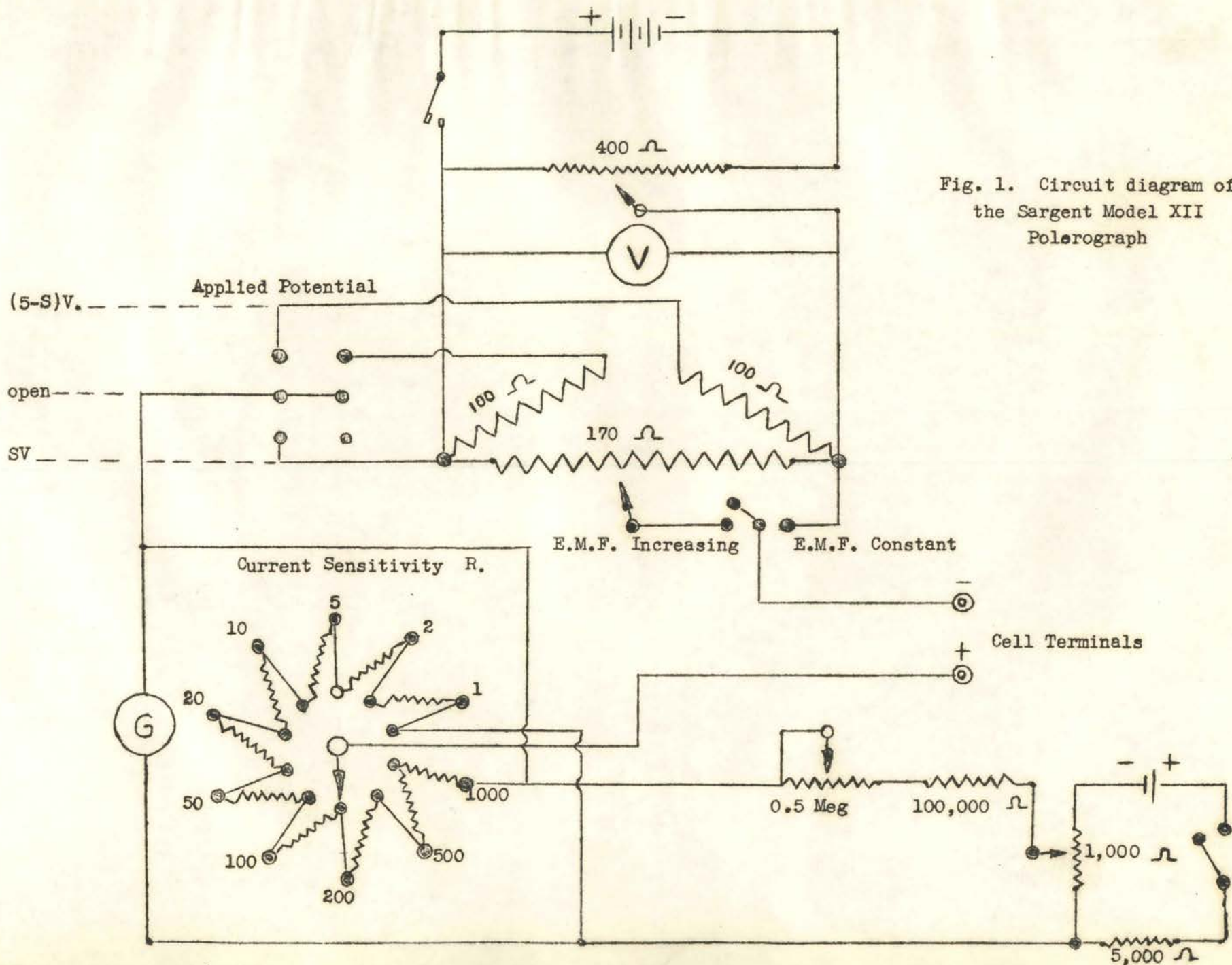
Fig. 1. Circuit diagram of the Sargent Model XII Polerograph

A reversing switch is provided to allow either anodic or cathodic voltages to be applied to the microelectrode. In one position, a shunt is connected by means of which one electrode may be connected to the middle of the slide wire allowing the other electrode to pass from positive through zero to negative potentials. In the other position, the slide wire is connected so as to apply a gradually increasing potential from zero to the maximum value given by the voltmeter.

The current sensitivity knob manipulates an Ayrton shunt in parallel with the galvanometer. The readings indicate the fraction of the total current actually passing through the galvanometer.

As was indicated, it is possible to use this instrument to obtain manual current-voltage curves. However, the manual curves obtained in this research were obtained by means of a manual apparatus assembled by Professor Paul Arthur of the Oklahoma A. and M. Chemistry staff. A wall-type Leeds and Northrup galvanometer was used in this assembly.

Assemblies and Results

Flowing Mercury Electrodes: The first form of microelectrode studied
utilizing a flow of mercury is shown in Fig. 2. The capillary, which
determines the area of mercury exposed to the test solution, was 1.5 mm.
in diameter, and with a flow of mercury of one gram per second gives
approximately the same sensitivity as the dropping mercury electrode.
The capillary at the end of the tubing through which the mercury flows,
makes the flow of mercury steady. The size needed to produce the
necessary back pressure was determined experimentally.

This electrode when used with the automatic polarograph acted
essentially like a stationary electrode, i.e., large time maxima occurred
and the diffusion current region, when present at all, was ill-defined.
When used with the manual apparatus, reproducible current-voltage curves
were obtained when a one-minute period was allowed to elapse at each
applied voltage before the current was recorded. As the waiting period
for a stationary microelectrode is two minutes, the advantage gained here
is insignificant.

This electrode has the advantage over a stationary electrode in that
there is some renewal of the electrode taking place; however, as the
electrode demonstrated that it is not applicable to automatic recording
instruments it was not tested further.

A second type of flowing mercury electrode studied is shown in
Fig. 3. Contact between the mercury and test solution is brought about
by drilling a hole 2 mm. in diameter into the tube conducting the mercury.
The remainder of the electrode is as the one previously described.
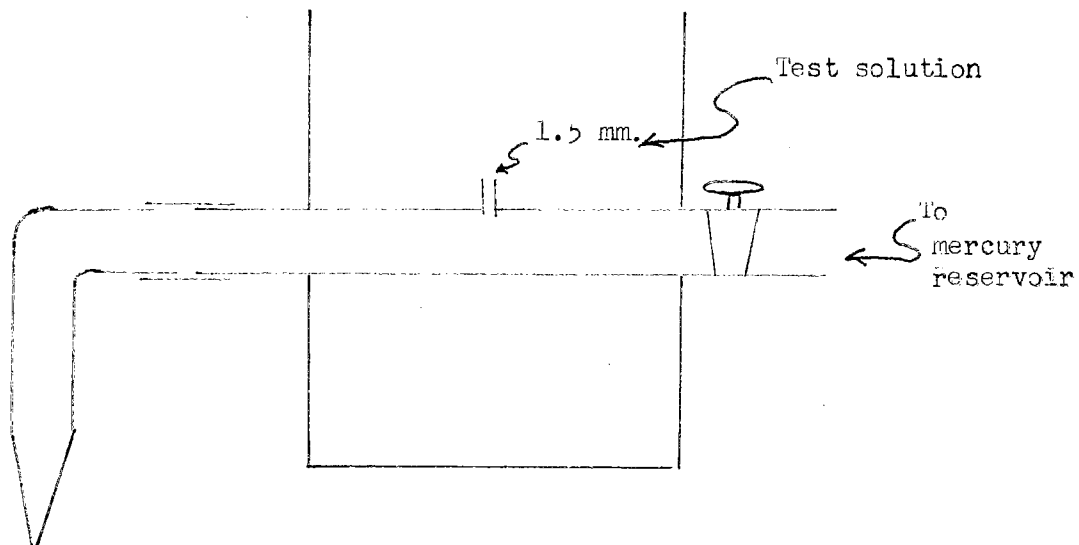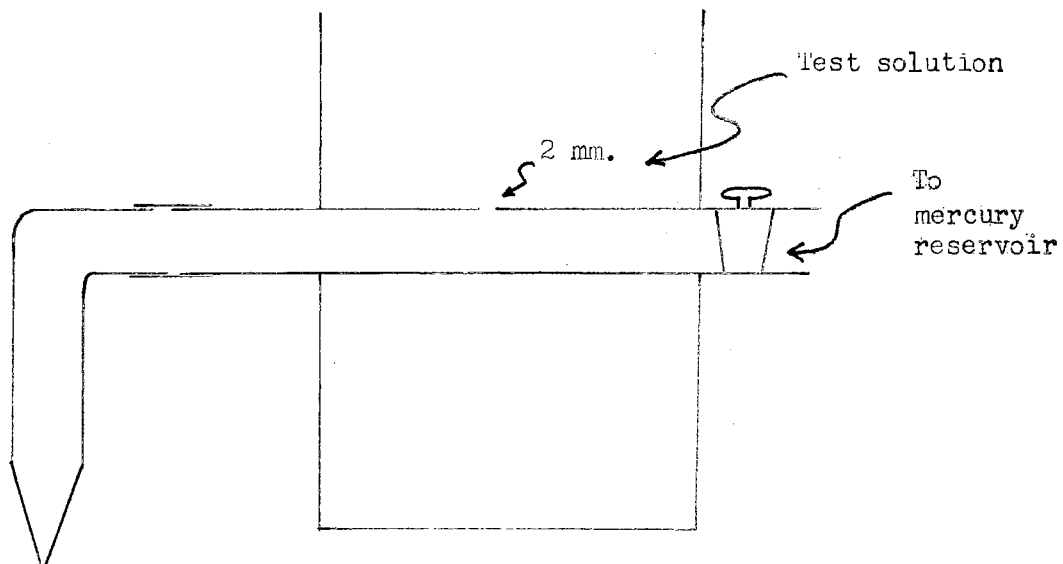
Fig. 2.   Type of Flowing Mercury Electrode

Fig. 3. Type of Flowing Mercury Electrode

A typical polarogram obtained with this electrode using the automatic polarograph is shown in Fig. 4. Maxima such as the one shown occurred in all cases; however, their magnitudes varied under apparently identical conditions. The maxima tend to indicate that the rate at which the system reaches diffusion equilibrium is slower than the rate at which the voltage changes.[22] Evidence for such an explanation is found in the observation that these maxima are not of the same type as those encountered with the dropping mercury electrode, in that the presence of gelatin does not suppress them. If this be the case, one would expect slower rates of polarization to produce curves with small maxima. Attempts were made to verify this conclusion, but the irregular occurrence of the maxima and the small variations in rate which could be attained with the apparatus available, prevented any quantitative conclusion concerning this effect.

Slight differences in the angle of the horizontal tube containing the mercury had considerable effect on the diffusion current and was probably largely responsible for the relatively poor precision attained, which was about 5 per cent.

The occurrence of the maxima and the relatively poor reproducibility of results obtained with this electrode discouraged further work on this type of electrode.

Rotating Electrodes: In view of the facts listed above, the investigation was directed toward different types of electrodes. The following is an investigation of the possibility of measuring half-wave potentials and diffusion current with rotating amalgamated electrodes at potentials where the rotating platinum electrode is ineffective.

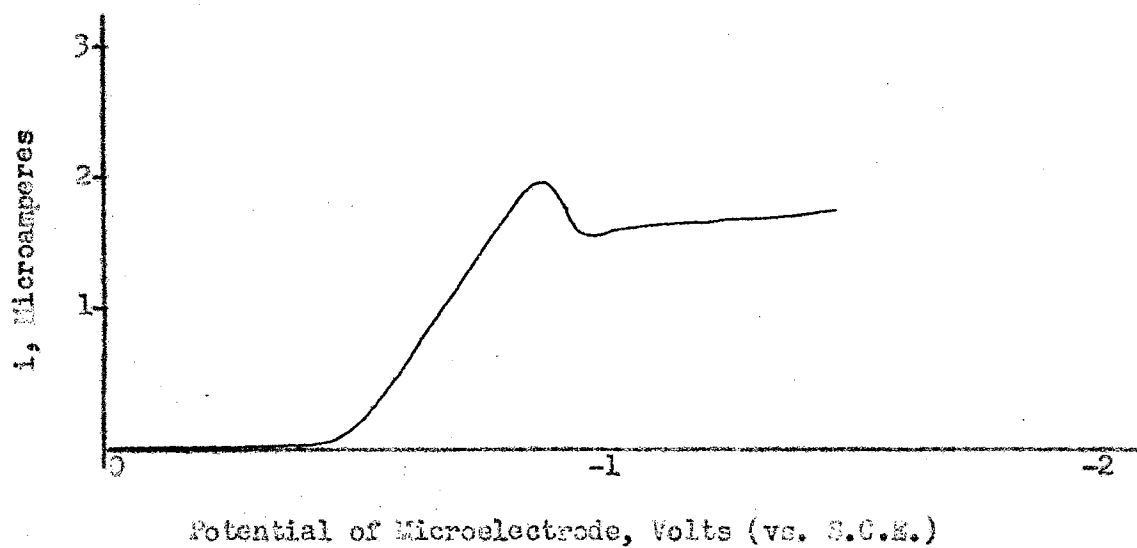[22] H. A. Laitinen and I. M. Kolthoff, J. Am. Chem. Soc., 61, 3344 (1939).

Fig. 4. Electrolysis of 10^{-3} $\underline{M}$ Cd^{++} in 0.1 $\underline{N}$ KCl using flowing mercury electrode.
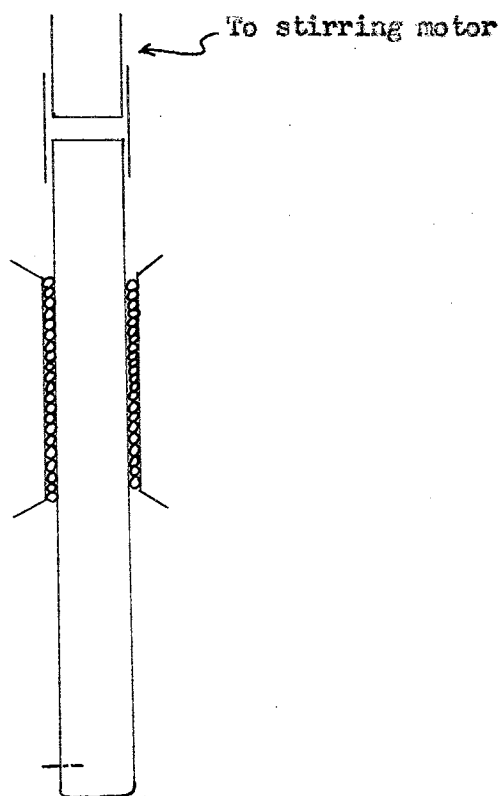

To stirring motor

Fig. 5. Rotating electrode assembly

Amalgamated electrodes were chosen so that the high hydrogen over-voltage of mercury could be utilized and to form an unstable surface so that metals which tend to deposit as crystals on platinum would fall off the surface and thus not appreciably increase the electrode area. The metals were plated on platinum instead of using the pure metal so that the electrode could be cleaned with acid and replated without significant change in its area. With this procedure various metals could be studied, removed and replaced with relative ease and good comparability.

The rotating-electrode assembly is shown in Fig. 5. The electrode consisted of a platinum wire 3.5 mm. long and 0.5 mm. in diameter on one side of an iron shaft. The iron shaft was coated with several layers of ceresin wax for electrical insulation, and the wax carefully scraped away from the platinum surface. One application of a thick coating was found to last indefinitely and to provide excellent electrical insulation and good protection from corrosion. The bearing was an ordinary bicycle front axle with a 5/16-inch shaft. The electrode was rotated with a variable-speed stirring motor whose rpm was checked occasionally by means of a tachometer. In all cases the speed of rotation was kept at 600 rpm. in accordance with the findings of Laitinen and Kolthoff.[23] Of the various types of electrical connections used, a brush contact, made of a strip of spring brass touching the shaft, proved to be the best.

A cork fitted into the electrolysis cell, with suitable openings, allowed an atmosphere of nitrogen to be kept above the solution in

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[23] H. A. Laitinen and I. M. Kolthoff, J. Phys. Chem., 45, 1061 (1941).

those cases where oxygen would interfere. Whenever possible, sodium
sulfite was used as the deoxygenating agent.

The electrodes used were gold and copper along with their amalgams.
They were prepared by plating the metal on the platinum electrode with a
known voltage and current. A 1 per cent alkaline solution of gold chloride
containing potassium cyanide and a 5 per cent solution of cupric chloride
in 50 per cent ethanol were used as the plating solutions. A potential of
two volts with a current of one milliampere for five minutes was used in
both cases. The gold electrode was amalgamated by dipping momentarily
into mercury whereas it was found necessary to dip the copper electrode
into 0.1 $\underline{N}$ mercuric chloride for one minute and then rub it lightly with
filter paper. As the polarographic set-up was used as the source of
potential and the voltage and current measuring device, the electrodes
could be prepared in a few minutes. The electrodes were cleaned between
runs by washing in about 5 per cent nitric acid and rinsing with distilled
water, it being found that several runs could be made in this way without
replating.

The voltage at which hydrogen was produced by decomposition of the
solvent is clearly indicated in Fig. 6. It can be seen that copper,
copper amalgam, and gold amalgam can be used at considerably more
negative potentials than can platinum.

The Deposition of Silver Ions

As the half-wave potential of silver is positive, it is possible to
use the rotating platinum electrode to obtain its polarogram. A number
of current-voltage curves for various concentrations of silver ion in
potassium nitrate were made using the rotating platinum electrode. In
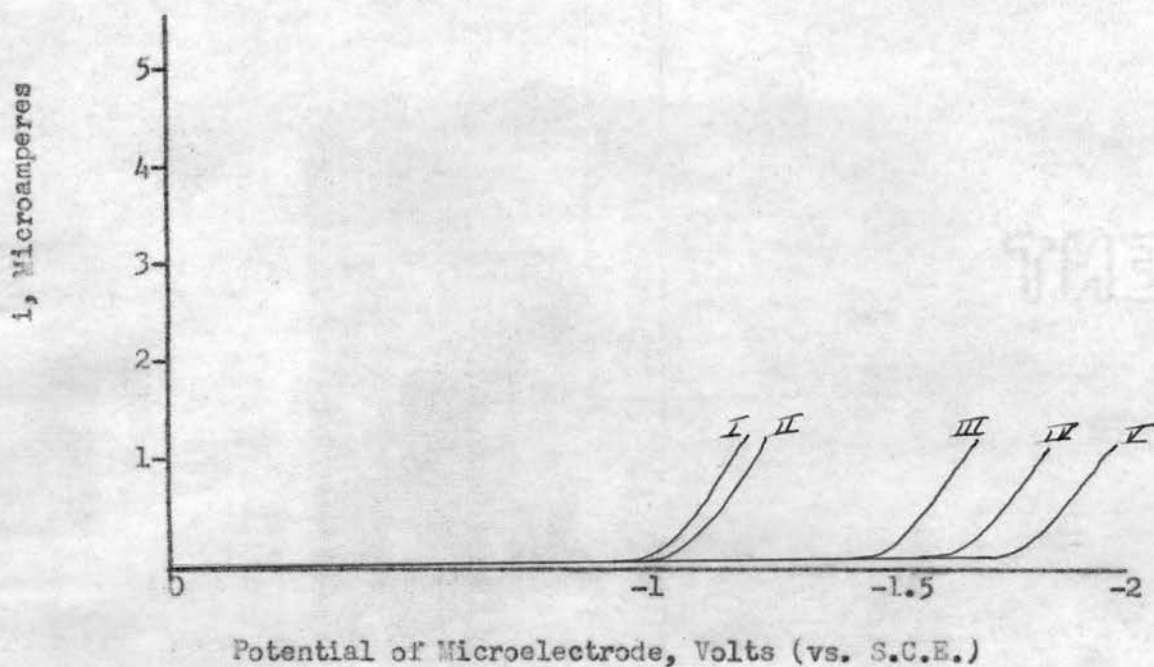
Fig. 6. Electrolysis in 0.1 $\underline{N}$ KCl. Curve I, platinum; Curve II, gold; Curve III, copper; Curve IV, gold amalgam; Curve V, copper amalgam.
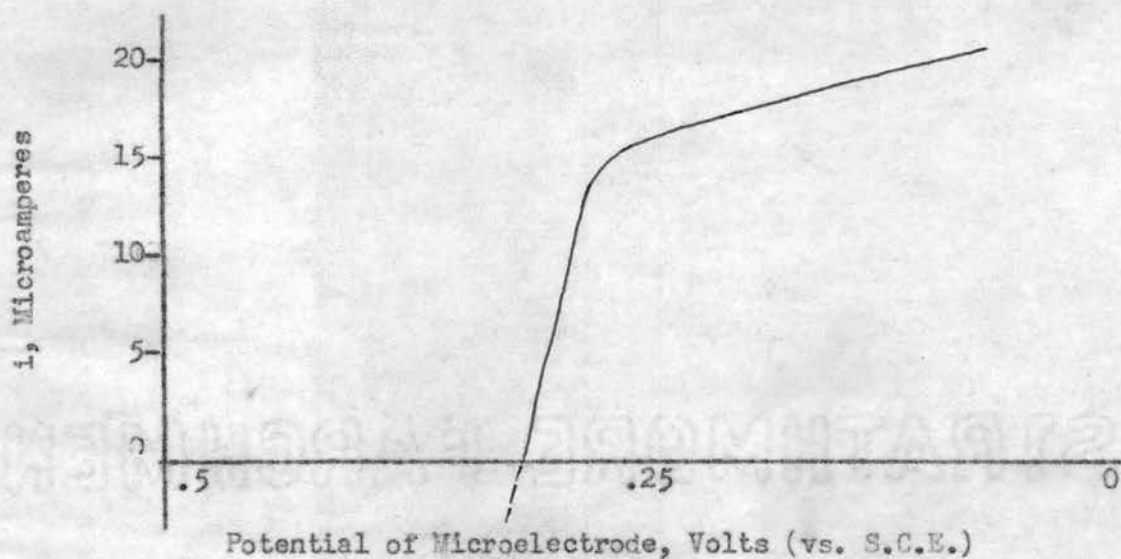

Fig. 7. Electrolysis of 10^{-3} $\underline{M}$ Ag^+ in 0.1 $\underline{N}$ KNO_3 using the amalgamated gold electrode.

the first experiments a flat residual current line followed by a steadily increasing current beginning at the decomposition potential of silver was observed. This seemed to be caused by a too high cell resistance, for when the salt bridge was redesigned to decrease the resistance, a diffusion current region was found. The diffusion current so obtained, however, increased with time and was not entirely reproducible. At the end of the electrolysis relatively large crystals of silver could be seen on the electrode, rather than a smooth coating. This would have the effect of increasing the electrode area considerably and thus the current should increase as the electrolysis proceeds. A simple calculation will show that the increase in area due to the formation of a smooth coating is quite small. On the addition of 0.01 per cent gelatin a smooth silver deposit was obtained and the diffusion current was found to be definite and reasonably constant.

In the use of the amalgamated gold electrode the diffusion current is found to be constant with or without the use of gelatin. In this case no crystal growth is observed presumably owing to the formation of a dilute silver amalgam and to the unstable nature of the surface to which the crystals would have to cling. A typical current-voltage curve obtained with 10^{-3} $\underline{M}$ silver nitrate in 0.1 $\underline{N}$ potassium nitrate is shown in Fig. 7.

The Deposition of Cadmium Ion

Excellent current-voltage curves (which could not be duplicated with the rotating platinum electrode owing to its limited voltage range) were produced with the rotating amalgamated electrodes. A typical polarogram is shown in Fig. 8 for 5×10^{-4} $\underline{M}$ cadmium chloride in 0.1 $\underline{N}$ potassium

chloride. As is to be expected, the diffusion current is much larger than with the dropping mercury electrode whereas the residual current is smaller. This, along with the fact that no oscillations occur, constitutes the principal advantages of the rotating electrode.

Fig. 9 shows the relationship between the diffusion current, as measured at a potential of -0.80 volt vs. the S.C.E., and the concentration of cadium. The amalgamated gold electrode was used.

The Deposition of Cupric and Nickelous Ions

The diffusion current for nickel was found to be much smaller than was expected and erratic results were obtained at concentrations greater than 10^{-4} M. As it cannot be assumed that concentration polarization is the only type of electrode reaction taking place with the rotating electrode, the action of each substance cannot always be predicted. Kolthoff and Laitinen[24] found ferrocyanide ion to give perfectly constant diffusion-current regions with the stationary platinum electrode but with the rotating electrode no well defined diffusion-current region was found. Evidently the appearance of a horizontal diffusion-current region on a current-voltage curve required the electrode reaction to be rapid in comparison with the rate of diffusion. With a rotating electrode the current density is increased greatly for a given solution as compared with a stationary electrode, and it is necessary to determine for each particular case whether current-voltage curves with well defined diffusion currents can be obtained.

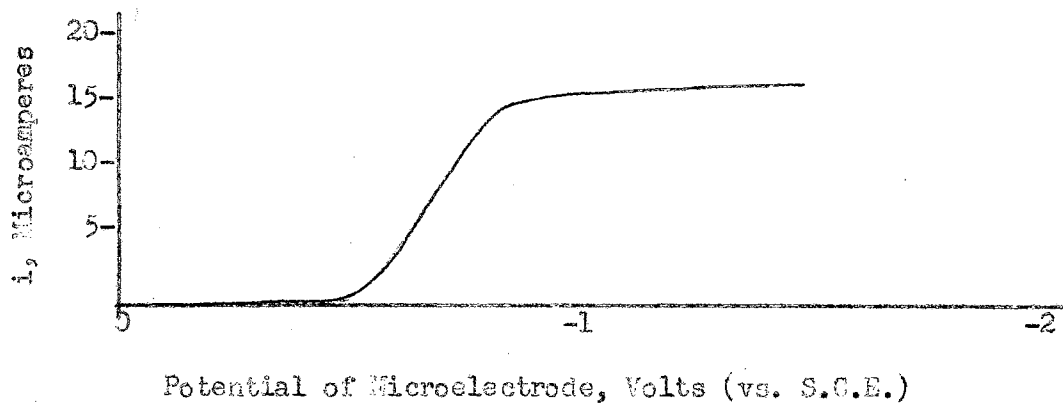[24] H. A. Laitinen and I. M. Kolthoff, J. Phys. Chem., 45, 1061 (1941).

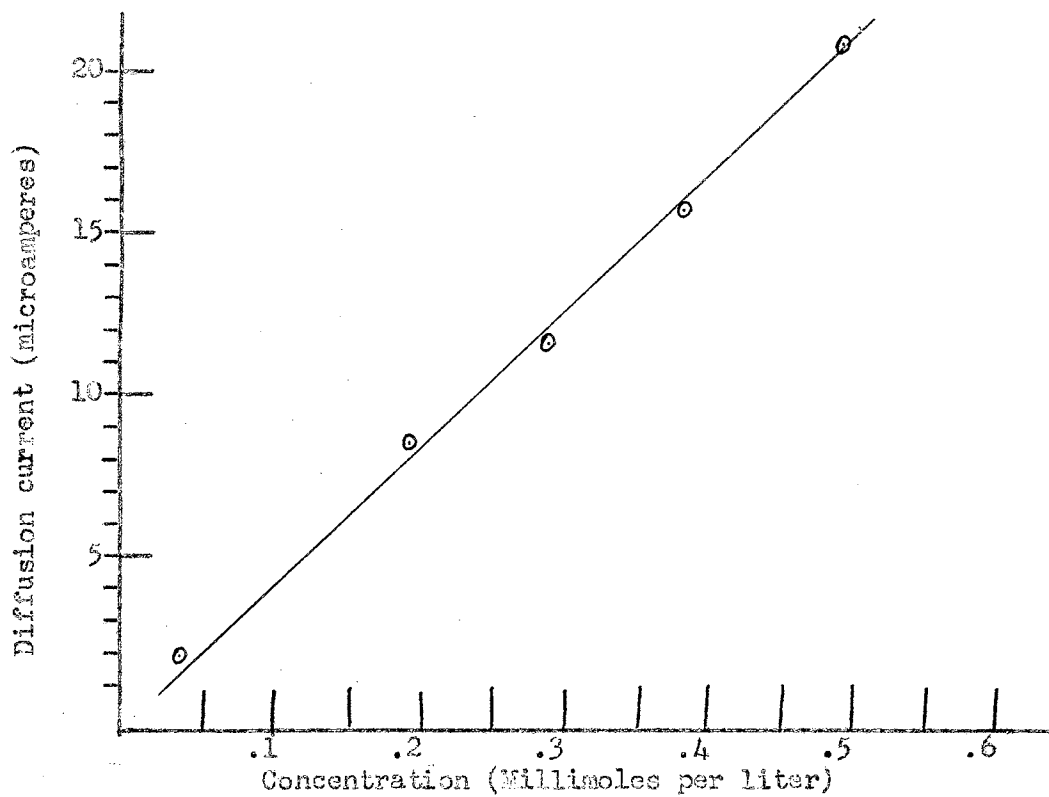Fig. 8. Electrolysis of 5×10^{-4} M Cd^{++} in 0.1 N KCl using the amalgamated gold electrode.

Fig. 9. Relationship between concentration of Cd^{++} and the diffusion current using the amalgamated gold electrode.

The current-voltage curve of cupric ion was unique in that a maximum invariably occurred which was not suppressed with gelatin. The height of the maxima could not be anticipated but the diffusion current regions beyond them were reasonably well defined.

Typical polarograms for the electrolysis of cupric and nickelous ion are shown in Fig. 10.

Electrolysis of Potassium Di-iodate

This electrolysis was run in order to demonstrate the usability of the amalgamated electrodes near their limits in the more negative regions. It can be seen from Fig. 11 that hydrogen evolution begins before the diffusion current is well defined with the amalgamated gold electrode. With the amalgamated copper electrode the diffusion current is well defined but represents almost the limit of usability of this electrode in the negative direction.
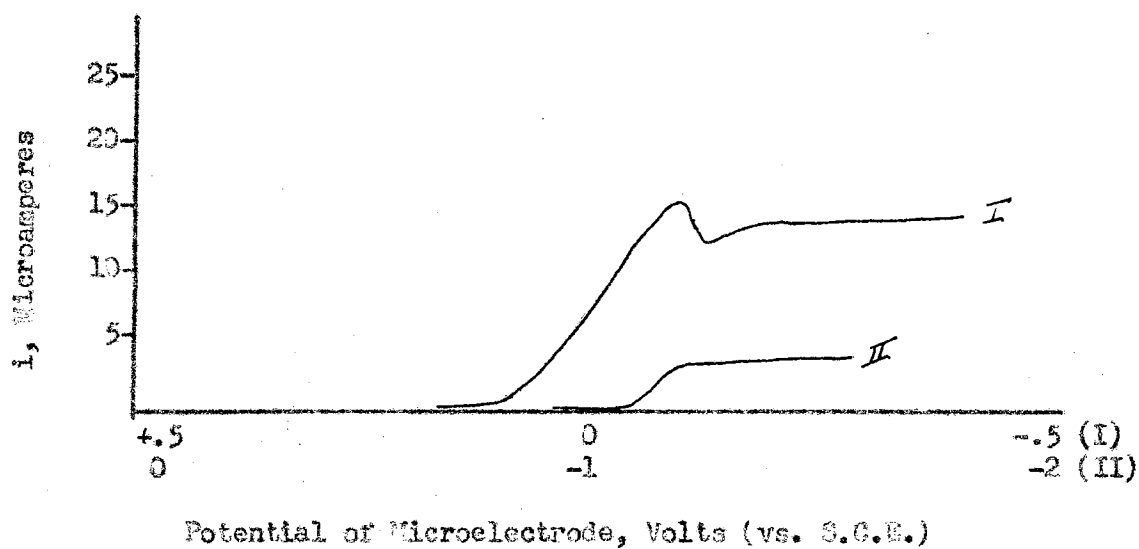
Fig. 10. Curve I, electrolysis of 10^{-3} $\underline{M}$ Cu.$^{++}$ in 0.1 $\underline{N}$ KCl.

Curve II, electrolysis of 10^{-4} $\underline{M}$ Ni^{++} in 0.1 $\underline{N}$ KCl.
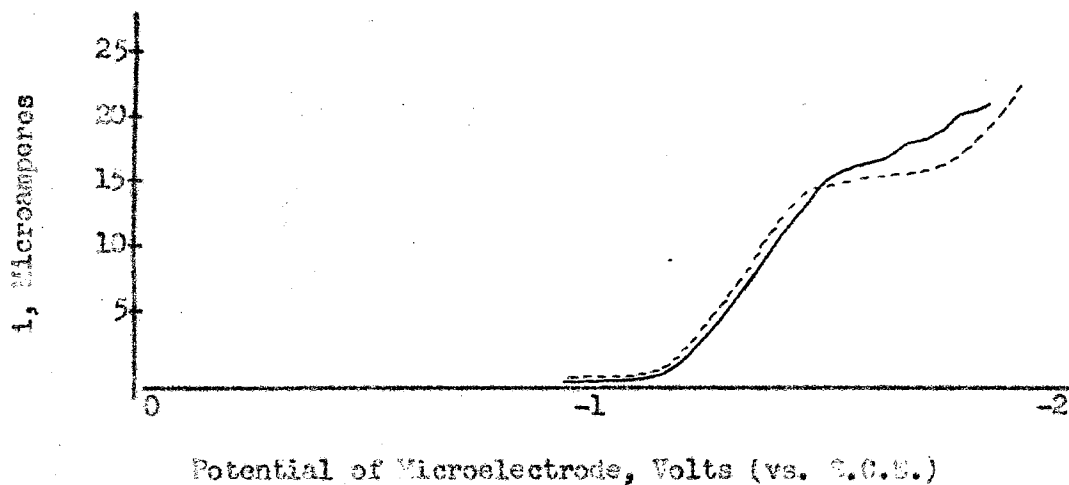
Fig. 11. Electrolysis of 10^{-4} $\underline{M}$ KH(IO$_3$)$_2$ in 0.1 $\underline{N}$ KCl.

Solid line, amalgamated gold electrode; dashed line, amalgamated copper electrode.

<u>Stationary Electrode with Stirred Solution</u>: One would expect the results from stirred solutions to be similar to those obtained either with a rotating electrode or by flowing the test solution past the electrode. Investigators[25,26] have reported, however, that stirring markedly decreases the reproducibility of both the half-wave potential and the diffusion current, and that in many cases no diffusion current plateau could be obtained. Nevertheless, it appeared reasonable that under properly controlled stirring conditions the half-wave potential and diffusion current would be well defined.

With this in mind a cell was made by sealing a length of thin-walled capillary tubing with an internal diameter of 2 mm. into the bottom of a test tube 2 cm. in diameter. The tubing projected 4 cm. into the test tube, the other end being attached to the usual leveling bulb. Mercury, which was placed in the leveling bulb, was allowed to flow into the capillary tubing until the meniscus was level with the top of the capillary. It was found in practice that the interfacial tension of the system mercury-solution changed enough to vary the height of mercury in the capillary tube by as much as 2 mm., as a varying potential of +0.5 to -0.5 volts was applied. This change in height was minimized by replacing the rubber tubing with glass and inserting a stopcock which when closed prevented flow of mercury between the capillary and the leveling bulb. The electrode as used is shown in Fig. 12. The piece of glass tubing sealed into the test tube and bent at 90° connects the

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[25] H. A. Laitinen and I. M. Kolthoff, J. Phys. Chem., 45, 1061 (1941).

[26] L. B. Rogers, H. H. Miller, R. B. Goodrich, and A. F. Stehney, Anal. Chem., 21, 777 (1949).

To stirring motor

burette for
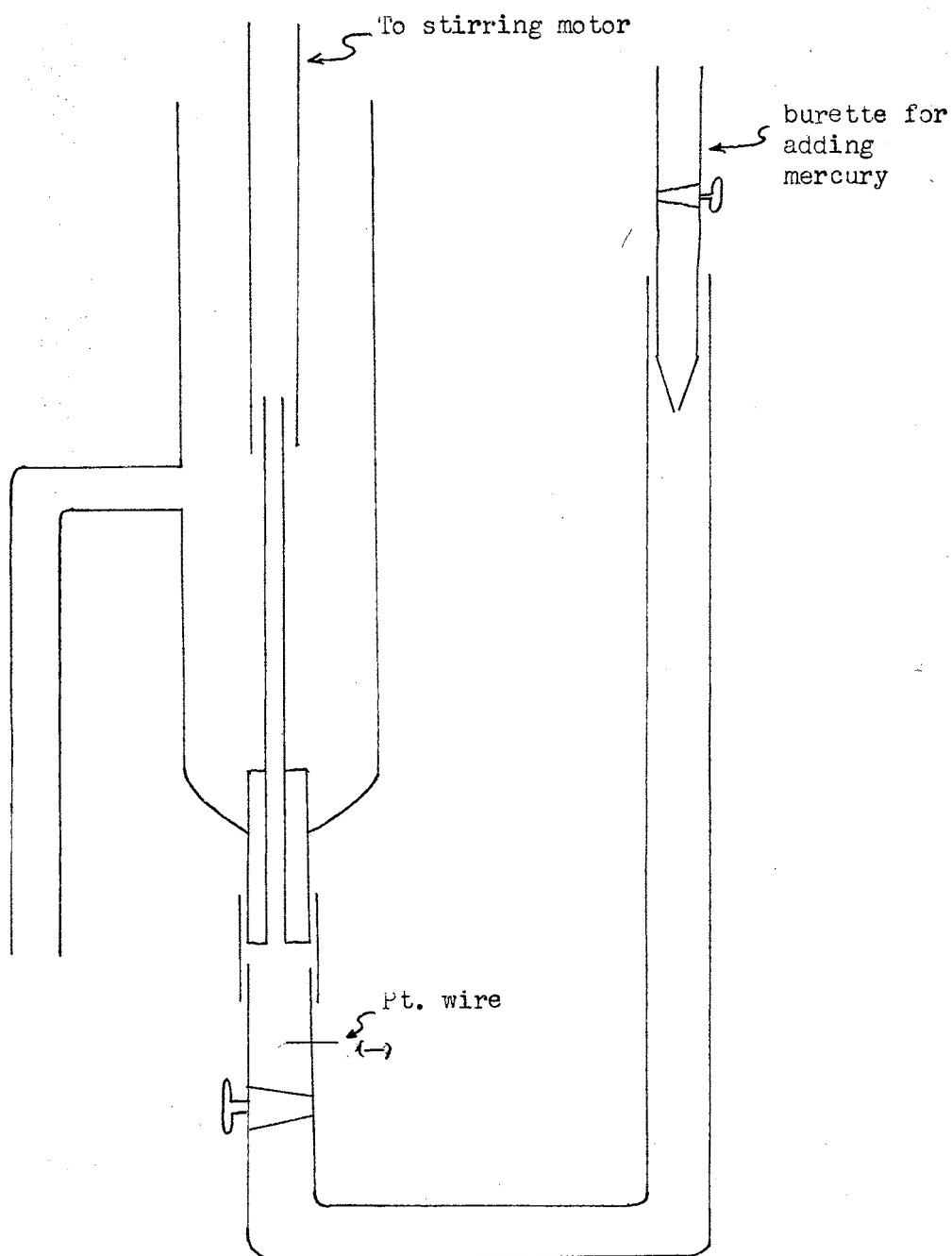adding
mercury

Pt. wire
(—)

Fig. 12. Stationary Mercury Electrode employing controlled stirring

cell to a saturated calomel half-cell by means of a salt bridge. This arrangement produces an electrode that is reproducible and which may be renewed after each run. To renew the electrode a quantity of mercury is added from the burette and the stopcock opened, which allows mercury to flow from the capillary. Small quantities of mercury are then added from the burette until the meniscus of the mercury is level with the top of the capillary. The stopcock is then closed.

A test solution of 5×10^{-4} $\underline{M}$ cadmium nitrate in 0.1 $\underline{N}$ potassium chloride was used. Sodium sulfite was used to remove oxygen from the solution. The addition of 0.1 gram of sodium sulfite to 50 ml. of test solution removed all traces of the oxygen wave.

Stirring was first accomplished by means of a glass rod 5 mm. in diameter rotated by means of a variable-speed stirring motor. The end of the rod was placed directly over and 1 cm. above the microelectrode. It was found that by stirring at 600 rpm, approximately the same sensitivity was attained as with the dropping mercury electrode.

Under these conditions polarograms were obtained in which the diffusion current was not well defined. A typical polarogram is shown in Fig. 13. It would appear that the fluctuations in the diffusion current are due either to vibrations, which may vary the size of the microelectrode, or to stray eddies in the solution. Subsequent investigations in which vibration was deliberately increased and decreased showed that vibration was not the primary cause of the fluctuations.

To reduce eddies in the solution, stirring was accomplished by means of 7 mm. glass tubing (internal diameter of 5 mm.), the lower end of which enclosed the capillary containing the microelectrode
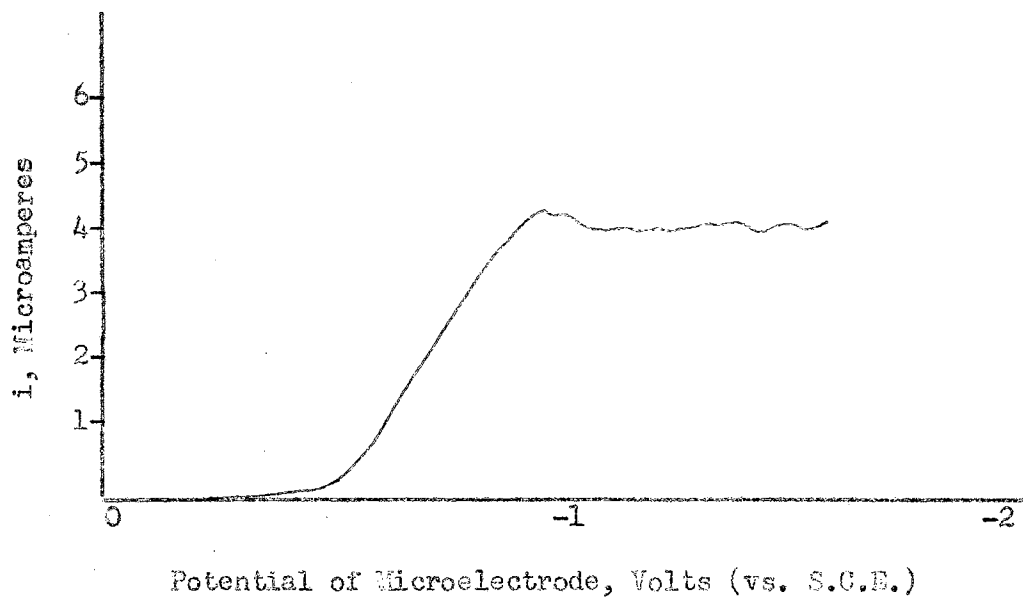
Fig. 13. Electrolysis of 5 x 10^{-4} $\underline{M}$ Cd^{++} in 0.1 $\underline{N}$ KCl using stationary mercury electrode and solid stirring rod.
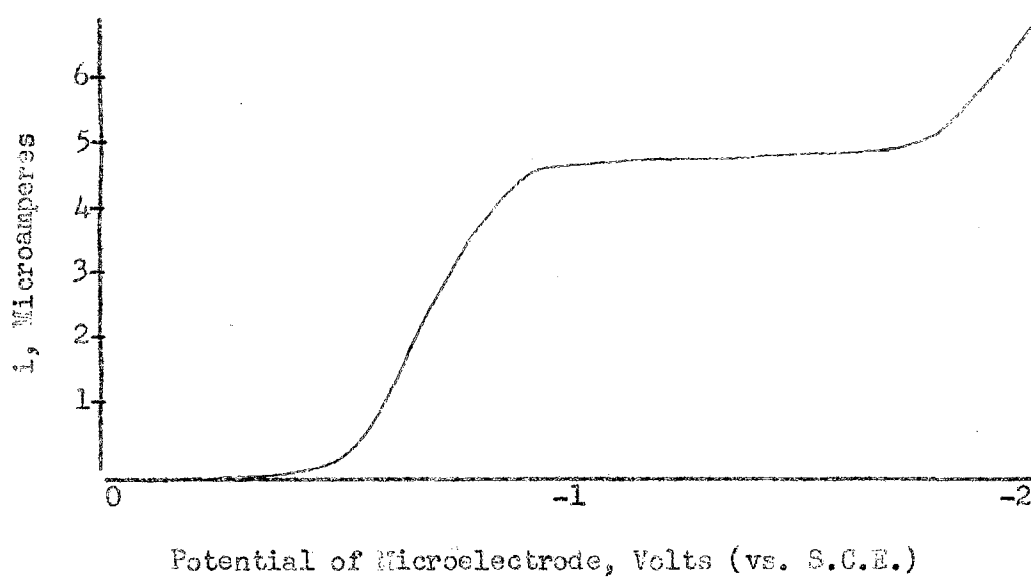
Fig. 14. Electrolysis of 5 x 10^{-4} $\underline{M}$ Cd^{++} in 0.1 $\underline{N}$ KCl using stationary mercury electrode and glass tubing as stirring rod. 0.01% gelatin added.

for a distance of 5 mm. Under these conditions the diffusion current was quite well defined. A typical polarogram is shown in Fig. 14. The same care must be used in stirring as is used with the rotating microelectrode in order to obtain polarograms free of fluctuations. When the tubing is inserted into the chuck of the stirring motor in such a way that a wobble is obtained, the polarograms have the same appearance as that shown in Fig. 13. By using the best of a half-dozen chucks inspected and by keeping the tubing short (about 5 cm.), the polarograms were kept free of fluctuations.

As would be expected, increasing the rate of stirring resulted in an increase in current. The increase, however, is quite slight for rotations greater than 550 rpm. With the apparatus used, irregularities were observed in the current-voltage curves when the speed of rotation was increased above 700 rpm. It is possible that if the rotating shaft was enclosed with a bearing which would keep the rotor running true at these higher speeds, the irregularities would not occur. However, as the current does not increase appreciably for rotations greater than 550 rpm., there appears to be no reason for using higher speeds of rotation. In the quantitative determinations a speed of 575 rpm. was used.

The height of mercury in the capillary also has some effect on the current and in these investigations the meniscus of the mercury was adjusted level with the top of the capillary. With the mercury 2 mm. below the top of the capillary the current is decreased about 40 per cent and at a distance of 3 mm. a time maximum occurs in the current-voltage curve. With the mercury meniscus adjusted level with the top of the capillary, slight variations in height had no great effect on the current.

Without the use of gelatin the polarograms of cadmium ion showed irregularities at voltages above 1.2 volts vs. the S.C.E. In a few cases the irregularities showed up at somewhat lower voltages. It might be thought that crystal formation was responsible for the variations, yet when the voltage was held at some point on the diffusion-current plateau below the point at which the irregularities occurred, the diffusion current remained steady for a period of time exceeding that of the normal electrolysis. No satisfactory explanation of this phenomenon was found.

The precision attained with the stationary electrode is comparable to that attained with the dropping mercury electrode. Fig. 15 shows the proportionality that exists between the diffusion current at a potential of -1.0 volt (vs. S.C.E.) and the concentration of cadmium, using the stationary and dropping mercury electrode. The average of three duplicate runs is shown in both cases.
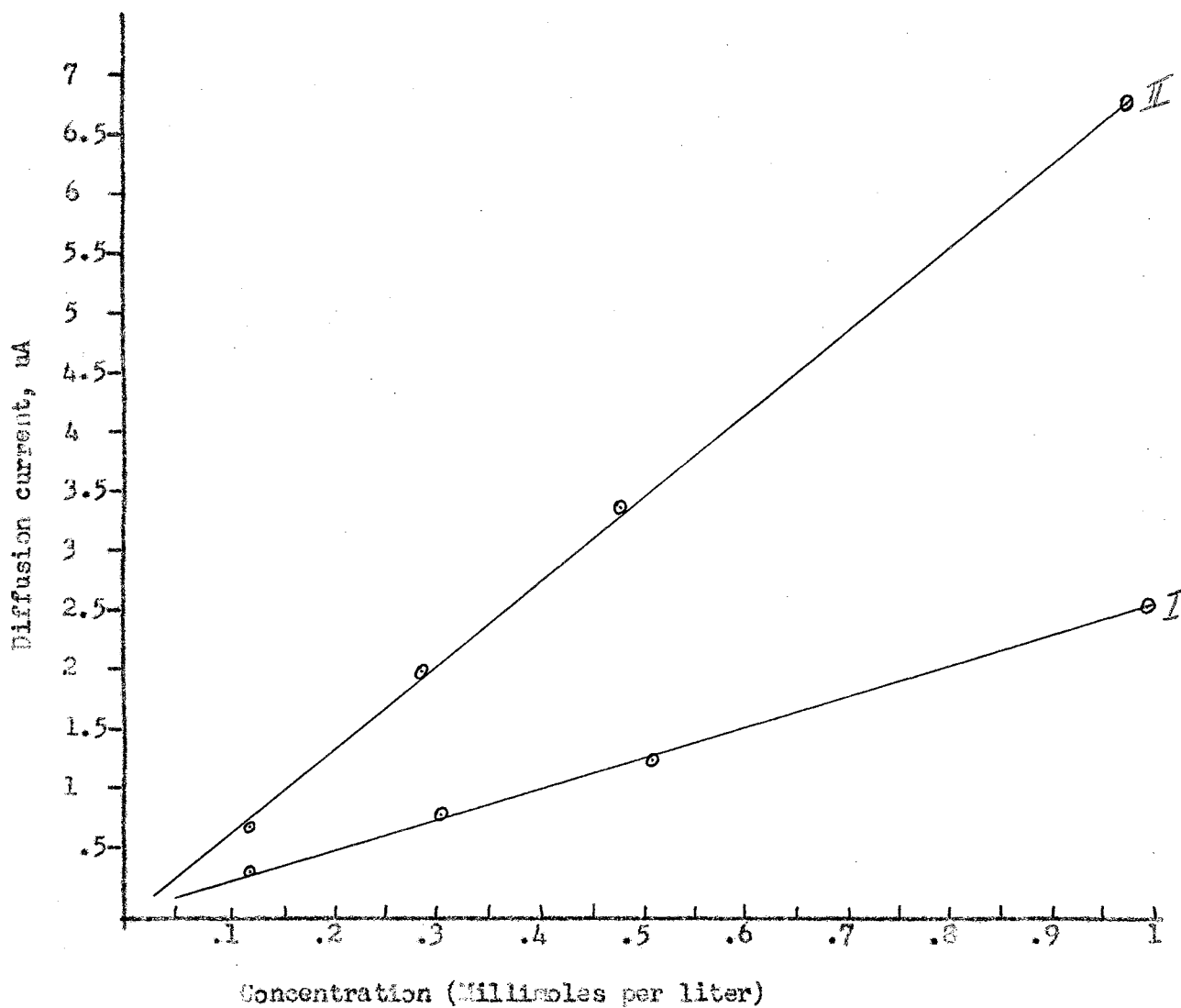
Fig. 15. Relationship between concentration of Cd^{++} and the diffusion current. Curve I, dropping mercury electrode; Curve II, stationary mercury electrode employing controlled stirring.

Discussion of Results

The results obtained with the two types of flowing electrodes studied indicate that considerable differences in design would have to be made before they would be applicable to polarographic analysis. The lack of reproducibility and the occurrence of the maxima are the two major obstacles that would have to be overcome. One serious disadvantage of the dropping mercury electrode would, however, be overcome in that oscillations in the current-voltage curves would be eliminated.

The rotating amalgamated electrodes proved to be superior to the rotating platinum electrode in that crystal formation was minimized or eliminated, and the range in the direction of negative potentials was considerably increased. The characteristic advantages of the rotating platinum electrode are retained in that the diffusion current is increased considerably whereas the residual current is small. Also smooth current-voltage curves are obtained. The cases in which the rotating electrodes may be used must be determined experimentally as the current density is increased tremendously and effects other than concentration polarization may occur.

So far as has been investigated the stationary mercury electrode employing controlled stirring seems to be superior in some respects to the dropping mercury electrode. The two chief disadvantages of the dropping mercury electrode, high residual current due to the condenser effect and oscillations in the current-voltage curves, are eliminated. The electrode used was approximately three times as sensitive as the dropping mercury electrode, and it seems reasonable to suppose, could be made still more sensitive without injurious effects. With this electrode an ordinary microammeter could be used in place of the sensitive galvanometer.

Summary

A review was conducted of available literature pertaining to indicator electrodes applicable to polarographic analysis.

It was decided that the ideal electrode would (1) give reproducible results, (2) give smooth current-voltage curves, (3) have a wide range, (4) develop a small residual current, (5) have a renewable surface, (6) be of a simple and sturdy design which would require a minimum of manipulation, and (7) not require large quantities of mercury.

Electrodes were designed employing the following features: (1) flow of mercury past the solution, (2) rotating amalgamated microelectrodes, and (3) stationary mercury surface employing controlled stirring.

Electrode (1) did not prove to be applicable to polarographic analysis. Time maxima occurred in the current-voltage curves which seemed to be inherent in the nature of the electrode and the reproducibility, as compared to that of the dropping mercury electrode, was poor. Electrode (2) possessed the characteristic features of the rotating platinum electrode in that smooth current-voltage curves were obtained with a minimum of residual current and a high diffusion current. In addition the range in the direction of negative potentials was extended and crystal formation on the electrode was minimized or eliminated. Electrode (3) gave the best results, and insofar as it was studied, seemed superior in some respects to the dropping mercury electrode. Smooth current-voltage curves were obtained with a minimum of residual current. The electrode as used was more sensitive than the dropping mercury electrode and could probably be made more sensitive without injurious effects.

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Biography

Roy F. Maness was born at Conway, Missouri, October 24, 1919. He completed grade school and high school at Gage, Oklahoma, graduating from high school in the spring of 1937. That fall he entered Panhandle A. and M. College at Goodwell, Oklahoma and received a Bachelor of Science degree in 1941.

In September of 1941 he was employed by the Guymon High School, Guymon, Oklahoma, as a science and mathematics teacher where he remained until called into the navy in 1944. Upon receiving his discharge in 1945 he spend a year in small business and a year as science instructor in the Wewoka High School, Wewoka, Oklahoma, before reentering school.

In september, 1947, he entered the Graduate School of Oklahoma A. and M. College where he has been employed as a graduate fellow in the Department of Chemistry until the present time.

Typed by:

Minniebel Richardson