THESIS TITLE: ANODIC POLAROGRAPHY OF INORGANIC IONS AT
VARIOUS ROTATING MICROELECTRODES

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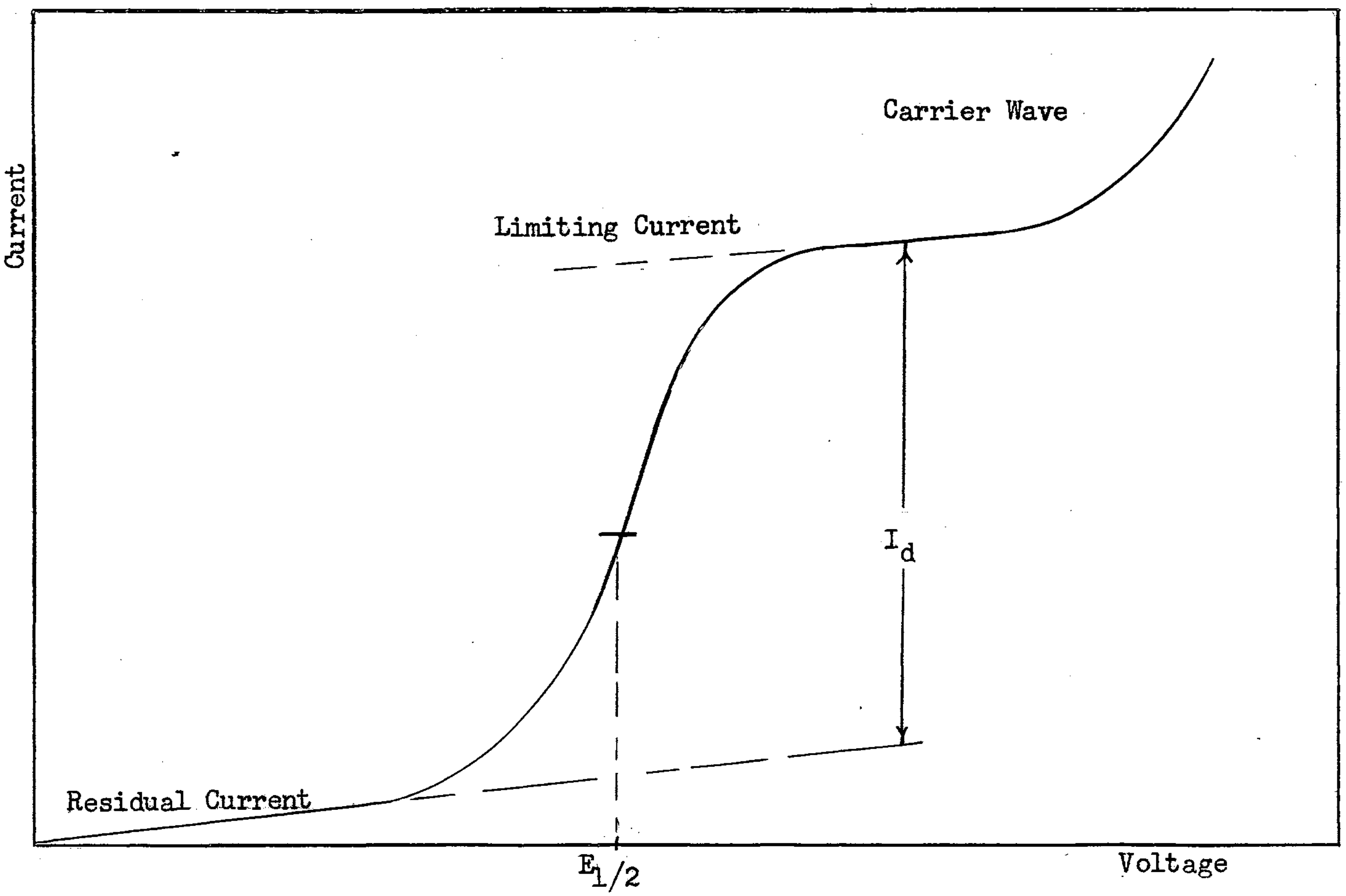
INTRODUCTION AND HISTORY

The polarographic method of chemical analysis is based on the interpretation of the current-voltage curve or polarogram obtained whenever a steadily-increasing potential is applied across an electrolysis cell consisting of a small easily polarizable electrode and a large nonpolarizable electrode. An ideal type of polarogram is shown in Figure 1. As electrolysis proceeds an increase in current will be noted when the applied voltage has reached the value at which some material present in the solution will react. This increase in current continues with increasing voltage but will reach a limit when the potential across the cell attains such a value that the reacting material is electrolyzed as fast as it reaches the electrode. Since this depends upon diffusion rate and the latter depends upon concentration, the height of the curve is a function of the concentration of the reacting material. The half-wave potential, on the other hand, is characteristic of the nature of the reacting material.

There may be several components to this limiting current. Among these are the residual current, the migration current, and the diffusion current, and in some cases, an adsorption current, a kinetic current, and a catalytic current. The migration current is usually minimized by employing a carrier electrolyte in concentrations fifty to one hundred times as great as that of the electrolyzable substance. The residual current consists of a condenser or charging current, which is proportional to the applied voltage, and a Faradaic current due to the reduction of traces of reducible impurities in the solution. In

FIGURE 1

IDEAL POLAROGRAM



quantitative polarographic analysis, the residual current must be subtracted from the total current observed in order to get the diffusion current. Adsorption currents appear on polarograms in the form of more-or-less pronounced maxima. They appear only under special conditions, and are the result of adsorption causing the reactive substance to be present in the layer around the electrode in concentrations in excess of that in the body of the solution. Usually such adsorption currents can be suppressed by the addition of surface active substances.

Electroactive materials reach the surface of the microelectrode under the influence of two more-or-less independent forces, a diffusive force proportional to the concentration gradient at the electrode surface and an electrical force proportional to the potential gradient at the electrode. As mentioned before, the migration current can be nearly eliminated if there is added to the solutions an indifferent electrolyte in concentrations from fifty to one hundred times larger than that of the salt under study. Such indifferent electrolytes are chosen to be of such nature that while they conduct the current, they do not react with the substance under investigation nor do they react at the electrode in the range of potentials being studied.

The diffusion current is caused by a nearly complete state of concentration polarization at the electrode surface. This state of concentration polarization is caused by the reaction of the electroactive ion at the electrode surface resulting in depletion of the ions at the electrode. To compensate for this depletion, more electroactive ions diffuse to the electrode surface from the body of the solution. As the applied voltage is increased, the depletion of the ions from the electrode surface increases until the difference of concentration of the electroactive ions at the electrode surface compared to the concentration in the body of the solution approaches a constant value. Consequently, the magnitude of the diffusion current (for a given ion in a given medium) is determined by the rate of diffusion of the electroactive ion. In most of the polarographic work reported in the literature the dropping mercury electrode (D. M. E.) was used as the microelectrode. Ilkovic (12) is to be credited with having given the theoretical and experimental proof for an equation which clearly defines the factors which govern the diffusion current at the D. M. E. The Ilkovic equation which holds for constant temperature is

$$I_d = 0.627\ nFD^{1/2}Cm^{2/3}t^{1/6} \qquad (1)$$

in which $\underline{I_d}$ is the mean diffusion current (in amperes), $\underline{n}$ is the number of electrons involved in the reduction of one molecule of reducible substance, $\underline{F}$ is the Faraday (96,500 coulombs), $\underline{D}$ is the diffusion coefficient of the reducible substance (in $cm.^2/sec.$), $\underline{C}$ its concentration (in moles/ml.), $\underline{m}$ the weight of mercury flowing from a capillary per second (in grams), and $\underline{t}$ (in seconds) the time necessary for the formation of one drop of mercury. This equation shows that, for the D. M. E., with all other factors held constant the diffusion current is proportional to the concentration of the electroactive substance. This is the basis for quantitative analysis in polarography.

A similar equation has been developed by Tsukamoto, Kambara, and Tachi (30) for one type of rotating platinum electrode. This type of electrode is formed by enclosing a platinum wire in the center of the end of the glass tube and bending the wire rectangularly to the horizontal direction and rotating so the wire moves in a horizontal plane.

The equation is

$$I_d = 0.807\ nFw_1{}^{1/3}D^{2/3}Chy_1{}^{2/3} \qquad (2)$$

where I_d is the diffusion current, n is the number of electrons involved in the reduction of one molecule of the reducible substance, F is the Faraday constant, D is the diffusion coefficient of the reducible substance, and C is the concentration of the electroactive substance in the body of the solution, w_1 is the velocity gradient of linear flow at the electrode surface and is proportional not only to the revolution number μ of the electrode but also to the linear velocity of the electrode surface, i.e., the product of μ and the radius of rotation. If the radius of the platinum wire is r_1, the distance measured from the axis of rotation ($\ell = 0$) is ℓ, and the entire length of the wire measured horizontally is ℓ_1, the term y_1 of equation (2) corresponds to the circumference, h to the height. Therefore, the limiting diffusion current dI_d which flows onto the microelectrode of length $d\ell$ at a distance ℓ from the axis of rotation is given by making the following substitutions into equation (2):

$$y_1 = 2\pi r_1$$

$$h = d\ell$$

$$w_1 \sim \mu\ell$$

It follows that

$$dI_d = k'\ r_1{}^{2/3}\ \ell^{1/3}\mu^{1/3}\ d\ell \qquad (3)$$

Integrating equation (3) gives

$$I_d = k'\ r_1{}^{2/3}\ \mu^{1/3}\int_0^{\ell_1} \ell^{1/3}\ d\ell \qquad (4)$$

or

$$I_d = k\ r_1{}^{2/3}\mu^{1/3}\ \ell_1{}^{4/3} \qquad (5)$$

where k' and k are constants.

These equations apply to an electrode which is rotated at a rate larger than about 200 rpm. A similar equation is necessary for rotations smaller than about 90 rpm, the main difference being the exponents on the constant term. These authors (30) tested the validity of the equation by making runs on 5×10^{-5} molar methylene blue at a pH of 3.07 in a MacIlvains buffer solution. These equations do not apply in the case where the platinum wire electrode projects horizontally from a cylindrical shaft of as large diameter as was used in this research. The only equation known to apply for such electrodes is a more-or-less empirical one showing the current to be proportional to the electrode area.

Kinetic currents are controlled by a mechanism which produces additional reducible material at a measurable rate on the electrode surface. These occur in instances when the drop-time is altered. The many conceivable reactions which might produce a kinetic current may be divided into three groups: (1) Hyperactive electrodes. In the reduction of metallic ions the deposited metal may be hyperactive and react immediately with the surrounding solution. The metallic ions thus formed are then once more deposited electrolytically. (2) Reconversion of products of electrode reaction in solution. In oxidation-reduction systems in which both oxidant and reductant are dissolved in solution, the end products of the electrode reaction may be catalytically converted at the interface to form more of the original starting material. This is redeposited electrolytically. (3) Reestablishment of disturbed equilibria. Given compounds reacting at the dropping mercury electrode may be in equilibrium with another compound which is either nonreacting or which reacts at a different electrode potential. The resulting kinetic current then depends on the rate at which this equilibrium is reestablished at the interface of the dropping mercury electrode.

Catalytic currents seem to depend upon the catalytic reduction of the hydrogen ion. Various substances, e.g., platinum metals, magnesium, calcium, and some organic compounds lower the hydrogen overvoltage on the dropping mercury electrode and thus make the reduction of the hydrogen ion possible at lower applied voltages. In addition these catalysts may produce current maxima which cannot be suppressed in the usual way.

The most widely used electrode for polarography is the dropping mercury electrode. The dropping mercury electrode consists of a mercury reservoir, arranged to maintain a constant head of mercury and connected to very fine capillary tubing. The tubing has a uniform bore of about 0.05 mm. in which case a length of from five to thirty centimeters will give the desired flow rate of a drop every three to six seconds. The dropping mercury electrode has the following advantages which cannot be matched by any other electrode: (1) its surface is reproducible, smooth and continually renewed; (2) the surface area can be calculated from the weight of the drops; (3) mercury amalgamates with most metals; and (4) the value of the overvoltage of hydrogen is very high on mercury so that much work can be done in acid solutions without interference arising from the evolution of hydrogen. The dropping mercury electrode is not well suited for anodic work because mercury itself is oxidized at a relatively low voltage of about + 0.4 volts vs. the saturated calomel electrode (S. C. E.)

Various types of solid microelectrodes have been proposed for polarographic analysis. The stationary platinum electrode consisting of a platinum wire about 4 mm. long and 0.5 mm. in diameter sealed in a piece of glass tubing has been studied by Laitinen and Kolthoff (20). They found that it takes two to three minutes for the current to reach a steady value for each value of the applied potential. The attainment of a steady diffusion state is dependent on the absence of mechanical and thermal disturbances so the polarographic analysis must be done in a set-up which is carefully thermostated and protected from vibration. Muller (23) has constructed an apparatus in which the solution under study flows through a constricted tube containing a platinum wire electrode having an area of only 0.3 sq. mm. Under the proper conditions the limiting current is a linear function of the concentration of the reacting substance and the logarithm of the rate of flow. Rogers (26) and co-workers have investigated the automatic recording of polarograms with both stationary and rotating electrodes. With the stationary electrode, current maxima were obtained when the voltage was continuously increased. The current maxima are due to the fact that the voltage change is more rapid than the rate at which a steady state of diffusion equilibria can be set up at the electrode. Skobets, Turov, and Ryabokon (28) have found that these current maxima may be eliminated by using operating temperatures of 50° to 60° C. Randles (25) and Airey (1) have used solid microelectrodes in conjunction with oscillographic polarography. Silver and copper (22) and amalgams (1) of these metals have also been recommended for use in polarographic analysis. Recently Gaylor, Elving, and Conrad (11) have reported the use of a graphite indicator electrode for polarographic analysis.

Many investigators have studied current-voltage curves using either a rotating platinum microelectrode or a microelectrode of various metals in stirred solutions. Nernst and Merriam (24) were the first to describe current-voltage curves obtained with a rotating platinum microelectrode. The main advantage of a rotating electrode over a stationary electrode is that the diffusion current, and, therefore, the sensitivity of the rotating electrode, is tremendously increased. Also a steady state of current is reached almost immediately. Laitinen and Kolthoff (20) describe a microelectrode of platinum wire about 3 mm. long and 0.5 mm. in diameter sealed in the side of a 10 mm. bulb on the end of a piece of 6 mm. soft glass tubing, rotated at 600 rpm. They studied the reduction of bromine and the reduction of the silver ion and found that the diffusion current was proportional to the concentration of the electroactive substance. However, for the oxidation of ferrocyanide and stannous and ferrous ions, a much smaller current was observed than was expected and no well-defined diffusion current regions were observed.

There is not complete agreement concerning the effect of rates of stirring of solutions on the rates of reaction at the electrode surface. Nernst and Merriam (24) found that the diffusion current increased with the six-tenths power of the rate of rotation of the microelectrode. Brunner (5) was of the opinion that the diffusion current with a stationary electrode in a stirred solution increased with the two-thirds power of the speed of rotation of the stirrer. Tsukamoto, Kambara, and Tachi (30) give the exponent for the rate of stirring as the two-thirds power for rates above 200 rpm. On the other hand, when the rate is about 90 rpm., they find that the diffusion is proportional to the three-fourths power of the rate of stirring. Rosenthal (27) et al. found that a speed of stirring could be reached beyond which there was no further effect on the current. However, if the speed of rotation is maintained constant at a value of somewhere between 600 and 900 rpm. good diffusion currents are usually obtained. This was confirmed by Komyathy (19) for a special stationary electrode employing controlled stirring.

Another type of solid electrode is the rotating silver amalgam electrode recently described by Cooke (6). The advantage of the solid electrode lies in the fact that there is no charging current and, hence, only a small residual current is present. Also the area of the electrode may be increased and a greater diffusion current thus obtained. Besides having a high hydrogen overvoltage, the amalgam electrode as well as the mercury has fluid surfaces which tend to reduce many irreversible surface effects. In addition, Cooke (6) reported that storage and pretreatment of the amalgam electrode are not as important as with other solid electrodes. With the silver amalgam electrode, he was able to obtain a sensitivity of approximately fifty times that of a dropping mercury electrode.

Most of the work in polarography to date has been with the dropping mercury electrode as a cathode. As was mentioned earlier, although the dropping mercury electrode has been used for some anodic work, it is quite limited in its application because of the low dissolution potential of mercury. On the other hand, ions which form insoluble or very slightly ionized salts with mercurous ions tend to decrease the potential of the mercury oxidation, and do so in a manner characteristic of the ion. In this manner Kolthoff and Miller (18) were able to obtain polarograms with chloride, bromide, iodide, sulfide, thiosulfate, cyanide, thiocyanate, and hydroxide ions. Struble (29) reports that the titanous ion gives an anodic wave in dilute hydrochloric acid. Verdier (31) has oxidized manganous tartrate with the dropping mercury electrode, while in later work Lingane and Meites (21) oxidized + 4 vanadium. The anodic wave of

+ 4 vanadium in a strongly alkaline medium has been employed by them for the determination of vanadium in steel. The wave is well-formed when the supporting electrolyte consists of 1 molal sodium hydroxide, with 0.1 N sodium sulfite to remove oxygen. The oxidation of + 3 antimony at the dropping mercury electrode has also been recorded (7).

The stationary platinum and the rotating platinum electrode should be more suitable than mercury for the study of anodic reactions, since the potential at which oxygen is evolved is much greater than is the dissolution potential of mercury. Cathodic, anodic, and composite cathodic-anodic curves of the ferric ion and of the ferrous ion all have been obtained with stationary platinum electrodes (15), linear proportionality between the diffusion current and the concentration being found. A similar proportionality was found in the case of ferricyanide and ferrocyanide ions when enough indifferent salt was present to eliminate the migration current.

Laitinen and Kolthoff (20) oxidized the ferrocyanide ion at a rotating platinum electrode, using potassium chloride as the carrier electrolyte, but in order to obtain reproducible results, they found it necessary to evolve oxygen from the electrode for a few minutes before each determination. Bortmes (3) was able to obtain good reproducible results for the ferrocyanide ion in a sodium sulfate carrier. In contrast to Laitinen and Kolthoff's results in chloride carriers, Bortmes depolarized the electrode by making it the cathode for about two minutes at about - 1.2 volts. However, he learned that ferrocyanide solutions have to be prepared just before the runs, and best results were obtained if the distilled water were freshly boiled before the nitrogen degassing treatment. DeFord and Davidson (9) oxidized potassium ruthenocyanide at both stationary and rotating platinum electrodes using a 0.2 molar potassium chloride carrier. With the rotating platinum electrode, they were able to obtain good waves by electrolyzing the solution several minutes at +1.5 volts before each run. Poor waves were obtained with no prior electrolysis. When using the stationary platinum electrode, they noticed that a green precipitate, which made runs difficult, formed during electrolysis.

Delahay and Stiehl (10) have reported the oxidation of the thallous ion at the rotating platinum electrode. Between runs they rinsed the electrode with concentrated sulfuric acid to remove the thallic hydroxide produced. Kolthoff and Jordan (13) also oxidized the thallous ion at the rotating platinum electrode. They stored their electrode in 10 N nitric acid between runs in order to obtain reproducible results. In more recent work they report the oxidation of the iodide ion by treating the electrode in the same manner. They found that iodide, in most supporting electrolytes, gives two anodic waves, the first of which they attribute to the oxidation of iodide to iodine and the second of which, to the oxidation of iodine to I^+. Bortmes (3) obtained good iodide waves in a carrier of 0.36 N sulfuric acid by limiting the maximum voltage to + 1.0 volt vs. the S. C. E. He was also able to obtain good polarographic waves for sulfide and stannous ions.

Bridgeman (4) studied the oxidation of phenol at a rotating platinum electrode in buffers of various pH and at different scanning rates. He found that for low scanning rates the half-wave potential decreased with an increase in pH. However, he obtained better waves at a higher scanning rate and found that the half-wave potentials were less dependent on pH. Phenol was also studied at a stationary, rather large-area graphite electrode by Gaylor, Elving, and Conrad (11). They found that the values of the half-wave potential decreased with increasing pH in a pH range of 1 to 10. They also found that more positive values for half-wave potentials were obtained with a higher polarization rate. In order to have a renewable surface they broke the lower tip off the electrode before each run. They also found that better results could be obtained by a ten-minute application of a constant potential at some point on the diffusion plateau of the sample before the run was made. Bridgeman (4) in his work on the oxidation of phenols scraped the electrode before each run. The rotating platinum electrode has also been used for the study of the oxidation of many other organic compounds.

SCOPE OF RESEARCH

The purpose of this research was to determine (1) the behavior of various so-called inert electrodes and the factors influencing their behavior when used as anodes in polarographic determinations and (2) to determine the feasibility of using attackable electrodes (solid or amalgam) for the determination of anions.

The anions chosen for this investigation were those inorganic ions which are easily oxidizable or which readily form insoluble substances with metallic ions.

MATERIALS AND EQUIPMENT

Reagents.

All reagents used were of chemically-pure or analytical reagent grade. Nitrogen used in the degassing solutions was purified by passing it through two gas-washing towers containing alkaline pyrogallol, through a solution containing the carrier electrolyte, and then finally to the electrolysis cell.

Triply-distilled mercury was used for the amalgamation of each of the wires used as an electrode and in the preparation of the silver amalgams.

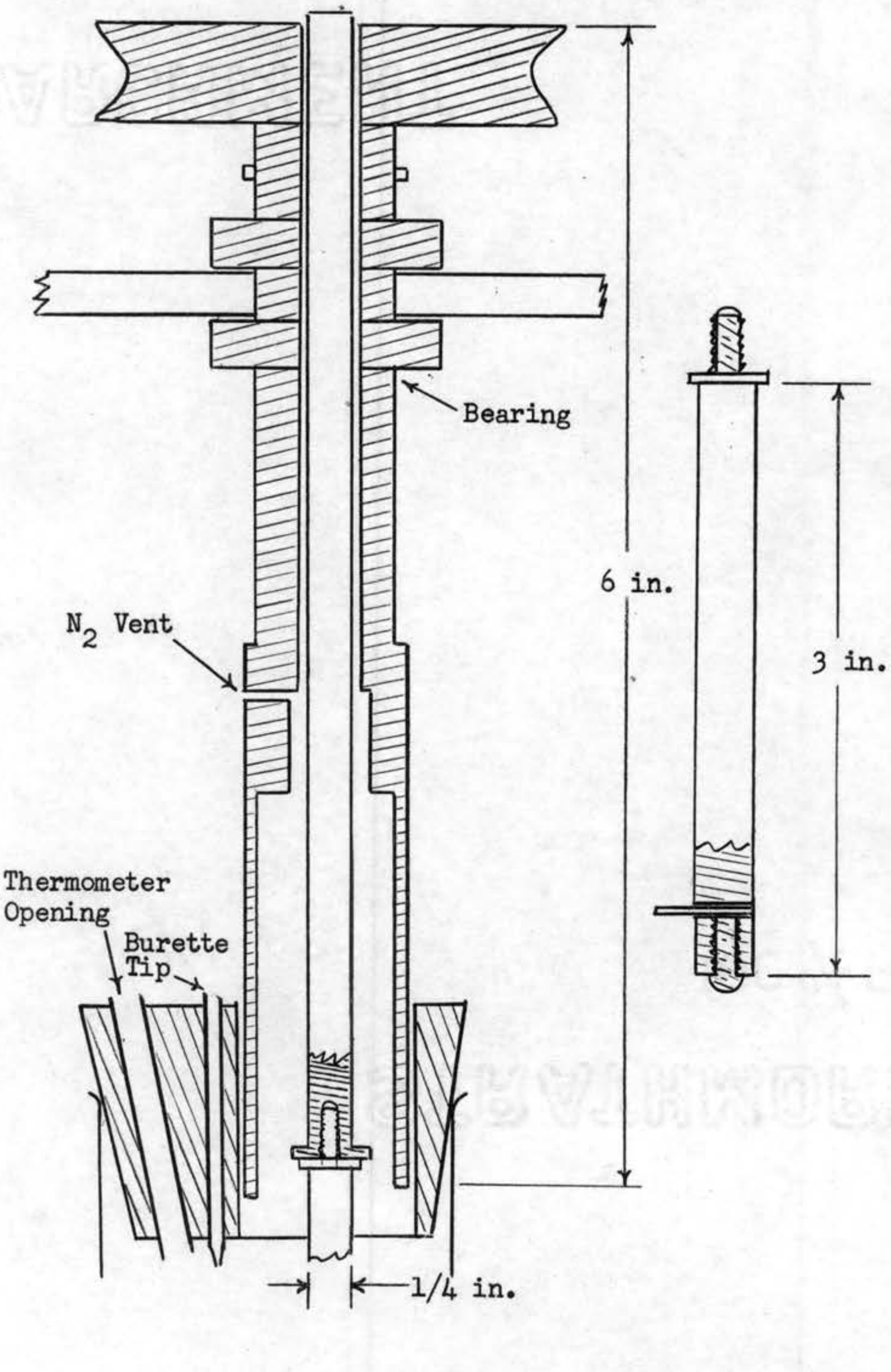
Apparatus.

The polarographs used in this study were a Sargent Model XXI polarograph and an experimental polarograph which was constructed so that it was possible to vary the time of electrolysis from twenty seconds to over five hours. This experimental polarograph was designed and constructed by Dr. Paul Arthur of the Department of Chemistry at Oklahoma A. and M. College. It was assembled from components of a Sargent Model XII photographic recording polarograph and was equipped for either strip-chart recording or photographic recording. For still faster runs, an especially-constructed polarograph was used which could cover the entire voltage span in three seconds. The polarograms were recorded by means of an oscilloscope with a camera attachment. The bridge operated in a continuous manner so that polarograms could be made in rapid succession.

The microelectrode and assembly used was built according to Figure 2. The assembly used first was not the same in all respects but differed

FIGURE 2

ELECTRODE ASSEMBLY

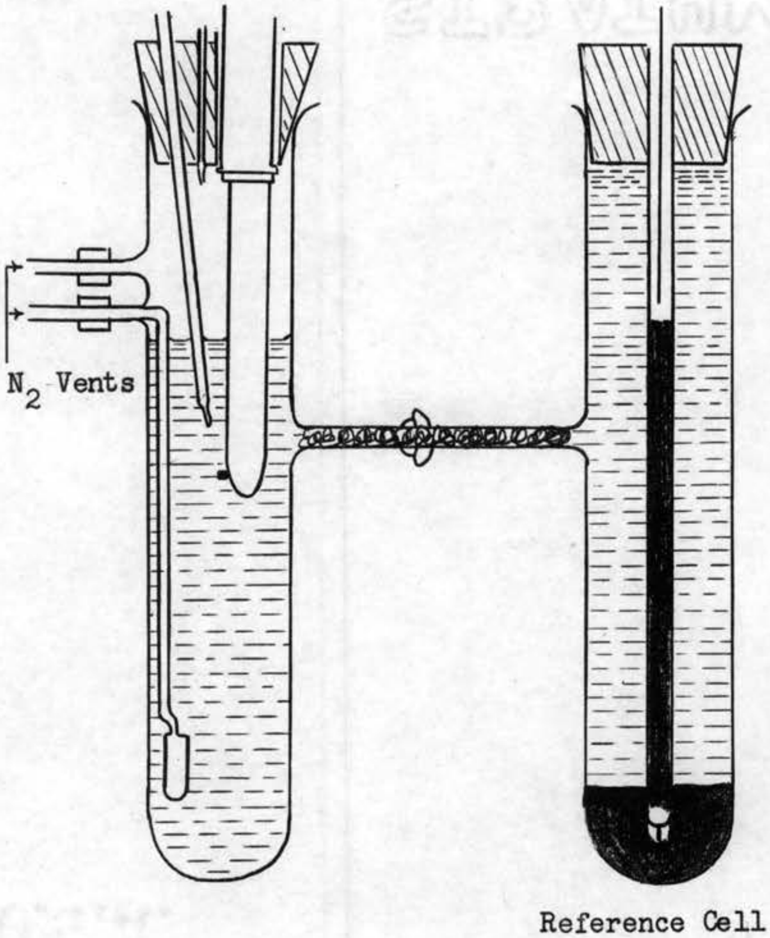


chiefly in the ease with which oxygen could be excluded. The set-up is essentially that used by Bortmes (3). The electrode holder was made of brass and had a set-screw at the bottom for holding the electrode in position. The holder was then screwed into a steel shaft. The shaft was mounted in a brass bushing which was in turn mounted in a metal stand attached to a wooden base. A shield extended over the electrode shaft when in the operating position and protruded to the top of the electrolysis cell in such a manner that a rubber stopper could be fitted over the shield and into the electrolysis cell. A tight fit was made here so as to prevent oxygen from diffusing into the cell. The small escape hole near the top of the shield allowed nitrogen to escape during the degassing procedure. To facilitate using the constant temperature bath, the shaft was made in such a way that the electrode could be lifted out of the cell and be protected by this shield while the constant temperature bath containing the electrolysis cell was moved into position. The electrode also could be held out of the solution during the degassing and then immediately returned to position. The electrode was rotated by means of a 0.05 horsepower motor connected to the pulley by a belt. The pulley ratio was such that the electrode rotated at approximately 640 rpm.

The polarographic cell is shown in Figure 3. The side arms of both the electrolysis and reference cells were packed with glass wool. The mercury-mercurous sulfate electrode was prepared by grinding together in a mortar mercury and mercurous sulfate moistened with saturated potassium sulfate solution. This was put in the cell to a depth of about 1 cm. over a pool of mercury, and saturated potassium sulfate solution was added to fill the cell. The cell containing the mercury-mercurous sulfate electrode was painted black to prevent light from decomposing the

FIGURE 3

POLAROGRAPHIC CELL



mercurous sulfate. Once the mercury-mercurous sulfate cell was made up, the side arm was left packed with the glass wool; the side-arm in the electrolysis cell, however, was repacked each time a new solution was added to the cell. A fritted-glass gas dispersion tube was sealed into the cell for degassing purposes. The polarographic cell was fitted with a stopper made to admit the shield, a thermometer, and a burette tip to permit addition of samples from the microburette. The capacity of the polarographic cell was 125 ml. Sample additions up to 10 ml. could then be made without the cell's being too full.

EXPERIMENTAL RESULTS

All determinations were made using a rotating microelectrode as the anode with a saturated mercury-mercurous sulfate half-cell as the cathode. Values are converted to the saturated calomel electrode by adding 0.40 volts to the value obtained in the determination or by presetting the instrument at 0.4 volts opposed. The mercurous sulfate cell was chosen in order to eliminate the possibility of diffusion of chloride ions from a calomel electrode. Also the side arms of the two half-cells were packed with glass wool since early investigations showed that agar, dissolving from the usual plug, gave irregular anodic waves.

Platinum Electrode

Oxidation of the Iodide Ion.

Bortmes (3), in his master's research, has shown that the platinum electrode is readily polarized by iodide in a 0.1 normal sodium sulfate carrier. By polarization we mean that a reaction has taken place which changes the characteristic of the electrode in such a manner that succeeding polarograms are not the same as the first polarogram of a series, the first wave itself usually having a pronounced dip in the limiting current. Polarization of an electrode is usually followed by a change in the wave shape of the polarogram and/or by a marked decrease in the wave height. This polarization was of a type which might be caused by the electrode's becoming coated by one of the products of electrolysis or by the electrode's combining chemically with one of the products in such a manner as to change the electrode characteristics.

To determine the nature of the polarization caused by the iodide ion several polarograms were made using 10^{-3} normal potassium iodide in 0.1 normal potassium sulfate. A new, freshly-scraped, platinum electrode in this solution gave one wave with a half-wave potential of + 0.57 volts followed by a second wave with a maximum at + 1.1 volts. When succeeding runs were made without depolarizing the electrode, the height of the two waves decreased until finally they disappeared.

Various methods of depolarization were tried in an effort to get reproducible waves and to determine the cause of the electrode polarization. These methods were based on the assumption that the polarization was due to an oxidation product which could be reduced electrolytically or by a strong reducing agent. It was also thought possible that the product might be dislodged by generation of hydrogen at the electrode or by volatilization by heat.

One method used was to reverse the polarity at the end of each run. This means that the voltage across the cells was - 1.2 volts. Thirty seconds was sufficient to do all the depolarizing it was possible to accomplish in this manner. Another method, partially effective, consisted of dipping the electrode in titanous chloride and then rinsing this off with water or with hydrogen peroxide followed by water, between runs.

Another method of depolarization consisted of putting a reducing agent directly in the solution. Stannous sulfate was tried, but this merely reduced the height of the iodide waves without depolarizing the electrode presumably because of complex ion formation between the iodide ion and the stannous ion.

Sodium hyposulfite was tried as an internal depolarizer, but since it itself gave a maximum which reached a peak at + 0.82 volts, it proved to be unsatisfactory. Sodium hypophosphite, although it did not itself give a wave, was, nevertheless, not effective in depolarizing the electrode.

Still another method consisted of heating the electrode between runs. This, of course, was usable only when a platinum electrode sealed in glass was employed. Depolarization seemed to occur all right, but, unfortunately, large residual currents were obtained. According to Kolthoff and Jordan (13) these irregularities are due to strains produced in the glass around the platinum wire and may be reduced by careful annealing of the glass seals.

Another technique used was the electrolytic generation of hydrogen at the electrode, this being used alone, or being followed by the washing of the electrode in a solution of iodine in potassium iodide.

In order to determine the nature of the maximum caused by the iodide ion, polarograms were made by allowing the run to continue well up on the first wave, at which point the voltage was held constant for five minutes. The results showed that if the run were stopped at about what would be the diffusion current region of the first wave, the current would change only slightly during the five minutes that the E. M. F. was constant. However, if the electrolysis were allowed to continue at a fixed voltage well up on the second wave, a pronounced decrease in current was noticed, the current decreasing each time until it reached a value slightly less than the diffusion current of the first wave. This indicates that a second oxidation reaction takes place in which the iodide is oxidized to a higher state than that represented by the product of the first oxidation. Kolthoff and Jordan (14) obtained similar polarograms with a solution of 2×10^{-4} N potassium iodide in a buffer having a pH of 4.

They attribute the first wave to oxidation of iodide to iodine and the second to the oxidation of iodide or of iodine to the one-plus oxidation state. These results also indicate that the so-called maximum is probably not a maximum at all; but instead the 'maximum' probably represents an approach to the normal wave height followed by a dip caused by decreasing electrode effectiveness.

In order to determine whether or not the dip on the second wave might be eliminated by allowing less time for polarization, runs were made at a speed of 100 millivolts per second instead of 3.72 millivolts per second. The dip appeared as before, but the hump was considerably higher. (See Figure 4). Also polarograms were made from a positive to a negative direction. (See Figure 5). In the latter case no hump or dip appeared. On the other hand, the heights of both waves were very much smaller, the first wave being only about 10% as high as in the forward run. This phenomenon might indicate an irreversible reaction, but more probably is due to the electrode's being strongly polarized and thus only a small part of it effective.

Bortmes (3) found that 0.36 N sulfuric acid carrier could be used for iodide determination for a concentration range of 10^{-2} to 10^{-5} N. These runs could be repeated without treating the electrode each time by stopping the run at + 1.0 volt vs. the S. C. E. He obtained normal polarograms for concentrations as great as 10^{-3} N potassium iodide in 0.36 N sulfuric acid. The 0.36 N sulfuric acid apparently itself depolarized the electrode sufficiently so that a series of runs could be made without further depolarization. However, a higher concentration, 5×10^{-3} N, produced the usual dip just ahead of the carrier current region.

FIGURE 4

POLAROGRAMS FOR 2 x 10^{-4} N KI IN 0.1 N K_2SO_4 AT Pt ELECTRODE

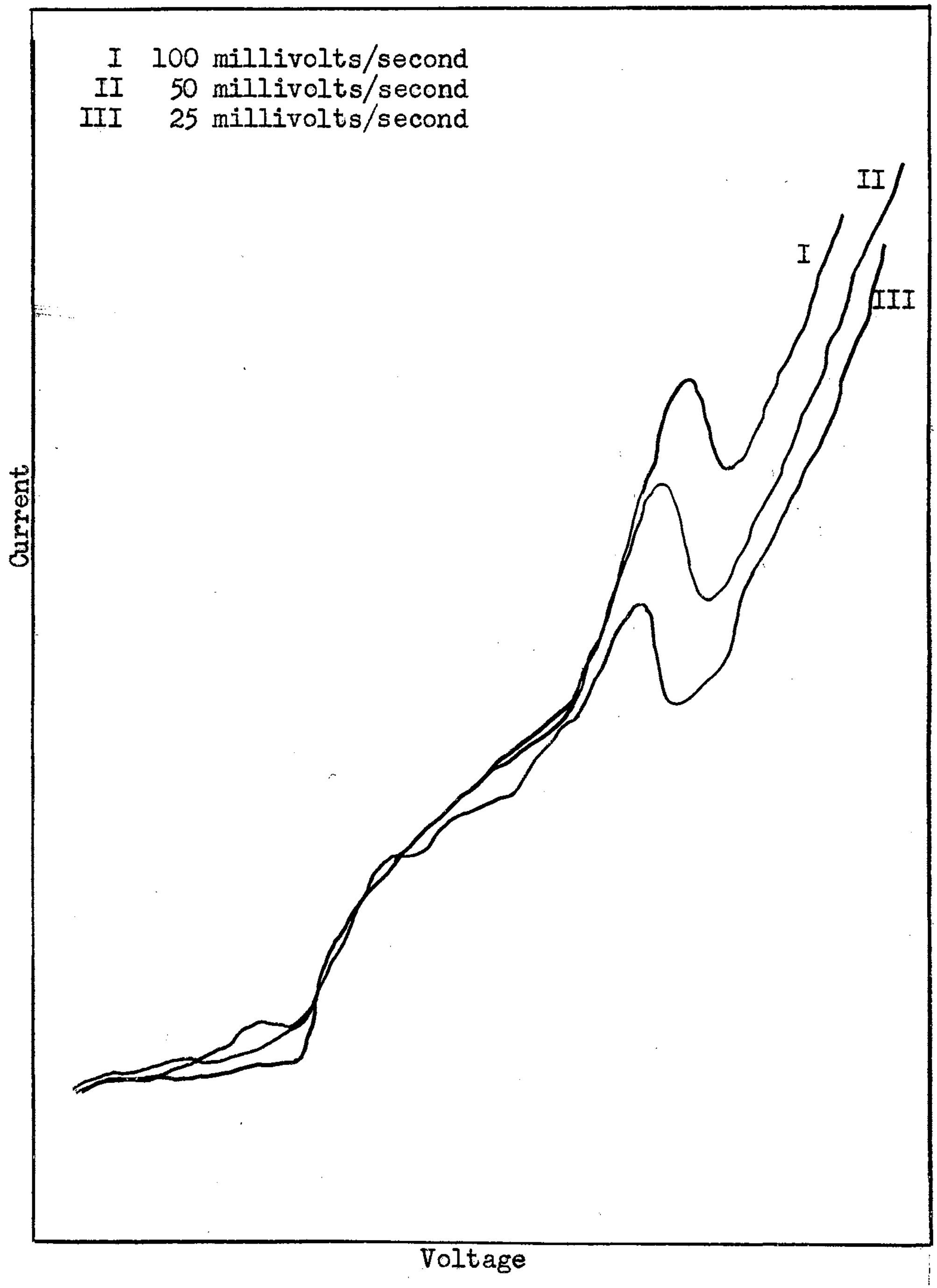
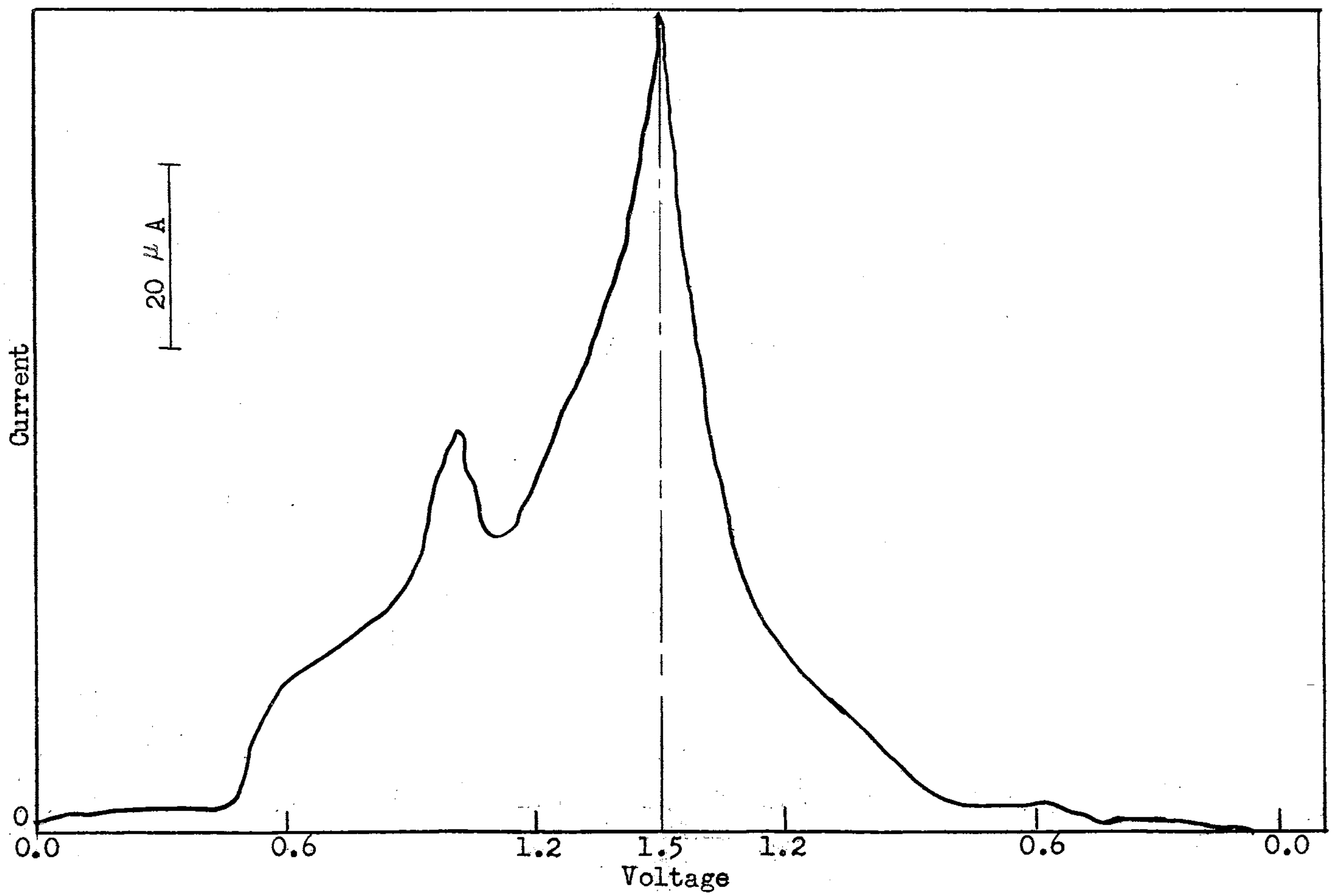


FIGURE 5

POLAROGRAM FOR 2 x 10^{-4} N KI IN 0.1 N K_2SO_4
AT ROTATING PLATINUM ELECTRODE



Kolthoff and Jordan (14) obtained similar waves for potassium iodide in 0.1 N perchloric acid carrier. They were able to determine the concentration of iodide in ranges from 10^{-5} N to 10^{-3} N by measuring the diffusion current at + 0.7 volts.

It was found in this investigation that the usual dip occurred when the run was extended to the carrier wave, the hump preceding the dip occurring at + 1.17 volts for 2×10^{-4} N potassium iodide in 0.36 N sulfuric acid. The apparent half-wave potential was + 0.57 volts. When these runs were made from a positive to a negative direction, the wave-shape was maintained, but the diffusion current was slightly less than in the negative to positive direction.

Oxidation of Potassium Bromide.

In a 0.1 N potassium sulfate carrier, a very slight indication of a wave appeared for 10^{-4} N potassium bromide solutions. A 10^{-3} N potassium bromide solution produced a wave with a half-wave potential equal to 0.94 volts. As the concentration of the bromide was increased to 4×10^{-3} N, a maximum appeared, but there was no apparent double wave as with potassium iodide--just a maximum and then after the dip, a carrier wave. When 2×10^{-4} normal potassium bromide was run in 0.36 N sulfuric acid, a wave was obtained with a half-wave potential equal to + 1.07 volts. When 2×10^{-4} N potassium iodide was added to this mixture, only one definite wave appeared. Its half-wave potential was + 0.55 volts which is very close to that of potassium iodide alone.

Oxidation of Sodium Hyposulfite and of Sodium Hypophosphite.

Sodium hyposulfite was run since it was thought that it might be a possible depolarizer for iodide. However, a 10^{-3} N solution of sodium hyposulfite in 0.1 N potassium sulfate gave a bluntly-humped curve, the maximum occurring at about + 0.82 volts. Sodium hypophosphite did not give a wave with the platinum electrode even though concentrations ranging from 10^{-4} N to 10^{-2} N were used.

Oxidation of Ferrous Ion.

Ferrous sulfate was dissolved in 1% sulfuric acid to make a 0.08 normal solution as a reductant. This was diluted with 0.1 N potassium sulfate carrier for the polarographic run. In a 10^{-4} N solution the curve produced had a half-wave potential of + 0.9 volts. (See Table I). As the concentration was increased, the wave height increased correspondingly. With the platinum electrode rather sloping residual currents were obtained while the gold electrode gave very smooth residual currents. Half-wave potentials were obtained with solution concentrations as high as 4×10^{-2} N with apparently good waves at high concentration and low sensitivity.

Oxidation of Stannous Ion.

It was found that 10^{-4} to 10^{-3} N stannous sulfate would not produce a wave at the rotating platinum electrode in either neutral or slightly acidified (with sulfuric acid) 0.1 N potassium sulfate carrier. Bortmes (3), on the other hand, obtained well-shaped waves for stannous chloride in hydrochloric acid and found that the half-wave potential decreased with an increase in the concentration of hydrochloric acid up to 3 N hydrochloric acid. He was able to make quantitative runs on the stannous ion in 2.5 N hydrochloric acid. This gave a half-wave potential of + 0.66 volts for 10^{-3} N stannous chloride.

In the present work, the half-wave potential of stannous chloride in 3 normal hydrochloric acid was found to be + 0.51 volts and in 1 N hydrochloric acid it was + 0.67 volts. Good waves were produced, but

TABLE I

HALF-WAVE POTENTIALS FOR OXIDATION REACTIONS AT INERT ELECTRODES

(vs. S. C. E.)

Ion	Molarity	Carrier	Pt	Au	Pd
I^-	1×10^{-5}	$0.1\ N\ K_2SO_4$	0.76	1.03	b
	3×10^{-5}	''	0.65, 0.82^c	0.67, 1.03^c	b
	1×10^{-4}	''	0.58, 0.82^c	0.67, 1.06^c	b
	2×10^{-4}	''	0.58, 0.82^c	0.67, 1.06^c	0.63, 1.1^c
	5×10^{-4}	''	0.60, 0.82^c	0.63, 0.94^c	b
	1×10^{-3}	''	0.58, a,c	0.63, a,c	b
	2.5×10^{-3}	''	0.58, a,c	0.63, a,c	b
	5×10^{-3}	''	0.64, 1.09^c	0.63,	b
	1×10^{-2}	''	0.63, a,c	0.64, a,c	b
	2×10^{-4}	$0.36N\ H_2SO_4$	0.57	0.79	0.79
	1×10^{-3}	''	0.54	b	0.54
Br^-	1×10^{-3}	$0.1\ N\ K_2SO_4$	0.94	b	b
	4×10^{-3}	''	b	0.88	b
	2×10^{-4}	$0.36N\ H_2SO_4$	1.07	1.02	1.20
$S_2O_4^=$	5×10^{-4}	$0.1\ N\ K_2SO_4$	0.64	0.92	b
	1×10^{-3}	''	0.64	0.97	b
	2×10^{-3}	''	0.64	a	b
	3.5×10^{-3}	''	0.70	a	b
	5×10^{-3}	''	0.70	a	b
Fe^{++}	1×10^{-4}	$0.1\ N\ K_2SO_4$	0.92	1.23	b
	2×10^{-4}	+	0.92	1.20	b
	5×10^{-4}	$0.36N\ H_2SO_4$	0.90	1.21	b
	1×10^{-3}	''	0.90	1.08	b
	2×10^{-3}	''	0.92	1.12	b
	4×10^{-3}	''	0.92	1.02	b
	8×10^{-3}	''	0.92	1.02	b
	1.2×10^{-2}	''	0.97	1.29	b
	2×10^{-2}	''	1.08	0.54	b
	4×10^{-2}	''	1.08	0.54	b
	2×10^{-4}	$0.36\ N\ H_2SO_4$	0.96	1.23	0.93
Sn^{++}	1×10^{-3}	3 N HCl	0.51	0.36	b
	1×10^{-3}	1 N HCl	0.67	0.29	b
$Fe(CN)_6^{-4}$	1×10^{-3}	$0.1\ N\ K_2SO_4$	0.6	0.21	b
$SO_3^=$	Unknown	$0.1\ N\ K_2SO_4$	0.51	0.87	b

---

a) Wave too poorly formed to make meaningful measurement.
b) Not tried.
c) Value refers to second wave.

it was necessary to protect the solution from air oxidation for good results since all of the stannous ion could be oxidized in a matter of only a few minutes.

Oxidation of Ferrocyanide Ion.

Bortmes (3) found that the half-wave potential of 10^{-3} N potassium ferrocyanide in 0.1 N sodium sulfate was + 0.29 volts for a depolarized electrode. For a polarized electrode it was + 0.58 volts. This was the only ion in which he noticed a shift in half-wave potential caused by polarization effect. He learned that best results could be obtained by making up a fresh solution of potassium ferrocyanide just before the run and using distilled water which had been freshly boiled before the nitrogen degassing treatment. He also noticed that if the potassium ferrocyanide solution were allowed to stand for a few hours and if the electrode were depolarized in the solution, a very prominent maximum would occur on the ensuing oxidation run.

In this work it was noticed that, for 10^{-3} N potassium ferrocyanide in 0.1 N potassium sulfate, the residual current was steeply climbing and merged directly into the wave. The half-wave potential was approximately + 0.6 volts. When the solution was allowed to stand for several hours, the residual current flattened somewhat although there was still an initial cathodic current at the beginning. When a fresh solution of 3×10^{-4} N potassium ferrocyanide was prepared, the waves still showed an initial negative current and a poor residual current. The break between the residual current and the polarographic wave seemed hardly noticeable. When this solution was allowed to stand, the wave height decreased and the initial current was more negative than previously. The polarograms obtained with the platinum electrode were thus not as good as those obtained with the gold electrode (described later).

Oxidation of Sodium Sulfite.

The results obtained at the rotating platinum electrode for sodium sulfite in 0.1 N potassium sulfate are in agreement with those of Bortmes (3); that is, a half-wave potential of + 0.51 volts is obtained. However, no quantitative study was made for the platinum electrode but rather runs were made to compare the platinum with the gold electrode. The same type maxima that Bortmes (3) described were also apparent. The best waves were obtained by not depolarizing the electrode between runs but by stopping the runs at + 1.2 volts. If the runs were allowed to proceed, however, the following runs showed waves with decreased diffusion currents. If the electrode were depolarized by setting the instrument at - 1.2 volts before the run, then a slight maximum would appear.

Platinum Black Electrode

Oxidation of Potassium Iodide.

When a platinum black electrode was used, a solution of 2×10^{-4} N potassium iodide in 0.1 N potassium sulfate gave a large initial cathodic carrier wave. The first anodic wave was the same as that of bright platinum. However, the second wave was ten times the height of the first, and a maximum occured at its top at about + 1.23 volts. A solution of 0.36 N sulfuric acid, with 2×10^{-4} N potassium iodide, gave waves which were not well formed and which had an initial negative current.

Gold Electrode

Oxidation of Potassium Iodide.

When a 10^{-4} N potassium iodide solution in 0.1 N potassium sulfate was oxidized at a gold electrode, the resulting curve had an apparent half-wave potential of 1.01 volts. As the concentration increased to

3×10^{-4} N, another wave appeared having a half-wave potential of + 0.67 volts. The second wave -- i.e., the one at the higher voltage--had a flat diffusion current region rather than showing the dip which appeared with the platinum electrode. After a series of runs, however, irregularities began to appear in the residual current region. This interference proved to be removable by scraping and rewaxing the electrode. At one time it was thought that the mercurous ion diffusing from the reference electrode might be causing the trouble. This theory was disproved when it was found that the deliberate addition of mercurous ions gave entirely different results. In all of these tests, the polarity was reversed at the end of each run.

In studying the possibility of using sodium hyposulfite as a depolarizer for the gold electrode, it was found that the hyposulfite itself gave a very nice curve with a half-wave potential of + 0.94 volts and therefore was not usable. Stannous sulfate, when tried as a depolarizer, merely reduced the iodide concentration and thus decreased the wave height. Sodium hypophosphite was added without changing the wave shape at all.

A solution of 10^{-3} N potassium iodide in 0.36 N sulfuric acid gave a wave which had the same half-wave potential as that obtained with a platinum electrode; that is, at + 0.54 volts. The curves were the same as with the platinum electrode except that with the gold electrode, there was no evidence of the second wave that had been obtained with the platinum electrode. When the concentration of the solution was increased to 5×10^{-3} N, a definite maximum appeared with both the gold and the platinum electrode. Later runs with the gold electrode showed that it did not become polarized when using potassium iodide in a potassium sulfate carrier. When 2 x 10^{-4} N potassium iodide was added to the carrier, the gold electrode gave a wave followed by a maximum. The wave height did not decrease in successive runs, however. When potassium iodide was used in 0.36 N sulfuric acid, a good curve was obtained with the half-wave potential at + 0.79 volts.

Oxidation of Potassium Bromide.

When 10^{-4} N potassium bromide was added to a 0.1 N potassium sulfate solution and the polarograph was set at a sensitivity of 0.08 microamperes per millimeter, no wave appeared for the gold electrode. Even a solution 2 x 10^{-3} N with bromide did not give a wave. A 4 x 10^{-3} N solution gave a small wave with a half-wave potential at + 0.88 volts; when the concentration was further increased to 10^{-2} N, the gold electrode curve had a maximum and the wave height was about one-tenth that of the platinum curve despite the fact that the electrodes were of approximately the same size. Later when 2 x 10^{-4} N potassium bromide was run in 0.36 N sulfuric acid, a curve was obtained having a half-wave potential of + 1.02 volts.

Oxidation of Sodium Hyposulfite.

When 10^{-3} N sodium hyposulfite was run in 0.1 N sodium sulfate at the gold electrode, a very nice wave occurred with a half-wave potential of + 0.94 volts. In a 2 x 10^{-3} N solution the wave changed, with a sharp-peaked maximum developing at + 1.01 volts. At higher concentrations the maximum went off scale. Even with the scanning speeds varying from 36 seconds to 10.9 minutes, little or no improvement was observed.

Oxidation of Ferrous Ion.

When 0.08 N ferrous sulfate in one per cent sulfuric acid was diluted to 10^{-4} N with a 0.1 N solution of sodium sulfate and a polarogram made, a very nice wave was obtained with the half-wave potential equal to + 1.23 volts. The wave height increased very regularly with increases in concentration, and the gold electrode gave much smoother residual currents than did platinum. In 10^{-3} N ferrous sulfate, gold gave a half-wave potential of + 0.96 volts. In a 2 x 10^{-3} N solution the half-wave potential was + 0.9 volts. Still higher concentrations, as high as 8 x 10^{-3} N, gave no further shift in the half-wave potential. However, more runs were made with the sensitivity changed from 0.4 to 1.5 microamperes per millimeter. The first run with gold gave a half-wave potential of + 1.29 volts. The next run gave two waves, one still at + 1.29 volts and one at + 0.57 volts. The following two runs produced waves each with a half-wave potential of + 0.55 volts and no evidence of a second wave. The platinum electrode did not exhibit this phenomenon.

Oxidation of Stannous Ion.

Stannous sulfate did not give a wave in either neutral or acid solution. With 10^{-3} N stannous chloride in 3 N hydrochloric acid, the gold electrode gave a wave with a half-wave potential at + 0.36 volts. The carrier wave went off scale at + 0.88 volts--which is exceptionally early for the gold electrode. With a gold electrode the wave height decreased from run to run probably due to air oxidation of the stannous chloride. A 10^{-3} N solution of stannous chloride in 1 N hydrochloric acid gave a half-wave potential at + 0.30 volts. Good runs were also obtained for 5 x 10^{-3} N stannous chloride in 1 N hydrochloric acid.

Oxidation of Potassium Ferrocyanide.

With a fresh solution of 10^{-3} N potassium ferrocyanide in 0.1 N potassium sulfate, good waves were obtained. The half-wave potential was + 0.21 volts. After the solution had stood overnight, the waves obtained were smaller, but still of good shape—as if oxidation of the ferrocyanide ion had occurred to give a lower concentration.

Oxidation of Sodium Sulfite.

With sodium sulfite in 0.1 N potassium sulfate, a maximum (apparently in the residual current) was obtained at + 0.36 volts, a normal wave with a half-wave potential of + 0.87 volts following this hump. The actual concentration of sodium sulfite is unknown because the apparatus was not protected from air oxidation.

Palladium Electrode

Oxidation of Potassium Iodide.

When 2×10^{-4} N potassium iodide was added to a 0.1 N potassium sulfate solution, the wave produced by the palladium electrode was similar to that produced by a platinum electrode. The half-wave potential was + 0.63 volts and the peak of the maximum was at + 1.17 volts. On further runs the electrode became polarized very badly. The electrode, however, could be depolarized by reversing the polarity.

When 2×10^{-4} N potassium iodide was added to 0.36 N sulfuric acid, good waves were obtained using the palladium electrode. The half-wave potential was at + 0.79 volts. The waves seemed to be better than those resulting from using either the platinum or the gold electrodes in that no tendency was noticed for a second wave to form. It was noted that the half-wave potential for the palladium electrode was greater than that for either the platinum or the gold electrodes. The electrode was scraped before each run.

Oxidation of Potassium Bromide.

When 2×10^{-4} N potassium bromide was run in 0.36 N sulfuric acid, the half-wave potential, at the palladium electrode, was + 1.20 volts. These curves were well formed with the exception of a slight maximum on the residual current just preceding the bromide wave. The technique of reversing the polarity was not satisfactory for depolarizing the palladium electrode because an additional large maximum then occurred almost immediately when starting a run, that is, at + 0.08 volts. The slight maximum at + 0.9 volts occurred whether or not the electrode was depolarized. The first maximum was formed by the pen's going immediately upscale when starting a run at zero volts and reaching a peak at + 0.08 volts.

When a mixture of 2×10^{-4} N potassium iodide and 2×10^{-4} N potassium bromide solutions was run in 0.1 N potassium sulfate, what appeared to be one wave, with a half-wave potential of + 0.76 volts, was obtained. Only the one wave occurred, but that was twice as high as that for potassium iodide alone.

Oxidation of Ferrous Sulfate.

When 2×10^{-4} N ferrous sulfate in 0.36 N sulfuric acid was run using the palladium electrode, a good wave, with a half-wave potential of + 0.93 volts, was obtained. These waves were of better form than those obtained with the platinum or gold electrode; however, there was some slope to the residual current line and the initial current was negative.

Oxidation of Sodium Hypophosphite.

Sodium hypophosphite in 0.36 N sulfuric acid was run in concentrations ranging from 2×10^{-4} N to 10^{-3} N without any wave being produced.

Platinum Amalgam Electrode

A platinum amalgam electrode was prepared by dipping a platinum wire in sodium amalgam, then treating with water to destroy the sodium. When this electrode was used in 0.1 N potassium sulfate, a maximum appeared on the residual current at + 0.43 volts followed by a wave at + 0.8 volts. In succeeding runs a maximum appeared near the top of the wave at + 1.2 volts. There was a variation in the shape of the second maximum from run to run. The potassium sulfate had been thoroughly degassed before the runs were made, but when the cathodic runs were made, maxima appeared at + 0.3 volts and - 0.3 volts, followed by a wave with a half-wave potential at - 1.5 volts. In succeeding runs these maxima disappeared, leaving only the wave with a half-wave potential of - 1.43 volts. The carrier waves then occurred at - 1.6 volts. When an anodic run was then made on the carrier, a maximum occurred on the residual current at zero voltage and another maximum occurred at the foot of the wave at + 0.5 volts. This wave had a half-wave potential of 0.8 volts and a maximum at + 1.2 volts. These maxima and waves were anodic.

When the amalgam was prepared by electroplating a wire in a solution of mercurous nitrate, a maximum appeared at + 0.48 volts followed by a wave with a half-wave potential of + 0.8 volts. A slight maximum occurred on this wave at + 1.00 volts. Quite a number of runs were made both anodically and cathodically at different initial positions trying to eliminate the maxima that appeared on the anodic run. When a cathodic run was made, maxima would appear on the cathodic side at - 0.54 volts and at - 0.75 volts. When anodic runs were made, several anodic maxima appeared, the most prominent ones being at - 0.75 volts and at - 0.33 volts.

Finally, however, when runs were made using the platinum amalgam electrode, it was found that a suitable carrier wave could be obtained by starting at + 0.5 volts. However, when stannous sulfate was added to the carrier, no indication of any wave was seen.

Gold Amalgam Electrode

A gold electrode was amalgamated by dipping it in mercury. When this was used in 0.1 N potassium sulfate, maxima occurred at + 0.48 volts and + 1.05 volts. These maxima were very pronounced in sharp contrast to those obtained with a pure gold electrode. Pure gold run in 0.1 N potassium sulfate gave a maximum at + 0.04 volts, when the run was started at - 0.3 volts vs. the S. C. E. When the run was started at zero versus the S. C. E., a maximum occurred at + 0.81 volts followed by a slight wave at + 1.02 volts. These maxima, though bothersome, were not nearly as pronounced as those obtained with the amalgamated gold electrode. When a run was started using the gold amalgam electrode on the anodic carrier and run cathodically, a maximum appeared on the cathodic wave at - 0.93. However, if the initial voltage were - 0.4, no maximum would appear on the cathodic wave.

Attackable Electrodes

Up to this point the electrodes investigated were of the so-called 'inert' type, which means that the ion in the solution, rather than the electrode material, is oxidized. Another type of electrode is the attackable electrode which becomes oxidized and forms a product with the ion under investigation, the latter remaining unoxidized; e.g.,

$$Ag + I^{-} - e \rightarrow AgI.$$

Even though the electrode material, not the dissolved ion, is oxidized, the diffusion current is dependent on the rate of diffusion of the ion to the electrode.

If the diffusion current produced by a given anion is to be separated from the carrier current so as to form a polarographic wave, the anion must be such as will combine with the metal of the electrode to form a slightly-soluble compound or a complex ion or a very weak electrolyte. The type it is most generally feasible to form is the slightly-soluble compound. These, however, are likely to coat the electrode and reduce the effective area of the latter--a phenomenon which probably occurs also when dipping polarograms are obtained with the so-called inert electrodes. To obtain more information on the behaviors of both types of electrodes, therefore, a number of attackable electrodes were studied. Included were some amalgamated electrodes, since certain amalgams might be expected to give a fluid surface to which the product would not adhere so tightly. The electrodes in the following section are examples of the attackable electrode.

Copper vs. Fluoride

The carrier used for these determinations was 0.1 N potassium nitrate. After several runs it was found that the range at which the copper electrode could be used anodically was only from - 0.4 volts to + 0.02 volts. Even than a cathodic wave occurred at - 0.29 volts. Potassium fluoride was then added in an attempt to get a wave due to reaction of copper with fluoride forming insoluble copper fluoride. However, no wave was produced even though potassium fluoride was added in concentrations from 10^{-4} N to 0.08 N.

Copper vs. Iodide.

When 2 x 10^{-4} N potassium iodide was added to 0.1 N potassium nitrate solution, the height of the carrier wave seemed to be increased, and an apparent cathodic wave with a half-wave potential of - 0.28 volts appeared. The entire wave occurred below the zero current line and an anodic maximum was produced at - 0.1 volts. The electrode was sometimes depolarized by reversing its polarity, by scraping it, or by dipping it momentarily in concentrated nitric acid. However, these treatments did not produce better waves than did the nondepolarized electrode.

Copper Amalgam vs. Fluoride.

After several anodic runs it was found that the useful range of the copper amalgam electrode was from - 0.9 volts to + 1.4 volts. If the solutions were not degassed, the cathodic carrier appeared earlier. When 10^{-3} N potassium fluoride was added, no wave appeared. The concentration was increased to 2×10^{-3} N with still no results.

Lead vs. Sulfate.

A lead electrode was prepared by rolling lead into a cylinder about one millimeter in diameter, waxing it, and scraping it. When a 0.1 N potassium nitrate carrier was used, it was found that the useful range of the electrode was from - 1.1 volts to - 0.80 volts. This particular plateau was considerably below the zero current line. Successive runs moved this residual current closer to the zero current line. However, with such a narrow range of usefulness and the negative current so large, the electrode is undesirable for use in analysis. If the electrode were allowed to stand in the carrier for thirty minutes before the run was made, the pen went off scale immediately in the positive direction. It was thought that since sulfate forms an insoluble precipitate with the lead ion, the reaction being

$$Pb - 2e + SO_4^{=} \rightarrow PbSO_4$$

this might be a method for determining sulfate concentration. Therefore, 2×10^{-4} N potassium sulfate was added to the potassium nitrate carrier.

The resulting curve consisted mostly of a cathodic current with a small maximum away from the zero current line at about + 0.88 volts. The following curves had much the same shape as the original carrier. When 10^{-3} N potassium sulfate was added, there was no significant difference in the results. This solution was then allowed to stand for two hours and run again; the pen went off scale in a positive direction almost immediately, just as had happened with the carrier alone. When the electrode was rewaxed and runs made with 10^{-3} N potassium sulfate, a dip in the curve occurred at - 0.88 volts; then what appeared to be a polarographic wave occurred at - 0.8 volts. However, this wave was entirely on the negative side of the zero current line; so the overall reaction was a reduction rather than an oxidation. When 5×10^{-3} N potassium sulfate was added, there was a small dip in the wave and an apparent polarographic wave still below the zero current line. However, this wave was smaller than that with the 10^{-3} N solution. With two successive runs, it would disappear entirely, but the minimum and the wave would also disappear. This wave shape did not seem to warrant the use of the lead electrode in sulfate determination.

Lead Amalgam vs. Sulfate.

The lead amalgam electrode was prepared by first plating a platinum wire with lead from a 0.1 N lead acetate solution and then plating it with mercury from a mercurous nitrate solution. After several runs, both anodic and cathodic, it was found that the anodic maxima at + 0.35 and ± 0.03 could be reduced by gradually reducing the initial voltage with a bridge until the current reached zero. In this manner zero volts could be obtained. From 2×10^{-4} N to 5×10^{-3} N potassium sulfate was then added to 0.1 N potassium nitrate, but no waves were produced. Later it it was found that when the lead electrode was replated and then the run started at - 0.5 volts, a linear, fairly rapidly-rising curve was obtained as far as + 0.37 volts at which time the current dropped rapidly. In the belief that the lead was being dissolved completely off the electrode, the lower limit of the electrode was changed to - 0.9 volts in order to prevent oxidation of lead itself. The useful range then was from - 0.9 volts to - 0.5 volts. This carrier wave is still below zero current. When 2 x 10^{-4} N potassium sulfate was added, no wave occurred, but there was a gradual increase in current. The following two runs then gave a maximum at - 0.06 volts and + 0.03 volts respectively. Succeeding runs were so irregular the electrode had to be replated. More runs showed maxima occurring at 0.1 volts and at 0.03 volts, and the following run was very irregular. Therefore, since no wave occurred except that of the carrier when potassium sulfate was added, the lead amalgam electrode was not satisfactory for the determination of sulfates.

<u>Silver</u> <u>vs</u>. <u>Halide</u>.

The first work done using a silver anode indicated that the useful range would be from 0.0 volts to + 0.4 volts. It was later discovered that by removing oxygen the range could be extended to more negative values. The halide tried first, potassium fluoride in a 0.1 N potassium nitrate carrier, gave no indication of a wave even though the runs were tried at a very high speed on both the experimental model polarograph and on the oscilloscope. A 10^{-3} N solution of potassium chloride in 0.1 N potassium nitrate was then tried. The only observable result was a seeming shift of the carrier wave to more negative values, the pen coming to rest at a large cathodic current at the beginning of each run.

Potassium iodide was also tried at the silver electrode. However, the pen went upscale almost immediately indicating that the iodide wave was already present at the beginning of the run. When the starting voltage was changed to - 0.2 volts in order to catch the foot of the wave, the resulting iodide wave rose to a maximum, dropped, then leveled off normally. The half-wave potential for this wave was - 0.38 volts. After each run a yellow precipitate (suspected to be silver iodide) was noticed on the electrode. Whenever the carrier was run, there was a large initial cathodic current which rose to an anodic maximum at + 0.03 volts, then leveled off a little above the zero current line. This initial negative current was later found to be due partially to oxygen. Several runs were made using 2 x 10^{-4} N potassium iodide, it being observed that the wave height was less for each run. When the electrode was washed in sodium thiosulfate to remove silver iodide, the wave height was again increased and the initial negative current was decreased.

Silver Amalgam vs. Halide.

Since silver electrodes gave a wave with potassium iodide, it was thought that by using a fluid amalgam surface the coating would not adhere so readily to the electrode thus allowing better duplication of results. For this study, 0.1 N potassium nitrate was chosen initially as carrier. When the run was started at - 0.2 volts, a maximum appeared at + 0.03 volts. When it was started at - 0.1 volts with 2 x 10^{-4} N potassium iodide, a large initial negative current followed and a maximum appeared at + 0.15 volts. Because of the undesirability of the maximum at + 0.03 volts, several attempts were made to eliminate it. During the series, the reference electrode was changed, the indicator cell was emptied and its sidearm repacked, and a fresh silver amalgam electrode was made from freshly-opened, triply-distilled mercury. Still the maximum appeared. To investigate the possibility of the carrier's being contaminated, some of the same solution was tested with a D. M. E. The results showed only oxygen interference and the necessity of degassing before runs.

A 0.1 N potassium sulfate carrier proved to display somewhat the same characteristics as those found with the nitrate and was chosen for iodide determinations. In early runs maxima appeared at + 0.09 volts and the diffusion currents were somewhat irregular. However, as the technique was improved, the results became better and indicated that it might be possible to use this method for iodide determination. At a later date when this type of analysis was made again, the initial carrier wave often was very good. Frequently, however, maxima would appear at from + 0.01 volts to - 0.03 volts during a series of runs. When 10^{-4} potassium chloride was added to 0.1 N potassium sulfate, a wave occurred with a half-wave potential of + 0.28 volts but it was so close to the carrier wave that the diffusion current region was very narrow.

When potassium bromide was added in addition to chloride, a wave with an apparent half-wave potential of + 0.13 volts was formed. When potassium iodide was added to this same mixture, the bromide and chloride wave seemed to merge so that the chloride wave was not easily discernible. The carrier was very thoroughly degassed for these runs. Early work indicated that at an initial voltage of - 0.2, a large negative current would be present but an increase of the voltage negatively made the current still more negative. This was followed by a sudden rise to near zero. It was then possible to get an initial voltage of - 0.8 without an appreciable cathodic current. However, there was still a maximum at 0.0 volts. It was noted early that, in successive runs using 10^{-4} N potassium iodide, there was a regular decrease in wave height. At higher speeds the decrease in wave height was not present.

Since it was recognized early that oxygen was an interfering substance, a new electrode and cell arrangement (See Figures 2 and 3.) was made so that it would be possible to exclude oxygen completely from the apparatus and to add potassium iodide quantitatively. It was thought that by eliminating oxygen a much better carrier wave could be obtained. Even with the new cell and thorough degassing, however, the carrier wave was not perfect. Several cathodic runs were made to confirm the belief that oxygen interfered. The addition of sodium sulfite, which is known to be especially effective in removing oxygen, resulted in the cathodic residual current's being considerably reduced. Although these results supported the theory of oxygen interference, sodium sulfite could not be used to remove oxygen in runs on halides because of the ease with which it itself is oxidized anodically.

In order to see whether or not peroxide formation interfered, hydrogen peroxide was added to the carrier but without any effect.

Another possible interference was diffusion of mercurous ions from the reference cell. To examine this possibility, mercurous sulfate was added directly to the indicator cell. No change was observed in the general shape of the carrier wave, but a definite cathodic current was produced.

Cooke (6) reported similar interference when he used a silver electrode sealed with ceresin wax; he reported the necessity of using Tygon tubing for connections between the nitrogen tank and the electrolysis cell. In order to prevent leakage of solution to the rotating shaft through breaks in the coating around the electrode, he made his electrode by threading a silver wire through a polyethylene sleeve attached to a steel shaft, then sealed the electrode with Duco cement. He also pointed out the necessity of degassing with the electrode out of the solution.

In this work, Tygon tubing was then put on the purifying train and the electrode left out of solution during degassing. It was thought that leakage around the electrode might be reduced by using a platinum electrode and silver plating only that portion used since it was possible that the leakage was caused by the amalgam dissolving part of the silver and consequently loosening the wax seal. When the silver electrode was removed from the brass shaft, it was seen that the shaft had actually become amalgamated even though it had been coated with ceresin wax. A platinum wire was then sealed in a glass bead and fastened to the shaft. This was plated and amalgamated. However, there was still trouble with a large initial negative current and a maximum. Since Kolthoff and Jordan (14) report that residual currents occur with the platinum electrode unless the electrode is carefully annealed in glass, it was thought the difficulty might be due to the seal of the platinum in glass. Since it was desirable to have a bead around the platinum wire to limit the area being scraped, it was decided to slip a snugly-fitting glass bead over the wire and to seal it with wax or cement without fusing the glass. This technique was used in all the remaining experiments.

Another anomaly occurring on the curve with a neutral 0.1 N potassium sulfate was a wave just preceding the carrier wave. Potassium perchlorate gave similar results; consequently in the belief that dissolved carbon dioxide or hydroxyl ions in the solution might be the cause of the difficulty, acidification was tried. Perchloric acid in the perchlorate or sulfuric acid in the sulfate removed this spurious wave effectively, only one part of sulfuric acid in 10,000 parts of solution being sufficient to eliminate the wave. Higher concentrations of sulfuric acid did not help the carrier wave, but sometimes seemed to make the initial portions worse.

Since sulfuric acid in potassium sulfate was suitable, it seemed that the salt, potassium acid sulfate, would be satisfactory. Indeed a few preliminary runs with potassium acid sulfate indicated that it might be satisfactory. Unfortunately, however, the carrier wave was such as to cast some doubts as to the purity of the salt. Consequently the carrier chosen for this work consisted of 0.1 N potassium sulfate and one part in 10,000 of sulfuric acid. Even then it was difficult to get good carrier waves consistently, and it was found necessary to be sure that the solutions was thoroughly degassed before each run and that the electrode was well sealed.

The quantitative data obtained for potassium iodide using the silver amalgam electrode was obtained by using the following procedure: After the electrode was fitted in the shaft, it was heated, especially if the electrode had been used for previous runs. This improved the carrier waves obtained. After the heating, the glass bead was slipped over the electrode and the whole shaft coated with ceresin wax. It was found best to keep the wax quite hot at first to allow thorough covering of the electrode and shaft. The electrode was dipped repeatedly until a coating of wax about 1 mm. in thickness covered the shaft and electrode. When the whole had cooled, the platinum wire beyond the glass bead was scraped with a razor blade in order to remove the wax.

The electrode was then plated with silver from a silver cyanide solution recommended by Dr. H. M. Trimble. The solution was prepared in the following manner: 3.4 grams (0.02 moles) silver nitrate were added to 200 milliliters of water. The silver from this was then precipitated as hydrated silver oxide by the addition of sodium hydroxide. The product was washed by decantation, then dissolved in 0.04 molar potassium cyanide. The resulting bath was diluted to 100 milliliters. The plating was done by using the silver cyanide bath with the platinum wire as a cathode and a silver wire as anode. According to Creighton and Koehler (8) silver plating should be done at about 0.4 amperes per square decimeter. For an electrode 0.81 millimeters in diameter and 1.70 millimeters long, the necessary current was calculated to be 194 microamperes. Care should be taken to see that an even crystalline deposit of silver is plated on to the electrode. After the electrode was plated at 200 microamperes and about 0.28 volts for thirty minutes, it was washed in distilled water.

At this point it was necessary to clean the electrode further before amalgamating since chloride-like waves appeared on previous runs when the electrode was not thoroughly clean. For this cleaning, hydrogen was evolved cathodically for five minutes from the electrode at 200 microamperes and 2.4 volts in dilute sulfuric acid, a platinum wire being used as the anode. The electrode was rinsed with distilled water, dried, and then amalgamated by dipping it in mercury or in mercury saturated with silver for five minutes. It was then ready for immediate use.

At one time it was thought a further cleaning could be accomplished by evolving hydrogen from the amalgam electrode. This, however, proved to give new oddities and was, therefore, discontinued.

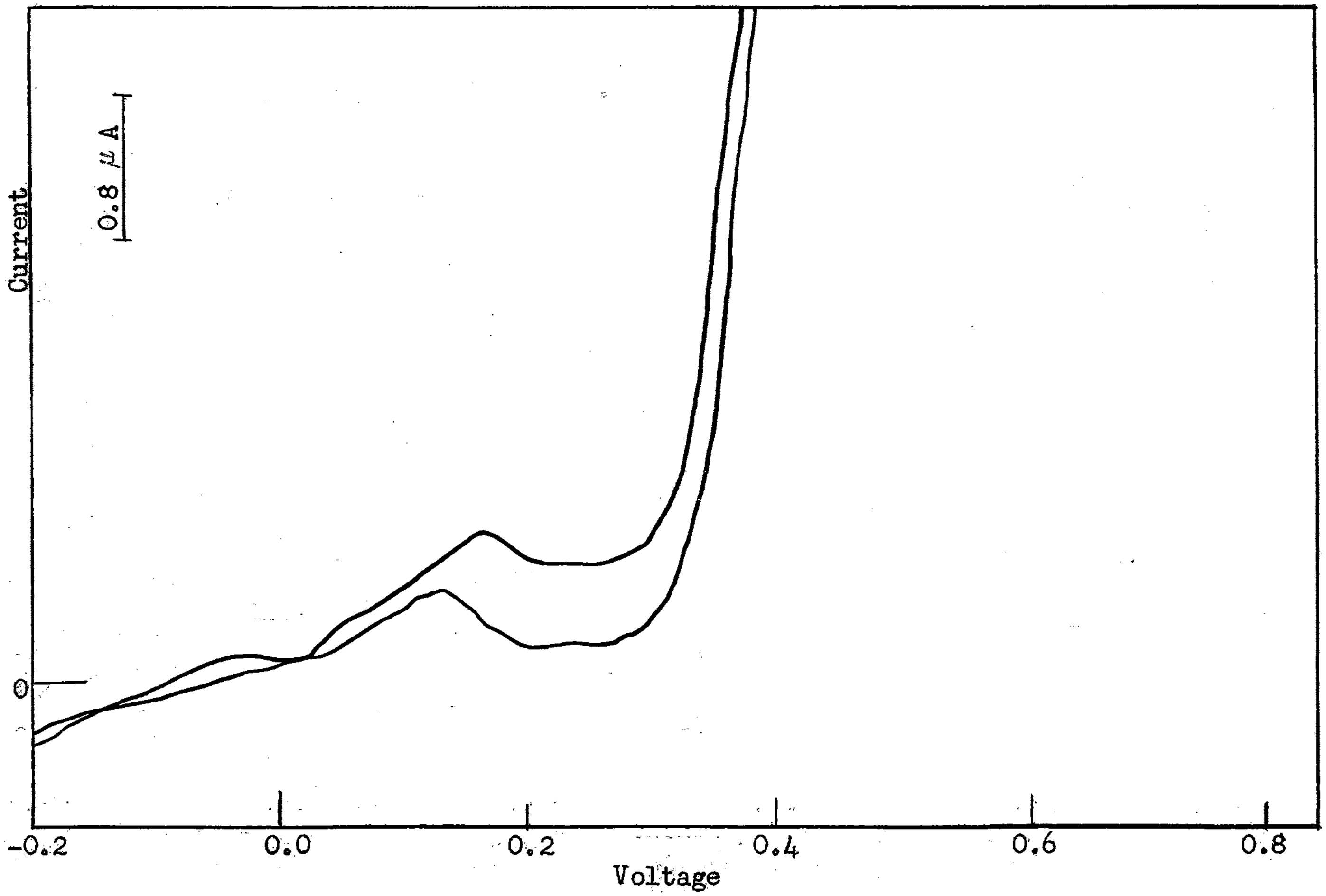
The electrode was then assembled in its holder and the solution degassed with the electrode out of the solution.

Before an anodic run was made, it was found beneficial to make at least two cathodic runs covering the range + 0.2 volts to - 0.8 volts. During the first run an irregular maximum appeared at - 0.6 volts. The maximum did not appear on the second run. If the electrolysis proceeded beyond the decomposition potential of the carrier, that is beyond - 1.0 volts, the maximum mentioned earlier as occurring at + 0.03 volts was increased in the following anodic run. During a series of runs, the anodic curve could sometimes be improved by applying a voltage of - 0.8 volts before the run until the current became constant. The - 0.8 volts was large enough to discharge the impurity due to the amalgamation and small enough to prevent decomposition of the carrier. The anodic runs were made, the starting voltage, unless otherwise described, being - 0.2 volts.

During actual iodide determinations it was found necessary to wash the electrode with sodium thiosulfate between runs to dissolve the silver iodide that had formed on the electrode during the preceding run. This was especially true for higher concentrations of potassium iodide made at conventional scanning rates. When the anodic diffusion current proved to be irregular it often could be improved by holding the electrode at - 0.8 volts again before the run. For new electrodes it was found best to make several anodic carrier runs before adding potassium iodide.

When, as sometimes happened especially if the electrode aged, the residual currents became too large, the amalgam was dissolved off the electrode with concentrated nitric acid and the electrode was rewaxed and replated. Although the maxima on the carrier waves were objectionable from the standpoint of obtaining well-formed waves (See Figure 6.) they did not seem to influence the actual wave height. The diffusion

POLAROGRAM FOR 4×10^{-6} N KI IN SLIGHTLY ACID 0.1 N K_2SO_4 AT ROTATING SILVER AMALGAM ELECTRODE



currents were obtained by subtracting the residual current from the total limiting current at + 0.25 volts.

The potassium iodide was weighed on an analytical balance immediately preceding use. It was then dissolved in water which had been freshly boiled to remove all the oxygen. The stock solution was diluted quantitatively to concentrations convenient for addition to the carrier solution in the cell. The final solution was made in the cell itself after the carrier solution had been degassed, by adding the standard iodide solution by means of a two-milliliter microburette with graduations of 0.01 milliliter. After each addition of the sample, the solution was further degassed, the nitrogen serving also to mix the potassium iodide throughout the solution. The cell was thermostated at 25.0° ± 0.1° C.

In making iodide runs at a concentration of 10^{-4} N, it was soon noticed that a constant decrease in wave height was obtained from run to run. At the same time a yellow deposit was observed on the electrode at the end of each run. Also in making concentration studies, it was noticed that the ratio of the diffusion current to the concentration decreased at higher concentrations. Since it was thought that the silver iodide covering the electrode might be effectively reducing its area, a method was tried whereby the electrode was washed with sodium thiosulfate between runs. This greatly improved the results by giving a fresh electrode surface for the reaction each time. Even washing with a stream of water from a wash bottle helped some. It was also found that the product could be at least partially removed from the electrode by applying a potential of - 0.8 volts across the cell for about two minutes at the end of each run. In making concentration studies it was found that the deposit became visible at a concentration of 10^{-5} N to 5×10^{-5} N. At 10^{-4} N, although well-formed waves were obtained (See Figure 7.), this coating was very pronounced, and at 3×10^{-4} N and greater, not only did the diffusion current decrease from run to run when the electrode was not washed, but also the diffusion current had a negative slope during any given run. (See Figure 8). Since this might have been caused either by the electrode's becoming coated with silver iodide and the effective area thus being reduced or by depletion of silver atoms from the surface of the amalgam, the atoms not diffusing to the surface fast enough to react with the iodide that was diffusing in, it was decided to check each of these possibilities. To do this, the run was carried to a point in the dip just preceding the carrier wave. In one case, the applied voltage then was cut off completely and the electrode allowed to stand for about three minutes. When the run was resumed, the current did not go up immediately, as it should have if the diffusion of the silver ion was responsible for the negative slope on the diffusion current. On the next try when the run was stopped at the same place, the electrode was removed and washed with sodium thiosulfate. When the run was started again at that same point, the current immediately jumped up to beyond the original diffusion current level indicating that now more surface was available for the reaction. Thus it was shown that the silver iodide on the surface of the electrode partially covered the electrode and rendered portions of it inactive for further reaction.

The upper concentration limit for which I_d vs. concentration was linear in the silver amalgam-iodide experiments made at a scanning rate of 1.24 millivolts per second, was about 3×10^{-4} N. It was thought that since the quantity of product formed should follow Faraday's law,

FIGURE 7

POLAROGRAM FOR 1 x 10^{-4} N KI IN SLIGHTLY ACID 0.1 N K_2SO_4
AT ROTATING SILVER AMALGAM ELECTRODE

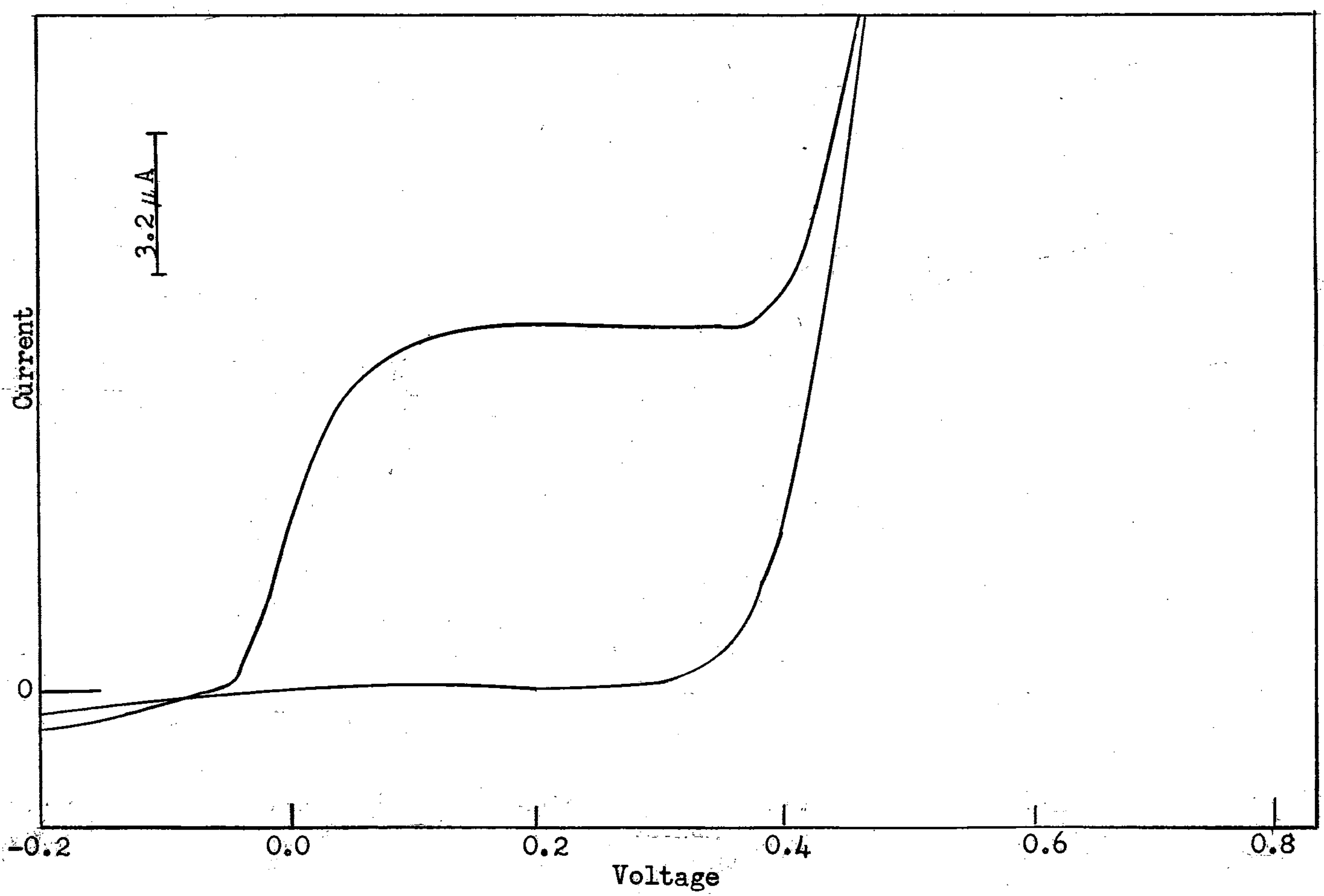
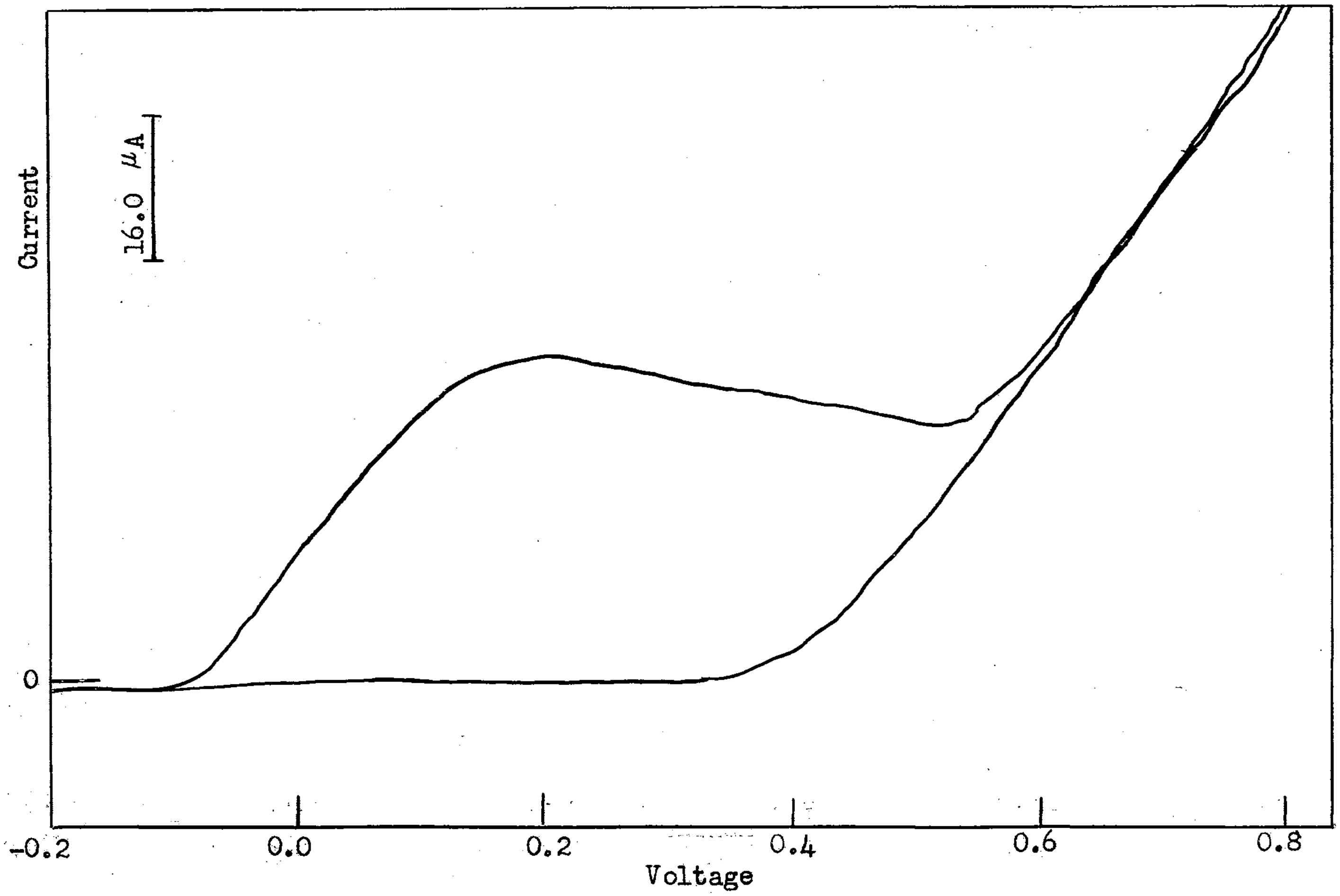


FIGURE 8

POLAROGRAM FOR 4.7 x 10^{-3} KI IN SLIGHTLY ACID 0.1 N K_2SO_4
AT ROTATING SILVER AMALGAM ELECTRODE



by making faster runs of 4.96 millivolts per second, higher concentrations of iodide could be analyzed quantitatively. When this was tried, it was found that concentrations up to 3 x 10^{-3} N could be analyzed if the electrode were washed between runs with sodium thiosulfate. These runs were fast enough so that in no case did the diffusion current decrease during the run. At still higher concentrations, up to 10^{-2} N, the wave seemed to shift to higher voltages, but the diffusion currents obtained still showed no polarization dip. Linearity between I_d and concentration fell off badly, however. At speeds of 1.24 millivolts per second the wave height decreased about 4% from run to run for 10^{-4} N potassium iodide. At lower concentrations it probably would not be necessary to wash the electrode with sodium thiosulfate before each run. However, if several runs are made, the sodium thiosulfate wash would be advisable. At higher speeds the concentrations could be increased without having to wash between runs.

Repeated trials on exactly the same solution and with the same basic electrode showed no significant differences in diffusion current when the electrode was dipped in amalgam, used for a run, then dipped again and retested. This indicates that reamalgamation can be done reproducibly.

TABLE II

EFFECT OF REPEATED RUNS WITHOUT DEPOLARIZATION

SILVER AMALGAM vs. IODIDE IN SLIGHTLY ACID 0.1 N K_2SO_4
Iodide Concentration = 9.25×10^{-5} N
Polarization Rate = 1.24 mv./sec.
Temperature = 25.0° ± 0.1° C.

Electrode Treatment Between Runs	I_d in μA/mml./liter
None	102.2
"	94.6
"	90.1
"	84.9
"	82.8
"	78.2
"	74.7
"	71.2
"	66.5
Washed with water	92.0

TABLE III

EFFECT OF REPEATED RUNS USING VARIOUS ELECTRODE TREATMENTS

SILVER AMALGAM vs. IODIDE IN SLIGHTLY ACID 0.1 N K_2SO_4
Iodide Concentration = 1.0×10^{-4} N
Polarization Rate = 1.24 mv./sec.
Temperature = 24.0° ± 0.2° C.

Electrode Treatment Between Runs	I_d in μA/mml./liter
None	99.0
"	89.0
"	80.0
Washed with water	97.0
None	82.0
"	75.0
Washed with $Na_2S_2O_3$	98.0
"	97.5
"	96.5
None	60.0

TABLE IV

DATA OBTAINED FOR IODIDE ION AT ROTATING SILVER AMALGAM ELECTRODE

(Saturated Silver Amalgam Dipped Type;
Carrier, Slightly Acid 0.1 N H_2SO_4)

Polarization Rate = 1.24 mv./sec.
Temperature = 25.0° ± 0.1° C.

Molarity of I^-	$E_{1/2}$ (vs. S.C.E.)	Diffusion Current, μA/mml./l.	
		At + 0.25 Volts	At Best Plateau
	Part a		
1.11×10^{-6}	0.07	90.1	
2.50×10^{-6}	0.10	82.4	
4.44×10^{-6}	0.08	86.9	
1.01×10^{-5}	0.06	93.1	
2.50×10^{-5}	0.04	95.2	
5.16×10^{-5}	0.03	96.3	
7.31×10^{-5}	0.02	94.4	
1.02×10^{-4}	0.01	95.2	
	Part b		
1.11×10^{-4}	0.02	87.2	
2.90×10^{-4}	0.03	86.8	
4.65×10^{-4}	0.02	76.5	77.5
6.35×10^{-4}	0.02	55.4	
1.10×10^{-3}	0.02	42.5	
1.96×10^{-3}	0.01	31.4	33.5

TABLE V

DATA OBTAINED FOR IODIDE ION AT ROTATING SILVER AMALGAM ELECTRODE

(Saturated Silver Amalgam Dipped Type;
Carrier, Slightly Acid 0.1 N H_2SO_4)
Polarization Rate = 4.96 mv./sec.
Temperature = 25.0° ± 0.1° C.

Molarity of I^-	$E_{1/2}$ (vs. S.C.E.)	Diffusion Current, μA/mml./l.	
		At + 0.25 Volts	At Best Plateau
6.30×10^{-6}	0.09	89.8	
3.79×10^{-5}	0.02	92.3	
6.98×10^{-5}	0.01	101.8	
1.01×10^{-4}	0.02	114.1	110.9
2.18×10^{-4}	0.00	102.4	104.1
4.06×10^{-4}	0.01	98.8	100.7
6.05×10^{-4}	0.04	93.5	100.8
8.33×10^{-4}	0.07	81.8	95.1
1.20×10^{-3}	0.10	70.5	94.0
1.97×10^{-3}	0.10	43.0	85.4
1.97×10^{-3} a	0.22	43.4	93.4
3.00×10^{-3} a	0.27	31.8	85.7
4.79×10^{-3} a	0.60	21.3	74.5
4.79×10^{-3} b	0.63	20.2	78.9
7.02×10^{-3} b	0.79	15.0	68.6
9.21×10^{-3} b	0.90	13.5	63.2

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a) Polarization Rate = 2.48 mv./sec.
b) Polarization Rate = 3.72 mv./sec.

CONCLUSIONS

Nature of Polarization.

As defined earlier, the term polarization is used in this thesis to denote any effect produced by electrolysis that prevents repeated use of an electrode without preliminary treatment. In this research it was found that polarization gives rise to at least two difficulties: (1) if successive runs are made without depolarizing the electrode, each succeeding run shows waves which are smaller and less reproducible than the preceding one as if the polarization is increasing from run to run; and (2) the original polarographic wave shows distortion from run to run in that the wave rises as if to follow a normal polarographic curve but reaches a limiting value and then rapidly drops off, leaving a peak in the curve. Bortmes (3) and Bridgeman (4) observed similar phenomena and showed that the types of polarization present vary with both the carrier electrolyte and with the oxidizable substance being studied. Bridgeman (4) found when he used a S. C. E. as the reference electrode, that chloride ion diffusing through the salt bridge caused trouble with the determinations even at potentials below that at which chloride is normally oxidized. Bridgeman also found that for a phosphate buffer polarization manifested itself in the form of a maximum on the residual current at from + 0.6 to + 0.9 volts vs. the S. C. E.

From the results obtained by Bortmes and Bridgeman, and those obtained in this research it seems highly probable that the so-called inert electrodes, therefore, seldom are really inert. One of the best evidences of this is the fact that different electrodes give different results with the same ion and the same carrier. In the case of iodide, for example, in a carrier of 0.1 N potassium sulfate, the waves obtained with the platinum and palladium electrodes are quite similar each showing a good wave followed by a second wave with a maximum and then a dip, while the gold electrode does not show the maximum on the second wave. Bamberger (2) has shown just recently that a carbon electrode does not seem to become polarized as readily as do the platinum, palladium, or even the gold electrode. In the case of gold electrodes polarization does not take place so readily as with platinum; but when the gold does become polarized it is depolarized only with great difficulty. With sodium hyposulfite platinum electrodes give waves with a dip, whereas gold electrodes give such maxima or dips only at very high concentrations. With ferrous sulfate, platinum, palladium, and gold electrodes give waves whose shapes are well formed; the half-wave potentials, however, vary with the electrode material. This indicates that the electrode itself must react with some component of the mixture, must catalyze the reaction, or must become polarized in such a manner that the electrode reaction cannot take place in the same manner for each electrode. Whatever the case, the electrode could scarcely be said to act as an inert electrode.

In some cases a change in solvent will eliminate or minimize these dips. Bortmes (3) found that the platinum electrode becomes polarized when iodide is used in a neutral sodium sulfate carrier; however, by adding sulfuric acid he was able to obtain good waves providing the maximum voltage used during the run did not exceed + 1.0 volts. In this investigation it was shown that by continuing the run to well up on the carrier wave, a maximum appears even with a 0.36 N sulfuric acid carrier but at a much higher voltage than with the neutral sulfate carrier. On the other hand, however, repeated runs were reproducible even without depolarizing between runs--which is not the case with neutral sulfate carriers.

In both this research and that of Bortmes, it was found that the stannous ion gives no evidences of a polarographic wave in a 0.1 N sodium sulfate carrier at the platinum electrode. This pointed to another type of polarization as being possible--i.e., the formation of a coating of insoluble oxidation product, thus decreasing the effective area of the electrode. When hydrochloric acid (in which the oxidation product, metastannic acid, is soluble) was used as carrier, very good waves were obtained. The half-wave potential shifted to less positive potentials as the concentration of the hydrochloric acid was increased, as might be expected when one considers the complexing action of chloride with stannic tin. On the other hand, the half-wave potential of the stannous ion was different at platinum than at gold (See Table I.)--which suggests that in this case both types of polarization were present, at one or both electrodes.

Higher speed runs in many cases give higher diffusion currents and better formed waves. Bridgeman (4) found that at a scanning rate of 10.5 mv./sec. the phenol anodic wave contained a very pronounced maximum, while when runs were made at the higher rate of 100 mv./sec., the wave was well formed. In this investigation, on the other hand, it was found that when iodide in potassium sulfate carrier is run at various speeds, although the diffusion current is higher for the higher speeds, the dip is not eliminated. In both cases, however, improvement resulted, the currents being greater for faster runs. If polarization is caused by product formation, the amount of product formed should follow Faraday's law. Consequently, polarization should be, and apparently is, less at the higher scanning rates.

Similarly, however, since the current is smaller with lower concentrations, polarization should be less if solutions of smaller concentration are used. This was, in general, found to be the case. For example, at gold electrodes 10^{-3} N sodium hyposulfite gave very well-formed waves; but when the concentration was increased to 2×10^{-3} N, a very sharp-peaked maximum occurred. Similarly, Bridgeman (4) was able to obtain much better phenol waves below a concentration of 5×10^{-3} N, and the relationship between I_d and concentration was much more linear for concentrations smaller than this. Likewise 10^{-3} N potassium iodide in sulfuric acid gives a very nice wave, while 5×10^{-3} N potassium iodide gives a wave with a strong dip. Naturally, a quantitative test of the application of Faraday's law to polarization could not be made; for some of the product must fall off and that which does cling would be expected to be at least somewhat permeable. The fact, however, that even a qualitative following of the law occurs, is strong evidence for the theory suggested.

The theory, therefore, accounts for the dip observed in the wave and also for the decreasing wave height when repeated runs are attempted without depolarization. It is equally obvious, however, that the product does not depend entirely on the electrolyte, but partly upon the electrode itself; i.e., the electrode may take part in the reaction. At lower concentrations smaller electrolysis currents flow since current is proportional to concentration which means that a smaller quantity of product would be deposited on the electrode. Also, since the amount of a material that deposits on the electrode is proportional to time elapsed, a smaller quantity would be deposited in a faster run than in a slower run.

Since several factors enter into the polarization of the electrode, the concentration range chosen for study must be tested for each ion to be analyzed and for each environment. If one carrier will not work, new ones should be tested, the idea in general being to get a good solvent for any oxidation product, whether the product is a compound of the electrode material or merely of the ion oxidized.

When a platinum black electrode was used for the analysis of potassium iodide in 0.1 N potassium sulfate, the second wave was nearly ten times the height of that obtained with the bright platinum electrode, the first wave in each case being approximately the same. The fact that the first waves are similar indicates that the effective area available for reaction is approximately the same since evidently polarization does not occur to any great extent on the first wave. Since the second wave with the black platinum is so much larger than that for the bright platinum, it is obvious that more surface is available for the reaction. The fact that the first wave was unaffected while the second was enhanced would seem to indicate that while the outer surface of the porous platinum black may become coated, when such happens, the inner structure of the mass takes over and acts as electrode surface, thus offsetting, to a great extent, the polarization.

In order to obtain a better understanding of the polarographic behavior of electrodes upon which an insoluble product was being formed, it was decided to study some electrodes which are known to be easily attacked. For this reason, such electrodes as copper, lead, and silver were chosen for investigation, with anions which would be expected to form insoluble precipitates with the cation of the metal used. In this manner, the surface of the electrode would be covered with insoluble material and rendered less effective in further reaction. Amalgams also were tried, since it was thought that their fluid surfaces would prevent a precipitate's adhering tightly, and thus make it more permeable. In addition an amalgam surface is more reproducible and less subject to irreversible effects. Of the electrodes tried, the silver seemed to be the most promising for use with halides. When potassium iodide was run using either silver or the silver amalgam electrode, a visible coating of yellow precipitate appeared. The waves obtained were very similar to those in which polarization had been observed with the so-called inert electrodes. The usual dip occurred, and repeated runs made without depolarization resulted in rapidly-decreasing wave heights. The amalgam, however, was, as expected, less strongly polarized than was the pure silver.

While the coating could be partially removed just by using a stream from a wash bottle, it was more effectively removed by washing the electrode with sodium thiosulfate. Since this product was formed by an oxidation reaction, it could also be partially removed by making the electrode the cathode and reducing the product. In each case the yellow precipitate disappeared, although the best results were obtained when the electrode was washed with sodium thiosulfate. The removal of silver iodide again allowed the diffusion current to reach its original value.

Theoretical Aspects.

At both low and high speeds, the half-wave potential decreased as the concentration of potassium iodide was increased from 10^{-6} N to

10^{-4} N. At higher concentrations the apparent half-wave potential again increased. This, however, was in a region in which polarization was becoming quite apparent and the waves, therefore, were becoming quite extended. At higher scanning rates, both the platinum and the silver amalgam electrode gave, with iodide, waves that were even more attenuated than those obtained at slower rates. The limiting currents became significantly less flat, at times resembling an Ohm's Law curve. It is quite possible, however, that the instrument lag was partially responsible for this, although it is also possible that the rate with which equilibrium was being established at the electrode was not great enough to keep up with the diffusion process. No definite explanation of this phenomenon can be given on the basis of evidence at present available.

It has been shown that better results are obtained at high scanning rates for the so-called inert electrodes. In the case of the iodide reacting with the silver ions formed by oxidation of the silver electrode, fast runs allowed higher concentrations to be analyzed because the silver iodide coating did not build up appreciably in the time required for the run to made. The upper limit of the concentration for 1.24 mv./sec. was about 3×10^{-4} N whereas for 4.96 mv./sec. the upper limit was about 3×10^{-3} N. For still higher scanning rates it might be possible to analyze even higher concentrations.

Present theories do not cover cases where the electrolysis forms an insoluble salt, particularly when the electrode becomes partially coated by this salt. According to Kolthoff and Lingane (16) the following equation holds for reduction of simple ions of metals that are soluble in mercury:

$$E_{d.e.} = E_{1/2} - \frac{0.0591}{n} \log \frac{I}{I_d - I} \qquad (6)$$

A plot of $E_{d.e.}$ vs. $\log \frac{I}{I_d - I}$ should produce a straight line with a slope of 0.0591/n, and the potential at which the logarithmic term becomes zero should be the half-wave potential. When this plot was made for the iodide determinations using a silver amalgam electrode, a slightly-curved line was obtained. A tangent drawn to this curve where $\log \frac{I}{I_d - I} = 0$ gives a slope of 0.055 making n equal to one. However, it would not be expected that this equation should hold in the case when an insoluble salt forms on the surface of the mercury and the product is allowed to accumulate. Therefore, the fact that a slope of 0.055 was obtained in comparison to a theoretical value of 0.059 for a one-electron change does not indicate that the reaction is necessarily reversible although the oxidation of silver to silver ion would be a one-electron reaction. The above equation indicates that the half-wave potential should be constant and independent of concentration; the experimental results showed the half-wave potential becoming less positive as the concentration increased.

Kolthoff and Lingane (17) give a similar equation for the case of reduction of ions of metals that are insoluble in mercury. The equation indicates that a plot of $\log (I_d - I)$ vs. $E_{d.e.}$ should give a straight line with the slope equal to 0.0591/n. When this plot was made for the case of iodide on the silver amalgam electrode, a straight line was obtained, but its slope was 0.11, indicating an n value of 0.5. However, since this equation was derived for the case of the dropping mercury electrode where the product on the surface of the mercury was removed with each drop, it would not apply in this case where the product continues to accumulate. Hence the fact that a straight line was obtained must be treated with caution until more is known of the behavior of such electrodes.

For an equation to extend to this latter case the lack of a continually renewed surface would have to be considered. An adequate equation would probably indicate a shift in half-wave potential to a less positive value for increase in concentration of the iodide ion. Cooke (6) points out that when in the case of a silver amalgam electrode the metal is allowed to accumulate in the amalgam, the plot of log $\frac{I}{I_d - I}$ vs. $E_{d.e.}$ does not hold and that a more complicated equation is necessary. In addition the equation would have to take into consideration the scanning rate since both the amount of product accumulating and the depletion of silver atoms in the surface of the amalgam would be governed by the length of time required for the electrolysis.

Quantitative Applications.

Observations from Bortmes (3), Bridgeman (4), and this study indicate that for quantitative applications to be made in anodic polarographs, the substance must actually be investigated over the concentration range to be used; otherwise, polarization is likely to spoil results, particularly at higher concentrations. For this same reason the medium must be taken into consideration. Bortmes' work indicated that sulfite concentrations could be determined quantitatively at concentrations from 2.5×10^{-4} N to 9×10^{-3} N, in a 0.1 N sodium sulfate carrier. When he ran iodide in 0.36 N sulfuric acid carrier, he found that the concentration versus the diffusion current was not linear over the range 10^{-2} to 10^{-5}. Better results were obtained with the oxidation of stannous ion in 2.5 N hydrochloric acid in the concentration range of 10^{-4} N to 10^{-2} N. Bridgeman found that better linearity could be obtained if high scanning rates were employed for phenol in the range from 10^{-3} M to 5 x 10^{-3} M; however, even then, to get good results, a calibration curve should be used.

Results in this research indicate that iodide concentrations from 10^{-6} N to 3 x 10^{-4} N show a linear relationship between diffusion current and concentration. Higher concentrations could be determined with the use of a calibration curve, i.e., up to about 10^{-3} N. At the higher scanning rate of 4.96 mv./sec., the linear relationship between the diffusion current and concentration holds to about 5 x 10^{-3} N, with it being possible to determine the concentrations as high as 10^{-2} N with a calibration curve. The best curves are obtained in the range of 10^{-5} N to 10^{-4} N. However, adequate measurements can be obtained in more dilute and more concentrated solutions. Some variation occurs in the ratio of diffusion current to concentration but in this study the concentrations are quite small, and for determination of iodide in such low concentrations, the accuracy is quite acceptable.

Results obtained in this research lead to the belief that other amalgams might be used for analysis of anions yielding an insoluble product. They also indicate high probability that liquid amalgams in the dropping mercury electrode might be even better, since polarization would be strongly limited. With the dropping amalgam electrode the product could not accumulate over the entire run but would be removed as each drop of amalgam fell from the capillary tip. It would, therefore, seem likely that higher concentrations could thus be determined without the necessity of using higher scanning rates.

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