ANODIC POLAROGRAPHY EMPLOYING VARIOUS ROTATING MICROANODES

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HISTORICAL

The polarographic method of chemical analysis, as developed by Professor Jaroslav Heyrovsky at Charles University in Prague, Czechoslovakia about 1920, is based on the unique characteristics of the current-voltage curves or polarograms obtained whenever a steadily-increasing potential is applied across an electrolysis cell consisting of a large nonpolarizable electrode and a small easily polarizable electrode.

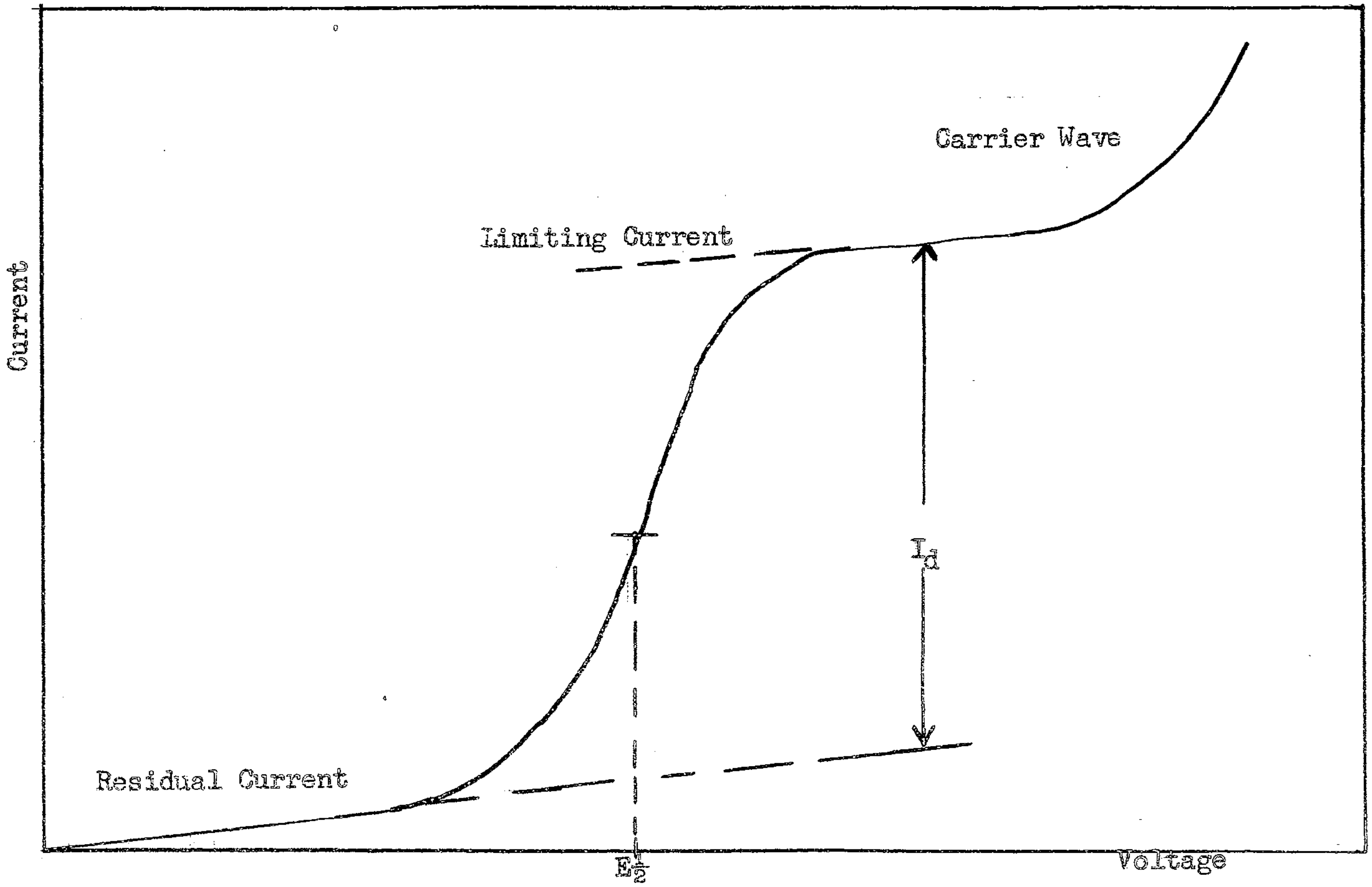
Most of the original work was done on a manual apparatus, the curve being plotted by hand. In 1925, however, Heyrovsky and Shikata (11) invented an instrument--the polarograph--which records current-voltage curves automatically in a small fraction of the time required to obtain them by the manual point by point method.

An ideal type of polarogram is shown in Figure 1. On such curves, the potential corresponding to the mid-point of the curve is characteristic of the particular oxidation-reduction system being investigated. This potential is called the "half-wave potential", $E_{\frac{1}{2}}$, and is measured with respect to a standard reference electrode--usually a saturated calomel electrode.

Before the beginning of the polarographic wave only a small residual current flows; consequently, the concentration of any electroactive material must be the same throughout the solution as at

Figure 1

IDEAL POLAROGRAM



the electrode interface. As soon as the decomposition potential is exceeded, some of the material undergoes a reaction involving an electron exchange at the interface, and as the concentration of the electroactive ions at the interface decreases, the rate of diffusion of these ions from the main body of the solution to the interface increases.

The current through the bulk of the solution is carried by the movement of all ions present, but only ions reducible or oxidizable at the microelectrode can undergo electron exchange and carry the current to the microelectrode. The movement of the reacting ions is partly by diffusion through a concentration gradient and partly by the action of an electrical force due to the charge of the ions and the electrical gradient between the electrodes of the cell. In order to reduce the latter effect, a relatively high concentration of an inert electrolyte must be present; for in the presence of such an electrolyte the migration of the electroactive ions is reduced to a negligible quantity. The current through the bulk of the solution thus is carried largely by the movement of the "indifferent" ions which are present in overwhelming concentration. The current that flows, therefore, is dependent upon the diffusion rate, which in turn is a function of the concentration gradient that exists between the depleted interface and the bulk of the solution. The limiting current is measured when a nearly complete state of concentration polarization exists at the electrode surface. Therefore, when the voltage is increased beyond the decomposition potential, electrolysis begins and the current increases until it gradually approaches a limiting value, becoming constant and independent of the increase in the applied E.M.F., and being limited only by the rate at which electroactive ions diffuse into the region around the microelectrode.

The dropping mercury electrode (D.M.E.) has been used as the microelectrode in most of the work that has been reported on polarography. From the laws regulating the conditions of diffusion at the D.M.E. and the nature of the growth of the mercury drop, Ilkovic (12) derived an equation to express the average current at the D.M.E. The Ilkovic equation, which holds for constant temperature is

$$I_d = 605\ nFD^{\frac{1}{2}}\ C\ m^{2/3}\ t^{1/6} \qquad (1)$$

in which the term 605 is simply a combination of numerical constants, arising in part from the geometrical characteristics of the dropping electrode; $\underline{I_d}$ 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 constant (96,500 coulombs); $\underline{D}$ is the diffusion coefficient of the reducible substance (in cm.^{2}/sec.); $\underline{C}$, its concentration expressed in moles per milliliter; $\underline{m}$ is the weight of mercury in grams flowing from the capillary each second; and $\underline{t}$ (in seconds) the time necessary for the formation of one drop of mercury. It can be seen from the quantities contained explicitly or implicitly in the Ilkovic equation that the diffusion currents are controlled by many factors. These factors include those concerned with diffusion itself, such as temperature, viscosity of the solution, ionic mobilities or diffusion coefficients, ionic strength of the solution, and the dielectric constant of the solvent; and those dealing with the characteristics of the capillary and of the electrode surface. The general usefulness of the Ilkovic equation is restricted by the unavailability of precise values of diffusion coefficients.

Tsukamoto, Kambara, and Tachi (29) have developed a similar equation for a particular type of rotating platinum electrode. The type considered was one made by enclosing a platinum wire in the center of the end of a glass tube and bending the platinum wire rectangularly to the horizontal plane. The equation applies to this electrode, when it is rotated at a rate greater than 200 r.p.m.; however, the equation does not apply to the more commonly used form which consists of a platinum wire projecting horizontally from a rotating cylindrical shaft.

Of several factors which affect the limiting current, the most important are the residual current, the migration current, and the diffusion current. The migration current of the electroactive material can almost be eliminated by employing a carrier electrolyte in concentrations 50 to 100 times as great as that of the electroactive material. The residual current, which is caused in part by minute traces of impurity, and in part by capacitance effects at the electrode surface, must be subtracted from the total current observed in order to get the actual diffusion current in quantitative polarographic analysis.

The most satisfactory microelectrode used in cathodic polarography is the D.M.E. The D.M.E. has the following advantages: (1) Its surface area is reproducible; (2) the electrode surface is smooth and continually being renewed; (3) mercury amalgamates with many metals and thereby lowers their decomposition potential; (4) hydrogen overvoltage is high on mercury, enabling work to be done at quite high values of applied voltages without interference from the evolution of hydrogen; (5) its surface area can be calculated from the weight of the drops; (6) the current assumes a steady value immediately and is reproducible.

In contrast to its value in cathodic work, the D.M.E. is limited in anodic polarography because mercury itself is oxidized at a relatively low voltage of about +0.4 volts vs. the saturated calomel electrode (S.C.E.). Consequently, save for the study of substances that are very readily oxidized, the D.M.E. is of little value in anodic studies.

Stationary solid microelectrodes of various forms and constructed from various metals have been used for determining current-voltage curves (16)(19). Usually noble metals are employed, but any metal would theoretically be suitable as long as the metal possesses an oxidation potential less positive than the region of voltage under investigation. In practice, the stationary type of microelectrode has the disadvantages that the current does not become constant upon applying a given voltage until after a period of several minutes, and even then the current slowly decreases with time. It often is not easy to obtain reproducible results; in fact the current at any instant is often found to depend on the pre-treatment of the electrode, the previous history of electrolysis, and similar factors difficult to control. Also the temperature coefficients of the observed diffusion currents are higher than with any other type of microelectrode, it being about 4% as compared with 2½% per degree for the D.M.E. or rotating electrodes. However, the stationary noble metal microelectrodes do have the definite advantage (also shared with the rotating microelectrodes) their range anodically would appear to be limited only by the potential at which oxygen would be evolved.

In their work with platinum, Kolthoff and Laitinen (17) have found that it takes two to three minutes for the current to reach a steady value for each applied potential when a 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 was employed. The achievement of a steady diffusion condition is dependent on the absence of mechanical and thermal disturbances; therefore, such polarographic analysis must be performed in a cell which is carefully thermostated and protected from vibrations. Rogers (26) and co-workers have investigated the automatic recording of polarograms with stationary electrodes. Current maxima were obtained when the voltage was continuously increased, these maxima resulting from the fact that the voltage change was more rapid than the rate at which a steady state of diffusion equilibria could be set up at the electrode. That these current maxima can be eliminated by using operating temperatures of 50° to 60° C., was reported by Skobets, Turov, and Ryablkon (27). Rotating electrodes do not show such so-called "time maxima", but Rogers (26) observed a second type of maxima when silver ion in 0.1 M. potassium nitrate carrier was run, and explained it as being due to a brief discharge of hydrogen at the surface of the freshly-deposited silver. The use of solid microelectrodes in union with oscillographic polarography has been described by Randles (25) and Airey (1). Instead of platinum, electrodes of silver, copper (23) and amalgams of these metals (1) have been recommended for use in polarographic analysis. The amalgamated electrodes have the advantage of being usable up to potentials as negative as -2.1 volts, but of course their use at positive potentials is limited (1).

Nernst and Merriam (24) were the first to describe current-voltage curves obtained with a rotating platinum electrode. A solid microelectrode rotating at constant speed yields steady diffusion currents without any period of waiting. Faster rates of stirring or rotation produced larger diffusion currents, but frequently also decreases the possibility of finding a definite diffusion current plateau. Laitinen and Kolthoff (16) have found that there is no significant increase in diffusion currents at speeds of rotation greater than 600 r.p.m.; consequently, this speed of rotation has been generally accepted as the ideal.

Cooke (4) recently described a rotating silver amalgam electrode as a type of solid electrode. The use of Cooke's electrode results in appreciably larger diffusion currents and surprisingly small residual currents. The amalgamated surface of the electrode has a reasonably high hydrogen overvoltage although not so high as does pure mercury. The magnitude of the diffusion current is stable over periods of time and the storage and pre-treatment of the electrode has been found to have little or no effect on the polarograms obtained. In addition, mercury and amalgam electrodes have fluid surfaces which tend to minimize irreversible surface effects.

As in cathodic work, most anodic work to date has been done at the D.M.E. As mentioned earlier, its anodic applications are limited because of the low dissolution potential of mercury; however, ions which form insoluble or very slightly ionized salts with mercurous ions tend to decrease the potential at which mercury is oxidized. Kolthoff and Miller (20) were able to employ this principle and thus obtain polarograms with chloride, bromide, iodide, thiosulfate, cyanide, thiocyanate, and hydroxide ions.

An anodic wave of the titanous ion in dilute hydrochloric acid was reported by Struble (28). The oxidation of +4 vanadium has been reported by Lingane and Meites (21) while in earlier work Verdier (30) has oxidized manganous tartrate with the D.M.E. Also the oxidation of +3 antimony at the D.M.E. has been reported (5).

There has been some anodic work with both the stationary and the rotating platinum electrodes. Glasstone (10) first used the stationary platinum electrode for such polarographic analyses, and found the diffusion current proportional to the concentration in the oxidation of ferrocyanide ion, ferrous ion, hydroquinone, and hydroxylamine. Julian and Ruby (13) have used this electrode also to determine half-wave potentials of several organic compounds. Using a stationary platinum electrode, cathodic, anodic, and composite cathodic-anodic polarograms of the ferric ion and of the ferrous ion have been reported (18).

Laitinen and Kolthoff (17) have found that the oxidation of the ferrocyanide ion at the rotating platinum electrode using KCl as the carrier electrolyte gave reproducible results if oxygen was evolved from the electrode for a few minutes before each determination. Bortmes (2) obtained reproducible results in the oxidation of the ferrocyanide ion in sodium sulfate carrier if he depolarized the electrode by making it the cathode for about two minutes at -1.2 volts. DeFord and Davidson (6) oxidized potassium ruthenocyanide using 0.2 molar potassium chloride carrier at both the stationary and the rotating platinum electrode. 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. These workers reported that a green precipitate formed when a stationary platinum electrode was used, and that this precipitate made runs very difficult.

Delahay and Stiehl (7) reported that in the oxidation of thallous ion at the rotating platinum electrode it was necessary to rinse the electrode with concentrated sulfuric acid between runs to remove the thallic hydroxide. Kolthoff and Jordan (14) also oxidized thallous ion at the rotating platinum electrode, storing their electrode in 10 N nitric acid between runs in order to obtain reproducible results. Bortmes (2) obtained good polarographic waves for sulfides in a sulfate carrier, stannous ions in HCl, and for iodides in a carrier of 0.36 N sulfuric acid, by limiting the maximum voltage employed to +1.0 volts vs. the S.C.E.

Oxidation studies of phenol at the rotating platinum electrode in various pH carriers (phosphate buffers) and at different scanning rates have been reported by Bridgeman (3). He found that certain polarization effects he observed in the wave were decreased when high speed runs were made, and that the half-wave potential decreased with an increase in pH. He showed that quantitative determinations of phenol could be made, but only at concentrations less than 5×10^{-3}M and at high scanning rates. Recently Gaylor, Elving, and Conrad (9) reported phenol studies using a stationary, large-area graphite electrode. They found that the half-wave potentials decreased with increasing pH in the pH range of 1 to 10.

INTRODUCTION TO PROBLEM

In the previously mentioned studies of anodic polarography by Gardels (8), Bortmes (2), and Bridgeman (3), marked evidence was obtained that some type of reaction-blocking occurrence (which will be referred to in this thesis as "polarization") very frequently took place at the surface of the electrode. Whenever such polarization occurred, it betrayed its presence through the fact that the second of two successive runs would give a much reduced wave, while the third often would give no wave at all. In addition, the original wave often would rise to a maximum, then dip downward in the limiting current region, sometimes rather abruptly, to form a dip as if something were rapidly decreasing the reaction rate.

The results obtained in the above-mentioned anodic studies indicated that two types of this so-called polarization might be encountered: (1) a type in which the electrode itself is attacked to form coatings which block off and make ineffective much of the electrode; and (2) a type in which the electrode is not itself attacked, but instead becomes coated with oxidation products formed from the oxidizable substance being investigated. The evidence for these two types of phenomenon were not conclusive, and it is possible that in some cases adsorption of substance at the surface of the electrode might be the source of the difficulty.

Various methods of depolarization were attempted by these investigators in an effort to get reproducible waves and to eliminate and determine the cause of electrode polarization. It was found by Bortmes (2) and Bridgeman (3) that the depolarization treatments needed depend upon the carrier electrolyte employed, the nature of the oxidizable substance being determined, and, in some cases, with the pH of the solution. Since evidence indicated that the polarization was due to coating of the electrode by some oxidation product, it was thought that by reversing the polarity (reducing electrolytically) or by the use of a strong reducing agent, this coating, and the consequent polarization, might be removed. Bortmes (2) found that reversing the polarity of the electrode for a few minutes gave acceptable results in some cases. Both Bridgeman and Bortmes tested the use of reducing agents. A number of such treatments were partially effective; e.g., dipping the electrode in hydrogen peroxide and rinsing with distilled water, or in titanous chloride solution followed by rinsing with distilled water between successive runs, seemed to work in a few cases.

A technique using a strong reducing agent such as stannous sulfate directly in the solution gave no signs of depolarizing the electrode in the case of the oxidation of iodides. Evidence indicated, however, that the hoped-for result was nullified by reaction of stannous ions with iodide ions to form complex ions.

Still another method that was applied in an attempt to condition the electrode involved the deliberate electrolytic evolution of hydrogen at the surface of the electrode, this being followed by immersing the electrode in iodine solution for 15 seconds then rinsing with distilled water. Bridgeman (3) found that this technique seemed to give excellent results with phenol, due either to the reduction of possible oxidation products by hydrogen or to loosening by the mechanical action of the bubbles, or both. After several treatments of the electrode with hydrogen, however, a new wave appeared, this wave appearing even in the carrier electrolyte solution alone. Bridgeman (3) thought that the wave could be eliminated by washing the electrode longer with iodine, his attempts to do this were unsuccessful.

Polarization with iodides can be easily removed by either heating the electrode between runs (an inconvenient procedure since it required a glass-mounted electrode and such a treatment frequently cracked the glass) or by using 0.36 N sulfuric acid as a carrier electrolyte. In using this technique of heating the electrode it was noticed that abnormally large residual currents were obtained. Kolthoff and Jordan (14) found that these irregularities were due to strains produced at the platinum-glass interface and could be minimized by carefully annealing of the platinum-glass joints.

Of all depolarization techniques tried only scraping with a sharp knife or razor blade worked in every case. This technique has the obvious disadvantage that eventually over a period of time, it will result in a change in the electrode area. When this technique was to be employed, a soft glass bead about 2.5 mm. in diameter was fused onto the platinum wire, and the electrode and bead were soldered in place in the steel shaft by Wood's metal. By scraping the electrode up to this bead it was possible to scrape always exactly the same length of electrode and thus keep the area of the electrode reasonably constant for many runs.

SCOPE OF RESEARCH

The purpose of this research was (1) to test a newly-designed disk-type rotating platinum electrode for use in anodic polarography; (2) to test the action of various continuous buffing methods as a way of combatting polarization of this electrode; and (3) to determine ways in which graphite might be employed as an electrode material.

Phenol, and various inorganic ions which are easily oxidizable, were chosen for this investigation.

MATERIALS AND EQUIPMENT

Reagents and Solutions:

All chemicals used were of reagent grade and all solutions were prepared from distilled water. The nitrogen used in degassing solutions was water-pumped nitrogen supplied by the Linde Co. and was purified by passing through a train consisting of a gas-washing tower containing alkaline pyrogallol, one containing carrier electrolyte solution, before it went into the electrolysis.

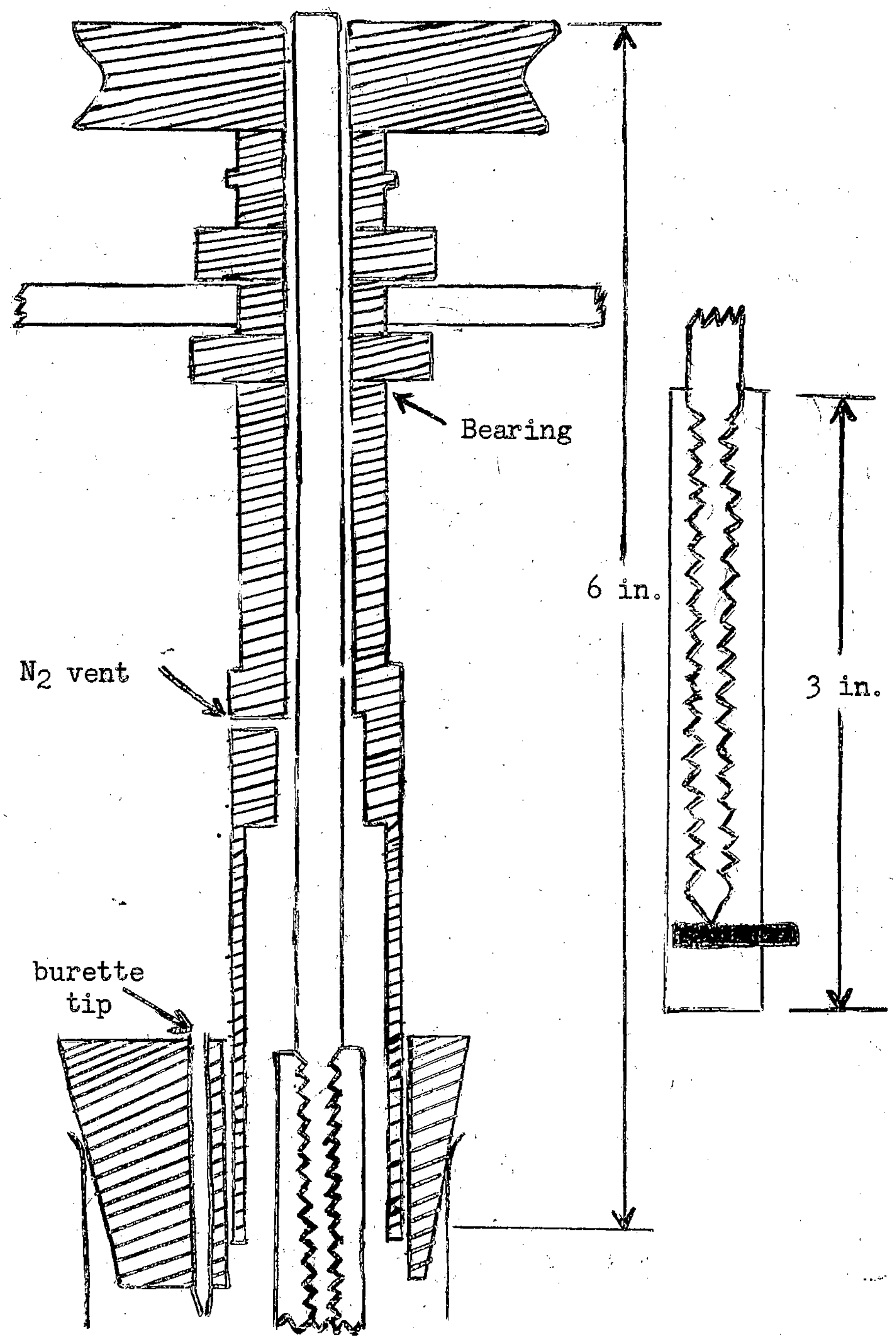
Apparatus:

The polarographs used in this investigation were a Sargent Model XXI polarograph and an experimental model polarograph. This latter polarograph was equipped with a chain of gears providing a variable speed drive, so that the full span could be transversed in a time that could be varied from 5 hours to 30 seconds, either strip-chart recording or photographic recording being employed.

The microelectrode and assembly used was built according to Figure 2. This set-up is practically the same as that used by Gardels (8). When impregnated graphite was used as the electrode, it was sealed into a hole drilled through the side of a polystyrene cylinder. The polystyrene cylinder which was threaded inside was screwed onto a threaded steel shaft equipped with a sharp-pointed end which served to make electrical contact between the graphite rod and the steel shaft. This whole electrode shaft was protected

Figure 2

Microelectrode and Assembly



by means of a shield when in operating position, the shield extending to the upper part of the electrolysis cell in such a way that a tight fit was made between the shield and the electrolysis cell by means of a rubber stopper. The rubber stopper, which together with the shield served to prevent oxygen from diffusing into the electrolysis cell, was drilled to admit not only the shield, but also a burette tip to allow the addition of samples from the 10 ml. microburette. The capacity of the electrolysis cell was 135 ml., permitting the use of 125 ml. of carrier electrolyte solution with room left so up to 10 ml. of sample could be added as desired. A minute opening near the top of the shield permitted the nitrogen to be discharged from the electrolysis cell during the degassing process. In degassing the solution, a coarse fritted-glass dispersion tube was constructed directly in the electrolysis cell.

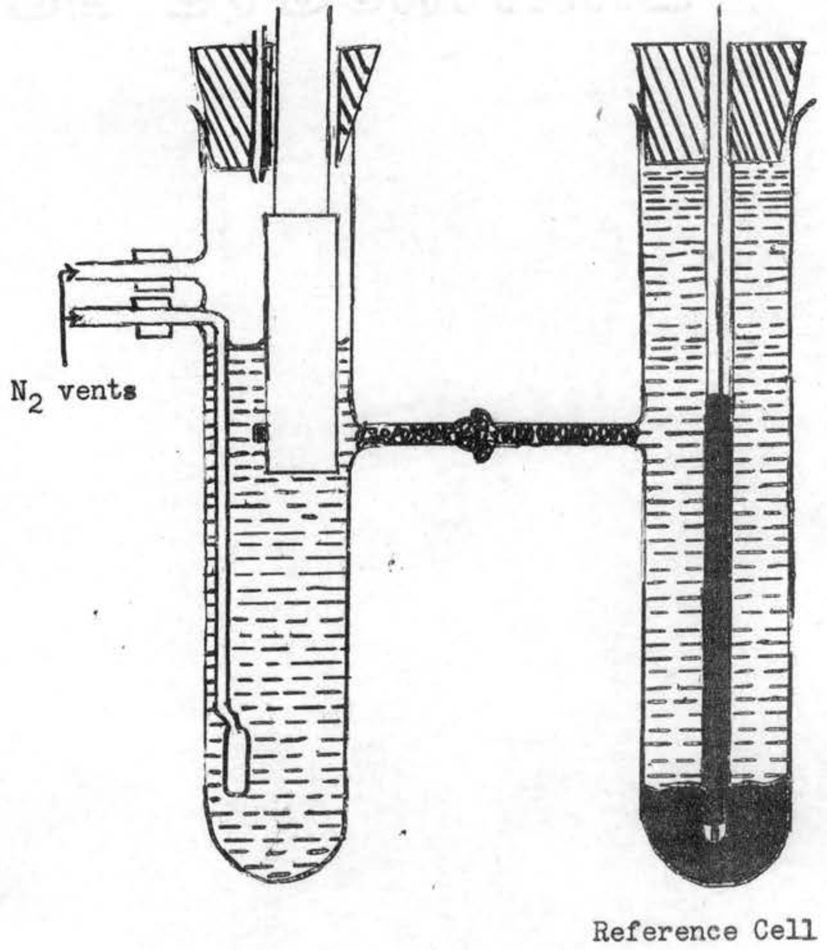
The electrode shaft was so constructed that the electrode could be raised out of the electrolysis cell and into the shield. Thus the cell, together with the constant temperature bath (which contained both the electrolysis cell and the reference cell) could be slipped from under the electrode assembly as one unit. The electrode could also be raised out of the solution during the degassing process whenever such was deemed necessary.

The electrode shaft, mounted in a brass bearing, was driven by means of a 0.05 horsepower motor, the motor and shaft being connected by means of a pulley and a drive belt which rotated the electrode at approximately 640 r.p.m. A three-inch blade driven by an electric stirrer served to keep the water inside the constant temperature bath thoroughly mixed.

The polarographic cell is shown in Figure 3. Side-arms of both the electrolysis and the reference cell were packed with glass wool to prevent diffusion and were connected together by a ground-glass ball and socket joint. The mercury-mercurous sulfate electrode was used instead of the saturated calomel electrode (S.C.E.) owing to the fact that it was found that unavoidable diffusion of chloride ions from the S.C.E. produced erratic results. The mercury-mercurous sulfate electrode was prepared by mixing together, in a mortar, mercury and mercurous sulfate moistened with saturated potassium sulfate solution. The mixture was placed in the reference cell to a depth of about 1 cm. over a pool of mercury, and then the rest of the cell was filled with a saturated potassium sulfate solution. Crystals of solid potassium sulfate were added on top of the paste of mercury and mercurous sulfate to insure that the potassium sulfate solution remained saturated. The mercury-mercurous sulfate cell (reference electrode) was painted black to prevent decomposition of the mercurous sulfate by light. The side-arm of the electrolysis cell was repacked each time a new solution was added to the cell.

Figure 3

Polarographic Cell



EXPERIMENTAL RESULTS

All determinations were made using a rotating (platinum or graphite) microelectrode as the anode, with a saturated mercury-mercurous sulfate half-cell as the cathode. In earlier work it was found that when the saturated calomel half-cell was used as the cathode, the resulting curves contained odd irregularities. Studies of this phenomenon finally led to the discovery that traces of chloride ions seeping from the calomel half-cell were causing the difficulty. Since agar plugs, which are ordinarily used to prevent diffusion, also gave irregularities, agar could not be employed to minimize diffusion. Consequently all experiments in this research were made using a mercury-mercurous half-cell saturated with potassium sulfate as the reference electrode, the polarograph being set to compensate for the difference between the potential of this electrode and that of the saturated calomel electrode (i.e., presetting the instrument 0.4 volts) so all readings would be referred to the latter in the usual way. This, of course, does not correct for liquid junction potential differences that exist between the two electrodes.

Platinum Disk-Type Electrode

Oxidation of the Iodide Ion:

Bortmes (2), in his work in the field of anodic polarography, has shown that the platinum electrode is readily polarized in 0.1N sodium sulfate carrier. In initial runs, 10^{-3} potassium iodide, at a fresh scraped platinum wire electrode, gave a fairly well-defined wave. However, when a second run was attempted at the moment the electrode was switched on the galvanometer quickly moved in a negative direction, then returned to the zero position. This would indicate that a reduction, rather than an oxidation, was taking place at the electrode surface. The resulting wave was ill-defined with no definite diffusion current region. When the electrode was scraped prior to each run, however, he obtained anodic waves with a definite diffusion current region. Polarization was noticed even in 0.1 N sodium sulfate carrier without any iodide being present when the previous run was carried to as high as +1.2 volts.

Since scraping proved to be quite universally workable as a depolarization technique for platinum, a new design of electrode was constructed and very briefly tested by Lloyd (22). This electrode consisted of a platinum disk sandwiched between the ends of two cylinders of nylon. A hole drilled longitudinally through the cylinders and disk permitted the whole to be bolted together to form a single cylinder, ceresin wax being used to seal any minute spaces between the nylon cylinders and the platinum disk. The whole was machined down so only the edge of the platinum, flush with the nylon, was exposed. The cylinder was revolved at 600 r.p.m. With a platinum disk 0.002" thick and the cylinder 3/4" in diameter, the same type of anodic waves were obtained as with the usual projecting platinum wire rotating electrode.

As was the intent in making this cylindrical or disk-type electrode, attempts were then tried to buff the surface of the electrode continuously during the making of the polarogram. Lloyd (22) tried using pads of cotton cloth and of glass cloth pressed against the edge of the rotating disk; but any improvement was unobservable.

The same disk-type electrode was used in the work reported in this thesis; a different approach, however, was made to the problem of buffing the platinum disk. It can readily be seen that when pads of cloth are pressed against the edge of a thin platinum disk, the platinum disk might never be buffed because it revolves between two strands of thread. It was believed, therefore, that by grooving the cylinder so that the edge of the platinum disk was at the bottom of the groove, a twisted string or cord pressing into this groove might buff the platinum disk more efficiently and thus keep its surface clean.

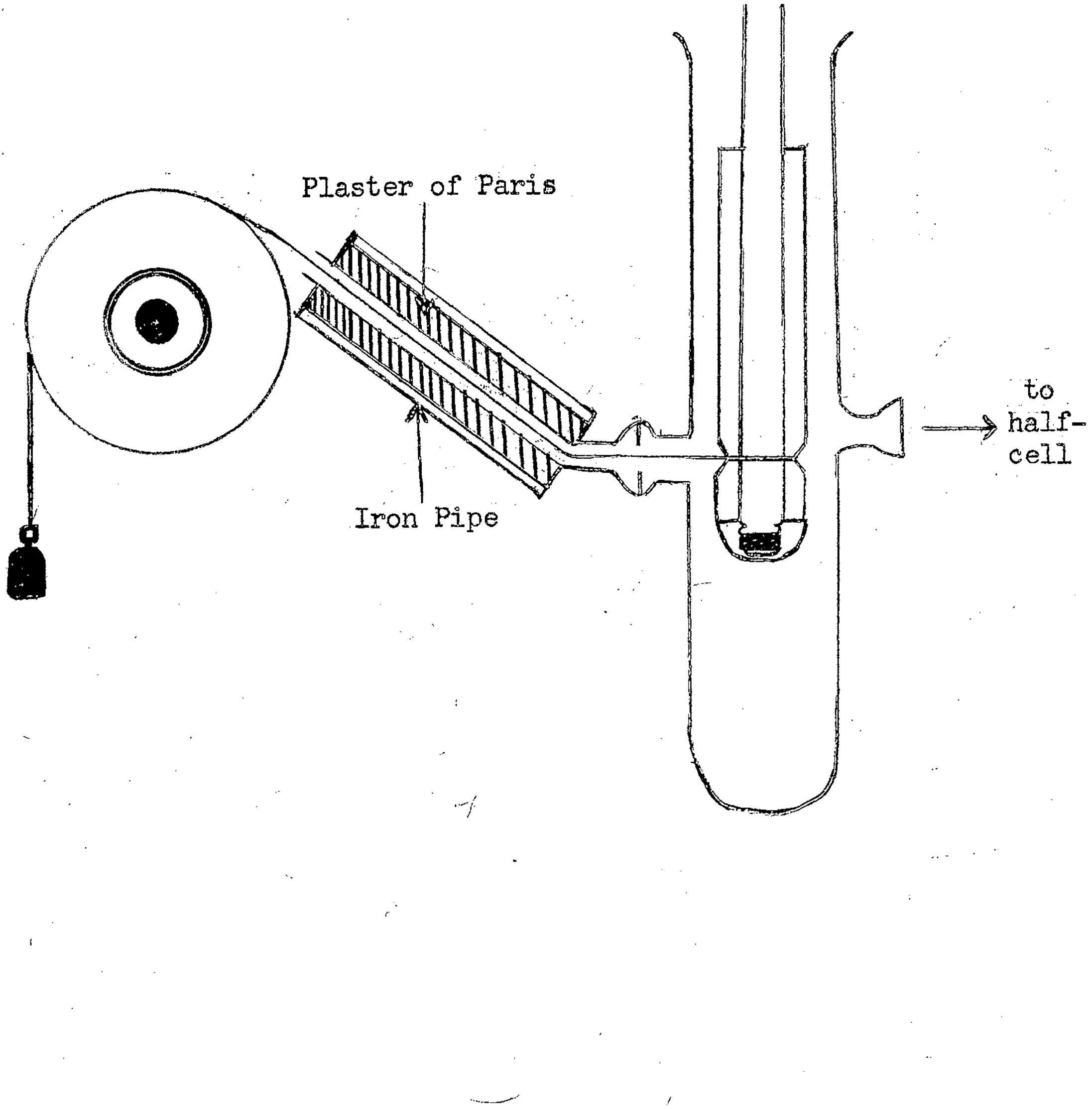
The first technique involving the use of a string or cord as a buffing agent was that of merely stretching the string through the cell horizontally, letting the string buff the platinum disk as the cylinder revolved against the string. The string was kept as tight as possible by means of screw-out clamp fastened to a rubber stopper. It was soon found, however, that constant tension could not be maintained owing to the fact that the string was constantly stretching.

It was thought that if in some way a pulley-weight arrangement could be employed, the string could be kept tight. The resulting arrangement is shown in Figure 4. Various sizes and weights or string and cord both of plain cotton and of nylon, were employed. The cotton cord didn't seem to last more than 3 to 4 runs; therefore, nylon string, which seemed to be more resistant to abrasion was used.

Figure 4

Rotating Platinum Disk Electrode

With a Pulley-Weight Arrangement



Various weights were tried in an attempt to see whether the tension on the cord was a significant factor in the effectivenss of buffing the disk electrode. It was found that the most effective buffing was reached by using a tension of approximately 5 pounds.

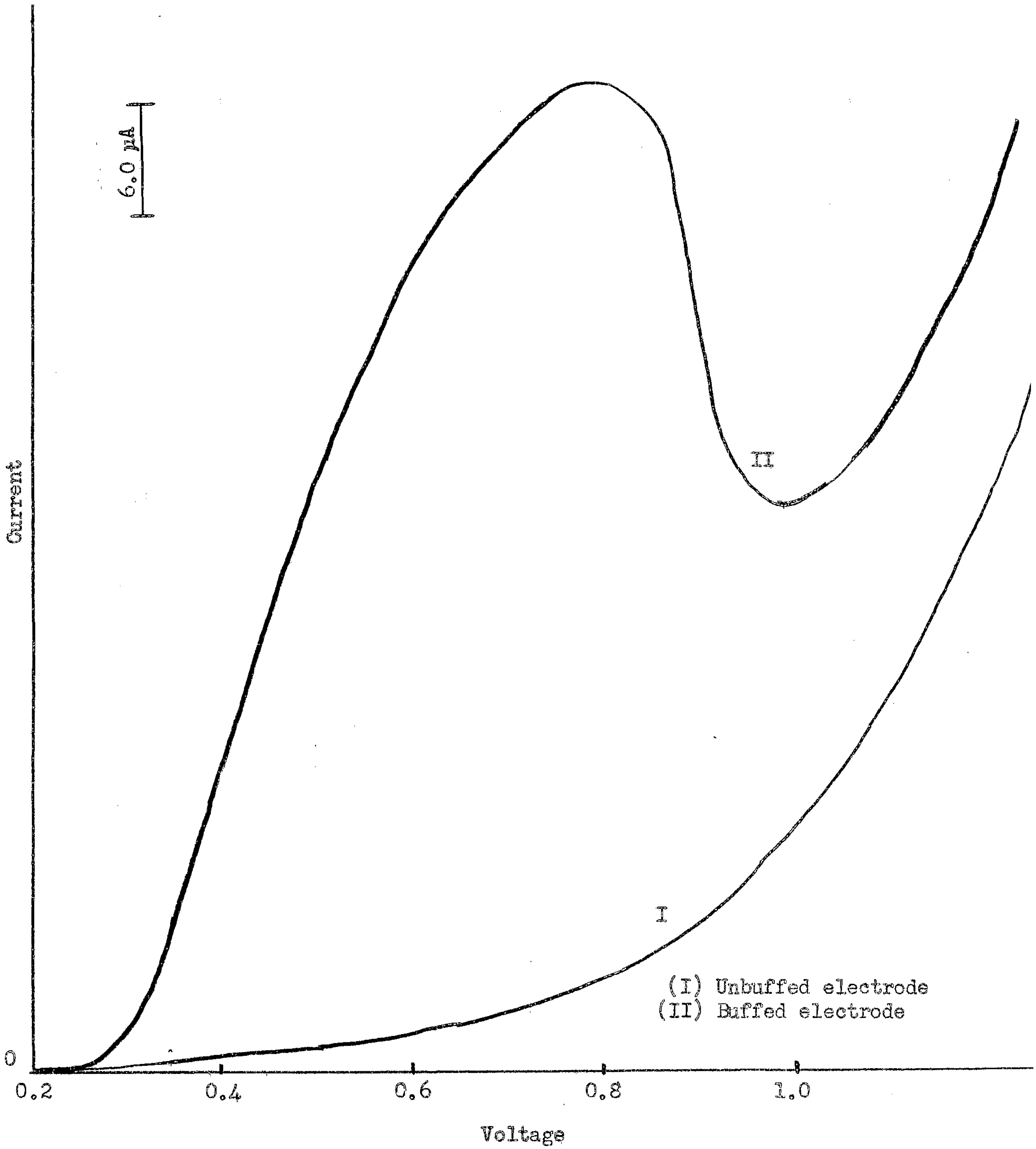
In using this idea of buffing, we would polarize the electrode by making several successive runs with iodide concentrations of $4x10^{-4}N$ in 0.1N sodium sulfate carrier without buffing the disk electrode, until the iodide wave finally obtained looked like a slightly irregular carrier wave. With the disk electrode thus quite completely polarized, the string was then placed around the groove of the electrode, the desired weight added, and the cord allowed to buff the surface of the electrode for approximately 10 minutes before making a polarogram. The polarograms obtained using this buffing technique indicated that some polarization still persisted. The iodide wave would rise to a maximum then dip downward in the limiting current region (Figure 5). Repeated runs with the buffing being contained throughout the run and with no extra buffing between runs gave the same kind of curve, reproducibly.

Oxidation of Phenol:

Bridgeman (3) found that reproducible phenol waves could be obtained only by scraping the rotating platinum wire electrode between successive runs. In an effort to obtain some idea of the effect of polarization on the wave shape, Bridgeman made runs at two speeds; i.e., scanning rates of 10.5 millivolts per second and 100 millivolts per second (a 3.0 volt span in 4 minutes 45 seconds and in 30 seconds, respectively). The polarization occurring with phenol resulted in a wave similar to that obtained with iodides; i.e., waves

Figure 5

Polarogram for 4×10^{-4} N KI in 0.1 N Na_2SO_4 at Rotating Platinum Disk-Type Electrode



with the usual dip in the limiting current. Bridgeman found that this effect was considerably reduced when runs were made at the higher speed of 100 millivolts per second. In his studies of the oxidation of phenol, he found that quantitative determinations of phenol could be made, but only at concentrations less than about 5×10^{-3}M. and only at high scanning rates.

By using the pulley-weight set-up as described in the oxidation of iodide, it was found that once the disk electrode became polarized in the oxidation of phenol, and the disk electrode was buffed for approximately 10 minutes, a wave similar to the one obtained in the oxidation of iodide resulted. The phenol wave rose to a maximum which was followed by the usual dip. The phenol studies were carried out in various standardized phosphate buffers, as carrier electrolytes, as in Bridgeman's work. In this research, however, the phenol studies were carried out using the phosphate buffer at a pH of 7.1. The original buffer solutions were made up as described in Bridgeman's thesis and checked with a Beckman Model H pH meter.

Graphite Electrode

Since much evidence pointed to the fact that platinum itself was being attacked in these anodic studies, it was decided to use graphite as an electrode and study its polarization effects with various ions and compare the results with those obtained with platinum. At first some attempts were made to make a disk-type carbon electrode. Some spectrographic-grade graphite was ground with a mortar and pestle until it was extremely fine, then mixed with various cements. The efforts made were not exhaustive, however, and none of the techniques employed proved satisfactory. Efforts along this line, therefore, were soon abandoned in favor of trying the more conventional form of electrode.

The second type of graphite electrode tested consisted of a rod of spectrographic-grade graphite about 2 mm. in diameter, inserted into the side of, and projecting about 3 mm. from the side of a polystyrene shaft (ca. 15 mm. in diameter). The graphite rod was sealed in place with Duco cement and allowed to dry 12 hours before it was used. Electrical contact was made by means of the threaded steel shaft (as described earlier). After 2 or 3 runs were made with this electrode it was noticed that curves obtained became very erratic and the recorder would go off scale very quickly. The trouble was soon found to be caused by leaks developing, either through the Duco cement, or through the porous graphite. A way, therefore, was sought to prevent the seeping of solution through the graphite rod. The problem was to find a method of decreasing the porosity of the graphite. The idea of filling the pores in the graphite with Duco cement, diluted with ethyl acetate, by using a side-arm test tube and evacuating it by means of a vacuum pump was used. After the system had been thoroughly evacuated, the graphite rod was pushed down into the solution of Duco cement and ethyl acetate by means of nichrome wire which held the graphite rod. The vacuum was released several times during the impregnation process. The graphite rod was then sealed into the polystyrene shaft with Duco cement and allowed to dry for 24 hours.

This new technique proved to be somewhat better; but still after making 5 to 6 runs, the electrode would not behave in a reproducible manner and shortly after that would become erratic as before.

Our next attempt was to try to impregnate the graphite rod with a monomer and allow the monomer to polymerize within the pores of the graphite. Methyl methacrylate was the monomer chosen, 1 per cent benzoyl peroxide being added as a catalyst. The same impregnation procedure was followed as in case of the Duco cement. After being thoroughly impregnated, the graphite rods were placed in an oven at 50°C. to hasten the polymerization. Finally, the impregnated graphite rod was fitted into the side of the polystyrene shaft and cemented with more of the partly polymerized methyl methacrylate which had been allowed to reach a viscous condition. The whole was then allowed to polymerize for 8 hours in the oven at 50°C. This technique proved to be quite satisfactory in eliminating our seeping problem and was adopted for the rest of the research problem.

Oxidation of Iodide Ion

Quantitative runs were made at 25.0 ± 0.2° C., with different concentrations of iodide in 0.1 N sodium sulfate or in 0.1 N sodium sulfate with 6 drops of concentrated sulfuric acid added to each 125 ml. of solution. The calculated amount of potassium iodide was weighed out and dissolved in carrier electrolyte solution which had been deoxygenated for 1 hour by a stream of purified nitrogen. This iodine stock solution was diluted quantitatively to concentrations convenient for addition to the carrier in the cell. Concentrations ranging from 10^{-2} to 10^{-5} N were employed. After each addition of the sample, the solution was further degassed, the nitrogen serving also to mix the solution. The iodide solution was added by means of a 10-milliliter burette with graduations of 0.1 milliliter. This burette was constructed so that nitrogen could pass thru a two-way stop cock and after each addition of sample, could be used to blow out the solution in the burette tip and in the surgical rubber tubing connecting the burette to the tip in the cell. This insured that there wasn't a drop of sample hanging to the burette tip.

The runs in which the slightly acidic sodium sulfate carrier was used, gave iodide waves that tend to have a flatter diffusion current regions than those obtained in the neutral sodium sulfate carrier.

Concentration studies made at the graphite electrode with iodide ion (See Table I) show that the usual linear relationship exists between I_d and concentration. Apparently, therefore, this electrode is quite suitable for use in quantitative analysis. Since the platinum disk electrode in its present state of development represents no improvement over the conventional form, no quantitative studies were made with it.

The variation of half-wave potential with concentration is not surprising since other evidences indicated that polarization was still influencing results and, undoubtedly, distorting the curves. In addition, if, as seems to be the case, the iodine formed in the oxidation of iodide at graphite remains deposited on the surface of the electrode, shifts in the direction observed would be predicted from polarographic theory.

In no case was any evidence of polarization observed until the concentration of iodide was approximately 5×10^{-3} N or greater. The polarization seemed to be more pronounced in the neutral carrier at this concentration than it was in the slightly acidic sodium sulfate

TABLE I

DATA OBTAINED FOR IODIDE ION AT ROTATING GRAPHITE ELECTRODE

Part (A)

(Carrier, slightly Acid 0.1N Na_2SO_4)
Electrode Diameter 1.80 mm.
Electrode Area 2.54 sq. mm.
Temperature 25.0° ± 0.2°C.

Concentration of I^-	I_d/conc. uA/millimole/liter	$E_{\frac{1}{2}}$ vs S.C.E.
0.99×10^{-5}M.	3.008×10^4	0.72 V
4.93×10^{-5}M.	3.058×10^4	0.62 V
1×10^{-4}M.	3.19×10^4	0.58 V
4.81×10^{-4}M.	3.259×10^4	0.55 V
0.966×10^{-3}M.	3.23×10^4	0.556V
2.47×10^{-3}M.	3.23×10^4	0.60 V

Part (B)

(Neutral carrier, 0.1N Na_2SO_4)
Electrode Diameter 1.80 mm.
Electrode Area 2.54 sq. mm.
Temperature 25.0° ± 0.2°C.

Concentration of I^-	I_d/conc.	$E_{\frac{1}{2}}$ vs S.C.E.
5.02×10^{-5}M.	2.27×10^4	0.66 V
1.009×10^{-4}M.	2.477×10^4	0.66 V
4.85×10^{-4}M.	2.58×10^4	0.59 V
1×10^{-3}M.	2.887×10^4	0.59 V

carrier. There was faint evidence of two waves in the oxidation of iodides which occured at 5 x 10^{-4}N. This second wave become more pronounced at 1 x 10^{-3}N. 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 (15) reported similar polarograms with a solution of 2 x 10^{-4}N. potassium iodide in a buffer having pH of 4. They postulated the first wave to be due to oxidation of iodide to iodine and the second to be due to the oxidation of iodide to the one-plus oxidation state.

Oxidation of phenol:

As mentioned earlier, Bridgeman (3) has found that quantitative determinations of phenol could be made, but only at concentrations less than about 5 x 10^{-3}M and only at high scanning rates. The depolarizing technique employed in Bridgeman's research was that of scraping the platinum wire between runs.

It was found in this research work that, when graphite was used as an electrode scraping the electrode between runs was again necessary despite the fact that, in the oxidation of iodides, scraping of the electrode wasn't necessary. Apparently the oxidation products that were formed were soluble in the carrier medium in the case of iodides, and were insoluble in the case of phenols.

At graphite, just as was true at platinum, increased polarization effects were noted in the low speed runs. In making runs using the Model XXI polarograph (3.0 volt span in 13 minutes) it was noticed that good phenol waves could be obtained by scraping between runs until the concentration of phenol was approximately 1×10^{-4}M. At this concentration the phenol rose to its normal height then dipped slightly downward near the carrier current region. This dip became more pronounced as the concentration of phenol was increased.

Runs were then made on an experimental model polarograph constructed by Dr. Paul Arthur of the Chemistry Department of Oklahoma A. and M. College. This polarograph is equipped for either strip-chart recording or photographic recording, and so constructed that various scanning rates could be employed. Runs were made at two speeds on this instrument; i.e., at scanning rates of 18.2 millivolts per second and at 25 millivolts per second. In the runs made using the scanning rate of 18.2 millivolts per second, polarization was first noticed when the concentration of phenol was approximately 5×10^{-4}M., but in the scanning rate of 25 millivolt per second, polarization was first encountered when the phenol concentration was approximately 1×10^{-3}M.

<u>Oxidation of ferrocyanide ion</u>:

Bortmes (2) found that, at platinum, there was a shift in the half-wave potential of ferrocyanide with concentration, he attributing these shifts to polarization effects. The half-wave potential of 10^{-3}N. potassium ferrocyanide in 0.1N sodium sulfate was +0.29 volts for a depolarized electrode, while on the same solution, but with a polarized electrode, the half-wave potential was +0.58 volts. He observed this shift of the half-wave potential for no other ion. Bortmes reported also that if the electrode was depolarized in slightly yellow ferrocyanide solution (ferrocyanide solutions turn slightly yellow upon standing several hours), a very pronounced maximum would appear on the ensuing oxidation runs. He obtained best results by making up fresh solution of potassium ferrocyanide just before the run in freshly boiled distilled water.

In this work it was noticed that for 10^{-5}N potassium ferrocyanide in 0.1N sodium sulfate, the current very slowly increased, flattening only slightly just before it went off in the carrier current region. When the ferrocyanide concentration was increased to 5 x 10^{-5}N, the current increased at a much faster rate, gradually climbing until again it looked as if it was going to form a limiting current plateau, but again going off into the carrier current. The break between the residual current and the slowly attenuated polarographic wave seemed to be lessened each time as the ferrocyanide concentration was increased. A plateau appeared in the limiting current region when the ferrocyanide concentration was approximately 5 x 10^{-4}N. The half-wave potential measured at this concentration was found to be approximately +0.47 volts, while the half-wave potential of 10^{-3} N potassium ferrocyanide was approximately +0.46 volts. However, there was no sign of a maximum or dip encountered in concentration runs from 10^{-2} to 10^{-5}N. From the results obtained in this work, the oxidation of the ferrocyanide ion at the graphite electrode seemed to indicate that the reaction is not diffusion controlled but probably rate controlled.

Oxidation of Sodium Thiosulfate:

Investigations were made on 10^{-5}N to 10^{-3}N sodium thiosulfate in 0.1N sodium sulfate. All attempts at oxidation of the thiosulfate ion, at the graphite microelectrode, gave no wave at all. Bortmes (2) reported that the oxidation of thiosulfate ion, at the platinum microelectrode, resulted in a pronounced maximum and no well-defined curves. He found that depolarization of the electrode in the thiosulfate solution resulted in an increased maximum.

<u>Oxidation of Sodium Hypophosphite and of Sodium Hyposulfite</u>:

Gardels (8) reported no waves with a rotating platinum electrode for sodium hypophosphite concentrations ranging from 2 x 10^{-4}N to 10^{-3}N.

It was found also by this investigator that sodium hypophosphite gave no wave with the rotating graphite electrode even though concentrations ranging from 10^{-5}N to 10^{-3}N were used. A slight hump which sometimes occurred very close to the carrier wave, may or may not have been due to hypophosphite.

In the case of sodium hyposulfite, Gardels (8) found that 10^{-3}N sodium hyposulfite in 0.1 N potassium sulfate, with a rotating platinum electrode, gave a bluntly-humped curve with the peak occurring at about +0.82 volts. With a gold electrode, however, he found that 10^{-3}N sodium hyposulfite in 0.1 N sodium sulfate produced a good wave with a half-wave potential of +0.94 volts. At a higher concentration, 2 x 10^{-3}N, the wave shape changed, a sharp-peaked maximum developing at +1.01 volts.

Sodium hyposulfite in 0.1 N sodium sulfate at concentrations ranging from 10^{-5} to 10^{-2} N, with a rotating graphite electrode, gave no wave. A slight hump occurred very close to the carrier wave, this being very similar to the one obtained with hypophosphite ion.

Oxidation of Potassium Bromide:

Investigations were made on 10^{-5} to 10^{-3} N potassium bromide in 0.1 N sodium sulfate, with the rotating graphite electrode. No wave was ever observed.

Gardels (8) found that 10^{-4} potassium bromide in a 0.1 N potassium sulfate carrier, at a rotating platinum electrode, gave a slight indication of a wave. With 10^{-3} N potassium bromide, a wave with half-wave potential of +0.94 volts, was produced. As the concentration of the bromide was increased to 4×10^{-3} N, a maximum occurred. With the gold electrode, he found that 4×10^{-3} N potassium bromide in 0.1 N potassium sulfate gave a small wave with a half-wave potential of +0.88 volts, and as the concentration was further increased to 10^{-2} N, a maximum was produced.

Oxidation of Stannous Sulfate:

In Bortmes' work it was found that the stannous ion gave no evidence of a polarographic wave in 0.1 N sodium sulfate at the rotating platinum electrode. In this work, however, it was found that a polarographic wave did appear at a concentration of 10^{-3} N when the graphite electrode was used. In neutral sodium sulfate, the wave had the usual pronounced peak; in 3.6 N sulfuric acid, the current climbed very slowly, finally merging into the carrier wave with no peak and no limiting current ever forming.

DISCUSSION AND CONCLUSIONS

The results obtained in this research indicate that the major problem in anodic polarography still is the one of depolarization of the electrode during or between runs. The most universally applicable method of depolarizing the electrode is by scraping the electrode between runs. This method is time-consuming, however, and undoubtedly in time results in a decrease of electrode area.

In using the buffing idea (pully-weight arrangement) with the platinum disk-type electrode in the oxidation of potassium iodide in 0.1 N sodium sulfate carrier, it was found that the polarization effects were decreased. After the disk-type electrode was completely polarized and after it was then buffed, the platinum disk electrode yielded iodide wave which rose to a maximum then dipped downward in the limiting current region, even though the buffing was continuing. Apparently the buffing technique eliminated polarization until the applied voltage exceeded the decomposition potential of the iodide ion; then the electrode reaction seemed to be producing polarization at a much faster rate than the buffing action could remove it.

In considering these results it seems highly probable that the platinum electrode itself is being attacked to form some product such as a hydrated lower oxide, an iodide of platinum, or both. If iodine alone were produced, it should dissolve in the solvent; or, if it adheres to the electrode, it should be easily removed by buffing.

Since quite vigorous buffing was required, and even then polarization was not entirely eliminated, it would seem that some much harder product must have been formed. Since a similar behavior was observed in the case of phenol oxidation--i.e., the wave dipped downward in the limiting current region even when the platinum disk-type electrode was buffed continuously during the making of the polarogram--it seems likely that the platinum disk electrode was again being attacked either to form insoluble phosphates with the carrier or to form hydrated oxides.

That electrode attacking is not the sole cause of polarization with unbuffed electrodes, however, seems equally evident. Carbon, if oxidized, should yield either carbon dioxide or carbon monoxide, both of which should escape readily from the surface of the electrode. When graphite was used as the electrode, however, although polarization with both iodides and phenol was very greatly reduced, some polarization still occurred. Consequently, it would appear that, while oxidation of the platinum itself accounts for part of the polarization at platinum electrodes, oxidation product of the iodide and of the phenol must contribute their parts to this phenomenon. A continuously buffed graphite electrode might eliminate all types of polarization therefore.

One outstanding fact that was determined is that the so-called "inert" electrodes, such as gold and platinum, are not truly inert. It has been shown in this thesis that graphite might be the most nearly true inert electrode, however, many substances would still give trouble by forming coatings of their own insoluble oxidation products on the electrode.

In addition, the results obtained in this research indicate that, in some cases, at least, the nature of the electrode surface itself may determine whether or not reaction will occur. Thus Gardels (8) was able to obtain, at the platinum electrode, waves with bromide and with hyposulfite, whereas at graphite, no wave was ever obtained. It would seem, therefore, that surface catalysis, or the formation of intermediates with the electrode material, may enter into the electrode reaction in such cases.

In future work, emphasis should be placed on developing a rotating graphite disk-type electrode, similar to the platinum disk-type electrode. If this type of graphite electrode is developed, then by some mild buffing technique both types of polarization might be eliminated. This would greatly enhance the general value of anodic polarography. In addition, however, the idea of buffing the platinum disk-type electrode should not be abandoned yet. A more efficient buffing action might be obtained by using an abrasive such as powdered carborundum directly in the solution or impregnated into the buffing cord. However, if the abrasion is too harsh, a decrease in electrode area will result after a period of time.

BIBLIOGRAPHY

(1) Airey, L., Analyst, 72, 306 (1947).

(2) Bortmes, E., 'Polarographic Studies Employing Rotating Microanodes.' Unpublished M.S. Thesis, Oklahoma A. and M. College (1951).

(3) Bridgeman, O. C., 'Polarography of Some Organic Compounds at the Rotating Microanode.' Unpublished M. S. Thesis, Oklahoma A. and M. College (1952).

(4) Cooke, W. D., Anal. Chem., 25, 215 (1953).

(5) Cozzi, D., and S. Vivarelli, Anal. Chim. Acta, 4, 300 (1950).

(6) DeFord, D., and A. Davidson, J. Am. Chem. Soc., 73, 1469 (1951).

(7) Delahay, P., and G. Stiehl, J. Am. Chem. Soc., 73, 1755 (1951).

(8) Gardels, M. C., 'Anodic Polarography of Inorganic Ions at Various Rotating Microelectrodes.' Unpublished Ph. D. Thesis, Oklahoma A. and M. College (1954).

(9) Gaylor, V. F., P. J. Elving, and A. L. Conrad, Anal. Chem., 25, 1078 (1953).

(10) Glasstone, S., Trans. Am. Electrochem. Soc., 59, 277 (1931).

(11) Heyrovsky, J., and M. Shikata, Rec. trav. chim., 44, 496 (1925).

(12) Ilkovic, D., Collection Czechoslov. Chem. Communs., 6, 498 (1934).

(13) Julian, D. B., and W. L. Ruby, J. Am. Chem. Soc., 72, 4719 (1950).

(14) Kolthoff, I. M., and J. Jordan, J. Am. Chem. Soc., 74, 382 (1952).

(15) Ibid., 75, 1571 (1953).

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

(17) Kolthoff, I. M., and H. A. Laitinen, J. Phys. Chem., 45, 1079 (1941).

(18) Kolthoff, I. M. and J. Lingane, Polarography, Vol. I, 2nd Ed., Interscience Publishers, Ind., New York, 1952, p. 406.

(19) Ibid., pp. 439-41.

(20) Kolthoff, I. M. and C. S. Miller, J. Am. Chem. Soc., 63, 1405 (1941).

(21) Lingane, J. J., and L. Meites, Ind. Eng. Chem., Anal. Ed., 19, 159 (1947).

(22) Lloyd, N. A., Private Communication, Oklahoma A. and M. College.

(23) Lyderson, D., Acta Chem. Scand., 3, 259 (1949).

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

(25) Randles, J. E. B., Trans. Faraday Soc., 44, 327 (1948).

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

(27) Skobets, E. M., P. P. Turov, and V. D. Ryabokon, Zavodskaya Lab., 15, 912 (1949).

(28) Struble, R., Collection Czechoslov. Chem. Commun., 10, 475 (1938).

(29) Tsukamoto, T., T. Kambara, and I. Tachi, Proceedings of the International Polarographic Congress in Prague, Part I, (1951), p. 525.

(30) Verdier, E. T., Collection Czechoslov. Chem. Commun., 10, 233 (1939).

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