A NEW POLAROGRAPH
FOR USE WITH HIGH RESISTANCE
NONAQUEOUS SOLUTIONS

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HISTORICAL

The beginning of polarography is usually attributed to Kucera (21), who in 1903 was using a dropping mercury electrode (D.M.E.) for the purpose of studying the electrocapillary curve of mercury in various solutions. During this study he noticed inflections in the electrocapillary curve when reducible substances were present. At Kucera's suggestion, Jaroslav Heyrovsky investigated these phenomena and from his work polarography was developed (11, 12).

In 1925 Heyrovsky and Shikata (14) invented an automatic recording instrument for this new analytical method. The instrument was called a polarograph and the waves obtained were called polarograms. However, the method was strictly empirical and rather unreliable until 1935, when Heyrovsky and Ilkovic (13) demonstrated the theoretical significance of the polarographic wave.

The polarograph, in its simplest form, consists of a direct current source (large-capacity batteries) which may be varied in known voltage steps by means of a potentiometer. This potential is applied across an electrolytic cell in which two electrodes, one, a very small, easily polarizable electrode (the microelectrode), the other a large and nonpolarizable electrode. A current-measuring device is inserted in the circuit to measure the resultant currents at each applied voltage (Figure 1a).

The most commonly used microelectrode is the dropping mercury electrode which consists of a mercury reservoir connected to a fine capillary of about 0.05 mm internal diameter. The drops from this

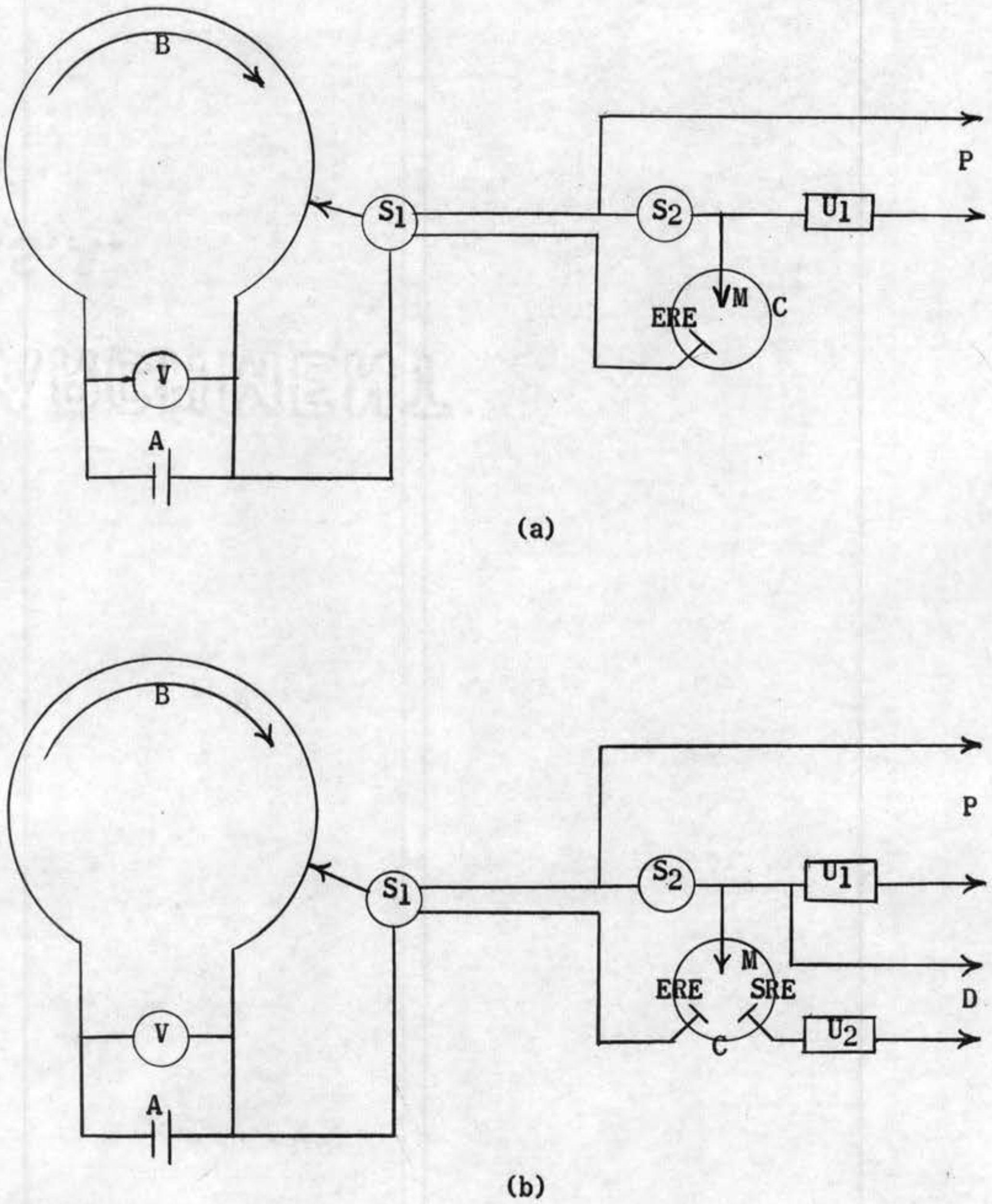


Figure 1.

(a) A Schematic Standard Polarographic Circuit.
(b) A Schematic Circuit for Polarography in High-Resistance Solutions.

Legend for both (a) and (b).

A.	Battery
B.	Bridge
S_1.	Reversing switch
S_2.	A series of resistors for varying the sensitivity
V.	Voltmeter
P.	To current-measuring device
M.	Microelectrode
E.R.E.	Electrolysis reference electrode
S.R.E.	Stable reference electrode
C.	Electrolysis cell
U_1.	Upscale control for pen
U_2.	Upscale control for chart
D.	To voltage-measuring device

capillary fall at a constant rate of one every 3 to 6 seconds. Capillary tubing of the proper bore may be obtained by selection from pieces of "marine barometer" tubing, from the Corning Glass Works, Corning, New York. The non-polarized electrode may be a pool of mercury in the bottom of the electrolysis vessel if the carrier electrolyte contains an anion which is capable of forming a reversible electrode with mercurous ion and if the pool is to act as the anode. However, a better electrode is the saturated calomel electrode, for not only is its behavior more reproducible but also it can be used in anodic polarography. Nearly all half-wave potentials are reported in the literature in terms of the S.C.E.

To permit a better understanding of the polarographic wave, a normal polarogram is shown in Figure 2, with its characteristic parts labeled. By studying this figure it will be seen that as an increasing voltage is applied across the electrolysis cell, a small current usually flows. This increasing current is shown as A in Figure 2, and is called the residual current. In the case of the D.M.E., this current is due, in part, to a small electrocapillary effect produced by certain ions which lower the interfacial tension between the mercury and the solution and concurrently permit the flow of a condenser current which results from the capacitance of the mercury-solution double layer at the interface. The rest of the residual current may be the result of the reduction of traces of oxygen or other impurities present in the solution--substances present in quantities so small it is almost impossible to remove them completely.

When the potential across the cell reaches the decomposition potential of the electro-reducible or electro-oxidizable substance,

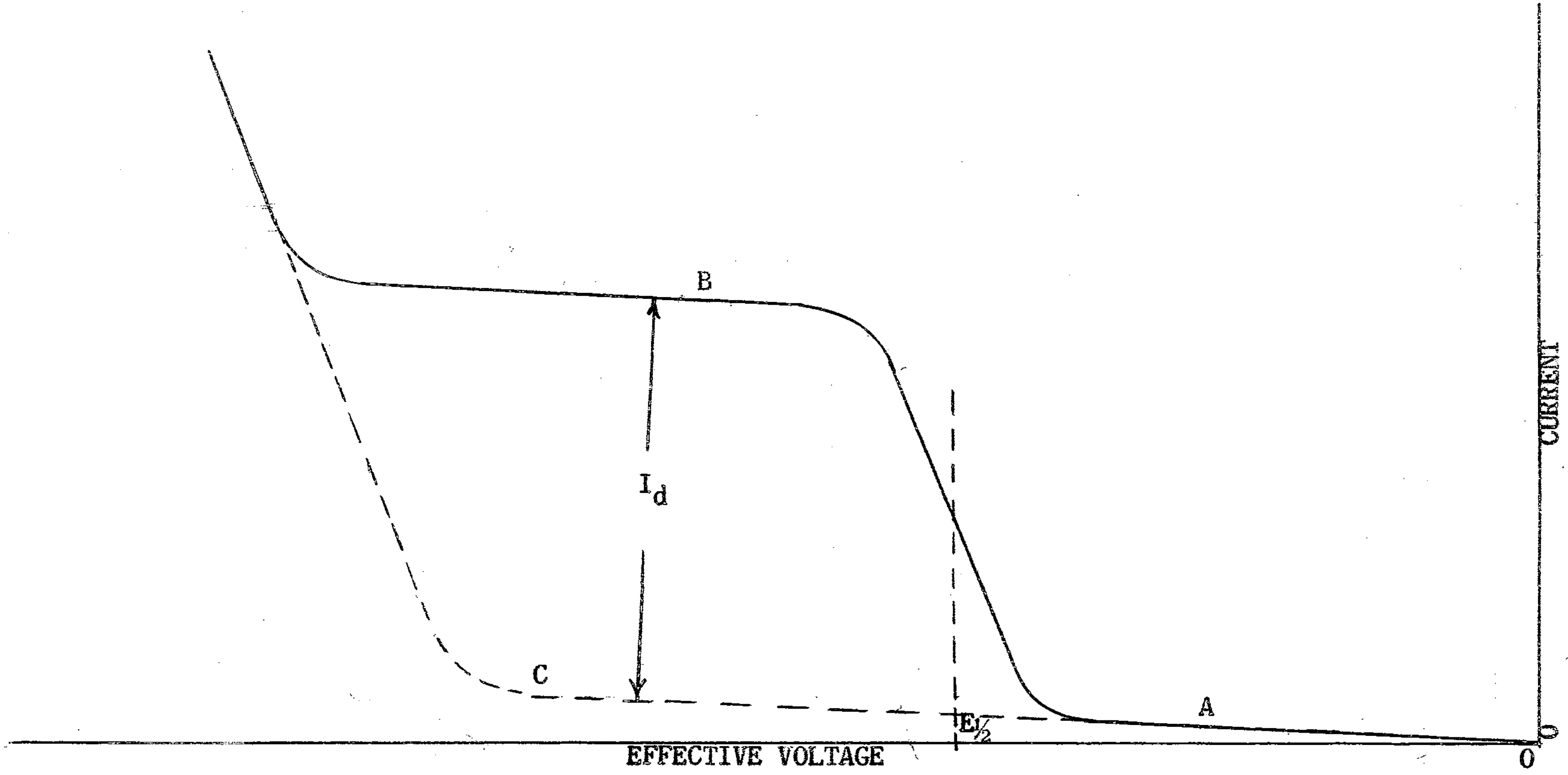


Figure 2. A Normal Polarogram

A. Residual current line
B. Limiting current line
C. Carrier curve

I_d. The diffusion current
$E_{1/2}$. The half-wave potential

the current increases rapidly until the limiting current B is reached. This limiting current is the sum of the residual current and the so-called diffusion current. The phenomenon of the limiting current obtained with the micro-electrode is caused by an extreme state of concentration polarization, due to the depletion of the ions (or molecules) at the electrode surface by the electrode reaction. When the limiting current is reached, the reducible or oxidizable substance reacts as rapidly as it reaches the electrode surface, and its concentration at the electrode surface, therefore, is maintained at a level which is negligibly small compared to its concentration in the bulk of the solution. Thus, the limiting current is practically independent of the applied E.M.F. and is governed by the rate at which the substance reaches the electrode from the body of the solution.

The oxidizable or reducible substance may arrive at the electrode, as a result of two forces; an electrical force, proportional to the potential difference between the two electrodes and a diffusion force, proportional to the concentration gradient between the solution at the electrode surface and the bulk of the solution. The first of these would tend to draw ions toward, or repel ions from the electrode, giving rise to the so-called migration current while the latter would give a diffusion current--for both would influence the rate at which ions would reach the electrode. However, by the addition of a salt, whose ions do not take part in the electrode reaction and of a concentration from 50 to 100 times that of the substance to be analyzed, the migration effect is expended largely on the ions of the supporting electrolyte (called the carrier electrolyte), and the migration current in the polarogram will be negligibly small. Thus, I_d (see Figure 2) is proportional to the rate of diffusion of the substance to be analyzed to the electrode. It can be seen then that the diffusion current is a function of the bulk-solution concentration, and that if conditions are constant and suitable standards are available, the wave height gives quantitative information.

The "half-wave" potential ($E_{1/2}$) is characteristic of the substance being oxidized or reduced. The half-wave potential is determined graphically by measuring the potential at which the midpoint of the wave, between the projected residual current line and the limiting current line, occurs. The half-wave potential is a function of temperature, of the nature of the carrier ions, of the concentration of the carrier ion, and of the reference electrode used. In many cases it is also a function of the concentration of the ion being determined; consequently, literature values should specify all of these variables.

It should be pointed out here that polarographs, to date, plot the current as a function of the applied potential. Thus, if the cell resistance is very high--4,000 or 5,000 ohms--the curve will be attenuated, giving an apparent shift in the half-wave potential. If the cell resistance is known, the curve may be corrected for the IR drop in the solution and the effective potential may be determined by the following equation:

$$E_{eff} = E_{app} - IR$$

where, "I" is the current at "E_{app}", "R" is the resistance of the cell plus the resistance of the circuit; and "E_{eff}" and "E_{app}" are the effective and the applied voltage, respectively. If the resistance is very large, it is difficult or impossible to correct the curve with the above equation chiefly because there is no recognizable wave to which the correction can be applied. If the cell resistance is low--less than 1,000 ohms--the IR correction is negligible and "E_{app}" may be assumed to be equal to "E_{eff}".

Diffusion Current Theory.

Ilkovic (16, 17) derived the following theoretical equation for the D.M.E.:

$$i_t = 706\ n\ D^{1/2}\ C\ m^{2/3}\ t^{1/6}$$

where; i_t is the current in amperes at any time "t", during the life of a drop,

706 is a constant arising from the geometry of the D.M.E. and includes Faraday's constant in coulombs,

n number of electrons involved in the electrode reaction,

D the diffusion coefficient of the substance involved in the electrode reaction, expressed in $cm^2\ sec^{-1}$,

C the concentration in moles per cm^3,

m the rate at which mercury flows from the capillary, expressed in grams per second,

t the time in seconds.

However, since the values involved are very small, it is more convenient to express "i_t" in microamperes, "C" in millimoles per liter, and "m" in milligrams per second.

More useful than "i_t" is the average current which may be defined as the theoretical current, which if allowed to flow for a length of time equal to the drop time, would pass the same number of coulombs as would the drop itself during its actual life. By substituting the above equation in the average current integral, and integrating, Ilkovic obtained for the average current:

$$i_{avg} = i_d = 605\ n\ D^{1/2}\ C\ m^{2/3}\ t^{1/6}.$$

It was recognized that the above equation of Ilkovic's was not wholly adequate, since it did not account for the observed variations of the diffusion current constant, $i_d/C\ m^{2/3}\ t^{1/6}$, with the characteristics of the D.M.E. However, it was not until 1950 that Strehlow and Von Stackelberg (31) and Lingane and Loveridge (25) independently demonstrated that the fault of the Ilkovic equation was due to the neglect of the curvature of the electrode surface. The new equation (at 25°C) is:

$$i_d = 607\ n\ D^{1/2}\ C\ m^{2/3}\ t^{1/6} \left(1 + \frac{A\ D^{1/2}\ t^{1/6}}{m^{1/3}} \right)$$

where "A" was evaluated as 17 by Strehlow and Von Stackelberg and as 39 by Lingane and Loveridge.

It can be seen that both the maximum current and the average current are directly proportional to the concentration of the oxidizable or reducible substance in the solution. However, since it is very difficult to measure the maximum current because of the sluggishness of the current-measuring devices employed in most polarographs, in practice the average current is usually measured.

Theories of the Half-Wave Potential and of Wave Form.

There are three general cases of metal ion reduction that should be considered when dealing with reduction at the D.M.E.

The first case is that of a metal ion that when reduced yields a metal which is soluble in mercury (e.g., cadmium). In this case

Heyrovsky and Ilkovic (13) have shown that (at 25°C)

$$E_{de} = E_{1/2} - \frac{0.0591}{n} \log \frac{i}{i_d - i} .$$

where; E_{de} is the potential of the D.M.E. at any point on the wave,

$E_{1/2}$ is the half-wave potential,

n is the number of electrons per ion taking part in the electrode reaction,

i is the current measured at the potential E_{de},

i_d is the diffusion current.

This is one form of the fundamental equation of the polarographic wave.

It can be seen from the above equation that for a polarogram of such an ion at 25°C., a plot of E_{de} versus log i/i_d-i should be a straight line with a slope of 0.0591/n. It can also be seen that the point where the log term becomes zero corresponds to the half-wave potential. One of the most valuable theoretical aspects of this curve is the slope, since it is possible from it to determine the value of "n". This is extremely important in reduction involving organic molecules, as it often explains the nature of the electrode reaction taking place.

The second case is that of a metal ion that is reduced to the metallic state but whose metal product is insoluble in mercury (e.g., nickel). In this case the important equation is,

$$E_{1/2} = E^{\circ}_{m} - \frac{RT}{nF} \ln \frac{k_s}{f_s} + \frac{RT}{nF} \ln \frac{i_d}{2} ,$$

where E°_{m} is the standard potential of the solid metal,

k_s is 605 n $D^{1/2}$ $m^{2/3}$ $t^{1/6}$ (from Ilkovic's equation),

f_s is the activity coefficient of the metal ion at the electrode surface.

This equation reduces to,

$$E_{1/2} = E^{\circ}_{ms} + \frac{0.0591}{n} \log \frac{i_d}{2.}$$

where $E^{\circ}_{ms} = E^{\circ}_{m} - RT/nF \ln k_s/f_s$, which is a constant at any given temperature, environment, and concentration. Since $i_d = k_sC$, it can be seen that in this case the half-wave potential is not independent of the concentration, but will shift 0.0591/n volts for a tenfold change in the concentration of the metal ion.

The third case is that of the reduction of a metal ion at one oxidation state to a lower state (e.g., ferric ion to ferrous ion in an oxalate carrier). The equation for this case has been shown to be the same as the equation in Case 1. This equation indicates that the general characteristics of the wave will be the same, and that the half-wave potential will be independent of the concentration.

Other situations have been treated theoretically and many equations for determining information useful to the theoretical chemist have been developed (20).

INTRODUCTION TO NON-AQUEOUS POLAROGRAPHY

A large volume of work has been and is being done using mixtures of organic solvents and water. However, these mixtures have only a limited application, since many organic compounds are insoluble in the presence of even small amounts of water, while others react with water. The amount of work that has been done in anhydrous organic solvents is relatively small.

A large part of the work in anhydrous solvents has been with the low molecular weight alcohols. Kikichi, Sakagachi, and Honda (19) were able to determine p-nitrosodiethylaniline in ethanol. Hans and von Sturm (9, 10) obtained good waves with $CuCl_2$ in methanol, ethanol, 1-butanol, and 1-pentanol, by plotting manually and correcting for the large IR drop in the solution. Vlcek (33) determined CO_2 in ethanol. Zurman, Zumanova, and Soucek (37) also used ethanol to determine CS_2, using diethylamine as a carrier. Methanol was used by Riccoboni and Popoff (29) to determine $SnCl_2$, and by Allison (1) to determine lead. Arthur and Lyons (2) were able to obtain good waves for lead and cadmium in methanol and ethanol and by means of special techniques were able to obtain good curves for several acid halides in anhydrous acetone.

Another popular solvent is a 1:1 mixture of benzene and methanol. Using methanol and benzene as a solvent, Willits, Ricciuti, Knight, and Swern (35) tabulated results for some forty-one oxygen-containing organic compounds (aldehydes, ketones, peroxides, etc.). In 1949, Lewis and Quackenbush (12, 24) published two papers on the use of this solvent to determine peroxides in fats and hydrocarbons. Hans and von Sturm (9) determined $CuCl_2$ in this mixture.

Bernard (6) also used methanol and benzene to determine peroxides of alcohols, pinene, and cyclohexanone.

Glacial acetic acid has been used as a solvent by several investigators. Bergman and James (5) used it to determine 46 nitro compounds. Bachman and Astle (3, 4) determined lead, cadmium, zinc, cobalt, chromium, antimony, nickel, copper, and ferric iron. Arthur and Lyons (2) used it for lead and cadmium.

Zan'ko and Manusova (36) used formamide and obtained good results with cadmium, lead, tin, and zinc. Letaw and Gropp (22) also used this solvent and obtained good waves with benzalacetone, benzophenone, fluorenone, lead, thallium, and zinc. Hood, Letaw, and Gropp (15) obtained good waves with this same series of compounds using mixtures of formamide and acetamide.

Parks and Hansen (28) used cellosolve (ethylene glycol monoethyl ether) to determine naphthalene, methylnaphthalene and also for a direct method for determining tetraethyllead.

Pyridine was used by Delimarshii and Abarbarchuk (7) for the determination of AgCl, $CoCl_2$, and $AsBr_3$, and by Hans and von Sturm (9) for $CuCl_2$.

Tetrahydrofuran was used by Kanngiesser (18), and he obtained excellent results for several types of compounds such as albumins, proteins, starch, and gelatine.

Liquid ammonia was used by Vecchi (32) to determine cadmium and lead; and by McElroy and Laitinen (27) to determine lead, cadmium, zinc, nickel, cobalt, chromium, and aluminum.

Wawzonek and Runner (34) reported excellent results in acetonitrile for lithium, potassium, cadmium, zinc, copper, lead, rubidium, cesium, sodium, calcium, and magnesium. Gentry (8) describes very briefly the use of ethylene glycol to determine cadmium, zinc, thallium, copper, and ferric iron.

As can be seen the use of anhydrous organic solvents has been largely restricted to the determination of inorganic ions, most of which can very easily be determined in water. However, these ions were used mainly to determine how well existing polarographic theories apply in such organic solvents, since very few organic compounds give the reversible waves to which such theories might be expected to apply. Only a few of the above mentioned papers dealt exclusively with organic compounds (2, 5, 18, 24, 35) in a particular organic solvent.

In almost all the above mentioned papers one of the points emphasized was that the cell resistance must not exceed a certain value, since it is then impossible to obtain good waves. Lewis, Quackenbush, and De Vries (24) could not obtain good results if the cell resistance exceeded 4,000 ohms. Arthur and Lyons (2) were unable to obtain good results if the cell resistance exceeded 8,000 ohms. In order to keep the resistance this low, as in acetone, it was necessary to place the capillary within 5 mm of the reference electrode, which meant that the reference electrode had to be a mercury pool. It also meant that the capillary must not be closer than this or the falling drops would stir the solution enough so that anodic products would come in contact with the cathode.

In all the above work the real solution to the use of organic solvents has been neglected. No reports have been made of any attempts to develop an instrument which would plot the current against the effective voltage rather than the applied voltage. Instead solvent-carrier combinations which had a low enough resistance were always employed, and then the curves were corrected for the IR drop in the solution. Arthur and Lyons (2) suggested that such an instrument would be a boon to the analytical chemist.

SCOPE OF INVESTIGATION

The primary purpose of this research was to develop an instrument that would be suitable for use in non-aqueous polarography. Such an instrument would plot the current as a function of the effective voltage in contrast to commercial instruments which plot the current as a function of the applied voltage. If this could be accomplished, then it would not be necessary to correct the polarograms obtained for the IR drop through the solution.

Since an instrument of this type must necessarily employ principles not employed in conventional polarographs, and since it was desired to eliminate water entirely from the system, it was also a part of the plan followed to develop and test suitable new cell designs and some non-aqueous reversible reference electrodes (the latter to take the place of the usual (S.C.E.)).

As is necessary with any new apparatus, it was also planned to test the instrument, both with high-resistance aqueous cells (to determine the effect of high resistance alone) and with organic solvents.

APPARATUS

An oscilloscope and a Brown Electronik Function Plotter, or X-Y recorder, were used as recording instruments in the polarographs designed in this research. A Dumont Cathode-Ray Oscillograph, Model 304-H, was used first, mostly, however, to test the polarographic circuits designed. This scope has a D.C. input with an impedance of 2 megohms and has quite stable, linear D.C. amplifiers.

The X-Y recorder was a special one, ordered from the Brown Instrument Division of the Minneapolis Honeywell Company. The specifications of the recorder were that the chart circuit operate with an input impedance of 100,000 ohms, have a sensitivity of 3.0 volts over ten inches of chart travel, and have a four-second response for full scale movement. The pen was to operate with an input impedance of 1,000 ohms and have a sensitivity of 2.5 millivolts full scale and a four-second response. This instrument was described by the manufacturers as a Model Y153X32(VV)-X-12(V).

The camera used for recording oscillographic traces and for copying work, was an Ibsor D.R.P., with a 13.5 cm lens. The camera uses a 3 1/4 x 4 1/4 sheet film back adapter. When used with the scope, the camera was adjusted to a setting of f:9 and was focused at a distance of 16 1/2 inches from the screen. The polarograms were recorded on Kodak Panatomic-X sheet film, the films then being developed in a tank according to the manufacturer's instructions.

Figure 3 illustrates the cell chiefly employed in testing the

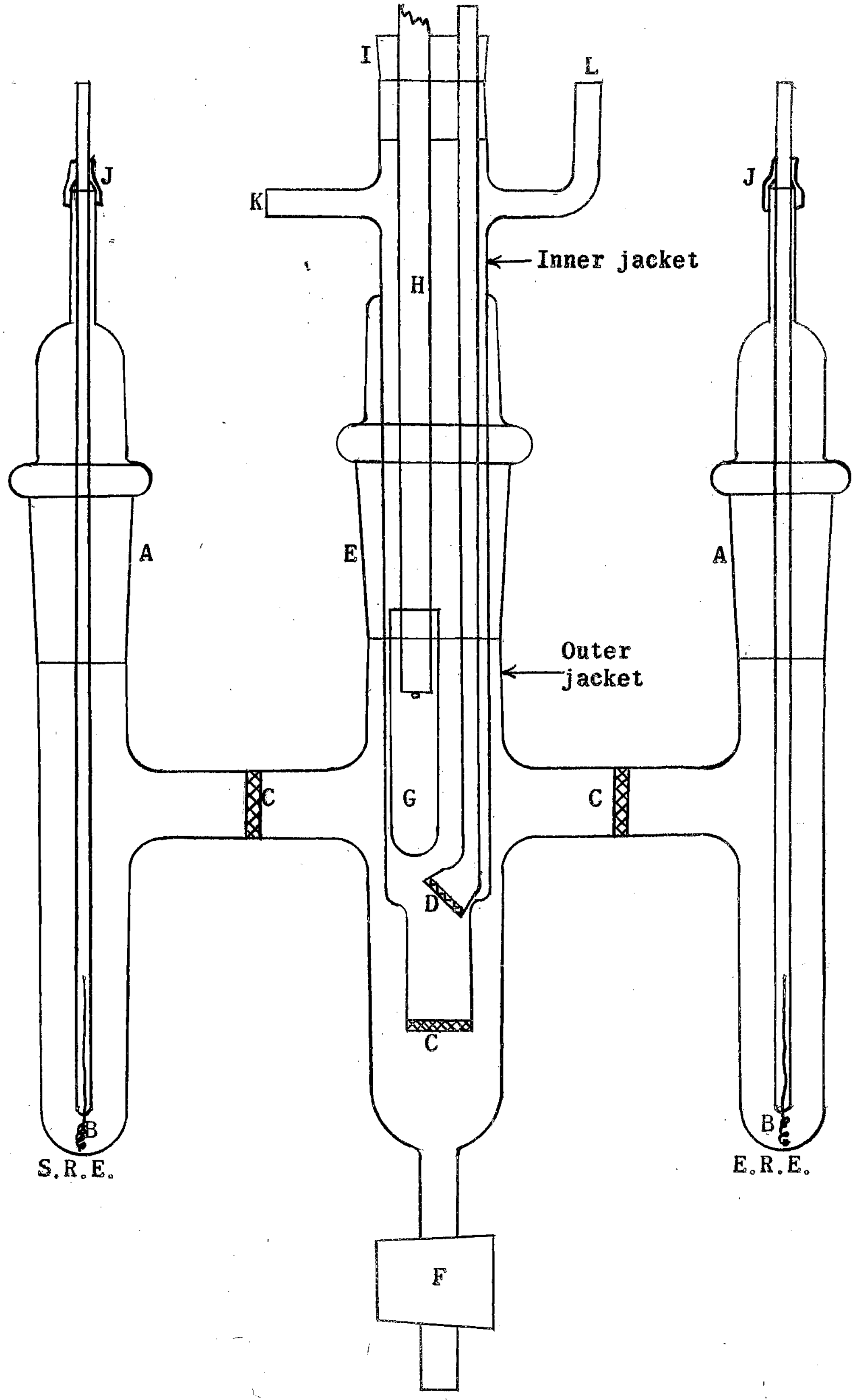


Figure 3. "Double-H" Polarographic Cell for Organic Solvents

Legend for Figure 3.

A. Standard taper joint, 19/38
B. Platinum wire
C. Sealing tubes, 10F, straight, with fritted disc
D. Gas dispersion tube, 10M, with fritted disc, for further degassing in the cell
E. Standard taper joint, 29/42
F. Stopcock, straight bore, #2
G. Small test tube, to catch drops from the D.M.E.
H. Dropping mercury electrode
I. Rubber stopper
J. Rubber tubing seals
S.R.E. Stable reference electrode
E.R.E. Electrolysis reference electrode
K. Nitrogen inlet tube
L. Nitrogen outlet tube

polarograph with organic solvents. The stable reference electrode (S.R.E.) and the electrolysis reference electrode (E.R.E.) were both acetone saturated calomel electrodes of the type described by Arthur and Lyons (2). A similar cell, but constructed so that the reference electrodes were connected to the D.M.E. compartment through 18/7 spherical joints, and with the inner jacket, the mercury-receiver G, and the dispersion tube D removed, was employed for use with aqueous solutions. For aqueous studies, conventional saturated calomel electrodes were used for both reference electrodes.

In the course of this research, it was found that the drop time of a dropping mercury electrode almost always became erratic if the same capillary were used in more than one solvent--sometimes even in the same solvent, but with different carrier electrolytes. Since several solvents were to be used in this research the apparatus shown in Figure 4 was constructed to facilitate the changing and reuse of electrode capillaries.

A 4 mm diameter tube was sealed onto the bottom of the male section of the 10/30 standard taper and then pulled down to about 1 mm I.D. With the hole this small, when the top stopcock is closed the mercury will not run out if the lower part of the apparatus (to which the capillary is attached) is removed. The latter can thus readily be replaced with a new female joint to which a different electrode is already attached. The standard taper joint is lightly greased and held in place with two small springs.
A nichrome wire is run through the top of the tube and then through the two stopcocks. This wire is used to make electrical contact with the mercury and serves also as a means of working out any small air bubbles which might be trapped in the bores of the

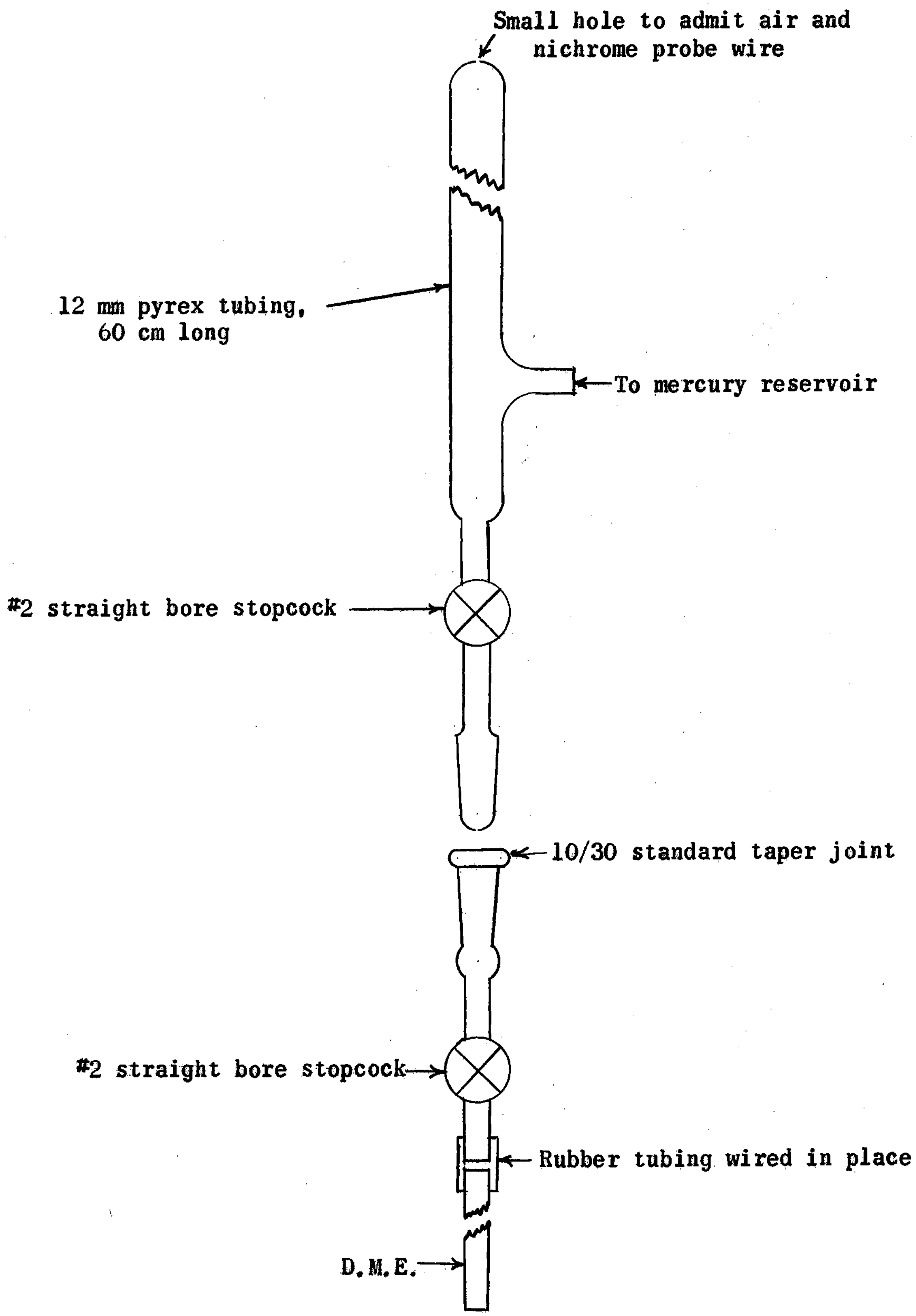


Figure 4. Dropping Mercury Electrode Assembly.

stopcock plugs.

A Gray Instrument Company, student-type potentiometer with a Leeds and Northrup galvanometer was used for all potential measurements. A Luder-type bridge (26) was used for all cell resistance measurements. The solutions were all thermostated in a kerosene bath at 25.0 ± 0.1°C.

REAGENTS

The following reagents were employed in this research:

Benzil - This was prepared by the oxidation of benzoin with nitric acid and recrystallizing twice from absolute ethanol.

Benzophenone - Eastman white label was used without further purification.

1-Butanol - Mallinckrodt analytical reagent grade was used after distillation from anhydrous potassium hydroxide. The distillation was done using a three-ball Snyder column, with all standard taper glass parts. To prevent formation of water by reaction of the KOH and butanol, distillation was stopped when about one-fourth of the butanol was left.

Cadmium chloride - Baker-Adamson reagent grade was used after drying overnight at 110°C.

Cetyldimethylethylammonium bromide - Matheson, Coleman and Bell C.P. was used without further purification.

Cinnamic acid - Coleman and Bell C.P. reagent grade was used without further purification.

Ethanol - A. S. Aloe absolute, reagent grade, was used after distillation as with 1-butanol above.

Ferric sulfate - Mallinckrodt analytical reagent grade was used without further purification after drying overnight at 110°C.

1-Hexanol - Eastman yellow label was used after drying over anhydrous potassium carbonate and then distillation as with 1-butanol.

Lead acetate - Baker's Analyzed C.P. was used after drying overnight at 110°C.

Lithium chloride - Mallinckrodt analytical reagent grade was used after drying several days at 110°C.

Mercurous chloride - Mallinckrodt analytical reagent grade was used without further purification.

Mercurous sulfate - Baker-Adamson C.P. was used without further purification.

Mercury - A. S. Aloe U.S.P. redistilled mercury was filtered on a gold filter and vacuum distilled in this laboratory.

Methanol - A. S. Aloe absolute reagent grade was treated as 1-butanol above.

m-Nitroaniline - Eastman white label was recrystallized from absolute ethanol before use.

Nitrogen - Linde water-pumped was used after passing successively through a tower of concentrated sulfuric acid, two towers of alkaline pyrogallol, and a tower of the solvent used.

Nickel chloride - Eimer and Amend C.P. was used after drying overnight at 110°C.

1-Octanol - Matheson, Coleman, and Bell was used after being treated as the 1-butanol above.

3-Pentanone - Matheson, Coleman, and Bell was used after drying over anhydrous potassium carbonate and then distilling over fresh potassium carbonate using the same apparatus as with the alcohols above.

Potassium carbonate - Anhydrous Mallinckrodt analytical reagent grade was used without further purification.

Potassium chloride - Merck reagent grade was used without further purification.

Potassium hydroxide - Merck reagent grade was used without further purification.

Potassium iodate - Baker analyzed C.P. was used after drying overnight at 110°C.

Potassium iodide - Baker analyzed C.P. was used after drying overnight at 110°C.

Potassium oxalate - Merck neutral reagent was used without further purification.

Potassium sulfate - Baker's analyzed C.P. was used without further purification.

1-Propanol - A. S. Aloe absolute reagent grade was used after treatment like 1-butanol above.

Sulfuric acid - A. S. Aloe C.P. reagent was used.

Sulfur - Merck, U.S.P., precipitated, was used without further purification.

Tetra-n-butylammonium iodide - was prepared by refluxing tri-n-butylamine and n-butyl iodide in ethanol for about 48 hours. The product was then recrystallized three times from benzene.

Zinc acetate - Mallinckrodt analytical reagent grade was used after drying overnight at 110°C.

PHOTOGRAPHIC TECHNIQUES

As was stated earlier, the traces on the oscillograph were photographed on Panatomic-X film. This gives a curve consisting of a black line on a white (clear film) background; but the need for enlargement, so that greater accuracy in measurements could be obtained, caused some difficulty. If the film was enlarged without reversing, a white line on a black background would result and necessary construction lines would not show up.

The problem was finally solved by simply making a contact print onto a very slow, high contrast film, Kodalith (a commercial film). An Airqupit Photocrat contact printer with a 25 watt bulb was used by cutting the line voltage to the bulb down to 40 volts. The film was exposed at this reduced illumination for approximately 5 seconds, depending upon the density of the original photograph. The Kodalith film was developed according to the manufacturer's recommendations with a special Kodalith developer. This produced a negative from which the desired black-on-white enlargements were made in the usual way on 8 1/2" x 11" Dupont Velour Black document-weight paper, Type AL, Grade 3. These same Kodalith negatives served also for the making of pictures for reports, articles, and this thesis.

Polarograms made on the chart paper of the strip-chart recorder were reproduced photographically, the same camera that was used with the oscillograph being employed. Kodak Contrast Process Ortho film, because of its very high contrast for line copy work, was used. With the camera set with its lens about 18 inches from the chart to be copied, and with the chart illuminated by two #2 photoflood lights as a distance of about two feet, the pictures were taken at one twenty-fifth of a second at f:9. The polarographs were placed under a sheet of plate glass, to hold them flat, and the lights were directed to strike the glass at about a 45° angle in order to minimize glare. The film was developed in Kodak D-11 according to the manufacturer's instructions. The blue grid lines of the chart paper showed up only faintly on this film, while the red pen trace was very strong and sharp. The few grid lines which showed up too plainly were touched up, on the negative, with opaque-red dye; then the polarograms were printed either by enlargement or contact. The enlargements were made in the usual way, using the above mentioned Dupont paper. The contact prints were made by using this same enlarging paper as a contact paper, the enlarger, set at about f:22, being used as the light source. All enlargements and prints were developed and processed according to the manufacturer's instructions with Kodak Dektol.

EXPERIMENTAL

Design of the Polarograph.

The idea for the construction of the instrument developed in this research came from the principle used in the limited cathode potential method of electrodeposition (30). This method involves the use of one cathode and two anodes. One of the anodes is used as an electrolysis electrode and the other is used as a stable reference electrode. The potential difference between the stable reference electrode and the cathode, measured in such a manner as to draw no current through the reference anode, serves as an index by means of which the effective cathode potential (involving no IR drop) can be determined and controlled throughout the electrolysis.

In order to apply this principle to high-resistance polarography, therefore, it is necessary to design and employ a new type of polarographic cell having two reference electrodes, at least one of which (the stable reference electrode (see Figure 3)) would preferably be a reversible electrode of the calomel type. In addition, a recorder, capable of plotting current as a function of the potential difference between the microelectrode and the stable reference electrode without drawing appreciable current through the latter, is needed.

Investigation revealed that there were two currently available types of recording instruments which would meet the specifications--i.e., which would measure the current flowing between the cathode and the electrolysis reference electrode (E.R.E.) and which would measure the effective voltage of the cathode as a function of the stable reference electrode (S.R.E.) and plot one as a function of the other. The first is the cathode-ray oscillograph and the second is the strip-chart function plotter such as the Brown Electronik Function Plotter or X-Y recorder.

A schematic circuit diagram showing the principle of the new polarograph is shown in Figure 1(b). Upon comparing this diagram with the one of the standard polarographic circuit, Figure 1(a), it can be seen that basically the circuit is the same except that a second reference electrode and a voltage-measuring device have been added.

The diagram of the complete polarographic circuit as finally adopted for use with the X-Y recorder is shown in Figure 5. In operating the instrument, S_1 and P_1 control the voltage supplied by B_1 to the motor-driven bridge--i.e., the span voltage--while S_2, S_3, B_2, and P_2 supply and control the potential at which the polarogram is actually started--i.e., the preset voltage. Switch S_4 controls the polarity of the microelectrode (upward is cathodic; downward is anodic) while S_7 is used to reverse the polarity of the electrolytic damping condenser C. Switch S_{10} controls the amount of damping, (closed upward gives moderate damping, closed downward gives a maximum damping, while in the center position gives no damping except that inherent in the recorder). Resistor R_2 is used to increase the amount of damping when the low sensitivity settings are used (for the measurement of large currents). This 1,000 ohm resistor, when placed in series with the sensitivity resistor, increases the RC time constant of the circuit, thus increasing the damping effect when the

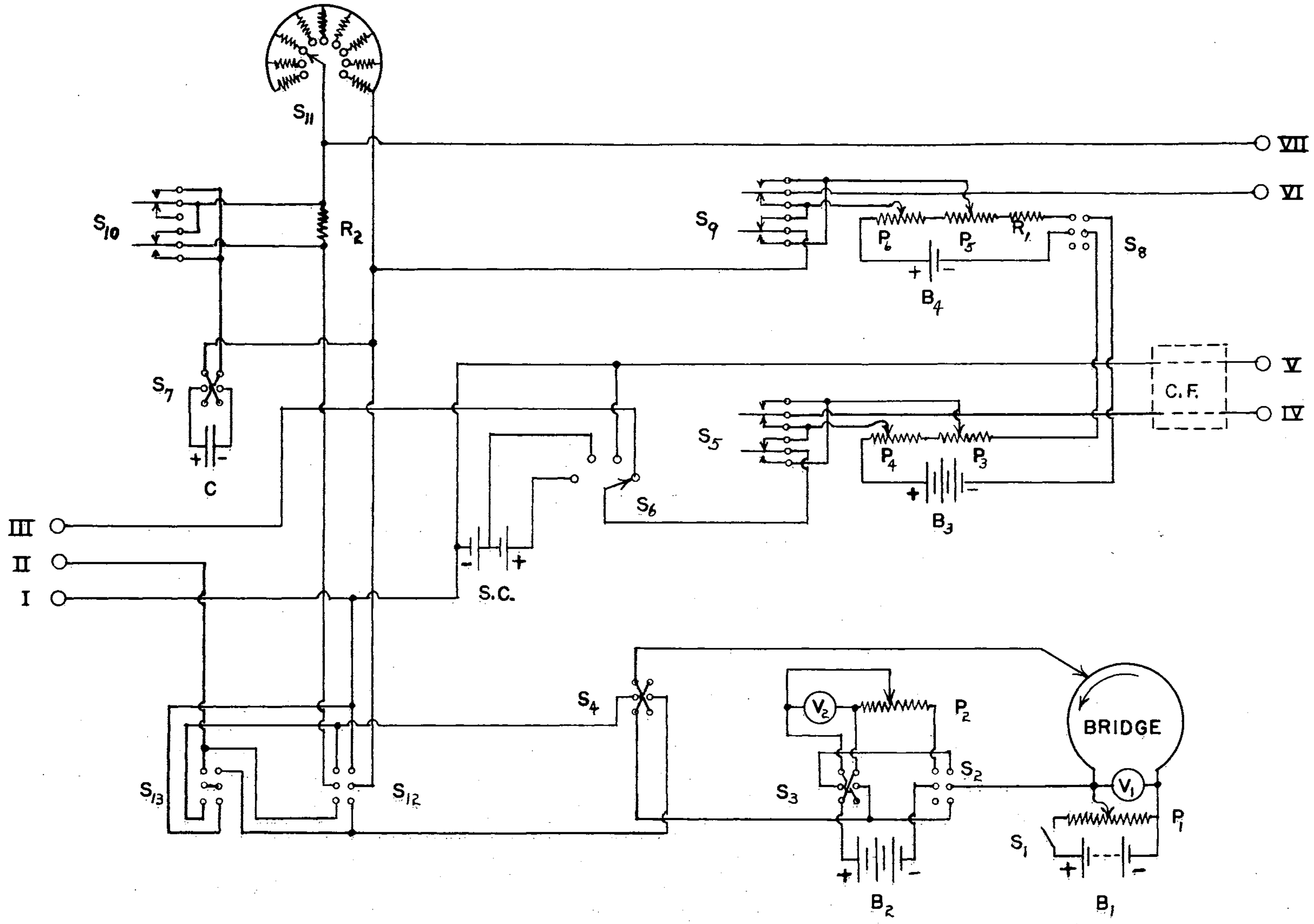


Figure 5. Final Polarographic Circuit

Legend for Figure 5.

I	Lead to microelectrode
II	Lead to electrolysis reference electrode
III	Lead to stable reference electrode
IV	Lead to chart positive
V	Lead to chart negative
VI	Lead to pen positive
VII	Lead to pen negative
B_1	One to three Eveready Hotshot 6-volt batteries, #1461, in series, as needed to provide maximum voltage required
B_2	Two to three Burgess #4F 1 1/2 volt batteries, in series
B_3	Two to three Burgess #4F 1 1/2 volt batteries, in series
B_4	One Burgess #4F 1 1/2 volt battery
C	Capacitor, Mallory, #WP041, 2000-mfd. electrolytic
C.F.	Cathode follower, high impedance (see Figure 10)
P_1	Industrial control (potentiometer), wire-wound, 4-watt, 00-ohm
P_2	Industrial control (potentiometer), wire-wound, 4-watt, 550-ohm
P_3	Industrial control (potentiometer), wire-wound, 4-watt, 25,000-ohm
P_4	Industrial control (potentiometer), wire-wound, 4-watt, 400-ohm
P_5	Industrial control (potentiometer), wire-wound, 4-watt, 100-ohm
P_6	Industrial control (potentiometer), wire-wound, 4-watt, 2-ohm
R_1	Resistor, Continental carbon, X-type, precision, 30,000-ohm
R_2	Resistor, IRC, type WW4J, wire-wound, 1% accuracy, 1000-ohm

The following resistors are those shown in S_{11} numbered in counter-clockwise order:

R_3	Resistor, IRC, type WW4J, wire-wound, 1% accuracy, 5000-ohm
R_4	Resistor, IRC, type WW4J, wire-wound, 1% accuracy, 2000-ohm
R_5	Resistor, IRC, type WW4J, wire-wound, 1% accuracy, 1000-ohm
R_6	Resistor, IRC, type WW4J, wire-wound, 1% accuracy, 500-ohm
R_7	Resistor, IRC, type WW4J, wire-wound, 1% accuracy, 200-ohm
R_8	Resistor, IRC, type WW4J, wire-wound, 1% accuracy, 100-ohm
R_9	Resistor, IRC, type WW4J, wire-wound, 1% accuracy, 50-ohm
R_{10}	Resistor, IRC, type WW4J, wire-wound, 1% accuracy, 20-ohm
R_{11}	Resistor, IRC, type WW4J, wire-wound, 1% accuracy, 10-ohm

Switches are as follows:

S_1 SPST toggle switch
S_2, S_3, S_8, S_{12}, and S_{13} DPDT toggle switches
S_4 and S_7 DPDT center-off toggle switches
S_5, S_9, and S_{10} Switchcraft Lever-Type No. 3036L, 3-position, locking type switches
S_6 and S_7 Ohmite power tap switches, Model III, eleven-contact switches

sensitivity resistors employed are themselves too small.

Switch S_6 is used for calibration of the chart movement. This calibration is necessary because of the cathode follower unit (C.F.) (to be discussed later), which is not included in the chart calibration unit of the recorder. When an oscillograph is used as the recorder, this calibration feature is doubly useful, since the oscillograph does not have a calibration circuit at all. The S.C. which supplies the known voltage for the calibration consists of two standard cells connected in series. The four switch positions are used as follows (reading counter-clockwise): position 1 (extreme right) is non-calibrating and is used for making polarograms; position 2 is to give a zero potential across the cathode follower input (this will be referred to as the <u>absolute</u> zero); position 3 applies a potential, equal to that of one of the standard cells, across the cathode follower input; and position 4 applies the full potential of the two standard cells, in series, across the cathode follower input.

Switch S_8 controls the batteries, B_3 and B_4, which provide the power for the upscale controls of the pen and chart. Potentiometers P_5 and P_6 control the pen upscale, while P_3 and P_4 control the chart upscale. Switches S_5 and S_9 are reversing switches, which allow the pen or the chart to be driven either up- or downscale. This set of controls is not used with the oscilloscope, since the latter has its own internal centering controls.

Switch S_{11} is the current-sensitivity selector switch. This switch places selected fixed resistors in the electrolysis circuit through which the current flows. Since the oscilloscope and the pen circuit of the recorder are both voltage-measuring devices, the voltage drop across any given resistor, and the proportionality of this IR drop to the current flowing through the resistor, is used for measuring the current.

Switch S_1 and S_{13} have not so far proved to be essential to the polarograph but provide a way of putting the current-measuring resistors into either the microelectrode circuit or into the electrolysis reference electrode circuit.

Connection I goes to the microelectrode, II goes to the electrolysis reference electrode (E.R.E.), and III goes to the stable reference electrode (S.R.E.). Connections IV, V, VI, and VII go to the recorder, IV going to the chart positive, V to the chart negative, VI to the pen positive, and VII to the pen negative. When the oscillograph is used, the leads V and VII are connected to the ground side, IV is connected to the X-input, and VI is connected to the Y-input.

Aqueous High-Resistance Cells.

As a means of testing the great variety of polarographic circuits tried and to see how polarograms obtained with such apparatus and with such high resistances compared with the conventionally-obtained polarograms, it was decided to employ aqueous cells for part of this work. One of the first problems encountered, therefore, was that of devising a method of obtaining suitably high cell resistances without changing carrier electrolyte concentrations from those customarily used in polarography. The method finally adopted involved the use of a modification of the cell illustrated in Figure 3. In this modification, the inner compartment of the illustration was omitted and the reference electrodes were connected to the D.M.E. compartment through 18/7 ball joints. In this way the parts of the cell could be connected directly to give a low resistance to the cell.

It was found by experiment that four feet of the 3 mm. I.D. tubing filled with 0.1M KCl solution gave a resistance of about 400,000 ohms to the arm or branch of the cell in which it was incorporated. This tubing was coiled to reduce its space requirements and make the cell assembly small enough to fit into the constant-temperature bath. For connecting purposes a pair of 18/7 ball joints were fastened to the ends of the coils with rubber tubing, small plugs of pyrex glass wool placed in the ends serving to retain the solution. Two sets of these coils were made, one giving about 400,000 ohms, and the other, 100,000 ohms resistance. Aqueous saturated calomel electrodes were used as reference electrodes.

When it was desired to use this cell, an aspirator was used to draw 0.1N KCl solution into each coil until completely filled. When the coils were full and all air bubbles were worked out, the cell was assembled and the solution to be tested (e.g., cadmium ion in 0.1N KCl) was placed in the D.M.E. compartment. The solution was degassed in the conventional way, then the D.M.E. was put in place and the flow of mercury started. The cell resistance (measured between the D.M.E. and each anode) was then determined. This measurement was necessary each time, because it was sometimes very difficult to remove all the tiny air bubbles from the side-arms. If the bubbles were not removed, resistances of several megohms were encountered and only straight lines were obtained when polarograms were run. It was sometimes possible to remove these small air bubbles by carefully squeezing the rubber tubing connectors; however, if this failed it was necessary to remove the side-arms and refill them. With the side-arms properly prepared, it was possible to reproduce the resistance to within about one percent.

Experiments with Oscillographic Recording.

The first polarograms actually run in this research were made with the polarograph employing oscillographic recording and with the aqueous cell described in the preceding section.

Some difficulty was immediately encountered. When the cell was thermostated in a water bath, it was found that it was impossible to focus the spot of light on the screen of the oscillograph down to the usual sharply-defined dot. All leads from the cell to the polarograph and from the latter to the oscillograph were immediately replaced with short shielded wires and the shields were grounded. This procedure helped, but the difficulty was not entirely overcome until the water in the constant-temperature bath was replaced by kerosene.

The explanation for this trouble is rather simple. Since the oscillograph (and the recorder, which was used later) measures all voltages, regardless of the source, all stray A.C. pick-up must be eliminated. Even with all the precautions taken it has been found difficult to use the instrument at all during electrical storms, owing to the fact that every time lightning flashes, the spot on the oscillograph or the chart gives a large jump.

After minimizing this stray pick-up, the first polarograms were made. The spot was set in the lower left-hand corner of the screen on the scope, and the attenuators were adjusted so that the polarograms would cover as much of the screen as possible.

Figures 6 and 7 show the types of curves obtained with oscillographic recording, when high-resistance (0.148 megohms) side arms were used, Figure 7 with damping and Figure 6 without. For purposes of comparison, Figures 8 and 9 show the types of polarograms obtained, with low (600 ohms) and high (0.48 megohms) resistances respectively, with damping, when the strip-chart recorder is used. As was anticipated, the curves obtained with cells of low resistance (Figure 8) proved to be identical to the curves obtained with the same solution in a conventional cell with a commercial (Sargent Model XXI) Polarograph.

The influence of high resistance, however, is readily seen in Figures 6, 7, and 9. In the damped polarograms, the oscillations caused by the D.M.E. appear to be horizontal rather than vertical,

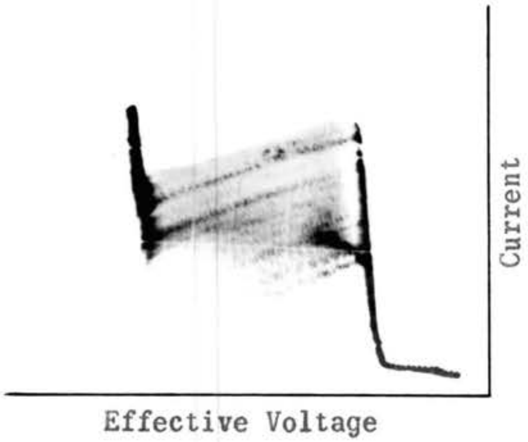


Figure 6. Cadmium in Water.

Concentration	10^{-3} M
Carrier	0.1N KCl
Reference electrodes, E.R.E.	S.C.E.
S.R.E.	S.C.E.
Cell resistance	0.15 megohm

Oscillographic recording, with no damping

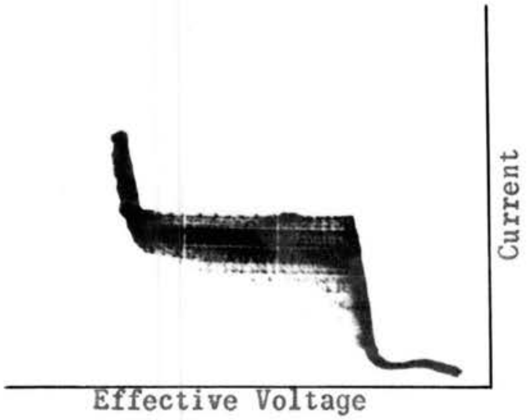


Figure 7. Cadmium in Water.

Concentration	10^{-3} M
Carrier	0.1N KCl
Reference electrodes, E.R.E.	S.C.E.
S.R.E.	S.C.E.
Cell resistance	0.15 megohm

Oscillographic recording, with damping

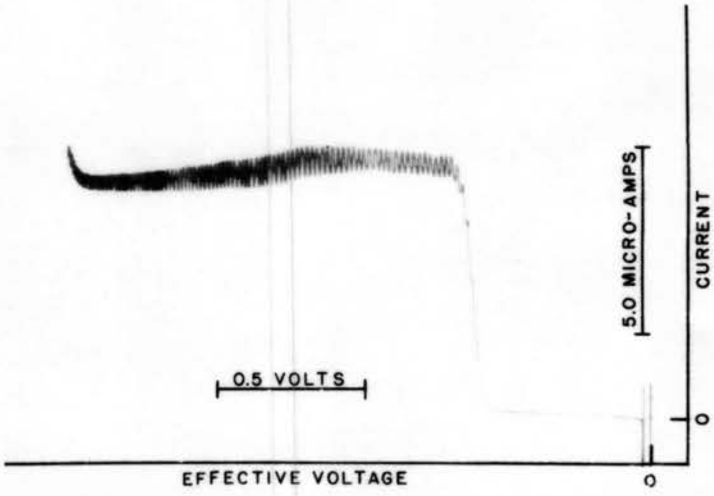


Figure 8. Cadmium in Water.

Concentration	10^{-3}M
Carrier	0.1N KCl
Reference electrodes, E.R.E.	S.C.E.
S.R.E.	S.C.E.
Cell resistance	600 ohms

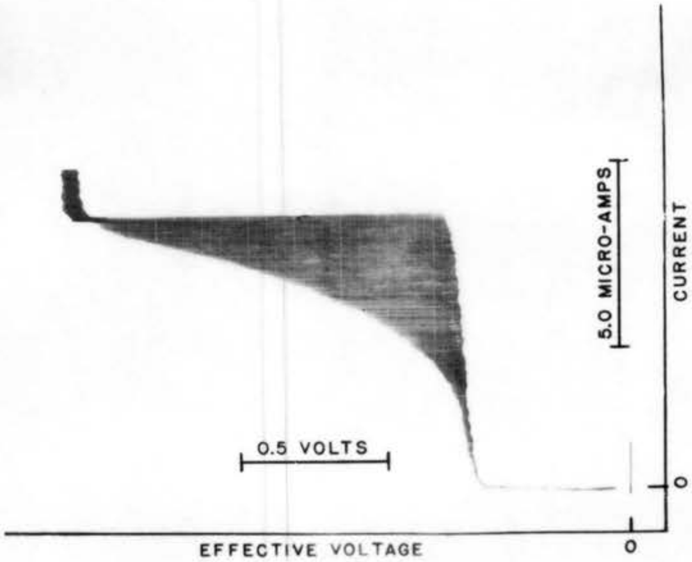


Figure 9. Cadmium in Water.

Concentration	10^{-3}M
Carrier	0.1N KCl
Reference electrodes, E.R.E.	S.C.E.
S.R.E.	S.C.E.
Cell resistance	0.47 megohm

but the envelope drawn through the outer and upper points of the curve corresponds closely to the form of normal polarograms. Without current damping (Figure 8), the oscillations are seen to slant, the damping obviously having the effect of removing the current (the vertical) component of a current-voltage vector. That these oscillations are due to the growth and falling off of the mercury droplets was determined by watching both the recorder and the D.M.E. simultaneously. In this same manner it was found that the maximum effective voltage (i.e., the farthest movement of the oscillation to the left) in any given oscillation occurred at the moment the droplet fell, leaving essentially no electrode, the current at this same instant dropping to its minimum value. This was as expected, since when the current decreases (minimum electrode area) the IR drop becomes small and the effective voltage approaches the magnitude of the applied voltage. At maximum current (maximum drop size) the IR drop is a maximum and the effective voltage reaches a minimum. The envelope mentioned earlier, therefore, should approach (and, without any damping influences, should reach) the conditions of a curve obtained at maximum drop size.

In continuing experiments with the oscillograph (and more accurately later with the strip-chart recorder) it was found that the diffusion current was not as large in the high-resistance solutions as it was in the low. To determine where the loss occurred, current measurements were made in each of the three electrode branches. It was soon found that a rather large part of the current was flowing in the S.R.E. branch, especially when the cell resistance was about 0.5 megohms. In the case cited, the current in the S.R.E. branch was about one-fifth as great as the current measured in the E.R.E.

branch. A re-examination of the circuit, the cell, and the oscillograph soon explained this phenomenon. The oscillograph employed has an input impedance of only two megohms. Normally this is considered a very high impedance; but compared to 0.5 megohms (the cell resistance) 2 megohms is not at all large. Consequently, considerable loss of current was occurring in the branch where current was not normally being measured. Since this meant that some IR drop must also be occurring, this condition had to be corrected.

Consultation with Dr. H. E. Harrington, Mr. Richard F. Buck, and Mr. Jack Tompkins of the Electronics Laboratory of the Oklahoma Agricultural and Mechanical College, Research Foundation, led to the conclusion that the best practical solution to the problem, was to place a high-impedance cathode follower (C.F.) into the S.R.E. circuit. Such a cathode follower will follow a D.C. voltage, has a linear output, can be designed to have a very high input impedance (100 megohms), and has an efficiency of from 90 to 95 percent.

The first cathode follower built employed a triode as the amplifier tube. This proved to be as bad as or worse than no amplifier at all, because of the high grid currents obtained with such tubes. The apparent impedance was 100 megohms, but because of the current flowing in the grid circuit, the effective impedance was less than 2 megohms.

The second cathode follower employed a pentode as the amplifier tube. The circuit used is shown in Figure 10, along with its power supply. To place this unit into operation, a 0.1 megohm fixed carbon resistor is placed across the output and a 1.0 megohm

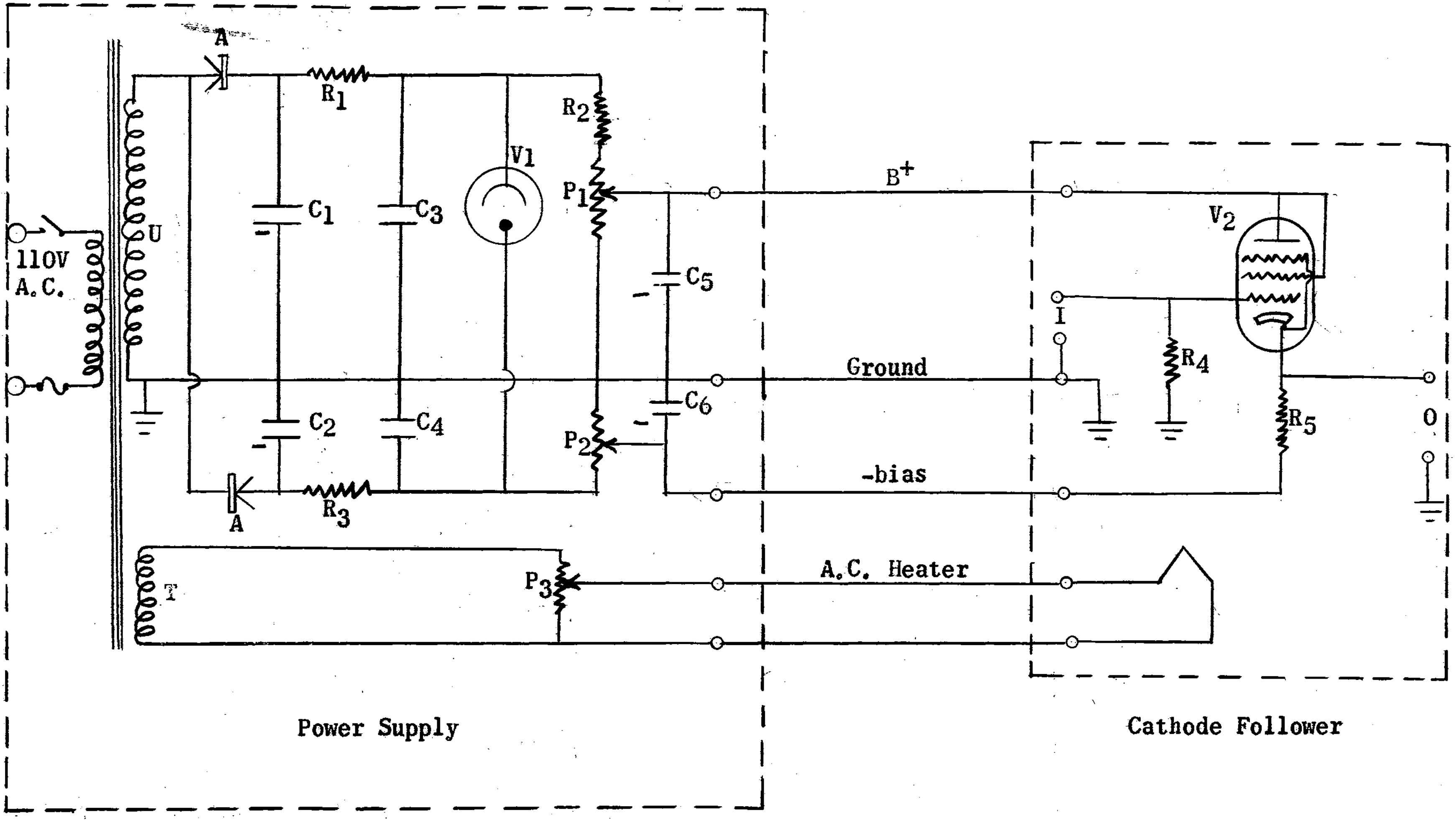


Figure 10. The Cathode Follower and Its Power Supply.

Legend for Figure 10.

A. Selenium rectifiers, 100 milliamps, D.C.
R_1. Resistor, 5,000 ohm, 5 watt
R_2. Resistor, 49,000 ohm, fixed carbon
R_3. Resistor, 5,000 ohm, 5 watt
R_4. Resistor, 100 megohm, fixed carbon
R_5. Resistor, 10,000 ohm, fixed carbon
P_1. Potentiometer, 50,000 ohm, wire-wound
P_2. Potentiometer, 50,000 ohm, wire-wound
P_3. Potentiometer, 250 ohm, wire-wound
C_1 and C_2. Condensers, 20 microfarad, electrolytic, 150 volts D.C.
C_3 and C_4. Condensers, 0.01 microfarad, 50 volts D.C.
C_5 and C_6. Condensers, 10 microfarad, electrolytic, 150 volts D.C.
V_1. Voltage regulator tube, OB2
V_2. Power pentode tube, 6AK5
T. Power transformer, 6.3-volt tap
U. Power transformer, 110-volt tap
I. Input terminals
O. Output terminals

fixed carbon resistor is placed across the input. The A.C. heater voltage is then adjusted with P_3 to exactly 2.9 volts. B^+ is adjusted to approximately 40 volts with P_1 and the bias is set to approximately -13 volts with P_2. Then by trial and error the output and the input of the cathode follower are set, by adjusting P_1 and P_2, to a minimum voltage, as measured across the fixed carbon resistors with a vacuum tube voltmeter. This adjustment is very critical and tedious, and is entirely different with each amplifier tube used (probably because the tube is used far below its rated filament voltage of 6.3). However, with care and patience the two values may be set to about 0.05 volts on the input side and to about -0.05 volts on the output side. On the input, when the cell with a resistance of 0.5 megohms is in place instead of the fixed carbon resistor, this corresponds to a current of about 0.001 microamps. The very small grid current is therefore negligible and the input impedance may be considered the input impedance of the cathode follower--i.e., 100 megohms. A resistance of 100 megohms as compared to a cell resistance of even one megohm is still very large, and the small amount of current which will flow in this branch may be neglected.

With the cathode follower installed, the waves obtained were like that in Figure 9 and the current was as large as expected. However, it was found necessary to operate the power supply of the cathode follower from a constant-voltage transformer, since the spot often would slowly move several divisions on the screen with no input signal. The line voltage sometimes fluctuated as much as 15 volts; however, a Sola constant-voltage transformer rated to smooth a 96 to 125 volt fluctuation to 115 volts to within one percent removed all but very tiny fluctuations from the filament voltage of the amplifier.

In addition to the work done in aqueous solutions, the work was also extended to include 1-butanol as a solvent. Sulfur and quinone were tried in 1-butanol, using 0.1N LiCl as the carrier electrolyte. Waves were obtained with both the sulfur and the quinone; however, the waves were not well formed. The reason for the poor quality of these waves was not clear at the time and the waves served only to show that sulfur and quinone are polarographically active in 1-butanol. These experiments were run before the need for the cathode follower was discovered, however, and during the time when the stability of the oscillograph still left much to be desired. It is highly probable, therefore, that much better waves could be obtained if the improved apparatus were employed.

At about this time the oscillograph started drifting badly during runs, i.e., the spot would move up and down on the screen and it was impossible to obtain good waves. It was thought that the fluctuations in the line voltage were causing most of the instability; therefore, all the filament leads of the oscillograph were removed from the oscillograph's power supply and connected to a 6-volt lead storage battery. A trickle charger was then connected to the battery to maintain a constant charge on the battery. It was also found that several of the I.R.C. resistors in the oscillograph were badly burned; consequently, they were replaced. With this arrangement and with the new resistors, the spot of the oscillograph was extremely stable. In running an IR plot (which required 12 minutes) photographing the trace, no visible fluctuations from the straight line could be seen on the film.

For reasons given in the next section, no further polarographic work was done with this apparatus.

Strip-Chart Recording Polarograph.

Owing to the much greater convenience of strip-chart recording and the fact that experience with other Brown recorders had indicated that great stability could probably be expected of the new recorder, it was the full intent from the beginning of this research to spend time on the oscillograph only while the X-Y recorder was being obtained. It was hoped that experiments with the oscillograph would permit the polarographic circuit to be perfected and would reduce the need for additional modifications after the recorder had arrived.

These hopes were only partially realized. As mentioned before, one connection of each the vertical and horizontal sweeps of the oscillograph is grounded--and they are therefore shorted to each other. In the X-Y recorder such is not the case. This would not have caused any trouble except for the fact that it was desired to design the polarograph so that anodic waves would rise in exactly the same way as cathodic waves. The X-Y recorder, with its completely separate chart and pen circuits, seemed to offer the opportunity to accomplish this.

Many circuit modifications were tried before the one shown in Figure 5 was finally adopted. The work was complicated by the fact that little was known about the behavior of either the apparatus or the solutions themselves, and the cause for a given odd behavior was therefore not readily apparent. An intermittent short-circuit occurring in the recorder itself caused no little trouble before it was discovered and led to the temporary discarding of circuits which actually were later found to work.

It was finally found that although the chart and pen circuits of the recorder are supposedly independent, actually, they either must remain completely disconnected (an impossibility in any polarographic circuit) or else the negative of the pen and that of the chart must be connected through a resistance not to exceed a few hundred ohms. A potential difference between the two negatives of even several volts has no apparent effect.

When this discovery was made, it was easy to see that the circuit shown in Figure 5 was probably the only one that would work with this recorder. Anodic waves can be made, but only by using the upscale controls (see Figure 5) to move both the pen and the chart as far as possible upscale. During the run, the potentials (current-measuring, and voltage) oppose the upscale potentials, thus tracing the anodic wave toward the left and bottom instead of to the right and upward. Since this way of representing anodic waves is actually preferred by some investigators, it is quite acceptable.

In order to test the behavior of this new instrument, a series of runs was made on aqueous solutions. The first runs were made in three different ways using the same solutions; (1) on the Sargent Model XXI, with a cell of low resistance; (2) on the new instrument, with a cell of low resistance; and (3) on the new instrument, with a cell of high resistance. The cells were kept at 25°C., and the following ions were used; cadmium, zinc, nickel, lead, and iodate in 0.1M potassium chloride, and ferric iron in 1.0M potassium oxalate. These ions were chosen because they represent all the cases that are normally considered, i.e., a metal which is soluble in the mercury electrode (cadmium), a metal which does not dissolve in the mercury (nickel), a metal ion which reversibly changes from one valence state to another but remains in the aqueous solution (ferric iron) and an ion which is irreversibly reduced and remains in solution (iodate). The half-wave potentials were then determined for all. The results of this series are shown in Table 1.

Table 1.
Half-Wave Potentials of Various Ions.

	$E_{1/2}$(Lit. 20)	$E_{1/2}$(XXI)	New Instrument $E_{1/2}$ Values (600 ohms)	(0.47 megohm)	Avg. $E_{1/2}$ (0.47 megohm)
Cd^{++}	0.599^a	0.598^a	0.597^a	0.572	0.600
Zn^{++}	0.995^a	0.997^a	1.04^a	0.982	1.09
Pb^{++}	0.396^a	0.404^a	0.403^a	0.334	0.384
IO_3^-	1.25^a	1.24^a	1.26^a	1.22	1.27
Ni^{++}	1.10^b	1.00^a	1.01^a	0.923	1.02
Fe^{+++}	0.240^c	0.245^c	0.236^c	0.199	0.233

a) Run in a carrier of 0.1N KCl. b) Run in a carrier of 1.0N KCl.
c) Run in a carrier of 1.0M $K_2C_2O_4$.

As can be seen, the results obtained on the Model XXI and on the new instrument, in low-resistance solutions, agree very well both with each other and with the literature values. The only serious deviation is zinc, which deviates by about four percent.

With high-resistance cells, on the other hand, a rather large shift in the half-wave potentials is obtained. It is felt that the reason for this shift may be due to the method used to measure the waves. As was mentioned earlier, owing to the shape of the wave (Figure 9) it is necessary to measure the envelope of the curve; and since the D.M.E. oscillations are horizontal, rather than vertical, it is probable that some average value of the effective voltage oscillations would more nearly correspond to the usual D.M.E. values. The way the curves are now measured, the minimum value of the effective voltage (at the half-wave potential) is measured, while the change in the effective voltage (for cadmium) at this potential is changing between the half-wave value extremes of 0.572 volts and 0.628 volts. The average of these two values is 0.600 volts, or very close to the accepted half-wave potential for cadmium. This average value for all the above ions is shown in the last column of Table 1.

The next series of aqueous runs made was a concentration study of cadmium in 0.1M KCl, in both high and low-resistance cells. In this case both the half-wave potential and the diffusion current were measured. The results of this study are shown in Table 2.

Table 2.
Influence of Concentration and Resistance on the Half-Wave Potential of Cadmium.

Cadmium Concentration	$E_{1/2}$ (600 ohms)	$E_{1/2}$ (0.34 megohm)	µA/mmole/l (600 ohms)	µA/mmole/l (0.34 megohm)
2.5×10^{-4}	0.627	0.605	8.68	8.76
5.0×10^{-4}	0.600	0.585	8.90	9.42
7.5×10^{-4}	0.623	0.590	8.87	9.79
10.0×10^{-4}	0.597	0.587	8.85	9.65
12.5×10^{-4}	0.607	0.595	9.27	9.66

The results as shown in Table 2 are not in too bad agreement. Actually, as much disagreement has appeared in the literature, even when ordinary polarographic techniques were employed. The agreement is far from perfect; however, the diffusion current measurements appear to be the most out of line. The first four values (in column 4) are very good, and it is felt that the last value probably can be disregarded, since the diffusion current is normally only linear to concentration in very dilute solutions. The values in the last column (for the high-resistance solutions), however, show a much larger deviation from the average. This deviation can probably be explained in the same way that the shift in the half-wave potential is explained. As was shown in the first part of this paper, only the maximum or the average current of the oscillations are expected to be proportional to the concentration. As mentioned before, the oscillations are largely horizontal in high-resistance solutions; consequently, it is not possible to determine what the average current is. Since the more concentrated the solution is, the higher the wave will be and, therefore, the greater this error or deviation from the average current will be.

The next series of runs was made for the purpose of testing a new cell design shown in Figure 11. This cell was designed in an effort to employ the much-used (in routine analysis) principle of the quiet pool mercury anode as the electrolysis reference electrode. With such a cell there would be one less easily-contaminated electrode involved, and in addition it was hoped that solutions of very high resistance could be run without need for excessively high voltages being applied to the bridge. The value of the latter becomes quite apparent when one considers that when cell resistances of 0.5 megohm were encountered, it frequently was necessary to apply 15 to 18 volts in order to top a normal wave. It was hoped also that this cell would be more useful with rotating electrodes, since the mercury pool is contained under a 30M fritted disk and the stirring of oxidation products from the anode into the main solution would thus be minimized. This would be an extremely valuable feature since mercury salts (Hg_2Cl_2) are more soluble in organic solvents than in water and are also readily reducible at the cathode.

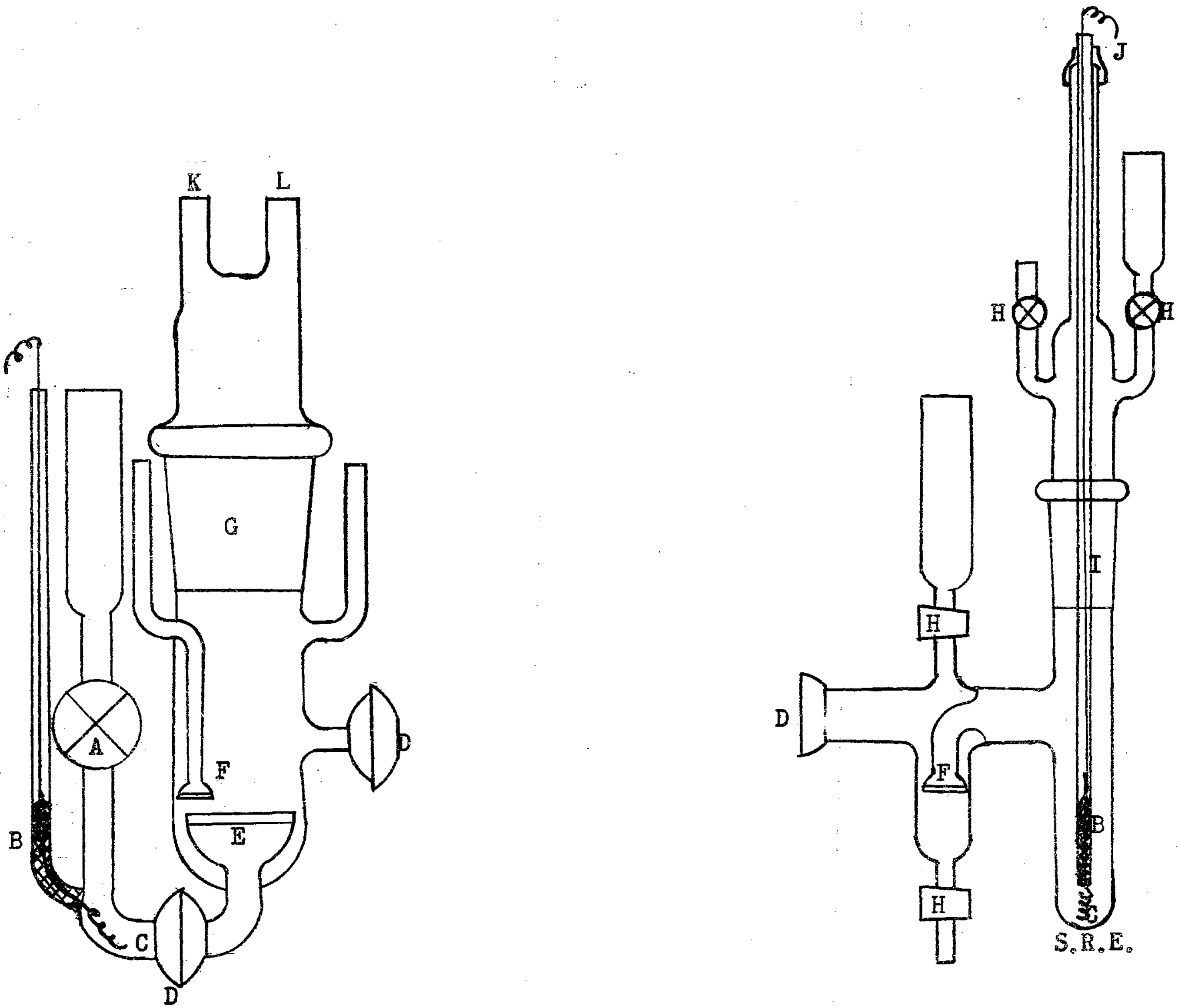


Figure 11.
Quiet Pool-Type Cell.

Legend for Figure 11.

A. Stopcock, straight bore, #2
B. Wood's metal
C. Platinum wire
D. Ball joint, 18/9
E. Immersion tube, 30C, with fritted disc, to contain the mercury pool anode
F. Immersion tube, 10M, with fritted disc
G. Standard taper joint, 45/50
H. Micro-stopcock
I. Standard taper joint, 19/38
J. Rubber seal
K. Tube to admit thermometer
L. Tube to admit D.M.E.

The fritted disk under which the pool is retained is set at a small angle with the horizontal, so that when the cell is used with a D.M.E., the falling droplets will spill off the disk rather than collect upon it. If this were not done, the disk would soon be covered with mercury and this would seal off the solution from the actual anode pool.

To use the new cell, a small pyrex wool plug is placed in the side-arm of the D.M.E.-pool compartment and the S.R.E. is clamped in place. The side-arm of the S.R.E. is filled with the carrier solution, and the cell is filled with the solution to be run. Mercury is placed in the S.R.E. compartment through the stopcock A. An aspirator bulb is then used to draw the mercury back up into the filling tube just far enough to draw a little of the solution in the electrolysis cell back through the fritted disk E. When the meniscus of the mercury just clears the bottom of the frit, stopcock A is closed. This operation is necessary in order to keep the anode reaction from taking place in the pores of the fritted disk. The cap or male part of the standard taper joint G is then put in place. The D.M.E. is placed in the cell, through one of the tubes in the top of the cap, and is lowered until it is exactly even with the bottom of the frit F. This setting of the D.M.E. gives a constant resistance, for a given solution, between the D.M.E. and the E.R.E. A thermometer is then placed in the other tube in the cap and the solution is degassed for the required length of time through the frit F.

A series of runs was made with this cell using water solutions of cadmium at a fixed concentration with the resistance between the D.M.E. and pool kept at either 600 ohms or 100,000 ohms and with the resistance of the other branch at 600 ohms, 0.1 megohm and 0.47 megohm (with the resistance in the S.R.E. branch always equal to or greater than the resistance in the E.R.E. branch). The results of these runs (see Table 3) showed that with the pool-type cell, not only did the half-wave potentials differ from those obtained on these solutions with the double-H cell, but also that two half-wave potentials had to be considered.

Table 3.
Half-Wave Potentials of Cadmium in 0.1M KCl.

ERE	ERE 600 ohms SRE 600 ohms		ERE 600 ohms SRE 100K ohms		ERE 600 ohms SRE 470K ohms		ERE 100K ohms SRE 470K ohms	
Used[a]	Abs.	App.	Abs.	App.	Abs.	App.	Abs.	App.
Pool	0.59	0.69	0.58	0.69	0.52	0.66	0.50 (0.53)[b]	0.68 (0.69)[b]
Calomel	0.60	0.60	0.59	0.59	0.57	0.59	0.58 (0.60)[b]	0.60 (0.62)[b]

a) SRE Calomel in both cases
b) $E_{1/2}$ measured as the average value of the horizontal oscillations at $E_{1/2}$

This table needs some explanation. As was mentioned earlier in the description of the instrument, the absolute zero on the chart is indicated when the input to the cathode follower is shorted, i.e., a zero input to the chart. This point is marked with the D.M.E. circuit open; then the calibration switch is turned to the "run" position and the D.M.E. switch is closed. With the pool electrode, the chart moves to a new position. This position (the actual starting point of the run) is also marked. Since the output of the bridge at the start of the run is not exactly zero, this output is measured by means of a potentiometer and the starting voltage (as indicated on the chart) is corrected by this amount. The difference in half-wave potentials on a given polarogram, therefore, arises from the fact that those in Table 3 designated as "Abs." were measured from the absolute zero, while those indicated as "App." (apparent) were measured from the corrected beginning of the actual run.

A consideration of the differences between the absolute and the apparent half-wave potentials obtained with the cell shown in Figure 11, and the fact that no such difference (or if any, very little difference) was encountered when the double-H cell was used, led to an interesting conclusion. An examination of the circuit shown in Figure 5 shows that when the D.M.E. switch (S_4) is closed at the beginning of a run, the D.M.E. and the electrolysis anode are essentially short-circuited. When the E.R.E. is identical with the S.R.E., the D.M.E. takes on a potential essentially the same as that of the S.R.E., and the potential at the start of the run is zero (i.e., the same as the absolute zero). When a pool is used, however, neither it nor the D.M.E. would have a potential corresponding to that of the calomel electrode being used for the S.R.E.; consequently, the starting point of the run would not be zero and probably would not be very stable.

In Table 3, therefore, the line marked "pool" contains data obtained with the pool cell, while that marked "calomel" lists values obtained with two calomel reference electrodes.

In view of the fact that only a low resistance could be obtained between the D.M.E. and the pool <u>within</u> the cell, the higher-resistance values were obtained by putting carbon resistors in the pool lead circuit--a device which earlier experiments indicated gave results similar to those obtained with high actual cell resistance.

To test the reasoning mentioned earlier--i.e., that the D.M.E. at the beginning of the run assumed a potential essentially the same as that of the E.R.E.--a double-H cell in which the E.R.E.

was a mercury-mercurous sulfate electrode and the S.R.E. was a saturated calomel electrode was constructed. Data obtained with this cell was intended to be included in Table 3. During the writing of this thesis, however, it was discovered that the roles of the sulfate and the calomel electrode unfortunately had been reversed, so that no direct comparison with the other cells could be made. A quick check of the cell, properly used with the calomel electrode as the S.R.E. but with no accurate temperature control, was made, and enough qualitative and semiquantitative data was obtained to add to that of Table 3 and make it possible to draw some conclusions. These conclusions are as follows:

(1) Values for the absolute half-wave potentials at low cell resistances are very close to the values obtained for cadmium with conventional polarographs. In other words, the same values are obtained as would be obtained conventionally if the reference anode of the conventional cell were the same as the S.R.E. On the other hand, the apparent half-wave values are much less dependent upon the cell resistance.

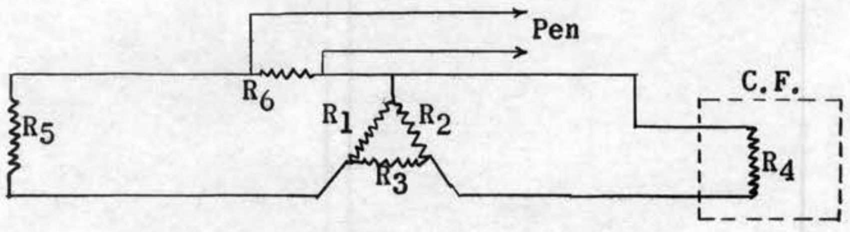
(2) Contrary to our earlier-expressed expectations, the D.M.E. was found not always to assume exactly the same potentials as that of the E.R.E. When the latter (whose potential is +0.40 volts with respect to the saturated calomel electrode) was used for the E.R.E., the potential at the beginning of the run was about 0.16 volts less than had been expected, indicating that the combination of the D.M.E. and mercury-mercurous sulfate electrode was less positive, by this amount, than the latter alone. A polarogram run with this cell showed a strong anodic wave at zero applied potential; consequently, it was obvious that the two

electrodes were forming a voltaic cell within their own branch of the polarographic cell.

(3) It is obvious, from the changes observed in Table 3, that until high-resistance polarography is more thoroughly understood, it would be best to work with a double-H cell in which similar reference electrodes are employed and in which the resistances of the two branches are approximately equal. It also appears at this time that if two calomel-type electrodes are used as the two reference electrodes, it probably will not make much difference what the resistances in the side-arms are.

It seems that there are at least two things that may partially explain the shift in the half-wave potentials with the different ratios of resistances in the two side-arms. The first of these is, as has been mentioned earlier, the method of measuring the half-wave potentials. In Table 3, the values for the average half-wave potential are shown in parentheses after the value measured from the envelope. However, this is listed only for the 0.47-megohm vs 0.10-megohm case since in the other cases, where the resistance of the E.R.E. branch is low (600 ohms), the oscillations are vertical. Even when the resistance in the S.R.E. branch is great, if the E.R.E. branch resistance is low the oscillations are always vertical.

The second explanation may lie in the cell structure itself. In the sketch below, which represents the schematic cell and circuit



arrangement, R_5 and R_6 are the bridge resistance and the current-measuring resistance, respectively, and are small enough to neglect; R_1 is 600 ohms; R_2 is 0.5 megohm; R_3 is 0.5 megohm; and R_4 is 100 megohms. It can be seen from this that although the cathode follower has a high enough impedance to hold any current passing through it to a minimum, it does not block such current entirely. Consequently, a very small IR drop might well be expected, and changes in the resistance of the cell (either one or both branches) might well influence this IR drop markedly.

The final test made in aqueous solutions was to determine if the instrument would also work anodically. As mentioned earlier, many circuits were tested for cathodic and anodic applications before the circuit in Figure 5 was finally adopted. When this final circuit was worked out, tests were made of its suitability for anodic work by applying it to situations already familiar to the investigators. The double-H cell with two saturated calomel elctrodes was employed in these anodic studies, and although no quantitative studies were undertaken, enough runs were made to show that the polarograph is quite suitable for such work.

These runs employed potassium iodide in K_2SO_4, H_2SO_4, and KNO_3, respectively, the D.M.E. being used with the KNO_3 carrier and the rotating platinum electrode with the others. The waves compared well with those obtained in low-resistance cells on the same solutions with the Sargent Model XXI polarograph.

Nonaqueous Studies with Strip-Chart Recording.

After the aqueous studies described in the previous section had been completed, it was decided that enough was now known about the apparatus to make nonaqueous experiments feasible. Consequently, some preliminary runs were made on various solvent-carrier systems to determine which ones might be usable for such purposes. A number of difficulties were immediately encountered and a large amount of time was used before these were finally overcome.

The first of these difficulties was caused by what appeared to be an unusually high solubility of oxygen in the alcohols and ketones tested. The form of the double-H cell first used had no provisions for degassing the solution in the cell itself. Degassing was done in an external container and the solution was then transferred through connecting tubes, and thus, supposedly, out of contact with air, to the cell while the latter was being flushed with nitrogen. Despite all precautions, however, the solution invariably picked up enough oxygen to show its two-stage reduction and give the two waves (at about 0.35 volts and 0.80 volts, respectively) seen in Figure 13. The quiet-pool-type cell (Figure 11), which was equipped for degassing within the cell, was then tried, and gave curves entirely free of oxygen.

Therefore, the method of degassing, in the double-H cell, was changed and the cell was slightly modified to the form shown in Figure 3. In using the cell, the solution was first degassed for fifteen minutes in an external cell and then was run into the electrolysis cell. The D.M.E., with the cup G and the frit D, were placed in the inner jacket of the cell, and the solution in the inner jacket was degassed for an additional fifteen minutes.

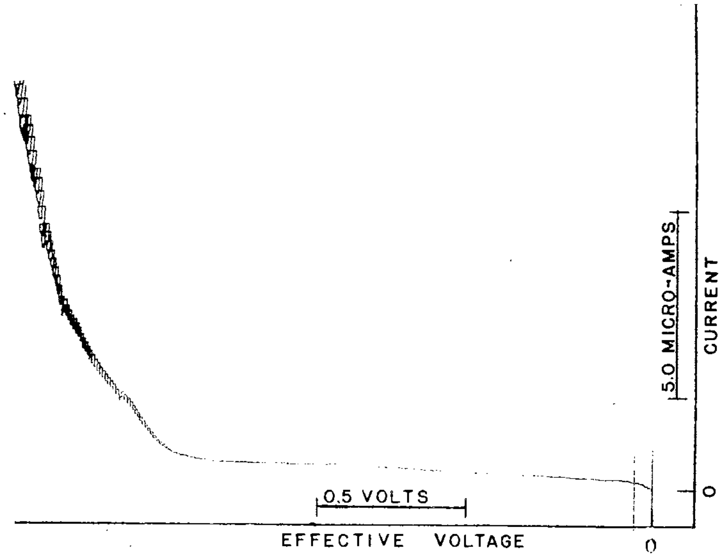


Figure 12. Properly Degassed Carrier Curve.

Carrier		0.1N LiCl in 1-butanol
Reference electrodes,	E.R.E.	A.S.C.E.
	S.R.E.	A.S.C.E.
Cell resistance		75,000 ohms

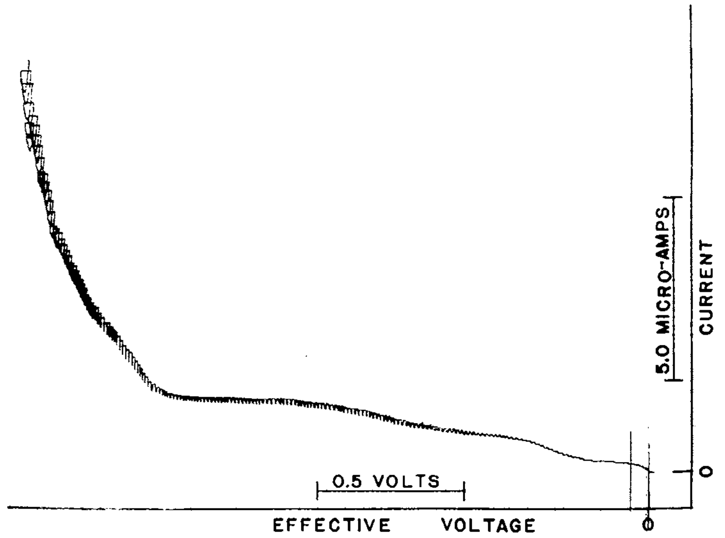


Figure 13. Improperly Degassed Carrier Curve.

Carrier		0.1N LiCl in 1-butanol
Reference electrodes,	E.R.E.	A.S.C.E.
	S.R.E.	A.S.C.E.
Cell resistance		75,000 ohms

During the latter degassing, the cup G was moved up and down several times by means of a small wire (not shown) through the rubber stopper. This was necessary in order to change the solution contained in the cup and to accomplish thorough degassing. With these changes, the carrier curve shown in Figure 12 was obtained with lithium chloride in 1-butanol. Even then, however, it will be noted that there is a small hump or wave at the base of the carrier decomposition wave. Evidence indicates that this wave, which was obtained with all the alcohols tested, is due to the reduction of aldehydes in the alcohol. The alcohol used to record this curve was distilled from potassium carbonate; when the alcohol was distilled from potassium hydroxide, this wave disappears.

The need for protecting organic solvents from oxygen at all times during the degassing and during a run, can not be emphasized enough. During a run, the protective stream of nitrogen over the surface of the solution must be very rapid--much more rapid than in the case of aqueous polarography. It was also found necessary to limit the size of the nitrogen exit opening. In the final modification of the double-H cell, the only exit for the nitrogen is through the same hole as that used for the wire used to manipulate cup G (see Figure 3), the extra side-arm being kept stoppered. In the quiet-pool cell, the only exit is around the D.M.E., the thermometer being sealed in with a piece of rubber tubing. These precautions were found necessary because with a normal flow of nitrogen and the regular-sized exit tube, there was enough back-diffusion of oxygen to give fairly large waves after a very few minutes.

The reaction of the alcohols with oxygen, on storage, was the next thing found to give trouble. All the alcohols tested were found to oxidize to form (presumably) peroxides and aldehydes. These oxidation products were formed only in polarographically-detectable amounts, but this is enough to ruin a solvent for use in polarography. The rate of this decomposition varied with each alcohol and seemed unpredictable even with a given alcohol. One batch of freshly distilled alcohol may keep for a week or two, but the next batch may deteriorate in two or three days. For this reason the alcohols were distilled either the same day or, at the most, the day before they were to be used. When this procedure was followed no further troubles of this type were encountered with the alcohols, and a similar procedure worked equally well with the ketones tried.

After preliminary investigations had been completed and the proper techniques had been developed, it was decided to undertake, first of all, a systematic study of the normal alcohols, starting with methanol and going to as high alcohols as would seem feasible. Experiments indicated that lithium chloride is sufficiently soluble in the normal alcohols up to and including 1-octanol, and that cadmium chloride is likewise sufficiently soluble to be used as polarographically-active substances. Since this would make comparison with aqueous cadmium solutions possible, this combination was selected for the series.

The alcohol carrier solutions were all 0.1M with lithium chloride. In the case of 1-butanol, 1-hexanol, and 1-octanol, the lithium chloride is only slowly soluble and it was necessary to shake them on a mechanical shaker for an hour or two. The cadmium chloride stock solutions were made by saturating small amounts of each of the alcohols with the anhydrous salt. This was done by shaking on a mechanical shaker for at least four hours and allowing the very finely divided salt to settle over night before using the solution.

The results for this series are shown in Table 4.

Table 4.
Half-Wave Potentials for Cadmium in Various Alcohols.

	Double-H Cell			Quiet-Pool Cell			
	ml of Cd*	$E_{1/2}$	Cell Resist.	$E_{1/2}$		Cell Resist.	
				Abs.	App.		
Methanol	0.10	0.538	10.8K ohms	. . .	. . .	. . .	. . .
Ethanol	0.20	0.596	11.2K ohms	. . .	. . .	. . .	. . .
1-Propanol	0.40	0.642	40.1K ohms	0.576	0.646	ERE 4.7K	SRE 28.8K
1-Butanol	1.00	0.768	75.0K ohms	0.631	0.701	ERE 11.4K	SRE 50.9K
1-Hexanol	3.00	. . .	. . .	0.585	0.712	ERE 59.3K	SRE 339.0K
1-Octanol	5.00	. . .	. . .	0.581	0.802	ERE 129K	SRE 1,037K

*Ml of Cd--indicates the number of milliliters of a saturated solution of cadmium chloride, in the corresponding alcohol, that was added to the carrier solution. The amounts shown were added to 55 ml of carrier in the case of the quiet-pool cell and to 75 ml of the carrier in the case of the double-H cell. The concentration of the solutions was not determined, but cadmium was added to give a concentration such that the wave heights were essentially the same in each of the alcohol carrier solutions.

Figure 14 shows the type wave obtained with the double-H cell, acetone saturated calomel electrodes being used for both reference anodes. This particular wave was obtained in a 1-butanol solution; however, the curves for all the lower alcohols had essentially the same form. The chief differences, i.e., the shape of the trace with each falling drop, were due to the different resistances. With methanol and ethanol the oscillations were straight up and down with no noticeable horizontal component. The double-H cell was not used with 1-hexanol or 1-octanol.

Figure 15 shows the type of curve obtained with the quiet-pool cell. The 1-octanol used in this series proved to have a resistance equivalent to the highest one it had been possible to use in aqueous solutions--i.e., about one megohm. It is not felt, however,

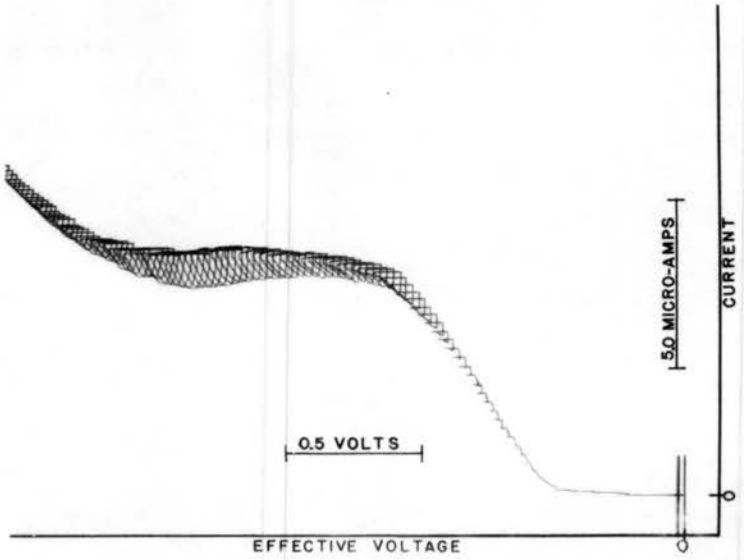


Figure 14. Cadmium in 1-Butanol.

Carrier		0.1N LiCl
Reference electrodes,	E.R.E.	A.S.C.E.
	S.R.E.	A.S.C.E.
Cell resistance		75,000 ohms

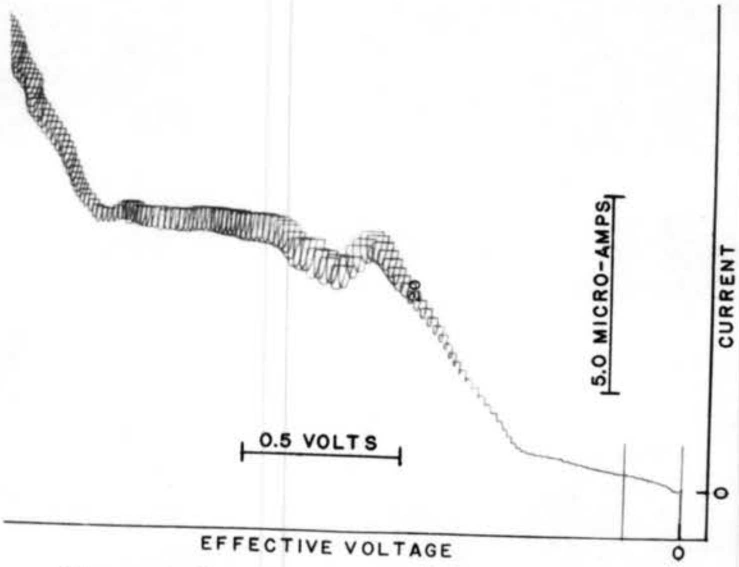


Figure 15. Cadmium in 1-Octanol.

Carrier		0.1N LiCl
Reference electrodes,	E.R.E.	Hg-pool
	S.R.E.	A.S.C.E.
Cell resistance,	E.R.E. branch	1.04 megohm
	S.R.E. branch	0.19 megohm

that this represents the maximum cell resistance that can be used.

An explanation for the minimum (see Figure 15) in the wave is lacking at the present time. This minimum was obtained only with the quiet-pool cell and when 1-butanol, 1-hexanol and 1-octanol were used.

Because the rising part of the wave obviously leaned more for cadmium in the alcohols than for cadmium in water (Figure 14 as compared to Figure 9), a plot of log i/i_d-i vs E was made for Figure 14. From the slope, a value of 0.42 was obtained for the number of electrons involved in the reaction. From this, it can be assumed that the reduction of cadmium in 1-butanol is different than its reduction in water. Whether this difference lies in the electrode reaction rate (a strong probability) or in the irreversibility of the reaction 1-butanol cannot be determined from this data.

It was now felt that enough information was available so that it would be feasible to try organic solutes in organic solvents.

Of several substances tested, the first one found to work well was m-nitroaniline. The waves obtained with this substance in 1-butanol were found to change considerably with concentration, even though the waves themselves were well formed. At a concentration of 1×10^{-4} and 2×10^{-4}M, only one wave can be seen; but at a concentration of 3×10^{-4}M the one wave appears to split into two (Figure 16). The two waves continue as the concentration is increased, with the first wave well defined and the limiting current line of the second gradually taking on a larger and larger slope (Figure 17) until finally this second wave can not be distinguished from the carrier decomposition curve. At very high concentrations,

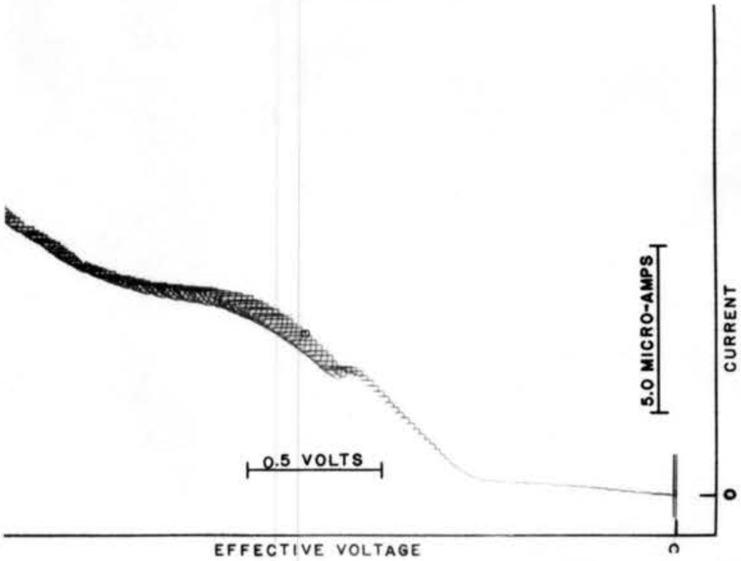


Figure 16. *m*-Nitroaniline in 1-Butanol.

Concentration	4×10^{-4}M
Carrier	0.1N LiCl
Reference electrodes, E.R.E.	A.S.C.E.
S.R.E.	A.S.C.E.
Cell resistance	193,000 ohms

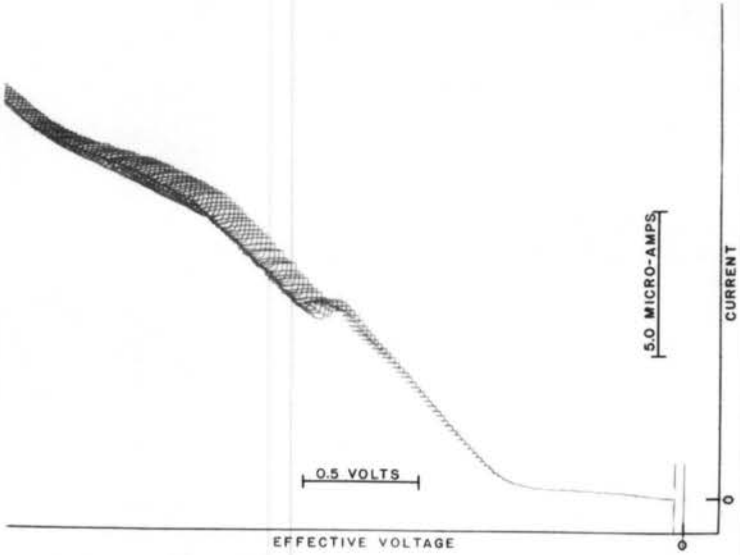


Figure 17. *m*-Nitroaniline in 1-Butanol.

Concentration	8×10^{-4}M
Carrier	0.1N LiCl
Reference electrodes, E.R.E.	A.S.C.E.
S.R.E.	A.S.C.E.
Cell resistance	193,000 ohms

5×10^{-3}M, the first wave also disappears, and the curve obtained looks like a carrier curve with its decomposition potential shifted to a more positive value. The results of a concentration study of m-nitroaniline are shown in Table 5.

Table 5.
m-Nitroaniline in 1-Butanol.
(in the double-H cell)

	I_d in μA/mmole/l			$E_{1/2}$ in Volts	
Concentration	1st Wave	2nd Wave	Total Wave	1st Wave	2nd Wave
1×10^{-4}M	. . .	. . .	15.6	0.936	
2×10^{-4}M	. . .	. . .	13.8	1.04	
3×10^{-4}M	8.33	5.13	13.5	0.930	1.26
4×10^{-4}M	7.92	5.95	13.9	0.988	1.42
5×10^{-4}M	8.42	4.84	13.3	1.01	1.43
6×10^{-4}M	8.35	4.87	13.2	1.08	1.64
7×10^{-4}M	7.48	5.33	12.8	1.04	1.71
8×10^{-4}M	7.40	5.76	13.2	1.11	1.77

From the curve made at a concentration of 8×10^{-4} molar m-nitroaniline, the "n" values were calculated from the plot of log i/i_d-i vs E. For the first wave the number of electrons involved was calculated to be 0.21 and for the second wave 0.29. Again this indicated that the reaction probably either was not reversible or was rate-controlled. It is not normally expected that the reduction of organic compounds will be reversible; consequently, such calculations are not often of too great value.

Another organic molecule which gave excellent results was benzil (dibenzoyl). The results of the studies with this substance in 1-butanol are shown in Table 6.

The results of this study are good. The only large deviation is the much too high value of the diffusion current at a concentration of 5×10^{-4}M. The half-wave potentials increase regularly with increases in concentration as is normally the case with either irreversible or rate-controlled reactions. A plot of log i/i_d-i vs

E for the curve obtained at 5×10^{-4}M concentration gives a value for "n" of 0.27, which confirms the assumption that the reaction is either irreversible or rate-controlled. The type of curve obtained is shown in Figure 18, and as can be seen it is quite normal.

Table 6.
Benzil in 1-Butanol with 0.1M LiCl.

Concentration	I_d in μA/mmole/l	Half-Wave Potentials in Volts
1×10^{-4}M	6.83	0.814
3×10^{-4}M	6.93	0.854
5×10^{-4}M	8.08	0.916
7×10^{-4}M	6.68	0.985
9×10^{-4}M	7.28	1.092
11×10^{-4}M	6.54	1.094

Benzophenone and cinnamic acid also gave fair waves in 1-hexanol, 0.1M with LiCl. Owing to the high resistance encountered, the quiet-pool cell was employed. The waves for these two molecules were too far out and merged with the carrier wave too quickly to be of much practical value. At a concentration of 4×10^{-4}, benzophenone had a half-wave potential of about 1.61 volts, measured from the apparent zero (1.45 volts measured from the absolute zero). At this same concentration, cinnamic acid gave a half-wave potential of 1.39 volts as measured from the apparent zero (1.22 volts as measured from the absolute zero).

In view of its importance to petroleum chemists, one of the most important substances studied in these organic solvents was sulfur. Since sulfur is practically insoluble in the alcohols used but is moderately soluble in benzene, a solution of sulfur in benzene was made with a concentration such that very small amounts (0.1 to 0.5 ml) could be added to the 1-hexanol solution to give the desired concentrations. Seemingly the sulfur, added in this manner, remained in solution. The quiet-pool cell was of necessity employed, and the curve obtained had the peculiar shape shown in Figure 19.

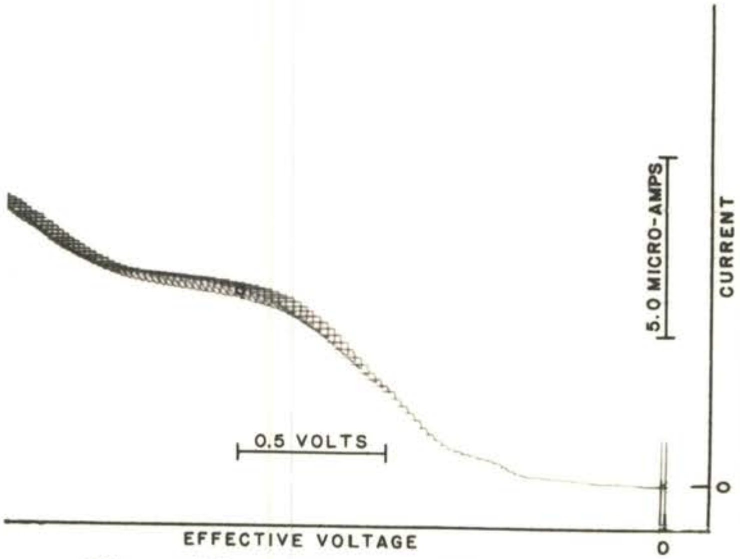


Figure 18. Benzil in 1-Butanol.

Concentration	7×10^{-4}M
Carrier	0.1N LiCl
Reference electrodes, E.R.E.	A.S.C.E.
S.R.E.	A.S.C.E.
Cell resistance	193,000 ohms

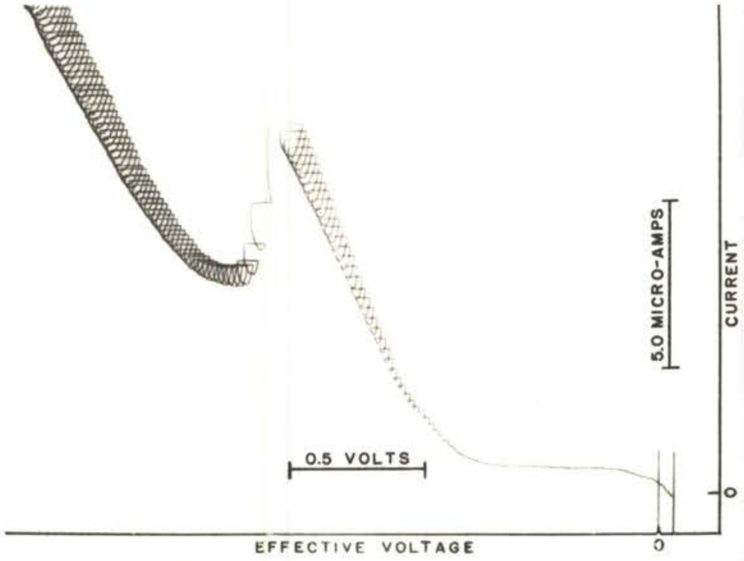


Figure 19. Sulfur in 1-Hexanol.

Concentration	4.5×10^{-3}M
Carrier	0.1N LiCl
Reference electrodes, E.R.E.	Hg-pool
S.R.E.	A.S.C.E.
Cell resistance, E.R.E. branch	59,300 ohms
S.R.E. branch	339,000 ohms

Since no flat plateau appears in these curves, the diffusion currents shown in Table 7 were obtained by measuring to the top of the peak.

Table 7.
Sulfur in 1-Hexanol.

Concentration	I_d in μA/mmole/l	Half-Wave Potentials in Volts	
		Apparent	Absolute
0.75×10^{-3}M	3.73	0.943	0.850
1.49×10^{-3}M	3.53	1.02	0.933
2.24×10^{-3}M	2.94	1.08	0.975
2.99×10^{-3}M	2.30	1.08	0.986
3.74×10^{-3}M	2.27	1.14	1.04
4.48×10^{-3}M	2.24	1.19	1.07

The diffusion current, measured at the maximum, is not too constant; however, when the concentration is plotted against the microamps/mmoles/liter, a smooth curve is obtained, which could be used analytically. The half-wave potentials vary in the same way as they do for all the other compounds tested in organic solvents. The plot of log $i/i_d - i$ vs $\underline{E}$ gave a value of 0.28 for "n"--which again indicates that the reaction is not the simple reversible diffusion-controlled type the polarographer likes to encounter. Despite this and the odd shape of the curve, however, the determination of sulfur by this method should be readily possible, although it would be necessary to carefully control all conditions and to employ a calibration curve of i_d vs the concentration.

The next solvents tried were 2-butanone and 3-pentanone. They were used with several carrier ions, lithium chloride, tetra-n-butylammonium iodide, and cetyldimethylethylammonium bromide. Lithium chloride did not work well with either of the ketones, probably due to its insolubility.

The cetyldimethylethylammonium bromide is also relatively insoluble, but fairly flat carrier curves could be obtained. As the applied voltage increased, however, the drop time became erratic and gradually decreased until the mercury was practically streaming. For this reason, no reducible substances were tested employing this carrier.

Tetra-n-butylammonium iodide in 3-pentanone gave pretty good flat carrier curves when the voltage was preset about 0.4 volts additive (i.e., so that the span runs from -0.4 volts to more negative values) to avoid the anodic wave caused by the reaction of the mercury with the iodide. The biggest difficulty encountered was the complete removal of all of the free iodine in the preparation of the salt. Recrystallization from benzene, which appeared to work well otherwise, did not remove this iodine. The purification was finally accomplished by recrystallizing the salt again from ethyl acetate.

It was found that a longer time of 30 minutes was required to degas 3-pentanone and that all the precautions required with alcohols were also necessary with this solvent.

The 2-butanone did not work well at all with tetra-n-butylammonium iodide. The carrier curves were not flat and the decomposition potential of the carrier came at a much too low voltage.

Since the ketones were investigated only with the thought of seeing if there was any possibility at all of employing them as solvents, no further work was done with them and no reducible substances (other than the free iodine inadvertently tested when it appeared as an impurity in the tetra-n-butylammonium iodide, and the oxygen appearing when solutions were improperly degassed) were tested in them.

DISCUSSION AND CONCLUSIONS

Instrument Design.

As was mentioned in the section describing the scope of this research, the primary objective in mind was the designing of a polarograph suitable for use with nonaqueous solutions of high resistance. This objective was accomplished and in addition a number of interesting facts were brought to light. The more important of these are as follows:

(1) The results of experiments with the many circuits tested in this research shows definitely that the voltage-measuring circuit of any recorder employed must have as high an input impedance as is feasible. It must not only measure the voltage, but must do so without drawing--or even permitting to pass--any appreciable current. There is some inconclusive evidence that even the cathode follower used in this research (Figure 10) does not entirely accomplish this, and that some of the shifts in half-wave potentials with changed cell resistance may be due to this.

(2) Either the strip-chart function plotter or a suitable oscillograph can be employed as the recorder. Although the oscillograph was not used for any quantitative studies in this research, enough evidence was obtained to show that properly stabilized, it should work well. Evidence indicates also that, if a cathode follower is used in the chart circuit, the special X-Y recorder used in this work could have been replaced by a more standard form of this instrument in which the 0.1 megohm impedance requirement is eliminated. This would make the instrument much cheaper and at the same time decrease the time required for delivery.

(3) When a double-H cell with identical calomel-type reference electrodes is used, cell resistances up to 0.1 or 0.2 megohm seem to make little difference in half-wave potentials. Some difference in diffusion currents were noted, but even reasonable care in duplicating conditions should eliminate any difficulty from this.

(4) The double-H cell does not, at present, seem feasible for use with organic solvents if branch resistances of around 0.3 megohm are encountered. This principle was properly tested only on 1-hexanol and 1-octanol, however; consequently, the results are indicative rather than conclusive.

(5) The pool-type cell of Figure 11 apparently is all right for routine work. In addition, through its use it is possible to extend the range of solvents usable to include some whose resistances in the double-H cell are too great to be workable. If half-wave potentials obtained with it are to be reported in the literature, however, all working conditions and all resistances must be carefully noted; otherwise, results obtained by others in the field may show marked disagreement. Adequate and intelligent use of this cell must also depend upon the obtaining of a better understanding of the reasons for the variations mentioned earlier in this thesis.

Influence of Reference Electrodes.

In discussing the results show in Table 3, it was pointed out that the absolute half-wave potential measured in low-resistance cells was the same as that obtained with standard polarographic equipment employing the same solution and with a saturated calomel electrode as the reference electrode. This was also shown to be the case when the E.R.E. was a mercury-mercurous sulfate electrode and the S.R.E. was a saturated calomel electrode. In all these cases, therefore, the E.R.E. differed, but the S.R.E. was always calomel. When a mercury-mercurous sulfate electrode was used as the S.R.E. and calomel for the E.R.E., however, the absolute half-wave potential was 0.40 volts greater. All this taken together, therefore, indicates that the absolute half-wave potential is, for low-resistance cells, independent of the nature of the E.R.E. and dependent only upon the nature of the S.R.E.

On the other hand, the starting point of the curve (and thus the apparent half-wave potential) is dependent upon the polarity and the potential difference between the two reference electrodes. In the case where the mercury-mercurous sulfate electrode was used as the E.R.E. (with the saturated calomel electrode as the S.R.E.) it was shown, by experiment, that the starting point also depended, to a small extent, on the magnitude of the resistance in the bridge and the current-measuring part of the circuit.

If it were not for the fact, therefore, that the absolute potential seems to change more with resistance, it would seem best to assign this the dominant role in polarography. Unfortunately, the apparent half-wave potential seems to be the least influenced by cell resistance changes. It is obvious that, therefore, until better understanding of these phenomena is acquired, both values should be reported.

Applications.

It was pointed out in an earlier discussion that by means of the double-H cell, normal alcohols up to and including 1-butanol can be employed as solvents in polarography, while in the pool-type cell, even 1-hexanol and 1-octanol can be employed. It was also shown that sulfur, metal ions (at least cadmium), and such organic substances as m-nitroaniline and benzil all gave usable waves in at least one representative of this group of solvents.

The curves obtained were definitely not the type to which existing polarographic theory could readily be applied, for one essential requirement is that the electrode reaction involved be both reversible and diffusion-controlled. That these reactions were clearly lacking in either one or both of these requirements was shown by the sprawling nature of the wave and the impossible "n" values calculated. For analytical purposes, however, the curves are usable, and it is possible that later developments will make theoretical applications possible. For the present, however, empirical relationships must serve.

It should also be emphasized that the instrument works as well with low-resistance aqueous polarography as do the conventional polarographs. It can be used in the way described earlier--in which case the usual precautions to make the cell with as low resistance as possible are much less important than is ordinarily the case. On the other hand, if the cell resistance is low enough to make its IR drop insignificant, the S.R.E. and E.R.E. outlets (II and III, Figure 5) can be connected to each other, then to the reference anode of the "H" cell used in conventional polarography, and runs made in this way. In either case, IR drop in the polarograph is eliminated.

In this instrument, therefore, we have a polarograph which can be used at any feasible cell resistance.

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