APPARATUS FOR POLAROGRAPHIC MILLICOULOMETRY IN NONAQUEOUS SOLVENTS

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APPARATUS FOR POLAROGRAPHIC MILLICOULOMETRY IN NONAQUEOUS SOLVENTS

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CHAPTER I

INTRODUCTION

The polarograph is essentially a micro-electrolysis instrument which delivers a potential that is increased by a rotating bridge at a uniform rate of speed and which automatically records a current-voltage curve. The electrolysis takes place between two electrodes, one of which is very small and easily polarized, while the other electrode is of large size and, due to the small currents encountered in polarography, essentially non-polarized. The current resulting from the electrolysis of electro-oxidizable or electro-reducible substances is measured continuously by following the voltage drop across a standard resistor by means of a strip chart recorder which is synchronized with the rotating bridge of the polarograph.

The electrolysis cell contains the reference electrode and the micro-electrode. The most commonly used reference electrode is the saturated calomel electrode. It can be used for both anodic and cathodic polarography and is easy to reserve in working condition. Other non-polarizable reference electrodes likewise can be used.

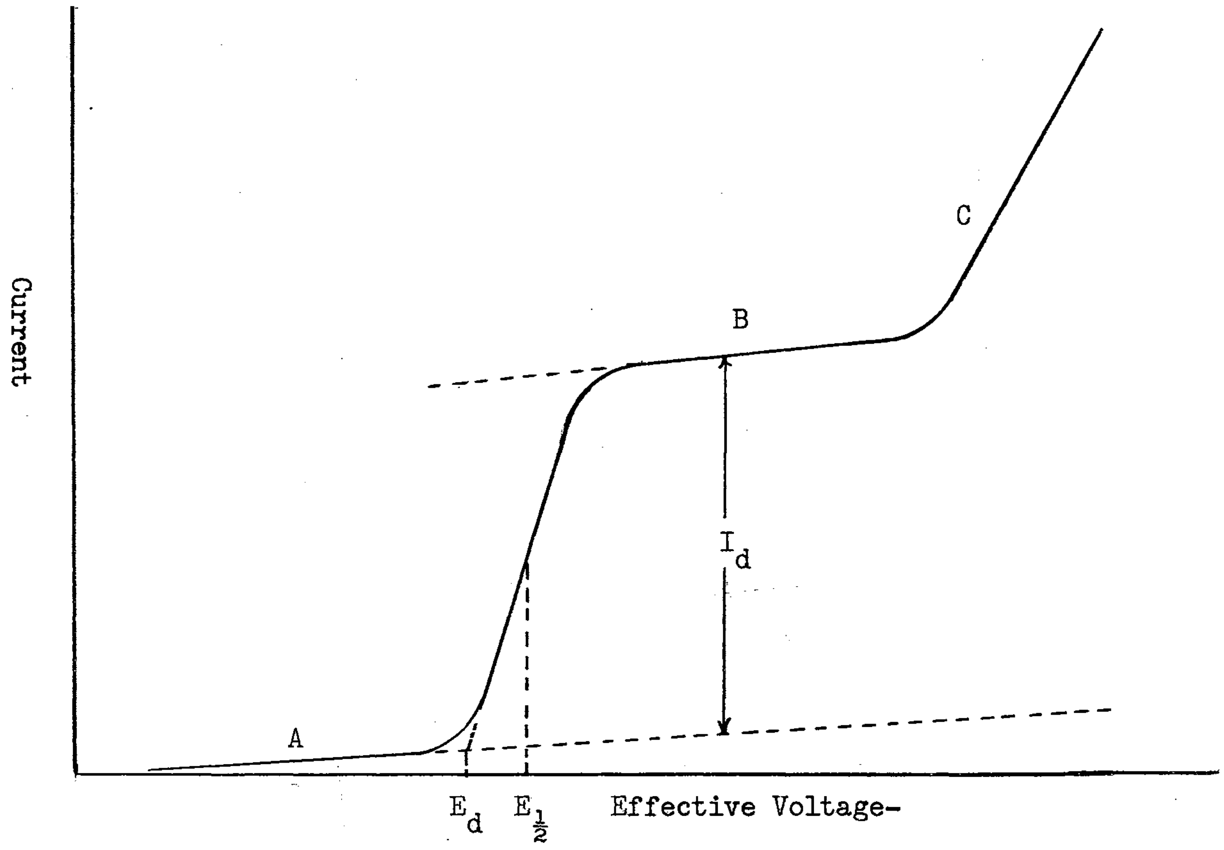
The most commonly used micro-electrode is the dropping mercury electrode (D.M.E.), which consists of a glass capillary tube of about 0.05 mm internal diameter connected to a mercury reservoir. The height of the bulb and the length of the capillary tube are adjusted so that a drop will form every three to six seconds at the lower end of the capillary. A constant pressure or head of mercury must be used in order to maintain a constant rate of flow through the capillary.

The D.M.E. has a number of advantages over other types of micro-electrodes. The surface area is reproducible and can be calculated from the weight of the drop. The surface itself is continuously being renewed by the dropping off of the old drop and the forming of a new drop with a clean surface. This prevents the electrode from becoming contaminated with the electrolysis products.

The current-voltage curves obtained during an electrolysis indicates by the half-wave potential, $E_{\frac{1}{2}}$, the nature of the electrolyzed substance and by the magnitude of the diffusion current the concentration of the substance. A typical polarogram is shown in Figure 1.

The initial current, termed the residual current, is small. In the case of the D.M.E., this current is due in part to a small electro-capillary effect produced by certain ions which lower the interfacial tension between the mercury and the solution, and in part to the flow of a capacitance current which results from the capacitance between the mercury and a double layer which forms at its interface in the solution. Traces of oxygen or residual impurities present even in the purest reagent chemicals also contribute to the height of the residual current.

As the potential applied across the cell increases, only the residual current flows until the decomposition potential (E_d) of an electro-oxidizable or electro-reducible substance is reached. When this decomposition potential is reached, the current rises quite rapidly until the limiting current is attained. The limiting current is the sum of the residual current and the so called "diffusion" current. The limiting current obtained with the micro-electrode represents a state of concen-



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

I_d = Diffusion current.
E_d = Decomposition potential.
$E_{\frac{1}{2}}$ = Half-wave potential.

Fig. 1. A Typical Polarogram

tration polarization, due to the depletion of ions (or molecules) at the electrode surface by the electrode reaction. When the current is at this limiting value, the reducible or oxidizable substance is reacting as rapidly as it reaches the electrode surface and the substance at the electrode surface is kept at essentially zero concentration compared to the bulk of the solution.

The rate at which electro oxidizable or electro-reducible ions reach the electrode surface is governed not only by diffusion but also by migration. In order to "blanket" the electrode and effectively reduce the migration forces, a supporting salt is added in a concentration 50 to 100 times that of the reacting substance. This supporting salt serves as a source of ions which can be attracted to the surface of the electrode but which are not discharged at voltages to be used for the main electrolysis. These ions form a cloud of ions around the electrode and serve to neutralize it in such a way as to minimize both the attraction and the repulsion of any ions under analysis. Since the migration effect thus is greatly reduced, the ions must reach the electrode almost entirely by diffusion. The rate of diffusion is dependent upon the concentration in the body of the solution; consequently the diffusion current is proportional to the concentration of the oxidizable or reducible substance. The supporting electrolyte also carries the current through the body of the solution and reduces the iR-drop in the cell.

In the case of electro-oxidizable or electro-reducible molecules, the migration forces are essentially non-existent. With molecules, therefore, the supporting salt's main function is as a carrier for the current.

As the potential across the cell is increased, the current changes very slowly after the limiting current is reached until the potential is high enough to discharge the carrier electrolyte ions or decompose the solvent. When this point is reached, the increase in current is quite rapid.

The half-wave potential, $E_{\frac{1}{2}}$, is the potential at the point on the current-voltage which is midway between the projections of the residual current and the limiting current. The half-wave potential is characteristic of the substance being reduced and is used for qualitative analysis. The half-wave potential is dependent on the solvent, on the nature and concentration of the supporting electrolyte, on the reference electrode used, and to a small extent upon the temperature. In certain cases it also is dependent upon the concentration of the ion being determined. Consequently, if the half-wave potentials are to be significant to others, all of these conditions must be reported.

The decomposition potential is located by the intersection of the extrapolated residual current line and the extrapolated wave front line.

Polarographic Millicoulometry

One of the chief applications of diffusion coefficient data in polarographic work is for the evaluation of the number of electrons ($\underline{n}$-value) involved per ion or molecule reacting at an electrode. For this purpose highly exact values of diffusion coefficients, $\underline{D}$, are not usually required because it is necessary only to differentiate between small integral values of $\underline{n}$. It is a fortunate circumstance in this connection that the diffusion current is proportional to the square root of $\underline{D}$, so that a given error in $\underline{D}$ itself is greatly minimized when it is applied in equations such as the Ilkovic equation. The determination of n is of particular importance in the study of reactions involving organic compounds where its value is often not obvious and where the n-value is needed to explain the electrode reaction taking place.

The n-values acquired directly from polarographic waves are frequently misleading. The shape of the polarographic wave is dependent upon several factors which are requirements that must be met for direct interpretation of the waves. Two of these requirements which most frequently are not met by organic compounds are (1) that the electrode reaction be reversible, and (2) that the wave be diffusion controlled. Failure of the reaction to meet these requirements leads to fractional n-values being calculated, although actually fractional values are impossible.

The principles of polarography can be utilized as a basis for a more direct method of determining n-values. In this method the voltage impressed across the two electrodes is held constant and the changes in current due to changes in concentration brought about by a lengthy electrolysis is recorded as a current-time curve by the recorder of the polarograph. By integration of the area under the current-time curve, the total quantity of electricity passed can be determined; then by using the percentage decrease in concentration of the substance reduced (by determining the drop in the diffusion current height) the n-value can be determined.

The total quantity of electricity can also be measured by means of a coulometer connected in series with the electrolysis cell whence all that is necessary to determine n-values is to determine the concentration changes of the substance studied by means of the decrease in its diffusion current.

To shorten the length of time required to electrolyze a measurable fraction of substance, the electrolysis can be done on small volumes, these volumes being as small as 0.1 milliliter. The technique of using small volumes and reducing them polarographically using the regular dropping mercury electrode has been termed <u>millicoulometry</u>.

In practice, the voltage is chosen so the current will correspond to the limiting current plateau of the substance to be studied[d]. If two substances are to be reduced simultaneously, the voltage is fixed on top of the last wave. The procedure is based on the same technique as those employed in amperometric titrations except that the titrations in millicoulometry are done completely by electrolysis and only a fraction of the sample need be reduced to get satisfactory results.

These ideas have been used quite frequently on large volumes with larger area electrodes. The drawback to using larger area electrodes, however, lies in the fact that the electrode processes are not always the same as with the regular dropping mercury electrode and frequently are poorly defined. Where they can be used, though, larger area electrodes have several advantages over the D.M.E. One advantage is that in the larger volumes employed, the anode may be more readily separated from the cathode by a fair distance. This is especially useful when mercury pool anodes are used. Another advantage has been the availability of several good macro-coulometers with which to measure the total quantity of electricity passed during the electrolysis. In millicoulometry, about the same percentage of the compound studied can be reduced in a given time and reduction is under the same conditions as those under which the actual polarograms are run. The total number of moles reduced, however, are of such extremely small magnitude that a small error in measuring the total quantity of electricity could mean a large error in determining the <u>n</u>-value. In addition, very little product for analysis is obtained.

CHAPTER II

HISTORICAL

Theoretical Developments and Coulometric Applications

In 1925 Heyrovsky and Shidata constructed an automatic instrument for recording voltametry curves (17), these current-voltage curves having previously been hand plotted. They called their instrument the *polarograph* and the photographically-recorded current-voltage curves they obtained were named *polarograms*. This instrument was developed to aid them in studying the phenomena encountered when reducible substances were present in solutions which were being electrolyzed by an electrocapillary electrode composed of mercury.

Theoretical significance was given to polarography when Ilkovic, in 1934, presented his original derivation of the famous Ilkovic equation (19) (20). From the diffusion current theory and on a purely theoretical basis, Ilkovic derived this equation and showed by this means the dependence of the diffusion current on several different quantities. The original Ilkovic equation is

$$i_d = 607\ n\ D^{\frac{1}{2}} C\ m^{2/3}\ t^{1/6}$$

where i_d is the average diffusion current in microamperes encountered during the life of the mercury drop, n is the number of faradays of electricity required for the reaction of one mole of the oxidizable or reducible species, D is the diffusion coefficient of the reducible or oxidizable ion or molecule in cm.^{2} sec.$^{-1}$, C is the concentration of the species in millimoles per liter, m is the mass of mercury that flows from the D.M.E., expressed in mg. sec.$^{-1}$, and t is the drop-time in seconds. It was shown that experimental results were essentially in agreement with the derived equation (27) (34).

It was recognized, however, that the Ilkovic equation was not wholly adequate in explaining the waves encountered with the D.M.E. In 1950 Strehlow and von Stackelbert (47) and Lingane and Loveridge (29), simultaneously and independently, arrived at the same conclusion and demonstrated that the fault of the Ilkovic equation was due to the neglect of the curvature of the electrode surface. A new equation derived by these investigators for solutions at 25°C. was

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

where A was evaluated as 17 by Strehlow and von Stackelbert and as 39 by Lingane and Loveridge. More recently, Macero and Rulfs (35), obtained results with six different ions that indicate the correct value for A should be 31.3 ± 1.6.

Heyrovsky and Ilkovic (16) showed that the potential at any point on the rising portion of a polarographic wave is given, for many substances, by the equation

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

where E_{de} is the potential at any point on the wave, $E_{\frac{1}{2}}$ 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}, and i_d is the diffusion current.

From the above equation it is apparent that a graph of E_{de} against $\log \frac{i}{i_d - 1}$ should give a straight line whose slope is a function of n; i.e.,

$$\text{Slope} = \frac{0.0591}{n}$$

The equation holds, however, only if the electrode reaction meets the following requirements: (a) the electrode reaction must be thermodynamically reversible, (b) the products of the electrode reaction must be soluble in the mercury of the electrode or in the solution, and (c) the electrode reaction must be diffusion controlled.

Lingane and Kolthoff (22, 27, 29) undertook what were possibly the first exhaustive studies of the principles and theories underlying polarography. They extensively tested the Ilkovic equation and reported that the postulates on which it was based and the equation itself were essentially correct. Other studies were devoted to the characteristics of the limiting current. They also were among the first to prepare a comprehensive review of studies at the dropping mercury electrode.

In 1945 Lingane (26) started the first coulometric work with the polarograph, this work being associated with his testing of the diffusion currents. Lingane used periodic measurements of the diffusion current of a substance in question during a prolonged electrolysis. His cathode was a stirred mercury pool which served as an electrode of very large area. The total quantity of electricity was measured by a hydrogen-oxygen coulometer in series with the polarographic cell, this technique allowing him to determine the number of electrons (n-value) without using the Ilkovic equation.

In this work, Lingane found that the coulometric method could be applied advantageously to the determination of the reduction states that correspond to polarographic waves observed in certain complicated cases where the Ilkovic equation was inadequate. His technique was improved by

Markacheva and Stromberg (38) through the control of several factors whose effects they had noticed.

Hume and Peattie (18) continued along the same line but changed to an iodine coulometer and measured the liberated iodine spectrophotometrically. Their work, as Lingane's, was done with a large area mercury pool as cathode. Although the employment of a large electrode gives large currents and shortens the time of electrolysis required to give an appreciable wave height difference, one cannot be certain that the electrode processes are the same as at the D.M.E. In some cases, they are known to be different, especially when solid electrodes are used.

Many methods have been tried in efforts to determine *n*-values of substances for which the Ilkovic equation was inadequate or for which knowledge of diffusion constants was too limited. A method was needed which could employ the D.M.E. so that the electrode reaction would be as clean-cut as in a regular polarographic electrolysis. Some success was obtained by using micro cells which employ very small volumes; but the chief difficulty was the development of a simple micro-coulometer that could be used with small quantities of electricity.

Bogan, Meites, Peters and Sturtevant (8) designed their own circuit to accomplish millicoulometry on a polarographic scale. Their calculations were based on the following integrating equation developed from Faraday's Law and the Ilkovic equation:

$$\log i_d = \log i_d^{\circ} - \frac{4.403\text{x}10^{-4}\ I\ m^{2/3}\ t^{1/6}}{nV}\ T$$

where i_d is the diffusion current after electrolysis for a length of time, T, i_d° is the original diffusion current, m is the mass of a mercury drop in mg. sec.$^{-1}$, t is the drop time in seconds for the electrode, I

is the average current passed during the electrolysis, V is the volume of sample used and n has its usual meaning.

Another type of current integrator, mentioned by Meites (41), is an Analytical Instruments, Inc., Integrator, with a 10,000 ohm input resistor. This instrument is driven at full speed by a current of 100 microamperes and was reported to give results which are in error by less than ± 0.1% with currents as small as 5 microamperes. Masaichiro, Masui and Sayo (40) also approached the problem electrically by employing a blocking oscillator attached to the polarograph. The oscillating frequency of this oscillator was proportional to the current and this reportedly allowed the total quantity of electricity passed during electrolysis to be measured more easily.

Gilbert and Rideal (13) worked with dyes in efforts to determine the products of reduction. They based their calculations on the dependance of the wave height on time of electrolysis, measuring the diffusion current before and after a timed electrolysis and using the average current multiplied by the time of electrolysis to determine the total quantity of electricity passed through the cell. However, as was pointed out by Meites (41) and observed by Bogan and coworkers (8), this method introduces error owing to the fact that the assumption that the current is an average of the initial and final diffusion currents can be far from true.

DeVries and Kroon (11) utilized two polarographic cells in series, and due to the larger volumes they employed, extended the length of the time of electrolysis. They determined the value of n from the ratio of changes in concentration of two different reducible substances, the two being in the separate cells and one serving as a standard. Kroon later designed a millicoulometer for better study of organic compounds (24).

Another problem encountered in the usual millicoulometric approach is that because in the forms usually employed, the sample sizes are as low as 0.1 milliliters. This means that the closeness of the polarizable and the non-polarizable electrode in the main electrolysis cell allows the reduced substances to be reoxidized at the anode. Most of the workers seem to have used the mercury pool anode--which increases this possibility. Recognizing this, Meites and Meites (42) developed a divided micro-cell with a saturated calomel reference electrode separated from the electrolysis compartment by an agar plug. Their cell could utilize either the S.C.E. or the mercury pool as the anode. The same type of divided micro-cell was used by Weaver and Whitnack (49). They integrated the area under recorded current-time curves to determine the number of coulombs passed during electrolysis. Then by applying Faraday's Law they calculated n by using the equations

$$n = \frac{c}{mF} \qquad \text{where } m = \left(1 - \frac{h_1}{h_2}\right) VC$$

where h_1 and h_2 are the heights of the polarographic waves which correspond to the initial and final concentrations, V is the volume of sample used, C is the original concentration in moles per liter, F is Faraday's constant and c is the total coulombs passed during electrolysis.

Cover and Meites (9) recently reported using a pilot ion method to determine n-values by millicoulometry. The pilot ion method requires the addition of an ion for which the n-value is known, then reduction of both substances at the same time and in the same cell. This requires a proper voltage setting as well as a very carefully selected pilot ion which will not react with, or interfere in any way with the substance to be analyzed. Their method has many advantages over other determinations of this type because the proportionality constant for the diffusion current to concentration relationship has a reasonable stability over small changes in temperature, in the height of the mercury head, in drop time, and in concentration. Another advantage is that the pilot ion works as the micro-coulometer and makes an external coulometer unnecessary.

Mark, Smith and Reilley (39) worked out a method of using the dropping mercury electrode in a constant current microcoulometric method employing a large (above 20 microfarads) capacitor connected in parallel with the micro-cell. The determination of the polarographic n-values was simpler than with the usual constant potential methods and the results obtained were comparable.

Nonaqueous Polarography

Glacial acetic acid was among the first anhydrous solvents used as a polarographic solvent. MacGillavery reported its use as early as 1936 (36), although his results were not completely satisfactory. Anhydrous acetic acid was used later by Bachman and Astle (6) who obtained very good polarographic waves for several inorganic metal ions in this solvent. Degassing of the solutions was reported a critical step in using this solvent due to the enhanced interference by dissolved oxygen.

Arthur and Lyons used anhydrous acetic acid for the determinations of lead and cadmium (4), while Bergman and James (7) studied nitro compounds in this solvent.

Low molecular alcohols have been used as solvents in a number of polarographic determinations. Ethanol was used by Vleck (48) to make determinations of several strong acids. Ethanol was also used by Zuman, Zumanova and Soucek (50) as a solvent for studying CS_2. Methanol was used by Allison to obtain lead waves (1). He found it necessary to degas with nitrogen which had been purified by bubbling through one or more wash bottles filled with an alkaline solution of pyrogallic acid to remove any oxygen present in the tank nitrogen. Hans and Von Strum (14) (15) obtained polarographic waves for copper in methanol, ethanol, 1-butanol and 1-pentanol, although they found it necessary to plot the curves manually to correct for the iR-drop in the cell.

There has apparently been no work in millicoulometry at the D.M.E. done in nonaqueous solvents. It is apparent, however, that other phases of polarography have been studied extensively in mixtures of nonaqueous and aqueous solvents in which there are low internal resistances. A smaller portion of the work has been done in anhydrous solvents. A number of workers have determined n-values using the Ilkovic equation in various forms and other theoretical methods which are based on the dependence of properties of polarographic waves on the number of electrons (4) (23) 46). The most common method which has been employed is to determine n-values from plots of E vs. log i/i_d-1. Manning, Ball and Menis (37) used a controlled-potential coulometric reduction on the four different waves they obtained with molybdenum salts in nitrilotriacetic acid.

Other solvents which have been used in polarographic work are cellosolve, pyridine, liquid ammonia, and sulfuric acid. The choice of solvents in earlier polarographic work was limited due to the high resistance of their solutions. On a convential polarograph the permissable resistance is limited, since good waves can not be obtained with resistances above certain limiting values. Thus Lewis, Quakenbush and De Vries (25) could not obtain good results if their cell resistance exceeded 4,000 ohms, while Arthur and Lyons (4) were unable to obtain good results if the cell resistance exceeded 8,000 ohms. In some cases the iR-drop of the cell could be calculated and graphs manually plotted to correct for the iR-drop. In other cases the waves were almost or wholly obliterated.

High Resistance Polarography

The problems encountered with solutions of high resistance have been approached in several ways, the main problem encountered being that, due to the high resistance, a larger potential must be applied to get the same effective voltage as in low resistance solvents. This causes the regular current-voltage curve obtained on a conventional polarograph to be distorted. The equation for correcting for the iR-drop and obtaining the effective voltage is

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

where *i* is the current at the applied voltage, *R* is the resistance of the cell and circuit, and E_{eff} and E_{app} are the effective and applied voltages respectively. The conventional polarograph plots current against E_{app}; consequently at high resistances, the wave may be completely unrecognizable and there is no way to calculate the effective voltage with satisfactory results. In aqueous solutions the iR term can be made very small and for most purposes may then be neglected.

Nicholson (43) modified a conventional polarograph so that the recorder pen drove an auxiliary bridge. The output of the auxiliary bridge applied to the cell a corrective voltage which was intended to be equal and opposite to the iR-drop. A similar corrective approach was reported by Jackson and Elving (21), who placed a standard resistor in series with the polarographic cell, amplifying the iR-drop across the resistor to make it equal to the iR-drop across the cell and feeding this correction into the circuit.

Arthur, Lewis and Lloyd devised a polarograph which plotted current against the actual effective voltage (3) (31). This method employed use of a stable third electrode which was connected to the D.M.E. by a high input impedance cathode follower. The current flow in this part of the circuit was negligibly low; therefore, when the output was connected to the chart circuit of a strip chart function plotter (X-Y recorder) the chart moved as a function of the effective voltage, while the current was recorded by the pen movement across the chart.

Utilizing the fact that the potential difference between the electrolysis reference electrode, E.R.E., and an identical stable reference electrode, S.R.E., should be equal to the iR-drop within the electrolysis cell, Arthur (5) recently designed an improved type of iR-compensator. This compensator can be used with almost any conventional polarograph and is the basis for the Model A IR-Compensator commercially produced by E. H. Sargent and Co. In this apparatus, the two reference electrodes are connected to a 1:1 amplifier of very high input impedance. Since the potential between the two reference electrodes is equal to the iR-drop, the output of the amplifier (compensator) also equals the iR-drop. The output side of the amplifier being of low impedance, when this output is connected in series with the polarograph, the latter provides (and plots) E_{eff} only, and compensation is achieved.

A similar approach was employed by Oka (44) who used an amplifier to drive a motorized bridge and by Kelley, et al, (32) (33) who used a much more complicated electronic circuit which was constructed as a complete polarograph. Both schools achieved compensation for the whole polarographic circuit, however, while Arthur, et al, compensated only for iR-drop in the polarographic cell.

CHAPTER III

SCOPE OF INVESTIGATION

The main objective of this research was to construct a cell suitable for nonaqueous polarography to achieve quantitative reductions at a dropping mercury electrode. What was desired was a cell that could be used with any conventional polarograph and which could employ both aqueous and nonaqueous solvents.

The cell needed to be constructed so as to allow very small samples to be reduced quantitatively over long periods of time. This was necessary to obtain another objective of the research, which was to determine whether the end products would be of sufficient quantity so as to allow possible identification by gas liquid-partition chromatography. The cell needed to employ a D.M.E. as the only reducing electrode so as to make certain the products (or any secondary products) would be the same as in a normal polarographic determination.

The cell was to be tested in aqueous and nonaqueous solutions employing commonly used ions such as Cd^{++}, then finally to experiment with organic compounds, of which the diketones, benzil and diacetyl, were chosen.

Another objective was to design a suitable millicoulometer which could be used in series with the polarographic cell and used for determinations of n-values for the electrode reaction in the cell.

CHAPTER IV

APPARATUS

The Sargent Model XXI polarograph was used in this investigation. All high resistance measurements were performed using the Model A IR-Compensator manufactured by E. H. Sargent and Company.

The polarographic cell, degassing cell, and coulometer used in this work was designed by Doctor Paul Arthur and will be described later since the main problem of research was in perfecting these items.

The cathode used in the polarographic cell was a dropping mercury electrode of the type described by Lloyd (31).

The nitrogen purifying apparatus consists of two chromous-chromic sulfate scrubbers as described by Arthur (2) followed by solvent-filled presaturators.

The mercury purifying apparatus consisted of a type G mercury oxifier and gold filter from Bethlehem Apparatus Company and a vacuum-still from Gaertner Scientific Company.

All experimental measurements utilizing the electrolysis cell were made in a mineral oil, constant temperature bath controlled to a temperature of plus or minus 0.1° Centigrade.

The gas chromatograph used was an Aerograph instrument equipped with a Model 500 electrometer, a Model 550 "Hy-Fi" oven, and a hydrogen flame ionization detector. The columns tested were 10% silicone rubber on 10/100 Chromosorb W, a 10% silicone gum, SE-30, on 80/100 acid-washed Chromosorb W, and a 5% Ucon-Polar on firebrick, in quarter-inch tubing, each six feet long.

CHAPTER V

REAGENTS

Ammonia. Anhydrous Matheson reagent grade was used without further purification.

Benzil. Matheson, Coleman and Bell white label grade was used without further purification.

Cadmium Chloride. Baker and Adamson Reagent grade was used without further purification.

Diacetyl. Matheson, Coleman and Bell white label grade was used without further purification.

Chromic Sulfate. Mallinckrodt analytical reagent grade was used without further purification.

Isooctane. Matheson, Coleman and Bell white label grade was used without further purification.

Lithium Chloride. Mallinckrodt analytical reagent grade was used after drying several days in an oven at 110-115° C.

Nitric Acid. Baker analytical reagent grade was used without further purification.

Nitrogen. Linde Laboratory Grade was used after being passed through two towers of chromous-chromic sulfate-amalgamated zinc scrubbers, a column of glass wool, a column of calcium sulfate drying agent, and a presaturator tower filled with the solvent system.

Potassium Carbonate. Fisher scientific reagent grade was used without further purification.

Potassium Hydroxide. Fisher scientific reagent grade was used without further purification.

2-Propanol. U. S. Industrial Chemicals Company reagent grade was used after being twice redistilled to remove impurities and the last traces of water. The first distillation was done after the alcohol, containing 5 grams of KOH per liter, had stood for twenty-four hours. The second distillation was done after the distillate from the above had been treated with K_2CO_3 for twenty-four hours in the ratio of 50 grams K_2CO_3 per liter of distillate. Both distillations were accomplished in a nitrogen atmosphere, the last 75 milliliters of each liter being discarded.

Silver Nitrate. Mallinckrodt analytical reagent grade was used without further purification.

Sodium Bisulfite. Baker reagent grade was used without further purification.

Sulfuric Acid. Fisher Scientific reagent grade was used without further purification.

Zinc Metal. Fisher Scientific reagent grade (in bars) was used without further purification.

CHAPTER VI

EXPERIMENTATION AND DISCUSSION

Polarographic Cell and Procedure. The polarographic cell used in this experiment was originally designed by Dr. Arthur, minor changes being made as it became obvious that they were necessary. Figure 2 shows the modified cell.

The main cell consists of a two-reference-electrode system for use with the Model A IR-Compensator. The reference electrodes are separated from the main electrolysis compartment by connecting sidearm tubes. The salt bridges connecting all compartments are asbestos fiber bridges.

The reference electrodes used were 0.1 N LiCl-calomel electrodes. The more commonly used saturated KCl-calomel electrode was tested as was also a saturated LiCl-calomel electrode, but due to the length of electrolysis and the limited solubility of the two salts in the 2-propanol used, precipitation occurred in the asbestos fibers at the liquid junction. This precipitation tended to increase the resistance in the asbestos fibers and the resulting increase in the iR-drop frequently exceeded the limits of the IR-Compensator. The 0.1 N LiCl-calomel electrodes were finally chosen, because this was the concentration of the LiCl used as carrier in the solvent. Other reference electrodes could probably have been used as long as the limits of solubility were not exceeded.

The 0.1 N LiCl-calomel electrodes, for convenience, were constructed

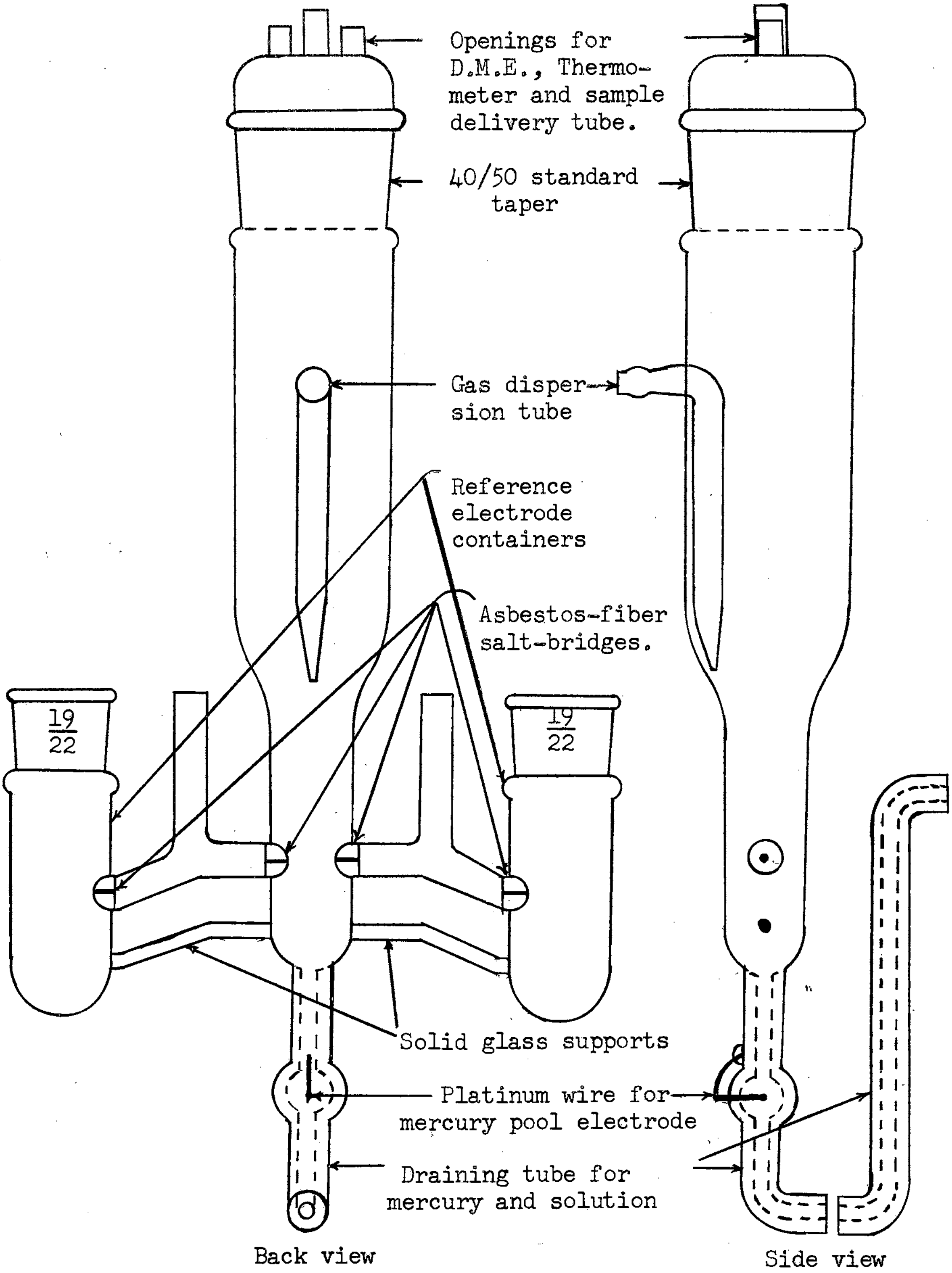


Figure 2. Polarographic Cell for Millicoulometric Work

as separate units from the main cell (see Figures 2 and 3). They could then be removed during cleaning of the cell and stored in the separate containers of Figure 3. In this way they could be left out of the polarographic cell until the degassing was accomplished.

The connecting side tubes separating the reference electrode compartments from the electrolysis compartment were filled with the solvent containing only carrier electrolyte. These compartments served to minimize the diffusion of water or acetone from the reference electrodes into the electrolysis compartment.

The asbestos fibers used were of a size to give with aqueous 0.1NKCl solution, approximately 30,000 ohms resistance for those separating the connecting tubes from the reference electrodes and approximately 70,000 ohms resistance for those fibers used to separate the connecting tubes from the electrolysis compartment. Smaller diameter fibers were tried in order to further minimize diffusion, but at the resulting higher resistances the iR-drop across the cell, when the limiting current was at a height corresponding to a cadmium concentration of 10^{-3}M, exceeded the limits of the IR-Compensator, and required the addition of voltage, in the form of batteries, to be added to the output of the Compensator.

The bottom of the cell with its sidearm attachment was designed mainly for excess mercury to drain out of the cell during the required long periods of electrolysis. The connection of the sidearm attachment to the cell was accomplished with rubber tubing. In this way the mercury height in the cell could be adjusted and kept at a constant level. In practice, when the 0.1 N LiCl-calomel reference electrodes were used, the mercury level was kept so that about three-fourths or less of the capillary tube was filled with mercury. The bulb enlargement of the

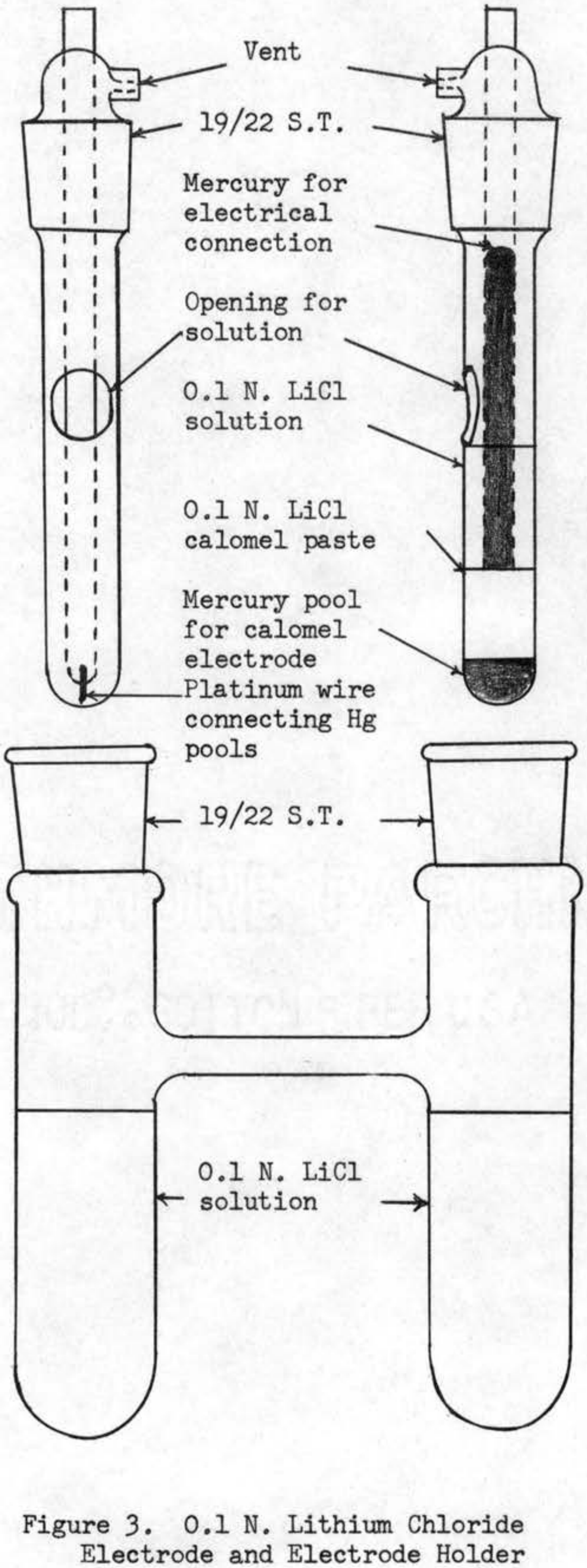


Figure 3. 0.1 N. Lithium Chloride Electrode and Electrode Holder

capillary with the platinum wire sealed into it enables the mercury pool to be used as the anode if desired. The size of the mercury pool can be controlled by raising or lowering the sidearm attachment. In this way, the mercury pool could also be used as a large area cathode for coulometric work by the method originally used by Lingane (26). The sidearm attachment can also be used to drain the electrolysis compartment by lowering it enough to allow the used sample to drain out. In this way a new sample could be introduced without disassembling the cell.

The degassing tube connected into the back of the cell was added to insure that the bottom of the electrolysis compartment and the capillary opening at the bottom would be swept clear of air.

The top closure of the cell consisted of a ground glass stopper with three openings. The middle opening was used for introduction of the D.M.E., while one of the remaining openings was used for introduction of the degassed sample via the delivery tube of the degassing cell and the third opening was used for insertion of a thermometer for direct measurements of the sample temperature.

The degassing and sampling cell, Figure 4, consisted of a large central compartment of approximately 30 milliliter volume where actual degassing of oxygen from the sample was accomplished. The nitrogen for degassing was dispersed into the solution by the use of a sintered glass end on the nitrogen introduction tube. The degassing cell and electrolysis cell were connected together during degassing so the nitrogen would flush the entire apparatus (including the cell) after passing through the solution.

The sample was not introduced into the main cell until degassing was complete—a process which usually required about 45 minutes. The

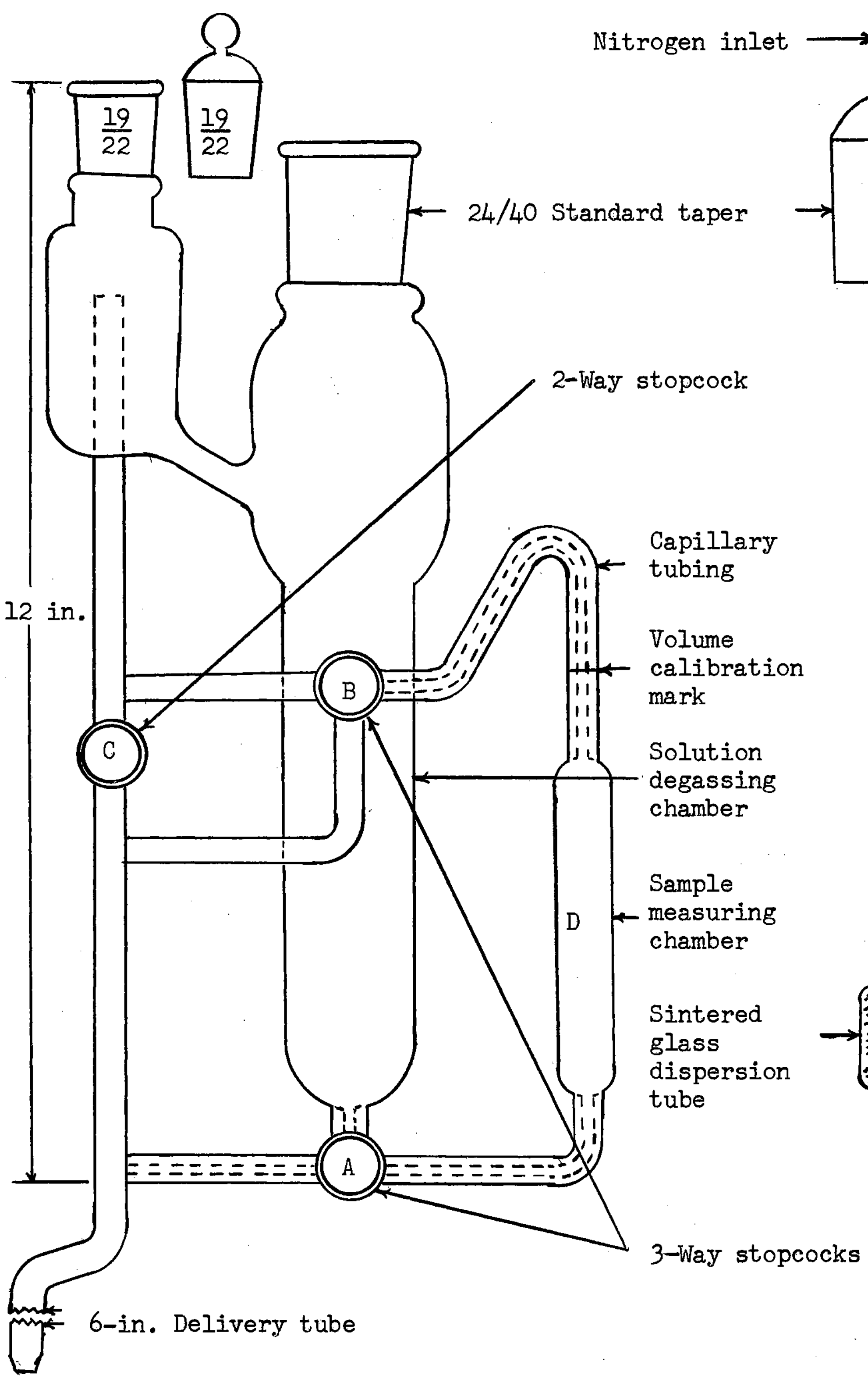


Figure 4. Degassing and Sampling Vessel

sample was introduced by the following procedure: Stopcock A was opened so as to allow the solution to pass into the calibrated sample measuring chamber, D. Stopcocks B and C were adjusted in such a way that the nitrogen pressure would force the solution into D. Around the tube above the chamber a line was etched so the chamber could be filled with a reproducible volume of solution. Calibration with water, employing the weight and density of that delivered, showed that 9.045 ml. was delivered to the cell when the measuring chamber was filled at 25° C. This known volume of sample could then be introduced into the main cell by adjusting stopcock A to connect the sidearm with the delivery tube. The delivery tube's length was constructed so that when it was completely inserted into the cell, the tip would be just above the final level of the sample in the cell. In this way, splashing on the sides was minimized. After the sample was delivered, the degassing cell could be raised so that nitrogen emerging from the delivery tube would not emerge directly onto the solution. The bend in the delivery tube enabled it to be inserted more easily.

The cell was originally tested with Cd^{++} in 2-propanol with 0.1 N. LiCl as carrier electrolyte. The cadmium, under these conditions, gave an $E_{\frac{1}{2}}$ of -0.75 V. versus the 0.1 N LiCl-calomel electrode. The polarogram obtained after introduction of the sample into the main electrolysis compartment was used to determine the diffusion current at the initial concentration. The voltage then was set at a constant potential which was on the level portion of the limiting current and the diffusion current was determined from the wave as soon as the limiting current stabilized. By allowing the wave to become steady and by then utilizing the downscaling attachment on the Model XXI polarograph, the sensitivity of the recorder could be increased stepwise to its maximum sensitivity of 0.003 microamp. per scale division without the graph going off scale. In this way a smaller percentage of change in the diffusion current would be more noticable and more accurately measured.

In practice, the temperature of the cell was maintained within ±0.05° C. of the original temperature throughout the run by means of a mineral oil bath. Therefore, all measurements were made at essentially the same temperature. A flow of nitrogen over the solution and through the cell was maintained throughout the run, and the diffusion current was continuously recorded at the selected constant voltage throughout the run. The chart speed was slowed by changing the gear ratio on the chart drive, and then calibrated by timing the chart rate with a stop watch. Results showed a speed of 40.45 seconds per division (0.1 inch) of the chart paper. The total length of time the solution was electrolyzed could then be calculated from the length of chart used. The currents were calculated from the heights of the waves and the sensitivity settings. The average current for the electrolysis was calculated from the decrease in wave height. This allowed the area under the curve to be determined approximately by multiplying the average current by the total time of electrolysis. The area under the curve thus calculated would be an approximation of the total quantity of electricity passed through the cell.

Although the above gives only an approximation of the quantity of electricity used, the ratio of the difference between the initial and the final diffusion currents, $\underline{i}_d^o - \underline{i}_d$, to the initial diffusion current, $\underline{i}_d^o$, gives quite accurately the percentage of substance that has been reduced. In this case the percentage of substance reduced was calculated from the decrease in the diffusion current at 0.003 microamp. per scale division sensitivity. A typical calculation of the n-value of cadmium obtained by using this method is given for a case where the original concentration of cadmium was 0.0008 M:

i_d° = 0.6999 microamp. (measured) + 2.0088 microamp. (compensated);
therefore i_d° = 2.7087 microamp.

i_d^f = 0.5811 microamp. (measured) + 2.0088 microamp. (compensated);
therefore i_d^f = 2.5899 microamp.

Therefore, $i_d^\circ - i_d^f$ = 0.1188 microamp.

$$\text{Average current} = \frac{2.7087 + 2.5899}{2} = 2.6493 \text{ microamp.}$$

Time of electrolysis = 563 div. x 40.45 sec./div. = 22773 sec.

$$\text{Equivalents reduced} = \frac{2.6493 \times 10^{-6} \text{ amp.} \times 22773 \text{ sec.}}{96{,}496 \text{ coulombs/equiv.}}$$

$$\text{Moles reduced} = 0.009045 \text{ liter} \times 0.000800 \text{ M} \times \frac{0.1188}{2.7087}$$

Therefore, by calculation, n = equiv./mole = 1.97 e^-

The final diffusion current was checked by stirring the solution and rerunning a polarogram at the original sensitivity of 0.010 microamp./div. The results obtained this way were in excellent agreement with the results obtained by calculating the decrease in current measured at the 0.003 microamp./ scale div. sensitivy. This would be an indication that the use of the down-scaling technique was all right.

On several runs, the n-values obtained for cadmium from electrolysis over a period of time not to exceed 6-8 hrs. agreed with the accepted value of 2.00 within an average error of about 8%; however, in several of the electrolyses which were extended overnight and for a length of time in which the room temperature could change considerably, variations of much larger percentages were noticed. These variations were noticed more when temperature drops occurred than when temperature raises occured.

In some cases when the temperature dropped, the final diffusion current actually exceeded the initial diffusion current. These results indicated that evaporation from the cell had occurred. This might be expected since the presaturators were located outside the constant temperature bath. Thus when the saturators were colder, the vapor pressure was lower and, since the temperature of the nitrogen was controlled before it entered the cell by passing it through copper coils in the constant temperature bath, the nitrogen would be unsaturated with vapor and cause evaporation of the solution in the cell. On the other hand, a rise in temperature would have its effect minimized by the condensing of excess solvent in the copper coils instead of in the cell.

Aqueous Cd^{++} solution was also tested with approximately the same results. The same cell was used, and since the asbestos fibers still gave high resistance, the IR-Compensator was still employed.

Benzil was tested in 2-propanol, 0.1 N with LiCl, using the same method as with Cd^{++}. The results obtained showed a value of 2.00 electrons within an average error of 10%, while the graph of E versus log $\frac{i}{i_d - i}$ gave a value of about one electron. The benzil gave only one polarographic wave and the half wave potential corresponded to a value of -0.97 V. The larger percentage of error was thought to be caused by a slow decreasing of the benzil's concentration due to other reactions besides electrolysis. The concentration of benzil in solution was found, by polarographic methods, to decrease on standing. This was shown by testing solutions identical in concentration, one of which had stood for 60 hours or longer and a second of which had been freshly prepared. Each run, therefore, required a fresh solution of benzil to assure that the original concentration was correct. The reasons for this loss was not determined.

To eliminate the errors encountered due to evaporation, it would be necessary to maintain the presaturators at the bath temperature, to completely seal off the cell to eliminate the gas flow over the sample, or to run the electrolysis completely at room temperatures. The first would require a very large constant temperature bath to contain all the apparatus, the second method was tried but was spoiled by oxygen leaking into the cell during the long electrolysis period, while the third method would allow the diffusion current to vary so that determination of an average current would be difficult. An electromechanical integrator was not available for the polarograph; consequently this method of determining the area under the curve obtained during the electrolysis could not be used.

Another method that would eliminate the need for determining the area under the curve is to use a coulometer in series with the polarographic cell. With a coulometer in series, the temperature could vary during the run, needing to be adjusted only when polarograms were being run. In an effort to use this method, it was necessary to design and test a coulometer that would work in series with a D.M.E., and which would accurately measure the small quantities of electricity used. The lack of a good coulometer has been discussed by several workers in millicoulometry. (41) (45)

The first coulometer tested was similar to the one employed by Lingane and Small (30). The coulometer was constructed from a test tube, with a silver anode and cathode. The electrodes were constructed by coiling several centimeters of #18 silver wire, the coils being separated by inserting one inside of a piece of 8 mm. (outside diameter) glass tubing which had been perforated with holes to allow diffusion of solution while the second electrode was coiled around the outside of the glass tubing. The solution used in the coulometer was aqueous 0.1 N LiCl. In this coulometer the lithium chloride salt serves as a carrier and also as a source of chloride ions. The resulting reactions are:

$$Ag + Cl^- \qquad AgCl + e^- \text{ (anode)}$$
$$2HOH + 2e^- \qquad H_2 + 2OH^- \text{ (cathode)}$$

If the solution was neutralized at the beginning of the electrolysis and CO_2 diffusion into the cell was kept at a minimum, the OH^- could be titrated with 0.001 N HCl and the equivalents of ion reduced could be calculated. Due to the extremely small currents employed, the total quantity of electricity was in the micro-coulomb range. The accuracy of the titrations, however, was found to be limited and errors of as much as 20% were common. The method of colorimetrically measuring the acid-base indicator response, as used by Franklin and Roth (12), was not tried.

There have been a number of workers who have tried different methods of comparing polarographic waves of two substances, for one of which _n_ is known, to obtain _n_-values (11) (19); but these methods have generally been restricted in their usefulness or are rather too complex to set up for convenient use.

What was desired in this investigation was some simple apparatus which would give maximum accuracy.

Various silver coulometers were tested using the difference in diffusion currents measured in cells consisting of a platinum electrode made of No. 24 platinum wire as cathode immersed in a solution 10^{-3} M with $AgNO_3$ and containing various other substances, with a saturated

KCl-calomel electrode as anode. The original design employed the use of an H-cell for the container. The silver solution and the reference anode electrode were connected by means of a 0.1 M NH_4NO_3 in $3\frac{1}{2}\%$ agar plug. The top for the electrolysis cell contained four openings, which were for (1) a solid platinum electrode consisting of 2 cm. of No. 24 platinum wire to be used as the cathode during the electrolysis, (2) a solid platinum electrode consisting of 1 cm. of No. 24 platinum wire to be used as the cathode during diffusion current measurements, (3) a thermometer graduated to 0.1° C. so that initial and final diffusion currents could be run at the same solution temperature, and (4) a degassing tube for degassing and stirring the solution. All platinum electrodes were made by sealing the platinum wire into a length of soft glass tubing, so that the wire extended past the seal on both the inside and the outside of the tube. Connection was accomplished by adding mercury to the inside of the soft glass tubing and inserting a nichrome wire into the mercury.

To avoid the time maximum always encountered in the silver wave at stationary platinum electrodes, the polarograms were run in reverse by starting the voltage at a potential which was on top of the silver wave and scanning with a positive bucking potential applied to the bridge.

Several silver solutions were tested in this coulometer. The solution which appeared to give the most accurate and reproducible results of all tested was a 0.001 M $AgNO_3$ solution with 0.1 N KNO_3 as carrier electrolyte. The solution was made 1 M with NH_4OH to assure that small quantities of chloride ion, which might seep into the cell from the reference electrode compartment if the agar plug were loosened during degassing, would not precipitate AgCl.

The sample used in the coulometer was a 4.992 ml. volume introduced by a standardized pipette. The percentage of silver reduced should then be twice the percentage of compound reduced in the 9.045 ml. nonaqueous solution if the latter was a one-electron reaction. When this was tested on cadmium, the accuracy was in general improved on long runs, but errors of the order of magnitude of 8 to 12% were still encountered.

This error was generally demonstrated by a too-large percentage drop in the silver concentration, even though the electrolysis compartment was covered with a black coating to prevent decomposition of silver salts by light. Leakage of silver solution through the bridge was thought to be one source of error. Different types of bridges were tried in an effort to reduce this error. A piece of "thirsty glass" (nonfused vicor) soaked in the carrier electrolyte was employed but this merely increased the error. Consequently, attention was turned toward the development of a single compartment cell. The apparatus first tested was simple to construct, since a test tube could be employed as the cell.

This second coulometer was tested using different solutions and different anodes, with platinum cathodes as before. Silver solutions containing thiosulfate and iodide were tested with anodes of carbon and platinum, but reproducible results were not obtained, the silver solutions containing thiosulfate alone appearing to give anodically controlled waves. The best results, however, were finally obtained using silver nitrate in a carrier consisting of sodium sulfite and made basic by adding ammonium hydroxide. This coulometer, which was the one finally adopted, was made as follows (see Figure 5).

The electrodes employed were (1) a 0.5 cm. electrode of No. 24 platinum wire used as cathode during the running of polarograms (2) a

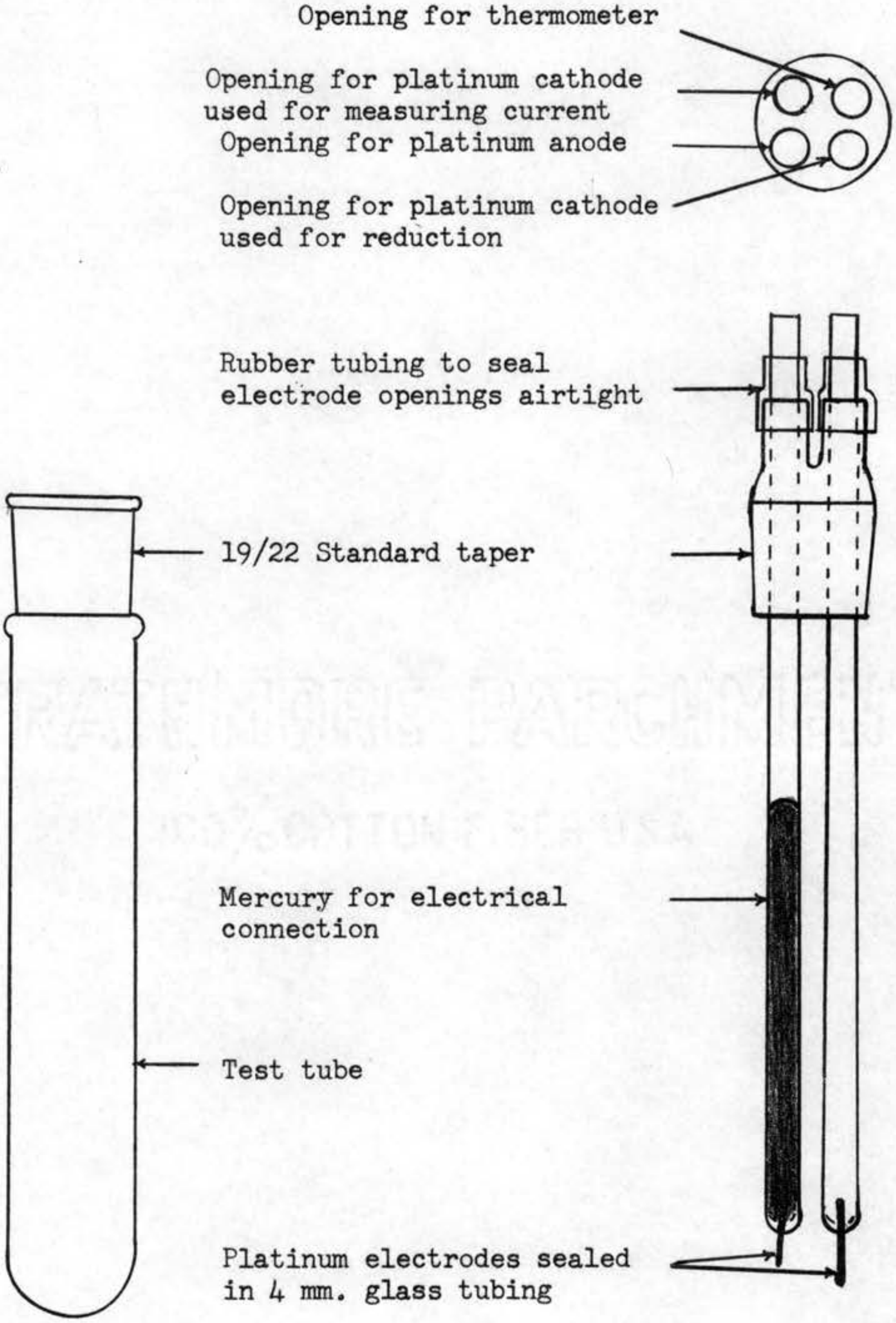


Figure 5. Microcoulometer

2 cm. length of No. 24 platinum wire used as cathode during the time of electrolysis, and (3) a 5 cm. length of No. 24 platinum wire used as the anode. A carbon anode first was tested but was soon replaced because the platinum anode was easier to handle and gave results that were comparable. These electrodes were inserted through a top which was designed to prevent entrance of air.

The silver solution used was 0.001 M $AgNO_3$, 0.1 N with $NaHSO_3$ and 2 M with NH_4OH. The basic solution of sulfite ions reacted with any oxygen present; consequently, it was unnecessary to degass the solution, and the sulfite could serve not only as carrier but also as an oxidizable ion for the anode reaction. The $Ag(NH_3)_2^+$ ion was the reducible ion and gave a half-wave potential of -0.15 V, under the described conditions. The equations for the electrode reactions would be

$$Ag(NH_3)_2^+ + e^- \longrightarrow Ag + 2\ NH_3 \quad \text{(cathode)}$$

$$SO_3^{-2} + HOH \longrightarrow SO_4^{=} + 2H^+ + 2\ e^- \quad \text{(overall anode reaction)}$$

$$2\ SO_3^{-2} + O_2 \longrightarrow 2\ SO_4^{-2} \quad \text{(reaction for oxygen removal)}$$

The sulfate ions produced by the reactions do not interfere with the $Ag(NH_3)_2^+$ wave and the amount of sulfite used is small in comparison to the quantity present; consequently, the wave does not become anodically controlled.

The silver waves were run to a maximum voltage of 1 V. and with as little damping as possible. The smaller cathode appeared to give waves which were both steadier and more reproducible. Ths diffusion current measurements were taken on the flat portions of the wave following the time maxima. Comparable waves were also obtained by setting the voltage at a potential well on top of the limiting current wave and measuring the current after the electrode reaction had equilibrated. Addition of maximum suppressors such as gelatine were found to have little effect on the time maxima and no effect on the wave heights.

The accuracy of the silver coulometer was checked by employing the polarograph as a constant-current source. This was accomplished by inserting a 1-megohm resistor in series with the silver coulometer and the polarograph, the amount of current thus being controlled by the resistance and by the constant voltage applied. The time was measured by an electric clock. Quantities of electricity in the range of 0.08 to 0.2 coulombs were used, these being comparable to the quantities used in the reduction of substances in the nonaqueous cell. The results of the calculated n-values for silver agreed with the accepted value by less than 5% error in the ranges mentioned.

In testing the whole apparatus (cell and coulometer) and in actual runs, the coulometer was connected in series with the nonaqueous polarographic cell by connecting the cathode of the coulometer to the electrolysis reference electrode and its anode to the corresponding lead from the IR-Compensator. In this way any extra iR-drop and back E.M.F. incurred from the silver coulometer would be compensated.

Nonaqueous solutions of Cd^{++}, diacetyl, and benzil were tested in the nonaqueous cell, with the silver coulometer in series with the cell. Separate polarograms were run on the $Ag(NH_3)_2^+$ and on the test solution before and after electrolysis to determine diffusion currents. Polarograms were also run with the two cells in series to make sure that the reduction was being controlled by the limiting current of the solution of the substance whose n-value was to be determined.

Using the difference between the diffusion current of the initial and final polarograms, the percentage of each compound reduced could be calculated. Since standardized volumes and solutions of known concentrations were used, the number of moles of each compound could be calculated.

The ratio of moles of tested ion or molecule reduced to the moles of silver reduced gave the *n*-value directly. The ratio would be

$$n = \frac{\Delta i'_d \text{ x } V' \ M' \text{ x } i_d}{\Delta i_d \text{ x } V \ M \text{ x } i'_d}$$

where Δi_d and $\Delta i'_d$ are the decreases in diffusion currents for the unknown and for the silver ammine complex respectively, V and V' are the volumes of unknown and of silver ammine solutions, respectively, and M and M' are the molarities of the unknown and the silver solutions.

The *n*-values obtained for cadmium using this method agreed with the accepted value within an error of 5.0% (see Table I).

TABLE I

n-VALUES OBTAINED WITH SILVER AMMINE COULOMETER FOR CADMIUM IN 2-PROPANOL, 0.1 N WITH LITHIUM CHLORIDE

Sample	Micromoles of Ag reduced	Micromoles of Cd reduced	n (calc.)	Deviation
1	1.045	0.5173	2.02	0.02
2	1.318	0.6340	2.08	0.08
3	0.923	0.4400	2.10	0.10
4	1.063	0.5165	2.08	0.08
5	1.022	0.4715	2.17	0.17
Mean			2.09	0.08

$$\text{Standard Deviation} = (\text{Mean of squared deviation})^{\frac{1}{2}} = 0.102$$

$$\frac{\text{Standard Deviation}}{\text{Accepted } n\text{-value}} = 0.0501 = 5.01\%$$

Benzil had only one polarographic wave when reduced in 2-propanol, 0.1 N with LiCl, the half wave potential corresponding to -0.97 V. As mentioned earlier, the benzil solution used was prepared fresh before each electrolysis; for electrolysis conducted on solutions over 48 hours old resulted in abnormally low n-values due to the decrease in concentration from the standardized molarity. The n-values obtained with fresh solutions of benzil showed a value of 2.00 within a standard deviation of 6.7% as shown by Table II.

TABLE II

n-VALUES OBTAINED WITH SILVER AMMINE COULOMETER FOR BENZIL IN 2-PROPANOL, 0.1 N WITH LITHIUM CHLORIDE

Sample	Micromoles of Ag reduced	Micromoles of Benzil reduced	n (calc.)	Deviation
1	3.625	1.672	2.18	0.18
2	3.492	1.670	2.20	0.20
3	0.7445	0.4290	1.88	0.12
4	1.930	0.9425	2.05	0.05
5	2.195	1.097	2.00	0.00
Mean			2.11	0.11

$$\text{Standard Deviation} = (\text{Mean of squared deviation})^{\frac{1}{2}} = 0.134$$

$$\frac{\text{Standard Deviation}}{\text{Accepted } n\text{-value}} = 0.0670 = 6.7\%$$

The cell circuit had an iR-drop of approximately 25 V. when 1 x 10^{-3} M. benzil solution was used in the nonaqueous solvent. Therefore, when the concentration was increased to 3 x 10^{-3} in an attempt to produce larger concentrations of products for analysis, the current was tripled and the iR-drop was correspondingly increased to approximately 75 V. The IR-Compensator employed gave a maximum of 30 V. compensation; therefore, it was necessary to place in series between the IR-Compensator and the E.R.E., two series-connected 22½ V. No. 412 Everready transistor batteries. The batteries thus compensated for 45 V. of the iR-drop, and the remainder was handled by the compensator. Any fluctuations in the voltage of the batteries also was compensated by the IR-Compensator.

Analysis of products was performed as follows. The electrolyzed solution was first separated by distilling out the low boiling compounds, employing a water bath as heater and an ice bath as condenser. This should distill out the alcohol and also all other compounds that boil below 100° C. The solid residue was then extracted with 5 ml. of isooctane to dissolve any organic matter out of the LiCl left by the evaporation. The two fractions were then tested separately employing the gas chromatograph.

When it was injected into the silicone rubber column at 55° C., ths distilled fraction gave one peak besides that for 2-propanol, with a retention time of 3.0 min. for the unknown peak and 1.0 min. for 2-propanol. Checks of the column with acetone, benzaldehyde, and benzene showed that none of these accounted for the second peak.

The isooctane fraction showed four major peaks besides the peaks corresponding to isooctane and benzil. The retention times on the silicone rubber column at 250° C. were 3.2 min., 4.1 min., 5.3 min. and 7.0 min. for the four unknown peaks, 0.8 min. for isooctane, and 4.4 min. for benzil. A check with benzoin showed that on none of the columns tested could benzil and benzoin be separated; therefore, there were four constituents present--and possibly benzoin, as well. No further attempts were made to identify these compounds at this time, or to ascertain whether or not benzoin was present.

Since some of these compounds might have been impurities, portions of the same benzil solutions were handled using the same procedure as for the electrolyzed sample except no reduction was done. The isooctane fraction yielded one peak besides the peaks corresponding to isooctane and benzil. This peak corresponded to the peak obtained at a retention time of 5.3 min. from the reduced fraction, and the substance responsible was apparently not produced by reduction. Therefore, the reduction of benzil in 2-propanol appeared to result in the formation of at least four products, with benzoin as a fifth possibility.

The second diketone studied, diacetyl, was found to be difficult to use because of the evaporation of the diacetyl from solution. The loss by evaporation caused such large drops in diffusion current that very low n-values were obtained. To overcome this a large volume of diacetyl solution was prepared and after a sample was poured into the degassing cell, the remainder of the solution was placed in presaturators located in the nitrogen flow just preceding the degassing cell. This tended to decrease the amount evaporated; however, it was found insufficient to stop evaporation enough so usable results could be obtained.

Attempts were made to seal the cell portion off after introduction of the sample. The cell, as designed, however, apparently still allowed enough air to leak into it so oxygen waves always showed on the polarograms. Therefore, no reproducible n-values for diacetyl could be obtained with the apparatus as constructed.

CHAPTER VII

SUMMARY AND CONCLUSIONS

Millicoulometry. As was described in the section describing the scope of this investigation, the primary objectives were those (a) of constructing a suitable nonaqueous polarographic cell for quantitative reductions at the dropping mercury electrode, and (b) of designing a suitable millicoulometer which could be connected in series with the cell and used for the determination of n-values for the electrode reaction in the cell. A third objective was that of seeing, with a suitable organic compound, whether enough product could be produced in the cell so that determinations of these products (or of any secondary products) could be done by means of G.L.P.C.

As would be expected for most organic compounds, the curve of benzil showed that the conventional method of determining n-values from the slope of the line obtained by plotting E versus log i/i_d-i would not work. With the millicoulometer, much more accurate results were obtained, those with cadmium being 2 electrons with a standard deviation of 5.0% and with benzil being 2 electrons with a standard deviation of 6.7%.

It will be noticed (Tables I and II) that (with one exception) results were always high. In these runs, nitrogen was passed over the solution being electrolyzed for the several hours of each run. Although the nitrogen was presaturated with solvent, there was evidence that this presaturation was not accurately accomplished. If the nitrogen were undersaturated, solvent would have been lost from the polarographic cell and this would lead to the high n-values obtained for cadmium and for benzil.

Although the work reported here represents a great improvement over other methods, still further improvement should be sought. Much reliance has been placed in the past upon the fact that a given electrode reaction could involve only whole-number n-values. This is, of course, true of a given electrode reaction. However, accurate measurement of n-values might lead to fractional values being measured, and these values, if trustworthy, could give valuable information as to occurrences within the solution and at the electrode. Thus, for example, fractional values would be measured:

(1) If some (but not all) of the electrode product reacted with some of the substance being examined to form a product that was not reducible at the voltage employed. Thus a 2-electron reaction would appear to be less than 2 electrons since more reactant would disappear than would be accounted for by the 2-electron process.

(2) If a slow rate-controlled reaction of one n-value were superimposed upon a normal diffusion-controlled reaction of another n-value, or if two rate-controlled reactions with different rate constants and different n-values were superimposed.

(3) If a wave were partly normal and partly adsorption, or partly normal and partly catalytic (the latter being the unexpected reduction of solvent, for example).

Thus, accurate measurement of experimental n-values could give clues as to unexpected happenings and help in the interpretation of mechanisms leading to products found in the final reaction mixture.

Application of G.L.P.C. to Product Analysis. Although in this research the products of the overall reaction were not identified for the benzil that was tested, the new peaks that were obtained showed that the method itself should be feasible. Likewise, the fact that several postulated products were shown to be absent is in itself proof of the value of this approach. Actual identification of less obviously expected products was beyond the intent of this research though it would have been desirable.

Future Investigations. From the results of this research and from the foregoing discussion, it is apparent that future efforts whould incorporate the following ideas:

(1) The microcoulometer itself probably is all right for most studies and the results would be quite accurate if the reaction in the microcoulometer were controlled entirely (as would be the case in practice) by the reaction in the polarographic cell containing the substances to be studied.

(2) The polarographic cell itself should be modified so continuous flow of nitrogen during the several hours of each run would be unnecessary. This would minimize changes in concentration of the substance by volatilization either of solvent (as in the case of cadmium and of benzil) or of solute (as in the case of diacetyl, which proved to be volatile).

(3) The efficiency of presaturators for the nitrogen which must be used at least to remove oxygen, should be improved so the concentration of the solution will not change significantly even in the preliminary degassing.

With these changes, experimental n-values could be determined with accuracy sufficient for use of these values, fractional or otherwise, in the interpretation of electrode and secondary reactions.

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