POLAROGRAPHIC BEHAVIOR OF CERTAIN

ORGANO-BORON COMPOUNDS IN

NONAQUEOUS SOLUTIONS

By

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DEDICATION

This work, a part of the requirements for the Doctor of
Philosophy degree, was inspired and aided by a number of people
whose cooperation and encouragement was a great help to the author.
As a small gesture of appreciation, the author wishes to dedicate
this thesis to his wife, Jean M. Ulrich; to his children, Sandra,
Richard, Nancy, and Mary; to his parents, Mr. and Mrs. E. B.
Ulrich; to his wife's parents, Mr. and Mrs. Emil J. Hetlinger;
and to Dr. and Mrs. Ted Hohm.

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HISTORICAL

Introduction.

The background for polarography was laid when Kucera (31),
while studying the intercapillary curve of mercury in various sol-
utions by the use of the dropping mercury electrode (D.M.E.), noticed
that when reducible substances were present peculiar inflections
appeared in the intercapillary curves. It was in 1922, however,
that Jaroslav Heyrovsky (18, 19), while following a suggestion from
Kucera that he investigate this phenomena, developed the polarograph
and established the basis for a new analytical method.

By 1925, Heyrovsky and Shikata (21) had developed an instrument
for recording automatically the curves which they called polarograms.
In 1935, Heyrovsky and Ilkovic (20) put polarography on a much sounder
basis by explaining the theoretical significance of the polarographic
wave.

A simple polarography consists of a direct current source with a
variable voltage output, together with a current measuring device by
means of which the resultant current at each applied voltage can be
measured (Figure 1 A). Two electrodes are used in the electrolysis
cell--one small and easily polarizable (the microelectrode) and the
other, large and non-polarizable.

The microelectrode most widely used is the dropping mercury
electrode. One form of this consists of a mercury resevoir fitted
with a stopcock to the lower end of which is attached a piece of
"marine barometer" capillary tubing. The capillary is about 0.05
mm. in diameter and such length that the mercury drops will fall at

a constant rate of one for every three to six seconds. This electrode acts as the cathode in the reduction process.

The larger non-polarizable electrode may be a calomel-type electrode or it may be merely a pool of mercury at the bottom of the electrolysis cell. The most generally useful electrode in this class is the saturated calomel electrode (S.C.E.).

A typical polarogram, with its main parts labelled, is shown in Figure 2. From this it will be seen that as the voltage is increased across the electrolysis cell, a small but increasing current (part A of the curve) flows. This current is called the residual current. This current in the case of the D.M.E. is due, in part, to the fact that as each mercury drop grows, a small current must flow in order to build up a condenser-type charge on the mercury, this charge increasing with the applied voltage. Another part of the residual current results from reduction or oxidation of impurities present which are beyond the range of the purification methods used on the components of the solution.

When the voltage across the cell has been advanced to the decomposition potential of the oxidizable or reducible substance, the current rises rapidly until the limiting current B is reached. The limiting current obtained with the microelectrode is due to the fact that owing to the depletion of reducible (or oxidizable) ions (or molecules) at the electrode surface, a high state of concentration polarization is attained. Since the number of ions present at the electrode is infinitesimal compared with that in the bulk of the solution, the limiting current becomes a function of the rate with which the substance reaches the electrode. Consequently, the limiting current is practically independent of the applied potential.
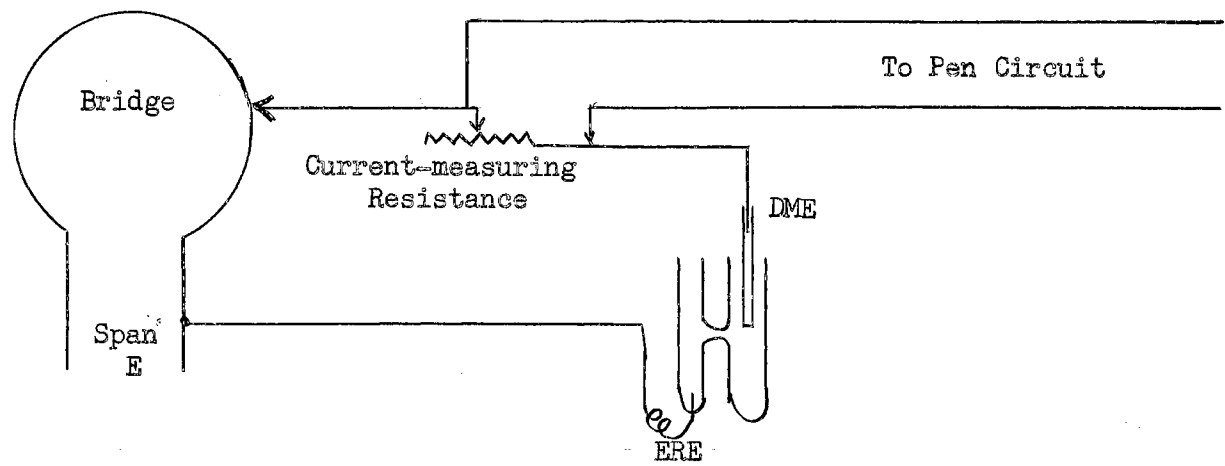
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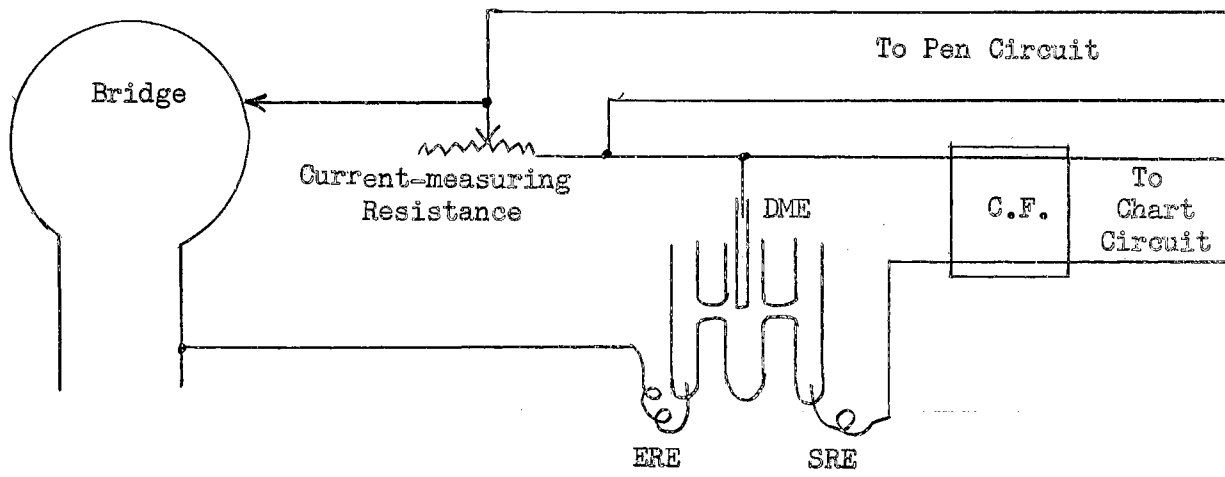
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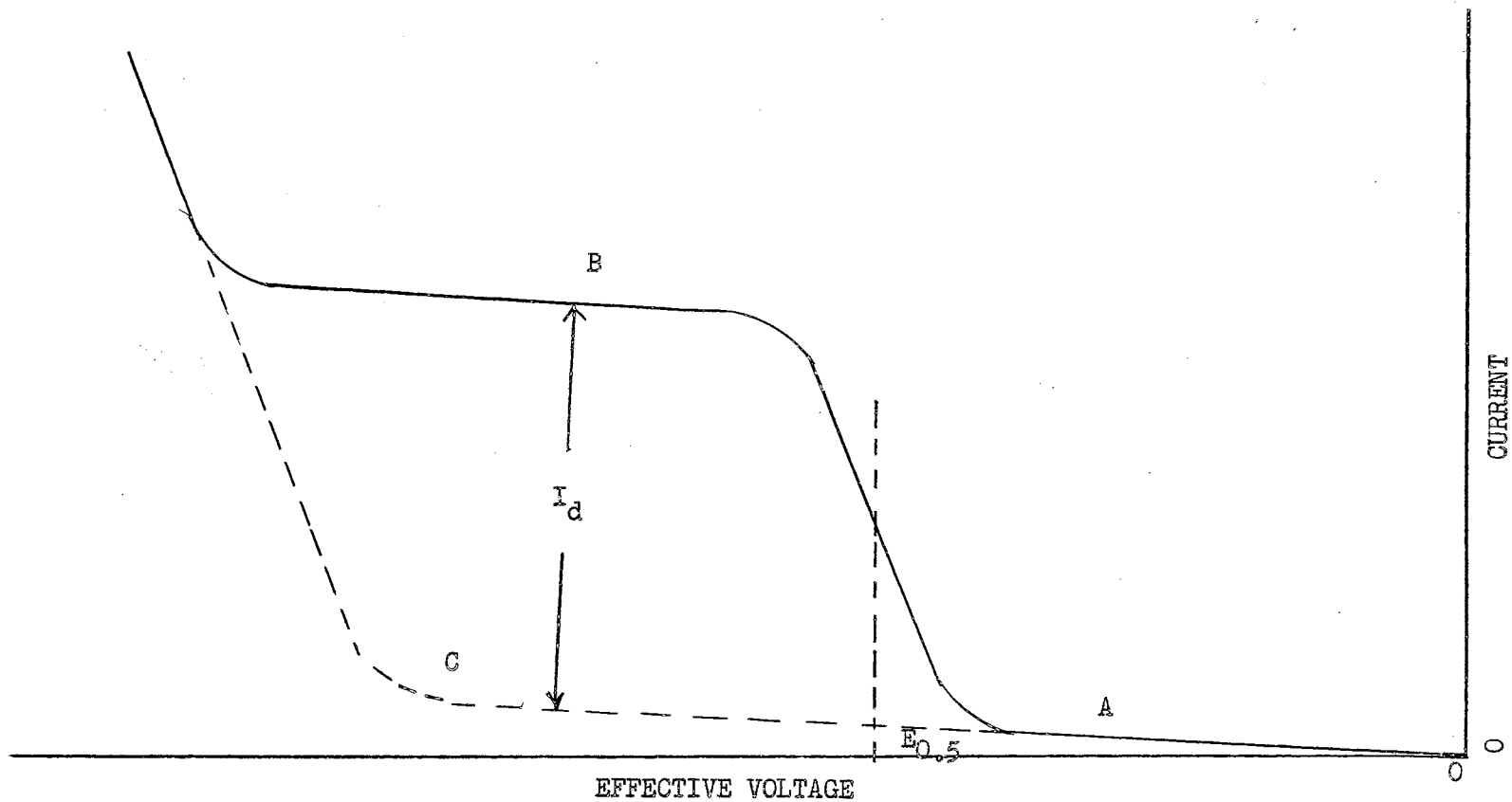
Figure 1.

Polarographic Circuits

Figure 2. A Normal Polarogram

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

I_d. The diffusion current
$E_{0.5}$. The half-wave potential

Two forces influence the rate at which the reducible or oxidizable substance moves toward the microelectrode. One force, an electrical force, attracts the ions to, or repels them from, the electrode, resulting in a migration current which is proportional to the potential difference between the electrodes. To minimize the influence of this upon the substance being determined, an inert carrier electrolyte (supporting electrolyte) is added at a concentration 50 to 100 times greater than the oxidizable or reducible substance present. As a result, the migration current in the polarogram is negligibly small. The second factor influencing the rate is the diffusion force which gives rise to the diffusion current (I_d). The I_d is a function of the bulk-solution concentration, and is proportional to the rate of diffusion of the reactive material to the microelectrode. With suitable standards and with controlled conditions, the wave height is found to be directly proportional to the concentration of the substance.

The "half-wave" potential $(E_{0.5})$ is characteristic of the oxidized or reduced substance. The function may be determined graphically by measuring the midpoint of the rapidly rising wave between the projected residual current and limiting current lines. Since the half-wave potential depends on the temperature, the nature and concentration of the carrier ion, the reference electrode used, and (at times) the concentration of the analyzed material, this information always should be specified.

The design of the conventional polarograph is such that the current is plotted as a function of applied voltage. When cell resistances of 5,000 ohms or more are encountered, curves obtained with such polarographs shift and flatten, giving the appearance of a shifted half-wave potential. By measuring the cell circuit resistance, a

correction for IR drop can be calculated and the curve replotted using 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 applied voltage, respectively. If the cell resistance becomes still larger, it is difficult or impossible to correct the curve with the above equation because of the poor quality of the curve. Actually, such polarographs are designed so that when the cell resistance is less than 1,000 ohms, "E_{app}" could be assumed to be equal to "E_{eff}".

With the high resistance polarograph developed by Arthur and Lloyd (43) (see Figure 1 (b)) in these laboratories, this IR correction is compensated for by the machine itself and the diffusion current is plotted against effective voltage. The need for correction is thus eliminated and distortion does not occur. A special cell with two calomel-type reference electrodes instead of the usual single electrode (see Figure 1 (a) and (b)) is employed, the microelectrode and one of the reference electrodes being used for the actual electrolysis while the potential of the microelectrode is measured, without flow of current in this part of the circuit, against the second reference electrode.

<u>Diffusion Current Theory.</u>

Ilkovic (23,24) derived the following theoretical equation to apply during the life of the drop 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 at any time, "t",

                n   is the number of electrons involved in the electrode reaction,

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

    C   is the concentration in moles per cm^3,

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

    t   is the time in seconds,

    706   is a constant involving the surface area of the drop and Faraday's constant.

It is more convenient to express "i_t" in microamperes, "C" in milli-moles per liter, and "m" in milligrams per second, since these values are easier to work with in polarography.

The _average_ current is defined as the theoretical current which, during the life of the drop, would pass the same number of coulombs as the drop itself actually passes. By integration of, and substitutions in the above equation, Ilkovic obtained for the average current:

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

To account for the variations in the diffusion current constant, $i_d / \; C \; m^{2/3} \; t^{1/6}$, when different D.M.E.'s were employed, Lingane and Loveridge (39) and Strehlow and von Stackelberg (49) included the curvature of the electrode surface. This modified Ilkovic's equation to become:

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

Lingane and Loveridge used 39 for the "A" value, while von Stackelberg used 17.

Both the maximum and the average current are directly proportional to the concentration of the reducible or oxidizable material present in the solution. It has been found more practical to use the average current because of the difficulty in measuring the maximum

current due to the slow response of the current-measuring devices of most recorders.

Half-Wave Potential and Wave Form Theory.

Since little work has been done in the field of nonaqueous polarography with organic compounds, theories to explain phenomena observed have not been developed. Consequently, theories developed for aqueous polarography will be discussed and comparisons with nonaqueous polarography will be noted.

There are three general situations that should be considered when dealing with reductions at the D.M.E. (30). Situation one, is that of a metal ion which upon reduction forms a metal soluble in mercury (e.g., cadmium). The second situation is that of a metal ion which upon reduction forms a metal that is insoluble in mercury (e.g., nickel); while the third situation is that of the reduction of a metal ion from a higher to a lower oxidation state (e.g., ferric to ferrous ion in oxalate carrier). Equations developed to cover situations one and three have been shown to be the same. Thus the general characteristics of the waves will be the same and the half-wave potentials will not be dependent upon concentration. Heyrovsky and Ilkovic (20) have shown that the potential at any point on the rising portion of the curve is given by the equation:

$$E_{de} = E_{0.5} - \frac{0.0591}{n} \log \frac{i}{i_d - i}$$

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

$E_{0.5}$ 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 of the most useful forms of the equation of the polarographic wave.

From the above equation it can be seen that a graph of $\log \frac{i}{i_d - i}$ versus E_{de} should be a straight line with a slope of $\frac{0.0591}{n}$ at $25^{\circ}C$. It also can be seen that the point at which the log term becomes zero should be the half-wave potential of the ion. The slope of the line is important since "n" may be calculated from it. The "n" value, when it approximates a whole number, can be used to help determine the nature of the electrode reaction. However, if the electrode process is ir-reversible or if the current is controlled by other than diffusion, the "n" values calculated are not whole numbers--in fact, are usually less than unity. The evaluation of the true "n" in such cases is not possible by this method.

If the diffusion coefficient of the reacting species is known and if the process is diffusion-controlled, an evaluation of "n" can be obtained from the Ilkovic equation. This method may be applied to either reversible or irreversible reactions. According to Reynolds and Shalgosky (47), if the diffusion coefficient is not known and the react-ion is irreversible, several "n" values may be assumed and the diffusion coefficient corresponding to each calculated. Examination of the values will lead to the elimination of the incorrect "n" values because of the absurdity of their values. For cases where neither of these methods apply, Lingane and others (42) have used coulometry on the macro scale for the calculation of "n" values. This method consists of electrol-yzing a solution at a stirred mercury pool cathode and employing a coulometer, such as a hydrogen, silver, or iodine coulometer, to integ-rate the current-time curve. A potentiostat (40) is used to maintain the potential difference between the cathode and the standard electrode

throughout the electrolysis. The initial and final concentration of the reacting ion species are usually determined polarographically and the number of electrons involved in the reduction is calculated by means of Faraday's laws. Mechanisms of reactions have been invest-igated by this method (40, 49).

Because there was some question as to whether the reaction at the large stirred electrode was identical with that carried out at the D.M.E., Reynolds and Shalgosky (47) have developed a micro coulo-metric method, which simulates actual polarographic conditions, for determining the number of electrons taking part in the reaction at the D.M.E. They made use of only the polarograph and a microcell in their work. Gilbert and Rideal (14) described a similar method using a micro polarographic cell to determine the number of electrons in the elec-trolytic reduction of an azo-sulphonate dye. Bogan, Mietes, Peters, and Sturtevant (7) designed a micro coulometer consisting of a com-plicated electronic circuit used to integrate current flowing through the polarographic cell. These workers employed their integrator with the micro electrode under conditions such that a big decrease in the concentration of the reduced material took place. DeVries and Kroon (11) described a micro coulometric method using two polarographic cells in series and extending the electrolysis until a reasonable decrease in the concentration of the reducible or oxidizable compound was made. This method, used for both inorganic and organic compounds gave results accurate within two per cent.

The above methods were developed for use in aqueous solutions, but with modifications they should be applicable to irreversible organic reactions in nonaqueous media.

In situation two, in which the reduced metal ion is insoluble in mercury (e.g., nickel) the important equation is

$$E_{0.5} = E_m^O - \frac{RT}{nF} \ln \frac{k_s}{f_s} + RT \ln \frac{i_d}{2} \, ,$$

where E_m^O 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 becomes,

$$E_{0.5} = E_{ms}^O + \frac{0.0591}{n} \log \frac{i_d}{2} \, ,$$

where $E_{ms}^O = E_m^O - \frac{RT}{nF} \ln \frac{k_s}{f_s}$ which is constant at any given temperature, environment and concentration. But $i_d = k_s C$; therefore in this case it can be seen that the half-wave potential is not independent of concentration, but will shift $\frac{0.0591}{n}$ volts for a ten fold change in concentration.

High Resistance Polarography.

In all the papers previously mentioned except that of Lloyd, it was emphasized that cell resistances must not exceed certain low values, since otherwise it was impossible to get good curves. Lewis, Quackenbush and De Vries (38) set 4,000 ohms as their maximum limit. Arthur and Lyons (2) while working in acetone found 8,000 ohms as their working limit. They used a special technique of placing the capillary within 5 mm. of a reference mercury pool electrode, the potential of this pool being measured, at significant points, against an external calomel-type electrode made in acetone. Even with 8,000 ohms resistance they found that the curve was distorted and it was necessary to correct the curve for IR drop by hand plotting.

With the development of the polarograph for high resistance

solutions by Arthur and Lloyd (43), the use of organic solvents with much higher resistances was made possible. Lloyd (43) and Lewis (37) were able to use cell resistances up to 500,000 ohms without appreciable distortion, as their machine plotted current against effective voltage instead of against applied voltage, thus eliminating the IR drop.

Boron Compounds.

The polarographic study of boron compounds has been very limited. Two aqueous studies were made on the behavior of boric acid, one by Kuta (32) and the other by Kemula and Witwicki (28). The latter obtained a single reduction wave of kinetic character with 0.01 M H_3BO_3, but two waves, one kinetic and one diffusion, with 0.001 M H_3BO_3. Tetramethylammonium iodide was used as the carrier electrolyte. An aqueous study of sodium borohydride was made by Lewis (37) which showed that this substance could be oxidized.

In nonaqueous media, several boron compounds were studied by Lewis. His investigation revealed that sodium borohydride could be reduced in methanol at the D.M.E. using 0.1 M LiCl as the carrier electrolyte. Further investigation revealed that sodium tetraphenylboron could be oxidized in 1-butanol at either the D.M.E. or a rotating platinum microelectrode; that acetanilide-boron trifluoride could be reduced in 1-butanol at the D.M.E.; that decaborane could be reduced at the D.M.E. in 1-butanol; and that sodium tetramethoxyborohydride could be reduced as well as oxidized at the D.M.E. in methanol.

Nonaqueous Polarography.

The literature records a large volume of work that has been done in polarography using mixtures of organic solvents and water. However, many organic compounds are unstable while others are insoluble in the water-organic solvent mixture. This led to the mixing of organic solvents

to improve solubility.

Many compounds found to be difficultly soluble in single organic solvents were found to be more soluble in mixtures of organic solvents. Certain of these mixtures yielded, with suitable carrier electrolytes, solutions of conductivity sufficient for polarographic purposes. One of the most popular of these solvent mixtures consisted of methyl alcohol and benzene. Willits, Ricciuti, Knight, and Swern (56) used this mixture to study forty-one oxygen-containing organic compounds (aldehydes, ketones, etc.). Lewis and Quackenbush (38) used this mixture to study the peroxides in fats and hydrocarbons; Hans and von Sturm (16) studied $CuCl_2$; Bohdanecky and Exner (8) determined peroxidic oxygen; and Bernard (6) determined peroxides of alcohols, pinene, and cyclohexanone; and Hall (15) determined oxygen in petroleum fractions.

Hook, Letaw, and Gropp (22) used various mixtures of formamide and acetamide in the investigation of benzalacetone, benzophenone, fluorenone, lead, zinc, and thallium.

Anhydrous normal alcohols, from methyl alcohol to 1-octanol, have been used, with the lower molecular weight alcohols being the most popular. Other solvents found useful were acetone, glacial acetic acid, formamide, ethylene glycol monoethyl ether (Cellosolve), ethylene glycol, pyridine, tetrahydrofuran, liquid ammonia, acetonitrile, concentrated sulfuric acid, and dimethyl formamide.

Hans and von Sturm (16, 17) reported good waves with $CuCl_2$ in methyl alcohol, ethyl alcohol, 1-butanol and 1-pentanol when the curves, corrected for IR drop, were plotted manually. Using methyl alcohol as a solvent, Allison (1) determined lead, and Riccoboni and Popoff (48) determined stannous chloride. Arthur and Lyons (2) were able to get good waves for lead in methyl and ethyl alcohol and by means of special

techniques were able to get good waves from several acid halides in acetone.

Ethanol has been very useful to a number of investigators. Kikichi, Sakagachi, and Honda (29) were able to determine p-nitroso-diethylaniline, and Vlcek (54) determined several strong acids in this solvent. Others include Zuman, Zumanova and Soucek (58) who studied CS_2 in ethanol with diethylamine as carrier. Runner (50) studied ortho, meta, and para nitroaniline reductions. Izmailov and Bez-uglyi (25) studied the influence of this solvent on the polarograms of benzene, acetophenone, codiene, dionine, papaverine, formaldehyde, and oxygen.

Lloyd, while testing the high resistance polarograph, used 1-butanol when he made studies of m-nitroaniline, benzil, benzophenone, and cinnamic acid. He also studied free sulfur in 1-hexanol by first dissolving it in 0.1 to 0.5 ml. benzene, then adding this to the hexanol-carrier solution. Lewis used 1-butanol when he studied the reduction of boron compounds (see later).

Several investigators found glacial acetic acid to be a useful solvent. Those using it were Bergman and James (5) when they studied forty six organic nitro compounds; Bachman and Astle (3, 4) published two papers covering their study of lead, cadmium, zinc, cobalt, chrom-ium, antimony, nickel, copper, iron (III), benzil, and benzoin; while Arthur and Lyons (2) used it in studies of lead and cadmium.

Zan'ko and Manusova (57) used formamide and obtained good results with cadmium, lead, tin, and zinc. This solvent was also used by Letaw and Gropp (36) in their study of benzalacetone, benzophenone, fluorenone, lead, zinc, and thallium. Hook, Letaw, and Gropp (22) used these same substances with various mixtures of formamide and acetamide.

Ethylene glycol monoethyl ether (Cellosolve) was used by Parks and Hanson (46) to determine naphthalene and methyl naphthalene. These investigators used it also in a direct method for lead tetra-ethyl. Ethylene glycol was chosen by Gentry (13) for his studies of cadmium, zinc, thallium, cobalt, and iron (III).

Delimarshii and Abarbarchuk (10) used pyridine for the determination of the chlorides of silver, cobalt (II), and arsenic (III), as did Hans and von Sturm (17) for cupric chloride.

Kanngeisser (27) reported excellent results with compounds such as albumins, proteins, starch, and gelatin in tetrahydrofuran.

Several investigators found liquid ammonia useful in their studies; Vecchi (52), to determine cadmium, and lead; McElroy and Laitinen (43), to determine cadmium, lead, zinc, nickel, cobalt, chromium, and aluminum; and Laitinen and Shoemacher (35) to determine mercury (II).

Acetonitrile was used with excellent results by Wawzonek and Runner (55) for determinations of lithium, potassium, cadmium, zinc, copper, lead, rubidium, cesium, sodium, calcium, and magnesium. This solvent was also used by Vlcek (52) in his study of various strong acids.

Edsberg, Eichlin, and Gavis (12) reported dimethylformamide as the solvent used in their study of anthraquinone.

Concentrated sulfuric acid was used by James (26) in his study of organic nitro compounds.

SCOPE OF INVESTIGATION

The primary purpose of this investigation was to further study the boron compounds which Mr. Lewis found to be reducible or oxidizable; and to work out procedures and carrier-solvent combinations which would give more reproducible polarograms upon which an analytical method could be based. In addition, however, the intent was to collaborate with Mr. Vander Kam to investigate improvements in electrolysis cell design and to construct a modified version of the high resistance polarograph to be used with the cathode ray oscillograph as a recording device.

APPARATUS

The high resistance polarograph, with X-Y strip recorder, was, except for the cathode follower (whose circuit diagram is given in Figure 3) the one described in Lloyd's thesis. The cell used is shown in Figure 5 and the D.M.E. assembly was the same as that used by Lloyd.

The stable reference electrode (S.R.E.) and electrolysis refer- ence electrode (E.R.E.) were both acetone saturated calomel electrodes of the type described by Arthur and Lyons (2).

A Gray Instrument Company, student-type potentiometer, with a Leeds and Northrup galvanometer, was used for the potential measure- ments. This potentiometer was calibrated against an Eppley standard cell. The polarograph itself was calibrated by Weston-type standard cells built into the polarograph (see Figure 4). A Luder-type bridge (44), in conjunction with a variable resistance box, was used in the resistance measurements.

The solutions for the boron determinations were thermostated in a mineral oil bath at $25.0 \pm 0.1^{\circ}C$.
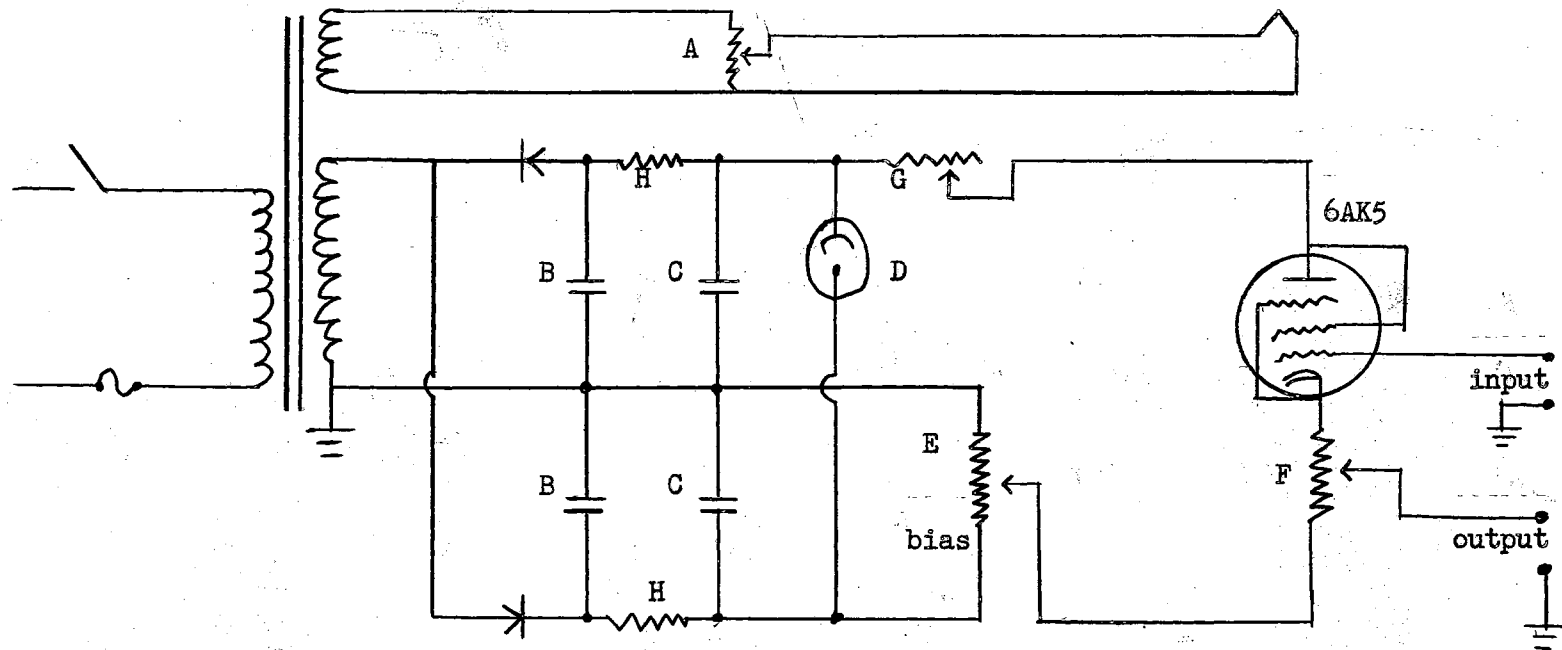
Figure 3

Cathode Follower Circuit

Legend for Figure 3.

A. Variable resistance, 250 ohms

B. Condensers, 20 ufd.

C. Condensers, .01 ufd.

D. Voltage regulator tube OA3 (VR75)

E. Variable resistance, 25 K ohms

F. Resistance, 10 K ohms

G. Variable resistance, 25 K ohms

H. Resistance, 5K15W

Figure 4.

New High Resistance Polarographic Circuit

Legend for Figure 4.

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 3)
P_1 Industrial control (potentiometer), wire-wound, 4 watt, 400-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

REAGENTS

The following reagents were employed in this research:

Acetanilide-boron trifluoride 10 grams of acetanilide was dissolved in 80 ml. chloroform and the resulting solution was poured into an excess of boron trifluoride in diethyl ether. Needle-like crystals appeared in 10 minutes. These were filtered and washed with ether, then stored in vacuo over calcium chloride. The product melted with decomposition at 143-149°C.

Acetone Aloe Scientific reagent grade was dried over anhydrous potassium carbonate and distilled from fresh anhydrous potassium carbonate.

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

1-Butanol Merck analytical reagent grade was distilled through a three-ball Snyder column from anhydrous potassium hydroxide. It was then redistilled from fresh anhydrous potassium carbonate to eliminate water.

Cadmium chloride Baker-Adamson reagent grade cadmium chloride was used after drying 12 hours at 110°C.

Decaborane This was supplied by the agency sponsoring this research and was used without further purification. *

1-Hexanol Eastman yellow label 1-hexanol was treated as described for 1-butanol.

Lithium chloride Mallinckrodt analytical reagent grade was used after it had been dried several hours at 110°C.

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*For security reasons, the name of the sponsoring agency is withheld.

Magnesium perchlorate Granular anhydrous magnesium perchlorate, from G. Frederick Smith Chemical Company, was used after it had been dried several hours at 110°C.

Mercurous chloride Mallinckrodt analytical reagent grade product was used without further treatment.

Mercury A. S. Aloe, U.S.P. redistilled mercury was used after filtration on a gold filter and distillation in a vacuum.

Nitrogen Linde water-pumped nitrogen was passed successively through alkaline pyrogallol, a trap, and concentrated sulfuric acid.

1-Octanol Matheson, Coleman, and Bell 1-octanol was purified as described for 1-butanol.

3-Pentanone Matheson, Coleman, and Bell 3-pentanone was distilled from anhydrous potassium carbonate.

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

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

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

Sulfuric acid A. S. Aloe, C. P. reagent grade was used.

Sodium borohydride Metal Hydride, technical grade sodium borohydride was purified by the method used by Lindemann (39).

Sodium trimethoxyborohydride This was prepared by the method of Brown, et. al. (9).

Sodium tetraphenylboron This was furnished by the sponsoring agency and was used without further purification.

Tetrabutylammonium perchlorate This was prepared by the method of Laitinen (33) and recrystallized from anhydrous ethyl acetate.

EXPERIMENTAL

The polarograph developed by Dr. Paul Arthur and Dr. Nelson Lloyd (43) for use with high resistance solutions was available for this investigation. From P. A. Lewis' thesis (37) was obtained the information that sodium borohydride, sodium tetramethoxyborohydride, acetanilide-boron trifluoride, and decaborane could be reduced at the D.M.E.; that sodium borohydride could be oxidized in water solution at the D.M.E.; and that sodium tetraphenylboron could be oxidized at the platinum rotating microelectrode (R.M.E.).

Mr. Lewis reported that the half-wave potentials of the above compounds were not reproducible and that the waves were continually shifting in such a manner as to make it difficult to say if the diffusion currents were proportional to concentration. In his research, no special effort was made to see if the cell design was the best obtainable. In addition, since it is not ordinarily necessary in polarography, Mr. Lewis did not degas the carrier-electrolyte solution before the solid reducible or oxidizable material was put into solution. It was the purpose of this investigation, therefore, to continue the work started by Mr. Lewis to see if, with suitable precautions, the above reducible and oxidizable boron compounds could be made to give reproducible polarograms upon which an analytical method could be based.

Electrolysis Cell Design.

The cell used by Lewis and Lloyd had, in the microelectrode compartment, an inner tube surrounding the microelectrode and fitted

at its lower end with a glass frit. This inner compartment was employed to reduce possibility of contamination from the reference electrodes while maintaining an electrolytic path between the micro-electrode and both reference electrodes. Peculiarities in the curves obtained with this cell, however, had brought about strong doubts as to whether this represented the best cell design. Consequently, experiments were run which showed definitely that any cell used for this work must be designed so no significant portion of the electrolyte path between the microelectrode and the stable reference electrode would fall in the path between the microelectrode and the electrolysis electrode. These experiments, which will be described in the thesis of Mr. Richard Vander Kam (who is working under another sponsor), led to the development of the cell illustrated in Figure 5. This cell was used in all of the work reported here.

With the new cell, excellent polarograms were made of sulfur in 1-hexanol (Figure 6), benzil in 1-butanol (Figure 7), and cadmium in 1-octanol (Figure 8). These are well formed polarograms from which calculations can easily be made. They may be compared with those in Mr. Lloyd's thesis using a cell of the same design as that employed by Mr. Lewis. It will be noted also that the resistance shown in Figure 8, is 6.5 megohms—roughly thirteen times the working resistance limit of 0.5 megohms employed by Mr. Lewis and Mr. Lloyd.

Boron Compounds.

Sodium tetraphenylboron. The first and most thoroughly studied boron compound was sodium tetraphenylboron. The compound was run anodically with the D.M.E. in 0.1 M LiCl in 1-butanol and found to give a wave which merged into the dissolution wave of mercury. There was a definite break in the wave but the diffusion current could not
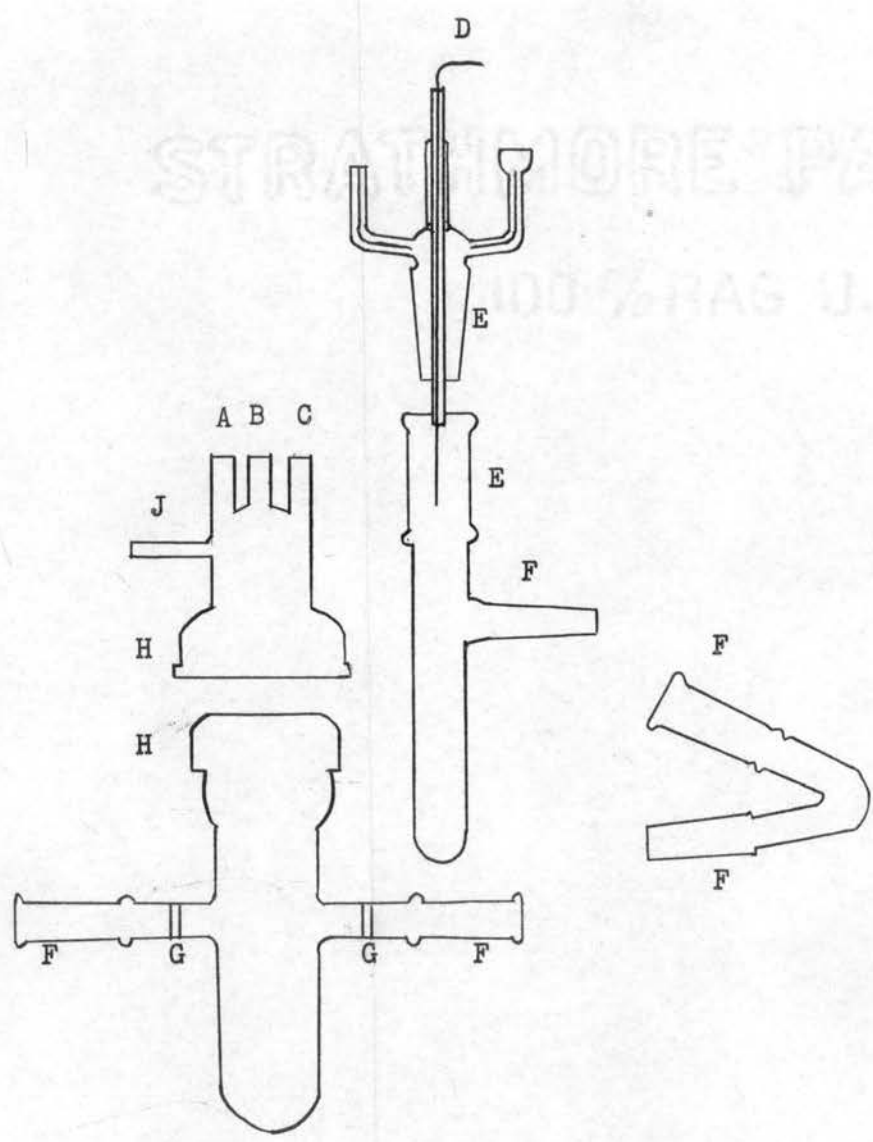
Figure 5.

Electrolysis Cell Assembly

Legend for Figure 5.

A. 6 mm. opening for thermometer

B. 6 mm. opening for dropping mercury electrode

C. 4 mm. opening for nitrogen inlet

D. Copper wire-solder-platinum

E. Standard Taper, 19/38

F. Standard Taper, 14/35

G. Fine fritted disc

H. Ball and socket joint, 50/30

J. 3 mm. opening for nitrogen outlet

Assembly includes-left, Electrolysis Cell, middle, Reference
  Electrode, right, Side Arm.

Carrier: 0.1 M LiCl
Resistance: ERE 368,000 ohms
SRE 466,000 ohms
Reference Electrode: both
saturated calomel in acetone
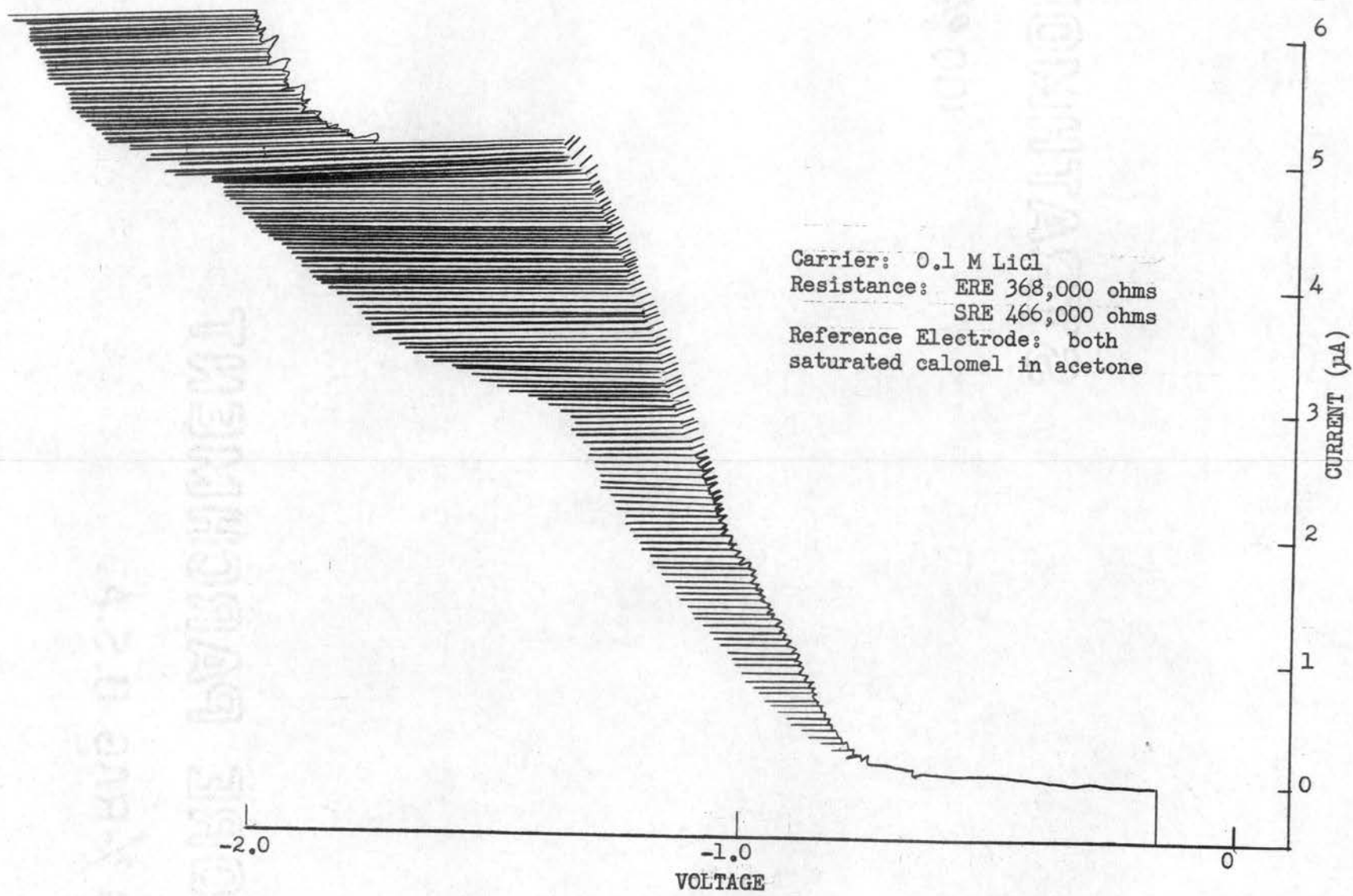
Figure 6.

Sulfur in 1-Hexanol (4.5x10^{-3}M)

Carrier: 0.1 M LiCl
Resistance: SRE 170,000 ohms
           ERE 150,000 ohms
Reference Electrode: both
saturated calomel in acetone
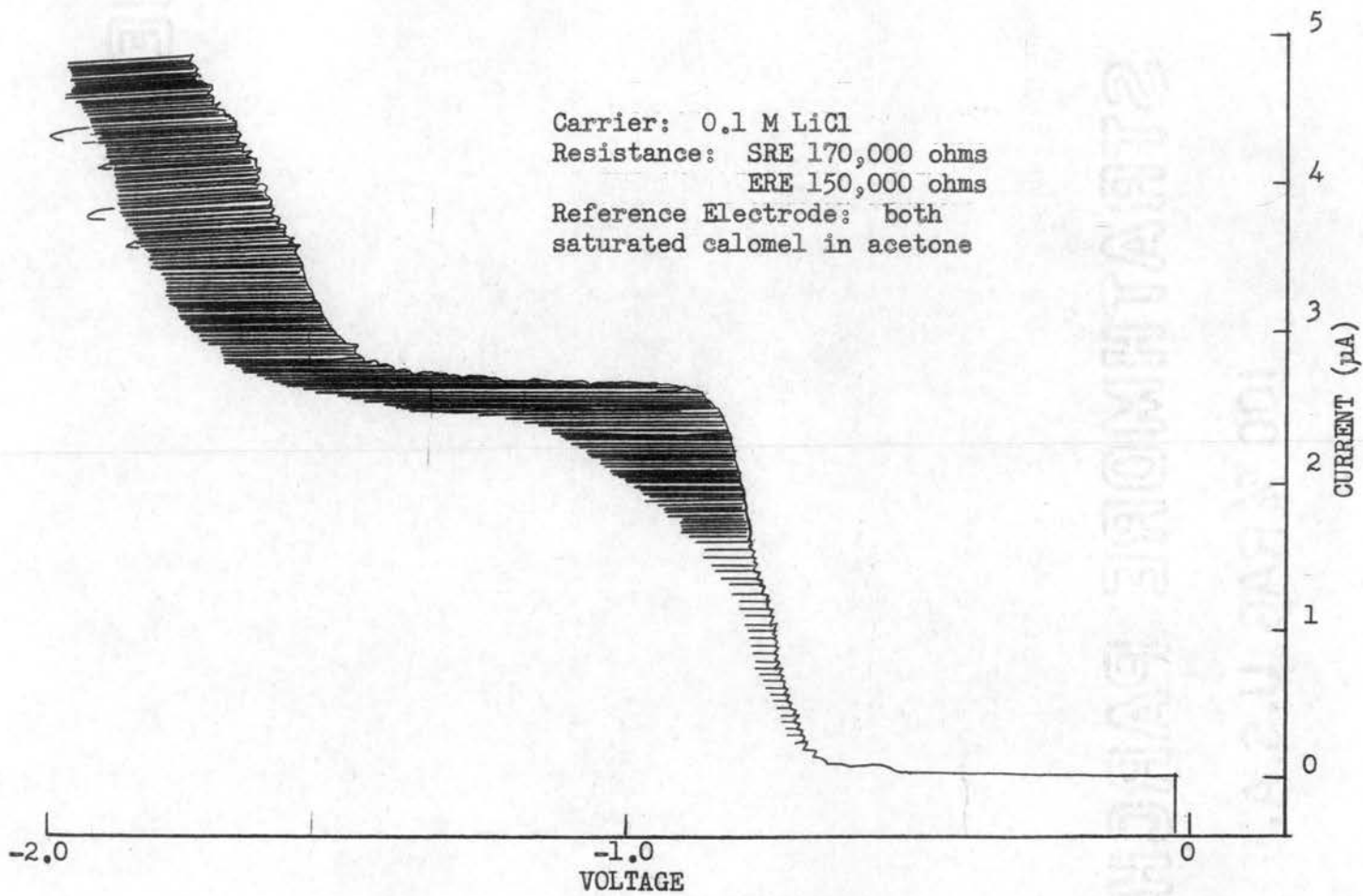
Figure 7.

Benzil in 1-Butanol (4×10^{-4})

Carrier: 0.1 M LiCl
Resistance: SRE 3.9 megohms
           ERE 2.6 megohms
Reference Electrode: both
saturated calomel in acetone

Figure 8.

Cadmium in 1-Octanol (1x10^{-3}M)

be determined accurately, for the previously-run carrier residual current was rapidly rising at the voltage at which measurements of the current had to be made.

The rotating platinum microelectrode (R.M.E.) was next tried on this same system. Unfortunately, however, the electrode proved to have a too small working voltage range anodically. The carrier wave began at about +1.4 volts, and sodium tetraphenylboron, instead of giving a definite limiting current, gave a wave which merged into the rapidly rising portion of the carrier wave. When $LiNO_3$ was tried as the carrier electrolyte, the voltage range was improved but the curves obtained were still not satisfactory.
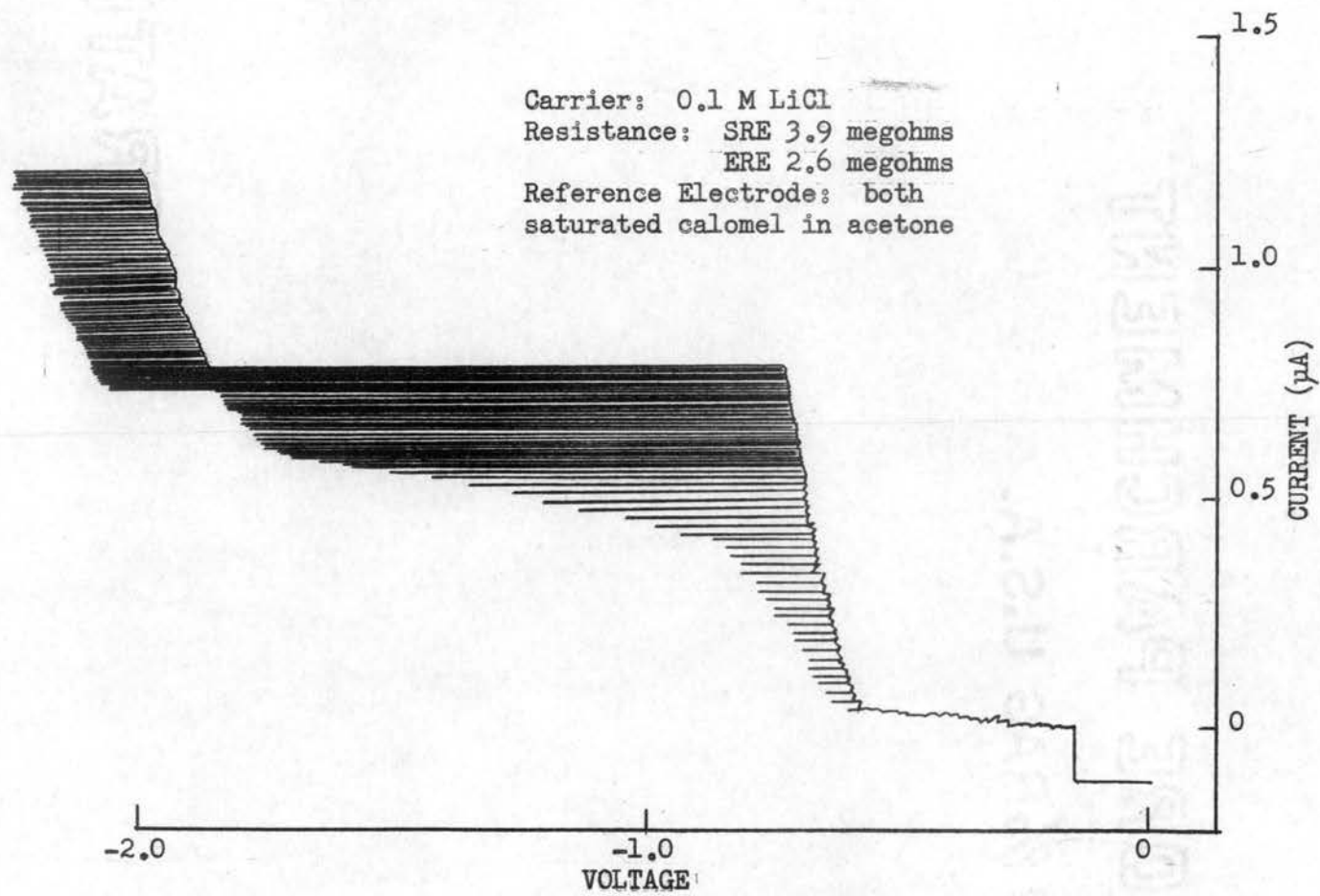
Since only certain types of compounds are soluble in 1-butanol, it was decided to use 3-pentanone in which nonpolar compounds would be expected to exhibit greater solubilities. Tetramethylammonium chloride, as a carrier electrolyte, proved to be too insoluble in this solvent. Tetrabutylammonium perchlorate in 3-pentanone with the R.M.E. gave a large voltage range both cathodically and anodically (-2.0 to +1.75 v.) but was not available in quantity. Magnesium perchlorate was found to give a good anodic voltage range (to about +1.75 volts) and therefore was employed.

When sodium tetraphenylboron was introduced into 0.1 M magnesium perchlorate in 3-pentanone, sometimes one and sometimes two waves in the polarogram were formed. When attempts were made to duplicate the runs, shifting half-wave potentials resulted. Finally, it was decided that an impurity was getting into the electrolysis cell and that the impurity might be mercurous ion from the saturated calomel electrode. A series of tests confirmed this, with the result that glass tube side arm extensions filled with absorbent cotton were inserted between

the electrolysis cell and each reference electrode as shown in Figure
5. The absorbent cotton was moistened with carrier electrolyte and
was found to prevent the passage of detectable quantities of mercurous
ion for as long as 4.5 hours.

With the new arrangement, studies of sodium tetraphenylboron were
again undertaken. The half-wave potentials became constant and only
one wave was found to be present, but the limiting current still did
not level off. This, however, was found to be a problem of developing
a proper procedure and when the following steps were followed rigidly,
excellent results were obtained:

1. Measure out 100 ml. of solvent.

2. In the dry box, weigh out the $Mg(ClO_4)_2$ and dissolve
   it in the solvent.

3. Measure out 25 ml. of the above carrier electrolyte
   solution, pour it into a 100 ml. flask, and degas
   through a gas dispersion tube for one hour.

4. Degas another 60 ml. portion of carrier solution for
   one hour in the electrolysis cell with sidearms in place.

5. Assemble the electrolysis cell, using the remaining 15
   ml. of solution to moisten cotton in side arms.

6. Check the electrolysis cell set-up for electrical
   continuity and measure the resistance of the cell from
   the microelectrode to each reference electrode.

7. Run the residual current curve.

8. With the degassed 25 ml. solution (3) in the dry box,
   weigh out the calculated amount of the compound to be
   run and dissolve it.

9. With a graduated 10 ml. pipette having a stopcock and
   suction bulb attached, pipette the calculated volume
   of solution (8) into the electrolysis cell. Mix by
   degassing for 2 minutes.

10. Run the polarogram.

Quadruplicate anodic runs employing the R.M.E. were made at each
of four concentrations of sodium tetraphenylboron with the cell

thermostated in a mineral oil bath at $25.0 \pm 0.1^{\circ}C$. Table I gives the results of these runs, and Figure 2 is a representative polarogram.

Some explanation of the first two columns in Tables I, II, and II is necessary. In the polarographic circuit, provision was made (see Figure 4, switch S_6) for calibrating the chart movement (voltage axis). This provided for, among other things, marking the short-circuit position or absolute zero voltage. In making polarograms, however, it was found that the actual polarographic curve usually started at a position measurably different from the true zero voltage. Consequently, half-wave potentials were measured from the short-circuit zero and also from the actual starting point of the curve. The resulting measurements of half-wave potential are designated as $E_{0.5}$-S (measured from the short-circuit position) and $E_{0.5}$-W (measured from the actual starting point of the curve)

Inspection of Table I will show that the half-wave potentials are reproducible usually within $\pm$ 0.01 volt, and that they show a small increase with an increase in concentration over a ten fold range of concentration. The average of 16 waves was +1.052 volts for the half-wave potential measured from the short position, with a maximum deviation of +0.025 volts. That measured from the starting point of the actual polarogram showed the more definite shift with concentration and gave an over all average of 0.931 volts with a much greater maximum deviation of 0.115 volts.

A graph of the diffusion current against concentration was not as linear as could be wished. It will be noted, however, that the number of microamperes per millimole per liter which should have remained constant, decreased from averages of 80.3 (for series of

four runs made within a 50-minute period) to averages of 77.0 and 75.1 (for series of four runs made within periods of 95 and 105 minutes, respectively). These evidences of decomposition undoubtedly account for the variations observed. Runs I and II, each completed after a 50 minute interval, gave the values 80.5 and 80.3--which compare very well. A quantitative method for sodium tetraphenylboron can be set up, therefore, but only when measurements are made at constant time intervals.

When the equation usually employed for calculating "n" values was applied to these curves, an average value of 0.4 was obtained. This indicates that the electrode reaction either is irreversible or is not diffusion controlled (possibly both). When such is the case, half-wave potentials frequently are less meaningful than the so-called decomposition potentials obtained by extrapolating the rising straight-line portion of the curve back to zero diffusion current. For comparative purposes, this was done and the values (E_d in Table I) were included. It will be observed that these potentials were surprisingly constant.

Table I.

Sodium Tetraphenylboron in 3-Pentanone
Anodic, R.M.E.

Run no.	$E_{0.5}$-S	$E_{0.5}$-W	E_d	I_d(in μA, at E=1.67)	Molarity $\times 10^{+4}$	μA/ mmole/l.
I. a	1.042	0.873	0.921	17.78*	2.76	64.5*
b	1.050	0.871	0.939	20.95	2.76	76.0
c	1.024	0.838	0.910	21.42	2.76	79.4
d	1.020	0.834	0.910	19.25	2.76	69.8
av.	1.034	0.854	0.920	20.54		75.1
II. a	1.060	0.904	0.930	44.8	5.74	78.0
b	1.044	0.906	0.916	46.5	5.74	81.0
c	1.050	0.905	0.920	47.0	5.74	82.0
d	1.058	0.909	0.916	46.3	5.74	81.0
av.	1.053	0.906	0.921	46.2		80.5
III. a	1.038	0.901	0.894	81.6	10.5	77.7
b	1.076	0.943	0.928	81.6	10.5	77.7
c	1.056	0.930	0.910	80.6	10.5	76.7
d	1.040	0.904	0.922	75.4	10.5	71.8
av.	1.053	0.919	0.914	79.7		76.0
IV. a	1.048	1.030	0.858	189.3*	22.1	86.0*
b	1.092	1.082	0.927	175.0	22.1	79.2
c	1.044	1.015	0.843	179.5	22.1	81.4
d	1.085	1.056	0.885	177.0	22.1	80.2
av.	1.067	1.046	0.878	177.2		80.3
Over-all av.	1.052	0.931	0.908			77.8

The time from the dissolving of sodium tetraphenylboron to the end of run I was 105 minutes; run II, 50 minutes; run III, 95 minutes; run IV, 50 minutes.

*Deviation greater than 2 1/2 times average deviation; consequently, omitted from average.

Note:

$E_{0.5}$-S: Half-wave potential measured from short position.
$E_{0.5}$-W: Half-wave potential measured from work position, but corrected for bridge error.
E_d: Voltage measured from short position to intersection of residual current line and the sloping line on the face of the curve--i.e., so called "decomposition potential".
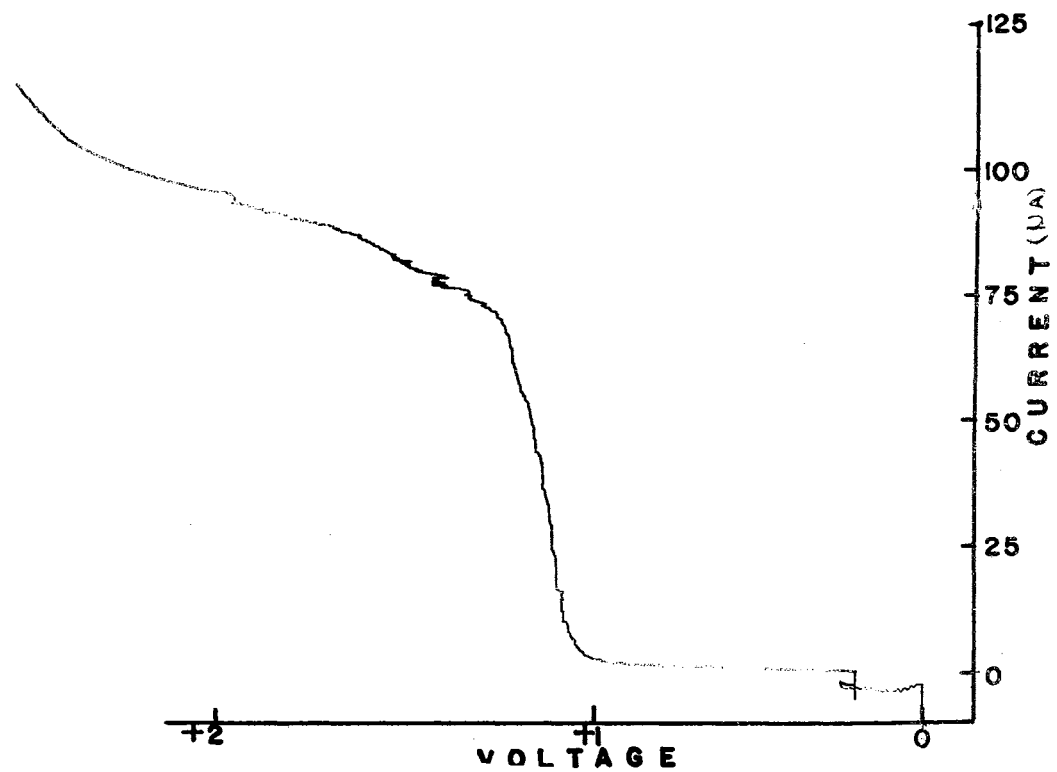
Figure 9.

Sodium Tetraphenylboron in 3-Pentanone
(1x10⁻³M)

Carrier: $0.1 \text{ M } Mg(ClO_4)_2$

Resistance: SRE to ERE, 758,000 ohms
              SRE branch   506,000 ohms
              ERE branch   104,000 ohms

Reference Electrodes: both saturated
calomel in acetone

<u>Acetanilide-boron trifluoride</u>. This compound was studied cath-
odically with the D.M.E. in 0.1 M LiCl in 1-butanol. Again the
mineral oil bath thermostated at 25.0 ± 0.1°C. was employed. Table
II gives the results of 16 runs and Figure 10 is a representative
polarogram.

<div align="center">Table II.</div>

<div align="center">Acetanilide-boron Trifluoride in 1-Butanol
Cathodic, D.M.E.</div>

Run no	$E_{0.5}$-S	$E_{0.5}$-W	E_d	I_d (in μA, at E=-1.28)	Molar- ity x10^{+3}	μA/ mmole/l.
I. a	-1.342	-1.454	-1.206	3.172	1.23	2.58
b	-1.342	-1.454	-1.213	3.172	1.23	2.58
c	-1.336	-1.440	-1.192	3.297	1.23	2.68
d	-1.336	-1.450	-1.198	3.320	1.23	2.70
av.	-1.339	-1.450	-1.179	3.240		2.64
II. a	-1.325	-1.446	-1.146	6.025	2.28	2.65
b	-1.377	-1.480	-1.215	6.025	2.28	2.65
c	-1.372	-1.459	-1.200	6.055	2.28	2.66
d	-1.325	-1.421	-1.147	6.235	2.28	2.73
av.	-1.349	-1.452	-1.177	6.085		2.67
III. a	-1.332	-1.436	-1.161	8.672	3.16	2.74
b	-1.338	-1.430	-1.168	8.672	3.16	2.75
c	-1.316	-1.407	-1.161	8.600	3.16	2.72
d	-1.330	-1.432	-1.155	8.770	3.16	2.77
av.	-1.329	-1.426	-1.159	8.680		2.74
IV. a	-1.520	-1.488	-1.109	26.45	10.0	2.65
b	-1.504	-1.476	-1.068	26.45	10.0	2.64
c	-1.484	-1.452	-1.060	26.35	10.0	2.64
d	-1.460	-1.442	-1.040	26.35	10.0	2.64
av.	-1.492	-1.465	-1.069	26.40		2.65
Over- all av.	-1.377	-1.448	-1.146			2.67

From Table II, it can be seen that the behavior of the half-wave
potentials were similar to that for the half-wave potentials of sodium
tetraphenylboron. The averages of runs I, II, and III were -1.34 with
a maximum deviation of 0.01 volt. Run IV, however, showed a definite
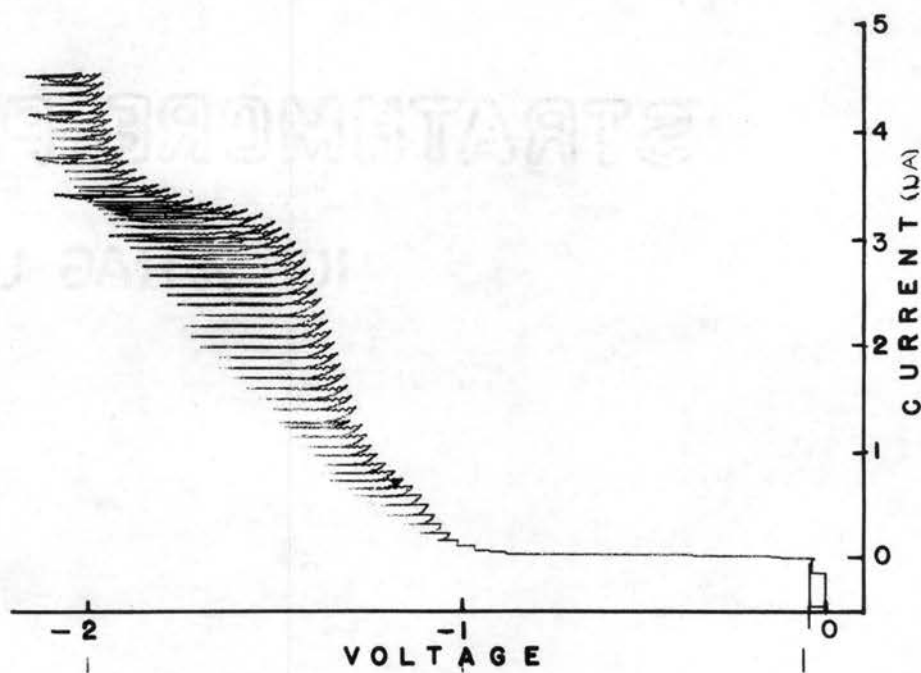
Figure 10.

Acetanilide-BF$_3$ in 1-Butanol
    (2.28x10^{-3}M)

Carrier: 0.1 M LiCl

Resistance: SRE to ERE 680,000 ohms
               SRE branch 508,000 ohms
               ERE branch 242,000 ohms

Reference Electrodes: Both saturated
calomel in acetone.

increase in half-wave potential with increased concentration.

The diffusion current was proportional to concentration over the whole range studied. The constancy of the function I_d/mmole/ liter was excellent which shows that quantitative determinations of this compound are quite feasible.

The "n" values calculated from the curves average 0.3—a fact which shows that this compound also either is not reversible or is not diffusion-controlled. Such results are not surprising, however, as many (probably most) organic compounds behave this way.

An attempt to get a cathodic wave from acetanilide in 1-butanol was not successful. This would indicate that this compound was not the factor involved in the formation of the polarographic wave obtained with the acetanilide-boron trifluoride.

In another experiment, boron trifluoride was bubbled through 1-butanol in the electrolysis cell to make a solution with a con- centration of 10^{-3} M. The compound was run cathodically with the D.M.E. in 0.1 M LiCl, and the polarographic curve that resulted was very similar to the curve from the acetanilide complex. The $E_{0.5}$-S was approximately the same, as was the wave height from the same order of concentration. Although boron trifluoride must be studied more before definite conclusions can be made, it seems probable that the boron trifluoride part of the acetanilide complex is responsible for the polarographic wave obtained with the latter.

Decaborane. This compound was run cathodically using the D.M.E. in 0.1 M LiCl in 1-butanol. A mineral oil bath thermostated at $25.0 \pm 0.1^\circ$C. was employed. Results are shown in Table III and Fig- ure 11.

Well-formed, reproducible waves were obtained. The half-wave

potentials did not change significantly with the concentration over the range of concentrations studied in runs I, II, and III; but with a 10 fold increase in concentration, the $E_{0.5}$-S showed a definite shift from -1.06 to -1.36 volts.

The plot of I_d (at E=-1.28 v.) versus concentration shows reasonable linearity and could be used as a basis of quantitative measurement. The decrease (see Table III) of current with time shows slow decomposition is occurring, however. Consequently, time should be considered an important factor in quantitative analysis. Decomposition is evidenced also by a slow evolution of gas bubbles.

Table III.

Decaborane in 1-Butanol
Cathodic, D.M.E.

| Run no.	$E_{0.5}$-S	$E_{0.5}$-W	E_d	I_d (in μA, at E=-1.28)	Molarity x10^{+3}	μA/ mmole/l.
I. a	-1.068	-1.066	-1.003	6.54	3.24	2.02
b	-1.065	-1.063	-0.996	6.32	3.24	1.95
c	-1.077	-1.082	-0.982	6.52	3.24	2.01
d	-1.054	-1.052	-0.982	6.01	3.24	1.86
av.	-1.066	-1.066	-0.991	6.35		1.96
II. a	-1.030	-1.027	-0.952	11.83	5.98	1.95
b	-1.056	-1.011	-0.976	11.63	5.98	1.93
c	-1.054	-1.050	-1.000	10.35	5.98	1.73
d	-1.065	-1.058	-1.004	10.14	5.98	1.70
av.	-1.051	-1.037	-0.983	10.99		1.83
III. a	-1.062	-1.047	-0.968	15.38	8.34	1.85
b	-1.058	-1.030	-0.968	15.33	8.34	1.84
c	-1.084	-1.061	-0.988	15.08	8.34	1.81
d	-1.079	-1.062	-0.974	15.04	8.34	1.80
av.	-1.071	-1.050	-0.975	15.21		1.83
IV. a	-1.344	-1.313	-1.045	55.92	30.7	1.82
b	-1.362	-1.312	-1.058	56.02	30.7	1.83
c	-1.362	-1.331	-1.072	55.05	30.7	1.80
d	-1.460*	-1.414*	-1.066	53.80	30.7	1.75
av.	-1.356	-1.319	-1.060	55.20		1.80
Over-all av.	-1.136	-1.118	-1.002			1.86
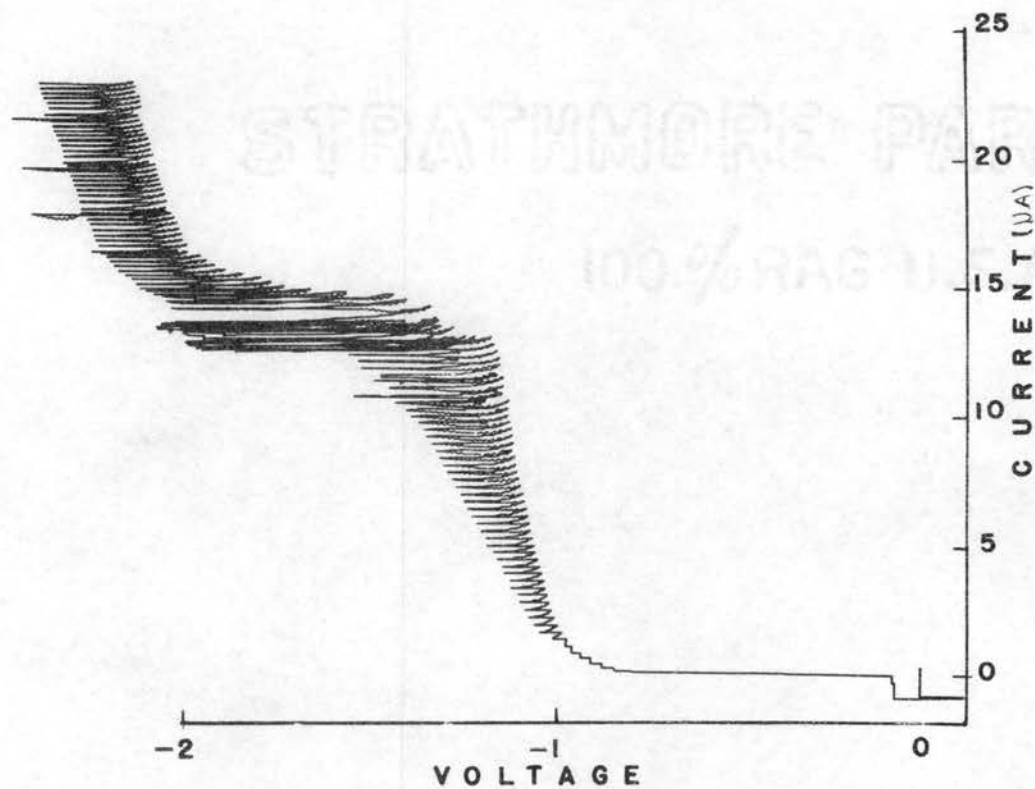
Figure 11.

Decaborane in 1-Butanol
(7.9x10-3M)

Carrier: 0.1 M LiCl

Resistance: SRE to ERE   700,000 ohms
              SRE branch   450,000 ohms
              ERE branch   230,000 ohms

Reference Electrode: both saturated
calomel in acetone.

* Had deviation greater than 2 1/2 times average deviation; so was omitted from averages.

The "n" values (an average of 0.81 for runs I and II; 0.54 for run III; 0.17 for run IV) again indicate that the electrode reaction either is not reversible or is rate controlled.

The time from the dissolving of decaborane to the end of run I was 40 minutes; run II, 80 minutes; run III, 124 minutes; run IV, 90 minutes. Concentration increases were made by accurately pipetting from a standard solution into the electrolysis cell, the total concentration being accumulative.

Sodium trimethoxyborohydride. This compound gave an anodic wave with the D.M.E. in 0.1 M LiCl in 1-butanol. The $E_{0.5}$-S was +0.2 volts. With a concentration of the order of 10^{-3} moles per liter, an increase in concentration did not alter the wave height of the diffusion curve. This compound need further investigation in more dilute solutions to see if I_d is proportional to concentration in lower ranges.

Sodium borohydride. This compound was run anodically with the D.M.E. in 0.1 M LiCl in 1-butanol. Reproducible waves were formed with no shift in half-wave potential with concentration ($E_{0.5}$-S +0.2 volts). The compound was difficultly soluble in degassed carrier solution, with a small amount remaining undissolved when 1×10^{-4} mole per liter was added. When aliquots were taken from the saturated solution, the I_d (at E= +0.31 v.) was found to be proportional to concentration. However, the straight line plot of these values takes the form

$$y = mx + c$$

as the extension of the line cuts the current axis above zero. Sodium borohydride is much more soluble in methyl alcohol and has been

analyzed cathodically with the polarograph in this solvent, as well
as with water (see Lewis' thesis); consequently, the investigation in
1-butanol was dropped.

Oscillographic Polarograph.

Early work by Lloyd (43) in these laboratories led to the develop-
ment of an oscillographic polarograph for use with solutions of high
resistance. Since such a polarograph would be much cheaper than the
type employing the X-Y strip-chart recorder, attempts were made early
in this research to modify Lloyd's apparatus to improve it to a
quality comparable with that of the instrument employing the X-Y
strip-chart recorder. Difficulties encountered with shielding and with
the cathode follower circuit needed to provide the necessary high
impedance for voltage measurements, however, led to the setting aside
of this portion of the research to permit more time for direct work
on compounds of interest with the apparatus already available.

DISCUSSION AND RESULTS

The improved electrolysis cell described here proved to give much better polarograms than those obtained with the cell of Lloyd and Lewis. The cell worked well even when the resistance measured as high as 6.5 megohms. This compares with less than 8,000 ohms for the Sargent model XXI polarograph with aqueous solutions, and about 500,000 ohms with previously-used cell in nonaqueous media.

Three organo-boron compounds, sodium tetraphenylboron, acet-anilide-boron trifluoride, and decaborane gave waves which were reproducible and whose diffusion currents were found to be reasonably proportional to concentration.

In all three cases there seemed to be a shift in half-wave poten-tial to higher values with increased concentration. This is difficult to explain by theories normally applicable to polarography, for shifts observed are normally in the opposite direction. For curves obtained with the dropping mercury electrode, it might be explained as resulting from the inability of the instrument to follow the rapid changes in IR-drop; for the oscillations caused by this are naturally much greater at higher concentrations where the current is large. Such an explan-ation would not be valid for the results obtained with sodium tetra-phenylboron, however; for it waves were obtained with the rotating platinum microelectrode where no such rapid changes are involved and where errors of this type, if any, should be in the opposite direction.

Although no supporting evidence was obtained, one other possible explanation exists. If some small duplication of electrolyte path

still exists in the S.R.E. and E.R.E. branches of the cell, the IR-drop (which increases as the concentration—and current—increases) would cause a proportionate leaning in the wave. This would make the measurements deviate in the direction observed. It should be obvious, at least, that the microelectrode must be exactly between the openings leading to the respective reference electrodes.

None of the shifts in half-wave potential are great enough to interfere with qualitative applications. For quantitative applications, however, it is clear that very careful control is needed. It seems probable that the method of standard additions or, better, the use of a pilot ion would be required if results with smaller than about 3% error are desired. In the cases of both sodium tetraphenylboron and decaborane, removal of oxygen before the compound is dissolved and careful timing are both definitely required.

Magnesium perchlorate in 3-pentanone which are found to be a good electrolyte-solvent combination for sodium tetraphenylboron, should be very usable for compounds which undergo anodic reaction but whose insolubility in common polarographic solvents have prevented their determination by polarographic means.

Tetrabutylammonium perchlorate in 3-pentatone gives a good residual current voltage range of about -2.0 to +1.75 volts with the platinum rotating microelectrode. The large cathodic range obtainable in it is of importance since this electrode in aqueous solutions with potassium chloride is limited to about -1.0 volts. This increase in range in nonaqueous media is open for exploration.

FUTURE WORK

Concentration studies of free sulfur in 1-hexanol and benzil in 1-butanol should be made to see if I_d is proportional to concentration. Sodium trimethoxyborohydride should have a concentration study made at very dilute solutions to see if its wave height can be made to change to become proportional to concentration.

Further concentration studies of boron trifluoride in 1-butanol should be made and further comparisons made with acetanilide-boron trifluoride in order to elucidate the mechanism of the reaction. It may be possible that a great number of boron trifluoride complexes may be polarographically determined.

The shielding problem for the polarograph used with the oscillograph and the cathode follower problem should be given further attention, since if this high resistance polarography is to become useful commercially, it should be made available at a reasonable cost.

BIBLIOGRAPHY

(1) Allison, B., "Polarographic Studies of Lead in Methanol Solution", unpublished M.S. thesis, Oklahoma A. and M. College (1950)

(2) Arthur, P., and Lyons, H., Anal. Chem., 24, 1422-25 (1952)

(3) Bachman, G. B., and Astle, M. J., J. Am. Chem. Soc., 64, 1303 (1942)

(4) Bachman, G. B., and Astle, M. J., J. Am. Chem. Soc., 64, 2177 (1942)

(5) Bergman, I., and James, J. C., Trans. Faraday Soc., 48, 956-64 (1952)

(6) Bernard, M. Y., Compt. rend., 236, 2412-14 (1953)

(7) Bogan, S., Mietes, L., Peters, E., and Sturtevant, J. M., J. Am. Chem. Soc., 73, 1584 (1951)

(8) Bohdanecky, M., and Exner, J., Chem. Listy., 48, 1506-10 (1954)

(9) Brown, H. C., Schlesinger, H. I., Sheft, I., and Ritter, D. M., J. Am. Chem. Soc., 75, 192 (1953)

(10) Delimarshii, Y. K., and Abarbarchuk, I. L., Zavodskays Lab., 16, 929-32 (1950)

(11) De Vries, T., and Kroon, J. L., J. Am. Chem. Soc., 75, 2484 (1953)

(12) Edsberg, R. L., Eichlin, D., and Gavis, J. J., Anal. Chem. 25, 798 (1953)

(13) Gentry, C. H. R., Nature, 157, 469-80 (1946)

(14) Gilbert, G. A., and Rideal, E. K., Trans. Faraday Soc., 47, 396 (1951)

(15) Hall, M. E., Anal. Chem., 23, 1382 (1951)

(16) Hans, W., and von Sturm, F., Agew. Chem., 65, 693-7 (1953)

(17) Hans, W., and von Sturm, F., Z. Elektrochem., 57, 416-19 (1953)

(18) Heyrovsky, J., Chem. Listy., 16, 256 (1922)

(19) Heyrovsky, J., Phil. Mag., 45, 303 (1923)

(20) Heyrovsky, J., and Ilkovic, D., Coll. Czech. Chem. Commun., 7, 198 (1935)

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

(22) Hook, J. H., Letaw, H., Jr., and Gropp, A. H., J. Phys. Chem., 58, 81-3 (1954)

(23) Ilkovic, D., Coll. Czech. Chem. Commun., 6, 498 (1934)

(24) Ilkovic, D., J. chim. phys., 35, 129 (1938)

(25) Izmailov, N. A., Bezuglyi, V. D., Komissii, T., Anal. Khim., Nauk 4, (VII) 29-41 (1952)

(26) James, J. C., Trans. Faraday Soc., 47, 1240 (1951)

(27) Kangiesser, W., Kolloid-Z., 128, 27-31 (1952)

(28) Kemula, W., and Witwicky, J., Roczniki Chem. 28, 305-6 (1954)

(29) Kilichi, S., Sakagachi, Y., and Honda, H., Bull Chem. Soc., Japan, 25, 98-101 (1952)

(30) Kolthoff, I. M., and Lingane, J. J., Polarography, 2nd Edition, Interscience Publishers, New York, (1952)

(31) Kucera, G., Ann. Physic., 11, 529 (1903)

(32) Kuta, J., Chem. Listy., 48, 1493-8 (1954)

(33) Laitenin, H. A., J. Am. Chem. Soc., 64, 1765 (1942)

(34) Laitenin, H. A., and Nyman, C. J., J. Am. Chem. Soc., 70, 2241 (1948)

(35) Laitenin, H. A., and Shoemacher, C. E., J. Am. Chem. Soc., 72, 663 (1950)

(36) Letaw, Jr., and Gropp, A. H., J. Phys. Chem., 58, 81-3 (1954)

(37) Lewis, P. A., "Polarographic Behavior of Organo-Boron Compounds in Nonaqueous Solutions", unpublished Ph. D. thesis, Oklahoma A. and M. College (1956)

(38) Lewis, W. R., Quackenbush, F. W., and De Vries, T., Anal. Chem., 21, 762-5 (1949)

(39) Lindemann, R. F., "The Reaction of Sodium Borohydride with N-acylanilines", unpublished M. S. thesis, Oklahoma A. and M. College (1954)

(40) Lingane, J. J., and Small, L. A., J. Am. Chem. Soc., 22, 1169 (1950)

(41) Lingane, J. J., and Loveridge, B. A., J. Am. Chem. Soc., 72, 438 (1950)

(42) Lingane, J. J., Ind. Eng. Chem., Anal. Ed., 16, 147 (1944); ibid 18, 429 (1946); Anal. Chim. Acta., 2, 584 (1948)

(43) Lloyd, N. A., "A New Polarograph for use with High Resistance Nonaqueous Solutions", unpublished Ph. D. thesis, Oklahoma A. and M. College (1955)

(44) Luder, W. F., J. Am. Chem. Soc., 62, 93 (1940)

(45) McElroy, A. D., and Laitenin, H. A., J. Phys. Chem., 57, 564-7 (1953)

(46) Parks, T. D., and Hansen, K. A., Anal. Chem., 22, 2168 (1950)

(47) Reynolds, G. F., and Shalgosky, J. J., Anal. Chim. Acta., 10, 386-99 (1954)

(48) Riccoboni, L., and Popoff, P., Gass. chim. ital., 79, 573-87 (1949)

(49) Rulfs, C. L., and Elving, P. J., J. Am. Chem. Soc., 22, 1169 (1950)

(50) Runner, M. E., J. Am. Chem. Soc., 74, 3567 (1952)

(51) Strehlow, H., and von Stackelbert, M., Z. Elektrochem., 54, 51 (1950)

(52) Vecchi, E., Atti. Accad. maze. Lincei, Rend., Classe Sci. fis., Mat. e nat., 14, 290-3 (1953)

(53) Vlcek, A. A., Nature, 172, 861-2 (1953)

(54) Vlcek, A. A., Chem. Listy., 45, 258, 297, 377 (1951)

(55) Wawzonek, S., and Runner, M. E., J. Electrochem. Soc., 99, 457-9 (1952)

(56) Willits, C. O., Ricciuti, C., Knight, H. B., and Swern, D., Anal. Chem., 25, 785-90 (1952)

(57) Zan'ko, A. M., and Manusova, F. A., J. Gen. Chem., (USSR), 10, 1171 (1940)

(58) Zuman, P., Zumanova, R., and Soucek, B., Chem. Listy., 47, 178-81 (1953)

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