THE POLAROGRAPHIC BEHAVIOR OF BORON COMPOUNDS IN NONAQUEOUS SOLVENTS

By

PHILLIP ALBERT LEWIS

Bachelor of Science
Aurora College
Aurora, Illinois
1942

Master of Science
Oklahoma A. and M. College
Stillwater, Oklahoma
1954

Submitted to the faculty of the Graduate School of
the Oklahoma Agricultural and Mechanical College
in partial fulfillment of the requirements
for the degree of
DOCTOR OF PHILOSOPHY
May, 1956

THE POLAROGRAPHIC BEHAVIOR OF BORON COMPOUNDS IN NONAQUEOUS SOLVENTS

Thesis Approved:

Paul Arthur
Thesis Adviser

Earl H. Gilmore

Ernest M. Hodnett

Harrington

Robert MacVicar
Dean of the Graduate School

ACKNOWLEDGMENT

The author wishes to express his appreciation and gratitude for the guidance given by Dr. Paul Arthur, whose desk was not labeled in jest.

Thanks is also due the outside sponsor, whose name is withheld for security reasons, and the Oklahoma A. and M. Research Foundation, for the financial aid which made this project possible. The author also wishes to acknowledge his debt to the Messrs. Lloyd, Donahoo, Annino, Lindemann and Beaver for their generous cooperation with equipment and materials.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Concluded)

LIST OF TABLES

LIST OF ILLUSTRATIONS

INTRODUCTION

Historical

The foundation of polarography is usually attributed to Kucera (26), who investigated the electrocapillary behavior of mercury in various solvents, using the dropping mercury electrode (D.M.E.). Kucera noticed inflections in the resulting curves in the presence of reducible substances; but passed this phase of the work on to Jaroslav Heyrovsky, who found that the results could be applied to both quantitative and qualitative analyses.

By 1925, Heyrovsky and Shikata (17) had invented an automatic recording instrument, called the polarograph, and termed the new analytical method polarography. By 1935, Heyrovsky and Ilkovic (16) had explained the theoretical significance of the half-wave potentials and wave heights. Others who became interested in this field, worked on both theory and application with the result that polarography has steadily increased in interest and usefulness until it now ranks as a major instrumental method of analysis.

The standard polarograph consists of a stable direct current source, the potential of which can be varied, applied across a special type of electrolysis cell, (see Figure 1a). One of the electrodes of

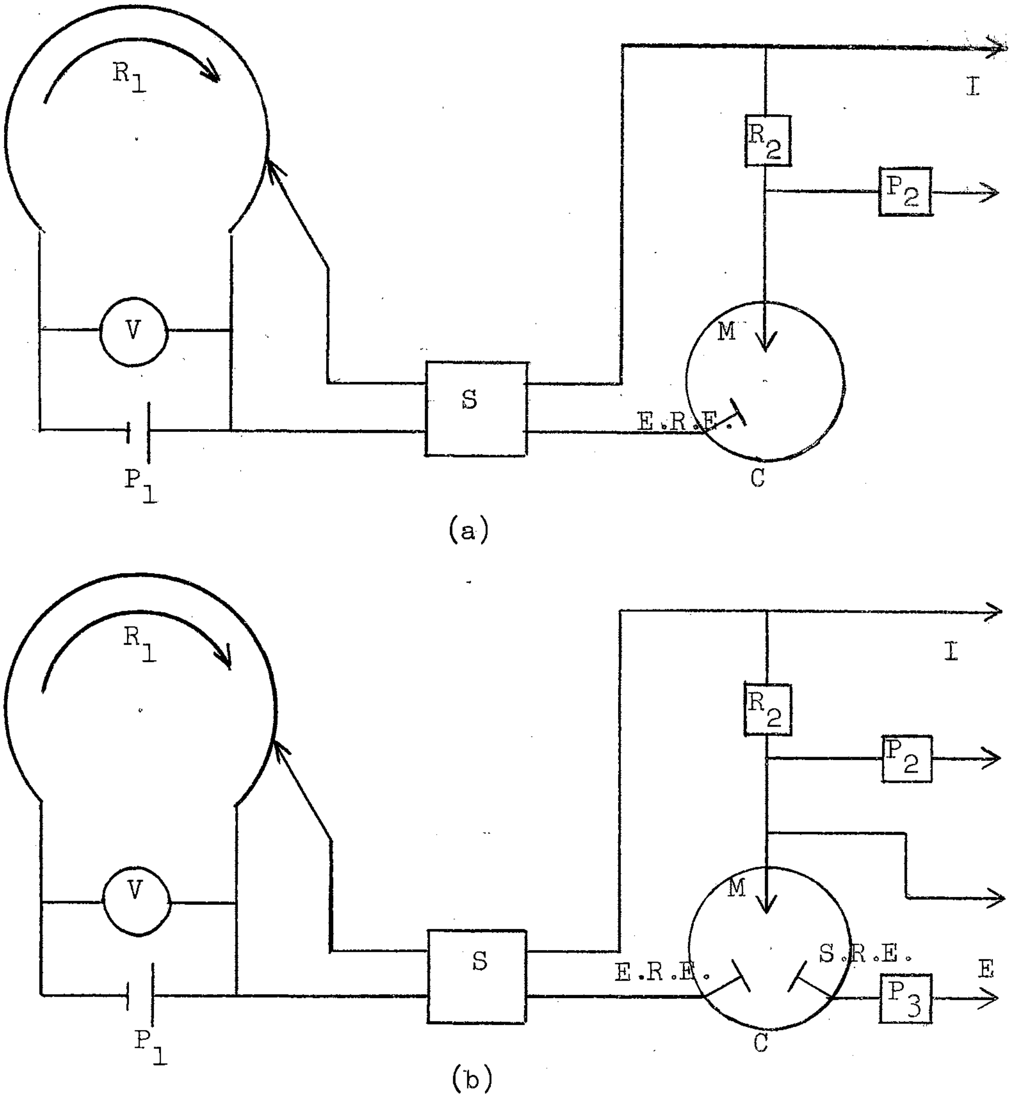

Figure 1.

(a) Schematic Diagram for Standard Polarographic Circuit

(b) Schematic Diagram for High-Resistance Polarographic Circuit

Legend

C - Electrolysis cell
E - To voltage-measuring device (Chart)
E.R.E. - Electrolysis reference electrode
S.R.E. - Stable reference electrode
I - To current-measuring device (Pen)
M - Microelectrode

P_1 - Applied potential
P_2 - Positioning control for pen circuit
P_3 - Positioning control for chart circuit
R_1 - Bridge
R_2 - Sensitivity control
S - Reversing switch
V - Voltmeter

this cell, the microelectrode, is very small and polarizable, while the other, the reference electrode, is large and non-polarizable. The applied potential is varied by means of a slide-wire potentiometer which may be coupled with a chart and driven by a constant-speed motor for automatic recording. A current-measuring device is also included in the circuit. For chart recording, this is a pen activated by the potential drop across a chosen standard resistor.

The most widely used microelectrode consists of the tiny drops of mercury formed by mercury flowing from a capillary tube. The mercury flows at a constant rate from a reservoir attached to, and at a fixed distance above, the capillary. Another form of microelectrode consists of a small piece of platinum wire embedded in an insulated shaft and rotated at a constant speed (27,30).

The non-polarizable electrode - the electrolysis reference electrode - is some suitable half-cell such as the saturated calomel electrode or even a quiet pool of mercury.

A typical polarogram is shown in Figure 2. As an increasing potential is applied across the electrolysis cell a small current, the residual current, flows. There are two contributing factors to the residual current when the microelectrode is the D.M.E., the major factor being the condenser current. Any electrolyte, especially any capillary-active electrolyte (one which reduces the interfacial tension between

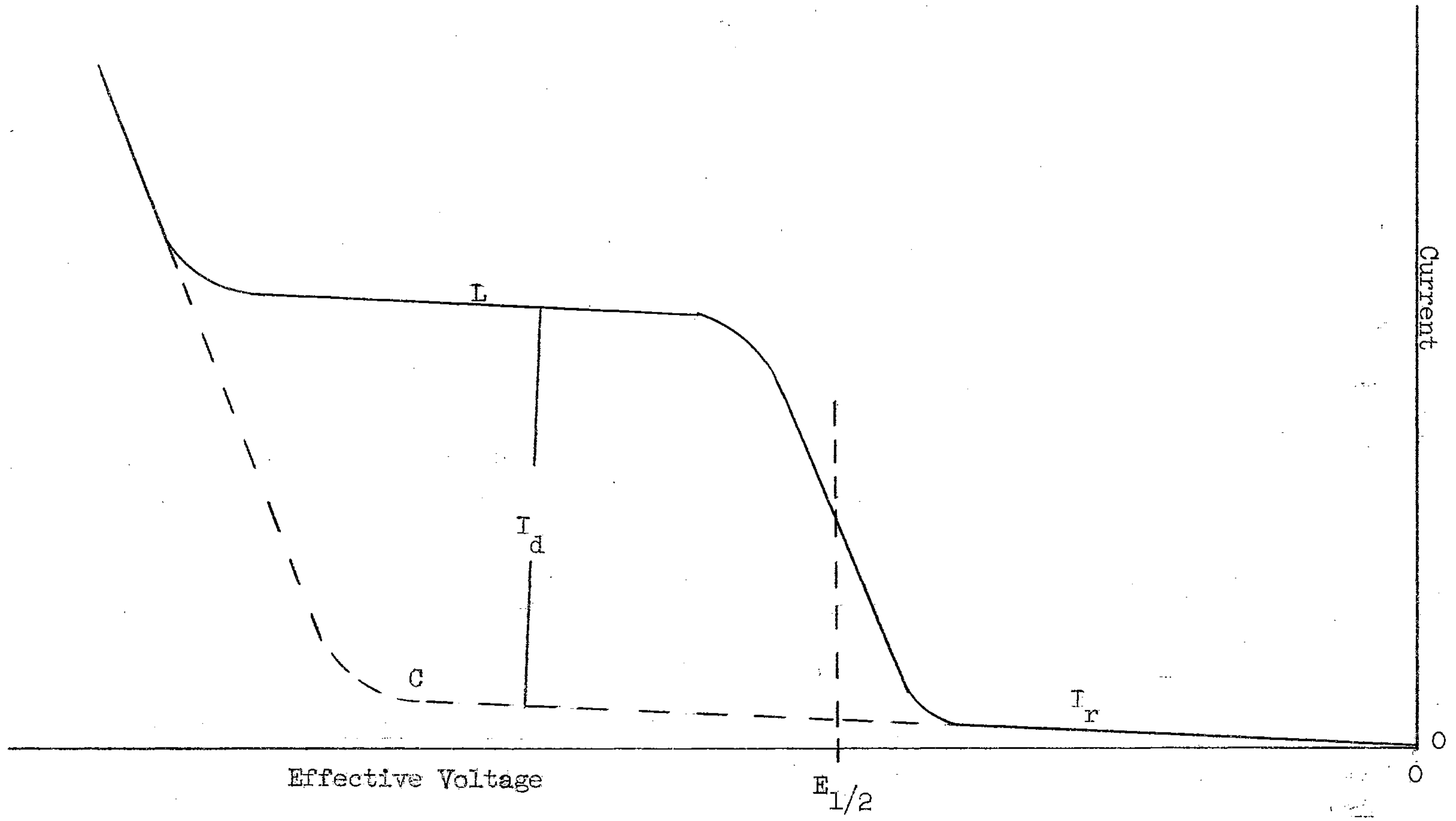

Figure 2. A Typical Polarogram

I_d - Diffusion current

I_r - Residual current

$E_{1/2}$ - Half-wave potential

C - Carrier curve

L - Limiting current line

mercury and the solution), sets up a double layer at the mercury-solution interface, resulting in an effective capacitance. Because of the constant growth and renewal of the mercury drops, the charging current does not drop to zero as it would for an ordinary condenser. Ilkovic (20) has both measured and calculated this effect, the magnitude of which is often as great as a few tenths of a microampere.

In practice, it is impossible to obtain solutions which are entirely free of traces of electro-reducible impurities. Reduction of these impurities, of which oxygen is the most troublesome, will add a small *faradaic* current as the second part of the residual current. Most of the dissolved oxygen is removed by bubbling nitrogen through the solution.

During the making of a polarogram, when the applied voltage reaches the decomposition potential of any electro-reducible substance present, reduction commences and the current begins to rise. As the voltage is increased, the rate of reduction and the current increase, while the solution immediately surrounding the microelectrode becomes depleted of reducible ions. The current very rapidly reaches a value which is limited by the rate at which the reducible substance can diffuse in to the electrode. This *limiting* current will thus consist of the residual current, which is still present, plus the *diffusion* current (I_d).

The rate at which the reducible ions reach the microelectrode normally depends upon both the concentration of the ions in solution and the rate of migration of the reducible ions. In polarography, however, the migration current is made negligible by adding a carrier electrolyte (sometimes called the indifferent or supporting electrolyte) at a concentration 50 to 100 times that of the reducible substance. The diffusion current is directly proportional to the concentration of the reducible substance in the solution, whether that substance be ionic or molecular. The migration current would never be an important factor in the limiting current of an uncharged reducible substance, unless an electric moment were easily induced in the molecule or the molecule possessed a permanent dipole. In the presence of a carrier electrolyte the migration current is so small that the limiting current can be assumed to be the sum of the residual and diffusion currents; and the magnitude of the latter can therefore readily be determined.

Ilkovic (19,21) and, later, MacGillavry and Rideal (37), have treated the problem of diffusion to the expanding spherical electrode (D.M.E.) mathematically and derived the equation for the resulting current. This is

$$i_t = 706nD^{1/2}Cm^{2/3}t^{1/6} \text{ microamperes}$$

where i_t is the current at any time "t" during the life of the drop

706 is a collection of constants - i.e., Faraday's constant, and area and volume constants

n is the number of electrons involved in the reduction

D is the diffusion coefficient of reducible substances in cm.^{2}/sec. (34)

C is the concentration of reducible substance in the body of the solution in mmoles/l.

m is the weight of mercury flowing from the capillary in mg./sec.

t is the time in seconds, or drop time for maximum current

The average current, defined as the constant current producing the same amount of electricity as the actual quantity produced by the drop, is

$$i_{av.} = 605nD^{1/2}Cm^{2/3}t^{1/6} \text{ microamperes}$$

The Ilkovic equation was derived assuming diffusion to a flat electrode surface, and so is not completely adequate for the small spheres of the D.M.E. Strehlow and von Stackelberg (55) and Lingane and Loveridge (33) corrected for this by the introduction of another constant, A , given the value of 17 by the former and 39 by the latter investigators. The corrected equation is

$$i_d = 607nD^{1/2}Cm^{2/3}t^{1/6}\left[1 + \frac{AD^{1/2}t^{1/6}}{m^{1/3}}\right] \text{ microamperes}$$

Most current-measuring devices are damped and so never register maximum current. For this reason, it is customary to measure the average current, although both are directly proportional to the concentration of the reducible substance.

The previous discussion and following remarks assume that the microelectrode is used as the cathode and the reaction taking place at the microelectrode is, therefore, a reduction. It should be understood, however, that the microelectrode may also be used as the anode, and that a suitable oxidation can be measured just as easily and with comparable results.

There is another capillary action which may take place if the concentration of reducible ion, through adsorption, becomes greater around the microelectrode than in the rest of the solution. Such adsorption results in a maximum in the limiting current which is neither predictable nor reproducible. This may be eliminated by addition of surface-active agents, such as gelatin, called maximum suppressors. Although it is concentration-dependent, there is no simple relationship between the height of the maximum and the concentration of the reducible substance (24).

Three types of product are possible in a polarographic reduction at the D.M.E. The product may be a solid soluble in mercury, a solid insoluble in mercury, or a substance which is soluble in the solution - e.g., an ion or a soluble molecule.

For the simplest case, in which the reduction product, usually a metal, is soluble in the mercury of the D.M.E., Heyrovsky and Ilkovic (16) have derived the equation for the polarographic wave. This is

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

where $\underline{E}_{de}$ is the potential of the dropping electrode

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

0.0591 is a constant at 25°C

$\underline{n}$ is the number of electrons involved in the reduction

$\underline{i}$ is the current at E_{de}

$\underline{i}_d$ is the diffusion current

This equation finds its greatest use in the calculation of "$\underline{n}$"; for the straight line obtained by plotting E_{de} vs. log (i/i_d-i) has a slope equal to 0.0591/n. Other factors remaining constant, for this case, $E_{1/2}$ is independent of the concentration of the reducible ion. This fact establishes the half-wave potential as a useful tool in qualitative analysis. The behavior of $\underline{E}_{1/2}$, and the calculation of "n", may also find use in postulating the mechanism of reactions.

The above equation also applies to the case where the reduction product is soluble in the solvent and is not, therefore, deposited at the microelectrode. It is strictly valid only when the original solution contains none of the reduction product.

For the case involving a product deposited on, but not soluble in, the mercury drop, the half-wave potential is given by:

$$E_{1/2} = E^{\circ}_{m} - \frac{0.0591}{n} \log \frac{k_s}{f_s} + \frac{0.0591}{n} \log \frac{i_d}{2} \text{ volts}$$

where E_m° is the standard potential of the solid metal

k_s is $605nD^{1/2}m^{2/3}t^{1/6}$ (Ilkovic equation)

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

$E_m^\circ - \frac{0.0591}{n} \log \frac{k_s}{f_s}$ is a constant when the temperature, the electrolyte environment, and the concentration of reducible material are constant. Furthermore, i_d is directly proportional to the concentration. Consequently, $E_{1/2}$, for this case, must vary with the concentration, although, as would be expected, the observed change is small.

The above equations should apply accurately only to reversible electrode reactions. These equations may not be used to test for reversibility entirely, however, since $E_{1/2}$ may be constant and the plot of E_{de} vs. $\log (i/i_d - i)$ may be a straight line for reactions which are not thermodynamically reversible. The simplest test of reversibility consists of tracing the polarographic wave cathodically, then retracing it anodically. The half-wave potentials should be identical (54).

Nonaqueous Polarography

All of the foregoing has been derived for, and largely applied to the study of aqueous solutions, with the instrument diagrammed in Figure 1a. It is obvious that a great many substances which should be easily oxidized or reduced are too insoluble to be studied in water, while others undergo hydrolysis too readily. When nonaqueous solutions are employed, the apparatus of Figure 1a is limited in application by the voltage drop across the electrolysis solution. This voltage drop is negligible if the resistance of the solution is less than 1000 ohms. For solutions of higher resistance, it is necessary to correct E_{de} for the IR drop through the solution; for the applied voltage then is no longer the effective voltage of the D.M.E. Maximum cell resistance for automatic recording instruments has been set at 4000 ohms by Lewis, Quackenbush and deVries (31) and at 8000 ohms by Arthur and Lyons (4). The latter find, also, that the D.M.E. must be kept far enough above the reference pool to avoid stirring of the solution by the drop, adding an additional practical limit to the method.

Despite these limitations, progress has been made using either mixtures of water and other solvents (42,57), or certain highly polar anhydrous solvents. Vitek (58) found the oxygen wave much larger in methanol than in water, and Allison (1) found removal of oxygen from the same solvent extremely important in obtaining good waves for lead. Several investigators have used ethanol with success (23,59). Hans and von Sturm (13,14) report good waves for $CuCl_2$ in 1-butanol and 1-pentanol.

Other anhydrous, nonaqueous solvents used with success include glacial acetic acid (4,5), the glycol ethers (43), liquid ammonia (39), and many more. All of these solvents give solutions of low resistance and provide, at best, only a beginning in the use of nonaqueous solvents.

An entirely new approach to nonaqueous polarography has been provided by Arthur and Lloyd (35) with the development of the instrument diagrammed in Figure 1b. The basic differences between this high resistance polarograph and the conventional polarograph of Figure 1a are (a) the addition of a second anode (the stable reference electrode, S.R.E.), and (b) the use of a recorder which measures both the current and the effective voltage of the cathode. The electrolysis reference electrode (E.R.E.) functions as before, and may be a quiet pool of mercury or other reference electrode, and the current-measuring circuit is also conventional. The effective voltage, however, is measured between the D.M.E. and the S.R.E., the recorder circuit being so designed as to draw essentially no current. The electrolysis current may thus be plotted as a function of the effective voltage and the IR drop through the solution is of no significance. This instrument was designed by Arthur and thoroughly tested by Lloyd (35), with good results. Included among the solvents tested were the alcohols, through 1-octanol, which gave cell resistances as great as 500,000 ohms.

Boron Compounds

Some boron compounds have been known and used from antiquity, but recent, intensive work in this field has resulted in a need for new methods for the analysis of such compounds. Little has been done polarographically. For those boron compounds for which water can be used as a solvent, good analytical procedures are already available; for the others, the polarograph in its conventional form has been inadequate. Development of the high-resistance instrument, however, should make polarography a useful tool in the analysis of boron compounds. The following systematic survey of the compounds of boron, using the Sidgwick classification (51), can be used as a guide to the possible applications of the new polarograph.

(1) Boron Hydrides and Derivatives. Of the simple boron hydrides, the non-volatile compounds are not available in pure form. Of the volatile compounds, decaborane is the only solid and the only one that can be handled easily.

There are many derivatives of the boron hydrides, but the addition compounds could probably best be studied as the component parts. The RBH_2 group shows singular instability. Tetramethyl borane and diethyl borane are solids, but the chemical properties are little known. Among the nitrogen derivatives, the ammonium salts and the tertiary ammines, both aliphatic and aromatic, are solid and stable; although the amines and imines are not. Triborine triamine, "inorganic benzene", is a stable solid with numerous addition derivatives but not much promise for oxidation-reduction reactions. The ether addition compounds, while solids, decompose so easily that either is a common solvent for other preparations. The boron alkyl oxides are unstable, volatile liquids.

Boric acid and the borates are reported as not polarographically active (10), but a typical hypoborate, $KOBH_3$, is a stable solid and a strong reducing agent. The hypoborates and sub-borates are intermediates in the hydrolysis of borane derivatives to boric acid or alkyl boric acids.

One mention of borates in connection with polarography is not promising. Elving and Callahan (11) studied the polarographic behavior of thenoyl trifluoroacetone in a series of buffers, obtaining two waves in chloride, acetate and ammonia solutions, but only one wave in the borate buffer. They postulated formation of a four-membered ring including polarographically-inactive bonds between boron and the two hydroxyl group oxygens. This would make the borates, boric oxide, and the boric acids poor prospects for polarographic investigation.

A wide variety of halogen derivatives is available, but all are unstable.

The borohydrides are the most promising boron compounds for polarographic study. At least one, $NaBH_4$, is commercially available and readily purified (32) and is finding increasing use as a reducing agent. It hydrolyzes in water and reacts with acetone and methanol, the latter reaction apparently being quantitative when the reactants are mixed in stoichiometric proportions (48). Despite obvious difficulties, polarographic studies of $NaBH_4$ have been made in aqueous solution. Marshall and Widing (38) report two anodic waves, with half-wave potentials at -0.15 volts and -0.64 volts vs. the S.C.E. in a buffer of pH 10. Pecsok (44) reports a single anodic wave at pH 9, the reaction being irreversible, and involving eight electrons. This investigator used this information to postulate the mechanism of the hydrolysis and to calculate the standard E.M.F. of the half-cell reaction involving oxidation of sodium borohydride to sodium borate. Pecsok's calculations gave a value of 1.23 volts as compared to a previously reported value of 1.37 volts (40). Both polarographic studies report that hydrolysis is so rapid in more acidic solutions that the polarograms obtained are meaningless.

(2) Metallic Borides. There seems to be no point in studying the polarographic behavior of these compounds in nonaqueous solvents because of their low solubilities and complex compositions.

(3) Boron-Carbon Bond Compounds. Owing to its insolubility, boron carbide would be of no interest for this study; however, there are many alkyl and aryl compounds and derivatives that are more promising. The trialkyl compounds are all gases or liquids. The triaryl compounds, on the other hand, are all solids, are not so easily flammable, and are quite stable. Water does not react with either class, although alcohols yield esters. They will also add the alkali metals. All are sensitive to oxidizing agents; and under controlled conditions the three alkyl or aryl groups may be removed stepwise, yielding a series of boric acids and oxides. The diaryl acids, salts, esters and anhydrides, again, are solids, insoluble in water, but soluble in organic solvents. There are certain striking differences in chemical behavior between the monoalkyls and monoaryls, plus the fact that both include stable solids insoluble in water, which would indicate that these classes should be investigated separately.

Some alkyl and aryl boron halides are known and a few of these are solids, but they have not been studied extensively. The boron triaryls will dissolve alkali metals in ether solution giving products which are extremely sensitive to oxidation.

(4) <u>Boron-Nitrogen Bond Compounds</u>. The compounds in which boron is bonded only to nitrogen are prepared by the reaction of ammonia and its derivatives with the boron halides or boron sulfide. The first product is an amine, which on heating, changes first to an imine and finally to boron nitride, the latter being inert chemically. Many derivatives of the boron amines have been prepared. Only the aryls exist as solids, however, and these are stable only when dry.

(5) <u>Boron-Oxygen Bond Compounds</u>. Boric oxide, the boric acids, the metallic borates, the borotungstates and the fluoroboric acids are of no particular interest at this time. Alkyl esters are readily formed by the reaction of boric acid or oxide with the appropriate alcohol and are as readily hydrolyzed by water. The polyalcohols form some stable chelate compounds; and there are stable esters of inorganic acids and organic anhydrides. The latter, however, hydrolyze in water and are insoluble in organic solvents.

(6) <u>Boron Sulfides</u>. There seems to be no reason to investigate the boron sulfide derivatives polarographically in nonaqueous solvents. The existence of only one boron sulfide has been proved and the derivatives are few and of little interest.

(7) <u>Boron Halides</u>. The boron halides, as such, with their well-known properties, would be of little interest here. No simple oxyhalides

have been prepared, but the mono- and di-halogen oxyhalide series are known, with the usual violence of boron trifluoride plus alcohol curiously controlled and even resulting in some stable solids.

(8) Boron Complexes. It is difficult to separate the complexes from the various classes of boron compounds discussed previously, but one of the most interesting and useful chemical characteristics of boron is its ability to form a large number of stable complex ions and compounds by gaining two electrons. The metal borohydrides, for instance, include the BH_4^- ion (see Section 1). There are also stable, solid, metal tetraaryl borates, but apparently the tetraalkyl derivatives exist only in solution.

The strongest electron donor of all in coordination with boron is nitrogen. Boron forms complexes with nearly all ammines, especially the tertiary amine derivatives. These decrease in stability in this order: boron hydrides, trifluorides, triaryls, trialkyls, trichlorides and esters, with the latter almost non-existent. The trifluoride, triaryl and trialkyl ammines are stable to air oxidation in contrast with the parent boron compounds, and most of them are solids.

The cyanides, organic nitriles, phosphine and arsine will coordinate to some extent with the boron halides.

The boron trihalides form crystalline complexes readily with ethers, as well as with aldehydes, ketones and hydroxyl compounds. The trialkyl and triaryl boron compounds form complexes only with the hydroxyl and alkyloxy groups. The stable chelate compounds of boron have the ring joined through two oxygen atoms.

Complex halides are confined mostly to the fluoride derivatives, which are numerous and stable. Boron triaryls coordinate with alkaline fluorides and there are many aryl borofluorides. The tetrafluoroborate anion is well known and very stable. The corresponding chlorides are known only in the case of the acyl derivatives.

SCOPE OF RESEARCH

Two circumstances combined to guide this project. The first was the development, in this laboratory, of a polarograph capable of use with solutions of very high resistance. To take full advantage of this new instrument, a series of compounds, not suitable for analysis by the usual commercial polarographs, was needed for investigation.

The second circumstance was the rapid growth of interest in boron chemistry in connection with national defense. Many of the boron compounds of greatest interest are not soluble in water or other highly polar solvents, and a large number of those which are soluble in water undergo reactions in aqueous solution that make polarographic analysis impractical. It was decided, therefore, to employ the new polarograph in a study of the behavior of certain boron compounds in nonaqueous solvents. Since the field was wide open, choice of individual compounds for investigation was dictated by solubility, stability and availability.

One of the first problems encountered, naturally, was that of finding suitable solvents and supporting electrolytes. In order to facilitate selection of solvent systems for future work, the conductivities of solvent carrier solutions were measured to see if this could be used as a criterion of their probable usefulness.

EQUIPMENT AND MATERIALS

Polarographs

The polarograph used for the major part of this work was designed by Dr. Paul Arthur and built in this laboratory (35). Because the instrument employs some principles not found in the standard polarographs, and because the designing, building, and testing of the instrument were partially concurrent with the work reported in this study, the description will be rather detailed.

Figure 1b shows the essential circuit diagram and Figure 3 is the complete wiring diagram. The span voltage is supplied to the bridge by B_1 and controlled by S_1 and P_1 . B_2, with S_2 and S_3 (reversing switches) and P_2 , supply the preset voltage to the bridge and provide a means for starting the polarogram at any desired potential. S_4 is the microelectrode reversing switch, operated in conjunction with S_7, which reverses the polarity of C, the electrolytic damping condenser. The amount of damping is controlled by S_{10}.

The chart is calibrated by means of S_6 and the two standard cells (S.C.). S_6 is shown in the operating position, with the calibration circuit eliminated. The other positions apply zero potential (absolute zero) or, selectively, the voltage from one or both standard cells across the input to the cathode follower (C.F.).

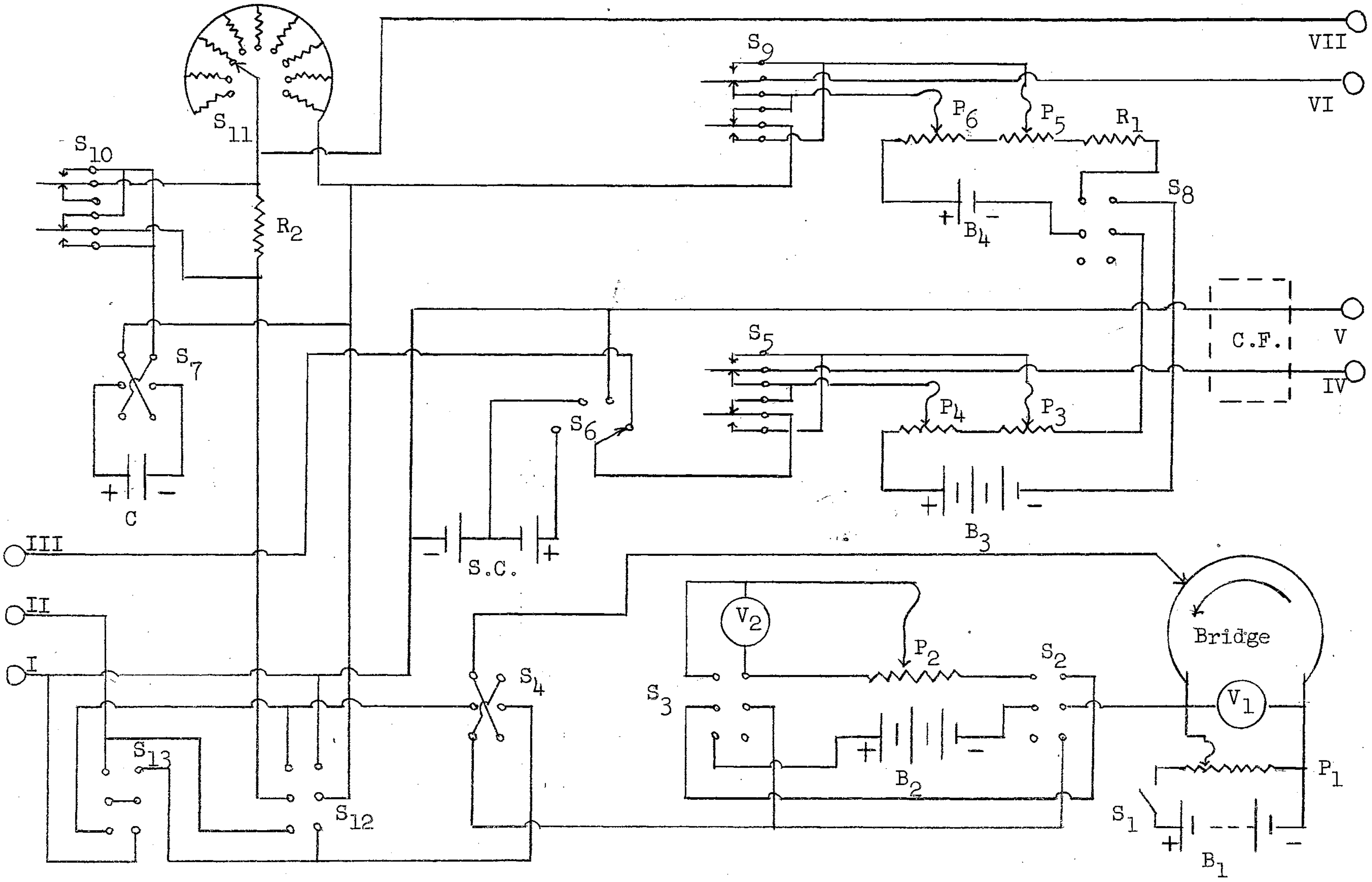

Figure 3. High-resistance Polarograph Circuit

Legend for Figure 3

I	Lead to microelectrode (M)
II	Lead to electrolysis reference electrode (E.R.E.)
III	Lead to stable reference electrode (S.R.E.)
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 desired
B_2	Two or three Burgess 1-1/2-volt batteries, in series
B_3	Two or three Burgess 1-1/2-volt batteries, in series
B_4	One Burgess #4F 1-1/2-volt battery
C	Condenser, Mallory, #WP041, 2000 mfd., electrolytic
C.F.	Cathode follower, high impedance (see Figure 4)
P_1	Potentiometer, wire-wound, 4 watt, 100 ohms
P_2	Potentiometer, wire-wound, 4 watt, 550 ohms
P_3	Potentiometer, wire-wound, 4 watt, 25,000 ohms
P_4	Potentiometer, wire-wound, 4 watt, 400 ohms
P_5	Potentiometer, wire-wound, 4 watt, 100 ohms
P_6	Potentiometer, wire-wound, 4 watt, 2 ohms
R_1	Resistor, Continental, carbon, X-type, precision, 30,000 ohms
R_2	Resistor, IRC type WW4J, wire-wound, 1%,1000 ohms
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, #3036L, 3 position, locking type switches
S_6	Ohmite power tap, Model III, 11 contact switch
S_{11}	Ohmite power tap, Model III, 11 contact switch with the following resistors attached, as shown, in counter-clockwise order:
R_3	Resistor, IRC, type WW4J, wire-wound, 1%, 5000 ohms
R_4	Resistor, IRC, type WW4J, wire-wound, 1%, 2000 ohms
R_5	Resistor, IRC, type WW4J, wire-wound, 1%, 1000 ohms
R_6	Resistor, IRC, type WW4J, wire-wound, 1%, 500 ohms
R_7	Resistor, IRC, type WW4J, wire-wound, 1%, 200 ohms
R_8	Resistor, IRC, type WW4J, wire-wound, 1%, 100 ohms
R_9	Resistor, IRC, type WW4J, wire-wound, 1%, 50 ohms
R_{10}	Resistor, IRC, type WW4J, wire-wound, 1%, 20 ohms
R_{11}	Resistor, IRC, type WW4J, wire-wound, 1%, 10 ohms

Positioning of the polarogram on the chart is done through the pen and chart upscale controls. Both controls go through $\underline{S}_8$. $\underline{B}_3$, $\underline{P}_3$ and $\underline{P}_4$ control the chart upscale, with $\underline{S}_5$ the reversing switch. $\underline{B}_4$, $\underline{P}_5$, $\underline{P}_6$ and $\underline{S}_9$ are the corresponding pen upscale controls.

Current sensitivity is controlled by $\underline{S}_{11}$. The pen circuit of the recorder is a voltage-measuring device; consequently, to obtain a pen recording proportional to the current, it is necessary to connect the pen circuit so it will measure the IR drop across a fixed known resistance. $\underline{S}_{11}$ provides a number of such fixed resistances, hence, a wide range of current sensitivities.

$\underline{S}_{12}$ and $\underline{S}_{13}$ are incorporated in the circuit as a means of putting the current-measuring resistors of $\underline{S}_{11}$ into either the microelectrode circuit or the electrolysis reference electrode circuit. These switches were not needed in this work.

The recorder used was the Minneapolis-Honeywell Brown Function Plotter, Model No. Y153X32(VV)-X-120(V), commonly known as the X-Y recorder. The pen range is 0 to 2.5 millivolts and the chart range 0 to 3 volts over 10 inches. Also specified for this use were the requirements that the chart circuit operate on an input impedance of 0.1 megohms and that of the pen on an input impedance of 1000 ohms. The chart paper used was the Brown Instrument No. 5873-NR. The speeds of both the pen and the chart movements were 4.5 seconds full scale.

The pen movement is proportional to the current (see above), as usual. The chart movement, however, is proportional to the effective voltage as measured between the microelectrode and the stable reference electrode, the chart moving forward and backward as the voltage increases and decreases. This differs from the action of the standard strip-chart recorders used on commercial polarographs, which have a constant-speed chart drive motor synchronized with the bridge drive to give a chart movement proportional to the applied voltage. To avoid IR drop in the chart circuit of the X-Y recorder, the input impedance of the recorder must be much greater than the resistance of the cell circuit. Since some cell resistances were as high as 0.5 megohm, the cathode follower had to be included in the circuit.

The cathode follower and power supply are shown in Figure 4, with the Sola constant-voltage transformer necessary to smooth out the line voltage. $\underline{P}_3$ is used to adjust the A.C. heater voltage for $\underline{V}_2$ to 2.9 volts. With a 1 megohm fixed carbon resistor across the input, the input and output of the cathode follower are set to minimum voltage by adjusting $\underline{P}_1$ (controlling the B+) and $\underline{P}_2$ (controlling the grid bias). The optimum operating values were approximately 40 volts and -13 volts, respectively. Very careful adjustment is necessary to achieve the rated 100 megohm input impedance of the cathode follower, but the IR drop through the input of the cathode follower - i.e., the chart circuit - is then negligible.

Due to the sensitivity of the instrument, all electrical leads were of shielded cable. The polarograph and all other pieces of

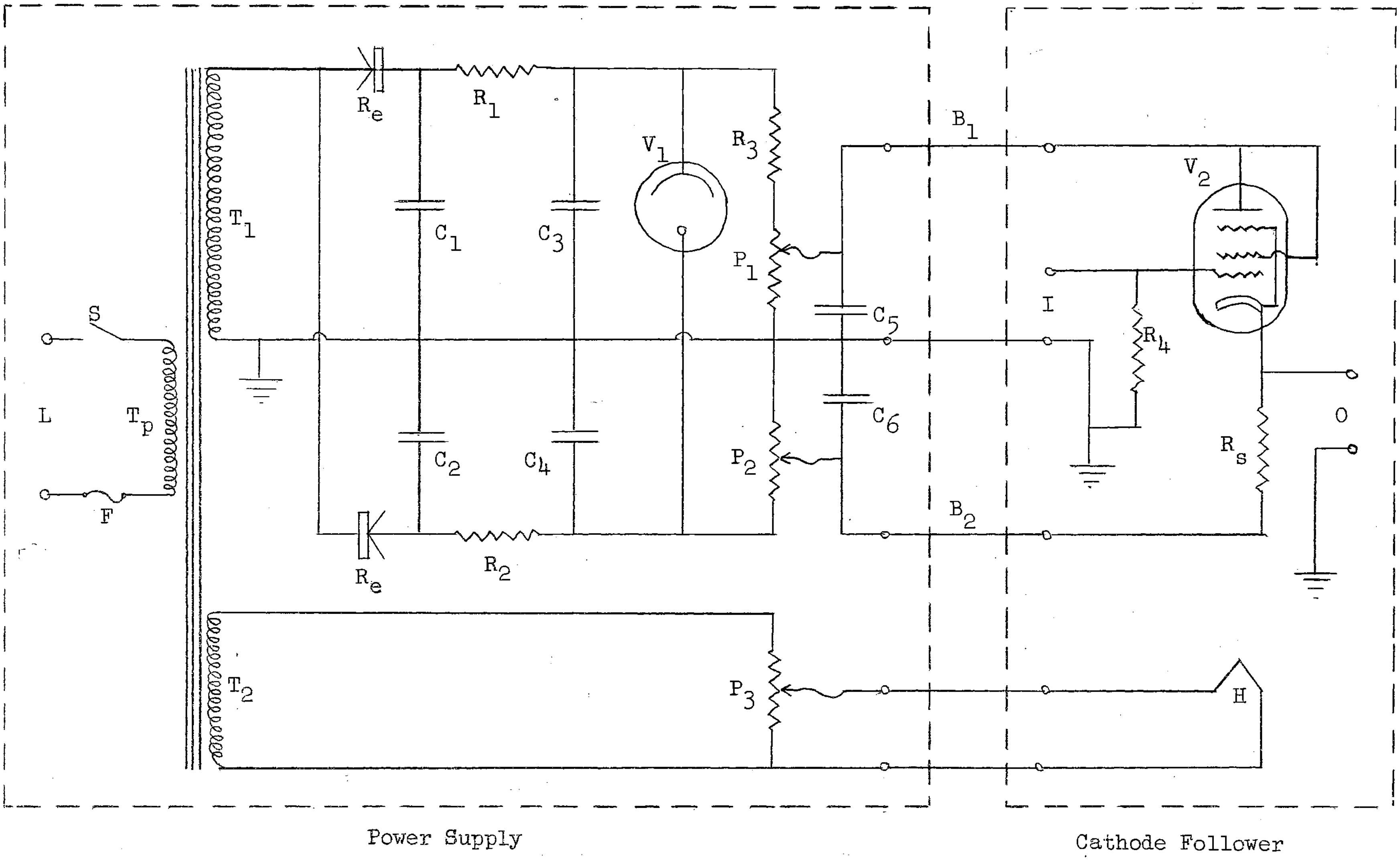

Figure 4. Cathode Follower and Power Supply

Legend for Figure 4

B_1	Plate supply for V_2
B_2	Negative bias for V_2
C_1 and C_2	Condenser, 20 microfarad, electrolytic, 150 volts D.C.
C_3 and C_4	Condenser, 0.01 microfarad, 50 volts, D. C.
C_5 and C_6	Condenser, 10 microfarad, electrolytic, 150 volts D. C.
F	Fuse
G	Ground line
H	Heater supply for V_2
I	Input to cathode follower
L	110 volt A. C. line input
O	Cathode follower output
P_1	Potentiometer, wire-wound, 25,000 ohms
P_2	Potentiometer, wire-wound, 50,000 ohms
P_3	Potentiometer, wire-wound, 250 ohms
R_1	Resistor, 5 watt, 5,000 ohms
R_2	Resistor, 5 watt, 5,000 ohms
R_3	Resistor, fixed carbon, 22,000 ohms
R_4	Resistor, fixed carbon, 100 megohms
R_5	Resistor, fixed carbon, 10,000 ohms
R_e	Selenium rectifier, 100 milliamperes, D. C.
S	Line switch
T_p	Power transformer, primary
T_1	Power transformer, secondary, 100 volts
T_2	Power transformer, secondary, 6.3 volts
V_1	Voltage regulator tube, OB2
V_2	Power pentode tube, 6AK5

electrical equipment possible in the room were grounded, with separate ground wires where needed. Kerosene was used in the constant-temperature bath (for the cell) to minimize conductance. In spite of this precaution, lightning produced pips on the polarographic waves when the instrument was operated during a thunderstorm.

In making cathodic waves the potentials move the chart down (i.e., the line representing voltage increase moves up) and the pen (current) to the right. In making anodic waves, the chart and pen are first moved upscale as far as possible and the voltage and current-measuring potentials then oppose the upscale potentials. Thus, the anodic waves are traced toward the bottom (voltage) and left (current). This difference has been retained in the figures to follow.

Some preliminary work was done on a Sargent Polarograph Model No. XXI, using a Brown Potentiometer Model No. Y153X12V-X-30AKN4(V) as the recorder.

Cell and Electrodes

The "Double-H" polarographic cell was used for all work with organic solvents (see Figure 5). The reference cells are the acetone saturated calomel (A.S.C.E.) type. The bottom layer is mercury; the next layer is a mercury-mercurous chloride-lithium chloride-acetone paste. On top of this paste is a thin layer of lithium chloride, and acetone saturated with lithium chloride and mercurous chloride is the electrolyte solution.

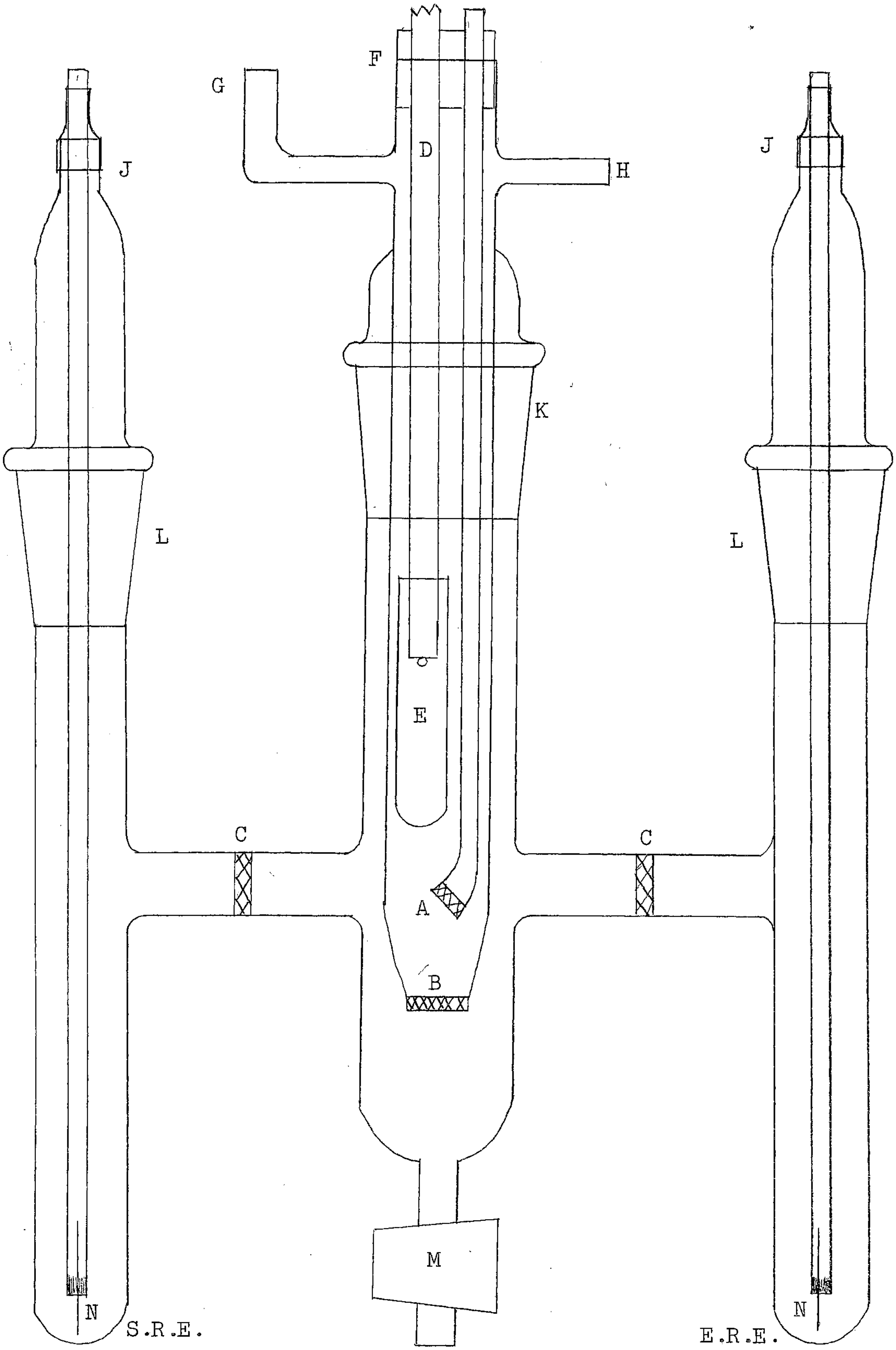

Figure 5. "Double-H" Polarographic Cell

Legend for Figure 5

A	Gas dispersion tube with fritted disc, 10M
B	Fritted disc, 10M
C	Sealing tubes, straight, with fritted disc, 10M
D	Dropping mercury electrode
E	Small test tube to collect mercury from D.M.E.
F	Rubber stopper
G	Solution inlet tube
H	Nitrogen inlet tube
J	Rubber tubing, surgical, seal
K	Standard taper joint, 29/42
L	Standard taper joint, 19/38
M	Stopcock, straight bore, No. 2
N	Platinum wire contact

A platinum wire, sealed into three millimeter soft glass tubing, dips into the mercury layer to make contact. Contact between the platinum and the external copper lead is made by means of Wood's metal. Evaporation of the acetone is minimized by use of the standard taper joint and the surgical rubber tubing seal where the tubing containing the contact wire enters at the top (J).

Marine barometer tubing, available from the Corning Glass Works, Corning, N.Y., was used for the dropping mercury electrode. The microelectrodes were selected to give a drop time of three to six seconds, the longer period being found most desirable. Since each solvent used had a different effect on the dropping characteristics of the D.M.E., it was necessary to use a separate electrode for each solvent and adjust the drop time accordingly. For ease of operation, the detachable D.M.E. developed by Lloyd (35) was adopted.

Although most of the work was done with the D.M.E., some exploratory work was done using the rotating platinum electrode described by Lewis (30), with the platinum wire sealed in soft glass tubing. The usual steel shaft covered with ceresin wax could not be employed, because the wax becomes soft in organic solvents. The glass tubing was cemented to the rotating shaft and contact made by means of copper wire and mercury. Because of the size of the electrode, the "Double-H" cell was used without the inner jacket.

Conductance and Resistance Measuring Apparatus

The conductance cell used was the vertical pipette type, with one centimeter plates two centimeters apart. The cell constant, determined from a series of standard potassium chloride solutions, was 0.6843. Due to the nature of the solutions used, the platinum plates were not coated with platinum black. All measurements were made at 25 ±0.1°C., with the cell immersed in a kerosene bath.

Resistances were determined with a Luder bridge (36). Because the need was for wide range rather than great accuracy, the variable resistance box shown in Figure 6 was constructed. This was used as the variable resistance for the Luder bridge, the connections being made at terminals III and IV. The appropriate resistance range was selected, using $\underline{S}_2$ and $\underline{S}_3$, and the cell (conductivity or electrolysis) resistance was balanced. The resistance box was then disconnected from the Luder bridge and connected across a potentiometer. With the battery turned on at $\underline{S}_1$, the ratio of the potentials across the fixed resistance, $\underline{R}_4$ (at VI and VIII), and across $\underline{R}_4$ plus the variable resistance (at VI and VII) could be used to calculate the variable resistance.

The above potentials were measured using a Gray Instrument Co. No. 9244 potentiometer with a Leeds and Northrup galvanometer. The potentiometer was calibrated against a standard cell obtained from The Eppley Laboratories, Inc.

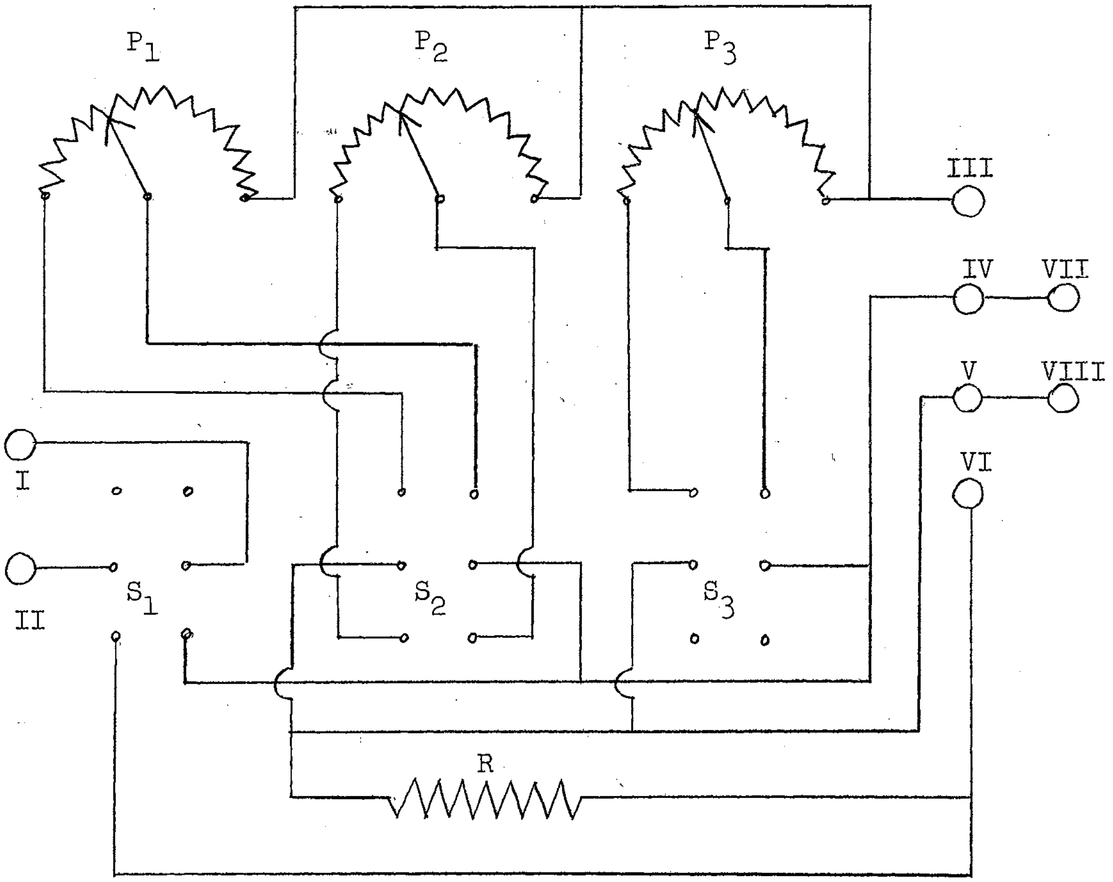

Figure 6.

Variable Resistance for Conductance Bridge

Legend

I	Positive lead to Burgess #4F 1-1/2 volt battery
II	Negative lead to battery connected at I
III	Positive lead for potentiometer measurement
IV	Positive lead for variable resistance measurement
V	Positive lead for fixed resistance measurement
VI	Negative lead for resistance measurements
VII	Variable resistance for conductance bridge
VIII	Variable resistance for conductance bridge
P_1	Potentiometer, 1.0 megohm, carbon
P_2	Potentiometer, 0.1 megohm, carbon
P_3	Potentiometer, 0.01 megohm, carbon
R	Resistor, IRC, Type WW4J, wire-wound, 1%, 100,000 ohms
S_1, S_2 and S_3	DPDT toggle switches, center off

The polarograph was calibrated using the potentiometer as a voltage source, with known resistances in place of the electrolysis and reference cells.

Reagents

The following reagents were used:

Acetone. A. S. Aloe reagent grade was used after drying over anhydrous potassium carbonate and distillation from fresh anhydrous potassium carbonate.

Acetanilide-boron trifluoride. This was furnished by Donahoo and Annino of these laboratories who had prepared the compound by the method of Muetterties and Rochow (41).

1-Butanol. Merck analytical reagent grade was used after drying over anhydrous potassium carbonate and distillation from potassium hydroxide pellets.

n-Butyl ether. Matheson, Coleman and Bell C.P. grade was used after drying over sodium wire and distillation from fresh sodium wire.

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

2-Chlorovinyl boric acid. This was prepared by the method of Arnold (2,3).

Decaborane. This was supplied by a source which, for security reasons, may not be disclosed. It was prepared by the method of Laubengayer and Bottei (28) and was used without further purification.

Ethyl ether. Mallinckrodt purified grade was used after drying over sodium wire and distillation from fresh sodium wire.

Hydrogen chloride. This was prepared by dropping sulfuric acid on sodium chloride and was dried by passing it over Hydralo.

Isobutylene. Matheson C.P. grade was used without further purification.

Isopropyl ether. Matheson, Coleman and Bell C.P. grade was used after drying over sodium wire and distillation from fresh sodium wire.

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

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

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

Methanol. A. S. Aloe reagent grade was used after drying over anhydrous potassium carbonate and distillation from fresh anhydrous potassium carbonate.

Methyl borate. This was prepared by the method of Schlesinger, et. al. (49).

2-Methyl-1-propenyl boronic acid. This was prepared by the method of Braude and Timmons (8) as modified by Letsinger and Skoog (29). The starting material was isobutylene.

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

Phenyl boric oxide. This was furnished by Donahoo and Annino, who prepared it by the reaction of the appropriate Grignard reagent with methyl borate.

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

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

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

Pyridine borine. This was furnished by the source mentioned earlier and was used without further purification.

Pyrogallic acid. Merck U.S.P. grade was used without further purification.

Sodium borohydride. Metal Hydrides technical grade was purified by the method of Lindemann (32).

Sodium chloride. Mallinckrodt analytical reagent grade was used without further purification.

Sodium tetramethoxyborohydride. This was prepared by the method of Schlesinger, et. al. (48).

Sodium tetraphenyl borate. This was furnished by the source mentioned earlier. Analysis showed 3.14% boron and 81.0% carbon, with the theoretical composition 3.16% boron and 84.1% carbon. It was used without further purification.

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

Sulfuric acid. A. S. Aloe C.P. reagent was used without further purification.

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

Tetramethylammonium chloride. Matheson practical grade was used after recrystallizing three times from benzene.

Tri-α-naphthylboron. This was furnished by Donahoo and Annino who prepared it by the method of Brown and Sujishi (9).

All distillations of organic reagents were carried out using a three-ball Snyder column. All parts were glass, with standard taper ground-glass joint connections.

EXPERIMENTATION AND DISCUSSION

Polarographic Cell

The use of glass frits in connection with the junction between the acetone saturated calomel electrode (A.S.C.E.) and the electrolysis cell (see Figure 5) caused some concern in the first stages of the experimental work. Evidence that the electrolyte solution from the reference cells did not enter the electrolysis section was obtained in the following manner: A solution of 1-butanol saturated with lithium chloride was used as the electrolyte and a polarogram was made. Several drops of acetone saturated with lithium chloride and mercurous chloride were added to the solution and the run repeated. The type of erraticity found in the resulting polarogram was not encountered in any other operation, and the amount of leakage through the frit could therefore be considered insignificant.

Solvents and Carriers

There is little precedence for selection of solvents and carriers for high-resistance polarographic work. The chemical nature of the boron compounds of interest precluded use of any organic solvent-water mixtures; and the availability of the new high-resistance polarograph afforded the opportunity of at least trying some entirely new polarographic solvents.

Methanol and ethanol are well known as solvents (24), and even 1-butanol has been used successfully as a solvent (13). Ethylene glycol (12), glycol ethers and Cellosolve have been found useful, but dioxane has not (43). In the light of the above information, the study was started from another viewpoint. The most promising solvents for boron compounds, from the standpoint of solute stability, solute solubility, solvent volatility, and possible solution conductivity, were selected. First, n-butyl ether, isopropyl ether, and, finally, ethyl ether, were tried; then 1-butanol, methanol and 3-pentanone.

It is impossible to separate the problems of suitable solvent and suitable carrier, but with the solvents selected, the type of carrier is limited. Lithium chloride, tetramethylammonium chloride, tetra-n-butylammonium iodide and anhydrous hydrogen chloride have often been used (15, 16, 58), and cetyldimethylethylammonium bromide might well present some advantage through the increased solubility induced by the presence of the cetyl group.

When it became apparent that some combinations were suitable and others were not, it was felt that a guide to the prospective usefulness of a solvent and/or carrier might be obtained by determination of conductivities. Although the number of combinations tried in this study was hardly large enough to make unequivocal predictions, the results should be of use in the future in evaluating prospective carrier solutions. The conductivities reported (see Table I) are intended to show an order of magnitude only.

Electrolysis cell resistances should furnish the same kind of information, especially (as in this case) where the same cell is used throughout. Cell resistances reported (see Table II) are an average of the resistances measured between the microelectrode and the respective reference electrodes. These values never differed by more than 10%, and were usually much closer.

Some important characteristics of the solvents considered are as follows:

n-Butyl ether. Saturated solutions of the carriers were used because none of them were soluble to the extent of 0.1 M. All solutions were run at maximum sensitivity, and with the applied voltage high enough (up to 20 volts) to register the maximum effective voltage on the chart. All were run cathodically; and the saturated tetra-n-butylammonium iodide solution was run anodically. There was no evidence of a carrier wave in any case.

Isopropyl ether. The same procedure was used, with identical results (as in the case of the n-butyl ether). In addition, the tetramethylammonium chloride and tetra-n-butylammonium iodide solutions were saturated with sulfur and cathodic runs were made. There was no evidence of either a sulfur or a carrier wave in any case.

Table I

Conductances of Solvents and Carrier Solutions

Solvent	Carrier*		Specific Conductance
	Nature	Concentration	$(\mathrm{Ohm}^{-1}\mathrm{cm.}^{-1})$
n-Butyl ether	None		5×10^{-9}
	1	(s)	5×10^{-7}
	2	(s)	5×10^{-7}
	3	(s)	5×10^{-7}
	4	(s)	5×10^{-7}
Isopropyl ether	None		3×10^{-8}
	1	(s)	5×10^{-7}
	2	(s)	5×10^{-7}
	3	(s)	5×10^{-7}
	4	(s)	5×10^{-7}
Ethyl ether	None		5×10^{-8}
	1	(s)	4×10^{-8}
	2	(s)	3×10^{-9}
	3	(s)	1×10^{-7}
	4	(s)	1×10^{-8}
	5	(s)	1×10^{-6}
1-Butanol	None		6×10^{-7}
	1	(0.1 M)	2×10^{-4}
	1	(s)	5×10^{-4}
Methanol	None		2×10^{-6}
	1	(0.1 M)	5×10^{-3}
3-Pentanone	None		2×10^{-7}
	3	(0.1 M)	2×10^{-3}
Water	None		1×10^{-6}
	2	(0.1 M)	9×10^{-3}
	3	(s)	5×10^{-3}
	6	(0.1 M)	1×10^{-2}
Acetone	1	(s)	3×10^{-4}

*(s) Solution saturated with respect to the solute
(1) Lithium chloride
(2) Tetramethylammonium chloride
(3) Tetra-n-butylammonium iodide
(4) Cetyldimethylethylammonium bromide
(5) Anhydrous hydrogen chloride
(6) Potassium chloride

Table II

Cell Resistances of Carrier Solutions

Solvent	Carrier* Nature	Carrier* Concentration	Average Resistance of Cell Arms (Ohms)
n-Butyl ether	1	(s)	1.0×10^6
	2	(s)	8.1×10^5
	3	(s)	6.7×10^5
	4	(s)	5.4×10^5
Isopropyl ether	1	(s)	8.0×10^5
	2	(s)	5.4×10^5
	3	(s)	6.7×10^5
	4	(s)	8.1×10^5
1-Butanol	1	(0.1 M)	8.5×10^4
	1	(s)	7.9×10^4
Methanol	1	(0.1 M)	6.2×10^3
3-Pentanone	3	(0.1 M)	2.4×10^4
Acetone	1	(s)	6.2×10^4

*(s) Solution saturated with respect to the solute
(1) Lithium chloride
(2) Tetramethylammonium chloride
(3) Tetra-n-butylammonium iodide
(4) Cetyldimethylethylammonium bromide

Ethyl ether. Conductivities were determined for the ethyl ether solutions as an exploratory experiment, primarily to evaluate the possibilities of anhydrous hydrogen chloride as a carrier. However, since ethyl ether has a boiling point of 34.6°C., and much of this work was done at a time of year when laboratory temperatures were seldom below 35°C., the ethyl ether solutions were not used polarographically.

1-Butanol. Both saturated and 0.1 M lithium chloride solutions are capable of giving good carrier waves in 1-butanol. Lithium chloride does not dissolve rapidly (the 0.1 M solutions had to be shaken mechanically for at least one hour), so rather than risk incomplete saturation, the 0.1 M solution was used for most of the work, although some of the boron compounds were run in the saturated solution in hopes that the increased conductivity would make a difference. There is evidence that the quaternary ammonium salts might interfere anodically (25, 45).

The first attempts to obtain cathodic polarographic carrier waves with 0.1 M lithium chloride in 1-butanol gave promising results, but the waves were not reproducible. There were three, small, erratic waves present, the first appearing almost immediately, the second at about -0.8 volts, and the third almost on the carrier. Elimination of these proved to be a major problem.

In the first procedure used, the 1-butanol was dried over anhydrous potassium carbonate, and then distilled from fresh anhydrous potassium carbonate into an Erlenmeyer flask. All joints were ground glass, the vacuum adaptor tube outlet was connected through a drying tube, and the distillate was stored in the collecting flask, with a ground glass stopper. The carrier solution was degassed outside the cell for 30 minutes while the cell was flushed with nitrogen. The degassing tube was connected to the cell at G (see Figure 5) after flushing out the connecting glass tube with degassed solution, and the cell was then filled. This procedure resulted in the erratic, non-reproducible waves mentioned above.

The degassing time was increased to 45 minutes, and then to one hour. Some improvement resulted. Solutions that had been standing for a week were compared with those freshly distilled, and fresh distillation was thus found to give further improvement. The sidearms were plugged with glass wool and the electrolysis cell flushed with degassed solution before filling, butthis had no favorable result.

Leakage from the reference electrodes through frit C was again suspected, but a test of this showed negative results (page 37). The degassing time was increased to two hours and the 1-butanol was distilled in an atmosphere of nitrogen, to no avail. 1-Butanol was able to dissolve very large amounts of oxygen.

The first two waves, apparently both due to oxygen, were finally eliminated by altering the electrolysis cell to allow degassing of the solution in the inner jacket. In the final procedure, which was used as standard for the remainder of the study, the solution was degassed outside the cell for 30 minutes, and was then added to the cell as before, the cell having been flushed out with nitrogen meanwhile. E (Figure 5) was provided with a hole and a wire hook extending through the stopper F, and the solution was degassed through frit A. By pumping E up and down, the entire inner jacket solution could be thoroughly degassed in 15 minutes. G was stoppered and a slit in F left as the only nitrogen outlet.

The third wave proved to be an aldehyde wave which was eliminated by distilling the 1-butanol from potassium hydroxide instead of anhydrous potassium carbonate. Smooth, reproducible carrier waves were then readily obtained.

The precautions outlined above were adopted for all other organic solvents, and no further trouble was encountered from oxygen. The importance of using freshly-distilled solvents and of properly degassing the electrolysis solutions cannot be overemphasized.

Methanol. Because methanol can be used as a solvent in low-resistance polarographic work (1, 58), it was not of interest per se in this study. During the investigation of sodium borohydride, however, it was felt that data on its behavior in the corresponding methanol solutions would be of some help in interpreting results (see page 5). For this reason, only the 0.1 M lithium chloride solutions were used with methanol. Methanol does not present the severe problems in technique encountered with 1-butanol, and, with due precautions, good results are readily obtained. As expected, conductances (Table I) and cell resistances (Table II) are comparable with those of water.

3-Pentanone. Tetra-n-butylammonium iodide is readily soluble in 3-pentanone, and was therefore used at a concentration of 0.1 M. The degassing problem is acute, as with 1-butanol, but the effect on the D.M.E. is even more serious. Even with a drop time of six seconds in the carrier solution before starting a polarographic run, by the end of the run the D.M.E. is almost a streaming electrode, and does not return to normal when the applied potential is removed. For this reason, although conductances (Table I) and cell resistances (Table II) indicate that tetra-n-butylammonium iodide in 3-pentanone might be a useful carrier solution, it was not investigated further.

Water. Water was used only in the preliminary investigation of sodium borohydride (see page 5) and is only included in Table I for comparison purposes. Water was never used in the cell of Figure 5.

Acetone. Acetone was not used as a solvent. The solution listed in Tables I and II is the solution used in the reference electrodes, and is included for comparison.

Boron Compounds

For convenience, the boron compounds studied have been arranged according to the classification system outlined in the "Introduction". The results were as follows:

Decaborane. Decaborane, $B_{10}H_{14}$, is the only stable, solid boron hydride known at present. The melting point is 99.5°C. and the vapor is monomeric. It hydrolyzes slowly in water (52), although it is only slightly soluble, and it is readily soluble in the common organic solvents, including 1-butanol. There was no immediate reaction visible with the carrier solution used, which was 0.1 M lithium chloride in 1-butanol; but when the solution was shaken after standing for 24 hours, some bubbles appeared.

Figure 7 shows the cathodic wave obtained with $1x10^{-3}$ M decaborane in 0.1 M lithium chloride in 1-butanol, which is about the lowest useful concentration which can be used under the conditions of this work. As the concentration was increased, a second wave appeared (see Figure 8). This was well-defined at a decaborane concentration of $2.5x10^{-3}$ M and was easily measurable up to $8x10^{-3}$ M. At the higher concentrations, however, the second wave was intermittent, and its

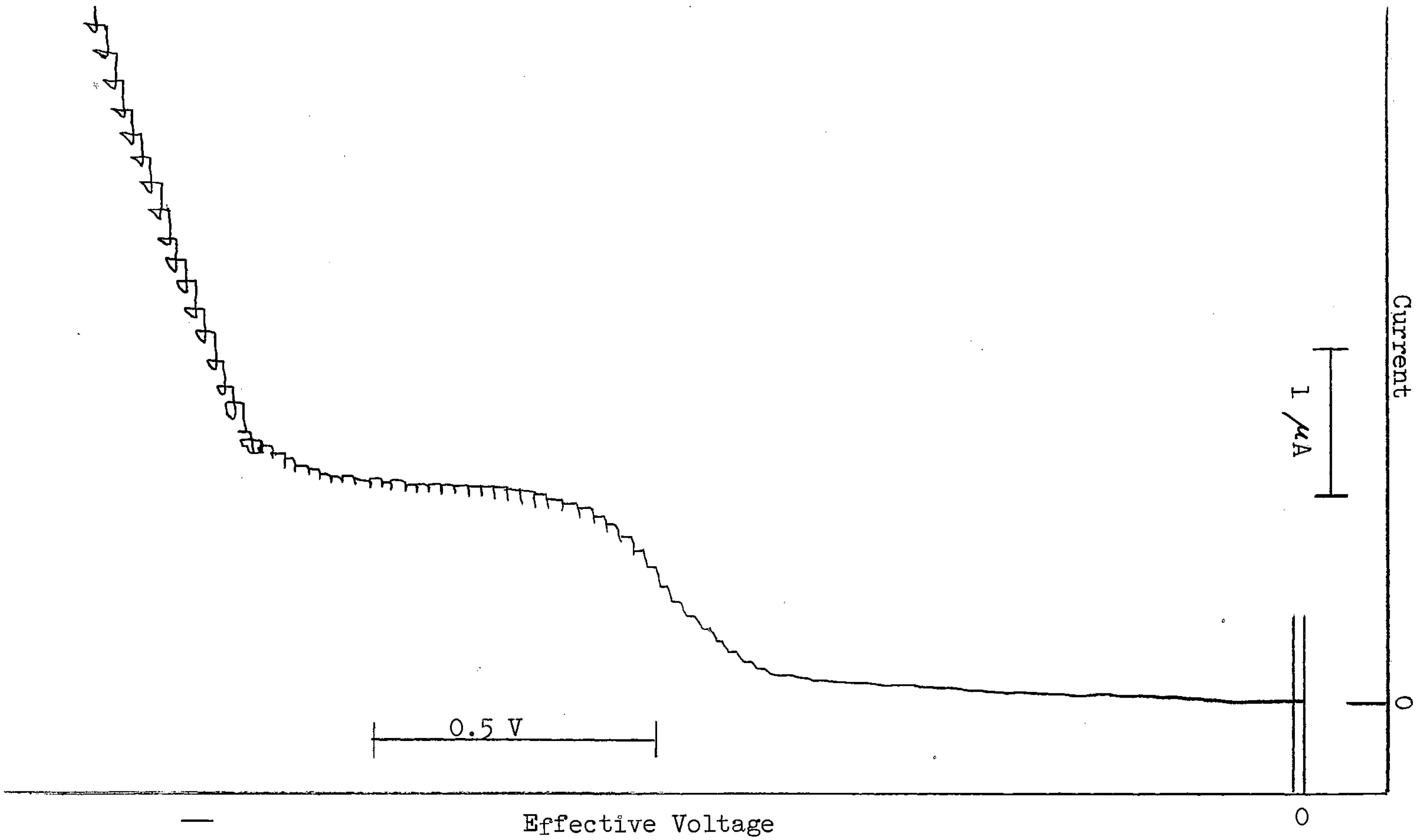

Figure 7. Decaborane in 1-Butanol

Concentration	1 x 10^{-3} M
Carrier	0.1 M LiCl
Reference electrodes	A.S.C.E.
Cell resistances, both	72,000 ohms

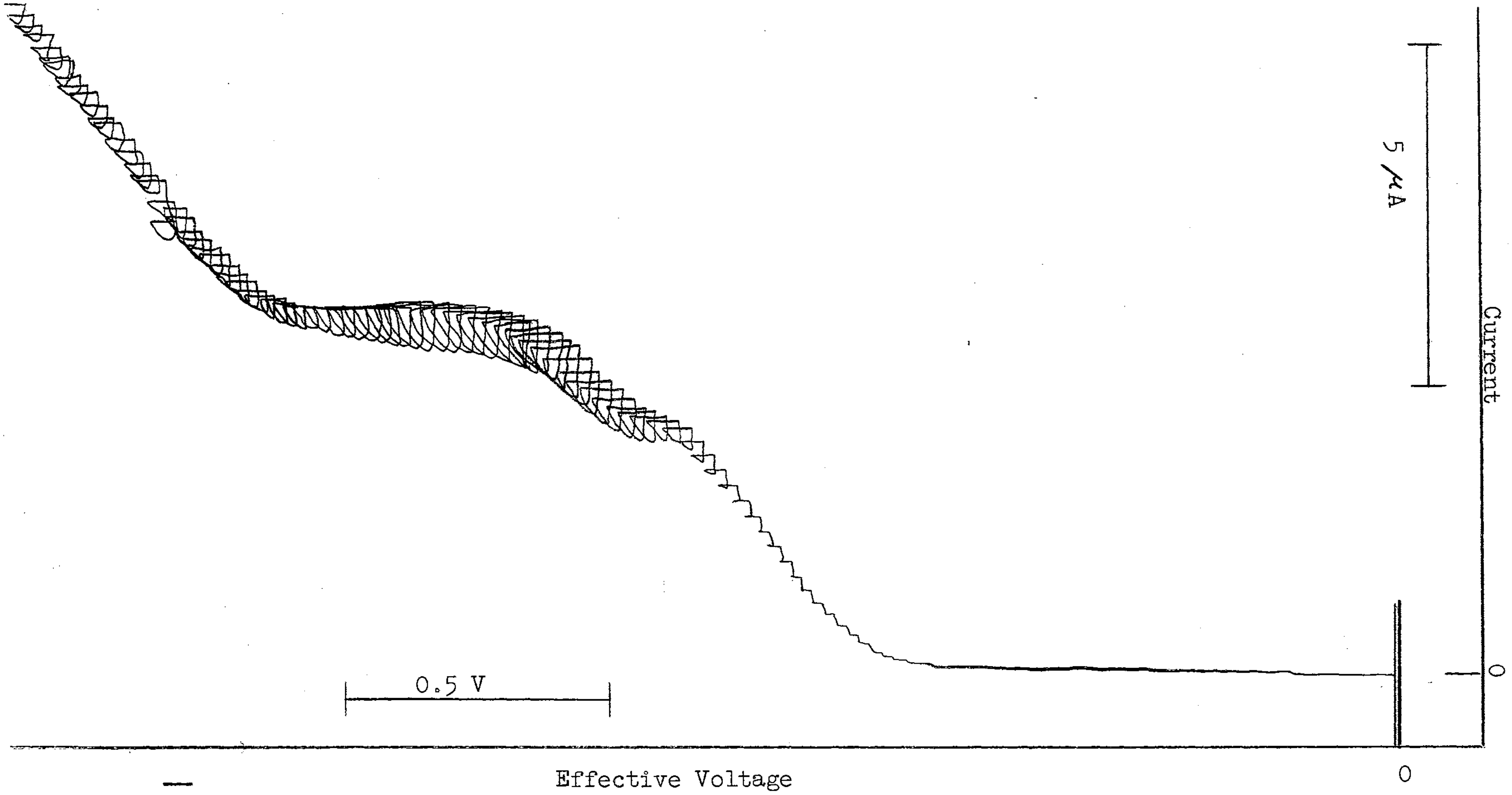

Figure 8. Decaborane in 1-Butanol

Concentration	4×10^{-3} M
Carrier	0.1 M LiCl
Reference electrodes	A.S.C.E.
Cell resistances, both	70,500 ohms

appearance seemed to be pure chance. For instance, on six consecutive runs, with the same solution, the second wave appeared on the first and fourth runs, but not on the others. At 10×10^{-3} M decaborane concentration the second wave had disappeared entirely.

Two reactions were apparent during the making of polarograms. First, there was a gray deposit in the sidearms and bottom of the electrolysis cell. This was thought to be mercury, obtained as a reduction product from a reaction between decaborane and the mercurous chloride of the reference electrodes. To check this theory, the outer jacket of the electrolysis cell was filled with a solution of 0.1 M lithium chloride in acetone, eliminating direct contact between the A.S.C.E. and the electrolysis solution, but eliminating only the decaborane-mercurous chloride in terms of possible reactants. The gray deposit did not appear under these conditions.

Evidence of a second reaction came in the form of bubbles in the electrolysis cell while making runs with the higher concentrations of decaborane. These bubbles appeared after electrolysis started, and did not cease when the potential across the cell was removed. As many as six consecutive runs were made, and the bubbling continued, but with no apparent effect on the wave height.

Allowing the electrolysis solution to stand in the cell in an atmosphere of nitrogen did not affect the wave height over a period of four hours. However, in another case a difference was noted. A sufficient quantity of solution was made up to furnish more than one set of runs and part of it was run immediately. The remainder was allowed to stand, in a stoppered bottle but not degassed, for 24 hours before using. The second portion gave a wave height approximately 20% of the wave height of the first portion, and with only the first wave appearing (see below). For this reason, all decaborane runs were made on a rigid time schedule, the timing beginning with the addition of the decaborane to the carrier solution.

Table III summarizes the relationships between the concentration, diffusion current, and half-wave potential. Comparison of the total wave height at a decaborane concentration of 2.5×10^{-3} M with the single wave at 1×10^{-3} M would seem to indicate that the second wave is merely a splitting of the original, but the slopes of the two waves are not the same. The half-wave potentials for both 1×10^{-3} M and 10×10^{-3} M seem to belong to the first wave series and not to a total wave combination. Separation of the two series of half-wave potentials increases with increasing concentration, and at 10×10^{-3} M the second wave disappears into the carrier.

Attempts to obtain an anodic wave were unsuccessful.

Table III

Decaborane in 1-Butanol

Concentration	I_d (μA/mmole/l.)			$E_{1/2}$ (Volts, neg.)	
x10^3	1st wave	2nd wave	Total wave	1st wave	2nd wave
1.0 M	1.20			1.094	
2.5 M	0.86	0.40	1.25	1.118	1.370
4.0 M	0.92	0.34	1.25	1.160	1.466
5.0 M	0.94	0.36	1.30	1.147	1.486
8.0 M	0.95	0.36	1.31	1.255	1.684
10.0 M	1.15			1.385	

Despite the shift of $E_{1/2}$ with concentration and the lack of anodic results, "n" was calculated from a plot of E vs. log (i/i_d-i). The values of "n" obtained (0.23 for the first wave and 0.55 for the second wave) indicate either that the reactions are irreversible or that they are rate-controlled.

<u>Pyridine Borine</u>. Pyridine borine, $C_5H_5NBH_3$, is produced by the reaction of diborane and pyridine at 0°C. At room temperature it is a liquid (melting point 11°C.), but its vapor pressure is so low it cannot be used satisfactorily in a vacuum apparatus (50). The pyridine can be displaced by compounds such as trimethylamine (47). It is apparently soluble in 0.1 M lithium chloride in 1-butanol, but a 2.65×10^{-3} M solution of pyridine borine in the carrier gave no polarographic wave with the dropping mercury electrode, cathodically or anodically.

Sodium Borohydride. Sodium borohydride, $NaBH_4$, was the first and most intensively-studied compound of this entire series. It had already been studied polarographically in aqueous solutions (38,44); it was already well-known and important chemically (7,18,32,49); and it was readily available in good purity. Most of the techniques used throughout the remainder of the work were evolved during the study of sodium borohydride.

Sodium borohydride is stable to 400°C. and dissociates in water, in which it is readily soluble, into sodium and borohydride ions (53). Hydrolysis is slow in cold water (10% per day), but decomposition is complete in two minutes at 100°C., and is even faster in alkali (18). This, plus the fact that sodium borohydride reacts with acetone and methanol (48), makes low-resistance polarographic methods difficult, at best. Sodium borohydride also is insoluble in ether (7), which might indicate difficulty in finding even a suitable high-resistance solvent.

To begin with, sodium borohydride was studied briefly in aqueous solution, with 0.1 M potassium chloride as the carrier. Using a solution buffered at pH 10, Marshall and Widing (38) found two anodic waves, one at a half-wave potential of -0.15 volts and the other at -0.64 volts, vs. the S.C.E. These results were confirmed in an unbuffered solution, with the D.M.E., using the Sargent Polarograph Model XXI. Both Marshall and Widing and Pecsok (44) used basic buffered solutions because of the rapid decomposition of the sodium borohydride in neutral and acidic solutions. Pecsok reported the formation of hydrogen gas as one of the products of the hydrolysis of sodium borohydride. An attempt was made to use the rotating platinum microelectrode, but, as might have been expected (44), gas bubbles collected on the microelectrode and the resulting waves were meaningless.

Of more significance was the rate at which the diffusion current of sodium borohydride in aqueous solution decreased with time compared with the rate of decrease of the diffusion current in the 1-butanol and methanol solutions used later. This is summarized in Table IV. After eight hours, the aqueous wave had disappeared.

Sodium borohydride was next run in 1-butanol, in which a slow rate of solvolysis is expected. Table IV shows this to be the case, with a small wave still present after 24 hours. Because of this slow reaction, the procedure was standardized and run on a carefully-timed schedule, as in the case of decaborane.

An additional difficulty was caused by the fact that although sodium borohydride is soluble in 1-butanol, it dissolves only slightly and very slowly. For this reason, the solutions called "saturated" were prepared by shaking excess solute with 100 ml. of a 0.1 M lithium chloride in 1-butanol solution in a 250 ml. volumetric flask for 30 minutes, at a setting of three on a Burrell Shaker Model DD. Analysis

Table IV

Sodium Borohydride*

Change of Diffusion Current with Time

Time in hours	Diffusion Current (in microamperes) in			
		Methanol		
	Water	1st wave	2nd wave	1-Butanol
0.0	0.34	1.67	2.45	3.7
0.5		1.19	2.41	3.8
1.0		1.11	2.03	4.1
1.5		0.80	1.97	4.0
2.0	0.10	0.65	1.67	4.0
2.5		0.49	1.55	4.0
3.0		0.42	1.46	
3.5		0.15	1.30	
4.0	0.07	--		

* Concentration of sodium borohydride at beginning was: in water, 1×10^{-3} M; in methanol, 1×10^{-2} M; in 1-butanol, 4.6×10^{-2}M.

showed that this produced a 0.046 M solution of sodium borohydride. This solution was then filtered and diluted with carrier solution to give the desired concentration for the polarographic studies; and this procedure was incorporated into the time schedule for making runs.

Figure 9 shows the anodic wave obtained with sodium borohydride, and Table V gives the concentration, diffusion current, and half-wave potential details. It will be noted that, due to the shift of $E_{1/2}$ with concentration, and the shape of the wave, it was impossible to measure the diffusion current for all of the waves at the

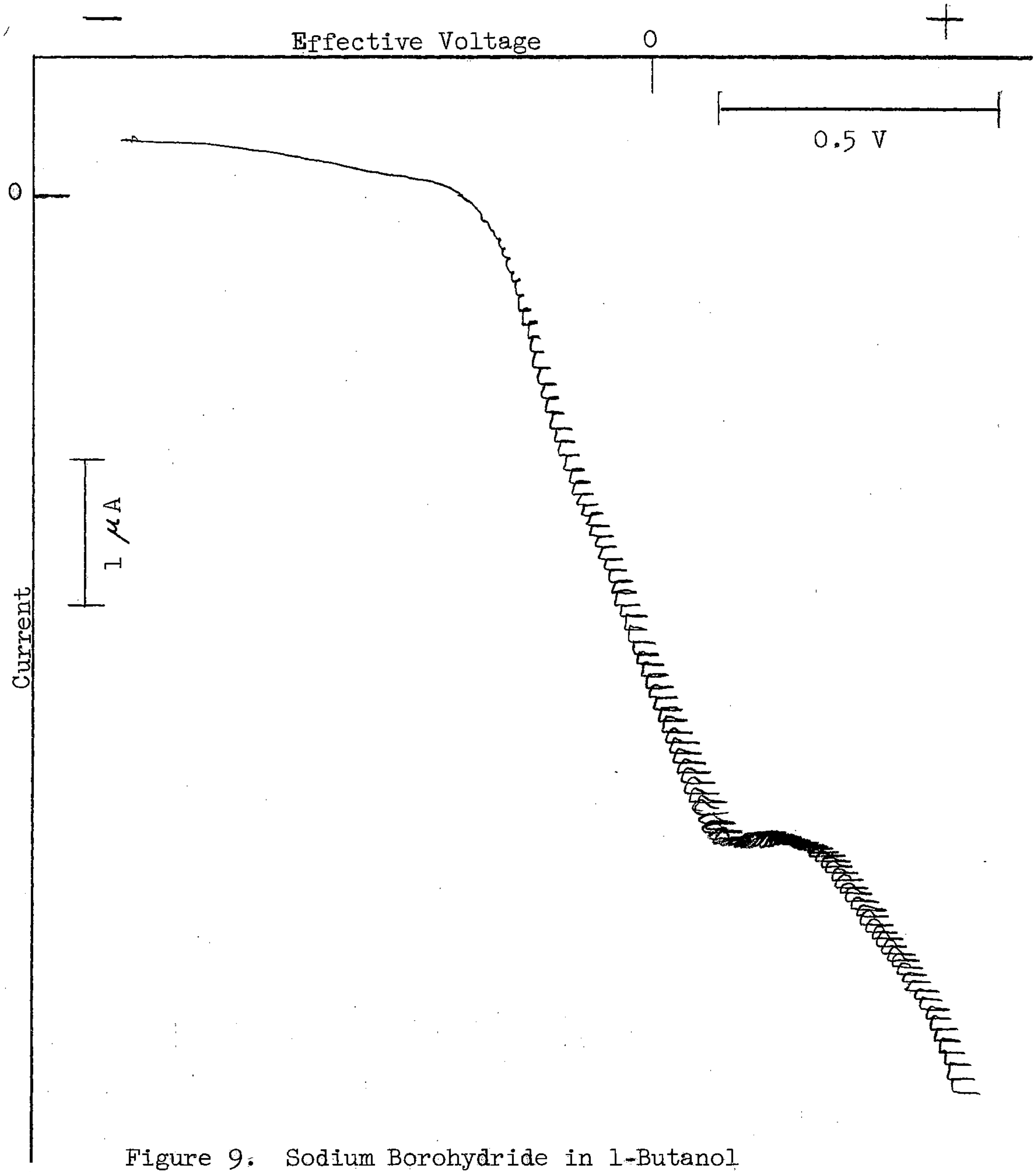

Figure 9. Sodium Borohydride in 1-Butanol

Concentration	3.68×10^{-2} M
Carrier	0.1 M LiCl
Reference electrodes	A.S.C.E.
Cell resistances, both	90,800 ohms

same effective voltage. At the highest concentration, the wave is very close to the carrier wave and measurements therefore cannot be considered reliable, the extreme values being ±10% as compared with ±3% for the other concentrations.

Table V

Concentration vs. Critical Constants for Sodium Borohydride in 1-Butanol

Concentration (Moles/l.)	Diffusion Current (Microamperes)	Half-wave Potential (Volts)
$9.2\text{x}10^{-3}$	1.20 (V = 0)	-0.249
$18.4\text{x}10^{-3}$	1.35 (V = 0)	-0.231
$27.6\text{x}10^{-3}$	2.27 (V = 0)	-0.216
$36.8\text{x}10^{-3}$	3.30 (V = 0.187)	-0.126
$46.0\text{x}10^{-3}$	3.96 (V = 0.373)	0.079

The diffusion current-concentration data from Table V are plotted in Figure 10. The shape of the curve and the fact that it does not go through the origin could readily be explained if one assumed (as was borne out by the evidence in Table IV) that some reaction took place prior to the electrolysis. In addition, oxygen may have reacted with some of the solute, for the sodium borohydride was dissolved in a carrier solution that had not been degassed (although the diluting solution had).

The wave does not give evidence of being satisfactorily reversible, although a plot of E vs. $\log(i/i_d - i)$ gives an "n" value of 2. A possible reaction would be

$$NaBH_4 + C_4H_9OH + 2e = C_4H_9ONa + BH_3 + H_2$$

$$2BH_3 = B_2H_6$$

No hydrogen bubbles appear, however.

There is no cathodic wave.

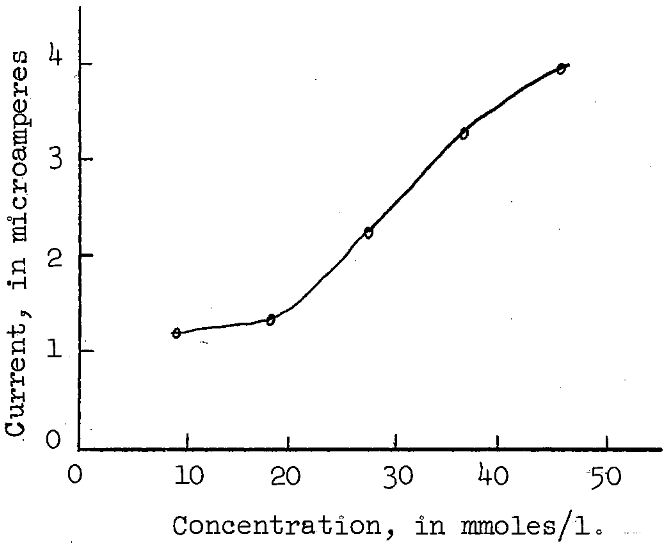

Figure 10

Sodium Borohydride in 1-Butanol

As a compromise between the rapid reaction of sodium borohydride with water and the limited solubility in 1-butanol, a 0.1 M solution of lithium chloride in methanol was used as the carrier. Sodium borohydride is readily soluble in this solution, but the rate of decrease of i_d with time is also rapid. As shown in Table IV, the first wave disappears completely in about four hours, which makes necessary a rigid time schedule similar to that for decaborane.

Sodium borohydride in methanol gives no anodic wave, but yields two cathodic waves, both of which are well-defined and easily measured (see Figure 11). The concentration, diffusion current, and half-wave potential relationships are summarized in Table VI. That the reactions are not reversible polarographically is indicated by the fact that "n" values calculated from a plot of E vs. $\log(i/i_d-i)$ are 0.27 and 0.25 for the first and second waves respectively. Lack of reversibility is also indicated by the shift of the half-wave potentials with concentration.

The appearance of single anodic waves with sodium borohydride in water and 1-butanol is as expected. The absence of an anodic wave and presence of two cathodic waves in methanol would indicate some entirely different type of reaction. Schlesinger and coworkers (48) report a reaction between sodium borohydride and methanol giving sodium tetramethoxyborohydride. Using stoichiometric

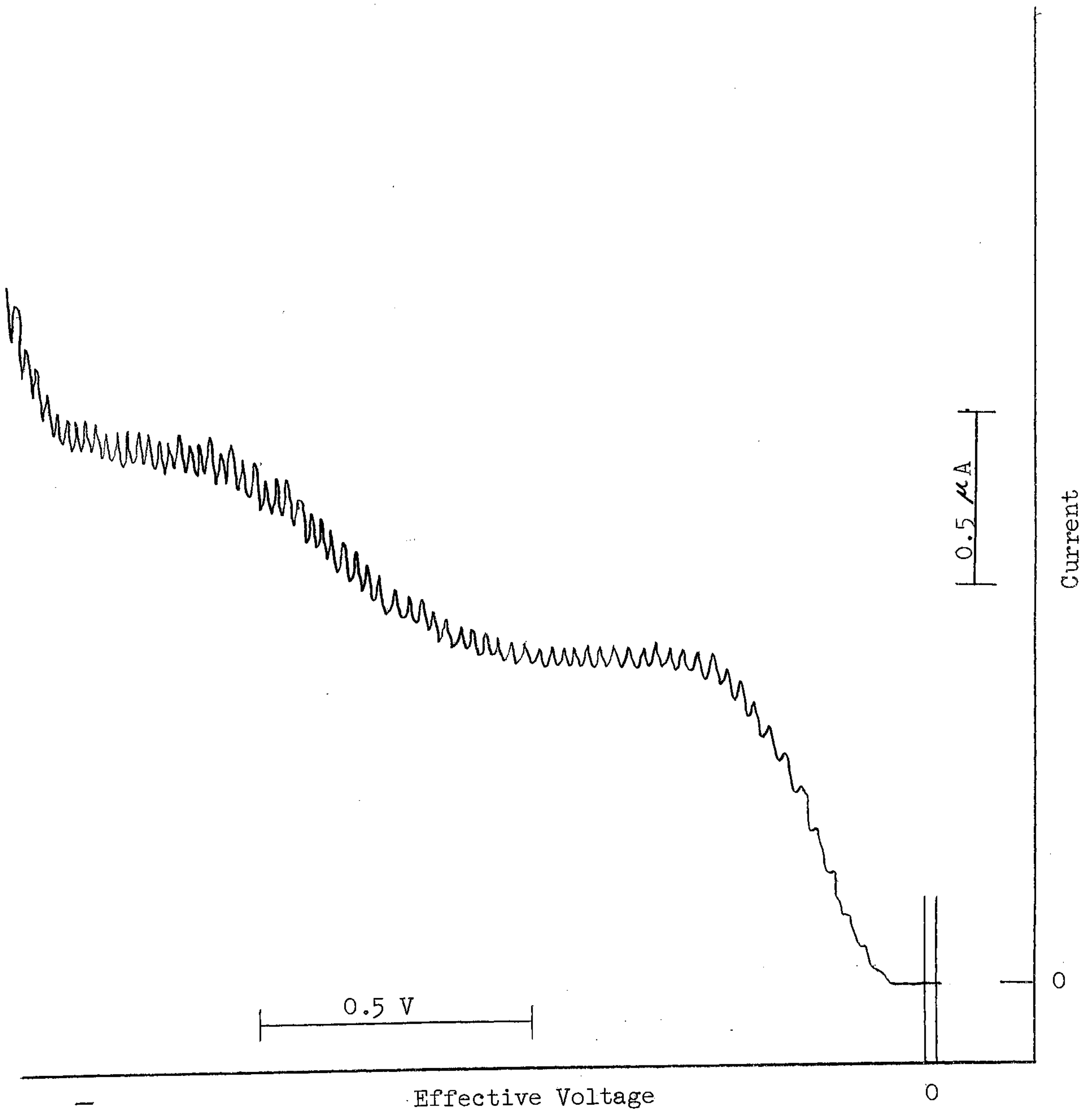

Figure 11. Sodium Borohydride in Methanol

Concentration	7×10^{-3} M
Carrier	0.1 M LiCl
Reference electrodes	A.S.C.E.
Cell resistances, both	6,700 ohms

quantities of reactants, they obtain a 90% yield, with an appreciable reaction even at -80°C. The sodium tetramethoxyborohydride is reported to give methanol at 145°C. and methyl borate at 250°C. In an effort to establish the reaction involved in the electrolysis of sodium borohydride in methanol, both the sodium tetramethoxyborohydride and methyl borate were prepared and run polarographically.

Table VI

Concentration vs. Critical Constants for
Sodium Borohydride in Methanol

Concentration (Moles/l.)	Diffusion Current (μA/mmole/l.)		Half-wave Potential (Volts, neg.)	
	1st wave	2nd wave	1st wave	2nd wave
1.0×10^{-3}	0.23	0.63	0.168	0.934
4.0×10^{-3}	0.18	0.38	0.215	0.989
7.0×10^{-3}	0.14	0.24	0.218	1.008
10.0×10^{-3}	0.17	0.24	0.218	1.035

Methyl Borate. Methyl borate, $B(OCH_3)_3$, is the simplest alkyl ester, easily prepared by refluxing boric oxide with methanol and separating the resulting azeotrope with lithium chloride (49). It is a liquid, very sensitive to hydrolysis like the other alkyl esters (46), and had to be handled in the dry box.

In connection with the previous sodium borohydride analyses, a study was made of methyl borate in 0.1 M lithium chloride in methanol, in which it is readily soluble. No polarographic waves were obtained with the

D.M.E., either cathodically or anodically, and anodic runs made with the rotating platinum electrode were equally fruitless.

Sodium Tetramethoxyborohydride. Sodium tetramethoxyborohydride, $NaB(OCH_3)_4$, like methyl borate was studied in an effort to shed light on the reactions involved in the polarographic reduction of sodium borohydride. The carrier solution was 0.1 M lithium chloride in methanol, with the time sequence of all runs kept identical with that used with the corresponding sodium borohydride solutions. The sodium tetramethoxyborohydride is readily soluble in methanol at the concentrations used.

Cathodically, a single wave appears. It is well-behaved except for the small diffusion current values, as shown in Table VII. These are smaller than the diffusion current values for the first wave of sodium borohydride, but the half-wave potentials compare favorably (see Table VI).

Table VII

Sodium Tetramethoxyborohydride in Methanol

	Cathodic		Anodic	
Concentration (Moles/l.)	I_d (μAmp/mmole/l.)	$E_{1/2}$ (Volts)	I_d (μAmp/mmole/l.)	$E_{1/2}$ (Volts)
$4.0x10^{-3}$	0.063	-0.185	7.0 (V = 0.230)	0.156
$7.0x10^{-3}$	0.084	-0.199	6.3 (V = 0.311)	0.206
$10.0x10^{-3}$	0.099	-0.207	5.8 (V = 0.374)	0.243
$40.0x10^{-3}$	0.042	-0.169	2.5 (V = 0.654)	0.386

Table VIII shows the change of diffusion current with time. The half-wave potential remains constant within the experimental limits. "n" for the cathodic wave, calculated as before, is 0.28.

Table VIII

Sodium Tetramethoxyborohydride in Methanol

Change of Diffusion Current with Time

Time (Hours)	Diffusion Current (Microamperes)
0	0.88
0.5	1.09
1.0	1.02
1.5	0.94
2.0	0.85
3.0	0.85

Anodically, there is another wave, shown in Figure 12. The relationship between concentration, diffusion current, and half-wave potentials is shown in Table VIII. It was impossible to measure all of the diffusion currents at the same potential because of the shift in half-wave potential. The higher concentrations again gave waves very close to the carrier wave; therefore the measured values for these cannot be considered as reliable as the others. "n" is 0.50, calculated as before, and the reaction gives evidence of being irreversible.

Tri-α-naphthylboron. Tri-α-naphthylboron, $B(C_{10}H_7)_3$, is a typical stable, solid boron triaryl compound. It does not react

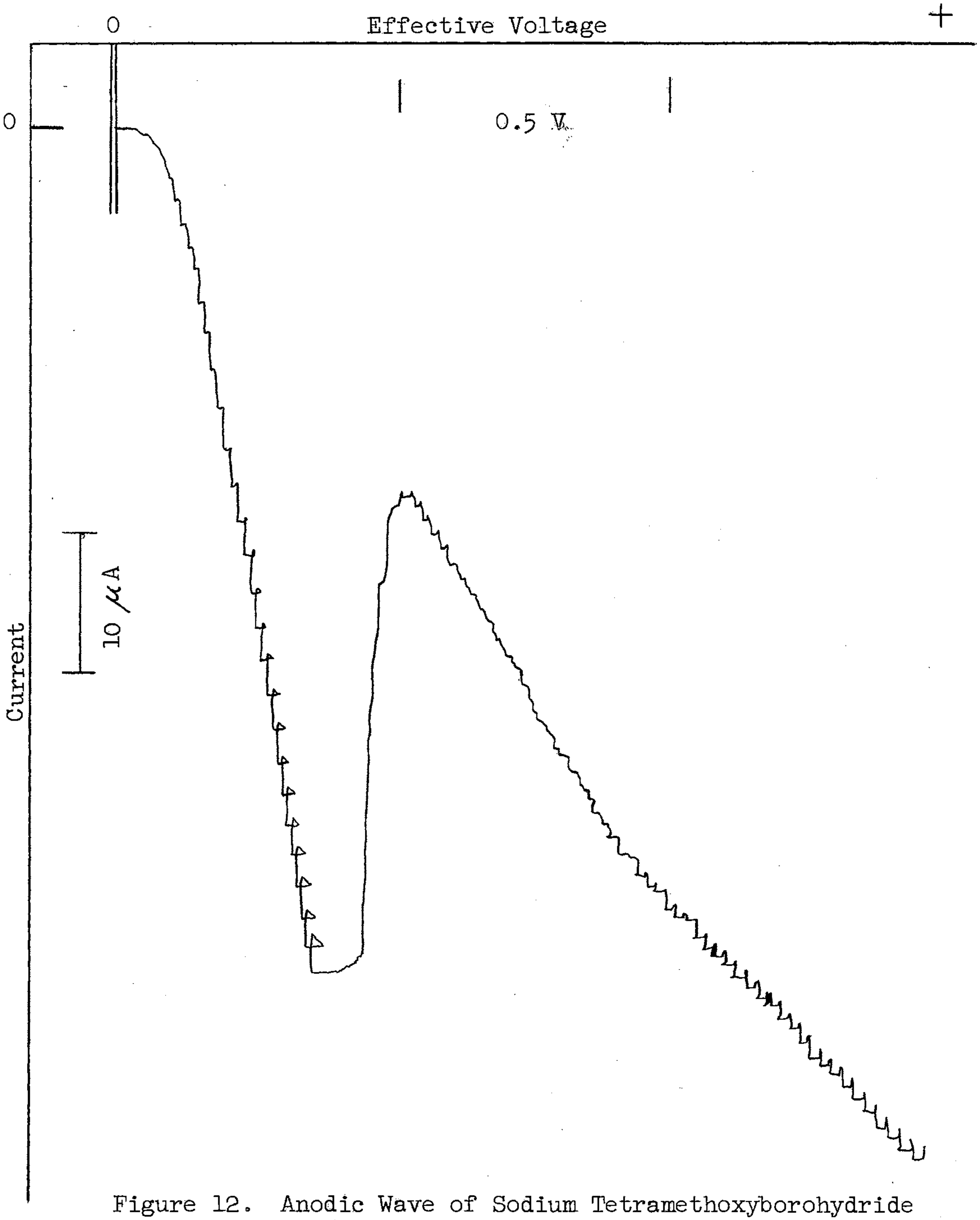

Figure 12. Anodic Wave of Sodium Tetramethoxyborohydride in Methanol

Concentration	1×10^{-2} M
Carrier	0.1 M LiCl
Reference electrodes	A.S.C.E.
Cell resistances, both	6,000 ohms

with water, but with alcohols it is reported to give esters.

The compound is soluble in 1-butanol to the extent of 1×10^{-3} M only after one hour of mechanical shaking. A saturated solution of tri-α-naphthylboron in saturated lithium chloride in 1-butanol carrier solution gave neither cathodic nor anodic waves, with either the D.M.E. or the rotating platinum electrode.

Tri-α-naphthylboron is more soluble in 3-pentanone than in 1-butanol, but the presence of the tri-α-naphthylboron, saturated, reduced the conductivity of 0.1 M tetra-n-butylammonium iodide in 3-pentanone carrier solution, so this was not run polarographically.

<u>Phenyl Boric Oxide</u>. Solid phenyl boric oxide, C_6H_5BO, is readily soluble in 1-butanol. Polarographic runs were made at a concentration of phenyl boric oxide of 1×10^{-3} M and 10×10^{-3} M in a carrier of 0.1 M lithium chloride in 1-butanol, and with the same at a concentration of 5×10^{-3} M in a saturated solution of lithium chloride in 1-butanol. There was no indication of polarographic activity anodically or cathodically with either the D.M.E. or the rotating platinum microelectrode.

<u>Unsaturated Aliphatic Boric Acids, Oxides and Halogen Derivatives</u>. Although no results were obtained with phenyl boric oxide, the monoaryl and monoalkyl boric oxides and acids differ enough in their chemical properties to warrant separate investigation.

There was also interest in the effect of unsaturated aliphatic groups and halogens on the polarographic activity. The existence of solid monoalkyl boric acids made this a convenient starting point for the investigation of several possible reactive groups.

The starting compound was chloroethylene boron dichloride, $ClHC::CHBCl_2$, prepared by passing acetylene and boron trichloride over a suitable catalyst (3). The product is a liquid (boiling point 91°C.) very sensitive to hydrolysis; consequently it was hydrolyzed to the corresponding solid acid (melting point 128°C.). The acid is readily purified, stable in air, and soluble in water and in the lower aliphatic alcohols (2).

Chloroethylene boric acid, $ClHC::CHB(OH)_2$, contains all of the desired groups since it is a halogenated, unsaturated alkyl boric acid. In addition, any group responsible for any observed polarographic activity can quickly be isolated. Thus, the acid can be dehydrated to the oxide, $(ClCH::CHBO)_3$, which is another solid (melting point 55°C.) (2). In addition, 2-methyl-1-propene-1-boronic acid, $(CH_3)_2C::CHB(OH)_2$, can be prepared by the method outlined by Braude and Timmons (8), using isobutylene and bromine as starting materials, and incorporating the lithium Grignard modification recommended by Letsinger and Skoog (29). The resulting solid acid (melting point 84°C.) is soluble in water and ethanol. Use of this series of compounds ought to isolate the effects of the halogen, unsaturated alkyl group, boric acid and the boric oxide.

The chloroethylene boric acid, being easiest to handle and deemed the most promising, was tried first. It is readily soluble in 0.1 M lithium chloride in 1-butanol, but showed no evidence of polarographic activity with the D.M.E.

Despite this failure, the 2-methyl-1-propene-1-boronic acid was also tried. It, too, was readily soluble in 0.1 M lithium chloride in 1-butanol, and it, too, gave no evidence of polarographic activity with the D.M.E. Because neither compound was polarographically active, there seemed to be no point in preparing the rest of the series.

Isobutylene, which was used as one of the starting materials in the preparation of the 2-methyl-1-propene-1-boronic acid, was also tried. It showed some solubility, but no polarographic activity in 0.1 M lithium chloride in 1-butanol.

The isobutylene did give a cathodic wave in 0.1 M lithium chloride in methanol, but since only boron compounds were considered in this research, no study of the wave was made.

Sodium Tetraphenyl Borate. Sodium tetraphenyl borate, $NaB(C_6H_5)_4$, is a stable solid, although the corresponding alkyl derivatives seem to exist only in solution (22).

The sodium tetraphenyl borate appeared to be soluble in the carrier used (0.1 M lithium chloride in 1-butanol), but the solutions were always cloudy. However, the solute did not precipitate on standing. Some evidence of a cathodic wave was obtained with this solution but the wave was poorly defined and not at all reproducible at any concentration in the range from 0.8×10^{-3} M to 3×10^{-3} M. Sometimes one wave appeared, at other times two, and occasionally no wave at all. The results could not be reproduced.

The anodic wave, on the other hand, was well-defined and was reproducible. Table IX shows that the correlation between the concentrations, diffusion currents and half-wave potentials is very poor. That this is due to the difficulty of making accurate measurements can be seen from Figure 13, which shows a carrier wave superimposed on the anodic wave. Even at this low concentration, the carrier merges rapidly with the wave for the compound, and the problem is not made any simpler by the dip which occurs in the wave.

There are two other possible explanations for the erratic results. The solutions were cloudy, which could mean they were actually colloidal suspensions rather than true solutions. There was always, in addition, a possibility that the samples were not of uniform composition. To minimize any influence of this type, the entire operating procedure was standardized and timed as carefully as possible;

the values reported are averages of at least four runs. The sensitivity setting of the instrument, where it could be varied, made no difference.

Table IX

Sodium Tetraphenyl Borate in 1-Butanol

Concentration (Moles/l.)	Diffusion Current (μA/mmole/l.)	Half-wave Potential (Volts)
$0.25\text{x}10^{-3}$	62	0.59
$0.50\text{x}10^{-3}$	15.5	0.39
$0.60\text{x}10^{-3}$	17.1	0.52
$0.80\text{x}10^{-3}$	10.4	0.40
$0.90\text{x}10^{-3}$	15.0	0.45
$1.0\ \text{x}10^{-3}$	13.1	0.64
$1.5\ \text{x}10^{-3}$	9.6	0.71
$2.0\ \text{x}10^{-3}$	8.5	0.66
$3.0\ \text{x}10^{-3}$	6.2	0.84

There is no evidence of decomposition or other reaction with time, the diffusion current and half-wave potential remaining constant over a period of two hours.

Owing to the fact that the D.M.E. has a limited anodic range, the sodium tetraphenyl borate was also run using the rotating platinum microelectrode. Figure 14 shows the wave obtained, with the carrier superimposed. Since this was actually no better than the other wave, and since, as can be seen by a careful study of Figure 14, there was obvious contamination of the carrier by products diffusing from the reference electrodes, this study was discontinued.

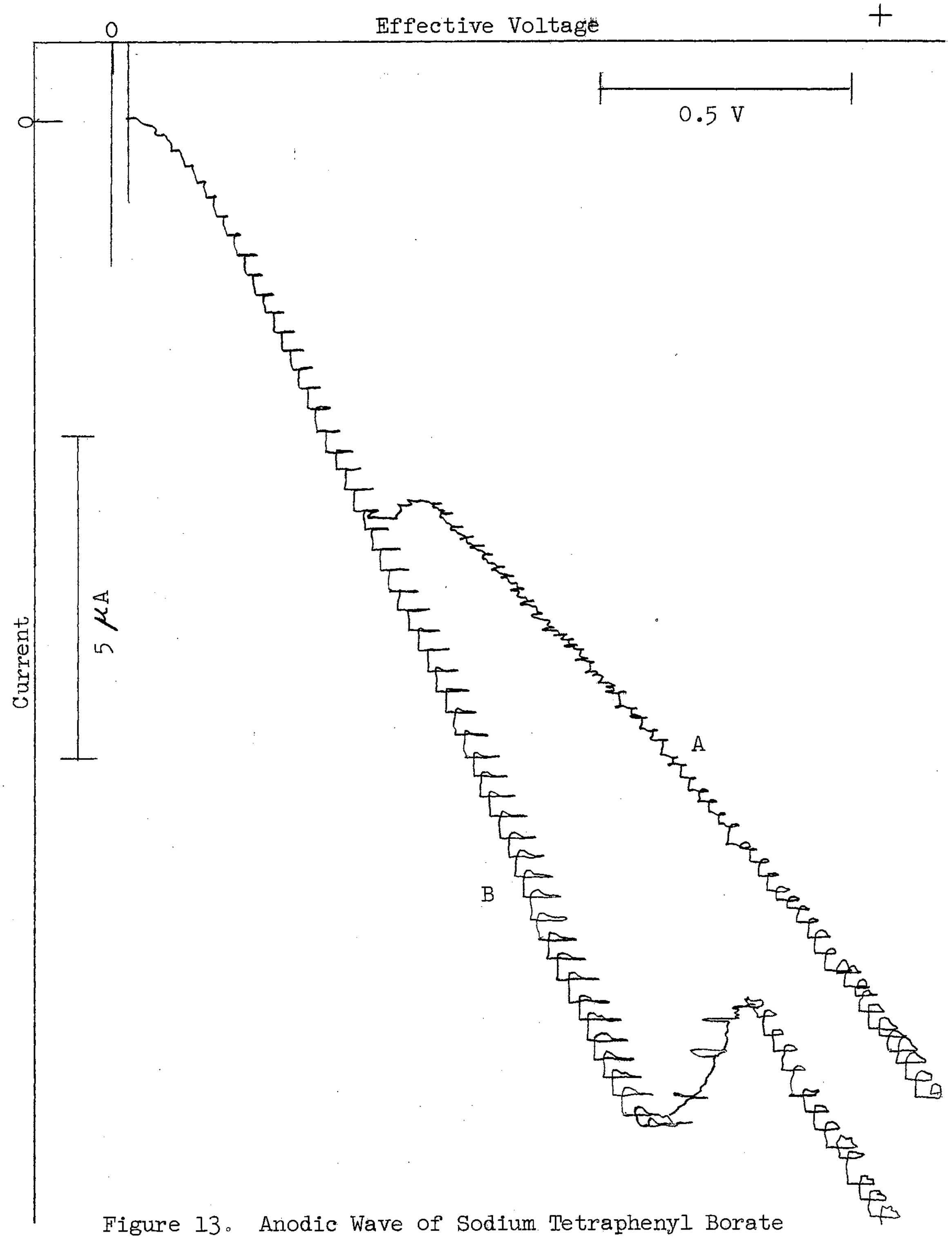

Figure 13. Anodic Wave of Sodium Tetraphenyl Borate in 1-Butanol at D.M.E.

A - Carrier

B - Sodium tetraphenyl borate

Concentration - 2.5 x 10^{-3} M

Carrier - 0.1 M LiCl

Reference electrodes - A.S.C.E.

Cell resistances, both - 76,000 ohms

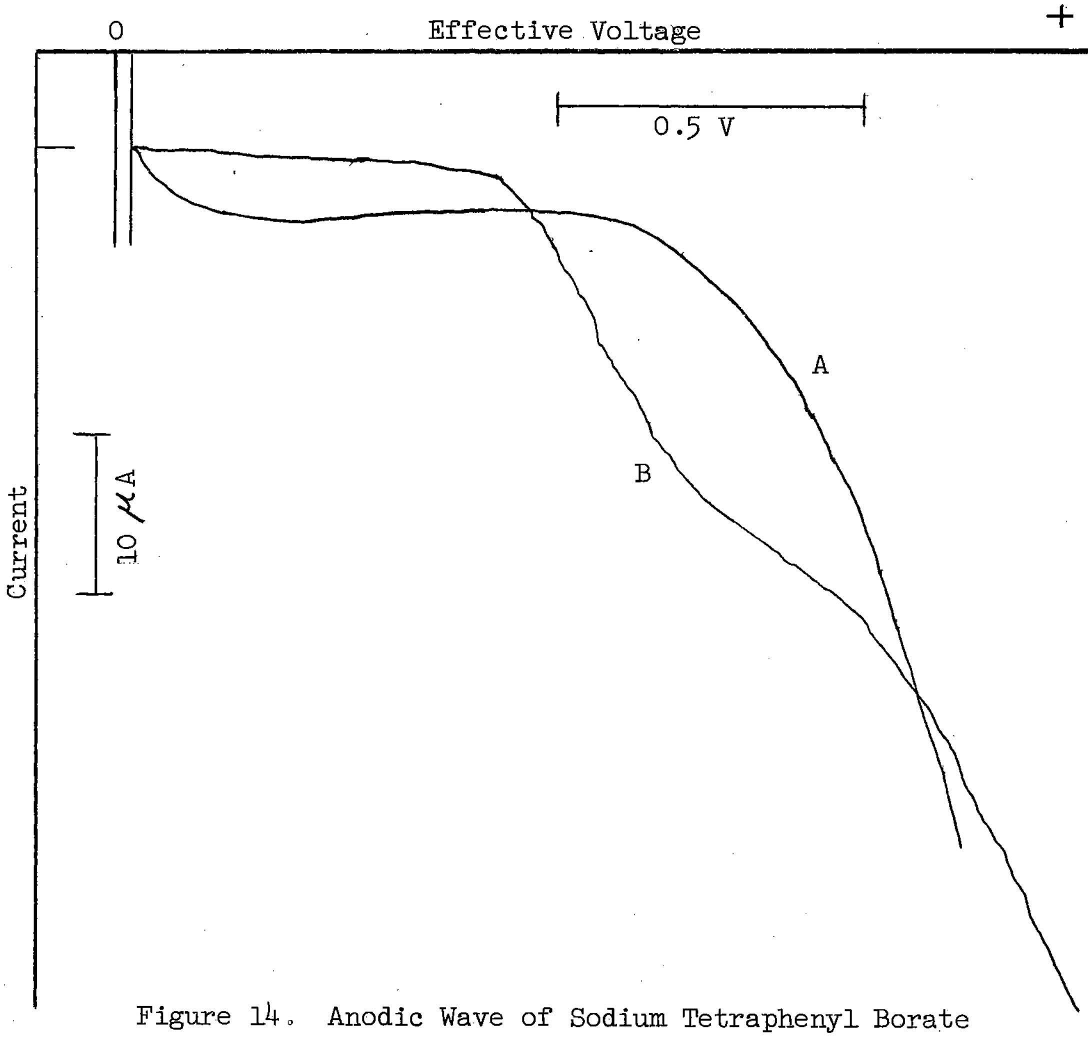

Figure 14. Anodic Wave of Sodium Tetraphenyl Borate in 1-Butanol

Rotating Platinum Microelectrode

A - Carrier curve

B - Sodium tetraphenyl borate

Concentration	1 x 10^{-3} M
Carrier	0.1 M LiCl
Reference electrodes	A.S.C.E.
Cell resistances, both	24,900 ohms

Acetanilide Boron Trifluoride. Acetanilide boron trifluoride, $BF_3 \cdot C_6H_5NHCOCH_3$, decomposes just above its melting point, which is 133°C., is not hygroscopic, is soluble in acetone and in ethyl alcohol but is insoluble in benzene and the ethers (56). It is readily soluble in 1-butanol, 0.1 M with lithium chloride.

A study of the complex in this medium gave results that changed with concentration changes. At the lower concentrations, there were two readily-distinguishable waves, as shown in Figure 15. The less-negative wave was easily measured and was, in fact, useful over the entire concentration range tested. As the concentration increased, another wave appeared at a half-wave potential less negative than the other two. Figure 16 shows all three waves, (which shall be referred to hereafter as a, b and c in order of increasingly-negative half-wave potentials).

Wave a first appeared at a concentration of acetanilide boron trifluoride of 3×10^{-3} M. As the concentration and diffusion current increased, the first two waves were sometimes hard to separate, because, if the instrument sensitivity was set high enough to give good values for the diffusion current, a and b tended to merge.

It was possible to measure the half-wave potential of c, only at very low concentrations, and it was never possible to measure the diffusion current with any real degree of certainty. This

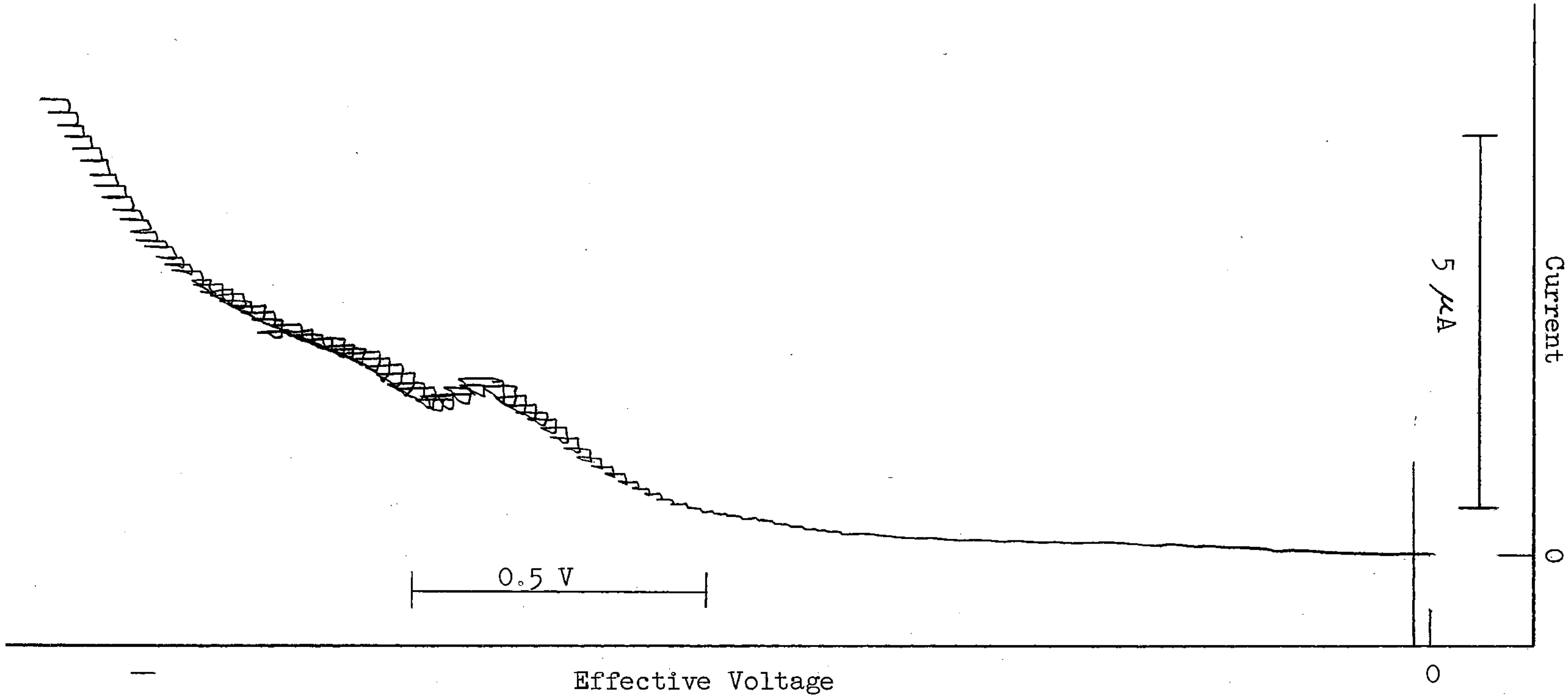

Figure 15. Cathodic Acetanilide-Boron Trifluoride in 1-Butanol

Concentration	1×10^{-3} M
Carrier	0.1 M LiCl
Reference electrodes	A.S.C.E.
Cell resistances, both	94,500 ohms

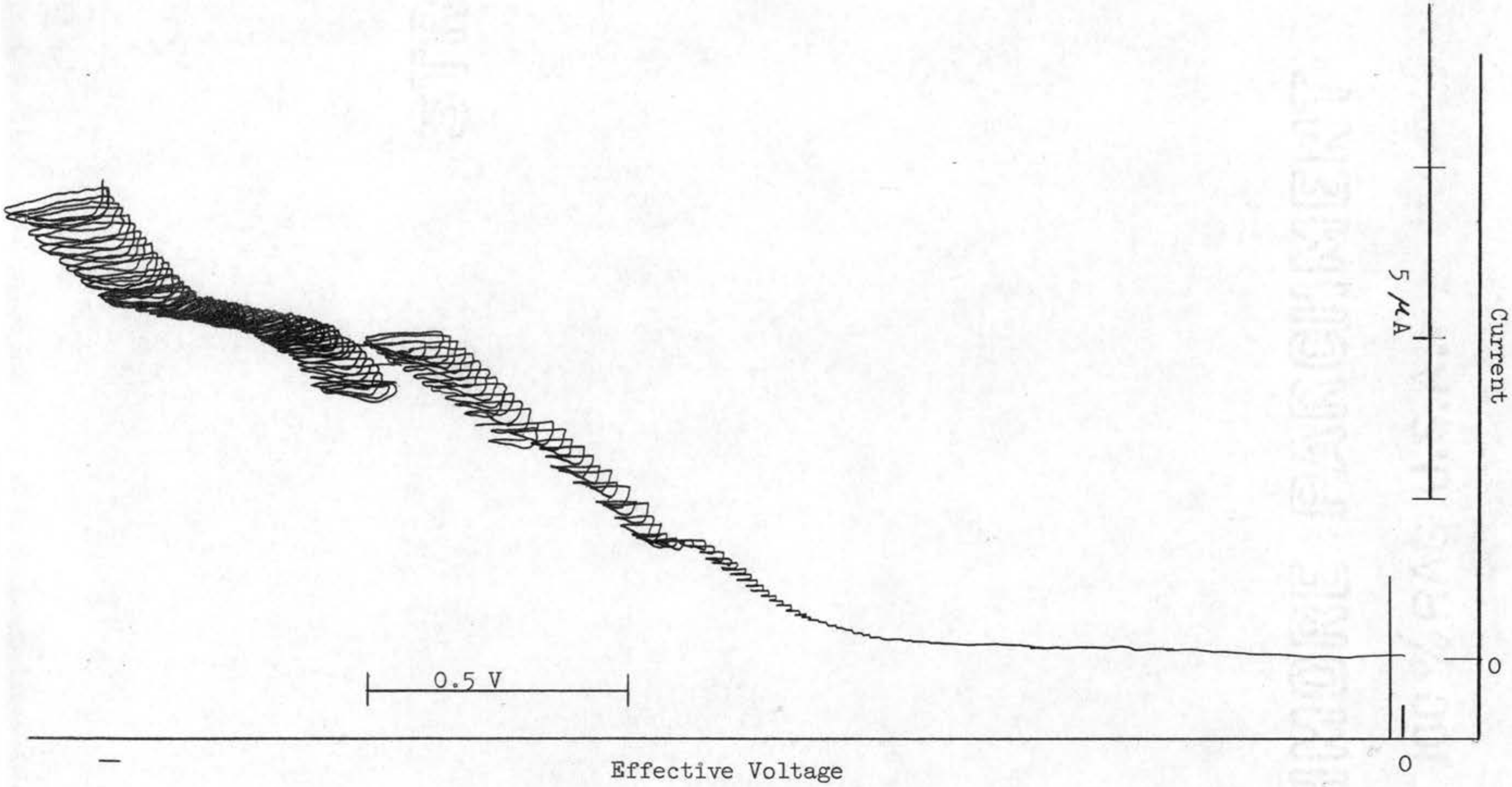

Figure 16. Cathodic Acetanilide Boron Trifluoride in 1-Butanol

Concentration	3×10^{-3} M
Carrier	0.1 M LiCl
Reference electrodes	A.S.C.E.
Cell resistances, both	94,100 ohms

was due to two factors: first, the drop time became erratic in the region of the c wave, although it was quite normal in the regions both preceding and following; and, second, the b wave showed a maximum. When the maximum dropped off, the bottom of the c wave became obscured since the separation was small (see Figure 17). The diffusion current for wave c was measured where possible, but only as the sum of all three waves, i.e., from the residual current line. At higher concentrations the c wave disappeared into the carrier.

The middle wave b, therefore, seemed to be the most useful analytical part of the polarogram. The relationships between the concentration, diffusion current and half-wave potential are summarized in Table 10. There was no decrease in wave height over a period of three hours, indicating no decomposition in the solution. The "n" value for a is 0.20 and for b is 0.25, calculated as before.

No anodic wave was ever observed.

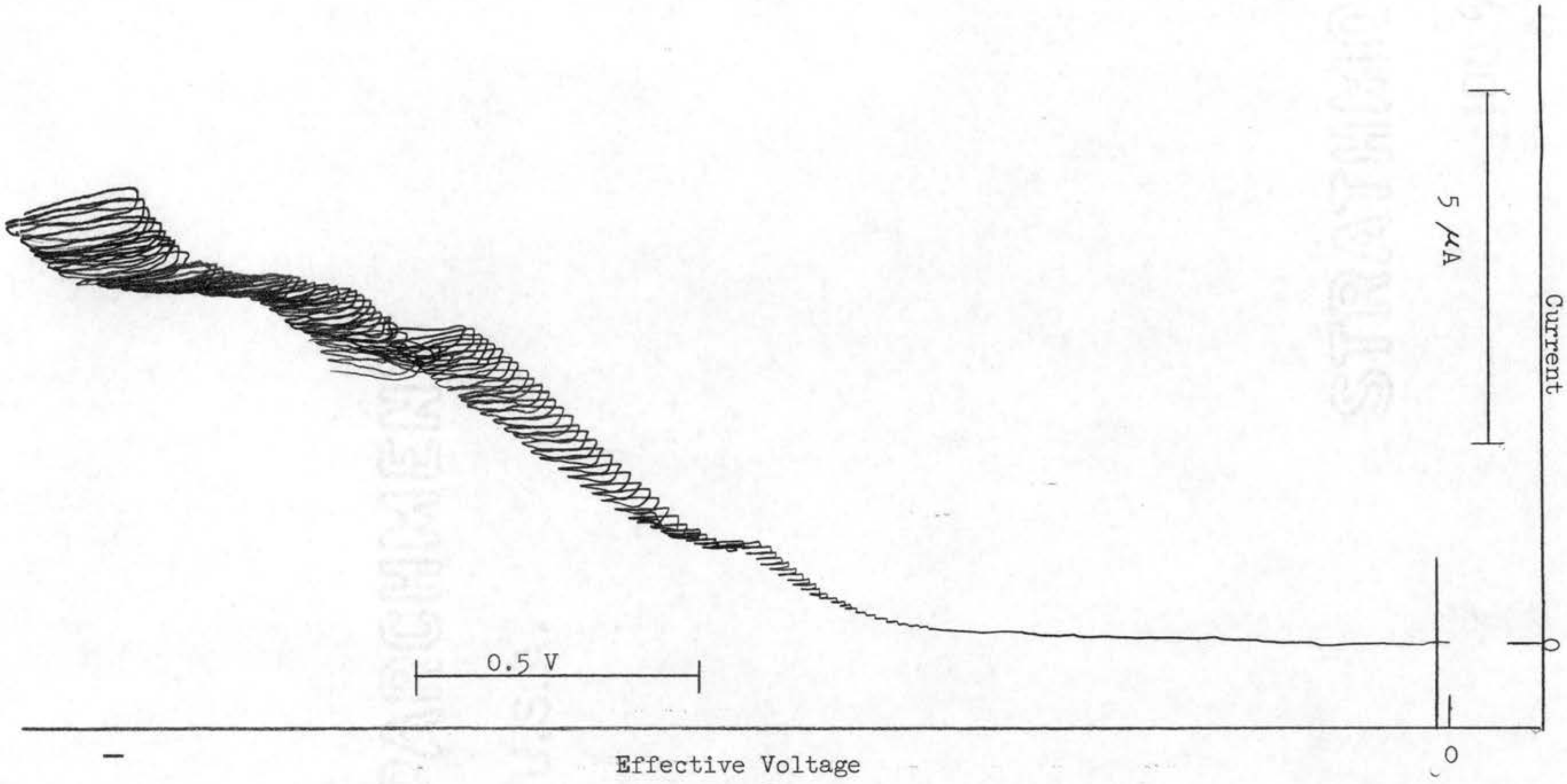

Figure 17. Cathodic Acetanilide Boron Trifluoride in 1-Butanol

Concentration	5×10^{-3} M
Carrier	0.1 M LiCl
Reference electrodes	A.S.C.E.
Cell resistance, both arms	92,800 ohms

Table X

Acetanilide Boron Trifluoride in 1-Butanol

Concentration (Mmoles/l.)	Diffusion Current (μ Amp/mmole/l.)				Half-wave Potential (Volts, neg.)		
	a		b	c	a		b
0.5		1.86				1.356	
1.0		2.02				1.395	
2.0		2.13				1.472	
3.0	0.47		1.55		1.145		1.544
4.0	0.73		1.84		1.196		1.665
5.0	0.58		1.56	1.69	1.217		1.723
6.0	0.77		1.26	1.66	1.293		1.843
8.0	0.94		1.31	1.69	1.348		1.870
10.0	1.15				1.519		

CONCLUSION

The high-resistance polarograph, at this stage of development and with the cell used in this study, will give good results with solutions of specific conductance of the order of 10^{-4}/ohm.-cm., or electrolysis cell resistance of the order of 90,000 ohms. This is in contrast with the previous maximum cell resistance (using the conventional polarograph) of some 8,000 ohms; and this opens up a whole new category of possible solvents and carriers. There seems to be no point in trying to use carrier solutions with specific conductance below 10^{-6}/ohm.-cm., but the intermediate range, between that used and the lower limit cited, may prove useful.

It seems clear that some types of bonds formed by boron are promising polarographically. The good results with decaborane indicate that either the boron-hydrogen bond or the boron-boron bond can be reduced, and that the polarographic method is certainly the simplest analytical method available for this hydride.

On the other hand, the boron-nitrogen, boron-oxygen and boron-carbon bonds as such, apparently are not polarographically active, as shown by the behavior of pyridine borine, tri-α-naphthylboron, methyl borate, phenyl boric oxide and chloroethylene boric acid.

Results obtained with sodium borohydride, sodium tetramethoxyborohydride and sodium tetraphenyl borate indicate that addition complexes of the boron hydrides, boron-oxy compounds and triarylborons are also promising, especially if the anodic range of the rotating platinum microelectrode is utilized. The problem of carrier solutions for the sodium borohydride cannot be considered solved. The propanols would be the next solvents for investigation.

The mechanism of the sodium borohydride reduction is still obscure, although the similarity in half-wave potential found in the case of the first wave of sodium borohydride and the sodium tetramethoxyborohydride may indicate a common reaction. A reaction common to both compounds could only be due to the sodium and complex boron ions (or sodium-boron bond), which does not seem likely, although there is the alternative possibility that some sodium tetramethoxyborohydride is formed when sodium borohydride is added to the methanol (48).

BIBLIOGRAPHY

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

(2) Arnold, H. R., U. S. Patent 2,402,509, (1946).

(3) Arnold, H. R., U. S. Patent 2,402,589, (1946).

(4) Arthur, P. and Lyons, H., Anal. Chem., 24, 1422 (1952).

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

(6) Black, H., "Polarographic Studies in Organic Solvents," unpublished M. S. thesis, Oklahoma A. and M. College, 1948.

(7) Boldebuck and Elliott, General Electric Co. Report No. R49A0534, Dec., 1949.

(8) Braude, E. A. and Timmons, C. J., J. Chem. Soc., 2000 (1950).

(9) Brown, H. C. and Sujishi, J. Am. Chem. Soc., 70, 2793 (1948).

(10) DeFord, D. D., Lucchesi, C. A. and Thoburn, J. M., "Analytical Chemistry of Boron," Dept. of Chemistry, Northwestern Univ., Evanston, Ill., June, 1953. (Unpublished)

(11) Elving, P. J. and Callahan, C. M., Nuclear Sci. Abs., 7, No. 9,2501, 303 (1953).

(12) Gentry, G. H. R., Nature, 157, 479 (1946).

(13) Hans, W. and von Sturm, F., Angew. Chem., 65, 693 (1953).

(14) Hans, W. and von Sturm, F., Z. Elektrochem., 57, 416 (1953).

(15) Heyrovsky, J. and Berezicky, S., Collection Czech. Chem. Communs., 1, 19 (1929).

(16) Heyrovsky, J. and Ilkovic, D., Collection Czech. Chem. Communs., 7, 198 (1935).

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

(18) Hoekstra, H. R., AEC Report No. AECD-2144, Sept. 19, 1947.

(19) Ilkovic, D., Collection Czech. Chem. Communs., 6, 498 (1934).

(20) Ilkovic, D., Collection Czech. Chem. Communs., 8, 170 (1936).

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

(22) Johnson, J. R., Snyder, H. R. and van Campen, M. G., J. Am. Chem. Soc., 60, 115 (1938).

(23) Kikichi, S., Sakagachi, Y. and Honda, H., Bull. Chem. Soc. Japan, 25, 98 (1952).

(24) Kolthoff, I. M. and Lingane, J. J., "Polarography," 2nd edition, Interscience Publishers, Inc., N.Y., 1952.

(25) Kolthoff, I. M. and Miller, C. S., J. Am. Chem. Soc., 63, 1405, 2732 (1941).

(26) Kucera, G., Ann. Physik., 11, 529 (1903).

(27) Laitinen, H. and Kolthoff, I., J. Phys. Chem., 45, 1079 (1941).

(28) Laubengayer, A. W. and Bottei, R., J. Am. Chem. Soc., 74, 1618 (1952).

(29) Letsinger, R. L. and Skoog, I. H., J. Org. Chem., 18, 895 (1953).

(30) Lewis, P. A., "Scanning Rates and the Rotating Microelectrode in Polarography," unpublished M. S. thesis, Oklahoma A. and M. College, 1954.

(31) Lewis, W. R., Quackenbush, F. W. and deVries, T., Anal. Chem., 21, 762 (1949).

(32) Lindemann, R. F., "The Reactions of Sodium Borohydride with n-Acyl Anilines," unpublished M. S. thesis, Oklahoma A. and M. College, 1954.

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

(34) Lingane, J. J. and Kolthoff, I. M., J. Am. Chem. Soc., 61, 825 (1939).

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

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

(37) MacGillavry, D. T. and Rideal, E. K., Rec. trav. chim., 56, 1013 (1937).

(38) Marshall and Widing, AEC Report No. AECD-2914, June 30, 1950.

(39) McElroy, A. D. and Laitinen, H. A., J. Phys. Chem., 57, 564 (1953).

(40) Metal Hydrides, Inc., Technical Bulletin 502-C.

(41) Muetterties, E. L. and Rochow, E. G., J. Am. Chem. Soc., 75, 490 (1953).

(42) Page, J. E. and Robinson, F. A., J. Chem. Soc., 133 (1943).

(43) Parks, T. D. and Hansen, J. A., Anal. Chem., 22, 1268 (1950).

(44) Pecsok, R. L., J. Am. Chem. Soc., 75, 2862 (1953).

(45) Revenda, J., Collection Czech. Chem. Communs., 6, 453 (1934).

(46) Scattergood, A., Miller, W. H. and Gammon, J., J. Am. Chem. Soc., 67, 2150 (1944).

(47) Schlesinger, H. I. and Brown, H. C., J. Am. Chem. Soc., 62, 3429 (1940).

(48) Schlesinger, H. I., Brown, H. C., Hoekstra, H. R. and Rapp, L. R., J. Am. Chem. Soc., 75, 199 (1953).

(49) Schlesinger, H. I., Brown, H. C., Mayfield, D. L. and Gilbreath, J. R., J. Am. Chem. Soc., 75, 213 (1953).

(50) Schlesinger, H. I. and Burg, A. B., Chem. Revs., 31, 1 (1942).

(51) Sidgwick, N. V., "Chemical Elements and their Compounds," Vol. I, Oxford Univ. Press, London, 1950.

(52) Silbiger, G. and Bauer, S. H., J. Am. Chem. Soc., 70, 115 (1948).

(53) Soldate, A. M., J. Am. Chem. Soc., 69, 987 (1947).

(54) Stackelberg, M. von, Z. Elektrochem., 45, 466 (1939).

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

(56) Sugden, S. and Waloff, M., J. Chem. Soc., 1492, 1932.

(57) Wawzonek, S. and Laitinen, H. A., J. Am. Chem. Soc., 63, 2341 (1941).

(58) Vitek, V., Collection Czech. Chem. Communs., 1, 537 (1935).

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

VITA

Phillip Albert Lewis
candidate for the degree of
Doctor of Philosophy

Thesis: The Polarographic Behavior of Boron Compounds in Nonaqueous Solvents

Major: Analytical Chemistry

Minor: Physical Chemistry

Biographical:

Born: February 11, 1921 at Indianapolis, Indiana

Education: Aurora College, 1938-1942; B.S. degree, 1942.
Illinois Institute of Technology, 1947-1949; graduate study.
Oklahoma A. and M. College, 1951-1954; M.S. degree, 1954.

Employment: Duluth Junior College, 1946; instructor, chemistry and mathematics.
Aurora College, 1946-1947, 1949-1951; assistant professor, chemistry.
University of Kansas City, 1954-; assistant professor, chemistry.

Military: Signal Corps Reserve, Sixth Service Command, 1942-1943.
A.S.T.P., Polytechnic Institute of Brooklyn, 1943-1944.
Signal Corps, Army of U.S., 1943-1946.

Professional: Member of the American Chemical Society, member of Phi Lambda Upsilon, associate member of The Society of Sigma Xi.

Date of Final Examination: November, 1955.

Thesis Title: The Polarographic Behavior of Boron Compounds
in Nonaqueous Solvents

Author: Phillip Albert Lewis

Thesis Adviser: Dr. Paul Arthur

The content and form have been checked and approved by the author and thesis adviser. The Graduate School Office assumes no responsibility for errors either in form or content. The copies are sent to the bindery just as they are approved by the author and faculty adviser.

Typist: R. Louise Weston