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POLAROGRAPHIC STUDIES OF LEAD IN METHANOL SOLUTIONS

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POLAROGRAPHIC STUDIES OF LEAD IN METHANOL SOLUTIONS

By

BIRT ALLISON, JR.

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East Central State College

Ada, Oklahoma

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APPROVED BY:

Paul Arthur

Chairman, Thesis Committee

Tom E. Moore

Member of the Thesis Committee

C. C. Danner

Head of the Department

H. M. T. T. T.

Dean of the Graduate School

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HISTORICAL

In 1903 Kucera¹ constructed a dropping mercury electrode for the purpose of studying the electrocapillary curve of mercury in various electrolyte solutions, this type of electrode being especially convenient for the determination of the surface tension of mercury under various conditions. During the course of his investigation he observed certain peculiar inflections in the electrocapillary curve when the solution contained reducible substances and it was his suggestion that further investigation be made of these "anomalies" that prompted Heyrovsky to begin the investigations which ultimately led to the development of polarographic analysis. The first reference to this new method of analysis was published by Heyrovsky in 1923².

In 1925 Heyrovsky and Shikata³ constructed an automatic instrument which recorded the results photographically. Present automatic instruments, although many show refinements and are far more complicated than this simple instrument, are based on the same principles and operate in much the same manner.

The value of the polarographic method of analysis was recognized almost immediately and efforts were made to apply the method to the field of organic as well as inorganic analysis. The first reference to an organic compound investigated with the polarograph was the work of Shikata⁴ with nitrobenzene. This was followed by studies of a great number of organic compounds, most of the work being done in the laboratories of Heyrovsky, Shikata and Semerano. The major developments, however, both theoretical and applied, came in the inorganic

¹ G. Kucera, Ann. Physik, 11, 529, (1903).

² J. Heyrovsky, Phil. Mag., 45, 303, (1923).

³ J. Heyrovsky and M. Shikata, Rec. trav. chim., 44, 496, (1925).

⁴ M. Shikata, Trans. Faraday Soc., 21, 42, (1925).

field of necessity since the reductions of organic compounds in most cases are irreversible or at least involve irreversible steps, and interpretation of the resulting current-voltage curves was impossible with the electrochemical data available to these pioneer workers at that time.

In an effort to fix upon some point on the current-voltage curve which would have sufficient significance to enable identifications and comparisons to be made, a number of suggestions were made by early workers in the field. At first⁵ that potential at which an increase in the applied voltage produced an increase in the current of 10^{-8} amperes was arbitrarily chosen, this being called the "deposition potential" of the ion. Later Semerano⁶ suggested as being more characteristic the applied potential at the point of maximum curvature of the polarographic wave which he obtained by placing a tangent at $35^{\circ} 16'$ to the curve. On the other hand Shikata⁷ chose to use that value of the applied voltage at which an increase of 10 mv. produced a rise in current of 1.9×10^{-8} amperes, calling this value the "reduction potential". All of these methods, however, possessed the very serious disadvantages that the potentials so observed changed with the concentration, with the sensitivity of the galvanometer, with the drop time, and with the rate of flow of the mercury. Consequently it was a great step forward when Heyrovsky and Ilkovic⁸ explained the theoretical significance of the polarographic wave and suggested the use of the half-wave potential for each ion. This value is independent of concentration, drop time, and galvanometer sensitivity.

The theory of the half-wave potential shows that this potential, when

⁵ J. Heyrovsky, Chem. Listy, 16, 256, (1922).

⁶ G. Semerano, Gazz. chim. ital., 62, 518, (1932).

⁷ M. Shikata, Mem. Coll. Agr. Kyoto Imp. Univ., Ser. No. 4, 1, (1927).

⁸ J. Heyrovsky and D. Ilkovic, Coll. Czech. Chem. Commun., 7, 198, (1935).

measured under certain conditions, is mathematically related to the potentiometrically determined oxidation-reduction potentials of these systems.^{9, 10} As a result of this discovery, many organic reactions are being studied with the dropping mercury electrode. A list, purporting to be complete, of all organic compounds which have been studied polarographically up to June 1938 has been compiled by O. H. Muller.¹¹ Subsequent references to such works may be found in the Bibliography of Polarographic Literature published by E. H. Sargent and Company covering the period from 1922 through 1945.

The use of indicator electrodes other than the dropping mercury has been reported. Of these the solid rotating platinum microelectrode is perhaps the most usable. Kolthoff and Lingane¹² and Laitinen¹³ have described various forms of these microelectrodes along with their respective characteristics.

⁹ J. Lingane, J. Am. Chem. Soc., 61, 2099, (1939).

¹⁰ O. H. Muller, The Polarographic Method of Analysis, Mack Printing Co., Easton, Pa., (1941).

¹¹ O. H. Muller, Chem. Revs., 24, 95, (1939).

¹² I. Kolthoff and J. Lingane, Polarography, Interscience Publishers, Inc., New York, 439-441, (1941).

¹³ I. Kolthoff and H. Laitinen, J. Am. Chem. Soc., 61, 3344, (1939).

INTRODUCTION

The polarographic method of analysis is based on the interpretation of current-voltage curves obtained when a cell containing an electrooxidizable or electroreducible substance is electrolyzed with a constantly increasing voltage between two electrodes, one of which is easily concentration-polarized, the other non-polarizable. Qualitative information is obtained from the voltage necessary to reduce or to oxidize the substance whereas the magnitude of the current flowing during electrolysis provides quantitative information.

Either an automatic continuously recording instrument or a manual instrument may be used to obtain this information. The former has the advantage of a constant rate of increasing the applied voltage during electrolysis and of yielding a continuous curve rather than a series of points. Slight peculiarities which might otherwise escape notice are automatically detected and recorded. This, plus the saving in time, makes the automatic instrument highly desirable. The major portion of this investigation was made using one of the more simple of the automatic instruments, Sargent's Model XII polarograph, which records the curves photographically. However, for studies where the time factor, i.e., for equilibrium to be reached, is important, a manual instrument was used. The schematic diagrams of these instruments are shown in Figs. 1 and 2.

For both instruments the basic theories and essential parts are the same. The apparatus necessary for the basic polarographic circuit consists of four units: (1) a source of electromotive force; (2) a means of varying the potential applied across the cell; (3) the electrolysis cell; and (4) the galvanometer circuit. The circuit of the automatic instrument is shown in Fig. 1. The galvanometer circuit consists of a low-internal-resistance d'Arsonval galvanometer of high sensitivity (10^{-9} amp/mm) and a long period of swing (15 seconds). The period of the galvanometer swing is increased by means of a damping resistance

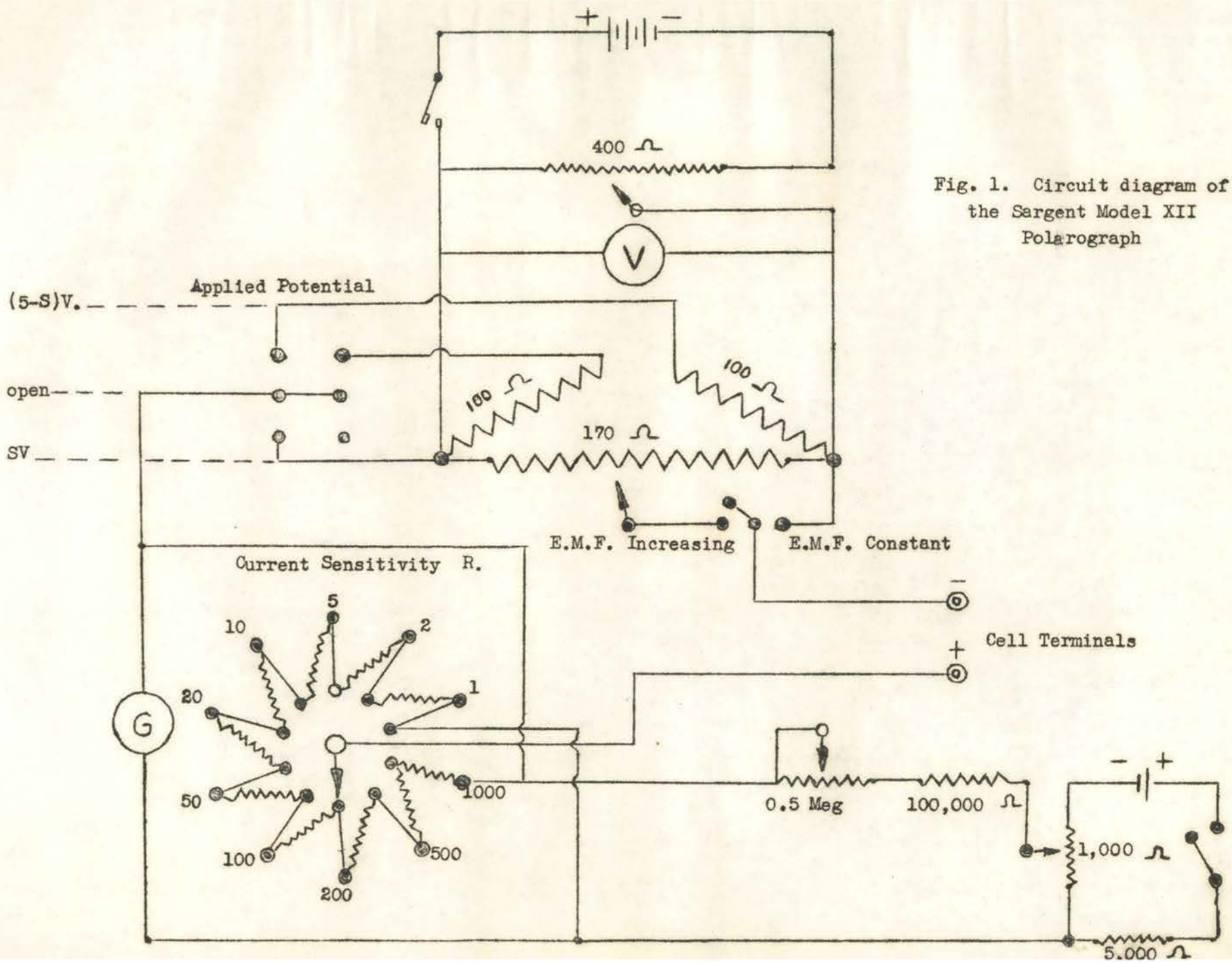


Fig. 1. Circuit diagram of the Sargent Model XII Polarograph

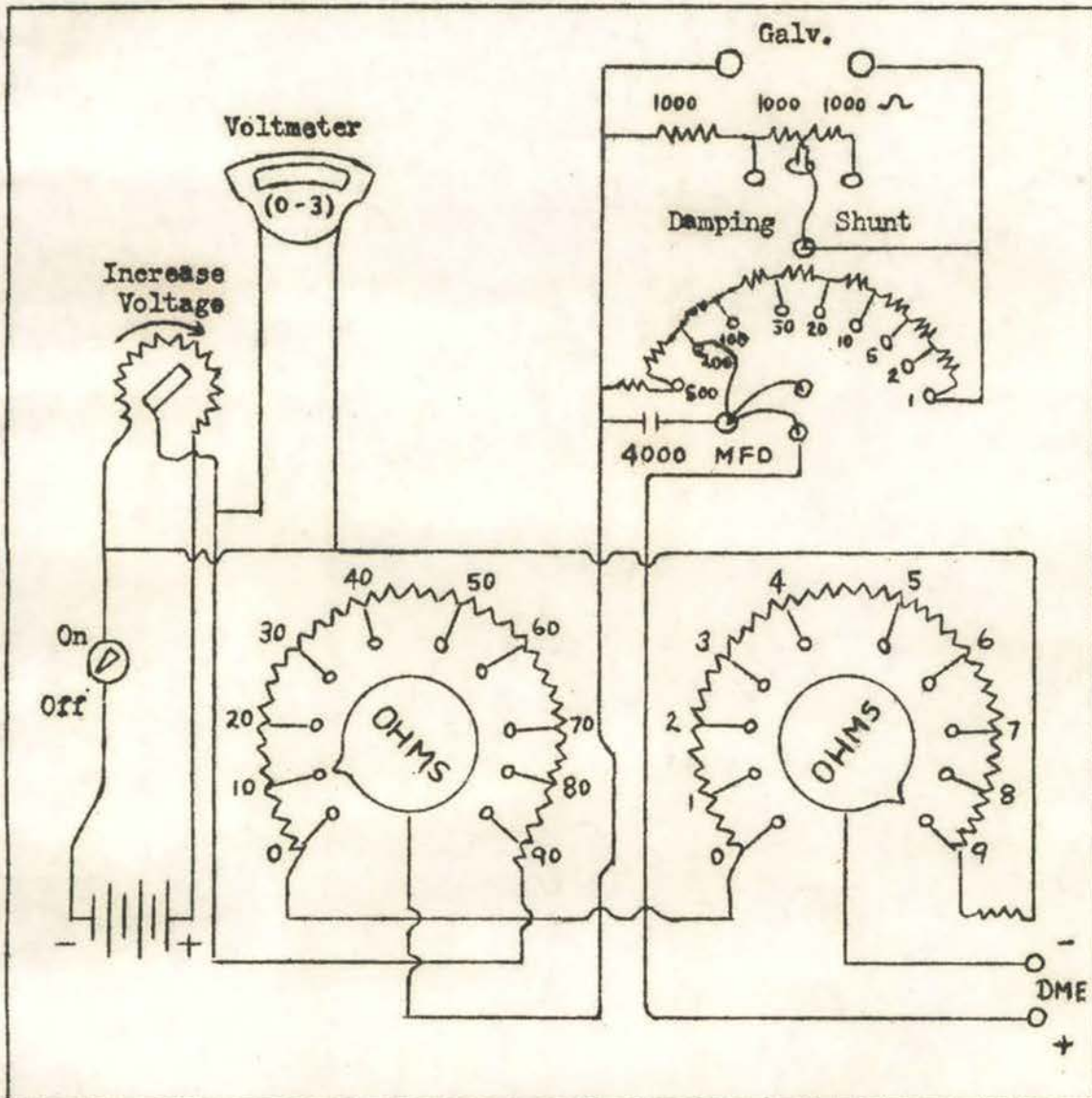


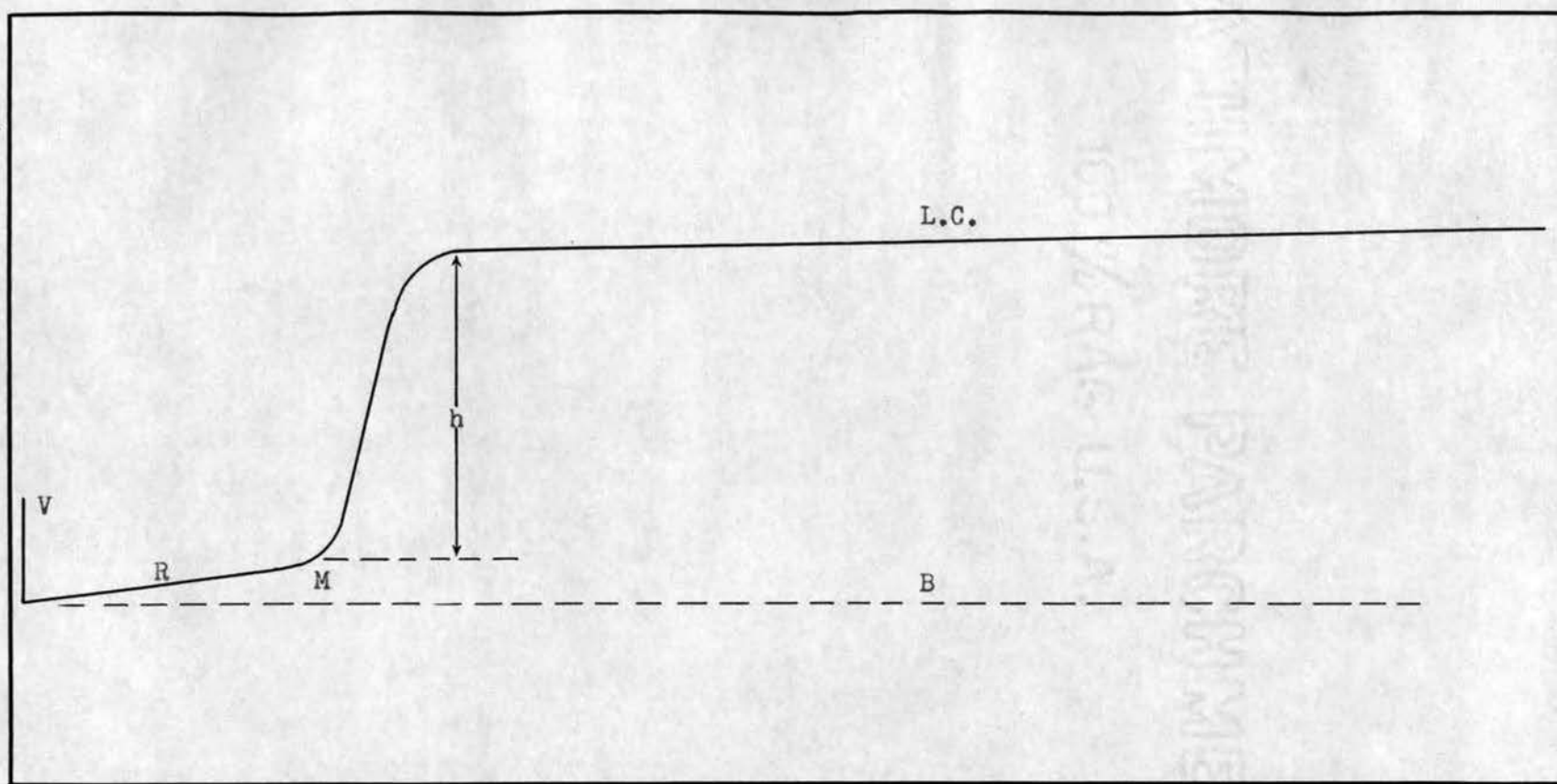
Fig. 2 Wiring Diagram of Manual Polarograph
(Designed and Constructed by Paul Arthur)

across the galvanometer since a period of 20 to 40 seconds is needed. The automatic instrument used for this investigation did not have a condenser to smooth out galvanometer oscillations, although the manual apparatus did have. (Fig. 2)

In operation the polarographic method involves the measurement of the currents flowing when known potentials are applied across the electrolysis cell. A graph of such data either plotted or automatically and continuously recorded is called a polarogram. A reproduction of a typical polarogram is shown in Fig. 3. The significance of the various parts of the polarogram itself will be presented after a brief discussion of underlying theoretical principles.

If the electrode is very small and the solution is not stirred during electrolysis, the reaction depletes the reacting substance in the solution in contact with the electrode and thus produces a concentration gradient between the body of the solution and the solution at the electrode surface. As the applied potential is increased this concentration gradient increases and the current, which is proportional to the rate of formation of products at the electrode, reaches a limiting value which is dependent only upon the rate at which the reacting particles move from the more concentrated body of the solution to the less concentrated solution at the surface of the electrode. The movement of these particles toward the less concentrated solution at the electrode is due to two forces: (1) migration of ions due to electrostatic attraction of the electrode for ions of opposite charge; (2) diffusion. Thus at sufficiently high potentials the total current which flows through the cell will be the sum of these two currents, i.e., a migration current and a diffusion current.

In polarographic analysis involving ionized substances it is desirable to minimize the migration current so that a well defined, reproducible wave due entirely to the diffusion of the reducible ions (or oxidizable ions, if the dropping mercury electrode is made positive) across the concentration gradient is obtained. This is accomplished by the addition of an indifferent electrolyte



R. Residual current line
 h. Height of diffusion current
 L.C. Limiting current line

B. Zero current line (base)
 V. Zero voltage line (base)
 M. Magnitude of residual current
 at indicated potential

Fig. 3 A Typical Polarogram

to the solution in sufficient concentration to blanket the charges on the droplets of mercury as they form, thereby minimizing migration of ions which are present in lower concentration. When a large excess of such an electrolyte (a salt whose ions are not involved in the electrode reaction) is added to a solution of relatively small concentrations of the oxidizable or reducible ion under consideration the current through the solution will be carried practically entirely by the indifferent ions. Under these conditions the tendency of the reducible ions to migrate under the influence of electrostatic influence is negligible and the measured limiting current becomes almost solely a diffusion current. In actual practice the concentration of the indifferent salt is usually at least ten times and preferably one hundred or more times as great as that of the ion under study. Obviously the potential at which the ion of the indifferent electrolyte will react at the electrode must be greater than that for the ion under study.

Diffusion at a dropping mercury electrode is spherically symmetrical but owing to the periodic growth and fall of the droplets, the area of the electrode surface changes continuously during the life of the drop. Although the problem of diffusion at the dropping mercury electrode is far more complicated than symmetrical diffusion at a fixed sphere, Ilkovic and other workers^{14, 15} have derived, for the resulting current for the dropping mercury electrode, an empirical equation which is reported to be most satisfactory.

An examination of Fig. 3 shows that the polarogram actually consists of several curves: (1) a linear curve (R) beginning, in this case, at zero voltage and current and rising slightly above the abscissa; (2) the wave proper; and (3) the limiting-current curve. The linear curve is finally interrupted by the

¹⁴ D. Ilkovic, Coll. Czech Chem. Commun., 6, 498, (1934).

¹⁵ I. D. MacGillavry and E. K. Rideal, Rec. Trav. Chim., 56, 1013, (1937).

"wave" when the deposition potential of a reacting ion is approached. This linear curve with a very slight rise is known as the residual current. It occurs even though no apparent electrolyzable material is present.

With the dropping mercury electrode this small residual current arises partially from the fact that as each new drop of mercury grows a small current must flow in order to build up a charge on the mercury corresponding to the applied potential. With stationary or rotating microelectrodes, the charging current is zero since the electrode area is constant; however, a small current due to unknown causes still flows. Obviously the residual current must be subtracted from the total current observed in quantitative determinations.

The wave portion of the polarogram is the most significant in polarographic analysis. From this comes the "half-wave" potential, i.e., a point halfway between the projected residual current line and the flat upper portion of the curve after the maximum change in current flow has been reached. This potential is, under the proper conditions, characteristic of the substance producing the wave. For example, the half-wave potential for the cadmium ion in 0.1 N aqueous solution of KCl will be found at -0.60 volts when determined against the saturated calomel electrode. Indifferent salts other than KCl may shift the half-wave potential slightly but literature values specify the potential vs. S.C.E. for a specific carrier salt.

The height of the wave ("h" in Fig. 3) is a function of the concentration of the ion whose deposition potential has been reached. If conditions are held constant and suitable standards are available, the wave height gives quantitative information. Accuracy is limited by the reproducibility of the wave and the accuracy with which measurement of the wave height may be made. Taylor¹⁶ has recently discussed the merits of various methods in use for evaluating quantitative

¹⁶ J. K. Taylor, Anal. Chem., 19, 368, (1947).

results.

The practically flat portion of the curve occurring at voltages beyond the deposition voltage for the ion is the "limiting current" curve. As was explained earlier, this phenomenon is caused by the extreme state of concentration polarization which results from the depletion of the electroactive material in the immediate vicinity of the electrode surface as a result of electrode reaction. The factors affecting the limiting current are: (1) the residual current, (2) the migration current, (3) the diffusion current, and (4) the adsorption current. Of these, only the last two merit additional discussion.

Ilkovic¹⁷ has derived the following equation for the diffusion current at the dropping mercury electrode at constant temperature with no stirring:

$$i_d = knFCD^{1/2}m^{2/3}t^{1/6}.$$

In this equation k arises from the geometric characteristics of the dropping mercury electrode; nF is the number of coulombs involved per mole of electrode reaction. C is the millimolar concentration of electroactive material per liter; D is the diffusion coefficient of the electroactive material in $\text{cm}^2/\text{sec.}$; m is the mass of mercury flowing through the capillary in milligrams per second; and t is the drop time in seconds at the half-wave potential.

The last two quantities in the Ilkovic equation, $m^{2/3}t^{1/6}$, are important because they establish a relationship by means of which diffusion currents measured with different capillaries and with the same capillary at different potentials may be compared. In actual practice, the drop time and the temperature are kept constant throughout a determination.

The occurrence of maxima is well known in polarography. Many of the current-voltage curves show this distortion unless measures are taken to prevent their occurrence. These maxima vary from sharp peaks that send the galvanometer off

¹⁷ D. Ilkovic, loc. cit.

the scale to rounded humps. Maxima have been variously attributed to the stirring effect of the droplet of mercury and to nonuniform adsorption of electro-active material on the surface of the droplet of mercury. In either case they seem to be due to an unbalanced charge on the droplet of mercury. A turbulence is thus produced and true concentration polarization is not reached. In many instances the curve shows a slight drop from the top of the maximum below the limiting-current line and then rises again to the flat portion of the curve. Whatever the cause, maxima must be eliminated in polarographic work. This is usually accomplished by the use of surface active agents such as dye ions or colloids. Gelatin is commonly used, but the amount present in the solution must be carefully controlled between 0.002 and 0.01%¹⁸ since a lower concentration is not an effective maxima suppressor and more tends to suppress the diffusion current.

Polarography has been applied quite extensively to the field of inorganic chemistry and to a far lesser extent to the reduction of organic substances in aqueous media. Some studies of cations in water-organic solvent mixtures have been reported but investigations conducted in anhydrous organic solvent media have been few in number. In most cases of this sort the curves obtained are erratic, non-reproducible and impossible to interpret. Exceptions may be found in the reported works of Bachman and Astle¹⁹ with anhydrous acetic acid. One reference has appeared in which anhydrous liquid ammonia was used as the solvent.²⁰

Investigators^{21,22} working with anhydrous organic solvents have reported

¹⁸ H. Hohn, Chemische Analysen mit dem Polarographen, Berlin: Springer, (1937).

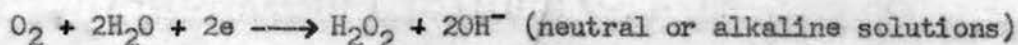
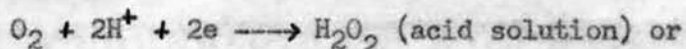
¹⁹ G. B. Bachman and M. J. Astle, J. Am. Chem. Soc., 64, 1303, (1942).

²⁰ H. D. Laitinen and C. J. Numan, J. Am. Chem. Soc., 70, 2241, (1948).

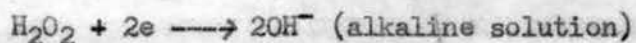
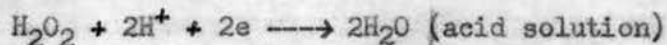
²¹ E. Perracho and V. Meloche, J. Am. Chem. Soc., 60, 1770, (1938).

²² H. Adkins and F. Cox, J. Am. Chem. Soc., 60, 1157, (1938).

that dissolved oxygen interferes with the wave of the ion under study. Oxygen, even in dilute aqueous solutions, is present in concentrations of about $2.5 \times 10^{-4} \text{ M}$ and is easily reduced to give a polarogram consisting of two waves of equal heights. According to Heyrovsky²³ the first wave is due to the reduction of molecular oxygen to hydrogen peroxide.



The second drawn-out wave corresponds to the reduction of hydrogen peroxide either to water or to the hydroxyl ion.



All these reactions are irreversible at the dropping mercury electrode and require considerable overvoltage.

The first oxygen wave is characterized by very pronounced maxima but these are easily suppressed by capillary active substances such as dyes or gelatin.

Kolthoff and Miller²⁴ reported that the potential at which the first wave appears is practically independent of the pH of the solution but that it varies somewhat with the nature and concentration of the anions that are present.

Strnad²⁵ reports that small concentrations of heavy metal ions exert a pronounced effect on the waves of oxygen; the effect of the lead ion was particularly marked. Vitek²⁶ has pointed out that the diffusion current of oxygen is several times larger when anhydrous methanol is used as the solvent than is the

²³ J. Heyrovsky, Trans. Faraday Soc., 19, 785, (1924).

²⁴ I. M. Kolthoff and C. S. Miller, J. Am. Chem. Soc., 63, 1013, (1941).

²⁵ F. Strnad, Coll. Czech. Chem. Commun., 11, 391, (1939).

²⁶ V. Vitek, Coll. Czech. Chem. Commun., 7, 537, (1935).

case for water. Vitek suggested that this might be due to a greater solubility of oxygen in alcohol than in water.

PURPOSE

This problem was undertaken in order to investigate the possibility of developing a direct polarographic means of analyzing for lead in motor fuels. Such an analysis, if successful, would be highly beneficial to the petroleum chemist, since present methods involve time consuming precipitation of the lead as either the sulfate²⁷ or chromate²⁸ along with frequent evaporations. The process as outlined by Birch²⁹ requires several hours for each analysis. An X-ray method, although requiring a much shorter time, requires exceedingly expensive equipment and a highly skilled operator. If such an analysis could be made polarographically, the saving in time and equipment would be of utmost importance.

An examination of pertinent literature^{30,31} showed that the concentration of lead varies from 0.5 to 3.0 mls. per gallon of gasoline (3.7854 liters) and up to 4.4 mls. per gallon in aviation type gasoline. One ml. per gallon is equivalent to ten parts in 1400 parts of gasoline by weight. This concentration is well within the concentration limitations of polarography. The direct polarographic determination of copper did not appear feasible since the maximum concentration of copper permissible in gasoline is too low, being of the order of 10^{-6} M.

Preliminary work with lead (II) salts in nonaqueous media failed to give reproducible interpretable results although the same salts did give reproducible

²⁷ R. Pierson, Scott's Standard Methods of Chemical Analysis, 5th Ed., D. Van Nostrand and Co., New York, N. Y., 1804 (1939).

²⁸ G. Ferreri, Giorn. Chim. ind. Applicata, 1, 625-626, (1925).

²⁹ S. F. Birch, J. Inst. Petroleum Tech., 10, 816-817, (1924).

³⁰ R. H. Aborn and R. H. Brown, Ind. Eng. Chem. Anal. Ed. 1, 26-27, (1929).

³¹ E. Droegemueller, ASTM Bulletin, TP 211, (1948).

curves in aqueous solutions under comparable conditions. This difficulty with nonaqueous solvents indicated that further knowledge of the behavior of lead ions in nonaqueous media was needed before a method of direct polarographic analysis of lead in gasoline could be perfected. Methyl alcohol was chosen as the solvent after conductance and solubility tests indicated that solutions of methyl alcohol with lithium chloride carrier compared favorably with aqueous 0.1 *N* potassium chloride solutions. Methyl alcohol was chosen also because it was believed that gasoline would be soluble in it to such an extent that the concentration of lead would be satisfactory for polarographic analysis. Too, alcohols in general are good solvents for many organic and inorganic compounds.

Black,³² working at this institution, reported that no limiting current for nickel was discernible in methanol-water solutions where the concentration of methanol exceeded 91% by volume. The main emphasis of this investigation was the study of the behavior of lead in nonaqueous media. Such a study is necessary before direct polarographic analysis for lead in gasoline can be accomplished. Owing to the lack of time it was not possible both to thoroughly investigate the behavior of the lead ion in anhydrous media and in addition to apply the acquired knowledge to perfecting a method for direct determination of lead in gasoline. This problem then is of a qualitative nature and no special effort was made to obtain quantitative data. The investigator was interested in perfecting a technique that would give reproducible interpretable results under anhydrous conditions; this technique in turn should point the way for later applications to the actual analysis of gasoline for lead.

³² H. Black, Polarographic Studies in Organic Solvents, Unpublished M. S. thesis, C.A.M.C., (1948).

EXPERIMENTAL

Instrumental Procedure

In a typical run using the dropping mercury electrode and a pool of mercury, about 10 ml. of the solution to be electrolyzed is placed in the electrolysis cell and purified nitrogen gas is bubbled through it for a minimum of fifteen minutes to remove dissolved oxygen. While the solution is being deoxygenated, the camera is loaded and inserted in the instrument. If desired, a zero-voltage line may be put on the film by opening the camera shutter and slowly moving the galvanometer light across the scale. Then, with only the galvanometer light on, the motor is turned on. These operations give a straight line along the bottom of the plate and a vertical line from which current and voltage measurements, respectively, can be made.

After deoxygenation is complete, the flow of gas is discontinued and a small quantity of mercury is poured into the electrolysis cell to serve as the anode. The dropping mercury electrode is inserted, the desired voltage and galvanometer settings are made, the camera is opened, and the motor switch is turned to the "on" position. The electrolysis is continued until the full voltage which was preset by the operator has been scanned, or it may be discontinued at any time by the operator. Several analyses or "runs" may be made on the same sheet of photographic paper.

When the runs are completed, the paper is removed from the camera and is developed and fixed by ordinary photographic methods.

Reagents

Since the reagents used in this investigation were of such nature that the only impurities which should interfere would be those which show up in polarograms, it was felt that polarographic tests for purity would be sufficient. Reagent grade chemicals were used where possible. The source and treatment of each of the reagents used in this investigation are as follows:

Acetone. Anhydrous C.P. acetone from the Mallinckrodt Chemical Works of St. Louis, Missouri, was kept dry over commercial Drierite.

Drierite. (CaSO_4). Both polarographic and conductivity tests showed no interference from this dehydrating agent. Drierite was manufactured by Hammond Company, Yellow Springs, Ohio.

Gelatin. Ground edible gelatin was obtained from the E. H. Sargent and Company, Chicago, Illinois.

Guanidine Hydrochloride. White-label guanidine hydrochloride obtained from the Eastman Kodak Company, Rochester, New York, was used without further purification.

Lead Acetate. Lead acetate was obtained from the J. T. Baker Chemical Company, Phillipsburg, New Jersey, and was used without further purification.

Lead Chloride. C.P. lead chloride from Eimer and Amend, New York, New York, was used without further purification.

Lead Nitrate. Lead nitrate was obtained from the J. T. Baker Chemical Company, Phillipsburg, New Jersey, and was C.P. grade, used without further purification.

Lithium Chloride. Lithium chloride was prepared from reagent grade hydrochloric acid and C.P. lithium hydroxide. Polarographic tests showed no interfering impurities up to 2.2 volts, so the reagent was used without further purification. It was necessary to dry this reagent in an oven at 105°C .

Mercury. U.S.P.C.P., triple-distilled mercury, obtained from the Metal-salts Corporation, Patterson, New Jersey, was used without further purification. The used mercury was reclaimed and purified by washing with 1 N nitric acid and then bubbling with air under 10% nitric acid for at least 24 hours. It was then washed repeatedly with distilled water, the excess water removed, and the mercury filtered through a very small hole punched in high grade filter paper.

The mercury was kept in a desiccator over concentrated sulfuric acid prior to use.

Methanol. Reagent grade absolute methyl alcohol obtained from Merck and Company, Rahway, New Jersey, was used without further purification.

Nickel Chloride. Reagent grade nickel chloride obtained from Merck and Company, Rahway, New Jersey, was used without further purification.

Nitrogen. Water-pumped nitrogen obtained from the Matheson Company, Joliet, Illinois, was bubbled through an oxygen absorber and through concentrated sulfuric acid prior to use for degassing purposes. It was finally passed through a wash bottle containing the same solution as that in the electrolytic cell.

Potassium Chloride. Reagent grade potassium chloride obtained from Merck and Company, Rahway, New Jersey, was used without further purification.

Pyrogalllic Acid. Pyrogalllic acid conforming with U.S.P. XI requirements was obtained from Eimer and Amend, New York, New York. An alkaline solution of this acid was used to absorb oxygen from the tank nitrogen.

Sodium Acetate. C.P. grade sodium acetate was obtained from Eimer and Amend, New York, New York, and was used without further purification.

Tetramethylammonium chloride. Practical grade tetramethylammonium chloride obtained from Eastman Kodak Company, Rochester, New York, was dried and maintained in a desiccator over calcium chloride before use.

Results and Conclusions

When pure water is electrolyzed with the dropping mercury electrode, a straight line with very little slope (the residual current line) is obtained until the decomposition potential of water is reached. By analogy, it was expected that an organic solvent or a mixture of water and organic solvent which produced a similar curve during electrolysis would be suitable for use as the medium in which soluble reducible substances could be studied polarographically.

In selecting the organic solvents to be used in the course of this investigation, it was necessary to consider several questions: (1) is the solvent stable to a minimum of two volts, this being the range arbitrarily set for work with the lead ion; (2) is the conductivity of a solution of the solvent saturated with a carrier salt of the same approximate order of magnitude as the conductivity of an 0.1 N potassium chloride solution in water; (3) are any available lead salts soluble to an appreciable extent in this solvent. The final criterion, of course, would be the ability of an anhydrous solution of the chosen solvent, carrier, and lead salts to give a reproducible lead wave. The two-volt range was chosen because at potentials less negative than this value most carrier salts and solvents show stability and it was thought desirable to follow changes caused by anhydrous solvents to as negative potentials as possible. A two-volt range across the potentiometer also is convenient since to determine a particular value for the applied voltage during a run, one need only multiply the value on the rotating camera by two.

Preliminary work was done with methyl alcohol, acetone and glacial acetic acid as solvents. Indifferent carrier salts tried in these solvents were potassium chloride, guanidine hydrochloride, tetramethylammonium chloride, sodium iodide, sodium acetate, potassium nitrate and lithium chloride. The source of lead ions was lead nitrate, lead acetate, or lead chloride. Degassing was accomplished originally by use of commercial water-pumped tank nitrogen with no purification. None of the curves obtained during this phase of the investigation could be interpreted since they showed no limiting current and were not reproducible. Even re-runs of the same solution failed to give similar curves.

Conductivity tests indicated that anhydrous methanol with lithium chloride as carrier compared favorably with an aqueous 0.1 N solution of potassium chloride. Because of this, a study was made of the curves obtained with anhydrous methanol and this carrier. The resulting curve showed the expected straight

line with a slight rise with no apparent instability up to the full negative two volts. Thus it was decided to use this solvent for all subsequent work either under anhydrous conditions or in mixtures of water-alcohol solutions. A check of solubilities showed that lead acetate and lead nitrate are both soluble in these solvents to an extent suitable for polarographic determinations.

Polarographic study of a solution of a lead salt dissolved in anhydrous methanol containing a carrier electrolyte, however, produced strange results. Poorly defined waves occurring at different potentials (not reproducible) were noticed. The currents were large in magnitude and seldom showed signs of leveling off to a true diffusion current. Since the only change in the solutions was the addition of the lead salt, it might be concluded that either the lead ion behaved erratically in alcoholic media or the interference was due to some reaction involving the anion of the lead salt. Changing the anions failed to improve the wave forms or to stabilize the potentials at which the waves began.

More and more, however, the evidence tended to point toward the enhanced oxygen wave in organic media in the presence of the lead ion. Vitek³³ had pointed out the increased difficulty of degassing methanol solutions and Strnad³⁴ had reported that the effect of a heavy ion such as that of lead is to give an enhanced oxygen wave, the effect of lead being seemingly catalytic in nature. These two investigators were studying the diffusion current of oxygen, being interested in the quantitative determination of oxygen in technical gases and solutions. Strnad attributed the seemingly catalytic effect of lead (most pronounced when the lead ion concentration was about 0.001 N) to

³³ V. Vitek, loc. cit.

³⁴ F. Strnad, loc. cit.

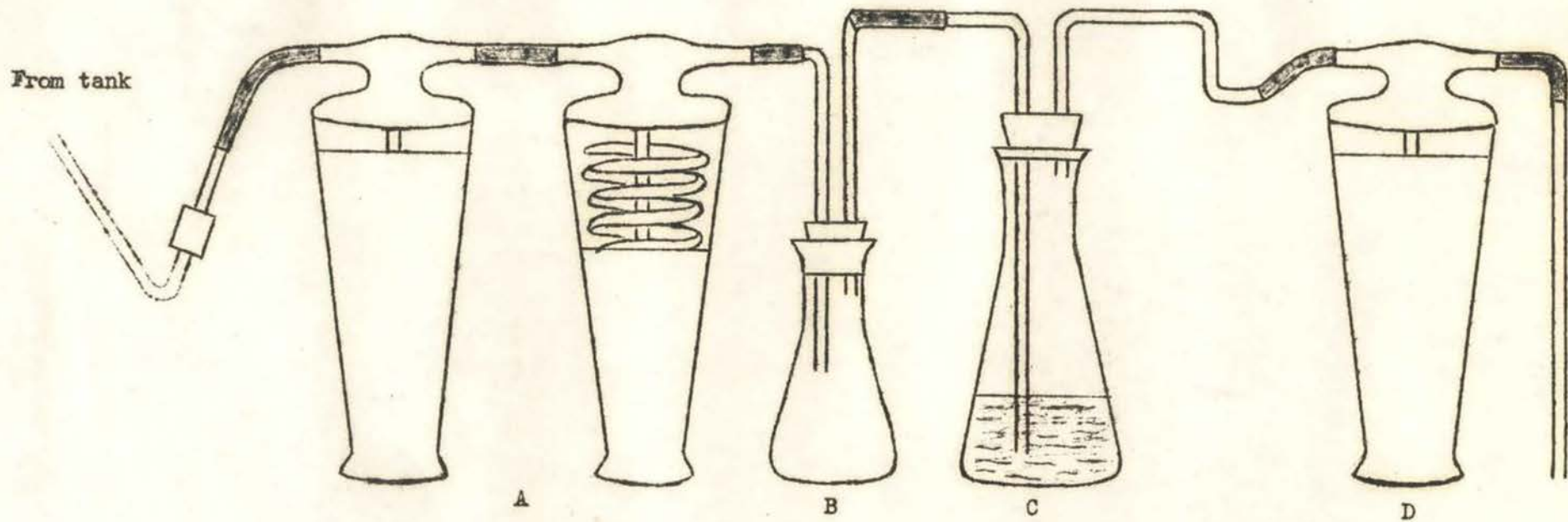
the formation of lead (IV) by the oxidation of the plumbous ion by the hydrogen peroxide first formed. This catalytic effect disappeared when traces of acids or bases were added to the solution. In a neutral solution any lead (II) compound ($PbO_2?$) formed would be immediately reduced and therefore the net result would be the reduction of the oxygen ion all the way to water or hydroxyl ion. Vitek claimed that the presence of a few hundredths of a percent of oxygen can be detected polarographically. The work of Black³⁵ with the nickel ion in anhydrous media has previously been mentioned. In considering our results and the results of the other investigators mentioned, it became increasingly apparent that none of the workers in this field had attributed sufficient importance to the role of oxygen as an interference in nonaqueous polarography where heavy metal ions are present. This is not surprising since the "waves" obtained resembled nothing which had ever been obtained in aqueous solutions and varied without any apparent reason.

To study the problem of dissolved oxygen and its effect on the half-wave potential of lead, it was decided to improve the efficiency of the degassing technique and to use various alcohol-water mixtures to see how this effect varied with the percentage of alcohol in the solution. Although ordinary tank nitrogen had proved satisfactory for degassing aqueous solutions, it apparently contained enough oxygen itself to cause interference when methanol was used as the solvent. After an examination of reported ways of removing oxygen from tank nitrogen, it was decided to bubble the nitrogen through one or more towers containing a solution of the sodium salt of pyrogallol acid. The gas was passed through an Erlenmeyer flask trap to catch any entrained material and thence through a container of concentrated sulfuric acid to remove any water vapor that might be present. After this treatment, the gas was bubbled through a gas-washing

³⁵ H. Black, loc. cit.

bottle containing the same solvent as that being used in the electrolysis cell. This saturated the stream of nitrogen with the solvent and thereby prevented loss of solvent in the cell by evaporation. A schematic drawing of the degassing apparatus is shown in Fig. 4. This apparatus was used for all subsequent degassing and proved to be satisfactory.

After this better degassing technique was developed and tested satisfactorily, it was decided to change from anhydrous conditions in order to study the effect of increasing alcohol concentration on degassing needs. Aqueous solutions of lead exhibit a well-defined half-wave with little or no special degassing whereas previous efforts to obtain a simple half-wave in anhydrous media gave erratic results. An attempt was made to establish the minimum concentration of alcohol in water necessary to eliminate the simple wave first without additional purification of the inert gas and then with the purified gas. In this work the concentration of alcohol was varied from 0 to 100% in steps of 25, 50, 75, 90, 95, and 100 percent. The result of increasing alcoholic content is shown in Figs. 5A and 5B. It should be noted that the diffusion current becomes progressively smaller with increasing amounts of alcohol. This is in accordance with accepted theories of ionization--that alcohol represses ionization. It is interesting to note that the half-wave potential of lead is not appreciably influenced by the concentration of alcohol up to a concentration of 50%. Also, up to 50% alcohol concentration, the solutions behave essentially like aqueous solutions with no particular degassing problems. When the concentration of alcohol reaches 75%, a longer degassing time is required; also the reproducibility of the half-wave potential is lessened. The same is true for the 90% methanol solution. Between 90 and 95% alcoholic content, the half-wave potential of lead disappears and no limiting current line is obtained. This confirms the observations of Black that the limiting current disappears in those solutions where the alcoholic content is greater than 91%. Apparently then, the



A. Gas washing bottles containing sodium pyrogallate
 B. Trap

C. Concentrated sulfuric acid
 D. Solvent

Fig. 4 Degassing Apparatus

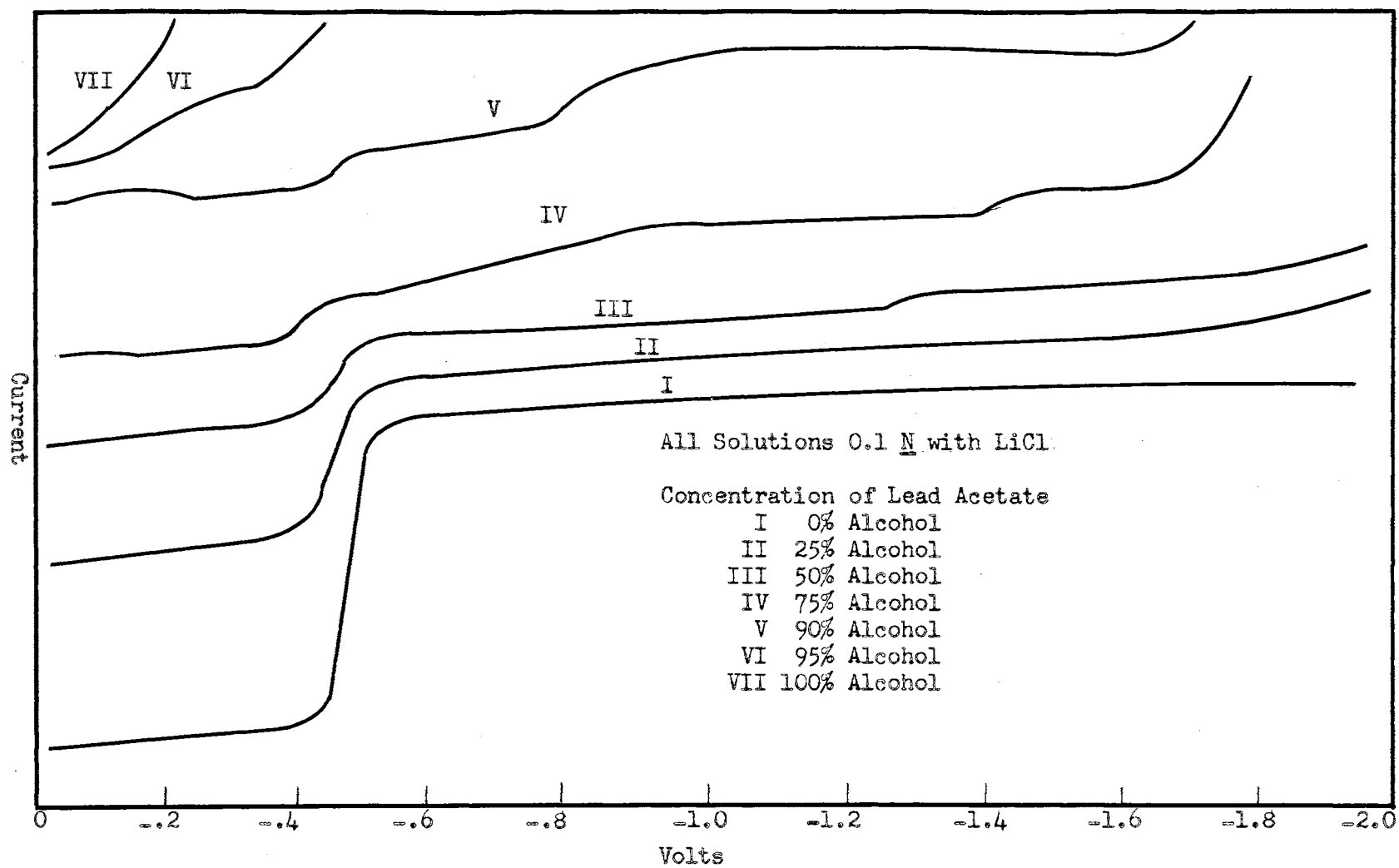


Fig. 5A Effect of Alcohol Concentration on Diffusion Current
(Untreated Nitrogen)

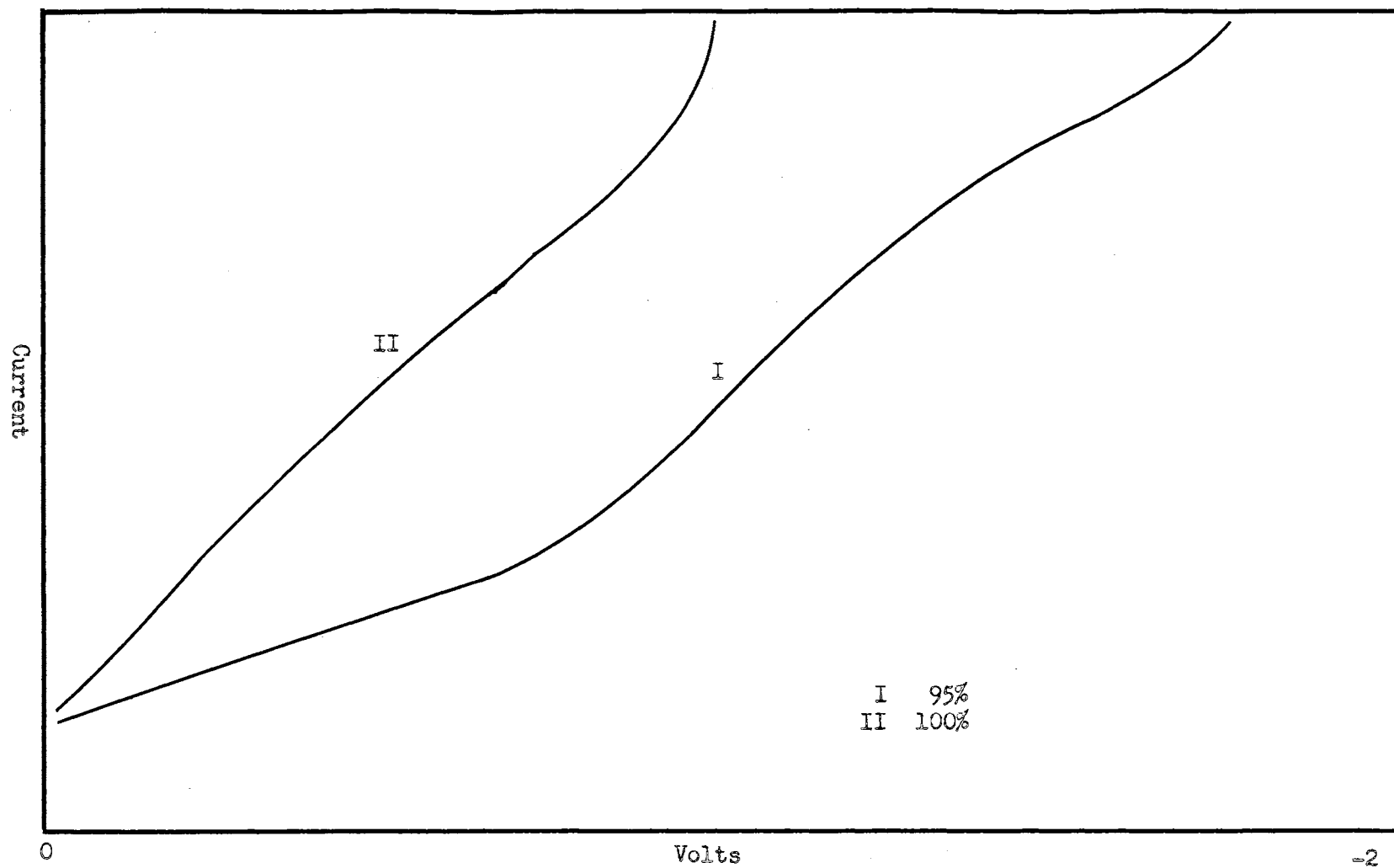


Fig. 5B
(Continuation of Fig. 5A)

problem of degassing reaches the critical state at a concentration of approximately 90% methanol and at higher concentrations better degassing technique is necessary.

Fig. 6 shows the effect of degassing time on a 0.1 N solution of lithium chloride in 100% methanol. When the degassing time was five minutes, the first oxygen wave showed at slightly less than -0.4 volts; with thirty minutes degassing, the first oxygen wave seems largely to have disappeared and what was apparently a displaced second oxygen wave appeared at about -1.0 volt. This degassing was accomplished with tank nitrogen with no further purification. Since the half-wave potential of lead is more positive than -1.0 volt, it seemed that it should be possible to analyze for lead in anhydrous media unless the presence of water is absolutely necessary for the electro-reduction of lead (which is doubtful). However, it will be recalled that in runs with the lead ion in anhydrous methanol no interpretable results were obtained. Thus the observations of Strnad³⁶ concerning the enhancement of the oxygen wave by lead in aqueous media seem equally applicable in methanol solutions. Apparently, therefore, we have a double enhancement to deal with--namely, the enhancement due to the methanol solvent and the enhancement due to the heavy metal. A more nearly complete removal of dissolved oxygen is required when methanol is used as the solvent and particularly when both methanol and lead are present.

The effect of using nitrogen gas that has been purified by bubbling through freshly prepared sodium pyrogallate is shown in Fig. 7. The solutions were 0.1 N lithium chloride and 0.05 N lead ions in anhydrous methanol. Curve 1 shows the result of no degassing. Curve 2 shows the result of degassing for 15 minutes. Curve 3 indicates that more than 15 minutes degassing with purified nitrogen is not necessary when lead is the only heavy metal present. Note that

³⁶ F. Strnad, loc. cit.

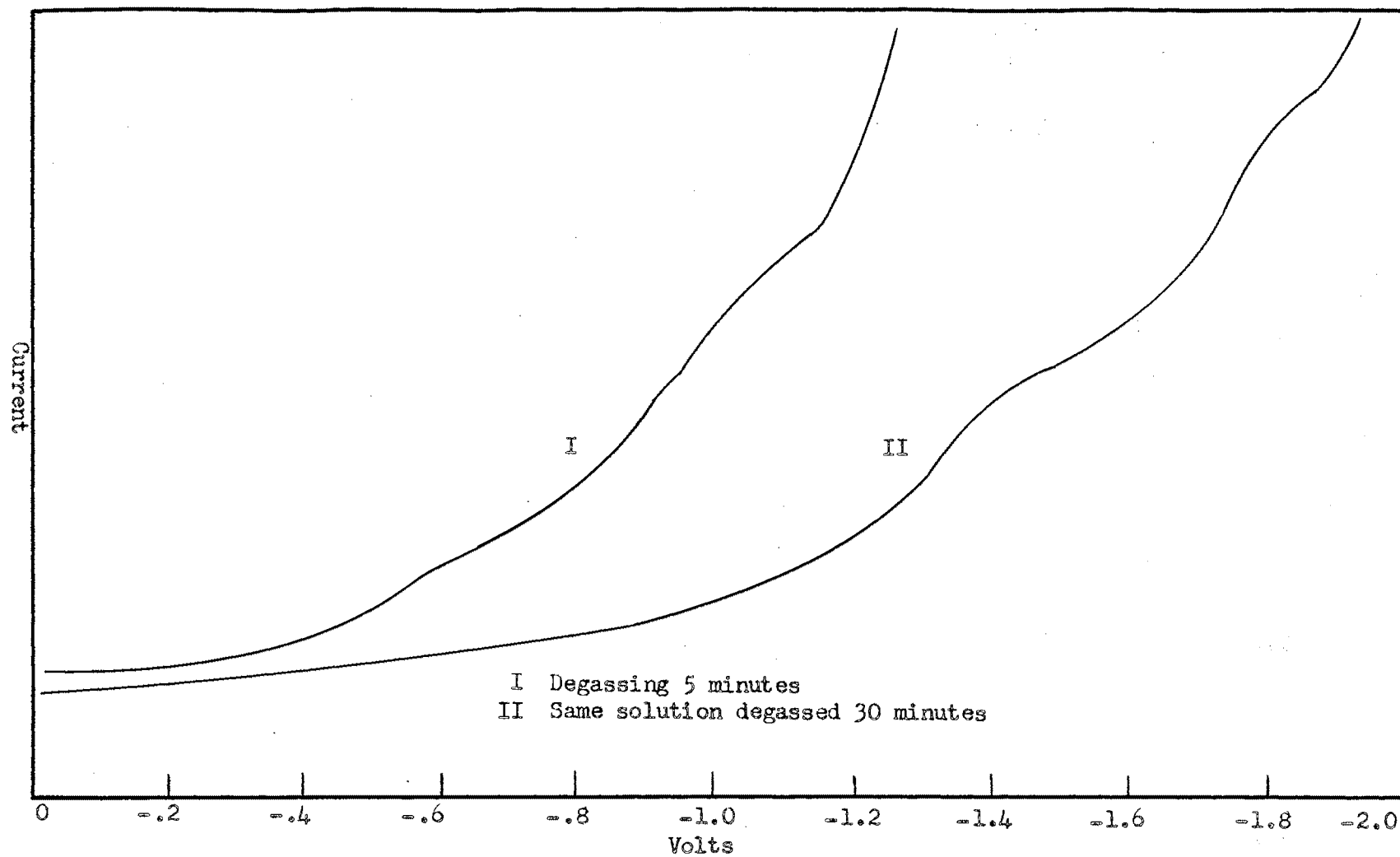


Fig. 6 Effect of Degassing Time on the Oxygen Wave
100% Methanol Solution with 0.1 N LiCl
Using Untreated Tank Nitrogen

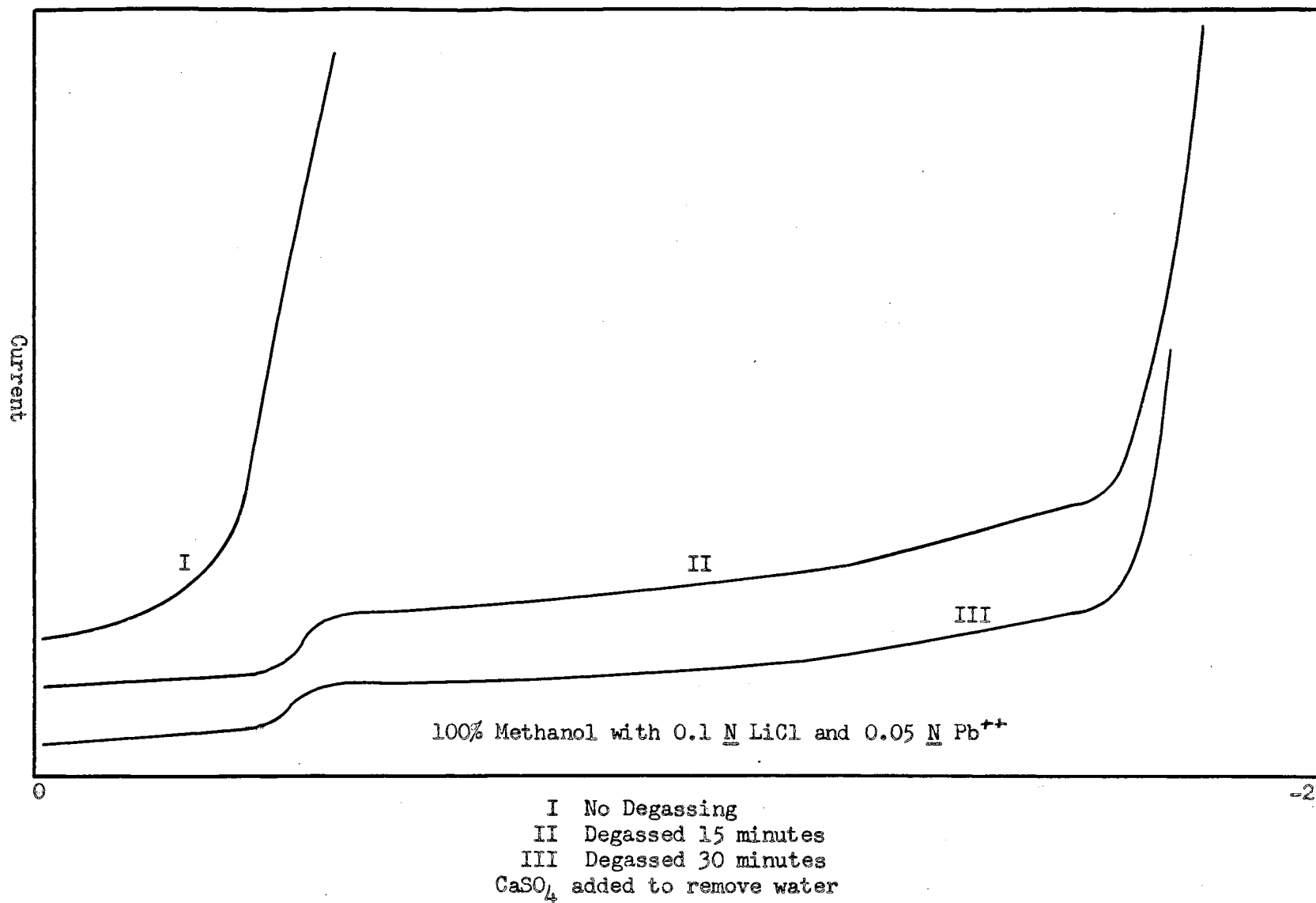


Fig. 7 Effect of Degassing Using Treated Nitrogen Gas

the lead wave appears at 0.325 volts and that the solution shows stability up to about -1.6 volts. Subsequent work has shown that by using two wash towers filled with a solution of sodium pyrogallate and by maintaining an atmosphere of nitrogen above the solution in the electrolysis cell during a run, the limiting current line is not disrupted up to two volts. Thus it appears that it is possible to analyze polarographically for lead in absolute methanol. Every effort was made to maintain anhydrous conditions. The mercury for the dropping mercury electrode and for the pool of mercury was carefully dried and kept in a desiccator over CaCl_2 . The rubber tubing that comprises part of the electrode was dried with warm air before a run. The lithium chloride used as carrier electrolyte was dried in an oven at 105° and stored in a desiccator until ready for use. C. P. anhydrous methanol was used as the solvent and the solvent and solutions were stored in contact with a large quantity of Drierite, it having been found that the addition of Drierite had no noticeable effect on either the conductivity of the solution or the curve itself. At the conclusion of each anhydrous run, a small quantity of anhydrous CuSO_4 was added to the solution in the electrolysis cell as a test for the presence of water; no change in color was noticed. Reproducible lead waves were obtained consistently under these conditions. These results were confirmed with a saturated calomel half-cell as the reference electrode.

It would appear from the foregoing that the degassing operation assumes tremendous importance in analyses involving methanol. Bachman and Astle³⁷ report that in work with anhydrous acetic acid solutions, it is necessary to bubble purified natural gas through the solution for four hours in order to free it from oxygen sufficiently for polarographic determination. A mere increasing solubility of oxygen in organic solvents in no way explains the fact that a

37 G. B. Bachman and M. J. Astle, loc. cit.

solution of methanol and carrier shows the regular residual current to the full two volts; but on adding a trace of lead to the same solution the galvanometer goes completely off the scale from the diffusion current of the oxygen. The effect seems catalytic in nature and makes effective degassing extremely difficult.

Since during the course of investigation of the effects and the removal of oxygen work was done with lead in various concentrations of methanol in water-methanol solutions, it was decided to examine these polarograms to see if the methanol concentration had any definite effect on the half-wave potential of lead. In solutions where the concentration of lithium chloride was 0.1 N and the lead content (always as lead acetate) was held constant, it was found that the following half-wave potentials were obtained with a quiet pool of mercury as reference electrode:

| <u>% Methanol Concentration</u> | <u>Observed Half-wave Potential</u> |
|---------------------------------|-------------------------------------|
| 0 | -0.47 volts |
| 25 | -0.45 volts |
| 50 | -0.43 volts |
| 75 | -0.41 volts |
| 90 | -0.48, -0.45 volts |
| 95 | Not observed |
| 100 | <u>-0.35</u> , -0.325, -0.37 volts |

It will be noted that there was slight change in the half-wave potential in the lower concentrations of alcohol. The results here also show good reproducibility. Solutions whose alcoholic contents were above 50% show considerable variance in the half-wave potential. This is believed due to the fact that up to about 50% concentration of alcohol, the solution behaves essentially like an aqueous solution. Previous work with degassing also tended to show that solutions whose methanol content was 50% or less behaved in a manner similar to water solutions. It was not possible to obtain clear-cut data concerning the effect of high concentration of methanol on the half-wave potentials. Even in solutions where the source of lead was the same, exact reproducibility was not

found. This may possibly be due to a loss of efficiency on the part of the alkaline pyrogallate although the latter was recharged frequently.

The effect of changing the lead salt is strikingly shown by the following half-wave potentials where lead chloride was the source of lead ions and 0.1 N lithium chloride the carrier. Conditions are comparable to those where lead acetate was used:

| <u>% Methanol Concentration</u> | <u>Observed Half-wave Potential</u> |
|---------------------------------|-------------------------------------|
| 0 | -0.28 volts |
| 50 | -0.23 volts |
| 75 | -0.18 volts |
| 90 | -0.17 volts |
| 100 | -0.17 volts |

Lead chloride is only slightly soluble in cold methanol. To overcome this and to insure a constant amount of both lead and carrier in each run, enough lead chloride was weighed out to make a liter of solution wherein the lead concentration would be 0.001 M. Then 4.240 g. of lithium chloride was added with the lead chloride to water and diluted to a volume of 200 ml. The water was heated until both salts had dissolved; then the solution was divided, 100 ml. being diluted with water to a volume of 500 ml. and the other portion evaporated to dryness. A small amount of hydrochloric acid was added to the residue to reverse hydrolysis and this solution was also evaporated to dryness. The residue was dissolved in warm methanol and diluted with methanol to a volume of 500 ml. This procedure not only increased the rate of solution of the salts in methanol but also insured the same concentration of lithium chloride and lead chloride in both water and alcohol.

One run was made with still another source of lead, lead nitrate, in a 50% methanol solution 0.1 N with lithium chloride; the half-wave potential here was found to be -0.61 volts as compared to -0.23 volts for lead chloride and -0.43 volts for lead acetate, the solvent and carrier electrolytes being the same in

all cases. In none of these trials was the anion involved in a reaction with the electrode at potentials more positive than -1.0 volt, yet the effect of the anion on the half-wave potential is apparently highly significant in qualitative determinations.

Appearance and Interpretation of a Second Lead Wave

During the work with the pool of mercury as the reference electrode a curious effect was often noticed; an apparent second wave appeared in many of the polarograms where the only addition to the solution was the lead salt. These waves began at applied potentials between -1.6 and -2.0 volts. No reducible material of such reduction potential was known to be present. Various lead salts were tried to see if the anion possibly could be involved in the cell reaction, the carrier salt in each case being lithium chloride, but this apparently had no effect on the formation of the second wave. The fact that waves did not appear in every case and that, if they did, their reduction potentials were not constant seemed to warrant further investigation. If this phenomenon showed the formation of a lead complex, it would be of the utmost importance in the quantitative determination of lead in anhydrous media. If a portion of the lead present in the solution were being tied up in a complex of recognizable potential, this fact should be available to an investigator so that the diffusion current for both reduction states of lead could be measured and evaluated.

The source of lead used in the early phases of this work was lead nitrate. When the applied potential reached -1.6 volts, the limiting current was disrupted and the galvanometer deflections showed a rapid increase. Changing the anion to acetate and holding the concentration of lithium chloride carrier constant gave similar results, as did changing to lead chloride. Apparently this phenomenon was not due to a cathodic reaction of the anion of the salt, unless all three

anions used here were being decomposed at the same voltage. To check this possibility, a run was made with 0.1 N potassium nitrate with no lead present. This solution alone showed instability at -1.6 volts. This shows that the reduction of the nitrate ion itself occurs at less than the full two volts and that lead nitrate is unsuitable as the source of lead for those runs covering this range of potential. The reported value for the reduction potential of the nitrate ion versus the saturated calomel electrode is -2.1 volts. Thus it was necessary to find other lead salts whose anions are not involved in a cell reaction within the desired range of potential. Both lead acetate and lead chloride were found to be suitable, runs with them showing no such instability through the full range of applied voltage. Owing to the slight solubility of lead chloride in cold water and in methanol, lead acetate was finally chosen and most of the subsequent work was done with this salt as the source of lead ions.

The effect of increasing alcohol concentration upon the second wave is not perfectly clear. The wave has appeared in solutions where the concentration of alcohol varied from 0 to 100 percent. However, when the chloride concentration is kept constant at 0.1 N and the alcohol concentration varied, there is a definite enhancement of the second wave with increasing alcohol content. This is shown in Fig. 8 where the lead was supplied as the chloride.

In an attempt to determine whether a chloro-lead complex might be responsible for this abrupt rise in the current, polarograms were made with lead in aqueous solutions when the carrier electrolyte, KCl, was increased in concentration in steps from 0.1 N to saturated. A well defined wave appeared at approximately the same position as did the abrupt rise in current in alcoholic media. These results are shown in Fig. 9 for cases when 0.01 N lead acetate was run in 0.1 N aqueous potassium chloride and when the same lead concentration was run in a saturated solution of potassium chloride in water. The saturated

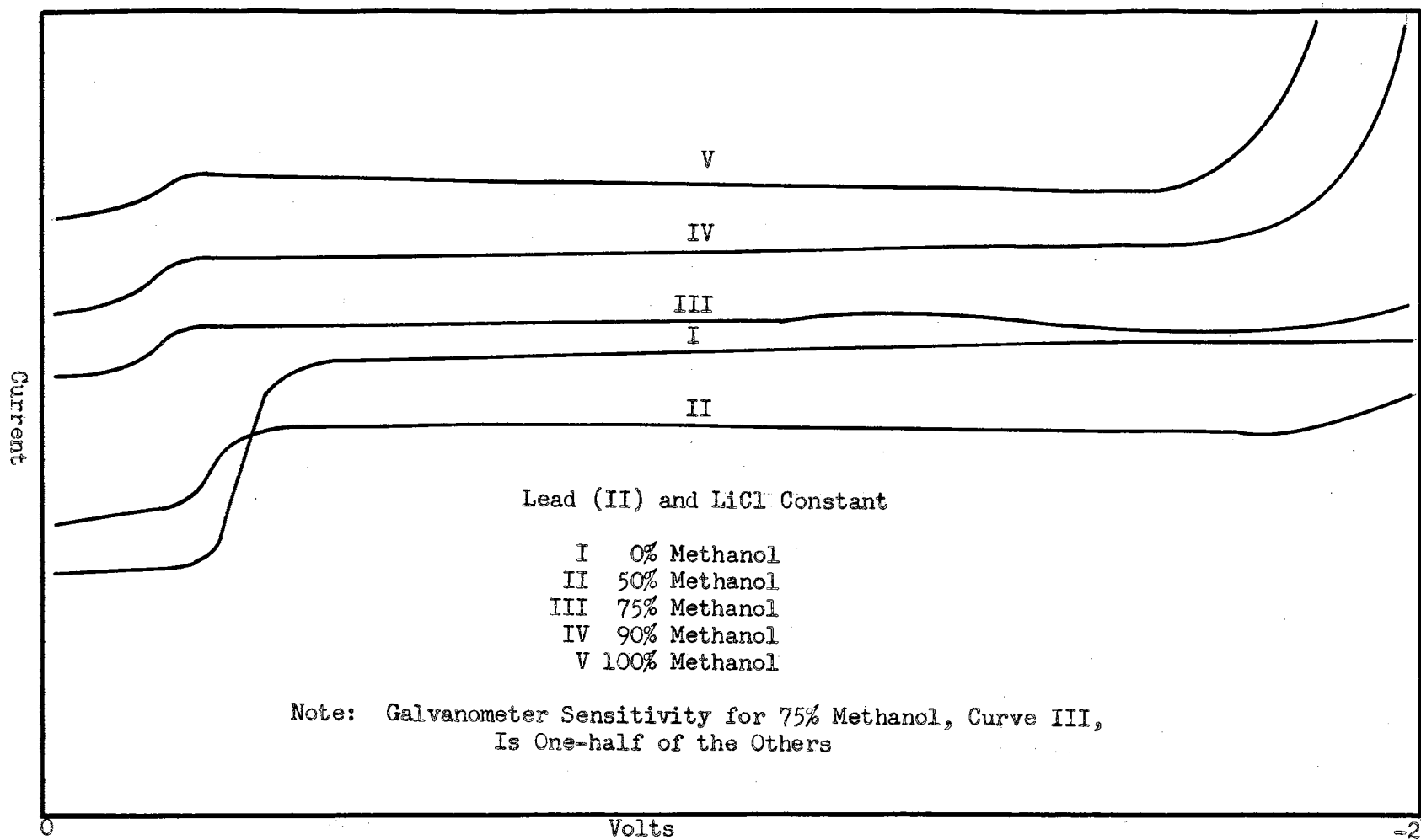


Fig. 8 Effect of Alcohol Concentration on Half-wave Potentials - $PbCl_2$ - Source

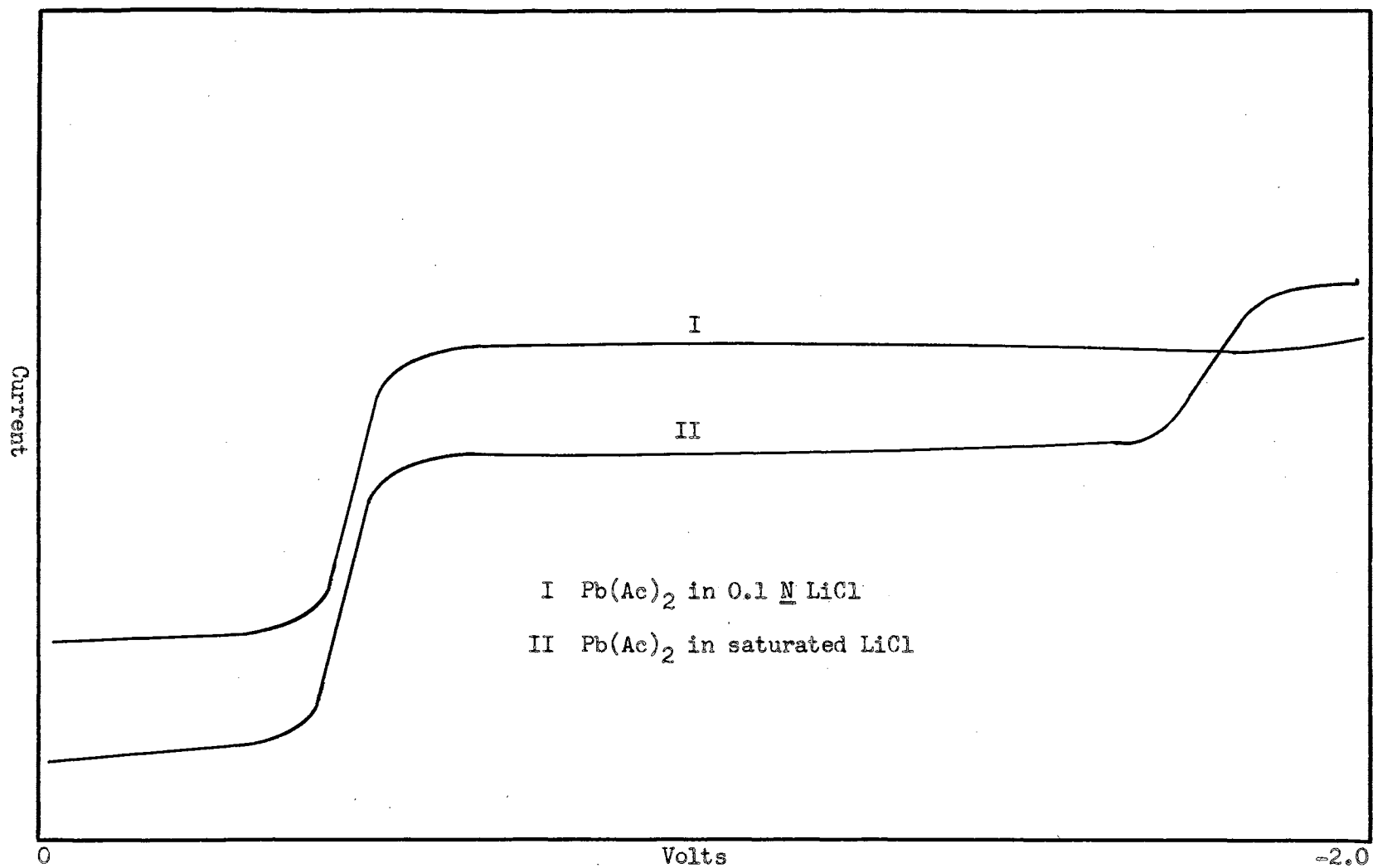


Fig. 9 Effect of Chloride Ion Concentration in Water Solutions

solution gives a well defined second wave complete with a normal limiting current whereas the 0.1 N solution shows no instability up to 2 volts.

An attempt was made to determine the effect of varying the chloride ion concentration in methanol solutions. The range of chloride ion concentration was limited, however, by the low solubility of the carrier salt in methanol. Consequently, no clear-cut results were obtained.

Some evidence exists that the combined presence of both acetate and chloride ions is more effective in producing the second wave in alcohol solutions than is the presence of chloride alone. It should be remembered, however, that the anion of the lead salt itself has an effect on half-wave potentials so this effect may well have caused a shift to lower values. In order to see if the presence of the chloride ion was necessary for the appearance of the second wave, a run was made with sodium acetate as carrier and lead acetate as the lead source. The polarograms of such salts in water and in 50% methanol show stability up to 2 volts. There was no wave present other than the usual lead wave although the second wave appeared if both chloride and acetate ions were present in these solutions. As would be expected, it apparently made no difference in these cases whether the source of chloride ions was potassium chloride, lithium chloride, or tetramethylammonium chloride, or whether the acetate ions came from the lead salt or from sodium acetate added when lead chloride was the source of lead. Additional degassing had no apparent effect on the appearance of the wave although a previous observation in the case of degassing an anhydrous solution pointed to this possibility. That the presence of acetate is not required is clearly shown in the work with lead chloride in various alcohol-water mixtures. The second wave appeared in all solutions containing alcohol even though no acetate was present. The chloride concentration here was known to be 0.1 M by the method used in preparing the solutions. The wave did not appear in

the aqueous solution of the same chloride concentration.

In attempting to explain the second wave, the possibilities are many. The wave could be due to a shift of reduction potential of the cation of the carrier salt to a more positive value. For example, potassium chloride shows stability to about -2.1 volts in water solutions. A shift of only 0.2 volts toward a less negative value would give some of the waves noticed. The concentration of potassium chloride when used as a carrier is known to have definite effect upon the half-wave potential of an ion. This effect, however, is usually toward more negative values as the chloride concentration increases. At least this is true for water solutions. Also the heights of the diffusion currents noticed do not correspond to the known concentration of the metallic ion of the carrier salt, these diffusion currents being of less magnitude than the diffusion current of lead. All other factors being equal, the diffusion current of the cation of the carrier should be at least ten times as high as that of lead. (See Fig. 9.)

In solutions where alcohol is present it has been noted that one effect of the alcohol is to shift the half-wave potentials to less negative values. If alcohol causes the potential of lead to be lowered, it appears reasonable that it would also lower the reduction potential of the carrier salt and possibly that of the solvent itself (in water-alcohol mixtures). This would explain the lack of a limiting current in alcohol solutions since the decomposition of the solvent gives a curve comparable to the hydrogen wave so often encountered in polarography when a micro platinum electrode is used. If it were the carrier salt showing instability, the high concentration of the metal ions would give a similar effect. Solutions of anhydrous alcohol and the carrier salt fail to show the second wave if thoroughly degassed.

The increasing difficulty of degassing solutions of high alcoholic content has been mentioned previously. A slight possibility remains that the second

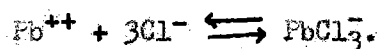
wave is due to the presence of dissolved oxygen although a specific investigation has been made with this in mind. Extra thorough degassing with nitrogen and also the use of sodium sulfite has had no apparent effect upon the second wave. The concentration of this oxygen in the solution must be extremely low after these degassing operations; the magnitude of the diffusion current does not indicate such a low concentration.

In work at this institution it has been found that amalgamation of metal surfaces has an appreciable effect on hydrogen overvoltage, this tending in each case to be less than that of mercury itself. It is quite possible that lead or nickel amalgams which were formed during this work catalyzed the decomposition of the solvent at a lower potential than that commonly found for mercury. This would not explain the second polarographic wave found in an aqueous solution saturated with potassium chloride and its absence in 0.1 N potassium chloride solutions. Nor would this explain the effect of increasing methanol content unless it were the alcohol that was being decomposed at voltages less negative than usual. This second wave effect may be a summation of several effects, i.e., the chloride concentration effect, the anion effect, and the decomposition of the solvent caused by a particular amalgam present during a run. This investigation has pointed to each of these as having possible effect on half-wave or "decomposition" potentials.

Nor does the evidence rule out the possibility of the formation of a chloro-lead complex although no conclusive data for this formation is yet available. One such complex, the $PbCl^+$ ion, has been reported in polarographic work³⁸ and its existence used to explain the difference in the half-wave potential of lead in 1 N potassium nitrate (-0.405 volts) and in 1 N potassium chloride (-0.435 volts), both versus the S.C.E. Also, the half-wave potential of lead in 1 N

³⁸ I. Kolthoff and J. Lingane, loc. cit.

potassium chloride is reported to be -0.435 volts whereas in 0.1 N potassium chloride it is -0.396 volts. It is evident from the studies made that the chloride ion concentration has definite influence upon the formation of this second wave, whatever the cause or causes of the wave. If a complex whose composition was, for example, PbCl_3^- were formed having a half-wave potential less negative than two volts, the importance of the chloride concentration would be evident:



According to the principle of Le Chatelier, an increase in the chloride ion concentration would tend to shift the equilibrium toward the formation of the complex. Doubling the chloride ion concentration should have an eight-fold effect on the concentration of the complex. Note that the second wave is invariably obtained in aqueous solutions saturated with potassium chloride or lithium chloride. Increasing the lead ion concentration would also tend to favor the formation of the complex. No definite information has been obtained concerning the effect of lead concentration upon the second wave. The question of solubility of the lead salt here would be of the utmost importance since the lead salts used in this work are at best only sparingly soluble in methanol.

Nickel is known to form complexes, so it was decided to see if waves comparable to the second lead wave could be obtained also with nickel. Runs were made of nickel in water and in 50 and 90% methanol solutions, all against the pool of mercury as reference electrode, and in 50 and 90% methanol solutions using the saturated calomel cell as reference electrode. Either lithium or potassium chloride was used as indifferent electrolyte. Aqueous solutions in which the chloride concentration was 0.1 N , whether with lithium chloride or with potassium chloride, did not show a second wave whereas saturated solutions of these salts did. The second wave for nickel showed a larger diffusion current

than did the second lead wave at equal concentrations.

The results with nickel in alcoholic media were similar to those obtained with lead, the second waves of both being poorly defined with no limiting current; however, like that for lead the potential shifted as alcohol content increased. The half-wave potential for the nickel ion in 50% methanol when measured against the pool of mercury was found to be -1.2 volts and to be -1.24 volts in 50% methanol against a saturated calomel electrode. In 90% methanol versus the calomel cell the half-wave potential measured -0.67 volts. The reported potential of nickel in aqueous solutions with 0.1 N potassium chloride as carrier when determined against the calomel electrode is -1.1 volt.³⁹

Thus, it has been impossible to ascertain definitely the cause of the second wave. The occurrence has been reported because of the possible importance of this wave in quantitative analysis for the lead ion by polarographic means.

During this investigation, both the quiet pool of mercury and the saturated calomel electrode have been used. An attempt was made to correlate the results obtained with the variable pool of mercury with those obtained with the constant calomel half-cell. The results with the lead ion in anhydrous alcohol, the results with degassing, and the results with the supposed lead and nickel complexes were similar for the two reference electrodes. It was also found that the sensitivity of the calomel electrode is much less than that of the pool of mercury, which means that higher concentrations of ions are necessary when the former is used. Also, the diffusion "wave" tends to be flattened in runs made with the calomel cell as reference. This was particularly marked when a non-polar solvent such as ligroin was added to anhydrous methyl alcohol. The increased resistance apparently causes this flattening to take place. The measured resistance of the dropping mercury electrode-calomel half-cell with salt

³⁹ I. Kolthoff and J. Lingane, loc. cit.

bridge was found to be approximately 3500 ohms whereas that of the dropping mercury electrode with the pool of mercury was consistently less than 1000 ohms. All values of half-wave potentials mentioned in this investigation are uncorrected for the IR drop. In the case of the calomel electrode this correction would be about 3.5 millivolts per microampere. Corrections were applied for the residual current but since quantitative measurements were not being made, there was no reason for an IR drop correction to be made for every polarogram obtained.

A recent article by Lewis, Quackenbush and De Vries,⁴⁰ all of Purdue University, reports successful results in their polarographic studies of organic peroxides in non-aqueous solution. These workers used as solvent equal volumes of anhydrous methanol and benzene. Lithium chloride and lithium methoxide were used as supporting electrolytes. The curves reproduced in their article show the flattened wave that was noticed by this investigator in work with methanol and ligroin.

The effect of non-polar solvents is to repress ionization and thereby reduce conductivity; the flattening of the diffusion wave is probably due to this factor. In the present investigation it was found that up to a maximum of 10% ligroin in 90% methanol reproducible lead waves could be obtained although the height of the diffusion current step was lessened considerably by increasing ligroin content. Solutions of more than 10% ligroin by volume failed to show enough wave height, even at maximum galvanometer sensitivity, to give a recognizable diffusion current. This work with ligroin was done in order to determine the effect of such a hydrocarbon upon the diffusion current for lead. Any direct determination of lead in gasoline by the polarographic method would of course require such a study. Judging from the range of concentrations of lead in gasoline, the solubility of hydrocarbons in methanol, and the ability

⁴⁰ W. Lewis, F. W. Quackenbush, and T. De Vries, Anal. Chem., 21, 762, (1949).

to obtain a diffusion current in anhydrous media in the presence of ligroin, it is at least theoretically possible that lead in gasoline may be determined by polarographic analysis.

SUMMARY

A brief discussion of the theory of polarography is presented with a description of the basic instrument and the characteristics of the different parts. Diagrams of the circuits of both the automatic and the manual instrument used in this investigation are shown. A typical polarogram is reproduced showing the significance of each part.

Methyl alcohol was chosen as the non-aqueous solvent after conductivity and polarographic tests indicated that this solvent gave sufficiently similar results to those obtained with 0.1 N potassium chloride in water. Lithium chloride was found to give the best results of all the salts tested in methanol for use as the indifferent electrolyte.

Early attempts to obtain a simple half-wave for lead in anhydrous media failed, so a study was made of possible underlying causes of this erratic behavior in the absence of water. It was found that with untreated tank nitrogen used for degassing the limiting current portion of the curve disappeared when the methanol concentration exceeded 90% by volume. Using nitrogen that had been bubbled through an oxygen absorber, it was possible to obtain reproducible lead curves consistently in anhydrous media. It was also found that the degassing of water-alcohol mixtures is not critical in solutions of low alcohol concentration since the behavior of these solutions is essentially the same as that of purely aqueous solutions. At concentrations of 75% and above degassing becomes more difficult.

A technique was developed for degassing solutions where the concentration of alcohol was high. It was found that tank nitrogen bubbled through one or more gas washing bottles filled with an alkaline solution of pyrogallol acid degassed solutions faster and more thoroughly than did untreated nitrogen and that by using this treated gas plus maintaining a stream of gas above the

solution during a run the usual oxygen waves encountered in alcoholic media did not appear. This indicated that the previously mentioned difficulties with anhydrous solvents are due to the increased oxygen concentration in the solvents. The results also tend to confirm the observation that the effect of lead on the dissolved oxygen wave in methanol solutions is to enhance it greatly.

It was found that the effect of increasing alcohol concentration on the height of the diffusion current is to reduce it as the alcohol content increases. There is also an effect on the half-wave potential itself, a higher alcohol concentration tending to shift these potentials to a more positive value. It was established that the particular anion of the lead salt had significant effect on the half-wave potentials observed for lead, acetate giving more negative values under comparable conditions than did chloride and nitrate giving more negative values than either of these two other anions. The nitrate ion itself was found to be unstable at an applied potential less than the desired range, whereas acetate and chloride ions were found stable for the full two volt range.

A second wave often appeared at potentials less negative than -2.0 volts. Work was done to ascertain the cause of this wave and although the results are still inconclusive, several factors apparently are involved either singly or collectively. It was established that the chloride ion concentration regardless of source has definite effect upon formation of the second wave in aqueous solutions although solubility limitations prevented clear-cut interpretations of results in alcoholic media. Measurements in water solutions were made for lead and nickel versus both the pool of mercury and the saturated calomel cell as reference electrodes. Early work had pointed out that the wave appeared in solutions where both acetate and chloride ions were present but it was conclusively shown that the presence of acetate is not a prime requirement for the

appearance of the second wave.

A definite enhancement of the second wave by increasing alcoholic content is indicated. Increasing degassing alone had no effect on this second wave so it is presumed that the phenomenon is not due solely to increased oxygen concentration in solutions where methanol is present.

A short discussion of the possible causes of the second wave is presented with evidence for and against each possibility. Further investigation of the wave using carefully controlled techniques seems advisable.

A comparison of results obtained with the pool of mercury and with a saturated calomel half-cell was given. The increased resistance of the calomel cell was pointed out, and its effect upon polarographic waves. Work with ligroin in methanol was briefly discussed, the results here showing that the addition of a non-polar solvent further flattens the lead wave. It was found that an interpretable wave could be obtained using a quiet pool of mercury as reference electrode up to a concentration of ligroin of 10% by volume in anhydrous methanol.

The evidence obtained in these studies of the behavior of the lead ion in anhydrous media seems to indicate that theoretically at least a determination of lead in gasoline by direct polarographic means is possible.

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BIOGRAPHY

Birt Allison, Jr., was born in Hartshorne, Oklahoma, on December 18, 1921. He attended public school in McAlester, Oklahoma, and Lincoln County, New Mexico, and was graduated from McAlester High School in 1938.

He entered Eastern Oklahoma A. & M. College, Wilburton, Oklahoma, and attended that school until entering the Army Air Forces in July 1940.

He was discharged from the service in December 1945 and entered East Central State College, Ada, Oklahoma, where he received the bachelor of science degree in May 1947.

In September 1947 he entered the Graduate School of Oklahoma A. & M. College and served as a graduate fellow until January 1950.

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