A Study of the Dissolution of Aluminum in Sodium-Hydroxide Solutions.

Citation

Stevenson, Robert Evans. *A Study of the Dissolution of Aluminum in Sodium-Hydroxide Solutions*. 1948, https://preserve.lehigh.edu/lehigh-scholarship/graduate-publications-theses-dissertations/theses-dissertations/study-96.

Lehigh University Bethlehem, Pa.

Rules covering use of manuscript theses.

Unpublished theses submitted for the Master's and Doctor's degree and deposited in the Lehigh University Library are open for inspection, but are to be used only with due regard to the rights of the authors. For this reason it is necessary to require that a manuscript thesis be read within the Library. If the theses is borrowed by another Library, the same rules should be observed by it. Bibliographical references may be noted, but passages, diagrams, and illustrations may be copied only with permission of the author, and proper credit must be given in subsequent written or published work. Extensive copying or publication of the thesis in whole or in part must have the consent of the author as well as the Dean of the Graduate School.

A Library which borrows this thesis for use by its readers is expected to secure the signature of each user.

This thesis by Michael Alfred Streider has been used by the following persons, whose signatures attest their acceptance of the above restrictions.

NAME	ADDRESS	DATE
Russell [illegible]	P. Elec. Corp. Blue Bell, Pa.	7/31/62

A STUDY OF THE DISSOLUTION OF ALUMINUM IN SODIUM HYDROXIDE SOLUTIONS

by

Michael Alfred Streicher

A DISSERTATION
Presented to the Graduate Faculty
of Lehigh University
in Candidacy for the Degree of
Doctor of Philosophy

Lehigh University
1948

249631

Approved and recommended for acceptance as a dissertation in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Jan. 24, 1948.
(Date)

Allison Butts
Professor in Charge

Accepted, ____________________
(Date)

Special committee directing the doctoral work of Mr. Michael Alfred Streicher

Gilbert E Doan Chairman

Joseph F. Libsch

Robert D. Stout

Harold V. Anderson

Allison Butts

The author wishes to express his thanks and appreciation to the many people whose unfailing encouragement and assistance made this study possible. To the following he extends particular thanks for their cooperation:

Professor Gilbert E. Doan, Head of the Department of Metallurgical Engineering of Lehigh University, without whose continued interest and aid this research would not have been possible

Professor Allison Butts, of the Department of Metallurgical Engineering of Lehigh University, under whose expert guidance and supervision this work was carried on

Mr. L. Reiss and Mr. V. J. Kublin, of the Squier Signal Laboratories of the United States Army Signal Corps, for their cooperation and encouragement throughout the progress of this study

Mr. R. H. Brown, Chief of the Chemical Metallurgy Division of the Aluminum Company of America, for his kind interest and assistance in the initial stages of the study

Mr. Robert L. Bovaird, student-physicist of Lehigh University, for his able and conscientious assistance with the experimental phases of the work

This project was carried out under Contract No. W 36-039 sc-32033 of the United States Army Signal Corps with the Department of Metallurgical Engineering of Lehigh University.

TABLE OF CONTENTS

TABLE OF SYMBOLS USED

C = concentration of electrolyte in milliequivalents per liter.

V_g = volume of hydrogen evolved from both anode and cathode in a corrosion couple (total volume).

V_e = volume of hydrogen calculated from quantity of current in external circuit (volume evolved at cathode).

V_{11} = volume evolved from freely dissolving specimen.

V_1 = volume of hydrogen evolved at anode while connected with more noble metal. (A measure of local-cell action at the anode of a corroding couple.)

$\triangle$ = "difference effect".

t = length of time of immersion in minutes.

T = temperature in degrees Kelvin.

W = weight-loss in milligrams per specimen (40.5 cm^2).

E = measured potential.

E' = open-circuit potential.

I = current density (in amps per specimen, 40.5 cm^2).

TABLE OF EQUATIONS

I $\frac{dw}{dt} = kC^n$

II $V_g - V_e = V_1$
or
$I_g - I_e = I_1$

III $V_{1i} - V_1 = \Delta$
or
$I_{1i} - I_1 = \Delta$

IV $\Delta = KI_{C.D.}$

V $W = at^b$

Va $\frac{dw}{dt} = abt^{(b-1)}$

Vb $\frac{dw}{dt} = \frac{w}{t}b$

VI $\frac{dw}{dt} = k' + k''t$

VIa $\frac{dw}{dt} = k' + k''w$

VII $W = me^{nT}$

VIII $\ln\frac{dw}{dt} = \ln A - \frac{E}{RT}$
or
$\frac{dw}{dt} = Ae^{\frac{-E}{RT}}$

IX $W = kC^d$

X $E = E' - P\frac{dw}{dt}$

Xa $W = \frac{(E' - E)t}{bP}$

XI $\Delta = K''I + N$

XII $E_a = E'_a - \frac{K_a}{A_a}I_a$

XIIa $E_c = E'_c + \frac{K_c}{A_c}I_c$

XIII $E_a - \phi_a(\frac{I_a}{A_a}) =$
$E_c + \phi_c(\frac{I_c}{A_c})$

XIIIa $E'_a = E'_c + \phi_c(\frac{I_c}{A_c})$

XIV $I_c = I_a + I_x$

XV $E'_c = E'_a - \phi(\frac{I_a}{A_a})$

XVI $K = \frac{R_p}{R_p + R_s}$

I. HISTORICAL AND THEORETICAL INTRODUCTION

The dissolution of metals in electrolytes may be considered a greatly accelerated form of corrosion. Almost all corrosion takes place in the presence of water (moisture) which usually has dissolved in it gases or salts which increase its conductivity. By substituting solutions of relatively concentrated acids and bases for this ever-present moisture, chemical reaction rates, diffusion, and effects related to local-cell action are greatly accelerated, while the effects of surface preparation and surface films may be minimized. The variables involved in the disintegration of metals by the more rapid dissolution in relatively concentrated electrolytes are more readily controlled than they are when disintegration takes place by the slower corrosion processes. The information gained from a study of the dissolution of metals on the mechanism of disintegration can then be applied to the problems of corrosion and corrosion protection.

There is much experimental evidence available which indicates that in many cases the dissolution and corrosion of metals are governed by an electrochemical process. For the instances in which the dissolution of a metal has been shown to be governed by an electrochemical process (1, 2, 3,)*,

---

* The figures appearing in parentheses refer to the bibliography at the end of the paper.

the local cell (or element) theory has proved to be the most satisfactory explanation. This theory was first proposed in 1830 by A. de la Rive (4), who observed that the rate of dissolution of such metals as zinc, aluminum, cadmium, and iron, as measured by the rate of hydrogen evolution, is much greater when these metals contain small quantities of impurities than when they are relatively pure. The increase in the rate of dissolution was attributed to the action of a current set up in local cells consisting of an anodic matrix and cathodic inclusions. When such a metal dissolves, the impurities often precipitate on the surface, thus setting up more local cells. Those impurities having the lowest hydrogen overpotential are most effective in accelerating the rate of dissolution (33).

This theory of local cell action was neglected until Ericson-Auren in 1901, at the suggestion of Palmaer (5), studied the controlling factors operative during the dissolution of zinc in dilute acids, taking into consideration the newer theories of solution pressure (Nernst), electrolytic dissociation (Arrhenius), and overpotentials (Caspari). At about the same time Whitney (6), Cushman (7), and Heyn and Bauer (8) also proposed an electrochemical mechanism for the dissolution and corrosion of metals. Before giving the discussion on the extension of these early concepts into the present-day theories of the dissolution of metals, a critical review of the experimental data found in the literature on the dissolution of aluminum and a description of the experimental work of the present study are given.

II. THE DISSOLUTION OF ALUMINUM IN VARIOUS ELECTROLYTES

A. General Introduction

The following section contains a critical summary of investigations which have contributed to an understanding of the dissolution process of aluminum in (inorganic) electrolytes.* Most investigators used systems which were open to air, i.e., no protective atmosphere. A dissolution process is considered entirely electrochemical when the loss in weight can be shown to agree with the change in weight predicted by Faraday's Law from current-time data. When the rate of dissolution is influenced by various degrees of agitation, a diffusion process is usually rate-controlling. The temperature coefficient of the dissolution rate is also sometimes used as a criterion for the dissolution mechanism. The temperature coefficient for a diffusion process is about 1.2 for a rise of 10°C, while the rate of a chemical reaction is practically doubled for a rise of 10°C (37). Centnerszwer (18, 66, 71) has found that agitation has no appreciable effect on the rate of dissolution of aluminum in hydrochloric acid or sodium hydroxide and that in both of these electrolytes the rate approximately doubles when the temperature is increased ten degrees.

---

* No general review of the resistance of aluminum and its alloys to various chemical agents is intended.

In nearly neutral solutions the attack on aluminum is of the pitting type. At low and high values of pH the attack covers the entire surface.

The oxide film on aluminum, which has non-reproducible break-down properties in various types of solutions, has often been the cause of confusing experimental results.* Usually three distinct, successive phases are observed during dissolution (17, 39): 1) incubation period during which there is no visible change, i.e., no hydrogen evolution, 2) induction period during which there is a sudden initiation of reaction and a rapid increase in hydrogen evolution, and 3) the reaction period during which the film has no further effect on the dissolution rate. In the interpretation of experimental work it is always necessary to know the relative effect of these various phases.

It has been found that dissolution rates of aluminum in acid and alkaline solutions are not reproducible, especially in the case of very pure aluminum (23, 38, 46).**

---

* Vernon (72) has shown that aluminum gains in weight as a result of oxidation for as long as 90 days at room temperature.

** Some of the reasons for the poor reproducibility of dissolution rates have been the neglect of control of the incubation and induction periods in experimental technique and the erroneous assumption that the dissolution rate is constant with immersion-time during the reaction period. In cases where there is an accelerating effect with time of immersion the impurities are effective in two ways: they reduce the incubation and induction periods by making the oxide film inhomogeneous, thus facilitating the attack on it, and by redepositing on the surface after dissolution during the reaction period.

The best reproducibility in alkaline solutions has been found when the aluminum contains about 0.5 to 0.7 percent impurities. One of the reasons for this is probably that, as Straumanis (30) has shown, the dissolution rate is very sensitive to small quantities of impurities, but beyond a certain content their effect falls off rapidly. Therefore, minor variations in the content of impurities above 0.5 percent do not affect the dissolution rate as decisively as below this value.

In addition to the composition of the aluminum and its surface properties, its thermal and mechanical history and its grain size affect the dissolution rate. Wiederholt (73) has shown that the annealing temperature influences the dissolution rate of aluminum in acid and alkaline solutions in a manner depending on the impurities present. Increasing amounts of cold working were found to increase the dissolution rate of 99 percent aluminum in hydrochloric acid as did a progressively decreasing grain size. This latter phenomenon may be explained by the observation made by Dix (66) that the potential of grain boundaries of high purity aluminum (and also of aluminum copper alloys (12)) is anodic to the centers of the grains in hydrochloric acid. By reducing the grain size the ratio of anodic area to cathodic area is increased. The effect of cold work may be explained, at least in part, by its action on the orientation of the crystallites.*

---

* The effect of stress may also be a contributing factor (12).

Increasing amounts of cold work intensify the preferred orientation. Walton (48) has found that various crystallographic planes of aluminum have different rates of dissolution in hydrochloric acid.*

B. Simple Dissolution

1. In acids. In studies on the dissolution of aluminum the most frequently used electrolyte is hydrochloric acid. When aluminum is dissolved in this medium, the three distinct phases previously described are observed (17, 39). Very pure (99.998%) aluminum is not attacked by hydrochloric acid until the concentration of acid reaches 4N (40), and then the attack is very slow (46, 51). Increasing the concentration of the acid accelerates the dissolution (25, 75).** According to Centnerszwer (51) the effect of concentration of hydrochloric acid on the rate of dissolution is given by

$$\frac{dw}{dt} = k\ C^n \qquad (I)$$

where C is the concentration of the acid and (k) and (n) are constants.

---

* This phenomenon has also been observed on zinc (29) and copper (74) single crystals.

** Maas and Widerholt (41) found that the rate of dissolution of aluminum in various electrolytes is independent of the hydrogen-ion concentration. However, their tests were made with relatively small volumes of dilute solutions over periods of three weeks or more, and after the acids were used up, attack continued in a solution of soluble corrosion products (salts) rather than in acids.

Several investigators have observed that the rate of dissolution of aluminum in acids may be increased several fold by the addition of other metals to the system as alloying elements (42, 46, 51, 76), in powdered form rubbed on the surface of the metal (43), or in the electrolyte in the form of salts (37, 44, 45, 46).* Those metals which reduce the hydrogen overpotential of the system accelerate the dissolution. Such metals (Pt, Fe, Cu, Ni, Au, Zn, and Hg) when added in the form of salts are observed to deposit on the dissolving aluminum by chemical replacement (cementation). The absence of an accelerating effect by cadmium and silicon is attributed to their large hydrogen overpotential (46) and, in the case of magnesium, to its more electronegative character (76).

Straumanis (46) found that additions of 0.01 percent iron or copper as alloying elements in aluminum did not accelerate the dissolution process. About 0.10 percent of these elements was necessary to increase the dissolution rate.** The effect of temperature on the dissolution rate of aluminum in hydrochloric acid is given by the Arrhenius equation (75).

---

* When impurities are added to the electrolyte in the form of salts not only the action of the cation, but also that of the anion must be considered (42, 50). This fact has sometimes been disregarded (46).

** A similar phenomenon in the case of magnesium was discovered by Hanawalt, Nelson, and Peloubet (77). It was found necessary to exceed a certain "tolerance limit" in concentration of impurities before an appreciable effect on the corrosion rate could be observed.

The rate of dissolution is usually determined by measuring the rate of hydrogen evolution, but the Mylius Test (44) can also be used. In this test aluminum specimens are allowed to dissolve in a certain volume of hydrochloric acid (about 3N) while the temperature is observed. The time-temperature plot reveals a maximum temperature, the position of which on the time axis is a measure of the reaction rate.

Hedges and Myers (47) found that the dissolution of aluminum in 2N hydrochloric acid is periodic as measured by hydrogen evolution. The periodic property, consisting of sudden increases in the rate of reaction, was observed to decrease throughout the course of the reaction and to vary directly with the concentration of the acid. The pulses are superimposed on the ordinary reaction curve and suggest that the reaction is being catalysed at definite intervals of time. These authors conclude that the periodic dissolution of metals depends not so much on the nature and condition of the dissolving metal itself as on some additional factor, such as the walls of the vessels used, colloidal substances, or the presence of a second metal. Walton (48) also observed periods of rapid attack of an unagitated hydrochloric acid solution on an aluminum single crystal. The variations of hydrogen evolution were superimposed on the normal reaction curve and could be related to sudden changes in solution potential, which Walton attributed to a polarization phenomenon. Werner (49) observed a similar effect but not the regularity in the periodicity as reported by Hedges and Myers.

According to Werner, the increases in the rate of hydrogen evolution are due to successive uncovering of "nests" of local cells.

In acids not only the hydrogen ion concentration is important, but also the nature and concentration of the anion of the acid. Centnerszwer (50) found that the rate of dissolution of pure aluminum in hydrochloric acid is accelerated by additions of F^-, Cl^-, Br^- and ClO_4^- and is retarded by I^-, $SO_4^=$ and NO_3^-.* The accelerating effect is dependent on a certain minimum hydrogen ion concentration. The anions which accelerate the dissolution of aluminum in hydrochloric acid remove the passivity of aluminum in nitric and sulfuric acids. Sulfuric acid does not attack aluminum of a certain purity so readily as does an hydrochloric acid solution of the same normality. In acid solutions containing only one anion the corrosion rate increases in this order: acetate, phosphate, sulfate, nitrate, chloride (112). Nitric acid in low and high concentrations attacks aluminum slowly, but when of medium concentration (30%) it attacks rapidly (39).

---

* Centnerszwer (50) also concluded from this study that the action of anions is independent of the cation present. This, of course, contradicts the result of later experiments described above. The reason for this erroneous conclusion is that the cations used by Centnerszwer were those of Li, Na, K, NH_4, Mg, Ca and Al. While it is probably correct that these cations do not have an accelerating effect, this generalization on the effect of cations does not apply to those of Cu, Fe, Pt, etc.

2. In Hydroxides. The attack of sodium hydroxide solutions is considerably more vigorous than the attack produced on the same metal by an hydrochloric acid solution of the same normality (41). A 0.5 N sodium hydroxide solution dissolves very pure (99.998%) aluminum, whereas 2-3N hydrochloric acid does not (30). The incubation and induction periods are considerably shorter in hydroxides than in hydrochloric acid. Even though the accelerating effects of impurities and concentration of the electrolyte on the rate of dissolution of aluminum in acids were already known in 1922 (43)*, the effects of these variables on the rate of dissolution in alkaline electrolytes were not definitely determined and recognized until 1938 (30).

Izgarischew and Jordansky in 1927 (42) and also Maas and Wiederholt in 1929 (78) found that increasing amounts of copper alloyed with aluminum accelerate its dissolution in both hydrochloric acid and potassium hydroxide. Without taking note of these results, Centnerszwer (51) and Schikorr (52, 53) found that the rate of dissolution of aluminum in sodium hydroxide is independent of its purity. These investigators used too small a volume of dilute solutions and aluminum of insufficient purity to permit conclusions on the effects of these variables. Not until 1938-39 did Müller (54) and Straumanis (30) prove again that the rate of dissolution

---

* Actually the accelerating effect of impurities was already demonstrated by A. de la Rive in 1830 (4).

of aluminum in alkaline solutions is accelerated by impurities in the metal or in the electrolyte. The rate of dissolution in alkalies is even more sensitive to small quantities of impurities than is the rate in hydrochloric acid. In contrast to the effect of impurities in acid solutions, only 0.01 percent iron or copper produce a definite increase in the rate of dissolution in hydroxides (30). The accelerating effect falls off rapidly. If the iron content is increased fifty times, the rate of dissolution is increased only 2-3 times.

The rate of dissolution increases with increasing concentration of hydroxide (21, 55) according to Centnerszwer. Equation (I) also applies in this case. Solutions of sodium, potassium, lithium, and barium hydroxide were found to act similarly on aluminum (39). The dissolution rate in sodium hydroxide of aluminum containing silicon is independent of the time of immersion but is increased linearly by increasing quantities of silicon (76).

The hydrogen absorbed by aluminum during dissolution in sodium hydroxide has been studied by several authors. Moreau and Chaudron (79) using an ion-bombardment extraction method found that the hydrogen content was 1,000 ml per 100 g of aluminum after 20-30 days of immersion in 0.01N sodium hydroxide. A value of an entirely different magnitude was found by Ransley and Neufeld (80). These authors used a volumetric method and found 0.4 ml per 100 g of aluminum under similar conditions of exposure. This quantity of hydrogen is considered normal for cast aluminum, and the authors conclude that no appreciable absorption of hydrogen takes place under the conditions studied.

3. <u>In Approximately Neutral Solutions</u>. The attack on aluminum of several solutions of salts has been investigated. Champion (56) studied the corrosion of pure aluminum in potassium chloride solutions by measuring the hydrogen evolved and the oxygen absorbed. Corrosion-time curves were thus obtained, but the irregularities in these curves were found to require further investigation. Schikorr (57) investigated the behavior of aluminum in neutral chloride solutions. Hydrogen is evolved in such solutions if the resulting sodium hydroxide and aluminum chloride do not react with each other but remain separated at the surface (no agitation). Brown and Mears (58) have studied the effect of external variables on corrosion probability* and intensity of attack. The occurrence of one pit influenced the occurrence of other pits in sodium chloride solutions. The average depth of attack decreased as the number of points of attack increased. Increasing the concentration of sodium chloride increased the probability of attack and the average depth of attack.

---

* Corrosion Probability, $P = \frac{N_c}{N_t} \times 100$

N_c = number of specimens on which one or more points of attack develop,
N_t = total number of specimens.

Increasing temperature also increased the probability of attack but decreased the average depth of attack. These results are in agreement with the predictions of electrochemical theory, that the attack at one area would reduce the chance and also the intensity of attack at adjacent areas (2).

In a study of the effect of pH on the rate of dissolution of aluminum, Akimov and Glukhova (70) found that the curve showing the dependence of the corrosion rate on the pH occupies approximately a symmetrical position with respect to the neutral region. In both the strongly alkaline region and the strongly acid region the rate of dissolution is of the same order. In neutral and acid solutions the rate is much higher in the presence of Cl^- ions than the presence of $SO_4^=$ ions. In strongly alkaline solutions the rate is unaffected by the presence of chloride, nitrate, sulfate, and acetate ions and is retarded by chromate ions (70, 111).
112

C. The Effect of an External E.M.F.

Maas and Wiederholf (41) observed that when two aluminum electrodes are immersed in water and a small current applied, pitting appears at the anode, while at the cathode dissolution occurs as in alkaline solutions because of the hydroxyl ion concentration caused by the release of hydrogen. This same effect was observed by Mears and Brown (68), who found that in sodium chloride and aluminum chloride solutions there is a critical potential at which attack can be prevented at both anode and cathode. Above this, attack takes place at the cathode even in aluminum chloride solutions, which cannot yield an alkali hydroxide. These authors suggest that, as above, the depletion of hydrogen ion concentration in the liquid immediately adjacent to the cathode results in a higher concentration of hydroxyl ions in this vicinity. Similar results were obtained by Caldwell and Albano (21), who found that when aluminum is made cathodic in sodium sulfate solution the rate of dissolution increases rapidly to a constant value as the current density is increased. At this constant value the rate of formation of hydroxyl ions at the cathode is equal to the rate of diffusion of these ions away from the layer at the surface of the cathode.

Brown and Mears (2) have shown that in solutions of potassium chloride, sodium chloride, and these same solutions containing hydrogen peroxide the corrosion of local aluminum anodes (isolated pits) and cathodes is entirely electrochemical in nature (i.e., the change in weight can be accounted for by Faraday's Law) and that the corrosion of the anode pits can be prevented by polarizing the cathodic areas to the open circuit potential of the pits (anodes) (3). When the number of sites of attack is increased the intensity of the attack decreases.

Several investigators (30, 38, 52, 53) have confirmed Thiel's (20, 23) original discovery of a positive "difference effect" when aluminum is dissolved anodically in sodium hydroxide solution. Thiel and Eckell observed that when aluminum dissolving in sodium hydroxide is connected to a more noble metal immersed in the same solution, the hydrogen evolution at the aluminum decreases while hydrogen is also evolved at the more noble metal. Connection of aluminum with a more noble metal actually increases its rate of dissolution even though the rate of hydrogen evolved at the aluminum is decreased.

When aluminum dissolves freely at a given temperature and concentration of electrolyte it has a certain rate of dissolution, (V_{11}), determined by measuring the hydrogen evolved over a given period. If this same run is now repeated while the aluminum specimen is connected to a more noble metal electrode also immersed in the same solution, the hydrogen evolved over the given period of time from the aluminum alone, (V_1), is less than V_{11}, while the total volume of hydrogen evolved, (V_g), is greater than V_{11}. From the current-time curve obtained from an ammeter connected between the two electrodes the volume of hydrogen evolved at the more noble electrode, (V_e), may be calculated. Then

$$V_g - V_e = V_1 \qquad \text{(II)}$$

and

$$V_{11} - V_1 = \triangle \qquad \text{(III)}$$

where "$\triangle$" is defined as the "difference effect." Thiel and Eckell (20, 23) found that within a certain range of current density the "difference effect" increases linearly with the current density as measured in the external circuit.

$$\Delta = K I \qquad (IV)$$

Straumanis (30) has found that the potential of aluminum dissolving in sodium hydroxide becomes more positive as the rate of dissolution is increased (by increasing the current density with an external current) and as the concentration of sodium hydroxide is decreased. The rate of dissolution consists of two factors, local element dissolution and dissolution caused by an external current.

The results obtained on making aluminum cathodic in alkaline solutions are contradictory. Hedges and Myers (47) found that an aluminum electrode connected to a platinum wire in 3N hydroxide solution when made cathodic does not dissolve even though it gives off gas. When the current is reversed, the aluminum dissolves, but the gas does not come from the aluminum. However, Caldwell and Albano (21) found that the rate of dissolution is unaffected (up to a current density of 90 ma per cm^2) when aluminum is made cathodic in sodium hydroxide solution and that the rate is dependent only on the concentration of the alkali.

In hydrochloric acid solutions the "difference effect" was found to be negative for aluminum (20, 26, 68) i.e., when the aluminum is connected with a more noble metal (is made anodic), its rate of hydrogen evolution is <u>increased</u>. Kroenig and Uspenskaja (28) have shown that the appearance of the negative "difference effect" is caused by the action of the oxide layer on aluminum when exposed to hydrochloric acid. According to these authors, making the dissolving aluminum more anodic increases the rate of dissolution in the pores of the oxide film, which is gradually destroyed. In this way a larger surface is exposed to the attack of the hydrochloric acid solution and the rate of hydrogen evolution is increased. When the oxide film is destroyed by amalgamation prior to immersion in the hydrochloric acid solution, the "difference effect" is found to be positive.

Caldwell and Albano (21) were able to reduce almost to zero the rate of dissolution of aluminum when cathodic in 0.5N hydrochloric acid containing some hydrogen peroxide.

D. Summary

The dissolution of very pure aluminum is very slow in both alkaline and acid solutions. When impurities are added either in the form of alloying elements or as salts in the electrolytes, the dissolution rate is increased. The effect of agitation in both types of solutions is negligible. An increase of ten degrees approximately doubles the dissolution rate. The dissolution process in approximately neutral solutions has been shown to be electrochemical. The "difference effect" of aluminum in alkaline solutions is positive, and in acid solution (hydrochloric) the effect depends on the oxide film. When the film is not removed from the surface, the effect is negative; otherwise, it, too, is positive.

The conditions determining the dissolution of aluminum in neutral solutions have been determined and shown to be largely electrochemical. Previous investigations have also indicated that an electrochemical mechanism is active in the dissolution of aluminum in acids and alkalies. However, for these solutions the evidence is sometimes contradictory and incomplete. It is the purpose of the experimental work to be described to investigate further the mechanism of the dissolution of aluminum in sodium hydroxide.

III. DESCRIPTION OF EXPERIMENTAL WORK

A. Experimental Details

1. Materials. The aluminum used for all experiments was taken from a sheet of 2S-O (about 99.1%)* aluminum, 0.0225 inch thick. Figure 1a gives the dimensions of the specimens used for all runs. A circular design was chosen to minimize edge effects. The electrode was punched in one piece by means of a steel die, thus avoiding a metal-to-metal junction between the disc and the handle. The handle was made 1 5/8 inches long, permitting immersion of the top of the electrode disc 1 1/4 inches below the surface of the solution. On removal from the steel die, the electrodes were filed at the edges and rubbed with 2/o emery paper to eliminate burrs. The discs were then flattened by a pressing operation. The electrodes now weighed about 3.7 g. To relieve stresses caused by cold working during punching and filing, the electrodes were annealed at 360°C in an electric furnace for thirty minutes at temperature and were then allowed to cool in the furnace.

In order to prepare the aluminum surfaces chemically, the electrodes were immersed in sodium hydroxide solutions of about the same concentration as the solution in which they were to be used until the surfaces were uniform and all

---

* The impurities consist primarily of iron, silicon, and a very small amount of copper.

scratches had been eliminated. During the dissolution process a black precipitate (Fig. 1b) gradually forms, which can be removed only by wiping the surface under running water. A stream of water alone does not wash off the precipitate. About 0.4 g of aluminum is lost during this chemical preparation, and the thickness is reduced about 0.0025 inch. The diameter of the specimen does not change appreciably during this process nor during subsequent dissolution tests.

The concentration of sodium hydroxide was controlled by titration with standard hydrochloric acid solution using phenolphthalein indicator. Reagent grade sodium hydroxide was used (A).* Initial concentrations were within ±0.004N of the given normality. The concentration of sodium hydroxide in effect remained constant throughout a run because of the large volume (4 liters) of solution used (100 ml solution per cm^2 of aluminum surface). No changes in the acid titration or dissolution rates were detected when 10 percent of the equivalents of the sodium hydroxide in the solution was used up as calculated by the weight of aluminum dissolved. Distilled water was used for all runs.

2. Specimen Coating. The use of the above described specimen depends entirely on an efficient coating for the handle. The part of the handle which is immersed in the solution must be completely protected from access by the electrolyte to insure a constant surface exposed (the disc). Also,

---

* Letters refer to sections in the Appendix.

when the specimen is used as an electrode in an electrolytic cell, the current density in an unshielded handle would be much greater than over the remainder of the specimen, resulting in rapid dissolution of the handle. Previous investigators have used paraffin-wax and similar coatings for shielding. The poor adherence of these substances often leads to penetration of the solution under the edges of the coatings, which also are generally not resistant to alkaline solutions.

After testing several types of coatings a laboratory cement* was tried which gave satisfactory performance. This cement is transparent and can be removed quantitatively from the specimens with acetone. To determine whether the weight of the coating remains constant during a dissolution run, several prepared electrodes were weighed and then their handles were coated. After drying at room temperature, these electrodes were dried at 110°C for twenty minutes, and, when they had cooled to room temperature, were used in a dissolution test. On removal from the solution, the precipitate was removed by wiping, and the specimens were dried at 110°C and weighed. The coating was now removed and the specimens were re-weighed. The greatest difference in weight-loss determined by weighing with and without coating was 2 milligrams (B). Therefore, it was not necessary to remove the

---

* DEKADHESE, made by Technical Specialties Company, Malden, Mass., under license from Decker Laboratories, Inc.

coating on the handle for weighings between runs. (Each specimen was used for several runs.) In summary, the properties of the laboratory cement of importance to this work are its

1) resistance and protection against concentrated hydroxides and acids (HCl),
2) adherence to aluminum without peeling at edges during exposure to various electrolytes,
3) constancy in weight during a dissolution test making removal for weighings unnecessary,
4) ability to dry rapidly (10 to 15 minutes).

3. Reproducibility. In order to obtain reproducible dissolution rates, the initial surface of the aluminum must be uniform in its break-down characteristics throughout all tests. At first a solution of chromic and phosphoric acids was used to remove completely all traces of precipitate and to produce a uniform surface on all specimens. However, it was found that all the precipitate formed during a dissolution run could be removed by wiping and that the surface obtained in this acid solution does not lead to reproducible dissolution rates. For these reasons the acid treatment was abandoned, and a pre-treatment in concentrated (6N) sodium hydroxide solution was substituted.

The action of this concentrated solution may be compared with some observations on the effect of more dilute solutions. When a drop of dilute (0.06N) sodium hydroxide is put on an untreated aluminum surface while its action is followed through a microscope, there is first an incubation period of no action (about 30 seconds), followed by a gradual, relatively slow evolution of hydrogen bubbles. The bubbles always come from a few points only. There is no over-all attack. When a bubble frees itself from the metal surface, another one forms at the same spot. After a certain period the number of active spots does not increase. More concentrated solution (0.6N) causes many more points to become active, each one more active than in the case of the more dilute solution. The active points are pores in the oxide film on the aluminum surface, which serve as local anodes.

After the electrodes were chemically prepared and coated, they were weighed and immersed in the concentrated sodium hydroxide solution until hydrogen bubbles appeared (10-20 seconds). The specimens were then rapidly withdrawn, rinsed immediately with water, and immersed in the test solution for a run. The weight-loss during the treatment in concentrated hydroxide solution is not more than one milligram.

The procedure for all runs using specimens prepared as described above was as follows:

a) Immersion in concentrated (6N) sodium hydroxide solu- until hydrogen bubbles appear.

b) Rinsing in water and immediate immersion in the test solution.

c) Removal of precipitate under running water by wiping after withdrawal from the test solution.

d) Drying in electric oven at 110°C, and cooling in desiccator.

e) Weighing.

The specimens are now ready for another run. The runs were timed by stopwatch.

Preliminary experiments revealed that the dissolution rates of aluminum in sodium hydroxide are sensitive to small fluctuations in temperature. A thermo-regulated bath was constructed which permitted temperature control of ±0.05°C. A mercurial thermo-regulator and a mercury relay were used for this control. The bath held five 4-liter beakers which were used simultaneously for dissolution runs.

A large number of runs were repeated to obtain information on the reproducibility of dissolution rates. In general, the percent maximum deviation from the arithmetic mean value did not exceed 3 percent. Only at small weight-losses (at low concentrations of sodium hydroxide, low temperatures or short times of immersion) was this value exceeded by one or two percent (C). The difference in weight-loss for repeated runs in the large majority of cases did not exceed 10 mg.

4. The Effect of Variables Other than C, t, T. In an effort to determine the cause of the variations within 10 mg, the effects of several other variables were studied. In

most cases agreement of repeated runs was excellent (within 2-3 mg) when two or more runs were made in the same solution. No variation could be found in the dissolution rates of the various specimens or in the action of various batches of sodium hydroxide pellets (D). Within the calculated 10 percent depletion of the sodium hydroxide solution previously mentioned, no difference was found in the action of a fresh solution and one which had already been used for a run.

The different surface conditions produced on the aluminum by various concentrations of sodium hydroxide had only a slight effect on the dissolution rates. At given conditions of t and T, specimens previously used in 0.05N solution gave slightly lower dissolution rates in a 0.05N solution than specimens previously used in 0.50N solutions. The same effect applied to dissolution rates in 0.5N solutions, i.e., the specimens previously used in a solution of the same concentration gave slightly higher dissolution rates than specimens having a surface produced in 0.05N solution (D).

In all runs only one specimen was used per beaker. However, when three specimens were immersed simultaneously the weight-loss of each of these was the same as that determined when only one specimen was used. To determine the effect of depth of immersion on the dissolution rate, a run was made with the specimen at the bottom of the 4-liter beaker. This did not change the rate. Thus, it was not possible to determine the factors which caused the variations in weight losses up to 10 mg in the case of repeated runs.

The variations were probably caused by the combination of the above discussed factors together with topochemical factors governing the formation and action of the precipitate. Heat was evolved during the dissolution process.

When the aluminum specimen dissolved without mechanical agitation, currents were set up as described in Fig. 2. The path of the small hydrogen bubbles evolved during dissolution made these currents visible.

To determine the effect of agitation on the dissolution rate, a stirrer was placed below the specimen. It was possible to place the specimen at the edge of the vortex produced by rapid stirring. Both sides of the panel were thus exposed to a rapid flow of liquid, which dispersed the hydrogen evolved throughout the beaker. In every case agitation produced a slight increase in the dissolution rate. The increases varied from 5 to 20 percent (E).

B. The Effect of Time of Immersion, Temperature and Concentration of Sodium Hydroxide.

1. Results. In Tables I-V* are given the weight-loss data obtained at concentrations between 0.05N and 0.50N and at temperatures between 8°C** and 40°C. All weight-loss data

---

* In Table VI are given additional values on the effect of concentration of sodium hydroxide on the loss in weight of aluminum.

** One run was made at 5°C in 0.10N NaOH.

are for 40.5 cm^2 (area of the specimens). Values marked with an asterisk are arithmetic mean weight-losses of two or more runs. The values from which these have been derived are given in (C). Figure 3 is a plot of Table III and represents typical curves on the effect of time of immersion and temperature on the weight-loss. The data plotted in Figure 4 were also taken from Table III. Figure 5 shows the effect of various concentrations of sodium hydroxide on the loss in weight at various temperatures. The data for Figure 5 were taken from Tables I-VI.

As indicated in Figure 3, the weight-loss is not directly proportional to the length of time of immersion. The rate of dissolution increases throughout the immersion period at all temperatures. This was found to be the case at all concentrations studied.* The increase in the rate of dissolution is accompanied by a progressive covering of the surface with a black precipitate (Fig. 9). This process continued until only a few pores revealing the metallic surface remain. The surface is then black to the unaided eye (Fig. 1). None of this precipitate was found in the solution, nor was there any colorless (aluminum hydroxide) precipitate observed.

The precipitate was collected from a number of specimens and submitted for analysis.** Both the spectrographic and

---

* One exception to this generalization occurred at 0.10N and 5°C. Here the weight-loss at 120 min. was only 57.1 mg. (See Table VII.)

** Analyses made at the "Squier Signal Laboratory", Fort Monmouth, New Jersey, through the courtesy of Mr. L. Reiss and Mr. V. J. Kublin.

X-ray diffraction analyses revealed that iron was the main constituent of the precipitate. A semi-quantitative (Harvey's) spectrographic method gave the following as the major constituents of the precipitate, with the percentage of each present: Fe - 8, Cu - 2.6, Al - 0.5, Mg - 0.4, Mn - 0.6, and Si - 0.6. The precipitate thus is formed chiefly from the impurities in the aluminum and contains little aluminum hydroxide. The dissolved aluminum apparently almost entirely enters the solution.

At all concentrations and lengths of times of immersion an increase in temperature resulted in an increase in the dissolution rate.

2. Discussion.

a) Effect of Length of Time of Immersion.

Empirical equations were found relating t, T, and C to the weight-loss, W. Figure 6 reveals that a plot of log W vs log t gives a straight line. The effect of immersion-time on the weight-loss (at constant T and C) may, therefore, be represented by a power function,

$$W = at^{b} \qquad (V)$$

where (a) and (b) are constants. These constants were calculated by the method of averages (83) for all conditions studied. Agreement of weight-losses calculated with these equations and observed values was well within experimental accuracy. The differences in these values were below 3 percent, with the exception of a few values involving weights below 50 mg (F). In Table VII are given values for (a) and (b). The values of (b) do not show a consistent trend with changes in T and C. The values of (a) increase with increasing temperature or concentration of sodium hydroxide. The constant (a) gives the weight-loss during the first minute of immersion.

The instantaneous rate of dissolution is given by differentiating (V),

$$\frac{dw}{dt} = abt^{(b-1)} \qquad \text{(Va)}$$

In Figure 7 are plotted calculated rates of dissolution against immersion time. The rate increases at a decreasing rate (Fig. 8). A series of runs up to 360 minutes revealed that the rate becomes constant after about 160 minutes of immersion in 0.30N solution at 23°C (Fig. 9).*

Figure 10 reveals that for any specified immersion-time the slope, $\frac{dw}{dt}/W$, is a constant for all concentrations studied. When the slopes of these lines are plotted against 1/t a straight line results. This relationship applies at all concentrations of sodium hydroxide and temperatures studied (Fig. 11). The slope of the line in Figure 11 is the constant (b). If equation (V) is solved for (a) and this expression is substituted in (Va), we get,

$$\frac{dw}{dt}/W = \frac{b}{t} \qquad \text{(Vb)}$$

---

* During these runs no solution was used longer than 180 minutes. After this period the specimens were rapidly removed to a new solution.

Thus, the values of (b) given in Table VII are slight deviations from a constant value, b = 1.11, obtained from the slope of the line in Figure 11, and (b) is a constant for the system, i.e., of the particular aluminum (2S) together with its impurities, dissolving in sodium hydroxide solutions within the ranges of t, T, and C studied.

Throughout these ranges the instantaneous rate is directly proportional to the average rate. From equation (Vb) it is seen that the rate of dissolution varies directly with the weight-loss and inversely with the immersion-time. The effectiveness of the impurities in each milligram of aluminum dissolved in increasing the rate of dissolution decreases with the immersion-time until finally further dissolution does not affect the rate, which then remains constant (Fig. 9).

Tammann and Neubert (76) have derived an equation for the effect on the rate of dissolution of impurities in the metal, which, on dissolving, precipitate on the surface in the metallic state or as compounds,

$$\frac{dw}{dt} = k' + k''t \qquad \text{(VI)}$$

Evans (33) has suggested a modification of this equation,

$$\frac{dw}{dt} = k' + k''W \qquad \text{(VIa)}$$

This equation holds only as long as the impurities adhere to the surface. Tammann agrees that (VIa) is the equation to be expected, as W is a measure of the impurities available for precipitation on the surface. Integration of (VIa) gives an equation for W for which a plot of W vs. t on semi-logarithmic coordinates is a straight line. The data of Tables I-VI do not give straight lines on these coordinates; log-log plots are required to give straight lines. Equation (VIa), therefore, does not apply to any part of the dissolution process studied. It will be shown in the section on electrode potential behavior that these equations (VI and VIa) do not apply in this case because they do not provide for the effect of polarization.

While there is continuous formation of a precipitate on the surface of the dissolving aluminum, the rate of dissolution increases at a decreasing rate until a constant rate is reached. Equation (V) described the reaction period (the incubation and induction periods having been eliminated by the pre-treatment) while the dissolution rate is increasing. The constant (b) is unique for this system, and (a) varies with the concentration and temperature.

b) Effect of Temperature. When the data of Tables I-VI are plotted on semi-logarithmic coordinates to show the effect of temperature on the weight-loss, straight lines result as shown in Figure 12. The relationship between the weight-loss and temperature may thus be given by an exponential function (at t and C constant)

$$W = me^{nT} \qquad \text{(VII)}$$

where T is the temperature in degrees absolute (K), e, the base of the natural logarithm, and (m) and (n) are constants. In Table VIII are given several values for these constants. There seems to be no correlation between the constants and the immersion-time or the concentration of sodium hydroxide. The agreement between observed weight-losses and those calculated by equation (VII) is of the same order as in the case of equation (V).

A plot of the logarithm of the instantaneous rate of dissolution against the reciprocal of the absolute temperature gives straight lines at various concentrations (Fig. 13) and immersion times. The effect of temperature on the instantaneous dissolution rate may thus be given by the Arrhenius equation (84),

$$\ln \frac{dw}{dt} = \ln A - \frac{E}{RT}$$

(VIII)

or

$$\frac{dw}{dt} = A_e^{-\frac{E}{RT}}$$

where R is the Gas Constant, E is the difference in the heat content between the activated and the inert molecules, the "experimental energy of activation", and A is a constant which is independent of the temperature. This relationship represents the temperature dependence of the specific reaction rates of most chemical reactions. Equation (VIII) is widely applicable not only to homogeneous reactions, but also to heterogeneous processes (16, 85).

The "experimental energy of activation" of the rate-controlling process in the dissolution of aluminum in sodium hydroxide was found to be about 13,700 cal. per mole for various concentrations and immersion times.*

The rate of dissolution approximately doubles with an increase of 10°C for all concentrations of sodium hydroxide and various immersion-times.** This is generally considered to be true for homogeneous chemical reactions (85). In contrast, for those heterogeneous reactions whose rate is determined by a diffusion process, the increase in reaction rate for a 10° rise is expected to be of the same order as the change in the diffusion constant, i.e., 2-3 percent (86).

c) The Effect of Concentration of Sodium Hydroxide.

A plot of the data of Tables I-VI made on logarithmic coordinates to reveal the effect of concentration on the weight-loss gives straight lines of which those in Figure 14 are typical. The dependence of the weight loss on the concentration of sodium hydroxide (at t and T constant) may be represented by a power function,

$$W = kC^d \qquad \text{(IX)}$$

where C is the concentration of sodium hydroxide in milliequivalents per liter and (k) and (d) are constants. A number

---

* The slope of the lines in Figure 13 is $-\frac{E}{R \times 2.3}$ where R is given in calories per degree (1.98).

** Typical coefficients are 1.92 and 2.16.

of these constants are given in Table IX.* Examination of the constant (d) reveals that it varies with the immersion time and with the temperature. This is in contrast to the constant (b) in (V), which does not vary with the analogous variables, t and C.

It was not possible to relate the rate of dissolution over the entire range of concentration of sodium hydroxide to any one property of the solution.** Neither the weight-loss nor the rate of dissolution is directly proportional to the pH, the conductivity, or the normality of the solution. The weight-loss was found to be directly proportional to the hydroxyl ion concentration up to 0.30N. Between 0.10N and 0.80N the rate of dissolution is proportional to the square root of the hydroxyl ion concentration as calculated from pH measurements.***

Centnerszwer (51, 63) found that the rate of dissolution is proportional to the square root of the concentration. Calculations based on the data from Tables I-VI give 0.46 rather than 0.50 as the exponent.

---

* A comparison of weight-losses, observed and calculated, using the three empirical equations developed for the effect of immersion-time, temperature, and concentration is given in Table X. All values fall within a range of 10 mg.

** It is shown in the section on "Electrode Potential Behavior" that the slope of the self-polarization curve is directly proportional to the pH of the solution.

*** Several runs made with potassium hydroxide gave results similar to those reported for sodium hydroxide.

C. The Effect of Gelatin and Potassium Permanganate

1. Gelatin. Röhrig (87) and also Rhodes and Berner (88) have found that the addition of gelatin to sodium hydroxide decreases the rate of dissolution of aluminum in such solutions. Gelatin retards (rather than delays) the dissolution to the same extent (on a percentage basis) in solutions of various concentrations of hydroxide. This effect becomes more pronounced as the quantity of gelatin is increased. To determine the action of gelatin in terms of the aluminum and concentration of hydroxides being studied, several runs were made using increasing quantities of gelatin* in 0.50N solutions at 25°. In Table XI and Figure 15 are given the data obtained. The weight-loss is reduced rapidly at first as increasing quantities of gelatin are added (0.10 percent gelatin reduces the weight-loss by 31.5 percent). When the solution contains 0.50 percent the weight-loss is reduced 80 percent. Agitation of these solutions does not affect the weight-loss. In general, the reproducibility of weight-losses in solutions containing gelatin is better than in gelatin-free solutions. As before, a black precipitate forms on the surface during the dissolution process.

2. Potassium Permanganate. It has been reported that potassium permanganate inhibits the dissolution of aluminum

---

* Bacto-Gelatin was used (made by Difco Laboratories, Detroit, Michigan). Ten grams of gelatin were dissolved in 500 ml of 0.50N solution with gentle heating up to 60°C.

in alkalies (89).* The protective effect increases with increasing quantities of permanganate. A series of runs was made using increasing quantities of potassium permanganate. The data obtained in these runs are given in Table XII and Figure 15.

From Figure 15 it is seen that below 0.06 percent potassium permanganate there is actually an increase in the weight-loss. In the case of 0.30N solution of sodium hydroxide at 23°C about 0.10 percent potassium permanganate is necessary to depress the weight-loss. A brown precipitate forms during dissolution in the presence of permanganate. This precipitate forms more readily than in permanganate-free solutions. At 0.27 percent permanganate the precipitate is so adherent that it becomes difficult to remove by wiping.

The accelerating effect of small quantities of permanganate is analogous to the action of sodium chromate reported by Fischer and Geller (90). Very small quantities of chromate were found to accelerate the dissolution rate and larger quantities were found to retard it. The action of gelatin and permanganate will be referred to again under the discussion on electrode potentials.

D. Electrode Potential Behavior

1. Theoretical Introduction.** Any general mechanism of corrosion must be able to account for all changes which take

---

* Inhibitors of the dissolution and corrosion of aluminum have been reviewed by Eldredge and Mears (81).

** The discussion in this section is based on that of Gatty and Spooner (91), "Electrode Potential Behavior of Corroding Metals in Aqueous Solutions", rather than on original references on this subject.

place in the electrode potential of the metal after immersion. The electrode potential of the bulk metal at any instant is dependent upon

1. The static potentials of the cathodic and anodic areas.
2. the relative magnitudes of the cathodic and anodic areas.
3. the degree of self-polarization (polarization due to currents in local cells).

These factors are not necessarily independent. For example, the current density of self-polarization at either area (anodic or cathodic) is dependent on the magnitude of that area. When the anode and cathode polarization curves are straight lines (potential vs current density), the slopes of these lines can be shown to be proportional to the exposed area of the respective electrodes at fixed conditions of exposure (2).

On immersion, the potential of an electrode usually changes until it finally attains a constant value. The conditions for a steady potential have been defined by Gatty and Spooner as such that the rates of the different electrode processes result in constant relative areas of all different fields existing on the solution-electrode interphase and that the total flow of electric charge from electrode to solution is zero.

<u>2. Experimental</u>. In Figure 16 is given a diagram of the experimental arrangement used for all electrochemical studies. During measurements of open-circuit electrode potentials the bridge connecting the two reaction beakers was

removed and the switch, S, was open. It was then possible to obtain two potential vs time curves during one run by connecting the potentiometer to each of the two independent circuits through the double-pole double-throw switch. The sodium hydroxide in the bridges and intermediary solutions was of the same concentration as that in the reaction beaker. The bridge connecting the reaction beaker with the other parts of the system was bent as indicated and drawn to a capillary opening which was brought as close to the surface of the aluminum specimen as possible. The tubulus could not be pressed against the surface because hydrogen bubbles fill the capillary when it is brought too close to the surface.

The calomel cells contained tenth-normal potassium chloride saturated with calomel. The potentiometer readings were made to 0.01 millivolt on a type K instrument (Leeds and Northrup Company). The beakers containing solutions and the calomel cells were immersed in the constant-temperature bath. All runs were made at 25°C except one series which was made to determine the effect of temperature. The temperature coefficient of the calomel cell was neglected in these measurements.* The concentration of sodium hydroxide used was 0.30N except in one series of runs which was made to determine the effect of concentration on the electrode potential. Junction potentials were computed by Henderson's

---

* The difference in e.m.f. of the calomel cell for a 15° change is 0.0007v.

equation (85).* When these corrections are applied to the measured potentials the sequence of curves in Figure 18 is not changed. Since changes in electrode potential rather than absolute values are of primary importance in this study, corrections for junction potentials were not made.

3. Results. Figure 17 illustrates the reproducibility of the electrode potential measurements. For these measurements the electrodes were pre-treated in concentrated sodium hydroxide solution. Immediately on immersion in the reacting solution measurements were made, timed with a stopwatch. The reproducibility of the potential-time curves is primarily an indication of the reproducibility of the pre-treatment and the formation of the precipitate. When no pre-treatment is used, the potential behavior is different and not reproducible. The gradual increase in potential is interrupted after about five minutes by a drop in potential also lasting about five minutes.

In Figures 18 and 19 are given the effects of temperature and concentration on the electrode potential behavior of dissolving aluminum. There is a continuous increase towards more noble electrode potentials in all the curves. Increasing temperature shifts the potential-time curve towards

---

* For 0.1N KCl and NaOH solutions of various concentrations these potentials were found:

0.05N	+0.014v	0.30N	+0.030v
0.10N	+0.019v	0.50N	+0.037v

more noble values, while increasing concentration causes a shift towards more negative values. Both of these effects increase the rate of dissolution.

Agitation shifts the electrode potential towards more noble values as shown in Figure 20. This effect becomes more pronounced with increasing time of immersion. When agitation is begun after sixty minutes' immersion-time, the electrode potential curve shifts to values determined on a specimen exposed to agitation throughout the entire run.

Data obtained to determine the cause of the change in electrode potential with immersion-time are given in Figure 21. It is seen that changing to a new solution after 60 minutes has no effect on the electrode potential. Various methods of wiping the surface free of precipitate cause an immediate change to a more negative value of electrode potential. Following such a change there are again regular increases in potential as more precipitate forms.

Electrode potential measurements were made on specimens immersed in solutions containing gelatin and potassium permanganate (Fig. 22). The addition of 0.25 percent gelatin gives lower (more negative) potentials which become constant after about 80 minutes. When 0.033 percent permanganate is added to the solution the dissolution rate is increased and the electrode potential is decreased. Thus, these two substances, one of which decreases the dissolution rate and the other of which increases the dissolution rate, both decrease the electrode potential. When enough permanganate is added to the solution to decrease the dissolution rate, the potential becomes constant at a low value within two minutes.

4. Discussion. The changes in the electrode potential caused by wiping the precipitate from the aluminum sheet during immersion and the absence of a change in the electrode potential when a specimen is removed to a new solution, after a precipitate has formed on the surface, indicate that the electrode potential behavior is largely determined by the action of the precipitate rather than by any changes taking place in the solution during the dissolution process.

There is a continuous change in electrode potential throughout the immersion-time studied. As previously described, there is also a continuous change in the rate of dissolution during the immersion periods studied. When the electrode potential is plotted against the rate of dissolution at a given time of immersion as shown in Figures 23 and 24, straight lines are obtained in every case.* Within the ranges of temperature and concentration of hydroxide studied the electrode potential of dissolving aluminum is directly proportional to the rate of dissolution.** The equations of these lines are of the type

$$E = E' - \frac{dw}{dt}P \qquad (X)$$

---

* The 32° line in Figure 24 was obtained graphically from calculated rates.

** This relationship was also found by Straumanis (29, 92) in the case of zinc dissolving in sulfuric acid, and by Hoar and Havenhand (33, 93) for iron.

where E is the measured potential, E', the open-circuit potential, and P, the slope. Rearrangement of (X) gives

$$\frac{dW}{dt} = \frac{(E' - E)}{P}\ [*]$$

The rate of dissolution is directly proportional to the difference between the open-circuit and the measured potential and inversely proportional to the polarizing function.

When equation (X) is combined with (Vb) and solved for W we get

$$W = \frac{(E' - E)t}{bP} \qquad (Xa)$$

The weight loss is thus dependent not only on the length of time of immersion but also on the polarization conditions.[**]

The fact that the rate of dissolution is dependent on the electrode potential indicates that the dissolution process is electrochemical. Therefore, the rate of dissolution may be converted (by means of Faraday's Law) to current density.[***] The current density thus obtained is determined

---

[*] Since P is always negative when (E' - E) is negative, the rate of dissolution will always be positive.

[**] From equations (V, Vb and X) it can be shown that

$$(E' - E) = abP(t^{(b-1)}).$$

This is the equation of the potential-time curves. A log-log plot of this equation gives a straight line. When the potential-time data are plotted in this manner straight lines are obtained.

[***] Rate in mg per 40.5 cm^2 x 4.42 = current density in milliamps per cm^2.

by the local cell current without an external current. We then have a typical polarization curve. In Table XIII are given the slopes P'[*] of these polarization curves. With increasing temperature and concentration the slopes increase in the positive direction (i.e., become less steep).[**]

When the polarizing function (slope P') is plotted against the pH of the hydroxide solution at various concentrations, a straight line results (Fig. 24a). The polarizing function is thus directly proportional to the pH of the solution. As the concentration is increased the polarisability is decreased. According to Figure 24a (on extrapolation), at a pH of 13.70 it is not possible to polarize anodically aluminum in sodium hydroxide solutions.

These electrode potential and polarization curves may now be interpreted in the light of information gained primarily in acid and neutral solution (53, 82, 91). It has been found that if, on immersion, the potential of a metal increases with time it may be inferred that cathodic processes predominate over anodic processes. This increasing potential may be obtained either by an increase in the self-polarization of the anodic areas or by a decrease in the

---

[*] $P' = P\ 4.42$

[**] The intercepts of these lines at zero current density are not absolute values as the electrode potentials have not been corrected for junction potentials. Figures 23 and 24 show that a given rate of dissolution does not correspond to a certain electrode potential. For a given electrode potential there are a number of dissolution rates which depend on the temperature and the concentration.

self-polarization at the cathodic areas. In every case an increase in potential with time has been observed during the dissolution of aluminum in sodium hydroxide solution. It may thus be concluded that this process is under cathodic control.

During dissolution the area of the cathodic phase increases. The slopes of the polarization curves are proportional to the extent of self-polarization and to the anodic area. Since the process is under cathodic control and the potential is directly proportional to the dissolution rate, the anode area must remain constant. The higher potential is thus a result of increasing self-polarization of the anodic areas.

The change in the electrode potential brought about by agitation can be accounted for on the basis of the local cell action just described. The effect of relative motion between electrode and electrolyte is to increase the rate of transfer of reactants and products of reaction between the solution-metal interphase and the bulk solution (91). The result is one or both of the two principal effects at the interphase:

a) cathodic area depolarization, with possible slight anodic area polarization, and/or

b) anodic area depolarization.

The direction of the electrode potential change on agitation depends on the relative magnitudes of a) and b). Predominance of a) gives a more positive potential. As indicated in Figure 20, the potential becomes more positive when the solution is agitated.*

The difference in potential, which increases with immersion-time, may thus be attributed primarily to cathodic area depolarization. The mechanism of this depolarizing action, which slightly increases the dissolution rate, probably consists of the removal of hydrogen bubbles from the surface by the action of the flowing solution. In this way the bubbles are removed while they are relatively small, giving rise to more contact between the solution and the precipitate. This effect increases as the cathodic area (quantity of precipitate) increases.

It was shown in a previous section that the rate of dissolution becomes constant when the immersion-time is extended beyond the period studied (120 minutes). The potential also approaches a constant value. One of the conditions for the steady state is that there be constant relative areas of all different fields (anodic and cathodic) existing on the solution-electrode interphase. This implies that when a constant potential and rate of dissolution are reached, the cathode area no longer increases.

---

* Gatty and Spooner (91) consider that any electro-kinetic effects, which may be produced by relative motion between the electrode and the solution, are in many cases outweighed by the simultaneous effect produced upon the local action process.

Figure 15 indicates that 0.25 percent of gelatin has about the same effect on reducing the weight-loss as 0.40 percent of potassium permanganate, yet the potential-time curves differ considerably (Fig. 22). The constant potential which is almost immediately established on immersion in solutions containing 0.40 percent of potassium permanganate indicates that the relative areas of local cathodes and anodes become constant within a few minutes of immersion. The precipitate formed in these solutions is very adherent and cannot be completely removed by wiping. Thus, the precipitate formed in solutions containing quantities of potassium permanganate sufficient to reduce the rate of dissolution in sodium hydroxide solutions (0.10 percent or more in 0.30M sodium hydroxide at 23°) forms a relatively thick layer within a few minutes of immersion, which impedes contact of the solution with the surface of the metal.

In the case of solutions containing gelatin and those containing small quantities of potassium permanganate which increase the rate of dissolution, the potential vs time curves give straight lines on logarithmic coordinates. This is in agreement with the results obtained from similar measurements made in solutions containing only sodium hydroxide. The slopes of these lines are given by (b-1). (See footnote pg. 42.) In the case of permanganate and gelatin additions this slope differs from that obtained for sodium hydroxide solutions without additions. Thus, the constant (b) is changed by gelatin and potassium permanganate.

While the effectiveness of the precipitate is decreased by the addition of gelatin, the mechanism of dissolution probably remains the same. It is probable that its effect is brought about by modification of the cathodic reaction, i.e., by retarding the evolution of hydrogen at the precipitate. In the case of permanganate additions which accelerate the rate of dissolution, a new kind of precipitate is formed, which is even more effective than the precipitate formed in permanganate free solutions. It might, therefore, be expected that this greater effectiveness is accompanied by increased anodic polarization. Figure 22 indicates that this is not so; there is actually less anodic polarization in the case of solutions containing permanganate than in permanganate-free solutions. Therefore, the accelerating effect of small quantities of potassium permanganate is probably a result of the rapid formation of an effective precipitate accompanied by some anodic depolarization.

E. Effect of an Externally Applied E.M.F.

The data obtained from electrode potential measurements indicated that the dissolution of aluminum in hydroxide solutions is electrochemical. Also, it is known that the "difference effect" on aluminum is positive in alkaline solutions. In order to supplement the information gained from electrode potential measurements and to study the reproducibility of the "difference effect" an external potential was applied to the dissolving aluminum by means of the experimental arrangement given in Figure 16.

1. Experimental. Two aluminum specimens, one an anode, the other a cathode, were used simultaneously. The switch S_1 was closed and the two large reaction beakers, one containing the anode, the other the cathode, were connected by a bridge. The concentration of sodium hydroxide was the same throughout all bridges and beakers for a series of runs.* Two series of runs were made, in a 0.30N and in 1.00N solutions. All runs were made at 23°C and 48 minutes immersion-time. The e.m.f. was supplied by a d.c. generator. By varying the resistance, the desired current (registered on the ammeter) was obtained. Throughout a run the current was held constant (±0.01A) by varying the resistance. As before, the specimens were given a pre-treatment.

Potential measurements were made using the same technique previously described.

For the lower current densities several sodium hydroxide bridges of the same concentration as the solution in the reaction beakers were used to complete the circuit between these beakers. This type of bridge could not be used where higher current densities were desired. The sodium hydroxide bridges were replaced by a platinum wire to increase the

---

* Originally it was intended to use a concentration cell, i.e., to depend on the current generated by the difference in concentration of hydroxide in the two reaction beakers. Several attempts were made using 0.01N and 1.0N solutions. However, the current generated by this cell, whose components differed by a factor of 100 in concentration, was not sufficient to produce the "difference effect".

current in the circuit. The ends of this wire were placed as far away as possible from the specimens as indicated in Figure 28a. The error introduced by using a platinum wire bridge (gases were evolved at both ends) was negligible.*

The two-beaker arrangement was used because the heat evolved, when the rate of dissolution is increased by an externally applied e.m.f., makes temperature control difficult. Also, by using separate beakers for the anode and the cathode the solutions were not depleted so rapidly as is the case when both are in the same solution.

2. Results. The results of runs made while an external current was applied to aluminum are given in Tables XIV and XV. The reproducibility of these runs is of the same order as that of simple dissolution runs previously described. In Figures 28 and 26 are plotted the data of Tables XIV and XV. For both the 0.30N and the 1.00N runs the aluminum specimen which was made the cathode lost only slightly less weight than under freely dissolving conditions. After an initial drop of about 10 mg at a current density of 0.3A, the cathodic weight-loss decreased very slightly with increasing

---

* A check run was made at 0.80A by immersing both anode and cathode in the same beaker (which eliminated the platinum wire connecting the solutions). The weight-loss obtained in this way agreed with that found when the wire was used. Anode-loss: with wire, 226.5, without wire, 219.1 mg.

current density.* As before, a precipitate formed on the surface.

In 0.30N solution there is no effect on the weight-loss of the anode until a c.d. of 0.3A (per specimen) is reached. At this value the weight-loss becomes proportional to the c.d. up to about 1.1A. From this point on, the slope changes and the proportionality of weight-loss and c.d. continues. When this last section of the curve is extrapolated it goes through the origin. The changes taking place on the surface as the c.d. is increased are given in a series of photomicrographs in Figure 27.

In 1.00N solutions there is a more continuous change in weight-loss of the anode as the c.d. is increased (Fig. 26). The curve cannot be divided into three parts of different slopes as was possible in the previous case.

When the c.d. reaches 0.3A in a 0.30N solution a definite decrease in hydrogen evolution was observed at the anode, while at the cathode there was a considerable increase in the hydrogen evolution. As the c.d. was increased this effect became more pronounced. Breaking of the circuit (restoring freely dissolving conditions) immediately increased evolution at the anode and decreased it at the cathode, until both evolved gas at about the same rate. At 0.9A and over, the

---

* This differs somewhat from the results of Caldwell and Albano (21), who found that making aluminum cathodic in sodium hydroxide solution does not affect the weight-loss. The temperature control used by these authors was 30.0 ± 0.5°C.

anode did not evolve hydrogen when first immersed. After about 10 minutes of immersion a slight precipitate formed and gas was evolved at an increasing rate. After 30 minutes the precipitate flaked off and bubbling ceased.

The action of the precipitate is further revealed in the following experiment. The platinum wire was placed near the edge of one specimen (Fig. 28b), giving very uneven current distribution over the surface of the specimen. The precipitate formed on only one-half of the specimen (the half away from the wire) while the other half remained clear. Hydrogen bubbles were evolved only on the side covered by the precipitate.

To the unaided eye the specimens exposed to current densities over 1.2A in 0.30N solution have a polished appearance. However, microscopic examination reveals that there are still traces of local cell action caused by the precipitate, which alternately slowly forms and flakes off (Fig. 27).

When an anode which has been exposed to polishing action at the higher current densities used is given the usual pretreatment in concentrated sodium hydroxide in preparation for re-use, it appears to have become "passive". Two to three minutes are required to initiate even slow hydrogen evolution.

In 1.00N solution these effects were similar with the exception that a c.d. of 2.4A was required to suppress hydrogen evolution at the anode on immersion. After about 3 minutes a precipitate formed, accompanied by very light bubbling. The gas evolution at the cathode in all cases was most vigorous. It was not possible to obtain a polished appearance at the anode in 1.00N solutions even at a c.d. of 2.4A.

When a current density of 4A was applied, there was immediate, slow evolution of large bubbles, probably oxygen, at the anode. At current densities above 2.4A the heat evolved became so great that it was not possible to control the temperature by the apparatus which was used in these experiments.

Slight agitation of a 0.30N solution at a current density of 1.0A increased the anode weight-loss considerably and reduced the cathode weight-loss about 10 mg.

Electrode potential measurements were difficult on specimens under the influence of an external current. There was a continual change in potential of both anode and cathode throughout all runs toward more noble (less negative) potentials. In general, the cathode potentials were found to be more negative than the potentials of the specimens which were made anodic. At higher current densities the potentials fluctuated considerably.

3. Discussion. When there is a precipitate on the surface a three-electrode system is formed, the anodic and cathodic areas on the aluminum and the cathodic precipitate. Brown and Mears (3, 32) have shown that, in cases where corrosion is entirely electrochemical in nature, it is necessary to polarize the cathodes in the local cells to the open-

circuit potential of the local anodes in order to obtain complete cathodic protection. Apparently one of the types of local cathodes (probably the precipitate) cannot be sufficiently polarized to produce complete cathodic protection. There is some cathodic polarization as indicated by the fact that the potential of the cathode specimen is more negative than that of the anode specimen.

The "difference effect" was calculated for runs in both concentrations of hydroxides studied. All values have been reduced to milligrams. These values and the method of calculation are given in Tables XVI and XVII and are plotted in Figure 29. At current densities below 0.3A there was no "difference effect" (this may be a result of the sensitivity of the experimental technique).

In 1.00N solutions the "difference effect" is linear with the current density up to about 0.8A and, on extrapolation, passes through the origin.

$$\Delta = KI \qquad \text{(IV)}$$

where K is a constant and I, the current density. The result is in agreement with that obtained by Thiel and Eckell (23) and Müller (38) in 1.00N sodium hydroxide. A current density of 0.8A is equivalent to 20 ma per cm². Thiel and Eckell found it to be linear up to 24 ma per cms. Müller (38) considers the "difference effect" linear over a larger range and attributes variations in K to experimental inaccuracies.

However, when Δ is plotted against the current density (Müller merely tabulates values of K) it is evident that the "difference effect" is linear up to about 22 ma per cm^2 and then falls off.

In 0.30N solutions the difference effect extends to about 1.0A; it is operative only in region (b) Figure 27. The effect is directly proportional to current density in this range. However, on extrapolation the line does not pass through the origin.

$$\Delta = K'I + N, \qquad (XI)$$

where N is the intercept at zero current density.

When the "difference effect" is complete, $W_1 = 0$ and dissolution by local cell action has ceased, making $\Delta = W_{1i}$. Therefore, the limiting value of the "difference effect" is W_{1i}. This limiting value is reached in 0.30N solution within the accuracy of these experiments.*

In 1.00N solutions the limiting value is approached but is not reached at the current densities studied. Even at 2.4A, there is no polishing action on the specimens and the precipitate is the usual powdery type rather than the flaking type observed in the runs using 0.30N solutions.

F. Summary of Experimental Work

The dissolution of (2S) aluminum in sodium hydroxide is accompanied by vigorous evolution of hydrogen and the formation

---

* $W_{1i} = 165.5$ and $\Delta_1 = 155.0$

of a powdery, black precipitate on the surface, which can be removed only by wiping. The precipitate consists primarily of compounds of the impurities in the aluminum (or a metallic deposit of these impurities). The weight-losses in all runs were found to be reproducible within a maximum deviation of 3 percent from the arithmetic, mean value of a series of repeat runs.

The summary given below of the effects of several variables applies within the ranges studied.

Time of Immersion: 0 -120 minutes
Concentration of Hydroxide: 0.05 - 0.5N
Temperature: 8.0° - 40.0°C

1. Effect of Length of Time of Immersion. The dissolution of aluminum in sodium hydroxide increases with length of time of immersion according to the equation $W = at^{b}$. The constant (a) varies with temperature and concentration. The rate of dissolution increases at a decreasing rate until a constant value is reached. The rate of dissolution is given by

$$\frac{dw}{dt} = \frac{W}{t}b \qquad \text{(Vb)}$$

The constant (b) applies under all conditions of temperature and concentration. (b = 1.11).

The electrode potential increases towards more noble values during the dissolution process and is directly proportional to the rate of dissolution. This relationship is given by the equation

$$\frac{dw}{dt} = \frac{(E' - E)}{P} \qquad \text{(X)}$$

The rate is a measure of the local-action current.

The electrode potential change with time can be related to the formation of the precipitate which is produced at the surface rather than to any changes taking place in the solution. The potential probably reaches a steady state when a constant rate of dissolution is reached.

2. <u>The Effect of Temperature.</u> The effect of temperature on the weight-loss is given by an exponential function,

$$W = me^{nT} \qquad \text{(VII)}$$

and the effect of temperature on the dissolution rate by the Arrhenius equation,

$$\frac{dw}{dt} = Ae^{\frac{-E}{RT}} \qquad \text{(VIII)}$$

An increase in temperature of ten degrees doubles the rate of dissolution. Increasing temperature makes the slope (P') of the polarization curve less steep.

3. <u>The Effect of Concentration.</u> The weight-loss increases with increasing concentration according to the equation

$$W = kC^{d} \qquad \text{(IX)}$$

The constants (k and d) vary with the immersion-time and temperature. The rate of dissolution cannot be related to any property of the solution over the entire range of concentrations studied. However, the slope (P') of the polarization curve is directly proportional to the pH of the solution.

4. <u>The Effect of an External E.M.F.</u> When aluminum is made cathodic in sodium hydroxide by an external e.m.f., after an initial drop of about 10 mg (at a c.d. of 0.3A) there

is only a very slight drop in the cathodic weight-loss as the current density is increased.

When the aluminum is made anodic at increasing current densities in 0.30N solution, there is first a range of current densities in which there is no apparent effect on the dissolution rate. Beyond this range the dissolution rate is directly proportional to the current density. This range is divided into two parts. In the second part the slope changes and the weight-loss becomes electrochemically equivalent to the current passing through the cell. In 1.00N solutions these changes are more gradual and the weight-loss approaches equivalence with the quantity of current passing through the cell at the higher current densities.

The "difference effect" is positive in both 0.30N and 1.00N sodium hydroxide. In 1.00N solution

$$\Delta = KI \qquad (IV)$$

up to a current density of about 20 ma per cm^2. At higher current densities the "difference effect" drops off. In 0.30N solution the "difference effect" (unagitated) follows the equation

$$\Delta = K'I + N \qquad (XI)$$

The degree of reproducibility of the "difference effect" is of the same order as all other dissolution runs when the time factor is considered.

Agitation markedly increases the anode weight-loss and decreases the cathode weight-loss in 0.30N solution. This has the effect of decreasing the "difference effect".

5. The Effect of Gelatin and Potassium Permanganate. Additions of gelatin reduce the dissolution rate. The weight-loss is reduced 50 percent by 0.50 percent gelatin in 0.30N solution. Small additions of permanganate accelerate the dissolution. About 0.10 percent potassium permanganate are necessary to depress the weight-loss.

6. A Note on Results Which Indicate the Nature of the Rate-Controlling Process. Vigorous agitation of the solution increases the weight-loss only slightly under freely dissolving conditions, and this increase may be attributed to a depolarization effect. In solutions containing gelatin agitation has no effect. The increase in the rate of dissolution for an increase in temperature of ten degrees is about 100 percent. The change in the diffusion coefficient expected for such an increase in temperature is of the order of 2 to 3 percent. All these facts indicate that, if diffusion processes have any effect at all on the rate of dissolution, it is very slight (for freely dissolving conditions). It is indicated that the rate-controlling process is a homogeneous chemical reaction.

IV. THEORETICAL DISCUSSION

A. The Electrochemical Nature of Metallic Surfaces

From the discussion of the literature survey and the experimental results just described, it is seen that electrochemical factors are decisive in the dissolution of metals in inorganic electrolytes. It follows that electrochemical principles have been used most frequently in explaining the mechanism of dissolution.*

The heterogeneous, topochemical character of corrosion reactions has led several investigators to a comparison with other reactions of this type, those of heterogeneous catalysis. Studies on adsorption in connection with solid metal catalysts resulted in the discovery that the surface of such catalysts is variable and contains active centers (16, 94). Pietsch and Josephy (16) consider these active centers to be active lines, crystal edges, crystal boundaries and imperfections in the crystal. Corrosion (dissolution) at these active lines (grain boundaries and inclusions) takes place according to this theory because they are also lines of preferential adsorption. At the same time, or as a result, these active centers are also centers of anodic activity.** Pietsch and

---

* Other methods which have been used to study the dissolution of metals include those dependent entirely upon diffusion theory and reaction kinetics.

** Müller (17) considers the activity of boundaries a result of larger concentrations of pores in the passive layer at such points.

Josephy (15) found that pure iron is attacked preferentially at grain boundaries and inclusions, and Dix (66) found that the grain boundaries of pure aluminum and of some aluminum alloys are anodic to centers of the grains. When aluminum surfaces are exposed to copper sulfate solutions (containing some hydrochloric acid), copper is deposited preferentially at certain parts of the surface such as edges, scratches, and cracks. On etching aluminum-copper alloys with the common reagents, the copper which goes into solution is redeposited over the surface so that an electron diffraction pattern of such a surface is that of polycrystalline copper (95). In addition to these effects, metallic surfaces are further modified by oxide films.

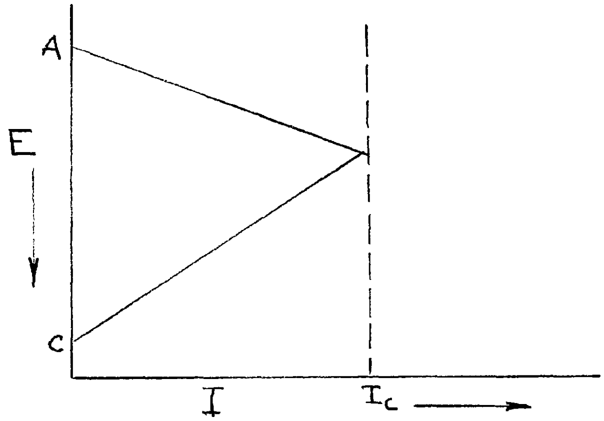
Cracks in these films, scratches, and grain boundary effects, produce differences of potential (local cells) on the surfaces of metals. Very pure metals dissolve slowly as a result of such local action. The most effective local action is produced by impurities either in the metal or precipitated on the surface. At the cathodes, areas of lower hydrogen overpotential, hydrogen is evolved, and at the anodes, areas of more negative potential, the metal goes into solution.*

---

* This discussion is concerned primarily with the hydrogen-evolution type of dissolution in the absence of oxidising agents (depolarisers).

B. Polarization

When a current flows in these local cells, polarization of the local anodes or cathodes or both (depending on the metal and the solution) takes place.



The anodes polarize to more noble potentials and the cathodes to more negative potentials. As indicated above, the polarization is often directly proportional to the current density. The equation for the polarization curves may then be given by

$$E_a = E'_a - \frac{K_a}{A_a}I_a \qquad \text{(XII)}^*$$

$$E_c = E'_c + \frac{K_c}{A_c}I_c \qquad \text{(XIIa)}$$

In these equations E_a and E_c are the polarized potentials of the anodes and cathodes, respectively; E'_a and E'_c are the open-circuit potentials; the constants K_a and K_c are the slopes when one unit area of the electrodes is exposed; and

---

* The notation of Brown and Mears (2, 3) is used throughout.

A_a and A_c are the exposed areas. The slopes are interpreted generally as "polarizing functions" by Brown and Mears (2, 3), Straumanis (92), and Evans (33). Müller (25, 96, 97, 98) has attempted to interpret these constants in terms of his "Bedeckungspassivität" theory. In this theory the surface of the metal is assumed to be covered by a film which contains numerous pores. The local-cell anodes are assumed to be at the bare surface of the metal (bottom of pores), and the local cathodes are assumed to be located on top of the film. The constants K/A are then replaced by R_s and R_p, respectively the resistance in the pore material and the resistance of the solution in the pores.

If the resistance of the metallic paths can be neglected and the resistance of the liquid is small, then at I_c in the above diagram $E_a = E_c$ and

$$E'_a - \phi_a\frac{(I_a)}{(A_a)} = E_c + \phi_c\frac{(I_c)}{(A_c)} \qquad \text{(XIII)}$$

where ϕ_a and ϕ_c are more general expressions for the polarizing functions (3).

In order to prevent dissolution the local anode current must be reduced to zero either by connecting the metal to a more noble electrode or by applying an external e.m.f. (cathodic protection). Brown and Mears (3) have shown that in this case ($I_a = 0$) equation (XIII) becomes

$$E'_a = E'_c + \phi_c\frac{(I_c)}{(A_c)} \qquad \text{(XIIIa)}$$

The local cathodes must be polarized to the open circuit potentials of the local anodes by an external current for complete cathodic protection (3, 32). From Kirchhoff's Laws

$$I_c = I_a + I_x \qquad (\overline{\underline{\text{XIV}}})$$

where I_x is the external current.

C. The "Difference Effect"

1. Theory. If equation (II) of the "difference effect" is converted from volumes of hydrogen evolved per unit of time to equivalent current density,* we have

$$I_g - I_e = I_l \qquad \text{(II)}$$

I_e, I_x = external current

I_g, I_a = current responsible for total weight-loss, a sum of the external current and the local cell current.

I_l, I_c = local cell current

Therefore,

$$I_c = I_a - I_x \qquad \text{(IIb)}$$

A comparison of equations (XIV) and (IIb) reveals that they are identical except for the sign of the external current. This is in agreement with experiment. To protect a metal cathodically, it is connected to a more anodic metal, and to produce a (positive) "difference effect" the metal is connected to a more cathodic electrode, or equivalent source of external current.

---

* This equivalence was first pointed out by Müller and Löw (99).

The limiting condition of the "difference effect" is given when I_1 (or I_e) is reduced to zero. Equation (XIII) then is given by

$$E'_c = E'_a - \phi_a \frac{(I_a)}{(X_a)} \qquad (XV)$$

Thus, in order to reach the limiting value of the "difference effect", the local anodes must be polarized to the open-circuit potential of the local cathodes. At this point local-cell action ceases and the weight-loss is equivalent to the applied current ($I_g = I_e$).

The above relationships do not imply that any given metal may be completely protected or dissolved anodically by merely reversing the external current.* Whether a surface can be polarized to the open-circuit potentials of the local anodes or cathodes depends on the nature of the metal and the solution, temperature, and concentration.

Inspection of the equations for the "difference effect"

$$I_g - I_e = I_1 \qquad (II)$$

$$I_{1i} - I_1 = \Delta \qquad (III)$$

reveals that it may become negative in two ways. Since for any run I_e and I_{1i} are fixed, the "difference effect" may be negative as a result of reversing the direction of the external current, i.e., making the specimen under consideration

---

* An example of both anodic and cathodic polarizability was described by Cupr (100). Zinc and copper electrodes were immersed in solutions of their sulfates.

cathodic, or, when the effect of making the specimen anodic is a large increase in I_g. This latter condition has been related to the break-down of a film by Kroenig and Uspenskaja (28) as previously described. To avoid confusion the expression "negative difference effect" is used in this discussion only when it is a result of a large value of I_g. If the "difference effect" is negative as a result of a reversal of the external current, the term "cathodic protection" is used.

2. __Historical Note__. The "difference effect" has been observed on a number of metals. The original work of Thiel and Eckell (20, 23) included studies on zinc and aluminum in hydrochloric acid (0.5N) and aluminum in sodium hydroxide (1.00N). Müller (38, 101) studied these same combinations in more detail. Both the "difference effect" and cathodic protection of zinc and copper were studied in solutions of their sulfates by Cupr (100). Cadmium also shows the "difference effect" in hydrochloric acid (23, 28). A negative effect was observed on magnesium in salt solutions (26), on aluminum in hydrochloric acid (23), and on magnesium-base alloys in sodium chloride solutions (102).*

In some instances, the experimental arrangement was such that the "difference effect" was operative but was not recognized. In these cases the freely dissolving rate (I_{1i}) is added to the weight calculated from the current in the couple (I_g). The difference between this sum and the value observed while the metal is made anodic is then usually attributed to experimental error (22, 103). This is permissible only when the local anodes do not polarize, i.e., when there is no "difference effect". Some of the data of Wesley (22) indicate that the "difference effect" is positive on commercially pure iron, cast iron (C-Si), austenitic-cast iron (Ni, Cu) in sodium chloride solution, on two steels in sea water, and commercially pure iron and Monel metal in sodium sulfate solution. In sulfuric acid the effect is negative for commercially pure iron.**

---

* The negative "difference effect" in these cases has been attributed to surface films (26, 102).

** Wesley (22) in his discussion on the discrepancy between calculated and observed values suggests that it "is probably an indication that the anode polarization accompanying the galvanic current reduced the normal (local cell) corrosion slightly".

3. Reproducibility. The reproducibility of the "difference effect" has also been studied. Thiel and Eckell report deviations of 35 percent in experimental values of the constant (K) for aluminum in hydrochloric acid. In sodium hydroxide this has been reduced to ±7 percent. Müller and Biberschick (101) have made a very careful study of the "difference effect" of zinc in 0.2N hydrochloric acid. These authors concluded that the "difference effect" in this case is not reproducible. In their discussion they note that the length of time of the run influenced the results.

In all previous studies of the "difference effect" and its theoretical treatment the assumption was made that the metal dissolves at a constant rate. In the experimental work a surface of 2 to 3 cm² was usually immersed in a round-bottom flask, which, in turn, was immersed in a constant-temperature bath, making the surface of the specimen inaccessible to observation. Successive readings were then made on the same specimen (because different specimens did not give reproducible results). The length of the runs was usually taken at 10 to 20 minutes. By alternately permitting the specimen to dissolve freely and applying an external e.m.f., a series of W_{li} and W_g values were obtained. The effect of time of immersion on the dissolution rate was disregarded.

For aluminum of highest purity the "difference effect" in sodium hydroxide was also not reproducible. Commercially pure aluminum gave somewhat better results (38).

4. Previously Proposed Theories. Only the more recent theories of the "difference effect" are reviewed at this point.* Straumanis (24, 92, 104) attributes the effect to polarization of the anodes with increasing current density. This reduced the potential difference between the anodes and the local cathodes with a consequent decrease in local cell action (I_o). While Straumanis has not further defined this polarization, Kroenig and Uspenskaja (28) attribute it to the increase in concentration of ions of the dissolving metal at the surface of the anodes. Thiel (31) has pointed out that this does not constitute an explanation of the phenomenon but is rather a substitution of one unknown for another. This is not entirely correct. While "polarization" does not "explain" the "difference effect", nevertheless, it has related

---

* The difference effect is discussed in references, 13, 14, 17, 20, 23, 24, 25, 26, 27, 28, 31, 33, 38, 61, 64, 92, 96, 97, 98, 99, 100, 101, 102, 104, 105.

the phenomenon to another variable, the electrode potential. Thiel and Eckell (13, 14) question the validity of electrode potential measurements on the grounds that their interpretation in terms of local cell action is impossible. However, since that time these difficulties have been largely clarified.

Müller (25, 99) has explained the "difference effect" in terms of his pore theory and has derived an equation for K.*

$$K = \frac{R_p}{R_p + R_s} \qquad (\Delta = KI) \qquad \text{(XVI)}$$

where R_p and R_s are the same resistances as previously described.

Straumanis (92) has also derived equation (IV) from Palmaer's (5)** original equation for local-cell action and the equation for the polarization curve (X). Both authors assumed a constant rate of dissolution.*** Experimentally, equation (IV) has been shown to apply in only two cases: zinc in 0.5N hydrochloric acid and aluminum in 1.0N sodium hydroxide.

5. The Effect of Agitation on the "Difference Effect".

It is probable that equation (IV) represents the purely electrochemical aspect of the "difference effect" and that the derivations of Müller and Straumanis are both descriptive

---

* Akimow and Tomaschow (106) later derived a similar expression which Müller (105) considers identical with his own.

** $V = \frac{k(E' - e)}{r}$, where V is the volume of hydrogen evolved during a given period, $(E' - e)$, the potential difference of the local cell, and r, the resistance of the local cell.

*** Müller and Straumanis (after years of discussion) agreed that their derivations are largely identical except for the interpretation of the constants. Müller defines these in terms of his pore theory, while Straumanis uses the term "polarization" without further definition (104).

of the electrochemical basis of the phenomenon of dissolving metals, if the fact that the dissolution rate may change with time (itself an electrochemical phenomenon) is taken into consideration.

In the experiments of the present study the effect of changes in dissolution rate with time was eliminated by keeping these changes constant throughout all runs. This was done by beginning all measurements at the instant of immersion of the specimen and by making all runs of equal length. In this way the action of the precipitate was kept constant.

As previously described, equation (XI) for the "difference effect" in 0.30N solution has an intercept at zero current density. This condition has not been previously described.*

Under "Experimental Work" a run was described in which mild agitation was used (to aid in temperature control) while the specimen was made anodic. The result was that the anode weight-loss increased considerably, increasing W_g, which, in turn, decreases Δ. Thus in 0.30N solutions there are factors in addition to electrochemical effects, probably diffusion phenomena.

---

* There is possibly one exception to this. In the original publication on the "difference effect" by Thiel and Eckell (23) there is a foot-note giving values of Δ at two current densities in 0.50N sodium hydroxide for aluminum. When these two points are plotted, the line connecting them does not pass through the origin but has an intercept on the Δ -axis. Neither Thiel and Eckell nor subsequent investigators have taken issue with this footnote.

When a certain current is passed through the solution during a given time interval, a quantity of aluminum is forced into solution determined by Faraday's Law. This greatly increases the concentration of the ion of the dissolving metal immediately adjacent to the metal. If the solution is relatively concentrated (1.00N), this effect is not so great as in more dilute solutions (0.30N). In the more concentrated solutions there are more hydroxyl ions left near the surface to take part in local-cell action than there are in a dilute solution. In this way local-cell action is decreased (and the difference effect is increased) in two ways: (1) by polarization of the anodes, and (2) by hydroxyl ion depletion at the metal-solution interphase. Agitation largely eliminates the second of these factors.

Under freely dissolving conditions the evolution of hydrogen causes considerable agitation of the solution at the interphase. When the specimen is made anodic, this evolution of hydrogen and its agitation effect are drastically reduced, and, at the same time, even more metal enters the metal-solution interphase than before.

D. Previously Proposed Theories of the Dissolution of Aluminum in Sodium Hydroxide

1. Historical Note. The dissolution of aluminum in alkaline solutions was first considered to be a "purely ionic" reaction by Centnerszwer and Zablocki (68) in which aluminum reacted with hydroxyl ions. Later, Centnerszwer (51) postulated that this is an oxidation reaction in which aluminum reacts with oxygen ions. This theory was derived from the fact that the rate of dissolution was found to be proportional to the square root of the sodium hydroxide concentration

(this, of course, is not equivalent to the hydroxyl ion concentration as assumed by Centnerszwer at that time).

The misleading results as to the absence of any accelerating effect of impurities on the rate of dissolution of aluminum in alkaline solutions led Centnerszwer (51) and Schikorr (52, 53) to state that local-cell action cannot be a part of the mechanism of dissolution in this case. Straumanis (13) offered electrochemical proof that the local-cell mechanism could not be operative on aluminum in alkaline solutions. More recently (109) the work of Müller (54) and Straumanis (30) proving that impurities do affect the rate of dissolution in alkaline solutions was used erroneously in support of a purely chemical theory proposed by Hedges (37) in 1932.

Theoretical considerations by Stranski based on crystallization phenomena have made it possible to predict etch figures on metals in some instances. Failure of these predictions in the case of aluminum led to the conclusion that the dissolution of aluminum is determined not by the structure of the metal but by an hypothetical, two-dimensional oxide layer. Straumanis (110) has discussed this hypothesis in terms of the known facts on the dissolution of aluminum and has found a number of contradictions.

Müller (98) has applied his pore theory to the dissolution of aluminum in alkalies. In the case of aluminum containing impurities the assumption is made that the film on the metal contains "metallic threads" which increase the conductivity of the film. Also the sizes of the pores are assumed to change under various conditions. The precipitate which forms is not discussed by Müller, and the fact that the rate changes with time is ignored.* These objections do not refer to the mathematical treatment of the theory but to the interpretation of the physical significance of the mathematical symbols.

2. The Most Recent Theory of Straumanis. The most inclusive theory as regards experimental facts has been proposed by Straumanis (30). According to this theory the dissolution of aluminum in hydroxides is governed by local-cell action. At the anodes the following reactions take place,

---

* Additional discussions of Müller's theory are given in references 92, 107, and 108.

$$Al \rightarrow Al^{+3} + 3e$$

$$Al^{+3} + 3OH^- \rightarrow Al(OH)_3$$

The number of aluminum atoms which can ionize is determined by the number of electrons which are discharged at the cathodes. At the cathodes it is assumed that water molecules are ionized under the influence of the potential gradient and the hydrogen ions thus formed are discharged.

$$3H_2O \rightarrow 3H^+ + 3OH^-$$

$$3H^+ + 3e \rightarrow 3H$$

$$2H \rightarrow H_2$$

The aluminum hydroxide formed is dissolved in excess hydroxide solution:

$$Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O$$

The dissolution of aluminum hydroxide is slower than the electrochemical reactions. Therefore, according to this theory, if the metal contains a small quantity of impurities, there is sufficient time for the dissolution of aluminum hydroxide, and the electrochemical reactions determine the rate of dissolution. When the aluminum contains larger quantities of impurities, the rates of the electrochemical reactions become so great that the aluminum hydroxide formed does not dissolve rapidly enough and precipitates on the surface as a film, which then increases the resistance of the local cells and reduces the rate of dissolution. In this case (large quantities of impurities) the rate of dissolution of aluminum hydroxide becomes rate-determining.

Straumanis considers this concept of the process a "working hypothesis". Even though potential measurements were made by Straumanis he does not make use of them in his theory of freely dissolving aluminum.*

E. The Mechanism of Dissolution Proposed on the Basis of the Present Study

On the basis of the experimental results of the present study, the dissolution of aluminum in a large volume of sodium hydroxide solution may be described as follows. The alloying constituents (impurities) in the aluminum form the cathode of local cells of which the aluminum matrix is the anode. The initial dissolution rate is a result of the action of these and any other cells, such as those caused by grain boundaries, etc. At the anodes aluminum goes into solution, while at the cathodes an equivalent quantity of hydrogen is evolved. As soon as some metal has dissolved, a black precipitate forms on the surface of the aluminum. This precipitate consists primarily of compounds of the impurities, hydroxides of iron and copper, interspersed perhaps with metallic deposits of these metals.

The precipitate acts as a cathode.** The progressive growth of the precipitate increases the total cathodic area

---

* The potential measurements were made by Straumanis (30) to provide evidence for a discussion with Müller that the potential changes with increasing current density. Müller repeatedly states that the potential of the metal remains constant. This disagreement was based on a misunderstanding. Müller referred to E' while Straumanis was considering the measured potential, E. (Equation X). Both authors were correct in their assertions. In a later paper this misunderstanding was resolved (104).

** There is now a three-electrode system at the surface, anodic areas and two kinds of cathodic areas, one on the metal and one the precipitate.

and, since the anodic area is not greatly diminished, the current density at the local anodes increases. As the weight-loss is directly proportional to the anodic current density, the dissolution rate is increased.* Increasing the anodic current density causes anodic polarization towards more noble potentials. The current density at the cathodes remains constant, and they do not polarise appreciably. As a result of anodic polarisation the potential difference of the local cells is decreased in proportion to the anodic current density.** For this reason the rate of dissolution increases at a decreasing rate until finally a constant rate and potential are reached. At this point the effective cathode area no longer increases. This may indicate that the precipitate now grows in depth only.

Thus the dissolution of aluminum in sodium hydroxide is under cathodic control. The rate of the cathodic reaction determines the rate of dissolution. The effects of temperature, agitation, and gelatin indicate that the rate-controlling reaction has the properties of a homogeneous chemical reaction.

---

* This is in contrast to the theory of Straumanis (30) in which the precipitate is considered a retarding factor.

** The equations for the rate of dissolution developed by Evans (33) and Tammann (76) do not provide for polarisation effects. Deviations from their equations are attributed to non-adherence to the surface of the precipitate. The equations (VI and VIa) are assumed to apply to the "hydrogen evolution" type of dissolution, which includes aluminum in sodium hydroxide. However, the data with which these equations have been compared were obtained in acid solutions only.

This rate-determining process is probably one of the steps in the series of reactions in which hydrogen ions from the solution are transformed to hydrogen gas at the cathodes. Diffusion effects do not appreciably influence the rate of dissolution under freely dissolving conditions.

The effect of temperature and concentration on the dissolution rate is two-fold. These variables affect the rate-determining or sluggish reaction at the cathodes and also influence the polarization of the anodes.

When the dissolving aluminum is made cathodic by an external current, the rate of dissolution is decreased only slightly. This is probably an indication that one of the two types of cathodes does not polarize appreciably (the precipitate). Making the dissolving aluminum anodic polarizes the local anodes and, as a result, decreases the potential difference of the local cells. Local-cell action is thus gradually eliminated. When the local anodes have been polarized to the open-circuit potential of the local cathodes, local-cell action ceases. The surface is now equipotential, and the weight-loss is electrochemically equivalent to the quantity of current passing through the cell.

SUMMARY

A critical review of the literature contributing to an understanding of the mechanism of dissolution of aluminum in electrolytes was made. This was followed by a description of an experimental study on the dissolution of commercially pure (2S) aluminum in sodium hydroxide solutions. The effect of time of immersion, temperature, concentration, external current, agitation, and additions of gelatin and potassium permanganate on the weight-loss and the rate of dissolution was studied within the following ranges:

Concentration of sodium hydroxide	0.05 - 0.5M
Temperature - - - - - - - - - - - -	8.0° - 40.0°C
Time of Immersion - - - - - - - - -	5-120 min.

A technique was developed which gave reproducible dissolution rates under all conditions studied.

1. When (2S) aluminum dissolves in sodium hydroxide solutions, hydrogen is evolved and a precipitate forms on the surface which increases the rate of dissolution at a decreasing rate until a constant rate is reached. The effect of time of immersion on the weight-loss is given by a power function. The instantaneous rate of dissolution (found by differentiating the equations derived empirically from weight-loss vs time data) is directly proportional to the weight-loss and inversely proportional to the time of immersion. The constant of proportionality in this relationship applies throughout all ranges of temperature and concentration studied.

2. Electrode potential measurements on dissolving specimens revealed that in every case the potential changes to more noble values during the dissolution process. The changes in potential appear to be a function of the precipitate rather than the result of any changes taking place in the solution. When the electrode potential is plotted against the rate of dissolution (which can be converted to current density of the local cells), straight lines are obtained.

3. The slopes of these polarization lines are directly proportional to the pH of the solution. Neither the weight-loss nor the rate of dissolution could be related to any property of the solution as a function of the concentration over the entire range. The effect of concentration on the weight-loss is also given by a power function.

4. The effect of temperature on the weight-loss is given by an exponential function and the effect on the rate of dissolution by the Arrhenius equation. An increase of ten degrees approximately doubles the dissolution rate.

5. When aluminum is made cathodic by an external current, there is only a very slight drop in the weight-loss as the current density is increased. When aluminum is made anodic, there is first a range of current densities in which there is no apparent effect on the weight-loss. Beyond this range the dissolution rate is directly proportional to the current density supplied by the external current. This

range is divided into two parts. In the first part there is dissolution as a result of both local-cell action and the external current. As the external current density is increased local-cell action is decreased ("difference effect") until it is almost completely suppressed. At this point the second part begins in which the weight-loss is electrochemically equivalent to the current passing through the cell.

6. The above described action of an external current was found in 0.30N solutions. In 1.00N solutions the transitions between the various phases, as the current density is increased, are less pronounced, and local-cell action cannot be reduced to zero.

7. The "difference effect" in 1.00N solutions was found to be directly proportional to the current density at lower values ($\Delta = KI$). However, at current densities over 20 ma per cm^2 the effect falls off. In 0.30N solutions the "difference effect" was also found to be linear with the current density, but an intercept on the Δ- axis at zero current density was revealed ($\Delta = K'I + N$). The effect of agitation on the "difference effect" indicates that this intercept is a result of the influence of concentration gradients set up in the more dilute solutions.

8. The effects of agitation, additions of gelatin, and temperature indicate that the rate-controlling reaction is an homogeneous chemical reaction.

9. About 0.10 percent of potassium permanganate is necessary to depress the dissolution rate of commercially pure aluminum in 0.30N sodium hydroxide. When it is added in quantities smaller than this, there is an accelerating effect.

10. In the last section, various theoretical implications resulting from the literature and experimental studies were discussed. It was shown that the "difference effect" is the counterpart of cathodic protection. The conditions defined by Brown and Mears for cathodic protection were found to apply also to the "difference effect" when the direction of the external current is taken into consideration. To reach the limiting value of the "difference effect" the local anodes must be polarized to the open-circuit potential of the local cathodes. Experiments indicate that this condition is met in 0.30N solutions. The "difference effect" is of the same order of reproducibility as other dissolution tests, when the fact that the dissolution rate changes with immersion-time is taken into account.

11. On the basis of the present investigation the process of the dissolution of commercially pure aluminum in sodium hydroxide solutions may be described as follows. The precipitate which forms on the surface of the dissolving aluminum, as a result of local-cell action at the surface, consists primarily of the impurities (iron or compounds of iron) in the aluminum, which precipitate on the surface.

This precipitate acts as a cathode in local cells. The progressive growth of the precipitate increases the total cathodic area, while the anodic area is not appreciably diminished. The local cell process is under cathodic control. The current density of the local anodes increases. As a result, the dissolution rate increases, the anodic areas are polarized to more noble potentials, and the potential difference of the local cells is diminished. For this reason the rate of dissolution increases at a decreasing rate (and is a function of the immersion-time) until finally a constant rate and potential are reached. At this point the effective cathodic area no longer increases. The cathodic precipitate does not polarize appreciably. This is in contrast to the theory of Straumanis, who considers the precipitate a retarding factor.

12. The rate of the cathodic reactions determines the rate of dissolution. Experimental results indicate that this rate-determining process is an homogeneous, chemical reaction, which probably is one of the steps in the series of reactions in which hydrogen ions from the solutions are transformed to hydrogen gas at the cathodes. Diffusion effects do not appreciably influence the rate of dissolution under freely dissolving conditions.

Thus, the various phenomena accompanying the dissolution of commercially pure aluminum in sodium hydroxide solutions may be explained in terms of electrochemical theory.

BIBLIOGRAPHY

1. Evans, U. R., and Hoar, T. P.; *Proc. Royal Soc.*, *A*, *137*, 343 (1932)

2. Brown, R. H., and Mears, R. B.; *Trans. Electrochem. Soc.* *74*, 495 (1938)

3. Brown, R. H., and Mears, R. B.; *Trans. Electrochem. Soc.* *81*, 455 (1942)

4. De La Rive, A.; *Ann. Chim. phys*. *43*, 425 (1830)

5. Palmaer, W.; "The Corrosion of Metals," Stockholm (1929)

6. Whitney, W. R.; *J. Amer. Chem. Soc*. *25*, 394 (1903)

7. Cushman, A. S.; *Proc. Amer. Soc. Test. Mat*. *7*, 211 (1906)

8. Heyn, E., and Bauer, O.; *Mitt. Materialprüfungsamt* *26*, 74 (1908)

9. Ericson-Auren, T., and Palmaer, W.; *Z. phys. Chem*. *39*, 1 (1901)

10. Liebreich, E.; *Korrosion u. Metallschutz* *5*, Beiheft, 20 (1929)

11. Guertler, W., and Blumenthal, B.; *Z. phys. Chem*. *152*, 197 (1931)

12. Mears, R. B., and Brown, R. H.; *Ind. Eng. Chem*. *33*, 1001 (1941)

13. Straumanis, M.; *Korrosion u. Metallschutz 9*, 1 (1933), *9*, 29 (1933)

14. Eckell, J.; *Z. Elektrochem*. *38*, 13 (1932)

15. Pietsch, E.; *Korrosion u. Metallschutz* *8*, 57 (1932)

16. Schwab, G. M., Taylor, H. S., and Spence, R.; "Catalysis," D. Van Nostrand Co., Inc., New York (1937)

17. Müller, W. J.; *Korrosion u. Metallschutz* *13*, 144 (1937)

18. Centnerszwer, M., and Straumanis, M.; *Z. phys. Chem*. *118*, 443 (1925)

19. Centnerszwer, M., and Straumanis, M.; *Z. phys. Chem.* **128**, 369 (1927)

20. Thiel, A.; *Z. Elektrochem.* **33**, 370 (1927)

21. Caldwell, B. P., and Albano, V. J.; *Trans. Electrochem. Soc.* **76**, 271 (1939)

22. Wesley, W. A.; *Trans. Electrochem. Soc.* **73**, 539 (1938)

23. Thiel, A., and Eckell, J.; *Korrosion u. Metallschutz* **4**, 121 (1928), **4**, 145 (1928)

24. Straumanis, M.; *Z. phys. Chem.* **148**, 349 (1930)

25. Müller, W. J.; *Trans. Electrochem. Soc.* **76**, 167 (1939)

26. Kroenig, W. O., and Uspenskaja, V. N.; *Korrosion u. Metallschutz* **11**, 10 (1935)

27. Thiel, A., and Ernst, W.; *Korrosion u. Metallschutz* **6**, 97 (1930)

28. Kroenig, W. O., and Uspenskaya, V. N.; *Korrosion u. Metallschutz* **12**, 123 (1936)

29. Straumanis, M.; *Z. phys. Chem.* **147**, 161 (1930)

30. Straumanis, M., and Barkss, N.; *Korrosion u. Metallschutz* **15**, 5 (1939)

31. Thiel, A.; *Z. phys. Chem.* **151**, 103 (1930)

32. Mears, R. B., and Brown, R. H.; *Trans. Electrochem. Soc.* **74**, 519 (1938)

33. Evans, U. R.; "Metallic Corrosion Passivity and Protection," Edward Arnold and Co., London, 1937

34. Walker, W. H., Cederholm, A. M., and Bent, L. N.; *J. Am. Chem. Soc.* **29**, 1251 (1907)

35. Akimow, G. W., and Oleschko, A. S.; *Korrosion u. Metallschutz* **11**, 125 (1935)

36. Goldowski, N.; *Korrosion u. Metallschutz* **13**, 128 (1937)

37. Hedges, E. S.; "Protective Films on Metals," D. Van Nostrand Co., Inc., New York (1932)

38. Müller, W. J., Löw, E., and Steiger, F.; *Korrosion u. Metallschutz* **15**, 1 (1939)

39. Bauer, O., Kröhnke, O., and Masing, G.; "Die Korrosion metallischer Werkstoffe," Verlag von S. Hirzel in Leipzig, 1936; Vol. II; Pg. 288

40. Müller, W. J.; *Aluminium 18*, 478 (1936)

41. Maass, E., and Wiederholt, W.; *Z. Metallk. 17*, 115 (1927)

42. Isgarischew, N., and Jordansky, W.; *Korrosion u. Metallschutz 3*, 54 (1927)

43. Mylius, F.; *Z. Metallk*. *14*, 233 (1922)

44. Hedges, E. S., and Myers, J. E.; *J. Chem. Soc*. *125*, 604 (1924)

45. Centnerszwer, M.; *Z. phys. Chem*. *131*, 214 (1927)

46. Straumanis, M.; *Korrosion u. Metallschutz 14*, 1 (1938)

47. Hedges, E. S., and Myers, J. E.; "The Problems of Physico-Chemical Periodicity," Longmans, Green and Co., New York, 1926; Page 42

48. Walton, C. J.; *Trans. Electrochem. Soc*. *85*, 239 (1944)

49. Werner, M.; *Z. anorg. Chem*. *154*, 275 (1926)

50. Centnerszwer, M.; *Z. Elektrochem*. *35*, 695 (1929)

51. Centnerszwer, M.; *Z. Elektrochem*. *37*, 598 (1931)

52. Schikorr, G.; *Z. Elektrochem*. *37*, 610 (1931)

53. Schikorr, G.; *Mitt. deut. Materialprüfungs anstalt Sonderheft 22*, 16 (1933)

54. Müller, W. J., and Löw, E.; *Aluminium 20*, 257 (1938)

55. Bailey, G. H.; *J. Soc. Chem. Ind*., Japan *39*, 118 (1920)

56. Champion, F. A.; *Trans. Faraday Soc*. *41*, 593 (1945)

57. Schikorr, G.; Mitt. deut. *Materialprüfungsanstalt Sonderheft 22*, 22 (1933)

58. Mears, R. B., and Brown, R. H.; *Ind. Eng. Chem*. *29*, 1087 (1937)

59. Liebreich, E., and Wiederholt, W.; *Z. Elektrochem*. *31*, 6 (1925)

60. Maass, E.; *Korrosion u. Metallschutz 3*, 25 (1927)

61. Akimow, G.; Korrosion u. Metallschutz 8, 197 (1932)

62. Straumanis, M.; Korrosion u. Metallschutz 18, 271 (1942)

63. Centnerszwer, M.; Z. phys. Chem. 141, 297 (1929)

64. Müller, W. J.; Korrosion u. Metallschutz 12, 133 (1936)

65. Centnerszwer, M., and Zablocki, W.; Z. phys. Chem. 122, 455 (1926)

66. Dix, E. H.; Trans. Am. Inst. Min. Met. Engrs., Inst. Metals Div. 137, 21 (1940)

67. Röhrig, H.; Z. Metallk. 22, 362 (1930)

68. Mears, R. B.; Corrosion Symposium, June 1, 1943, Amer. Soc. Refrig. Engineers.

69. Akimow, G. W.; Korrosion u. Metallschutz 6, 84 (1930)

70. Akimow, G. W., and Glukhova, A. I.; Comptes Rendus (Doklady) de l'Academie des Sciences de l' URSS 41, 194 (1943)

71. Schikorr, G.; "Die Zersetzungserscheinungen der Metalle," Verlag von Johann Ambrosius Barth, Leipzig (1943)

72. Vernon, W. H. J.; Second Experimental Report, Trans. Faraday Soc. 23, 117 (1927)

73. Wiederholt, W.; Z. anorg. allg. Chemie 154, 226 (1926)

74. Glauner, R., and Glocker, R.; Z. Kristallographie A 80, 377 (1931)

75. Waché, M. X.; Revue de Métallurgie 25, 331 (1928)

76. Tammann, G., and Neubert, F.; Z. anorg. allg. Chemie 201, 225 (1931)

77. Hanawalt, J. D., Nelson, C. E., and Peloubet, J. A.; Trans. Amer. Inst. Min. Met. Eng. 147, 273 (1942)

78. Maass, E., and Wiederholt, W.; Korrosion u. Metallschutz 5, 265 (1929)

79. Moreau, and Chaudron; C. R. Acad. Sci. Paris 219, 554 (1944)

80. Hansley, C. E., and Neufeld, H.; Nature 159, 709 (1947)

81. Eldredge, G. G., and Mears, R. B.; Ind. Eng. Chem. 37, 736 (1945)

82. Brown, R. H., Fink, W. L., and Hunter, M. S.; Trans. A.I.M.E. 143, 115 (1941)

83. Davis, D. S.; "Empirical Equations and Nomography," McGraw-Hill Book Co., Inc., New York, 1943

84. Glasstone, S., Laidler, K. J., and Eyring, H.; "Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, 1941

85. Glasstone, S.; "Textbook of Physical Chemistry," D. Van Nostrand Co., Inc., New York, 1946, Pg. 1088

86. Eucken, A.; "Grundriss der Physikalischen Chemie," Akademische Verlagsgesellschaft, Leipsig, 1943, Pp. 385 and 407

87. Röhrig, H.; Korrosion u. Metallschutz 5, 41 (1929)

88. Rhodes, F. H., and Berner, F. W.; Ind. Eng. Chem. 25, 1336 (1933)

89. Collari N; Alluminio 15, 13 (1947)

90. Fischer J., and Geller, W.; Korrosion u. Metallschutz 12, 297 (1936)

91. Gatty, O., and Spooner, E. C. R.; "The Electrode Potential Behaviour of Corroding Metals in Aqueous Solutions," Oxford, At the Clarendon Press (1938)

92. Straumanis, M.; Korrosion u. Metallschutz 14, 67 (1938)

93. Hoar, T. P., and Havenhand, J.; J. Iron Steel Inst 133, 248 (1936)

94. Taylor, H. S.; J. Phys. Chem. 30, 145 (1926)

95. Heidenreich, R. D., and Sturkey, L., and Woods, H. L.; J. App. Physics 17, 127 (1946)

96. Müller, W. J.; Korrosion u. Metallschutz 16, 1 (1940)

97. Müller, W. J.; Korrosion u. Metallschutz 14, 49 (1938)

98. Müller, W. J.; Korrosion u. Metallschutz 14, 77 (1938)

99. Müller, W. J., and Löw, E.; Z. Elektrochem. 42, 789 (1936)

100. Cupr, V.; *Korrosion u. Metallschutz* **15**, 256 (1939)

101. Müller, W. J., and Biberschick, W.; *Korrosion u. Metallschutz* **17**, 77 (1941)

102. Fox, F. A., and Davies, J. K.; *J. Inst. Met.* **14**, 553 (1947)

103. Hoar, T. P.; *Trans. Faraday Soc.* **30**, 480 (1934)

104. Straumanis, M.; *Korrosion u. Metallschutz* **14**, 81 (1938)

105. Müller, W. J.; *Korrosion u. Metallschutz* **14**, 63 (1938)

106. Akimow, G. W., Tomaschow, N. D.; *Korrosion u. Metallschutz* **13**, 114 (1937)

107. Weiner, R., and Halla, F.; *Z. Elektrochem.* **48**, 361 (1942)

108. Halla, F.; *Z. Elektrochem.* **48**, 618 (1942)

109. Kroehnke, O., Masing., G.; "Der Korrosionsschutz Metallischer Werkstoffe und Ihrer Legierungen," Verlag von S. Hirzel, Leipzig (1940)

110. Straumanis, M.; *Korrosion u. Metallschutz* **19**, 157 (1943)

111. Kühnrich, E.; *Korrosion u. Metallschutz* **14** (1938) Beiheft NR. 1

112. McKee, A. B., and Brown, R. H.; *Corrosion* **3**, 595 (1947)

TABLES

TABLE I

Loss in Weight of Aluminum in 0.05N Sodium Hydroxide Solution at Various Temperatures

Time of Immersion in Minutes	Loss in Weight of Aluminum in Milligrams per 40.5 cm² Temperature in °C 25	28	32	40
10	16.1	18.2	29.7	43.9
15	21.7	29.5	42.7	67.9
20	--	--	--	96.9
30	47.3*	52.0	90.6	149.4
45	71.9*	90.0	140.9	240.1*
60	94.4	129.4	196.0	324.5
80	141.0	161.1	271.1	--
100	165.0	229.2	351.6	--
120	223.1*	265.1	431.2	--

* Average of several values.

TABLE II

Loss in Weight of Aluminum in 0.10N Sodium Hydroxide Solution at Various Temperatures

Time of Immersion in Minutes	Loss in Weight of Aluminum in Milligrams per 40.5 cm^2 ---Temperature in °C--- 5	23	26	32	40
5	--	9.9	11.1	17.3	--
10	--	19.7	23.1	34.8	63.8
15	7.7	29.6	37.2*	53.8	103.2
20	10.2	40.2	48.5	76.6	--
30	14.2	60.2	78.8*	117.5	218.3
45	20.2	94.8*	114.7	188.8	343.9
60	27.4	124.5	171.1*	248.0*	478.2
80	36.1	177.4	221.9	365.1	--
100	49.6	228.5	287.9*	446.9	--
120	57.1	281.4*	343.5*	553.3	--

* Average of several values.

TABLE III

Loss in Weight of Aluminum in 0.20N Sodium Hydroxide Solution at Various Temperatures

Time of Immersion in Minutes	Loss in Weight of Aluminum in Milligrams per 40.5 cm^2				
	Temperature in °C				
	8	25	26	32	40
10	8.2	25.8	29.9	49.5	87.0
15	12.8	38.9	47.0	78.5	136.3
30	23.8	81.6	102.3	171.1	290.2
45	36.6	135.5*	162.9	263.0	466.3
60	52.7	178.6*	225.7	362.4	--
80	72.1	244.3	312.1	--	--
100	91.0	318.3*	407.3	--	--
120	112.8	387.5	495.0	--	--

* Average of several values.

TABLE IV

Loss in Weight of Aluminum in 0.30N Sodium Hydroxide Solution at Various Temperatures

Time of Immersion in Minutes	Loss in Weight of Aluminum in Milligrams per 40.5 cm^2 Temperature in °C 8.5	23	26	40
10	11.8	32.7	42.2	107.5*
15	16.7	50.9	58.9	172.6*
30	31.1	102.7*	124.6*	367.4*
45	46.4	162.7*	205.1*	544.3*
60	65.1	224.2*	276.3*	--
80	89.1	309.5*	369.3	--
100	112.5	395.0*	487.0*	--
120	138.7	479.6*	599.8	--

* Average of several values.

TABLE V

Loss in Weight of Aluminum in 0.50N Sodium Hydroxide Solution at Various Temperatures

Time of Immersion in Minutes	Loss in Weight of Aluminum in Milligrams per 40.5 cm²			
	Temperature in °C			
	8.5	25	26	40
10	12.2	38.6	49.0	133.0
15	18.8	59.5	74.6	204.1
30	38.8	118.5	164.9	454.5
45	58.7	196.9*	256.1	706.2
60	80.8	266.7	349.8*	--
80	106.7	366.7	470.3	--
100	147.6	480.2	576.1	--
120	175.0	603.0	744.6	--

* Average of several values.

TABLE VI

Loss in Weight of Aluminum at 23° in NaOH Solutions of Various Concentrations

Time of Immersion in Minutes	Loss of Aluminum in Milligrams per 40.5 cm^2 Concentration of NaOH in Equivalents per Liter, (N) 0.15	0.25	0.35	0.40
45	111.4	144.6	179.8	182.0
60	156.7	190.4	247.0	253.9
100	276.7	348.9	427.0	442.6
		At 26°		
45	140.0	182.6	221.6	231.8
60	193.6	250.5	312.5	319.8
100	340.6	441.5	549.2	573.8

TABLE VII

Constants (a) and (b) for Equation $W = at^b$

W = mg/40.5 cm^2
t = minutes

Temperature °C	Concentration of NaOH in Equivalents per Liter 0.05	0.10	0.20	0.30	0.50
			-(a)-		
5.0	--	0.530	--	--	--
8.0	--	--	0.658	--	--
8.5	--	--	--	1.060	1.020
25.0	1.175	1.714	1.895	2.660	2.855
26.0	1.378	1.880	2.178	3.220	4.041
32.0	2.210	2.791	3.819	--	--
40.0	3.350	5.017	6.785	9.678	9.860
			-(b)-		
5.0	--	0.973	--	--	--
8.0	--	--	1.072	--	--
8.5	--	--	--	1.012	1.071
25.0	1.084	1.057	1.113	1.085	1.112
26.0	1.101	1.088	1.134	1.089	1.086
32.0	1.099	1.103	1.116	--	--
40.0	1.117	1.111	1.108	1.070	1.124

TABLE VIII

Constants (m) and (n) for Equation $W = me^{nT}$

W = mg/40.5 cm^2
T = absolute temperature in °K
e = base of natural logarithm

Time of Immersion in Minutes	Concentration of Sodium Hydroxide Solution in Equivalents per Liter				
	0.05	0.10	0.20	0.30	0.50
			$-(m \times 10^{+9})-$		
15	113	15.3	--	23.6	11.9
45	27.5	3.47	6.07	14.6	9.9
120	--	7.19	--	12.7	23.2
			$-(n)-$		
15	0.0647	0.0722	--	0.0725	0.0754
45	0.0732	0.0809	0.0802	0.0780	0.0800
120	--	0.0822	--	0.0822	0.0809

TABLE IX

Constants (k) and (d) in Equation $W = kC^d$

W = weight loss in mg/40.5 cm^2
C = concentration of sodium hydroxide in
milli-equivalents per liter

Time of Immersion in Minutes	Temperature in °C 23	 26	 32	 40
		-(k)-		
15	3.90	6.01	--	10.77
30	7.76	7.47	--	23.66
45	9.64	12.27	23.1	38.94
60	12.79	18.84	--	--
80	24.44	25.79	--	--
100	26.74	33.27	--	--
120	38.59	40.42	--	--
		-(d)-		
15	0.440	0.396	--	0.482
30	0.447	0.496	--	0.477
45	0.491	0.491	0.460	0.468
60	0.499	0.474	--	--
80	0.438	0.469	--	--
100	0.475	0.473	--	--
120	0.440	0.471	--	--

TABLE X

Comparison of Observed and Calculated Weight-losses in Milligrams per 40.5 cm^2 at 0.30N and 23°

Immersion	----------Source of Calculated Value----------			
Time	Observed	$W = at^b$	$W = kC^d$	$W = me^{nT}$
15	50	50	48	51
30	107	106	99	--
45	163	165	158	157
60	224	226	222	--
80	310	308	298	--
100	396	394	386	--
120	480	479	475	454

TABLE XI

The Effect of Gelatin on the Rate of Dissolution in 0.30N Sodium Hydroxide at 23° and 60 Minutes Immersion-time

Percent Gelatin	-------Weight-Loss in mg per 40.5 cm^2-------		
	Observed	Mean	With Agitation
0.00	225.7	225.7	---
0.0083	207.3 207.3 209.5	208.0	---
0.0208	188.7 188.9 189.8	189.1	---
0.0416	176.3 177.9 171.5	175.2	175.0
0.0833	160.8	160.8	161.5
0.1666	139.4	139.4	141.0
0.2500	132.2 133.5	132.8	133.5
0.5000	112.2 114.3	113.2	---

TABLE XII

Effect of Potassium Permanganate on the Rate of Dissolution in 0.30N Sodium Hydroxide Solution at 23°

Immersion-time: 60 minutes

Percent Potassium Permanganate	----Weight-Loss in mg per 40.5 cm^2----- Observed	Mean	With Agitation
0.0	226.7	---	---
0.00271	256.3 253.9	255.1	---
0.01085	268.3 268.6	268.4	---
0.0217	277.3 276.3	276.8	---
0.0325	280.8 275.6	278.2	267.5 265.5
0.0500	261.8 266.3	263.9	---
0.1000	201.5 212.9	207.2	---
0.1355	195.4 186.1	190.7	---
0.2710	158.1 157.3 154.5	156.6	152.8
0.4000	149.3 144.4	146.8	---
0.5420	138.7 132.5	135.6	---

TABLE XIII

Slopes of Polarization Curves (P')

$$\frac{\text{volt - cm}^2}{\text{amps}}$$

At 23°		At 0.30N	
0.05	-0.0610	23°	-0.0252
0.30	-0.0252	32°	-0.0166
0.50	-0.0167	40°	-0.0111

$$\frac{dw}{dt} \times \frac{1}{50} \times \frac{1}{9} \times \frac{96,500}{40.5 \times 1000} = \text{ma/cm}^2$$

pH Measurements Made with Beckman pH Meter
Using "Type E" (Blue Glass) Electrode

Normality in Equivalents per Liter	pH
0.05	12.52
0.10	12.83
0.20	13.09
0.30	13.22
0.50	13.38
1.00	13.58

TABLE XIV

Effect of An External E.M.F. on the Dissolution of Aluminum in Sodium Hydroxide at 25° in 0.30N Solution

Current Density in Amps per Panel	Weight-Loss in mg per 40.5 cm² in 45 min. Anode	Mean	Cathode	Mean
0.30	162.8		149.3	
0.40	174.9		152.3	
0.50	185.0		150.3	
0.60	191.3		146.8	
	200.5	195.9	156.1	151.5
0.70	211.2		144.4	
0.80	225.5		140.0	
0.80*	219.1	222.3	142.7	141.3
0.90	237.7		150.0	
1.00	250.3		144.9	
	257.1		146.1	
	258.6	255.3	141.7	144.2
1.20	281.3		151.5	
1.40	339.3		142.5	
1.60	386.2		138.3	
	400.5	393.3	157.4	147.8
1.80	435.1		145.2	
2.00	476.0		141.5	
2.40	576.1		144.2	

* Run made with anode and cathode in same beaker.

Without applied e.m.f.: 165.4

TABLE XV

Effect of An External E.M.F. on the Dissolution of Aluminum in Sodium Hydroxide at 25° in 1.00N Solution

Current Density in Amps per 40.5 cm^2	Weight-Loss in mg per 40.5 cm^2 in 45 min. Anode	Cathode
0.40	303.0	281.0
0.60	310.8	271.6
0.80	320.6	274.1
1.00	344.0	276.1
1.20	372.0	270.0
1.40	406.3	272.6
1.60	431.5	269.6
1.80	471.2	265.9
2.00	528.2	269.7
2.40	620.3	263.7

Without applied e.m.f.: 290.0
290.5

TABLE XVI

The Difference Effect on Aluminum in 0.30N Sodium Hydroxide at 23°

$W_g - W_e = W_1$ $\qquad$ $W_{ii} = 165.4$

$W_{ii} - W_1 = \Delta$ $\qquad$ $W_e = \dfrac{A \times 45 \times 60 \times 9 \times 1000}{96{,}500}$

W_{ii} = weight-loss determined under freely dissolving conditions
W_t = total weight-loss observed when external e.m.f. was applied anodically
W_e = weight-loss calculated from current in external circuit
W_s = weight-loss due to simple dissolution while specimen was made anodic by external e.m.f.
Δ = difference effect

C.D. per Specimen	Weight-Loss in mg per 40.5 cm² in 45 minutes W_g	W_e	$W_g - W_e$	$W_{ii} - W_1 = \Delta$
0.30	162.8	75.5	87.3	78.1
0.40	174.9	100.6	74.3	91.1
0.50	185.0	126.0	59.0	106.4
0.60	195.9	151.0	44.9	120.5
0.70	211.2	176.0	35.2	130.2
0.80	222.3	201.8	20.5	144.9
0.90	237.7	226.8	10.9	154.5
1.00	255.3	252.0	3.3	162.1
1.00*	266.5	252.0	14.5	150.9*

* With mild agitation

TABLE XVII

The Difference Effect on Aluminum in 1.00N Sodium Hydroxide at 25°

All Runs 45 Minutes

C.D. per Specimen	W_g	W_e	$W_g - W_e = W_1$	$W_{ii} - W_1 = \Delta$
0.40	303.0	100.6	202.4	87.6
0.60	310.8	151.0	159.8	130.5
0.80	320.6	201.8	118.8	170.6
1.00	344.0	252.0	92.0	198.0
1.20	372.2	302.0	70.2	219.8
1.40	406.3	352.0	54.3	235.7
1.60	431.5	402.5	29.0	261.0
1.80	471.2	452.0	19.2	270.8
2.00	528.2	504.0	24.2	265.8
2.40	620.3	605.0	15.3	274.7

$W_{ii} = 290.0$

ILLUSTRATIONS

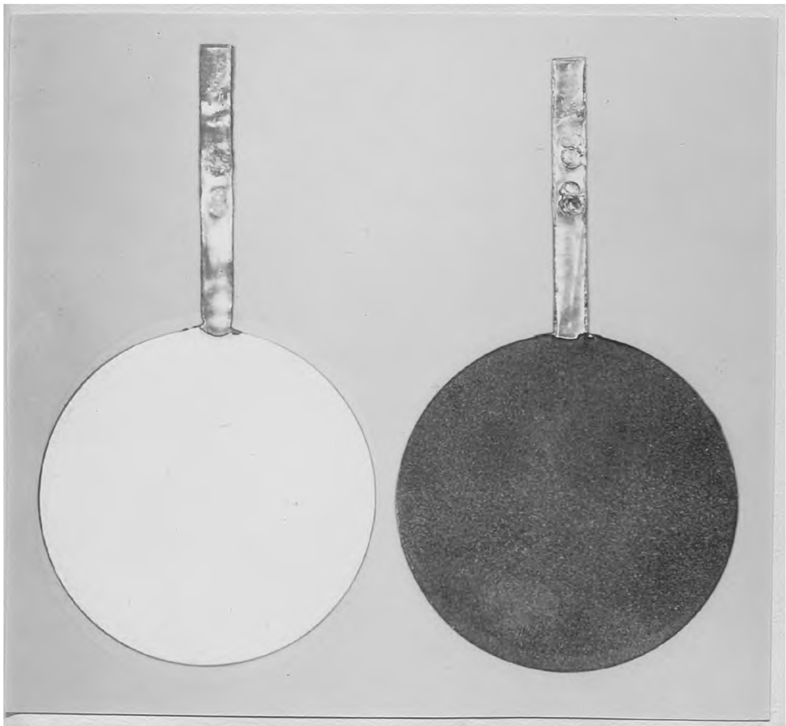


Fig. 1a
Specimen Dimensions
Radius of Disc--1 inch
Handle 1 5/8 x 3/16"
Original Thickness--0.0225 in.
At left, appearance before a run.
At right, specimen covered with precipitate after 60 min. immersion in 0.30N solution at 23°.

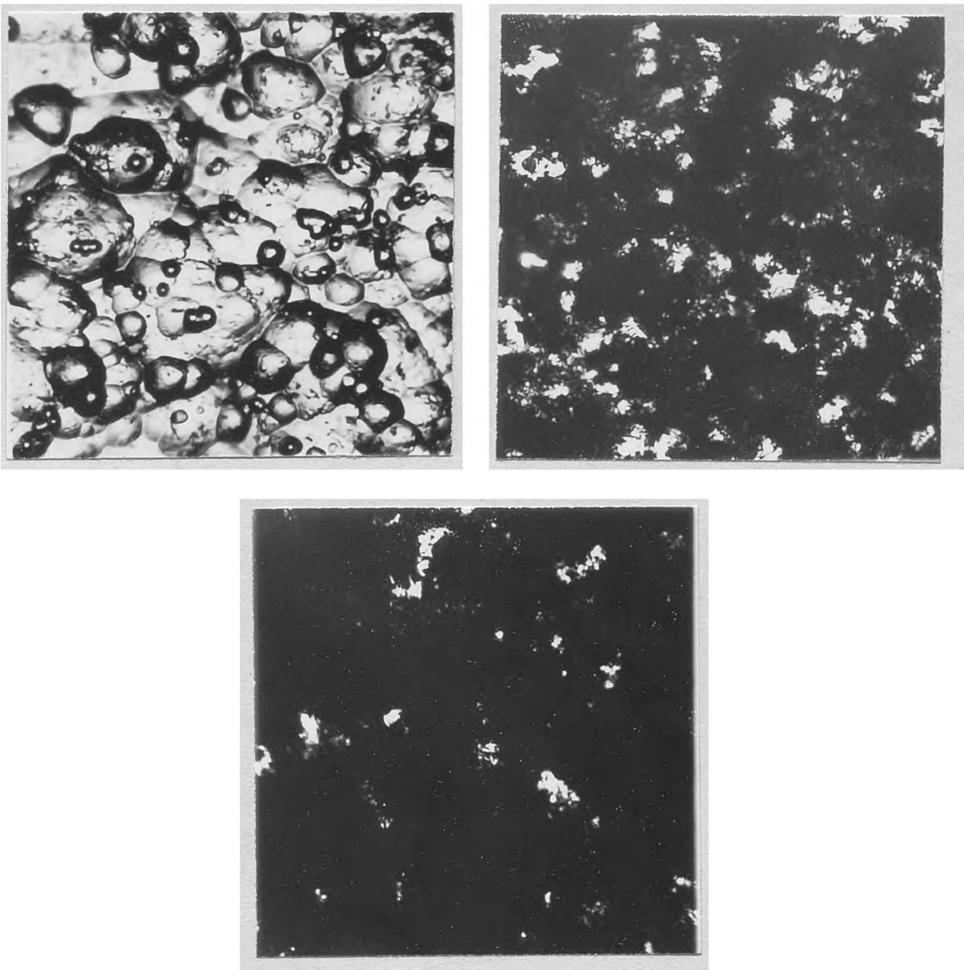
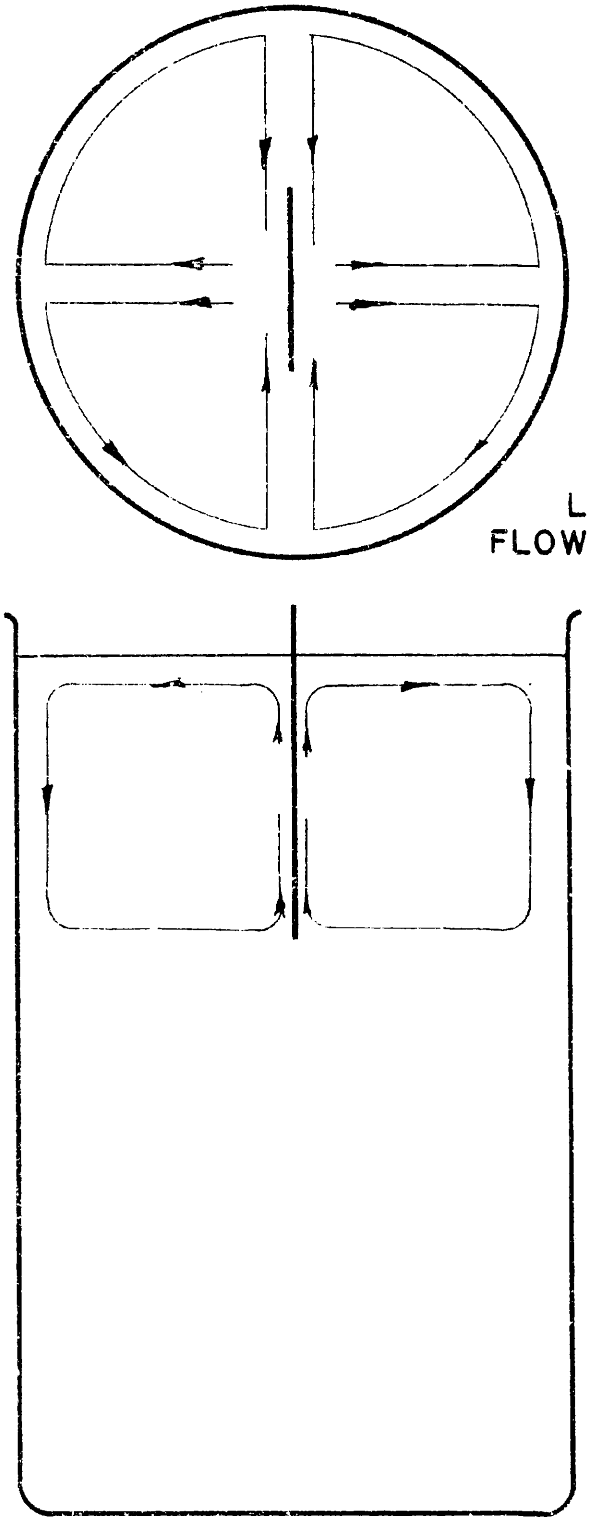


Fig. 1b. 475X
(1) Surface of a prepared specimen.
(2) After 60 min. and (3) after 100 min. immersion in 0.30N solution at 23°.

FIG. 2


LINES INDICATE FLOW OF HYDROGEN BUBBLES

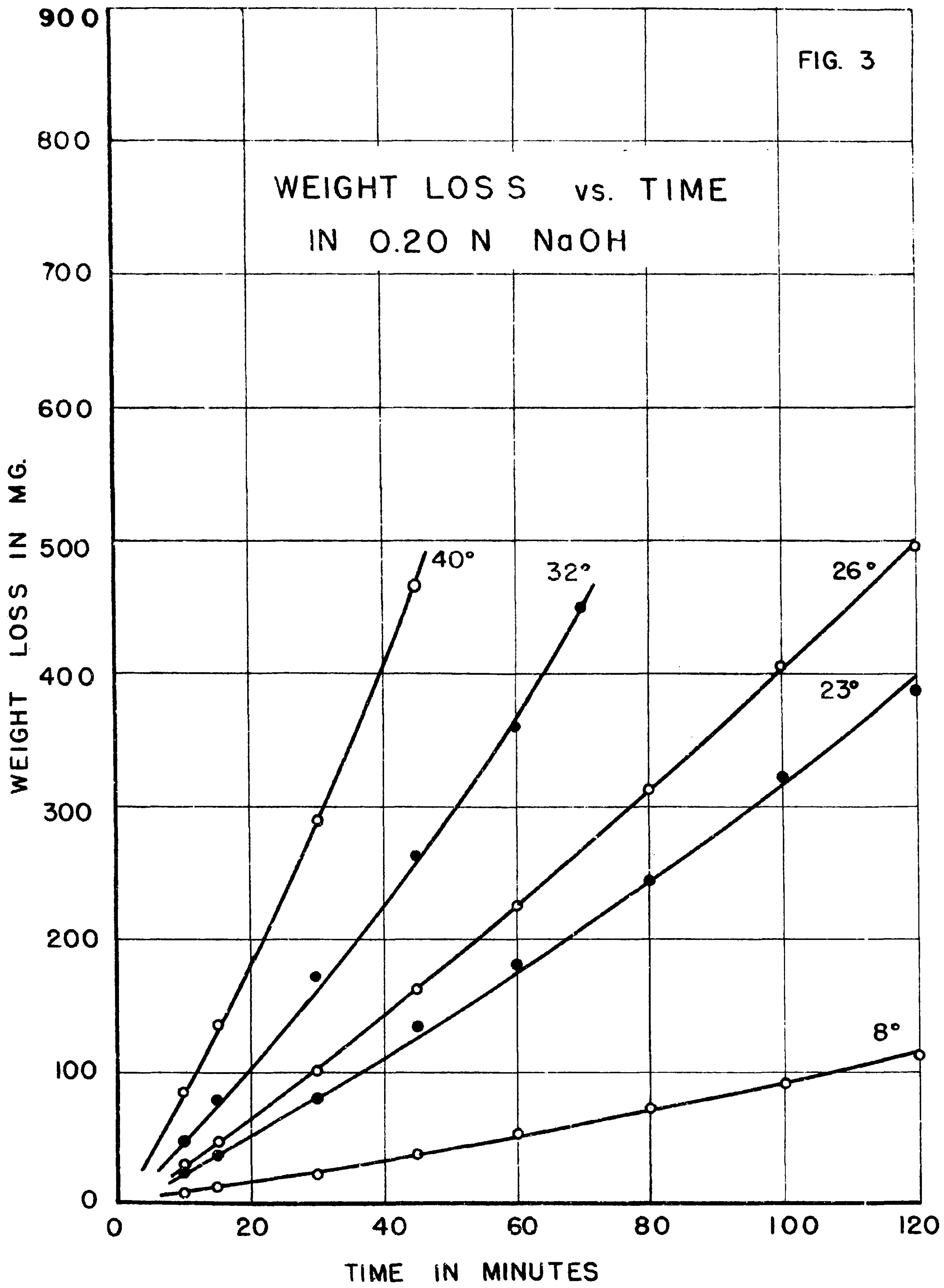


FIG. 3

WEIGHT LOSS vs. TIME IN 0.20 N NaOH

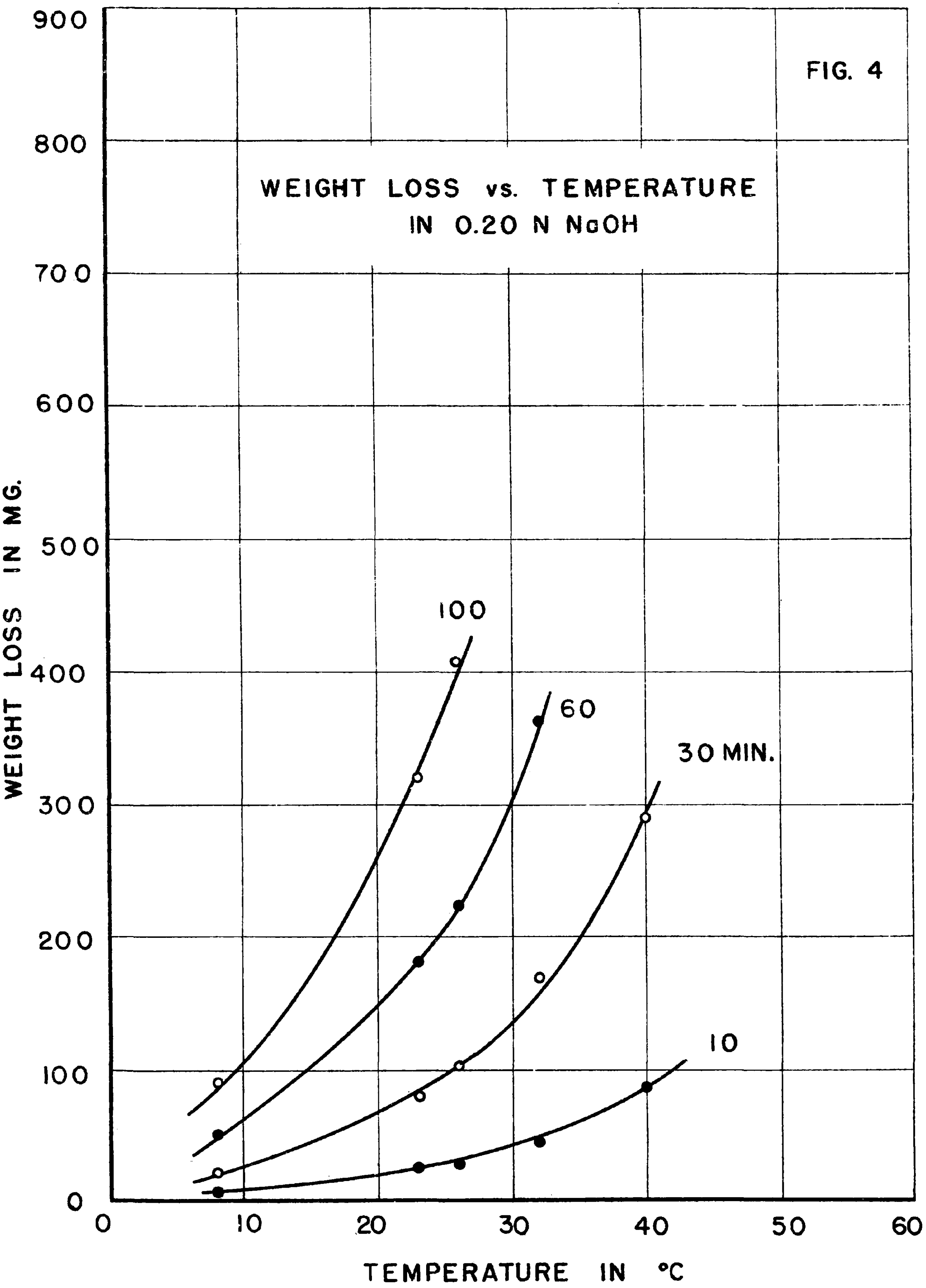


FIG. 4

WEIGHT LOSS vs. TEMPERATURE IN 0.20 N NaOH

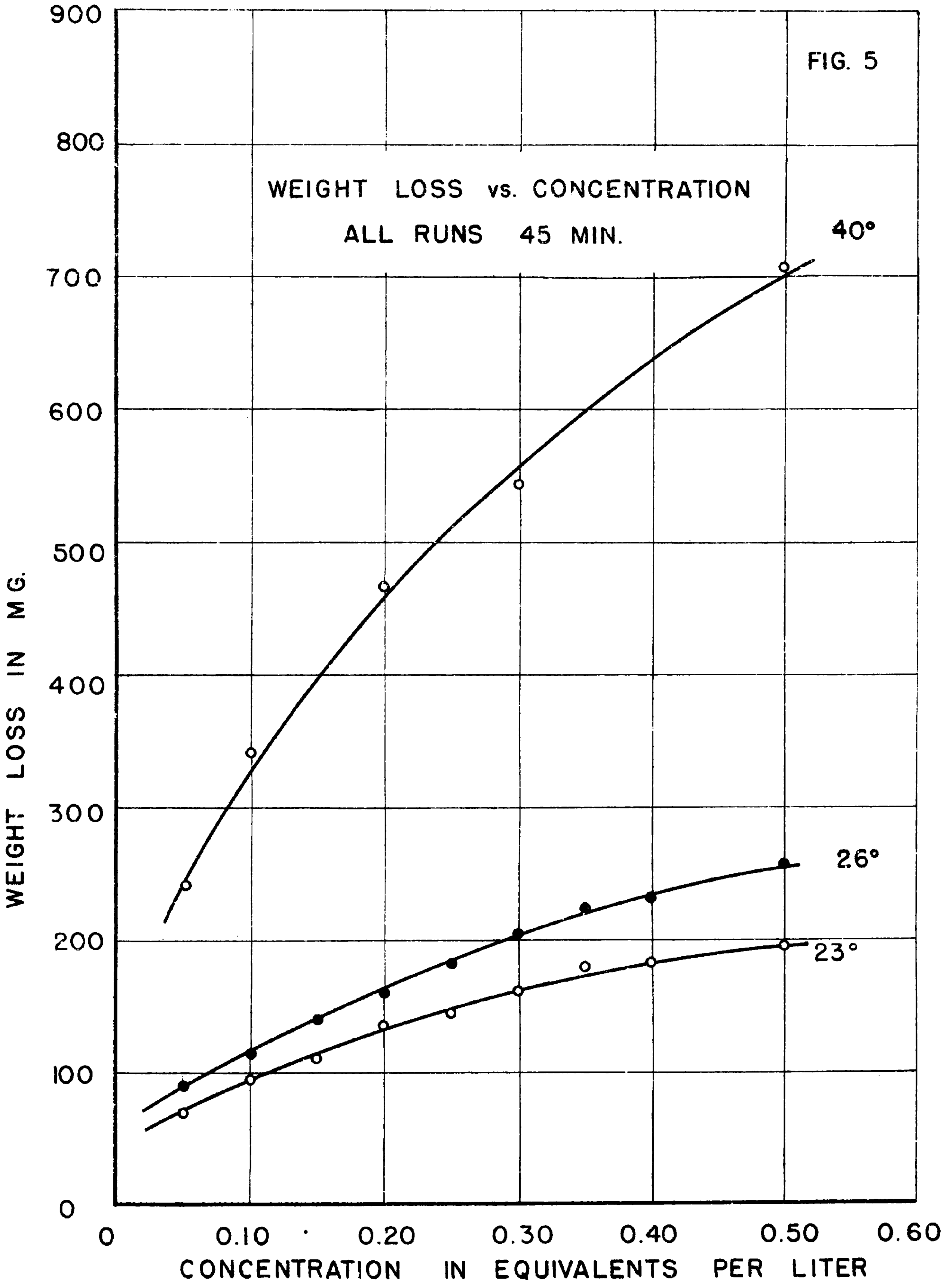


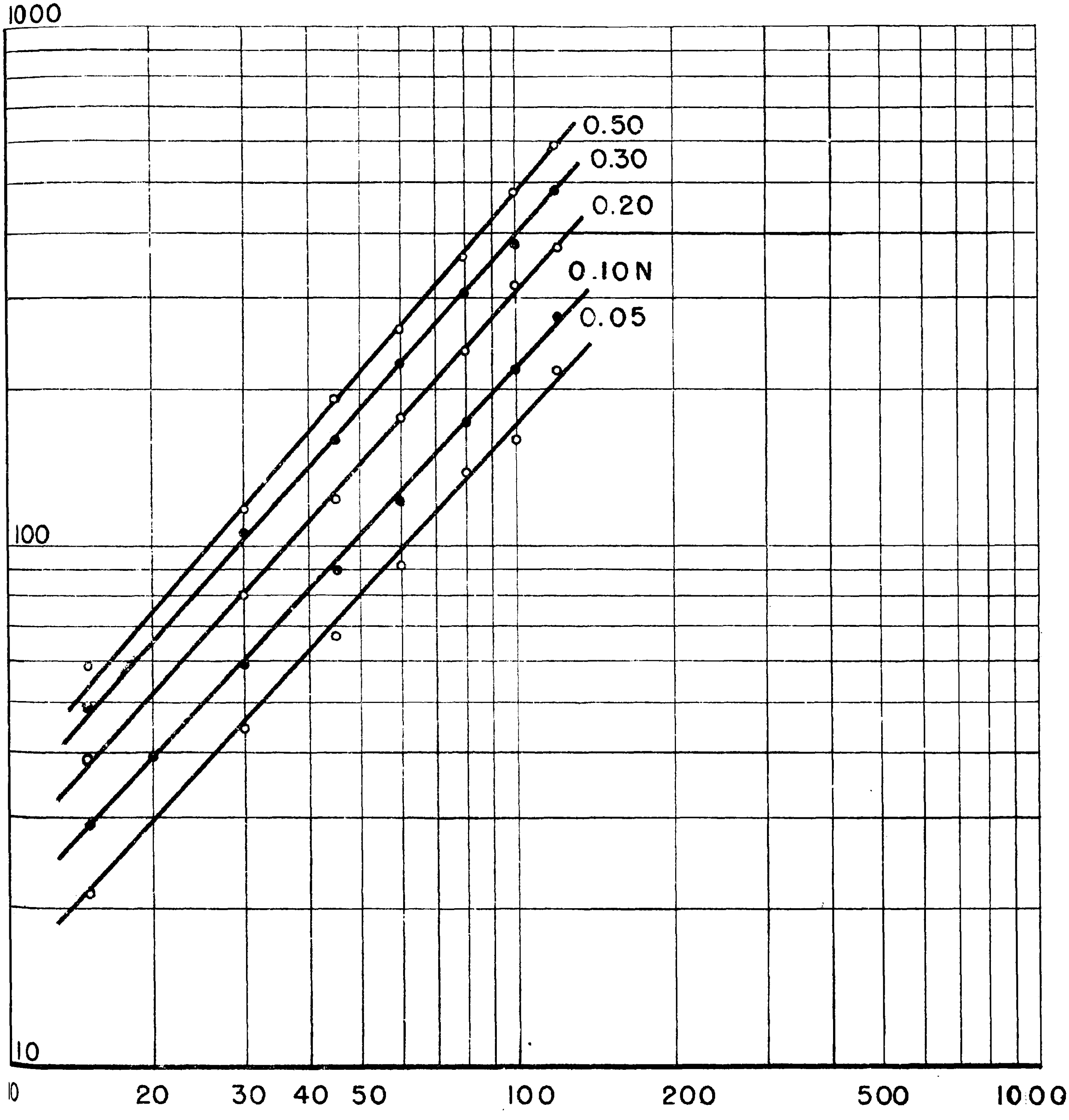
FIG. 5

WEIGHT LOSS vs. CONCENTRATION

ALL RUNS 45 MIN.

FIG. 6

WEIGHT LOSS vs. TIME OF IMMERSION
AT 23°



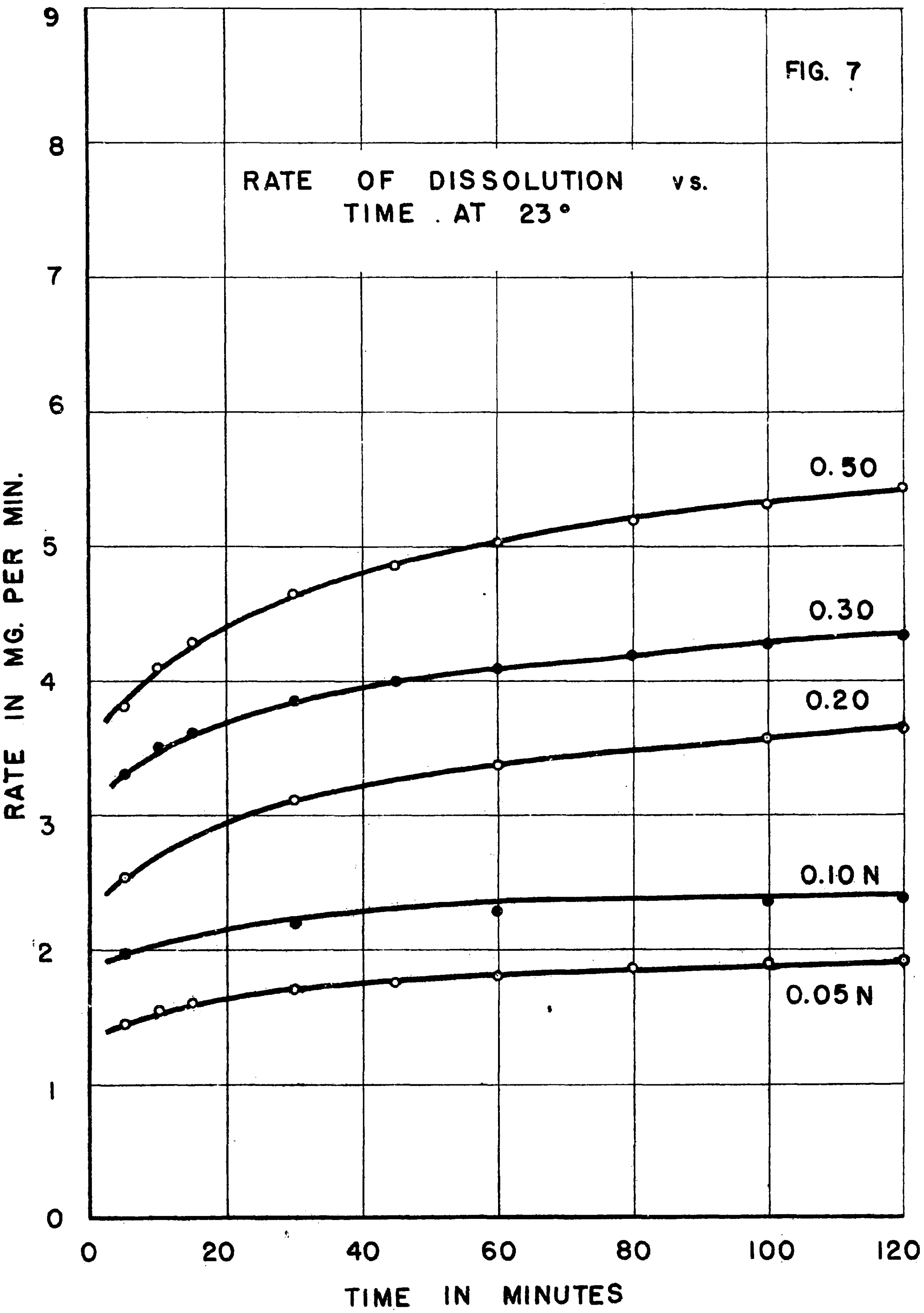


FIG. 7

RATE OF DISSOLUTION vs. TIME . AT 23°

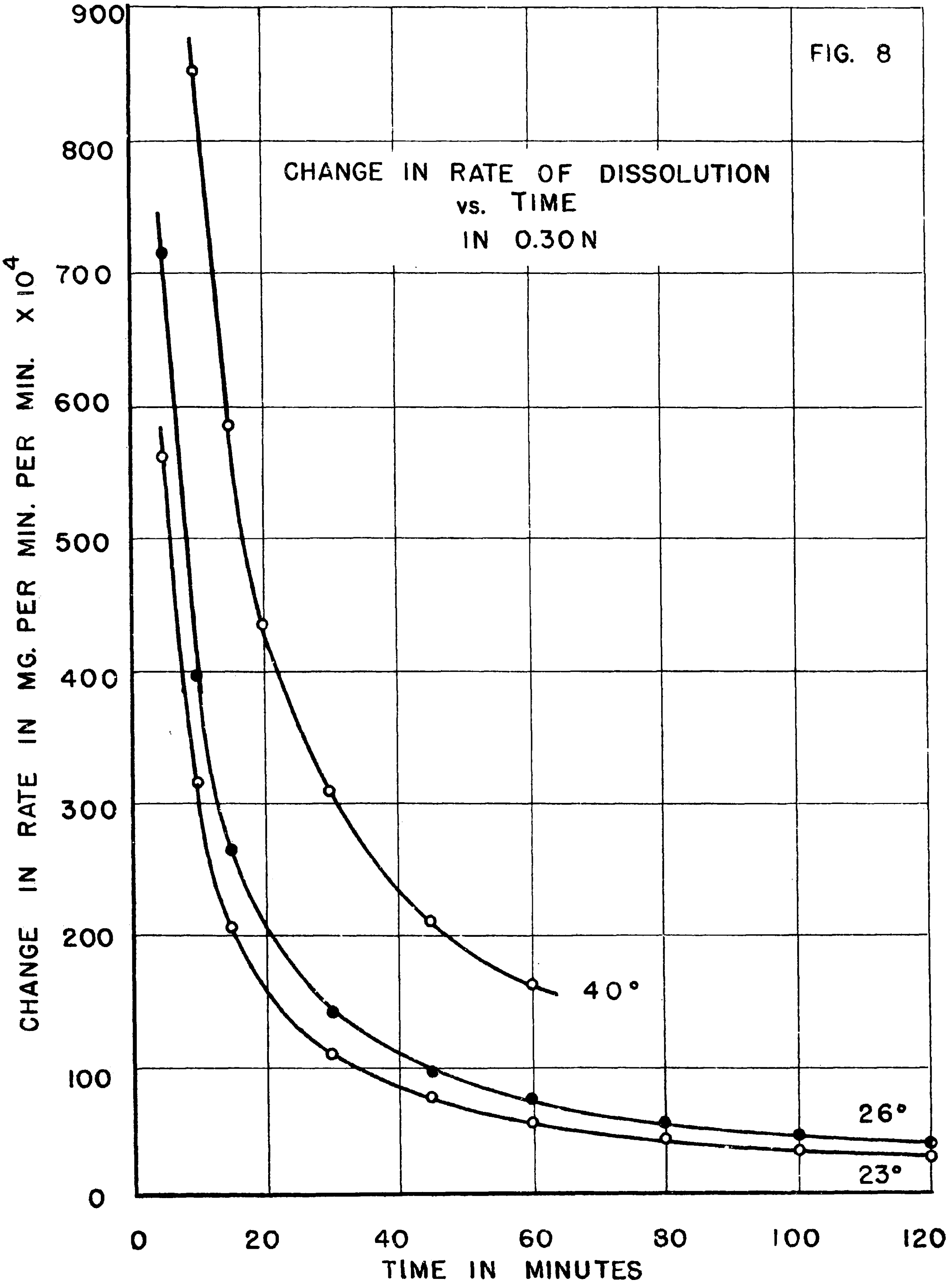


FIG. 8

CHANGE IN RATE OF DISSOLUTION vs. TIME IN 0.30N

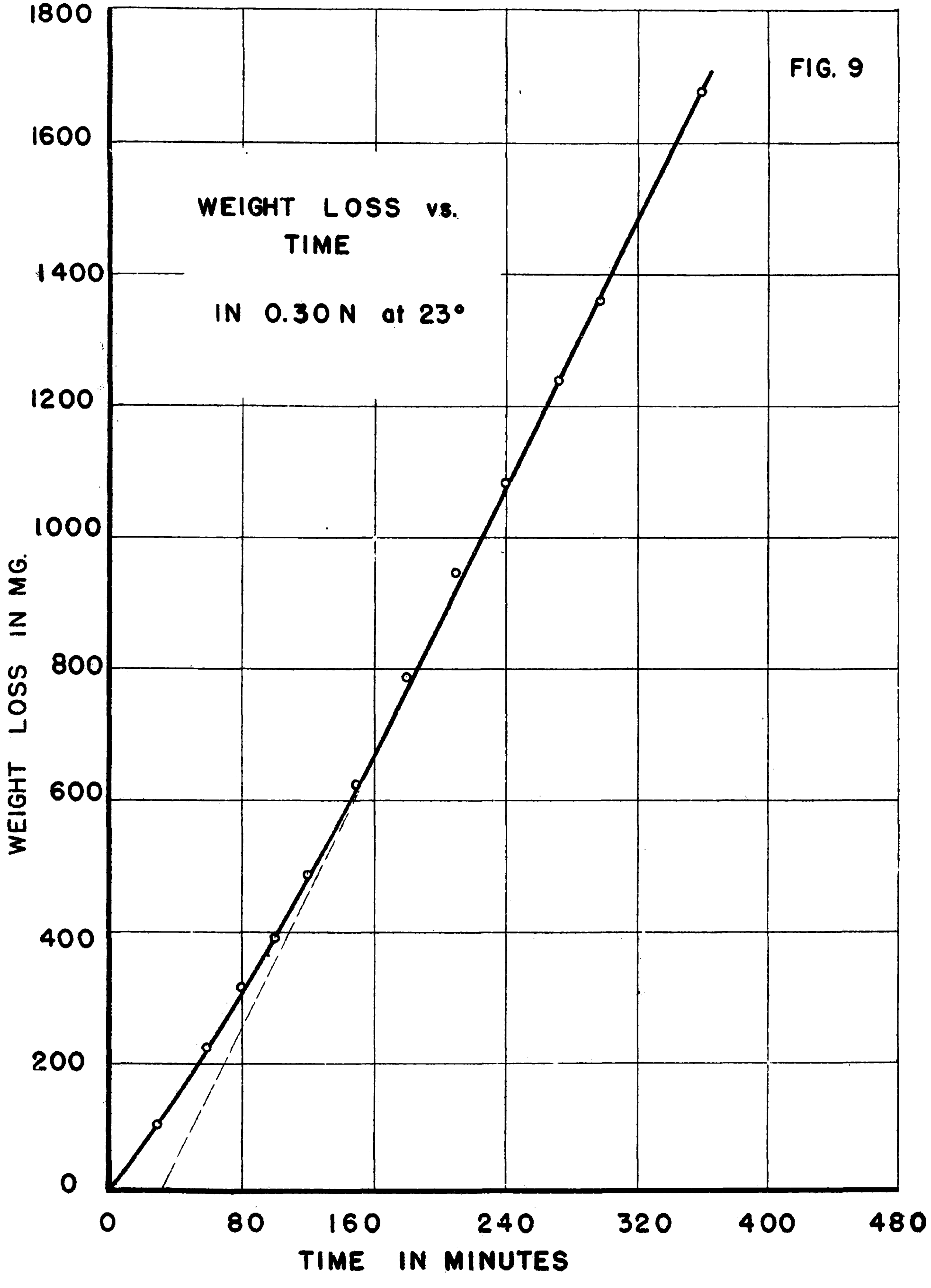
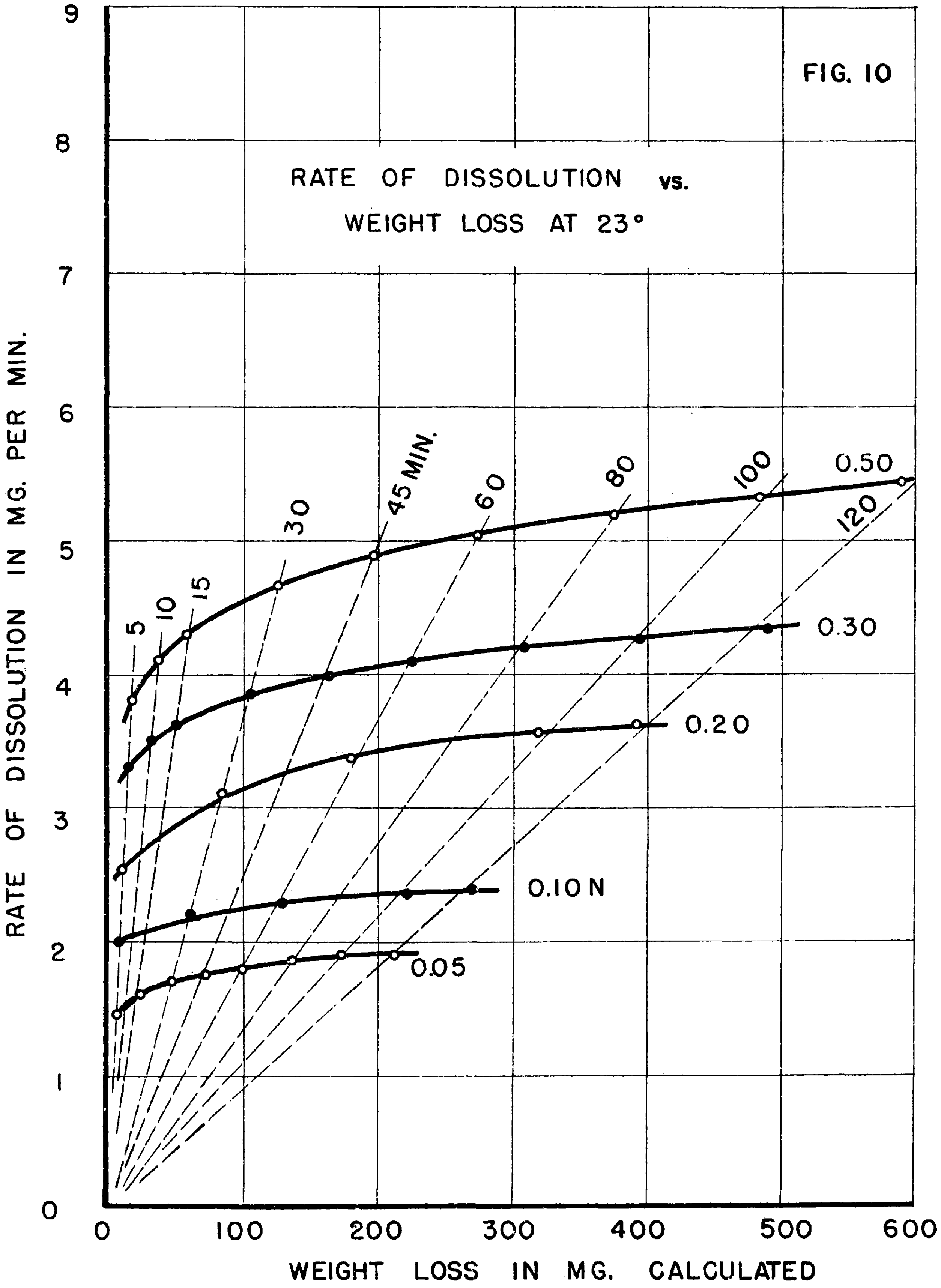
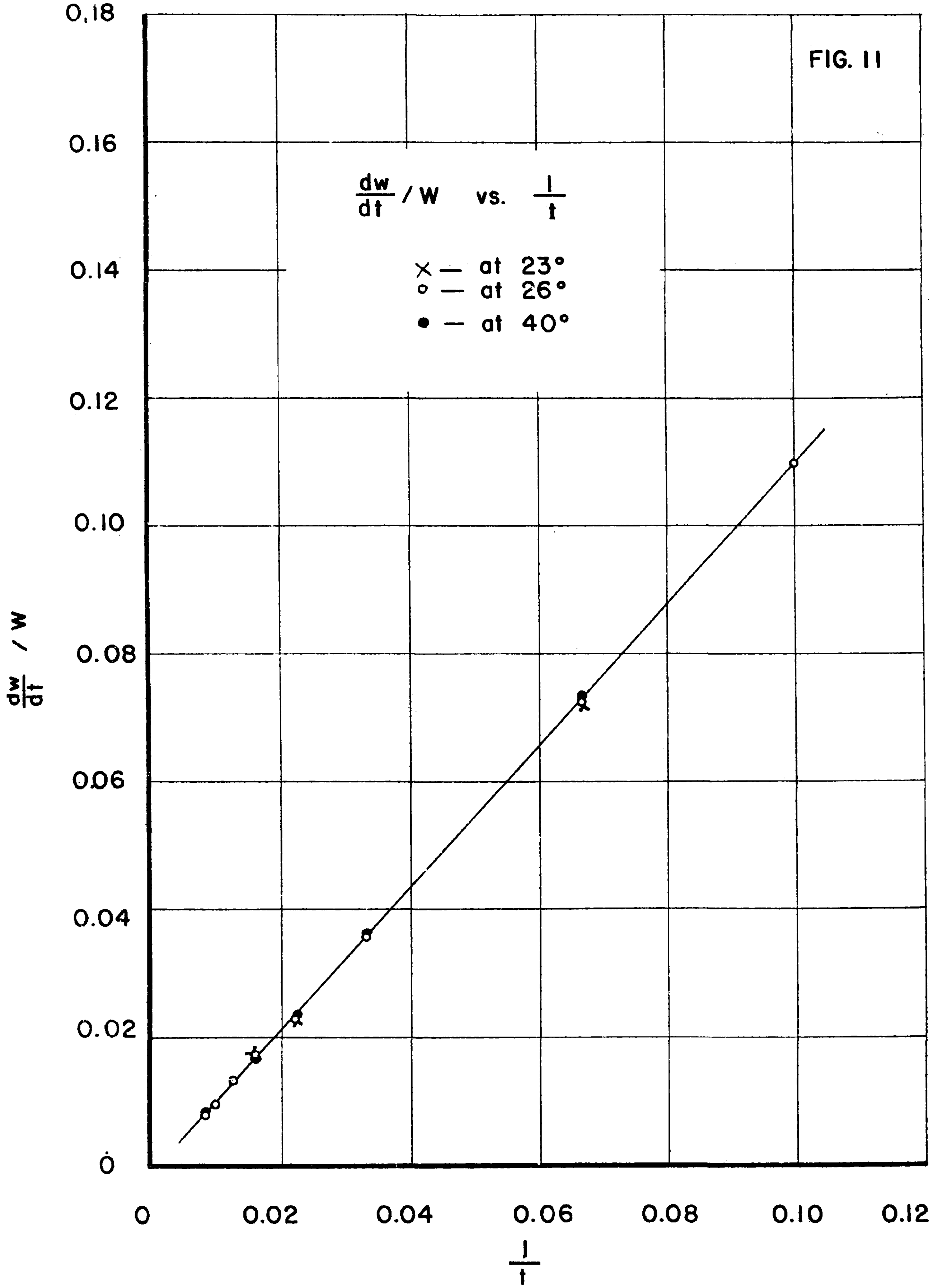


FIG. 9
WEIGHT LOSS vs. TIME
IN 0.30 N at 23°
WEIGHT LOSS IN MG.
TIME IN MINUTES
1800
1600
1400
1200
1000
800
600
400
200
0
0
80
160
240
320
400
480

FIG. 10



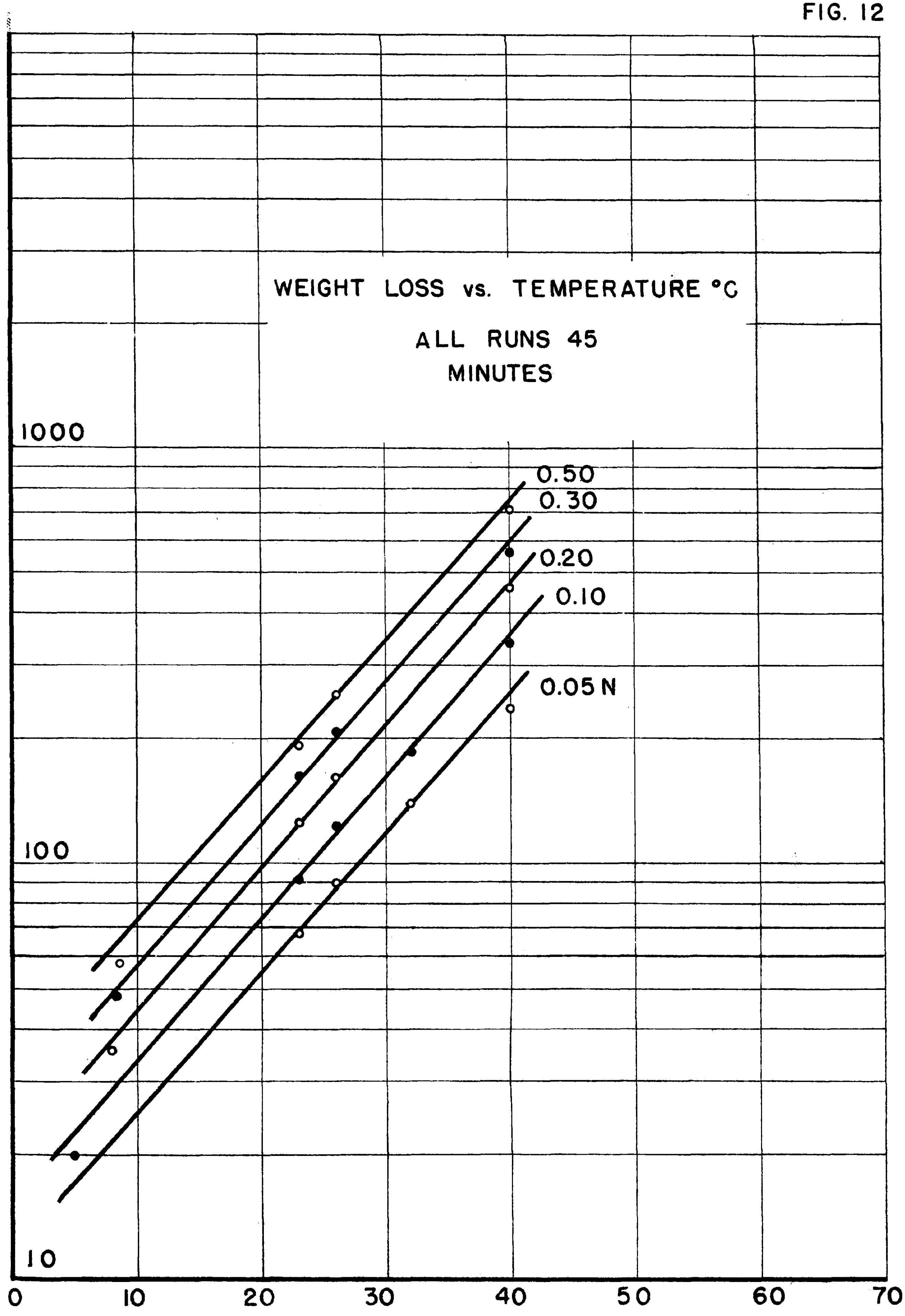
RATE OF DISSOLUTION vs.
WEIGHT LOSS AT 23°

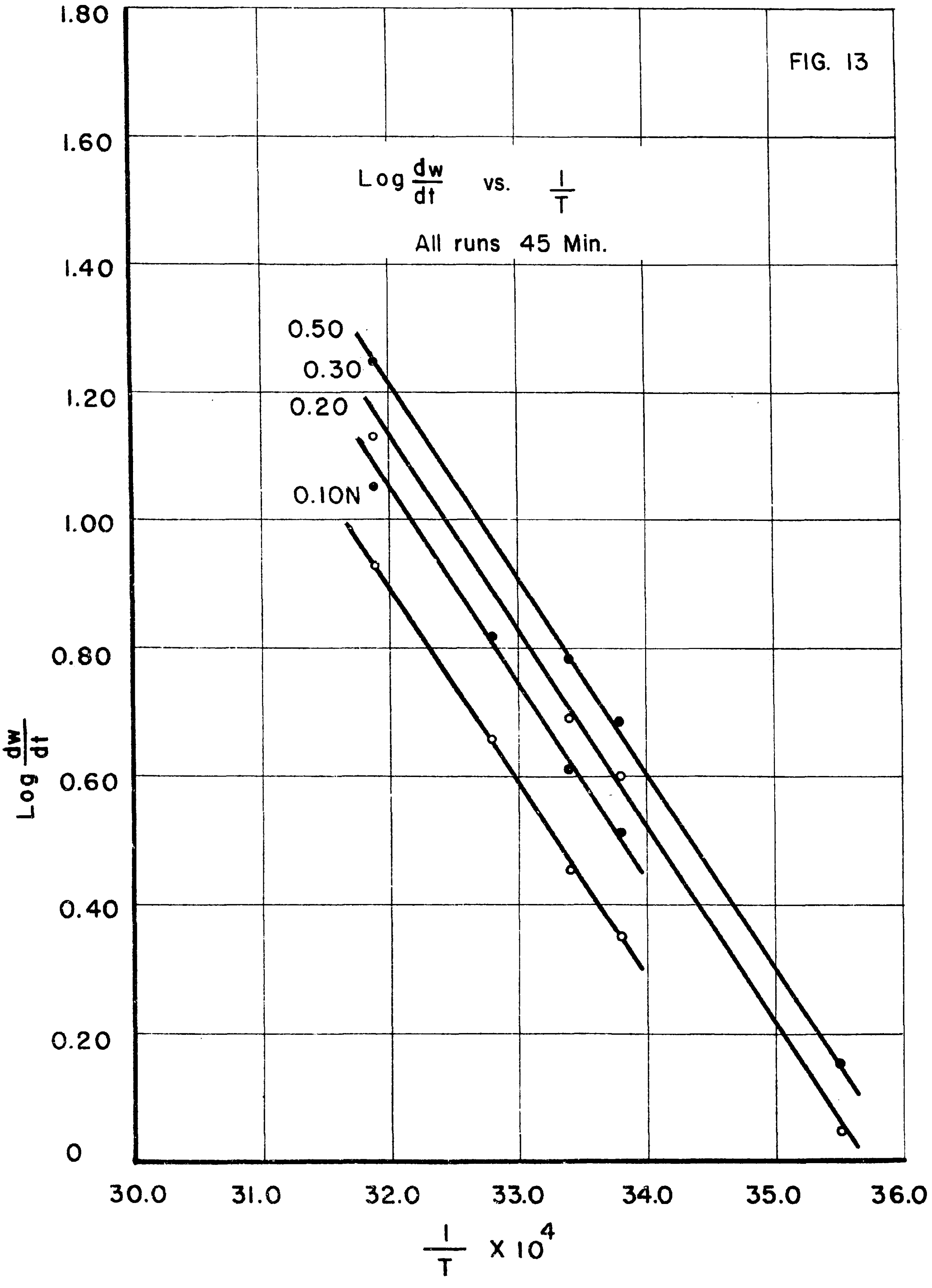


$\frac{dw}{dt}/W$ vs. $\frac{1}{t}$
× — at 23°
○ — at 26°
● — at 40°
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0
$\frac{dw}{dt}$ / W
0
0.02
0.04
0.06
0.08
0.10
0.12
$\frac{1}{t}$

FIG. 11

FIG. 12


WEIGHT LOSS vs. TEMPERATURE °C
ALL RUNS 45 MINUTES
1000
100
10
0.50
0.30
0.20
0.10
0.05 N
0
10
20
30
40
50
60
70



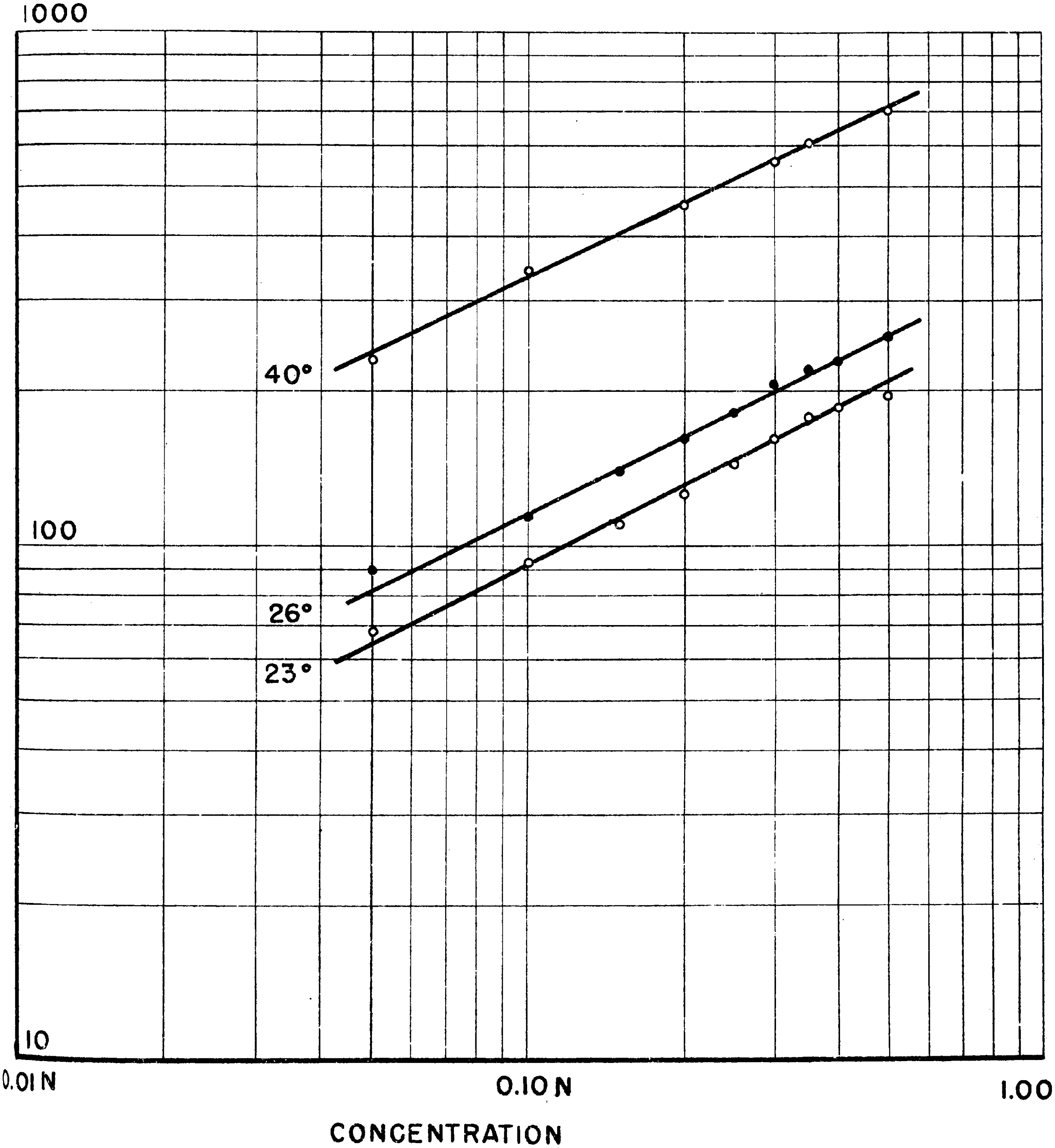
Log $\frac{dw}{dt}$ vs. $\frac{1}{T}$
All runs 45 Min.
0.50
0.30
0.20
0.10N
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0
Log $\frac{dw}{dt}$
30.0
31.0
32.0
33.0
34.0
35.0
36.0
$\frac{1}{T} \times 10^4$

FIG. 13

FIG. 14

WEIGHT LOSS vs. CONCENTRATION

All Runs 45 Min.



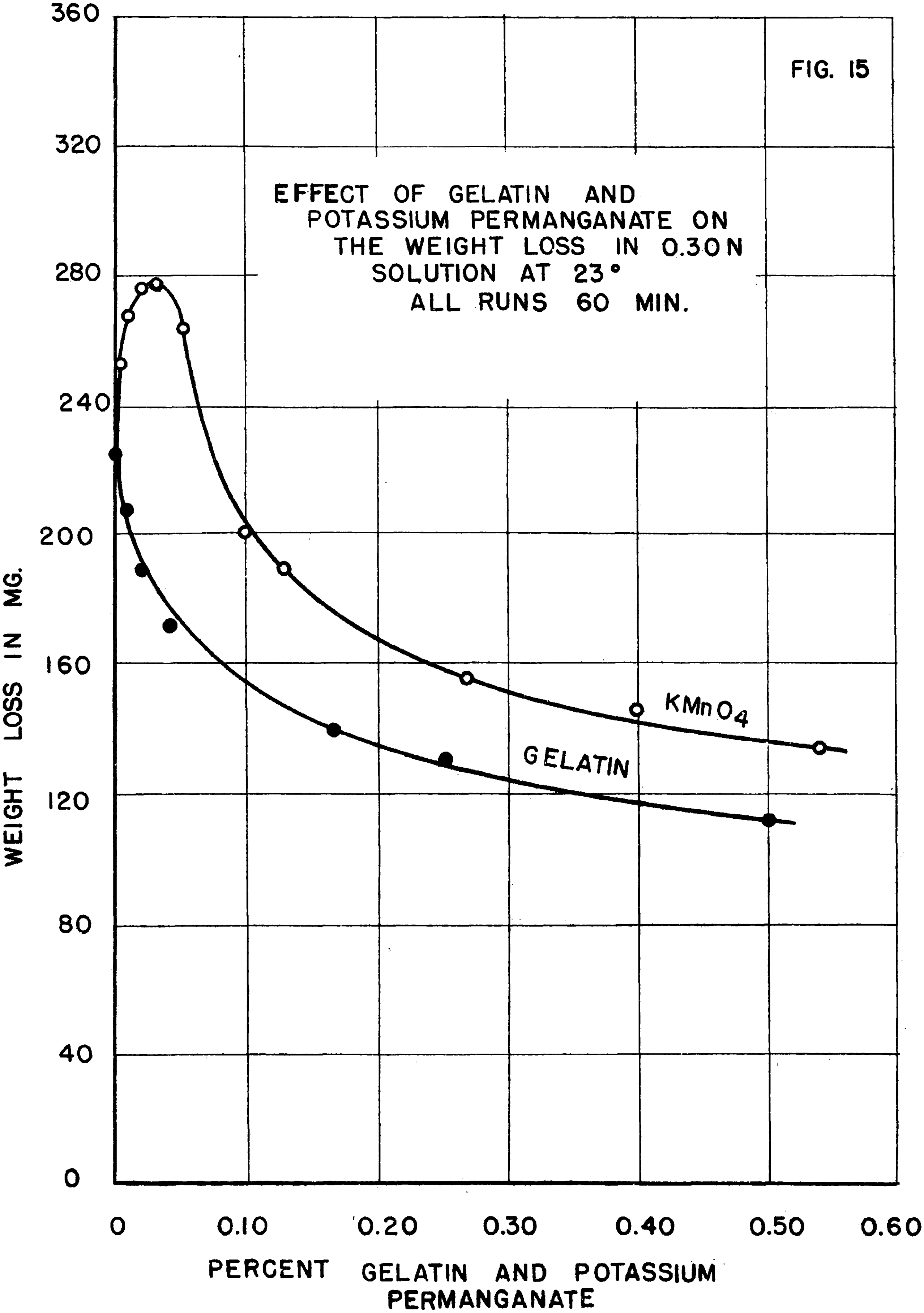


FIG. 15

EFFECT OF GELATIN AND POTASSIUM PERMANGANATE ON THE WEIGHT LOSS IN 0.30 N SOLUTION AT 23°
ALL RUNS 60 MIN.

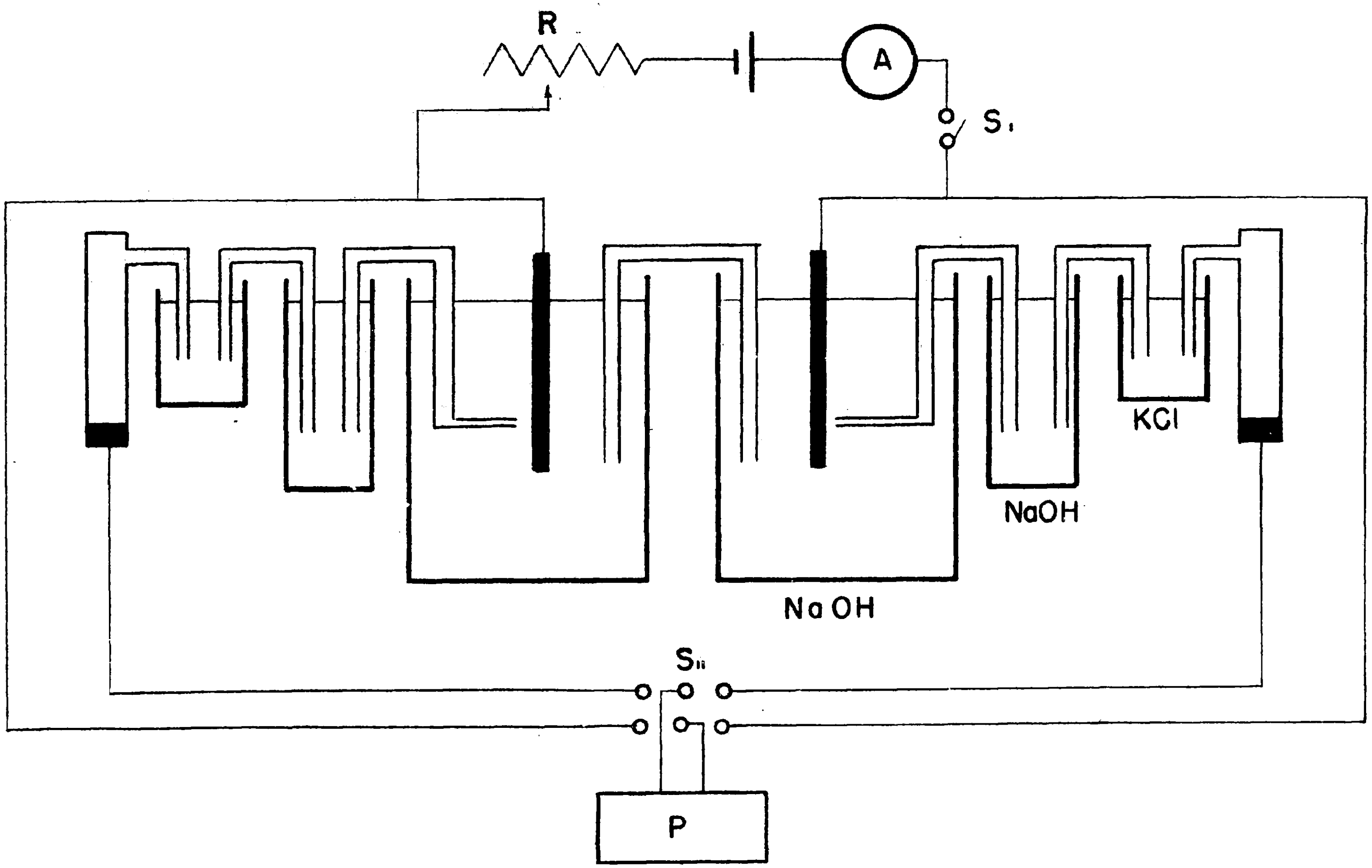


FIG. 16 WIRING DIAGRAM

FIG. 16

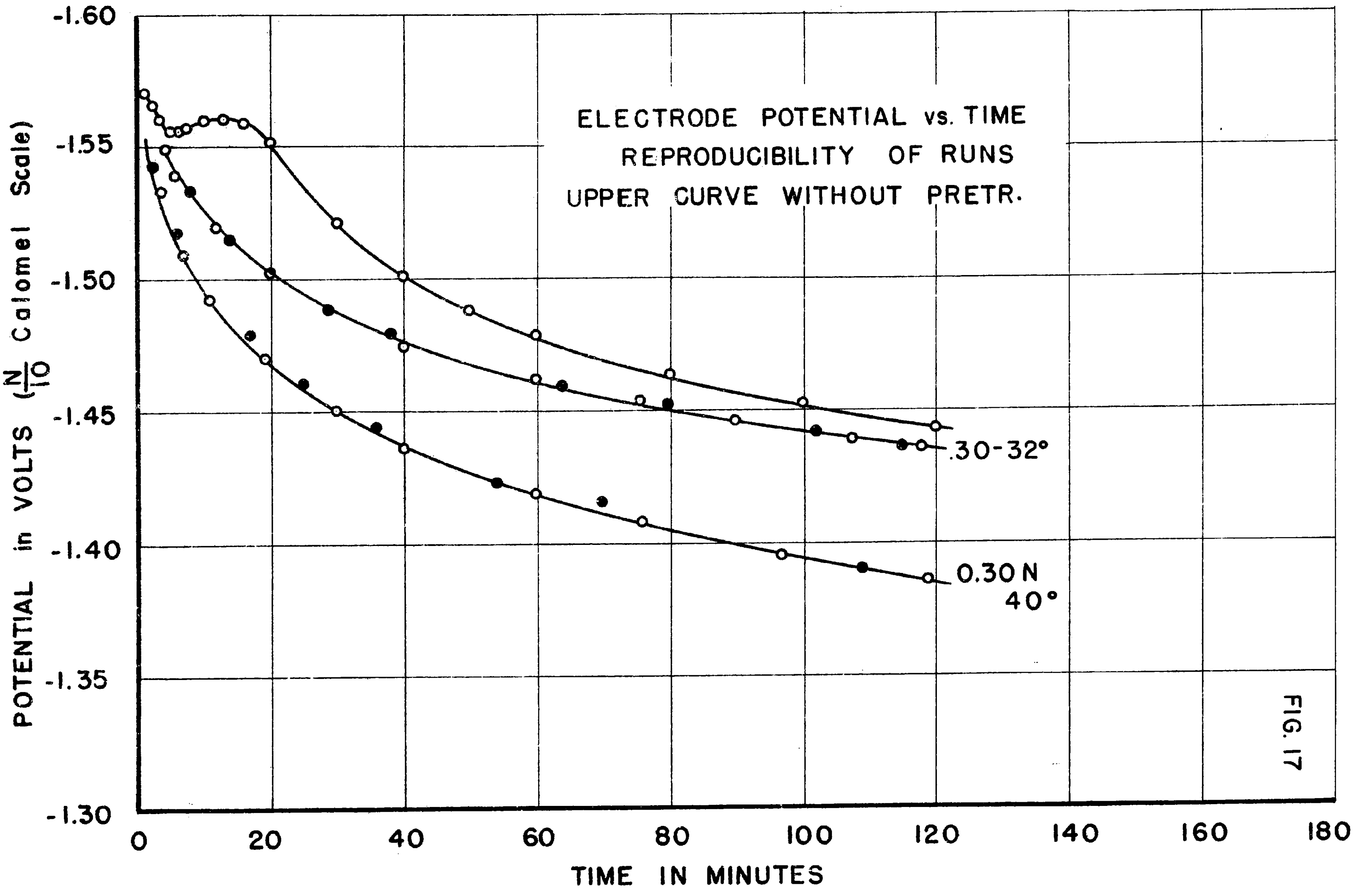

ELECTRODE POTENTIAL vs. TIME
REPRODUCIBILITY OF RUNS
UPPER CURVE WITHOUT PRETR.
.30-32°
0.30 N
40°
-1.60
-1.55
-1.50
-1.45
-1.40
-1.35
-1.30
POTENTIAL in VOLTS ($\frac{N}{10}$ Calomel Scale)
0
20
40
60
80
100
120
140
160
180
TIME IN MINUTES

FIG. 17

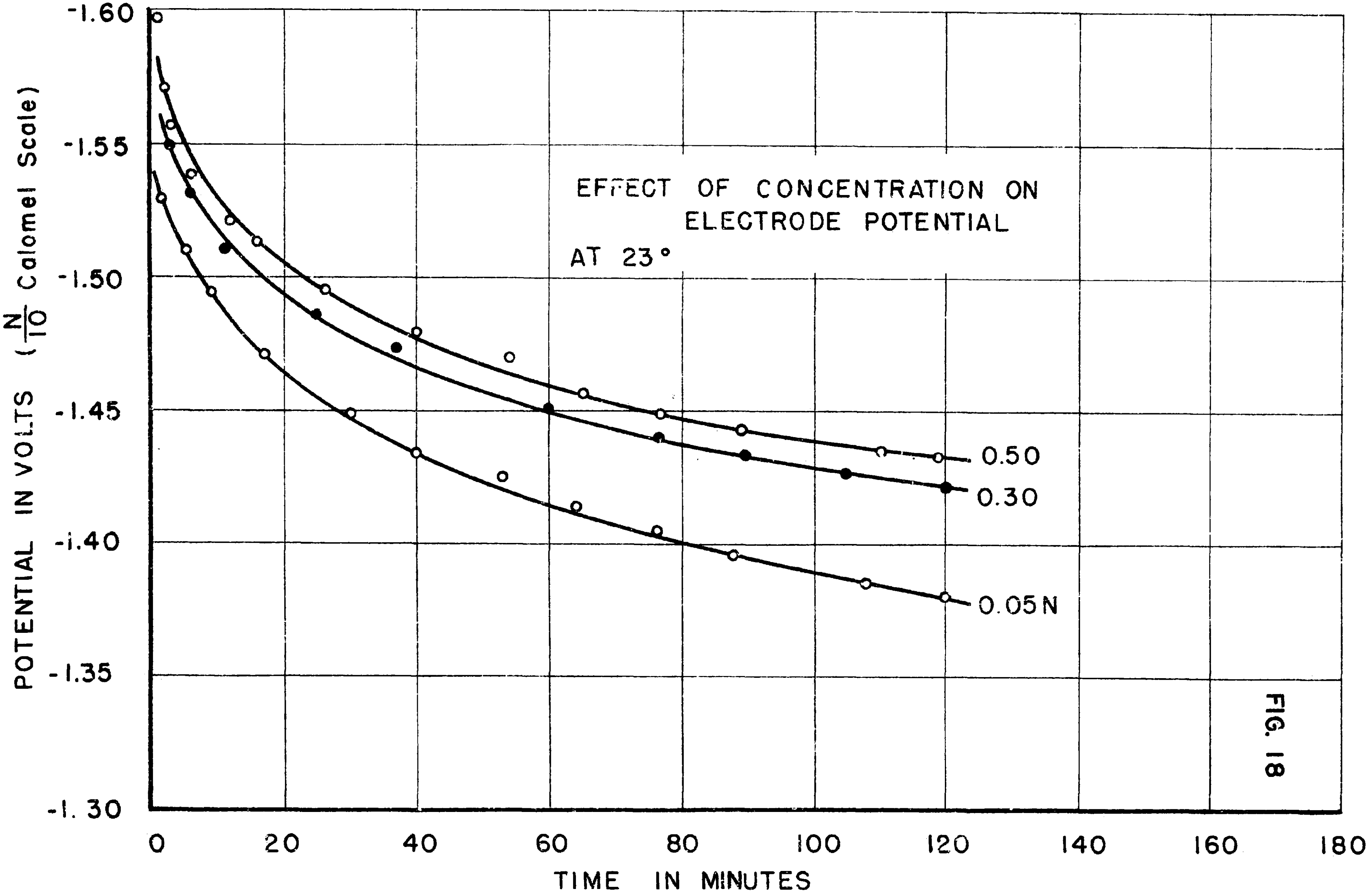

EFFECT OF CONCENTRATION ON
ELECTRODE POTENTIAL
AT 23°
0.50
0.30
0.05N
-1.60
-1.55
-1.50
-1.45
-1.40
-1.35
-1.30
POTENTIAL IN VOLTS ($\frac{N}{10}$ Calomel Scale)
0
20
40
60
80
100
120
140
160
180
TIME IN MINUTES

FIG. 18

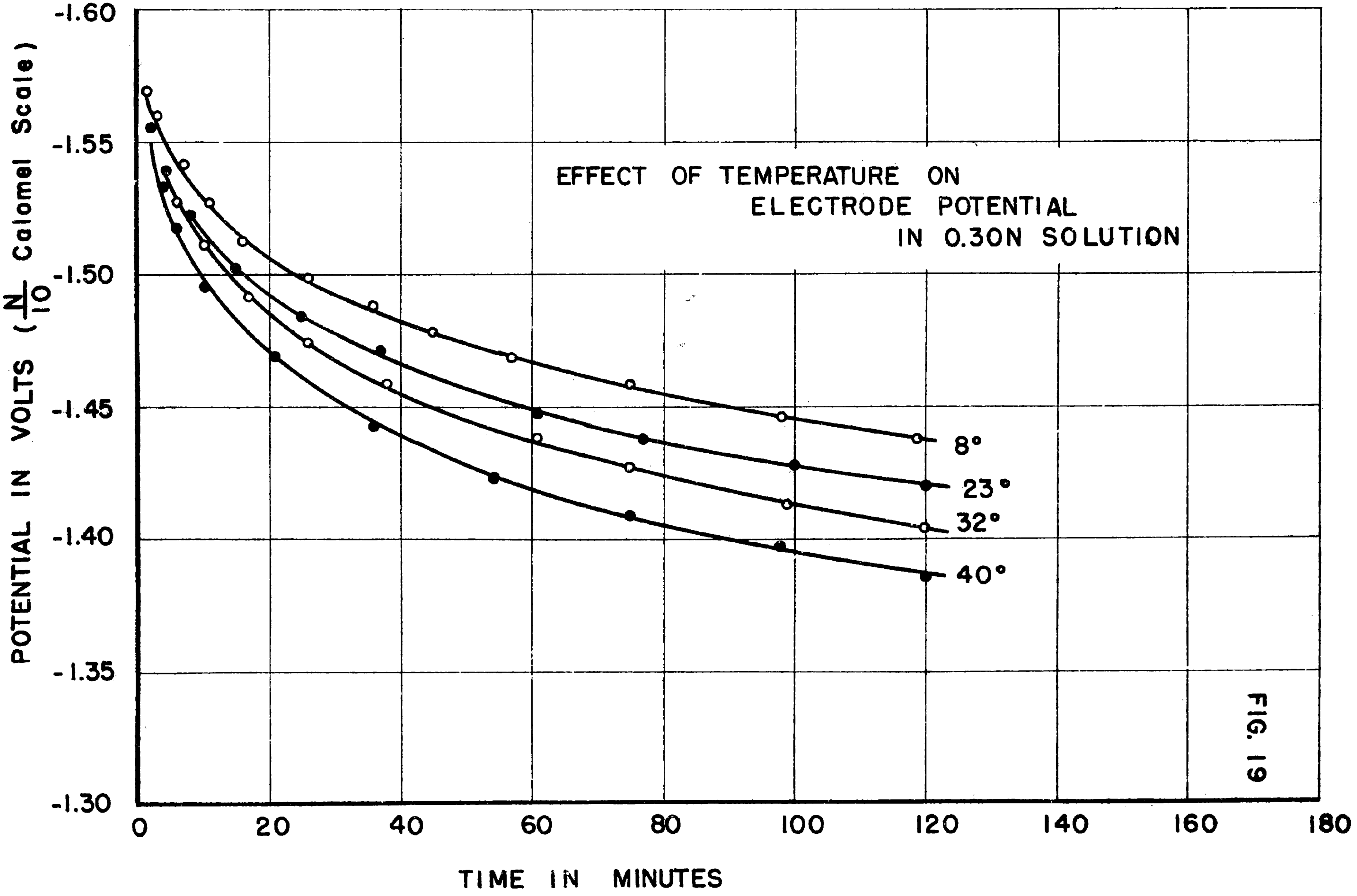

EFFECT OF TEMPERATURE ON
ELECTRODE POTENTIAL
IN 0.30N SOLUTION
POTENTIAL IN VOLTS ($\frac{N}{10}$ Calomel Scale)
TIME IN MINUTES
-1.60
-1.55
-1.50
-1.45
-1.40
-1.35
-1.30
0
20
40
60
80
100
120
140
160
180
8°
23°
32°
40°

FIG. 19

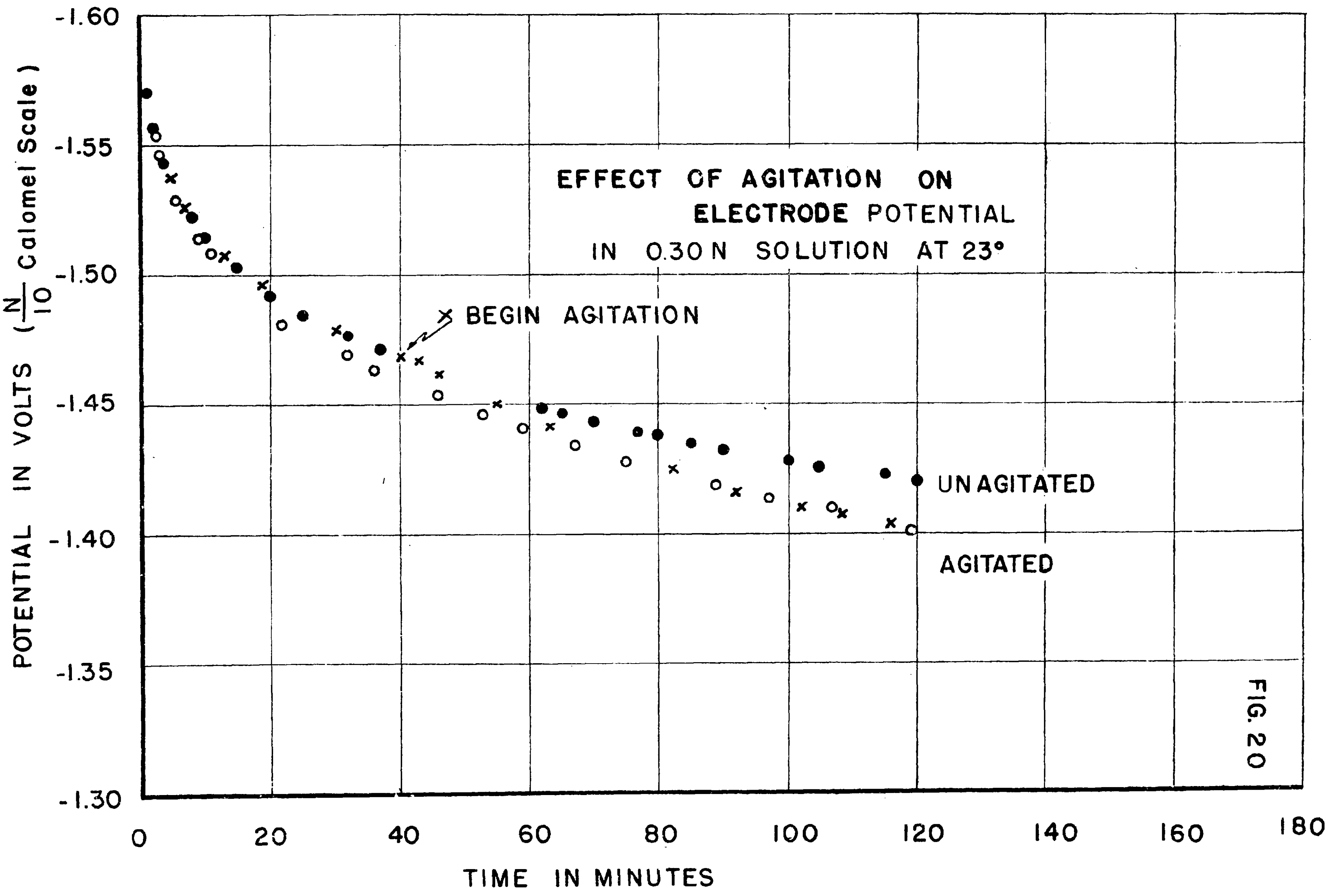


FIG. 20

EFFECT OF AGITATION ON ELECTRODE POTENTIAL IN 0.30 N SOLUTION AT 23°

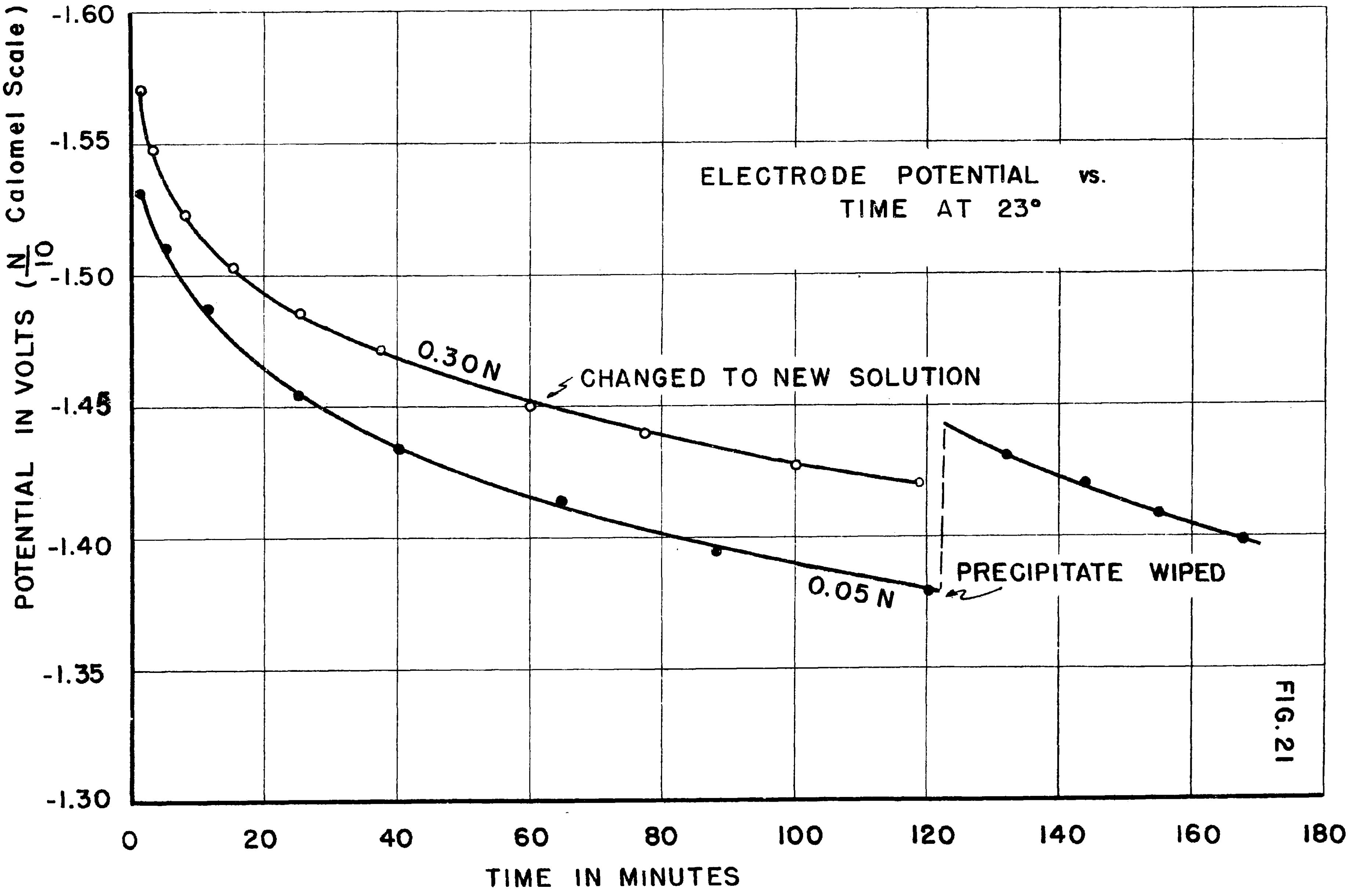
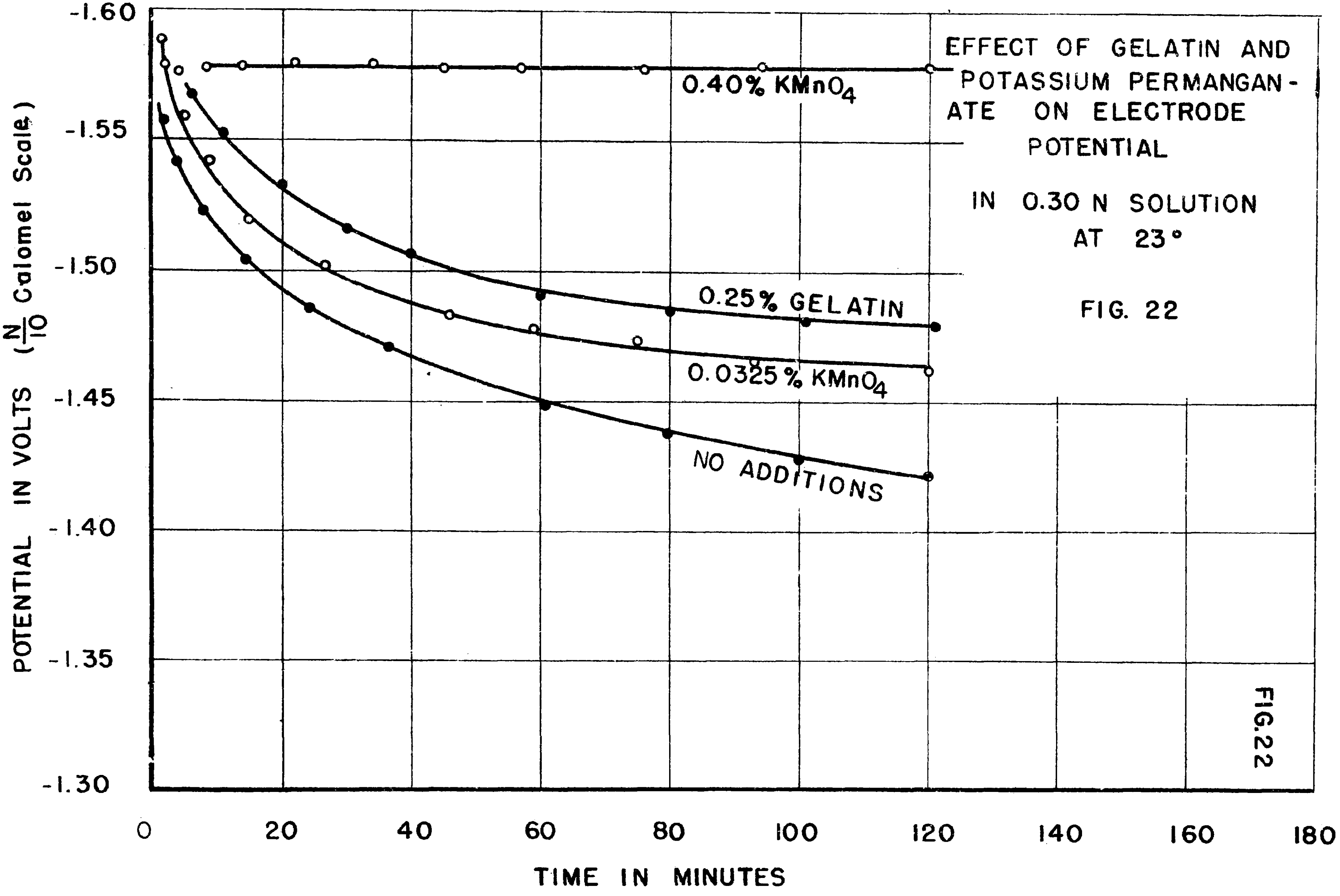

ELECTRODE POTENTIAL vs.
TIME AT 23°
0.30 N
CHANGED TO NEW SOLUTION
0.05 N
PRECIPITATE WIPED
POTENTIAL IN VOLTS ($\frac{N}{10}$ Calomel Scale)
-1.60
-1.55
-1.50
-1.45
-1.40
-1.35
-1.30
0
20
40
60
80
100
120
140
160
180
TIME IN MINUTES

FIG. 21


EFFECT OF GELATIN AND POTASSIUM PERMANGANATE ON ELECTRODE POTENTIAL

IN 0.30 N SOLUTION AT 23°

FIG. 22

FIG.22

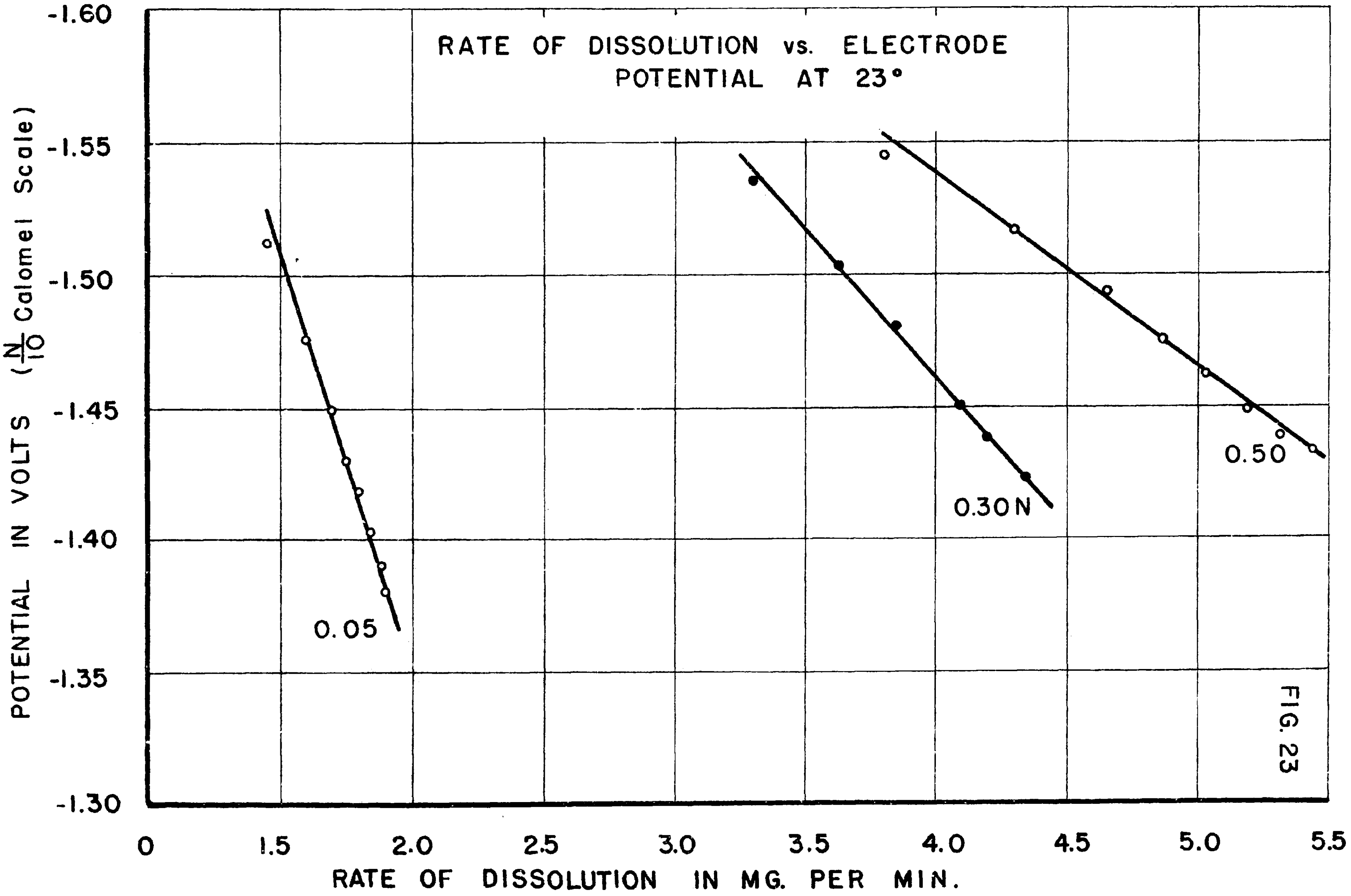

RATE OF DISSOLUTION vs. ELECTRODE
POTENTIAL AT 23°
POTENTIAL IN VOLTS ($\frac{N}{10}$ Calomel Scale)
-1.60
-1.55
-1.50
-1.45
-1.40
-1.35
-1.30
0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
RATE OF DISSOLUTION IN MG. PER MIN.
0.05
0.30N
0.50

FIG. 23

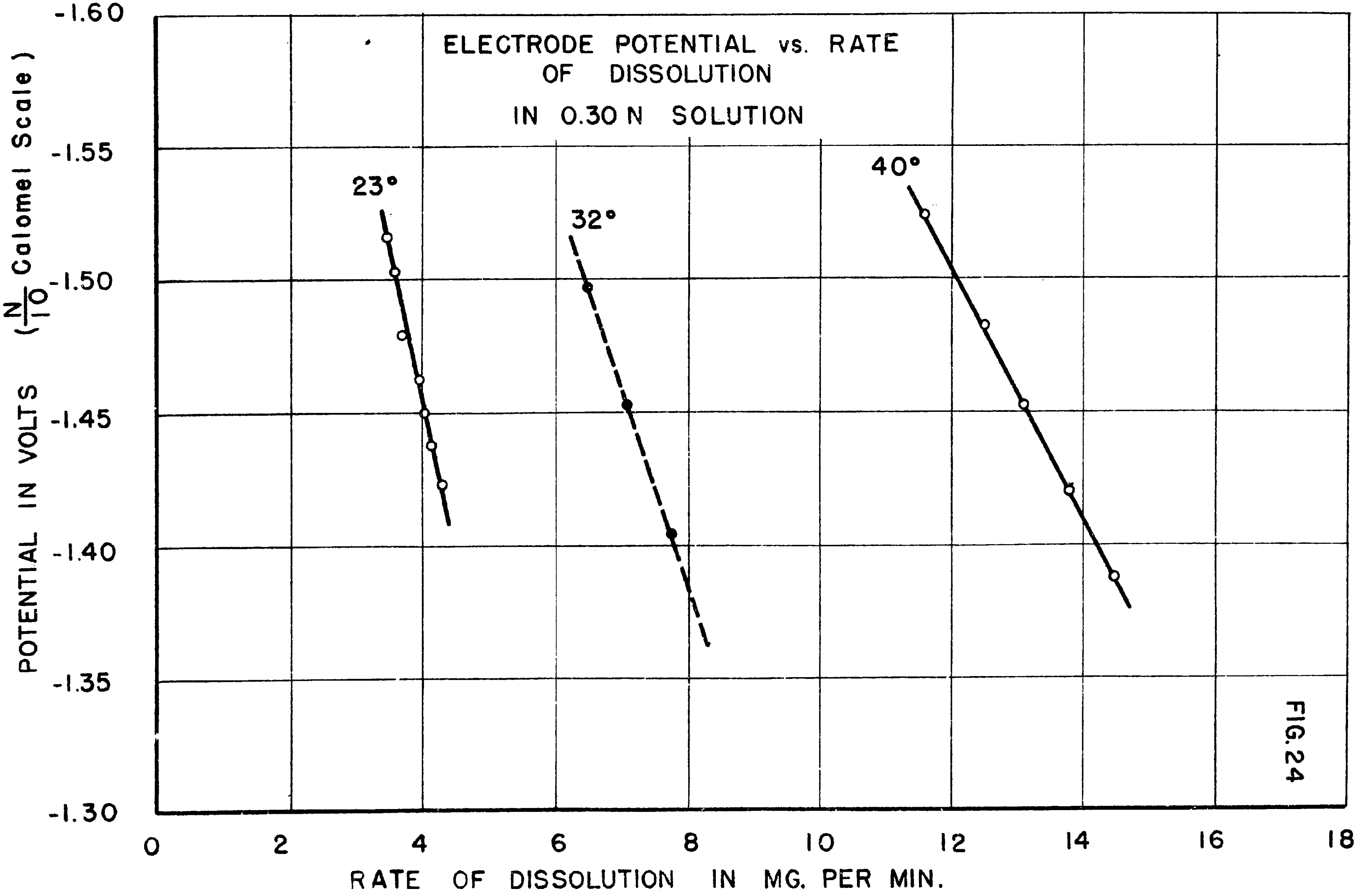

ELECTRODE POTENTIAL vs. RATE OF DISSOLUTION
IN 0.30 N SOLUTION
23°
32°
40°
-1.60
-1.55
-1.50
-1.45
-1.40
-1.35
-1.30
0
2
4
6
8
10
12
14
16
18
POTENTIAL IN VOLTS ($\frac{N}{10}$ Calomel Scale)
RATE OF DISSOLUTION IN MG. PER MIN.

FIG. 24

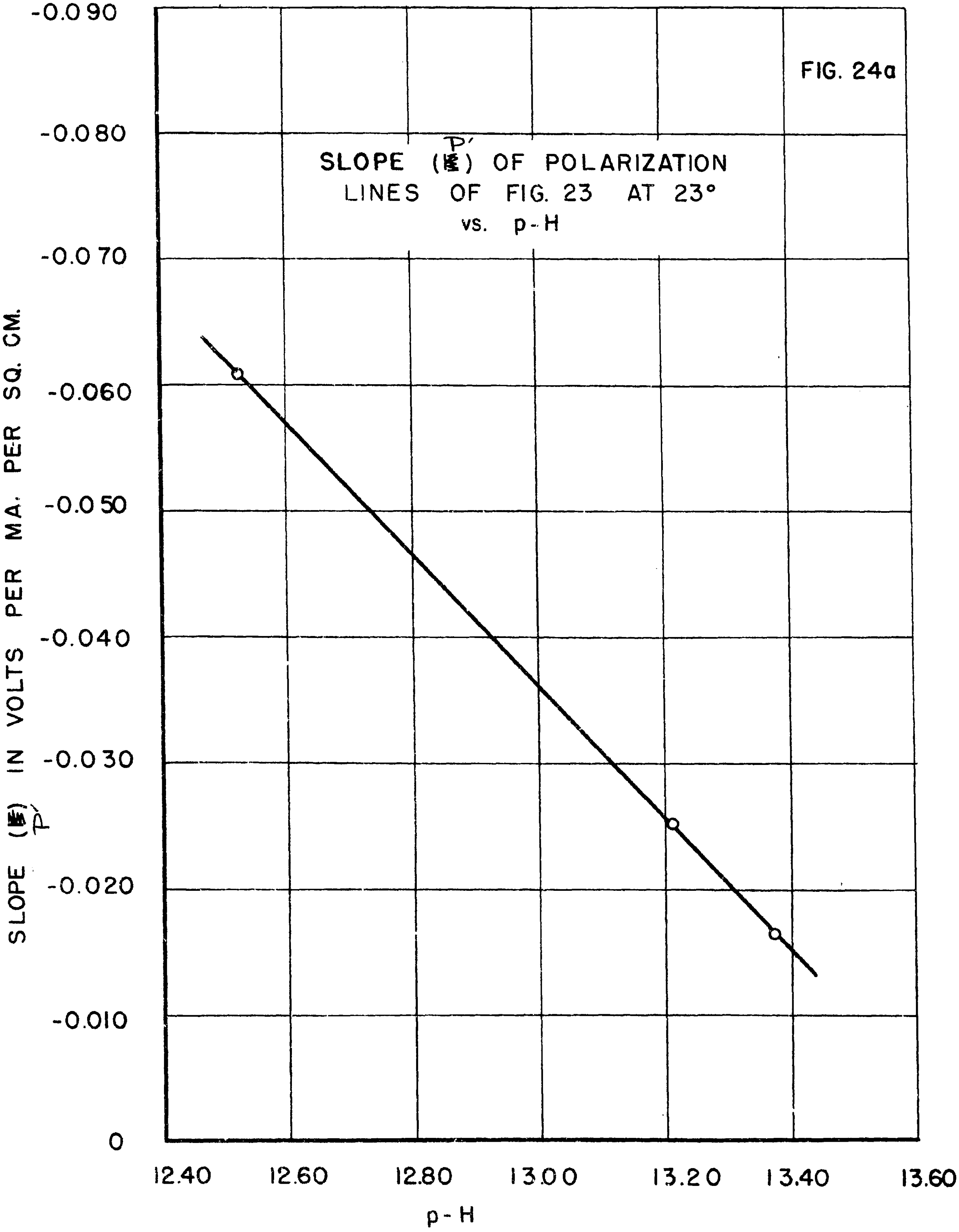


FIG. 24a

SLOPE (P') OF POLARIZATION LINES OF FIG. 23 AT 23°
vs. p - H

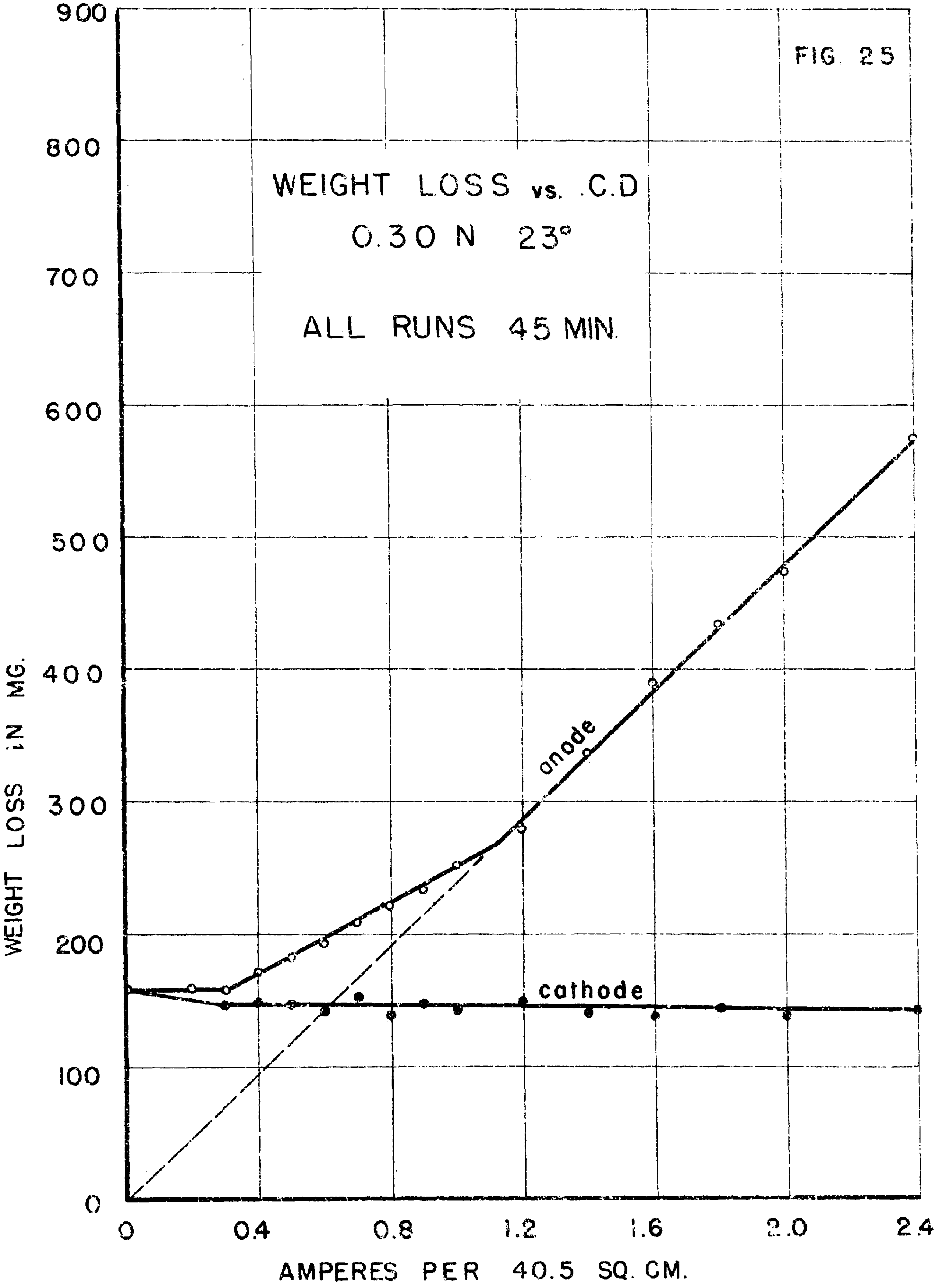


FIG. 25
WEIGHT LOSS vs. C.D
0.30 N 23°
ALL RUNS 45 MIN.
WEIGHT LOSS IN MG.
900
800
700
600
500
400
300
200
100
0
anode
cathode
0
0.4
0.8
1.2
1.6
2.0
2.4
AMPERES PER 40.5 SQ. CM.

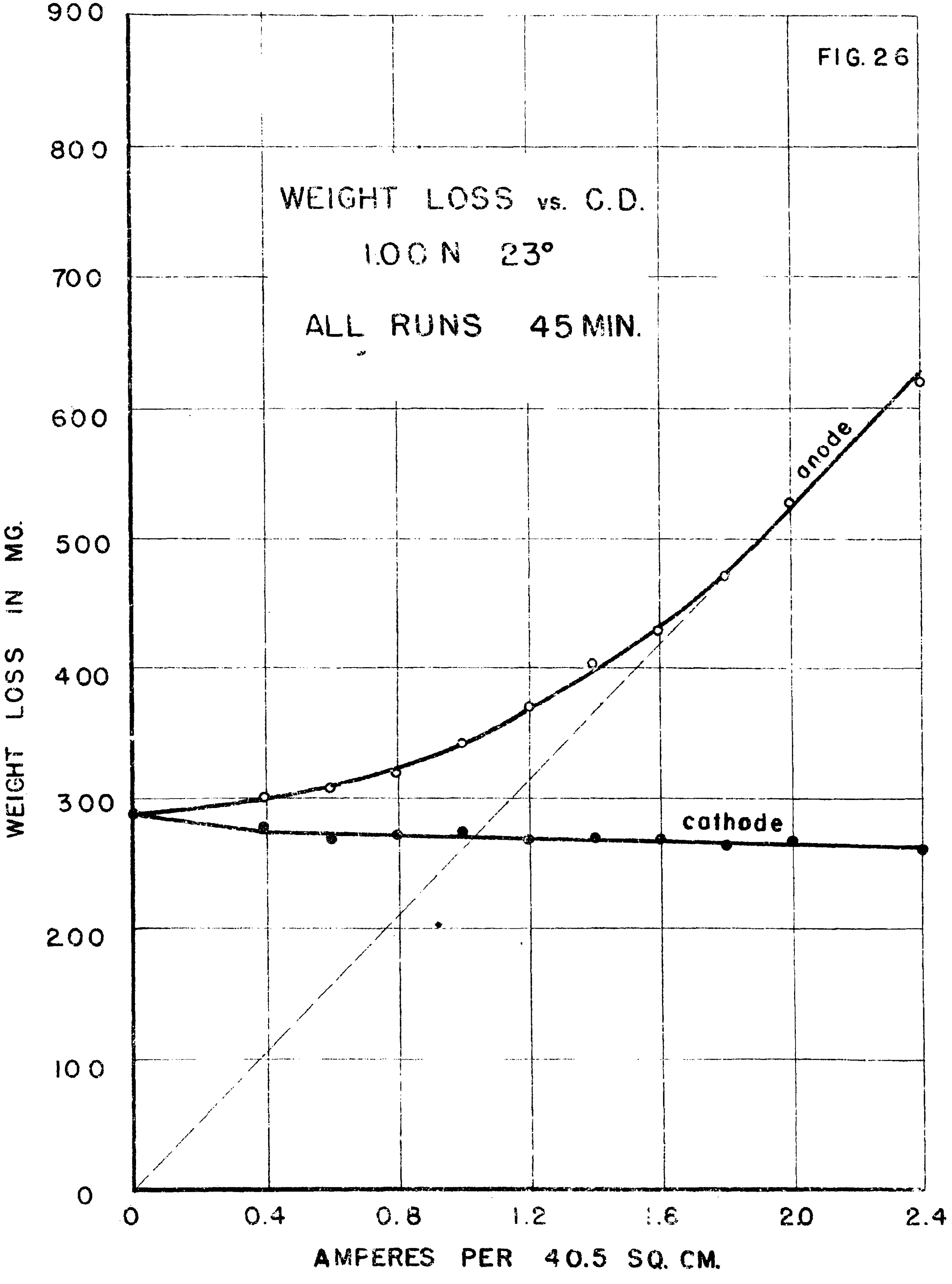
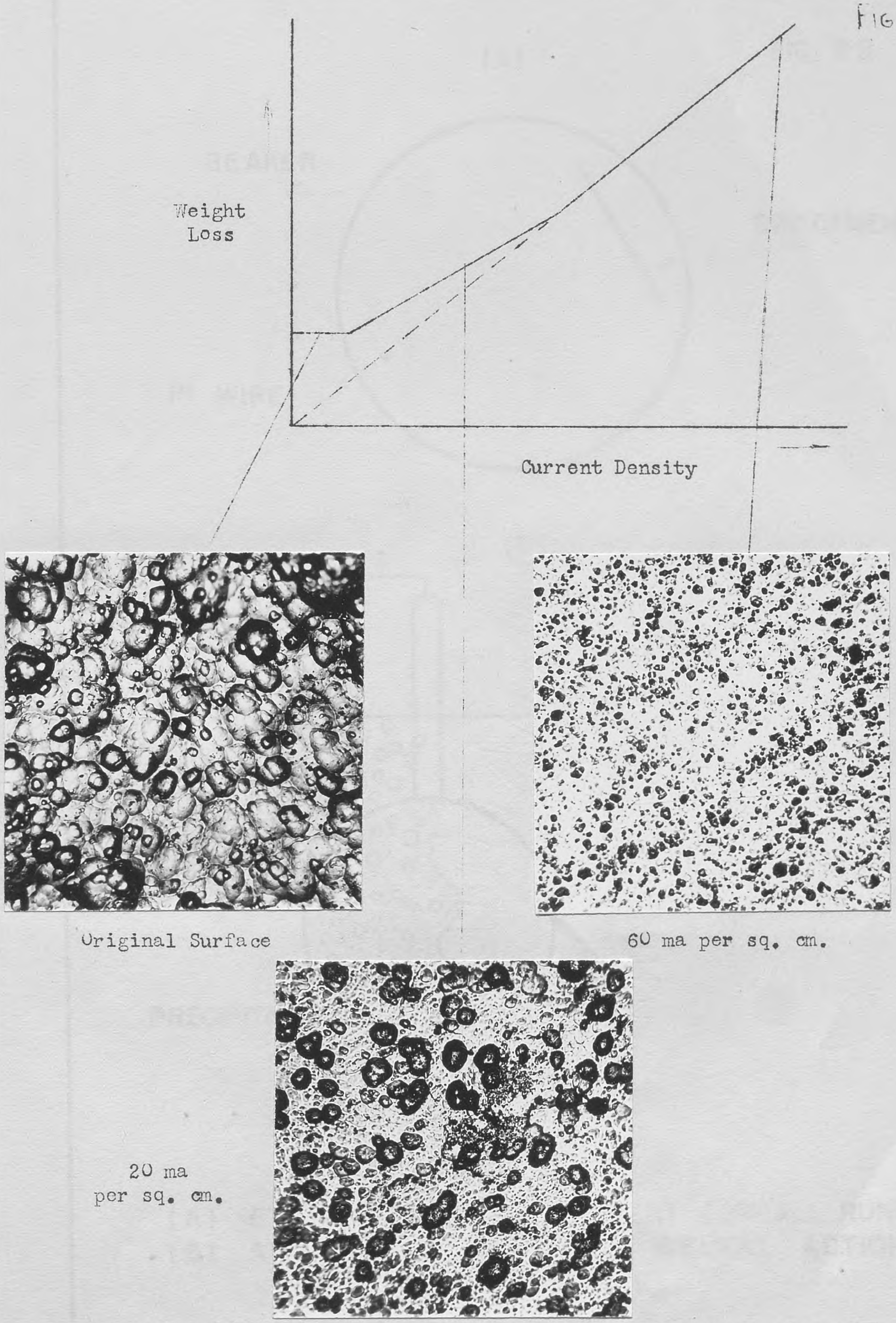


FIG. 26
WEIGHT LOSS vs. C.D.
1.00 N 23°
ALL RUNS 45 MIN.
anode
cathode
WEIGHT LOSS IN MG.
900
800
700
600
500
400
300
200
100
0
0
0.4
0.8
1.2
1.6
2.0
2.4
AMPERES PER 40.5 SQ. CM.

FIG 27



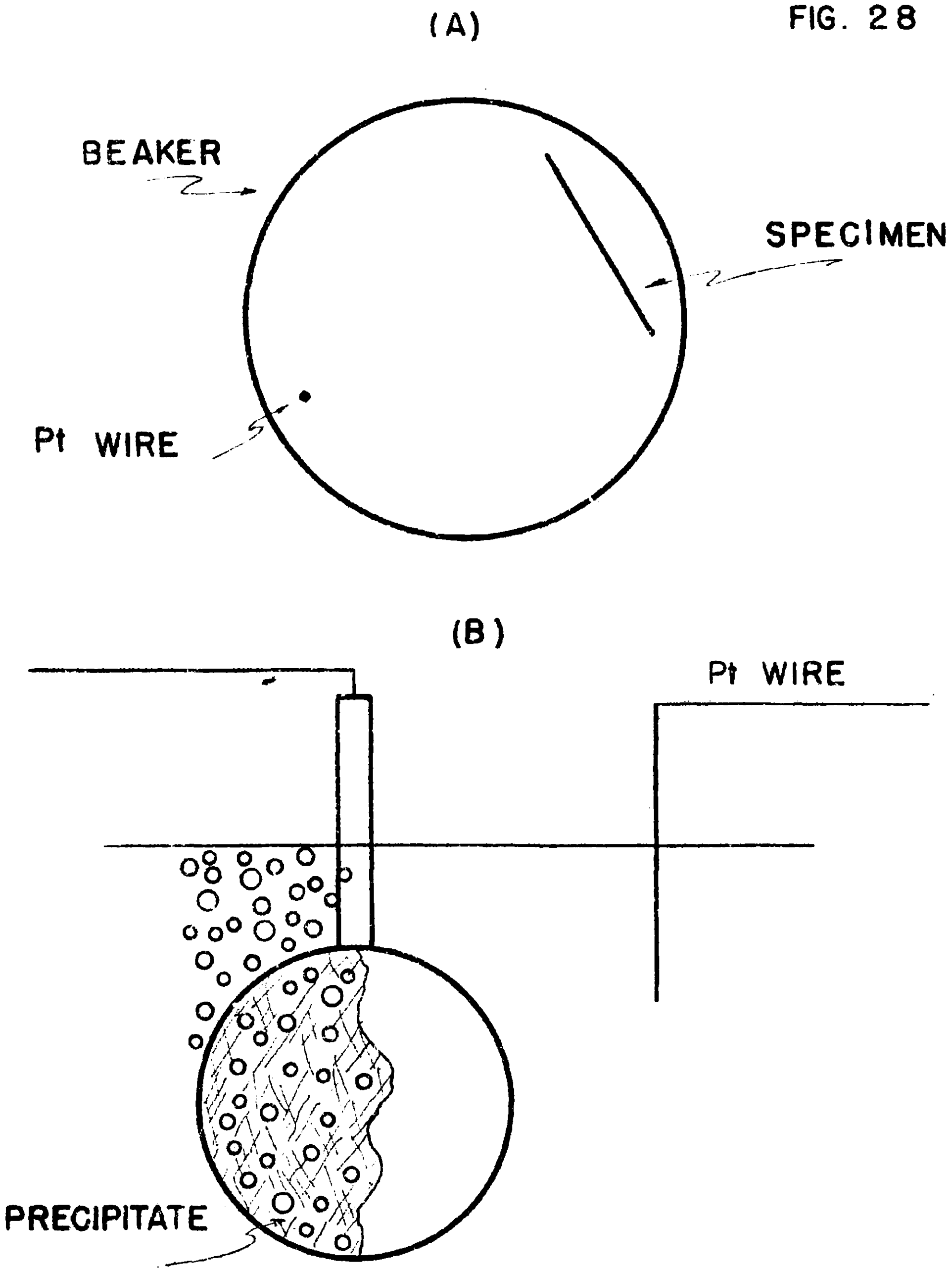
Original Surface

60 ma per sq. cm.

20 ma per sq. cm.

Fig. 27. 265X Change of appearance of anode surface as current density is increased. Precipitate has been removed by wiping.

FIG. 28



(A) EXPERIMENTAL ARRANGEMENT FOR ALL RUNS
(B) ARRANGEMENT USED TO REVEAL ACTION OF PRECIPITATE

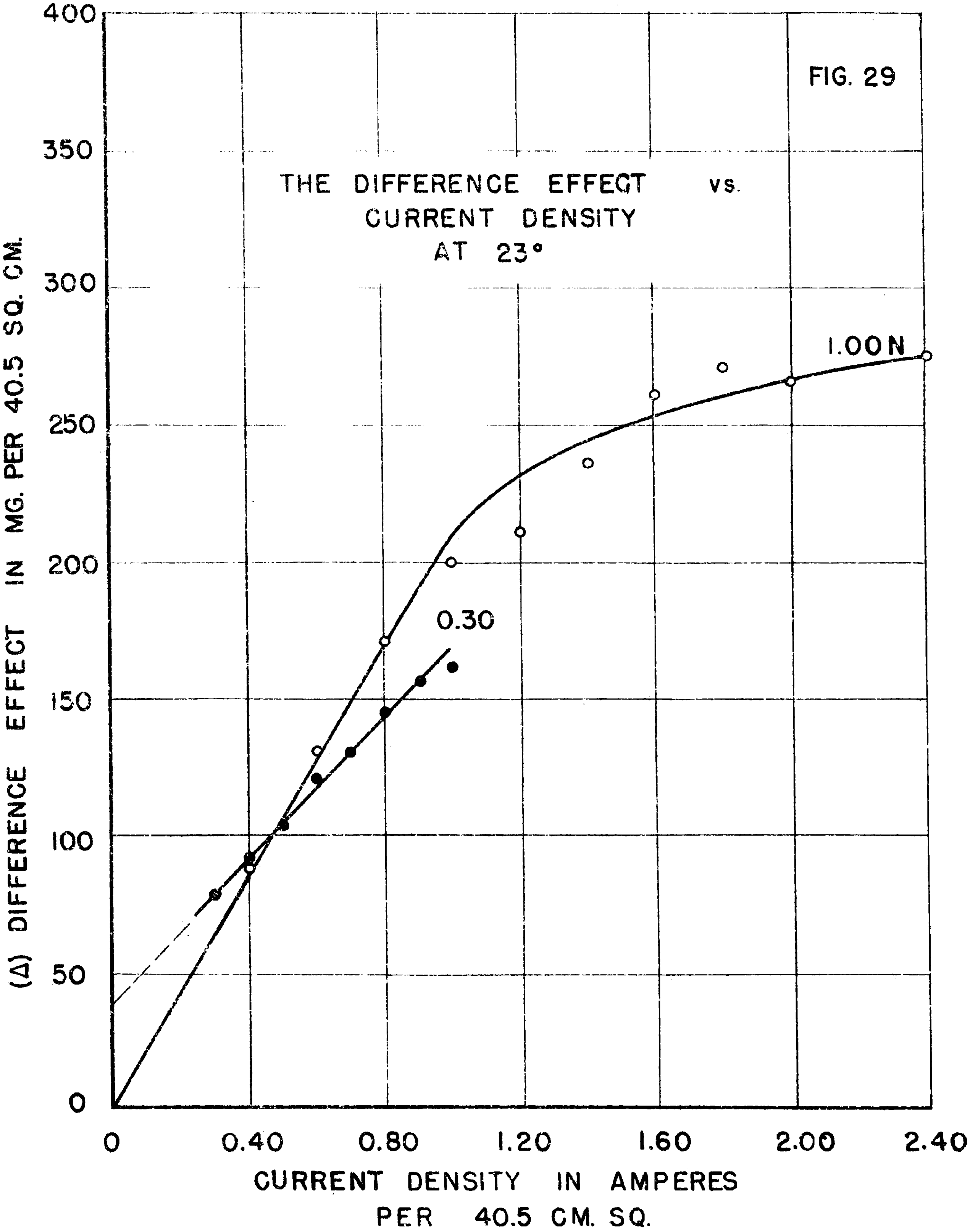


FIG. 29
THE DIFFERENCE EFFECT vs. CURRENT DENSITY AT 23°
1.00 N
0.30
(Δ) DIFFERENCE EFFECT IN MG. PER 40.5 SQ. CM.
0
50
100
150
200
250
300
350
400
0
0.40
0.80
1.20
1.60
2.00
2.40
CURRENT DENSITY IN AMPERES PER 40.5 CM. SQ.

APPENDICES

(A) Analysis of Sodium Hydroxide

Assay	97.3%	Cl	0.001%
PO_4	0.001%	N	0.0001%
SO_4	0.000%	Fe	0.001%
H.M. (as Ag)	0.001%	K	0.02%

Sodium Carbonate	1.5%
SiO_2 and NH_4OH ppt.	0.005%

(B) Comparison of Weight-Losses Determined by Weighing with and without Coating on Specimen

	------Weight Loss, Milligrams---			
Specimen No.	1	2	3	4
with coating	802.5	770.3	871.7	860.9
without coating	802.0	768.1	872.7	860.4
difference	0.5	2.2	1.0	0.5

(C) Data on Reproducibility of Dissolution Rates

C	T	t	W	Mean	Percent Maximum Deviation
0.05	23	30	49.8 44.9	47.3	5.0
0.05	23	45	69.2 72.5 70.1 70.2 69.9	71.9	3.7
0.05	23	120	221.8 224.5	223.1	0.6
0.05	40	45	236.5 243.7	240.1	1.5
0.10	23	45	96.8 92.8	94.8	2.2
0.10	23	120	281.3 281.6	281.4	0.0
0.10	26	15	36.4 38.0	37.2	2.1
0.10	26	30	73.4 84.3	78.8	3.4
0.10	26	60	165.2 177.0	171.1	3.5
0.10	26	100	285.4 290.5	287.9	0.9
0.10	26	120	341.4 345.6	343.5	0.6
0.10	32	60	248.1 247.9	248.0	0.0
0.15	23	45	111.4 110.6	111.0	0.4

(C) (continued)

C	T	t	W	Mean	Percent Maximum Deviation
0.20	23	45	135.3 138.3 137.3 131.1	135.5	3.2
0.20	23	60	175.0 182.3	178.6	2.0
0.20	23	100	312.8 323.9	318.3	1.8
0.30	23	30	107.0 104.3 100.8 103.2 100.6 100.6	102.7	4.2
0.30	23	45	163.1 162.3	162.7	0.2
0.30	23	60	228.8 223.3 219.0 226.5 227.0 219.8	224.2	2.2
0.30	23	80	316.5 302.5	309.5	2.3
0.30	23	100	391.2 398.9	395.0	1.2
0.30	23	120	473.0 486.2	479.6	1.4
0.30	26	30	126.7 122.5	124.6	1.7
0.30	26	45	208.4 201.9	205.1	1.6
0.30	26	60	270.2 282.5	276.3	2.2

<u>(C)</u> (continued)

C	T	t	W	Mean	Percent Maximum Deviation
0.30	26	100	486.1 488.0	487.0	0.2
0.30	40	10	103.7 111.4	107.5	3.7
0.30	40	15	166.5 179.1	172.8	3.6
0.30	40	30	362.7 372.2	367.4	1.3
0.30	40	45	546.4 562.2	544.3	1.4
0.40	23	45	181.2 183.1	182.1	0.6
0.40	23	100	437.4 447.8	442.6	1.1
0.50	23	45	194.2 193.3 200.1 200.9 195.0 197.8	196.9	2.0
0.50	26	60	353.4 346.3	349.8	1.0
1.00	23	60	400.3 400.7	400.5	0.0

(D) The Effect on the Dissolution Rate of Variables Other Than C, t, T

1. Source of Sodium Hydroxide at 23° and 0.30N

t	-Weight in Milligrams----	
	Batch I	Batch II
30	103.2 101.7 100.6	108.8 106.2
60	223.3 227.0 219.8	226.5 230.2

2. Use of New and Used Solutions at 32° - 0.10N - 60 Min.

New Solution	248.1
Solution Previously used 30 minutes	247.9

3. Effect of Surfaces Produced in Solutions of Various Concentrations

All runs at 23° for 45 min.

in 0.50N Solution	200.9) 200.9)	previously in 0.50N
	196.0) 197.6)	previously in 0.05N
in 0.05N Solution	72.5) 70.2)	previously in 0.50N
	70.1) 69.9)	previously in 0.05N

4. Effect of Specimen Position and Number of Specimens Used Simultaneously

at 0.30N - 23° - 45 min.

a. normal position: 163.1
b. at bottom of beaker: 167.4

(D) (continued)

at 0.20N - 23° - 45 min.

a. one specimen: 131.1
b. three specimens simultaneously: 135.3
138.3
137.3

The slight increase in weight-loss of the three specimens can be attributed to a 0.10° rise in temperature of the solution because of the greater quantity of heat liberated from three specimens than from one specimen.

(E) The Effect of Agitation on Weight-Loss

C	T°C	t	---Wt. Loss in Mg---- Unagitated	Agitated	W	Percent Increase
0.05	23	80	141.0	149.5	8.5	6.0
0.05	23	45	68.6	76.6	8.0	11.8
0.05	26	80	161.1	195.3	34.2	21.2
0.05	32	80	271.1	292.1	21.0	7.7
0.10	5	80	36.1	43.3	7.2	20.0
0.10	23	45	96.8	104.5	7.7	8.0
0.10	23	80	177.4	211.0	33.6	19.0
0.10	26	80	211.9 221.9	252.7	30.8	13.9
0.30	7	80	77.1	83.4	6.3	8.2
0.30	23	45	163.1	190.2	27.1	16.6
0.50	23	45	194.2	233.4	39.2	20.0

(F) Comparison of Observed and Calculated Weight-Loss Data

Data Calculated from $W = at^b$

t	-Weight in Milligrams-- Observed	Calculated	Deviation	Percent Deviation
		at 0.05N - 40°C		
10	43.9	43.9	0.0	0.0
15	67.9	69.0	-1.1	1.6
20	96.9	95.1	+1.8	2.0
30	149.4	149.0	0.0	0.0
45	236.5	235	+2	0.9
60	324.5	324	0	0.0
		at 0.10 - 26°C		
5	11.1	10.8	+0.3	2.8
10	23.1	22.9	+0.2	0.9
15	36.4	35.6	+0.8	2.2
20	48.5	48.5	+0.0	0.0
30	73.4	76.1	-2.7	3.5
45	114.7	118	-3	2.5
60	165.2	161	+4	2.5
80	221.9	220	+2	0.9
100	285.4	280	+5	1.8
120	341.4	342	-1	0.3
		at 0.30N - 26°C		
10	42.2	39.3	+2.9	7
15	58.9	61.5	-2.6	4
30	126.7	131	-4	3
45	205.1	203	+2	1
60	282.5	277	+6	2
80	369.3	380	-11	3
100	487.0	483	+4	1
120	599.8	592	+8	1

VITA

Michael Alfred Streicher, the son of Johann S. and Olga (Schmidt) Streicher, was born September 6, 1921, in Heidelberg, Germany. In 1928 he entered the Waldorfschule at Stuttgart, Germany. From 1932 until 1936 he attended Ridge Street Grammar School, Newark, New Jersey. This elementary schooling was followed by attendance at the following institutions.

1. Barringer High School
   Newark, New Jersey
   1936 - 1940

2. Rensselaer Polytechnic Institute
   Troy, New York
   B. Ch.E. December 1943

3. Syracuse University
   Syracuse, New York
   M. Ch.E. 1945

4. Lehigh University
   Bethlehem, Pennsylvania
   October 1945----