A Study of the Dissolution of Magnesium in Hydrochloric Acid.

Citation

Roald, Bernt. *A Study of the Dissolution of Magnesium in Hydrochloric Acid.* 1950, https://preserve.lehigh.edu/lehigh-scholarship/graduate-publications-theses-dissertations/theses-dissertations/study-95.

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Unpublished theses submitted for the Master's and Doctor's degree and deposited in the Lehigh University Library are open for inspection, but are to be used only with due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 ....Bernt....Porsild.......... has been used by the following persons, whose signatures attest their acceptance of the above restrictions.

NAME	ADDRESS	DATE

A STUDY OF THE DISSOLUTION
of
MAGNESIUM
in
HYDROCHLORIC ACID

by

Bernt Roald

A DISSERTATION

Presented to the Graduate Faculty

of Lehigh University

In Candidacy for the Degree of

Doctor of Philosophy

Lehigh University
1950

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

March 15, 1950. (Date)

W. Beck. (Professor in Charge)

Accepted, ________ (date)

Special committee directing the doctoral work
of Mr. Bernt Roald.

Gilbert E. Doan Chairman
Frank E. Myers
R D Stout
C. A. Shook
H. V. Anderson
____

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:

Dr. 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.

Dr. Walter Beck, of the Department of Metallurgical Engineering of Lehigh University, under whose supervision this work was carried on, for his unfailing counsel and advice.

Dr. Michael A. Streicher, formerly of the Department of Metallurgical Engineering of Lehigh University, for stimulating discussions and valuable suggestions throughout the course of this study.

Mr. L. Reiss, of the Squier Signal Laboratories of the United States Army Signal Corps, for his unfailing cooperation and encouragement.

Mr. W. S. Loose and Mr. H. Robinson, of the Dow Chemical Company, for their continued interest and assistance.

Dr. D. E. Mack, of the Department of Chemical Engineering of Lehigh University, for his expert advice on the agitation problems.

The magnesium alloys used in this study, as well as the spectrographic analyses of these, were made available by the Dow Chemical Company, Midland, Michigan. The project was carried out under Contract No. W 36-039 sc-32033 (Department of the Army Project 3-99-15-022) of the United States Army Signal Corps with the Department of Metallurgical Engineering of Lehigh University, Bethlehem, Pennsylvania.

TABLE OF CONTENTS

INTRODUCTION

Most of the commonly used metals are thermodynamically unstable in their service environments. The fact that properly selected metals show a good, serviceable corrosion resistance under various conditions of exposure is due to a number of factors, which retard or completely stifle the corrosive attack. For proper selection of materials for various service conditions, and for effective protection against corrosion it is important to understand the mechanism that controls the corrosion process.

Almost all corrosion at ordinary temperatures is caused by the action of electrolytic solutions, since even metals that are exposed to the atmosphere will be covered with films of moisture which have gases and salts dissolved in them. The dissolution or corrosion[1] of metals in electrolytic solutions is now commonly regarded as an electrochemical process (1). The emission of metal ions into solution is considered to take place at anodic areas on the surface of the metal, while an equivalent number of electrons from the metal combine with ions or molecules in the solution at cathodic surface areas. In most cases the cathodic process is either the discharge of hydrogen ions to form gaseous hydrogen (hydrogen evolution type of corrosion), or the

---

[1] When the rate of attack is low, as on magnesium in neutral solutions where the metal is protected by a film of corrosion products, the term corrosion is commonly used. When the rate of attack is high, as on magnesium in hydrochloric acid, where the protective films break down, the term dissolution is preferred. The two terms do not denote any differences in mechanism of attack, and are to some extent used as synonyms.

reduction of dissolved oxygen to hydroxyl ions (oxygen absorption type of corrosion).

Since the conductivity of metals is high, the rate of the overall corrosion process depends on the rates of the anodic and the cathodic processes, the rate of diffusion of reactants and reaction products to and from the anodic and cathodic surface areas, and the conductivity of the solution. Depending on the conditions, any one of these processes may be the slowest one and thus determine the actual dissolution rate of the metal. This complexity of the dissolution process has been overlooked by many investigators who have attempted to describe the dissolution process in terms of a chemical rate constant only.

The mechanism of attack depends on the composition and metallography of the metal, the composition of the solution, and the conditions at the solution-metal interface. Of particular importance is the presence of protective films on the surface of the metal. These films may be formed prior to the exposure, they may be formed by precipitation of corrosion products, or they may be formed by adsorption of constituents in the solution. Such films are instrumental in affording protection against corrosion, but they also obscure the electrochemical processes on the corroding surface. In solutions of acids and alkalies where the protective films break down, the conditions are much simpler, and the mechanism of attack can be evaluated more readily. Through dissolution studies in such solutions information which may lead to a better understanding of the corrosion behavior under actual service conditions where the protective films are stable can be gained. Such an understanding is a substantial aid in developing alloys with enhanced corrosion resistance and in devising more effective methods for protection against corrosion.

It is the purpose of this investigation to study the dissolution of magnesium in hydrochloric acid. The report on this study is preceded by a review of available information on the corrosion of magnesium in aqueous solutions. It is well known that the corrosion resistance of magnesium is seriously impaired by small amounts of impurities. The mechanism whereby these impurities act to lower the corrosion resistance is, however, not clearly understood. The present study was undertaken with a view towards obtaining information which might throw some light on these and related problems.

II. THE DISSOLUTION OF MAGNESIUM IN AQUEOUS SOLUTIONS.

A. Introduction.

When magnesium is immersed in aqueous solutions, hydrogen is evolved in amounts corresponding to the quantity of metal dissolved. Oxygen does not appear to play a major role, with a possible exception in strongly alkaline solutions (2, 3). The corrosion process thus consists of the cathodic evolution of hydrogen and the anodic dissolution of magnesium until the pH at the metal-solution interface rises to a point at which $Mg(OH)_2$ is precipitated (2).

The standard potential of magnesium has not been measured directly, but calculations from thermal data give a value of -2.37 V (4) which makes magnesium the most electronegative of the commonly used metals. Consequently, the corrosion resistance of magnesium and its alloys depends on the formation of protective films in the media to which the alloys are exposed. The ability of these films to offer protection varies with the medium. In acids, where the films are unstable[2], rapid attack takes place. In alkalies stable hydroxide films are formed which offer good protection.

In acids, as well as in alkalies, alloying elements and impurities have little or no influence on the rate of attack. This is in sharp contrast to the conditions in neutral solutions where minute amounts of certain detrimental impurities may increase the corrosion rate several hundred times (3). The detrimental effect of impurities in neutral solutions has been known for a long time, but a poor correlation between the data of different investigators existed until the action and interaction of the metallic impurities and alloying elements normally present in magnesium alloys was evaluated in an extensive series of careful investigations carried out by Hanawalt and his co-workers (3, 5, 6). The mechanism whereby these impurities act to lower the corrosion resistance is, however, not clearly understood.

B. The Corrosion of Magnesium in Neutral Solutions.

In 1941, Hanawalt, Nelson and Peloubet (5) showed that "controlled purity" alloys with the amounts of certain detrimental impurities below their "tolerance limits"[3] have a very good resistance to corrosion, even under the drastic conditions of alternate immersion in a 3% NaCl solution.

---

[2] Stable films are formed in hydrofluoric acid and in chromic acid (3).

[3] The "tolerance limit" is defined as the critical concentration of an alloyed component of magnesium at which a discontinuity in the corrosion rate occurs (3).

The tolerance limit of iron in magnesium is 0.017%, for nickel less than 0.0005%[4], and for copper close to 0.1%. With increasing amounts of these impurities the corrosion rate stays constant (below 0.2 mg/sq.cm.day) until the tolerance limit is reached. At this point a very sharp rise in the corrosion rate is observed. More recent work shows that these same impurities largely control the rate of attack in severe exposure, and to a lesser extent in atmospheric exposure (3).

Other metals, such as aluminum, zinc, manganese, etc., have much higher tolerance limits, and their effect in increasing the corrosion rate is small as compared with that of iron, nickel, and copper. More important is their effect in shifting the tolerance limits of iron and nickel, since these are the only impurities liable to cause trouble in commercial alloys. Thus, aluminum and zinc which are added to commercial alloys for enhanced mechanical properties influence the tolerance limits in such a way that zinc has a beneficial effect while aluminum seriously lowers the limits. The detrimental effect of aluminum is to some extent counteracted by a small addition of manganese which raises the tolerance limits and also reduces the corrosion rate of impure alloys (5, 6). Calcium is reported to have a similar effect (7).

While the initial corrosion rate of various magnesium alloys in 3% NaCl solutions in all cases is high, it rapidly falls off to a low value for controlled purity alloys, whereas impure alloys corrode at an increasing rate (8, 3).

Hanawalt showed that the tolerance limit of any given element was not identical with its solid solubility in the alloy considered, and

---

[4] Cobalt apparently has a similar tolerance limit.

explained the mechanism of attack by assuming that the active element was dispersed throughout the lattice in the form of minute particles, each of which functions as the cathode in a local cell. The corrosive attack is concentrated around the particle, and in due course sufficient material is corroded away to leave the particle unsupported, whereupon it falls away from the metal bulk. If the amount of the impurity is below the tolerance limit, no new particles will be discovered before the initiating particle is dislodged, and corrosion will eventually be stifled. If, on the other hand, one or more particles are laid bare, an accelerating type of attack occurs.

This theory is supported by microscopic evidence which shows that while the tolerance limits of iron in pure magnesium and in magnesium containing 8% aluminum are widely different (0.017% and 0.002%), yet the mean distance of separation of the iron-bearing particles in the two alloys is about the same at the tolerance limits.

Hanawalt (5) has also pointed out that there may exist a critical anodic current density below which protective film formation takes place but above which corrosion can continue. Thus, when the relative size of the cathodic areas (which determines the current density) falls below a certain limit, the cathodic areas will be made inactive by encroachment of the anodic films. This explanation of the tolerance limits is in accord with the observation that magnesium in neutral solutions exhibits a negative "difference effect" (5, 9), i.e., the corrosion due to local action increases when the specimen is made anodic by coupling with a nobler metal. Kroenig and Uspenskaja (9) have explained this phenomenon as a breakdown of the anodic film due to the increased anodic current density with the result that additional cathodic points are laid bare. This effect is exhibited by controlled purity as well as by impure alloys.

It has been suggested that the mechanism whereby iron and nickel accelerate the corrosion of magnesium and its alloys may depend on redeposition of the metal, either as metal or as hydroxide (10, 11).

The corrosion behavior of magnesium in neutral solutions is thus largely determined by the amounts of certain low overvoltage impurities in the metal. The phenomenon of tolerance limits has been explained by the removal of the cathodic particles by undermining, and by anodic films being able to cover the cathodic particles when their relative surface areais reduced to a critical value. Hanawalt considers that both mechanisms may be operative, but states that additional information is required before a complete explanation can be given.

C. The Dissolution of Magnesium in Acids.

In acids the protective films on magnesium are destroyed and rapid attack ensues. Because of the strongly electronegative character of magnesium the potential difference between metal and solution is sufficiently high to overcome the overvoltage for hydrogen discharge on magnesium. For this reason hydrogen is freely liberated without the aid of low overvoltage impurities. Accordingly, impurities have been found to have little or no influence on the dissolution rate (12, 21)[5].

---

[5] This is in contrast to the behavior of the more noble zinc which is hardly attacked by acids unless low overvoltage impurities or cathodic depolariz~~z~~ers are present.

Kilpatrick and co-workers (13, 14) measured dissolution rates of magnesium in dilute solutions of hydrochloric acid and various weak organic acids. Based on Brönsted's theory of generalized acids, they concluded that the rate controlling step was a slow, chemical reaction between the metal and the acid. In particular, they claimed that the metal can react with undissociated acid molecules as well as with hydrogen ions. In contrary to this belief, King and co-workers (15, 21) stated that the dissolution rate is controlled by diffusion, and supported this theory by a series of careful investigations which gave results in convincing agreement with the following criteria of diffusion controlled reactions[6]:

a. Different solids dissolve at nearly the same rate in the same reagent under the same conditions.

b. The stirring rate has a very large influence on the observed dissolution rates (this is not typical of chemical processes).

c. The dissolution rate is nearly inversely proportional to the viscosity of the solution.

d. The rates observed with different acids follow, in general, the diffusion coefficients of the acids rather than their acid strengths.

e. The temperature coefficient is usually between 1.1 and and 1.5 per 10°C rise, while chemical reactions seldom have temperature coefficients below 2.

The electrode potential[7] of magnesium becomes more anodic with increasing acid concentration up to a maximum of -1.6 to -1.7 V on the hydrogen

---

[6] A discrepancy in the case of chloracetic acid, quoted against the diffusion theory by James (22), was shown by Coates (23) to be due to side reactions.

[7] According to the convention adopted by The Electrochemical Society and National Bureau of Standards, a positive potential refers to a noble or cathodic potential, whereas a negative potential applies to an active or ~~cathodic~~ anodic potential (29).

scale (23, 24, 25). At higher concentrations it remains fairly constant in the case of strong acids, while in weak acids the trend is reversed, and the potential becomes more cathodic. Agitation of the solution shifts the potential to a value corresponding to a higher acid concentration (24, 26, 27).

Gatty and Spooner (2) considered that the surface of the metal is covered with a "hydride film"[8] and that this film is the site of hydrogen discharge, while the emission of metal ions into solution takes place through "pores" in this film. "Under these conditions self-polarization will be almost entirely anodic and the electrode potential determined by the potential of the hydride film which, for given system conditions, will be negative to the reversible hydrogen electrode in that solution by an overvoltage corresponding to the cathodic current density", (Ref. 2, p. 425). Coates (23) has pointed out that an overvoltage of 1.65 V, corresponding to the measured potentials of magnesium in acid solutions, is 0.4 V greater than has been observed for any other metal. This discrepancy is removed, however, when concentration polarization, which is a necessary consequence of the diffusion control theory, is taken into account. Coates considered that the hydrogen ions in the immediate vicinity of the surface of the metal will be depleted to the point where a transitory formation of magnesium hydroxide may take place[9]. When the corresponding concentration polarization is subtracted from the observed potential of about 1.65 V, the hydrogen overpotential appears to be of the order of 1 V, which is quite reasonable and comparable with that of other

---

[8] More accurately interpreted as a layer of adsorbed hydrogen atoms (23).

[9] $Mg(OH)_2$ is precipitated at a pH of 10.5 (28).

non-catalytically active metals.

Summarizing, the dissolution of magnesium in acids appears to be a diffusion controlled reaction. The electrode potential is determined by the potential of the cathodic areas, and is probably the sum of the hydrogen overvoltage corresponding to the cathodic current density and a concentration polarization term corresponding to the decrease in hydrogen ion concentration in the vicinity of the surface of the metal. No explanation has been given for the variations in electrode potential with acid concentration.

D. The Corrosion of Magnesium in Alkaline Solutions.

Magnesium and its alloys exhibit good resistance to attack by alkalies at normal temperatures. At temperatures above 60°C the attack becomes appreciable (3).

III. DESCRIPTION OF EXPERIMENTAL WORK.

A. Introduction.

Previous investigators studying the dissolution of magnesium in hydrochloric acid have concluded that the dissolution rate is controlled by diffusion and that impurities have no appreciable influence on the dissolution rate. Most of these investigators have regarded the dissolution process as a chemical rate process without taking the electrochemical aspect into consideration. For this reason data on electrode potentials and external polarization are scarce and inconclusive. Most of the earlier studies have been made in acids of low concentrations (below 0.1 N) and the observed rates have been reported in terms of a rate constant k, computed by means of the equation

$$k = \frac{2.3\ V}{A\ t} \log \frac{c_0}{c} \qquad (1)$$

where V is the volume of acid, A the exposed surface area, t the time, and c_0, and c the concentration before and after the run. Equation 1 is derived by integration of the rate equation for a first order chemical reaction

$$\frac{dn}{dt} = k\ c \qquad (2)$$

Where dn/dt is the dissolution rate in an acid of concentration c. The rates computed by means of Equation 1 thus represent mean dissolution rates for rather wide ranges of acid concentration.

In the present investigation the dissolution rate of high purity magnesium in hydrochloric acid has been studied by measuring dissolution rates and electrode potentials as functions of the acid concentration, the temperature, and the rate of agitation. By using a large volume of acid the changes in concentration during each run were kept at a minimum. The effect of agitation was studied by using cylindrical specimens which were rotated about their own axes at different speeds. This arrangement ensures reproducible rates of agitation, whereas the use of stationary specimens and agitation of the solution is strongly affected by minor changes in the geometry of the system. With the results of these experiments as a basis for comparison the effects of different alloy compositions and different additions to the acid solution have been studied. Finally, the effect of external polarization on the dissolution rate has been measured.

B. Experimental Details.

1. Materials. The compositions of the magnesium alloys used in this study, as determined by spectroscopic analysis, are given in Table I. The beryllium-settled metal is commercial magnesium ("cell magnesium") which has been purified by beryllium settling. This alloy has been used for most of the dissolution experiments and, unless otherwise specified, the results given in subsequent sections, have been obtained with specimens of this composition. The distilled magnesium is of the highest purity currently available.

The test specimens were in the form of cylindrical bars of 11 mm diameter which were machined from extruded bars. The bars were covered with a plastic coating[10], leaving 3 to 4 cm (corresponding to 10 to 15 sq.cm.) of the cylindrical surface exposed to the acid.

The specimens of the J-1 alloy were heated at 410°C for 24 hours and quenched in water in order to put the aluminum and the zinc into solid solution. The manganese remained as a separate phase. The other alloys were used in the as-extruded condition, except for one batch of specimens of the beryllium-settled magnesium which was heated at 610°C

---

[10] DEKADHESE, a laboratory cement made by Technical Specialties Co., Malden, Mass., under license from Decker Laboratories, Inc. This material dries rapidly to form a tough, impermeable coating which is very resistant to strong acids and alkalies. The coating adheres well without peeling at edges, provided the magnesium base is properly cleaned before application. The coating shows no change in weight during dissolution tests and drying operations, and does not have to be removed for weighing (30).

for 15 hours and quenched in water. Aside from ensuring a homogeneous solid solution, this treatment resulted in considerable grain growth, to an average grain diameter of about 1 mm.

The concentration of hydrochloric acid was controlled by titration with standard sodium hydroxide using phenolpthalein as an indicator. The hydrochloric acid used was C.P. grade reagent[11], with a content of heavy metals (as Pb) of 0.00005%. The iron content was 0.00001%.

2. Experimental Arrangement. The specimens were rotated by a synchronous motor with adjustable gears; an arrangement which ensures constant and reproducible rates of agitation. By mounting the motor with the specimen holder in a sliding fixture and suspending it by a counterweight arrangement, the rotating specimen could easily be immersed in or lifted out of the acid bath. The volume of acid used in each run was four liters in order to minimize the changes in acid concentration as dissolution proceeds. This large volume of acid has the additional advantage of reducing the unavoidable temperature increase during runs at the higher acid concentrations. The beakers with the acid were immersed in a thermo-regulated bath with provisions for heating and cooling. A mercurial thermo-regulator in connection with a Fisher-Serfass electronic relay maintained the temperature constant within ± 0.05°C.

Electrical contact to the specimen for potential measurements and for external polarization was made by means of a mercury contact. The electrode potentials were measured against a 0.1N calomel cell using a salt bridge of saturated potassium chloride in order to minimize the liquid-junction potential. The potential readings were made with a

---

[11] Supplied by J. T. Baker Chemical Co., Phillipsburg, New Jersey

Leeds and Northrup type K potentiometer, using the higher range which permitted reading of the potentials with an accuracy of 0.1 mV.

In the experiments with external polarization an EMF from a d.c. generator was applied to the dissolving specimen, using a platinum wire as an auxiliary electrode. The platinum wire was bent to form a circle of 15 cm diameter and mounted inside the beaker with the exposed surface area of the specimen in its center. This arrangement ensures a reasonably uniform current density on the exposed surface. The current was adjusted by a variable resistance in series with the current, and its magnitude was measured with a Weston multi-range amperemeter.

3. Experimental Procedure. Before being used in the dissolution experiments the specimens were cleaned by immersion in 5% hydrochloric acid and immediately flushed by a jet of distilled water from a wash-bottle. They were then dried in an electric oven at 110°C and cooled in a desiccator before weighing. This pre-treatment produces perfectly clean, mirror-bright surfaces, and when the specimens were immersed in the acids there was no delay in the evolution of hydrogen. With specimens that had been exposed to the atmosphere for any considerable length of time the evolution of hydrogen was markedly delayed, particularly in the weaker acids, and a non-uniform attack developed.

The time of immersion varied from 15 to 20 minutes at the lowest acid concentrations down to 1.5 or 1 minute at concentrations above 1N. The short immersion times were used in order to keep the changes in acid concentration during the runs at a minimum. At the higher acid concentrations the decrease in diameter as dissolution proceeds, as well as the temperature increase of the solution, also becomes appreciable.

At the end of a run the specimen was pulled from the solution and immediately flushed with a jet of distilled water from the wash-bottle while it still was rotating. Following drying and weighing the area of exposed surface was carefully measured and, finally, the dissolution rate in mg per sq. cm per min. was evaluated. Corrections were made for the decrease in diameter which decreases the area, and for the temperature increase due to the heat of reaction which increases the rate of dissolution. These corrections become appreciable at the higher acid concentrations. The acid concentration was recorded as the mean of the initial and final concentrations. The decrease in acid concentration during the runs was generally below 4%.

The electrode potential measurements were partly made in combination with the determinations of dissolution rates, and partly in separate runs. In the latter case the specimens were immersed in the acid immediately after cleaning in 5% hydrochloric acid and flushing with distilled water.

The experiments with external polarization were made in 0.045N acid. The duration of the runs was decreased from 10 to 3 minutes as the current density increased. In the experiments with anodic polarization the dissolution rate due to local action was found by subtracting the dissolution rate due to the external polarizing current (calculated by means of Faraday's law) from the total dissolution rate which was given by the observed weight loss.

An attempt to measure the variations in electrode potential with the polarizing current was unsuccessful because the large potential drop in the solution due to the ohmic resistance overshadowed any changes that might occur in the electrode potential.

4. Limits of Error. Due to the large number of variables that affect the dissolution rate (acid concentration, temperature, rate of agitation, time of exposure, weighing, and measurement of the exposed area) an estimation of the experimental accuracy from the accuracy of the individual variables is hardly justified. However, from three representative groups of data[12] the standard deviation from the mean is found to be ± 2.7%, with a maximum deviation of ±4%.

At rates of agitation below 947 r.p.m. the scatter in the observed rates of dissolution is ±10% due to anomalies in the dissolution process within this range. With no agitation the reproducibility is normal.

The electrode potentials, which were measured to the nearest millivolt, are generally reproducible within ±10mV. At rates of agitation below 947 r.p.m. (including no agitation) the reproducibility is poor in acids of concentrations less than 0.1 N. At higher rates of agitation the reproducibility is normal.

In the experiments with external polarization the scatter in the data is somewhat higher than normal on account of the difficulties in maintaining accurate control of the polarizing current.

C. Results.

1. Dissolution Rates. Preliminary experiments have shown that the dissolution rate of magnesium in hydrochloric acid is constant with

---

[12] Using the values of the rate constant k for 1364, 2880, and 6400 r.p.m. from Table II for the lower concentration range where k is constant. The values for k for the two lowest acid concentrations at 1364 r.p.m. were omitted since the total weight losses in these two determinations were only 8.5 and 13.5 mg respectively.

time, unless changes in acid concentration, temperature, and area of the exposed surface become significant. Additions of magnesium chloride do not affect the dissolution rate appreciably.

Table II and Fig. 1 show the dissolution rates of high purity (beryllium-settled) magnesium in hydrochloric acid of concentrations ranging from 0.001 to 1.5 N at 25°C. The measurements have been made at rates of agitation ranging from 0 to 6400 revolutions per minute (r.p.m.), corresponding to a peripheral speed of 0 to 22100 cm. per minute. At the lower acid concentrations the dissolution rates appear to be directly proportional to the acid concentration, corresponding to a slope of 1 of the dissolution rate - concentration curves on logarithmic coordinates (Fig. 1). With no agitation the increase is more rapid, or rather, the dissolution rate decreases more rapidly with decreasing acid concentration. Coates (23) attributed this to the formation of obstructive films, as indicated by the dull and slightly pitted appearance of the specimens that had been exposed to the most dilute acids.

At the higher acid concentrations the slopes become steeper. The concentrations at which the breaks in the curves occur increase with increasing rates of agitation, whereas the break becomes less sharp as the rate of agitation increases. As a result the curves converge; i.e., the effect of agitation on the dissolution rate decreases with increasing acid concentration. Thus, in 1.4 N acid a stirring rate of 2880 r.p.m. has practically no effect on the dissolution rate.

The first runs at 380 r.p.m. gave dissolution rates that were about 15% lower than those of later runs. The reproducibility of the early runs was considerably less than for the later runs. The reason for this inconsistency seems to be an instability in the dissolution process in this range of stirring rates.

Table II also gives values of the rate constant k, as defined by Equation 1 (p. 11)[13]. In Fig. 2 the rate constants for various rates of agitation are plotted against the corresponding dissolution rates.

In Table III and Fig. 4 are given the dissolution rates obtained with specimens of beryllium-settled magnesium which had been heated at 610°C and quenched in water (broken lines). Fig. 4 shows that while this heat treatment has no effect on the dissolution rate at the lower acid concentrations, there is an appreciable decrease in dissolution rate at the highest concentrations.

The effect of agitation on the dissolution rate is given in Tables IV and V, and in Fig. 5, for rates of agitation up to 8030 r.p.m., corresponding to a peripheral speed of 27800 cm./min. The rate constants apply to the lower range of acid concentrations where the dissolution rate is proportional to the concentration. The slope of 0.71 for the straight line in Fig. 5 shows that the rate constant increases with the rate of agitation to a power of 0.71 for speeds of rotation above about 1000 r.p.m.

2. Effect of Temperature. In Table VI and Fig. 6 is shown the effect of temperature on the dissolution rate at 947 r.p.m. A temperature increase of 10° C appears to increase the dissolution rate

---

[13] The values of k are calculated by means of Equation 2 (p. 11) in the form

$$k = 0.0822 \frac{\text{(diss. rate in mg./sq.cm.min.)}}{\text{(acid conc. in mols/liter)}}$$

The factor 0.0822 is introduced for conversion to the proper units (cm./min.).

about 25% for concentrations up to 0.5N. In Table VII are given the mean values of the rate constants for acid concentrations below 0.8N. From these data the temperature coefficient per 10°C rise ($\frac{k_{35}}{k_{25}}$) is calculated to be 1.24. In Fig. 7 log k is plotted against the reciprocal of the absolute temperature, using data from Table VII. From the slope of the resulting straight line, the activation energy of the dissolution process is found by means of Arrhenius' equation to be 4100 cal/mol.

3. Heating Effects During Dissolution. During the runs at the higher acid concentrations there is an appreciable increase in temperature on account of the large heat of dissolution. Since this heat is evolved at the metal-solution interface, the temperature of the dissolving specimen will be higher than that of the solution. In order to measure the temperature difference between specimen and solution, a thermometer was placed inside the dissolving specimen through a hole drilled in from the top, in such a way that the thermometer bulb was inside the exposed surface area. The temperature difference was measured at no agitation and with the specimen placed on the edge of the vortex formed in rapidly stirred solutions[14]. In 0.1N acid this intensity of stirring gave dissolution rates about 4 times as high as in unstirred solutions, e.g. about the same as if the specimen were rotated at a rate of 1000 r.p.m.

The results of these measurements are given in Table VIII and Fig. 8. The agitation is seen to reduce the temperature difference between the specimen and the solution. Thus the larger evolution of heat on account of the higher dissolution rate is more than offset by the more rapid heat transfer.

---

[14] The specimen with the thermometer inside could not be rotated with the available equipment.

4. Electrode Potentials. Fig. 11 shows the electrode potentials of beryllium-settled magnesium in hydrochloric acid at different rates of agitation. The potentials are plotted against the corresponding rates of dissolution rather than against the acid concentration. By this method of plotting the potentials for rates of agitation above 1000 r.p.m. appear to fall on the same line, within the limits of reproducibility. At the higher acid concentrations the potentials rapidly reach steady values which do not change appreciably with time. At the lower dissolution rates a longer time is needed, with the potentials drifting in a cathodic direction until steady values are reached.

With no agitation, and at 947 r.p.m., the potential curves show a rather surprising discontinuity. At dissolution rates below 0.1 mg./sq. cm.min. the potentials drift slowly in a cathodic direction. At somewhat higher dissolution rates this trend is reversed after a few minutes, and the potentials gradually become more anodic until steady states are approached.

The effect of temperature on the electrode potentials at 947 r.p.m. is shown in Fig. 12. These measurements are to some extent rendered undertain by the above-mentioned anomalies in the potential curve at 947 r.p.m. However, at the lower rates of dissolution a temperature increase of 10°C appears to shift the potential about 0.05 V in a cathodic direction. At the higher dissolution rates, where the potentials level off to a constant value, the temperature has no appreciable influence on the potentials.

5. Effect of Alloy Composition. In Tables X and XI, and in Figs. 9 and 13, are given the dissolution rates and electrode potentials of different alloys in hydrochloric acid at 1364 r.p.m. Cell magnesium

(with iron in excess of the tolerance limit) appears to have dissolution rates similar to those of the purer beryllium-settled metal (Fig. 9). A few tests with distilled magnesium also gave similar dissolution rates.

Fig. 13 shows that the solution heat treatment of the beryllium-settled magnesium shifts the potential at the lower dissolution rates to more anodic values. The greater amount of impurities in cell magnesium appears to retard the approach of the potential towards a steady value as the dissolution rate increases.

The dissolution rates of the J-1 alloy (containing 6.2% Al and 0.27% Mn) correspond to those of pure magnesium at the highest acid concentrations (Fig. 9). At acid concentrations around 0.3N a curious bump appears in the rate curve. Specimens that have been immersed in acids within this concentration range exhibit a considerable roughening of the surface. Microscopic examination (Fig. 18) reveals that channels have been etched in the surface along stringers of manganese inclusions[15]. At lower acid concentrations this surface roughness does not appear, but a black coating which uniformly covers the surface is formed. This effect of manganese on the dissolution rates is accompanied by a marked effect on the electrode potentials, as shown by Fig. 13.

6. Effects of Additions to the Solution. Table IX and Fig. 10 show the dissolution rates of magnesium in solutions of hydrochloric acid which contain 0.5 mols per liter of aluminum chloride. At the

---

[15] The manganese inclusions were lined up as stringers in the extrusion operation used in producing the bars from which the specimens were machined.

lower acid concentrations a white film of aluminum hydroxide was formed on the specimens. This precipitate interfered with the weighing, and reliable dissolution rates could not be obtained. At the higher acid concentrations the precipitate did not form. Fig. 10 shows that the break in the dissolution rate-concentration curve for pure acid does not appear for solutions containing aluminum chloride. In acids containing aluminum chloride the hydrogen bubbles were small even at the highest acid concentrations, whereas in pure acids very large bubbles were formed in the strongest acids. The effect of aluminum chloride on the bubble size in 1.5N acid at 1364 r.p.m. is shown in Fig. 20. From Fig. 14 it appears that the addition of aluminum chloride to the acid shifts the electrode potential about 0.08 V in an anodic direction over the whole range of dissolution rates.

When salts of iron, copper, or manganese are added to the weaker acids, a dark precipitate is formed on the surface of the dissolving specimens. This precipitate does not form at the higher acid concentrations. Fig. 14 shows the effect on the potential of increasing additions of ferric chloride. At the lower acid concentrations where the precipitate forms, a marked change in the potential to more cathodic values is observed. At the lowest acid concentrations the precipitate exhibits the brown color typical of ferric hydroxide. With increasing acid concentration the color changes to black. At the higher concentrations where the precipitate does not form, the addition of ferric chloride has no effect on the electrode potential.

In Fig. 15 are shown the effects of additions of manganous chloride, ferric chloride, and cupric chloride in changing the electrode potentials of magnesium in 0.1 N hydrochloric acid at 1364 r.p.m. to more cathodic values. The magnitude of the effect increases markedly in the succession $MnCl_2$, $FeCl_3$, $CuCl_2$. The amounts of precipitate formed on the specimens increases in the same succession. Thus, practically no precipitate was formed in an acid with 0.001 M $MnCl_2$, whereas a corresponding amount of $CuCl_2$ formed a heavy precipitate which continually flaked off. The formation of these precipitates makes it difficult to obtain reliable weight loss determinations. However, the precipitates do not seem to have any significant influence on the dissolution rates.

X-ray diffraction patterns of the precipitates formed in 0.1 N acids containing cupric chloride and ferric chloride respectively showed that they consist of metallic copper or iron which have been plated out by cementation.

7. Effect of External Polarization. The effect of external polarization on the dissolution rate of magnesium in 0.045 N hydrochloric acid at 1364 r.p.m. is shown in Tables XII and XIII, and in Fig. 16. When the specimen is made anodic, the observed dissolution rate is the sum of the dissolution rate due to the external current and the dissolution rate due to local action. In Fig. 16 the dissolution rate due to the anodic current is indicated by a broken line. The dissolution rate in anodic polarization is seen to approach this line as the current density is increased, indicating that the dissolution rate due to local action is reduced. The effect of anodic polarization in reducing the dissolution rate of a metal was first described by Thiel (31, 32), who introduced the term "difference effect"

for the phenomenon[16]. The effect of cathodic polarization in reducing the dissolution rate (cf. Fig. 16) is called "cathodic protection" (33).

In Fig. 17 the effect of external polarization in reducing the dissolution rate due to local action is shown as a function of the current density. The difference effect as well as cathodic protection are seen to increase linearly with the current density up to a current density of about 0.07 amp./sq.cm. In anodic polarization a dark precipitate appeared on the specimens at this current density. This precipitate interfered with the weighing, and reproducible values of the dissolution rate could not be obtained at current densities above 0.1 amp./sq.cm. The curve for cathodic protection (Fig. 17) also shows a break at a current density of about 0.07 amp./sq.cm. Specimens that have been subjected to a higher current density exhibit a dull, slightly pitted appearance, apparently on account of the formation of a surface film.

The broken line through the origin in Fig. 17 indicates what the change in dissolution rate would be if it were equivalent to the polarizing current density. A comparison of the slope of this line with the slopes of the curves for the difference effect and cathodic protection show that for current densities below about 0.07 amp./sq.cm. the difference effect is equivalent to about 2/3 of the anodic current density while cathodic protection is equivalent to about 1/3 of the cathodic current density.

8. Microscopic Examination of the Etched Surfaces. Microscopic examination revealed the presence of dark spots on the surface of the specimens of the beryllium-settled magnesium which had been dissolving

---

[16] When the dissolution rate due to local action is increased as a result of anodic polarization, as in the case of magnesium in neutral solutions (cf. p. 6), the difference effect is said to be negative.

in the weaker acids. As shown by Figs. 21 to 24, these spots decrease in number and size as the acid concentration (or rather the dissolution rate) increases, until in 0.2 N acid there are only few left. The solution heat-treated specimens exhibited a considerably smaller number of such spots, as shown by comparison of Fig. 22 with Fig. 25. These spots appear to be protrusions on the surface rather than pits.

At the higher acid concentrations the attack became non-uniform, apparently because the rate of attack depends on the orientation of the grains. This effect was very pronounced in the acids containing aluminum chloride, as shown by Fig. 26. Figs. 27 and 28 show the appearance of distilled magnesium after immersion in acids of two different concentrations. In Fig. 29 is shown the precipitates formed by increasing additions of ferric chloride to the acid.

Fig. 30 shows the precipitate which is formed at an anodic current density of about 0.07 amp./sq.cm. in 0.045 N acid. As the precipitate is formed, the attack is seen to become non-uniform.

IV. DISCUSSION OF THE RESULTS.

A. Dissolution Rates.

1. General Theory. The classical theory for the dissolution of solids in liquids was developed by Noyes and Whitney (34), Nernst (35), and Brunner (36). They postulated that in such cases the rate of the chemical reaction at the surface of the solid is very high compared to the rate of diffusion of reactant to the surface through the reaction products as they diffuse away.

This theory is not as generally applicable to heterogeneous reactions as was supposed by the originators. There are cases where the rate of the surface reaction itself is lower than that of the diffusion process, and thus determines the reaction rate (activation controlled reactions). Also, the rates of the diffusion process and the surface reaction may be comparable in magnitude, and the observed rate will depend on both (37). Thus, when metals dissolve, the dissolution process consists of several steps, each of which may be the rate determining one.

Nernst (35) postulated that when a solid is in contact with a moving liquid, a stationary layer of liquid will be present on the surface of the metal, and that transport of reactant through this "diffusion layer" can take place by diffusion only. The reaction rate $\frac{dn}{dt}$ is then given by Fick's law,

$$\frac{dn}{dt} = \frac{DA}{\delta}(c_o - c), \qquad (3)$$

where D is the diffusion coefficient, A the surface area, $(c_o - c)$ the concentration difference between the solution in the bulk and the solution at the surface of the solid, and δ the thickness of the diffusion layer. The thickness δ will depend on the velocity of liquid past the surface of the solid, i.e., on the rate of agitation. Equation 3 is analogous to the equation for the rate of a first order chemical reaction

$$\frac{dn}{dt} = kA(c_o - c) \qquad (4)$$

where k is the rate constant. When c is very small compared to c_o, as when magnesium dissolves in hydrochloric acid, Equation 4 becomes identical with Equation 2,

$$\frac{dn}{dt} = kc \qquad (2)$$

where $\frac{dn}{dt}$ is the dissolution rate per unit area. Combination of Equations

3 and 4 gives

$$k = \frac{D}{\delta} \qquad (5)$$

i.e., the rate constant is inversely proportional to the thickness of the diffusion layer.

Numerous investigators have reported evidence in favor of this theory[17]. The rate constant has been found to vary with the rate of agitation according to a power function

$$k = \text{const. } U^n \qquad (6)$$

where U is the rate of agitation, and n a constant with values ranging from 0.5 to 1, according to the type of apparatus and stirring used.

Attempts to evaluate the effect of agitation on the thickness of the diffusion layer by hydrodynamical methods have been made by Eucken (38), Levich (39, 40), and Agar (41). They have shown that the essential feature of the Nernst theory is correct, namely that there exists a very steep concentration gradient across a thin layer of solution contingent to the surface of the solid. This layer is, however, not immobile, as postulated by Nernst; it is rather in a laminar state of flow, i.e., the velocity component normal to the surface is zero, while the tangential component increases from zero with the distance from the surface according to a parabolic relation. At low liquid velocities, and in the absence of conditions that may cause turbulence, the state of flow will be laminar throughout the liquid. This condition is hardly ever realized in the case of diffusion controlled reactions, since convection currents due to

---

[17] Reviews of the voluminous literature on the subject are given by Taylor (42) and Levich (39).

gradients in temperature and gravity will always be present. Wagner (43, 44) found a correlation between the dissolution rate of sodium chloride in water and the convection currents set up by the concentrated solution near the surface of the salt crystals. If gas bubbles are evolved during the reaction, they will be particularly effective in setting up convection currents.

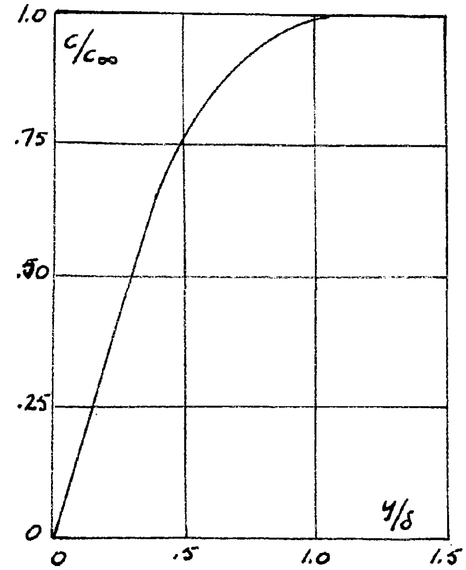
As the liquid velocity increases, the flow in the main stream becomes turbulent, while a layer of liquid in contact with the surface remains in an essentially laminar condition (Prandtl's boundary layer). Turbulence sets in when the Reynold's number reaches a critical value. Reynold's number (Re) is a dimensionless quantity defined as

$$Re = \frac{Ul\rho}{\eta} \tag{7}$$

where l is a linear dimension characteristic of the surface, η the viscosity, and ρ the density of the liquid. The critical Reynold's number at which turbulence appears depends on the geometry of the flow system. For flow in straight channels values of about 2000 are found.

At very high Reynold's numbers, of the order $\sim 10^5$, the flow within the boundary layer becomes turbulent, and laminar motion is restricted to a "viscous (laminar) sub-layer" in contact with the surface (39). With perturbed flow and rough surfaces the transition from laminar to viscous flow in the boundary layer may take place at Reynold's numbers considerably lower than 10^5.

Inside the boundary layer there is a small amount of turbulence which increases with the distance from the surface of the solid. At a certain distance, which corresponds to the thickness of the Nernst diffusion layer, the transport of reagent by diffusion and by convection are equal in magnitude. Inside the diffusion layer the reagent is transported essentially by diffusion along a very steep concentration gradient; outside it diffusion is negligible in comparison with convection, and the concentration is essentially constant.



Change in concentration with distance from the surface (Levich (39)).

Levich (39) has pointed out that the diffusion layer is several times thinner than the laminar boundary layer due to the smallness of the diffusion coefficient in aqueous solutions. The thermal boundary layer, however, is about equal in thickness to the laminar boundary layer. For this reason, the use of analogies between the related processes of diffusion and heat transfer is somewhat restricted.

Levich (39) has calculated the thickness of the diffusion layer for a flat plate in a moving liquid and for a rotating disc in a stagnant liquid for laminar boundary layer conditions. He found in both cases that the thickness of the diffusion layer was inversely proportional to the square root of Reynold's number (i.e., the exponent n in Equation 6 was equal to 0.5), in good agreement with experiment. For the case of a rotating cylinder, the difficulties in solving the equations of flow appear almost insurmountable. No solutions have been found for turbulent conditions in the boundary layer. Levich considers, however, that values of the exponent n in the range of 0.5 to 1, are to be expected.

Due to a certain amount of drag within the turbulent region of flow, the velocity of liquid past the surface of the solid will be less at the outside of the boundary layer than it is in the main stream. In the case of a rotating cylinder, this means that the difference in velocity between the surface of the cylinder and the turbulent region of flow is less than the peripheral velocity of the cylinder. The magnitude of this difference in velocity (often referred to as "swirl") depends on the geometry of the system. By introducing baffles it can be reduced practically to zero. Although no studies have been made on the effect of baffling on the exponent n in Equation 6, other work on agitation suggests that n increases with the degree of baffling until it is unity at fully baffled conditions[18]. Thus, it seems possible that the exponent n in Equation 6 is a measure of the degree of "swirl", and that the difference in velocity (U') between

---

[18] Dr. D. F. Mack, Lehigh University, Department of Chemistry, (private communication).

the surface of the solid and the solution at the outside of the boundary layer is given by the relation

$$U' \sim \text{const. } U^n \qquad (8)$$

where U is the rate of agitation.

2. The Dissolution Rate of Magnesium in Hydrochloric Acid. The results of the dissolution rate measurements are in general agreement with data reported in the literature and with the theory of diffusion controlled dissolution reactions. Thus, the determined activation energy of 4100 cal/mol agrees with the value of 4110 cal/mol determined by Coates (23). For the lower acid concentrations the dissolution rate increases with the rate of agitation to a power of 0.71. King and Braverman (15) reported that the dissolution rate increases linearly with the rate of agitation for peripheral speeds above 5000 cm./min. When their data are plotted on logarithmic coordinates, however, a straight line with a slope of about 0.77 is obtained. These values are in agreement with previous determinations of the effect of agitation on the rate of diffusion controlled reactions, which have given values of the exponent ranging from 0.5 to 1 depending on the experimental arrangement (39).

Alloying elements and impurities in the metal, as well as additions of metal salts to the solution, seem to affect the dissolution rate only insofar as they interfere with the rate of acid transfer to the metal by diffusion and convection. Thus, the bump in the dissolution rate - concentration curve for the J-1 alloy (Fig. 9) at acid concentrations around 0.3 N is explained by the accompanying roughening of the surface of the specimen (cf. Fig. 18). Increasing surface roughness is known to increase the turbulence within the laminar boundary layer, with a consequent increase in the rate of acid transfer by convection.

The effect on the dissolution rate of the precipitates of iron, copper, and manganese which are formed in the more dilute acids could not be determined accurately because of their interference with the weight loss determinations. However, heavy precipitates of iron seemed to increase the dissolution rate slightly, probably on account of an increase in the surface roughness. Since aluminum hydroxide is precipitated at a pH of about 4.1 (28) it was expected that additions of aluminum ions to the acid might lead to the precipitation of aluminum hydroxide within the diffusion layer. Such a precipitation was found to take place in the more dilute acids (below 0.1 N) containing 0.5 mol/liter of aluminum chloride. In the more concentrated acids no visible precipitate was formed. Fig. 10 shows that the break in the dissolution rate - concentration curve which appears with pure acids does not appear with acids containing 0.5 mol/liter of aluminum chloride. For reasons to be discussed later, this is taken as an indication that precipitation of aluminum chloride within the diffusion layer takes place even at acid concentrations above 0.1 N. A further indication of this is given by the decrease in dissolution rate (resp. rate constant) of about 10% which is caused by the addition of aluminum chloride (Fig. 10 and Table IX). This may be partly due to an increase in the viscosity which decreases the diffusion coefficient of the acid (no literature data available). However, a comparison of Figs. 9 and 10 shows that a similar lowering of the dissolution rate is observed with the J-1 alloy (which contains 6.2%

aluminum) in pure acid at concentrations around 0.1 N where the conditions are comparable. This is taken as an indication that the decrease in dissolution rate is due to the shielding effect of an aluminum hydroxide gel which is precipitated close to the surface of the metal.

3. The Stirring Effect of the Hydrogen Bubbles. The breaks in the dissolution rate - concentration curves (Fig. 1) at the higher acid concentrations have not been reported in the literature. Coates (23) determined the curve for no agitation for acid concentrations up to 0.5 N, and attributed the increase in slope at concentrations approaching 0.5 N to heating effects. Although the local temperature increase, which becomes appreciable in this concentration range (cf. Fig. 8), has an effect in increasing the dissolution rate, it cannot alone account for the breaks in the dissolution rate - concentration curves. Thus, at 947 r.p.m. in 0.5 N acid the dissolution rate is 1.8 times higher than it would be if the break did not occur. If local heating alone were the cause, this increase in dissolution rate would require a temperature increase of more than 25°C. However, the actual temperature difference between the specimen and the solution is only about 3.5°C. At lower rates of agitation this discrepancy becomes even larger.

At the higher acid concentrations the hydrogen evolution becomes vigorous, and it seems probable that the breaks in the dissolution rate - concentration curves (Fig. 1) are caused by the stirring action of the hydrogen bubbles. This explanation is consistent with the observation that the effect of external agitation becomes less as the dissolution rate (and with it the rate of hydrogen evolution) increases. The stirring efficiency of the hydrogen bubbles can best be evaluated from Fig. 2 where the rate constant is plotted against the rate of dissolution. At a given temperature the rate constant is a measure of the effective rate of agitation, while the dissolution rate is a measure of the rate of hydrogen evolution. Hence, Fig. 2 is in effect a plot of the total stirring efficiency against the rate of gas evolution at different levels of external agitation.

From Fig. 2 it appears that the dissolution rate at which the stirring action of the gas bubbles becomes significant increases with increasing speed of rotation, as indicated by the broken line which has a slope of 0.5. When the dissolution rates corresponding to the intercepts of this line with the curves in Fig. 2 is plotted against the corresponding speeds of rotation on logarithmic coordinates (Fig. 3), a straight line with a slope of 1.40 is obtained. Accordingly, the dissolution rate at which the stirring action of the gas bubbles becomes significant increases with the speed of rotation to a power of 1.40. Figs. 2 and 3 show that as the rate of agitation is increased, the stirring action of the gas bubbles is suppressed up to quite appreciable rates of hydrogen evolution. This explains why previous investigators who used dilute acids did not find any stirring effect due to the gas bubbles (36).

For dissolution rates above 1 mg/sq.cm.min. the curve for no stirring in Fig. 2 appears to be a straight line with a slope of 0.59. Accordingly, the rate constant increases with the rate of hydrogen evolution (V) according to a power function

$$k = \text{const.}\ V^{0.59}. \qquad (9)$$

This increase in the rate constant with the dissolution rate is accompanied by an appreciable increase in temperature at the solution - metal interface (cf. Fig. 8). An accurate correction for this temperature increase cannot be made since the temperature distribution in the solution close to the surface of the metal is not known. However, an estimate based on data from Tables VII and VIII indicates that such a correction would reduce the exponent in Equation 9 to a value approaching 0.5. Accordingly, the stirring action of the gas bubbles is approximately proportional to the square root of the rate of gas evolution. This relationship does not hold at low rates of gas evolution. The curve for no agitation in Fig. 2 indicates that as the dissolution rate increases, the stirring action of the gas bubbles becomes increasingly important as compared to the stirring due to thermal and gravitational convection currents which predominate at the lowest dissolution rates. At dissolution rates above 1 mg/sq.cm.min. (corresponding to about 1 ml H_2/sq.cm.min.) the stirring action of the gas bubbles predominates.

The square root relationship between the stirring effect of the gas bubbles and the rate of gas evolution is in formal agreement with the inverse square root relationship between the rate of agitation and the thickness of the diffusion layer which was derived by Levich (cf. p. 30) for special conditions of flow. This correlation is, however, hardly more than a coincidence, on account of the differences in type of stirring in the two cases. The calculations of Levich are valid for special cases of liquid flow past the surface of the metal, where an increase in velocity results in a decrease in thickness of the diffusion layer. On the other hand, Equation 9 applies to a condition where the stirring action is due to gas bubbles which continuously break away from the surface of the metal.

Since the space vacated by them at the solution - metal interface will be filled by acid flowing in from the outside, the stirring action of the gas bubbles will be one of supplying acid to the surface of the metal by creating convective currents rather than by reducing the thickness of a laminar diffusion layer[19].

When external stirring is applied, a laminar boundary layer will be formed. Because of the high rate of shear within this layer, it seems probable that the hydrogen bubbles will be detached from the magnesium surface while their diameter is small compared to the thickness of the diffusion layer. Such small bubbles may traverse the boundary layer without causing any appreciable degree of turbulence, until the rate of gas evolution reaches a certain limiting value. This explanation is in reasonable accord with the curves in Fig. 2. Thus, at 6400 r.p.m. a rate of hydrogen evolution of 10 ml/sq.cm.min. (corresponding to about 10 mg/sq.cm.min.) has no effect on the rate constant. The limiting value of gas evolution at which the stirring action of the gas bubbles becomes significant would, according to the explanation given above, be expected to depend on the rate of shear in the solution at the surface of the metal. An approximate measure of this shearing rate is given by the relation

$$\frac{dv}{dx} \sim \text{const.} \frac{U'}{\delta} \qquad (10)$$

---

[19] Coates (23) attributed the increase in rate constant at no external stirring within the range of acid concentrations from 0.04 to 0.2 N to the stirring action of the hydrogen bubbles. His calculations showed that the stirring action of the gas bubbles increased with the rate of gas evolution to a power of about 0.3. This result is in agreement with hydrodynamical calculations by Eucken (38) according to which the thickness of the diffusion layer varies inversely as the one-third power of the stirring rate. However, Levich (39) has later shown that Eucken's calculations were in error due to incorrect assumptions.

Combination with Equations 5, 6, and 8 gives

$$\frac{dv}{dx} \sim \text{const.} \frac{U^n}{U^{-n}} = \text{const.}\ U^{2n} \qquad (11)$$

Introducing the experimental value 0.71 for the exponent n, we obtain

$$\frac{dv}{dx} \sim \text{const.}\ U^{1.42} \qquad (12)$$

The dissolution rate at which the stirring action of the hydrogen bubbles becomes significant was found to increase with the rate of agitation to a power of 1.4 (cf. p. 34). The agreement between this exponent and the exponent in Equation 12 suggests that the efficiency of the external stirring in suppressing the stirring action of the gas bubbles is proportional to the rate of shear in the solution contiguous to the surface of the metal.

The break in the dissolution rate - concentration curve for 1364 r.p.m. did not appear when 0.5 mol/liter of aluminum chloride was added to the acid (Fig. 10)[20]. In pure acids very large hydrogen bubbles were formed at the higher acid concentrations (Fig. 19). In acids containing aluminum chloride, however, the hydrogen bubbles were small even at the highest acid concentrations, (Fig. 20). It seems probable that the bubble growth in acids containing aluminum chloride is restricted by an aluminum hydroxide gel which is precipitated within the diffusion layer in the low pH region at the surface of the metal. Thus the hydrogen bubbles will, even at the highest dissolution rates, be detached from the surface before they can coalesce to form bubbles which are sufficiently large to disrupt the laminar flow in the diffusion layer.

---

[20] The small increase in rate constant at the highest acid concentrations (Table IX) is probably due to the increase in temperature.

At acid concentrations of about 1.5 N, the increase in the dissolution rate with the acid concentration at no stirring (and to a smaller extent at 1364 r.p.m.) becomes less than at the lower acid concentrations (Fig. 1). This phenomenon is evidently due to the violent evolution of hydrogen (more than 60 ml/sq.cm.min.) which reduces the dissolution rate by preventing the acid from coming in contact with the metal. Agitation reduces this effect by removing the gas more rapidly. From Fig. 4 it is seen that the solution heat-treated specimens (of beryllium-settled magnesium) dissolve slower than the as-extruded specimens in the more concentrated acids. At these high concentrations the attack on the magnesium is non-uniform, apparently because the rate of attack depends on the grain orientation. Since the solution heat-treatment resulted in considerable grain growth, the resulting differences in surface roughness between the solution heat-treated specimens and the as-extruded ones will change the conditions for bubble formation as well as the efficiency of the hydrogen gas in reducing the contact area between the acid and the metal. These circumstances may account for the reduction in dissolution rate caused by the solution heat-treatment.

The poor reproducibility at 360 r.p.m. is probably due to an instability in the dissolution process. At such low rates of agitation the laminar flow in the boundary layer will be rather unstable, and the ability of the hydrogen bubbles in disrupting it may be appreciably influenced by minor differences in experimental conditions between different runs, such as the small amount of excentricity in mounting the specimen, etc.

B. Electrode Potentials.

1. The Electrochemical Nature of Metallic Corrosion. In 1830 de la Rive (45) observed that the dissolution rate of such metals as zinc, aluminum, cadmium, and iron, as measured by the rate of hydrogen evolution, is much greater when the metals contain small amounts of impurities than when they are relatively pure. De la Rive attributed this increase in the dissolution rate to the action of a current set up in "local cells" consisting of an anodic matrix and cathodic impurities. This theory of local-cell action was neglected until Ericson-Auren in 1901, at the suggestion of Palmaer (46), 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 overpotential (Caspari). At about the same time Whitney (47), Cushman (48), and Heyn and Bauer (49) also proposed an electrochemical mechanism for the dissolution and corrosion of metals. Since this time the electrochemical theory of corrosion has been developed through the work of numerous investigators until it, at the present time, is generally accepted.

a. The Electrode Potential. When a metal is immersed in an electrolytic solution, a potential difference is found to exist between the metal and the solution. This potential difference, the electrode potential, is established by electrochemical reactions which take place at the metal - solution interface. If a metal electrode is in thermodynamic equilibrium with a solution of its own ions, the electrode reaction, which proceeds with equal velocities in both directions, is

$$Me_{(s)} - n\,\theta \rightleftharpoons Me_{(l)}^{n+} \qquad (13)$$

The electrode potential (E) is given in Nernst's equation

$$E = E^{o} + \frac{RT}{nF} \ln a_{Me^{n+}} \qquad (14)$$

where E^{o} is the standard electrode potential which is measured when the activity $a_{Me^{n+}}$ of the metal ions is unity[21].

In general, if the electrode reaction is

$$A + n\Theta \rightleftharpoons B, \qquad (15)$$

the reversible electrode potential is given by

$$E = E^{o} - \frac{RT}{nF} \ln \frac{a_A}{a_B} \qquad (16)$$

b. Polarization. When a galvanic current is passed through a reversible electrode, the electrode potential may be shifted in a positive or negative direction depending on whether the electrode is the anode or the cathode in the galvanic couple. This change in electrode potential from its reversible value which is caused by the flow of a polarizing current is called polarization. The measured polarization comprises three different terms, viz., (1) activation overvoltage, (2) concentration polarization, and (3) resistance polarization.

The activation overvoltage is the difference between the potential drop across the metal - solution interface of the polarized electrode and the corresponding reversible potential difference. In a number of cases,

---

[21] Since no way has been found to measure the potential of single electrodes, electrode potentials are given with reference to that of a standard electrode, usually that of the hydrogen electrode, whose standard potential by definition is zero. In the present report the electrode potentials are given with reference to that of the 0.1 N calomel electrode, which is positive to standard hydrogen electrode by an EMF of 0.3338 V (50).

notably in the case of hydrogen discharge, the activation overvoltage (η) is given by Tafel's equation

$$\eta = a + b \log I \tag{17}$$

where a and b are constants, and I the polarizing current density.

Due to the electrochemical reactions which takes place at a polarized electrode, differences in concentration will be established in the solution. Thus, if the electrode reaction is the discharge of hydrogen ions, the solution at the surface of the electrode will be depleted of hydrogen ions and, as a result, a potential difference which enters into the measured overvoltage is established between the surface of the electrode and the solution in the bulk. The magnitude of this potential difference, the concentration polarization (P_c), is given by Nernst's equation

$$P_c = \frac{RT}{F} \ln \frac{a_H}{a_{H'}} \tag{18}$$

where a_H and $a_{H'}$ are the hydrogen ion activities in the bulk of the solution and at the electrode surface respectively.

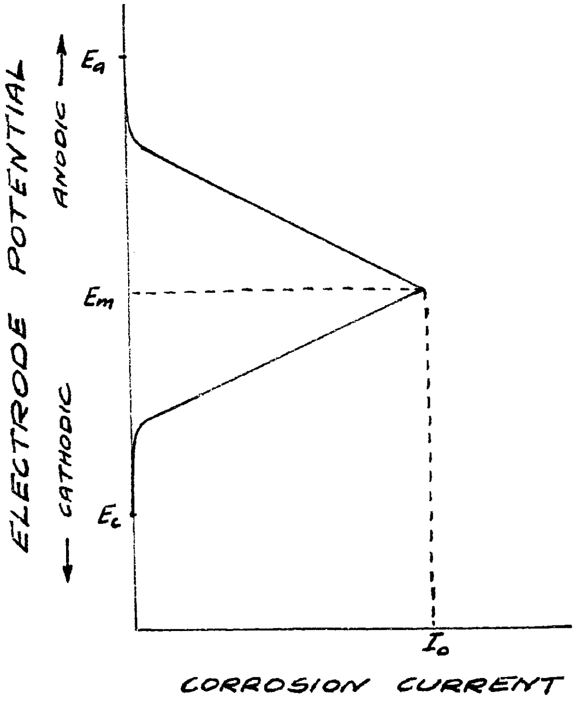
The flow of a current through the solution also gives rise to an ohmic potential drop between the solution at the electrode surface and the solution at the tip of the salt bridge to the reference electrode. This resistance overpotential (often referred to as the "IR-drop") can be reduced by bringing the tip of the salt bridge close to the surface of the electrode[22].

c. The Electrode Potential of a Corroding Metal. If the reversible electrode potential of a metal which is immersed in an electro-

---

[22] This may, however, change the polarizing conditions and give rise to erroneous potential readings.

lytic solution is negative to the red.-ox. potential of reducible ions or molecules in the solution, the metal may corrode by electrochemical action. Ions of the metal may then go into solution at anodic surface areas, while an equivalent number of electrons are consumed in the cathodic reduction process at cathodic surface areas. Thus, the metal electrode is in effect an array of short-circuited local cells, where a galvanic current equivalent to the dissolution rate flows from the cathodic areas through the metal to the anodic areas and back through the electrolyte. Due to the flow of current, the local anodes polarize to more noble potentials, while the local cathodes polarize to more negative potentials, as indicated in the diagram below. In this diagram E_a and E_c are the reversible electrode potentials of the local anodes and cathodes respectively. E_m is the measured ("mixed") potential of the corroding metal, and



I_o is the corrosion current. The shape of the polarization curves depends on the properties of the anodic and cathodic areas as well as on the electrolyte.

Due to the heterogeneous nature of metallic surfaces, the polarization characteristics of the anodic and cathodic reactions may vary greatly between different areas on the surface of an electrode. Areas of low hydrogen or oxygen overvoltage will become cathodic, as in the case of low overvoltage impurities (iron, copper, etc.) in metals such as zinc and aluminum which themselves have high hydrogen overvoltages. Similarly, areas where the anodic polarization is low will become anodic. In the great majority of cases, the anodic polarization is largely governed by films which cover the surface of the metal. For this reason anodic dissolution is usually found to take place at surface areas where the films are impaired, i.e., around inclusions, at grain boundaries, edges, scratches, etc.

Under certain conditions the overvoltage relationships are such that the cathodic and anodic reactions may proceed at the same surface areas. This is the case when magnesium dissolves in hydrochloric acid, since the electrode potential of magnesium is sufficiently negative to overcome the overvoltage for hydrogen discharge on magnesium. Under these conditions the anodic and cathodic reactions will not be confined to definite surface areas, i.e., there are no local cells. However, Wagner and Traud (51) have shown that the dissolution process even in such cases is electrochemical in nature. The different surface areas will alternately be anodic and cathodic, and electrochemical principles will govern the dissolution process as in the cases where the local anodes and cathodes are fixed in a stationary pattern of local cells.

2. The Electrode Potential of Magnesium in Hydrochloric Acid. As shown in Fig. 11, the electrode potential of beryllium-settled magnesium in hydrochloric acid becomes more anodic as the dissolution rate increases until, at a certain point, it levels off to a constant (or slightly decreasing) value. The anomalous results obtained at no stirring and at 947 r.p.m. are apparently connected with the irregularities in the dissolution process at the lower rates of agitation. At the higher rates of agitation, however, the potentials fall on the same line within the limits of reproducibility.

The experiments with additions of ferric, cupric, and manganous chlorides to the acid show that the ions of these metals are plated out on the magnesium by cementation at the lower acid concentrations, and that the formation of these precipitates is accompanied by a marked shift in the electrode potential to more cathodic values (Figs. 14 and 15). As shown by Figs. 21 to 24, a similar kind of precipitate appears on the specimens of beryllium-settled magnesium in pure acids. The amount of this precipitate decreases with increasing acid concentration until it has practically disappeared at the acid concentration where the electrode potential levels off to a constant value. These observations indicate that the changes in electrode potential at the lower acid concentrations are connected with a replating of impurities of heavy metals (iron, copper, etc.) on the surface of the magnesium.

Gatty and Spooner (2) concluded that the surface of magnesium dissolving in acids is covered by a cathodic "hydride film", while the anodic areas are located at the bottom of "pores" in this film. According to their view, the anodes will be strongly polarized due to a high resistance in these "pores", and the electrode potential will be determined by the potential of the cathodic area. Coates (23) has pointed out that, as a necessary consequence of the theory of diffusion controlled reactions, the hydrogen ion concentration at the surface of the metal will be reduced. Based on measurements of critical current densities (52), he concluded that the pH at the magnesium surface is raised to a point where a transitory formation of magnesium hydroxide may take place. As a consequence of this observation it seems necessary to assume that the magnesium surface is at least partially covered by a film of magnesium hydroxide, and that the cathodic hydrogen evolution takes place at surface areas where this film is destroyed by acid diffusing in from the outside. Under these conditions, the IR-drop in the solution will be small, and the electrode potential will be given by the potential of the cathodic areas, which is negative to the reversible hydrogen electrode in the solution under consideration by an amount corresponding to the cathodic polarization (activation overvoltage and concentration polarization). Hence

$$E_m = E_H - \eta - P_c - E_{cal.} \qquad (19)$$

where E_H is the potential of the reversible hydrogen electrode and $E_{cal.}$ the potential of the o.1 N calomel reference electrode. Introducing Equations 16 and 18 ($E_H^o = 0$), we obtain

$$E_m = \frac{RT}{F} \ln a_H - \eta - \frac{RT}{F} \ln \frac{a_H}{a_{H'}} - E_{cal.} \qquad (20)$$

Introducing $pH' = - \log a'_H$, we obtain

$$E_m = - \frac{2.3RT}{F} pH' - \eta - E_{cal.} \qquad (21)$$

where pH' is the pH at the metal-solution interface. According to Britton (28), magnesium hydroxyde is precipitated at a pH of about 10.5. Introducing this value of pH', and the value of 0.3338 V for $E_{cal.}$, we obtain

$$E_m = -\eta - 0.95 \tag{22}$$

From Fig. 11 is seen that the electrode potential for dissolution rates above 1 mg/sq.cm.min.[23] levels off to an approximately constant value of -1.96 V. Inserted in Equation 22, this value of E_m gives a value of about 1 volt for the hydrogen overvoltage. This may mean that the cathodic areas increase in proportion with the corrosion current with the result that the cathodic current density, and hence the cathodic overvoltage, stays constant. This is, however, not necessarily the case, since Hickling and Salt (53) have shown that the hydrogen overvoltage of high overvoltage metals such as mercury, cadmium, lead, etc., approach constant maximum values at high current densities. Coates (23) measured the hydrogen overvoltage of magnesium in 0.2 N sulphuric acid for current densities up to 1.5 amp./sq.cm. using an electronic interrupter method in order to eliminate the IR-drop and the concentration polarization. He found that the overvoltage increased from about 1 V at a current density of 0.1 amp./sq.cm. (corresponding to the dissolution rate on open circuit) to a

---

[23] A dissolution rate of 1 mg/sq.cm.min. is according to Faraday's law equivalent to a current density of 0.132 amp.sq.cm. It should be noted that current densities calculated by this conversion represent anodic as well as cathodic current densities per sq.cm. of electrode surface. The true anodic and cathodic current densities cannot be calculated unless the actual sizes of the anodic and cathodic areas are known.

constant value of about 1.3 amp./sq.cm. at current densities above 1 amp.sq.cm. These values are, however, rather doubtful on account of the interference of the surface films which form at high cathodic current densities (cf. p. 24). It seems more probable that the overvoltage of about 1 V which is indicated by Equation 22 for dissolution rates above 1 mg/sq.cm.min. represents the hydrogen overvoltage of magnesium at the current densities in consideration (above 0.15 amp./sq.cm.).

At dissolution rates below 1 mg/sq.cm.min. the electrode potential changes to more cathodic values as the dissolution rate decreases. This is clearly due to the impurities of heavy metals (iron, copper, etc.) which are replated on the surface of the magnesium in increasing amounts as the dissolution rate decreases. Since these metals have hydrogen overvoltages considerably lower than that of magnesium (54), they will, when precipitated on the surface of the magnesium, become active as cathodes. As a result the electrode potential will become more noble as the surface coverage increases until it approaches a constant value which corresponds to the hydrogen overvoltage of the precipitate (cf. Fig. 15).

Fig. 14 shows that with increasing additions of ferric chloride to the weakest acids, the initial change in potential to more cathodic potentials is soon reversed, and the potentials slowly become more anodic. This is evidently due to a precipitation of ferric hydroxide, as indicated by the brown color of the precipitates formed in the weakest acids. In the more concentrated acids the precipitates were black. The effect of precipitated hydroxides on the electrode potential is also shown by the effect of 0.5 M aluminum chloride in the acid in changing the potentials about 0.7 V in an anodic direction over the whole range of dissolution rates (Fig. 14).

From Fig. 11 is seen that the electrode potential of beryllium-settled magnesium for different rates of agitation (above 1364 r.p.m.) fall on the same line when plotted against the dissolution rate. This indicates that the amounts of heavy metals plated out by cementation decrease as the rate of the competing process of hydrogen evolution increases. On the other hand, the precipitation increases with the concentration of heavy metal ions in the solution. The amounts of precipitate formed also depends on the metal which is being plated out. Thus, even small additions of cupric chloride to 0.1 N acid forms a heavy precipitate. With ferric chloride the precipitation is substantially less, and with manganous chloride a visible precipitate forms only after relatively large additions have been made. This behavior is reflected in the potential curves in Fig. 15. From Fig. 12 is seen that the electrode potential at the higher dissolution rates is not appreciably affected by the temperature. At the lower dissolution rates, however, the potentials are shifted in a cathodic direction, probably because an increase in temperature favors the replating of impurities.

Although it has long been known that low overvoltage impurities is a controlling factor in the dissolution of metals, the effect has not been reported previously in the case of magnesium dissolving in acids. It has been suggested, however, that the replating of impurities may be of importance in connection with the corrosion of magnesium in neutral solutions.

The effect of different alloy compositions on the electrode potential is shown in Fig. 13. The cathodic potentials of the J-1 alloy are evidently due to the presence of 0.27% manganese as a separate phase in this alloy. Thus, the manganese inclusions may account for the potential shift of about 0.1 V in a cathodic direction at the higher dissolution rates where no replating takes place. At the lower acid concentrations a heavy precipitate is formed, which probably to a large extent consists of manganese inclusions which accumulate on the surface as the magnesium matrix dissolves.

The somewhat higher impurity content of cell magnesium as compared with beryllium-settled magnesium (cf. Table I), is seen to retard the approach of the electrode potential towards a constant value as the dissolution rate increases (Fig. 13). The solution heat treatment of the beryllium-settled metal appears to change the electrode potential to more anodic values at the lower dissolution rates (Fig. 13). This heat treatment will partially or completely put into solid solution metallic impurities which may be present as separate phases in the as-extruded metal. Since such particles are likely to be preferred sites for the replating of low overvoltage impurities, the elimination of second phase constituents in the solution heat treatment may reduce the amounts of replated impurities and thus give rise to more anodic potentials. A comparison of Figs. 22 and 25 reveals that the replated impurities tend to accumulate at separate points rather than uniformly cover the surface.

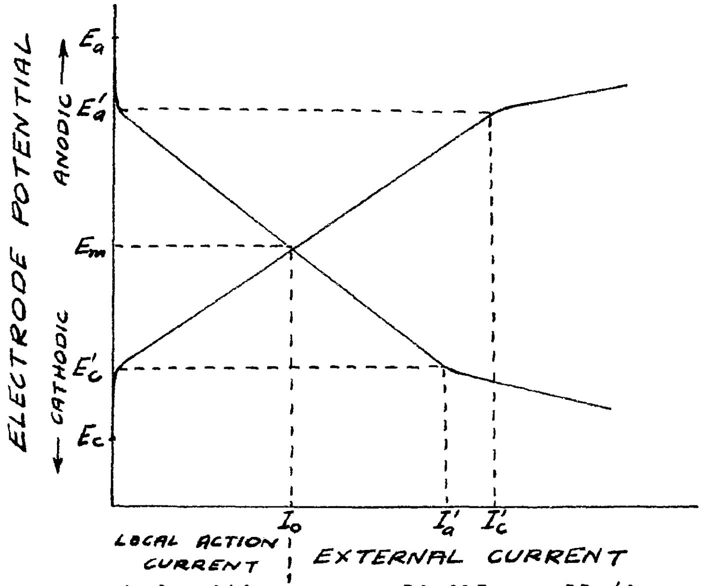
It is also seen that the solution heat treatment resulted in a substantial reducion in number and size of the areas of replated impurities, in accord with the explanation given above.

From Fig. 13 is seen that the potentials of the distilled magnesium are considerably anodic to those of the beryllium-settled alloy. Figs. 27 and 28 which show the surface appearance of the distilled magnesium after exposure to two acids of different concentrations indicate that some kind of a surface film has been formed. This film must be somewhat similar in properties to the film formed on beryllium-settled magnesium in acids containing aluminum chloride, as shown by the similarities in surface appearance in the two cases after immersion in more concentrated acids (Figs. 26 and 28), and also by a comparison of the effects of the two films on the electrode potentials (Figs. 13 and 14). The only possible cause of such a film formation on the distilled magnesium seems to be the silicon content of 0.01% of the metal. The silicon will, when going into solution, form a silica gel which is insoluble in acids and thus may accumulate on the surface of the magnesium.

C. External Polarization.

1. Theoretical Considerations. The electrochemical nature of metallic corrosion is clearly demonstrated by the changes in dissolution rate and electrode potentials which are observed when a corroding metal is made anodic or cathodic by an external polarizing current. The information obtained in such polarization studies may be of great value in the evaluation of the mechanism of the corrosion process. The reduction

in local action, which in many cases is observed when the specimen is made anodic, is called the "difference effect", whereas the reduction in local action which is usually observed when the specimen is made cathodic is called "cathodic protection" (cf. p. 23). These effects have been attributed to the increases in anodic (52, 53, 54) and cathodic (55) polarization respectively which are caused by the applied currents. These conditions may be represented by the diagram given below (56). In this diagram E'_a and E'_c represent the "open circuit" potentials of the local anodes and cathodes, which are measured when the anodic resp. cathodic current densities are negligibly small (i.e., the anodic resp. cathodic polarization corresponds to the a-term in Tafel's equation (Equation 17)). I_o and E_m represent the dissolution rate and the electrode potential with no external polarization (cf. diagram on p. 42).



When the specimen is made anodic, the anodic polarization will increase with a consequent decrease in local cell action. At an applied current density of I'_a the local anodes have been polarized to the open circuit potential of the local cathodes (E'_c). As a result local action is suppressed, and the dissolution rate is equivalent to the applied current density. Similarly, when the specimen is made cathodic, the cathodic polarization increases and the local action decreases until, at a current density of I'_c, the local cathodes have been polarized to the open circuit potential of the local anodes (E'_a), with the result that no further dissolution can take place. The current densities at which local action is suppressed are usually indicated by a change in slope of the polarization curves (cf. the above diagram).

According to this explanation, the effect of external polarization in suppressing local action depends entirely on the polarizing characteristics of the local anodes and cathodes. Thus the widely used method of making metal structures cathodic by external polarization in order to eliminate corrosion (cathodic protection) is only effective when the local cathodes are readily polarized. Streicher (30, 57, 58) has shown that when aluminum dissolves in 0.3 N sodium hydroxide, the local anodes are readily polarized, whereas the local cathodes are virtually non-polarizable. Accordingly, the difference effect is very pronounced, and local action is suppressed at relatively low anodic current densities. On the other hand, the dissolution rate is hardly affected by externally applied cathodic currents.

In some cases the dissolution rate due to local action is increased as a result of external polarization, particularly at relatively high current densities. Thus, magnesium in neutral salt solutions (9, 59) and aluminum in hydrochloric acid (32) exhibit a negative difference effect, apparently because the increase in anodic dissolution results in a damage of protective surface films (9, 59). Similarly, the dissolution rate of aluminum in neutral salt solutions is increased when the specimens are made cathodic, apparently because the consumption of hydrogen ions in the cathodic process leads to an increase in the hydroxyl ion concentration at the surface of the metal with the result that the protective films are attacked (60, 61, 62).

2. Effect of External Polarization on the Dissolution of Magnesium in Hydrochloric Acid. As explained in the preceding section, the effect of external polarization on the dissolution rate due to local action of a corroding metal has been attributed to the effect of the external current on the polarization of the local anodes and cathodes. This explanation applies to corrosion reactions where the dissolution rate is determined by the electrochemical reactions at the surface of the metal, i.e., the anodic and cathodic processes and the conduction of current through the solution. Under these conditions the dissolution rate due to local action will be reduced when either the anodic or cathodic polarization is increased by an external polarizing current. In the case of magnesium dissolving in hydrochloric acid, however, the dissolution rate is determined by the rate of diffusion of hydrogen ions to the surface of the metal. For this reason, an external polarizing current would be expected to affect the dissolution rate due to local action only insofar as it affects the rate of transport of hydrogen ions to the surface of the metal by diffusion and migration.

Fig. 16 shows the effect of external polarization on the dissolution rate of magnesium in 0.045 N hydrochloric acid at 1364 r.p.m. and 25°C. When the specimen is made anodic, the dissolution rate is seen to increase linearly with the applied current density up to a current density of about 0.07 amp./sq.cm. The broken line indicates what the increase in dissolution rate would be if it were equivalent to the applied current density. A comparison of the slopes of these two lines shows that the increase in dissolution rate when the specimen is made anodic is equivalent to about one-third of the applied current density. Similarly, when the specimen is made cathodic, the dissolution rate appears to decrease by an amount which is equivalent to about one-third of the applied current density for current densities up to about 0.07 amp./sq.cm.

When magnesium dissolves in hydrochloric acid, hydrogen ions diffuse from the bulk of the solution to the surface of the metal, while an equivalent amount of magnesium ions diffuse in the opposite direction. Since these ions carry electrical charges, the two diffusion currents may be regarded as electrical currents, which in effect represent the local cathodic ($I^o_{H^+}$) and anodic ($I^o_{Mg^{++}}$) currents respectively. When an external current (I_e)[24] is applied, its magnitude will be equal to the difference between the anodic and cathodic currents (now denoted by I_{H^+} and $I_{Mg^{++}}$ respectively), i.e.,

$$I_{Mg^{++}} - I_{H^+} = I_e \qquad (23)$$

As explained above, the dissolution rate increases or decreases by an amount equivalent to about one-third of the current density of an applied

---

[24] An anodic polarizing current (I_e) is taken as positive, a cathodic current as negative.

anodic resp. cathodic current. Hence,

$$I_{Mg^{++}} - I^{o}_{Mg^{++}} \sim \frac{1}{3} I_e \tag{24}$$

By combining Equations 23 and 24 we obtain (since $I^{o}_{Mg^{++}} = I^{o}_{H^{+}}$),

$$I_{H^{+}} - I^{o}_{H^{+}} \sim -\frac{2}{3} I_e \tag{25}$$

Equations 24 and 25 are valid when the specimen is made anodic as well as cathodic. This is taken as a strong indication that the effect of external polarization on the dissolution rate of magnesium in hydrochloric acid is related to the effect of the external current on the movement of the current-carrying ions in the diffusion layer rather than to its effect on the polarization of the local anodes and cathodes.

When the specimen is made anodic, the dissolution rate due to local action is given by the cathodic current ($I_{H^{+}}$). Accordingly, the difference effect ($\triangle$), is given by Equation 25, i.e.,

$$\triangle = I^{o}_{H^{+}} - I_{H^{+}} \sim \frac{2}{3} I_e \tag{26}$$

Similarly, when the specimen is made cathodic, the dissolution rate due to local action is given by the anodic current ($I_{Mg^{++}}$). Hence, cathodic protection (C.P.) is given by Equation 24 (a cathodic current has minus sign),

$$(\text{C.P.}) = I^{o}_{Mg^{++}} - I_{Mg^{++}} \sim \frac{1}{3} (-I_e) \tag{27}$$

The relationships shown by Equations 26 and 27 are also brought out by Fig. 17, where the difference effect and cathodic protection are plotted against the applied anodic and cathodic currents respectively. The broken line through the origin indicates what the reduction in dissolution rate due to local action would be if it were equivalent to the applied current density. A comparison of slopes shows that the difference effect and cathodic protection are equivalent to 2/3 resp. 1/3 of the applied current density for current densities up to about 0.07 amp./sq.cm.

Proportionality between the difference effect and the applied current density has been found for zinc in hydrochloric acid (32) and for aluminum in sodium hydroxide solutions (30, 32, 57). However, since these reactions are not under diffusion control, they are not directly comparable to the dissolution of magnesium in hydrochloric acid. Mouquin and Steitz (63) studied the effect of external anodic polarization on the dissolution rate of zinc in hydrochloric acid. In this case the reaction was diffusion controlled since the acid contained an excess of hydrogen peroxide ("cathodic depolarizer"). The results of these investigators indicate that the difference effect for zinc in 0.0054 N hydrochloric acid is proportional to the applied current density up to a dissolution rate which is about equivalent to the dissolution rate at no external polarization (as in the case of magnesium). However, the difference effect seems to be equivalent to about one-half of the applied current, whereas in the case of magnesium the ratio is about two-thirds. The magnitude of this ratio will,in the case of diffusion controlled reactions, probably depend on the valencies and mobilities of the current-carrying ions.

As shown in Fig. 17, the difference effect does not reach its limiting value (complete suppression of local action) which is indicated by the horizontal broken line, but levels off at an applied current density of about 0.07 amp./sq.cm. At this current density a dark precipitate begins to form on the surface of the specimen and, at the same time, the attack on the metal surface becomes very irregular (Fig. 30). When a sample of this precipitate was added to hydrochloric acid, a brief surge of hydrogen evolution was observed before the precipitate dissolved. Apparently the precipitate consists of magnesium hydroxide with embedded particles of magnesium which give the precipitate its dark color.

When the specimen is made cathodic, a precipitate which probably consists of magnesium hydroxide appears on the surface of the metal at current densities higher than 0.07 amp./sq.cm. (Fig. 31). At the same time the decrease in local action with increasing current density becomes less. The decreasing effect of the current in reducing the dissolution rate may be due to the increase in surface roughness caused by the precipitate as well as to the increase in hydrogen evolution as the current density increases. Both of these factors will tend to increase the turbulence within the diffusion layer and thereby increase the supply of hydrogen ions to the surface of the metal. Coates (23) found that the dissolution rate of magnesium in 0.2 N sulphuric acid with no agitation is decreased to some extent when the specimen is made cathodic. His results, however, are inconclusive due to the pronounced stirring effect at no external agitation of the hydrogen bubbles which are liberated in the cathodic process.

Attempts to measure the changes in the electrode potential which are caused by the external polarizing currents were unsuccessful on account of the large IR-drop in the solution which overshadowed any changes that might occur in the electrode potential.

SUMMARY

Following a critical review of the literature on the dissolution of magnesium in solutions of electrolytes, a report is given of an experimental study of the dissolution of magnesium in hydrochloric acid. The dissolution process was studied by measuring dissolution rates and electrode potentials as functions of acid concentration, rate of agitation, temperature, external polarization, alloy composition, and different additions to the acid solution.

1. The results of the dissolution rate measurements are in agreement with the theory of diffusion-controlled-reactions, which requires that the dissolution rate is determined by the rate at which acid is transported to the surface of the metal by diffusion and convection. Thus, impurities in the metal and different additions to the acid affect the dissolution rate only insofar as they affect the physical process of acid transfer, either by forming obstructive films which tend to shield the surface of the metal; by increasing the surface roughness which, in the case of stirred solutions, reduces the thickness of the diffusion layer by increasing the turbulence in the solution; or by increasing the viscosity of the solution with a consequent decrease in the diffusion coefficient of the acid. Diffusion control is also indicated by the temperature coefficient (k_{35}/k_{25}) of 1.24, corresponding to an activation energy of 4100 cal/mol.

2. The theory of diffusion-controlled reactions requires that the dissolution rate is proportional to the acid concentration, and also that it is strongly influenced by agitation. These conditions were found to be fulfilled at the lower acid concentrations and at the higher rates of

agitation (above about 1000 revolutions per minute of the cylindrical specimens, corresponding to peripheral velocities above 3500 cm./min.). At the higher acid concentrations the increase in dissolution rate with increasing acid concentration was more rapid, particularly at the lower rates of agitation. This phenomenon is attributed to the stirring effect of the hydrogen bubbles which are liberated in the dissolution process. While external agitation increases the dissolution rate by reducing the thickness of the diffusion layer, the stirring action of the hydrogen bubbles is considered to be one of creating turbulent convection currents by disrupting the laminar flow in the diffusion layer.

3. With no external agitation the stirring effect of the hydrogen bubbles was found to be about proportional to the square root of the rate of hydrogen evolution. When external agitation is used, the stirring action of the hydrogen bubbles is completely suppressed up to a certain limiting rate of hydrogen evolution. This limiting rate at which the stirring effect of the gas bubbles becomes significant is proportional to the rate of agitation to a power of 1.4. It is suggested that the effect of external agitation in suppressing the stirring action of the hydrogen bubbles depends on the rate of shear in the solution contiguous to the surface of the metal. At the highest acid concentrations (about 1.5 N) the hydrogen evolution becomes so violent that it tends to reduce the dissolution rate by reducing the contact area between the acid and the metal.

4. At low rates of agitation the reproducibility of the dissolution rates is very poor, apparently because the ability of the external agita-

tion to suppress the stirring effect of the hydrogen bubbles is appreciably influenced by minor differences in experimental conditions between different runs.

5. When aluminum chloride was added to the acid, the stirring action of the hydrogen bubbles (at 1364 r.p.m.) was completely suppressed at even the highest acid concentrations, probably because the precipitation of an aluminum hydroxide gel within the diffusion layer prevents the gas bubbles from coalescing to form bubbles which are sufficiently large to disrupt the laminar flow within the diffusion layer.

6. At the lower acid concentrations the magnesium surfaces were uniformly attacked by the acid. With increasing acid concentration the attack became non-uniform, apparently because the rate of attack depends on the orientation of the grains. This effect was very pronounced in acids containing aluminum chloride.

7. A solution heat treatment at 610°C which had no appreciable effect on the dissolution rate at the lower acid concentrations affected a considerable decrease in the dissolution rate at the higher acid concentrations. The heat treatment resulted in considerable grain growth, and in the more concentrated acids where the non-uniform attack develops, the difference in surface roughness caused by the increase in grain size may have changed the conditions for bubble formation as well as the efficiency of the hydrogen gas in reducing the contact area between the acid and the metal, thus reducing the rate of dissolution.

8. The electrode potential of magnesium in hydrochloric acid becomes more anodic as the acid concentration increases until, at a certain acid

concentration, it levels off to a constant value. When the electrode potentials were plotted against the dissolution rate rather than against the acid concentration, the observed values for different rates of agitation above 1364 r.p.m. fell on the same line. At the lower rates of agitation the electrode potentials were irregular, and the reproducibility was poor, probably on account of the instability in the dissolution process at the lower rates of agitation.

9. The observed changes in the electrode potential with the acid concentration are attributed to a replating of metallic impurities on the surface of the magnesium at the lower acid concentrations. The electrode potential is considered to be given by the potential of the cathodic surface areas (2, 23), which is negative to the reversible hydrogen electrode in the solution under consideration by an amount which corresponds to the hydrogen overvoltage of the cathodic areas and a concentration polarization term which corresponds to the difference in hydrogen ion concentration between the solution at the surface of the metal and the solution in the bulk. In the more concentrated acids where the electrode potential does not vary with the acid concentration, the amounts of replated impurities are nominal, and the cathodic evolution of hydrogen takes place at the magnesium surface. With decreasing acid concentration impurities of iron, copper, manganese, etc., are replated in increasing quantities on the magnesium surface. Since the hydrogen overvoltages of these metals are considerably lower than that of magnesium, the electrode potential will be shifted to more cathodic values as the amounts of replated impurities on the magnesium surface increase. This explanation is supported by microscopic evidence which shows that increasing amounts of a

dark precipitate accumulate on the magnesium surface as the acid concentration decreases. It is also shown that when small amounts of ferric, cupric, or manganous chloride are added to the acid, the corresponding metal is plated out on the magnesium by cementation with the result that the electrode potential is shifted to more cathodic values. The precipitation of the heavy metals decreases with increasing acid concentration until it is completely suppressed.

10. When magnesium dissolving in hydrochloric acid is made anodic in an external circuit, the dissolution rate due to local action is decreased by an amount which is equivalent to about two-thirds of the applied current density (i.e., the "difference effect" is positive). Before the applied current density can be increased to a point where local action is suppressed, a film of magnesium hydroxide is precipitated on the magnesium surface, and the attack on the surface becomes irregular with particles of magnesium being dislodged and embedded in the magnesium hydroxide film. When the specimen is made cathodic, the dissolution rate due to local action is decreased by an amount equivalent to about one-third of the applied current density ("cathodic protection"). At the higher current densities a film, probably consisting of magnesium hydroxide, is formed on the magnesium surface, and the effect of increasing current densities in reducing the dissolution rate due to local action decreases. The effect of external polarization in reducing the dissolution rate due to local action has been attributed to the effect of the applied EMF on the rate of transport of hydrogen ions to the surface of the metal by diffusion and migration. The effect of external polarization on the electrode potential could not be determined on account of experi-

mental difficulties.

11. The results of the present study of the dissolution of magnesium in hydrochloric acid offer additional evidence in favor of a diffusion-controlled mechanism of reaction. By studying the dissolution process at acid concentrations up to 1.6 N, it has been possible to evaluate the stirring efficiency of the hydrogen bubbles which are evolved during the dissolution process. This is a factor which must be kept under control in reactions which are affected by agitation.

The changes in the electrode potential with the acid concentration have been shown to depend on a replating of low overvoltage impurities on the surface of the dissolving metal. When this condition is taken into account, the observed electrode potentials are readily explicable in terms of the electrochemical theory of metallic corrosion. This result supports the view that the dissolution of metals in electrolytes is electrochemical in nature, even in cases such as the dissolution of magnesium in hydrochloric acid where stationary local cells are absent, and where the dissolution rate is diffusion-controlled.

The effect of external polarization in reducing the dissolution rate due to local action has been related to the effect of the externally applied EMF on the rate of transfer of hydrogen ions to the surface of the metal by diffusion and migration rather than to the effect of the external current in increasing the polarization of the local anodes and cathodes.

BIBLIOGRAPHY

1. O. P. Watts, Trans. Electrochem. Soc., 64, 125 (1933).
2. O. Gatty and E. R. C. Spooner, "The Electrode Potential Behavior of Corroding Metals in Aqueous Solutions", Clarendon Press, Oxford (1938).
3. W. S. Loose, in "Corrosion Handbook", pp. 218-252, John Wiley & & Sons, Inc., New York (1948).
4. G. E. Coates, J. Chem. Soc., 1945 (July), p. 478.
5. J. D. Hanawalt, C. E. Nelson, and J. A. Peloubet, Trans. A.I.M.E. , 147, 273 (1942).
6. F. A. Fox and C. J. Bushrod, J. Inst. Met., 70, 525 (1944).
7. G. C. Kuczynski and F. Schonfeld, Trans. Electrochem. Soc., 93, 41 (1948).
8. R. E. McNulty and J. D. Hanawalt, Trans. Electrochem. Soc., 81, 423 (1942).
9. W. O. Kroenig and V. N. Uspenskaya, Korrosion u. Metallschutz, 11, 10 (1935).
10. U. R. Evans, J. Inst. Met., 73, 837 (1947).
11. C. J. Bushrod, J. Inst. Met., 73, 843 (1947).
12. L. Whitby, Trans. Farad. Soc., 29, 415, 853 (1933).
13. M. Kilpatrick and J. H. Rushton, J. Phys. Chem., 34, 2180 (1930); 38, 269 (1934).
14. M. Sclar and M. Kilpatrick, J. Amer. Chem. Soc., 59, 584 (1937).
15. C. V. King and M. M. Braverman, J. Amer. Chem. Soc., 54, 1744 (1932).
16. C. V. King, J. Amer. Chem. Soc., 57, 828 (1935).
17. C. V. King and M. Schack, J. Amer. Chem. Soc., 57, 1212 (1935).
18. C. V. King and H. Catchart, J. Amer. Chem. Soc., 59, 63 (1937).
19. C. V. King and M. B. Abramson, J. Amer. Chem. Soc., 61, 2290 (1939).
20. C. V. King, Trans. N. Y. Acad. Sci., (Ser. II, Vol. 10) 262, (1948).

21. C. V. King, "Pittsburgh International Conference on Surface Relations", Corrosion Publishing Co., Pittsburgh, Pa. (1948).

22. T. H. James, J. Amer. Chem. Soc., 65, 39 (1943).

23. G. E. Coates, J. Inst. Met., 71, 457 (1945).

24. S. Bodforss, Z. Phys. Chem., 153, 83 (1931).

25. S. Bodforss and H. Kajmer, Z. Phys. Chem., 171, 190 (1934).

26. Wl. Kistiakowsky, Z. Elektrochem., 14, 111 (1908); 31, 625 (1925).

27. Wl. Kistiakowsky, Z. Phys. Chem., 70, 206 (1910).

28. H. T. S. Britton, "Hydrogen Ions", Chapman & Hall, Ltd., London (1932).

29. H. Uhlig, "Corrosion Handbook", John Wiley & Sons, Inc., New York (1948).

30. M. A. Streicher, "A Study of the Dissolution of Aluminum in Sodium Hydroxide Solutions", Dissertation, Lehigh University, Bethlehem, Pa., (1948).

31. A. Thiel, Z. Electrochem., 33, 370 (1927).

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

33. W. A. Wesley and R. H. Brown, "Corrosion Handbook", p. 482, John Wiley & Sons, Inc., New York (1948).

34. A. A. Noyes and W. R. Whitney, Z. Phys. Chem., 23, 689 (1897).

35. W. Nernst, Z. Phys. Chem., 47, 52 (1904).

36. E. Brunner, Z. Phys. Chem., 47, 56 (1904).

37. J. Zimmerman, J. Phys. Coll. Chem., 53, 562 (1949).

38. A. Eucken, Z. Electrochem., 38, 341 (1932).

39. B. Levich, Acta Physicochim. U.S.S.R., 17, 257 (1942); 19, 117, 133 (1944).

40. B. Levich, Farad. Soc. Discussions, 1, 37 (1947).

41. J. N. Agar, Farad. Soc. Discussions, 1, 26 (1947).

42. H. S. Taylor, "A Treatise on Physical Chemistry", Second Ed., Chapt. XV, D. vanNostrand Co., Inc., New York (1931).

43. C. Wagner, *J. (and Trans.) Electrochem. Soc.*, *95*, 161 (1949).

44. C. Wagner, *J. Phys. Coll. Chem.*, *53*, 1030 (1949).

45. A. de la Rive, *Ann. Chim. Phys.*, *43*, 425 (1830).

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

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

48. A. S. Cushman, *Proc. A.S.T.M.*, *7*, 211 (1906).

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

50. D. A. MacInnes, "The Principles of Electrochemistry", Reinhold Publishing Corp., New York (1939).

51. C. Wagner and W. Traud, *Z. Elektrochem.*, *44*, 391 (1938).

52. M. Straumanis, *Z. Phys. Chem.*, *148*, 349 (1930).

53. M. Straumanis, *Korrosion u. Metallschutz*, *14*, 67, 81 (1938).

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

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

56. R. B. Mears and R. H. Brown, *J. (and Trans.) Electrochem. Soc.*, *97*, 75 (1950).

57. M. A. Streicher, *Trans. Electrochem. Soc.*, *93*, 285 (1948); *96*, 170 (1949).

58. M. A. Streicher, "Pittsburgh International Conference on Surface Relations", p. 105, Corrosion Publishing Co., Pittsburgh, Pa. (1948).

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

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

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

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

63. H. Mouquin and W. A. Steitz, *Trans. Electrochem. Soc.*, *67*, 339 (1935).

TABLE I

Spectroscopic analysis of the magnesium alloys.

	Be-settled magnesium	J-1 alloy	Cell Magnesium	Distilled Magnesium
Al	.01	6.2	.011	.002
Be	.035			
Cd		< .01		<.01
Ca	< .01		< .01	
Cu	.017	< .01	.003	< .001
Fe	< .001	< .001	.03	< .001
Mn	.002	.27	.08	.002
Ni	< .001	< .001	< .001	< .001
Pb	< .002	< .001	< .002	.001
Si	< .001	< .01	.001	.01
Sn	< .001	< .001	< .001	< .001
Zn	< .01	.70	< .01	< .01

TABLE II

Dissolution rates of magnesium in hydrochloric acid at 25° C for various rates of agitation.

No stirring

Conc. of HCl mols/l	Diss. rate MCM**	Rate const. k
.0103	.0087	.070
.0106	.0078	.061
.0210	.0229	.094
.0218	.0239	.086
.0370*	.0713	.154
.0592	.139	.193
.0612	.151	.205
.0836	.212	.209
.0870	.235	.222
.100	.272	.224
.118	.341	.238
.181	.625	.284
.270	1.30	.396
.389	3.00	.634
.487	4.95	.836
.590*	8.19	1.14
.680	11.63	1.41
.800	16.90	1.74
.942	25.5	2.18
1.08	36.0	2.74
1.39	63.8	3.78
1.55	68.5	3.67

200 r.p.m.

Conc. of HCl mols/l	Diss. rate MCM	Rate const. k
.0105	.036	.282
.0216	.080	.305
.0372	.135	.298
.0607	.237	.321
.0859	.360	.344
.115*	.533	.381
.179	.925	.425
.267	1.72	.530
.386	3.67	.782
.575	8.66	1.24

---

* Mean values of 2 or 3 determinations.

** Abbreviation for mg/sq. cm. min.

TABLE II cont'd

380 r.p.m.

Conc. of HCl mols/l	Diss. rate MCM	Rate const. k
.00926	.055	.488
.0180	.107	.498
.0193	.106	.426
.0339	.199	.483
.0417	.230	.453
.0540	.336	.512
.0837	.500	.492
.0903	.565	.514
.143*	.972	.530
.193	1.44	.614
.202	1.62	.659
.264	2.34	.728
.360*	4.06	.928
.508	7.29	1.18
.518	7.70	1.22
.616	10.2	1.36
.764	15.8	1.70

947 r.p.m.

Conc. of HCl mols/l	Diss. rate MCM	Rate const. k
.00474*	.047	.815
.00970*	.094	.797
.0198	.195	.810
.0208	.205	.810
.0341	.349	.842
.0429	.442	.847
.0589	.604	.838
.0856	.897	.867
.0900	.937	.856
.129	1.40	.892
.142	1.60	.927
.201*	2.44	.998
.265	3.63	1.13
.320	4.47	1.15
.359	5.53	1.30
.459	7.78	1.40
.513	9.38	1.50
.622	12.3	1.63
.758	17.4	1.89
.882	23.4	2.18

---

* Mean values of 2 or 3 determinations.

TABLE II cont'd

1364 r.p.m.			2880 r.p.m.		
Conc. of HCl mols/l	Diss. rate MCH	Rate const. k	Conc. of HCl mols/l	Diss. rate [illegible]	Rate const. k
.00292	.0415	1.17	.00537	.122	1.87
.00475	.066	1.14	.0108	.234	1.78
.00682	.089	1.07	.0185	.408	1.81
.00975	.137	1.15	.0209	.453	1.78
.0139	.179	1.06	.0323	.708	1.80
.0219	.283	1.06	.0326	.743	1.88
.0310	.411	1.09	.0420	.898	1.76
.0467	.615	1.08	.0518	1.18	1.87
.0624	.820	1.08	.0856	1.92	1.84
.0909	1.22	1.10	.0877	2.04	1.91
.116	1.57	1.11	.120	2.68	1.84
.173	2.45	1.14	.138	3.14	1.88
.232	3.49	1.24	.167	3.90	1.92
.308	5.07	1.35	.231	5.47	1.95
.423	7.85	1.53	.334	8.50	2.09
.566	12.7	1.84	.443	12.2	2.25
.761	19.8	2.14	.575	16.9	2.42
.900	26.6	2.45	.748	24.9	2.74
1.03	34.3	2.74	.889	32.2	2.98
1.35	60.6	3.69	1.03	40.0	3.20
1.63	85.8	4.33	1.32	62.6	3.90

TABLE II cont'd

6400 r.p.m.

Conc. of HCl mols/l	Diss. rate MDF	Rate const. k
.00110	.046	3.44
.00404	.167	3.40
.00968	.404	3.44
.0207	.872	3.46
.0346	1.53	3.23
.0593	2.30	3.21
.0988	4.18	3.48
.108	4.22	3.23
.144	5.64	3.25
.166	6.65	3.30
.222	9.07	3.36
.297	12.0	3.32
.404	17.2	3.50
.474	21.4	3.71
.587	26.8	3.75
.669	31.2	3.83
.788	38.3	4.00
.926	47.3	4.20
1.06	56.5	4.37
1.57	89.7	4.70

TABLE III

Dissolution rates of magnesium in hydrochloric acid at 25° C for various rates of agitation*.

No stirring.

Conc. of HCl mols/l	Diss. rate MCM	Rate const. k
.0390	.072	.152
.119	.338	.234
.203	.757	.307
.363	2.23	.505
.435	3.31	.626
.605	8.02	1.09
.878	18.5	1.73
.941	20.3	1.77
1.20	31.4	2.15
1.59	53.1	2.75

1364 r.p.m.

Conc. of HCl mols/l	Diss. rate MCM	Rate const. k
.371	6.43	1.43
.622	12.6	1.67
.961	24.6	2.11
1.23	33.3	2.21
1.65	53.1	2.65

2880 r.p.m.

Conc. of HCl mols/l	Diss. rate MCM	Rate const. k
.557	15.6	2.30
.773	23.0	2.43
.911	27.9	2.52
.993	32.0	2.65
1.37	47.5	2.85

6400 r.p.m.

Conc. of HCl mols/l	Diss. rate MCM	Rate const. k
.367	14.6	3.27
.614	26.5	3.55
.952	39.2	3.39
1.21	52.2	3.55
1.61	72.0	3.68

---

* The specimens were heated at 610° C for 15 hours and quenched in water.

TABLE IV

Determination of rate constants for the dissolution of magnesium in hydrochloric acid at 25° C for various rates of agitation.

Speed of rotation r.p.m.	Conc. of HCl mols/l	Diss. rate MCM	Rate const. k	$k_{average}$
1780	.0593	.951	1.32	1.31
	.0619	.974	1.30	
4500	.0604	1.90	2.59	
	.0614	1.91	2.55	2.57
8030	.0576	2.65	3.78	
	.0567	2.61	3.78	3.78

TABLE V

Rate constants* and calculated values of the thickness of the diffusion layer at 25° C for various rates of agitation.

Speed of rotation r.p.m.	Rate const. k	δ cm. 10^4
0	.20	89
200	.30	59
380	.46	39
947	.831	22
1364	1.08	16
1780	1.31	14
2880	1.82	9.8
4500	2.57	6.9
6400	3.36	5.3
8030	3.78	4.7

* Average values from Tables II and IV for the lower concentration range where k is constant.

TABLE VI

Effect of temperature on the dissolution rate of magnesium in hydrochloric acid at 947 r.p.m.

35° C.			45° C.		
Conc. of HCl mols/l	Diss. rate MCH	Rate const. k	Conc. of HCl mols/l	Diss. rate MCH	Rate const. k
.00506	.065	1.06	.00509	.073	1.18
.0103	.123	.982	.0102	.150	1.21
.0204	.251	1.01	.0199	.295	1.22
.0352	.443	1.04	.0345	.535	1.28
.0609	.770	1.04	.0592	.920	1.28
.0875	1.14	1.07	.0870	1.42	1.34
.132	1.85	1.15	.147	2.66	1.49
.197	3.27	1.37	.209	4.35	1.71
.306	5.52	1.48	.333	8.48	2.19
.439	10.2	1.91			

TABLE VII

Effect of temperature on the rate constant* and the temperature coefficient per 10°C at 947 r.p.m.

Temperature °C	Rate const. k	Temp. coeff. per 10° C.
25	.823	
35	1.02	1.24
45	1.23	1.21

* Mean values for acid concentrations less than 0.8N .

TABLE VIII

Heating of Specimens during dissolution.

Conc. of HCl mols/l	Temperature difference between specimen and solution (^{o}C). No stirring	External stirring
.10	.70	.55
.16	1.05	.85
.20	1.45	1.15
.26	2.0	1.5
.31	2.4	1.8
.36	3.1	2.3
.55	5.3	3.9
.60	5.8	4.2
.74	8.2	5.9
.87	10.6	8.0
.94	10.9	8.0
.98	12.9	9.5
1.19	15.9	12.2
1.27	19.8	14.5
1.54	22.8	-

TABLE IX

Dissolution rates* of magnesium in solutions of HCl 0.5 N $AlCl_3$ at 1364 r.p.m. and 25° C.

Conc. of HCl mols /l	Diss. rate MCM	Rate const. k
0	.074	-
.0096	.095	.81
.0220	.159	.596
.0448	.425	.780
.139	1.65	.985
.284	3.34	.966
.768	9.34	1.00
1.45	18.2	1.04

* Each value represents the mean of two single determinations.

TABLE X

Dissolution rates of cell magnesium in hydrochloric acid at 1364 r.p.m. and 25° C.

Conc. of HCl mols /l	Diss. rate MCM	Rate const. k
.00654	.0855	1.08
.0160	.228	1.17
.0398	.530	1.10
.0930	1.28	1.13
.199	3.00	1.24
.410	7.43	1.49

TABLE XI

Dissolution rates of the J-1 alloy* in hydrochloric acid at 1364 r.p.m. and 25° C.

Conc. of HCl mols /l	Diss. rate MCM	Rate const. k
.0070	.068	.799
.0142	.130	.753
.0296	.300	.834
.0304	.312	.844
.0576	.636	.908
.0882	1.01	.942
.0905	1.07	.972
.138	1.66	.989
.191	2.76	1.19
.195	2.87	1.21
.234	3.77	1.33
.265	5.02	1.56
.288	6.34	1.81
.295	6.65	1.85
.395	8.83	1.84
.402	8.87	1.82
.612	14.9	2.00
.866	25.2	2.39
.874	25.6	2.41
1.35	56.2	3.42

---

* The specimens of this alloy, which contains 6.2 % Al and 0.27 % Mn, were solution heat treated at 415° C for 15 hours and quenched in water.

TABLE XII

Effect of anodic polarization on the dissolution rate of magnesium in 0.045 N hydrochloric acid at 1364 r.p.m. and 25° C.

Current density Amp. /cm^2	Total diss. rate MCM	Simple diss. rate MCM	Difference effect (Δ) MCM
0	.576	.576	0
.0073	.597	.541	.035
.0091	.616	.547	.029
.0150	.604	.490	.086
.0259	.664	.468	.108
.0357	.659	.389	.187
.0570	.745	.314	.262
.0744	.792	.230	.346
.0940	.879	.168	.408

TABLE XIII

Effect of cathodic polarization on the dissolution rate of magnesium in 0.045 N hydrochloric acid at 1364 r.p.m. and 25° C.

Current density Amp. /cm^2	Dissolution rate MCM	Cathodic protection MCM
0	.576	0
.0312	.499	.077
.0406	.492	.084
.0590	.421	.155
.0785	.384	.192
.117	.325	.251
.162	.280	.296
.201	.252	.324
.236	.193	.383
.282	.193	.383
.325	.134	.442
.364	.137	.439

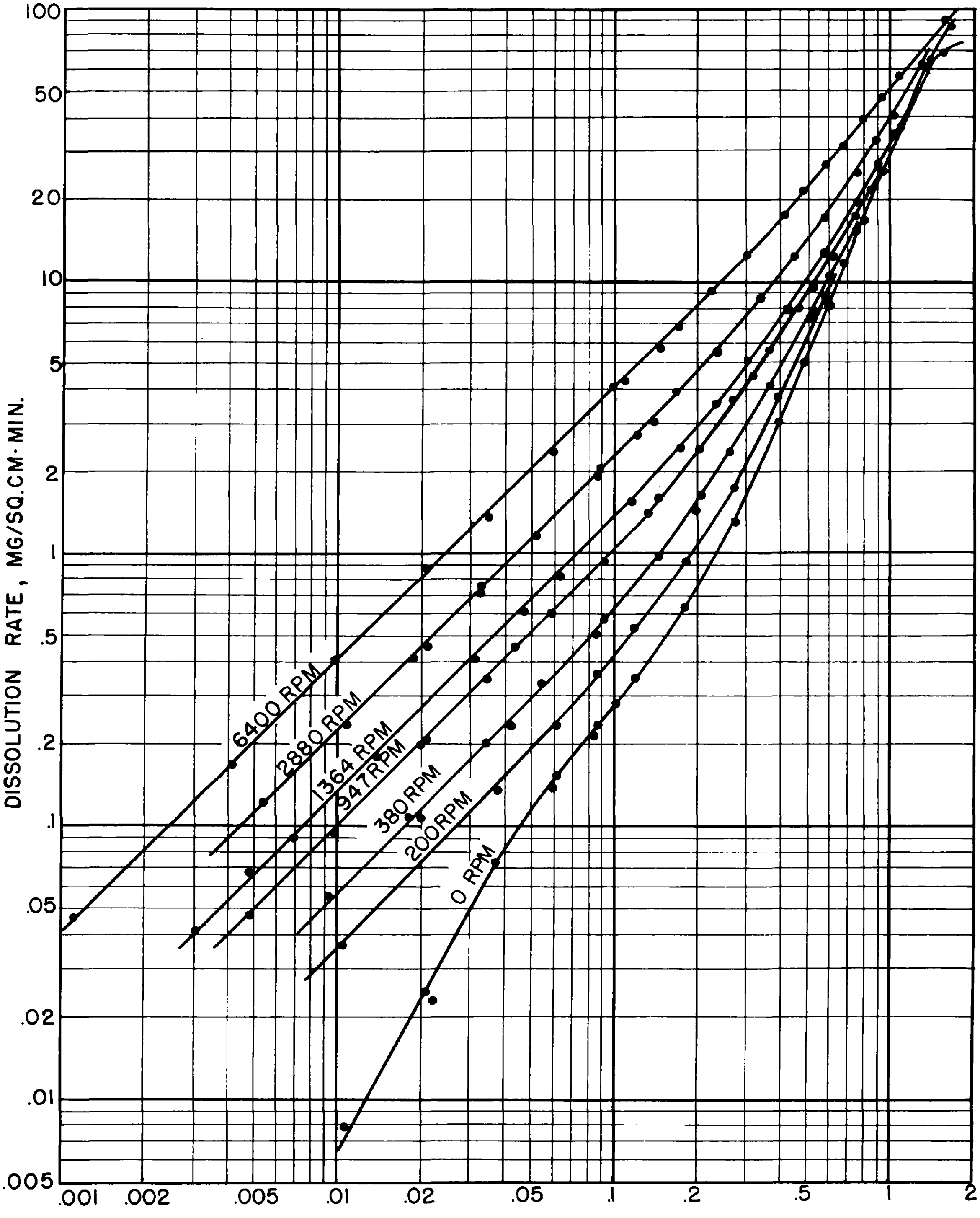


FIG I. DISSOLUTION RATES OF MAGNESIUM IN HYDROCHLORIC ACID AT 25°C. THE CYLINDRICAL SPECIMENS (11mm in diameter) WERE ROTATED AT THE INDICATED SPEEDS.

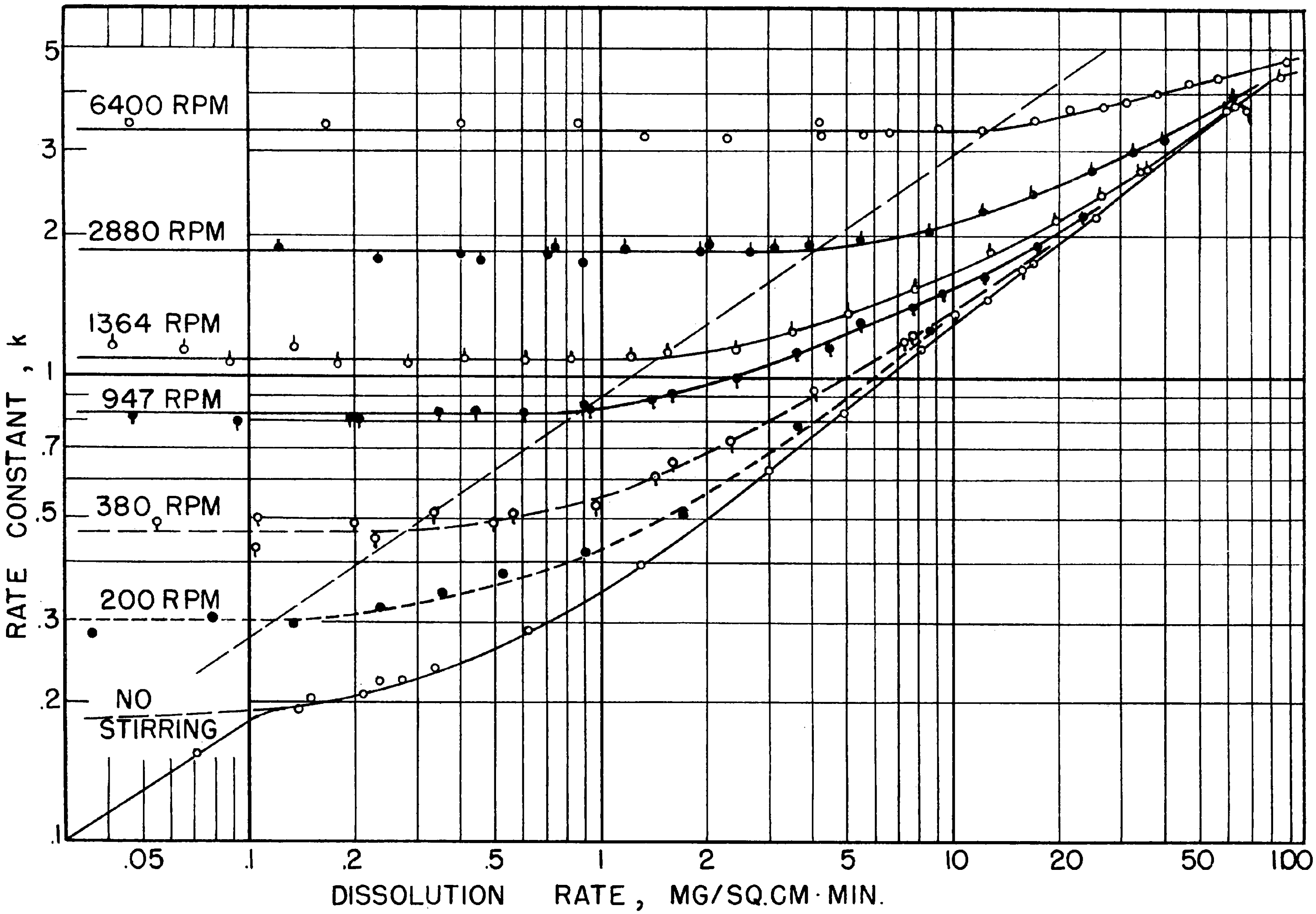


FIG. 2. RATE CONSTANTS vs. DISSOLUTION RATES FOR DIFFERENT RATES OF AGITATION AT 25° C.

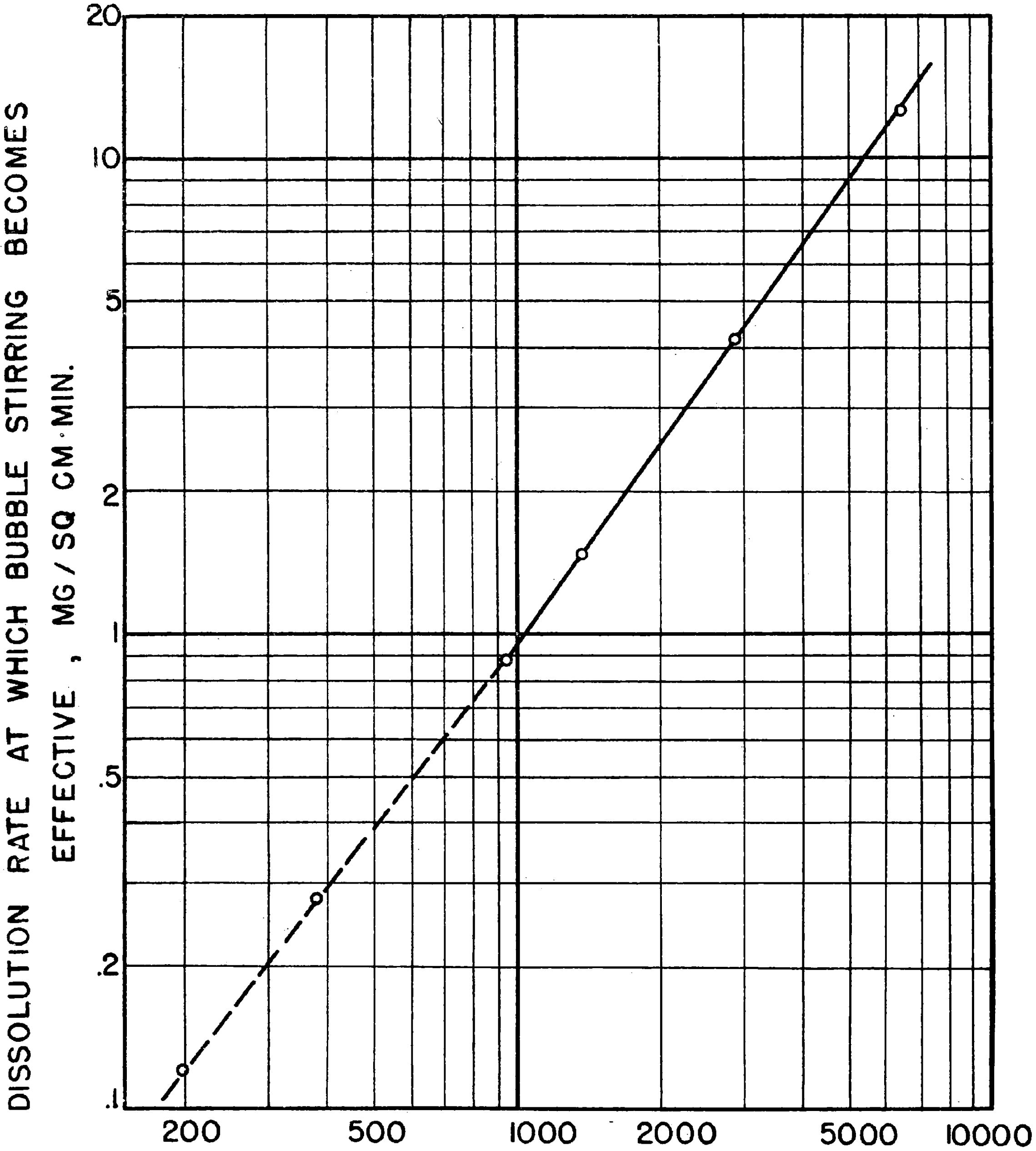


FIG. 3. EFFECT OF EXTERNAL STIRRING IN SUPPRESSING THE STIRRING ACTION OF THE GAS BUBBLES.

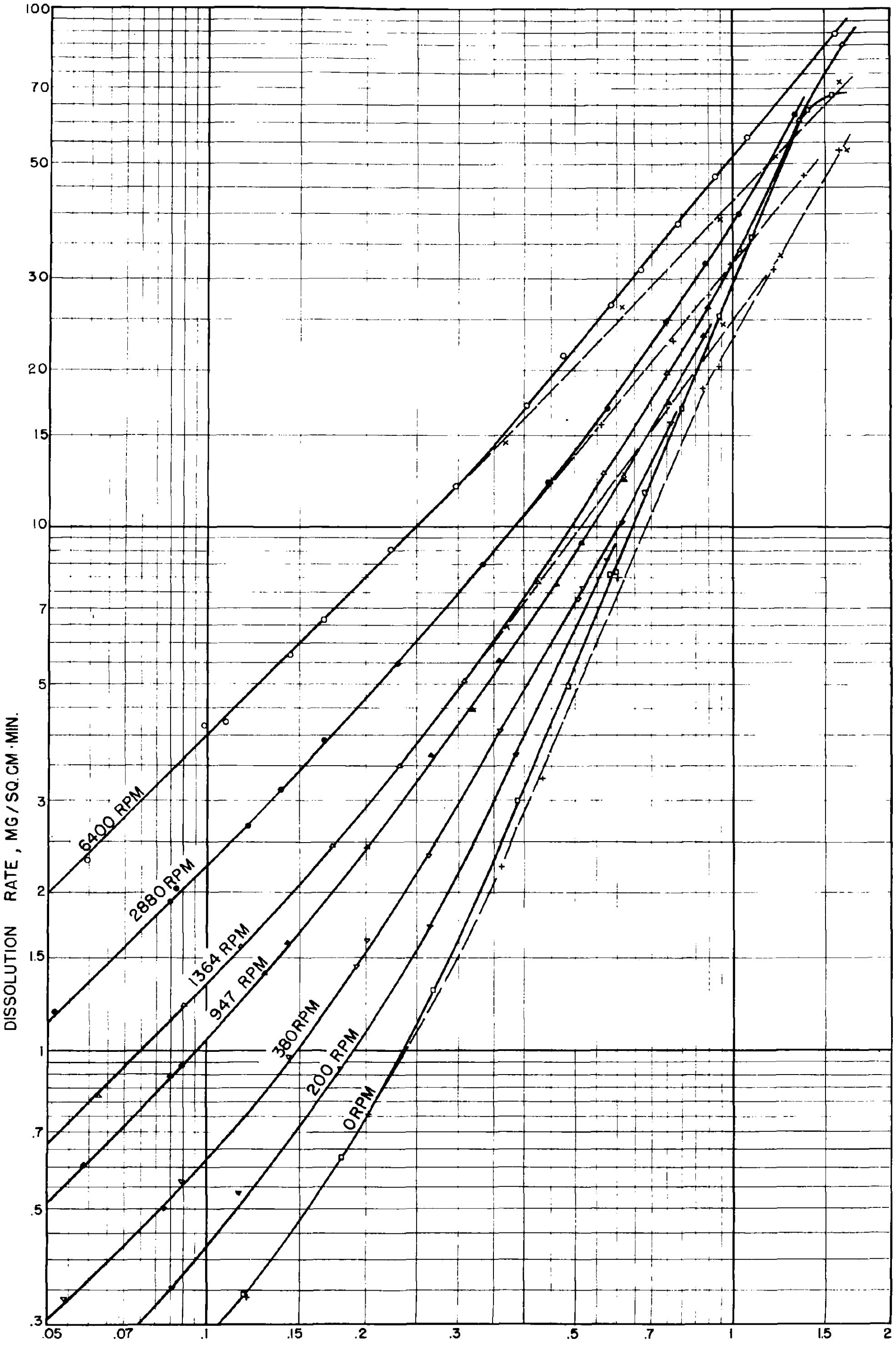


FIG. 4. EFFECT OF HEAT TREATMENT ON THE DISSOLUTION RATE OF Be-SETTLED MAGNESIUM AT 25°C (BROKEN LINES)

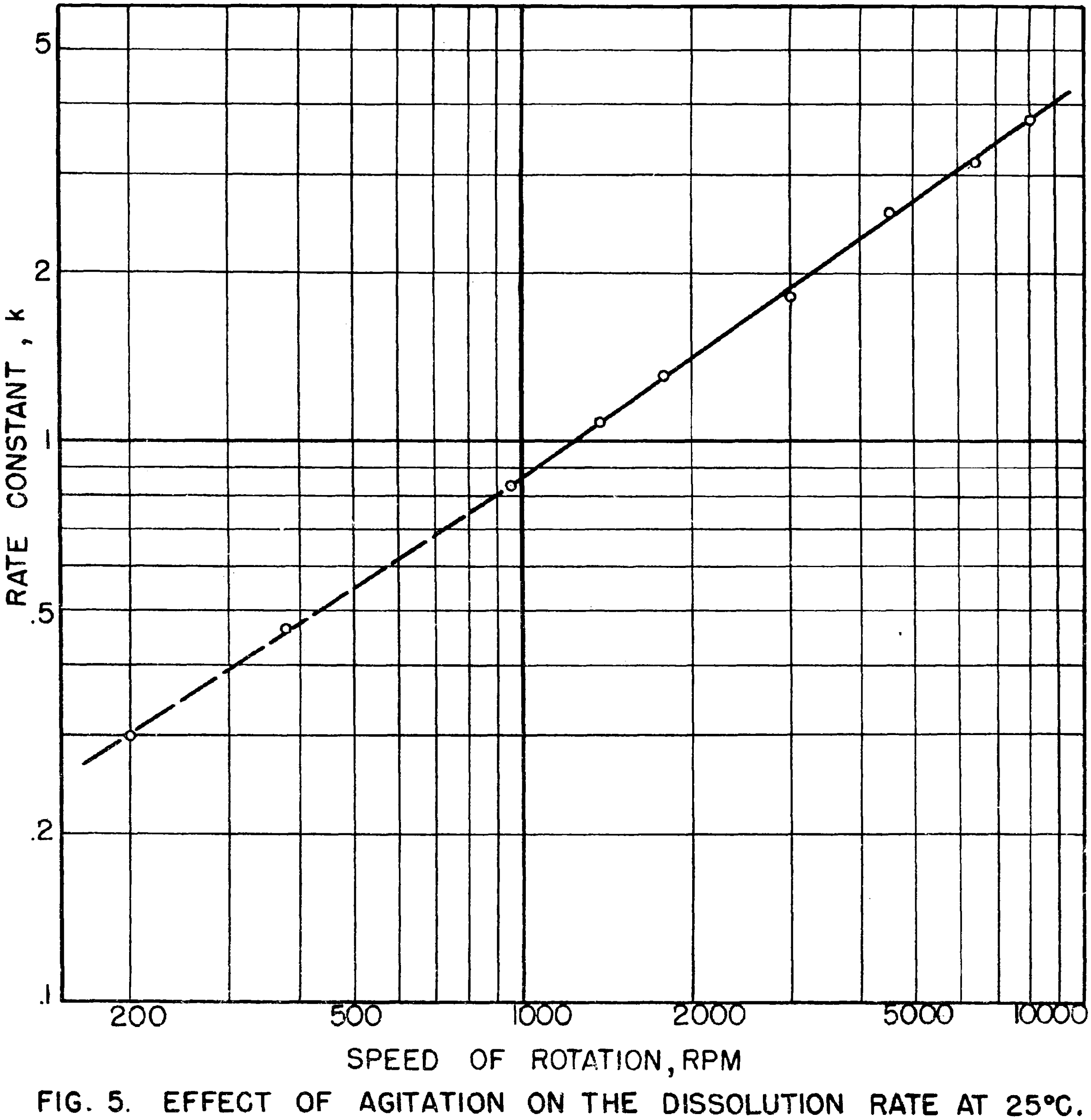


FIG. 5. EFFECT OF AGITATION ON THE DISSOLUTION RATE AT 25°C.

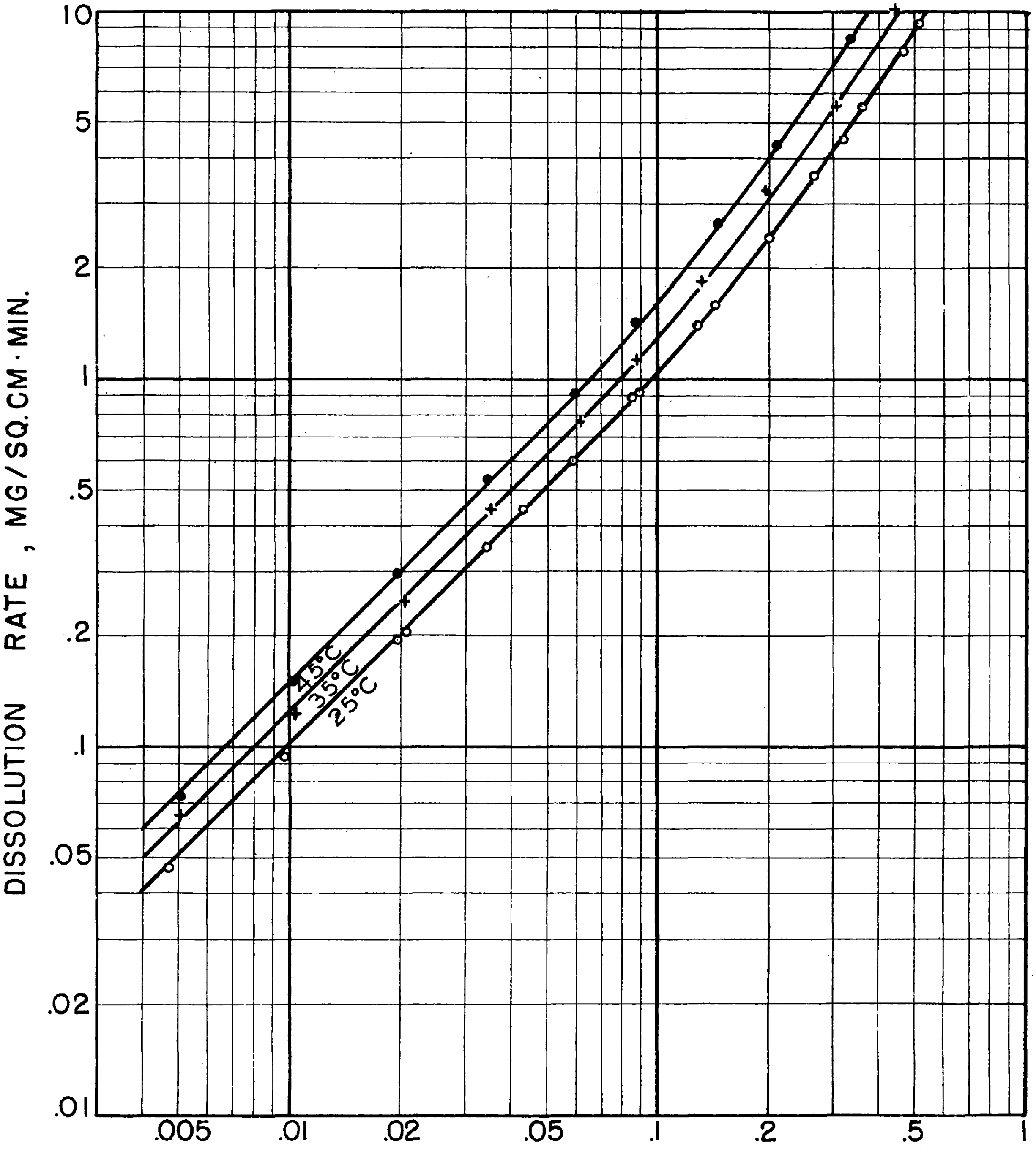


FIG. 6. EFFECT OF TEMPERATURE ON THE DISSOLUTION RATE AT 947 RPM.

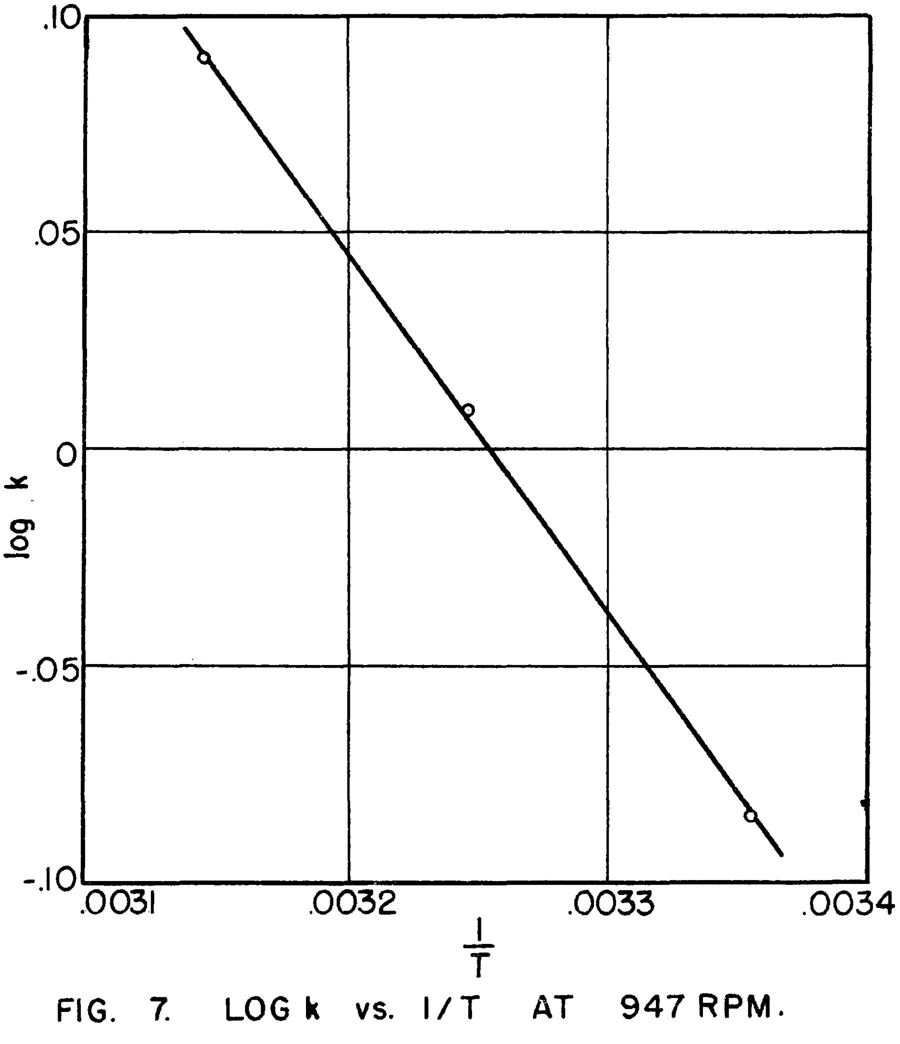


FIG. 7. LOG k vs. 1/T AT 947 RPM.

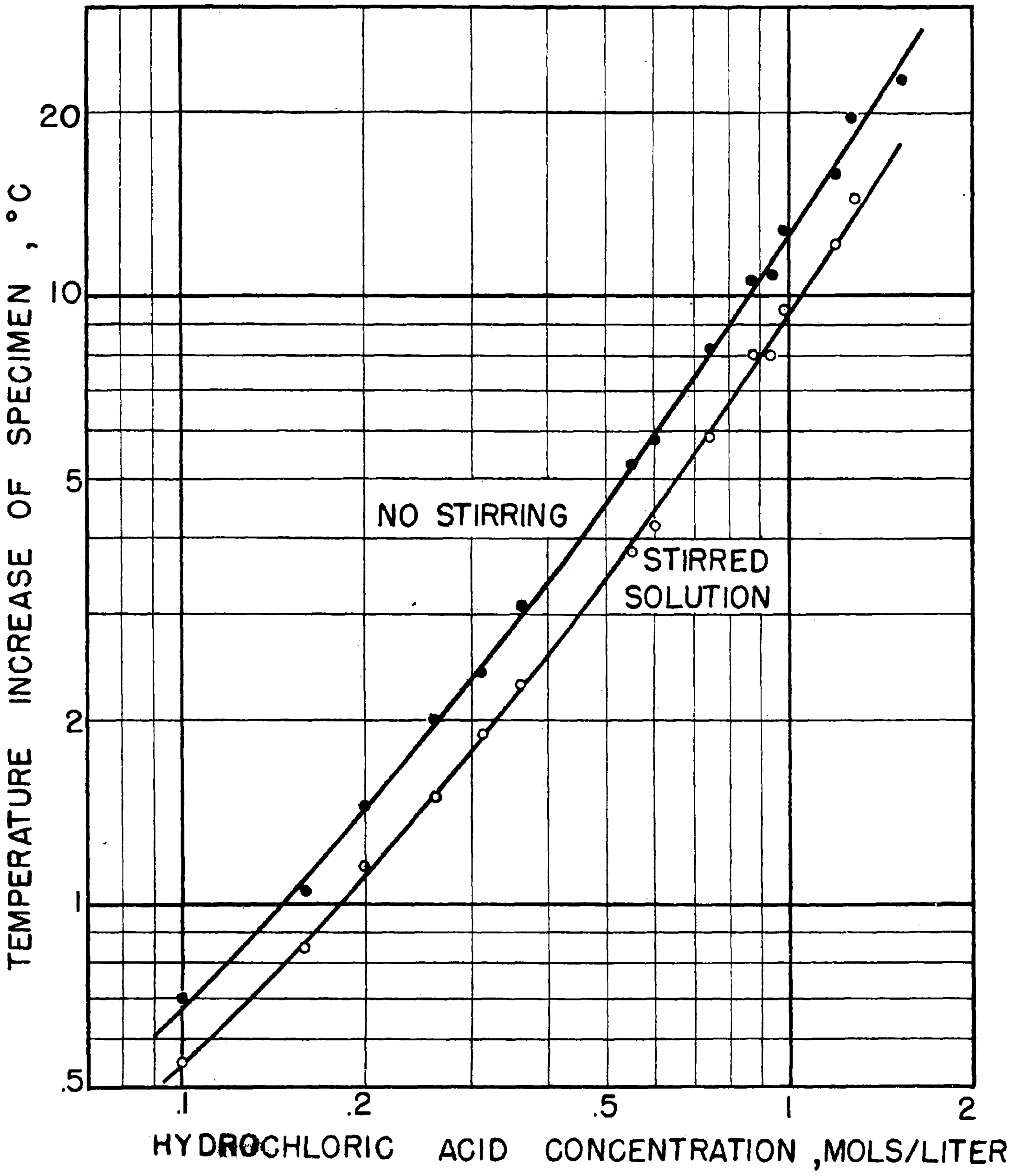


FIG. 8. HEATING OF SPECIMEN DURING DISSOLUTION.

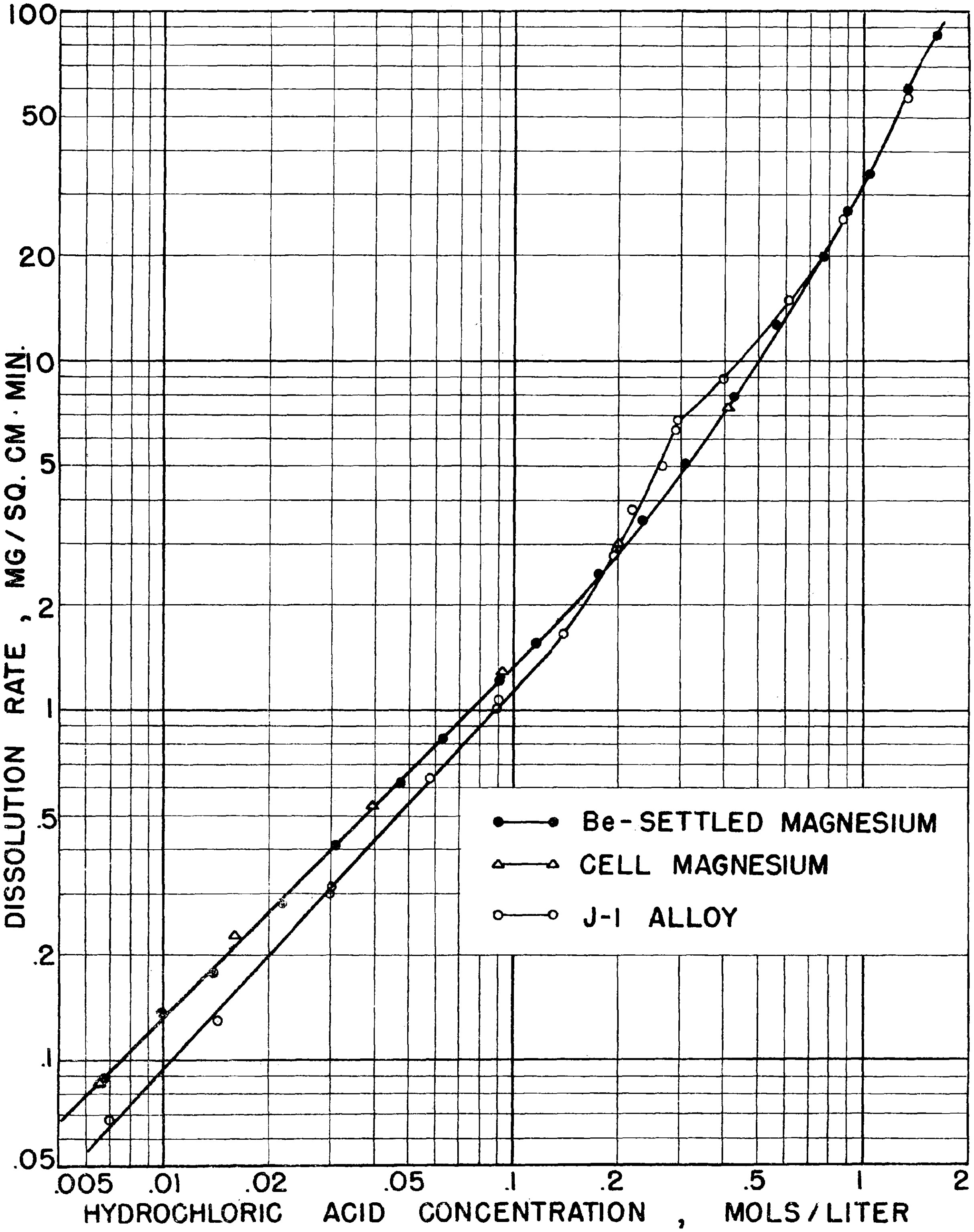


FIG. 9. DISSOLUTION RATES OF DIFFERENT ALLOYS AT 1364 RPM AND 25°C.

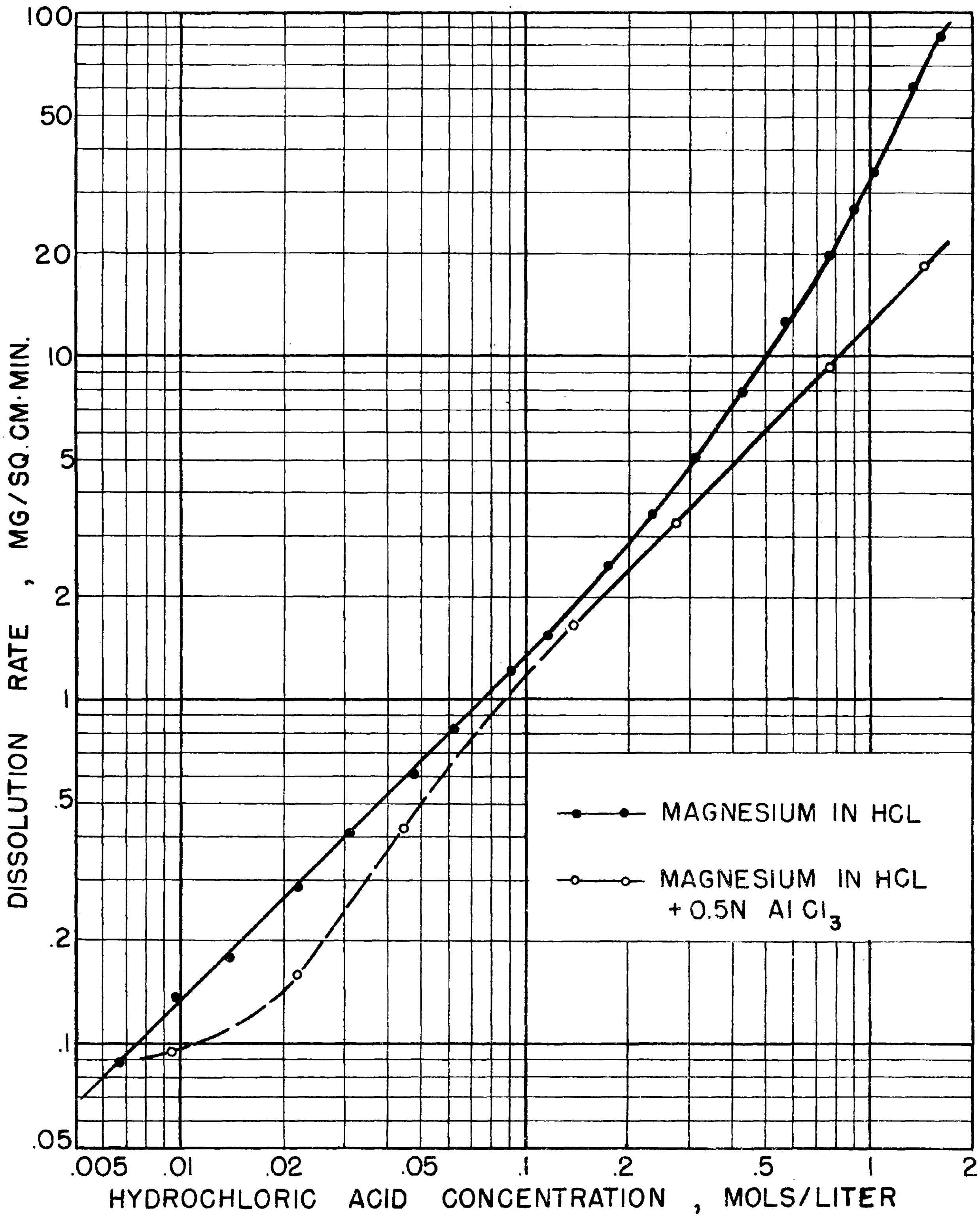


FIG. 10. EFFECT OF $AlCl_3$ ON THE DISSOLUTION RATE AT 1364 RPM AND 25° C.

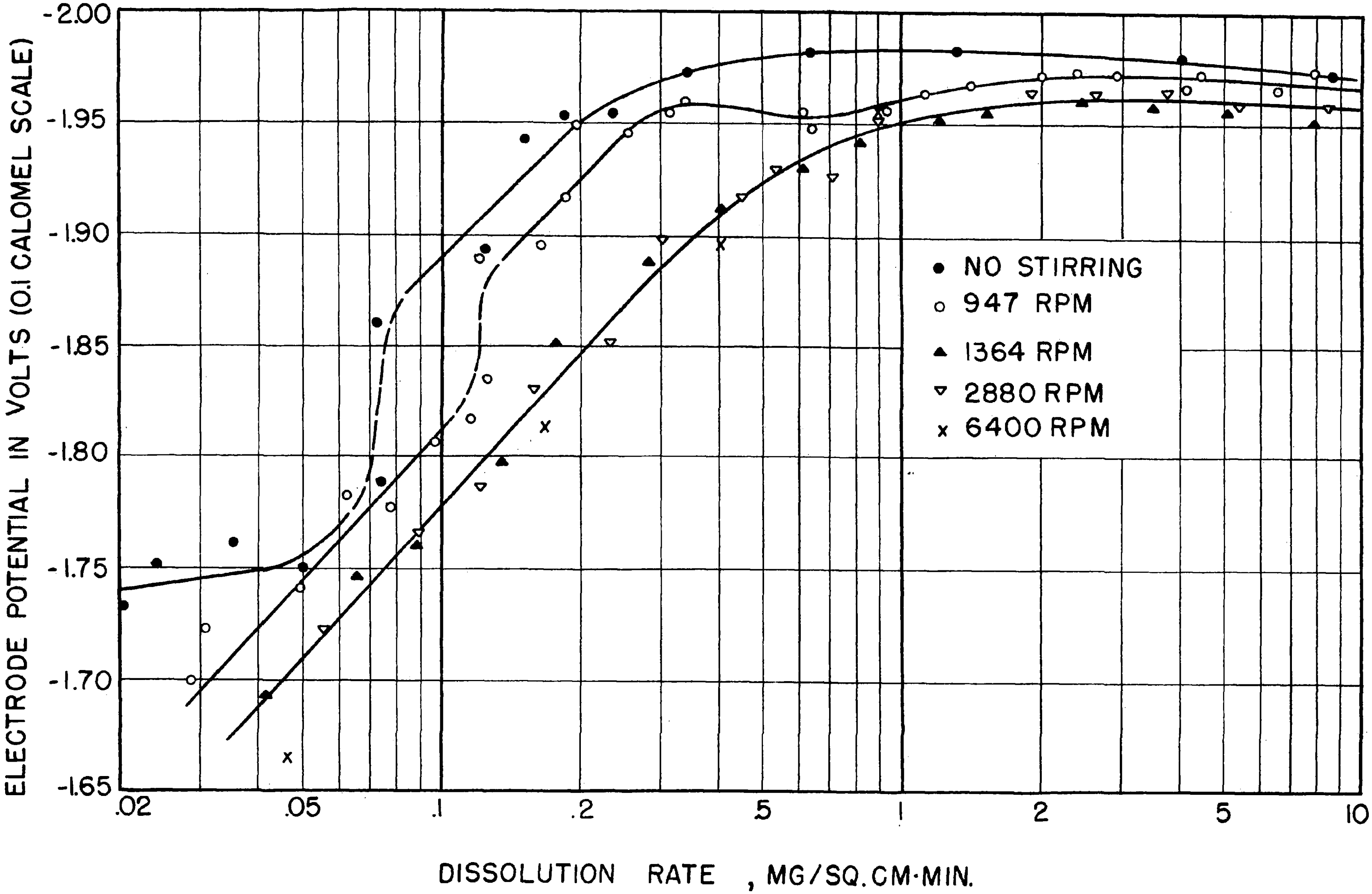


FIG. 11. ELECTRODE POTENTIALS AT VARIOUS RATES OF AGITATION. TEMP.: 25°C.

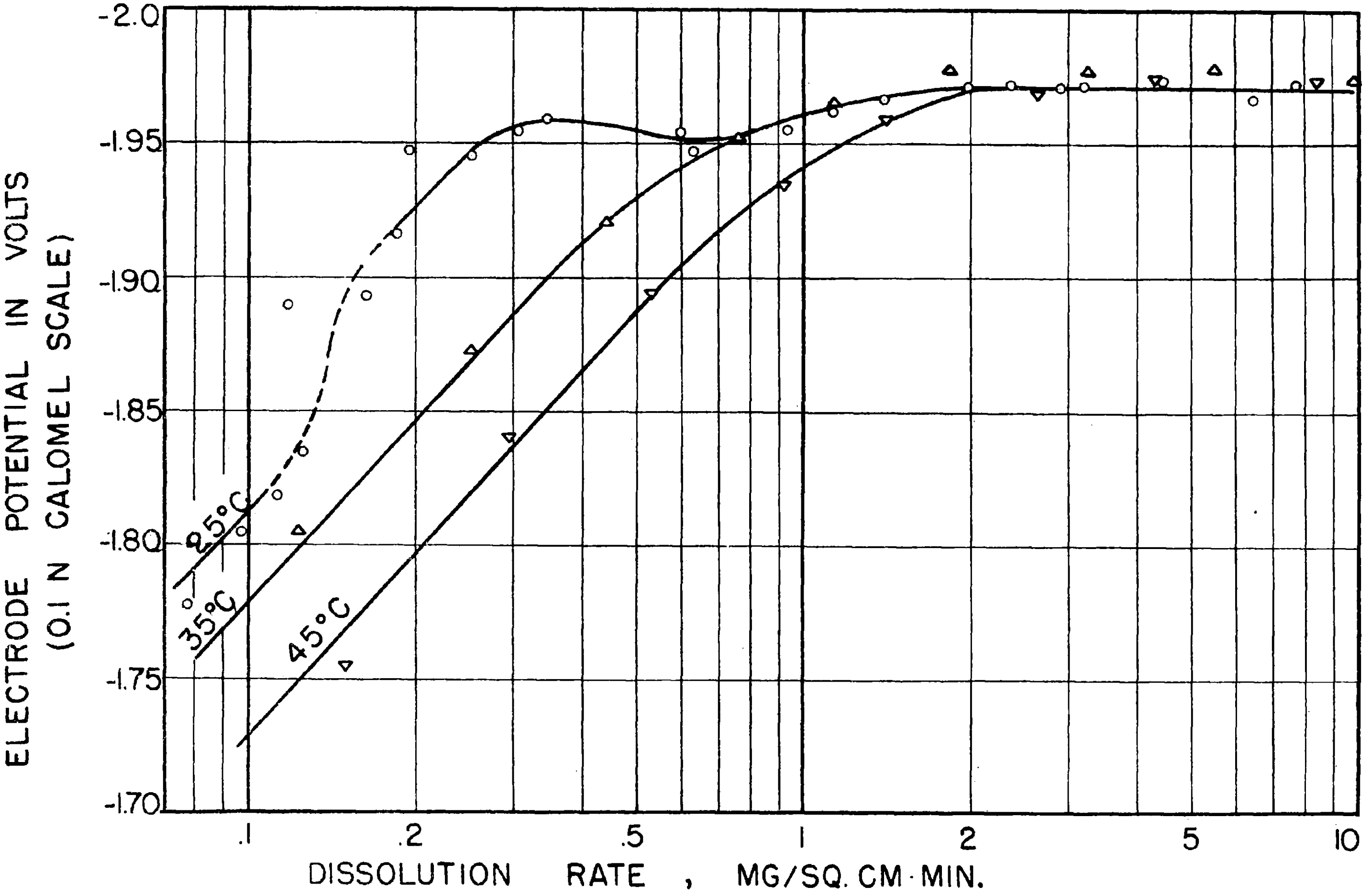


FIG. 12. EFFECT OF TEMPERATURE ON THE ELECTRODE POTENTIALS AT 25°C.

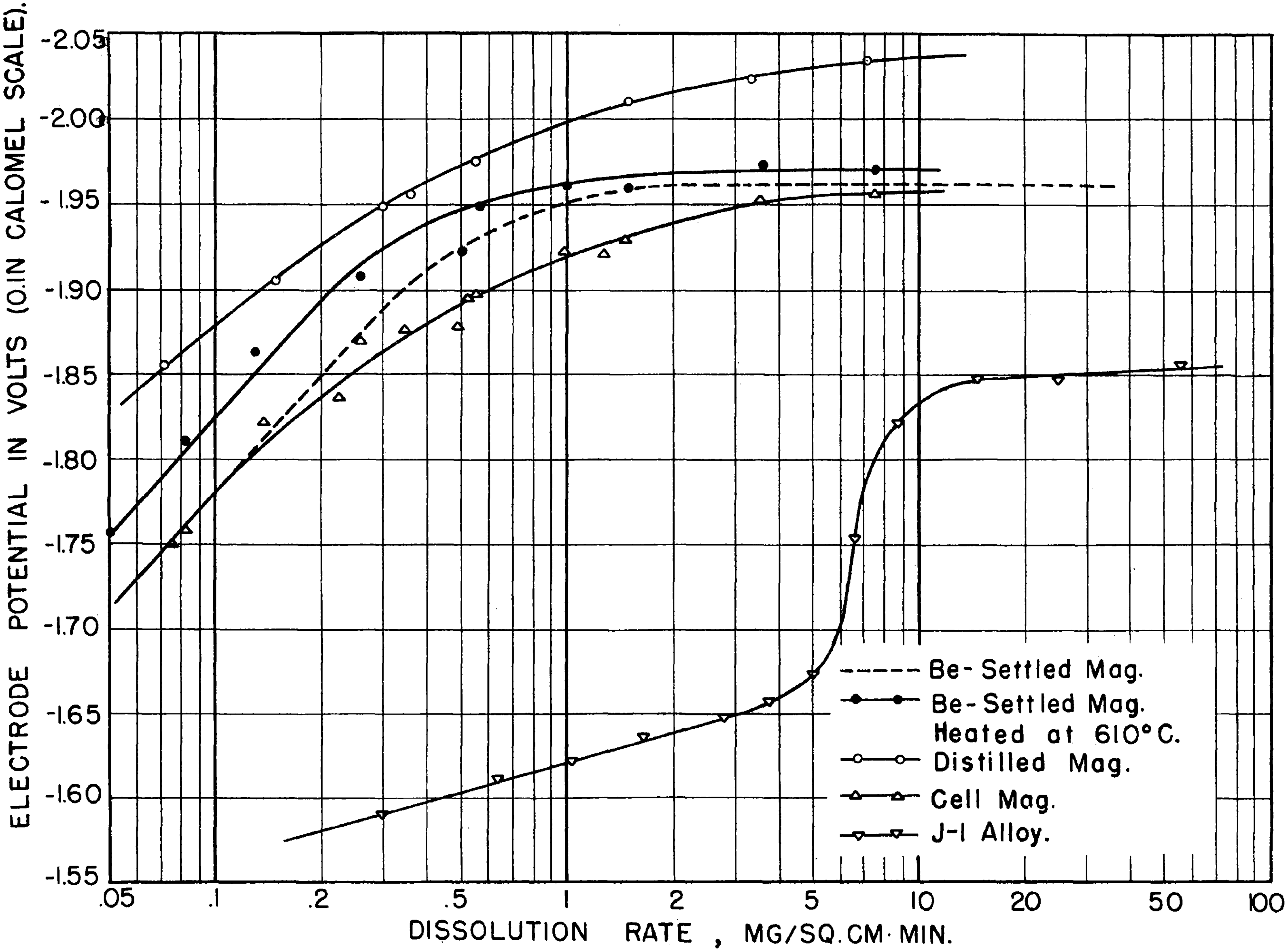


FIG. 13. ELECTRODE POTENTIALS OF DIFFERENT ALLOYS AT 1364RPM AND 25°C.

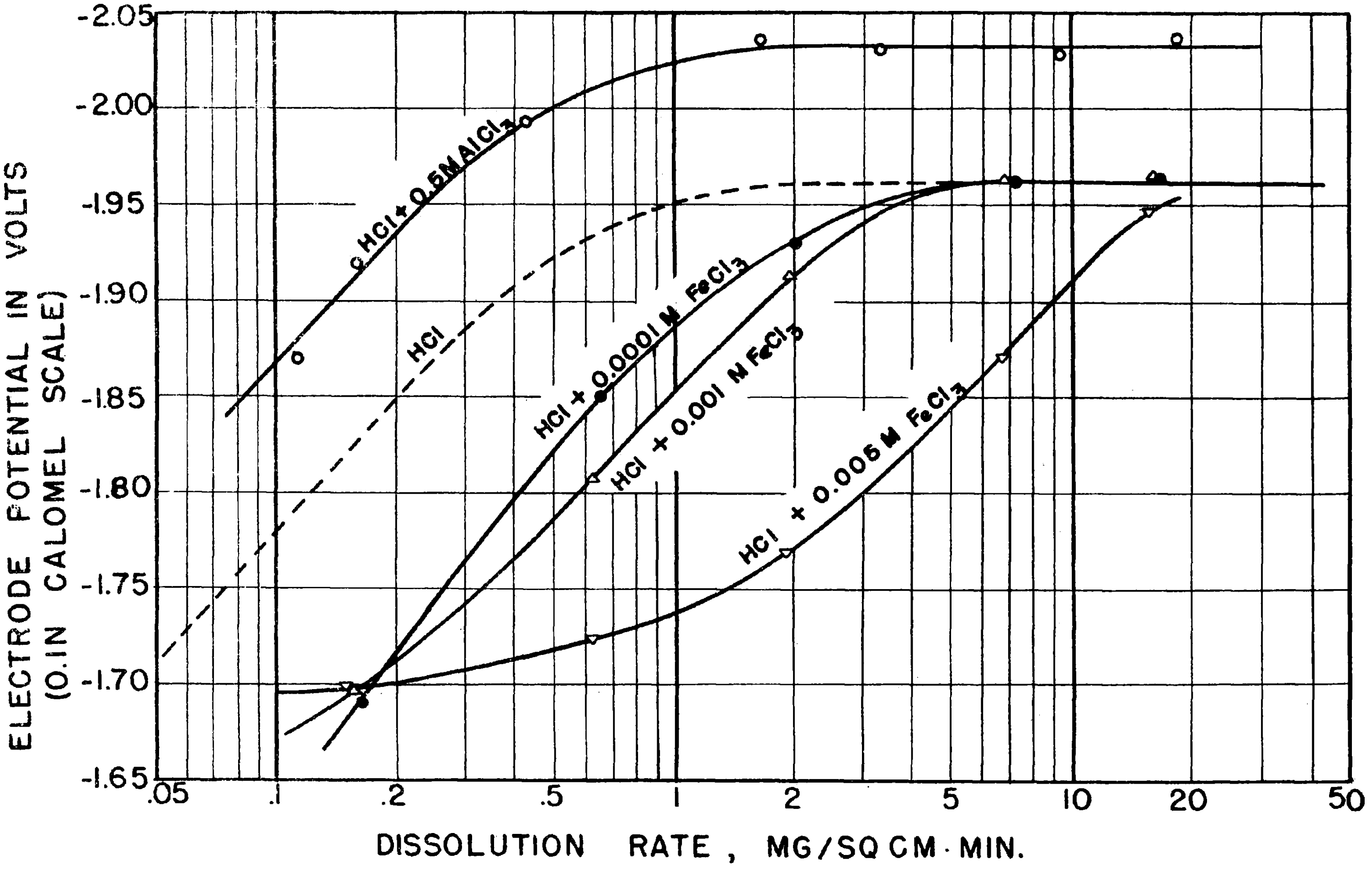


FIG. 14. EFFECT OF $AlCl_3$ AND $FeCl_3$ ON THE ELECTRODE POTENTIALS AT 1364 RPM AND 25°C.

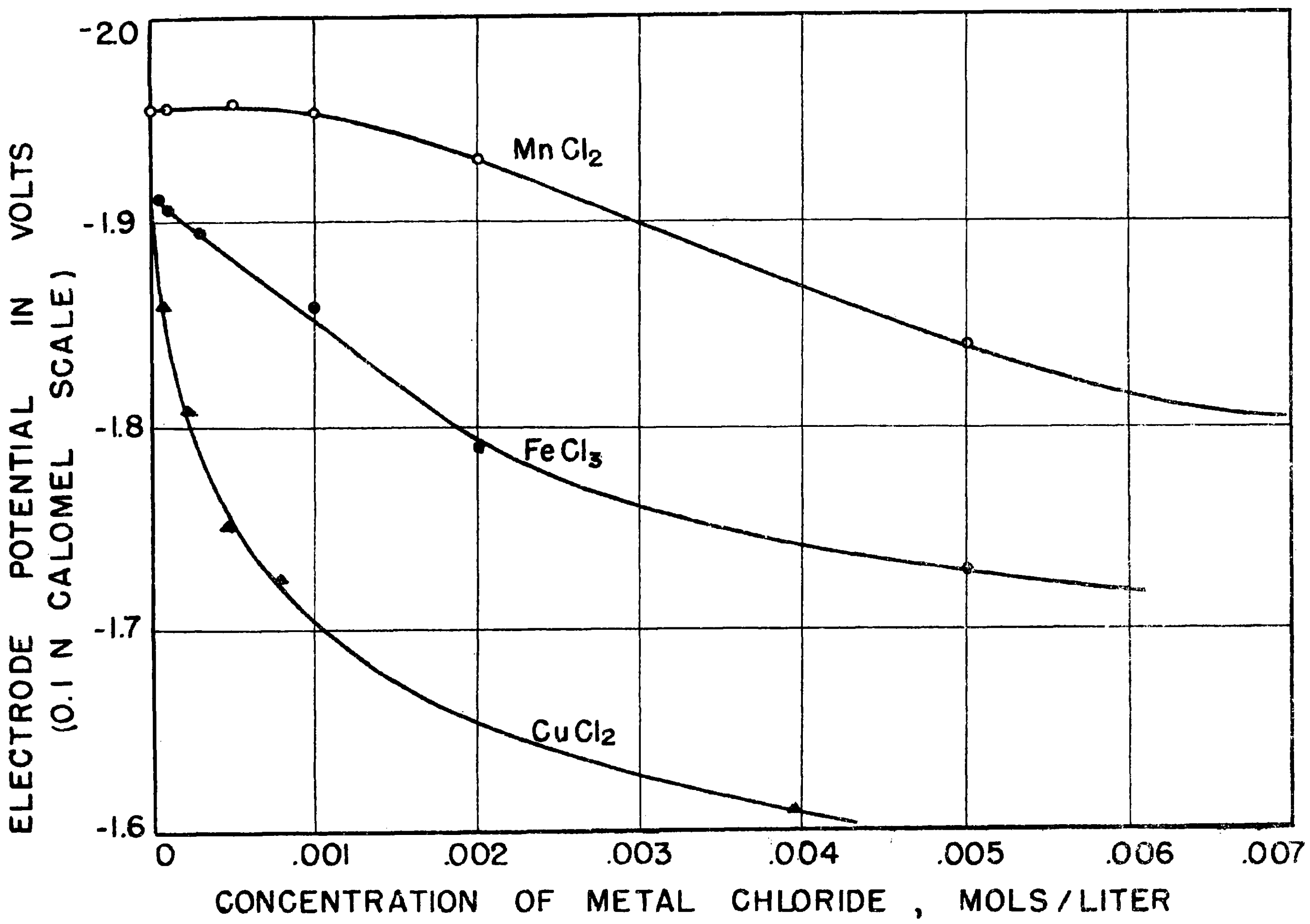


FIG. 15. EFFECT OF DIFFERENT METAL CHLORIDES ON THE ELECTRODE POTENTIAL AT 1364 RPM AND 25° C.

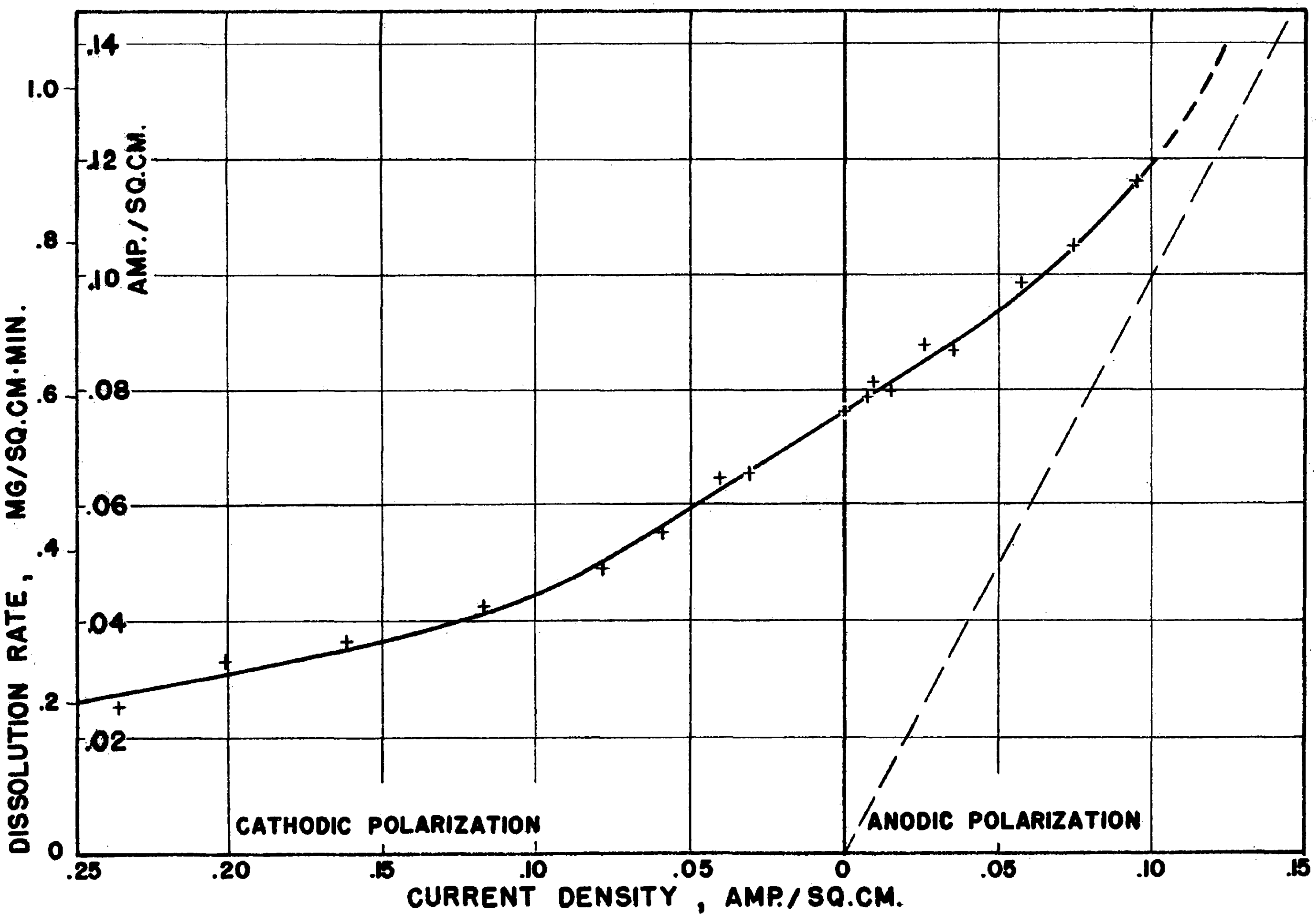


FIG. 16. EFFECT OF ANODIC AND CATHODIC POLARIZATION ON THE DISSOLUTION RATE OF MAGNESIUM IN 0.045 N HCl AT 1364 RPM AND 25° C.

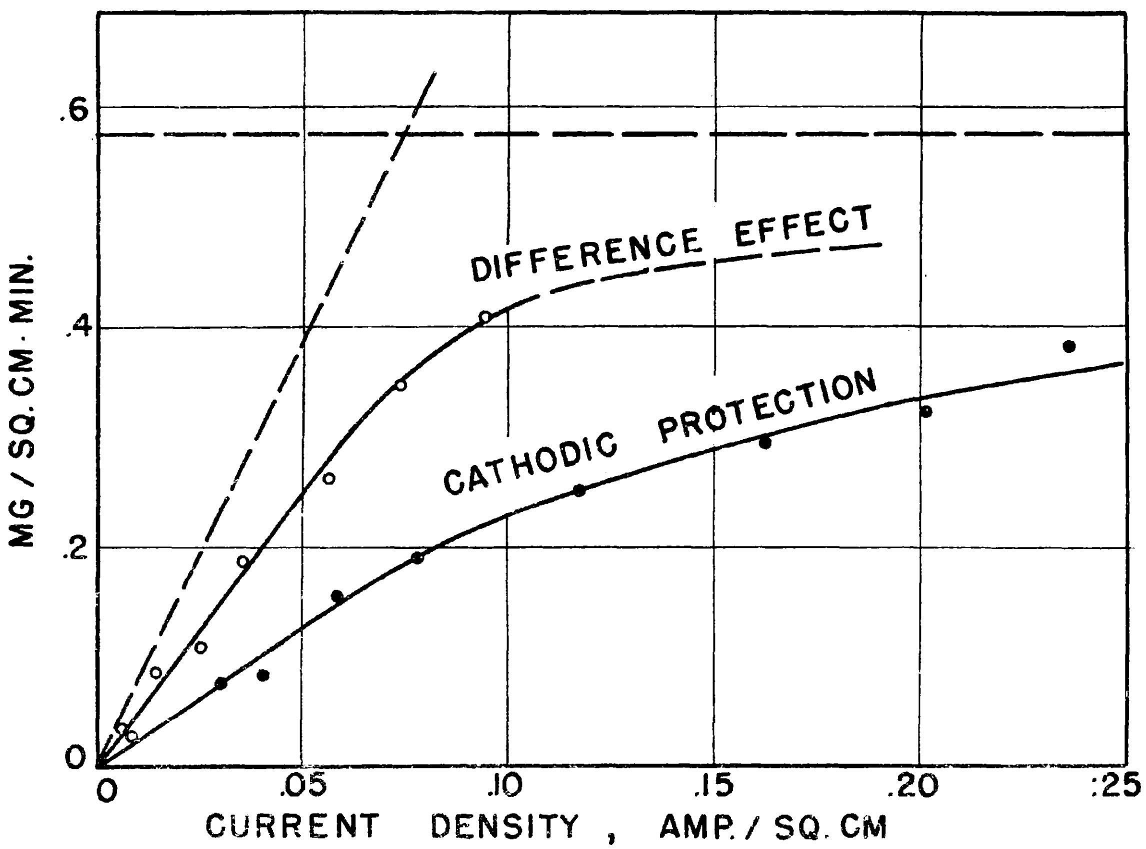


FIG. 17. EFFECT OF ANODIC AND CATHODIC POLARIZATION IN REDUCING THE DISSOLUTION RATE DUE TO LOCAL ACTION ("DIFFERENCE EFFECT" resp. "CATHODIC **PROTECTION**") AT 1364 RPM AND 25°C.

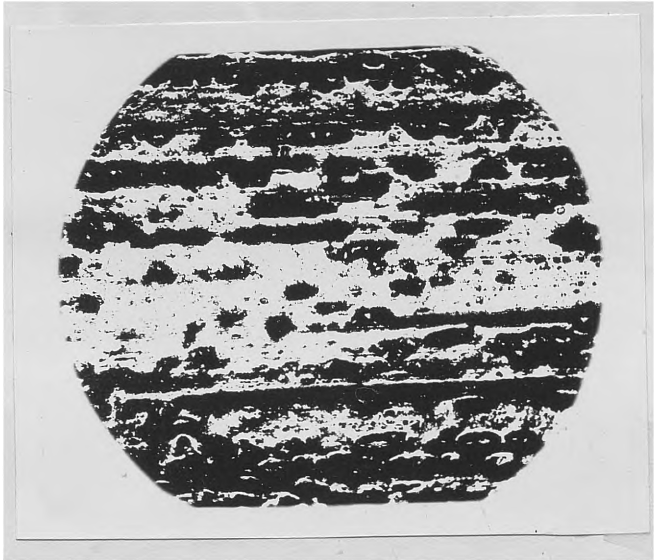


Fig. 18. J-1 alloy (containing 6.2% Al and 0.27% Mn) after immersion in 0.40 N HCl at 1364 r.p.m. (25°C). The attack is concentrated around stringers of manganese inclusions. 75 X.

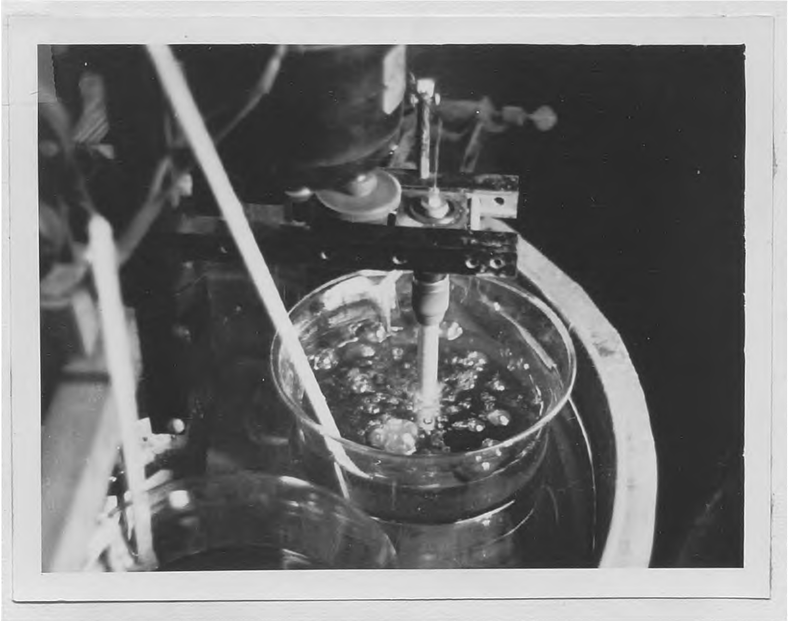


Fig. 19. Magnesium dissolving in 1.5 N HCl at 1364 r.p.m. (25°C). The hydrogen bubbles are large.

Fig. 20. Magnesium dissolving in 1.5 N HCl containing 0.5 mol/liter of $AlCl_3$ (1364 r.p.m. and 25°C). The hydrogen bubbles are small, giving diffuse reflection of light.

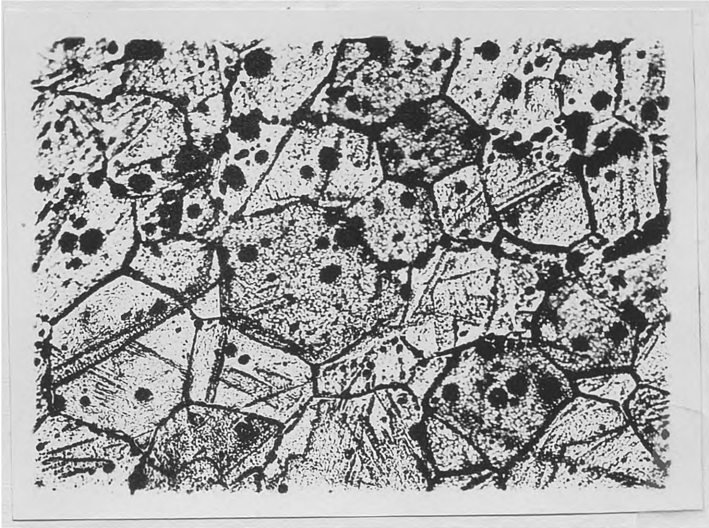


Fig. 21. Be-settled magnesium after immersion in 0.005 N HCl (1364 r.p.m. and 25°C). The amounts of the dark precipitate decrease as the acid concentration increases, as seen by comparison with Figs. 22, 23, and 24. 250 X.

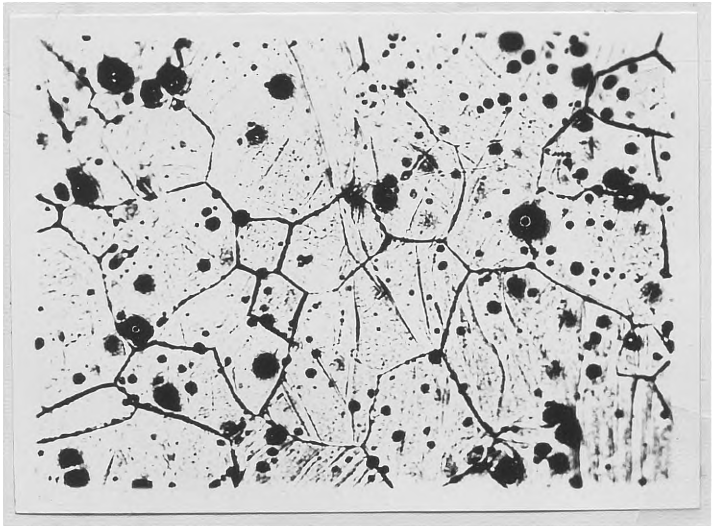


Fig. 22. Be-settled magnesium after immersion in 0.020 N HCl (1364 r.p.m. and 25°C). 250 X

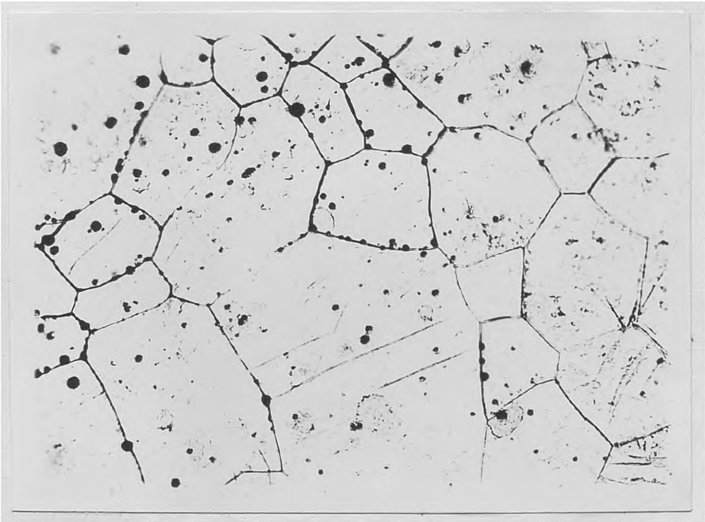


Fig. 23. Be-settled magnesium after immersion in 0.042 N HCl (1364 r.p.m. and 25°C). 250 X.

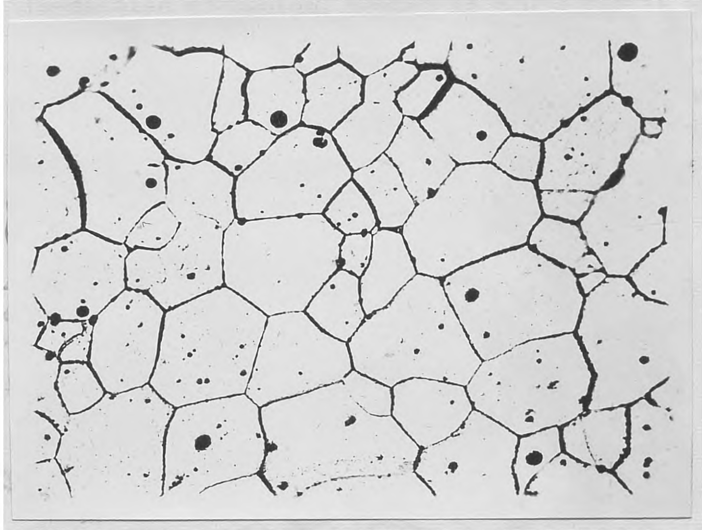


Fig. 24. Be-settled magnesium after immersion in 0.20 N HCl (1364 r.p.m. and 25°C). 250 X

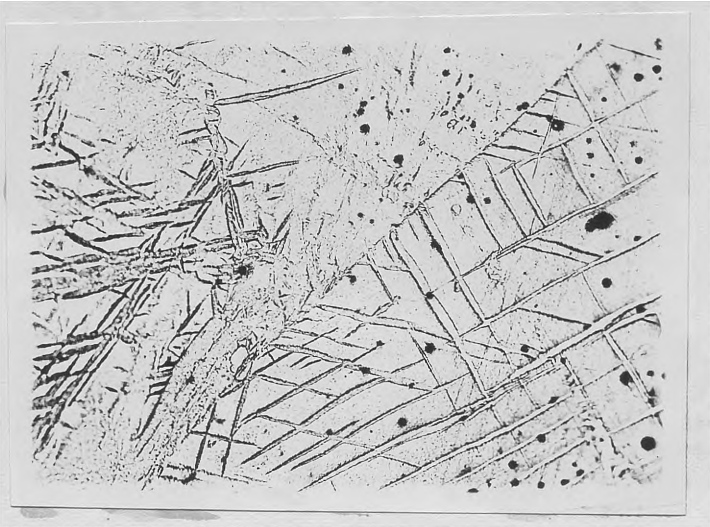


Fig. 25. Be-settled magnesium, heated at 610°C for 15 hours and quenched in water after immersion in 0.020 N HCl (1364 r.p.m. and 25°C). Comparison with Fig. 22 shows that the solution heat treatment has resulted in a decrease in the formation of the dark precipitate. 250 X

Fig. 26. Be-settled magnesium after immersion in 1 N HCl containing 0.5 mol/liter of $AlCl_3$ (1364 r.p.m. and 25°C). Stepwise attack at grain boundaries indicates that the rate of attack depends on the orientation of the grains. 250 X.

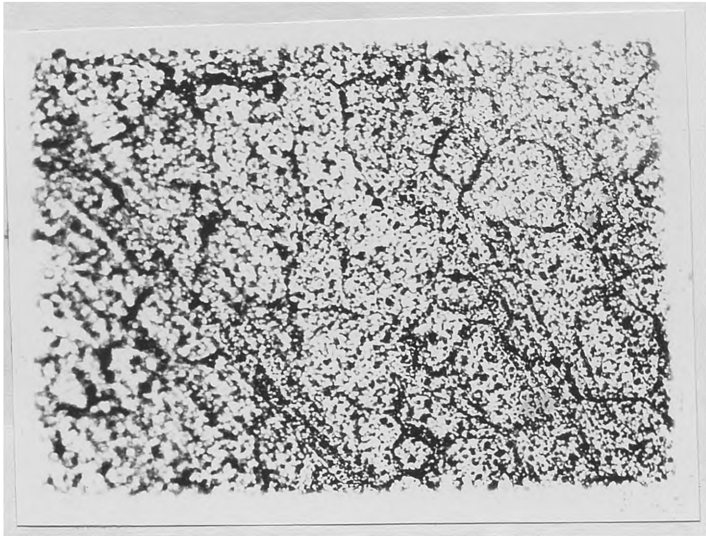


Fig. 27. Distilled magnesium after immersion in 0.020 N HCl (1364 r.p.m. and 25°C). Mottled appearance indicates that an insoluble film has been formed. 250 X.

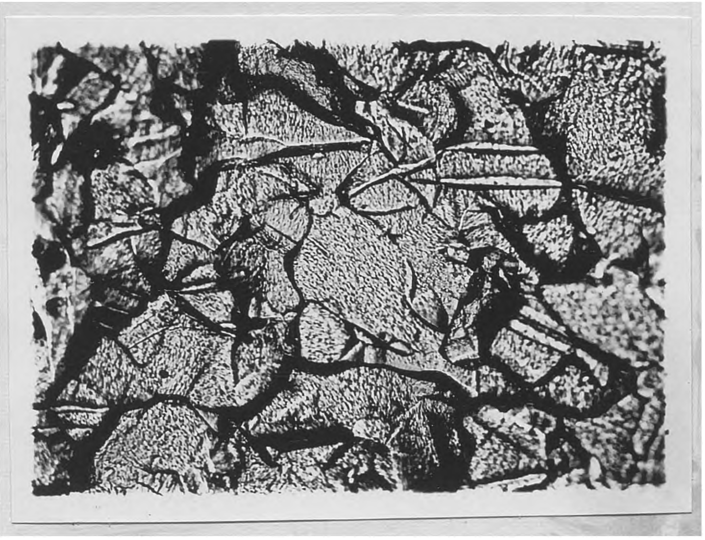


Fig. 28. Distilled magnesium after immersion in 0.5 N HCl (1364 r.p.m. and 25°C).

a. (0.042 N HCl + 0.0001% $FeCl_3$) b. (0.042 N HCl + 0.0005% $FeCl_3$) c. (0.042 N HCl + 0.001% $FeCl_3$)

Fig. 29. Be-settled magnesium after immersion in 0.042 N HCl containing (a) 0.0001% $FeCl_3$, (b) 0.0005% $FeCl_3$, and (c) 0.001% $FeCl_3$ (1364 r.p.m. and 25°C). Shows precipitates of iron which are plated out by cementation. 250 X.

Fig. 30. Be-settled magnesium after immersion in 0.042 N HCl (1364 r.p.m. and 25°C) at an applied anodic current density of 0.07 amp./sq.cm. At this current density a dark precipitate is formed, and the attack on the surface becomes irregular. 375 X.

Fig. 31. Be-settled magnesium after immersion in 0.042 N HCl (1364 r.p.m. and 25°C) at an applied cathodic current density of 1 amp./sq.cm. At this current density a precipitate, probably consisting of $Mg(OH)_2$, is formed. 250 X.

VITA

Bernt Roald, son of Andreas and Severine (Gjøsund) Roald, was born in Vigra, Norway, on October 24, 1921. After graduating from Volda Gymnasium, Volda, Norway, he was in 1940 admitted to the Norwegian Institute of Technology, Trondheim, Norway. His studies were interrupted for three years by conditions connected with the German occupation of Norway. In 1944 he went to England where he joined the Norwegian Army, and was commissioned as a second lieutenant in the Intelligence Corps. After the war he left the army to complete his engineering studies, and received his diploma as a chemical engineer in 1947. Since September, 1947, he has been a graduate student in the Department of Metallurgy of Lehigh University, Bethlehem, Pennsylvania. He is the co-author of a paper "The Equilibrium $CaCo_{3(melt)} = CaO_{(s)} + CO_2$. The activity Coefficients of Calcium Carbonate in Alkali Carbonate Melts" (*Journ. Amer. Chem. Soc.*, *71*, 572 (1949)) which is based on part of his Trondheim thesis.

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 - 1346 USA