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THE ANODIC DISSOLUTION OF MAGNESIUM IN AQUEOUS SOLUTIONS

BY

CHEN-I LU -1938-

A

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ABSTRACT

The anodic dissolution of magnesium was studied in $MgCl_2$-KCl and $MgBr_2$-KBr mixtures at 25, 40, and 55 °C. The parameters of the study were current density, concentration of magnesium ion, and temperature. The concentration of magnesium ions was varied from 0.001 to 1 N holding the ionic strength constant at 1.5. The weight loss of magnesium from the electrode during electrolysis was determined by weighing the electrode both before and after electrolysis. The current was measured with a sensitive milliammeter. The range of the current densities was varied from 0.001 to 0.1 $amps \cdot cm^{-2}$. The apparent valence of magnesium ions going into solution was determined. The following was concluded:

(1) The apparent valence of magnesium dissolving anodically is decreased rapidly as current density is increased at current densities below 0.03 $amps \cdot cm^{-2}$. From 0.03 to 0.1 $amps \cdot cm^{-2}$, the apparent valence decreases slowly with increasing density.

(2) The effect of concentration of magnesium ions and temperature on the apparent valence of magnesium dissolving anodically in KCl-$MgCl_2$ and KBr-$MgBr_2$ mixtures is small.

(3) The apparent valence of magnesium dissolving in 1 N $MgCl_2$ and $MgBr_2$ solutions has a much more pronounced temperature and current density effect at low current densities.

(4) The apparent valence-current density plots for the anodic dissolution of magnesium can be separated into two regions where there exists linear relationships between them.

The potential measurements of magnesium dissolving anodically under similar conditions led to the following conclusions:

(1) The overpotential is very slightly affected by temperature and concentration, except in 1 N $MgCl_2$ and $MgBr_2$ solutions.

(2) The electrode is not appreciably polarized at current densities below 0.03 $amps \cdot cm^{-2}$. Above 0.03 $amps \cdot cm^{-2}$, the electrode polarizes rapidly indicating passivation.

On the basis of the above, it is concluded that the behavior of magnesium is consistent with the model proposed by Sun (1) in which the anodic dissolution consists of three simultaneous processes, an electrochemical reaction, local corrosion, and disintegration. The deviation of the valence of the magnesium ions from the normal valence, i.e., deviation from Faraday's law, is accounted for by local corrosion and disintegration. A mathematical model is derived that gives the observed influence of current density.

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NOTATION

A = Atomic weight of magnesium

a_{Mg} = Activity of magnesium metal

$a_{Mg^{+2}}$ = Activity of magnesium ion, gmole/l

c = Mg^{+2} concentration, gmole/l

E_i = Steady dissolution potential at current density i, volts

E_o = Standard potential, volts

E_r = Reversible potential, volts

F = Faraday constant = 96,500 coulomb/gmequiv.

f = Activity coefficient

I = Current, amps

i = Current density, amp/cm^2

$k_1, k_2, k_3, k'_3, k', k'', k_4$, a, b, c, A, and B = Constants

n = Normal cationic charge of magnesium = 2

R = Gas constant = 8.314 joules/gmole °K

r_D = Rate of anodic dissolution by disintegration, gmole/liter sec

r_E = Rate of anodic dissolution from Faraday's law, gmole/liter sec

r_L = Rate of anodic dissolution by local corrosion, gmole/liter sec

r_T = Total rate of anodic dissolution (experimental), gmole/liter sec

T = Temperature, °K

t = Time of run, sec

V_i = Apparent valence

W_a = Apparent weight of magnesium dissolved, gm

W_e = Experimental weight of magnesium dissolved, gm

Z = Number of charges transferred

η = Overpotential, volts

σ = Standard deviation

I. INTRODUCTION

Magnesium has recently advanced from the position of being a "curiosity" metal to one of vast industrial and military importance. At the present time, the production of magnesium on an industrial scale is based almost exclusively on an electrolytic process, which consists of the electrolysis of fused magnesium salts, particularly magnesium chloride.

① The increasing demand for zinc magnesium and zinc alloys magnesium alloys in the manufacture of aircraft, space materials, and transportation vessels has stimulated a great amount of research into the corrosion characteristics of these materials. The result of such research has been the development of suitable zinc magnesium zinc alloys and protective coatings to retard corrosion.

② The electrolysis of zinc magnesium in various electrolytes has been studied by several investigators. The metal usually dissolves anodically with a current efficiency of less than 100 per cent. The dissolution is also accompanied by an evolution of hydrogen at the surface of the electrode. A detailed mechanism for this dissolution process is still forthcoming.

The purpose of this investigation was to study the effect of magnesium undergoing dissolution in various electrolytes containing appreciable concentrations of magnesium ions. Comprehensive work of this nature has not been reported previously and it could be helpful in formulating a detailed mechanism.

II. LITERATURE REVIEW

In the past sixty years, extensive investigations have been reported pertaining to the anodic dissolution of magnesium in aqueous solutions. This literature review includes a brief survey of these reports.

A. Anodic Dissolution of Magnesium in Aqueous Solution

In studies of magnesium dissolving in various electrolytes, it has been observed that the electrode potential of magnesium is considerably more noble than the reversible potential. Hydrogen evolution has been observed both on magnesium cathodes and anodes, (2) and during anodic dissolution, more magnesium is found in solution than is predicted by Faraday's law assuming a normal valence of +2. In order to account for these facts, two hypotheses have been proposed. The first assumes the metal enters into solution as "uncommon valence" ions. The second explains the behavior by a "film controlled" theory in which there may be a disintegration of the electrode as well as local corrosion.

Petty, Davidson, and Kleinberg (3) proposed a mechanism for the anodic dissolution of magnesium metal in aqueous solutions using the concept of the uncommon valence ion. They observed an initial mean valence number which was appreciably lower than two. They studied the dissolution in various electrolytes using magnesium anodes and platinum cathodes. The electrode compartments were divided. The current was supplied by a full-wave mercury rectifier and measured both with a silver coulometer and an ammeter. The initial valence number, V_i, of the metallic ions formed was calculated by means of the equation:

$$V_i = \frac{(\text{Weight of Ag deposited in coulometer})(24.32)}{(107.88)(\text{Weight of Mg lost from anode})} \qquad (1)$$

The values of V_i for Mg dissolving in various concentrations of Na_2SO_4 and $MgSO_4$ solutions were found to be around 1.4; for $KClO_3$, about 1.65.

These results were explained on the hypothesis that the primary reaction at the surface of the magnesium anode consisted of a stepwise oxidation, the first step being the oxidation of magnesium to the unipositive ion:

$$Mg \longrightarrow Mg^{+} + e \qquad \text{(at the electrode)} \qquad (2)$$

The unipositive ion, being very unstable, would readily form the dipositive ion. This was thought to occur in two ways: (1) further electrochemical oxidation at the magnesium anode, and (2) chemical oxidation by an oxidizing agent in the electrolyte, i.e.,

$$Mg^{+} \longrightarrow Mg^{+2} + e \qquad \text{(at the electrode)} \qquad (3)$$

$$Mg^{+} + \text{oxidant} \longrightarrow Mg^{+2} + \text{reductant (in the electrolyte)} \qquad (4)$$

In non-reducible electrolytes, reaction (4) could not occur and consequently an initial mean valence number of two would be obtained. In reducible electrolytes, reactions (3) and (4) would be competitive and the predominant reaction would depend on conditions of the experiment. Thus, the initial mean valence could range from 1 to 2 depending upon the relative extents of reactions (3) and (4).

Raijola and Davidson (4), and Laughlin, et al., (5) have supported the theory for unipositive ion formation for metals such as Zn, Cd, Be, and Al based on anodic dissolution experiments in perchlorate and nitrate solutions.

Greenblatt (6) has reported a study in which magnesium goes into solution as univalent ions and these are further oxidized by water. He used a magnesium anode and a silver-silver chloride cathode in 3 per cent NaCl solution. He determined the amount of Mg in the anolyte (both dissolved and as a solid product), the hydrogen evolved at the anode, and the total weight loss of the anode. The quantities of soluble Mg, insoluble Mg, and the magnesium calculated from the current passed were in approximately a one to one ratio to each other and all were roughly one-half of the total weight loss. This relationship was not affected by temperature, surface area, or current density. He proposed four reactions that would explain his observations:

$$Mg \longrightarrow Mg^{+} + e \qquad (5)$$

$$2Mg^{+} + H_2O \longrightarrow MgO + Mg^{+2} + H_2 \qquad (6)$$

$$2Mg^{+} \longrightarrow Mg^{+2} + Mg \qquad (7)$$

$$Mg \longrightarrow Mg^{+2} + 2e \qquad (8)$$

Reaction (5) followed by reaction (6) would explain the one to one ratios of soluble, insoluble, and calculated Mg which were one-half the total weight loss. The possible occurrence of reactions (7) or (8) shows that the amount of hydrogen evolved would be decreased. That the relative extent of reactions (5) and (8) can be changed is shown by the variation of apparent valence with electrolyte as reported by Petty, Davidson and Kleinberg (3). Recently, Greenblatt (7) reported further studies in which magnesium was anodically and cathodically electrolyzed in a three per cent NaCl solution containing D_2O and H_2O in known molar ratios. The gases evolved at the anode and cathode were separately collected and analyzed with a mass spectrometer. They were found to contain approximately the same ratios of D_2 and H_2. This indicated that the electron transfer mechanism at both electrodes was the same. If the reaction of univalent magnesium ions were involved, a different reaction, depending on the specific properties of the postulated univalent ion, would be taking place. Thus, he suggested that the gas discharge reaction at the anode was produced at local cathodes and not by oxidation of monovalent ions by the electrolyte. For the dissolution mechanism, Greenblatt suggested that when magnesium ions leave the metal lattice, a finite time is required for them to diffuse through the oxide film, thus creating an excess of positive ions. The film with excess positive ions must also have an equal number of anion vacancies. To obtain electrical neutrality, electrons must flow across the film, filling the anion vacancies and therefore do not pass through the external circuit. Thus, the amount of current measured through the external circuit is deficient due to this flow of electrons through the film. This results in a greater amount of metal being dissolved than the number of coulombs passed through the external circuit would indicate. The electrons flowing through the film at the anode would react with water to produce hydrogen in the same manner as they would at the local cathodes.

The film theory mechanism has been accepted by several investigators. Robinson and King (8) have explained the electrochemical behavior of the magnesium by this process. They attributed the excess anodic consumption rate of Mg with increasing anodic current density (above that predicted by Faraday's law for divalent ion formation) as due to the "negative difference effect". This, thought to result from film control in aqueous solutions of $MgBr_2$ and NaBr, is responsive to processes of film repair and film damage. In the absence of external current, the magnesium anode forms a protective magnesium hydroxide film. Upon the passing of anodic current, such a film was postulated to be damaged due to a build-up of soluble magnesium salts and thereby the unprotected areas react with water in a fashion comparable to the reaction between sodium and water. Thus, the increased rate was explained to be directly proportional to the unprotected areas. This explanation is limited to electrolytes containing anions capable of forming soluble magnesium salts.

Hoey and Cohen(9) have also studied magnesium dissolution in NaCl solution. They found thick, white films of $Mg(OH)_2$ containing small Mg particles formed on the surface of the metal anode. Hubber (10) also found evidence of thin films of MgO and/or $Mg(OH)_2$. They proposed that the corrosion rate was film controlled and suggested the following reaction to explain the hydroxide film which spalled off the surface carrying the metallic particles:

$$2Mg \rightleftharpoons Mg^{+2} \cdot Mg + 2e \qquad (9)$$

$$Mg^{+2} \cdot Mg + 2H_2O \rightleftharpoons Mg^{+2} + Mg(OH)_2 + H_2 \qquad (10)$$

$$Mg^{+2} \cdot Mg + 2OH^- \rightleftharpoons Mg \cdot Mg(OH)_2 \qquad (11)$$

$$Mg \cdot Mg(OH)_2 + 2H_2O \rightleftharpoons 2Mg(OH)_2 + H_2 \qquad (12)$$

These reactions also account for the hydrogen evolution by the corrosion products.

Straumanis, et al., (11,12) studied the anodic dissolution of Mg in HCl solutions. At high current densities, they observed dark flakes containing metal magnesium particles which were formed on the surface of the anode. These were shown to be magnesium particles held in a matrix of $Mg(OH)_2$. They discounted the concept of uncommon valency, and explained both positive and negative difference effects on the basis of anodic polarization, film disruption, and disintegration of the magnesium anode.

The fact that metal particles can be suspended in solution by electrode disintegration at high current densities has been observed by many investigators. Burton (13) produced colloidal solutions of metals in water by electrolysis. He observed that "clouds of finely divided metal particles would scatter from the cathode during sparking and would remain suspended in the water for a time depending on the nature of the metal." Metal particles were obtained from platinum, gold silver, bismuth, lead, and iron electrodes. He occasionally found some large coarse particles or "chunks" in the colloidial solutions.

Del Boca (14) studied the dissolution of various metals in liquid ammonia and suggested a mechanism to explain the deviation from Faraday's law. He suggested the dissolving metal entered into solution by formation of complex ions such as $Zn \cdot Zn^{+2}$, $Cd \cdot Cd^{+2}$, or $Al \cdot Al^{+3}$.

Straumanis and Poush (15) observed that gallium dissolved with a valence somewhat less than its normal oxidation state of three. They proposed that the reason more metal is found in solution than predicted by Faraday's law is also due to anodic disintegration. They applied the technique of using amalgamated gallium as an anode. The amalgam was made by dissolving 15 milligram samples of the metal in mercury. Anodic dissolution tests were performed on the amalgam in HCl, H_2SO_4, and $HClO_4$ solutions. The amalgam prevented anodic disintegration. The apparent valence obtained was approximately three which is the normal oxidation state for gallium. Next they performed anodic dissolution tests in cold H_2SO_4 solutions using pure gallium anodes. As soon as the current was started, a stream of grayish particles were observed droping from the anode. Under high magnification, aggregates of small metallic particles could be seen.

B. The Relationship Between the Current Density and Potential of the Magnesium Anode in Aqueous Solutions

Normal electrochemical behavior of the magnesium anode can be considered in terms of the following aspects: (a) The steady state working potential is usually on the order of a volt more noble than the standard potential of -2.43 volts, (b) the steady state potential is relatively insensitive to increasing anodic current in some environments, (c) the rate of magnesium anode dissolution increases almost linearly with current in many environments, and (d) the anode consumption rate is greater than that predicted by Faraday's law. This excess consumption is accompanied by an increase in hydrogen evolution at the anode with increasing anodic current density. (16,17,18)

Gatty and Spooner (16) pointed out that it was impossible to explain the polarization at open circuit potential by a high magnesium ion activity at the metal surface. They postulated the formation of a hydride film to explain the nobility of the observed potential.

Akimov and Rozenfeld (19) observed the effects of pH on potential and corrosion rate. They found the potential of magnesium at open circuit was practically constant in the pH range 3 to 11. Wetmore (20) observed that the potential curve showed a sharp bend toward more noble potentials at pH's$>$11. The corrosion rate showed a corresponding decrease. In buffered solutions, the potential increased sharply at pH 9.2. In acid solutions an obvious increase in potential and corrosion rate also occured at pH's$<$3.

Though the anodic dissolution of Mg has been studied extensively, proposed mechanisms have not satisfactorily explained the following observations: (a) the anodic current efficiency in aqueous solutions which is less than 100 per cent for various electrolytes (the anodic current efficiency is defined as the ratio of the actual coulombs passed to the theoretical coulombs obtained from the actual weight loss assuming a magnesium valence of two), (b) the amount of hydrogen evolved at the anode that is equivalent to the excess Mg dissolved, and (c) the corrosion film formed on Mg anode that is composed of Mg, MgO, and $Mg(OH)_2$.

The electrochemical formation of monovalent Mg (5-9) has been used to account for the low current efficiencies, and the hydrogen and corrosion product formation. Robinson (17) has suggested that the low current efficiencies might be due to an enhanced corrosion rate at the anode, since in unbuffered solutions, the acidity at the metal-solution interface is higher than in the bulk of the solution for anodically polarized Mg. He found, in the presence of ions such as OH^-, F^-, $CO_3^=$, BO_2^-, and $PO_4^{\equiv}$, that the anodic polarization curves of Mg were flat up to current densities of 1 $ma \cdot cm^{-2}$ when the solutions contained ions which formed soluble Mg salts.

Hoey and Cohen (9) also supported Robinson's concept. However, this explanation was not satisfactory for buffered solutions. They explained that the formation of thick films of $MgMg(OH)_2$ on anodically polarized Mg might possibly lead to an enhancement of the rate of local corrosion at the anode. This depended on two assumptions: (a) the film on the anodic areas being $Mg \cdot Mg(OH)_2$ and (b) the amount of Mg in the film. They observed that the resistance of the film was inversely proportional to the anodic current density, and that the rate of corrosion at the anode was directly proportional to the current density. The current efficiencies observed at room temperature were considerably lower than at higher temperatures. This might be accomplished by the lesser solubility of $Mg(OH)_2$ at higher temperatures which would stifle the local corrosion. They also found that the current efficiency increased with current density at low currents, but became independent of current density at higher values. The current efficiency also increased with pH in the lower pH range.

King (21) suggested that magnesium was normally in either the passive or transpassive state in various electrolytes. He defined "passivity" as the behavior of an electrochemically active metal when it appears to be less active or more noble. He stated that if magnesium was in the transpassive state, its corrosion rate could be decreased by lowering the potential into the passive region. When magnesium was polarized in the negative direction to the region of its reversible potential, a considerable weight loss was observed which might be due to the incipient breakdown of passivity. It was also pointed out that the increased corrosion rate at low pH values could be due to depolarization of both the local anodes by breakdown of the $Mg(OH)_2$ protective film and the local cathodes by the increased availability of protons for discharge. He showed that the pH decreased appreciably with increasing magnesium ion concentration and suggested that the local corrosion rate might well be expected to rise with increasing current density.

Muller, et al., (22) studied the anodic passivity of Mg in H_2SO_4, HNO_3, NaOH, and $MgCl_2$ solutions. They found that the current-time curves were similar to those obtained with other metals in H_2SO_4 solutions. Magnesium became passive in HNO_3 solutions, but side reactions complicated the phenomenon. Passivity was not reached in $MgCl_2$ solutions. Passivity in NaOH solutions resulted quickly.

III. EXPERIMENTAL

The purpose of this investigation was study the anodic dissolution of magnesium in constant ionic strength solutions containing magnesium ions. The solutions were mixtures of $MgCl_2$ with KCl, and $MgBr_2$ with KBr.

The experimental plan consisted of the following major phases: (1) the effect of electrolyte, concentration, temperature, and current density on the apparent valence of magnesium undergoing anodic dissolution, and (2) polarization studies of magnesium undergoing anodic dissolution under the same conditions as phase (1).

A. Materials

The list of materials is given in Appendix A.

B. Equipment

The list of apparatus is given in Appendix B.

C. The Effect of Concentration, Temperature, and Current Density on the Apparent Valence of Magnesium Undergoing Anodic Dissolution in Various Electrolytes

1. Apparatus. The apparatus consisted of a separated compartment electrolytic cell of 400 ml capacity, a magnesium anode, a platinum cathode, a sensitive milliammeter, a decade power resistor, a d.c. power supply, and a knife-blade switch, all connected in series. A diagram of the apparatus is shown in Figure 1. An electric timer was used for measuring the elapsed time. The cell was immersed in a water bath which was controlled at a constant

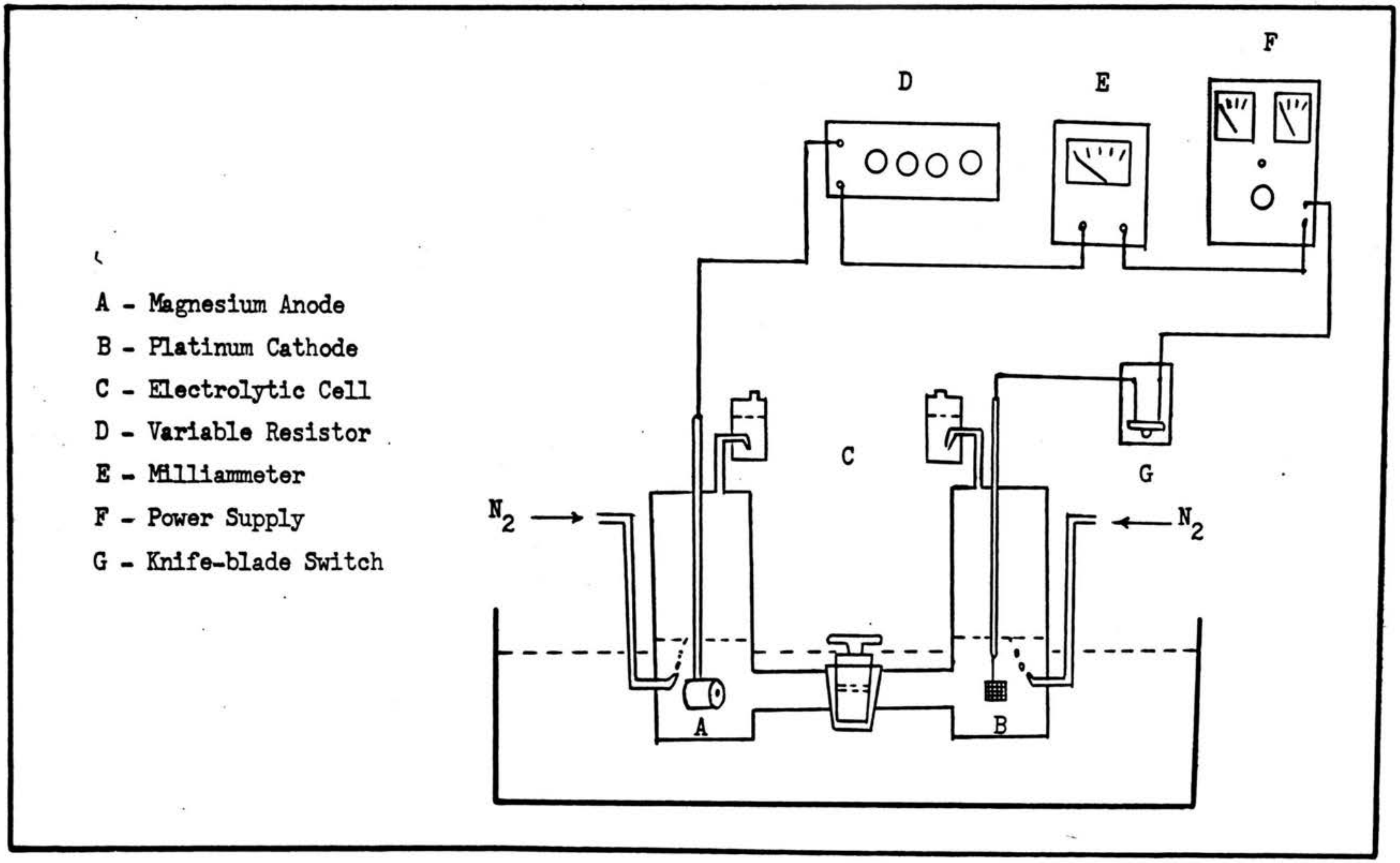

Figure 1. Apparatus used for measurement of apparent valence of magnesium undergoing anodic dissolution.

temperature within ± 0.1 °C.

2. Procedure. A platinum cathode of 9 cm^2 area was constructed from platinum gauze. A cylindrical magnesium specimen with a cross-sectional area of 1.0 cm^2 and 2.0 cm long was cut from a polycrystalline bar of 99.999 per cent purity and mounted in a teflon holder. The electrode was polished immediately before each run as previously decribed (23), dried, and weighed as decribed the following section. A measured quantity (250 ml) of electrolyte was transferred to the electrolytic cell. The cell was placed in the constant temperature bath in such a position as to insure complete submergence of the solution. The solution was allowed to remain in the water bath for about one hour to bring the system to constant temperature before starting a run. Nitrogen was bubbled through the anodic and cathodic compartments. The magnesium anode and the platinum cathode were then immersed into the anodic and cathodic compartments of the electrolytic cell and connected into the external circuit as shown in Figure 1. The knife-blade switch was closed and the current was kept at a steady value by adjusting the resistance box. The timer and milliammeter were used for measuring the number of coulombs (amp-seconds) passed. After a predetermined time interval, the knife-blade switch was opened and the electrodes were removed from the electrolytic cell. The magnesium anode was put into distilled water and the white film brushed off with a soft nylon brush. It was then dried with heated air for 30 minutes, put into a desiccator for 8 hours, and weighed on a balance with a

sensitivity of 0.1 milligram to determine the weight loss of magnesium. The procedure employed was the same for all electrolysis experiments.

3. Data and Results. The anodic dissolution of magnesium was observed in two electrolytes, $MgCl_2$-KCl and $MgBr_2$-KBr mixtures, at a constant ionic strength of 1.5. The range of current densities was from 0.001 to 0.100 amps$\cdot$cm^{-2}, and the temperature range was from 25 to 55 ^{o}C.

a. Magnesium chloride-potassium chloride mixtures. The concentration of magnesium ions was varied from 0.001 to 1.0 N. Data for these runs are shown in Tables I to XXI, Appendix C. A graphical representation is shown in Figures 2 to 4. It can be seen that the apparent valence decreases rapidly with increasing current density from 0.001 to 0.01 amps$\cdot$cm^{-2}. Above 0.01 amps.cm^{-2}, it changes very slightly in the region studied. There is no pronounced temperature effect except in $MgCl_2$ solution where the rate of local corrosion is of comparable magnitude to the anodic dissolution rate. The conditions of the electrode surface and the electrolyte for the different experiments are shown in Tables XXII and XXIII, Appendix C.

b. Magnesium bromide-potassium bromide mixtures. The concentration of magnesium ions in these solutions was also varied from 0.001 to 1.0 N. Data from these runs are shown in Tables XXIV to XLIV, Appendix C. The effect of current density and concentration on the apparent valence at different temperatures is also shown in Figures 5 to 7. The apparent valence again decreases rapidly with increasing current density from 0.001 to 0.01 amps$\cdot$cm^{-2}. Above

0.01 amps$\cdot$cm^{-2}, the apparent valence decreases slightly. Here again, there was only a slight effect on the apparent valence by temperature except in $MgBr_2$ solutions. Surface conditions, pitting, etc., are shown in Tables XLV and XLVI, Appendix C.

4. Sample Calculations. The method used to calculate the apparent valence in the Cl^- and Br^- solutions was the same. The data from the experiment in 1.0 N $MgCl_2$ (Table VII) have been used to illustrate these calculations.

a. Calculation of the apparent weight of magnesium dissolved from coulombic data. The apparent weight of magnesium dissolved according to Faraday's law, assuming the normal valence of 2, was calculated as follows:

$$W_a = \frac{(I)(t)(A)}{(n)(F)} \qquad (13)$$

$$= \frac{(0.01)(20{,}000)(24.32)}{(2)(96{,}500)} = 0.0252 \text{ gm}$$

b. Calculation of the apparent valence. The apparent valence was calculated by means of the equation:

$$V_i = \frac{(W_a)(\text{normal valence})}{(W_e)} \qquad (14)$$

$$= \frac{(0.0252)(2)}{(0.0353)} = 1.43$$

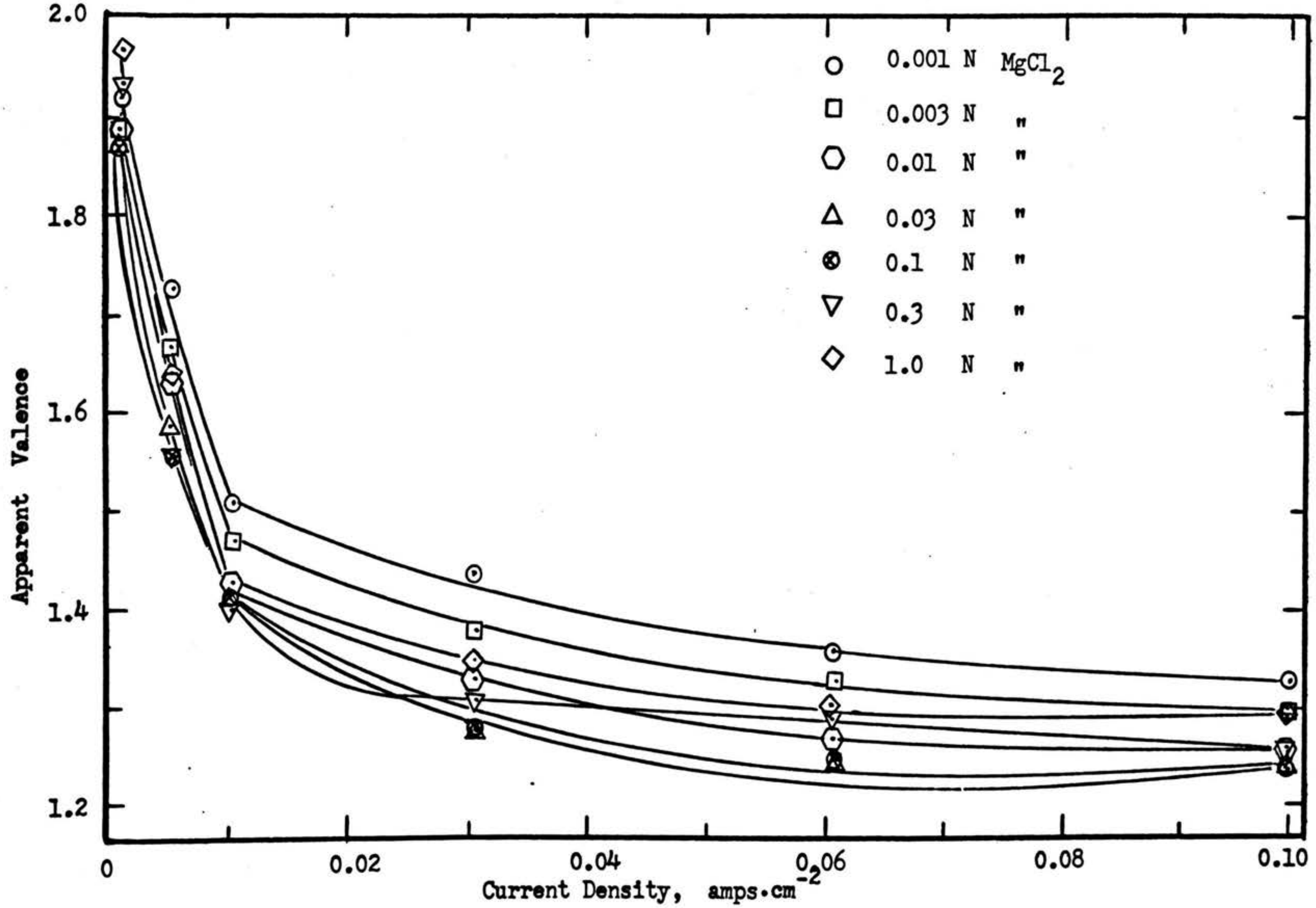

Figure 2. The apparent valence of magnesium dissolving anodically in $MgCl_2$ - KCl solutions (ionic strength = 1.5) at 25 °C.

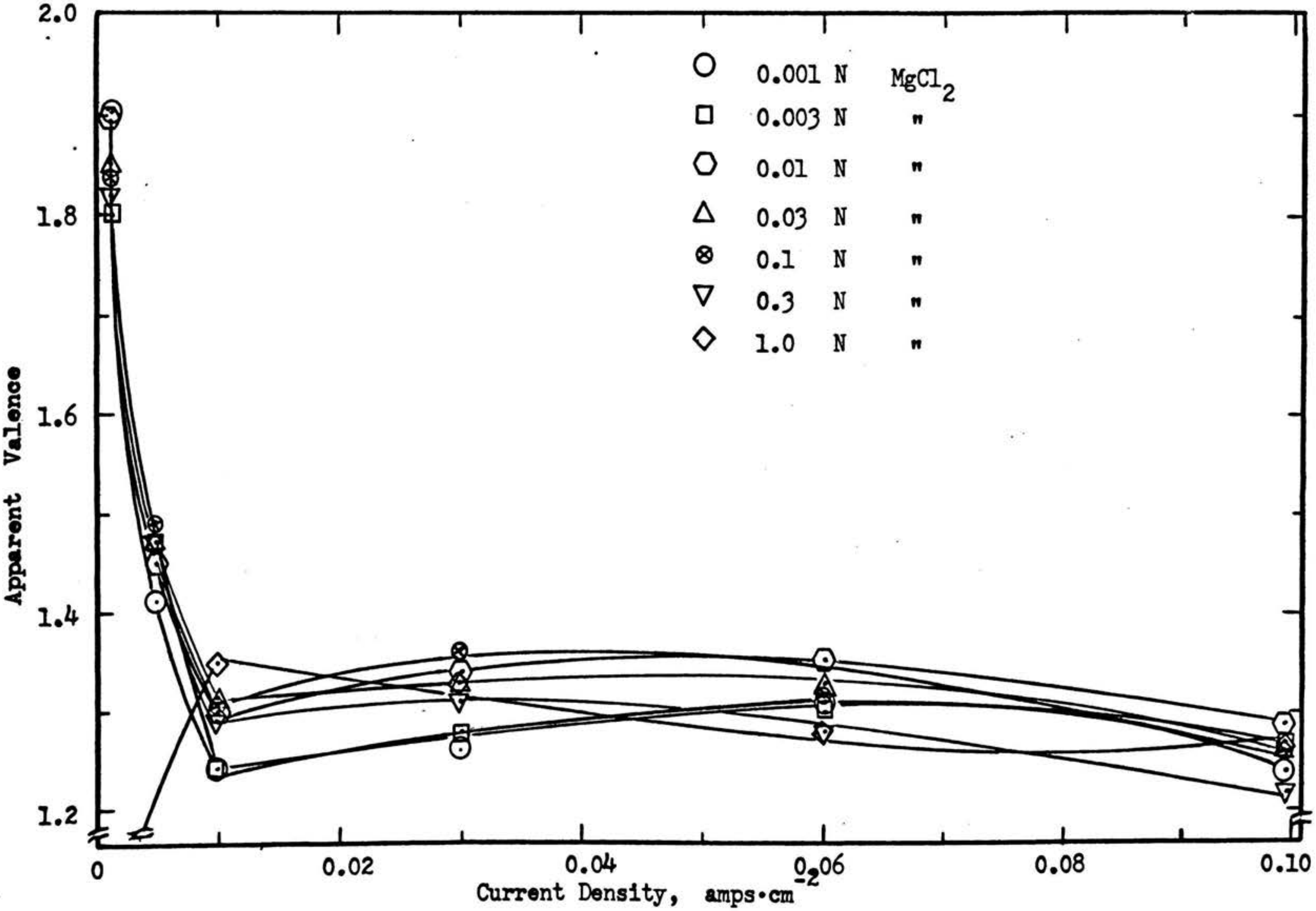

Figure 3. The apparent valence of magnesium dissolving anodically in $MgCl_2$ - KCl solutions (ionic strength = 1.5) at 40 °C.

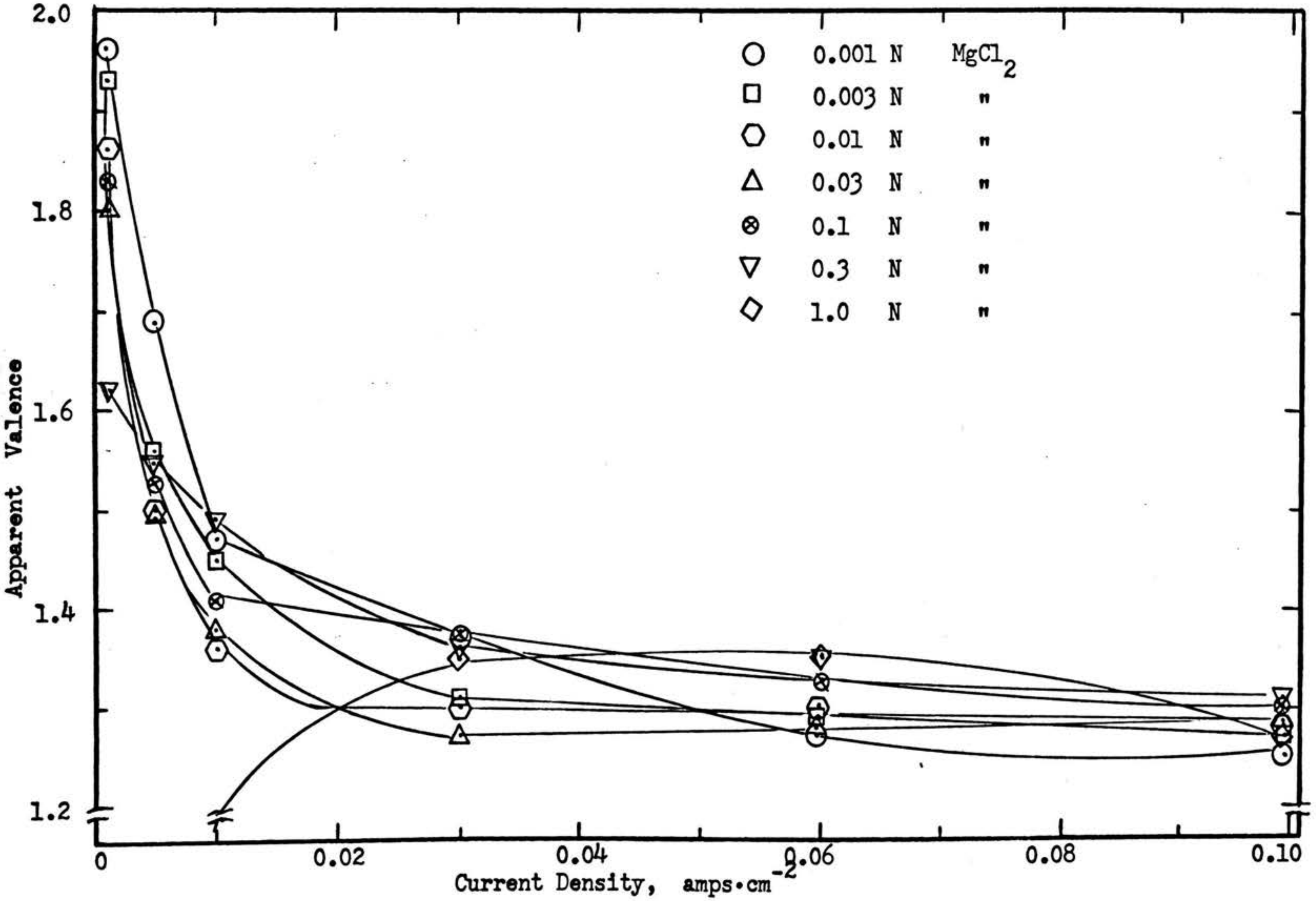

Figure 4. The apparent valence of magnesium dissolving anodically in $MgCl_2$ - KCl solutions (ionic strength = 1.5) at 55 °C.

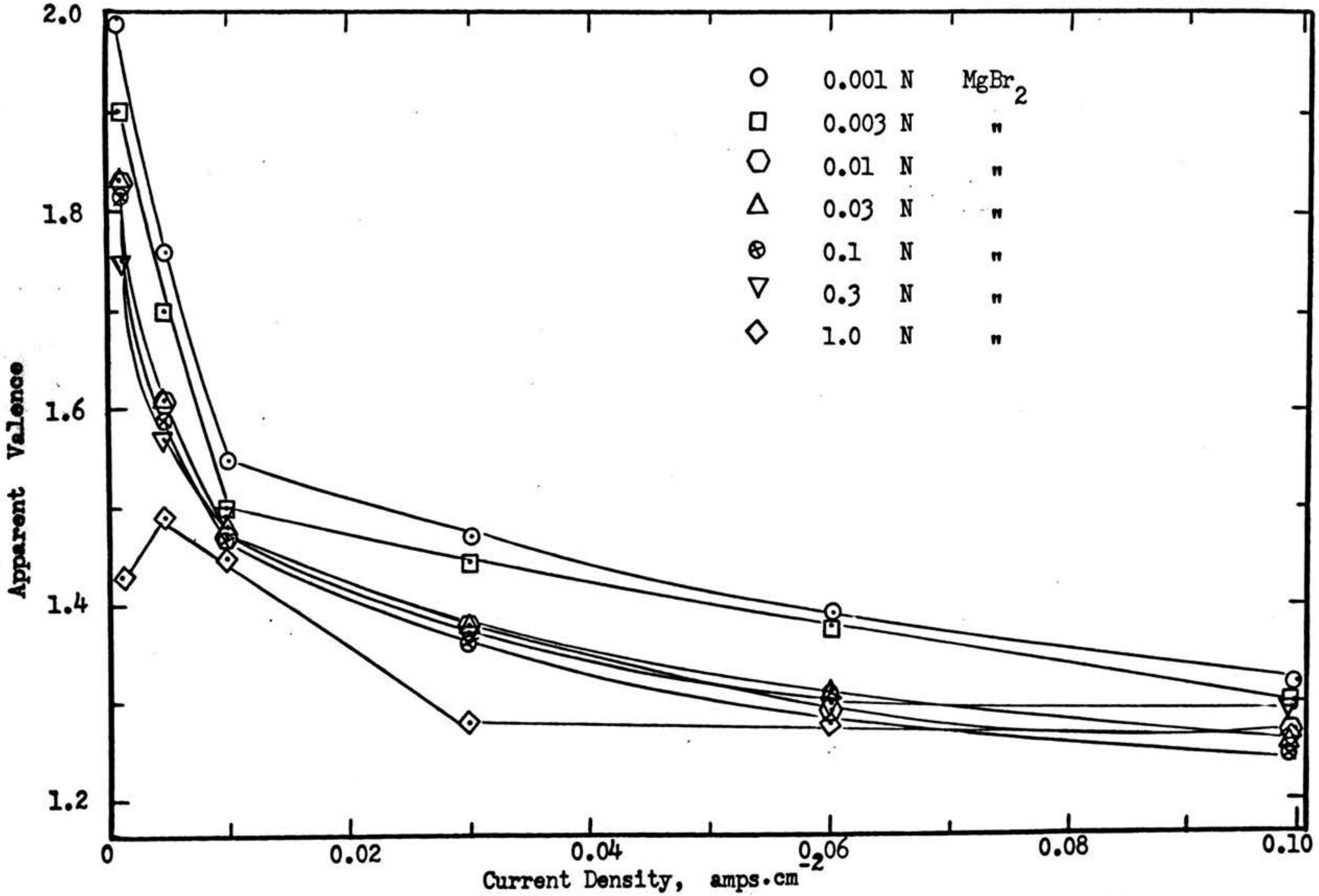

Figure 5. The apparent valence of magnesium dissolving anodically in $MgBr_2$ - KBr solutions (ionic strength = 1.5) at 25 °C.

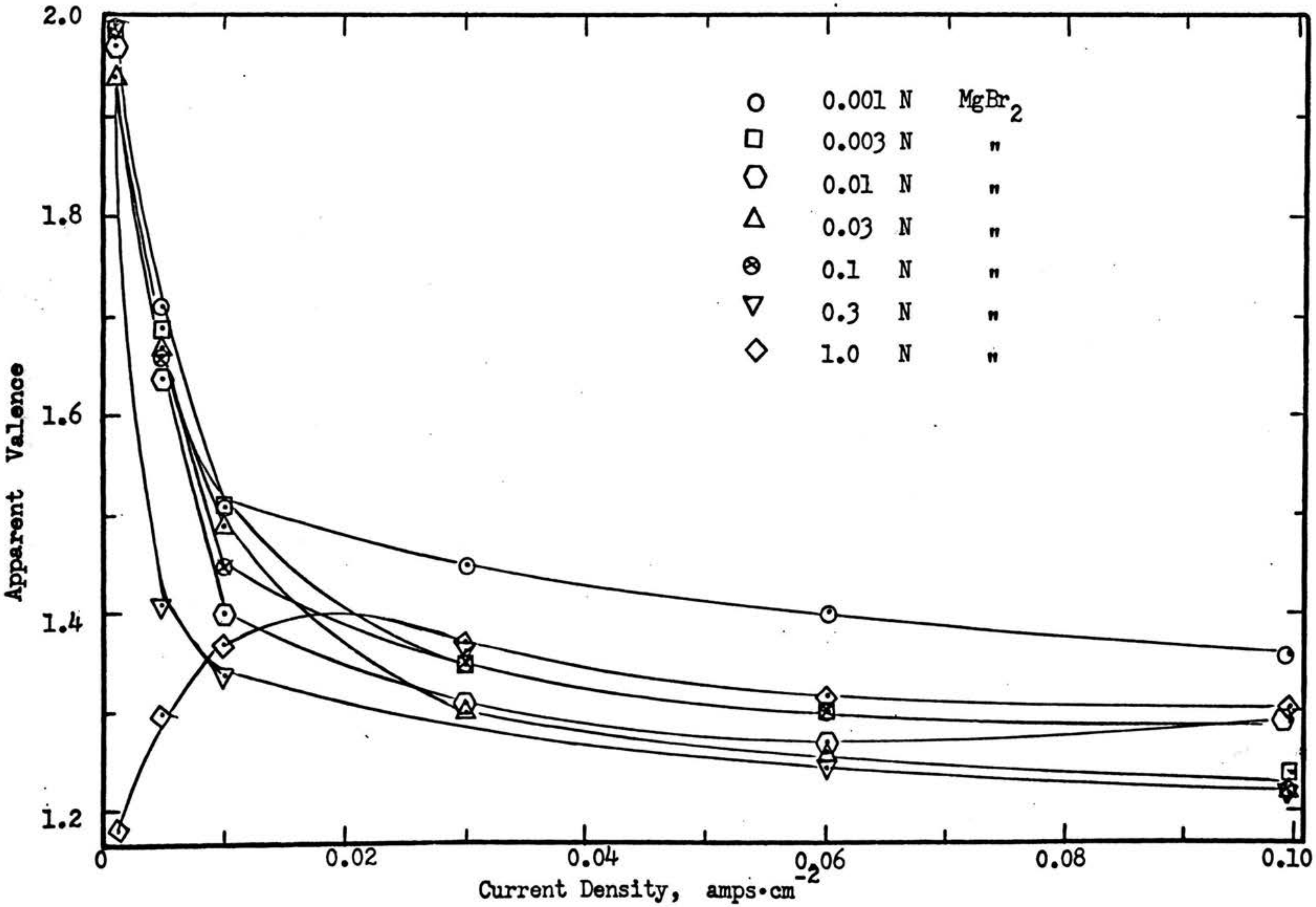

Figure 6. The apparent valence of magnesium dissolving anodically in $MgBr_2$ - KBr solutions (ionic strength = 1.5) at 40 °C.

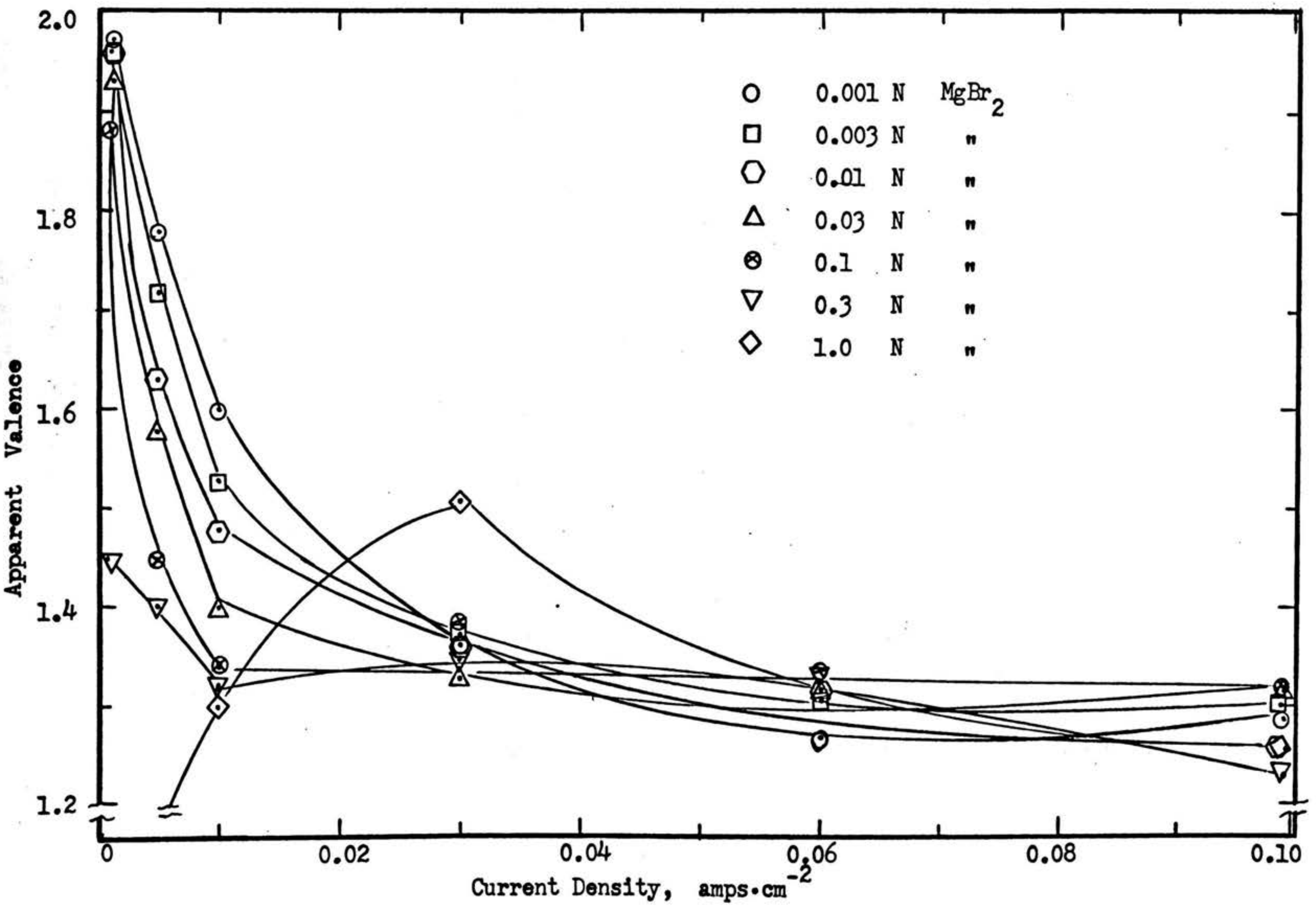

Figure 7. The apparent valence of magnesium dissolving anodically in MgBr$_2$ - KBr solutions (ionic strength = 1.5) at 55 °C.

D. The Polarization Study of Magnesium Undergoing Anodic Dissolution in Various Electrolytes

1. Apparatus. The apparatus was the same as described previously except that a 1 N calomel reference electrode was connected to the magnesium anode through a salt bridge and Luggin capillary. A high impedence electrometer was used to measure the potential. A diagram of the apparatus is shown in Figure 8.

2. Procedure. The procedure was similar to that decribed previously. Initially, the anode was allowed to came to a steady potential with no current flowing (rest potential). After reaching this state, different currents, varying from 0.001 to 0.1 amps$\cdot$cm^{-2}, were impressed on the anode. Potentials were noted at 15 minutes intervals until they became steady.

3. Data and Results. The anodic dissolution potentials of magnesium were observed under the same conditions as those for which the apparent valences were determined. A brief summation of the experimental results follows:

a. Magnesium chloride-potassium chloride mixtures. The anodic dissolution potentials of magnesium were measured in $MgCl_2$-KCl solutions (constant ionic strength = 1.5) in which the magnesium ion concentration was varied from 0.001 to 1.0 N. Data from these runs are shown in Tables XLVII to LVIII, Appendix C. Tafel plots are shown in Figures 9 to 11. The potentials (or overpotentials) were nearly constant at current densities below 0.030 amps$\cdot$cm^{-2}. Above 0.03 amps$\cdot$cm^{-2}, the overpotentials increased rapidly with increasing current density.

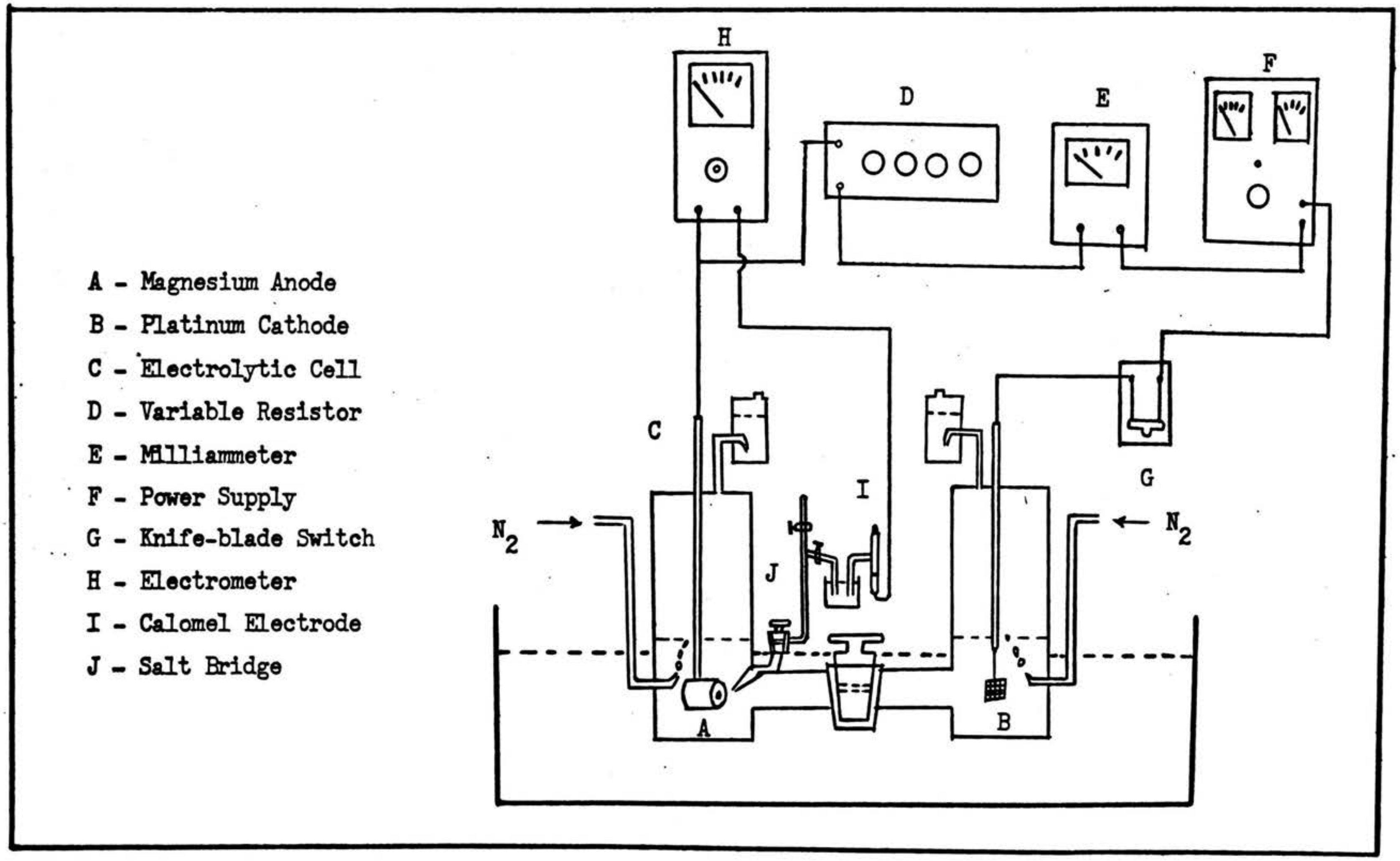

Figure 8. Apparatus used for measurement of dissolution potential of magnesium.

b. Magnesium bromide-potassium bromide mixtures. The anodic dissolution potentials of magnesium were also obtained in $MgBr_2$-KBr solutions in which the Mg^{+2} concentration was varied from 0.001 to 1.0 N. Data from these runs are shown in Tables LIX to LXX, Appendix C. Tafel plots are shown in Figures 12 to 14. The overpotential behavior was similar to that in Cl^- solution except that 0.010 $amps \cdot cm^{-2}$ seemed to divide the regions of slowly and rapidly increasing overpotentials.

4. Sample Calculations. The method used to calculate the overpotentials in $MgCl_2$-KCl and $MgBr_2$-KBr solutions was the same. The data from Table LIX, Appendix C have been used to illustrate these calculations.

a. Calculation of the overpotential of the magnesium from dissolution potential data. The overpotential of magnesium was calculated by means of the equation:

$$\eta = E_i - E_r \qquad (15)$$

Therefore,

$$\eta = (-1.28) - (-2.38) = 1.10 \text{ volts}$$

b. Calculation of the reversible potential. The reversible potential of the electrode was calculated using the Nernst equation:

$$E_r = E_o - \frac{2.303\ R\ T}{Z\ F} \log \frac{a_{Mg}}{a_{Mg^{+2}}} \qquad (16)$$

Therefore,

$$E_r = -2.38 - \frac{(2.303)(8.314)(298)}{(2)(96,500)} \log \frac{1}{0.04} = -2.42 \text{ volts}$$

The calculated value of the reversible potential for each Mg^{+2}

concentration used in this study is shown in Table LXXI, Appendix C.

c. Calculation of ionic activity. The activity coefficient of the magnesium ion was obtained from Falkenhagen (24) for a Mg^{+2} solution of ionic strength 1.5. The ionic activity was calculated from the equation:

$$a_{Mg^{+2}} = fc \qquad (17)$$

Therefore,

$$a_{Mg^{+2}} = (0.08)(0.5) = 0.04 \text{ gmoles/liter}$$

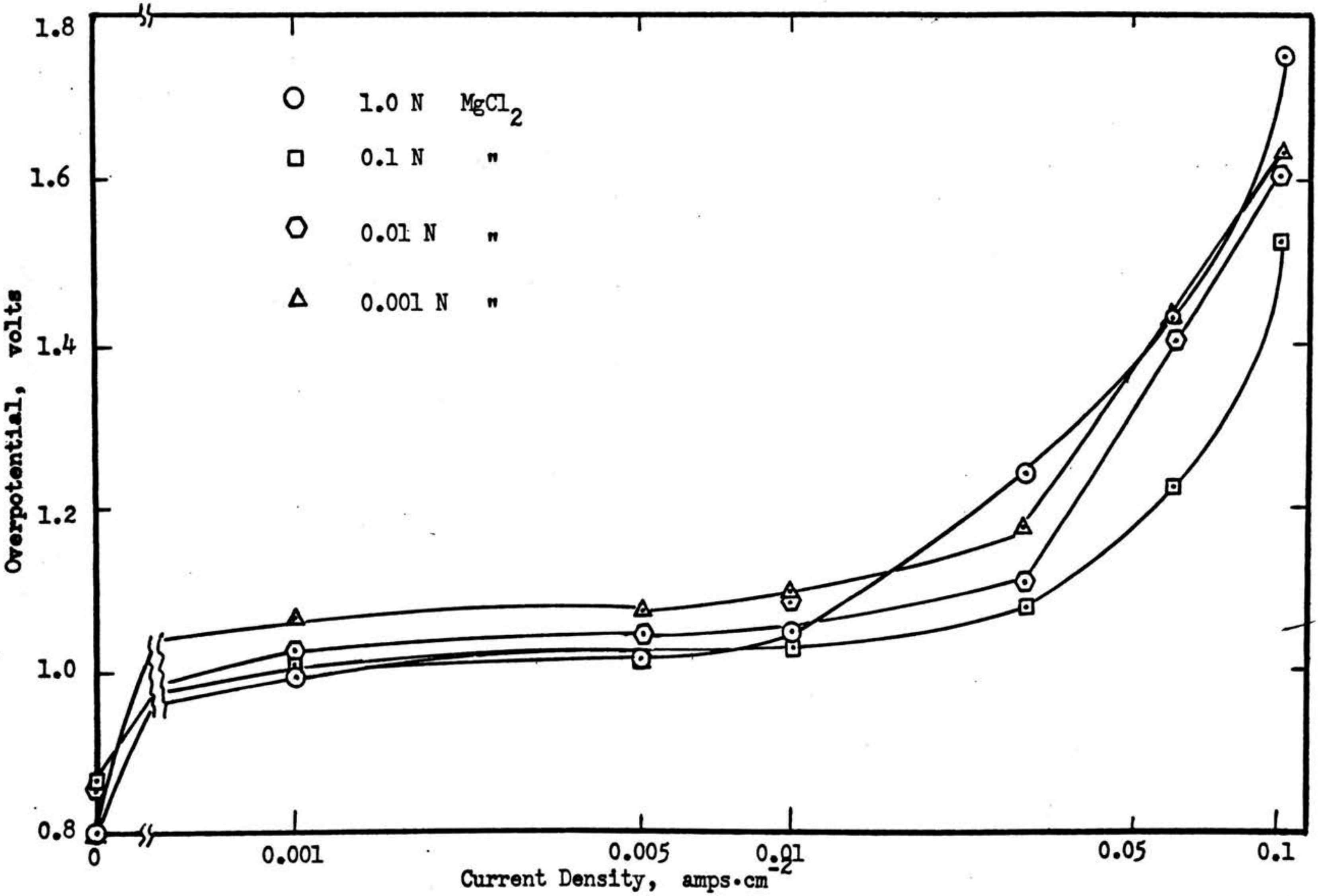

Figure 9. Tafel curves for magnesium undergoing anodic dissolution, $MgCl_2$ - KCl solutions (ionic strength = 1.5) at 25 °C.

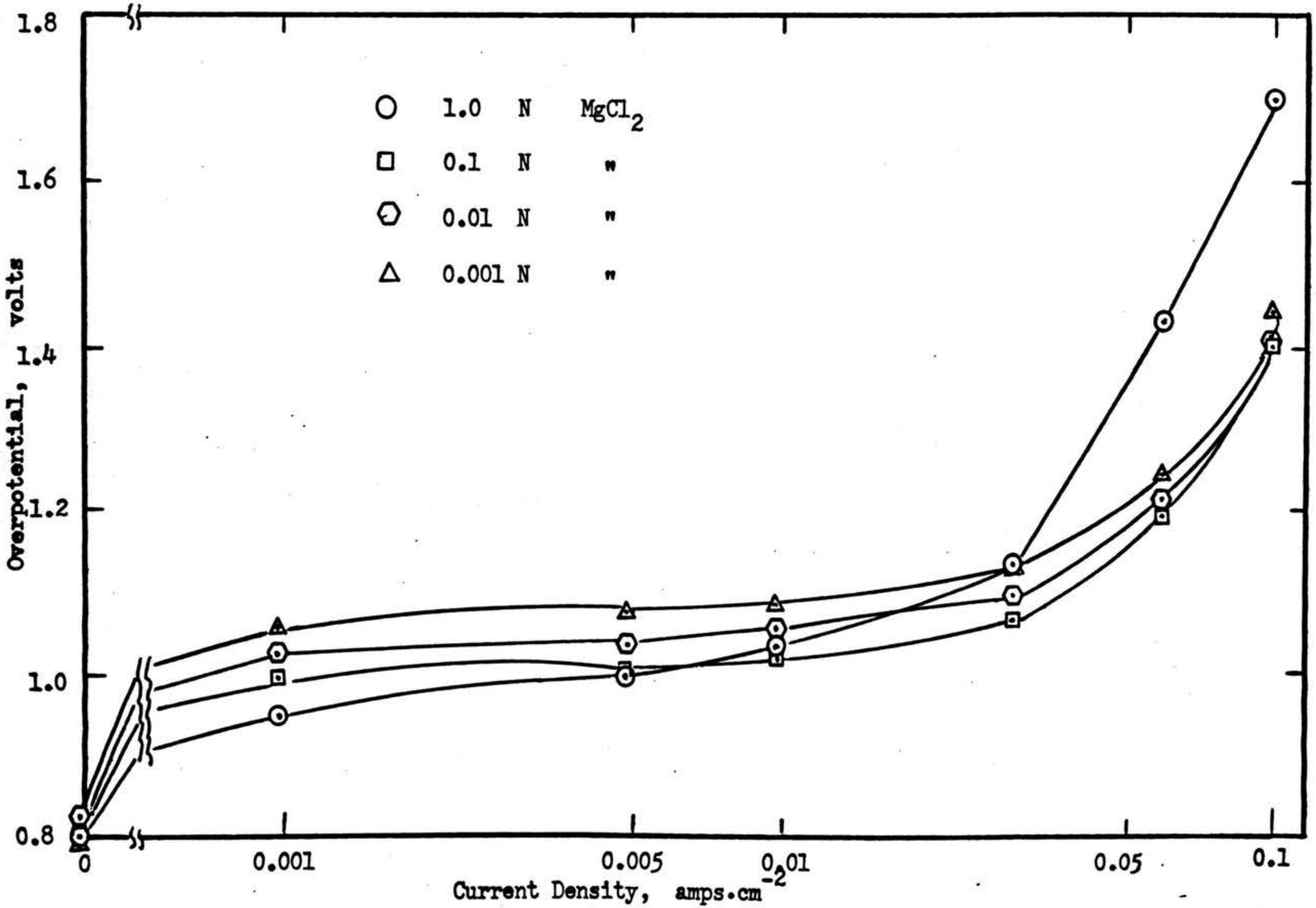

Figure 10. Tafel curves for magnesium undergoing anodic dissolution, $MgCl_2$- KCl solutions (ionic strength = 1.5) at 40 °C.

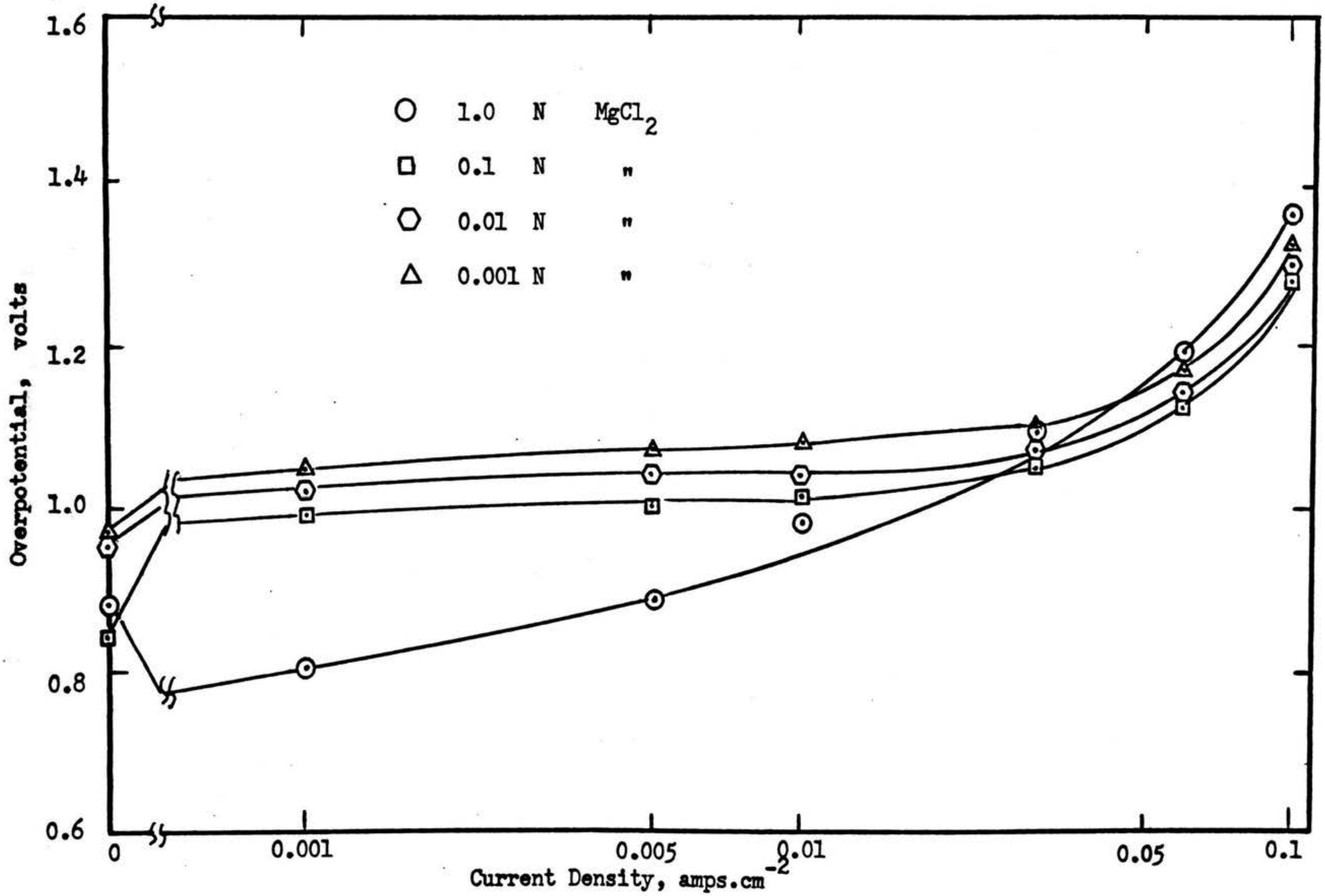

Figure 11. Tafel curves for magnesium undergoing anodic dissolution, MgCl$_2$ - KCl solutions (ionic strength = 1.5) at 55 °C.

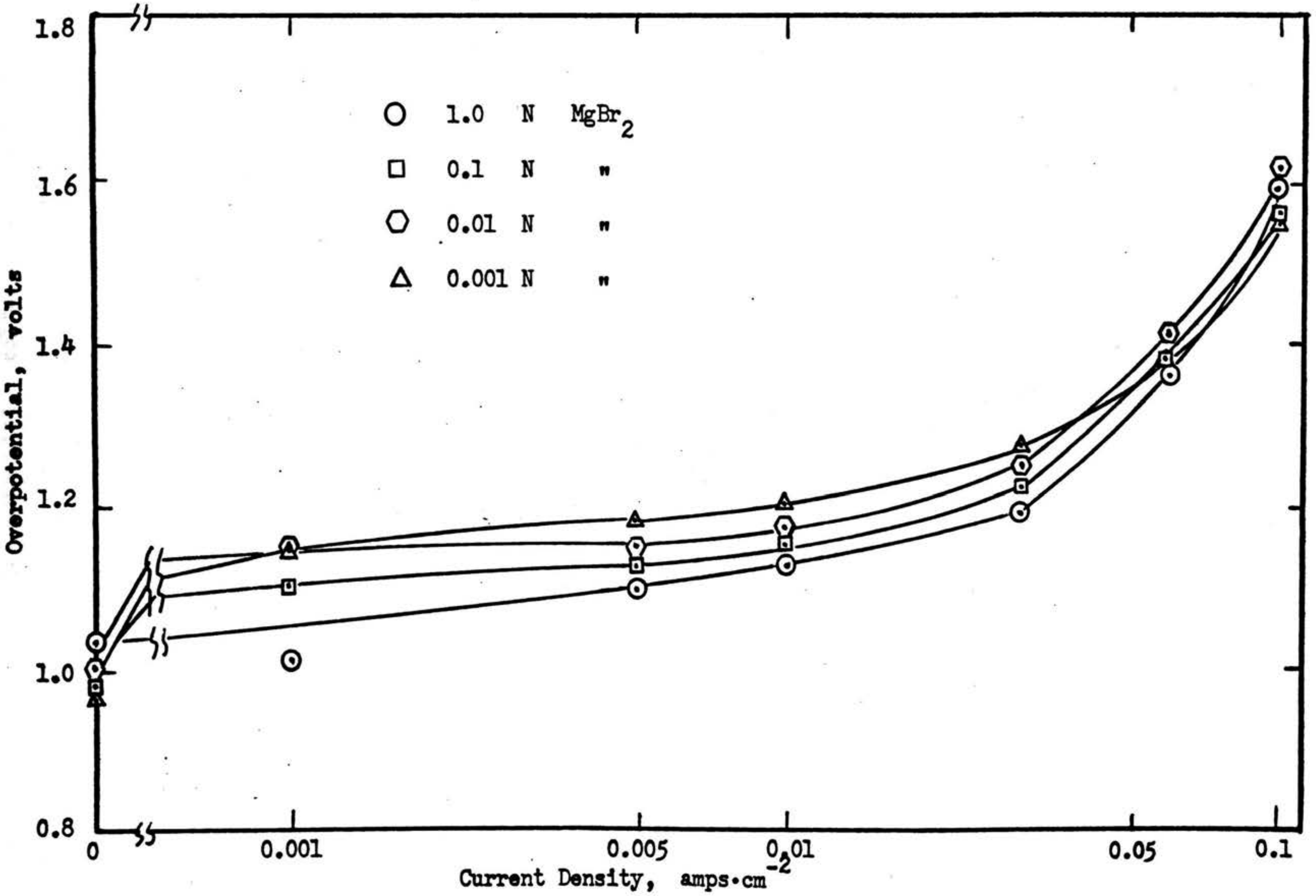

Figure 12. Tafel curves for magnesium undergoing anodic dissolution, $MgBr_2$ - KBr solutions (ionic strength = 1.5) at 25 °C.

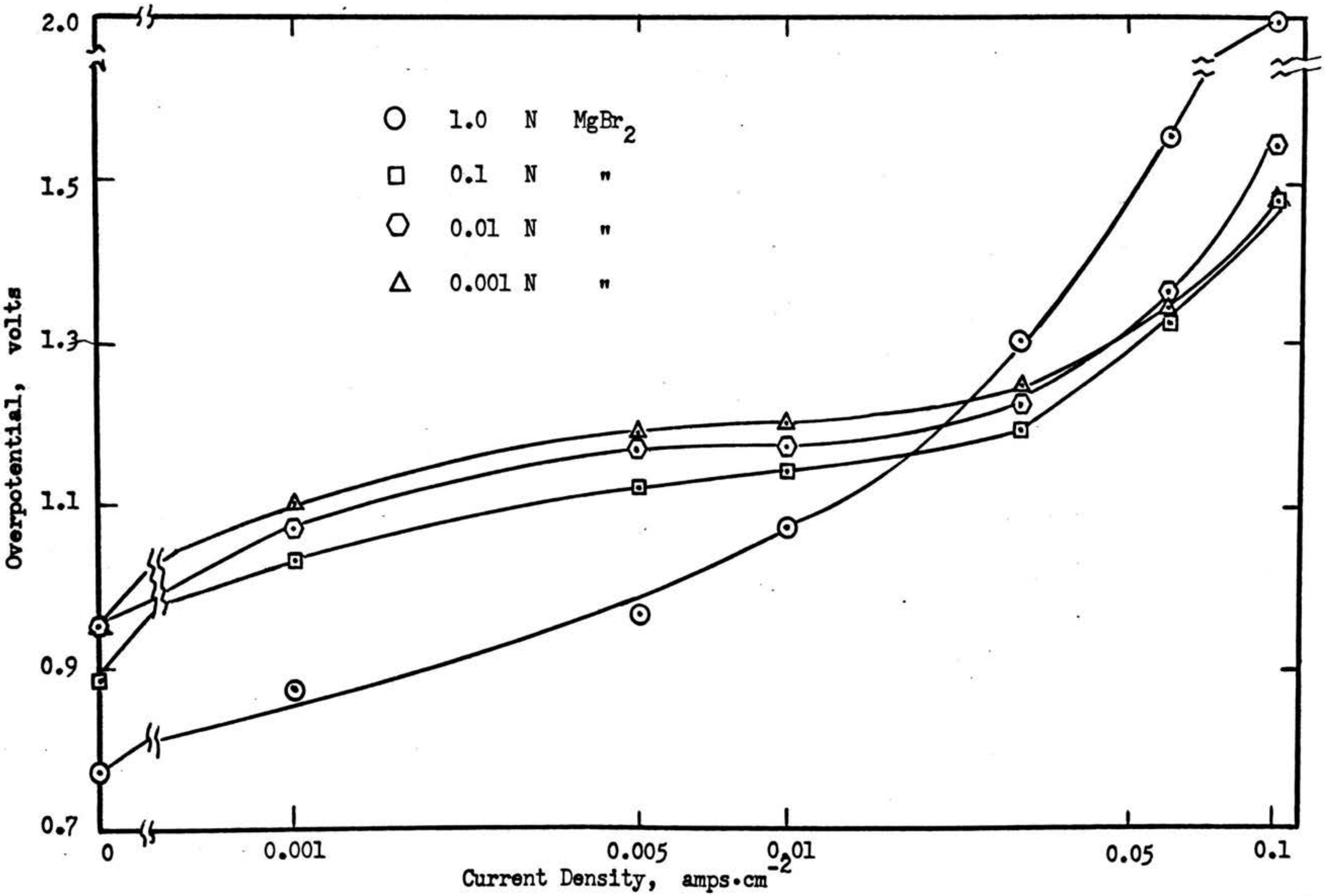

Figure 13. Tafel curves for magnesium undergoing anodic dissolution, MgBr$_2$ - KBr solutions (ionic strength = 1.5) at 40 °C.

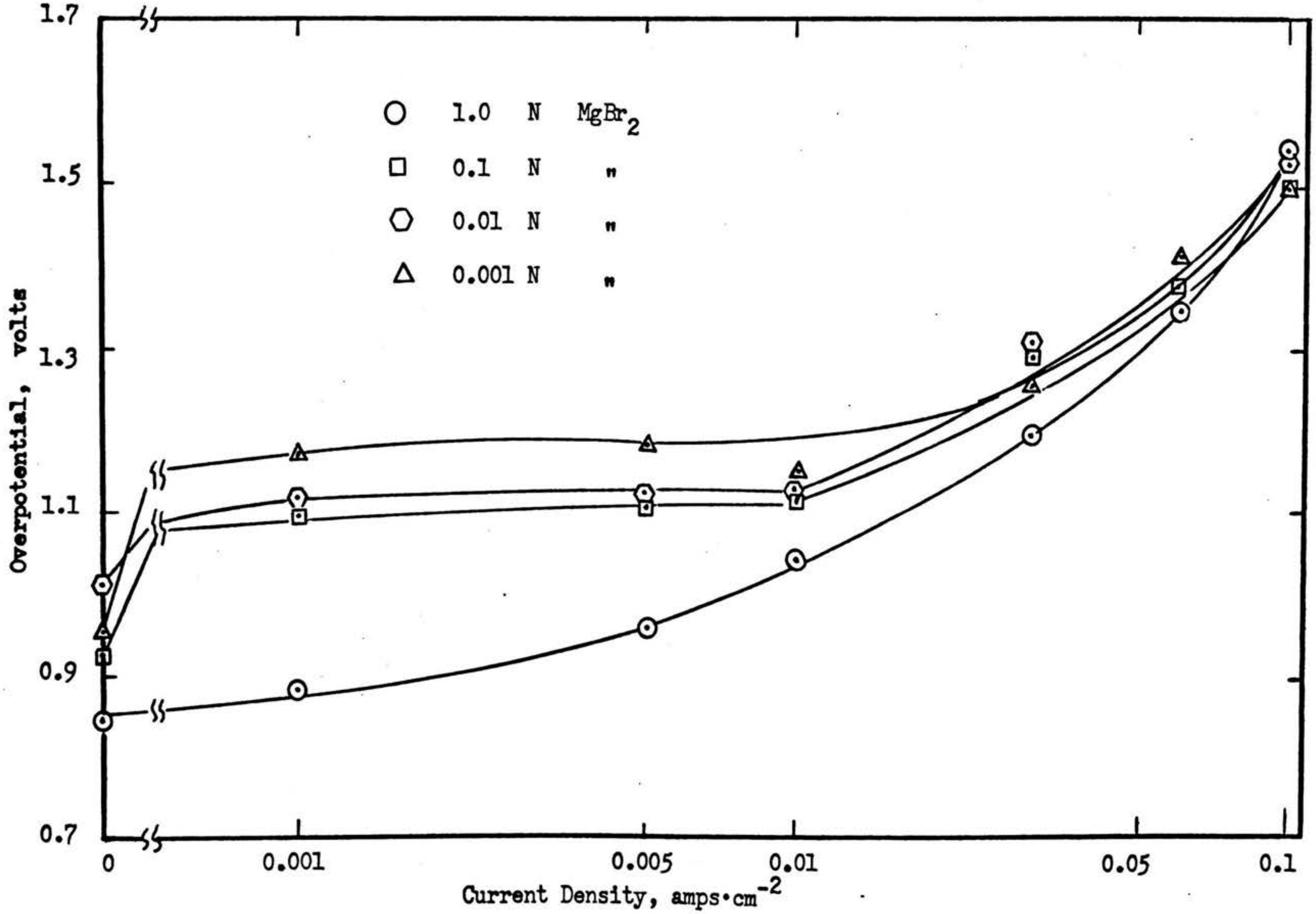

Figure 14. Tafel curves for magnesium undergoing anodic dissolution, MgBr$_2$ - KBr solutions (ionic strength = 1.5) at 55 °C.

IV. DISCUSSION

None of the work to date has given a clear picture of the mechanism of the anodic dissolution of magnesium. The present work was undertaken to study the effect of magnesium ions on the dissolution in an attempt to further clarify mechanisms that have been suggested.

In a recent study by Sun on zinc, (1) a mechanism has been suggested that accounts for the majority of the phenomena that is observed upon the anodic dissolution of reactive metals. This mechanism begins with the observation that metal anodes such as Zn, Cd, Be, Pb, Mg, and Ti are initially covered with a protective film (oxide or hydroxide) prior to electrolysis. As an external current is applied, the expulsion of metallic ions from the electrode surface disrupts the film and uncovers local elements consisting of local cathodes and anodes. These local elements allow corrosion to occur. If corrosion is to proceed on a metal with a high hydrogen overpotential, e.g., zinc, the H^o formed on the local cathodes must be removed by oxidizing agents (NO_3^- or ClO_4^-) in the electrolyte. In other words, the nitrate or chlorate ions serve as depolarizers. The hydrogen forming on the local cathodes protects these areas from corrosion, but allows metal from surrounding areas to be dissolved until the local cathodes are detached from the electrode. This causes the so-called "disintegration" of the anode. Thus, it is proposed that the disintegration rate is proportional to the local corrosion rate and that these phenomena are responsible for the observed deviation of the apparent valence from the normal value. Sun found that when zinc is dissolved anodically in nitrate solutions, the apparent valence reaches a limiting value above current densities of approximately 0.03 amps•cm^{-2}. Below 0.03 amps•cm^{-2}, the apparent valence increases and approaches the normal valence as a limiting value. He suggested that at low current densities, the local corrosion (and disintegration) rate is increasing exponentially with external current due to the large ratio of protected area to local elements which allows the local elements to spread laterally. At high current densities, the local corrosion rate increases linearly with external current due to the small ratio of protected area to local elements, thus, the local elements increase linearly with increasing current density. He also found that the apparent valence was a function of nitrate concentration. This is in conformity with the mechanism as the concentration of the depolarizer (NO_3^-) would control the local corrosion rate. Thus, disintegration is facilitated by the action of oxidizing agents when corrosion is cathodically controlled by the combination of hydrogen atoms.

With metals such as magnesium, the corrosion potential is large enough that the hydrogen overpotential is overcome and local corrosion can occur without a depolarizer. Thus magnesium shows an uncommon valence in most all aqueous solutions. Concentration effects are those associated with changes in the corrosion potential.

Current density effects on the apparent valence of magnesium have been shown in Figures 2 to 7 for $MgCl_2$ and $MgBr_2$ solutions.

Similar data taken by Chi (21) in 1 N solutions of KCl and KBr are shown in Figure 15. For comparison, data from this study for 1 N solutions of $MgCl_2$ and $MgBr_2$ have also been plotted. Generally speaking for a given anion, the apparent valences are higher in the solutions containing Mg^{+2} ions. This is in conformity with the effect of magnesium ions on the corrosion potential, i.e., the corrosion potential increases as the Mg^{+2} concentration decreases. Most of the apparent valence curves for $MgCl_2$-KCl mixtures lie between the curves for $MgCl_2$ and KCl solutions. All of the apparent valence curves of $MgBr_2$-KBr mixtures solution are above the $MgBr_2$ and KBr curves.

The data from this study have been correlated with a least squares technique. By separating the data into two current density regions, linear equations were obtained. For $MgCl_2$-KCl solutions at current densities below 0.01 $amps \cdot cm^{-2}$:

$$V_i = 1.88 - 50.9\ i$$
$$\sigma = 0.10$$

At current densities between 0.01 to 0.1 $amps \cdot cm^{-2}$ (the upper limit of current density studied):

$$V_i = 1.35 - 0.77\ i$$
$$\sigma = 0.04$$

For $MgBr_2$-KBr solutions at current densities below 0.01 $amps \cdot cm^{-2}$, the equation is:

$$V_i = 1.92 - 48.1\ i$$
$$\sigma = 0.12$$

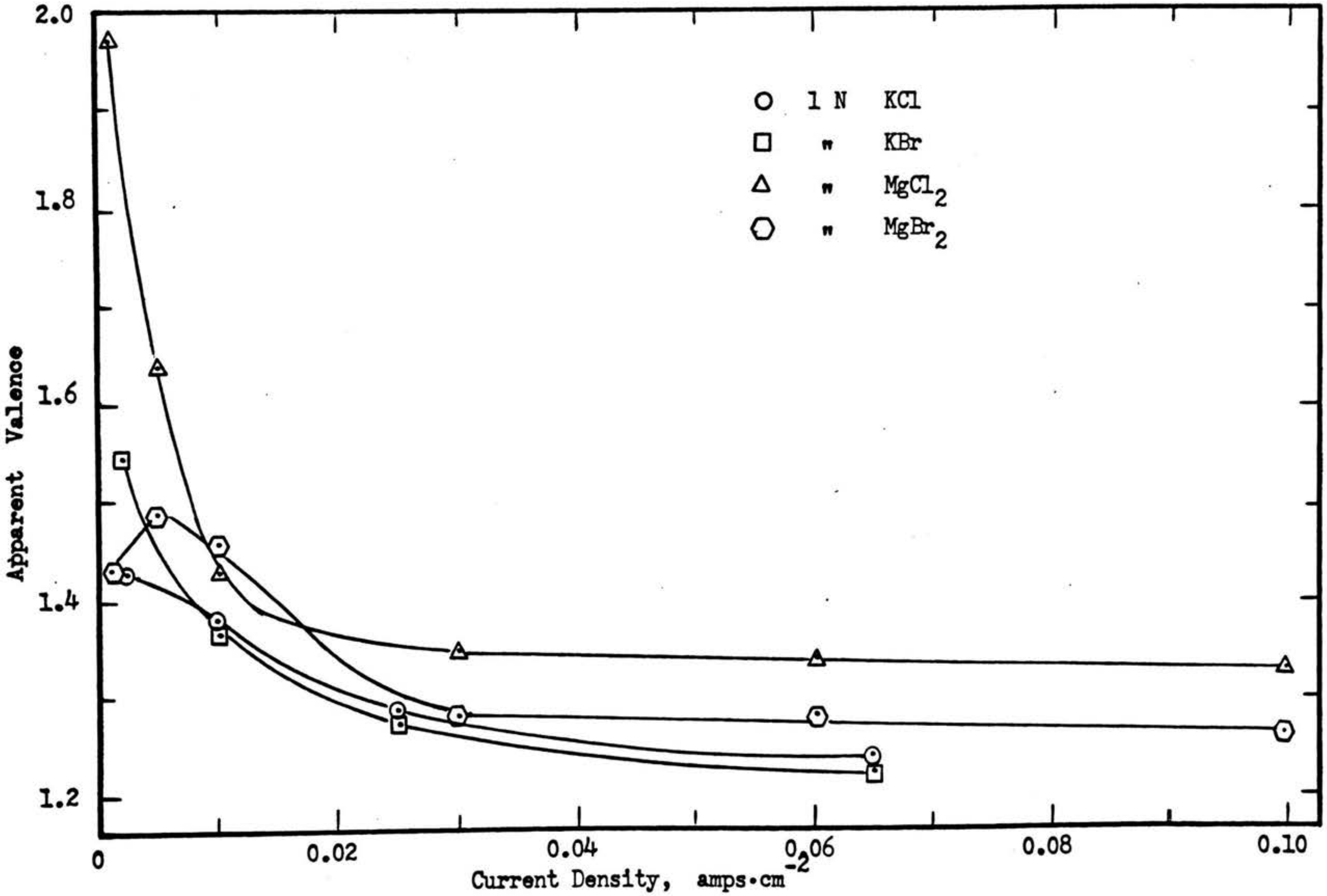

Figure 15. The apparent valence of magnesium dissolving anodically in Cl$^-$ and Br$^-$ solutions at 25 °C

At current densities between 0.01 to 0.1 amps•cm^{-2}:

$$V_i = 1.41 - 1.34\, i$$

$$\delta = 0.04$$

The apparent valence in Cl$^-$ solutions is slightly affected by Mg^{+2} concentration and temperature at current densities below 0.01 amps•cm^{-2}. There is no appreciable effect at current densities above 0.01 amps•cm^{-2}. The apparent valences in Br$^-$ solutions are similar to those in Cl$^-$ solutions. The only exception is at 55 °C where local corrosion has obviously been enhanced in some manner.

It appears that the mechanism for the anodic dissolution of magnesium in aqueous solutions can be expressed as the summation of three distinct reactions: (1) an electrochemical reaction, (2) local corrosion, and, (3) disintegration. Magnesium dissolving by reaction (1) gives two electrons to the external circuit. The Mg^{+2} ions produced are driven through the protective film into solution, thus damaging the film and exposing the metallic surface underneath to the electrolyte which allows local corrosion to occur. The rate of local corrosion depends on several variables. Among these are the electronegativity of the metal, the area of the metallic surface exposed, the number of local cathodes (impurities, dislocations, and imperfections), and the concentration of the electrolyte. The disintegration is a direct consequence of local cell action. These three reactions occur simultaneously on the Mg electrode and their relative rates depend on the current density, electrolyte nature and concentration, and the temperature. In general, the rate of the electrochemical reaction is greater than local corrosion and disintegration which are retarded by film formation. However as more metallic surface is exposed by an increased anodic dissolution (increased current), the rate of local corrosion and disintegration will increase and the apparent valence will decrease.

Accordingly, the reactions involved in the dissolution process may be written:

<u>Electrochemical reaction</u> (reaction responsible for current in the external circuit)

$$Mg_{(s)} = Mg^{+2}_{(aq)} + 2e$$

<u>Local corrosion reaction</u>

$$Mg_{(s)} = Mg^{+2}_{(aq)} + 2e \qquad \text{(anodic)}$$

$$2H_2O + 2e = H_2 + 2OH^- \qquad \text{(cathodic)}$$

$$(\text{or} \quad 2H^+ + 2e = H_2)$$

$$Mg_{(s)} + 2H_2O = Mg(OH)_2 + H_2 \qquad \text{(overall reaction)}$$

<u>Disintegration reaction</u> (particles detached by corrosion)

$$Mg_{(electrode)} = Mg_{(particles)}$$

$$Mg_{(particles)} + 2H_2O = Mg(OH)_2 + H_2$$

On the basis of these reactions, a mathematical model for the anodic dissolution of Mg can be derived as follows:

The total dissolution rate of Mg is the sum of the electrochemical reaction, local corrosion, and disintegration rates,

$$r_T = r_E + r_C + r_D \qquad (18)$$

The electrochemical dissolution rate is proportional to the current, therefore,

$$r_E = k_1 \, i \qquad (19)$$

As mentioned previously, the rate of local corrosion would be dependent on several variables. Since hydrogen is readily evolved during local corrosion, the corrosion potential (rather than the depolarizer concentration as in the case of zinc and cadinum) is an important rate determining factor for the corrosion rate. The corrosion potential is:

$$E_C = \text{constant} - \frac{RT}{2F} \ln a_{Mg}{+2} \qquad (20)$$

This gives a Mg^{+2} dependence to the local corrosion rate. Thus for a particular specimen of magnesium in a given electrolyte, the local corrosion rate is:

$$r_C = k_2 \, f(i) \, F(a_{Mg}{+2}) \qquad (21)$$

Since disintegration results directly from corrosion, a first approximation would be to assume that the disintegration rate is directly proportional to it, i.e.,

$$r_D = k'_3 \, r_C = k_3 \, f(i) \, F(a_{Mg}{+2}) \qquad (22)$$

Therefore,

$$\begin{aligned} r_T &= k_1 i + k_2 f(i) F(a_{Mg}{+2}) + k_3 f(i) F(a_{Mg}{+2}) \\ &= k_1 i + k_4 f(i) F(a_{Mg}{+2}) \qquad (23) \end{aligned}$$

but,

$$V_i = \frac{2\, r_E}{r_T}$$

$$= \frac{2k_1 i}{k_1 i + k_4 f(i)F(a_{Mg}+2)} = \frac{2}{1 + k'G(i)F(a_{Mg}+2)}$$

$$= 2(1 - k'G(i)F(a_{Mg}+2) + \cdots\cdots) \qquad (24)$$

Experimentally, the concentration dependence of the apparent valence was slight. Assuming it approximately constant, that $k'G(i)<1$, and that $G(i)$ can be expressed as a power series; then,

$$2 - V_i = k''G(i) = k''(a + bi + ci^2 + \cdots\cdots)$$

$$= A + Bi + Ci^2 + \cdots\cdots \qquad (25)$$

If the higher terms are omitted, we obtain:

$$V_i = (2 - A) - Bi \qquad (26)$$

This is of the form of the empirical equations found to correlate the data.

Magnesium is found to disintegrate in almost all aqueous solutions. As hydrogen can be readily seen evolving from its surface, it apparently is reactive enough or has such a low hydrogen overpotential that local corrosion (and disintegration) can occur without a depolarizer.

The concentration of magnesium ions doesn't have a pronounced effect on the dissolution potential (or overpotential) of the magnesium anode (Figures 9 to 14).

V. RECOMMENDATIONS

In this study, the corrosion rates of magnesium in solutions containing Mg^{+2} are found to vary with current density. This corrosion of Mg decreases the apparent valence (or current efficiency) of Mg. Since current density seems to be the most important factor, a study over a large region of current densities (such as 10^{-5} to 10 amp/cm^2) might be of interest. A study of amalgamated electrodes could also be informative.

VI. APPENDICES

A. Materials

The following is a list of the major materials used in this investigation.

1. Potassium Chloride. Reagent grade, meets ACS specifications. Fisher Scientific Company, Fair Lawn, N. J.

2. Potassium Bromide. Reagent grade, meets ACS specifications. Fisher Scientific Company, Fair Lawn, N. J.

3. Magnesium Chloride. Reagent grade, meets ACS specifications. Fisher Scientific Company, Fair Lawn, N. J.

4. Magnesium Bromide. Reagent grade, meets ACS specifications. Matheson Coleman & Bell, Inc., Norwood (Cincinnati), Ohio.

5. Magnesium. 99.999 per cent purity, obtained by Dr. M.E. Straumanis from Dr. R. Gadeau, Director, Centre Technique de l' Aluminum, Paris, France.

B. Equipment

1. Surface Preparation of Magnesium Specimens

a. Belt surfacer. Buehler No. 1250, Buehler Ltd., Evanston, Ill.

b. Hand grinder. Handimet, 4 stage, Buehler No. 1470, Buehler Ltd., Evanston, Ill.

2. Electrolysis Apparatus

a. Ammeter. Model 931, Weston Electric Instrument Corporations, Newark, N. J.

b. Resistance box. Decade type, graduated from 0 to 999,999 ohms in 1 ohm divisions, Clarostat Mfg. Co., Inc., Dover, New Hampshire.

c. D.C. power supply. Model 711 A, Hewlett-Packard Co., Loveland, Colorado.

d. Electrometer. Multi-range type, Model 610 B, Keithley Instruments, Inc., 12415 Euclid Avenue, Cleveland, Ohio 44106.

C. Appendix C (Tables I to LXX)

TABLE I

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.001 N $MgCl_2$ - 1.4985 N KCl at 25 °C

Time (sec)	Current Density (amps•cm^{-2})	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
100000	0.001	0.0126	0.0131	1.92
40000	0.005	0.0252	0.0292	1.73
20000	0.010	0.0252	0.0333	1.51
7000	0.030	0.0265	0.0367	1.44
3500	0.060	0.0265	0.0388	1.36
2000	0.100	0.0252	0.0379	1.33

TABLE II

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.003 N $MgCl_2$ - 1.4955 N KCl at 25 °C

Time (sec)	Current Density (amps•cm^{-2})	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
100000	0.001	0.0126	0.0133	1.89
40000	0.005	0.0252	0.0301	1.67
20000	0.010	0.0252	0.0343	1.47
7000	0.030	0.0265	0.0383	1.38
3500	0.060	0.0265	0.0397	1.33
2000	0.100	0.0252	0.0387	1.30

TABLE III

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.01 N $MgCl_2$ - 1.485 N KCl at 25 °C

Time (sec)	Current Density ($amps \cdot cm^{-2}$)	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
90000	0.001	0.0113	0.0120	1.89
40000	0.005	0.0252	0.0310	1.63
20000	0.010	0.0252	0.0352	1.43
7000	0.030	0.0265	0.0399	1.33
5000	0.060	0.0378	0.0595	1.27
2000	0.100	0.0252	0.0400	1.26

TABLE IV

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.03 N $MgCl_2$ - 1.455 N KCl at 25 °C

Time (sec)	Current Density ($amps \cdot cm^{-2}$)	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
100000	0.001	0.0126	0.0135	1.87
40000	0.005	0.0252	0.0317	1.59
20000	0.010	0.0252	0.0358	1.41
7000	0.030	0.0265	0.0413	1.28
3500	0.060	0.0265	0.0422	1.25
2000	0.100	0.0252	0.0401	1.26

TABLE V

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.1 N $MgCl_2$ - 1.35 N KCl at 25 °C

Time (sec)	Current Density ($amps \cdot cm^{-2}$)	Weight of Magnesium Calc. (gm)	Expt. (gm)	Apparent Valence
100000	0.001	0.0126	0.0135	1.87
40000	0.005	0.0252	0.0323	1.56
20000	0.010	0.0252	0.0355	1.42
7000	0.030	0.0265	0.0415	1.28
5000	0.060	0.0378	0.0605	1.25
2000	0.100	0.0252	0.0406	1.24

TABLE VI

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.3 N $MgCl_2$ - 1.05 N KCl at 25 °C

Time (sec)	Current Density ($amps.cm^{-2}$)	Weight of Magnesium Calc. (gm)	Expt. (gm)	Apparent Valence
102000	0.001	0.0129	0.0133	1.93
40000	0.005	0.0252	0.0323	1.56
20000	0.010	0.0252	0.0360	1.40
7000	0.030	0.0265	0.0404	1.31
3500	0.060	0.0265	0.0400	1.32
2000	0.100	0.0252	0.0400	1.26

TABLE VII

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 1 N $MgCl_2$ at 25 °C

time (sec)	Current Density ($amps \cdot cm^{-2}$)	Weight of Magnesium Calc. (gm)	Expt. (gm)	Apparent Valence
90000	0.001	0.0113	0.0115	1.97
40000	0.005	0.0252	0.0307	1.64
20000	0.010	0.0252	0.0353	1.43
8000	0.030	0.0302	0.0447	1.35
5000	0.060	0.0378	0.0563	1.34
2000	0.100	0.0252	0.0379	1.33

TABLE VIII

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.001 N $MgCl_2$ - 1.4985 N KCl at 40 °C

Time (sec)	Current Density ($amps \cdot cm^{-2}$)	Weight of Magnesium Calc. (gm)	Expt. (gm)	Apparent Valence
90000	0.001	0.0113	0.0119	1.91
40000	0.005	0.0252	0.0358	1.41
20000	0.010	0.0252	0.0407	1.24
7100	0.030	0.0268	0.0425	1.26
5000	0.060	0.0378	0.0576	1.31
2000	0.100	0.0252	0.0406	1.24

TABLE IX

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.003 N $MgCl_2$ - 1. 4955 N KCl at 40 °C

Time (sec)	Current Density (amps·cm^{-2})	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
100000	0.001	0.0126	0.0140	1.80
40000	0.005	0.0252	0.0343	1.47
20000	0.010	0.0252	0.0405	1.24
7000	0.030	0.0265	0.0412	1.28
3050	0.060	0.0231	0.0356	1.30
2000	0.100	0.0252	0.0397	1.27

TABLE X

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.01 N $MgCl_2$ - 1.485 N KCl at 40 °C

Time (sec)	Current Density (amps·cm^{-2})	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
120000	0.001	0.0151	0.0160	1.89
40000	0.005	0.0252	0.0348	1.45
20000	0.010	0.0252	0.0388	1.30
7020	0.030	0.0265	0.0397	1.34
5000	0.060	0.0378	0.0575	1.31
2000	0.100	0.0252	0.0390	1.29

TABLE XI

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN $0.03\ MgCl_2 - 1.455\ N\ KCl$ at 40 °C

Time (sec)	Current Density (amps•cm^{-2})	Weight of Magnesium Calc. (gm)	 Expt. (gm)	Apparent Valence
100000	0.001	0.0126	0.0136	1.85
44000	0.005	0.0277	0.0377	1.47
20000	0.010	0.0252	0.0383	1.32
7000	0.030	0.0265	0.0395	1.34
3500	0.069	0.0265	0.0397	1.33
2000	0.100	0.0252	0.0399	1.26

TABLE XII

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN $0.1\ N\ MgCl_2 - 1.35\ N\ KCl$ at 40 °C

Time (sec)	Current Density (amps•cm^{-2})	Weight of Magnesium Calc. (gm)	 Expt. (gm)	Apparent Valence
120000	0.001	0.0151	0.0164	1.84
40000	0.005	0.0252	0.0338	1.49
20000	0.010	0.0252	0.0382	1.32
7000	0.030	0.0265	0.0390	1.36
5000	0.060	0.0378	0.0574	1.32
3000	0.100	0.0378	0.0600	1.26

TABLE XIII

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.3 N $MgCl_2$ - 1.05 N KCl at 40 °C

Time (sec)	Current Density (amps•cm^{-2})	Weight of Magnesium Calc. (gm)	Expt. (gm)	Apparent Valence
105000	0.001	0.0132	0.0145	1.83
40000	0.005	0.0252	0.0339	1.49
20000	0.010	0.0252	0.0391	1.29
7100	0.030	0.0268	0.0410	1.31
3550	0.060	0.0268	0.0420	1.28
2050	0.100	0.0258	0.0424	1.22

TABLE XIV

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 1 N $MgCl_2$ at 40 °C

Time (sec)	Current Density (amps•cm^{-2})	Weight of Magnesium Calc. (gm)	Expt. (gm)	Apparent Valence
100000	0.001	0.0126	0.0339	0.74
40000	0.005	0.0252	0.0482	1.05
20000	0.010	0.0252	0.0374	1.35
7000	0.030	0.0265	0.0399	1.33
5000	0.060	0.0378	0.0593	1.28
3000	0.100	0.0378	0.0589	1.28

TABLE XV

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.001 N $MgCl_2$ - 1.4985 N KCl at 55 °C

Time (sec)	Current Density ($amps \cdot cm^{-2}$)	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
91000	0.001	0.0115	0.0117	1.96
50000	0.005	0.0315	0.0372	1.69
20000	0.010	0.0252	0.0342	1.47
8000	0.030	0.0302	0.0442	1.37
3500	0.060	0.0265	0.0416	1.27
2000	0.100	0.0252	0.0403	1.25

TABLE XVI

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.003 N $MgCl_2$ - 1.4955 N KCl at 55 °C

Time (sec)	Current Density ($amps \cdot cm^{-2}$)	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
92000	0.001	0.0116	0.0120	1.93
33000	0.005	0.0208	0.0266	1.56
20200	0.010	0.0255	0.0352	1.45
7000	0.030	0.0265	0.0405	1.31
3700	0.060	0.0280	0.0433	1.29
2000	0.100	0.0252	0.0396	1.27

TABLE XVII

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.01 N $MgCl_2$ - 1.485 N KCl at 55 °C

Time (sec)	Current Density ($amps \cdot cm^{-2}$)	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
87000	0.001	0.0110	0.0118	1.86
42500	0.005	0.0268	0.0357	1.50
15800	0.010	0.0199	0.0292	1.36
7300	0.030	0.0276	0.0426	1.30
5100	0.060	0.0386	0.0592	1.30
2000	0.100	0.0252	0.0394	1.28

TABLE XVIII

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.0 N $MgCl_2$ - 1.455 N KCl at 55 °C

Time (sec)	Current Density ($amps \cdot cm^{-2}$)	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
100000	0.001	0.0126	0.0140	1.80
40000	0.005	0.0252	0.0338	1.49
20000	0.010	0.0252	0.0367	1.38
7200	0.030	0.0272	0.0428	1.27
3500	0.060	0.0265	0.0412	1.28
2000	0.100	0.0252	0.0391	1.29

TABLE XIX

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.1 N $MgCl_2$ - 1.35 N KCl at 55 °C

Time (sec)	Current Density ($amps \cdot cm^{-2}$)	Weight of Magnesium Calc. (gm)	Expt. (gm)	Apparent Valence
89400	0.001	0.0113	0.0123	1.83
43100	0.005	0.0272	0.0354	1.53
24500	0.010	0.0309	0.0438	1.41
7000	0.030	0.0265	0.0384	1.38
4300	0.060	0.0325	0.0488	1.33
2000	0.100	0.0252	0.0387	1.30

TABLE XX

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.3 N $MgCl_2$ - 1.05 N KCl at 55 °C

Time (sec)	Current Density ($amps \cdot cm^{-2}$)	Weight of Magnesium Calc. (gm)	Expt. (gm)	Apparent Valence
89400	0.001	0.0113	0.0139	1.62
44000	0.005	0.0277	0.0357	1.55
24000	0.010	0.0302	0.0406	1.49
7400	0.030	0.0280	0.0410	1.36
3600	0.060	0.0272	0.0403	1.35
2000	0.100	0.0252	0.0385	1.31

TABLE XXI

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 1 N $MgCl_2$ at 55 °C

Time (sec)	Current Density (amps•cm^{-2})	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
86400	0.001	0.0109	0.0237	0.92
41200	0.005	0.0260	0.0567	0.92
20000	0.010	0.0252	0.0472	1.07
8400	0.030	0.0318	0.0472	1.35
3500	0.060	0.0265	0.0388	1.36
2000	0.100	0.0252	0.0396	1.27

TABLE XXII

THE CONDITION OF ELECTRODE SURFACE IN ANODIC DISSOLUTION OF MAGNESIUM

Temp. & Conc.	1 ma/cm^2	5 ma/cm^2	10 ma/cm^2	30 ma/cm^2	60 ma/cm^2	100 ma/cm^2
25 °C						
0.001 N Mg^{+2}	○	◎	□	◎	○	○
0.003 N "	○	△	□	◎	○	◎
0.01 N "	○	□	□	◎	○	○
0.03 N "	◎	□	□	◎	○	○
0.1 N "	◎	△	△	◎	△	△
0.3 N "	◎	○	○	○	△	△
1.0 N "	△	○	○	○	□	△
40 °C						
0.001 N Mg^{+2}	○	○	△	△	○	○
0.003 N "	○	○	□	□	○	○
0.01 N "	○	○	△	□	○	◎
0.03 N "	○	○	◎	□	○	◎
0.1 N "	○	○	◎	△	△	○
0.3 N "	○	○	◎	□	○	◎
1.0 N "	◎	○	○	○	□	△
55 °C						
0.001 N Mg^{+2}	○	△	◎	○	◎	◎
0.003 N "	○	△	◎	○	□	△
0.01 N "	□	○	△	△	□	◎
0.03 N "	□	○	◎	○	△	△
0.1 N "	□	○	○	△	□	△
0.3 N "	△	○	○	○	□	◎
1.0 N "	△	○	◎	○	□	△

○ Bright ⬡ Brown □ Gray △ Light Gray ◎ Mixture of Bright and Gray

TABLE XXIII

CLARITY OF ANOLYTE AFTER ELECTROLYSIS IN $MgCl_2$-KCl SOLUTIONS

Temp. & Conc.	1 ma/cm^2	5 ma/cm^2	10 ma/cm^2	30 ma/cm^2	60 ma/cm^2	100 ma/cm^2
25 °C						
0.001 N Mg^{+2}	△	△	○	○	○	△
0.003 N "	△	○	○	○	○	○
0.01 N "	○	○	○	○	○	△
0.03 N "	△	○	○	○	△	△
0.1 N "	○	○	○	○	□	○
0.3 N "	○	○	○	○	○	○
1.0 N "	○	○	○	○	○	○
40 °C						
0.001 N Mg^{+2}	○	○	○	□	△	□
0.003 N "	○	△	△	□	○	□
0.01 N "	○	△	□	□	○	□
0.03 N "	○	△	○	○	○	○
0.1 N "	○	○	○	△	△	□
0.3 N "	○	○	○	○	○	○
1.0 N "	○	○	○	○	○	○
55 °C						
0.001 N Mg^{+2}	○	○	○	□	□	△
0.003 N "	○	○	○	○	○	○
0.01 N "		○	○	○	○	○
0.03 N "	○	○	○	○	○	○
0.1 N "	○	○	○	○	○	○
0.3 N "	○	○	○	○	○	○
1.0 N "	○	□	□	○	△	○

○ Clear □ Cloudy △ Part Cloudy

TABLE XXIV

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.001 N $MgBr_2$ - 1.4985 N KBr at 25 °C

Time (sec)	Current Density ($amps \cdot cm^{-2}$)	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
90500	0.001	0.0114	0.0114	2.00
31200	0.005	0.0197	0.0224	1.76
15600	0.010	0.0197	0.0253	1.55
5000	0.030	0.0189	0.0258	1.47
2510	0.060	0.0190	0.0274	1.39
2000	0.100	0.0252	0.0382	1.32

TABLE XXV

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.003 N $MgBr_2$ - 1.4955 N KBr at 25 °C

Time (sec)	Current Density ($amps \cdot cm^{-2}$)	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
89700	0.001	0.0113	0.0119	1.90
30000	0.005	0.0189	0.0223	1.70
15000	0.010	0.0189	0.0252	1.50
5000	0.030	0.0189	0.0260	1.45
2600	0.060	0.0197	0.0285	1.38
2000	0.100	0.0252	0.0388	1.30

TABLE XXVI

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.01 N $MgBr_2$ - 1.485 N KBr at 25 °C

Time (sec)	Current Density $(amps \cdot cm^{-2})$	Weight of Magnesium Calc. (gm)	Expt. (gm)	Apparent Valence
153000	0.001	0.0193	0.0211	1.83
30000	0.005	0.0189	0.0235	1.61
15000	0.010	0.0189	0.0258	1.47
5000	0.030	0.0189	0.0274	1.38
2510	0.060	0.0190	0.0294	1.29
2000	0.100	0.0252	0.0396	1.27

TABLE XXVII

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.03 N $MgBr_2$ - 1.455 N KBr at 25 °C

Time (sec)	Current Density $(amps \cdot cm^{-2})$	Weight of Magnesium Calc. (gm)	Expt. (gm)	Apparent Valence
143000	0.001	0.0180	0.0196	1.84
32100	0.005	0.0202	0.0251	1.61
15100	0.010	0.0190	0.0257	1.48
5000	0.030	0.0189	0.0274	1.38
2600	0.060	0.0197	0.0307	1.28
2000	0.100	0.0252	0.0401	1.26

TABLE XXVIII

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.1 N $MgBr_2$ - 1.35 N KBr at 25 °C

Time (sec)	Current Density (amps•cm^{-2})	Weight of magnesium Calc. (gm)	Expt. (gm)	Apparent Valence
95600	0.001	0.0120	0.0132	1.83
40000	0.005	0.0252	0.0316	1.60
15100	0.010	0.0190	0.0259	1.47
5000	0.030	0.0189	0.0278	1.36
2500	0.060	0.0189	0.0289	1.31
2100	0.100	0.0265	0.0413	1.28

TABLE XXIX

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.3 N $MgBr_2$ - 1.05 N KBr at 25 °C

Time (sec)	Current Density (amps.cm^{-2})	Weight of Magnesium Calc. (gm)	Expt. (gm)	Apparent Valence
106000	0.001	0.0134	0.0152	1.76
31000	0.005	0.0195	0.0248	1.58
15000	0.010	0.0189	0.0253	1.49
5000	0.030	0.0189	0.0275	1.37
2500	0.060	0.0189	0.0290	1.30
2100	0.100	0.0265	0.0409	1.29

TABLE XXX

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 1 N $MgBr_2$ at 25 °C

Time (sec)	Current Density ($amps \cdot cm^{-2}$)	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
136000	0.001	0.0171	0.0239	1.43
30200	0.005	0.0190	0.0255	1.49
22600	0.010	0.0285	0.0391	1.46
5000	0.030	0.0189	0.0296	1.28
2500	0.060	0.0189	0.0295	1.28
2100	0.100	0.0265	0.0420	1.26

TABLE XXXI

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.001 N $MgBr_2$- 1.4985 N KBr at 40 °C

Time (sec)	Current Density ($amps \cdot cm^{-2}$)	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
100300	0.001	0.0126	0.0126	2.00
36700	0.005	0.0231	0.0270	1.71
15000	0.010	0.0189	0.0251	1.51
5000	0.030	0.0189	0.0261	1.45
2500	0.060	0.0189	0.0270	1.40
2000	0.100	0.0252	0.0371	1.36

TABLE XXXII

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.003 N $MgBr_2$ - 1.4955 N KBr at 40 °C

Time (sec)	Current Density ($amps \cdot cm^{-2}$)	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
100300	0.001	0.0126	0.0127	1.99
31700	0.005	0.0200	0.0236	1.69
15100	0.010	0.0190	0.0251	1.52
5100	0.030	0.0193	0.0286	1.35
2500	0.060	0.0189	0.0291	1.30
2000	0.100	0.0252	0.0406	1.24

TABLE XXXIII

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.01 N $MgBr_2$ - 1.485 N KBr at 40 °C

Time (sec)	Current Density ($amps \cdot cm^{-2}$)	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
119400	0.001	0.0150	0.0153	1.97
35000	0.005	0.0221	0.0269	1.64
15000	0.010	0.0189	0.0271	1.40
5700	0.030	0.0215	0.0329	1.31
2500	0.060	0.0189	0.0297	1.27
2000	0.100	0.0252	0.0390	1.29

TABLE XXXIV

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.03 N $MgBr_2$ - 1.455 N KBr at 40 °C

Time (sec)	Current Density (amps•cm^{-2})	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
140000	0.001	0.0176	0.0182	1.94
36900	0.005	0.0232	0.0278	1.67
15000	0.010	0.0189	0.0254	1.49
5500	0.030	0.0208	0.0320	1.30
2500	0.060	0.0189	0.0300	1.26
2000	0.100	0.0252	0.0414	1.22

TABLE XXXV

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.1 N $MgBr_2$ - 1.35 N KBr at 40 °C

Time (sec)	Current Density (amps•cm^{-2})	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
114400	0.001	0.0144	0.0142	2.03
34400	0.005	0.0217	0.0261	1.66
15000	0.010	0.0189	0.0260	1.45
5100	0.030	0.0193	0.0286	1.35
2500	0.060	0.0189	0.0291	1.30
2100	0.100	0.0265	0.0434	1.22

TABLE XXXVI

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.3 N $MgBr_2$ - 1.05 N KBr at 40 °C

Time (sec)	Current Density ($amps \cdot cm^{-2}$)	Weight of Magnesium		Apparent Valence
		Calc. (gm)	Expt. (gm)	
120100	0.001	0.0151	0.0151	2.00
30300	0.005	0.0191	0.0270	1.41
15300	0.010	0.0193	0.0286	1.35
5000	0.030	0.0189	0.0278	1.36
2500	0.060	0.0189	0.0295	1.28
2200	0.100	0.0277	0.0455	1.22

TABLE XXXVII

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 1 N $MgBr_2$ at 40 °C

Time (sec)	Current Density ($amps \cdot cm^{-2}$)	Weight of Magnesium		Apparent Valence
		Calc. (gm)	Expt. (gm)	
102000	0.001	0.0129	0.0218	1.18
34000	0.005	0.0214	0.0330	1.30
15100	0.010	0.0190	0.0277	1.37
5100	0.030	0.0193	0.0282	1.37
2500	0.060	0.0189	0.0285	1.33
2000	0.100	0.0252	0.0385	1.31

TABLE XXXVIII

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.001 N $MgBr_2$ - 1.4985 N KBr at 55 °C

Time (sec)	Current Density ($amps \cdot cm^{-2}$)	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
88600	0.001	0.0112	0.0113	1.98
30000	0.005	0.0189	0.0212	1.78
15000	0.010	0.0189	0.0237	1.60
5000	0.030	0.0189	0.0278	1.36
2500	0.060	0.0189	0.0297	1.27
2000	0.100	0.0252	0.0390	1.29

TABLE XXXIX

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.003 N $MgBr_2$ - 1.4955 N KBr at 55 °C

Time (sec)	Current Density ($amps \cdot cm^{-2}$)	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
90000	0.001	0.0113	0.0116	1.96
34000	0.005	0.0214	0.0249	1.72
15000	0.010	0.0189	0.0247	1.53
5000	0.030	0.0189	0.0275	1.37
2600	0.060	0.0197	0.0301	1.31
2100	0.100	0.0265	0.0416	1.27

TABLE XL

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.01 N $MgBr_2$ - 1.485 N KBr at 55 °C

Time (sec)	Current Density ($amps \cdot cm^{-2}$)	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
79600	0.001	0.0100	0.0102	1.97
30000	0.005	0.0189	0.0232	1.63
15100	0.010	0.0190	0.0258	1.48
5100	0.030	0.0193	0.0283	1.36
2500	0.060	0.0189	0.0286	1.32
2000	0.100	0.0252	0.0399	1.26

TABLE XLI

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.03 N $MgBr_2$ - 1.455 N KBr at 55 °C

Time (sec)	Current Density ($amps \cdot cm^{-2}$)	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
91200	0.001	0.0115	0.0119	1.93
37200	0.005	0.0234	0.0297	1.58
15000	0.010	0.0189	0.0271	1.39
5500	0.030	0.0208	0.0312	1.33
2500	0.060	0.0189	0.0286	1.32
2000	0.100	0.0252	0.0383	1.32

TABLE XLII

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.1 N $MgBr_2$ - 1.35 N KBr at 55 °C

Time (sec)	Current Density ($amps \cdot cm^{-2}$)	Weight of magnesium Calc. (gm)	Weight of magnesium Expt. (gm)	Apparent Valence
93600	0.001	0.0118	0.0125	1.89
40600	0.005	0.0256	0.0352	1.45
20000	0.010	0.0252	0.0374	1.35
6500	0.030	0.0246	0.0354	1.39
2500	0.060	0.0189	0.0283	1.34
2000	0.100	0.0252	0.0382	1.32

TABLE XLIII

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 0.3 N $MgBr_2$ - 1.05 N KBr at 55 °C

Time (sec)	Current Density ($amps \cdot cm^{-2}$)	Weight of magnesium Calc. (gm)	Weight of magnesium Expt. (gm)	Apparent Valence
84000	0.001	0.0106	0.0146	1.45
42500	0.005	0.0268	0.0382	1.40
15000	0.010	0.0189	0.0285	1.33
5000	0.030	0.0189	0.0280	1.35
2500	0.060	0.0189	0.0282	1.34
2000	0.100	0.0252	0.0408	1.24

TABLE XLIV

APPARENT VALENCE OF MAGNESIUM DISSOLVING ANODICALLY IN 1 N $MgBr_2$ at 55 °C

Time (sec)	Current Density $(amps \cdot cm^{-2})$	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
86300	0.001	0.0109	0.0246	0.88
32000	0.005	0.0202	0.0425	0.95
15000	0.010	0.0189	0.0291	1.30
5100	0.030	0.0193	0.0254	1.52
2500	0.060	0.0189	0.0279	1.36
2000	0.100	0.0252	0.0398	1.27

TABLE XLV

THE CONDITION OF ELECTRODE SURFACE IN ANODIC DISSOLUTION OF MAGNESIUM

Temp. & Conc.	1 ma/cm^2	5 ma/cm^2	10 ma/cm^2	30 ma/cm^2	60 ma/cm^2	100 ma/cm^2
25 °C						
0.001 N Mg^{+2}	○	○	◎	△	○	◎
0.003 N "	○	○	◎	△	◎	◎
0.01 N "	○	○	◎	□	○	◎
0.03 N "	○	⬡	⬡	◎	◎	◎
0.1 N "	○	○	◎	◎	◎	◎
0.3 N "	○	○	□	◎	◎	◎
1.0 N "	□	⬡	⬡	□	◎	◎
40 °C						
0.001 N Mg^{+2}	○	⬡	⬡	◎	◎	◎
0.003 N "	○	⬡	⬡	◎	△	◎
0.01 N "	○	○	⬡	□	◎	◎
0.03 N "	○	⬡	⬡	□	△	◎
0.1 N "	○	○	○	□	△	◎
0.3 N "	○	⬡	⬡	□	△	△
1.0 N "	△	○	○	△	△	△
55 °C						
0.001 N Mg^{+2}	⬡	○	○	△	□	□
0.003 N "	○	○	○	◎	△	△
0.01 N "	⬡	○	○	◎	△	◎
0.03 N "	○	⬡	○	○	△	□
0.1 N "	□	⬡	○	◎	△	△
0.3 N "	□	⬡	○	○	○	○
1.0 N "	□	○	⬡	○	□	○

○ Bright ⬡ Brown □ Gray △ Light Gray ◎ Mixture of Bright and Gray

TABLE XLVI

CLARITY OF ANOLYTE AFTER ELECTROLYSIS IN $MgBr_2$-KBr SOLUTIONS

Temp. & Conc.	1 ma/cm^2	5 ma/cm^2	10 ma/cm^2	30 ma/cm^2	60 ma/cm^2	100 ma/cm^2
25 °C						
0.001 N Mg^{+2}	○	△	△	○	○	○
0.003 N "	○	○	○	○	○	○
0.01 N "	○	○	○	△	○	○
0.03 N "	○	○	○	△	○	△
0.1 N "	○	○	○	○	○	△
0.3 N "	○	○	○	○	○	○
1.0 N "	○	○	○	○	○	○
40 °C						
0.001 N Mg^{+2}	○	□	△	○	△	○
0.003 N "	○	○	△	○	○	○
0.01 N "	□	○	△	△	○	□
0.03 N "	○	○	○	△	○	○
0.1 N "	○	○	○	○	○	○
0.3 N "	○	○	○	○	○	○
1.0 N "	○	○	○	○	○	○
55 °C						
0.001 N Mg^{+2}	○	□	△	○	△	□
0.003 N "	○	□	○	○	○	△
0.01 N "	○	□	△	○	○	△
0.03 N "	○	○	○	○	○	○
0.1 N "	○	○	○	○	○	○
0.3 N "	○	○	○	○	○	○
1.0 N "	○	□	△	○	△	△

○ Clear □ Cloudy △ Part Cloudy

TABLE XLVII

THE DISSOLUTION POTENTIAL OF MAGNESIUM IN 1 N $MgCl_2$ at 25 °C

I (amps•cm^{-2})	t (min)	E (volts)[a]	I (amps•cm^{-2})	t (min)	E (volts)[a]
0.000	0	1.98	0.030	30	1.56
	15	1.94		45	1.55
	30	1.94		60	1.54
	45	1.92		75	1.52
	60	1.91		90	1.50
	75	1.90		105	1.48
	90	1.90		120	1.45
	105	1.90		135	1.45
				150	1.45
0.001	0	1.70			
	15	1.70	0.060	0	1.24
	30	1.70		15	1.26
				30	1.26
0.005	0	1.68		45	1.26
	15	1.68			
	30	1.68	0.100	0	0.97
				15	0.93
0.010	0	1.65		30	0.99
	15	1.65		45	0.98
	30	1.65		60	0.94
				75	0.94
0.030	0	1.57		90	0.94
	15	1.56			

[a] Normal hydrogen scale.

TABLE XLVIII

THE DISSOLUTION POTENTIAL OF MAGNESIUM IN

0.1 N $MgCl_2$ - 1.35 N KCl at 25 °C

I (amps·cm^{-2})	t (min)	E (volts)[a]	I (amps·cm^{-2})	t (min)	E (volts)[a]
0.000	0	1.85	0.030	0	1.65
	15	1.79		15	1.65
	30	1.80		30	1.65
	45	1.81			
	60	1.82	0.060	0	1.56
	75	1.83		15	1.53
	90	1.84		30	1.50
	105	1.85		45	1.47
	120	1.86		60	1.50
	135	1.86		75	1.50
	150	1.86		90	1.50
0.001	0	1.73	0.100	0	1.32
	15	1.73		15	1.21
	30	1.73		30	1.29
				45	1.29
0.005	0	1.71		60	1.27
	15	1.71		75	1.15
	30	1.71		90	1.20
				105	1.20
0.010	0	1.70		120	1.20
	15	1.70			
	30	1.70			

---

[a] Normal hydrogen scale.

TABLE XLIX

THE DISSOLUTION POTENTIAL OF MAGNESIUM IN 0.01 N $MgCl_2$ - 1.485 N KCl at 25 °C

I (amps•cm^{-2})	t (min)	E (volts)[a]	I (amps•cm^{-2})	t (min)	E (volts)[a]
0.000	0	1.92	0.060	0	1.35
	15	1.91		15	1.40
	30	1.90		30	1.36
	45	1.90		45	1.35
	60	1.90		60	1.35
				75	1.35
0.001	0	1.73			
	15	1.73	0.100	0	1.05
	30	1.73		15	1.23
				30	1.25
0.005	0	1.71		45	1.25
	15	1.71		60	1.05
	30	1.71		75	1.25
				90	1.25
0.010	0	1.69			
	15	1.67			
	30	1.67			
	45	1.67			
0.030	0	1.64			
	15	1.65			
	30	1.65			
	45	1.65			

[a] Normal hydrogen scale.

TABLE L

THE DISSOLUTION POTENTIAL OF MAGNESIUM IN 0.001 N $MgCl_2$ - 1.4985 N KCl at 25 °C

I (amps·cm^{-2})	t (min)	E (volts)[a]	I (amps·cm^{-2})	t (min)	E (volts)[a]
0.000	0	1.79	0.060	0	1.45
	15	1.95		15	1.43
	30	1.98		30	1.38
	45	1.98		45	1.35
	60	1.98		60	1.35
				75	1.35
0.001	0	1.73			
	15	1.73	0.100	0	1.17
	30	1.73		15	1.08
				30	1.13
0.005	0	1.71		45	1.18
	15	1.71		60	1.21
	30	1.71		75	1.05
				90	1.00
0.010	0	1.71		105	1.28
	15	1.69		120	1.25
	30	1.69		135	1.15
	45	1.69		150	1.15
0.030	0	1.61			
	15	1.61			
	30	1.61			

[a] Normal hydrogen scale.

TABLE LI

THE DISSOLUTION POTENTIAL OF MAGNESIUM IN 1 N $MgCl_2$ at 40 °C

I ($amps \cdot cm^{-2}$)	t (min)	E (volts)[a]	I ($amps \cdot cm^{-2}$)	t (min)	E (volts)[a]
0.000	0	1.95	0.030	0	1.58
	15	1.91		15	1.56
	30	1.90		30	1.56
	45	1.90		45	1.56
	60	1.90			
			0.060	0	1.40
0.001	0	1.71		15	1.37
	15	1.73		30	1.33
	30	1.76		45	1.27
	45	1.76		60	1.27
	60	1.76		75	1.27
0.005	0	1.71	0.100	0	1.05
	15	1.71		15	1.06
	30	1.71		30	1.03
				45	1.00
0.010	0	1.68		60	1.00
	15	1.67		75	1.00
	30	1.67			
	45	1.67			
	60	1.67			

[a] Normal hydrogen scale.

TABLE LII

THE DISSOLUTION POTENTIAL OF MAGNESIUM IN

0.1 N $MgCl_2$ - 1.35 N KCl at 40 °C

I (amps•cm^{-2})	t (min)	E (volts)[a]	I (amps•cm^{-2})	t (min)	E (volts)[a]
0.000	0	1.95	0.060	0	1.61
	15	1.95		15	1.59
	30	1.95		30	1.55
	45	1.95		45	1.54
	60	1.95		60	1.54
				75	1.54
0.001	0	1.74			
	15	1.74	0.100	0	1.40
	30	1.74		15	1.37
				30	1.35
0.005	0	1.73		45	1.33
	15	1.73		60	1.31
	30	1.73		75	1.33
				90	1.33
0.010	0	1.71			
	15	1.71			
	30	1.71			
0.030	0	1.67			
	15	1.67			
	30	1.67			
	45	1.67			

[a] Normal hydrogen scale.

TABLE LIII

THE DISSOLUTION POTENTIAL OF MAGNESIUM IN

0.01 N $MgCl_2$ - 1.485 N KCl at 40 °C

I $(amps \cdot cm^{-2})$	t (min)	E (volts)[a]	I $(amps \cdot cm^{-2})$	t (min)	E (volts)[a]
0.000	0	1.90	0.060	0	1.60
	15	1.92		15	1.58
	30	1.92		30	1.55
	45	1.94		45	1.55
	60	1.94			
	75	1.94	0.100	0	1.50
				15	1.46
0.001	0	1.74		30	1.43
	15	1.74		45	1.44
	30	1.74		60	1.40
				75	1.41
0.005	0	1.73		90	1.36
	15	1.73		105	1.36
	30	1.73		120	1.36
	45	1.73			
0.010	0	1.71			
	15	1.71			
	30	1.71			
0.030	0	1.68			
	15	1.67			
	30	1.67			
	45	1.67			

[a] Normal hydrogen scale.

TABLE LIV

THE DISSOLUTION POTENTIAL OF MAGNESIUM IN $0.001\ N\ MgCl_2$ - 1.4985 N KCl at 40 °C

I (amps•cm^{-2})	t (min)	E (volts)[a]	I (amps•cm^{-2})	t (min)	E (volts)[a]
0.000	0	1.94	0.030	0	1.68
	15	1.96		15	1.67
	30	1.96		30	1.66
	45	1.96		45	1.66
				60	1.66
0.001	0	1.74			
	15	1.74	0.060	0	1.58
	30	1.74		15	1.55
	45	1.74		30	1.55
				45	1.55
0.005	0	1.72		60	1.55
	15	1.72			
	30	1.72	0.100	0	1.43
				15	1.39
0.010	0	1.70		30	1.35
	15	1.71		45	1.35
	30	1.71		60	1.35
	45	1.71			

[a] Normal hydrogen scale.

TABLE LV

THE DISSOLUTION POTENTIAL OF MAGNESIUM IN 1 N $MgCl_2$ at 55 °C

I (amps·cm^{-2})	t (min)	E (volts)[a]	I (amps·cm^{-2})	t (min)	E (volts)[a]
0.000	0	-0.65	0.005	90	1.80
	15	-1.50		105	1.82
	30	1.83		120	1.82
	45	1.82			
	60	1.82	0.010	0	1.72
	75	1.82		15	1.72
				30	1.72
0.001	0	1.68			
	15	1.75	0.030	0	1.63
	30	1.80		15	1.61
	45	1.82		30	1.61
	60	1.83		45	1.61
	75	1.86			
	90	1.87	0.060	0	1.51
	105	1.90		15	1.51
	120	1.90		30	1.51
	135	1.90			
			0.100	0	1.36
0.005	0	1.71		15	1.34
	15	1.70		30	1.34
	30	1.71		45	1.34
	45	1.73			
	60	1.75			
	75	1.78			

[a] Normal hydrogen scale.

TABLE LVI

THE DISSOLUTION POTENTIAL OF MAGNESIUM IN 0.1 N $MgCl_2$ - 1.35 N KCl at 55 °C

I (amps·cm^{-2})	t (min)	E (volts)[a]	I (amps·cm^{-2})	t (min)	E (volts)[a]
0.000	0	1.91	0.060	0	1.62
	15	1.90		15	1.61
	30	1.89		30	1.61
	45	1.89		45	1.61
	60	1.89			
			0.100	0	1.53
0.001	0	1.74		15	1.51
	15	1.74		30	1.49
	30	1.74		45	1.47
				60	1.46
0.005	0	1.73		75	1.46
	15	1.73		90	1.46
	30	1.73			
0.010	0	1.72			
	15	1.72			
	30	1.72			
0.030	0	1.69			
	15	1.68			
	30	1.68			
	45	1.68			

[a] Normal hydrogen scale.

TABLE LVII

THE DISSOLUTION POTENTIAL OF MAGNESIUM IN 0.01 N $MgCl_2$ - 1.455 N KCl at 55 °C

I (amps·cm^{-2})	t (min)	E (volts)[a]	I (amps·cm^{-2})	t (min)	E (volts)[a]
0.000	0	1.93	0.060	0	1.64
	15	1.89		15	1.63
	30	1.86		30	1.63
	45	1.83		45	1.63
	60	1.82			
	75	1.81	0.100	0	1.54
	90	1.81		15	1.51
				30	1.49
0.001	0	1.75		45	1.47
	15	1.75		60	1.47
	30	1.75			
0.005	0	1.72			
	15	1.73			
	30	1.73			
	45	1.73			
0.010	0	1.71			
	15	1.72			
	30	1.72			
0.030	0	1.69			
	15	1.69			
	30	1.69			

---

[a] Normal hydrogen scale.

TABLE LVIII

THE DISSOLUTION POTENTIAL OF MAGNESIUM IN

0.001 N $MgCl_2$ - 1.4985 N KCl at 55 °C

I ($amps \cdot cm^{-2}$)	t (min)	E (volts)[a]	I ($amps \cdot cm^{-2}$)	t (min)	E (volts)[a]
0.000	0	1.94	0.060	0	1.64
	15	1.89		15	1.63
	30	1.88		30	1.63
	45	1.85		45	1.63
	60	1.83			
	75	1.83	0.100	0	1.54
	90	1.83		15	1.51
				30	1.49
0.001	0	1.74		45	1.48
	15	1.74		60	1.47
	30	1.74		75	1.47
0.005	0	1.72			
	15	1.72			
	30	1.72			
0.010	0	1.71			
	15	1.71			
	30	1.71			
0.030	0	1.69			
	15	1.69			
	30	1.69			

---

[a] Normal hydrogen scale.

TABLE LIX

THE DISSOLUTION POTENTIAL OF MAGNESIUM IN

1 N $MgBr_2$ at 25 °C

I (amps•cm^{-2})	t (min)	E (volts)[a]	I (amps•cm^{-2})	t (min)	E (volts)[a]
0.000	0	1.87	0.030	0	1.52
	15	1.87		15	1.50
	30	1.80		30	1.50
	45	1.75		45	1.50
	60	1.68		60	1.50
	75	1.65			
	90	1.65	0.060	0	1.40
	105	1.65		15	1.36
				30	1.34
0.001	0	1.59		45	1.33
	15	1.61		60	1.33
	30	1.65		75	1.33
	45	1.68			
	60	1.68	0.100	0	1.14
	75	1.68		15	1.13
				30	1.15
0.005	0	1.60		45	1.10
	15	1.60		60	1.11
	30	1.60		75	1.10
	45	1.60		90	1.10
				105	1.10
0.010	0	1.57			
	15	1.57			
	30	1.57			

[a] Normal hydrogen scale.

TABLE LX

THE DISSOLUTION POTENTIAL OF MAGNESIUM IN 0.1 N $MgBr_2$ - 1.35 N KBr at 25 °C

I (amps•cm^{-2})	t (min)	E (volts)[a]	I (amps•cm^{-2})	t (min)	E (volts)
0.000	0	1.82	0.030	45	1.50
	15	1.77		60	1.50
	30	1.78		75	1.50
	45	1.74			
	60	1.74	0.060	0	1.35
	75	1.74		15	1.33
				30	1.34
0.001	0	1.60		45	1.34
	15	1.61		60	1.34
	30	1.62			
	45	1.62	0.100	0	1.21
	60	1.62		15	1.16
				30	1.17
0.005	0	1.60		45	1.30
	15	1.60		60	1.26
	30	1.60		75	1.16
				90	1.16
0.010	0	1.58		105	1.16
	15	1.58			
	30	1.58			
0.030	0	1.53			
	15	1.53			
	30	1.51			

[a] Normal hydrogen scale.

TABLE LXI

THE DISSOLUTION POTENTIAL OF MAGNESIUM IN

0.01 N $MgBr_2$ - 1.485 N KBr at 25 °C

I ($amps \cdot cm^{-2}$)	t (min)	E (volts)[a]	I ($amps \cdot cm^{-2}$)	t (min)	E (volts)[a]
0.000	0	1.86	0.030	30	1.50
	15	1.76		45	1.50
	30	1.75		60	1.50
	45	1.75			
	60	1.75	0.060	0	1.38
				15	1.39
0.001	0	1.60		30	1.38
	15	1.60		45	1.35
	30	1.60		60	1.34
				75	1.34
0.005	0	1.60		90	1.34
	15	1.60			
	30	1.60	0.100	0	1.20
				15	1.20
0.010	0	1.60		30	1.14
	15	1.58		45	1.14
	30	1.58		60	1.14
	45	1.58			
0.030	0	1.55			
	15	1.53			

[a] Normal hydrogen scale.

TABLE LXII

THE DISSOLUTION POTENTIAL OF MAGNESIUM IN

0.001 N $MgBr_2$ - 1.4985 N KBr at 25 °C

I ($amps{\cdot}cm^{-2}$)	t (min)	E (volts)[a]	I ($amps{\cdot}cm^{-2}$)	t (min)	E (volts)[a]
0.000	0	1.84	0.030	30	1.53
	15	1.80		45	1.51
	30	1.83		60	1.51
	45	1.81		75	1.51
	60	1.81			
	75	1.81	0.060	0	1.42
				15	1.40
0.001	0	1.60		30	1.40
	15	1.65		45	1.40
	30	1.64			
	45	1.64	0.100	0	1.26
	60	1.64		15	1.28
				30	1.23
0.005	0	1.60		45	1.23
	15	1.60		60	1.20
	30	1.60		75	1.25
				90	1.23
0.010	0	1.59		105	1.23
	15	1.58			
	30	1.58			
	45	1.58			
0.030	0	1.55			
	15	1.54			

[a] Normal hydrogen scale.

TABLE LXIII

THE DISSOLUTION POTENTIAL OF MAGNESIUM IN 1 N $MgBr_2$ at 40 °C

I (amps•cm^{-2})	t (min)	E (volts)[a]	I (amps•cm^{-2})	t (min)	E (volts)[a]
0.000	0	1.96	0.030	0	1.38
	15	1.93		15	1.25
	30	1.93		30	1.40
	45	1.93		45	1.40
				60	1.40
0.001	0	1.75			
	15	1.76	0.060	0	1.31
	30	1.77		15	1.28
	45	1.78		30	1.26
	60	1.79		45	1.24
	75	1.81		60	1.20
	90	1.81		75	1.15
	105	1.83		90	1.10
	120	1.84		105	1.15
	135	1.85		120	1.15
	150	1.86		135	1.15
	165	1.86			
	180	1.86	0.100	0	0.85
				15	0.80
0.005	0	1.65		30	0.76
	15	1.68		45	0.71
	30	1.70		60	0.66
	45	1.72		75	0.66
	60	1.74		90	0.71
	75	1.74		105	0.56
	90	1.74		120	0.66
				135	0.66
0.010	0	1.62			
	15	1.63			
	30	1.63			
	45	1.63			

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[a] Normal hydrogen scale.

TABLE LXIV

THE DISSOLUTION POTENTIAL OF MAGNESIUM IN

0.1 N $MgBr_2$ - 1.35 N KBr at 40 °C

I (amps·cm^{-2})	t (min)	E (volts)[a]	I (amps·cm^{-2})	t (min)	E (volts)[a]
0.000	0	1.96	0.030	0	1.54
	15	1.85		15	1.54
	30	1.85		30	1.54
	45	1.85	0.060	0	1.46
0.001	0	1.66		15	1.44
	15	1.66		30	1.43
	30	1.68		45	1.42
	45	1.70		60	1.41
	60	1.70		75	1.41
	75	1.70	0.100	0	1.26
0.005	0	1.61		15	1.26
	15	1.61		30	1.26
	30	1.62			
	45	1.55			
	60	1.56			
	75	1.59			
	90	1.61			
	105	1.61			
0.010	0	1.59			
	15	1.59			
	30	1.59			

[a] Normal hydrogen scale.

TABLE LXV

THE DISSOLUTION POTENTIAL OF MAGNESIUM IN

0.01 N $MgBr_2$ - 1.485 N KBr at 40 °C

I (amps·cm^{-2})	t (min)	E (volts)[a]	I (amps·cm^{-2})	t (min)	E (volts)[a]
0.000	0	1.88	0.030	0	1.54
	15	1.86		15	1.54
	30	1.83		30	1.54
	45	1.81			
	60	1.81	0.060	0	1.46
	75	1.81		15	1.44
				30	1.43
0.001	0	1.61		45	1.42
	15	1.68		60	1.41
	30	1.61		75	1.40
	45	1.69		90	1.40
	60	1.69			
			0.100	0	1.20
0.005	0	1.58		15	1.21
	15	1.59		30	1.22
	30	1.59		45	1.22
	45	1.59			
0.010	0	1.56			
	15	1.59			
	30	1.59			

[a] Normal hydrogen scale.

TABLE LXVI

THE DISSOLUTION POTENTIAL OF MAGNESIUM IN

0.001 N $MgBr_2$ - 1.4985 N KBr at 40 °C

I (amps•cm^{-2})	t (min)	E (volts)[a]	I (amps•cm^{-2})	t (min)	E (volts)[a]
0.000	0	1.88	0.060	0	1.48
	15	1.84		15	1.46
	30	1.84		30	1.46
	45	1.84		45	1.46
				60	1.46
0.001	0	1.62			
	15	1.69	0.100	0	1.31
	30	1.69		15	1.30
	45	1.69		30	1.32
				45	1.31
0.005	0	1.60		60	1.31
	15	1.60			
	30	1.60			
0.010	0	1.59			
	15	1.59			
	30	1.59			
0.030	0	1.55			
	15	1.55			
	30	1.55			

[a] Normal hydrogen scale.

TABLE LXVII

THE DISSOLUTION POTENTIAL OF MAGNESIUM IN 1 N $MgBr_2$ at 55 °C

I (amps•cm^{-2})	t (min)	E (volts)[a]	I (amps•cm^{-2})	t (min)	E (volts)[a]
0.000	0	1.94	0.010	0	1.76
	15	1.96		15	1.76
	30	1.96		30	1.76
	45	1.96		45	1.76
0.001	0	1.86	0.030	0	1.60
	15	1.89		15	1.61
	30	1.91		30	1.61
	45	1.92			
	60	1.92	0.060	0	1.48
				15	1.46
0.005	0	1.60		30	1.46
	15	1.72			
	30	1.76	0.100	0	1.34
	45	1.82		15	1.31
	60	1.83		30	1.30
	75	1.84		45	1.27
	90	1.85		60	1.26
	105	1.85		75	1.26
	120	1.85		90	1.26

[a] Normal hydrogen scale.

TABLE LXVIII

THE DISSOLUTION POTENTIAL OF MAGNESIUM IN 0.1 N $MgBr_2$ - 1.35 N KBr at 55 °C

I (amps•cm^{-2})	t (min)	E (volts)[a]	I (amps•cm^{-2})	t (min)	E (volts)[a]
0.000	0	1.91	0.030	0	1.40
	15	1.91		15	1.50
	30	1.91		30	1.60
	45	1.91		45	1.59
				60	1.54
0.001	0	1.63		75	1.54
	15	1.71		90	1.54
	30	1.74			
	45	1.74	0.060	0	1.47
	60	1.74		15	1.46
				30	1.46
0.005	0	1.63			
	15	1.64	0.100	0	1.36
	30	1.69		15	1.34
	45	1.73		30	1.32
	60	1.73		45	1.35
	75	1.73		60	1.36
				75	1.34
0.010	0	1.61		90	1.34
	15	1.67			
	30	1.72			
	45	1.72			

[a] Normal hydrogen scale.

TABLE LXIX

THE DISSOLUTION POTENTIAL OF MAGNESIUM IN 0.01 N $MgBr_2$ - 1.485 N KBr at 55 °C

I (amps•cm^{-2})	t (min)	E (volts)[a]	I (amps•cm^{-2})	t (min)	E (volts)[a]
0.000	0	1.90	0.010	0	1.65
	15	1.92		15	1.68
	30	1.94		30	1.69
	45	1.92		45	1.51
	60	1.90		60	1.74
	75	1.90		75	1.74
	90	1.88		90	1.74
	105	1.86			
	120	1.85	0.030	0	1.56
	135	1.85		15	1.56
				30	1.56
0.001	0	1.61		45	1.56
	15	1.67			
	30	1.73	0.060	0	1.50
	45	1.74		15	1.50
	60	1.75		30	1.50
	75	1.75			
			0.100	0	1.41
0.005	0	1.61		15	1.38
	15	1.61		30	1.37
	30	1.74		45	1.34
	45	1.75		60	1.34
	60	1.75		75	1.34
	75	1.75			

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[a] Normal hydrogen scale.

TABLE LXX

THE DISSOLUTION POTENTIAL OF MAGNESIUM IN 0.001 N $MgBr_2$ - 1.4985 N KBr at 55 °C

I (amps•cm^{-2})	t (min)	E (volts)[a]	I (amps•cm^{-2})	t (min)	E (volts)[a]
0.000	0	1.93	0.010	60	1.74
	15	1.94		75	1.75
	30	1.94		90	1.75
	45	1.94			
			0.030	0	1.59
0.001	0	1.61		15	1.61
	15	1.67		30	1.64
	30	1.73		45	1.64
	45	1.73			
	60	1.73	0.060	0	1.50
				15	1.46
0.005	0	1.61		30	1.54
	15	1.67		45	1.53
	30	1.74		60	1.52
	45	1.75		75	1.40
	60	1.74		90	1.48
	75	1.68		105	1.48
	90	1.71			
	105	1.71	0.100	0	1.43
				15	1.35
0.010	0	1.68		30	1.40
	15	1.72		45	1.40
	30	1.74			
	45	1.75			

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[a] Normal hydrogen scale.

APPENDIX D

TABLE LXXI

REVERSIBLE POTENTIALS OF THE Mg^{+2}/Mg ELECTRODE

Mg^{+2} Concentration	Reversible Potential (volts)[a] 25 °C	40 °C	55 °C
1.000 N	-2.41	-2.41	-2.42
0.100 N	-2.44	-2.45	-2.45
0.010 N	-2.47	-2.48	-2.48
0.001 N	-2.50	-2.51	-2.51

[a] Normal hydrogen scale.

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