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THE DISSOLUTION OF MAGNESIUM IN STRONG ACIDS AND NEUTRAL SOLUTIONS

BY

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A

THESIS

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I. INTRODUCTION

The increasing demand for magnesium and magnesium-base alloys in the manufacture of aircraft 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 magnesium alloys and protective coatings to retard corrosion.

The basic mechanism of the anodic dissolution of metals such as magnesium, zinc, and cadmium in salt solutions is not completely known. Several schools of investigators have proposed different and opposing theories to explain the discrepancies which often arise between coulometer data and the weight loss of metal electrodes in certain salt solutions.

The purpose of this investigation was to study the anion effect on the dissolution and disintegration of magnesium. If anion adsorption is important in these processes, then varying the ionic species present should alter kinetic parameters for the dissolution reaction and the apparent valence for the disintegration. To this end, the self-dissolution was studied in hydrochloric, hydrobromic, and hydriodic acids and the anodic dissolution in one normal solutions of potassium sulfate, potassium chloride, potassium nitrate, potassium bromide, and potassium iodide.

II. LITERATURE REVIEW

The mechanism of dissolution of magnesium metal in aqueous solution has been investigated both under self-dissolution and anodic conditions. This review of literature is divided into two major topics: (1) chemical kinetics of the dissolution of magnesium, and (2) anodic dissolution of magnesium in aqueous solution.

Chemical Kinetics of the Dissolution of Magnesium

The mechanism of dissolution of magnesium in acid has been discussed from the point of view of both the diffusion theory and chemical rate theory. Kilpatrick and Rushton(1) measured dissolution rates of magnesium in dilute solutions of hydrochloric acid and various weak organic acids. They concluded that the rate-controlling step was a slow chemical reaction between the metal and the acid. They have attempted to show that the rates are dependent on the acid strength in the same manner as in homogeneous acid-base catalysis; i.e., that:

$$k_a = GK_A^x$$

where, k_a = velocity constant

K_A = dissociation constant of the reacting acid

G, x = numerical constants, the latter a proper fraction.

In particular, they claimed that when the metal dissolves in strong acids at temperatures above 50°C, at least two reactions occur. One is a reaction with water independent of hydrogen ion concentration, and the second, a reaction with water dependent on hydrogen ion concentration. An explanation is offered from the extended theory of acids and bases. For a strong acid such as hydrochloric acid, it is assumed that the following reaction goes practically to completion:

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^- \qquad (1)$$

In the case of the reaction of the acid with magnesium, the primary reaction is:

$$H_3O^+ + e \longrightarrow H_2O + H^\bullet \qquad (2)$$

This is followed by the reactions:

$$\underset{\text{(solid)}}{Mg^{++}} \longrightarrow \underset{\text{(dissolved)}}{Mg^{++}} \qquad (3)$$

$$2H^\bullet \longrightarrow H_2 \qquad (4)$$

It is assumed that the metal is composed of magnesium ions in the solid state (Mg^{++}) and free electrons.

In weak acids, such as acetic acid, the authors emphasized that two reactions take place at the surface of the metal, one due to a reaction with protons and the other with undissociated acid molecules, i.e.,

$$H_3O^+ + e \longrightarrow H^\bullet + H_2O \qquad (5)$$

$$HAc + e \longrightarrow H^\bullet + Ac^- \qquad (6)$$

For the weak acids, it was found that for a constant hydrogen ion concentration, the rate of reaction was proportional to the concentration of undissociated acid present. This is support for a chemical rate theory in which the rate would be proportional to the concentration of acid present.

The effect of stirring on the dissolution rate was studied. The relationship reported for their equipment was:

$$V = aR^n$$

where, V = reaction rate in $cm^3 cm^{-2} min^{-1}$

R = velocity of the metal surface in $cm \cdot min^{-1}$

a, n = numerical constants

The values of a and n for the reaction of magnesium with hydrochloric acid were 0.139 and 0.365, respectively. For the reaction of magnesium with acetic acid, the values of a and n were 0.0197 and 0.362, respectively.

The effect of viscosity on the rate of dissolution of magnesium in hydrochloric acid was also studied. The viscosity of the acid solution was varied by adding sodium chloride, potassium chloride, magnesium chloride, and potassium nitrate. No general relationship was found between the rate of solution and the viscosity for these additions. However, there was a finite decrease in dissolution rates when the viscosity of hydrochloric acid and acetic acid solutions was increased by adding sugar and glycerine.

The effect of temperature on the rate of dissolution of magnesium in acidic solution was also found. The temperature coefficient for the reaction with hydrochloric acid was reported to be 1.75 and that for acetic acid was 1.69. Since the temperature coefficients were less than two, a diffusion controlled mechanism was again favored. However, the authors considered that the general criterion of the statement that chemical reactions usually have temperature coefficients greater than two usually apply to reactions taking place in one phase and not to reactions at an interface.

In contrast to Kilpatrick and Rushton's belief, King and co-workers(2,3,4) state that the dissolution rate is controlled by diffusion and support this theory by a series of careful investigations. The principal conclusions from their measurements were: (1) different solids dissolve at nearly the same rate in the same reagent under the same conditions, (2) the stirring rate has a very large influence on the observed dissolution rates, (3) the dissolution rate is nearly inversely proportional to the viscosity of the solution, (4) the rates observed are proportional to diffusion coefficients, and (5) temperature coefficients are usually between 1.1 and 1.5 per $10^{o}C$ rise, values which are typical of diffusion coefficients and much too low to be considered typical of chemical reaction rates.

Ivan Sekerka and co-workers(5) considered the dissolution of metal in acids to be controlled by two steps depending on the concentration. For concentrations up to 0.1N, the rate is controlled by the diffusion of H^+ ions to the metal surface; at concentrations greater than 0.5N, the rate controlling step is the discharge of H^+ ions. In the concentration range from 0.1 to 0.5N, the dissolving action is influenced by both steps.

King and Cathcart(4) determined the diffusion coefficients of a number of weak and strong acids in the presence of their magnesium salts. Dissolution rates of magnesium were also determined under similar conditions. A linear relationship was found between the dissolution rate constants k(cm min^{-1}) and the diffusion coefficients D(cm^2 min^{-1}) and was represented by the equation $k = 0.36D^{0.70}$. According to the authors, this exponential relationship is consistent with a diffusion layer whose thickness increases with increasing diffusion coefficients. It was concluded that the dissolution rates were in agreement with their proposed modification of Nernst's theory which states that the layer involved in diffusion can not be a stagnant layer and that the thickness of the layer varies with the diffusion coefficient of the reagent, increasing as the latter increases.

James(6) claimed that he obtained dissolution rates in various acids in which diffusion effects were eliminated.

It was found that the reaction rates were not affected by shaking above a critical shaking speed of 220 cycles per minute. In the reaction vessel, one millimole of magnesium metal was employed in the form of finely divided shavings (60-80 mesh) with an excess amount of acid. A shaking speed of 400 cycles per minute was normally employed. All runs were carried out in an atmosphere of nitrogen. In the case of reaction with hydrochloric acid, the observed rates were considered due to reaction with hydrogen ions. In the case of weak organic acids, such as acetic acid, the measured rates were those with undissociated molecules. The effect of salt additions on the reaction rate was also investigated. Sodium chloride was found to have a negligible effect upon the reaction of magnesium with acetic acid, although it affected the diffusion coefficients. However, the salt did increase the rate of dissolution in hydrochloric acid. Magnesium chloride increased the rate of dissolution in hydrochloric acid to the same extent. Sucrose was added to a 0.01 molar acetic acid solution in two different concentrations. The rate constant decreased with an increase in sucrose concentration, indicating an effect of viscosity on the dissolution rates. Activation energies for the acetic acid and hydrochloric acid reactions were reported to be 5100 and 4920 calories, respectively.

Roald and Beck(7) considered the dissolution of metals to be electrochemical in nature. When magnesium is immersed in aqueous solutions, hydrogen is evolved. The corrosion process thus consists of the cathodic evolution of hydrogen and the anodic dissolution of magnesium until the pH at the solution-metal interface rises to a point where $Mg(OH)_2$ is precipitated. In neutral and alkaline solutions, the magnesium surface is covered by films of magnesium hydroxide which protect the metal against corrosion attack. In acids, however, the protective films are destroyed and rapid attack ensues. Because of the strong electronegative character of magnesium, the potential difference between the metal and solution is sufficiently high to overcome the overvoltage of impurities which have been found to have little or no influence on the dissolution rate.

The electrode potential of magnesium in acids becomes more anodic with increasing acid concentration reaching a maximum of -1.6 to -1.7V on the hydrogen scale. At higher concentrations it remains fairly constant for strong acids, but 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.

Gatty and Spooner(8) concluded that the surface of the metal is covered with a "hydride film" and that the emission of metal ions into solution takes place through "pores" in this film. According to these authors, the local anodes will be strongly polarized and the electrode potential is thus determined by the potential of the cathodic area (the "hydride film"). Assuming concentration polarization to be negligible, they concluded that the electrode potential will be negative to the hydrogen electrode in the solution considered by an overvoltage corresponding to the cathodic current density.

Roald and Beck(7) also showed that the dissolution rate of magnesium in hydrochloric acid is constant with time, unless changes in acid concentration, temperature, or area of the exposed surface become significant. At the lower acid concentrations, the dissolution rate appeared to be proportional to the acid concentration.

The electrode potentials of magnesium in hydrochloric acid at different rates of agitation were also studied. At the higher acid concentrations, the potentials rapidly reached steady values which did not change appreciably with time. At the lower acid concentrations a longer time was needed, with the potentials drifting in a cathodic direction. They also discovered that at the lower rates of dissolution, a temperature increase of 10°C shifts the potential about 50 mV in a cathodic direction. At the higher dissolution rates, where the potential leveled off to a constant value, temperature had no appreciable influence on the potentials.

The authors pointed out that the stirring effect of hydrogen bubbles influenced the dissolution rate. The action of the gas bubbles was approximately proportional to the square root of the rate of the gas evolution. Without agitation, the stirring action of the gas bubbles became 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 $cm^{-2}min^{-1}$ (corresponding to about 1 ml H_2 $cm^{-2}min^{-1}$), the stirring action of the gas bubbles predominates. At acid concentrations of about 1.5N, the increase becomes less than at the lower acid concentrations. This phenomenon was apparently due to the violent evolution of hydrogen which reduced the dissolution rate by preventing the acid from coming in contact with the metal. Agitation reduced this effect by removing the gas more rapidly.

The effect of anions, such as Cl^-, Br^-, and I^- ions, on the dissolution kinetics of metals was studied by Kolotyrkin(11). This author pointed out that the dissolution of metals in electrolytic solutions is an electrochemical process, and the rate depends not only on the usual variables of chemical kinetics, concentration and temperature, but also on electrochemical parameters of the system, first and foremost, on the electrode potential and the structure of the electric double layer at the metal-solution interface. In acidic solutions, Cl^-, Br^-, and I^- ions increased the true anodic dissolution rate of cadmium and of indium amalgam. This is accounted for by the direct participation of these ions in elementary processes of ionizing metal atoms. The chemisorptive interaction of halide ions with surface atoms of a metal takes place at potentials much more negative than the dissolution potential of the metal. The extent of "filling" the surface with adsorbed anions increases considerably with shift of potential to more positive values. The dissolution of metals occurs with the direct participation of halide ions and, consequently, the kinetics of these reactions at constant pH may be expressed as follows:

$$i = kC^{a}\exp(\ FE/RT)$$

where, i = dissolution rate in terms of electric current
E = electrode potential
= transfer coefficient
k = constant depending on the metal and surface condition
C = concentration of halide salt
a = constant equal to 3 for the cadmium dissolution reaction in presence of I^- ions, and 1, 2, and 3 respectively, for the dissolution of the indium amalgam in iodide, bromide, and chloride solutions.

H. H. Uhlig(12) explains that chloride ions, and to a lesser extent other halogen ions, break down passivity or prevent it on Fe, Cr, and the stainless steels. From the point of the oxide film theory, Cl^- penetrates the protective oxide film through pores or defects easier than do other ions such as $SO_4^=$ or Cl^- which may colloidally disperse the oxide film and increase its permeability. On the other hand according to the adsorption theory, Cl^- favors hydration of metal ions and increases the ease with which metal ions enter into solution just opposite to the effect of adsorbed oxygen which decreases the rate of metal dissolution. In other words, adsorbed chloride ions increase the exchange current (decrease overvoltage) for anodic dissolution of the above metals over the value prevailing when oxygen covers the surface. Breakdown of passivity by Cl^- occurs locally rather than generally over the passive surface, the preferred sites being determined perhaps by small variations in the passive film structure and thickness.

Halogen ions have less effect on the anodic behavior of titanium, tantalum, molybdenum, tungsten, and zirconium. Their passivity may continue in media of high chloride concentration in contrast to Fe, Cr, and Fe-Cr alloys which lose passivity. This is sometimes explained by formation of insoluble protective Ti-, Ta-, Mo- etc, basic chloride films.

U. R. Evans(27) considers that in a very dilute solution, the potential gradient will cause the water molecules near the anode surface to orient themselves with the oxygen portion nearest the metal, providing an easy mechanism for film-formation. Cations from the metal, instead of passing out into the liquid, take up places between the oxygen ions, and in their stead hydrogen ions from the water molecules move out into the liquid. If, however, the liquid contains an appreciable concentration of anions carrying a negative charge, the same potential gradient will cause them to displace the water molecules, which carry no net charge, from the metal surface. Chloride ions, thus, will displace water molecules and break up the water phalanx without providing any new mechanism for passivation. Hence, their presence is unfavorable to passivity.

Anodic Dissolution of Magnesium Metal in Aqueous Solution

In the past sixty years considerable work has been done to arrive at a mechanism for the anodic dissolution of magnesium metal in aqueous solutions. It has been found that magnesium anode consumption is very much greater than predicted by Faraday's Law for divalent magnesium ion formation. To account for this, three hypotheses have been reported. The first explanation is based on the assumption that the metal enters solution as a univalent ion. The second assumes that the anodic dissolution is film controlled and as such the behavior of magnesium can be explained without the need of uncommon valency ions. More recently the "chunk effect" has been advanced as a third possibility.

Davidson, Kleinberg, and Sorensen(13,14,15,16) have given support to the concept of "uncommon valence". They calculated the initial valence number (V_i) of magnesium ions in various electrolytic cells connected in series with a full-wave rectifier (the current source), a silver coulometer, and an ammeter. The quantity of electricity passing through the circuit was measured with the silver coulometer. An oxygen-free nitrogen atmosphere was maintained over the solution in the anode compartment. The initial valence number of the magnesium ions formed was calculated by means of the equation:

$$V_i = \frac{(\text{wt. of silver deposited in coulometer})(24.32)}{(107.88)(\text{wt. of magnesium lost from anode})}$$

The valence number was found to lie between one and two. The results were explained on the hypothesis that the primary reaction at the metal anode consisted of a stepwise oxidation, the first step being the oxidation of the metal to the unipositive ion:

$$Mg = Mg^{+} + e \text{ (at the electrode)} \qquad (7)$$

The unipositive ion would be expected to be very unstable and would readily form the normal bipositive ion. There are two ways in which this second step can occur:

1) by further electrolytic oxidation at the anode:

$$Mg^{+} = Mg^{++} + e \text{ (at the electrode)} \qquad (8)$$

2) by chemical oxidation by the oxidizing agent in solution:

$$Mg^{+} + \text{oxidant} = Mg^{++} + \text{reductant (in solution)} \qquad (9)$$

With nonreducible electrolytes, reaction (9) cannot occur and consequently an initial mean valence number of two would be observed. With reducible electrolytes, however, the two possible mechanisms of the step would be competitive and the one which will predominate depends on the nature of the oxidizing electrolyte and the conditions of the experiment. The initial mean valence might then range from +1 to +2, depending upon the relative extents of the reactions (8) and (9) which in turn depend upon the concentration of the oxidizing electrolyte and the temperature.

Another mechanism suggested by Greenblatt$^{(17)}$ for anodic dissolution of magnesium was that as 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 containing excess positive ions must also have an equal number of anion vacancies. To obtain electrical neutrality, electrons flow across the film, filling the anion vacancies and 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 which fill anion vacancies. This results in a greater amount of metal being dissolved than the number of coulombs passing through the external circuit would indicate.

Hoey and Cohen$^{(18)}$ give several possibilities for anodic dissolution, among which the following was mentioned:

$$2Mg \longrightarrow Mg{\cdot}Mg^{++} + 2e \qquad (10)$$

$$Mg{\cdot}Mg^{++} + 2H_2O \longrightarrow Mg^{++} + Mg(OH)_2 + H_2 \qquad (11)$$

Reaction (11) shows why the corrosion products have a tendency to evolve hydrogen.

The film controlled behavior of the magnesium anode was postulated by Robinson and King(19). They termed the increase in hydrogen evolution on magnesium with increasing anodic current density as the negative difference effect. The negative difference effect, thought to be resulting 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 formed 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.

Higgins(20) also supported the hypothesis that the increase in hydrogen evolution on the magnesium anode while a current is flowing is due to the breakdown of a protective $Mg(OH)_2$ film. This allows hydrogen to be formed at local cathodes due to impurities.

Marsh and Schaschl(21) have proposed the "chunk effect" to explain the negative difference effect on steel. They suggested that when steel corrodes at a high rate, the corrosion proceeds with the removal of "chunks" of iron containing several atoms. Therefore, the metal anode does not dissolve as predicted by Faraday's Law because of the expulsion of metallic particles.

Later Straumanis and Bhatia(22) showed that magnesium disintegrated partially into very small metallic particles under certain conditions of dissolution or corrosion. The dark color of the flakes separating from the anode was caused by the presence of minute magnesium particles held in a matrix of $Mg(OH)_2$, as confirmed under high magnification employing both reflected and transmitted light. They discounted the concept of uncommon valency and explained both positive or negative difference effects as a result of the ease with which a passivating film on the anode is removed, and the ease with which the metallic particles are separated from the anode surface.

III. EXPERIMENTAL

The purpose of this present investigation was to study the self-dissolution of magnesium in strong acids and the anodic dissolution of magnesium in neutral solutions. The strong acids were hydrochloric, hydrobromic, and hydriodic acids. The neutral solutions included potassium chloride, potassium bromide, potassium iodide, potassium sulfate, and potassium nitrate.

The experimental plan consisted of the following major phases: (1) the effect of acid concentration on the dissolution rates, (2) the effect of various electrolytes and current densities on the apparent valence of magnesium undergoing anodic dissolution, and (3) the polarization curves of magnesium undergoing anodic dissolution in various electrolytes.

Materials

The list of the materials used in this investigation is given in the Appendix.

1. The Effect of Acid Concentration on the Dissolution Rates.

Apparatus. The apparatus used was the same for the rate studies in hydrochloric, hydrobromic, and hydriodic acids. It consisted of a reactor flask of 500 milliliters capacity, equipped with a mercury-sealed stirrer to which a polyvinylchloride foot was fitted to hold the mounted magnesium sample, and a gas burette for collection and measurement of the hydrogen evolved during dissolution. The reaction flask was immersed in a constant-temperature water bath, which was controlled within 0.1°C. A stirring speed of 200 revolutions per minute was employed in the rate studies. The apparatus used for the rate studies has been described previously(23).

Procedure. A specimen of approximately one square centimeter area was cut from a bar of magnesium metal of 99.999 per cent purity. It was filed to reduce the area to one square centimeter, plus or minus two per cent. This was checked by using a micrometer. The specimen was mounted in lucite in a metallographic mounting press. The mounted specimen had one side exposed, leaving an area of 1 cm^2 for the reaction. This side was ground and polished in a manner previously described(23). Before being used for a dissolution rate study, the specimen was etched with an acid solution of the concentration under consideration. The sample was attached to the stirrer foot with beeswax.

Three hundred milliliters of the acid solution were used in the reaction flask for the rate studies. The reaction flask was placed in the constant-temperature water bath in such a position so as to submerge that part of the flask which contained the acid. The reaction flask was allowed to stay in the water bath for about one hour to bring the system to constant temperature before starting a run. The hydrogen gas evolved during the reaction was collected in the gas burette. The rate of dissolution was followed by recording the gas burette reading at definite time intervals. The temperature and pressure were recorded at which the gas was collected. Using this information, the volume at standard pressure and temperature was calculated. The rate was expressed in cubic millimeters of hydrogen at STP per square centimeter of magnesium surface per second ($mm^3\ cm^{-2}sec^{-1}$).

The procedure employed was the same for all acids. A detailed step-by-step procedure for this phase of experimentation has been described previously(23).

Data and Results. The data obtained from these measurements are shown in the Appendix.

Since the rate studies were investigated in hydrochloric, hydrobromic, and hydriodic acids, a brief account of the results for each follows separately.

Hydrochloric Acid. The dissolution of magnesium in hydrochloric acid was carried out in four different acid concentrations (0.0297, 0.100, 0.293, and 1.00N) at 25°C. The plot of acid concentration versus the dissolution rate showed a linear relationship to about 0.3N. In general, the direct relationship (up to 0.3N) can be expressed by the following equation:

$$dv/dt = k(HCl)^n \tag{12}$$

where, dv/dt = hydrogen evolution rate, $mm^3cm^{-2}sec^{-1}$

k = reaction rate constant

(HCl) = hydrochloric acid concentration, equivalents/liter

n = order of the reaction

Figure 1, page 25, shows the effect of hydrochloric acid concentration on the dissolution rate at 25°C. The data used to make the plot are shown in Table I, page 22. The slope of the straight line in the log-log plot (Figure 2) was calculated by the method of least squares, giving a reaction order of 1.02.

Hydrobromic Acid. The dissolution of magnesium in hydrobromic acid was observed in concentrations varying from 0.0295 to 0.97N. The data are summarized in Table II, page 23. The effect of acid concentration on the dissolution rate is shown in Figure 1, page 25. It can be seen that the rate of hydrogen evolution is linear up to a concentration of 0.3N. Figure 2, page 26, shows the log-log plot of rate versus acid concentration. The slope of the straight line was 1.08, indicating an approximate first order reaction.

Hydriodic Acid. Table III, page 24, shows the rate of hydrogen evolution in solutions of 0.0300, 0.100, and 0.300N. Figure 2, page 26, shows the log-log plot of rate versus acid concentration. Again, the straight line relationship exists up to 0.3N.

TABLE I

Hydrogen Evolution Rate for the Dissolution of Magnesium in Hydrochloric Acid at 25°C

HCl Concentration equivalents/liter		Hydrogen Evolution Rate $mm^3cm^{-2}sec^{-1}$ at STP
0.0297		3.71 3.40 3.34
	Average	3.48
0.100		11.5 11.5 11.5
	Average	11.5
0.293		37.0 36.8 34.5
	Average	36.1
1.00		340 335 327
	Average	334

TABLE II

Hydrogen Evolution Rate for the Dissolution of Magnesium in Hydrobromic Acid at 25°C

HBr Concentration equivalents/liter		Hydrogen Evolution Rate $mm^3cm^{-2}sec^{-1}$ at STP
0.0295		3.04
		2.89
		2.92
	Average	2.95
0.100		10.8
		10.5
		10.6
	Average	10.6
0.300		35.2
		37.1
	Average	36.1
0.970		364
		367
		372
	Average	368

TABLE III

Hydrogen Evolution Rate for the Dissolution of Magnesium in Hydriodic Acid at 25°C

HI Concentration equivalents/liter		Hydrogen Evolution Rate $mm^3 cm^{-2} sec^{-1}$ at STP
0.0300		2.98
		2.58
		3.00
	Average	2.85
0.100		12.5
		15.1
		13.9
	Average	13.8
0.300		36.6
		44.0
		46.8
	Average	42.5

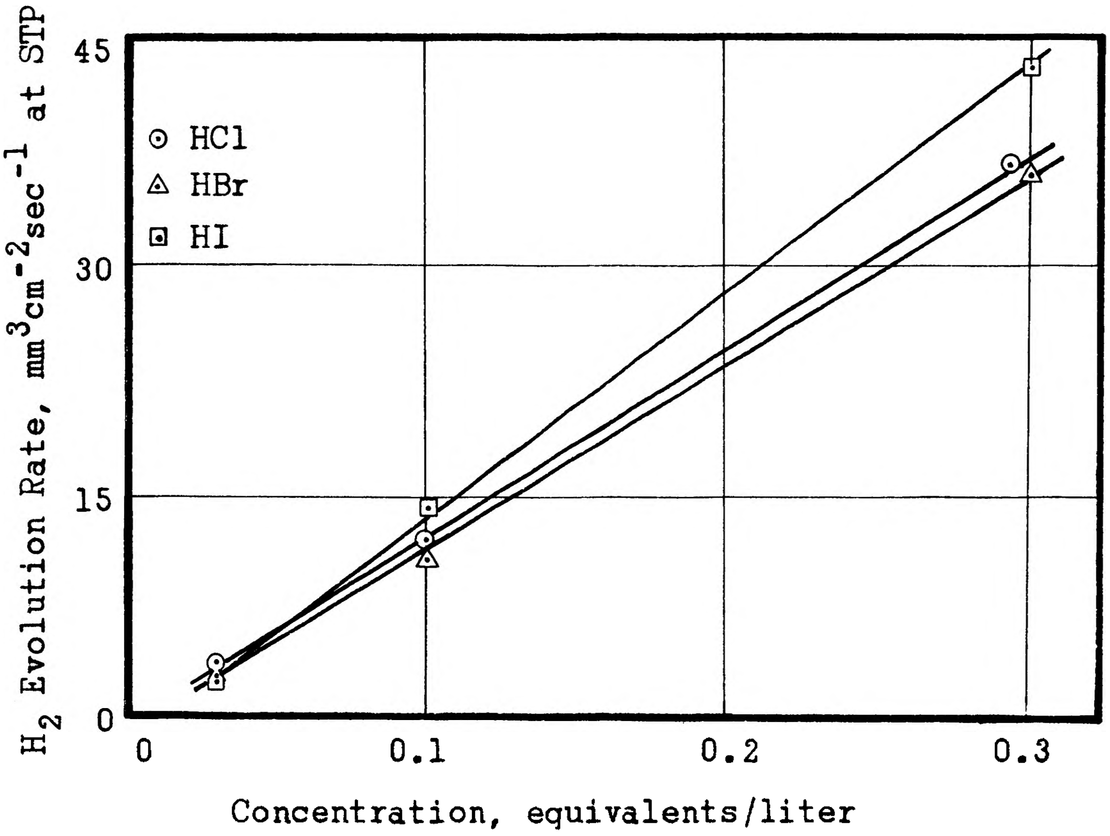

Figure 1. Rates of hydrogen evolution for magnesium dissolving in hydrochloric, hydrobromic, and hydriodic acids.

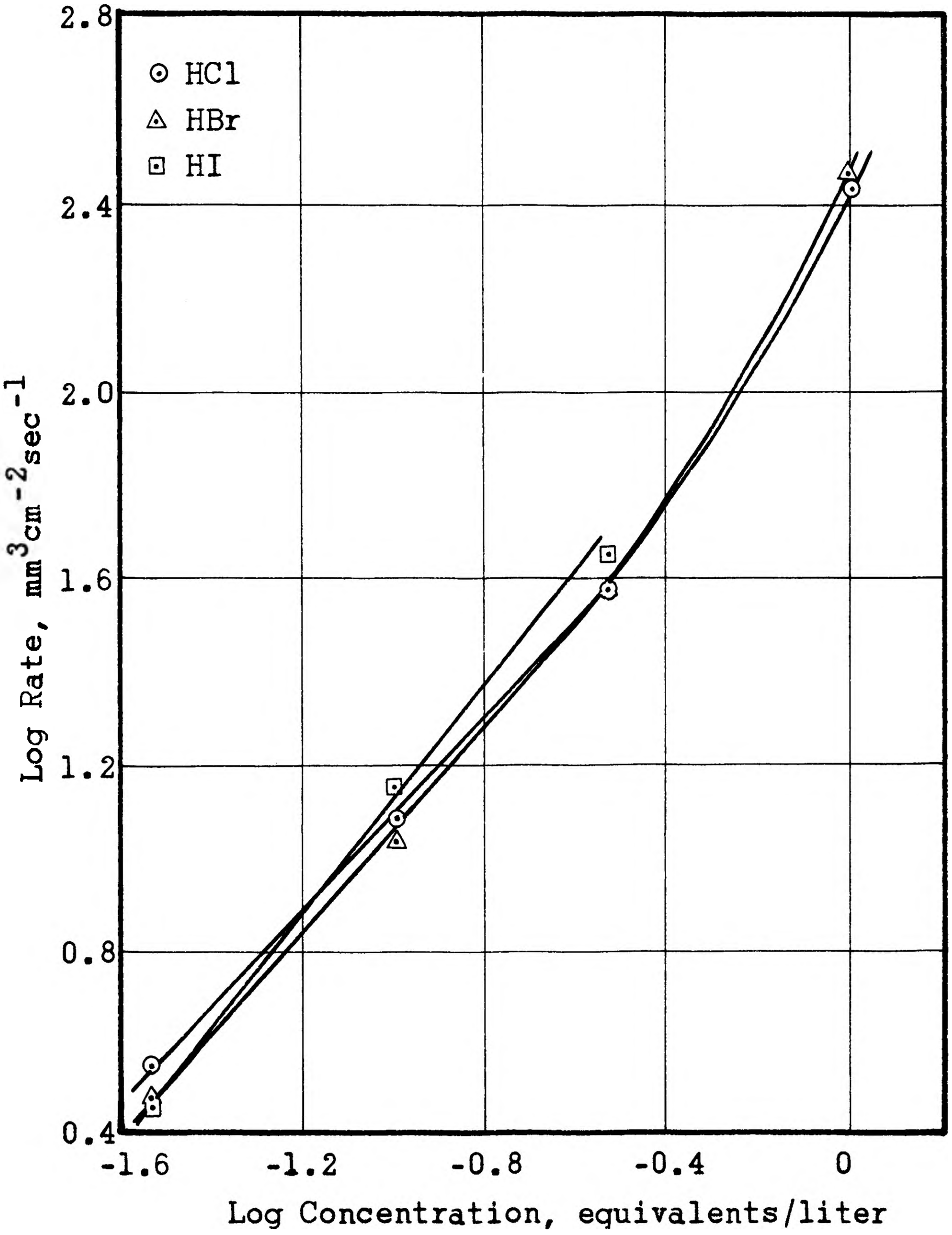

Figure 2. Rates of hydrogen evolution for magnesium dissolving in hydrochloric, hydrobromic, and hydriodic acids.

The activity of each of the above acids at 25°C was calculated using activity coefficients from the literature(28). The values for low concentrations were obtained by interpolating these data. A plot of hydrogen evolution rate versus activity at 25°C is shown in Figure 3, page 28. The log-log plot of hydrogen evolution rate versus activity at 25°C is shown in Figure 4, page 29. The hydrogen evolution rates in hydrochloric, hydrobromic, and hydriodic acids are about the same at a given acid concentration. This shows that the mechanism in these three acids may be similar. The slopes of these three lines were calculated to be 1.08, 1.13, and 1.21 for hydrochloric, hydrobromic, and hydriodic acids, respectively. Thus, at low concentrations (below 0.3N) the dissolution of magnesium is approximately first order in the three acids.

Sample Calculations. The method used for calculation of rates in hydrochloric, hydrobromic, and hydriodic acids was the same.

Calculation of Dissolution Rates. For purposes of illustration, the dissolution in hydrochloric acid has been selected. The following shows the calculation of the average hydrogen evolution rate at STP (0°C and 760 mm Hg). The data used are taken from Table XVII, page 78.

t = average thermometer reading during the run

= 26.6°C

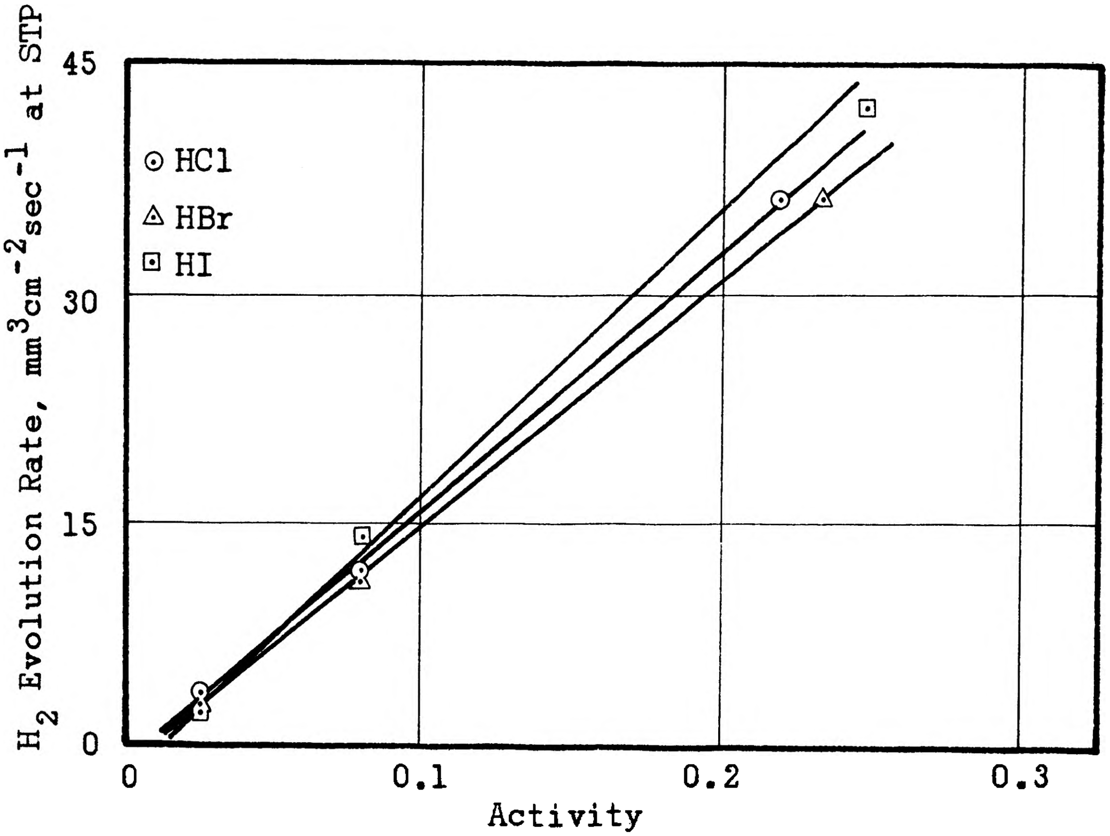

Figure 3. Rates of hydrogen evolution for magnesium dissolving in hydrochloric, hydrobromic, and hydriodic acids.

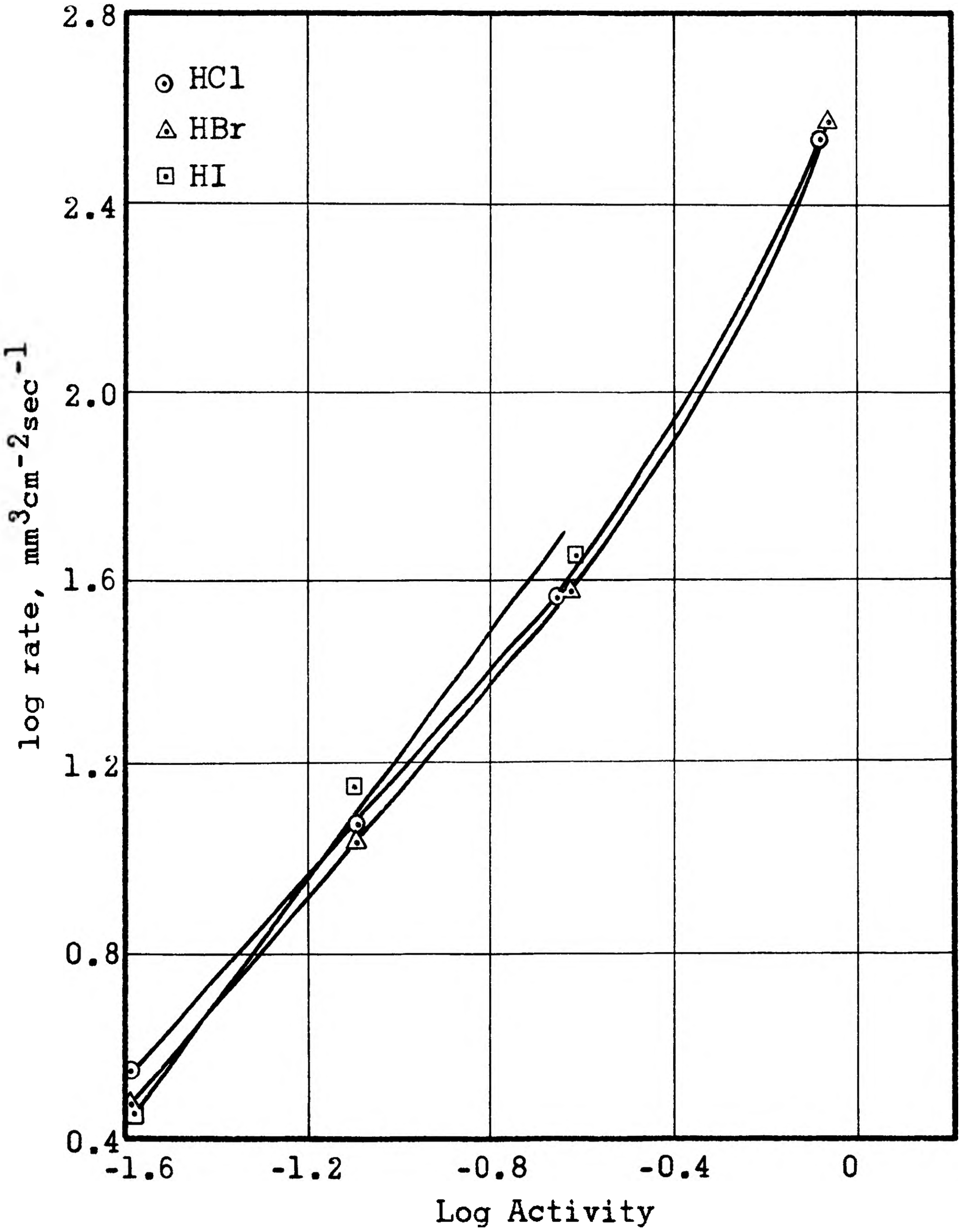

Figure 4. Rates of hydrogen evolution for magnesium dissolving in hydrochloric, hydrobromic, and hydriodic acids.

T = absolute temperature of hydrogen

= 26.6 + 273.1 = 299.7°K

P = average barometric pressure

= 725.5 mm Hg

Pressure corrections:

(1) correction for vapor pressure of water at 26.6°C

= 26.1 mm Hg

(2) = temperature correction for brass-scale barometer

= 3.1 mm Hg

Corrected average pressure of hydrogen = 725.5 -26.1 - 3.1 = 696.3 mm Hg

dv = increase in volume of hydrogen over each definite time interval, mm^3

dv STP = the increase in volume of hydrogen reduced to standard temperature and pressure during the time interval, mm^3

$$= (dv)\left(\frac{696.3}{760.0}\right)\left(\frac{273.1}{299.7}\right) = 0.8350 \text{ dv mm}^3$$

The values of dv STP have been calculated by the above method and are shown in the third column of the table from which the data were taken. The average maximum dv was calculated by averaging those values which were practically constant during a period of the run. This value was calculated to be 2672 mm^3 for a time interval of 720 seconds. The average maximum rate per second was obtained from the equation:

$$R = \frac{dv(ave)}{A\ dt}$$

where, R = rate, $mm^3cm^{-2}sec^{-1}$

$dv(ave)$ = average maximum value, mm^3

A = surface area of the specimen, cm^2

dt = the time interval over which the measurements were made, sec

Substituting the values obtained for this illustration gives:

$$R = \frac{2672}{(1)(720)} = 3.71\ mm^3cm^{-2}sec^{-1}$$

<u>Calculation of Activities</u>. For 0.100N HCl at 25°C, the value of the activity coefficient is 0.796. Thus, the activity is given by the equation:

$$a_{HCl} = (0.796)(0.1) = 0.0796$$

The activities of the other acids were calculated in the same manner.

<u>Calculation of Reaction Rate Constants</u>. The data used are taken from Table I, page 22, for the reaction at 25°C. From equation 12, page 20:

$$dv/dt = k(HCl)^n$$

Using n=1 as the order of reaction for 0.297N HCl

$$k = \frac{dv/dt}{(HCl)} = \frac{3.48}{0.0297}$$

$$= 117\ mm^3cm^{-2}sec^{-1}(equiv/l)^{-1}$$

TABLE IV

Reaction Rate Constant for the Dissolution of Magnesium in Hydrochloric Acid at 25°C

HCl Concentration equivalents/liter	Reaction Rate Constant, k $mm^3cm^{-2}sec^{-1}(equiv/l)^{-1}$
0.0297	117
0.100	115
0.293	123
1.00	334
Average k	118[a]

[a] The value of k for 1.00N HCl was not included to obtain the average k.

TABLE V

Reaction Rate Constant for the Dissolution of Magnesium in Hydrobromic Acid at 25°C

HBr Concentration equivalents/liter	Reaction Rate Constant, k $mm^3cm^{-2}sec^{-1}(equiv/l)^{-1}$
0.0295	100
0.100	106
0.300	120
0.970	379
Average k	109[a]

[a] The value of k for 0.970N HBr was not included to obtain the average k.

TABLE VI

Reaction Rate Constant for the Dissolution of Magnesium in Hydriodic Acid at 25°C

HI concentration equivalents/liter	Reaction Rate Constant, k $mm^3 cm^{-2} sec^{-1} (equiv/l)^{-1}$
0.0300	95
0.100	138
0.300	142
Average k	125

2. The Effect of Various Electrolytes and Current Densities on the Apparent Valence of Magnesium Undergoing Anodic Dissolution.

Apparatus. The apparatus consisted of a separated electrolytic cell of 300 milliliter capacity, a magnesium anode, a platinized-platinum cathode, an electric stirrer, a sensitive milliammeter, a decade-type resistance box with graduations from 0 to 9999 ohms in one-ohm divisions, a power source, and a knife switch, all connected in series. A diagram of the apparatus is shown on page 35. A timer with one-second divisions was used for measuring time passed. Pipettes with capacities of 5, 10, 25, and 50 milliliters were used to withdraw aliquots from the cell and a microburette of 10 milliliter capacity with 0.05 milliliter graduations was employed to measure the magnesium content of the aliquots by E.D.T.A. (ethylenedinitrilotetraacetic acid) titration. The cell was immersed in a water bath which was controlled at a temperature of 25.0°C within 0.1°C.

Procedure. A specimen with a cross-sectional area of approximately one square centimeter was cut from a bar of magnesium metal of 99.999 per cent purity. It was filed to reduce the area to one square centimeter, plus or minus two per cent. This was checked by using a micrometer. It was then mounted in lucite by means of a metallographic mounting press. The magnesium electrode was prepared as previously

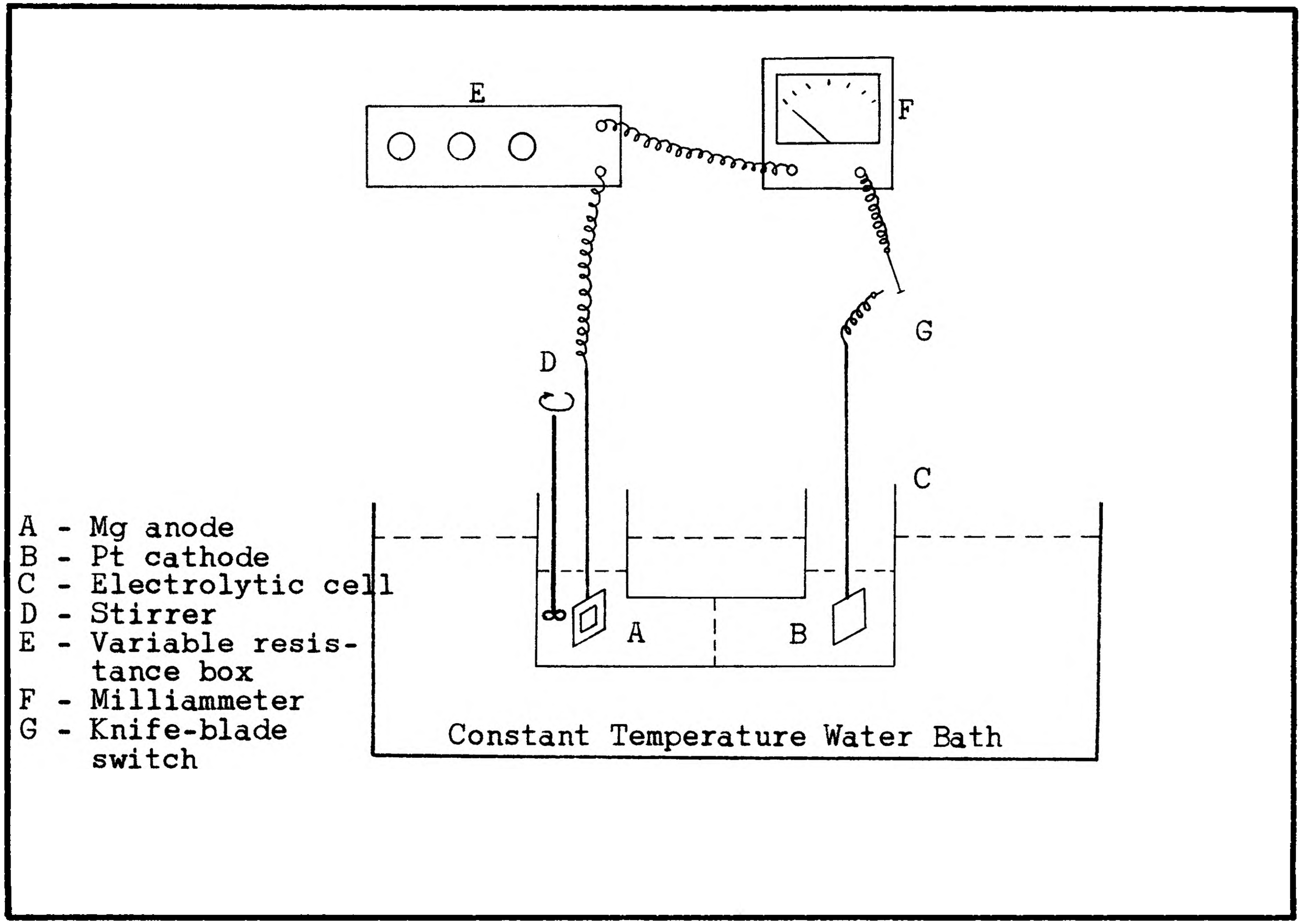

Figure 5. Diagram of apparatus used for measurement of apparent valence of magnesium undergoing anodic dissolution.

described(23). The electrode was polished immediately before each run according to the procedure listed in the appendix. A measured quantity of electrolyte was transferred to the electrolytic cell with pipettes. The electrolytic cell was then placed into 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. The mounted metal anode and the platinized-platinum cathode were then immersed into the anodic and cathodic compartments of the electrolytic cell and connected in series with the external circuit. The knife switch was closed and the current was kept at a steady rate by means of the resistance box. The timer and milliammeter were used for measuring the number of coulombs passed. A 10 milliliter aliquot was withdrawn from the electrolyte at the end of a run, diluted to approximately 100 milliliters with distilled water, buffered to a pH of 10, and titrated with a standard E.D.T.A. solution using the organic dye Erichrome Black-T as an internal indicator. The E.D.T.A. solution had been previously standardized against a weighed amount of pure magnesium obtained from the same bar as the mounted specimen. The time was recorded in seconds, the current in amperes, and the weight loss of the magnesium (determined by the E.D.T.A. titration) in grams. The procedure employed was the same for all electrolysis experiments and is described in the appendix. A detailed description of the procedure for standardizing the E.D.T.A. has been described(24).

Data and Results. The anodic dissolution of magnesium was observed in five different electrolytes. They were potassium sulfate, potassium nitrate, potassium chloride, potassium iodide, and potassium bromide. The range of current densities was from 0.0020 to 0.070 amps·cm^{-2}. A brief summation of the results for each electrolyte follows.

Potassium Sulfate. The anodic dissolution of magnesium in 1.00N potassium sulfate was carried out at a temperature of 25°C. The range of current densities was from 0.0020 to 0.065 amps.cm^{-2}. Data from these runs are shown in Table VII, page 38. The effect of current density on the apparent valence is also shown in Figure 6, page 44. It can be seen that the apparent valence approaches the normal valence of 2 at a very low current density (0.002 amps·cm^{-2}) and decreases with increasing current density.

Potassium Nitrate. Magnesium was anodically dissolved in 1.00N potassium nitrate and at various current densities ranging from 0.0020 to 0.070 amps·cm^{-2}. The data collected are shown in Table VIII, page 39. The plot of apparent valence versus current density is shown in Figure 6, page 44. At the lowest current

TABLE VII

Effect of Current Density on the Apparent Valence of Magnesium Dissolving Anodically in 1.0N K_2SO_4 at 25°C

Time (sec)	Current Density (amps·cm^{-2})	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
50400	0.0020	0.0127	0.0262	2.02
36000	0.0020	0.00907	0.00912	1.99
19860	0.0050	0.0125	0.0154	1.63
36000	0.010	0.0454	0.0634	1.43
14400	0.025	0.0454	0.0663	1.37
7260	0.045	0.0412	0.0709	1.16
5400	0.065	0.0442	0.0741	1.19

TABLE VIII

Effect of Current Density on the Apparent Valence of Magnesium Dissolving Anodically in 1.0N KNO_3 at 25°C

Time (sec)	Current Density $(amps \cdot cm^{-2})$	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
36000	0.0020	0.00907	0.00947	1.92
36000	0.0020	0.00907	0.00872	2.08
36000	0.0020	0.00907	0.00902	2.01
18000	0.0050	0.0113	0.0115	1.96
18000	0.0050	0.0113	0.0119	1.91
18000	0.0050	0.0113	0.0115	1.96
12600	0.0070	0.0111	0.0119	1.86
9000	0.010	0.0113	0.0125	1.82
14400	0.025	0.0454	0.0491	1.85
14400	0.025	0.0454	0.0498	1.82
5400	0.070	0.0476	0.0520	1.83

density, the apparent valence approaches the normal valence of 2 and decreases slowly with increasing current density. It seems to reach a limiting value of about 1.8 for current densities larger than 0.01 amps$\cdot$cm^{-2}.

Potassium Chloride. Table IX, page 41 and Figure 6, page 44, show the anodic dissolution of magnesium in 1.00N potassium chloride. It can be seen that the apparent valence is much lower than the normal valence of 2 even at low current densities (0.002 amps$\cdot$cm^{-2}), and that it decreases slowly with increasing current density.

Potassium Iodide. The effect of current densities, ranging from 0.0020 to 0.065 amps$\cdot$cm^{-2}, on the apparent valence of magnesium undergoing anodic dissolution in 1.00N potassium iodide is shown in Table X, page 42. At the lowest current density, the apparent valence deviates from its normal value of 2, and is almost independent of current density up to 0.065 amps$\cdot$cm^{-2}.

Potassium Bromide. Table XI, page 43 and Figure 6, page 44, show the effect of current density on the apparent valence of magnesium undergoing anodic dissolution in 1.00N potassium bromide. When the current density changes from 0.0020 to 0.065 amps.cm^{-2}, the apparent valence changes from 1.52 to 1.20 respectively.

TABLE IX

Effect of Current Density on the Apparent Valence of Magnesium Dissolving Anodically in 1.0N KCl at 25°C

Time (sec)	Current Density (amps·cm^{-2})	Weight of Magnesium Calc. (gm)	Expt. (gm)	Apparent Valence
36000	0.0020	0.00907	0.0127	1.43
36000	0.0020	0.00907	0.0127	1.43
21600	0.010	0.0272	0.0396	1.38
21600	0.010	0.0272	0.0392	1.39
10800	0.025	0.0340	0.0534	1.27
10800	0.025	0.0340	0.0525	1.30
5400	0.065	0.0442	0.0718	1.23
5400	0.065	0.0442	0.0709	1.25

TABLE X

Effect of Current Density on the Apparent Valence of Magnesium Dissolving Anodically in 1.0N KI at 25°C

Time	Current Density	Weight of Magnesium		Apparent
(sec)	(amps·cm^{-2})	Calc. (gm)	Expt. (gm)	Valence
36000	0.0020	0.00907	0.0117	1.55
36000	0.0020	0.00907	0.0114	1.55
10800	0.025	0.0340	0.0451	1.51
10800	0.025	0.0340	0.0445	1.53
5400	0.065	0.0442	0.0498	1.48
5400	0.065	0.0442	0.0611	1.45

TABLE XI

Effect of Current Density on the Apparent Valence of Magnesium Dissolving Anodically in 1.0N KBr at 25°C

Time (sec)	Current Density (amps·cm^{-2})	Weight of Magnesium Calc. (gm)	Weight of Magnesium Expt. (gm)	Apparent Valence
36000	0.0020	0.00907	0.0118	1.54
36000	0.0020	0.00907	0.0117	1.55
21600	0.010	0.0272	0.0401	1.36
10800	0.025	0.0340	0.0534	1.27
10800	0.025	0.0340	0.0525	1.30
5400	0.065	0.0442	0.0728	1.22
8000	0.065	0.0655	0.111	1.18

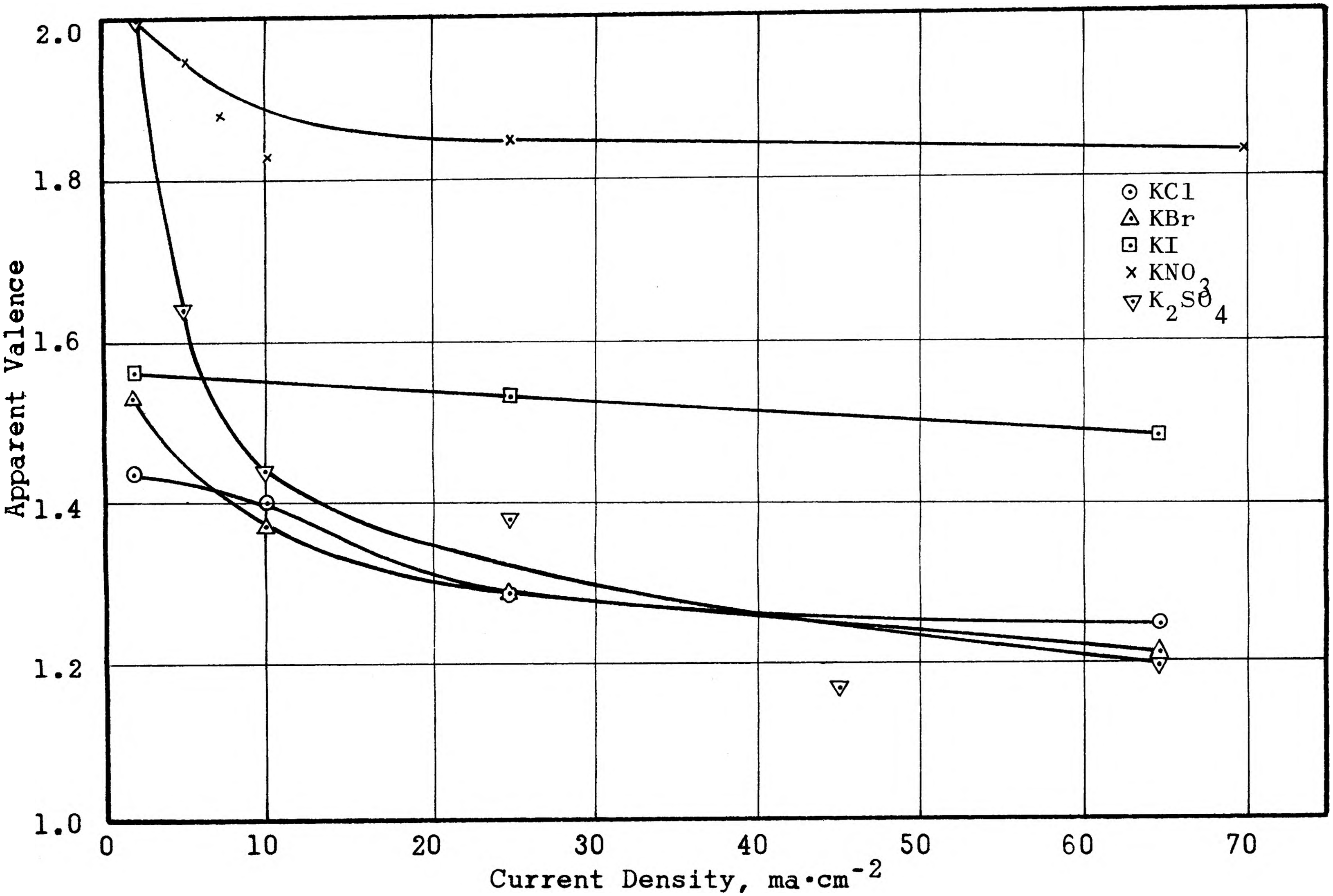

Figure 6. Effect of current density on the apparent valence of magnesium dissolving anodically in neutral solutions.

Sample Calculations. The method used for calculation of the apparent valence in potassium sulfate, potassium nitrate, potassium chloride, potassium iodide, and potassium bromide was the same. The data from the effect of current density on magnesium anodic dissolution in 1.00N K_2SO_4 (Table VII, page 38) have been used to illustrate the calculations involved in this part of the experimentation.

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:

$$\text{Wt. of magnesium (apparent)} = \frac{(It)(\text{Atomic weight of Mg})}{(nF)}$$

where, t = time interval of run = 36000 sec

I = current = 0.010 amp

Atomic weight of magnesium = 24.32 gm/gmol

F = Faraday constant = 96,500 amp sec/equiv

n = normal cationic charge of magnesium = 2

Therefore,

$$\text{Wt. of magnesium (apparent)} = \frac{(0.01)(36{,}000)(24.32)}{(96{,}500)(2)}$$

$$= 0.00454 \text{ gm}$$

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

V_i (apparent valence)

$$= \frac{(\text{Wt. of magnesium apparent})(\text{normal valence})}{(\text{Wt. of magnesium experimental})}$$

$$= \frac{(0.00454)(2)}{(0.00634)} = 1.43$$

where, Wt. of magnesium experimental =
Wt. of magnesium determined by E.D.T.A. titration

Wt. of magnesium apparent =
Wt. of magnesium determined by Coulombic data

3. The Polarization Curves of Magnesium Undergoing Anodic Dissolution in Various Electrolytes.

Apparatus. The apparatus consisted of a separated electrolytic cell of 300 milliliter capacity, a magnesium anode, a platinized-platinum cathode, a calomel electrode and a salt bridge (both containing 1.00N KCl solution), a milliammeter, a decade-type resistance box with graduations from 0 to 9999 ohms in one-ohm divisions, a power source, a knife switch, and an electrometer. A diagram of the apparatus is shown on page 48. The cell was immersed in a water bath which was controlled at a temperature of 25.0°C within 0.1°C.

Procedure. A specimen with a cross-sectional area of approximately one square centimeter was cut from a bar of magnesium metal of 99.999 per cent purity. It was filed to reduce the area to one square centimeter, plus or minus two per cent. It was then mounted in lucite by means of a metallographic mounting press. The magnesium electrode was prepared by the same method as previously described.

The electrode was polished immediately before each run. A measured amount of the electrolyte in the cell was then placed into 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. The mounted metal anode and the platinized-platinum cathode were then immersed into the anodic and cathodic compartments of the electrolytic cell and connected in series with the external circuit. The calomel reference electrode and magnesium anode were connected to the electrometer in order to measure the magnesium electrode potential at the various current densities. First, without any current passing, potential values were recorded at fifteen minute intervals until they became constant. Similar measurements were then made at various current densities until steady values were obtained.

Data and Results. The polarization curves for magnesium undergoing anodic dissolution were obtained in five different electrolytes. They were potassium sulfate, potassium nitrate, potassium chloride, potassium iodide, and potassium bromide. The range of current density was changed from zero to 0.080 amps$\cdot$cm^{-2}. A brief summation of the results for each electrolyte follows separately.

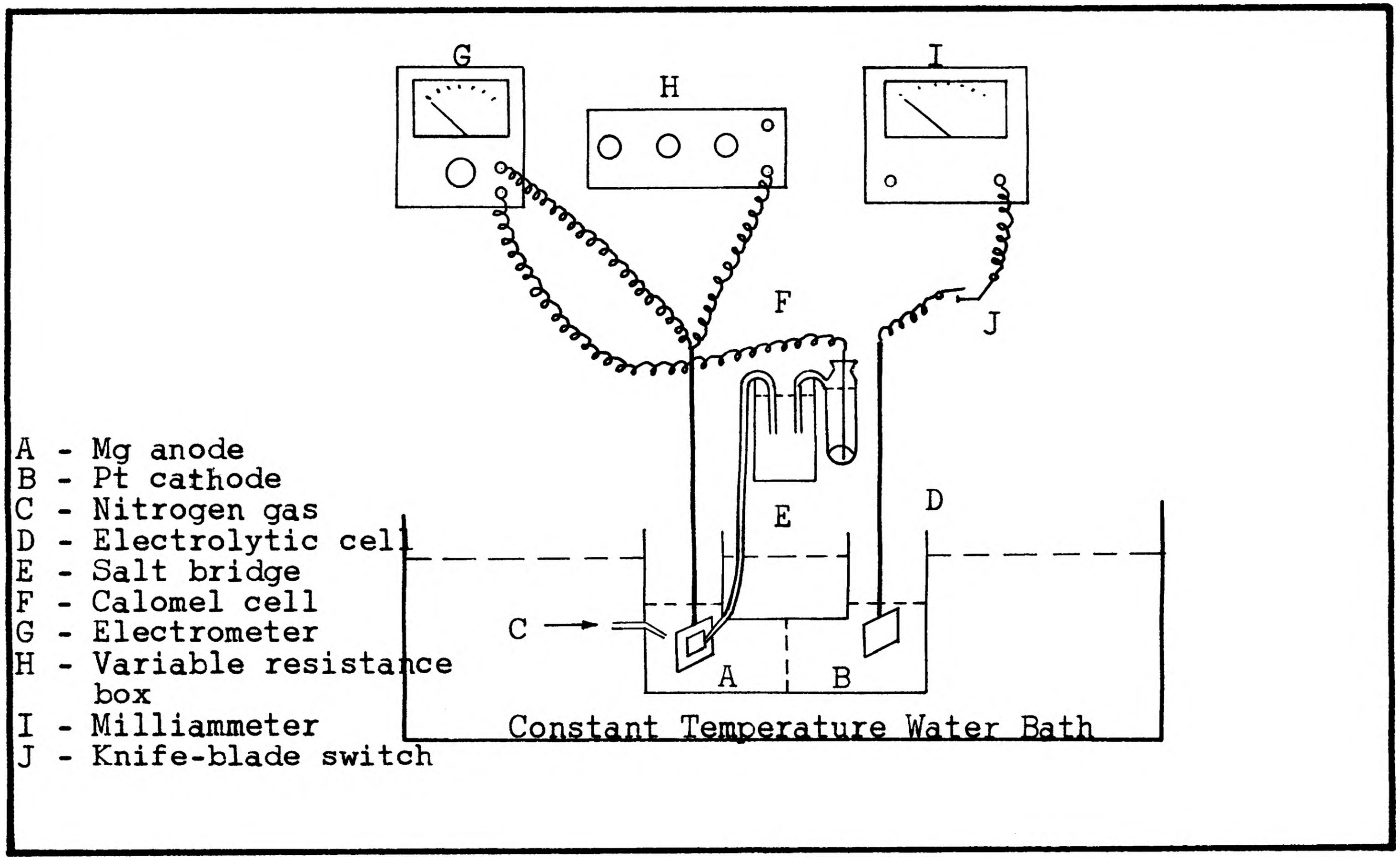

Figure 7. Diagram of apparatus used for measurement of dissolution potential of magnesium with various current densities.

Potassium Sulfate. The anodic dissolution of magnesium in 1.00N potassium sulfate solution was observed. The range of current densities was from zero to 0.030 amps$\cdot$cm^{-2}. Data for this run are shown in Table XII, page 50. The plot of potential versus log current density is shown in Figure 8, page 57. The potential increased slowly for current densities up to 0.01 amps.cm^{-2}. Above this, it increased rapidly with current density and became passivated.

Potassium Nitrate. Magnesium was anodically dissolved in 1.0N potassium nitrate at various current densities, ranging from zero to 0.080 amps$\cdot$cm^{-2}. The data collected are shown in Table XIII, page 52. A plot of potential versus log current density is shown in Figure 8, page 57. The potential shifted in the cathodic direction as the current density increased. At a current density of 0.0060 amps$\cdot$cm^{-2}, the anode became passivated.

Potassium Chloride. Table XIV, page 53, and Figure 8, page 57, show the relationship between potential and current density for magnesium undergoing anodic dissolution in 1.0N potassium chloride. The current density has almost no specific influence on the potential in the range from 0.0010 to 0.010 amps$\cdot$cm^{-2}. At high current densities (above 0.10

TABLE XII

The Dissolution Potential of Magnesium in 1.0N K_2SO_4 at Various Current Densities at 25°C

I (amps·cm^{-2})	t (min)	E (volts)[a]	I (amps·cm^{-2})	t (min)	E (volts)[a]
0.00000	0	-1.76	0.010	0	-1.23
0.00000	15	-1.74	0.010	15	-1.30
0.00000	30	-1.74	0.010	30	-1.31
			0.010	45	-1.32
0.00025	0	-1.65	0.010	75	-1.32
0.00025	15	-1.62			
0.00025	30	-1.56	0.030	0	-1.24
0.00025	45	-1.56	0.030	15	-1.18
			0.030	30	-1.12
0.00050	0	-1.50	0.030	45	-1.10
0.00050	15	-1.52	0.030	75	-0.98
0.00050	30	-1.52	0.030	90	-0.98
0.0010	0	-1.42			
0.0010	15	-1.46			
0.0010	30	-1.46			
0.0040	0	-1.39			
0.0040	15	-1.37			
0.0040	30	-1.37			

[a] Normal hydrogen scale.

amps•cm^{-2}), the potential increases rapidly with increasing current density.

Potassium Bromide. The change of potential with current density is shown in Table XV, page 54, and Figure 8, page 57. In the range from 0.0010 to 0.010 amps•cm^{-2}, the potential changes slowly. With current densities larger than 0.030 amps•cm^{-2}, it increases rapidly.

Potassium Iodide. Table XVI, page 55, and Figure 8, page 57, show the relationship between potential and current density when magnesium undergoes anodic dissolution in 1.0N potassium iodide. When the current density is larger than 0.0040 amps•cm^{-2}, the potential increases very slowly with increasing current density. It can be seen that the magnesium anode was difficult to passivate in this solution.

Runs were made in which the anolyte was stirred externally. This had no effect on the individual points. Duplicate measurements of the Tafel curves (see Figure 8a, page 56) for magnesium dissolving in 1.0N KCl were also made. The deviation was small.

TABLE XIII

The Dissolution Potential of Magnesium in 1.0N KNO_3 at Various Current Densities at 25°C

I ($\text{amps}\cdot\text{cm}^{-2}$)	t (min)	E (volts)[a]	I ($\text{amps}\cdot\text{cm}^{-2}$)	t (min)	E (volts)[a]
0.00000	0	-1.32	0.010	0	-1.17
0.00000	15	-1.36	0.010	15	-1.16
0.00000	30	-1.36	0.010	30	-1.16
0.00025	0	-1.32	0.030	0	-0.91
0.00025	15	-1.32	0.030	15	-0.86
0.00025	30	-1.32	0.030	30	-0.86
0.00050	0	-1.29	0.060	0	-0.73
0.00050	15	-1.29	0.060	15	-0.73
			0.060	30	-0.73
0.0010	0	-1.25			
0.0010	15	-1.25	0.080	0	-0.66
			0.080	15	-0.66
0.0040	0	-1.21			
0.0040	15	-1.18			
0.0040	30	-1.18			

[a] Normal hydrogen scale.

TABLE XIV

The Dissolution Potential of Magnesium in 1.0N KCl at Various Current Densities at 25°C

I (amps.cm^{-2})	t (min)	E (volts)[a]	I (amps.cm^{-2})	t (min)	E (volts)[a]
0.00000	0	-1.76	0.030	0	-1.32
0.00000	15	-1.76	0.030	15	-1.31
			0.030	30	-1.28
0.00025	0	-1.61	0.030	45	-1.26
0.00025	15	-1.63	0.030	60	-1.23
0.00025	30	-1.61	0.030	75	-1.26
0.00025	45	-1.56	0.030	90	-1.23
0.00025	60	-1.56	0.030	105	-1.23
0.00050	0	-1.42	0.060	0	-0.92
0.00050	15	-1.46	0.060	15	-1.20
0.00050	30	-1.46	0.060	30	-1.11
			0.060	45	-1.08
0.0010	0	-1.41	0.060	60	-1.03
0.0010	15	-1.41	0.060	75	-1.02
0.0040	0	-1.39	0.080	0	-0.86
0.0040	15	-1.40	0.080	15	-0.86
0.0040	30	-1.40			
0.010	0	-1.38			
0.010	15	-1.39			
0.010	30	-1.39			

[a] Normal hydrogen scale.

TABLE XV

The Dissolution Potential of Magnesium in 1.0N KBr at Various Current Densities at 25°C

I (amps•cm^{-2})	t (min)	E (volts)[a]	I (amps•cm^{-2})	t (min)	E (volts)[a]
0.00000	0	-1.73	0.030	0	-1.16
0.00000	15	-1.75	0.030	15	-1.16
0.00000	30	-1.75			
			0.060	0	-1.01
0.00025	0	-1.63	0.060	15	-0.96
0.00025	15	-1.62	0.060	30	-0.92
0.00025	30	-1.61	0.060	45	-0.88
0.00025	45	-1.61	0.060	60	-0.93
			0.060	75	-0.89
0.00050	0	-1.50	0.060	90	-0.84
0.00050	15	-1.48	0.060	105	-0.88
0.00050	30	-1.47	0.060	120	-0.88
0.00050	45	-1.47			
			0.080	0	-0.72
0.0010	0	-1.30	0.080	15	-0.59
0.0010	30	-1.36	0.080	30	-0.64
0.0010	45	-1.35	0.080	45	-0.56
0.0010	60	-1.33	0.080	60	-0.63
0.0010	75	-1.35	0.080	75	-0.62
0.0040	0	-1.28			
0.0040	15	-1.28			
0.010	0	-1.25			
0.010	15	-1.25			

[a] Normal hydrogen scale.

TABLE XVI

The Dissolution Potential of Magnesium in 1.0N KI at Various Current Densities at 25°C

I (amps·cm^{-2})	t (min)	E (volts)[a]	I (amps·cm^{-2})	t (min)	E (volts)[a]
0.00000	0	-1.77	0.0040	0	-1.17
0.00000	15	-1.74	0.0040	30	-1.21
0.00000	30	-1.76	0.0040	45	-1.21
0.00000	45	-1.76			
			0.010	0	-1.18
0.00025	0	-1.41	0.010	15	-1.20
0.00025	15	-1.61	0.010	30	-1.20
0.00025	30	-1.64			
0.00025	45	-1.59	0.030	0	-1.17
0.00025	60	-1.59	0.030	15	-1.18
			0.030	30	-1.18
0.00050	0	-1.49			
0.00050	15	-1.47	0.060	0	-1.14
0.00050	30	-1.45	0.060	15	-1.14
0.00050	45	-1.45			
			0.080	0	-1.11
0.0010	0	-1.35	0.080	15	-1.11
0.0010	15	-1.31			
0.0010	30	-1.33			
0.0010	45	-1.33			

[a] Normal hydrogen scale.

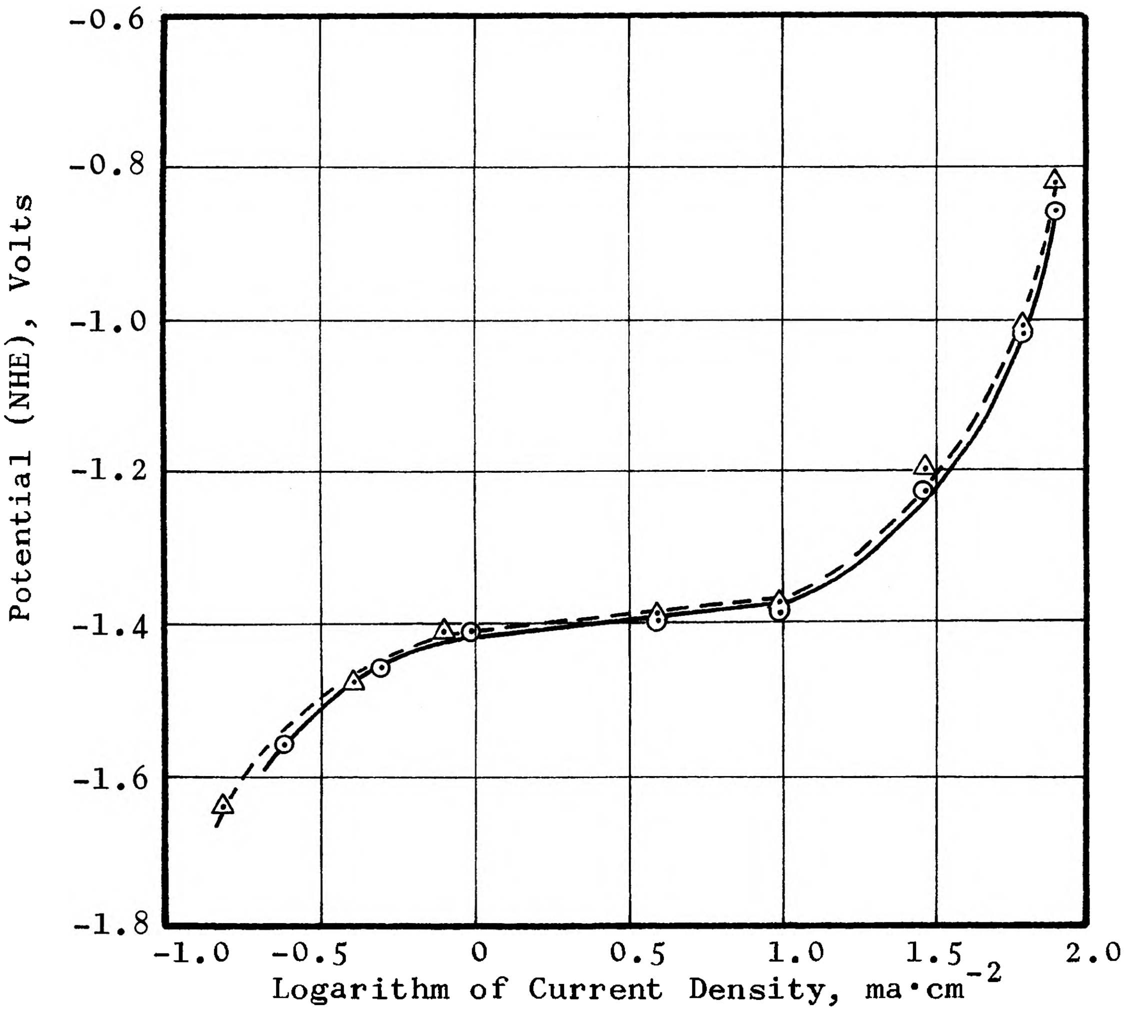

Figure 8a. The polarization curves of magnesium undergoing anodic dissolution in 1.0N KCl solutions.

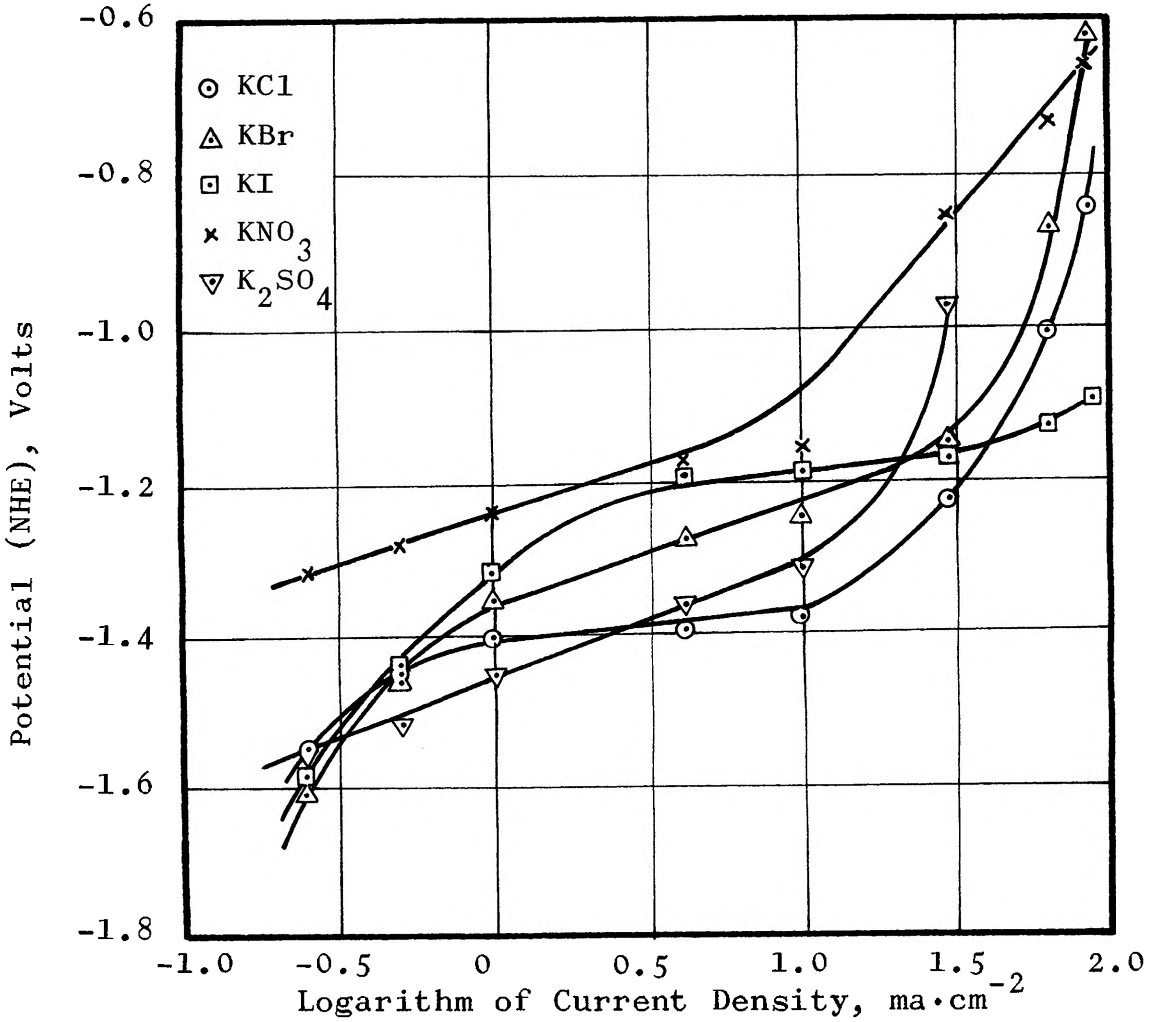

Figure 8. The polarization curves of magnesium undergoing anodic dissolution in neutral solutions.

IV. DISCUSSION

Discussion of the results is presented in two parts: (1) free dissolution of magnesium in acids, and (2) anodic dissolution of magnesium in neutral solutions.

Free Dissolution of Magnesium in Acids

The stoichiometry for the dissolution of magnesium in strong acids was checked by the hydrogen evolution method. It was found that magnesium enters into solution according to the following reaction:

$$Mg + 2H^{+} \longrightarrow Mg^{++} + H_2 \qquad (13)$$

Free dissolution of magnesium in hydrochloric, hydrobromic, and hydriodic acids was studied over a concentration range of 0.03 to 1.0N at 25°C. The reaction rate was found to be directly proportional to the acid concentration up to 0.3N, i.e., first order with respect to the acid concentration. Plots of dissolution rate versus acid concentration show that the dissolution rate deviates from linearity at higher acid concentrations (above 0.3N). Roald and Beck(7) have considered the deviation to be caused by the heating effect and also by the stirring effect of the hydrogen bubbles coming off the surface of metal. They have suggested that at higher acid concentrations the size and the action of the bubbles increase, thereby removing the reaction products faster than usual. It is also possible that the high dissolution rates may be caused by the more complete removal of protective films, possibly $Mg(OH)_2$, on the surface of metal which would be more soluble at higher acid concentrations, allowing reaction with water or increasing the reaction area. Another possibility is that appreciable amounts of magnesium disintegrate at these higher acid concentrations, thereby causing higher dissolution rates.

In the present studies at 25°C, activities of hydrochloric, hydrobromic, and hydriodic acids were calculated using activity coefficients available from the literature. These activities were plotted versus the hydrogen evolution rates. Corresponding log-log plots were also prepared. It was found that in hydrochloric, hydrobromic, and hydriodic acids, the hydrogen evolution rates were approximately the same at the same acid activity. Thus, the halide ions have no pronounced specific effect on the rate of self-dissolution of magnesium in these acids. The very close values of the dissolution rates indicate a similar mechanism of reaction in these three acids. In general, the rate equation for these acids can be expressed as:

$$R = k(H^+)$$

where, R = rate, $mm^3cm^{-2}sec^{-1}$

(H^+) = concentration of hydrogen ions, equivalents/liter

k = rate constant

Bhatia et al$^{(10)}$ have studied the effect of temperature on the dissolution rates of magnesium in strong acids. The activation energies in hydrochloric, sulfuric, and perchloric acids were 3.6 ± 0.3, 3.7 ± 0.1, and 4.4 ± 0.3 kilocalories, respectively.

It is suggested for the conditions of this study that the rate of hydrogen evolution is dependent upon the diffusion of hydrogen ions to the surface of the metal as proposed by Kilpatrick and Rushton$^{(1)}$ and Roald and Beck$^{(7)}$. They propose the actual reactions taking place at the surface of magnesium to be:

$$Mg + 2H^+ \longrightarrow Mg^{++} + 2H^\cdot \tag{14}$$

followed by

$$2H^\cdot \longrightarrow H_2 \tag{15}$$

The first step of the reaction is electrochemical in nature. Although the magnesium used was of high purity, aggregation of a few impurities at the grain boundaries and the presence of minute "peaks" (high points) on the surface could act as local cathodes and thus discharge hydrogen ions.

The main characteristics of diffusionally controlled reactions are: (1) the reaction is first order, (2) the activation energy is about 4 kilocalories, (3) the reaction proper takes place very rapidly at the surface of the metal, and (4) a diffusion layer is present which is formed by accumulation of reaction products during the initial stages(25).

The results of dissolution rate measurements in hydrochloric, hydrobromic, hydriodic, sulfuric, and perchloric acids are all in general agreement with the theory of diffusion controlled reactions.

Anodic Dissolution of Magnesium in Neutral Solutions

The purpose of this part of the investigation was to study the effect of anions on the disintegration of magnesium during electrolysis in neutral salt solutions. The solutions used were one normal in potassium sulfate, potassium nitrate, potassium chloride, potassium bromide, and potassium iodide.

Figure 8, page 57, shows the Tafel curves of magnesium undergoing anodic dissolution in one normal solutions of potassium nitrate, potassium sulfate, potassium chloride, potassium bromide, and potassium iodide. Between current densities of 0.0010 to 0.010 amps$\cdot$cm^{-2}, the slopes of the polarization curves for magnesium in potassium nitrate, potassium bromide and potassium sulfate are almost the same, approximately 120 mV. The polarization curves for magnesium in potassium iodide and potassium chloride are also parallel and approximately equal to 30 mV. At high current densities (above 0.010 amps$\cdot$cm^{-2}), the magnesium anode becomes passive probably due to film formation on the surface of the metal. Compared with potassium sulfate and potassium nitrate, it can be seen that the magnesium anode was difficult to passivate in halide solutions as many investigators have pointed out before(11,12,13).

From Figure 6, page 44, it is seen that in potassium nitrate solution the apparent valence changes slowly from 2 to 1.83 with increasing current density, but in potassium sulfate, the apparent valence drops rapidly from 2 to 1.19 when current density changes from 0.0020 to 0.065 amps$\cdot$cm^{-2}. The apparent valence of magnesium with current density in potassium iodide, potassium bromide, and potassium chloride is intermediate between that of the first two electrolytes. It should be noted that the apparent valence of magnesium with halide ions present deviates appreciably from two at the lowest current densities used in this study. Under these conditions, any specific adsorption of the anion would be more pronounced. As the current density is increased, the electrode becomes more positive and probably all anions are adsorbed.

The effect of various electrolytes and current density on the apparent valence of magnesium undergoing anodic dissolution may be explained by an anion adsorption and a passivative mechanism of magnesium in these electrolytes.

The electrostatic attractions between the magnesium anode and the anions at the higher current densities tend to increase as the ionic radius becomes smaller and the negative charge becomes larger. The ionic radii of $SO_4^=$, NO_3^-, Cl^-, Br^-, and I^- are 2.36 Å[a], 2.02 Å[a], 1.81 Å, 1.95 Å, and 2.16 Å, respectively. Based on this viewpoint, the adsorption of the anions at the anode surface would be in the order of $SO_4^=$, Cl^-, Br^-, NO_3^- and I^- at high current densities.

For electrolysis in potassium nitrate, at current densities 0.010 to 0.070 amps•cm^{-2}, the apparent valence of magnesium is relatively constant at 1.83 ± 0.02. However, when the current density drops below 0.010 amps•cm^{-2}, the valence increases and approaches the normal valence of 2 at 0.0020 amps•cm^{-2}. Also, during the electrolysis, a gray film was observed on the surface of the magnesium electrode. It is suspected that this film formed on the metal anode plays an important role in the abnormal behavior of the anodic dissolution. The film formed at the surface of the metal was $Mg(OH)_2$ mixed with small metallic magnesium particles as reported previously(14,22).

[a] Estimated by Pauling's Rule assuming covalent bonding.

For electrolysis in one normal potassium sulfate solution, the apparent valence drops continuously and rapidly from the normal valence of 2 to 1.43 as current densities increase from 0.0020 to 0.010 amps$\cdot$cm^{-2}. It then drops slowly with increasing current density. When no current was passing through the electrolytic cell, gas bubbles were formed on surface of the magnesium anode but no such phenomenon was observed in potassium nitrate solution. During electrolysis, a white and spongy film was built up on the surface of the magnesium anode. After removal of the film, the surface of the metal was shiny, but in potassium nitrate solution the surface of the metal was gray. These phenomena indicate some difference in the mechanism of magnesium undergoing anodic dissolution.

When magnesium was undergoing anodic dissolution in potassium sulfate, potassium bromide, potassium chloride, and potassium iodide solutions, gas bubbles came off the anode as well as the cathode. Especially during electrolysis in potassium chloride solution at low current density, gas bubbles were observed coming from pitting sites. At higher current densities, because of the high rate of hydrogen evolution, it became difficult to see the surface of the magnesium anode. During prolonged electrolysis, white and spongy films were observed to form on the surface of the magnesium anode. Upon removal of the film, the surface of the metal was gray-black. During electrolysis in potassium iodide solution, a lot of black spots appeared on the surface. A white film was built up on the surface of the metal. Upon removal of the film, an uneven gray-black surface containing many pits could be seen. During electrolysis in potassium bromide solution, a white film was observed to form on the surface of the magnesium anode. Upon removal of the film, small metallic particles could be seen protruding from the gray-black surface.

It is proposed that the anodic dissolution of magnesium in neutral solutions consists of two reactions: (1) a normal electrochemical reaction involving Mg as the anode and the platinized-platinum as the cathode, and (2) a local cell action producing corrosion or self-dissolution. It appears that the overall mechanism for this anodic dissolution is film controlled with the uncommon valence being accounted for by both local corrosion and disintegration. The disintegration is a direct consequence of local cell action. Film behavior is very important as it controls the extent of the local corrosion, i.e., when the film is promoted by the anodic reaction (and/or nature of the electrolyte), local corrosion is suppressed and the valence approaches two. Under conditions unfavorable for formation of the film, local corrosion is promoted and the valence becomes less than two, depending on the extent of local corrosion.

Film formation can be affected several ways. In acid media, the film is soluble thereby allowing the metal to dissolve entirely by local cell action, and equivalent Mg-H_2 production is noted. In electrolysis in neutral solutions, various things can influence the film formation: (1) adsorption of anions on the metal can hinder formation of $Mg(OH)_2$, (2) precipitation of Mg^{+2} ions as a salt on the metal surface can hinder the formation of $Mg(OH)_2$ by both surface coverage with salt and Mg^{+2} removal, and (3) complexing of Mg^{+2} by anions can hinder $Mg(OH)_2$ formation by removal of Mg^{+2}. These are all associated with increased local cell action. Decreasing the precipitation of a magnesium salt by the choice of anion or introducing an anion that may be reduced will favor $Mg(OH)_2$ formation.

The anions used in this experiment can be placed in the following categories:

Nitrate Ion. Promotes film formation by the reaction of magnesium with nitrate or water to form insoluble $Mg(OH)_2$ film as proposed by Sun(24).

$$Mg + NO_3^- + H_2O \longrightarrow Mg(OH)_2 + NO_2^- \qquad (16)$$

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + 2H^{\bullet} \qquad (17)$$

This should inhibit local cell action and lead to a valence higher than with other non-oxidizible anions of comparable solubility.

Figure 9, page 69, shows the effect of current density on the anodic potential and valence. In potassium nitrate solution, the apparent valence decreases with increasing current density up to 0.010 amps$\cdot$cm^{-2} and then the apparent valence remains constant because of the protective film $Mg(OH)_2$ formed on the magnesium anode surface which hinders the local corrosion.

Sulfate Ion. From Figure 9, page 69, it can be seen that the apparent valence deviates continuously and rapidly from the normal valence of 2 as the current density increases. The reason may be the large electrostatic attraction between the $SO_4^=$ ions and the magnesium anode. $SO_4^=$ ions are not oxidizing agents and therefore do not promote film formation. Furthermore, $MgSO_4$ is relatively insoluble leading to precipitation of salt on the surface. Both of these promote local cell action which leads to a decreased valence.

Chloride, Bromide, and Iodide Ions. Figure 9, page 69, also shows that the decrease of the apparent valence varies linearly with the increase of the current density even though the magnesium anode is becoming passive. These halide anions are not oxidizing agents and therefore do not promote film formation. They also would complex with Mg^{+2}, as pointed out by other investigators(9,26). This makes Mg^{+2} unavailable for $Mg(OH)_2$ formation and promotes the local cell reaction. Hence, even at low current densities, the apparent valence deviates from a normal valence of 2 and continuously drops with increasing current densities.

It seems that the anodic disintegration may be a direct consequence of the local corrosion on the electrode. Activation of the surface (or film removal) occurs by the impact of cations (Mg^{+2}) forced into solution by the anodic current or by the changed conditions in the interface while the current is flowing. This uncovers local anodes and cathodes and allows self-dissolution to begin. Cathodic sites would not be as susceptible to attack due to the evolution of hydrogen at these regions. For this reason, the metal around and underneath the cathodic area would be dissolved and a magnesium chunk disloged. Once separated from the metal, the chunk would react by local action until passivated or consumed.

Recommendations

In this study, the dissolution rates of magnesium in hydrochloric, hydrobromic, and hydriodic acids are found to vary with the concentration of hydrogen ion. As the hydrogen ion concentration is changing during the course

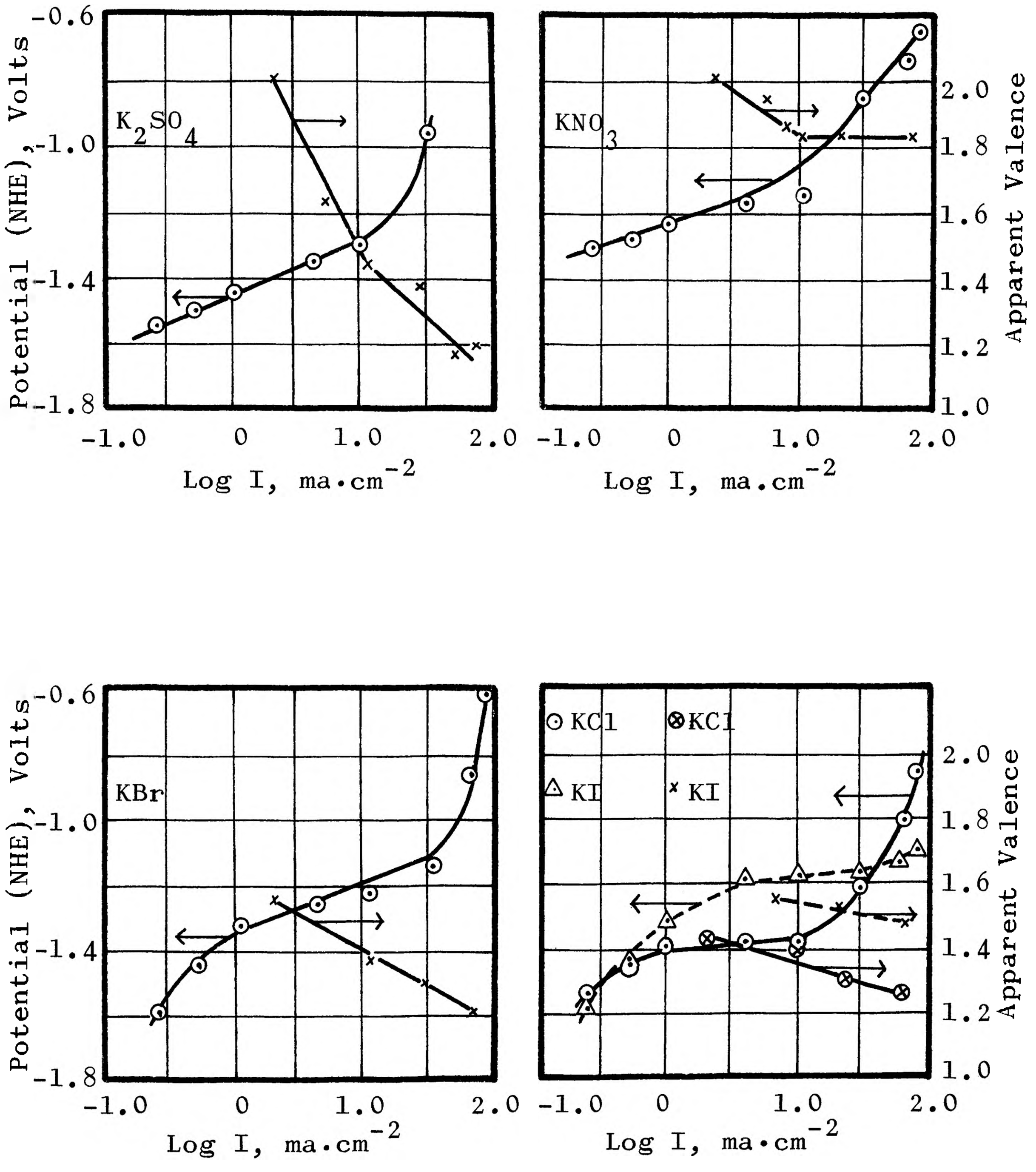

Figure 9. The effect of current density on the potential and apparent valence of magnesium dissolving anodically in 1.0N neutral salt solutions. (NOTE: The apparent valence is read on the right-hand scales and potential on the left-hand scales of the diagrams.)

of reaction, an apparatus should be developed to follow this changing concentration. A suitable pH meter might be coupled with the reaction flask, so that pH of the acid could be recorded simultaneously with the burette reading.

The objective of the anodic dissolution of magnesium in neutral solutions was to study the effect of anions on the disintegration of magnesium during electrolysis. In this study, it is interesting to note that the more insoluble the magnesium salts, the lower the apparent valence in some cases. A study with various magnesium salts and with varying anion concentrations in other electrolytic solutions might be of value.

V. SUMMARY AND CONCLUSIONS

The purpose of the present studies was to investigate the anion effect on the dissolution and disintegration of magnesium undergoing free and anodic dissolution.

Free dissolution of magnesium was studied in hydrochloric(1), hydrobromic, and hydriodic acids. A gas burette was used to collect the hydrogen gas evolved during the dissolution in a reaction flask. The temperature of the reaction flask was controlled by a constant-temperature water bath at 25 ± 0.1°C. The concentration of the acids was varied from 0.0300N to 1.00N. This led to the following results:

(1) The reaction of magnesium in hydrochloric, hydrobromic, and hydriodic acids obeys first order reaction kinetics with respect to hydrogen ion concentration for the acid concentration range of 0.0300 to 0.300N. Above these concentrations, the reaction rates increase exponentially.

(2) The hydrogen evolution rates are approximately the same for the same activities of hydrochloric, hydrobromic, and hydriodic acids.

These observations are in agreement with previous observations that the free dissolution in acids is electrochemical in nature and diffusionally controlled. The halide ions have no pronounced specific effect on the rate of self-dissolution of magnesium in these acids.

The anodic dissolution of magnesium was carried out in one normal solutions of potassium sulfate, potassium nitrate, potassium chloride, potassium bromide, and potassium iodide at 25 ± 0.1°C. A titration with the disodium salt of E.D.T.A. was used to determine the weight loss of magnesium from the electrode during electrolysis. The current densities were varied from 0.0020 to 0.070 amps.cm^{-2}. This led to the following conclusions:

(1) The slopes of the polarization curves in potassium sulfate, potassium nitrate, and potassium bromide solutions are the same and approximately 120 mV. The slopes in potassium iodide and potassium chloride are parallel and approximately equal to 30 mV. At high current densities (above 0.010 amps.cm^{-2}), the potential rapidly becomes more positive, probably due to film formation on the surface of the metal.

(2) The apparent valence of magnesium dissolving anodically in potassium nitrate solution at current densities ranging from 0.0020 to 0.070 amps.cm^{-2} is 2.00 to 1.83, respectively. In potassium sulfate solution, the apparent valence drops rapidly from 2 to 1.43 when the current density changes from 0.0020 to 0.010 amps.cm^{-2},

then decreases slowly to 1.19 as the current density increases to 0.065 amps·cm^{-2}. The apparent valence in potassium iodide, potassium bromide, and potassium chloride are intermediate between those of the first two electrolytes except that valences of 2 are not approached at current densities as low as 0.0020 amps·cm^{-2}.

(3) It is postulated that the overall mechanism for the anodic dissolution of magnesium in neutral solutions is film controlled with the uncommon valence being accounted for both by local corrosion and disintegration. The disintegration is a direct consequence of local cell action.

VI. APPENDIX

Materials

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

1. (Ethylenedinitrilo) Tetraacetic Acid, Disodium Salt. Reagent grade. Distillation Products, Eastman Organic Chemicals, Rochester 3, New York.

2. Acid, Hydrochloric. Reagent grade, meets ACS specifications. Fisher Scientific Company, Fair Lawn, N.Y.

3. Acid, Hydrobromic. Reagent grade, meets ACS specifications. Fisher Scientific Company, Fair Lawn, N.Y.

4. Acid, Hydriodic. Reagent grade, meets ACS specifications. Fisher Scientific Company, Fair Lawn, N.Y.

5. Potassium Chloride. Reagent grade, meets ACS specifications. Allied Chemical Corp., New York, N.Y.

6. Potassium Nitrate. Reagent grade, meets ACS specifications. Allied Chemical Corporation, New York, N.Y.

7. Potassium Sulfate. Reagent grade, meets ACS specifications. Fisher Scientific Company, Fair Lawn, N.Y.

8. Potassium Bromide. Reagent grade, meets ACS specifications. J. T. Baker Chemical Co., Phillipsburg, N.J.

9. Potassium Iodide. Reagent grade, meets ACS specifications. J. T. Baker Chemical Co., Phillipsburg, N.J.

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

Miscellaneous Experimental Procedures

Standardization of Disodium Salt of E.D.T.A.

The procedure for this part of the experimentation follows as a step-by-step operation.

1. Accurately weigh out approximately three-tenths of a gram of magnesium metal of 99.999 per cent purity.
2. Transfer to a 100 milliliter volumetric flask and dissolve in a small amount of 3N hydrochloric acid.
3. Dilute to 100 milliliters, mix throughly.
4. Withdraw a 3 milliliter aliquot with a pipette.
5. Dilute to 100 milliliters with distilled water.
6. Add 10 milliliters of a pH 10 buffer solution.
7. Add one drop of Erichrome Black-T indicator solution.
8. Titrate with 0.05M disodium salt of E.D.T.A. with a microburette until one drop turns the solution blue.
9. Determine the magnesium equivalent of the disodium salt of E.D.T.A. solution in gm magnesium/ml of solution.

Surface Preparation of Magnesium Specimens

The following procedure was used for the magnesium metal surface preparation.

1. Remove all pits and irregularities from the metal surface with a belt surfacer equipped with a No. 150 grit abrasive cloth belt.
2. Finish the sample surface on a water-flushed four-stage hand grinder equipped with No.'s 240, 320,400, and 600 abrasive strips, proceeding from the coarsest to the finest.
3. Rinse the sample with distilled water.

TABLE XVII

Dissolution of Magnesium in 0.0297N HCl at 25°C

	T=26.6°C P=725.5 mm Hg		T=23.4°C P=715.0 mm Hg		T=21.5°C P=732.5 mm Hg	
Time	Vol	dv STP	vol	dv STP	Vol	dv STP
sec	ml	ml	ml	ml	ml	ml
0	2.00	--	14.8	--	15.4	--
720	4.40	2.004	17.7	2.428[a]	18.1	2.340[a]
1440	7.60	2.672[a]	20.5	2.344[a]	20.9	2.428[a]
2160	10.8	2.672[a]	23.4	2.428[a]	23.7	2.428[a]
2880	13.9	2.589[a]	26.6	2.679[a]	26.5	2.428[a]
3600	17.2	2.756[a]	29.4	2.344[a]	29.1	2.254
4320	20.1	2.422	31.9	2.093	31.7	2.254
5040	23.0	2.422			34.3	2.254
5760	25.8	2.338			36.8	2.168
6480	28.5	2.255				
7200	31.4	2.422				
Average Rate $mm^3cm^{-2}sec^{-1}$		3.71		3.40		3.34

[a] Values averaged to get average maximum rate.

TABLE XVIII

Dissolution of Magnesium in 0.100N HCl at 25°C

	T=19.9°C P=723.8 mm Hg		T=22.6°C P=734.0 mm Hg		T=22.5°C P=734.1 mm Hg	
Time	Vol	dv STP	Vol	dv STP	Vol	dv STP
sec	ml	ml	ml	ml	ml	ml
0	12.8	--	15.3	--	20.0	--
180	15.1	1.986	17.8	2.160	22.4	2.074
360	17.5	2.073[a]	20.2	2.073[a]	25.0	2.247
540	19.9	2.073[a]	22.6	2.073[a]	27.5	2.161
720	22.3	2.073[a]	25.0	2.073[a]	30.0	2.161
900	24.7	2.073[a]	27.4	2.073[a]	32.4	2.074[a]
1080	27.1	2.073[a]	29.8	2.073[a]	34.8	2.074[a]
1260	29.5	2.073[a]	32.1	1.987	37.2	2.074[a]
1440	31.7	1.900	34.4	1.987	39.6	2.074[a]
1620	34.0	1.987	36.6	1.900	41.9	1.988
1800	36.2	1.900	38.9	1.987	44.3	2.074
Average Rate $mm^3cm^{-2}sec^{-1}$	11.5		11.5		11.5	

[a] Values averaged to get average maximum rate.

TABLE XIX

Dissolution of Magnesium in 0.293N HCl at 25°C

	T=24.5°C P=737.0 mm Hg	
Time sec	Vol ml	dv STP ml
0	19.3	--
120	24.8	4.723
240	30.3	4.723
360	35.7	4.637
480	41.0	4.551
600	46.2	4.465[a]
720	51.3	4.379[a]
840	56.5	4.465[a]
960	61.7	4.465[a]
1080	66.9	4.465[a]
1200	72.0	4.379[a]
Average Rate $mm^3cm^{-2}sec^{-1}$		37.0

[a] Values averaged to get average maximum rate.

TABLE XX

Dissolution of Magnesium in 0.293N HCl at 25°C

	T=24.4°C P=738.0 mm Hg		T=23.2°C P=736.0 mm Hg	
Time	Vol.	dv STP	Vol	dv STP
sec	ml	ml	ml	ml
0	19.8	--	20.8	--
60	22.1	1.979	23.3	2.159
120	24.6	3.151	25.8	2.159
180	27.0	2.065	28.3	2.159
240	29.8	2.409	30.8	2.159
300	32.4	2.237[a]	33.3	2.159
360	35.0	2.237[a]	35.7	2.072[a]
420	37.5	3.151[a]	38.1	2.072[a]
480			40.5	2.072[a]
540			42.9	2.072[a]
600			45.3	2.072[a]
660			47.7	2.072[a]
Average Rate $mm^{3}cm^{-2}sec^{-1}$		36.8		34.5

[a] Values averaged to get average maximum rate.

TABLE XXI

Dissolution of Magnesium in 1.0N HCl at 25°C

Time	T=23.5°C P=735.5 mm Hg Vol	dv STP	T=24.0°C P=735.5 mm Hg Vol	dv STP	T=23.6°C P=734.5 mm Hg Vol	dv STP
sec	ml	ml	ml	ml	ml	ml
0	19.5	--	12.6	--	11.0	--
20	24.5	4.307	19.0	5.499	18.0	6.019
40	33.4	6.806[a]	26.3	6.272	25.8	6.706
60	41.4	6.892[a]	33.6	6.272	33.4	6.534[a]
80	49.2	6.719[a]	41.3	6.616	41.0	6.534[a]
100	57.2	6.892[a]	49.1	6.702	48.6	6.534[a]
120	65.0	6.719[a]	56.6	6.444	56.2	6.534[a]
140	72.6	6.547	64.4	6.702[a]	64.2	6.878
160	80.4	6.719	72.3	6.788[a]	71.8	6.534
180			80.0	6.616[a]	79.4	6.534
Average Rate $mm^3cm^{-2}sec^{-1}$		340		335		327

[a] Values averaged to get average maximum rate.

TABLE XXII

Dissolution of Magnesium in 0.0295N HBr at 25°C

	T=26.4°C P=730.0 mm Hg		T=28.7°C P=731.6 mm Hg		T=28.9°C P=732.1 mm Hg	
Time	Vol	dv STP	Vol	dv STP	Vol	dv STP
sec	ml	ml	ml	ml	ml	ml
0	18.4	--	18.6	--	18.4	--
720	20.8	2.019	20.5	1.581	20.4	1.663
1440	23.5	2.272[a]	23.1	2.163[a]	23.0	2.162[a]
2160	26.2	2.272[a]	25.6	2.080[a]	25.6	2.162[a]
2880	28.8	2.187[a]	28.1	2.080[a]	28.1	2.079[a]
3600	31.3	2.103[a]	30.5	1.997[a]	30.5	1.996[a]
4320	33.8	2.103[a]	32.8	1.914	32.8	1.913
5040	36.2	2.109	35.0	1.830	35.2	1.996
5760	38.6	2.109	37.2	1.830	37.6	1.996
6480	41.0	2.109	39.4	1.830	39.8	1.830
Average Rate mm^{3}cm^{-2}sec^{-1}		3.04		2.89		2.92

[a] Values averaged to get average maximum rate.

TABLE XXIII

Dissolution of Magnesium in 0.100N HBr at 25°C

	T=25.0°C P=733.0 mm Hg		T=25.7°C P=720.0 mm Hg		T=22.3°C P=725.4 mm Hg	
Time	Vol	dv STP	Vol	dv STP	Vol	dv STP
sec	ml	ml	ml	ml	ml	ml
0	19.2	--	17.2	--	17.0	--
360	23.2	3.406	21.4	3.497	21.5	3.847[a]
720	27.8	3.917[a]	26.1	3.913[a]	26.1	3.932[a]
1080	32.4	3.917[a]	30.7	3.830[a]	30.6	3.847[a]
1440	36.9	3.832[a]	35.2	3.747[a]	34.9	3.676[a]
1800	41.4	3.832[a]	39.6	3.663[a]	39.1	3.590
2160	45.7	3.661	44.0	3.663[a]	43.3	3.590
2520	50.0	3.661	48.2	3.497	47.3	3.419
2880	54.2	3.576	52.4	3.497	51.4	3.505
3240	58.4	3.576	56.5	3.414	55.5	3.505
3600	62.6	3.576	60.7	3.497	59.5	3.419
Average Rate $mm^3 cm^{-2} sec^{-1}$	10.8		10.5		10.6	

[a] Values averaged to get average maximum rate.

TABLE XXIV

Dissolution of Magnesium in 0.300N HBr at 25°C

	T=26.1°C P=731.6 mm Hg		T=26.6°C P=732.9 mm Hg	
Time	Vol	dv STP	Vol	dv STP
sec	ml	ml	ml	ml
0	19.6	--	19.0	--
60	21.8	1.858	21.1	1.772
120	24.2	2.027	23.4	1.941
180	26.8	2.196[a]	25.8	2.026
240	29.5	2.280[a]	28.4	2.194[a]
300	32.1	2.196[a]	30.9	2.110[a]
360	34.7	2.196[a]	33.4	2.110[a]
420	37.4	2.280[a]	35.9	2.110[a]
480	40.0	2.196[a]	38.4	2.110[a]
540	42.5	2.112	40.8	2.026[a]
600	45.1	2.196	43.3	2.110
Average Rate $mm^3cm^{-2}sec^{-1}$	37.1		35.2	

[a] Values averaged to get average maximum rate.

TABLE XXV

Dissolution of Magnesium in 0.970N HBr at 25°C

	T=25.8°C P=732.7 mm Hg		T=26.0°C P=732.7 mm Hg		T=26.0°C P=732.7 mm Hg	
Time sec	Vol ml	dv STP ml	Vol ml	dv STP ml	Vol ml	dv STP ml
0	11.5	--	2.8	--	1.0	--
20	19.8	7.035	11.8	7.618	9.2	6.940
40	28.2	7.205[a]	20.5	7.364[a]	18.6	7.110[a]
60	36.8	7.289[a]	29.2	7.364[a]	27.4	7.448[a]
80	45.4	7.289[a]	37.8	7.279[a]	36.0	7.279[a]
100	54.0	7.289[a]	47.4	8.125	45.2	7.787[a]
120	62.6	7.289[a]	56.2	7.448	54.2	7.618[a]
140	71.8	7.798	67.8	0.818	63.8	8.125
160	80.2	7.120	75.4	7.279	72.4	7.279
180	89.0	7.459	84.0	7.279		
Average Rate mm^{3}cm^{-2}sec^{-1}		364		367		372

[a] Values averaged to get average maximum rate.

TABLE XXVI

Dissolution of Magnesium in 0.0300N HI at 25°C

	T=27.2°C P=737.6 mm Hg		T=27.5°C P=738.0 mm Hg		T=26.2°C P=737.4 mm Hg	
Time	Vol	dv STP	Vol	dv STP	Vol	dv STP
sec	ml	ml	ml	ml	ml	ml
0	10.7	--	10.5	--	11.0	--
720	13.5	2.370[a]	12.8	1.945[a]	13.6	2.176[a]
1440	16.2	2.286[a]	15.1	1.945[a]	16.2	2.176[a]
2160	18.2	1.693[a]	17.1	1.691[a]	19.0	2.344[a]
2880	20.6	2.032[a]	18.2	0.930	21.3	1.925[a]
3600	23.5	2.455[a]	19.4	1.015	23.3	1.674
4320	25.9	2.032[a]	21.4	1.691	25.1	1.506
5040	27.8	1.608	22.5	0.930	26.8	1.423
5760	29.4	1.354	23.4	0.761	28.2	1.172
6480	30.9	1.269	24.1	0.592	29.7	1.255
7200	32.5	1.354	24.9	0.676	30.8	0.921
7920	34.0	1.269	25.6	0.592	31.8	0.837
Average Rate mm^{3}cm^{-2}sec^{-1}		2.98		2.58		3.00

[a] Values averaged to get average maximum rate.

TABLE XXVII

Dissolution of Magnesium in 0.100N HI at 25°C

	T=25.2°C P=734.9 mm Hg		T=27.7°C P=739.8 mm Hg		T=25.1°C P=741.9 mm Hg	
Time	Vol	dv STP	Vol	dv STP	Vol	dv STP
sec	ml	ml	ml	ml	ml	ml
0	10.7	--	11.0	--	12.2	--
180	12.6	1.621	13.3	1.947	14.4	1.896
360	15.2	2.218[a]	16.8	2.963	17.4	2.585
540	17.9	2.303[a]	20.2	2.878	20.3	2.499
720	20.5	2.218[a]	23.6	2.878	21.6	1.120
900	23.2	2.303[a]	27.0	2.878	24.5	2.499[a]
1080	25.8	2.218[a]	30.2	2.709[a]	27.4	2.499[a]
1260	28.3	2.132	33.4	2.709[a]	30.3	2.499[a]
1440	30.8	2.132	36.6	2.709[a]	33.2	2.499[a]
1620	33.2	2.046	39.9	2.793[a]	36.1	2.499[a]
1800	35.6	2.218	43.1	2.709[a]	39.0	2.499[a]
Average Rate						
$mm^3cm^{-2}sec^{-1}$		12.5		15.1		13.9

[a] Values averaged to get average maximum rate.

TABLE XXVIII

Dissolution of Magnesium in 0.300N HI at 25°C

	T=27.5°C		T=27.9°C		T=25.8°C	
	P=726.0 mm Hg		P=737.8 mm Hg		P=736.0 mm Hg	
Time	Vol	dv STP	Vol	dv STP	Vol	dv STP
sec	ml	ml	ml	ml	ml	ml
0	15.6	--	11.6	--	11.0	--
60	18.3	2.244	14.0	2.024	13.9	2.469
120	21.1	2.327	16.4	2.024	16.6	2.299
180	24.1	2.493	19.0	2.193[a]	19.6	2.554
240	27.5	2.826[a]	21.6	2.193[a]	22.7	2.639[a]
300	30.8	2.743[a]	24.2	2.193[a]	25.8	2.639[a]
360	34.2	2.826[a]	26.8	2.193[a]	28.9	2.639[a]
420	37.6	2.826[a]	29.4	2.193[a]	32.0	2.639[a]
480	41.0	2.826[a]	31.9	2.108	35.1	2.639[a]
540	44.3	2.743	34.5	2.193	38.2	2.693[a]
600	47.6	2.743	37.1	2.193	41.2	2.554
660	50.9	2.743	39.7	2.193	44.3	2.638
Average Rate $mm^3cm^{-2}sec^{-1}$	46.8		36.6		44.0	

[a] Values averaged to get average maximum rate.

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