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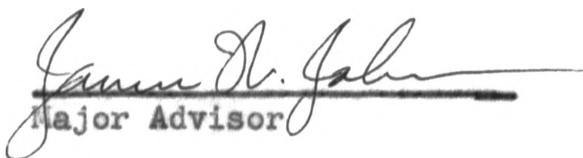
THE DISSOLUTION OF MAGNESIUM
IN STRONG ACIDS

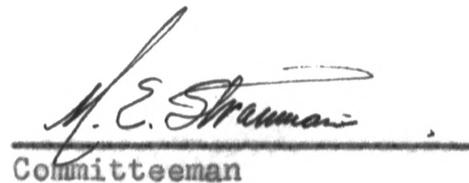
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Baldev K. Bhatia

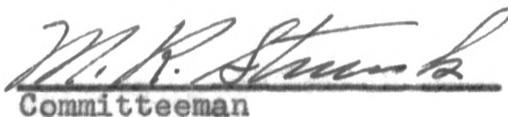
Thesis submitted to the faculty of the
Missouri School of Mines and Metallurgy
in partial fulfillment of the requirements for the
Degree of

MASTER OF SCIENCE
in
Chemical Engineering

APPROVED:


Major Advisor


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I. INTRODUCTION

The rapidly growing demand for magnesium and magnesium-base alloys in the manufacture of aircraft has led to 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 standard electrode potential of magnesium lies between -2.35 volts and -2.54 volts at 25°C (hydrogen scale). Thus, magnesium lies next to aluminium in the electrochemical series of elements. The atmospheric corrosion of magnesium has been studied under conditions of indoor and outdoor exposure. Under these conditions the initial attack is formation of a hydroxide film which has a tendency to absorb carbon dioxide and moisture from the air. As a pure metal, magnesium is attacked rapidly by hydrochloric, perchloric, sulfuric, and nitric acids. In hydrofluoric acid the metal does not corrode at an appreciable rate. Magnesium metal is rarely, if ever, used in unalloyed conditions for structural purposes. The corrosion rate is retarded by alloying the metal with small quantities of aluminium, manganese, and zinc.

The purpose of this present investigation was to study the dissolution of magnesium in strong acids. It was also

aimed to investigate whether magnesium metal exhibits uncommon valence characteristics as reported in the literature. The strong acids included hydrochloric, perchloric, and sulfuric acids.

II. LITERATURE REVIEW

The mechanism of dissolution of magnesium metal in aqueous solutions 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 solutions.

Chemical Kinetics of the Dissolution of Magnesium

Magnesium rapidly dissolves in hydrochloric, sulfuric, perchloric, and nitric acids. In hydrofluoric acid the reaction is very slow. The factors affecting the rate of dissolution of magnesium in acidic solutions have been the subject of many investigations^(1,5,7,8).

Kilpatrick and Rushton⁽⁷⁾ have shown that at temperatures above 50°C there are at least two reactions in aqueous solutions of strong acids. First, a reaction with water independent of hydrogen ion concentration, and second, a reaction with water dependent on hydrogen ion concentration. An explanation is offered from the extended theory of acid and bases. For a strong acid such as hydrochloric acid, it is assumed that the following reaction goes practically to completion:



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



This is followed by the reactions:



It is assumed that the metal is composed of magnesium ions in solid state (Mg^{++}) and free electrons. In weak acids, such as acetic acid, the two authors emphasized that both 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.,



The effect of stirring on the dissolution rate was studied and the relationship $k=aR^n$ was reported (for their equipment), where k is the reaction rate constant in $\text{cm}^3/\text{cm}^2 \cdot \text{min}$, and R is the velocity of the metal surface in cm/min . The values of a and n for the reaction of magnesium with hydrochloric acid were 0.139 and 0.362, respectively. For the reaction of magnesium with acetic acid, the values of a and n were 0.0179 and 0.362, respectively.

The effect of viscosity on the rate of solution 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 definite decrease in dissolution rates when the viscosity of hydrochloric acid and acetic acid solutions was increased by adding sugar and glycerine. A plot of rate of dissolution of magnesium versus acid concentration showed an intercept on the y-axis. In the case of the reaction with the strong acid, the intercept was attributed to the rate due to reaction with water. In the case of a weak acids, it was thought to represent the rate due to reaction with both water and hydrogen ions. (The reaction with water molecules is plausible, but there would be no appreciable concentration of hydrogen ions at zero acid concentration corresponding to the intercept.)

A mechanism of dissolution of magnesium in acid was discussed from the point of view of both the diffusion theory and chemical rate theory. The increase in rate with stirring speed indicated that the rate was probably diffusion controlled. In strong acids, the rate would be controlled by the diffusion of hydrogen ions to the metal surface. In the case of weak acids, it would be both the

diffusion of hydrogen ion and of the molecular acid. No explanation for a diffusion reaction of magnesium with water was offered because no diffusion layer was thought to exist. A hydrogen film had been eliminated as a diffusion layer by showing that the rate was not affected by the addition of a depolarizer. The temperature coefficient for the reaction with hydrochloric acid was found to be 1.75 (temperature coefficient = $k_{35^{\circ}\text{C}}/k_{25^{\circ}\text{C}}$). The temperature coefficient for the reaction with acetic acid was reported to be 1.69. Since the temperature coefficients were less than two, a diffusion controlled mechanism was favored again. This still offered no explanation for the water reaction mechanism.

In the case of 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 supports an argument of chemical-rate theory which states that for a chemical reaction, the rate is proportional to the concentration of acid present. It was also mentioned that this rate could be diffusion controlled. The results of experiments to test the influence of viscosity on the rate of dissolution were reported to be definitely contradictory to the diffusion theory. According to diffusion theory, the rate of dissolution should decrease with an increase in viscosity of the solution. It should be pointed

out that the authors may have affected other variables of the reaction solution and surface as well as the viscosity by the salt additions.

The principal conclusion from their measurements was that the dissolution of magnesium could not be explained with "the old diffusion theory" whose criteria are: (1) different solids dissolve at nearly the same rate, (2) stirring has marked effect on the rate, (3) the rate of solution is inversely proportional to the viscosity, (4) the rates observed are proportional to diffusion coefficients for comparable conditions, and (5) the temperature coefficients are small compared to those of chemical reactions.

King and Cathcart⁽⁸⁾ determined the diffusion coefficients of a number of weak and strong acids in the presence of their magnesium salts. The diffusion rates were measured in porous glass disk cells of the type described by McBain and Dawson⁽¹²⁾. Dissolution rates of magnesium were also determined in these acids containing the same salts under similar conditions of acid strength and salt concentration. The dissolution rates were measured by rotating magnesium cylinders (approximately 2.5 cm long and 2.0 cm in diameter) in 250 ml of the acid solution. The temperature of the solution was maintained at $25 \pm 0.5^\circ\text{C}$. The dissolution rate constants ($k = \text{cm}^3/\text{cm}^2 \cdot \text{min}$) were found not to vary in the

same manner as the diffusion coefficients ($D = \text{cm}^2/\text{min}$). The weak acids yielded low dissolution rates apparently explained by the fact that these acids have salts of low solubility which form a film on the magnesium surface. Other discrepancies among certain acids could not be explained.

A log-log plot of k versus D gave a straight line for their data. This straight line was represented by the equation $k = 0.36D^{0.70}$. According to the authors, this exponential relation 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 modified Nernst's theory which states that the layer involved in diffusion can not be a stagnant layer, and that the thickness of this layer must vary with the diffusion coefficient of the reagent, increasing as the latter increases.

James⁽⁵⁾ claims that he obtained dissolution rates in various acids by eliminating diffusion effects. The diffusion effects were eliminated by using an apparatus similar to that employed by Weissberger, Mainz, and Strasser⁽²³⁾. 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 (H_3O^+). 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 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 solution 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.

It is generally considered that the reaction of a metal with aqueous solutions consists of three steps: (1) diffusion of reactants to the metal surface, (2) reaction of the metal with the reactant, and (3) diffusion of reaction products away from the metal surface. Since James claims

that the diffusion effects were eliminated, he assumes that the rate controlling step is that of the acid reaction with electrons at the metal surface. As such, the activation energies of 5,100 calories and 4,920 calories would indicate that the chemical reaction at the metal surface has a low activation energy compared to that for a "normal" chemical reaction which is 14,000 calories or above. The results obtained by James could also favor a diffusion controlled mechanism, because these activation energy values lie in the range where diffusion is usually controlling, i.e., the diffusion temperature coefficient is equal to or greater than the chemical activation energy. Too, since the rate of reaction decreases with sucrose additions, it seems that the diffusion effects have not been completely eliminated. It is possible that for the geometry of his apparatus, the diffusion effects just are not observable above the critical shaking speed of 220 cycles per minute.

Anodic Dissolution of Magnesium Metal in
Aqueous Solutions

In the last sixty years considerable work has been done to explain a mechanism for the anodic dissolution of magnesium metal in aqueous solutions. It has been found that magnesium anode consumption measured in terms of hydrogen

evolution is very much greater than predicted by Faraday's Law for divalent magnesium ion formation. To account for such an excess consumption, two hypotheses have been reported in the literature. The first one explains the anodic dissolution based on the assumption that the metal enters the solution as the univalent ion. The second hypothesis assumes that the anodic dissolution is film controlled and as such the behavior of magnesium can be explained by divalent ion formation. Recently, the "chunk effect"⁽¹¹⁾ has been proposed as a third possible explanation.

In the electrolysis of sodium sulfate solution between a magnesium anode and a platinum cathode, Turrentine⁽²²⁾ explained the behavior of the magnesium anode on a basis of univalent ion formation. However, the existence of the univalent ion was not proved.

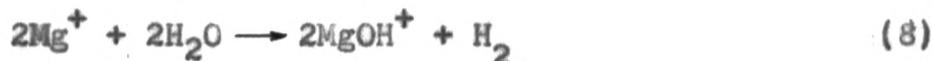
Kleinberg and co-workers^(14,15,16) have tried to prove the existence of magnesium ions of lower valence, but their attempts to identify such ions were unsuccessful. Recently, Petty, Davidson, and Kleinberg⁽¹⁴⁾ calculated the initial valence number (V_1) of magnesium ions in various electrolytes using magnesium electrodes. The electrolytic cell was 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, V_i , 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.

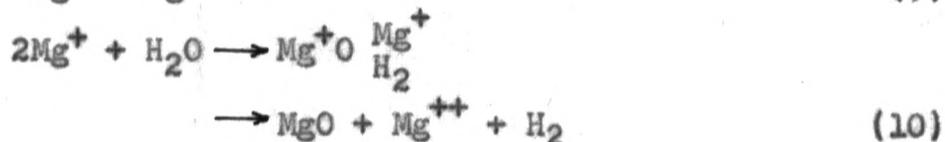
This was explained by the hypothesis that "the primary reactions at the magnesium anode consists in the oxidation of the metal to both the unipositive and the dipositive state". The former, a strong reducing agent, undergoes the following secondary reaction with the solvent:



In order to prove the existence of univalent magnesium ions, further electrolysis was carried out with electrolytes containing oxidizing agents other than hydrogen ion. Agents such as MnO_4^- , and ClO_3^- gave reduction products in the anolyte other than gaseous hydrogen, indicating a possible existence of Mg^+ . The appearance of an insoluble black product was also reported. However, the efforts to identify unipositive magnesium ions were unsuccessful.

Greenblatt⁽²⁾ electrolysed 3% NaCl solution using a magnesium anode of 99.92% purity and determined the magnesium in the anolyte, the magnesium in the corrosion product, the

total hydrogen gas evolved, and the weight loss of magnesium anode. He found that the magnesium entering into the solution, the insoluble magnesium retained in the corrosion product, and the weight of magnesium calculated from the current were approximately in a one to one ratio with each other and that all of these quantities were roughly equal to one half of the total weight loss (50% current efficiency). To account for the 50% efficiencies of the magnesium anode, he assumed that the self-corrosion reaction, both under anodic conditions and while the circuit was open, proceeded at the same rate. The conclusions were that the magnesium dissolved in the solution primarily as a univalent ion, followed by a reaction of the univalent ion with water leading to the normal divalent state. This latter reaction was speculated as occurring at the surface between an absorbed water molecule and univalent magnesium ion. The following series of reactions were proposed to explain the data obtained:



Reaction (9) was favored over reaction (12) as the heat of hydration of magnesium is 33 kilocalories less than the ionization potential of Mg^{++} .

Kakoulina and Kabanov⁽⁹⁾ investigated the anodic dissolution of magnesium in magnesium sulfate solution. Their results were in accord with the conclusions drawn by Greenblatt. They also assumed that the hydrogen evolution from the anode was not film controlled.

Hoey and Cohen⁽⁴⁾ give several possibilities for anodic dissolution, among which the following is mentioned:



Reaction (15) shows why the corrosion products have a tendency to evolve hydrogen. A $Mg(OH)_2$ film was identified on the magnesium anode by X-ray analysis and the presence of free magnesium particles in the corrosion products was observed by microscopic examination.

The film controlled behavior of the magnesium anode has been postulated by Robinson and King⁽¹⁸⁾, Higgins⁽³⁾, and Roald and Beck⁽¹⁷⁾. The increase in hydrogen evolution on magnesium with increasing anodic current density has been termed as the negative difference effect. Robinson and King consider this negative difference effect to result from film control in aqueous solutions of $MgBr_2$ and $NaBr$, and to be

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 is postulated to be damaged due to a build-up of soluble magnesium salt 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 also supports 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.

Roald and Beck studied the anodic and cathodic dissolution of magnesium in 0.045 N hydrochloric acid and found that the difference effect (under anodic conditions) was equivalent to two thirds of the current density up to 0.07 amp/cm². They concluded that the external current has some effect on the current-carrying-ions in the diffusion layer rather than on the local anodes. These authors also reported the formation of a dark precipitate on the magnesium anode, and suggested that the presence of free magnesium particles gave the precipitate its dark color.

Recently, Marsh and Schaschl⁽¹¹⁾ have proposed the "chunk effect" to explain the negative difference effect on steel. They discard the film disruption theory in highly corrosive solutions because there is the least possibility of the film to be present under such conditions. They suggest that when steel corrodes at a high rate, the corrosion proceeds with the removal of "chunks" of iron containing several atoms. According to the authors, dissolution by chunks would explain the negative difference effect, if it is assumed that the chunks are being also removed during free corrosion. Thus, under the anodic condition, the metal would not dissolve as predicted by Faraday's Law, and the observed corrosion rate would be given by

$$I_u = I_x + I_a + I_b \quad (16)$$

where, I_u = observed corrosion rate expressed as equivalent current density

I_x = corrosion current in accordance with Faraday equivalence

I_a = local action current density

I_b = chunk effect corrosion rate expressed as equivalent current density

If I_x is zero, the observed corrosion rate (I_u) equals the freely corroding rate (I_o). Under this condition

$$I_o = I_{oa} + I_{ob} \quad (17)$$

In this case I_{oa} and I_{ob} are the particular local action and chunk effect rates occurring together which are measured as the freely corroding rates.

It was also suggested that the chunk effect and anodic polarization occur on the same piece of corroding metal. Thus either the positive or negative difference effect may be observed, depending on the corrodent.

III. EXPERIMENTAL

The purpose of this present investigation was to study the dissolution of magnesium in strong acids. It was also aimed to investigate whether magnesium metal exhibits uncommon valence characteristics as reported in the literature^(2,14). The strong acids included hydrochloric, perchloric, and sulfuric acids.

The experimental plan consisted of the following major phases: (1) the effect of acid concentration on the dissolution rates, (2) the influence of temperature on the dissolution rates, (3) the difference effect on magnesium metal dissolving in the acids, and (4) the electrolysis in aqueous solutions using a magnesium anode.

The description of each phase will include apparatus, method of procedure, data, results, and sample calculations.

Materials

The list of the materials used in this investigation is given in the Appendix, pages 96.

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

Apparatus. The apparatus used was the same for the rate studies in hydrochloric, perchloric, and sulfuric 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 $\pm 0.10^\circ\text{C}$. A stirring speed of 200 revolutions per minute was employed in the rate studies. The apparatus used for the rate studies was the same as that employed by Johnson⁽⁶⁾.

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⁽⁶⁾. Before being subjected to a dissolution rate study the specimen was etched with a concentrated solution of the acid under consideration. The sample was then 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 bath in such a position so as to insure the submergence of 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 at which the gas volume was measured were recorded. 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 minute ($\text{mm}^3/\text{cm}^2.\text{min}$).

The procedure employed was the same for all the acids. A detailed step-by-step procedure for this phase of experimentation has been described previously⁽⁶⁾.

Data and Results. The data obtained for this part of the measurements are shown in the Appendix, pages 97 through 173.

Before attempting to investigate the rate, it was necessary to establish the stoichiometry of the dissolution of magnesium. The apparatus used was the same as described above with the exception that no stirrer was used. A weighed quantity of pre-etched magnesium metal (unmounted) was dropped into the reaction flask containing the acid. The total volume of hydrogen gas evolved was collected in

the gas burette. This volume was corrected to standard conditions and compared with the calculated standard volume theoretically evolved from this weight of metal dissolving with the normal valence of two. The data for this part of experimentation is given in Table I, page 22. The deviation of experimental volume from the calculated volume was not more than three per cent.

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

Hydrochloric Acid. The dissolution of magnesium in hydrochloric acid was carried out in four different acid concentrations (0.05, 0.10, 0.25, and 0.50 N) for each temperature under investigation. The plot of acid concentration versus the dissolution rate showed a linear relationship up to 0.25 N HCl. This indicated that the dissolution rate is directly proportional to the HCl concentration up to 0.25 N. In general, the direct relationship (up to 0.25 N) can be expressed by the following equation:

$$dv/dt = k (HCl)^n \quad (18)$$

where, dv/dt = hydrogen evolution rate, mm^3/cm^2min

k = reaction rate constant

(HCl) = hydrochloric acid concentration,
equivalent/liter

TABLE I

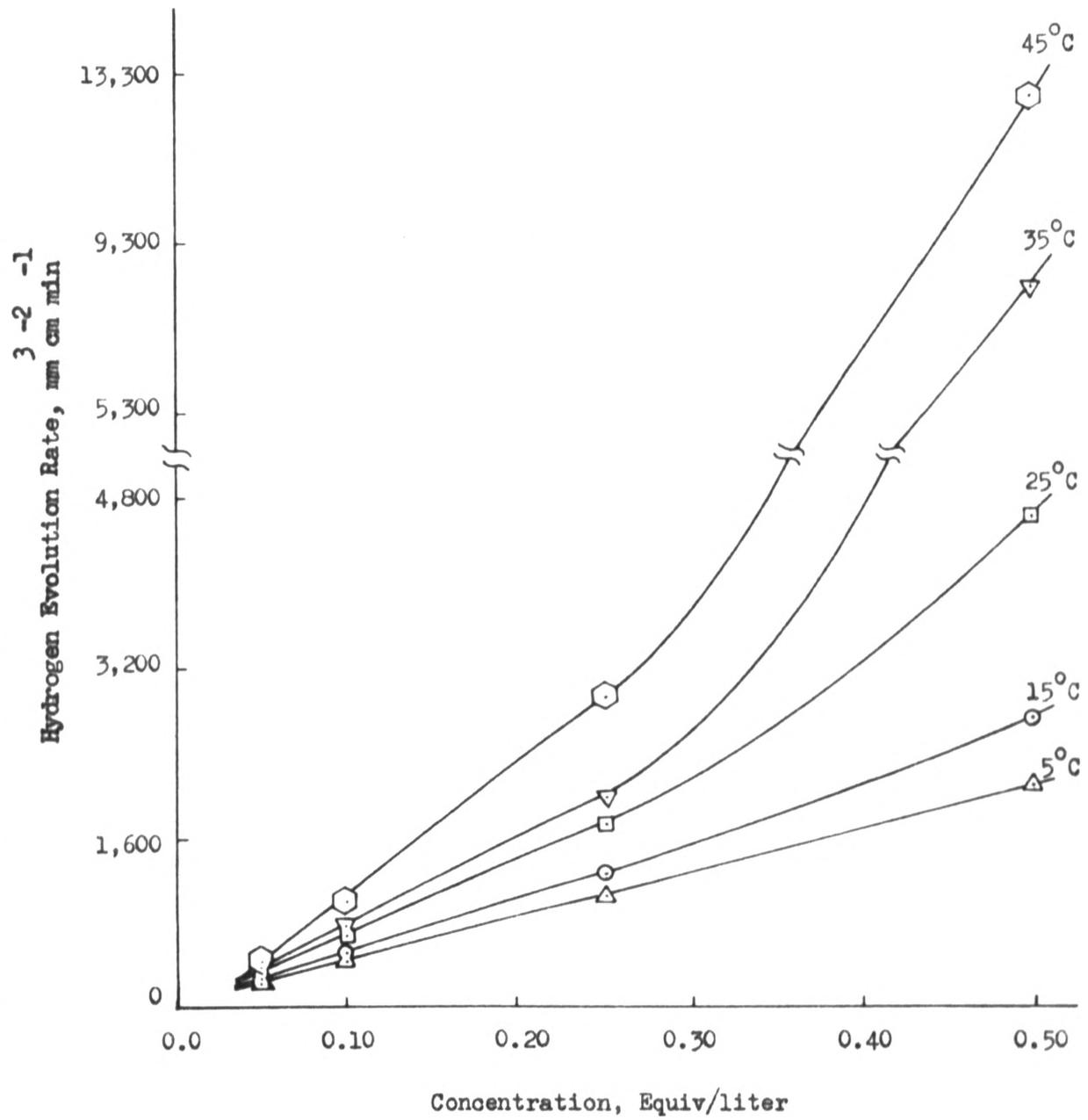
Data Used to Check the Stoichiometry of Magnesium

Wt. of Mg	Volume of H ₂ at STP	
	Expt. ml	Calculated ml
0.0746	70.40	68.75
0.0709	64.16	65.34
0.0661	61.60	60.92
0.0655	61.32	60.37

TABLE II

Hydrogen Evolution Rate for the Dissolution of Mg Metal in Hydrochloric Acid

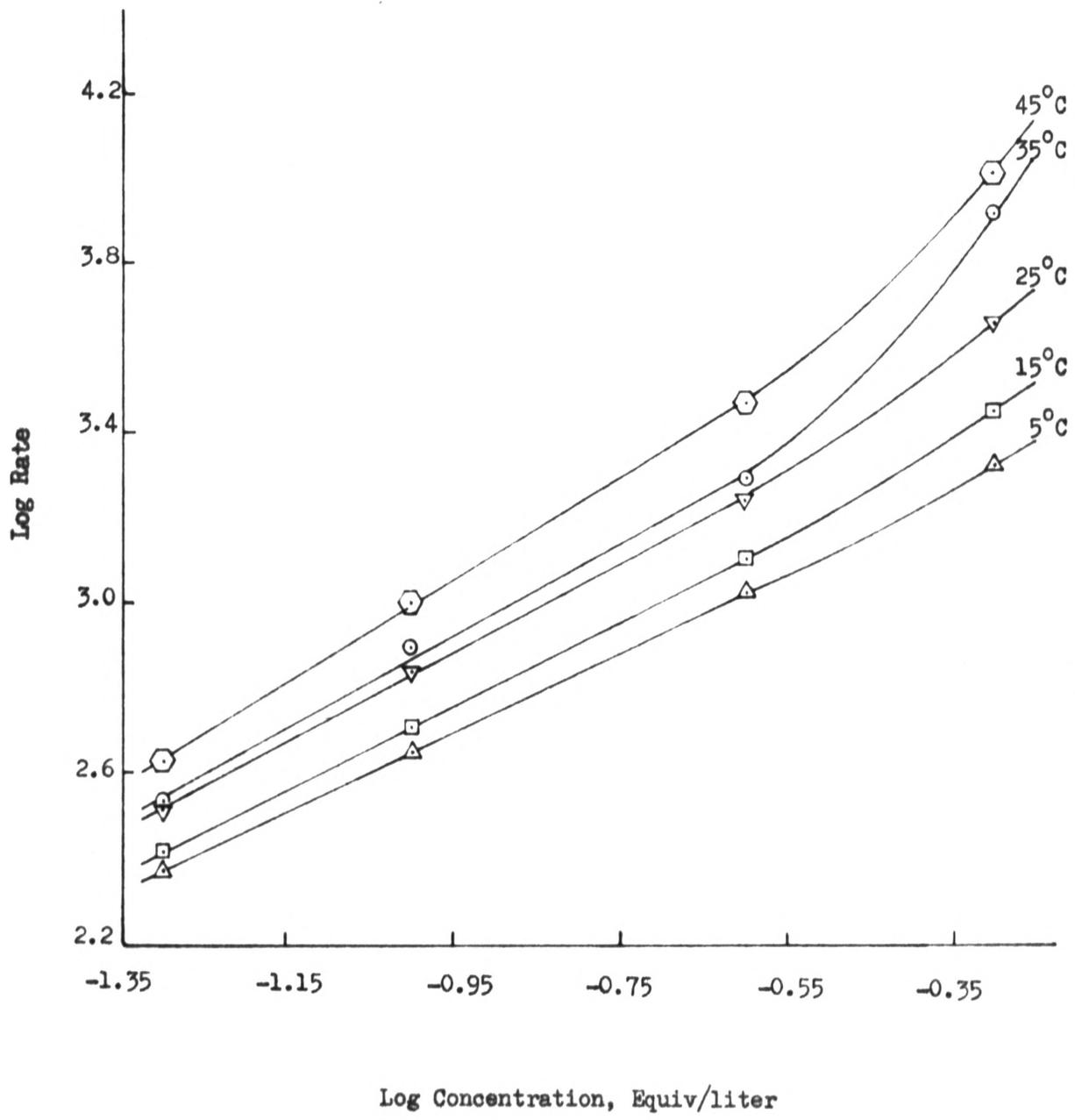
HCl conc.		Hydrogen Evolution Rate - mm ³ /cm ² min at STP				
<u>Equiv.</u> <u>liter</u>		5°C	15°C	25°C	35°C	45°C
0.05		235.7	271.6	326.4	339.7	418.0
		233.5	250.0	323.9	344.8	427.0
	Ave.	234.6	260.8	325.2	342.3	422.5
0.10		418.3	514.9	684.6	796.7	995.8
		472.6	502.3	693.0	770.1	1,003.0
	Ave.	445.5	508.6	688.8	783.4	999.4
0.25		1,063.6	1,310.0	1,742.3	1,897.5	2,944.0
		1,035.9	1,216.5	1,714.3	2,052.3	2,903.0
	Ave.	1,049.7	1,263.3	1,728.3	1,975.0	2,923.5
0.50		2,063.6	2,800.0	4,483.1	8,217.0	12,606.3
		2,230.1	2,785.0	4,519.6	8,297.0	12,834.0
	Ave.	2,146.9	2,792.6	4,501.3	8,257.0	12,720.2



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RATE OF HYDROGEN EVOLUTION FOR MAGNESIUM
METAL DISSOLVING IN HYDROCHLORIC ACID

SCALE:	DATE	CASE NO:
DRAWN BY:		FILE NO:
CHECKED BY:		FIGURE NO: 1
APPROVED BY:		SHEET NO:



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RATE OF HYDROGEN EVOLUTION FOR MAGNESIUM
METAL DISSOLVING IN HYDROCHLORIC ACID

SCALE:	DATE	CASE NO:
DRAWN BY:		FILE NO:
CHECKED BY:		FIGURE NO: 2
APPROVED BY:		SHEET NO:

n = order of reaction

Figures 1 and 2 on pages 24 and 25 show the effect of hydrochloric acid concentration on the dissolution rate at various temperatures. The data used to make the plots are shown in Table II, page 23. The slopes of the straight lines in the log-log plot (Figure 2) were calculated by the method of least squares, giving an order of reaction varying from 0.93 to 1.20. The order of reaction was considered to be equal in all of these concentrations, although a slight increase in order with the increase of temperature seems to follow from the plot.

Perchloric Acid. The dissolution of magnesium in perchloric acid was observed in concentrations varying from 0.05 to 0.64 N. The data are summarized in the Table III, page 27. The effect of acid concentration on the dissolution rate is shown in Figures 3 and 4 pages 29 and 30. It can be seen that the rate of hydrogen evolution is proportional to the perchloric acid concentration up to 0.32 N. Figure 4 shows the log-log plot of rate versus acid concentration. This plot was used to calculate the order of reaction. The slopes of the straight lines vary from 0.98 to 1.14, indicating that at low concentrations (below 0.32 N) the reaction obeys first-order kinetics with respect

TABLE III

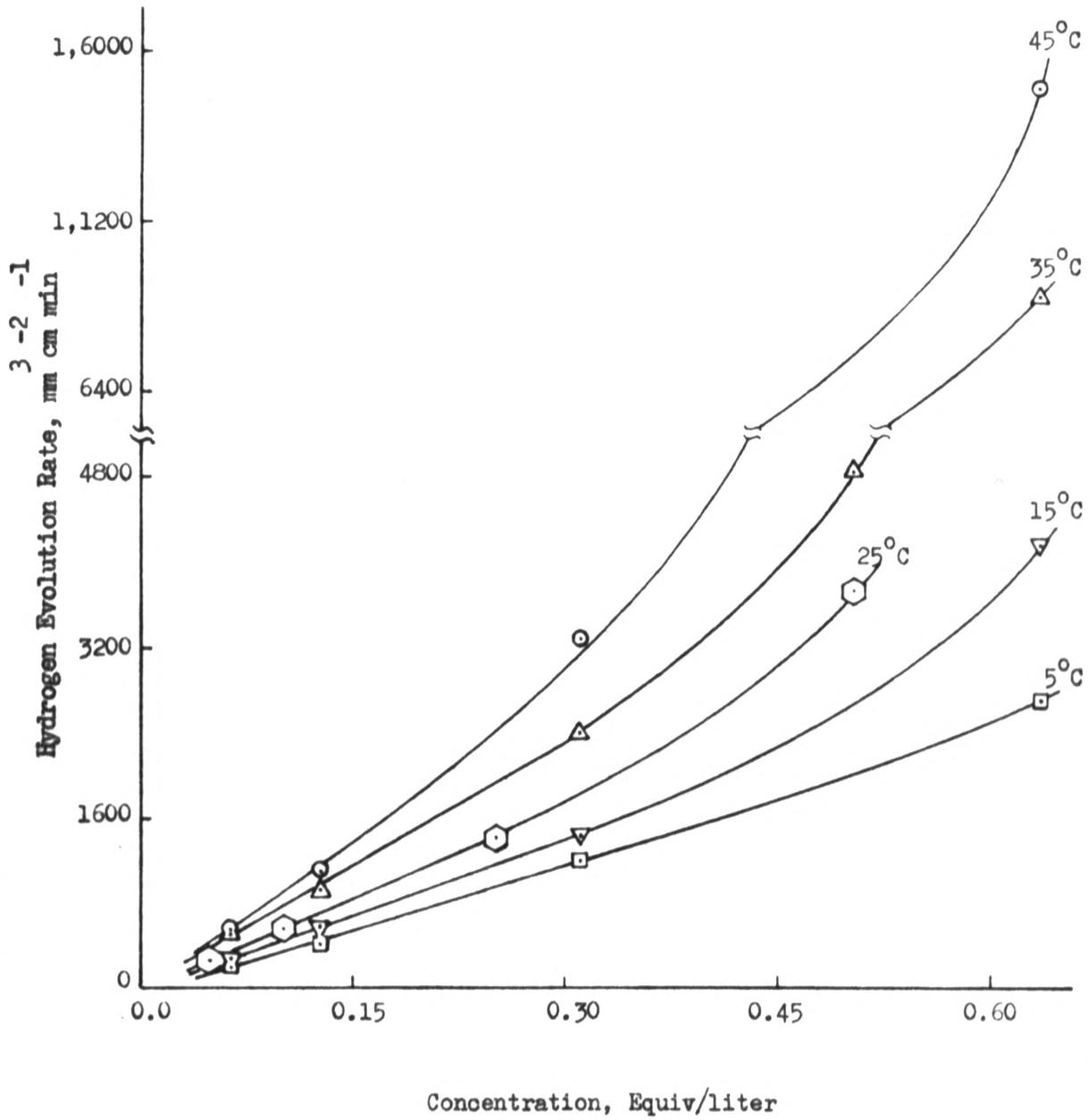
Hydrogen Evolution Rate for the Dissolution of Mg Metal in
Perchloric Acid

HClO ₄ Conc. <u>Equip.</u> liter	Hydrogen Evolution Rate - mm ³ /cm ² min at STP			
	5°C	15°C	35°C	45°C
0.64	2,724.6	4,122.5	8,895.8	14,945.4
	2,650.3	4,184.1	9,208.6	14,897.7
	Ave. 2,687.5	4,153.3	9,052.2	14,921.5
0.32	1,162.0	1,418.9	2,434.0	3,270.6
	1,203.9	1,456.5	2,382.4	3,294.3
	Ave. 1,183.0	1,437.7	2,408.2	3,282.5
0.13	422.6	585.4	887.4	1,129.5
	419.8	580.7	956.4	1,100.8
	Ave. 421.2	583.1	921.9	1,114.7
0.064	203.9	291.3	504.3	516.6
	207.4	291.8	497.0	529.6
	Ave. 205.7	291.6	500.7	523.1
0.50			4,723.1	
			4,872.6	
			4,934.3	
Ave.		4,843.3		

TABLE III

Hydrogen Evolution Rate for the Dissolution of Mg Metal in
Perchloric Acid (con't)

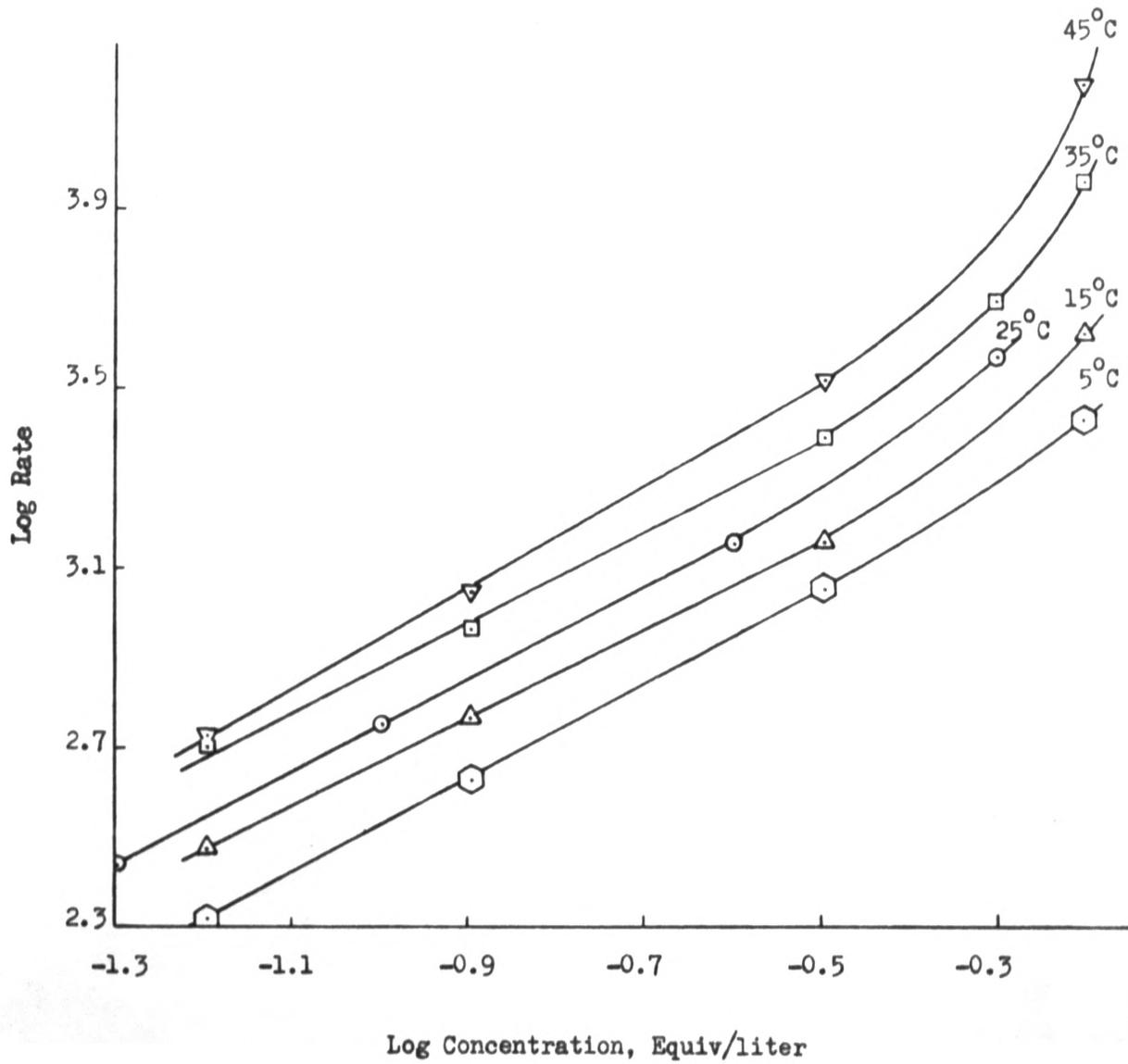
<u>HClO₄ Conc.</u>	<u>Hydrogen Evolution Rate - mm³/cm²min at STP</u>
<u>Equiv.</u> <u>liter</u>	<u>25°C</u>
0.50	3,727.8 3,718.6
	Ave. 3,723.2
0.25	1,420.5 1,429.8
	Ave. 1,423.2
0.10	556.8 560.8
	Ave. 558.8
0.05	268.2 275.7
	Ave. 272.0



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SCALE:	DATE	CASE NO:
DRAWN BY:		FILE NO:
CHECKED BY:		FIGURE NO: 3
APPROVED BY:		SHEET NO:



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RATE OF HYDROGEN EVOLUTION FOR MAGNESIUM
METAL DISSOLVING IN PERCHLORIC ACID

SCALE:	DATE	CASE NO:
DRAWN BY: <i>Robert White</i>		FILE NO:
CHECKED BY:		FIGURE NO: 4
APPROVED BY:		SHEET NO:

to perchloric acid concentration. Using the nomenclature of equation (18), the rate of hydrogen evolution in perchloric acid is expressed as follows:

$$dv/dt = k(\text{HClO}_4)^1 \quad (19)$$

where, (HClO_4) = perchloric acid concentration,
in equivalent/liter

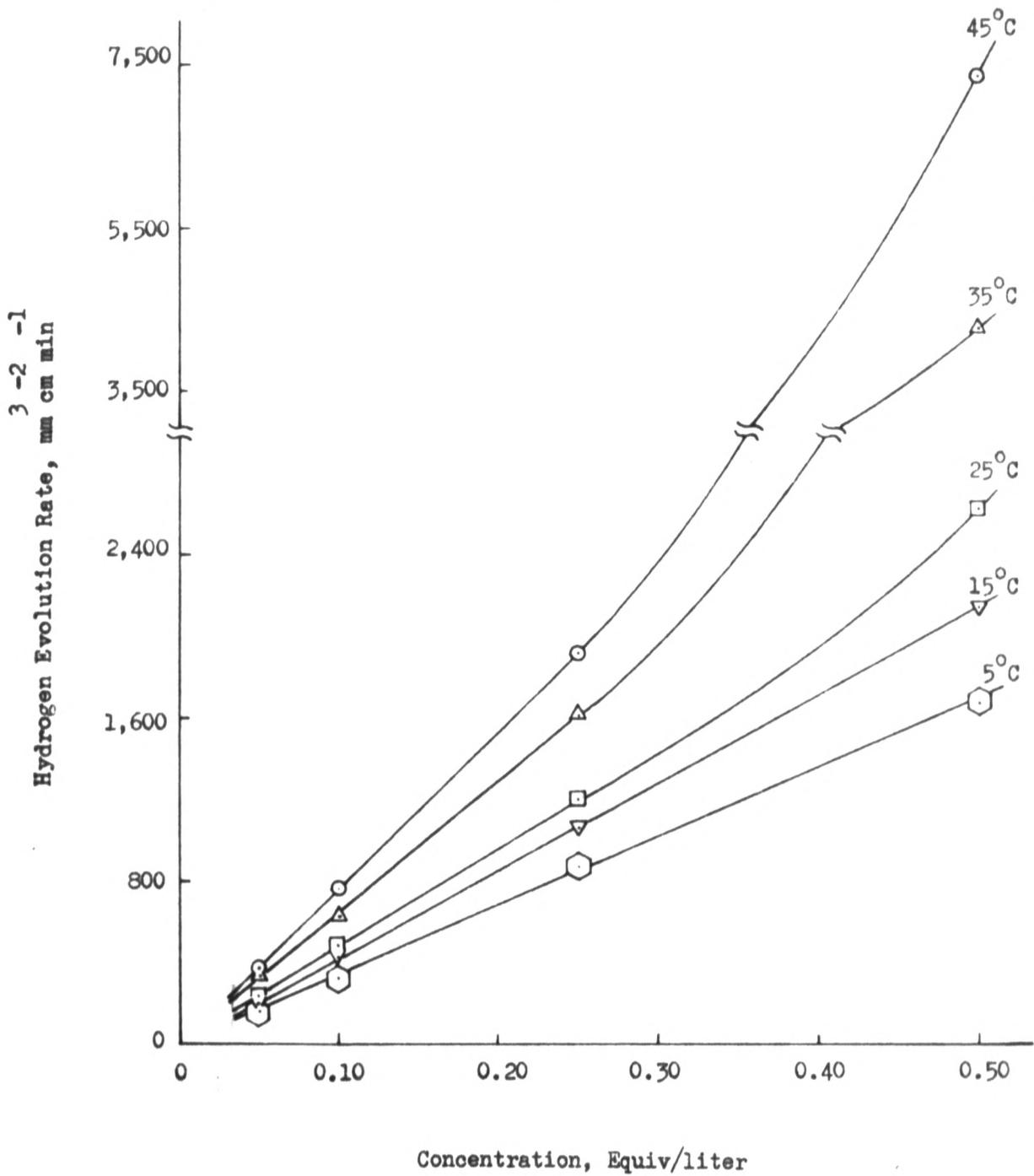
Sulfuric Acid. Table IV page 32, and Figures 5 and 6, pages 33 and 34 show the rate of hydrogen evolution in solutions of 0.05, 0.10, 0.25, and 0.51 N H_2SO_4 . Again, the straight line relationship exists up to 0.25 N H_2SO_4 . Above 0.25 N the dissolution rate increases rapidly at temperatures of 25°C, 35°C, and 45.2°C. This causes the curve at higher concentration to become exponential. From the log-log plot (Figure 6) the slopes of the straight lines vary between 0.99 to 1.05. This indicates that the reaction is first order within experimental error at concentrations below 0.25 N H_2SO_4 .

The hydrogen ion concentration in each of the above acids at 25°C was calculated using the per cent dissociation values from the literature. For sulfuric and hydrochloric acids the apparent per cent dissociation values were available in very dilute solutions⁽²⁴⁾. The per cent dissociation values of perchloric acid were available at concentrations above one normal⁽¹⁰⁾.

TABLE IV

Hydrogen Evolution Rate for the Dissolution of Mg Metal in Sulfuric Acid

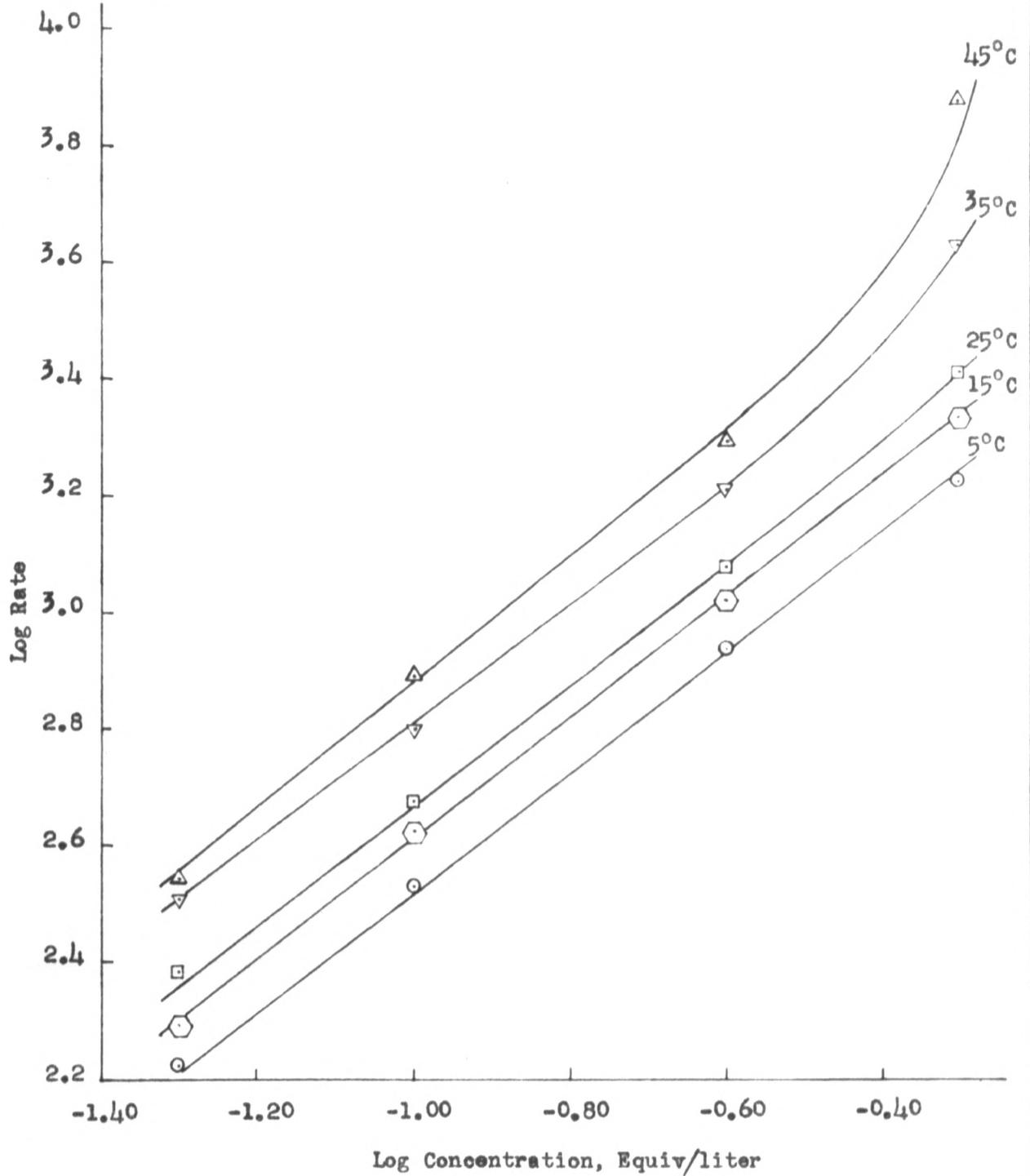
H ₂ SO ₄ Conc. <u>Equiv.</u> liter	Hydrogen Evolution Rate - mm ³ /cm ² min at STP				
	5°C	15°C	25°C	35°C	45.2°C
0.05	165.2	186.4	230.4	327.7	331.4
	156.4	208.3	246.7	329.7	373.1
	167.1	-	243.9	322.5	339.2
	Ave.	162.9	197.3	240.1	326.6
0.10	349.2	424.0	478.0	659.3	726.0
	337.1	423.6	467.0	605.0	793.3
	339.9	433.6	471.0	615.4	-
	Ave.	342.0	427.1	472.0	626.6
0.25	822.7	1,047.8	1,208.0	1,640.0	1,881.0
	900.6	1,054.0	1,174.0	1,572.0	2,012.0
	-	1,044.7	1,198.0	1,609.0	1,838.0
	Ave.	861.7	1,049.0	1,193.3	1,607.0
0.51	1,731.3	2,221.8	2,715.0	4,453.0	7,090.0
	1,658.7	2,116.0	2,528.0	4,138.0	7,679.0
	1,600.6	2,101.0	2,602.0	4,153.0	-
	Ave.	1,663.5	2,146.3	2,615.0	4,247.8



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RATE OF HYDROGEN EVOLUTION FOR MAGNESIUM
METAL DISSOLVING IN SULFURIC ACID

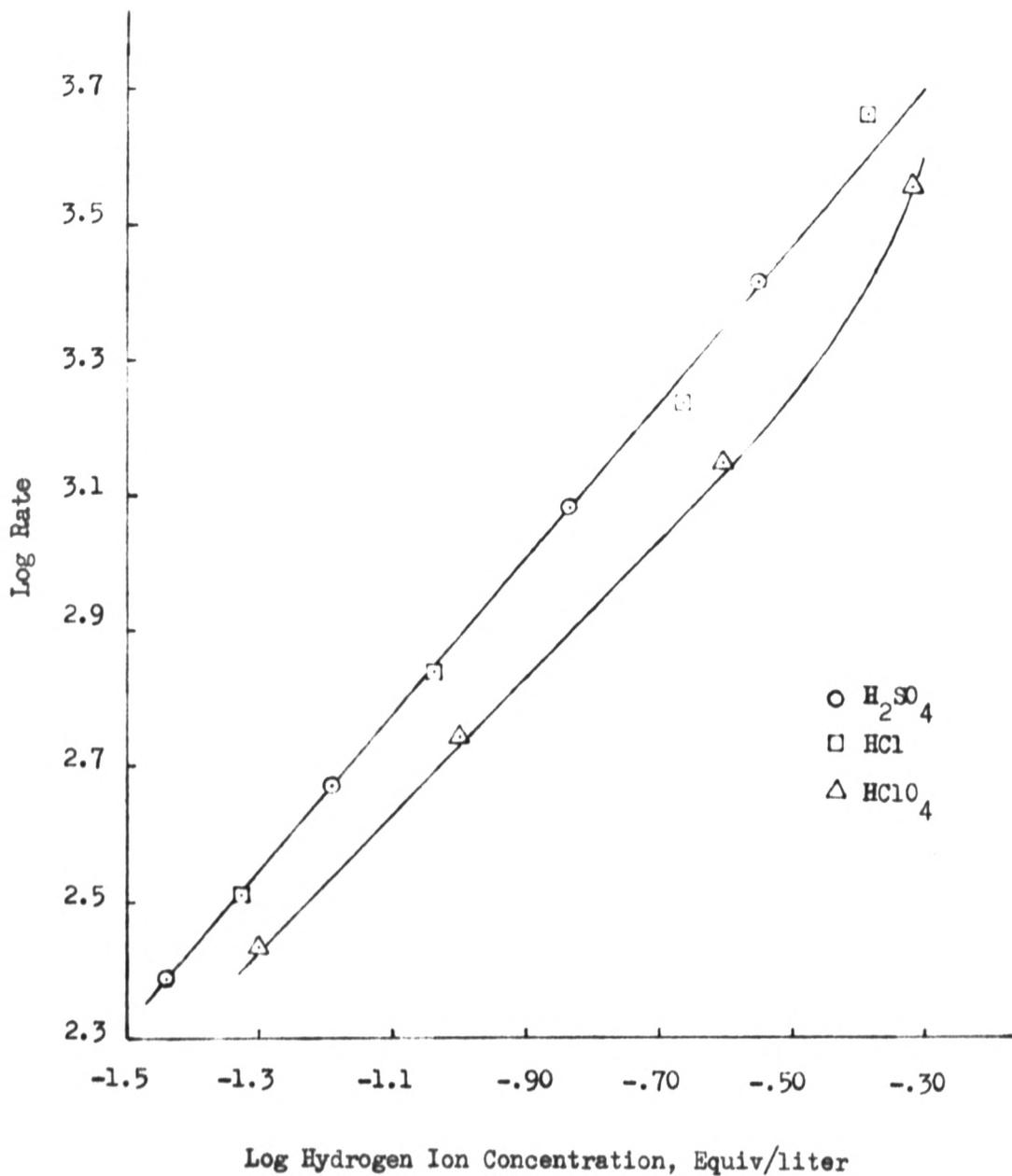
SCALE:	DATE	CASE NO:
DRAWN BY:		FILE NO:
CHECKED BY:		FIGURE NO: 5
APPROVED BY:		SHEET NO:



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RATE OF HYDROGEN EVOLUTION FOR MAGNESIUM
METAL DISSOLVING IN SULFURIC ACID

SCALE:	DATE	CASE NO:
DRAWN BY: <i>Balden Bhatia</i>		FILE NO:
CHECKED BY:		FIGURE NO: 6
APPROVED BY:		SHEET NO:



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RATE OF HYDROGEN EVOLUTION AS FUNCTION
OF HYDROGEN ION CONCENTRATION IN
ACIDS AT 25° C

SCALE:	DATE	CASE NO:
DRAWN BY:		FILE NO:
CHECKED BY:		FIGURE NO: 7
APPROVED BY:		SHEET NO:

The values for low concentrations were obtained by extrapolating this data. A log-log plot of hydrogen evolution rate versus hydrogen ion concentration at 25°C is shown in Figure 7, page 35. The hydrogen evolution rates in hydrochloric and sulfuric acids are about the same at a given hydrogen ion concentration. However, for the same concentration in perchloric acid, the rates are lower than those in hydrochloric and sulfuric acids. This shows that the reaction mechanism in hydrochloric and sulfuric acids may be similar. A linear relationship between the dissolution rates and hydrogen ion concentrations in hydrochloric and sulfuric acid extends over the concentration range covered in this study. The slope of this line is calculated to be 1.16. Thus, the dissolution of magnesium in hydrochloric and sulfuric acids is approximately first order with respect to the concentration of hydrogen ions. In perchloric acid the direct proportionality between the dissolution rates and hydrogen ion concentrations exists up to 0.32 N. Above 0.32 N, the dissolution rate increases rapidly in a manner similar to that shown in Figure 4, page 30.

Sample Calculations. The method used for calculation of rates in sulfuric, hydrochloric, and perchloric acids is the same.

Calculation of Dissolution Rates. For purposes of illustration, the dissolution in sulfuric acid has been selected. The following shows the calculation of average maximum hydrogen evolution rate at STP (0°C and 760 mm Hg). The data used is taken from Table LXX, page 158.

$$t = \text{average thermometer reading during the run} \\ = 30.2^{\circ}\text{C}$$

$$T = \text{absolute temperature of hydrogen} \\ = 30.2 + 273.2 = 303.4^{\circ}\text{K}$$

$$P = \text{average barometric pressure} = 735.7 \text{ mm Hg}$$

Pressure corrections:

(1) corrections for vapor pressure of water at
 $30.2^{\circ}\text{C} = 32.2 \text{ mm Hg}$

(2) temperature correction for brass-scale
barometer = 3.6 mm Hg

$$\text{Corrected average pressure of hydrogen} = 735.7 - 35.8 \\ = 699.9 \text{ mm Hg}$$

$$dv = \text{increase in volume of hydrogen over each} \\ \text{definite interval of time } dt, \text{ mm}^3\text{cm}^{-2}$$

dv_{STP} = the increase in volume of hydrogen during
the time interval dt , reduced to standard
temperature and pressure.

$$= (dv) \left(\frac{699.9}{760.0} \right) \left(\frac{273.2}{303.4} \right) = 0.8292 \text{ dv in cubic} \\ \text{millimeters (mm}^3\text{)}.$$

The values of dv STP have been calculated by the above method and are shown in the third column of the table from which data was 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 $2,239 \text{ mm}^3$ over the time interval of 6 minutes. The average maximum rate per unit area per minute was obtained from the equation:

$$R = \frac{dv}{A dt}$$

where R is the rate in $\text{mm}^3 \text{cm}^{-2} \text{min}^{-1}$, dv is the average maximum value in cubic millimeters, A is the surface area of the specimen in square centimeters, and dt is the time interval (minutes) over which the measurements were made. Substituting the values just obtained for this illustration gives:

$$R = \frac{2,239}{(1)(6)} = 373.1 \text{ mm}^3 \text{cm}^{-2} \text{min}^{-1}$$

Calculation of Hydrogen Ion Concentration. The complete dissociation of hydrochloric acid is given by the expression:



For 0.50 N HCl at 25°C the value of per cent dissociation is about 84 per cent ⁽²⁴⁾. As such the hydrogen ion concentration is given by

$$\text{H}^+ = 0.50 \times 0.84 = 0.42 \text{ equivalent/liter}$$

The values of hydrogen ion concentration in other acids were calculated in the same manner. A log-log plot of hydrogen ion concentration in all the acids (at 25°C) versus the corresponding hydrogen evolution rates is shown in Figure 7, page 35.

2. The Influence of Temperature on the Dissolution Rates.

Apparatus. The apparatus used was the same as that described previously⁽⁶⁾, and as briefly discussed in the previous section on the measurement of rate studies in acids.

Procedure. The procedure employed was the same as described in the dissolution rate studies. A detailed step-by-step procedure has been described previously⁽⁶⁾.

Data and Results. The data collected are presented in the Appendix, pages 97 to 163 and have been summarized in Tables II, III, IV, pages 23, 27, and 32. The values of the reaction rate constant k were calculated by assuming that the order of reaction n was equal to one (calculated values of n were very close to one, see pages 26 and 31). Values of k at different concentrations for a specific temperature are given in Tables V, VI, and VII on pages 40 through 42. The average values of k shown do not include the values of k at 0.50 N or higher acid concentrations because the log-log plots of reaction rate versus acid concentration (Figures 2, 4, and 6, pages 25, 30, and 34) show a linear relationship

TABLE V
Reaction Rate Constants for the Dissolution of Mg Metal in
Hydrochloric Acid

HCl Conc.	Reaction Rate Constant, k, $\frac{\text{mm}^3}{(\text{cm}^2 \cdot \text{min})(\text{equiv/lit})}$				
<u>Equiv.</u> <u>liter</u>	5°C	15°C	25°C	35°C	45°C
0.05	4,692	5,216	6,504	6,846	8,450
0.10	4,455	5,086	6,888	7,834	9,994
0.25	4,199	5,053	6,913	7,900	11,690
0.50	4,294	5,585	9,002	16,510	25,440
	4,449*	5,118*	6,768*	7,527*	10,010*

*The value of k at 0.50 N HCl was not included to obtain average k.

TABLE VI

Reaction Rate Constants for the Dissolution of Mg Metal in
Perchloric Acid

HClO ₄ Conc.	Reaction Rate Constant, k, $\frac{\text{mm}^3}{(\text{cm}^2 \cdot \text{min})(\text{equiv}/\text{lit})}$				
<u>Equiv.</u> <u>liter</u>	5°C	15°C	25°C	35°C	45°C
0.05	-	-	5,418	-	-
0.064	3,224	4,571	-	7,848	8,199
0.10	-	-	5,566	-	-
0.13	3,301	4,570	-	7,225	8,736
0.25	-	-	5,670	-	-
0.32	3,708	4,507	-	7,549	10,290
0.50	-	-	7,417	9,648	-
0.64	4,212	6,510	-	14,190	23,390
Ave. k	3,411*	4,549*	5,551*	7,541*	9,075*

*The value of k at and above 0.50 N HClO₄ were not included to obtain the average k.

TABLE VII

Reaction Rate Constants for the Dissolution of Mg Metal in Sulfuric Acid

<u>H₂SO₄</u> Conc.	Reaction Rate Constant, k, $\frac{\text{mm}^3}{(\text{cm}^2 \cdot \text{min})(\text{equiv}/\text{lit})}$				
<u>Equiv.</u> liter	5°C	15°C	25°C	35°C	45.2°C
0.05	3,258	3,946	4,802	6,532	6,958
0.10	3,420	4,271	4,720	6,266	7,597
0.25	3,447	4,196	4,773	6,428	7,640
0.51	3,271	4,221	5,143	8,354	14,521
Ave. k	3,375*	4,138*	4,765	6,409*	7,398*

*The value of k at 0.50 N H₂SO₄ was not included to obtain the average k.

at all temperatures only for the lower concentrations. Average values of k at various temperatures for hydrochloric, perchloric, and sulfuric acids are summarized in Table VIII, page 44. Data from Table IX, page 45 were used to make the Arrhenius plots ($\log k$ versus $1/T$) shown in Figure 8, page 46. From these, the activation energies were calculated. The activation energy for the dissolution of magnesium in perchloric acid is 4.4 ± 0.3 kilocalories, in hydrochloric acid 3.6 ± 0.3 kilocalories, and in sulfuric acid 3.7 ± 0.1 kilocalories. The values for hydrochloric and sulfuric acids can be considered equal within the limits of experimental error.

Sample Calculations. The following shows a sample calculation of the reaction rate constant k , activation energy E_a , and the deviation of the activation energy for the dissolution of magnesium in hydrochloric acid. The same method of calculation was used for the other acids.

Calculation of Reaction Rate Constant. Data used were taken from Table II, page 23 for a reaction temperature of 15°C .

$$dv/dt = k(\text{HCl})^n \quad (\text{Equation 18, page 21})$$

But $n = 1$, since the order of reaction is equal to one.

Therefore,

$$k = \frac{dv/dt}{(\text{HCl})} = \frac{260.8}{0.05} = 5216 \frac{\text{mm}^3}{\text{cm}^2 \cdot \text{min}} \text{ for } 0.05 \text{ N HCl.}$$

TABLE VIII

Summary of Reaction Rate Constants for the Dissolution of
Mg Metal in Hydrochloric, Perchloric, and Sulfuric Acids

Acid	Reaction Rate Constant, k, (mm ³ /cm ² .min)(liter/Equiv)					
	5°C	15°C	25°C	35°C	45°C	45.2°C
Perchloric	3,411	4,549	5,551	7,541	9,075	-
	3.5329*	3.6580*	3.7444*	3.8775*	3.9578*	-
Hydrochloric	4,449	5,118	6,768	7,527	10,010	-
	3.6483*	3.7091*	3.8304*	3.8766*	4.0000*	-
Sulfuric	3,375	4,138	4,765	6,409	-	7,398
	3.5282*	3.6168*	3.6781*	3.8068	-	3.8691*

*Logarithm of the preceding number.

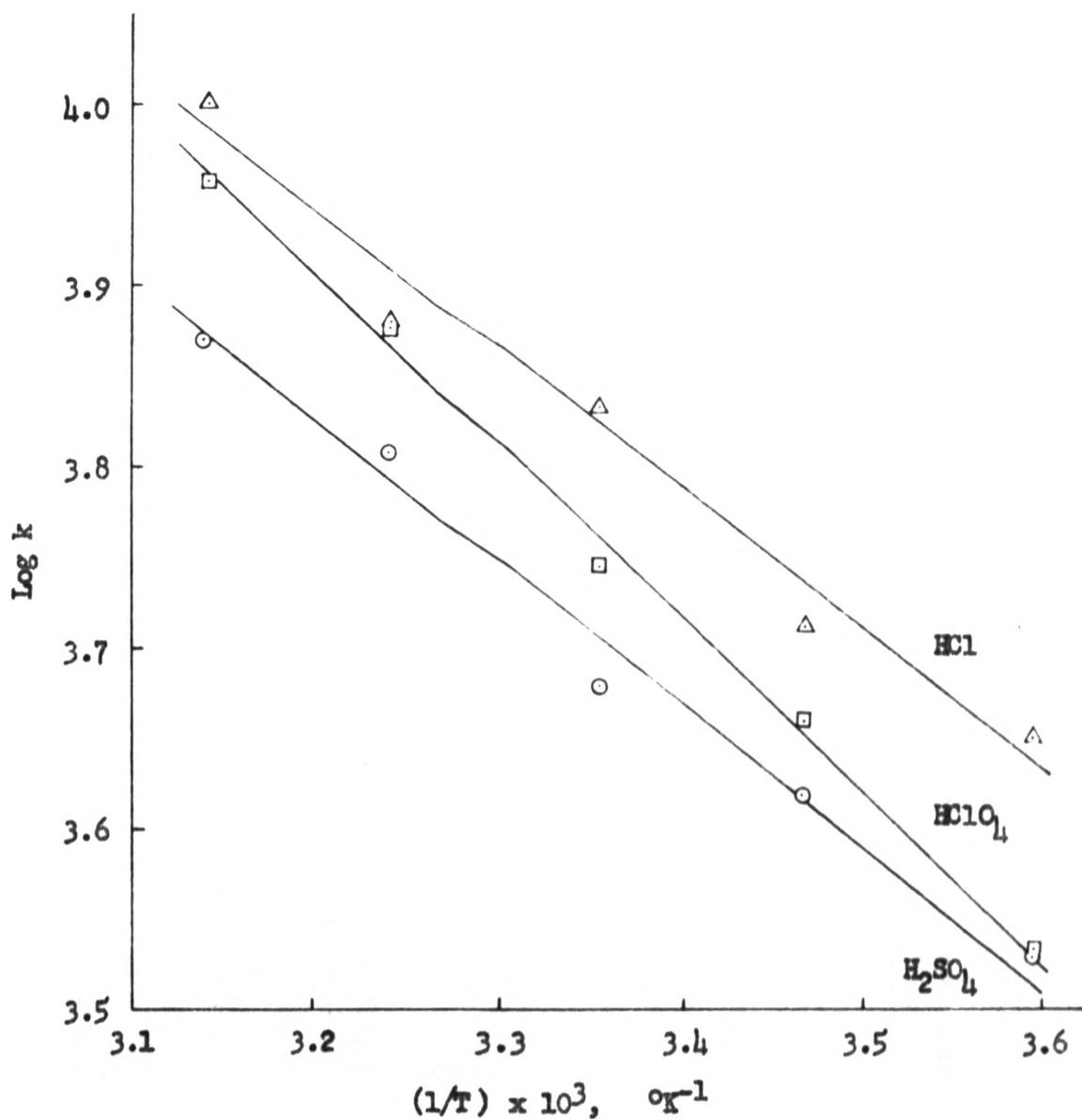
-47-

TABLE IX

Data Used to Make the Arrhenius Plots for the Dissolution
of Mg Metal in Hydrochloric, Perchloric, and
Sulfuric Acids

Temperature		(1/T)(10 ³)	Log k		
°C	°K	°K ⁻¹	H ₂ SO ₄ *	HClO ₄ *	HCl*
5	278.2	3.595	3.5282	3.5329	3.6483
15	288.2	3.467	3.6168	3.6580	3.7091
25	298.2	3.3534	3.6781	3.7440	3.8304
35	308.2	3.2446	3.8068	3.8775	3.8766
45	318.2	3.1426	-	3.9578	4.0000
45.2	318.4	3.1407	3.8691	-	-

*Average value obtained from Table VIII.



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**ARRHENIUS PLOTS FOR THE DISSOLUTION
OF MAGNESIUM IN ACIDS**

SCALE:	DATE	CASE NO:
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Similarly,

$$k = 5,086 \text{ for } 0.10 \text{ N HCl}$$

$$= 5,53 \text{ for } 0.25 \text{ N HCl}$$

$$= 5,585 \text{ for } 0.50 \text{ N HCl}$$

Excluding the value of k at 0.50 N HCl, the average value is

$$k = \frac{5,216 + 5,086 + 5,053}{3} = 5,118 \text{ at } 15^\circ\text{C}$$

Calculation of Activation Energy. The data for this calculation were taken from Figure 8, page 46 for the dissolution of magnesium in hydrochloric acid.

$$\log k = \frac{-E_a}{RT} \log e + \log A \quad (\text{Arrhenius Equation})$$

or

$$\log k = -0.434 \frac{E_a}{R} (1/T) + \log A$$

The slope of the straight line from the Arrhenius plot is -773.6. Thus,

$$-0.434 \frac{E_a}{R} = -773.6$$

$$E_a = 3,560 \text{ calories} = 3.56 \text{ kilocalories}$$

A similar method of calculation was used to obtain the activation energies for sulfuric and perchloric acids.

Calculation of the Deviation of the Activation Energy. The data used in this calculation were taken from Table V. From the Arrhenius equation,

$$\ln k = \ln A - E_a/RT \quad (21)$$

Taking the differential,

$$\frac{dk}{k} = 0 - \frac{dE_a}{RT} + \frac{E_a}{RT^2} dT \quad (22)$$

where,

k = reaction rate constant

T = reaction temperature

R = gas constant

E_a = activation energy

A = frequency factor (a constant)

The numerical values to be substituted in the above equation (22) will be such as to maximize the error in E_a.

$$R = 1.987 \text{ cal/gm mol}^\circ\text{K}$$

T = 45.0°C = 318.2°K (the largest value for the reaction temperature used to maximize the error in E_a).

ΔT = 10° = 1K° (the water bath temperature was set within ± 0.1°C. As such the maximum error allowed from the set temperature is taken as equal to 10°).

$$1/T^2 = \frac{1}{(273.2 + 5)^2} = \frac{1}{(278.2)^2} \quad (\text{The minimum value of the reaction temperature}).$$

Δk = 11,694 - 10,012 = 1,682 (Maximum deviation of k from the average value).

$$k = 4,199 \frac{\text{mm}^3}{(\text{cm}^2 \cdot \text{min})(\text{Equiv/liter})} \quad (\text{Minimum})$$

value of k).

$E_a = 3,560$ calories (value of experimentally determined activation energy).

$$\Delta E_a = (1.987)(318.2)\left(\frac{1.682}{4,199}\right) + \frac{3,560}{(1.987)(278.2)^2}$$
$$= 268 \text{ calories} = 0.268 \text{ kilocalories} = 0.3$$

kilocalories approximately

The deviation of ± 0.30 kilocalories for the activation energy of 3,560 kilocalories in hydrochloric acid should be a conservative estimate.

3. The Difference Effect on Magnesium Metal Dissolving in Acids. The difference effect on magnesium metal was measured in hydrochloric, perchloric and sulfuric acids at 25°C. The concentration of the acids employed varied from 0.05 N to 0.50 N.

Apparatus. The apparatus used was the same as described previously⁽⁶⁾. A three-necked reaction flask of 500 milliliter capacity was used to hold the acid. A magnesium anode and a platinized-platinum cathode was placed in the center neck, a mercury-sealed stirrer in one side neck and teflon tubing from the third neck led to a gas burette for collection and measurement of hydrogen gas evolved during a run. The reaction flask was immersed in a water-bath, which was controlled at a temperature of 25°C within $\pm 0.10^\circ\text{C}$. A stirring speed of 200 revolutions per minute was employed.

The anodic current flowing through the circuit was measured by a milliammeter and was varied by changing the resistance in the circuit.

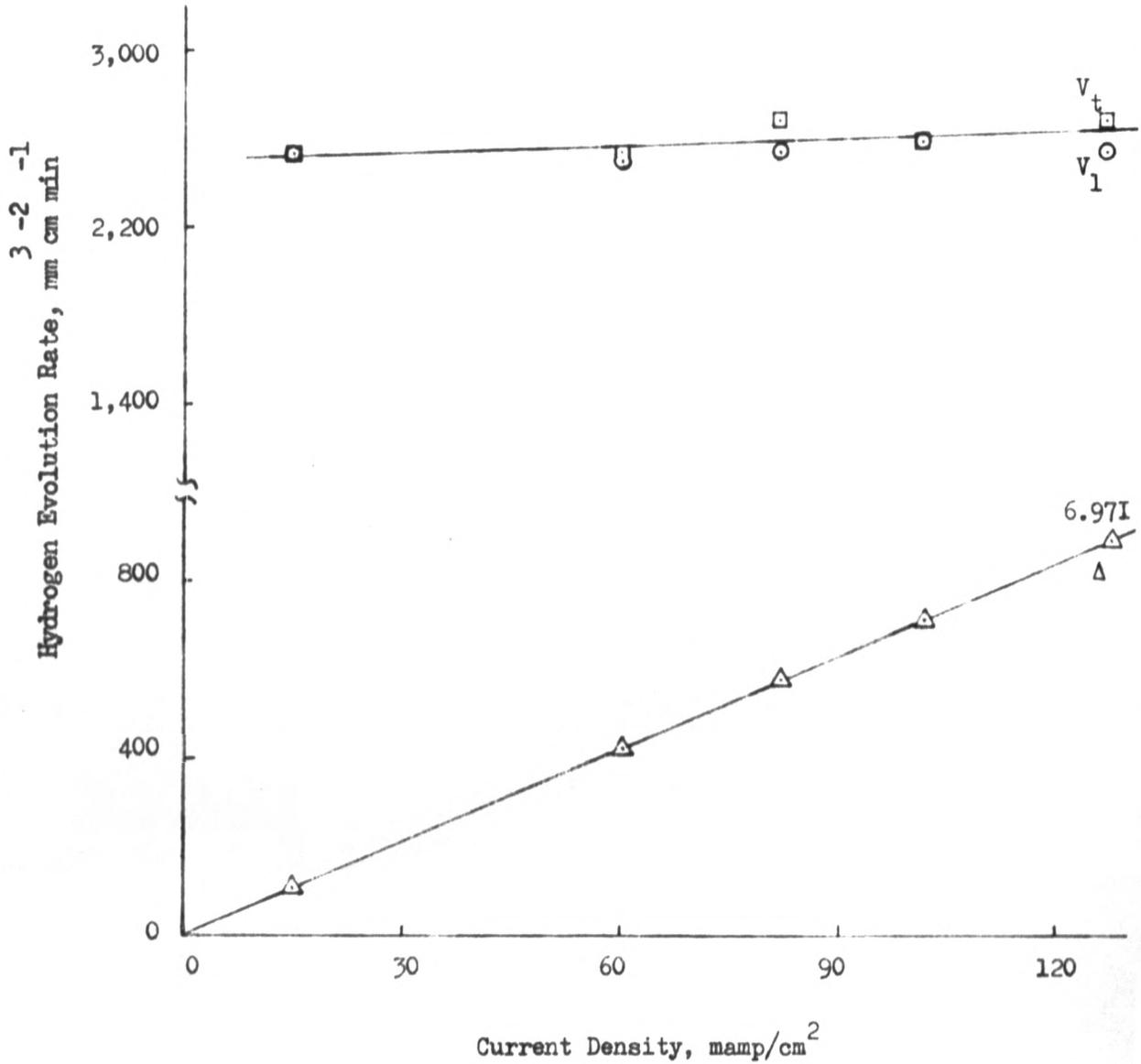
Procedure. A detailed procedure has been described previously⁽⁶⁾. A magnesium electrode of one square centimeter surface area was prepared with the same technique as described previously⁽⁶⁾. A platinized-platinum cathode having a surface area of approximately four square centimeters was used in all the runs. The distance between the electrodes was 0.25 centimeters. Three hundred milliliters of the acid of known concentration was poured into the reaction flask and the system was allowed to come to the temperature of the water-bath (about one hour required). After this time had passed, the electrodes were immersed (with external circuit switch open) in the acid, the stirring mechanism was turned on, and the hydrogen evolved during the dissolution was collected in the gas burette. The volume of the gas was recorded for definite time intervals until the rate became fairly constant. At this time, the external circuit was closed with the knife-blade switch and two consecutive burette readings were taken at equal time intervals. The average milliammeter reading was also recorded for each time interval. The above procedure of taking two burette readings without an external current

flowing, and two burette readings with an external current flowing was repeated at several current densities. The current flowing through the circuit was adjusted with a resistance box. The procedure was the same for all the acids used.

Data and Results. The data from these measurements are presented in the Appendix, pages 164 to 173. These tables show the average hydrogen evolution rate V_1 from the magnesium electrode without the current flowing and the total hydrogen evolution rate V_t from the anode and the cathode with the current flowing, both at standard temperature and pressure. The values of V_1 and V_t have been plotted against the corresponding current densities I (milliamperes per square centimeter) in Figures 9 through 18, pages 52 through 61. Curves were drawn through the plotted points to obtain average values of V_1 and V_t . From these curves, values of V_1 and V_t were obtained at various current densities to find the difference effect values Δ (see equation 24 on page 62). The difference effect is defined as the difference between hydrogen evolution rate V_1 from an electrode without the current flowing and hydrogen evolution rate V_2 from the same electrode with the current flowing, i.e.,

$$\Delta = V_1 - V_2$$

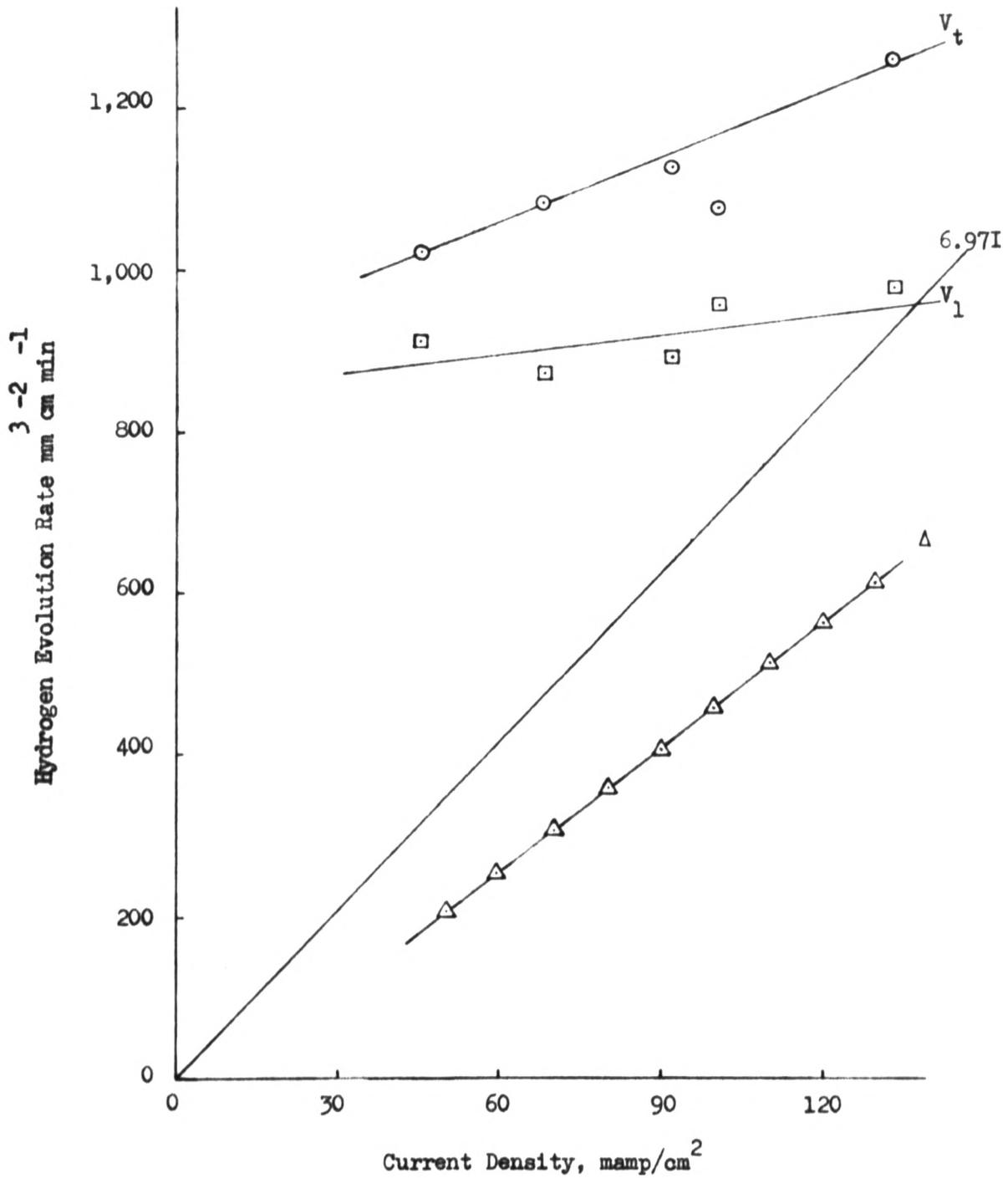
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ANODIC DISSOLUTION OF MAGNESIUM IN
0.50 N HCl AT 25°C

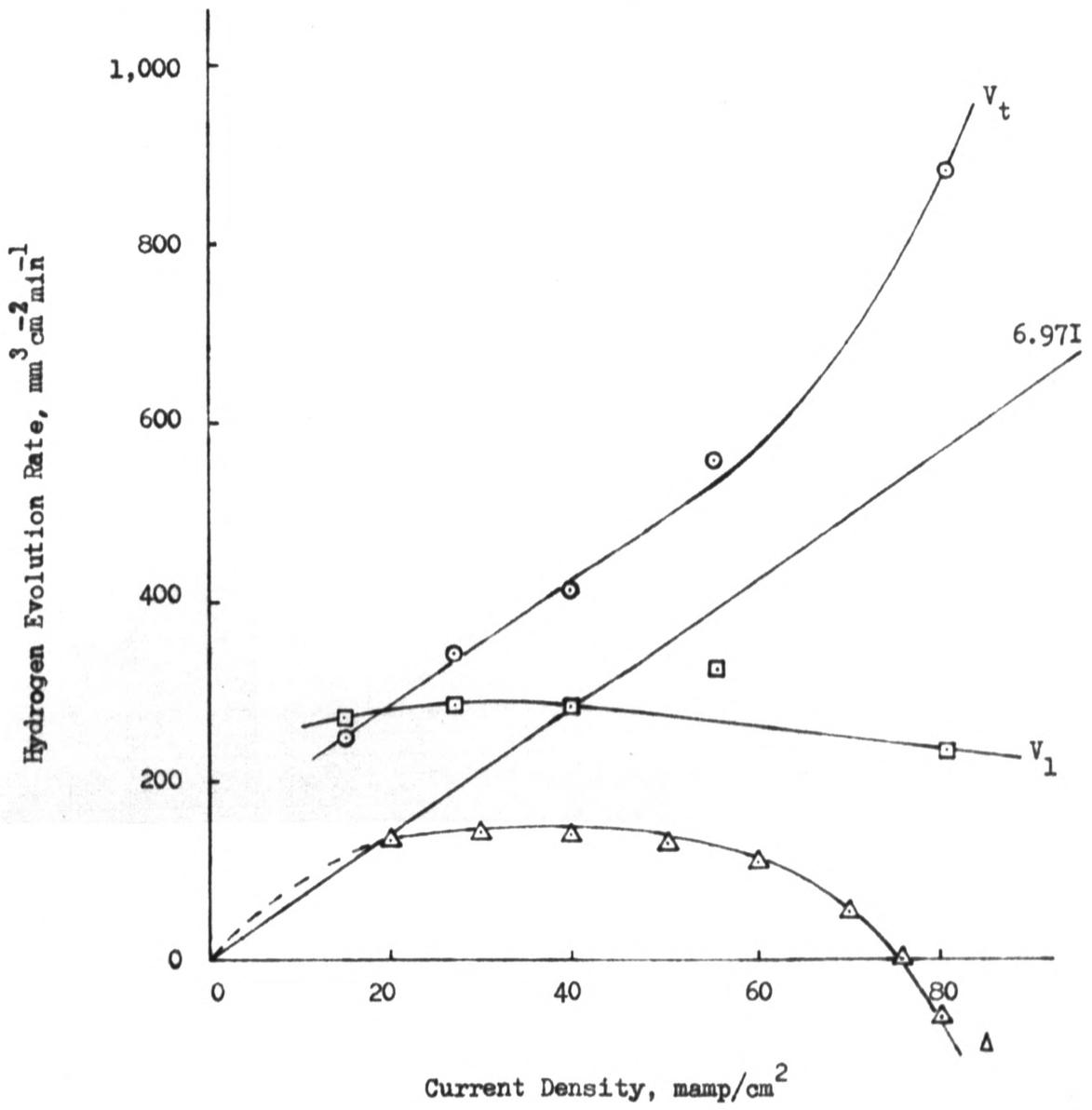
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ANODIC DISSOLUTION OF MAGNESIUM IN
0.25 N HCl AT 25°C

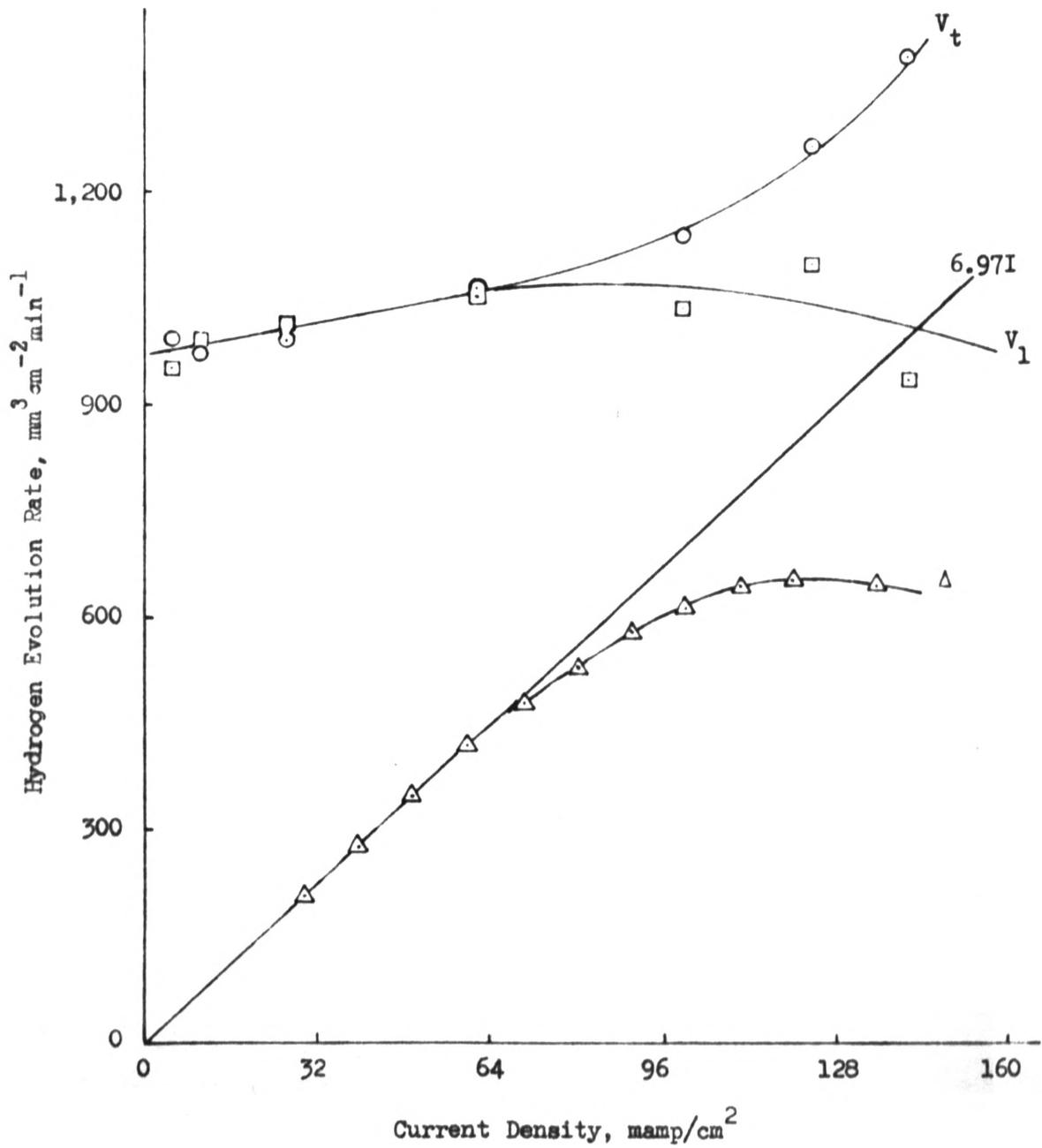
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**ANODIC DISSOLUTION OF MAGNESIUM IN
0.10 N HCl AT 25°C**

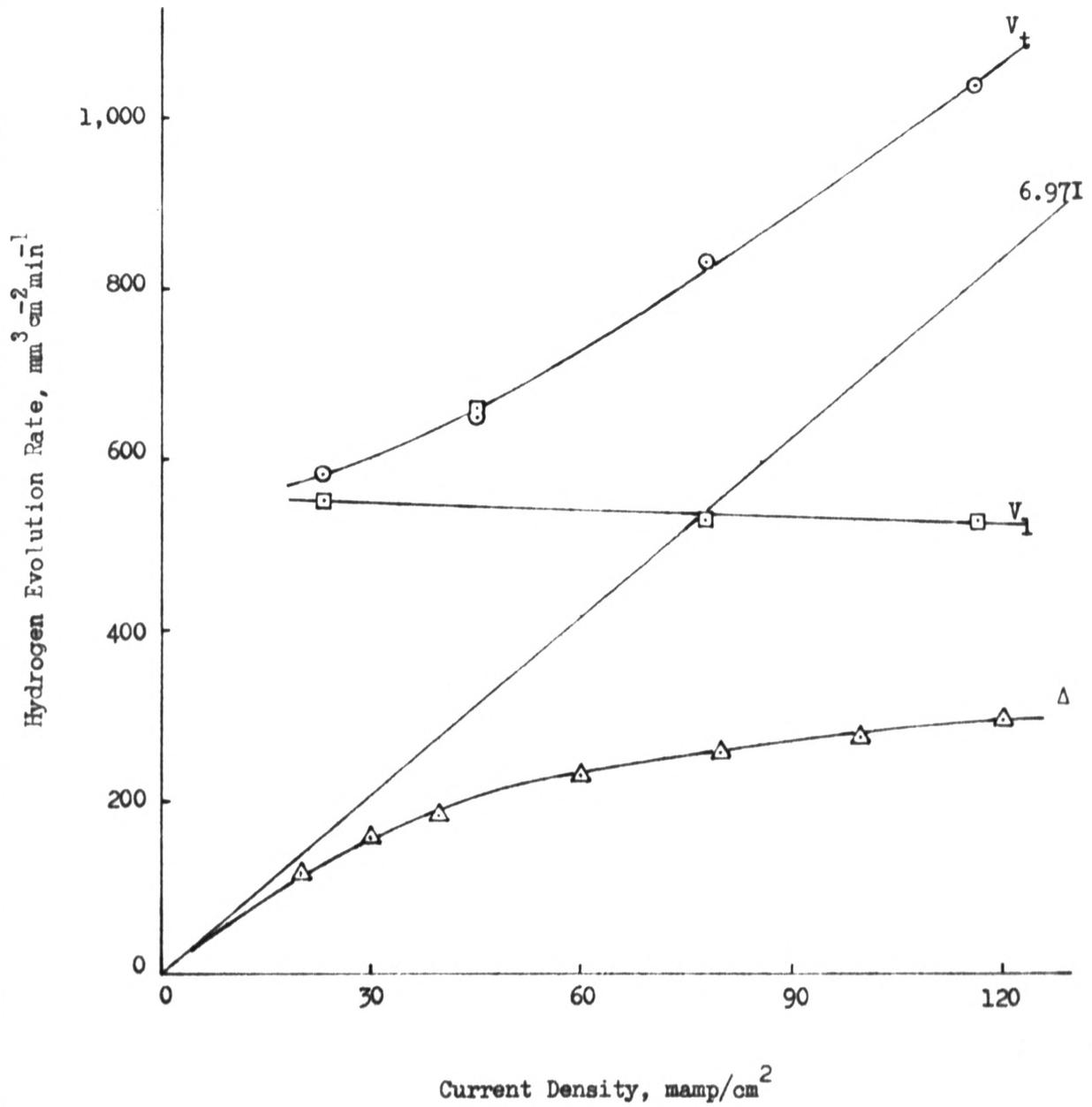
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ANODIC DISSOLUTION OF MAGNESIUM IN
0.25 N HClO₄ AT 25°C

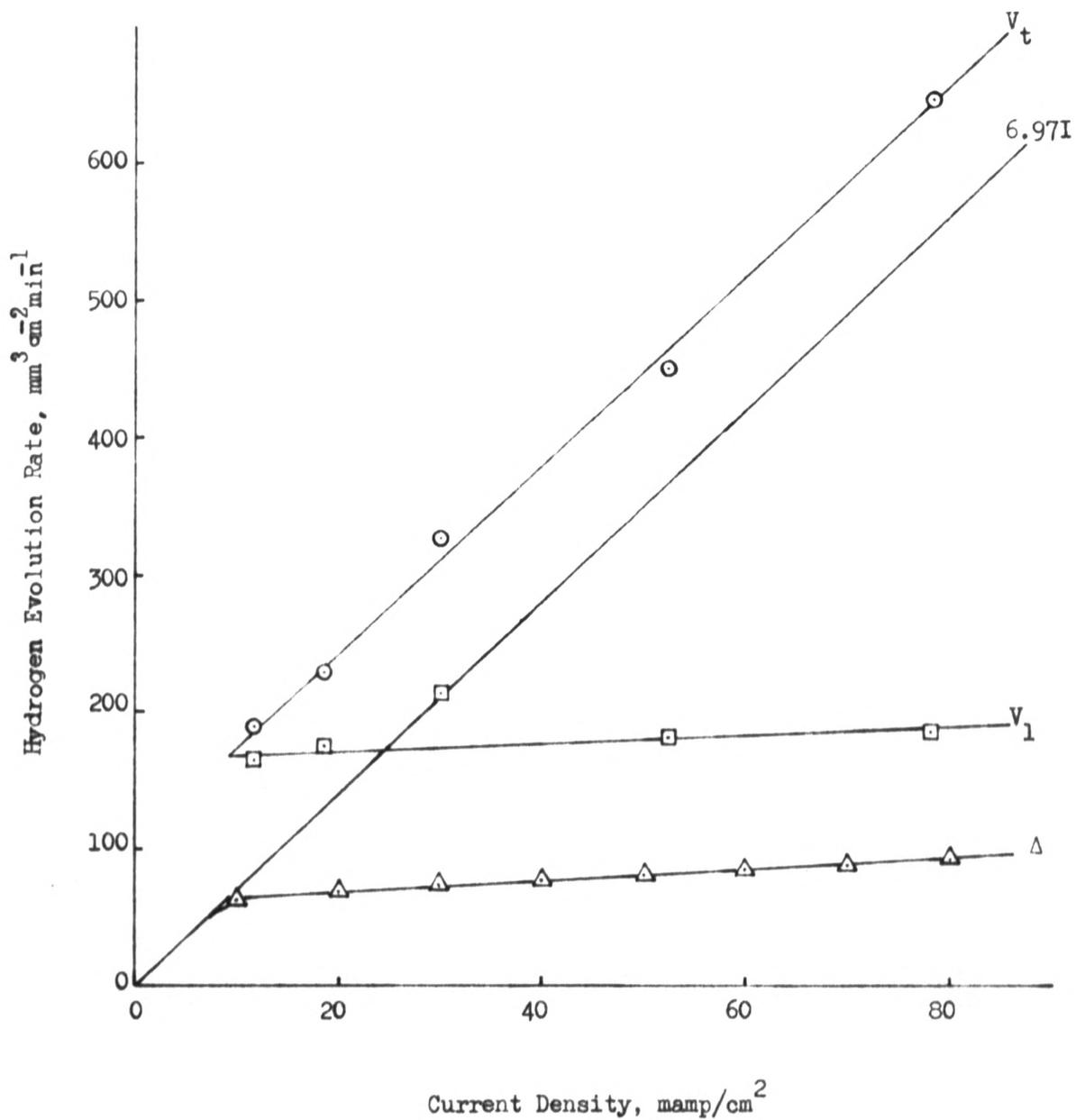
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ANODIC DISSOLUTION OF MAGNESIUM IN
0.10 N HClO₄ AT 25°C

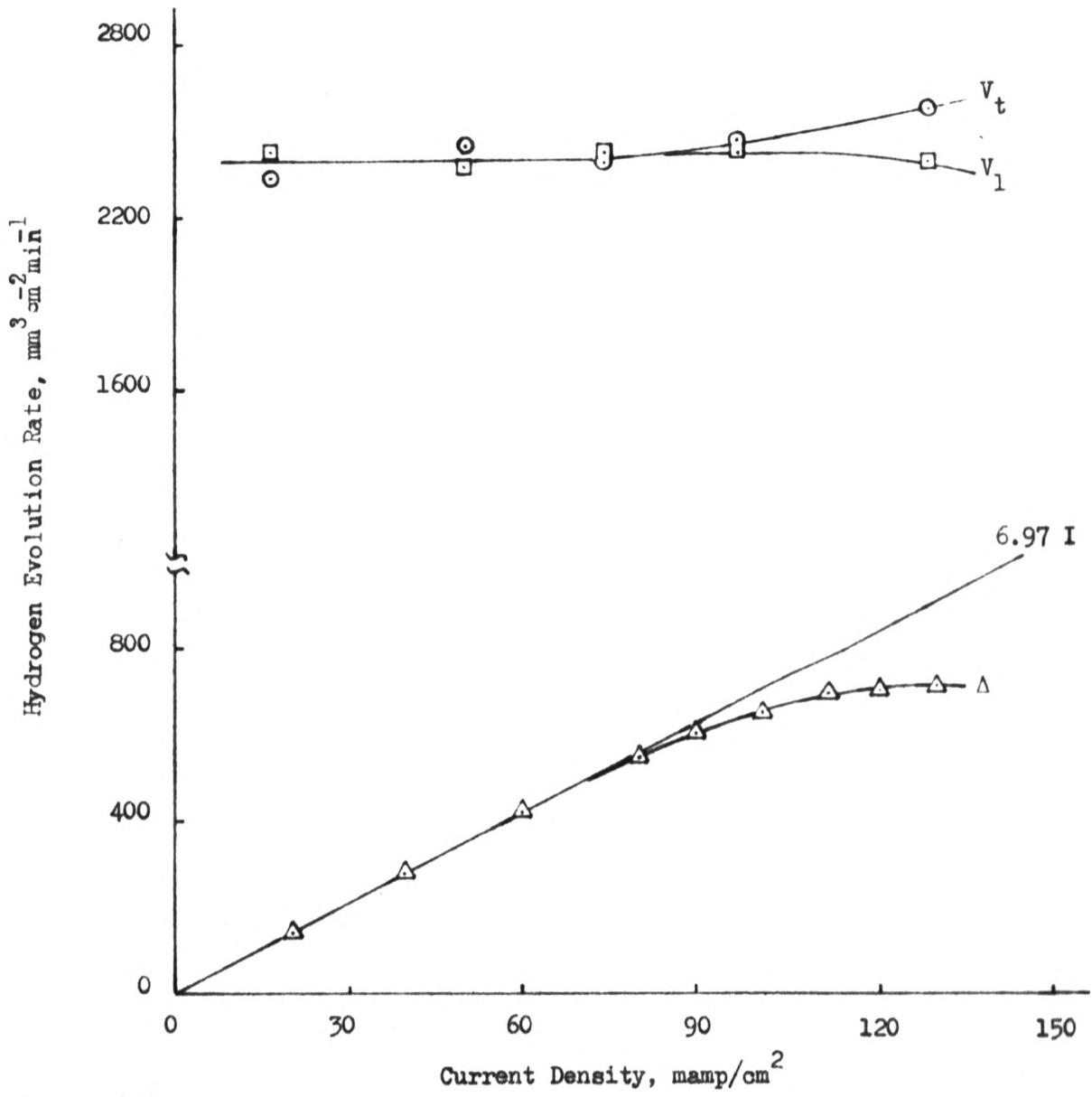
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ANODIC DISSOLUTION OF MAGNESIUM IN
0.05 N HClO₄ AT 25°C

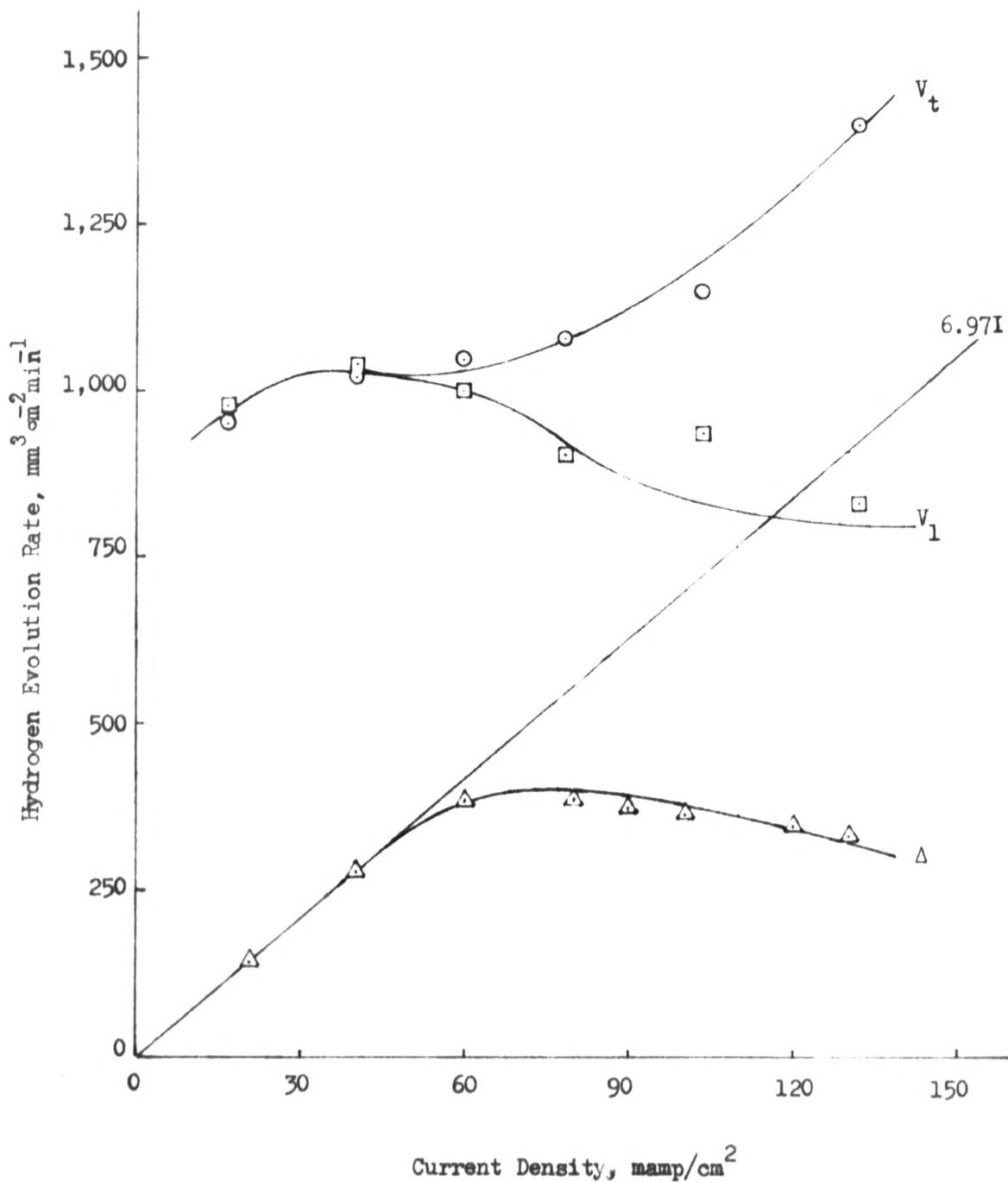
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ANODIC DISSOLUTION OF MAGNESIUM IN
0.50 N H₂SO₄ AT 25°C

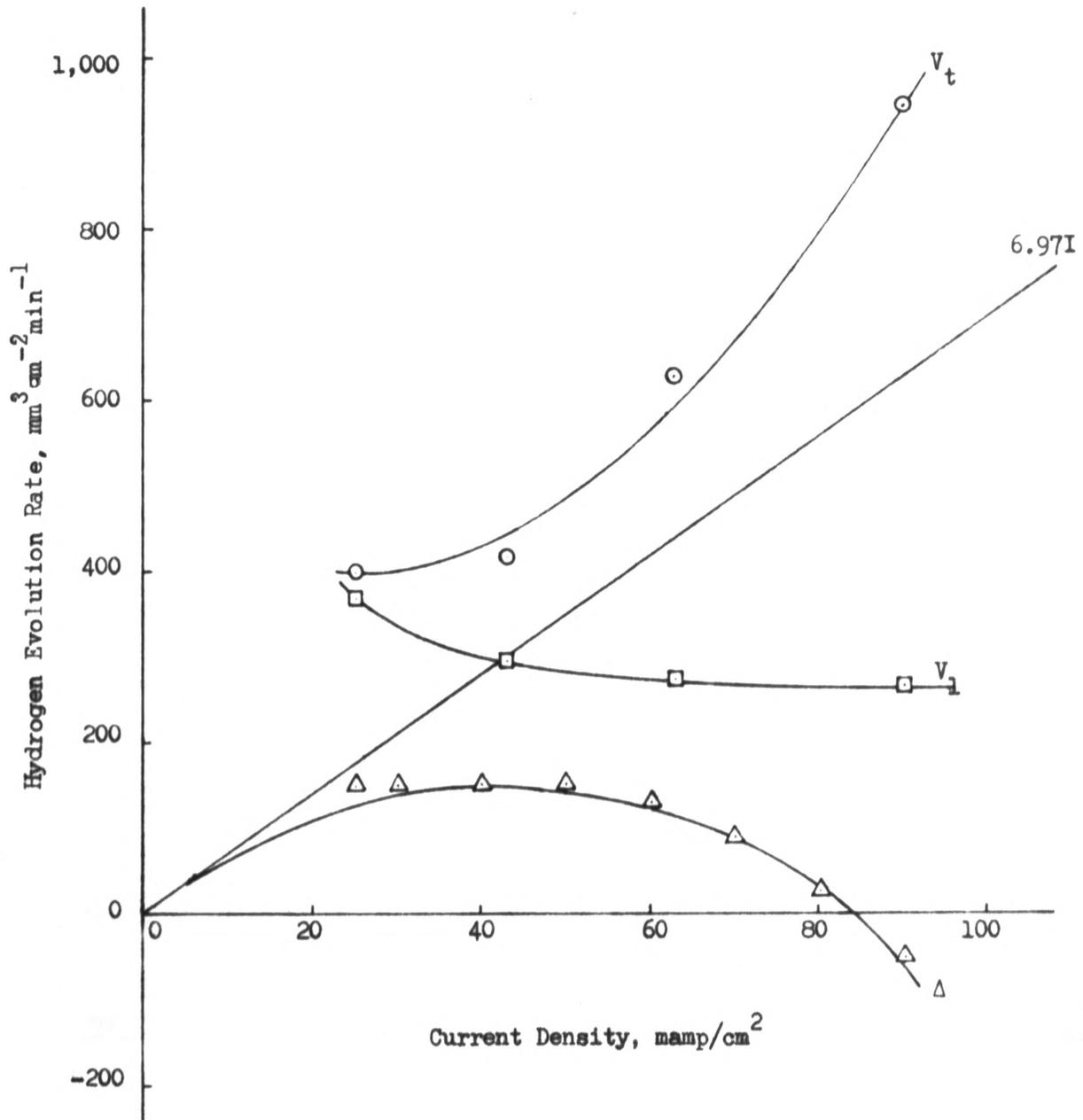
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ANODIC DISSOLUTION OF MAGNESIUM IN
0.25 N H₂SO₄ AT 25°C

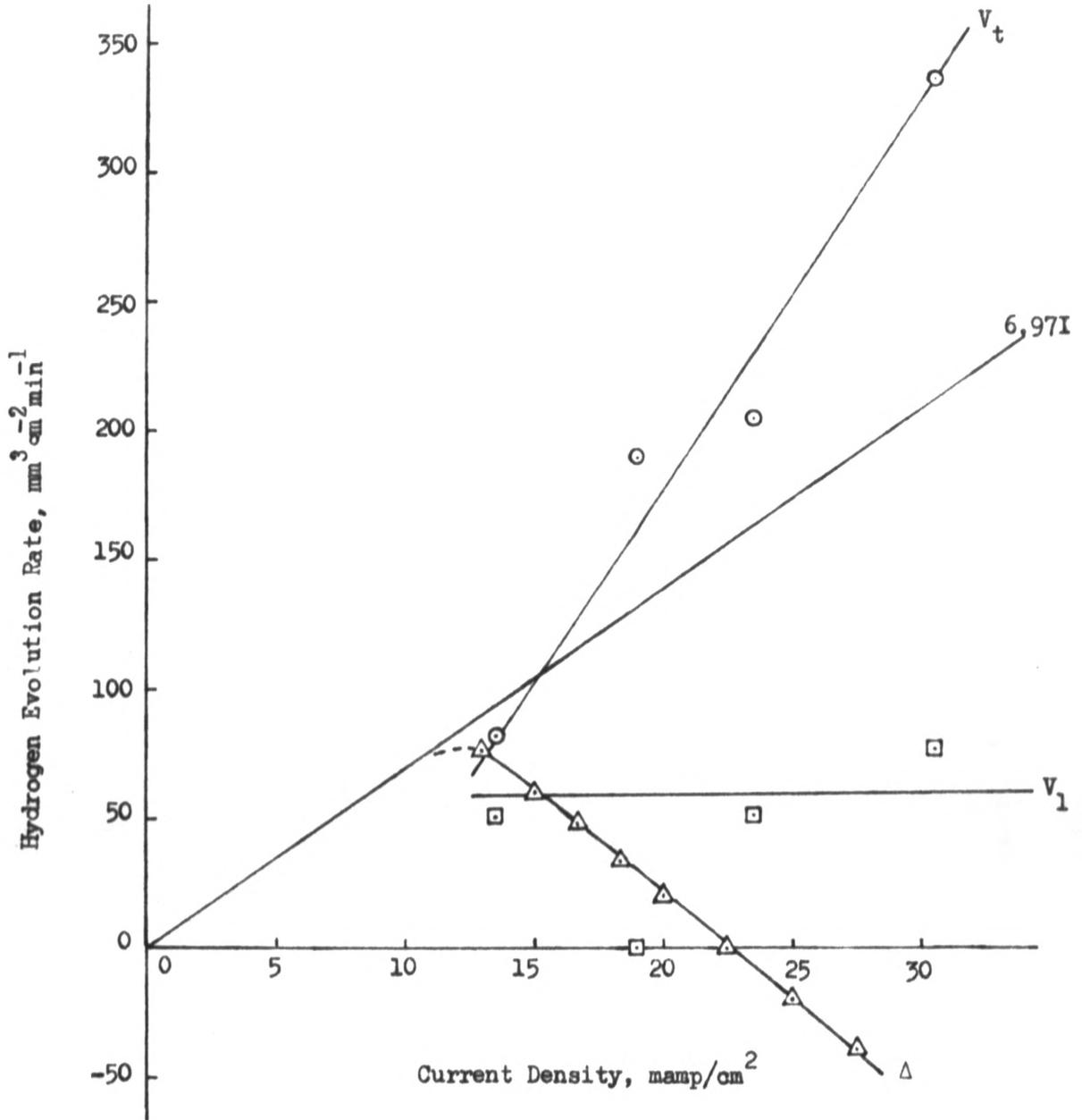
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ANODIC DISSOLUTION OF MAGNESIUM IN
0.10 N H₂SO₄ AT 25°C

SCALE:	DATE	CASE NO:
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ANODIC DISSOLUTION OF MAGNESIUM IN
0.05 N H₂SO₄ AT 25°C

SCALE:	DATE	CASE NO:
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Usually the two rates are not equal, and a 'positive' difference effect results when the rate is decreased by passing an anodic current ($V_1 > V_2$). A 'negative' difference effect results when the rate of dissolution is increased by passing an anodic current ($V_2 > V_1$). The difference effect Δ expressed in $\text{mm}^3 \text{cm}^{-2} \text{min}^{-1}$ is calculated by the equations

$$\Delta = V_1 - (V_t - 6.97I)$$

or,
$$\Delta = V_1 + 6.97I - V_t \quad (24)$$

where the factor 6.97 converts the milliamperes of current flowing through the electrodes for one minute into cubic millimeters of hydrogen (cathodic) at standard conditions. The values of Δ so calculated are also plotted on the same figures. The experimental values of V_1 and V_t were not used to calculate Δ because scatter in the data gave inconclusive results. This was thought to be due in part to the removal of a film on the magnesium anode, and the dissolution by chunks originating from the magnesium anode (as shown in the next experimentation section).

As can be seen from the figures, a linear relationship between Δ and I exists only at a low current. The deviation from linearity becomes more pronounced with increasing current densities and decreasing acid concentrations. In almost all the acids, the difference effect is positive over a considerable range of current densities, i.e., the hydrogen

evolution rate on magnesium anode is decreased on passing the anodic current. In 0.50 N sulfuric acid (Figure 15), Δ is proportional to I up to 80 mamp/cm², and above this Δ increases exponentially. In 0.25 N sulfuric acid (Figure 16), Δ is proportional to I up to 41 mamp/cm², but above this current density Δ increases slowly reaching a maximum value at 80 mamp/cm² and then begins to drop. In 0.10 N sulfuric acid (Figure 17), however, the relation between Δ and I is exponential over the whole range covered. The Δ curve reaches a maximum value at about 40 mamp/cm² and then begins to drop reaching a zero value at about 84 mamp/cm². Above this current density a negative difference effect results, i.e., the hydrogen evolution rate on the magnesium anode increases on passing the anodic current. At very low concentrations of sulfuric acid (0.05 N), the Δ values decrease with increasing current densities resulting in zero Δ value at about 22.5 mamp/cm². Above this current density the negative difference effect results on the magnesium anode. Thus, there is a change from a positive difference effect to a negative one with increasing current densities and decreasing sulfuric acid concentrations. Similar results are obtained in hydrochloric acid (Figures 9, 10 and 11). However, in perchloric acid a positive difference effect is observed within the experimental data covered,

although it is not proportional to all the current densities applied (Figures 12, 13 and 14).

Using the values of Δ and I obtained from these plots, the apparent cationic charge C^+ on magnesium during the anodic dissolution in an acid was calculated using the following equation⁽¹⁹⁾

$$C^+ = n_m \frac{11,207 I}{1,608.2 (V_t - V_1)} \quad (25)$$

where, $n_m = 2$, the normal cationic charge on magnesium. In this equation it is assumed that the free self-dissolution rate V_1 does not change during anodic dissolution. Tables X, XI and XII, pages 65, 66 and 67 show the cationic charges with which magnesium ions enter solution in hydrochloric, perchloric and sulfuric acids at 25°C. This variation of C^+ with I is shown in Figures 19, 20 and 21, pages 70, 71 and 72 for each acid at various concentrations. The cationic charge varies from infinity at low current densities to approximately the normal cationic charge of two at high current densities. In 0.50 N HCl, C^+ is infinity for the measured range of current densities. This is due to V_t and V_1 having approximately the same values at these current densities.

Sample Calculations. The data from the difference effect on magnesium dissolving in 0.25 N HCl (Table LXXV, page 165) has been used to illustrate the calculations involved in this part of the experimentation.

TABLE X

Apparent Cationic Charge on Magnesium Ions During Anodic
Dissolution in Hydrochloric Acid at 25°C

I mamp	0.25 N HCl		0.10 N HCl	
	Δ $\text{mm}^3 \text{cm}^{-2} \text{min}^{-1}$	C^+	Δ $\text{mm}^3 \text{cm}^{-2} \text{min}^{-1}$	C^+
10	-	-	-	-
20	-	-	133.0	43.56
30	-	-	142.0	6.22
40	-	-	140.0	4.00
50	206.0	4.9	128.0	3.16
60	258.0	5.2	107.0	2.68
70	306.0	5.4	102.0	2.52
75.7	-	-	0.0	2.00
80	359.0	5.6	-65.0	1.79
90	409.0	5.8	-	-
100	460.0	5.9	-	-
110	513.0	6.0	-	-
120	553.0	5.9	-	-
130	612.0	6.2	-	-

TABLE XI

Apparent Cationic Charge on Magnesium Ions During Anodic Dissolution in
Perchloric Acid at 25°C

I	0.25 N HClO ₄		0.10 N HClO ₄		0.05 N HClO ₄	
	Δ	c ⁺	Δ	c ⁺	Δ	c ⁺
mamp	mm ³ cm ⁻² min ⁻¹		mm ³ cm ⁻² min ⁻¹		mm ³ cm ⁻² min ⁻¹	
10	-	-	60.0	14.37	52.0	7.88
20	139.4	∞	118.0	13.03	68.0	3.90
30	-	-	158.0	8.18	72.0	3.05
40	278.8	∞	185.0	5.94	75.0	2.74
50	-	-	-	-	80.0	2.56
60	418.2	∞	228.0	4.40	84.0	2.50
70	-	-	-	-	88.0	2.44
80	528.0	37.67	256.0	3.70	-	-
90	-	-	-	-	-	-
100	608.0	15.66	275.0	3.30	-	-
110	-	-	-	-	-	-
120	650.0	8.97	296.0	3.10	-	-

TABLE XII

Apparent Cationic Charge on Magnesium Ions During Anodic
Dissolution in Sulfuric Acid at 25°C

I ma/cm ²	0.25 N H ₂ SO ₄		0.05 N H ₂ SO ₄	
	Δ mm ³ cm ⁻² min ⁻¹	C ⁺	Δ mm ³ cm ⁻² min ⁻¹	C ⁺
13.0	-	-	77.0	13.32
15.0	-	-	62.0	8.91
18.0	-	-	37.0	2.84
20.0	139.4	∞	20.0	2.34
22.5	-	-	0.0	2.00
25.0	-	-	-20.0	1.79
27.5	-	-	-40.0	1.65
40.0	278.8	∞	-	-
50.0	335.0	51.63	-	-
60.0	375.0	19.36	-	-
70.0	395.0	10.50	-	-
80.0	395.0	6.86	-	-
90.0	392.0	5.33	-	-
100.0	380.0	4.38	-	-
120.0	343.0	3.39	-	-

TABLE XII

Apparent Cationic Charge on Magnesium Ions During Anodic
Dissolution in H₂SO₄ at 25°C (con't)

I	0.50 N H ₂ SO ₄		0.10 N H ₂ SO ₄	
	Δ	C ⁺	Δ	C ⁺
mamp/cm ²	mm ³ cm ⁻² min ⁻¹		mm ³ cm ⁻² min ⁻¹	
10.0	-	-	62.0	18.10
13.0	-	-	-	-
15.0	-	-	-	-
18.0	-	-	-	-
20.0	139.4	∞	108.0	8.88
22.5	-	-	-	5.72
25.0	-	-	-	-
27.5	-	-	-	-
30.0	-	-	136.0	5.72
40.0	278.8	∞	150.0	4.33
50.0	-	-	142.0	3.38
60.0	418.2	∞	122.0	2.82
70.0	-	-	88.0	2.44
80.0	550.0	146.74	32.0	2.12
90.0	605.0	52.26	-54.0	1.84
100.0	650.0	29.66	-	-
110.0	690.0	19.99	-	-
120.0	700.0	12.26	-	-
130.0	710.0	9.24	-	-

Calculation of V_1 and V_t .

t = average room temperature during the run
= 25.7°C

T = absolute temperature of hydrogen
= 273.2 + 25.7 = 298.9°K

P = average barometric pressure during the run
= 736.5 mm Hg

Pressure Corrections:

(1) correction for vapor pressure of water at
25.7°C = 24.8 mm Hg

(2) temperature correction for brass-scale barometer = 3.1 mm Hg

Corrected average pressure of hydrogen

$$= 736.5 - 27.9 = 708.6 \text{ mm Hg}$$

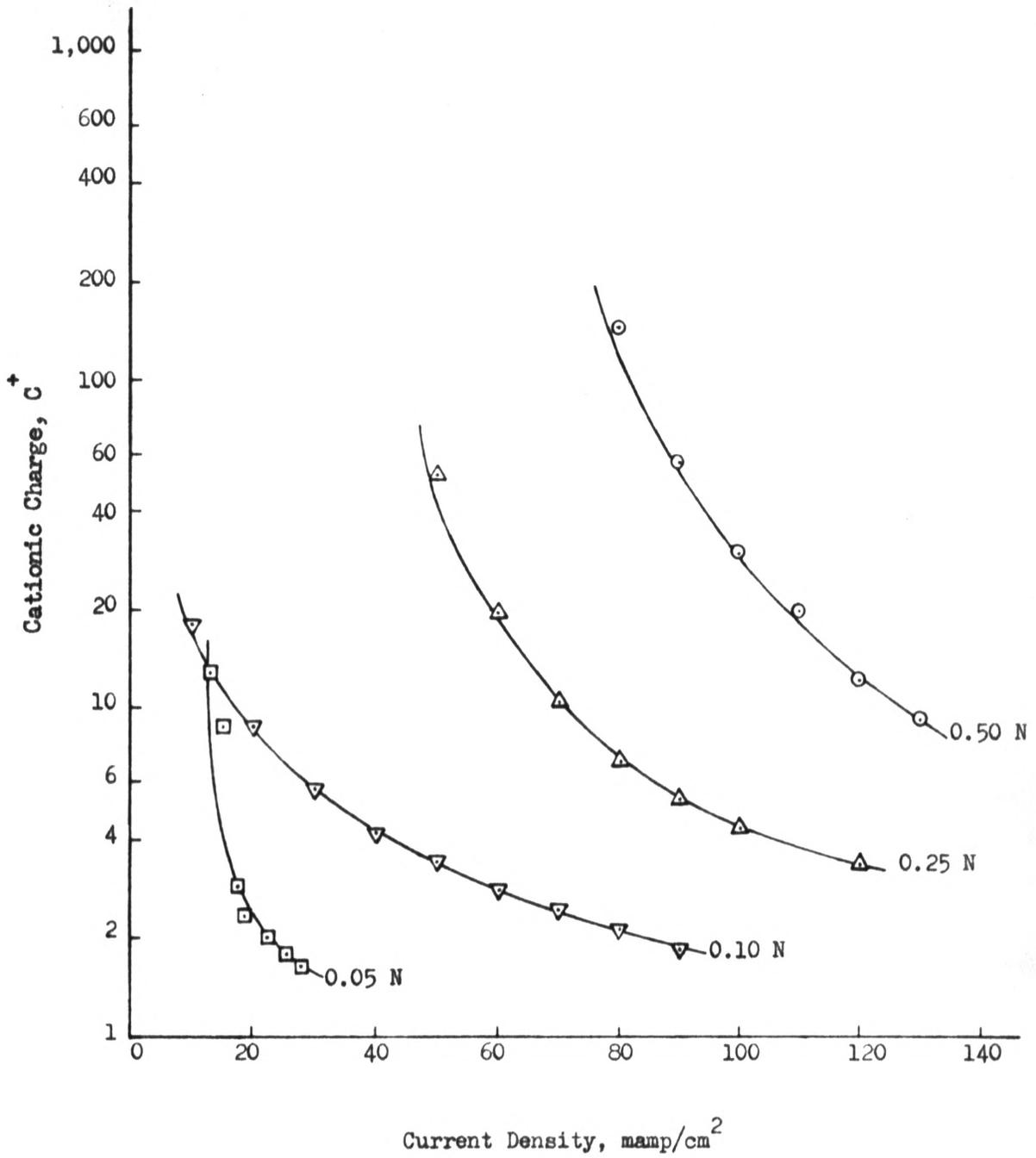
dv = increase in volume of hydrogen over each
definite interval of time dt , $\text{mm}^3\text{cm}^{-2}$

dv_{STP} = the increase of hydrogen during the time
interval dt reduced to standard pressure
and temperature

$$= (dv/2) \left(\frac{273.2}{298.9} \right) \left(\frac{708.6}{760.0} \right) = 0.426 \text{ } dv \text{ } \text{mm}^3\text{cm}^{-2}\text{min}^{-1}$$

V_1 = the average value of self-dissolution rate
before and after the current flow ($I = 0$)

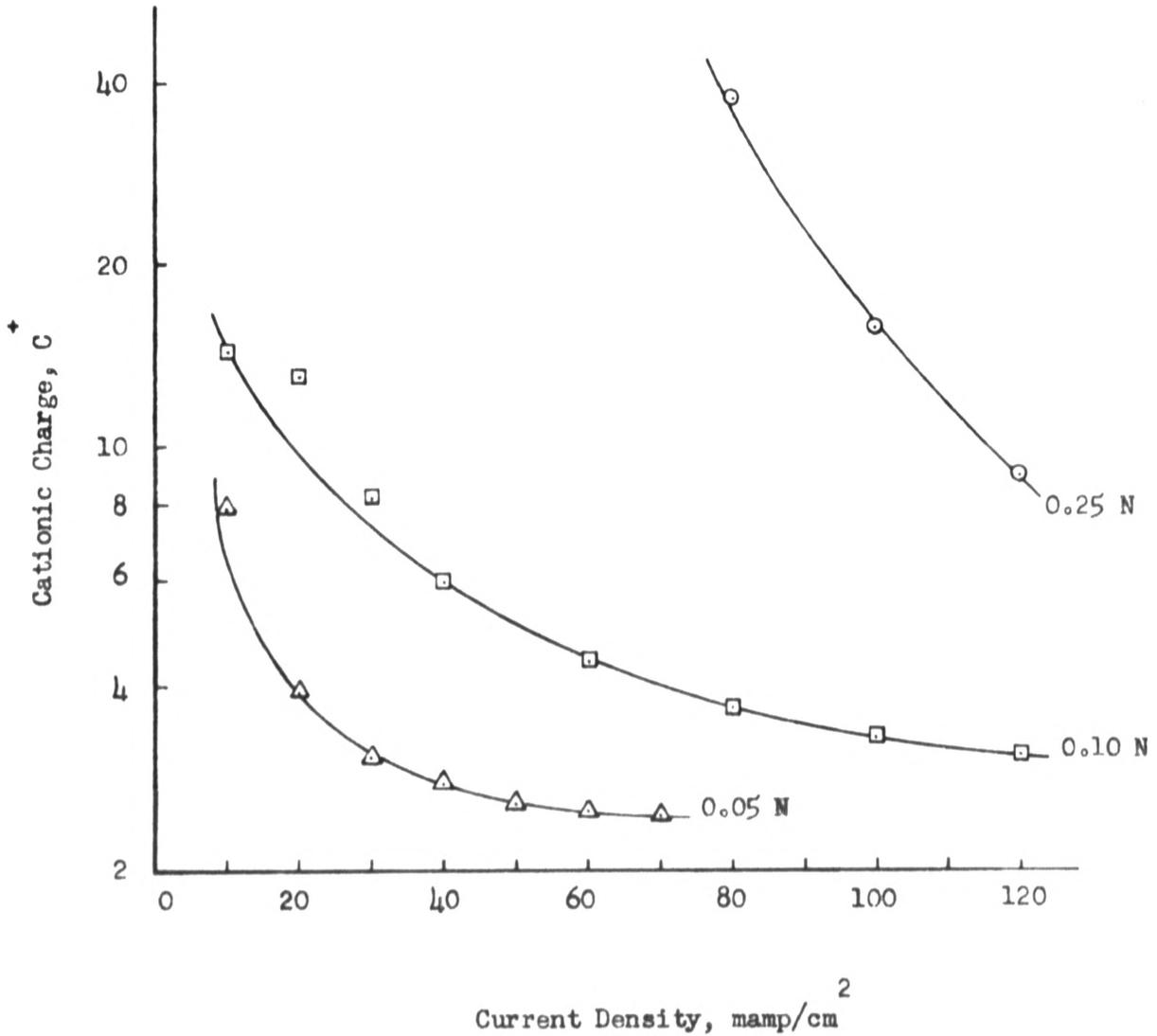
$$= (937.5 + 980.0)/2 = 959 \text{ } \text{mm}^3\text{cm}^{-2}\text{min}^{-1} \text{ (The values of } dv \text{ STP at the 10th and 18th minutes)}$$



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APPARENT CATIONIC CHARGES ON MAGNESIUM
DURING ANODIC DISSOLUTION IN SULFURIC
ACID AT 25°C

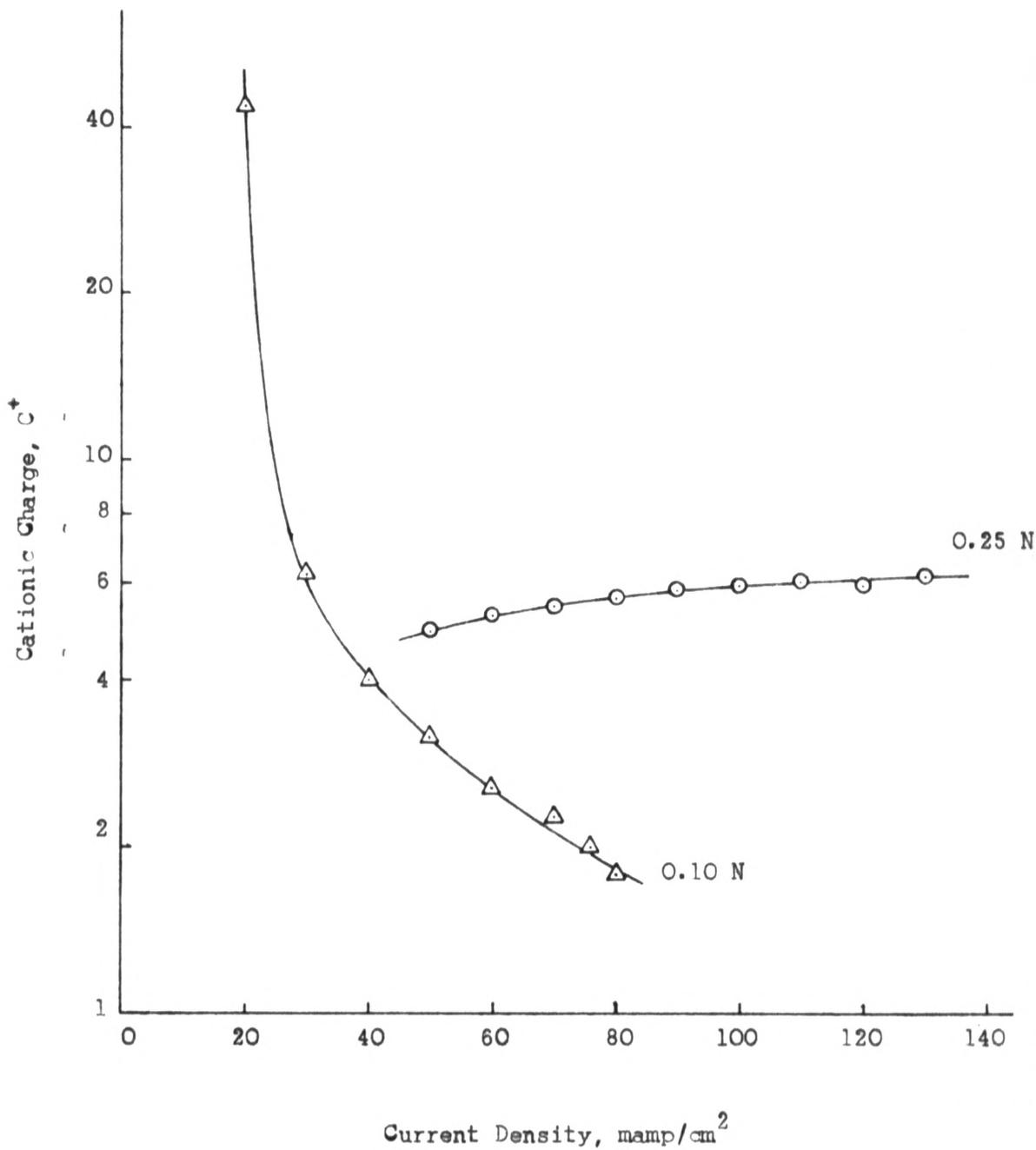
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APPARENT CATIONIC CHARGES ON MAGNESIUM
DURING ANODIC DISSOLUTION IN
PERCHLORIC ACID AT 25°C

SCALE:	DATE	CASE NO:
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APPARENT CATIONIC CHARGES ON MAGNESIUM
DURING ANODIC DISSOLUTION IN
HYDROCHLORIC ACID AT 25°C

SCALE:	DATE	CASE NO:
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V_t = the total hydrogen evolution rate from the anode and the cathode with the current flowing ($I = 111.2$ milliamperes/cm²)

$$= \frac{(980 + 1,151 + 1,108)}{3} = 1,080 \text{ mm}^3\text{cm}^{-2}\text{min}^{-1}$$

(The values of dv STP at the 12th, 14th and 16th minutes)

The calculated values of dv STP, V_1 and V_t are shown in the fourth, fifth, and the sixth columns of the table from which the data were taken. The values of V_1 and V_t so calculated are plotted against the corresponding I in Figures 9 through 18.

Calculation of Δ . The difference effect expressed in $\text{mm}^3\text{cm}^{-2}\text{min}^{-1}$ is calculated by the equation:

$$\Delta = V_1 + 6.97I - V_t \quad (\text{Equation 24, page 62})$$

The values of V_1 and V_t are taken from the plots since the individual experimental values are not used. From Figure 10, at a current density of 50 mamp/cm², the values of V_1 and V_t are 892 and 1,035 $\text{mm}^3\text{cm}^{-2}\text{min}^{-1}$, respectively. Substituting these values

$$\Delta = 892 + 348.5 - 1,035 = 205.5 \text{ mm}^3\text{cm}^{-2}\text{min}^{-1}$$

This value of Δ is shown in Table X for 0.25 N HCl.

The Δ values at other current densities were calculated in the same manner.

Calculation of C^+ . From page 64 the apparent cationic charge is calculated by the equation:

$$C^+ = n_m \frac{11.207 I}{1,608.2(V_t - V_1)} \quad (25)$$

But

$$\Delta = V_1 + 6.97 I - V_t$$

Therefore, rewriting equation (25):

$$C^+ = n_m \frac{6.97 I}{6.97 I - \Delta} \quad (26)$$

This equation was used to calculate the apparent cationic charge on the magnesium ions during the anodic dissolution. From Figure 10, at a current density of 50 mamp/cm², the value of Δ is about 206 mm³cm⁻²min⁻¹.

Substituting these values in equation (26):

$$C^+ = \frac{(2)(6.97)(50)}{(6.97)(50) - 206} = 4.9$$

This value of cationic charge is shown in Table X for 0.25 N HCl. The method of calculation is similar at other current densities and is the same for other acids used.

If $\Delta = KI$ had been substituted in equation (26), the following expression could be obtained:

$$C^+ = n_m \frac{6.97}{6.97 - K} \quad (27)$$

This shows that for a constant value of K as has been found in several instances (with Al, Ti, Zr, and Hf), normal valency ions are formed only if K is zero, i.e.,

when there is no difference effect. When there is a difference effect, $C^+ \rightarrow n_m$ only when K becomes small (no polarization). If as in this case $\Delta \neq KI$, then C^+ varies with the relative magnitude of V_t and V_1 . It will only approach normal valencies when V_t and V_1 are far apart and will become infinite when V_t and V_1 are close together. Since K was not constant for this study, then the valencies of the magnesium ions were calculated using the equation involving Δ values (above equation 26).

4. Electrolysis in Aqueous Solutions Using a Magnesium Anode.

Electrolysis in Aqueous Salt Solution. During the anodic dissolution of magnesium metal in aqueous solutions, it has been reported that a black corrosion product is given off from the magnesium anode⁽¹⁴⁾. Qualitative studies were carried out to produce the black deposit and analyse it for the possible presence of magnesium chunks. The electrolysis was carried out with a magnesium anode and a platinum cathode in approximately three per cent NaCl solution. The current was varied from 250 to 300 milliamperes per square centimeter of surface area. The electrolyte was maintained at a low temperature during the electrolysis by immersing the reaction beaker in ice water.

This was to reduce the possible reaction of any magnesium chunks formed with water.

A black corrosion product began coming off the magnesium anode immediately after starting the electrolysis. While the products were settling, the solution began to show a white turbidity. The electrolysis was stopped when the turbidity became heavy. The black corrosion product was washed several times with ice water to remove the salt solution. The product was next washed several times with cold ethanol (95 per cent) to remove the last traces of water and then dried at room temperature. Upon drying, some of the product turned white, while some retained its black color for several hours. This product was observed under a microscope at 1430 magnification. A multitude of bright metallic particles were observed mixed with the white corrosion product. The size of these particles varied approximately from 7×10^{-5} mm to 7×10^{-4} mm. The accompanying photomicrograph (Figure 22, page 77) shows these metallic particles in the corrosion product. The corrosion product evolved minute gas bubbles (probably hydrogen) when placed in fresh acid. As another means of identification, the darkest flakes were picked from the corrosion product and subjected to x-ray analysis. The analysis yielded diffraction lines belonging to $Mg(OH)_2$ and two of the strongest

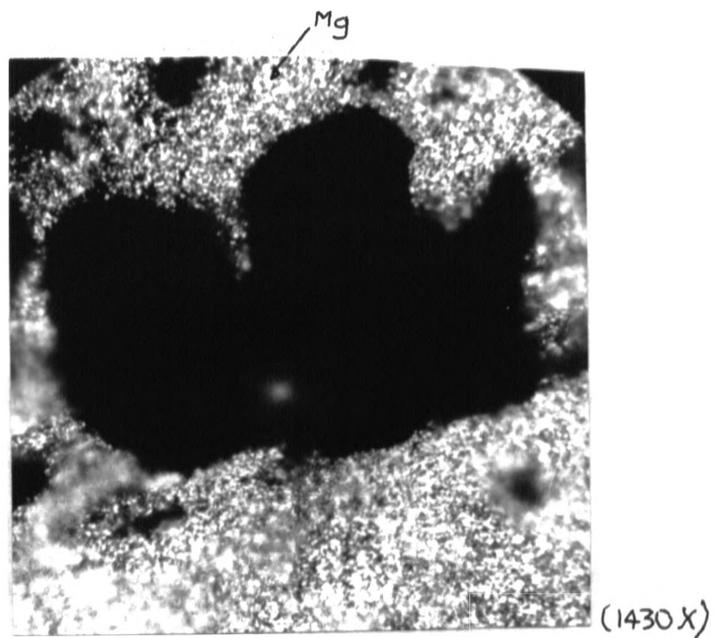


Figure 22. The Magnesium Chunks that Appear
During the Anodic Dissolution of Magnesium
in Three per cent Sodium Chloride Solution

lines of metallic magnesium. These strongest lines correspond to those of pure magnesium metal having the relative intensities of 100 and 41. The former is very weak although sharp. The latter is barely visible. The third strong line of pure magnesium with relative intensity of 20 and all other lines which are lower in intensities are missing. It is thought that the third strong line of magnesium could not be obtained due to the small quantity of magnesium present, the small size of the particles, and a very thin hydroxide coating which was probably formed on the particles. A hazy background also appeared on the film together with the broad lines of the hydroxide and metal. The background probably aggravated the appearance of other weaker lines of magnesium.

Electrolysis in Hydrochloric Acid. The electrolysis in hydrochloric acid was carried out as described above. The concentration of the acid employed was approximately 0.05 N.

The magnesium anode was allowed to dissolve freely in the electrolyte with the external circuit switch open. After a few minutes, the circuit was closed. The bubbles of hydrogen gas began to develop immediately upon the platinum electrode. Also, the magnesium electrode developed a dark coating as seen through the solution. While the current was flowing, dark flakes were coming off the anode.

These flakes turned white on settling. The quantity of electricity passed through the solution was about 200 milliamperes per square centimeter of surface area as recorded on the milliammeter. No dark corrosion product could be obtained for analysis.

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 acids and salts.

Free Dissolution of Magnesium in Acids

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



Free dissolution of magnesium in hydrochloric, perchloric, and sulfuric acids was studied over a temperature range of 5°C to 45°C and a concentration range of 0.05 N to 0.64 N. The reaction rate was found to be directly proportional to the acid concentration up to 0.25 N (0.32 N in HClO_4) at all the temperatures investigated, and resulted in first order reaction with respect to the acid concentration.

The log-log plots of dissolution rate versus acid concentration showed that the dissolution rate deviates from linearity at higher acid concentration (above 0.25 N) and with increasing reaction temperature. Coates⁽¹⁾ has determined these curves for hydrochloric acid concentrations up

to 0.50 N without employing external agitation. He found a similar deviation and attributed the increase in slope to heating effects. Roald and Beck⁽¹⁷⁾ 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 action of the bubbles increase, thereby possibly removing the reaction products faster than usually. However, it is possible that high dissolution rates might be caused also by the presence of a porous film (possibly that of $Mg(OH)_2$) on the surface of metal which could be more soluble at higher acid concentrations.

In the present studies at 25°C, the hydrogen ion concentration in sulfuric, hydrochloric, and perchloric acids was calculated from the per cent dissociation values available in the literature and plotted against the hydrogen evolution rates (log-log plots). It was found that in sulfuric and hydrochloric acids, the hydrogen evolution rates are the same at the same hydrogen ion concentration. However, for the same hydrogen ion concentration in perchloric acid the rates are relatively lower. These results are in accord with those reported in literature by Kilpatrick and Rushton⁽⁷⁾. The lower rate in perchloric acid might be due to the manner in which the hydrogen ion concentrations were obtained at low concentrations (see

page 31). A lower value of the diffusion coefficient in perchloric acid could also reduce the rate in this acid, as well as an incomplete removal of the surface film, or an absorption of the perchlorate ion on the metal surface. In general, the rate expression in sulfuric and hydrochloric acids may be expressed as

$$R = k (H^+) \quad (29)$$

where, R is the rate in $\text{mm}^3 \text{cm}^{-2} \text{min}^{-1}$, and H^+ is the concentration of hydrogen ions in equiv./liter.

The effect of temperature on the dissolution rates yielded activation energies in sulfuric and hydrochloric acids of 3.7 ± 0.1 kilocalories and 3.6 ± 0.3 kilocalories respectively, whereas that in perchloric acid of 4.4 ± 0.3 kilocalories. The very close values of activation energies in sulfuric and hydrochloric acids indicate that there may be a similar mechanism of reaction in these two acids.

The main characteristics of a diffusionally controlled reactions are: (1) the reaction is first order, (2) the activation energy is about 4.6 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 the accumulation of reaction products during the initial stages⁽¹³⁾. The results of dissolution rate measurements in perchloric, sulfuric, and hydrochloric acids

are in general agreement with the theory of diffusion controlled reactions. The low values of activation energies in sulfuric and hydrochloric acids as compared to that in the perchloric acid indicate that in the latter case there may be a slightly higher resistance to the diffusion of hydrogen ions (or other reactants) to or from the surface of the metal. This higher resistance in perchloric acid could be offered by a thin surface film on the metal as mentioned previously.

It is suggested that for the conditions of this study, the rate of hydrogen evolution is dependent upon the diffusion of hydrogen ions to the surface of the metal as also proposed by Kilpatrick and Rushton⁽⁷⁾ and Roald and Beck⁽¹⁷⁾. Thus, the actual reaction taking place at the surface of magnesium can be expressed by the equations:



followed by



The first step of the reaction is of electrochemical 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 evolve hydrogen gas. The contribution to the rate by a chemical reaction taking place at the

surface should be very small because the quantity of unionized acid molecules is very small compared to the hydrogen ion concentration in acid solutions employed. (The direct reaction of an acid molecule with the metal resulting in hydrogen evolution is a characteristic of a chemical reaction.)

Anodic Dissolution of Magnesium in Acids and Salt

When a metal dissolves anodically in an aqueous solution either by an external or an internal current, the self-dissolution rate may be reduced or increased depending upon the corroding solution. In most aqueous salt solutions, this self-dissolution rate is found to increase with current density thereby resulting in what is called the "negative" difference effect. In most acid solutions, the self-dissolution rate is observed to decrease⁽²¹⁾ thereby resulting in the "positive" difference effect. In the latter case, the decrease in the self-dissolution rate is attributed to polarization of the local anodes by the current.

Difference effect studies were carried out with magnesium in perchloric, sulfuric, and hydrochloric acids at 25°C over a concentration range of 0.05 N to 0.50 N. The difference effect values were not calculated by using the individual experimental values. Instead, a smooth curve was drawn

through the points representing the self-dissolution rate V_1 and total hydrogen evolution rates V_t (under anodic conditions) to obtain the average values of these rates. This was done to compensate for the scatter in the data obtained. This method gave difference effect values which showed a definite trend when plotted against the current densities. At high current densities and low acid concentrations, the difference effect values showed a pronounced deviation from linearity. Thus, in sulfuric acid (Figures 15, 16, 17 and 18) at 0.50 N, the departure from linearity occurs at 80 milliamperes whereas in 0.25 N it occurs at about 40 milliamperes. At still lower acid concentration, this departure from linearity is more pronounced, and occurs at about 5 milliamperes in 0.10 N and the slope of the curve is almost completely reversed in 0.05 N sulfuric acid. Assuming that the dissolution rate due to local action does not change while the current is passing, the cationic charges with which magnesium ions entered the solution were calculated using the respective equation (see page 64).

The calculated cationic charges vary from infinity at low current density to approximately two at high current density. The very fact that such large values of cationic charges are calculated show the invalidity of the

assumption that the self-dissolution rate due to local actions remain unchanged under anodic conditions. As such the calculated valencies are only apparent resulting because of false assumptions.

The results of difference effect studies showed that the positive difference effect results in most circumstances on magnesium under anodic conditions, i.e., the self-dissolution rate of the anode is decreased on passing the anodic current. Also, at high current densities in aqueous solutions, chunks of metal originate from the anode in the reaction solution.

The difference effect studies on metals such as titanium and aluminum^(20,21) have shown that Δ is directly proportional to I and is nearly independent of acid concentration. It was shown that the difference effect is caused by the polarization of the local anodes, the extent of which is given by the value of the proportionality constant K and by I . As such the extent of polarizability of the dissolving metal is constant in absence of any complications. In the case of magnesium, if it is considered that the extent of polarization remains constant, the deviation from linearity between Δ and I is caused by some other effects. One of these effects may be the removal of a thin or very thin film from the surface. The removal of this

film definitely seems to accelerate the corrosion due to local actions, thus lowering the Δ values. Another factor which may cause one of these effects is the dispersion of the magnesium anode in the form of microscopic chunks. That this is happening is supported by the evidence that chunks of magnesium do result from the electrolysis in aqueous solutions at high current densities. The magnesium chunks were actually found to be present in aqueous salt solutions and they were observed on the anode during the electrolysis in dilute hydrochloric acid. In the latter case, the chunks dissolved rapidly in the acid solution when the external current was cut off. This indicated that in the difference effect studies at higher current densities, chunks may be present on the anode but are not observable because as soon as the current is turned off, they enter the solution. The dislodgement of chunks is probably caused by the high current density affecting the grain boundaries where the impurities are usually aggregated. Thus, under the positive difference effect as long as the Δ curve shows linearity with I , the extent of polarization of local anodes (caused by a passivating film on anode) remains constant, i.e., the self-dissolution rate V_2 under anodic conditions decreases in proportion to current density. When the curve begins to deviate from linearity, but the Δ values rise and reach a maximum value, it seems probable that the

passivating film on the anode starts to come off allowing the self-dissolution rate V_2 to increase slightly but not in proportion with the current density. At higher current densities when the Δ values begin to decrease with I , the dissolution of the anode by chunk formation and by removal of a passivating film becomes effective, thereby rapidly increasing V_2 which is still less than V_1 (the dissolution rate when no current is passing the anode) to result in a 'positive' difference effect ($\Delta = V_1 - V_2$). As the current density increases, more and more chunks leave the anode until the self-dissolution rate V_2 reaches a value equal to V_1 resulting in zero Δ effect. Above this current density the dissolution of the anode by chunks formation is much more pronounced giving V_2 values greater than V_1 and thus, resulting in a 'negative' difference effect ($V_2 > V_1$). Thus, a change from a 'positive' to a 'negative' difference effect results from the gradual removal of a passivating film from the anode and by its dissolution by chunk formation. It may be pointed out once more that the magnesium ions could not enter the solution in form of ions of uncommon valency as has been calculated here because this would assume production of cationic charges of very high values. Rather it seems better to assume a change in self-dissolution rate of the anode while an anodic current is passing.

Recommendations

In this study the dissolution rates of magnesium in perchloric acid were found to differ from those in hydrochloric and sulfuric acids at the same hydrogen ion concentrations. A study of the diffusion coefficients of hydrogen ions in these acids might be helpful in determining what factors (if any) influence the reaction.

The dissolution rates in these acids have been found to vary with the concentration of hydrogen ion. As the hydrogen ion concentration is changing during the course of reaction, a method should be developed to follow this changing concentration. A suitable P_H meter might be coupled with the reaction flask, so that P_H of the acid could be recorded simultaneously with the burette reading. A plot of dissolution rates versus the average P_H of the acid might give an additional insight into the reaction kinetics of magnesium in acids.

In the difference effect studies the internal current developed between the Mg-Pt electrodes was employed. It would be interesting to see whether the similar effects are more pronounced when an external source of current is employed through a magnesium anode.

Further studies should be conducted to measure the dissolution potential of magnesium in these acids. Since the

difference effect values have been found to vary with the current density such a variation might also exist in the dissolution potentials.

Limitations

Reduction Products. During the difference effect studies it was assumed that the reduction product from the anode as well as cathode was hydrogen gas. However, it is possible that gases other than hydrogen are being evolved. Thus, in the electrolysis of hydrochloric acid the chloride ions on losing their charge at the anode might combine with magnesium to form magnesium chloride or combine with another chlorine atom to form molecular chlorine gas. Thus, the analysis of reduction products could be useful in determining the actual quantity of hydrogen gas evolved from the anode.

Sample Area. The surface area of magnesium sample exposed for the reaction was measured by means of a micrometer. This apparent area was assumed to be the actual area in the rate measurements. However, as the sample becomes corroded during the reaction, the actual area might be changing from time to time.

Distribution of Impurities in Sample. The dissolution of magnesium in strong acids is of electrochemical nature,

depending upon the distribution of impurities. Uneven distribution of impurities might be giving the fluctuation in dissolution rates, although the average rates appear to remain constant.

V. SUMMARY AND CONCLUSIONS

The purpose of the present studies was to investigate the chemical or electrochemical nature of magnesium during free dissolution in strong acids. It was also aimed to see whether magnesium might be entering the solution with valencies other than two during the anodic dissolution.

Free dissolution of magnesium was studied in hydrochloric, perchloric, and sulfuric 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. The concentration of the acids was varied from 0.05 to 0.62 N. The temperature was varied from 5° to 45.2°C. This led to the following results:

- (1) The reaction of magnesium in sulfuric and hydrochloric acids obeyed a first order reaction kinetics with respect to hydrogen ion concentration for the acid concentration range of 0.05 to 0.51 N. In perchloric acid the first order kinetics with respect to hydrogen ion concentration extended up to 0.32 N HClO_4 . Above these concentrations, the reaction rates increased exponentially.
- (2) The energies of activation in hydrochloric and perchloric acids were same within the experimental

errors. It was 3.7 kilocalories in sulfuric acid and 3.6 kilocalories in hydrochloric acid. In perchloric acid, the activation energy was 4.4 kilocalories.

- (3) The reaction proper taking place at the surface of the metal is as follows:



It is thus concluded that the reaction of magnesium in hydrochloric, perchloric, and sulfuric acids is diffusionally controlled and that it is of electrochemical nature.

Difference effect studies were carried out on magnesium anode at 25°C. The acids employed were hydrochloric, perchloric, and sulfuric acids. The concentration of each acid was varied from 0.05 to 0.50 N. A magnesium anode of one square centimeter surface area was employed. The hydrogen evolution rates were compared with and without the anodic current passing giving difference effect values. The apparent cationic charges with which magnesium ions entered the solution under anodic conditions were also calculated. This led to the following:

- (1) A positive difference effect was observed in most circumstances under anodic conditions. A change to negative difference effect resulted at high current densities and low acid concentrations.

- (2) At high current densities dissolution by microscopic chunks and by removal of a passivating film controlled the self-dissolution rates on magnesium anode. A change from positive to negative difference effect resulted because of these two effects.
- (3) The large values of cationic charges on magnesium ions resulted from the false assumption that the self-dissolution rate of magnesium anode did not change when the current was passing.

On the basis of above, it is concluded that the normal valency of magnesium ions does not change under the anodic conditions. Rather, the self-dissolution rates are affected under these conditions. A positive or negative difference effect results depending upon the ease with which a passivating film on the anode is removed, and the ease with which the chunks can come off the anode.

VI. APPENDIX

Materials

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

1. Acid, Hydrochloric. Reagent grade, meets ACS specifications. Allied Chemical Corporation, New York, N.Y.

2. Acid, Perchloric. 60 per cent, Reagent grade, meets ACS specifications. Allied Chemical Corporation, New York, N.Y.

3. Acid, Sulfuric. Reagent grade, meets ACS specifications. Allied Chemical Corporation, New York, N.Y.

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

TABLE XIII

Dissolution of Mg Metal in 0.05 N HCl at 5°C

Time	T=32.1°C P=736.0 mm Hg		T=33.3°C P=734.8 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	6.0	-	6.0	-
20	7.9	1.558	6.8	0.650
28	10.3	1.968	9.0	1.787
36	12.8	2.050	11.4	1.949*
44	15.2	1.968*	13.9	2.030*
52	17.6	1.968*	16.2	1.868*
60	19.8	1.804*	18.4	1.786*
68	22.0	1.804*	20.6	1.786*
76	24.3	1.886*	22.9	1.868*
84	26.6	1.886*	25.2	1.868*
92	28.7	1.722	27.4	1.786*
100	31.0	1.886	29.5	1.705
Ave. Rate mm ³ /Min.		235.7		233.5

*Values averaged to get average maximum rate.

TABLE XIV

Dissolution of Mg Metal in 0.1 N HCl at 5°C

Time	T=31.0°C P=738.3 mm Hg		T=32.6°C P=738.0 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min.	ml	ml	ml	ml
0	0.0	-	0.0	-
10	1.6	1.325	1.5	1.230
15	3.9	1.905	4.2	2.213
20	6.6	2.236	7.4	2.623
25	9.2	2.153*	10.2	2.295
30	11.8	2.153*	13.0	2.295*
35	14.4	2.153*	15.9	2.377*
40	17.0	2.153*	18.9	2.459*
45	19.2	1.822*	21.8	2.377*
50	21.6	1.988*	24.7	2.377*
55	24.1	2.071*	27.5	2.295*
60			30.2	2.213
65			33.0	2.295
Ave. Rate mm ³ /Min.		418.3		472.6

*Values averaged to get average maximum rate.

TABLE XV

Dissolution of Mg Metal in 0.25 N HCl at 5°C

Time	T=30.8°C P=739.2 mm Hg		T=31.0°C P=738.7 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
3	2.0	1.661	1.8	1.492
6	4.8	2.325	4.6	2.320
9	8.1	2.574	8.0	2.818
12	12.0	3.238*	11.8	3.149*
15	16.3	3.570*	15.5	3.066*
18	19.9	2.989*	19.2	3.066*
21	23.6	3.072*	22.9	3.066*
24	27.3	3.072*	26.8	3.232*
27	31.2	3.238*	30.5	3.066*
30	35.0	3.155*	34.2	3.066*
33	38.3	2.740	38.0	3.149*
36	41.7	2.823	41.8	3.149
Ave. Rate mm ³ /Min.		1,063.6		1,035.9

*Values averaged to get average maximum rate.

TABLE XVI

Dissolution of Mg Metal in 0.5 N HCl at 5°C

T=30.0°C P=736.3 mm Hg			T=30.0°C P=736.4 mm Hg		
Time	Vol	dvSTP	Time	Vol	dvSTP
Min	ml	ml	Min	ml	ml
0	0.0	-	0	0.0	-
1	2.0	1.662	2	4.2	3.491
2	4.0	1.662	4	8.6	3.657
3	6.0	1.662	6	13.3	3.906
4	8.1	1.745	8	18.2	4.072
5	10.3	1.828	10	23.0	3.989
6	12.5	1.828	12	28.0	4.156*
7	14.7	1.828	14	33.2	4.322*
8	17.0	1.911	16	38.6	4.488*
9	19.3	1.911	18	44.4	4.820*
10	21.6	1.911	20	49.4	4.488*
11	23.8	1.828	22	55.3	4.488*
12	26.1	1.911	24	60.3	4.156
13	28.4	1.911	26	65.5	4.322
14	30.8	1.994			
15	33.3	2.078			
16	35.8	2.078			
17	38.2	1.994			
18	40.6	1.994			
19	43.0	1.994			
20	45.4	1.994*			
21	47.9	2.078*			
22	50.4	2.078*			
23	52.9	2.078*			
24	55.4	2.078*			
25	57.9	2.078*			
Ave. Rate mm ³ /Min:					
		2,063.6			2,230.1

*Values averaged to get average maximum rate.

TABLE XVII

Dissolution of Mg Metal in 0.05 N HCl at 15°C

T=31.5°C P=733.3 mm Hg			T=28.7°C P=736.3 mm Hg		
Time	Vol	dvSTP	Time	Vol	dvSTP
Min	ml	ml	Min	ml	ml
0	0.0	-	0	0.0	-
15	2.0	1.640	10	2.0	1.661
23	4.4	1.968*	18	4.6	2.159
31	7.0	2.132*	26	7.4	2.325*
39	9.9	2.378*	34	10.0	2.159*
47	12.1	1.804	42	12.6	2.159*
55	14.5	1.968*	50	15.0	1.993*
63	17.2	2.214*	58	17.7	2.242*
71	19.8	2.132*	66	20.3	2.159*
79	21.9	1.722*	74	22.7	1.993
87	24.3	1.768*	82	24.8	1.744
95	26.4	1.722*			
Ave. Rate mm ³ /Min.		250.0			271.6

*Values averaged to get average maximum rate.

TABLE XVIII

Dissolution of Mg Metal in 0.1 N HCl at 15°C

T=30.2°C P=731.1 mm Hg			T=29.7°C P=736.3 mm Hg		
Time	Vol	dvSTP	Time	Vol	dvSTP
Min	ml	ml	Min	ml	ml
0	0.0	-	0	0.0	-
6	1.7	1.401	5	1.0	0.833
12	5.5	3.131	10	4.0	2.498*
18	9.5	3.296	15	7.4	2.831*
24	13.3	3.131	20	10.2	2.331*
30	17.7	3.460*	25	13.4	2.664*
36	21.3	3.131*	30	16.2	2.331*
42	25.0	3.048*	35	19.1	2.414*
48	28.5	2.884*	40	22.8	3.080
54	32.2	3.048*	45	25.9	2.581
60	35.8	2.966*	50	29.0	2.581
66	39.2	2.801	55	31.9	2.414
72	43.0	3.131	60	34.6	2.248
Ave. Rate mm ³ /Min.		514.9			502.3

*Values averaged to get average maximum rate.

TABLE XIX

Dissolution of Mg Metal in 0.25 N HCl at 15°C

Time	T=31.3°C P=731.6 mm Hg		T=29.3°C P=731.0 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
2	1.9	1.556	1.9	1.574
4	4.6	2.211	4.0	1.739
6	7.4	2.293	6.4	1.988
8	10.3	2.375	9.2	2.319
10	13.7	2.784	12.1	2.402*
12	17.1	2.784	15.2	2.568*
14	20.3	2.620*	18.2	2.485*
16	23.4	2.538*	21.0	2.319*
18	26.6	2.620*	24.0	2.485*
20	29.8	2.620*	26.9	2.402*
22	33.1	2.702*	29.7	2.319*
24	36.3	2.620*	32.7	2.485*
26	39.6	2.702*	35.4	2.236
28	42.7	2.538*	38.3	2.402
30	45.5	2.293		
Ave. Rate mm ³ /Min.		1,310.0		1,216.5

*Values averaged to get average maximum rate.

TABLE XX

Dissolution of Mg Metal in 0.5 N HCl at 15°C

Time	T=30.7°C P=732.5 mm Hg		T=31.4°C P=732.3 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
1	3.2	2.635	3.2	2.621
2	6.6	2.800	6.3	2.539
3	9.5	2.388	9.7	2.785
4	13.3	3.130	13.3	2.949
5	16.5	2.883	16.7	2.785
6	20.2	3.047	19.7	2.457
7	23.6	2.800*	23.2	2.867
8	26.9	2.718*	26.6	2.785*
9	30.2	2.718*	30.0	2.785*
10	33.6	2.800*	33.4	2.785*
11	37.0	2.800*	36.8	2.785*
12	40.4	2.800*	40.2	2.785*
13	43.9	2.883*	43.6	2.785*
14	47.4	2.883*	46.9	2.703
15	50.9	2.883		
16	54.3	2.800		
Ave. Rate mm ³ /Min.		2,800	2,785	

*Values averaged to get average maximum rate.

TABLE XXI

Dissolution of Mg Metal in 0.05 N HCl at 25°C

Time	T=29.0°C P=737.9 mm Hg		T=30.2°C P=737.5 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
8	1.7	1.424	2.0	1.663
16	4.8	2.597*	5.7	3.076
24	7.9	2.597*	9.1	2.826
32	11.2	2.765*	12.7	2.993
40	14.2	2.513*	15.8	2.577*
48	17.2	2.513*	19.1	2.577*
56	20.4	2.681*	22.2	2.577*
64	23.2	2.346	25.3	2.577*
72	26.1	2.430	28.4	2.577*
80	28.9	2.346	31.6	2.660*
88			34.8	2.660
96			37.9	2.577
Ave. Rate mm ³ /Min.		326.4		323.9

*Values averaged to get average maximum rate.

TABLE XXII

Dissolution of Mg Metal in 0.1 N HCl at 25°C

Time	T=33.5°C P=736.8 mm Hg		T=30.2°C P=737.7 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
4	1.8	1.464	2.5	2.079
8	5.0	2.603	5.9	2.827
12	8.4	2.766*	9.4	2.911*
16	11.8	2.766*	12.7	2.744*
20	15.2	2.766*	16.1	2.827*
24	18.6	2.766*	19.4	2.744*
28	21.9	2.684*	22.6	2.661*
32	25.2	2.684*	25.9	2.744*
36	28.4	2.603	29.0	2.578
40	31.8	2.766	32.2	2.661
Ave. Rate mm ³ /Min.		684.6		693.0

*Values averaged to get average maximum rate.

TABLE XXIII

Dissolution of Mg Metal in 0.25 N HCl at 25°C

Time	T=33.0°C P=737.3 mm Hg		T=33.0°C P=737.0 mm Hg	
	Vol	dvSTP	Vol	dvSTP
	ml	ml	ml	ml
0	0.0	-	0.0	-
2	3.5	2.859	3.3	2.694
4	7.2	3.022	7.0	3.020
6	11.2	3.267	11.0	3.265
8	15.4	3.430	15.2	3.429*
10	19.7	3.512*	19.4	3.429*
12	23.9	3.430*	23.6	3.429*
14	28.2	3.512*	27.8	3.429*
16	32.5	3.512*	32.0	3.429*
18	36.8	3.412*	35.9	3.184
20	41.0	3.430*	39.9	3.265
22	45.3	3.512	44.0	3.347
24	49.4	3.349		
Ave. Rate mm ³ /Min.		1,742.3	1,714.3	

*Values averaged to get average maximum rate.

TABLE XXIV

Dissolution of Mg Metal in 0.5 N HCl at 25°C

Time	T=31.9°C P=737.3 mm Hg		T=32.1°C P=737.4 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
1	5.4	4.442	5.4	4.363
2	10.7	4.360	10.8	4.363
3	16.2	4.524*	16.3	4.518
4	21.7	4.524*	21.6	4.354
5	27.1	4.442*	27.0	4.363*
6	32.5	4.442*	32.5	4.518*
7	37.8	4.360*	38.0	4.518*
8	43.4	4.607*	43.5	4.518*
9	48.9	4.524	49.1	4.600*
10	53.1	3.455	54.7	4.600*
11			60.2	4.518
12			65.8	4.600
Ave. Rate mm ³ /Min.		4,483.1	4,519.6	

*Values averaged to get average maximum rate.

TABLE XXV

Dissolution of Mg Metal in 0.05 N HCl at 35°C

Time	T=31.8°C P=734.2 mm Hg		T=29.5°C P=735.3 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
6	2.2	1.805	2.6	2.164
12	5.1	2.544	5.3	2.247
18	7.8	2.216	7.8	2.081
24	10.4	2.134	10.5	2.247
30	13.1	2.216	13.2	2.247
36	15.9	2.298	15.8	2.164
42	18.4	2.052*	18.1	1.914
48	20.9	2.052*	20.7	2.164*
54	23.4	2.052*	23.2	2.081*
60	25.9	2.052*	25.6	1.998*
66	28.3	1.970*	28.0	1.998*
72	30.8	2.052*	30.6	2.164*
78	33.6	2.298	33.0	1.998*
84			35.5	2.081*
Ave. Rate mm ³ /Min.		339.7		344.8

*Values averaged to get average maximum rate.

TABLE XXVI

Dissolution of Mg Metal in 0.1 N HCl at 35°C

Time	T=30.4°C P=732.2 mm Hg		T=31.5°C P=737.8 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
3	2.6	2.143	2.2	1.815
6	5.8	2.637	5.0	2.310
9	9.0	2.637	7.7	2.228*
12	11.9	2.390	10.7	2.475*
15	15.0	2.555	13.6	2.393*
18	18.0	2.473*	16.3	2.228*
21	21.0	2.473*	19.1	2.310*
24	23.8	2.308*	21.8	2.228*
27	26.6	2.308*	24.6	2.310*
30	29.5	2.390*	27.4	2.310*
33	32.3	2.308*	29.9	2.063
36	35.4	2.555*	32.4	2.063
39	38.2	2.308*		
42	41.2	2.473		
Ave. Rate mm ³ /Min.		796.7	770.1	

*Values averaged to get average maximum rate.

TABLE XXVII

Dissolution of Mg Metal in 0.25 N HCl at 35°C

Time	T=33.2°C P=733.9 mm Hg		T=34.3°C P=733.1 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
1	2.3	1.867	2.2	1.771
2	4.7	1.948	4.6	1.932
3	7.1	1.948	7.1	2.012
4	9.6	2.030	9.7	2.093
5	12.0	1.948*	12.4	2.173
6	14.4	1.948*	15.0	2.093*
7	16.7	1.867*	17.6	2.093*
8	19.0	1.867*	20.2	2.093*
9	21.4	1.948*	22.7	2.012*
10	23.7	1.867*	25.2	2.012*
11	26.0	1.867*	27.8	2.093*
12	28.3	1.867*	30.3	2.012*
13	30.6	1.867	32.8	2.012*
14	33.0	1.948	35.4	2.093
Ave. Rate mm ³ /Min.		1,897.5	2,052.3	

*Values averaged to get average maximum rate.

TABLE XXVIII

Dissolution of Mg Metal in 0.5 N HCl at 35°C

Time	T=32.8°C P=733.7 mm Hg		T=32.1°C P=733.9 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0.0	0.0	-	0.0	-
0.5	5.2	4.230	5.2	4.251
1.0	10.5	4.312	10.4	4.251
1.5	15.8	4.312	15.5	4.169
2.0	21.1	4.312	20.5	4.087
2.5	26.2	4.149*	25.5	4.087
3.0	31.3	4.149*	30.6	4.169*
3.5	36.4	4.149*	35.6	4.087*
4.0	41.4	4.068*	40.7	4.169*
4.5	46.5	4.149*	45.8	4.169*
5.0	51.4	3.986*	50.9	4.169*
5.5	56.5	4.149*	56.0	4.169*
6.0	61.5	4.068*	61.0	4.087*
6.5			66.0	4.087*
Ave. Rate mm ³ /Min.		8,217	8,297	

*Values averaged to get average maximum rate.

TABLE XXIX

Dissolution of Mg Metal in 0.05 N HCl at 45°C

Time	T=31.2°C P=735.8 mm Hg		T=32.1°C P=735.1 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
4	2.5	2.073	2.6	2.130
8	4.4	1.575	4.9	1.883
12	6.8	1.990	7.2	1.883
16	8.8	1.658*	9.3	1.720*
20	10.8	1.658*	11.3	1.638*
24	12.5	1.409*	13.4	1.720*
28	14.8	1.907*	15.5	1.720*
32	16.9	1.741*	17.4	1.556*
36	18.9	1.658*	19.6	1.801*
40	20.6	1.409	21.8	1.801*
44	22.6	1.658	23.8	1.638
48	24.6	1.658	25.8	1.638
52			27.7	1.556
Ave. Rate mm ³ /Min.		418		427

*Values averaged to get average maximum rate.

TABLE XXX

Dissolution of Mg Metal in 0.1 N HCl at 45°C

Time	T=28.6°C P=733.9 mm Hg		T=30.1°C P=735.7 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
2	2.7	2.255	2.4	1.992
4	5.2	2.088	5.1	2.240
6	7.6	2.004*	7.6	2.075*
8	10.0	2.004*	10.0	1.992*
10	12.4	2.004*	12.4	1.992*
12	14.7	1.921*	14.7	1.909*
14	17.2	2.088*	17.2	2.075*
16	20.5	1.921*	19.6	1.992*
18	21.7	1.002	21.8	1.826
20	24.4	2.004	24.1	1.909
22			26.4	1.909
Ave. Rate mm ³ /Min.		995.8	1003.0	

*Values averaged to get average maximum rate.

TABLE XXXI

Dissolution of Mg Metal in 0.25 N HCl at 45°C

Time	T=28.4°C P=734.8 mm Hg		T=27.6°C P=735.0 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
1	3.6	3.014	3.6	3.029
2	7.1	2.930	7.1	2.945
3	10.7	3.014*	10.8	3.113
4	14.2	2.930*	14.6	3.197
5	17.7	2.930*	18.1	2.945
6	21.3	3.014*	21.4	2.777
7	24.5	2.679*	24.5	2.608
8	28.2	3.097*	27.9	2.861*
9	31.7	2.930	31.3	2.861*
10	35.1	2.846	34.7	2.861*
11	38.3	2.679	38.3	3.029*
12	41.8	2.930	41.7	2.861*
13	45.3	2.930	45.2	2.945*
14	48.6	2.762	48.4	2.692
15	51.9	2.762	51.6	2.692
16			55.1	2.945
17			58.6	2.945
18			61.8	2.692
Ave. Rate mm ³ /Min.		2,944		2,903

*Values averaged to get average maximum rate.

TABLE XXXII

Dissolution of Mg Metal in 0.5 N HCl at 45°C

Time	T=30.0°C P=733.8 mm Hg		T=27.1°C P=734.8 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0.0	0.0	-	0.0	-
0.5	0.0	-	8.1	6.765
1.0	16.0	13.248	16.2	6.765
1.5	24.1	6.707	24.3	6.765
2.0	31.8	6.376*	32.0	6.431*
2.5	39.5	6.376*	39.8	6.515*
3.0	47.3	6.568*	47.6	6.515*
3.5	54.6	6.044*	55.3	6.431*
4.0	62.6	6.624*	62.8	6.264*
4.5	70.0	6.127*	70.4	6.348*
5.0	77.5	6.210*	77.7	6.097
5.5	85.0	6.210*	85.0	6.097
Ave. Rate mm ³ /Min.		12,606.3	12,834.0	

*Values averaged to get average maximum rate.

TABLE XXXIII

Dissolution of Mg in 0.064 N HClO₄ at 5°C

T=30.5°C P=737.7 mm Hg			T=30.4°C P=736.8 mm Hg		
Time	Vol	dvSTP	Time	Vol	dvSTP
Min	ml	ml	Min	ml	ml
0	0.0	-	0	0.0	-
30	1.7	1.411	30	2.7	2.240
42	4.8	2.574	40	5.2	2.074*
52	7.6	2.325	50	7.5	1.908*
62	10.4	2.325	60	10.1	2.157*
72	12.8	1.993*	70	12.6	2.074*
82	15.2	1.993*	80	15.2	2.157*
92	17.9	2.242*	90	17.6	1.991*
102	20.3	1.993*	100	19.8	1.825*
112	22.8	2.076*	110	22.7	2.406*
122	25.1	1.910*	120	24.9	1.825
132	27.5	1.993*	130	27.3	1.991
142	30.2	2.242*	140	29.6	1.908
152	32.5	1.910*			
Ave. Rate mm ³ /Min.		203.9			207.4

*Values averaged to get average maximum rate.

TABLE XXXIV

Dissolution of Mg in 0.13 N HClO₄ at 5°C

T=30.9°C P=736.4 mm Hg			T=31.0°C P=736.2 mm Hg		
Time	Vol	dvSTP	Time	Vol	dvSTP
Min	ml	ml	Min	ml	ml
0	0.0	-	0	0.0	-
16	2.4	1.984	14	2.0	1.652
20	4.4	1.654*	20	5.0	2.477*
24	6.4	1.654*	26	8.0	2.477*
28	8.5	1.736*	32	11.4	2.808*
32	10.9	1.984*	38	14.4	2.477*
36	13.0	1.736*	44	17.6	2.643*
40	14.8	1.488*	50	20.4	2.312*
44	16.8	1.654*	56	23.5	2.560*
48	18.8	1.654*	62	26.5	2.477*
52	20.8	1.654*	68	29.4	2.395*
56	22.7	1.571	74	32.5	2.560*
60	24.6	1.571	80	35.3	2.312
64	26.4	1.488			
Ave. Rate mm ³ /Min.		422.6			419.8

*Values averaged to get average maximum rate.

TABLE XXXV

Dissolution of Mg in 0.32 N HClO₄ at 5°C

Time	T=30.5°C P=737.6 mm Hg		T=30.4°C P=737.4 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
4	2.2	1.826	2.0	1.661
6	4.6	1.992	4.1	1.744
8	7.2	2.158	6.9	2.325*
10	9.8	2.158	9.9	2.491*
12	12.6	2.324*	12.9	2.491*
14	15.2	2.158*	15.7	2.325*
16	18.1	2.407*	18.6	2.408*
18	21.1	2.490*	21.5	2.408*
20	23.7	2.158*	24.5	2.491*
22	26.4	2.241*	27.3	2.325*
24	29.5	2.573*	30.2	2.408
26	32.3	2.324*	33.2	2.491
28	35.18	2.324*	35.9	2.242
30	37.8	2.241*	38.9	2.491
Ave. Rate mm ³ /Min.		1,162		1,203.9

*Values averaged to get average maximum rate.

TABLE XXXVI

Dissolution of Mg in 0.64 N HClO₄ at 5°C

T=30.2°C P=737.0 mm Hg			T=30.0°C P=738.1 mm Hg		
Time	Vol	dvSTP	Time	Vol	dvSTP
Min	ml	ml	Min	ml	ml
0	0.0	-	0	0.0	-
10	14.0	11.631	1	1.9	1.583
11	17.0	2.492	2	4.1	1.833
12	20.1	2.576	3	6.1	1.666
13	23.1	2.492	4	8.6	2.083
14	26.3	2.659*	5	11.1	2.333
15	29.4	2.576*	6	13.9	2.500
16	32.5	2.576*	7	16.9	2.666
17	35.7	2.659*	8	20.1	2.583
18	39.0	2.742*	9	23.2	2.583
19	42.2	2.659*	10	26.3	2.666
20	45.5	2.742*	11	29.5	2.583
21	48.5	2.492*	12	32.6	2.500
22	51.7	2.659*	13	35.6	2.583
23	55.0	2.742*	14	38.7	2.750
24	58.2	2.659	15	42.0	2.750*
			16	45.3	2.750*
			17	48.5	2.666*
			18	51.8	2.750*
			19	55.0	2.666*
			20	58.2	2.666*
			21	61.6	2.833*
			22	64.8	2.666*
			23	68.1	2.750*
			24	71.4	2.750*
Ave. Rate mm ³ /Min.					
2,650.3			2,724.6		

*Values averaged to get average maximum rate.

TABLE XXXVII

Dissolution of Mg in 0.064 N HClO₄ at 15°C

T=31.6°C P=736.9 mm Hg			T=31.0°C P=736.6 mm Hg		
Time	Vol	dvSTP	Time	Vol	dvSTP
Min	ml	ml	Min	ml	ml
0	0.0	-	0	0.0	-
18	2.3	1.894	16	2.8	2.314
26	5.0	2.223*	24	5.7	2.396*
34	7.9	2.388*	32	8.3	2.148*
42	10.5	2.141*	40	11.1	2.314*
50	13.4	2.388*	48	14.1	2.479*
58	16.0	2.141*	56	16.9	2.314*
66	18.9	2.388*	64	19.8	2.396*
74	21.6	2.223*	72	22.9	2.562*
82	24.7	2.553*	80	25.4	2.066*
90	27.8	2.553*	88	28.0	2.148
98	30.6	2.306*	96	30.8	2.314
106	32.8	1.812	104	33.8	2.066
Ave. Rate mm ³ /Min.		291.3			291.8

*Values averaged to get average maximum rate.

TABLE XXXVIII

Dissolution of Mg in 0.13 N HClO₄ at 15°C

T=30.6°C P=731.0 mm Hg			T=30.6°C P=730.3 mm Hg		
Time	Vol	dvSTP	Time	Vol	dvSTP
Min	ml	ml	Min	ml	ml
0	0.0	-	0	0.0	-
8	4.5	3.697	6	2.0	1.642
12	7.6	2.547	10	4.7	2.216
16	10.4	2.300	14	7.5	2.298*
20	13.6	2.629	18	10.4	2.380*
24	16.5	2.383*	22	13.2	2.298*
28	19.4	2.383*	26	16.1	2.380*
32	22.5	2.547*	30	18.8	2.216*
36	25.2	2.218*	34	21.6	2.298*
40	28.0	2.300*	38	24.6	2.462*
44	31.0	2.465*	42	27.2	2.134*
48	33.7	2.218*	46	30.1	2.380*
52	36.4	2.218*	50	33.0	2.380*
Ave. Rate mm ³ /Min.		585.4			580.7

*Values averaged to get average maximum rate.

TABLE XXXIX

Dissolution of Mg in 0.32 N HClO₄ at 15°C

Time	T=27.2°C P=734.0 mm Hg		T=29.9°C P=732.0 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
2	1.9	1.600	1.8	1.488
4	4.6	2.274	4.6	2.314
6	7.9	2.779*	8.1	2.892*
8	11.3	2.863*	11.4	2.727*
10	14.5	2.695*	14.9	2.892*
12	18.1	3.032*	18.6	3.058*
14	21.5	2.863*	22.2	2.975*
16	24.9	2.863*	25.7	2.892*
18	28.2	2.779*	29.3	2.975*
20	31.7	2.947*	32.8	2.892*
22	35.0	2.779*	35.7	2.397
24	38.3	2.779*	39.0	2.727
26	41.9	3.032	42.4	2.810
28	45.0	2.611	45.9	2.892
Ave. Rate mm ³ /Min.		1,418.9		1,456.5

*Values averaged to get average maximum rate.

TABLE XL

Dissolution of Mg in 0.64 N HClO₄ at 15°C

Time	T=31.0°C P=735.1 mm Hg		T=31.2°C P=734.8 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
1	3.9	3.216	4.1	3.375
2	8.1	3.463	8.3	3.457
3	12.2	3.381	12.8	3.704
4	16.8	3.793	17.5	3.869
5	21.5	3.875	22.5	4.116*
6	26.1	3.793	27.4	4.033*
7	31.0	4.040*	32.3	4.033*
8	35.9	4.040*	37.4	4.198*
9	40.9	4.123*	42.5	4.198*
10	45.8	4.040*	47.8	4.362*
11	50.8	4.123*	52.9	4.198*
12	55.8	4.123*	58.0	4.198*
13	60.9	4.205*	63.3	4.280*
14	66.0	4.205*	68.3	4.116*
15	71.2	4.287*	73.6	4.362*
16	76.2	4.040*	78.6	4.116*
Ave. Rate mm ³ /Min.		4,122.5	4,184.1	

*Values averaged to get average maximum rate.

TABLE XLI

Dissolution of Mg Metal in 0.05 N HClO₄ at 25°C

Time	T=30.6°C P=736.5 mm Hg		T=31.0°C P=736.4 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
8	1.2	0.994	1.3	1.074
16	3.8	2.153*	3.9	2.148*
24	6.5	2.236*	6.8	2.395*
32	9.1	2.153*	9.6	2.313*
40	11.9	2.319*	12.3	2.230*
48	14.4	2.071*	15.0	2.230*
56	17.0	2.153*	17.7	2.230*
64	19.6	2.153*	20.3	2.148*
72	22.0	1.988*	22.9	2.148*
80	24.5	2.071*	25.4	2.065*
88	27.1	2.153*	28.0	2.148*
Ave. Rate mm ³ /Min.		268.2		275.7

*Values averaged to get average maximum rate.

TABLE XLII

Dissolution of Mg Metal in 0.1 N HClO₄ at 25°C

Time Min	T=30.2°C P=737.3 mm Hg		T=30.2°C P=737.0 mm Hg	
	Vol ml	dvSTP ml	Vol ml	dvSTP ml
0	0.0	-	0.0	-
4	1.4	1.164	1.4	1.163
8	4.0	2.161	4.2	2.326*
12	6.8	2.327*	6.8	2.160*
16	9.6	2.327*	9.5	2.243*
20	12.3	2.244*	12.3	2.326*
24	15.1	2.327*	14.9	2.160*
28	17.6	2.078*	17.5	2.160*
32	20.4	2.327*	20.3	2.326*
36	23.0	2.161*	22.7	1.994
40	25.6	2.161*	25.0	1.911
44	28.2	2.161*	27.4	1.994
48	30.8	2.161*		
52	33.3	2.078		
Ave. Rate mm ³ /Min.		556.8		560.8

*Values averaged to get average maximum rate.

TABLE XLIII

Dissolution of Mg Metal in 0.25 N HClO₄ at 25°C

Time	T=30.3°C P=735.3 mm Hg		T=29.4°C P=737.0 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
2	2.2	2.733	2.2	1.837
4	5.5	2.899*	5.5	2.755*
6	9.0	2.982*	8.9	2.839*
8	12.6	2.816*	12.5	3.006*
10	16.0	2.899*	16.0	2.922*
12	19.5	2.816*	19.5	2.922*
14	22.9	2.816*	22.9	2.839*
16	26.3	2.816*	26.3	2.839*
18	29.7	2.816*	29.6	2.755*
20	33.1	2.816*	32.7	2.588*
22	36.4	2.733*	36.3	3.006
24	39.8	2.816*	39.6	2.755
Ave. Rate mm ³ /Min.		1,420.5	1,429.8	

*Values averaged to get average maximum rate.

TABLE XLIV

Dissolution of Mg Metal in 0.5 N HClO₄ at 25°C

Time	T=32.0°C P=737.6 mm Hg		T=31.8°C P=737.6 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
1	3.7	3.043	3.7	3.046
2	7.7	3.289	7.8	3.376
3	11.8	3.371	12.1	3.540
4	16.2	3.454	16.5	3.623
5	20.5	3.536	20.7	3.458
6	25.1	3.783	25.1	3.623
7	29.5	3.618	29.7	3.787*
8	34.0	3.700*	34.2	3.705*
9	38.5	3.700*	38.6	3.623*
10	43.1	3.783*	43.1	3.705*
11	47.6	3.700*	47.7	3.787*
12	52.2	3.783*	52.2	3.705*
13	56.7	3.700*	56.7	3.705
14	61.5	3.947	61.2	3.705
15	66.2	3.865		
16	71.9	3.848		
Ave. Rate mm ³ /Min.		3,727.8	3,718.6	

*Values averaged to get average maximum rate.

TABLE XLV

Dissolution of Mg in 0.064 N HClO₄ at 35°C

Time Min	T=30.4°C P=739.5 mm Hg		T=30.2°C P=739.0 mm Hg	
	Vol ml	dvSTP ml	Vol ml	dvSTP ml
0	0.0	-	0.0	-
4	2.3	1.915	1.3	1.083
8	4.6	1.915	3.4	1.750
12	7.1	2.082*	5.6	1.833
16	9.6	2.082*	8.1	2.083*
20	12.1	2.082*	10.6	2.083*
24	14.6	2.082*	13.0	2.000*
28	17.1	2.082*	15.3	1.916*
32	19.4	1.915*	17.7	2.000*
36	21.7	1.915*	19.9	1.833*
40	24.0	1.915*	22.3	2.000*
44	26.4	1.999*	24.5	1.833
48	28.6	1.832*	26.7	1.833
52	31.1	2.082	28.9	1.833
56	33.4	1.915		
Ave. Rate mm ³ /Min.		504.3		497.0

*Values averaged to get average maximum rate.

TABLE XLVI

Dissolution of Mg in 0.13 N HClO₄ at 35°C

Time	T=29.3°C P=738.4 mm Hg		T=30.0°C P=740.0 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
2	2.0	1.677	2.0	1.671
4	4.1	1.758*	4.4	2.005*
6	6.2	1.758*	6.6	1.838*
8	8.4	1.842*	8.8	1.838*
10	10.5	1.758*	11.2	2.005*
12	12.6	1.758*	13.7	2.088*
14	14.8	1.842*	15.9	1.838*
16	17.0	1.842*	18.2	1.921*
18	19.1	1.758*	20.4	1.838*
20	21.2	1.758*	22.6	1.838*
22	23.2	1.675*	24.9	1.921*
24	25.3	1.758	27.1	1.838
Ave. Rate mm ³ /Min.		887.4		956.4

*Values averaged to get average maximum rate.

TABLE XLVII

Dissolution of Mg in 0.32 N HClO₄ at 35°C

Time	T=30.5°C P=738.2 mm Hg		T=28.0°C P=740.4 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
1	2.5	2.077	2.8	2.368
2	5.3	2.326	5.4	2.199
3	8.1	2.326	8.3	2.453*
4	11.0	2.409*	11.1	2.368*
5	14.0	2.492*	13.9	2.368*
6	16.9	2.409*	16.8	2.453*
7	19.9	2.492*	19.6	2.368*
8	22.8	2.409*	22.4	2.368*
9	25.8	2.492*	25.1	2.284*
10	28.7	2.409*	28.0	2.453*
11	31.6	2.409*	30.7	2.284*
12	34.5	2.409*	33.6	2.453*
13	37.4	2.409*	36.5	2.453*
14	40.3	2.409	39.2	2.284*
Ave. Rate mm ³ /Min.		2,434.0		2,382.4

*Values averaged to get average maximum rate.

TABLE XLVIII

Dissolution of Mg Metal in 0.5 N HClO₄ at 35°C

Time	T=33.4°C P=736.3 mm Hg		T=30.1°C P=738.9 mm Hg	
	Vol	dvSTP	Vol	dvSTP
	ml	ml	ml	ml
0	0.0	-	0.0	-
1	5.6	4.557	5.5	4.584
2	11.3	4.639	11.2	4.751
3	17.1	4.720	17.2	5.001*
4	22.9	4.720	22.9	4.751*
5	28.8	4.801*	28.9	5.001*
6	34.7	4.801*	34.8	4.918*
7	40.7	4.883*	40.7	4.918*
8	46.7	4.883*	46.6	4.918*
9	52.7	4.883*	52.7	5.084*
10	58.8	4.964*	58.6	4.918*
11	64.8	4.883*	64.5	4.918*
12	70.8	4.883*	70.4	4.918*
Ave. Rate mm ³ /Min.		4,872.6		4,934.3

*Values averaged to get average maximum rate.

TABLE XLVIII

Dissolution of Mg Metal in 0.5 N HClO₄ at 35°C (con't)

T=31.0°C P=736.6 mm Hg			
Time	Vol	dvSTP	
Min	ml	ml	
0.0	0.0	-	
0.5	2.4	1.983	
1.0	4.4	1.652	
4.0	17.2	10.575	
4.5	20.2	2.479*	
5.0	23.0	2.313*	
5.5	26.0	2.479*	
6.0	28.6	2.148*	
6.5	31.5	2.396*	
7.0	34.3	2.313*	
7.5	37.2	2.396*	
8.0	40.0	2.313*	
8.5	42.9	2.396*	
9.0	46.0	2.561*	
9.5	48.7	2.231*	
10.0	51.5	2.313*	
10.5	54.4	2.396	
11.0	57.3	2.396	
Ave. Rate mm ³ /Min.		4,723.1	

*Values averaged to get average maximum rate.

TABLE II

Dissolution of Mg Metal in 0.64 N HClO₄ at 35°C

Time	T=31.6°C P=738.7 mm Hg		T=30.8°C P=738.6 mm Hg	
	Vol	dvSTP	Vol	dvSTP
	Min	ml	ml	ml
0	0.0	-	0.0	-
1.0	9.6	7.926	10.2	8.462
1.5	14.7	4.211	15.6	4.480
2.0	19.7	4.128	20.9	4.397
2.5	24.8	4.211	26.4	4.563*
3.0	30.0	4.293	31.8	4.480*
3.5	35.3	4.376*	37.4	4.646*
4.0	40.5	4.293*	42.9	4.563*
4.5	45.9	4.458*	48.4	4.563*
5.0	51.3	4.458*	54.0	4.646*
5.5	56.6	4.376*	59.6	4.646*
6.0	62.1	4.541*	65.2	4.646*
6.5	67.6	4.541*	70.8	4.646*
7.0	73.1	4.541*	76.4	4.646*
Ave. Rate mm ³ /Min.		8,895.8		9,208.6

*Values averaged to get average maximum rate.

TABLE L
Dissolution of Mg in 0.064 N HClO₄ at 45°C

Time	T=33.0°C P=736.5 mm Hg		T=33.0°C P=735.7 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
3	2.4	1.958	4.2	3.422
6	4.4	1.631*	7.0	2.281
9	6.3	1.550*	9.6	2.119*
12	8.1	1.468*	12.4	2.282*
15	10.1	1.631*	14.9	2.037*
18	12.0	1.550*	17.7	2.282*
21	14.0	1.631*	20.2	2.037*
24	15.9	1.550*	22.8	2.119*
27	17.8	1.550*	25.4	2.119*
30	19.7	1.550*	28.0	2.119*
33	21.5	1.468*	30.6	2.119*
36	23.4	1.550*	33.0	1.956*
39	25.2	1.468*	35.6	2.119*
42	27.1	1.550*	38.0	1.956
Ave. Rate mm ³ /Min.		516.6	529.6	

*Values averaged to get average maximum rate.

TABLE LI

Dissolution of Mg in 0.13 N HClO₄ at 45°C

Time	T=31.9°C P=737.0 mm Hg		T=31.9°C P=737.3 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
2	3.5	2.877	3.2	2.632
4	6.2	2.220*	6.0	2.303
6	9.1	2.384*	8.7	2.221
8	12.0	2.384*	11.4	2.221
10	14.7	2.220*	14.2	2.303
12	17.4	2.220*	16.8	2.138
14	20.1	2.220*	19.5	2.221
16	22.8	2.220*	22.2	2.221
18	25.6	2.302*	24.8	2.138
20	28.2	2.137*	27.4	2.138
22	31.0	2.302*	30.1	2.221
24	33.7	2.220*	32.6	2.056
26			35.4	2.303
28			38.0	2.138
Ave. Rate mm ³ /Min.		1,128.5		1,100.8

*Values averaged to get average maximum rate.

TABLE LII

Dissolution of Mg in 0.32 N HClO₄ at 45°C

Time	T=31.2°C P=738.0 mm Hg		T=32.0°C P=737.2 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
1	4.3	3.560	4.5	3.698
2	8.6	3.560	8.7	3.451
3	12.8	3.478	13.0	3.533
4	16.9	3.395	17.0	3.287*
5	20.9	3.312*	21.2	3.451*
6	24.8	3.229*	25.1	3.205*
7	28.7	3.229*	29.2	3.369*
8	32.7	3.312*	33.2	3.287*
9	36.6	3.229*	37.1	3.205*
10	40.5	3.229*	41.1	3.287*
11	44.4	3.229*	45.1	3.287*
12	48.4	3.312*	49.1	3.287*
13	52.4	3.312*	53.0	3.205*
14	56.4	3.312*	57.1	3.369*
Ave. Rate mm ³ /Min.		3,270.6		3,294.3

*Values averaged to get average maximum rate.

TABLE LIII

Dissolution of Mg in 0.64 N HClO₄ at 45°C

Time	T=30.9°C P=738.3 mm Hg		T=30.6°C P=738.3 mm Hg	
	Vol	dvSTP	Vol	dvSTP
	ml	ml	ml	ml
0.0	0.0	-	0.0	-
0.5	8.9	7.376	8.6	7.141
1.0	17.8	7.376*	17.5	7.390*
1.5	26.8	7.459*	26.4	7.390*
2.0	35.8	7.459*	35.3	7.390*
2.5	44.6	7.293*	44.4	7.556*
3.0	53.5	7.542*	53.4	7.473*
3.5	62.8	7.708*	62.5	7.556*
4.0	71.6	7.293*	71.5	7.473*
4.5	80.6	7.459*	80.6	7.556*
Ave. Rate mm ³ /Min.		14,897.7		14,945.4

*Values averaged to get average maximum rate.

TABLE LIV

Dissolution of Mg Metal in 0.05 N H₂SO₄ at 5°C

		T=29.0°C P=736.9 mm Hg	
Time	Vol	dvSTP	
Min	ml	ml	
0	0.0	-	
30	0.0	-	
40	1.5	1.255	
50	3.4	1.590*	
60	5.3	1.590*	
70	7.3	1.673*	
80	9.4	1.757*	
90	11.4	1.673*	
100	13.5	1.757*	
110	15.2	1.422*	
120	17.3	1.757*	
Ave. Rate mm ³ /Min.		165.2	

*Values averaged to get average maximum rate.

TABLE LIV

Dissolution of Mg Metal in 0.05 N H₂SO₄ at 5°C (con't)

T=33.1°C P=737.3 mm Hg			T=33.6°C P=736.0 mm Hg		
Time	Vol	dvSTP	Time	Vol	dvSTP
Min	ml	ml	Min	ml	ml
0	0.0	-	0	0.0	-
28	0.0	-	30	0.9	0.731
37	2.1	1.714*	39	2.5	1.300*
46	3.9	1.469*	48	4.1	1.300*
55	5.7	1.469*	57	6.2	1.705*
64	7.1	1.143*	66	7.8	1.300*
73	9.0	1.551*	75	9.7	1.542*
82	11.0	1.632*	84	11.3	1.300*
91	12.9	1.551*			
Ave. Rate mm ³ /Min.		167.1			156.4

*Values averaged to get average maximum rate.

TABLE LV

Dissolution of Mg Metal in 0.1 N H₂SO₄ at 5°C

Time	Run No. 1 T=31.5°C P=738.2 mm Hg		Run No. 2 T=32.0°C P=736.8 mm Hg		Run No. 3 T=31.3°C P=737.3 mm Hg	
	Vol	dvSTP	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml	ml	ml
0	0.0	-	0.0	-	0.0	-
8	0.5	0.413	0.1	0.082	0.4	0.330
16	3.6	2.559	2.2	1.725	3.0	2.147
24	6.5	2.394	5.6	2.792*	7.4	3.633
32	10.2	3.054	8.8	2.628*	10.5	2.559
40	12.9	2.229	12.1	2.710*	14.0	2.890*
48	16.2	2.724*	15.3	2.628*	17.5	2.890*
56	19.3	2.559*	18.8	2.875*	20.9	2.807*
64	22.7	2.806*	21.9	2.546*	24.3	2.807*
72	26.1	2.806*	24.7	2.300	27.6	2.724*
80	29.3	2.641*	27.6	2.382	30.8	2.642*
88	32.5	2.641*	30.6	2.464	33.8	2.477
96	35.9	2.806*	33.7	2.546	36.8	2.477
104	38.7	2.311			40.6	3.137
112	41.1	1.981			43.9	2.724
120					47.2	2.724
Ave. Rate mm ³ /Min.		339.9		337.1		349.2

*Values averaged to get average maximum rate.

TABLE LVI

Dissolution of Mg Metal in 0.25 N H₂SO₄ at 5°C

Time	T=31.4°C P=738.0 mm Hg		T=31.0°C P=738.0 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
4	1.6	1.321	1.3	1.076
8	4.5	2.395	4.2	2.401
12	8.6	3.385	7.9	3.063
16	12.9	3.551*	12.0	3.395
20	17.2	3.551*	16.1	3.395*
24	21.8	3.798*	20.1	3.312*
28	26.2	3.634*	24.4	3.560*
32	30.5	3.551*	28.1	3.063*
36	35.2	3.881*	31.9	3.146*
40	39.2	3.303*	35.7	3.146*
44	43.5	3.551*	39.6	3.229*
48			43.8	3.477*
52			46.6	2.318
56			50.5	3.229
60			54.3	3.146
Ave. Rate mm ³ /Min		900.6		822.7

*Values averaged to get average maximum rate.

TABLE LVII

Dissolution of Mg Metal in 0.51 N H₂SO₄ at 5°C

Time	Run No. 1 T=31.2°C P=739.0 mm Hg		Run No. 2 T=27.8°C P=737.6 mm Hg		Run No. 3 T=30.5°C P=737.9 mm Hg	
	Vol	dvSTP	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml	ml	ml
0	0.0	-	0.0	-	0.0	-
2	3.0	2.484	3.1	2.614	3.2	2.657
4	6.2	2.649	6.1	2.530	6.6	2.823
6	9.8	2.980	9.7	3.036	10.3	3.072
8	13.5	3.068	13.4	3.121	14.3	3.322
10	17.0	2.898	17.1	3.121	18.2	3.238
12	20.7	3.068	20.9	3.205*	22.3	3.405*
14	24.5	3.146	24.8	3.289*	26.3	3.322*
16	27.9	2.815	28.8	3.374*	30.6	3.571*
18	31.8	3.229*	32.7	3.289*	34.8	3.488*
20	35.7	3.229*	36.7	3.374*	39.0	3.488*
22	39.6	3.229*	40.7	3.374*	43.2	3.488*
24	43.4	3.146*	44.7	3.374*	47.3	3.405*
26	47.3	3.229*	48.5	3.205*	51.4	3.405*
28	51.1	3.146*	52.5	3.374*	55.6	3.488*
30	54.9	3.146	56.5	3.374	59.9	3.571*
Ave. Rate mm ³ /Min.		1,600.6		1,658.7		1,731.3

*Values averaged to get average maximum rate.

TABLE LVIII

Dissolution of Mg Metal in 0.05 N H₂SO₄ at 15.0 °C

Time	Run No. 1 T=32.0 °C P=734.9 mm Hg		Run No. 2 T=32.3 °C P=736.1 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
20	3.0	2.375	1.4	1.146
40	8.3	4.341*	4.7	2.703*
60	13.8	4.505*	7.9	2.621*
80	19.2	4.423*	11.5	2.949*
100	24.1	4.013*	15.4	3.194*
120	29.1	4.095*	18.4	2.457*
140	33.5	3.686*	23.3	3.194*
160	38.5	4.095*	25.3	2.457*
Ave. Rate mm ³ /Min.		208.3		186.4

*Values averaged to get average maximum rate.

TABLE LIX

Dissolution of Mg Metal in 0.1 N H₂SO₄ at 15°C

Time	T=32.1°C P=735.5 mm Hg		T=32.3°C P=735.4 mm Hg	
	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml
0	0.0	-	0.0	-
8	1.6	1.310	1.0	0.818
16	5.9	3.523	4.9	3.190*
24	10.9	4.096	9.4	3.681*
32	14.7	3.932	13.7	3.517*
40	18.9	3.441*	17.8	3.354*
48	23.2	3.523*	22.0	3.436*
56	27.5	3.523*	25.9	3.190*
64	31.6	3.359*	30.0	3.354*
72	35.9	3.523*	34.0	3.272
80	40.1	3.441*	37.9	3.190
88	43.8	3.031		
96	47.8	3.277		
Ave. Rate mm ³ /Min.		433.6	423.6	

*Values averaged to get average maximum rate.

TABLE LIX

Dissolution of Mg Metal in 0.1 N H₂SO₄ at 15°C (con't)

		T=32.3°C P=737.6 mm Hg	
Time	Vol	dvSTP	
Min	ml	ml	
0	0.0	-	
6	1.5	1.231	
12	4.5	2.462	
18	7.5	2.462*	
24	9.7	1.805*	
30	13.4	3.036*	
36	16.2	2.298*	
42	19.8	2.954*	
48	22.8	2.462*	
54	26.1	2.708*	
60	29.3	2.626*	
66	32.2	2.380	
72	35.1	2.380	
Ave. Rate mm ³ /Min.		424.0	

*Values averaged to get average maximum rate.

TABLE LX

Dissolution of Mg Metal in 0.25 N H₂SO₄ at 15°C

Time	Run No. 1 T=33.5°C P=738.6 mm Hg		Run No. 2 T=33.5°C P=738.1 mm Hg		Run No. 3 T=33.2°C P=738.0 mm Hg	
	Vol	dvSTP	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml	ml	ml
0	0.0	-	0.0	-	0.0	-
2	1.8	1.468	1.9	1.548	2.3	1.633
4	4.1	1.875	4.0	1.711	4.3	1.633
6	6.3	1.794	6.3	1.874	6.4	1.715
8	8.8	2.038	8.7	1.955	8.0	1.306
10	11.4	2.120	10.9	1.792	10.6	2.123
12	14.0	2.120	13.5	2.118	13.2	2.123
14	16.6	2.120	16.1	2.118	15.8	2.123
16	18.9	1.875	18.8	2.200	18.4	2.123*
18	21.3	1.957	20.9	1.711	21.0	2.123*
20	24.0	2.202*	23.6	2.200*	23.5	2.041*
22	26.5	2.038*	26.1	2.037*	26.1	2.123*
24	29.1	2.120*	28.9	2.281*	28.7	2.123*
26	31.5	1.957*	31.5	2.118*	31.2	2.041*
28	34.2	2.202*	34.1	2.118*	33.8	2.123
30	36.8	2.120*	36.6	2.037*	36.3	2.041
32	39.3	2.038*	39.1	2.037*	38.2	1.551
34	41.8	2.038*	41.6	2.037*	41.0	2.286
Ave. Rate mm ³ /Min.		1,044.7		1,054.0		1,047.8

*Values averaged to get average maximum rate.

TABLE LXI

Dissolution of Mg Metal in 0.51 N H₂SO₄ at 15°C

Time	Run No. 1 T=34.1°C P=737.7 mm Hg		Run No. 2 T=33.0°C P=737.7 mm Hg		Run No. 3 T=29.9°C P=739.0 mm Hg	
	Vol	dvSTP	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml	ml	ml
0	0.0	-	0.0	-	0.0	-
1	2.4	1.947	2.6	2.124	2.6	2.170
2	4.8	1.947	5.1	2.042	5.3	2.253
3	7.4	2.109*	7.6	2.042*	7.1	1.502
4	10.1	2.190*	10.2	2.124*	9.8	2.253*
5	12.7	2.109*	12.8	2.124*	12.4	2.170*
6	15.2	2.028*	15.5	2.206*	15.1	2.253*
7	17.8	2.109*	17.9	1.961*	17.8	2.253*
8	20.4	2.109*	20.6	2.206*	20.4	2.170*
9	22.8	1.947*	23.1	2.042*	23.0	2.170*
10	25.4	2.109*	25.8	2.206*	25.7	2.253*
11	28.1	2.190*	28.5	2.206	28.4	2.253*
12	30.7	2.109*	30.6	1.715	30.7	1.919
13	33.1	1.947	33.1	2.042	33.6	2.420
14	35.9	2.271	35.7	2.124	36.3	2.253
15	38.3	1.947	38.6	2.369	39.0	2.253
16	40.7	1.947	41.4	2.288		
17	43.4	2.190	43.9	2.042		
Ave. Rate mm ³ /Min.		2,101.0		2,116.0		2,221.8

*Values averaged to get average maximum rate.

TABLE LXII

Dissolution of Mg Metal in 0.05 N H₂SO₄ at 25 °C

Time	Run No. 1 T=25.8 °C P=741.8 mm Hg		Run No. 2 T=26.3 °C P=740.9 mm Hg		Run No. 3 T=25.5 °C P=740.2 mm Hg	
	Vol	dvSTP	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml	ml	ml
0	0.0	-	0.0	-	0.0	-
10	1.9	1.630	2.0	1.709	1.5	1.286
20	4.7	2.402*	5.1	2.649*	4.2	2.315*
30	7.6	2.488*	8.0	2.478*	7.1	2.487*
40	10.6	2.488*	10.9	2.478*	9.9	2.401*
50	13.4	2.488*	13.9	2.564*	12.7	2.401*
60	16.1	2.316*	16.7	2.393*	15.3	2.230*
70	19.0	2.488*	19.6	2.478*	17.9	2.230*
80	21.8	2.402*	22.4	2.393*	20.5	2.230*
90	24.3	2.145	25.1	2.307*	23.0	2.144*
100	27.1	2.402				
Ave. Rate mm ³ /Min.		243.9		246.7		230.4

*Values averaged to get average maximum rate.

TABLE LXIII

Dissolution of Mg in 0.1 N H₂SO₄ at 25°C

Time	Run No. 1 T=26.9°C P=739.6 mm Hg		Run No. 2 T=26.3°C P=739.5 mm Hg		Run No. 3 T=25.6°C P=741.9 mm Hg	
	Vol	dvSTP	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml	ml	ml
0	0.0	-	0.0	-	0.0	-
6	2.4	2.040	2.3	1.962	2.5	2.148
12	5.8	2.891*	5.7	2.901	5.9	2.921*
18	9.2	2.891*	9.1	2.901*	9.4	3.007*
24	12.7	2.976*	12.5	2.901*	12.7	2.835*
30	16.0	2.805*	15.8	2.815*	16.1	2.921*
36	19.4	2.891*	19.2	2.901*	19.5	2.921*
42	22.7	2.805*	22.4	2.730*	22.7	2.749*
48	26.1	2.891*	25.6	2.730*	25.9	2.749*
54	29.4	2.805*	28.9	2.815*	29.1	2.749*
60	32.5	2.635	32.2	2.815*	32.3	2.749
Ave. Rate mm ³ /Min.		478		471		467

*Values averaged to get average maximum rate.

TABLE LXIV

Dissolution of Mg Metal in 0.25 N H₂SO₄ at 25°C

Time	Run No. 1 T=24.4°C P=738.9 mm Hg		Run No. 2 T=26.0°C P=739.2 mm Hg		Run No. 3 T=24.8°C P=739.3 mm Hg	
	Vol	dvSTP	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml	ml	ml
0	0.0	-	0.0	-	0.0	-
2	2.2	1.895	2.2	1.879	2.3	1.977
4	4.8	2.240	4.9	2.306	4.9	2.235
6	7.5	2.326*	7.7	2.391*	7.7	2.407*
8	10.4	2.498*	10.5	2.391*	10.6	2.493*
10	13.2	2.412*	13.2	2.306*	13.5	2.493*
12	16.0	2.412*	16.0	2.391*	16.4	2.493*
14	18.8	2.412*	18.7	2.306*	19.2	2.407*
16	21.5	2.326*	21.4	2.306*	22.0	2.407*
18	24.2	2.326	24.2	2.391	24.8	2.407*
20	26.9	2.326	27.0	2.391	27.5	2.321*
22	29.6	2.326	29.7	2.306	30.2	2.321*
24	32.3	2.326	32.4	2.306	33.0	2.407
26	35.0	2.326	35.1	2.306	35.8	2.407
Ave. Rate mm ³ /Min.		1,198		1,174		1,208

*Values averaged to get average maximum rate.

TABLE LXV

Dissolution of Mg Metal in 0.51 N H₂SO₄ at 25°C

Time	Run No. 1 T=28.0°C P=734.0 mm Hg		Run No. 2 T=28.2°C P=733.1 mm Hg		Run No. 3 T=28.2°C P=732.5 mm Hg	
	Vol	dvSTP	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml	ml	ml
0	0.0	-	0.0	-	0.0	-
2	5.5	4.613	5.5	4.572	6.1	5.096
4	11.5	5.032	11.6	5.071	12.4	5.263
6	17.6	5.116	17.8	5.154	18.9	5.430*
8	23.8	5.200*	23.9	5.071*	25.4	5.430*
10	29.7	4.948*	30.2	5.237*	31.9	5.430*
12	35.9	5.200*	36.4	5.154*	38.4	5.430*
14	41.8	5.116*	42.7	5.237*	45.0	5.514*
16	47.9	5.116*	49.0	5.237*	51.4	5.347*
18	53.9	5.032*	55.2	5.154*	57.9	5.430*
20	59.9	5.032*	61.4	5.154*	64.4	5.430
22	65.9	5.032*	67.8	5.320*	70.9	5.430
24	71.8	4.948*	74.1	5.237*	77.3	5.347
26	77.7	4.948*	80.4	5.237*		
Ave. Rate mm ³ /Min.		2,528		2,602		2,715

*Values averaged to get average maximum rate.

TABLE LXVI

Dissolution of Mg Metal in 0.05 N H₂SO₄ at 35.0 °C

Run No. 1 T=27.0 °C P=731.4 mm Hg		
Time	Vol	dvSTP
Min	ml	ml
0	0.0	-
8	2.9	2.436
16	6.1	2.688*
24	9.3	2.688*
32	12.3	2.520*
40	15.4	2.604*
48	18.4	2.520*
56	21.4	2.520*
64	24.4	2.520*
72	27.3	2.436
80	30.3	2.520
Ave. Rate mm ³ /Min.		322.5

*Values averaged to get average maximum rate.

TABLE LXVI

Dissolution of Mg Metal in 0.05 N H₂SO₄ at 35.0 °C (con't)

Time Min	Run No. 2 T=25.3 °C P=735.4 mm Hg		Run No. 3 T=25.4 °C P=732.3 mm Hg	
	Vol ml	dvSTP ml	Vol ml	dvSTP ml
0	0.0	-	0.0	-
6	2.5	2.132	2.4	2.037
12	5.0	2.132*	4.8	2.037*
18	7.4	2.047*	7.1	1.952*
24	9.7	1.961*	9.5	2.037*
30	12.1	2.047*	11.7	1.867*
36	14.3	1.876*	14.0	1.952*
42	16.6	1.961*	16.3	1.952*
48	18.9	1.961*	18.4	1.782
54	21.2	1.961*	20.6	1.867*
60	23.4	1.876*	22.7	1.782
66	25.7	1.961*	24.4	1.442
72	27.9	1.876	26.8	2.037*
78	30.1	1.876	28.8	1.697
84	32.4	1.961	30.9	1.782
90	34.7	1.961	33.1	1.867*
Ave. Rate mm ³ /Min.		329.7		327.7

*Values averaged to get average maximum rate.

TABLE LXVII

Dissolution of Mg Metal in 0.1 N H₂SO₄ at 35.0 °C

Time	Run No. 1 T=38.9 °C P=732.3 mm Hg		Run No. 2 T=24.5 °C P=731.8 mm Hg		Run No. 3 T=26.4 °C P=731.3 mm Hg	
	Vol	dvSTP	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml	ml	ml
0	0.3	-	0.0	-	0.0	-
4	3.1	2.328	3.2	2.727	3.2	2.696
8	6.2	2.578*	6.2	2.557*	6.4	2.696*
12	9.2	2.495*	9.2	2.557*	9.6	2.696*
16	12.3	2.578*	12.0	2.386*	12.7	2.612*
20	15.3	2.495*	14.8	2.386*	15.9	2.696*
24	18.3	2.495*	17.6	2.386*	19.1	2.696*
28	21.2	2.412*	20.4	2.386*	22.2	2.612*
32	24.1	2.412*	23.1	2.301*	25.2	2.528*
36	27.0	2.412*	25.9	2.386*	28.3	2.612*
40	29.9	2.412*	28.6	2.301	31.2	2.528*
44	32.7	2.328*	31.4	2.386	34.5	2.696*
48	35.6	2.412	34.1	2.301	37.4	2.443
52					40.6	2.696
Ave. Rate mm ³ /Min.		615.4		605.0		659.3

*Values averaged to get average maximum rate.

TABLE LXIX

Dissolution of Mg Metal in 0.51 N H₂SO₄ at 35°C

Time	Run No. 1 T=27.1°C P=738.2 mm Hg		Run No. 2 T=27.7°C P=738.2 mm Hg		Run No. 3 T=28.0°C P=734.5 mm Hg	
	Vol	dvSTP	Vol	dvSTP	Vol	dvSTP
Min	ml	ml	ml	ml	ml	ml
0	0.0	-	0.0	-	0.0	-
1	5.0	4.238	5.3	4.763	5.5	4.613
2	9.9	4.153	10.6	4.763	10.9	4.529
3	14.8	4.153*	15.6	4.223	16.3	4.529*
4	19.8	4.238*	20.5	4.138*	21.7	4.529*
5	24.6	4.068*	25.4	4.138*	26.8	4.278*
6	29.5	4.153*	30.4	4.223*	32.1	4.445*
7	34.5	4.238*	35.3	4.138*	37.3	4.361*
8	39.3	4.068*	40.1	4.054*	42.6	4.445*
9	44.1	4.068*	44.9	4.054*	47.8	4.361*
10	49.0	4.153*	49.8	4.138*	53.2	4.529*
11	54.0	4.238*	54.7	4.138*	58.6	4.529*
12	58.9	4.153*	59.4	3.969	64.0	4.529*
13	63.7	4.068*	64.1	3.969	69.3	4.445*
14			69.1	4.223		
Ave. Rate mm ³ /Min.		4,153		4,138		4,453

*Values averaged to get average maximum rate.

TABLE LXX

Dissolution of Mg Metal in 0.05 N H₂SO₄ at 45.2 °C

Time Min	Run No. 1 T=31.5 °C P=736.6 mm Hg		Run No. 2 T=30.2 °C P=735.7 mm Hg		Run No. 3 T=30.4 °C P=736.1 mm Hg	
	Vol ml	dvSTP ml	Vol ml	dvSTP ml	Vol ml	dvSTP ml
0	0.0	-	0.0	-	0.0	-
6	3.4	2.800	3.2	2.653	3.4	2.817
12	6.2	2.306	6.1	2.404*	6.4	2.486
18	9.1	2.388	8.9	2.321*	8.9	2.071*
24	11.6	2.059*	11.7	2.321*	11.4	2.071*
30	14.2	2.141*	14.3	2.156*	13.5	1.740*
36	16.8	2.141*	17.0	2.239*	15.9	1.988*
42	19.3	2.059*	19.6	2.156*	18.3	1.988*
48	21.7	1.976*	22.1	2.073*	20.8	2.071*
54	24.0	1.894*	24.4	1.907	22.8	1.657
60	26.4	1.976*	26.8	1.990	24.8	1.657
66	28.6	1.812	29.1	1.907	27.2	1.988
72	31.0	1.976	31.6	2.073	29.7	2.071
78	33.2	1.647	34.0	1.990	31.9	1.823
84	35.6	1.976	35.9	1.575	33.9	1.657
90	37.9	1.894	38.3	1.990	36.1	1.823
Ave. Rate mm ³ /Min.		339.2		373.1		331.4

*Values averaged to get average maximum rate.

TABLE LXXI

Dissolution of Mg Metal in 0.1 N H₂SO₄ at 45.2 °C

		Run No. 1 T=28.2 °C P=736.2 mm Hg	
Time	Vol	dvSTP	
ml	ml	ml	
0	0.0	-	
2	2.4	2.015	
4	4.8	2.015	
6	6.9	1.763*	
8	8.8	1.595*	
10	10.8	1.679*	
12	12.8	1.679*	
14	14.7	1.595*	
16	16.4	1.427*	
18	18.1	1.427*	
20	20.0	1.595*	
22	21.9	1.595*	
24	23.7	1.511*	
26	25.3	1.343*	
28	27.2	1.595	
30	28.8	1.343	
Ave. Rate mm ³ /Min.		793.3	

*Values averaged to get average maximum rate.

TABLE LXXI

Dissolution of Mg Metal in 0.1 N H₂SO₄ at 45.2 °C (con't)

Time Min	Run No. 2 T=30.1 °C P=737.2 mm Hg		Run No. 3 T=30.4 °C P=737.0 mm Hg	
	Vol ml	dvSTP ml	Vol ml	dvSTP ml
0	0.0	—	0.0	—
4	4.1	3.409	4.3	3.567
8	7.7	2.993	8.0	3.069
12	11.1	2.827	11.4	2.821*
16	14.5	2.827	15.0	2.987*
20	17.4	1.579	18.5	2.904*
24	20.9	2.910	22.0	2.904*
28	23.9	2.494*	25.5	2.904*
32	27.1	2.660*	29.0	2.904*
36	30.1	2.494*	32.1	2.572
40	33.1	2.494*	35.0	2.406
44	36.1	2.494*	38.2	2.655
48	39.1	2.494*	41.5	2.738
52	42.1	2.494	44.8	2.738
56	45.1	2.494	48.1	2.738
60	48.1	2.494	51.2	2.572
Ave. Rate mm ³ /Min.		630.4		726.0

*Values averaged to get average maximum rate.

TABLE LXXII

Dissolution of Mg Metal in 0.25 N H₂SO₄ at 45.2°C

Time Min	Run No. 1 T=28.0°C P=736.1 mm Hg		Run No. 2 T=28.0°C P=739.1 mm Hg		Run No. 3 T=28.0°C P=735.8 mm Hg	
	Vol	dvSTP	Vol	dvSTP	Vol	dvSTP
	ml	ml	ml	ml	ml	ml
0	0.0	-	0.0	-	0.0	-
2	4.0	3.362*	5.0	4.221*	5.3	4.448
4	8.3	3.615*	10.2	4.391*	10.0	3.944*
6	12.5	3.531*	15.3	4.306*	14.5	3.776*
8	16.5	3.362*	20.3	4.221*	19.0	3.776*
10	20.5	3.362*	25.1	4.052*	23.5	3.776*
12	24.4	3.279*	30.0	4.137*	28.2	3.944*
14	28.2	3.195*	34.4	3.715*	32.6	3.692*
16	32.1	3.279*	39.1	3.968*	37.1	3.776*
18	35.8	3.111*	43.9	4.052*	41.5	3.692*
20	40.0	3.531*	48.1	3.546*	45.9	3.692*
22	44.1	3.447*	53.1	4.221*	50.3	3.692*
24	48.1	3.362*	58.0	4.137*	54.5	3.524*
26	52.3	3.531*	62.1	3.461*	59.1	3.860*
28	56.3	3.362*	66.9	4.052*	63.4	3.608
30	60.4	3.447*	71.5	3.883*	67.7	3.608
Ave. Rate mm ³ /Min.		1,692		2,012		1,881

*Values averaged to get average maximum rate.

TABLE LXXII

Dissolution of Mg Metal in 0.25 N H₂SO₄ at 45.2°C (con't)

		Run No. 4 T=30.0 °C P=731.0 mm Hg	
Time	Vol	dvSTP	
Min	ml	ml	
0	0.0	-	
1	2.2	1.814*	
2	4.5	1.897*	
3	6.7	1.814*	
4	8.9	1.814*	
5	11.1	1.814*	
6	13.2	1.814*	
7	15.5	1.897*	
8	17.5	1.649	
9	19.6	1.731	
10	21.7	1.731	
11	23.8	1.731	
12	25.9	1.731	
13	28.0	1.731	
14	30.0	1.649	
15	32.0	1.649	
16	34.1	1.731	
17	36.3	1.814	
18	38.3	1.649	
19	40.3	1.649	
20	42.3	1.649	
21	44.3	1.649	
22	46.4	1.731	
23	48.4	1.649	
24	50.6	1.814	
25	52.7	1.731	
26	54.7	1.649	
Ave. Rate mm ³ /Min.		1,838	

*Values averaged to get average maximum rate.

TABLE LXXIII

Dissolution of Mg Metal in 0.51 N H₂SO₄ at 45.2°C

Time Min	Run No. 1 T=30.1°C P=733.6 mm Hg		Run No. 2 T=30.7°C P=730.8 mm Hg		Run No. 3 T=31.0°C P=730.9 mm Hg	
	Vol ml	dvSTP ml	Vol ml	dvSTP ml	Vol ml	dvSTP ml
0	0.0	-	0.0	-	0.0	-
1	9.2	7.611	8.9	7.309	8.5	6.965
2	18.6	7.776*	17.4	6.981*	15.9	6.064
3	27.8	7.611*	26.2	7.227*	23.4	6.146*
4	37.1	7.693*	34.8	7.063*	30.9	6.146*
5	46.4	7.693*	43.6	7.227*	38.4	6.146*
6	55.7	7.693*	52.2	7.063*	46.1	6.310*
7	64.9	7.611*	60.7	6.981*	53.7	6.228*
8	73.9	7.445	68.8	6.652	61.2	6.146*
9	82.9	7.362	77.3	6.981	68.8	6.228*
10	91.7	7.362	85.7	6.899	76.2	6.064*
11					83.7	6.146*
Ave. Rate mm ³ /Min.		7,679		7,090		6,187

*Values averaged to get average maximum rate.

TABLE LXXIV

Difference Effect on Mg in 0.1 N HCl at 25°C

Average barometric pressure = 737.6 mm Hg
 Average room temperature = 27.7°C

Time	Vol	I	dvSTP*	V ₁ *	V _t *
Min	ml	ma/cm ²	mm ³ /Min	mm ³ /Min	mm ³ /Min
0	5.2	0	-		
8	8.9	0	390		
16	12.1	0	337		
24	15.5	0	359		
32	20.7	59.0	548		
40	26.0	56.5	560	322	554
48	28.7	0	285		
56	31.6	0	306		
64	34.5	0	306		
72	43.2	84.5	918		
80	51.1	77.5	833	232	876
88	52.6	0	158		
96	55.2	0	274		
104	57.8	0	274		
112	61.6	40.0	401		
120	65.6	40.0	422	280	412
128	68.3	0	285		
136	71.0	0	285		
144	74.2	27.5	338	285	343
152	77.5	27.0	348		
160	80.2	0	285		
168	82.8	0	274		
176	85.1	15.0	242	269	248
184	87.5	15.0	253		
192	90.0	0	264		
200	92.4	0	253		

*Per square centimeter of surface area.

TABLE LXXV

Difference Effect on Mg in 0.25 N HCl at 25°C

Average barometric pressure = 736.5 mm Hg Average room temperature = 25.7°C					
Time	Vol	I	dvSTP*	V ₁ *	V _t *
Min	ml	ma/cm ²	mm ³ /Min	mm ³ /Min	mm ³ /Min
0	5.4	0	-		
2	7.9	0	1,065		
4	10.2	0	980		
6	12.2	0	853		
8	14.6	0	1,023		
10	16.8	0	938		
12	19.1	111.5	980		
14	21.8	111.5	1,151	959	1,080
16	24.4	110.5	1,108		
18	26.7	0	980		
20	29.2	0	1,065		
22	32.0	135.5	1,193		
24	35.2	134.0	1,278	980	1,264
26	38.3	132.0	1,321		
28	40.4	0	895		
30	42.8	0	1,023		
32	45.0	0	938		
34	47.6	92.5	1,108		
36	50.3	92.5	1,150	895	1,129
38	52.3	0	852		
40	54.2	0	810		
42	55.4	69.5	512		
44	59.8	69.0	1,875		
46	62.4	69.0	1,108**		
48	64.9	69.0	1,065**	874	1,087
50	67.1	0	938		
52	69.3	0	938		
54	71.5	45.5	938		
56	74.0	45.5	1,065	916	1,023
58	76.5	45.5	1,065		
60	78.6	0	895		
62	80.8	0	937		
64	82.9	0	895		

*Per square centimeter of surface area.

**Values selected to get average V_t.

TABLE LXXVI

Difference Effect on Mg in 0.5 N HCl at 25°C

Average barometric pressure = 736.9 mm Hg
 Average room temperature = 26.1°C

Time	Vol	I	dvSTP*	V ₁ *	V _t *
Min	ml	ma/cm ²	mm ³ /Min	mm ³ /Min	mm ³ /Min
0	7.0	0	-		
1	10.6	0	3,063		
2	13.6	0	2,553		
3	16.6	0	2,553		
4	19.7	16.0	2,638		
5	22.6	14.0	2,468	2,553	2,553
6	25.6	14.0	2,553		
7	28.6	0	2,553		
8	31.7	0	2,638		
9	34.7	127.5	2,553	2,681	2,553
10	37.7	127.5	2,533		
11	40.9	0	2,723		
12	43.9	0	2,553		
13	47.0	0	2,638		
14	50.1	102.0	2,638	2,596	2,596
15	53.1	102.0	2,553		
16	56.1	0	2,553		
17	59.2	0	2,638		
18	62.2	82.0	2,553	2,681	2,553
19	65.2	82.0	2,553		
20	68.4	0	2,723		
21	71.4	0	2,553		
22	74.3	0	2,468		
23	77.4	60.5	2,638		
24	80.4	60.5	2,553	2,553	2,496
25	83.1	60.5	2,298		
26	86.2	0	2,638		
27	89.2	0	2,553		

*Per square centimeter of surface area.

TABLE LXXVII

Difference Effect on Mg in 0.05 N HClO₄ at 25°C

Average barometric pressure = 734.0 mm Hg
 Average room temperature = 26.2°C

Time	Vol	I	dvSTP*	V ₁ *	V _t *
Min	ml	ma/cm ²	mm ³ /Min	mm ³ /Min	mm ³ /Min
0	6.8	0	-		
8	8.2	0	148		
16	9.9	0	180		
24	11.9	0	212		
32	13.9	0	212		
40	16.9	34.0	318		
48	20.1	33.0	338	212	328
56	22.1	0	212		
64	24.0	0	201		
72	30.2	78.5	656		
80	36.2	76.5	635	185	646
88	37.8	0	169		
96	39.5	0	180		
104	43.8	54.0	455		
112	48.0	51.5	444	180	450
120	49.7	0	180		
128	51.3	0	169		
136	53.4	18.5	222		
144	55.6	18.5	233	175	228
152	57.3	0	180		
160	58.8	0	159		
168	60.3	0	159		
176	61.8	11.4	159		
184	63.7	11.4	201	164	187
192	65.6	11.4	201		
200	67.2	0	169		
208	68.8	0	169		

*Per square centimeter of surface area.

TABLE LXXVIII

Difference Effect on Mg in 0.1 N HClO₄ at 25°C

Average barometric pressure = 735.2 mm Hg
 Average room temperature = 29.7°C

Time	Vol	I	dvSTP*	V ₁ *	V _t *
Min	ml	ma/cm ²	mm ³ /Min	mm ³ /Min	mm ³ /Min
0	5.8	0	-		
4	7.2	0	291		
8	8.9	0	353		
12	11.0	0	436		
18	14.7	0	513		
24	18.4	0	513		
30	22.2	0	527		
36	29.5	116.0	1,011	527	1,039
42	37.2	118.0	1,067		
48	41.0	0	527		
54	44.8	0	527		
60	50.8	78.0	831	527	831
66	56.8	77.0	831		
72	60.6	0	527		
78	64.6	0	554		
84	69.2	45.5	637	561	651
90	74.0	45.5	665		
96	78.1	0	568		
102	82.0	0	540		
108	86.3	23.3	596	554	582
114	90.4	23.3	568		
120	94.5	0	568		

*Per square centimeter of surface area.

TABLE LXXIX

Difference Effect on Mg in 0.25 N HClO₄ at 25°C

Average barometric pressure = 733.7 mm Hg
 Average room temperature = 30.3°C

Time	Vol	I	dvSTP*	V ₁ *	V _t *
Min	ml	ma/cm ²	mm ³ /Min	mm ³ /Min	mm ³ /Min
0	6.8	0	-		
2	9.4	0	1,075		
4	11.8	0	992		
6	14.3	0	1,033		
8	16.6	62.0	950	1,054	1,061
10	19.2	62.0	1,075		
12	22.0	62.0	1,157		
14	24.6	0	1,075		
16	27.3	0	1,115		
18	30.4	123.0	1,281	1,095	1,260
20	33.4	123.0	1,240		
22	36.0	0	1,075		
24	38.5	0	1,033		
26	41.3	100.0	1,157	1,033	1,136
28	44.0	100.0	1,115	1,033	1,136
30	46.5	0	1,033		
32	48.9	0	992		
34	51.3	26.5	992	1,012	992
36	53.7	26.5	992		
38	56.2	0	1,033		
40	58.5	0	950		
42	60.9	0	992		
44	63.2	10.5	950	992	971
46	65.6	10.5	992		
48	68.0	0	992		
50	70.3	0	951		
52	72.8	5.3	1,033		
54	75.1	5.3	950	951	992
56	77.5	5.3	992		
58	79.8	0	951		
60	82.1	0	951		
62	85.5	142.5	1,405	930	1,384
64	88.8	142.5	1,364		
66	91.0	0	909		

*Per square centimeter of surface area.

TABLE LXXX

Difference Effect on Mg in 0.05 N H₂SO₄ at 25°C

Average barometric pressure = 740.9 mm Hg
 Average room temperature = 25°C

Time	Vol	I	dvSTP*	V ₁ *	V _t *
Min	ml	ma/cm ²	mm ³ /Min	mm ³ /Min	mm ³ /Min
0	4.8	0	-		
10	6.8	0	172		
20	8.6	0	155		
30	10.0	0	121		
40	12.0	0	172		
50	13.8	0	155		
60	20.1	44.0	542		
70	24.3	33.0	362**		
80	27.9	28.0	310**	77.5	336
90	27.9	0	0		
100	27.9	0	0		
110	28.6	19.5	146		
120	31.5	18.5	250	0	189
130	33.5	18.5	172		
140	33.5	0	0		
150	33.5	0	0		
160	34.4	13.5	77.5		
170	35.4	13.6	86.0	51	82
180	36.6	0	103		
190	37.6	0	86		
200	39.6	24.0	172		
210	42.0	23.5	207	52	206
220	44.6	23.0	238		
230	44.8	0	17		
240	45.0	0	17		

*Per square centimeter of surface area.

**Values selected to get average V_t.

TABLE LXXXI

Difference Effect on Mg in 0.1 N H₂SO₄ at 25°C

Average barometric pressure = 737.3 mm Hg
 Average room temperature = 25.4°C

Time	Vol	I	dvSTP*	V ₁ *	V _t *
Min	ml	ma/cm ²	mm ³ /Min	mm ³ /Min	mm ³ /Min
0	5.5	0	-		
6	7.9	0	342		
12	10.5	0	370		
18	13.0	0	356		
24	15.4	25.0	342		
30	18.2	25.0	399	363	399
36	21.4	25.0	456		
42	24.0	0	370		
48	26.4	0	342		
54	32.5	95.0	869		
60	40.0	90.0	1,067	264	940
66	46.2	85.0	883		
72	47.5	0	185		
78	49.7	0	313		
84	52.0	0	327		
90	56.6	64.5	655		
96	60.9	62.5	612	270	627
102	65.2	61.5	612		
108	66.7	0	213		
114	68.6	0	271		
120	70.6	0	285		
126	73.2	44.0	370		
132	76.2	42.5	427	292	413
138	79.3	42.5	441		
144	81.4	0	299		
150	83.4	0	285		

*Per square centimeter of surface area.

TABLE LXXXII

Difference Effect on Mg in 0.25 H₂SO₄ at 25°C

Average barometric pressure = 734.4 mm Hg
 Average room temperature = 25.4°C

Time	Vol	I	dvSTP*	V ₁ *	V _t *
Min	ml	ma/cm ²	mm ³ /Min	mm ³ /Min	mm ³ /Min
0	5.2	0	-		
2	7.5	0	979		
4	9.8	0	979		
6	11.9	16.5	894		
8	14.2	16.5	979	979	951
10	16.5	16.5	979		
12	18.8	0	979		
14	21.2	0	1,022		
16	23.7	40.0	1,064		
18	26.0	40.0	979	1,043	1,022
20	28.4	40.0	1,022		
22	30.9	0	1,064		
24	33.1	0	936		
26	33.5	0	1,022		
28	38.0	59.5	1,064		
30	40.4	59.5	1,022	1,000	1,043
32	42.7	0	979		
34	44.8	0	894		
36	46.9	0	894		
38	49.5	79.0	1,107		
40	51.9	78.5	1,022	894	1,078
42	54.5	78.5	1,107		
44	56.6	0	894		
46	58.6	0	851		
48	61.9	132.5	1,405		
50	65.2	132.5	1,405	830	1,405
52	67.1	0	809		
54	69.2	0	894		
56	71.3	0	894		
58	74.0	103.5	1,149		
60	76.7	103.5	1,149	936	1,149
62	79.0	0	979		
64	81.0	0	851		
66	82.9	0	809		
68	84.8	0	809		

*Per square centimeter of surface area.

TABLE LXXXIII

Difference Effect on Mg in 0.5 N H₂SO₄ at 25°C

Average barometric pressure = 732.4 mm Hg
 Average room temperature = 27.6°C

Time	Vol	I	dvSTP*	V ₁ *	V _t *
Min	ml	ma/cm ²	mm ³ /Min	mm ³ /Min	mm ³ /Min
0	7.4	0	-		
1	10.4	0	2,515		
2	13.3	0	2,431		
3	16.2	0	2,431		
4	19.0	17.3	2,347		
5	21.8	15.7	2,347	2,431	2,347
6	24.9	0	2,431		
7	27.8	0	2,431		
8	30.6	50.0	2,347		
9	33.6	50.0	2,515	2,389	2,459
10	36.6	50.0	2,515		
11	39.4	0	2,347		
12	42.5	0	2,599		
13	45.4	0	2,431		
14	48.4	129.0	2,515		
15	51.6	129.0	2,683	2,389	2,571
16	54.6	129.0	2,515		
17	57.4	0	2,347		
18	60.4	0	2,515		
19	63.3	0	2,431		
20	66.2	97.5	2,431		
21	69.2	97.5	2,515	2,431	2,473
22	72.1	0	2,431		
23	75.0	0	2,431		
24	78.0	74.5	2,515		
25	80.9	74.5	2,431	2,431	2,403
26	83.6	74.5	2,263		
27	86.5	0	2,431		
28	89.3	0	2,347		

*Per square centimeter of surface area.

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IX. VITA

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