

Part I

THE ANODIC OXIDATION OF MAGNESIUM IN AQUEOUS SOLUTION

Part II

THE OXIDATION OF MAGNESIUM BY TRIIODIDE ION

by

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Part I

THE ANODIC OXIDATION OF MAGNESIUM IN AQUEOUS SOLUTION

Introduction

It has been known for many years that evolution of hydrogen occurs, in addition to the dissolution of magnesium, during the anodic oxidation of magnesium in aqueous salt solutions (1). This behavior is obviously extraordinary, since the primary electrochemical action at the anode is one of oxidation, and hydrogen must be produced from the water by reduction. These facts indicate either that a non-electrolytic reaction occurs simultaneously with electrolysis, or that an unstable intermediate, which is capable of undergoing further oxidation, is formed during the anodic electrolytic reaction. Turrentine (2) assumed the latter of these alternatives to be the correct one, and suggested that unipositive magnesium was formed as the unstable intermediate. The evidence for the validity of this assumption, however, is not conclusive.

The present work was undertaken to characterize the anodic behavior of magnesium in aqueous salt solutions. Experiments were carried out to distinguish between the two alternatives presented above. The

results of these experiments leave little doubt that during the anodic oxidation of magnesium at least some of the metal is converted to the unipositive state.

Historical Review

The existence of lower oxidation states of the Group II elements has long been the subject of considerable controversy*. The idea has been prevalent that the Group II elements, in particular, can exist in no form intermediate between the metallic state and that in which they exhibit their maximum oxidation number of two (3). However, evidence has been available for the existence, under certain conditions, of sub-halides of some of the alkaline earth metals (Ca, Sr and Ba) (4). More recently, evidence has accumulated for the existence of sub-halides of magnesium and aluminum (5, 6 and 7), of sub-oxides of other elements (5), and of lower valence states for the Group III elements (8, 9, 10 and 11).

*Since the previous evidence for the lower oxidation states of metals other than magnesium has no direct bearing on the results of the work to be presented here, a complete bibliography will not be given. However, extensive bibliographies are to be found in the following references: Wöhler and Rodewald, Z. anorg. Chem., 61, 54 (1909); Gomberg and Bachmann, J. Am. Chem. Soc., 49, 236 (1927); Schäfer, Chem. Ztg., 75, 48 (1951).

Gomberg and Bachmann (12) postulated that "magnesium iodide" was formed as an intermediate in the reduction of ketones to pinacols either by magnesium and iodine, or by magnesium and magnesium iodide mixture, in ether-benzene mixtures. Thus, evidence for the existence of anomalous oxidation states of regular elements has been accumulating through the years.

Modern atomic theory has indicated, insofar as ionization energy is concerned, that successive electrons may be removed from an atom one at a time. Specifically, in the case of the alkaline earth elements, it requires approximately twice as much energy to remove the second electron as to remove the first. However, the ionization energy is not the sole criterion for the formation of a stable entity. Other factors may oppose the effect of the ionization energy by bringing about conditions under which the entity in question is quite unstable. Nevertheless, one fact remains clear: that is, that it is not the inherent nature of the elements to utilize under all circumstances all available valence electrons; rather, the experimental conditions and environment determine whether only one or more than one of these electrons are to be used in the formation of the stable entity.

Experimental Methods

The electrolyses were carried out in a cell consisting of two compartments separated by a sintered glass plate. Each compartment had a capacity of 25 milliliters. All electrolyses were made with similar magnesium electrodes cut from the same gross piece of magnesium. This magnesium, of 99.8% purity, was furnished by the Aluminum Company of America through the courtesy of Dr. P. V. Faragher. The chemicals used for the preparation of electrolytic solutions were of C. p. or Reagent grades. The source of direct current was a mercury tube rectifier capable of supplying up to 1000 volts.

If a coulometer is placed in series with the electrolytic cell, it is found that more magnesium is dissolved from the anode than can be accounted for on the assumption that magnesium is oxidized uniformly to the dipositive state. A convenient measure of this anomaly is to be found in the mean valence number (\bar{n}). The initial mean valence number of magnesium in anodic oxidation is defined as the number of faradays of electricity passed through the cell per gram-atomic weight of magnesium lost from the anode. With the use of a

silver coulometer, this number, designated as V_1 , is calculated from the equation

$$V_1 = \frac{\text{Wt. of Ag deposited in coulometer} \times 24.32}{107.88 \times \text{Wt. of Mg lost from anode}}$$

Since gas was evolved at the magnesium anode during electrolysis, a complete and quantitative analysis of the gas liberated was necessary for the characterization of the anodic reaction. A schematic representation of the gas analysis apparatus is shown in Figure 1.

The anode compartment A of the divided electrolytic cell was sealed into the system, whereas, since the cathodic reaction as such was not under study in this investigation, the cathode compartment C was left open to the atmosphere. With stopcock 3 open, nitrogen, from which oxygen had been removed by means of a train of pyrogallol and chromium(II) sulfate solution, was allowed to flow through stopcock 2 into bulb B_1 , which contained the electrolyte to be used in the electrolytic experiment. Nitrogen was allowed to flow also through stopcock 6 into the anode compartment and out into the atmosphere through stopcocks 7 and 8. This procedure was followed in order that all gases other than nitrogen might be excluded from the system and the solution. After passage of nitrogen for one to

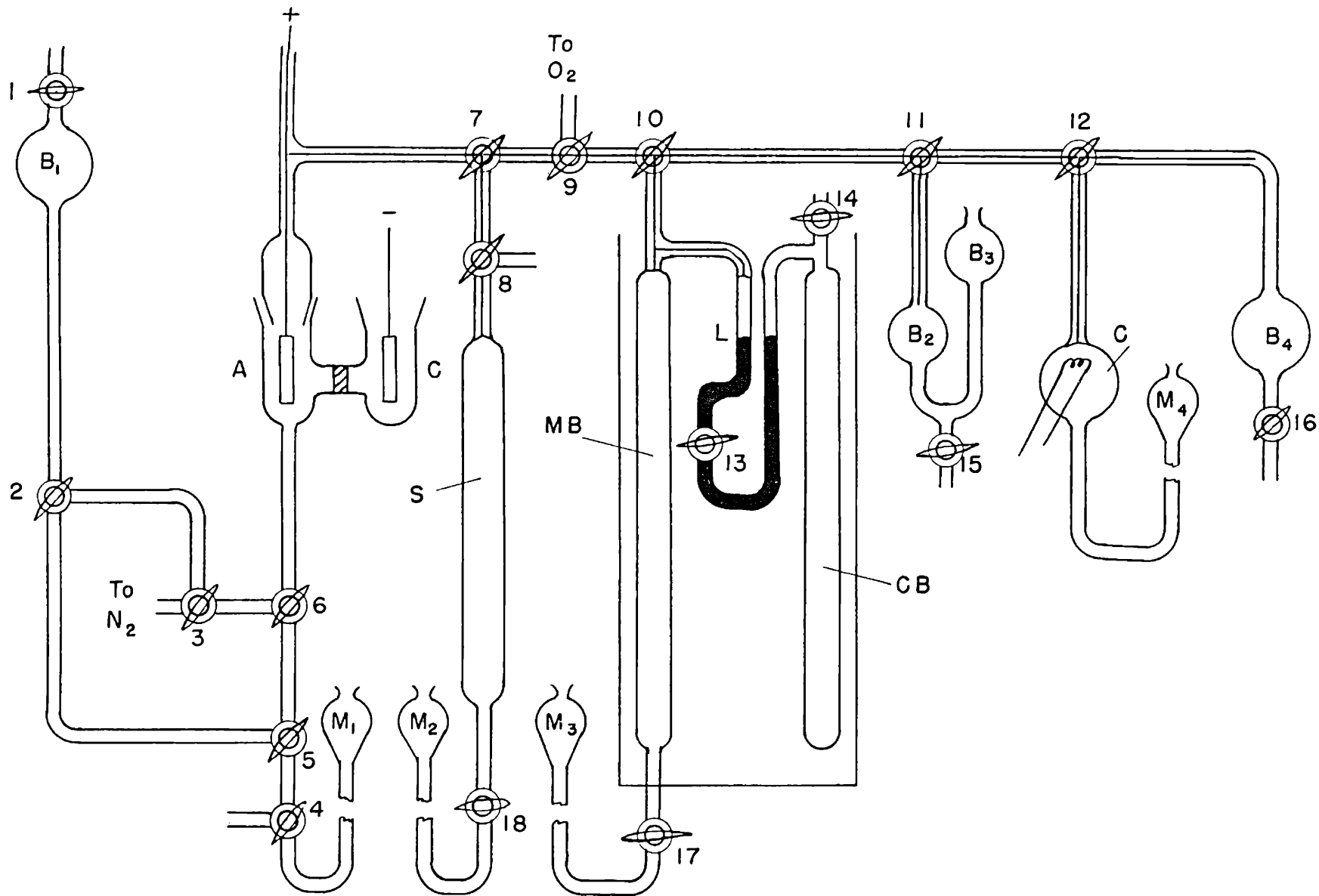


Figure 1 Gas Analysis Apparatus

two hours, the electrolytic solution was allowed to flow from bulb B_1 through stopcocks 2 and 5 up to stopcock 6. Nitrogen was then permitted to flow for an additional interval of time through the anode compartment to remove the air which had been previously trapped between stopcocks 2 and 5.

After the nitrogen flow had been discontinued and stopcock 8 closed, the electrolyte was allowed to flow into the anode compartment to the desired level. Identical electrolyte was added to the cathode compartment and electrolysis was started. As the gas was evolved from the anode it was allowed to expand through stopcocks 7 and 8 into the reservoir S. Approximately atmospheric pressure was maintained by appropriate adjustment of mercury bulb M_2 . At the end of the electrolysis, water was allowed to flow from bulb M_1 through stopcocks 4, 5 and 6 into the anode compartment. This action forced all the gas, both evolved and residual, into the reservoir S. The water was allowed to flow until the electrolyte had been forced just through the bore of stopcock 7.

At this point, all of the gas was contained in the reservoir S below stopcock 7. The remainder of the system to the right of stopcock 7 (except the compensating burette CB) was completely filled with mercury. By raising mercury bulb M_2 and lowering mercury bulb M_3

and by opening stopcocks 7, 8, 9, 10 and 17, the gas was forced into the calibrated measuring burette MB, the mercury being stopped at the end of the bore of stopcock 10. The measuring burette MB and the compensating burette CB were enclosed in a water jacket in order to maintain a uniform temperature. By closing stopcock 14 and observing the barometric pressure, a known and constant reference pressure was maintained in the compensating burette CB. Since the collected gases were saturated with water vapor from the electrolytic cell, no correction for this vapor pressure was necessary if a small quantity of water was maintained in the compensating burette CB.

With stopcocks 13 and 17 open, the mercury level in the measuring burette MB was raised or lowered by appropriately raising or lowering bulb M_3 until the two mercury levels were the same at L. The temperature of the bath, the pressure in the compensating burette CB, and the calibrated volume of the gas in the measuring burette MB were then recorded.

With stopcocks 10 and 11 opened appropriately, the gas was transferred to bulb B_2 by raising mercury bulb M_3 . Bulb B_2 contained a chromium(II) sulfate solution to absorb oxygen. The gas was allowed to remain in contact with this solution for thirty minutes with shaking at frequent intervals. The gas was then

returned to the measuring burette MB by lowering mercury bulb M_3 until the chromium(II) sulfate solution had risen to stopcock 11. The gas was then forced entirely into the measuring burette MB by appropriately opening stopcocks 11 and 12 and raising mercury bulb M_4 . The volume and temperature were recorded after adjusting mercury bulb M_3 until the mercury levels at L were the same. The reference pressure set in the compensating burette CB remained constant throughout these operations. The gas was again returned to bulb B_2 , as previously, and this procedure was repeated until there was no further change in the volume of the gas. Any decrease in volume was due to the absorption of oxygen by the chromium(II) sulfate solution. If there were no changes in volume, it was assumed that no oxygen was present.

With stopcocks 10, 11 and 12 opened appropriately, the gas was transferred completely to the combustion bulb C by raising mercury bulb M_3 and lowering mercury bulb M_4 . Oxygen was then drawn into the measuring burette MB by opening stopcocks 9 and 10 appropriately and lowering mercury bulb M_3 . It was necessary to make only an approximate calculation to insure that an excess of oxygen was added over that necessary to unite completely with the hydrogen present. After the volume of oxygen had been measured, as above,

the platinum coil in the combustion chamber was heated to a dull red heat and the oxygen was slowly forced from the measuring burette MB into the combustion chamber C. Extreme caution was necessary during this operation, since the heat of combustion of the hydrogen was sufficient to destroy the platinum coil if the oxygen were added too rapidly.

As soon as all of the oxygen had been transferred to the combustion chamber C the gas was returned to the measuring burette MB by raising mercury bulb M_4 and lowering mercury bulb M_3 . The volume of gas was again measured as before. This volume was then subtracted from the combined volumes of the original gas, after oxygen absorption, plus the added oxygen. The difference gave the amount of hydrogen and oxygen consumed in the combustion. Since the volume of water produced was negligible, and since two moles of hydrogen were consumed for every mole of oxygen in the combustion, the volume of hydrogen was determined as two-thirds of the decrease in volume on combustion.

A further check was made by transferring the measured volume of gas after combustion to the bulb B_2 , where the excess oxygen was absorbed. The remaining volume plus the calculated volume of hydrogen should have been equal to the volume of gas measured after the original oxygen absorption.

Results and Discussion

The evolution of hydrogen at a magnesium anode during the electrolysis of aqueous salt solutions was confirmed. As stated previously, this phenomenon requires the assumption either of a non-electrolytic reaction or of the formation of an unstable intermediate, capable of further oxidation. The first qualitative indication that an intermediate is formed is the fact that, whereas evolution of gas at the magnesium cathode used instantaneously ceases (except for the very slow evolution encountered with metallic magnesium in aqueous salt solutions without electrolysis) when the current is interrupted, evolution of gas at the anode continues for several minutes. Experiment has shown that approximately 40% of the total gas evolved occurs after the current has been interrupted. This gas, therefore, cannot be formed by an electrochemical reaction. As further evidence is presented it will become clear that the gas evolution is not a result of direct reaction between metallic magnesium and water.

At room temperature there is scarcely any reaction between pure metallic magnesium and pure water. Impure magnesium may, of course, evolve gas as a result of couple action. It is also well known that the addition of any of several electrolytes causes a noticeable

reaction between pure magnesium and water. The extensive literature on this subject (13, 14, 15, 16 and 17) need not be covered in detail in this discussion. In general, however, any electrolyte which increases the hydrogen ion concentration by hydrolysis promotes the liberation of hydrogen from water by magnesium, and any electrolyte which decreases the hydrogen ion concentration by hydrolysis retards the liberation of hydrogen. These results are to be expected; but the reaction is not so simple, since some electrolytes which do not undergo hydrolysis promote the liberation of hydrogen. This catalytic activity has never been satisfactorily explained.

The significant point, however, is the fact that, since hydrogen is evolved at the magnesium anode during electrolysis, the anolyte becomes definitely basic. Yet the anode continues to evolve gas in this basic solution, although there is only extremely slight evolution of gas from the magnesium cathode in the basic catholyte. The evolution of gas, therefore, cannot be a direct function of the hydrogen ion concentration, and the delayed evolution of gas at the anode strongly supports the postulate of an unstable intermediate.

These ideas will be strengthened by the evidence to be presented. This evidence is centered about the reducing action in the anode compartment, and will be

concerned with both qualitative and quantitative aspects of this reducing action. Since the techniques of measuring the various facets of this reducing action differ somewhat, each is discussed separately in the following sections.

A. Mean Valence Number Determinations

A greater quantity of magnesium is dissolved from the anode than can be accounted for coulometrically on the assumption that magnesium is oxidized to the dipositive state. In other words, the initial mean valence number of the magnesium dissolved from the anode is somewhat less than two. This mean valence number can be determined quantitatively by means of the equation presented in the section dealing with experimental methods.

Table I shows a series of typical initial mean valence numbers in a variety of electrolytes. These values were all obtained in a divided cell with magnesium anode and cathode. The current density was approximately 0.05 amp. per square centimeter. In all cases, there was no detectable loss in weight of the magnesium cathode. Gas was liberated at both electrodes, but the cathodic evolution was considerably greater than the anodic evolution. In most cases, the anode tended to acquire a superficial dark film which turned white on

Table I

Typical Mean Valence Numbers

<u>Electrolyte</u>	<u>Conc. (gm/100 cc. H₂O)</u>	<u>V_i</u>
MgSO ₄	2.5	1.38
MgSO ₄	saturated	1.33
Na ₂ SO ₄	7	1.41
NaCl	15	1.50
KClO ₃	5	1.66
KI	20	1.54
CaCl ₂	32	1.66

drying. This aspect will be discussed more fully in a later section. The film caused no electrolytic passivity, but, in general, it could not be completely wiped from the anode in order to make accurate weighing possible. On this account, the measured loss in weight of the magnesium was less than the actual loss by oxidation, and hence the initial mean valence numbers recorded in Table I are a little too high.

Although there appears to be some variation in mean valence number with the electrolyte used, it will be noted that in all cases listed the mean valence number is significantly less than two. The range of mean valence numbers is from 1.66 to 1.33, which

indicates that from one to four unipositive magnesium ions are produced for every two dipositive magnesium ions.

The results of a study of the variation of the mean valence number with electrolyte concentration and with current density are indicated in Table II. These results were obtained with a divided cell and a

Table II

Variation of Electrolyte Concentration and Current Density

<u>Electrolyte</u>	<u>Current (amps.)</u>	<u>Approx. Current Density (amps./sq. cm.)</u>	<u>V₁</u>
MgSO ₄ (5 gms. per 200 cc. H ₂ O)	0.2	0.033	1.41
	0.4	0.067	1.44
	0.7	0.12	1.43
	1.0	0.16	1.40
	2.0	0.33	1.38
	3.0	0.50	1.38
MgSO ₄ (saturated)	0.2	0.033	1.32
	0.4	0.067	1.31
	0.7	0.12	1.33
	1.0	0.16	1.57
	1.5	0.25	1.56
	2.0	0.33	1.54
	3.0	0.50	1.65

magnesium anode and a platinum cathode. The dilute magnesium sulfate solution contained 5 grams of magnesium sulfate heptahydrate in 200 cc. of water.

It is obvious that there are no significant trends in the value of the mean valence number with variation in either the concentration or the current density. However, in the case of the saturated magnesium sulfate solution, there is a definite change in the mean valence number between total current values of 0.7 and 1.0 amp. The occurrence of the higher value of the mean valence number at currents above 1.0 amp. was accompanied by a peculiar cyclic phenomenon. Very soon after the start of the electrolysis, the anode turned black. This discoloration slowly disappeared with evolution of gas. During this time the current gradually decreased, while the voltage increased. Whenever the current had decreased to approximately one-half its original value, it would start to increase again, with decreasing voltage. By this time the black deposit had completely disappeared from the anode and the gas evolution had stopped. When the current had increased to approximately three-fourths of its original value there was a flash appearance of black color over the entire anode surface, while the current and voltage simultaneously jumped to their original values. The appearance of the black color was

accompanied by a vigorous evolution of gas. The entire cycle was repeated over and over again during the course of electrolysis. Since this cyclic phenomenon had no direct connection with the ultimate goals of this work and was not susceptible of simple explanation, it was not investigated further; and the region of current density at which this phenomenon occurred was avoided during all subsequent experiments.

Some electrolytes caused deviations in the behavior of the magnesium anode. With potassium fluoride as the electrolyte, the anode became passive. It is believed that this was due to the fact that a very adherent white substance, presumably magnesium fluoride, covered the anode. In the case of potassium cyanide as the electrolyte, a brown flocculent material, which qualitatively exhibited the behavior of paracyanogen, a polymer of composition $(CN)_x$, was formed at the anode.

B. Anodic Reductions

It is assumed that unipositive magnesium is formed as part of the primary anodic electrolytic process, and that this unipositive magnesium reacts non-electrolytically with the water to liberate hydrogen. However, if another species capable of being reduced were present, it also could undergo reaction with the

unipositive magnesium. In such a case there would be a competitive reaction between this added species and the water, and both the evolution of hydrogen and reduction products of the added species should be observed. The qualitative aspects of several such reactions which have been observed will be discussed in the following sub-sections. All of these experiments were performed in a divided cell with two magnesium electrodes, both cut from the same gross piece of magnesium. In some instances the added species was used as the sole electrolyte, whereas in other cases the species were added to magnesium sulfate solution. This was deemed appropriate, since no reduction products of sulfate ion have ever been detected in the anode compartment, either during or after electrolysis. Likewise, no peroxy compounds, such as the peroxydisulfate ion, have ever been detected in the anolyte. The magnesium sulfate solutions used contained approximately 10% by weight of this solute.

1. Potassium permanganate with magnesium sulfate as electrolyte.

A considerable amount of brown material was isolated from the anolyte. This material dissolved in 6M nitric acid, and gave a violet color when sodium bismuthate was added to the acid solution. The brown

material could scarcely have been other than manganese dioxide. No brown material was found in the catholyte. There was some gas evolution at the anode. A control test showed no loss in weight of a piece of magnesium left overnight in pure potassium permanganate solution without electrolysis.

2. Potassium dichromate with magnesium sulfate as electrolyte.

A dark brown material was formed at the anode. This material behaved qualitatively like chromium dioxide, but its composition was not determined. No brown substance was formed at the cathode. There was some gas evolution at the anode. A control test showed no loss in weight of a piece of magnesium left overnight in pure potassium dichromate solution without electrolysis.

3. Potassium hexacyanoferrate(III) with magnesium sulfate as electrolyte.

At the end of electrolysis a positive test was obtained for hexacyanoferrate(II) ion in the anolyte. No hexacyanoferrate(II) ion was detected either in the catholyte or in the original solution. A control test did indicate a slow reaction between magnesium

and the potassium hexacyanoferrate(III) solution, since hexacyanoferrate(II) ion could be detected after one and one-half hours without electrolysis. The electrolytic experiments, however, lasted only fifteen minutes.

4. Magnesium nitrate as electrolyte.

Gas was evolved at the anode, but no solid products were formed. However, nitrite ion was detected in both anolyte and catholyte. It is quite possible that the cathodic reduction of the nitrate ion occurred electrochemically, as evidenced by a marked decrease, in this instance, in the amount of gas evolved at the cathode. A control test showed no evidence of nitrite ion when a piece of magnesium was left overnight in the magnesium nitrate solution. There was some evolution of gas, however, in the control test.

5. Potassium chlorate as electrolyte.

At the conclusion of electrolysis, the anolyte gave a positive test for chloride ion. Gas was evolved at the anode. The catholyte gave only a faint turbidity upon the addition of silver nitrate solution. The

control test indicated no trace of chloride ion at the end of two hours without electrolysis.

6. Sodium tungstate with magnesium sulfate as electrolyte.

The only detectable effect was a black deposit on the anode. This product was not identified. The cathode showed no trace of the black material. The control test indicated no apparent effect without electrolysis.

7. Ammonium metavanadate with magnesium sulfate as electrolyte.

The anode developed black scales, and the original yellow color of the solution gradually disappeared in the anolyte. The solid product was not identified. There was no trace of the black material on the cathode, and the catholyte retained its original yellow color. The control test indicated no apparent effect without electrolysis.

These qualitative observations indicate that reduction of the oxidizing species present usually does occur at the anode. In some cases, it was obvious that some reduction, possibly electrochemical, occurred also at the cathode, and others tended to show a very slow reaction in the control tests without electrolysis.

These cases, therefore, cannot be used as conclusive evidence. However, most of the listed observations show unequivocally that reduction of the oxidizing species occurred solely at the anode during electrolysis. Other observations, which are not listed, were discarded due to their inconclusive nature as a result of either reaction in the control test or passivity effects. Among the oxidizing species used in these tests were uranyl nitrate, sodium arsenate, ammonium molybdate, iodine, and potassium iodate. The observations which have been described are summarized in Table III.

Table III

Summary of Anodic Reductions With Mg Electrodes

<u>Electrolyte</u>	<u>Oxidizing Species</u>	<u>Reduced Products</u>		
		<u>Anolyte</u>	<u>Catholyte</u>	<u>Control</u>
1. MgSO ₄	MnO ₄ ⁻	MnO ₂	None	None
2. MgSO ₄	Cr ₂ O ₇ ⁼	Brown Substance	None	None
3. MgSO ₄	Fe(CN) ₆ ⁻³	Fe(CN) ₆ ⁻⁴	None	Slow
4. Mg(NO ₃) ₂	NO ₃ ⁻	NO ₂ ⁻	NO ₂ ⁻	None
5. KClO ₃	ClO ₃ ⁻	Cl ⁻	Trace	None
6. MgSO ₄	WO ₄ ⁼	Black Substance	None	None
7. MgSO ₄	VO ₃ ⁻	Black Substance	None	None

Anodic reductions of this nature are not peculiar to magnesium. Similar qualitative effects of varying degree were observed with aluminum, zinc, cadmium and copper. Some of these effects are listed in Table IV.

Table IV

Summary of Anodic Reductions With Various Electrodes

<u>Electrodes</u>	<u>Electrolyte</u>	<u>Oxidizing Species</u>	<u>Reduced Anolyte</u>	<u>Products Catholyte</u>	<u>V_1</u>
Aluminum	KNO_3	NO_3^-	NO_2^- and gas	NO_2^-	-
	KClO_3	ClO_3^-	Cl^- and gas	Cl^-	2.00
	$\text{K}_3[\text{Fe}(\text{CN})_6]$	$\text{Fe}(\text{CN})_6^{-3}$	Blue ppt. and gas	$\text{Fe}(\text{CN})_6^{-4}$	-
Zinc	KClO_3	ClO_3^-	Cl^-	None	1.88
	KNO_3	NO_3^-	NO_2^- and gas	NO_2^-	-
	$\text{K}_3[\text{Fe}(\text{CN})_6]$	$\text{Fe}(\text{CN})_6^{-3}$	Blue ppt. and gas	$\text{Fe}(\text{CN})_6^{-4}$	-
Cadmium	KNO_3	NO_3^-	NO_2^-	NO_2^-	1.46
	KClO_3	ClO_3^-	None	None	1.98
	$\text{K}_3[\text{Fe}(\text{CN})_6]$	$\text{Fe}(\text{CN})_6^{-3}$	Blue ppt. and gas	$\text{Fe}(\text{CN})_6^{-4}$	-
Copper	KNO_3	NO_3^-	None	None	1.98
	KClO_3	ClO_3^-	Cl^-	None	1.73
	KCN	-	None	None	0.99

These observations were made in a divided cell with similar metal electrodes. In all cases, the anion of the electrolyte served as the oxidizing species under investigation. It is obvious that, in some cases, reduction to a varying degree has occurred at both electrodes. In other cases, there was no reduction at either electrode. However, in the particular instance when the hexacyanoferrate(III) ion was the oxidizing species, different products were obtained in the anolyte and catholyte. At the cathode a positive test for hexacyanoferrate(II) ion was obtained, whereas at the anode a precipitate of Prussian blue was obtained, indicating that not only had reduction occurred but the complex ion had been broken down as well.

The initial mean valence number was determined in a few cases, and these data are listed, also, in Table IV. It is apparent that, in the cases studied, whenever a mean valence number lower than normal was obtained, reduction of the oxidizing species did occur at the anode. When normal valence numbers were obtained, no reduced products were formed. A striking example of this is furnished by copper. In the presence of nitrate ion, no reduction occurred and a mean valence number of essentially two was obtained. In the presence of cyanide ion, which is known to stabilize the unipositive state, a mean valence number of one

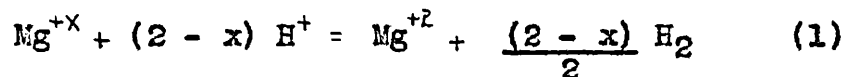
was observed. However, in the presence of chlorate ion, an intermediate mean valence number was obtained and chloride ion was detected in the anolyte.

It is possible, of course, that some of these reactions may proceed by other mechanisms. However, several cases indicate the validity of the postulate of an unstable intermediate. It is evident that much more work needs to be performed in this field, as no other data are available at present; and, since this particular subject was not the original goal of the present work, such investigations will have to be left to others.

C. Gas Evolution Studies

The purpose of the studies of the gas evolved at the anode was to correlate quantitatively the amount of hydrogen evolved with the excess magnesium (beyond that required for oxidation to the dipositive state) dissolved from the anode. However, it cannot be determined from such a study, in itself, whether the hydrogen is produced by non-electrolytic reaction between metallic magnesium and water, or by reaction between a unipositive magnesium ion and water. The initial mean valence number and the amount of hydrogen evolved would be identical by both mechanisms.

Irrespective of the mechanism involved, the amount of hydrogen evolved at the anode is governed by the following equation:



where x is the mean valence number.

This is true, of course, only if the reducing substance, whether metallic magnesium or unipositive magnesium ion, is oxidized solely by hydrogen ion. It would not be true if another oxidizing species, capable of reaction, were present. However, since it has been shown previously that metallic magnesium does not react with the anion of the salt which was reduced during electrolysis, the amount of hydrogen liberated from a direct reaction between water and metallic magnesium would be expected to be independent of the presence of the reducible anion. Experiments have shown that the presence of the reducible anion did decrease the amount of hydrogen. Therefore, both by far the greater part of the liberation of hydrogen, as well as the reduction of the added oxidizing species must be due to products formed during electrolysis.

The gas evolution data are listed in Table V. The gas measurements were made in the gas analysis apparatus shown in Figure 1 and described in the

Table V

Gas Evolution Measurements

<u>Electrolyte</u>	<u>Concentration</u> (gms/100 cc. H ₂ O)	<u>Wt. Hg</u> <u>Dissolved</u>	<u>Wt. Ag</u> <u>Deposited</u>	<u>V₁</u>	<u>Vol. H₂</u> <u>Exptl. STP</u>	<u>Vol. H₂</u> <u>Calc. STP</u>
Na ₂ SO ₄	7	0.0388gms	0.2431gms	1.41	11.5 ml	10.5 ml
Na ₂ SO ₄	7	0.0408	0.2549	1.41	11.9	11.1
Na ₂ SO ₄	7	0.0470	0.2912	1.39	14.2	13.2
Na ₂ SO ₄	7	0.0489	0.3074	1.42	14.2	13.1
Na ₂ SO ₄	7	0.0513	0.3260	1.43	14.1	13.5
*KClO ₃	5	0.0626	0.4479	1.61	11.3	13.2
*KClO ₃	5	0.0642	0.4607	1.62	11.8	12.9

*Cl⁻ detected in the anolyte.

section dealing with the experimental methods. The results indicate that, in the sodium sulfate solutions in which the only reduced product ever detected was hydrogen, approximately one milliliter more of hydrogen was found than was calculated from the initial mean valence number according to equation (1) of this section. Part of this slight difference may be attributed to experimental error. However, in this and other cases, it has been noticed that a small amount of gas was liberated on the anode side of the porous disc separating the anode compartment from the cathode compartment. Although this phenomenon has not been satisfactorily explained, it may account, at least in part, for the fact that slightly more than the calculated quantity of hydrogen was evolved.

In the cases where potassium chlorate was used as the electrolyte, from one to two milliliters less hydrogen was actually found than was to be expected from the mean valence number of the magnesium dissolved. It will be remembered that, in the studies of anodic reductions, the chlorate ion was found to undergo some reduction to chloride ion. Chloride ion was detected in the anolyte after the gas evolution measurement also. The decrease in the amount of hydrogen evolved is to be expected from consideration of the above discussion concerning reaction between the unipositive magnesium

ion and both water and chlorate ion. Further quantitative determinations were not undertaken.

D. Reduction at a Distance from the Anode

One of the more difficult tasks associated with the present work has been to show conclusively that the previously discussed phenomena are the result of a reaction of an oxidizing species with an intermediate produced during the anodic oxidation, rather than of a reaction between the oxidizing species and metallic magnesium. Practically all of the observations could be explained, with reservations, in terms of either mechanism. However, if it could be shown, by means of an experiment in which direct contact between the oxidizing agent and the anode is prevented, that reduction can take place at some distance from the anode, this would prove the reducing species to be not metallic magnesium but something present in the solution.

In order to accomplish this goal, a so-called "sweep" electrolytic apparatus was devised. A diagram of this apparatus is shown in Figure 2. A reservoir R of one to two liters capacity, and filled with the electrolyte to be used, was mounted three to four feet above the electrode assembly. The electrolyte was allowed to flow through the tube, past the anode A and into the large beaker B. The added oxidizing species

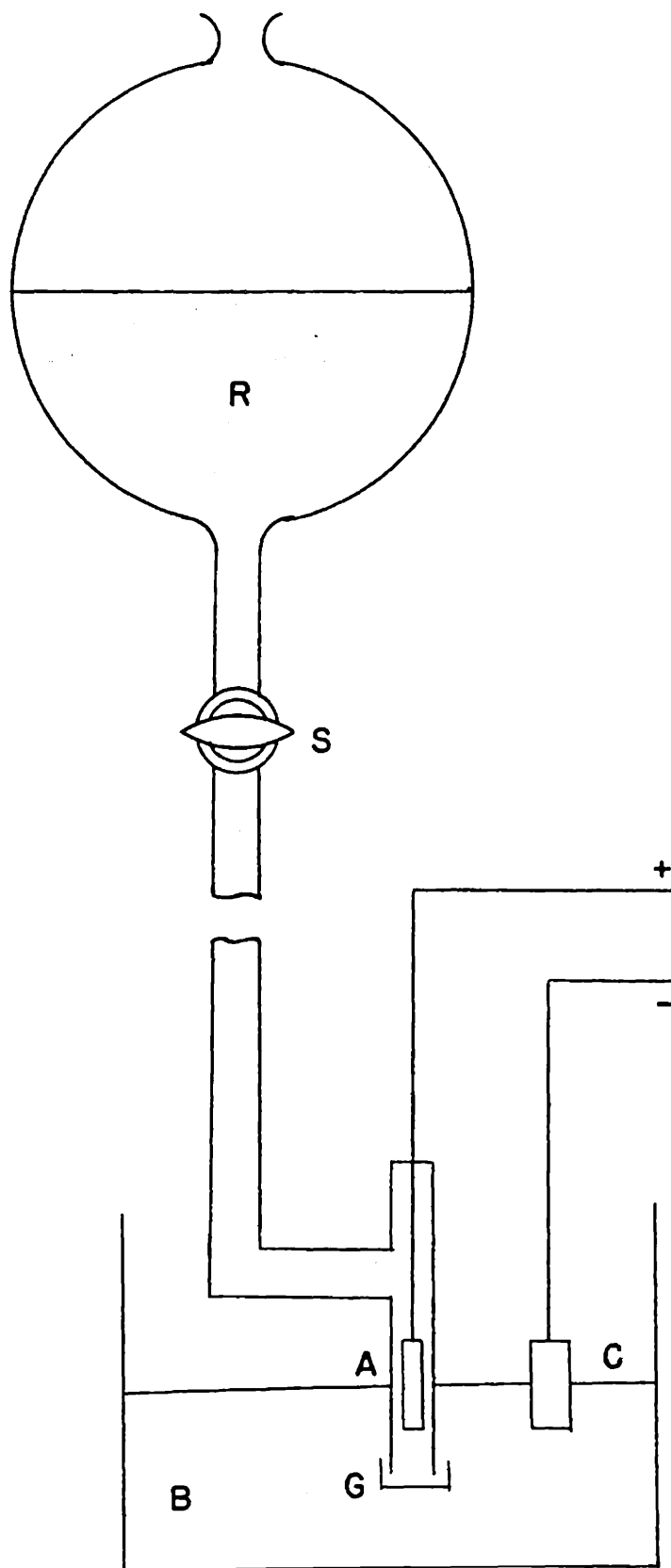


FIGURE 2. ELECTROLYTIC "SWEEP" APPARATUS

was contained in this beaker, so that, so long as the electrolyte was flowing at the appropriate rate, this oxidizing species could not come into direct contact with the anode. A layer of glass wool G, to prevent any solid material from entering the main beaker, covered the end of the anode delivery tube. To prevent any cathode products from entering the main beaker, the cathode C was shielded by a porous cup.

In operation, the beaker B was mounted in such a way that the level of solution was slightly below the end of the anode delivery tube. Stopcock S was then opened and adjusted so that the electrolyte flowed at a fairly rapid rate. After the level had risen to establish contact, the current was started and electrolysis was allowed to proceed until the electrolyte was nearly exhausted from the reservoir. At this point, the current was stopped and the beaker removed. The oxidizing species contained in the beaker had never come into contact with the anode. The solution was then filtered and any solid products were examined.

It was found possible to effect reductions of added oxidizing species by means of this apparatus and technique. For example, with silver ion as the oxidizing species contained in the main beaker, a black finely divided solid was obtained which on qualitative

test proved to be metallic silver. A series of such qualitative observations is given in Table VI.

Table VI

Anodic Reductions Using a "Sweep" Technique

<u>Electrolyte</u>	<u>Concentration (gms/100 cc. H₂O)</u>	<u>Oxidizing Species</u>	<u>Observations</u>
Mg(NO ₃) ₂	10	AgNO ₃	Black finely divided substance which gave qualitative tests for metallic silver.
Na ₂ SO ₄	7	Ammoniacal AgNO ₃	Black finely divided substance which gave qualitative tests for metallic silver.
Na ₂ SO ₄	7	KMnO ₄	Brown substance which gave qualitative tests for MnO ₂ .
NaCl	10	KMnO ₄	Brown substance which gave qualitative tests for MnO ₂ .
Na ₂ SO ₄	7	KClO ₃	No chloride ion detected.

Although the actual amounts of reduced products obtained by this technique were necessarily small, they were nevertheless sufficient for positive identification, except when chlorate ion was used as the oxidizing

species. This exception can be explained by noting that, in previous cases, the mean valence number obtained with a chlorate electrolyte was considerably higher than with other electrolytes. The potassium permanganate solution was filtered prior to use in the later electrolytic experiments. The amount of manganese dioxide isolated from the solution after electrolysis was definitely greater than the trace amount of manganese dioxide found when the original solution was filtered. Sodium sulfate was chosen as the "sweep" electrolyte because no reduced or peroxy compounds of the sulfate ion have ever been detected. However, as an additional proof, sodium chloride was used also, since chloride ion cannot be reduced and there is no possibility of the formation of peroxy compounds. The same effect was obtained as with sodium sulfate as the "sweep" electrolyte.

The results of this experiment show that the data previously accumulated cannot be accounted for in terms of a non-electrolytic reaction between the metallic magnesium anode and the oxidizing species present, since the reducing action was found to take place a short distance from the anode even when the oxidizing species was never allowed to come into direct contact with the magnesium anode. The only other possibility is that unipositive magnesium is formed, and that this

product is sufficiently stable in the solution so that it can be removed at least a short distance from the anode.

E. Electrolysis With an Intermittent Direct Current

Although appropriate control tests have indicated that metallic magnesium undergoes no non-electrolytic reaction with various oxidizing species previously discussed, there has been some speculation from other laboratories concerning a sort of "anodic activation", in which the anode is supposed temporarily to acquire the ability to react with the oxidizing species during and as a result of the current passage. Such speculation would appear to have little basis, since most existing activation-passivation theories have indicated that it is the cathode which becomes activated and the anode which becomes passive. Nevertheless, considerable doubt was cast on the anodic activation postulates by a simple type of experiment, consisting of electrolysis by an intermittent direct current instead of the continuous direct current. This was accomplished by the use of only a single tube of the mercury tube rectifier, so that a direct current flowed only during one half-cycle and no current flowed during the other half-cycle.

If the anode becomes activated during the time when current is flowing so that it can react

non-electrolytically with an oxidizing species, this activation should carry over, at least in part, into the half-cycle when no current is flowing. If this were true, considerably lower mean valence numbers would be obtained with an intermittent than with a continuous direct current. However, if an intermediate is formed, the amount of which is dependent, in a given situation, on the amount of current passed, then the same mean valence number should be obtained whether an intermittent or a continuous current is used. The results of these experiments are presented in Table VII.

Table VII

Intermittent Electrolysis				
<u>Electrolyte</u>	<u>Conc. (gms. per 100 cc. H₂O)</u>	<u>Current</u>	<u>Time</u>	<u>V_f</u>
MgSO ₄	7	Continuous 0.3 amp.	20 min.	1.39
MgSO ₄	7	Intermittent 0.3 amp.	20 min.	1.37
MgSO ₄	7	Intermittent 0.15 amp.	40 min.	1.38
Na ₂ SO ₄	7	Continuous 0.3 amp.	20 min.	1.40
Na ₂ SO ₄	7	Intermittent 0.15 amp.	40 min.	1.37

These results indicate that essentially the same mean valence number was obtained regardless of whether

the current was continuous or intermittent. Another indication that there was no non-electrolytic reaction with metallic magnesium is given by those instances in which the electrolysis was carried out for a longer period of time. Any direct non-electrolytic reaction between the magnesium and water would have resulted in a lower mean valence number in the cases in which the anode was in contact with the solution for a longer period. In other words, the degree of non-electrolytic reaction should be dependent, to some extent at least, on the time of exposure to the solution. On the other hand, the amount of an intermediate produced by electrochemical means should be dependent only on the current and the efficiency of the process, and not on the time during which the anode is in contact with the solution.

F. Unidentified Substance

It was mentioned in a previous section that the anode tended to develop, under certain conditions, a dark film which turned white on drying. Moreover, in certain cases, black particles of varying size were observed to fall from the anode. At room temperature, most of these particles soon disappeared, leaving a white solid which proved to be magnesium hydroxide. Gas bubbles were observed coming from the larger

particles which fell to the bottom of the anode compartment. It seemed of interest, therefore, to attempt to obtain this dark colored product in quantity, and, if possible, to identify it.

Beetz (1) also reported the formation of a black substance during electrolysis, but Turrentine (2) reported no evidence of such a substance. Faivre (18) reported the x-ray diffraction analysis of a black product obtained by slow oxidation of metallic magnesium in a moist atmosphere. His conclusions were that there was no significant difference between this product and ordinary brucite (magnesium hydroxide), although the black compound contained excess magnesium which would not react with ethyl bromide. This paper repudiates the earlier one by Faivre and Michel (19), in which they reported that the excess magnesium did react with ethyl bromide, and that the x-ray analysis indicated the black material to be magnesium hydroxide with magnesium atoms inserted in the lattice. Such evidence as this is, at best, indecisive.

Frary and Berman (20) reported a black material which they characterized as a sub-oxide of magnesium. This material was formed at the cathode during the electrolysis of molten $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ if magnesium oxide were present. The material reacted with water, and this action was shown not to be due to finely

divided metallic magnesium by the fact that the black material would not react with a solution of anhydrous nickel chloride in absolute alcohol, whereas powdered magnesium liberated nickel from such a solution.

Still other instances have been reported in which a black product containing magnesium has been obtained. Baborovsky (21) repeated the work of Beetz (1) and obtained a black product which he concluded had to be either a sub-oxide of magnesium or magnesium oxide and metallic magnesium. Christamanos (22) reported the formation of a black product when magnesium ribbon was burned in contact with cold glass. He reported the substance to be a sub-oxide of indefinite composition.

It is interesting to note that, in every case reported except one, the black materials were formed as the result of oxidation of metallic magnesium. Frary and Berman could obtain their black product only by cathodic reduction, and the presence of magnesium oxide was necessary for its formation. They believed that their product was not the same as those formed in oxidation processes. However, it is only reasonable to assume that, if the black products do contain unipositive magnesium, they could be formed by reduction of dipositive magnesium as well as by oxidation of metallic magnesium, provided only that the appropriate conditions existed.

In the present work it was found that the black material was formed in greater quantities, and did not disappear so quickly, when the electrolysis was carried out at the temperature of an ice bath with sodium chloride as electrolyte. However, the black material formed even under these conditions still turned white if the wet material was allowed to warm to room temperature. Various methods were tried to remove the bulk of the water from the black material while it was maintained at 0°C. The only suitable technique in which the material remained fairly black was to wash the material with water at 0°C. to remove traces of electrolyte, and then wash two or three times with a cold 95% alcohol solution. After this treatment the material could be allowed to warm to room temperature and the drying process could be completed in a desiccator.

The dark gray to black product obtained as just described liberated hydrogen from acid solution and reacted with potassium permanganate solution to give manganese dioxide. This reducing property might be accounted for either on the assumption that the dark substance was colloidal metallic magnesium or on the assumption that it was a colored compound of unipositive magnesium. Although it had been determined previously that bulk metallic magnesium does not react with pure potassium permanganate solution, this fact

does not insure that very finely divided metallic magnesium might not do so. Yet, from the evidence to be considered in the ensuing discussion, it seems extremely unlikely that the black material can be finely divided metallic magnesium. For one reason, simple anodic oxidation is not a general method for the preparation of colloidal solutions of metals. The usual electrochemical method requires that an arc be struck between two electrodes under a liquid.

When observed under an ordinary microscope, the black material appeared quite inhomogeneous. The material consisted of irregular black masses surrounded by a colorless layer, presumably magnesium hydroxide. Upon the addition of a drop of acid, the colorless layer dissolved fairly rapidly, whereas the black masses dissolved more slowly with the liberation of gas. As will be brought out later, chemical analysis did indeed show that the bulk of the material consisted of magnesium hydroxide.

The following procedure was employed for the analysis of the black material. The reducing power was determined by measuring the amount of hydrogen evolved from a weighed sample. Hydroxide ion was determined by dissolving a weighed sample in standard acid and titrating the excess acid with standard base. Obviously, for this determination, the number of

equivalents of reducing power must be subtracted from the total number of equivalents of standard acid used, since hydrogen ion is involved in both reactions. Magnesium was determined by the pyrophosphate method. Since the black material was obtained from a sodium chloride solution, chloride ion was determined by the standard Volhard method. A typical analysis of a sample of the material, dried as described above, follows:

Total Mg	-	32.77%	
OH ⁻	-	36.67%	
Cl ⁻	-	5.11%	
Mg ⁺	-	6.76%	} from reducing power.
{ or metallic Mg	-	3.38%	

Undoubtedly, the remainder of the material was water, although it was not determined as such. Attempts to dry the black material indicated that it could be dried at 105°C. without apparent change in properties. Even at this temperature, however, not all the water was lost. This behavior was to be expected from the presence of magnesium hydroxide.

The percentage of chloride ion may have no significance, since later experiments indicated that the chloride ion content could be reduced to about 2% by grinding and re-washing the black material with water. The reducing power is expressed alternatively

as percentage of univalent magnesium and as percentage of metallic magnesium.

When heated at 300°C., the black material turned white within two or three minutes. Also, all of the chloride ion was lost, a behavior which parallels the familiar hydrolysis of magnesium halides at higher temperatures. After the material had turned white, it no longer had any reducing properties.

All attempts to analyze the black material by means of x-ray diffraction techniques were of no avail. Control investigations were made on magnesium hydroxide, on metallic magnesium, and on a physical mixture of the two. If the reducing property of the unknown black material were due to metallic magnesium, the above analysis would require that the metallic magnesium be present to the extent of about 3.4% by weight. The x-ray diffraction pattern of the control mixture of magnesium hydroxide and powdered magnesium (3.41% by weight) indicated that metallic magnesium could be detected at this concentration in magnesium hydroxide, since the three most intense metallic magnesium peaks were distinguishable in the x-ray pattern of the control mixture. However, for the black substance, in every case, the x-ray diffraction pattern showed only two broad, ill-defined peaks, as is characteristic of amorphous substances.

The black material obtained in this work was also subjected to a test similar to that of Frary and Berman (20). The work of Gomberg and Bachmann (12) showed that magnesium reacts quite vigorously with iodine solutions in ether. The black material did not undergo reaction with the iodine solution in ether and was recovered unchanged. A control test with powdered magnesium gave a vigorous reaction. Likewise, the black material did not react, as does finely divided magnesium, with ethyl bromide.

Obviously, the structure of unipositive magnesium ion is unknown. However, even as Turrentine (2) suggested, the structure may involve a magnesium to magnesium linkage in which the effective valence of the magnesium is unity. This would pair the odd electrons and might account for the observed stability of the unknown compound. Such behavior is already well recognized in the case of the mercurous ion.

It is unfortunate that the characteristics of the reported black products are such as to prevent isolation in a form pure enough for chemical analysis. Because of this fact, in order to support the hypothesis of the presence of unipositive magnesium, one must clearly demonstrate that the properties of the material cannot be explained by any alternative hypothesis. It is believed that the failure of the black material

to undergo certain reactions characteristic of metallic magnesium strongly indicates that the material does not contain finely divided magnesium.

G. Liquid Ammonia Electrolyses

Since, in electrolysis in aqueous solutions, water is reduced at the magnesium anode, it is obvious that data obtained by the use of non-aqueous solvents would be desirable. Preliminary investigations were undertaken with liquid ammonia as solvent. Since liquid ammonia is more difficult to reduce than water, the unstable intermediate encountered in the previous work might be expected to exhibit greater stability in liquid ammonia than in water.

Del Boca (23) reported that magnesium did not dissolve and no gas was evolved from a magnesium anode in liquid ammonia solutions. However, he used a potential of only 12 volts. By means of the mercury tube rectifier used in the present work much greater potentials could be applied. Bergstrom (24) found that only a trace of magnesium amide was formed from the action of pure liquid ammonia on magnesium ribbon over a period of five months. However, he did find that magnesium reacted slowly with liquid ammonia

solutions of salts of the alkali metals to form magnesium amide. This behavior parallels that in aqueous solutions.

Techniques involving the use of liquid ammonia as a solvent have been well established and need not be considered here. The electrolytic apparatus used in the present work consisted of a simple cell equipped with a reflux condenser cooled by means of a dry ice-isopropyl alcohol mixture. Platinum leads to which the magnesium electrodes were connected were sealed through the glass cell. Ammonia gas from a cylinder of anhydrous ammonia was condensed in the cell by means of the cooling mixture. No special precautions were taken to dry the ammonia gas prior to use. The electrolyses were performed at the boiling point of liquid ammonia, the reflux condenser preventing loss of ammonia.

Three salts were used in the preparation of the electrolytic solutions. Sodium chloride, which was found to be sufficiently soluble in liquid ammonia to give appreciable currents without the use of excessive voltages, was pulverized and dried at 110° C. for 24 hours prior to use. The sodium chloride was transferred to the electrolytic cell, and, after the cell had been connected to the condenser, ammonia gas was allowed to flow through it for two hours in order to remove air and moisture. Ammonia was then condensed

and electrolysis started. In a separate determination, magnesium iodide was used as the electrolyte. Since magnesium iodide is relatively unstable in the presence of light and moisture, the salt initially had a yellow appearance and appeared to contain some moisture. However, after ammonia gas had been passed over the magnesium iodide in the electrolytic apparatus for two hours the salt turned completely white. Some ammonia was then condensed on the salt and allowed to evaporate to facilitate the removal of moisture. After this treatment, ammonia was condensed and electrolysis started. Magnesium nitrate was treated similarly to magnesium iodide. In this instance, however, it is uncertain whether or not all the water had been removed prior to electrolysis.

Since the investigations were of an exploratory nature, the only quantitative data obtained were the initial mean valence numbers. These were determined by means of the equation given in the section dealing with experimental methods. The mean valence numbers obtained are presented in Table VIII.

With sodium chloride as the electrolyte, the mean valence number was greater than two, indicating that an electrochemical oxidation in addition to the dissolution of magnesium occurred. A blue color developed at the cathode and diffused throughout the

Table VIII

Mean Valence Numbers in Liquid Ammonia Solutions

<u>Electrolyte</u>	<u>Wt. Mg Dissolved</u>	<u>Wt. Ag Deposited</u>	<u>V₁</u>
NaCl	0.0259 gms	0.2753 gms	2.39
MgI ₂	0.0443	0.3625	1.84
Mg(NO ₃) ₂	0.0235	0.2249	2.16

entire solution. The blue color persisted until after the conclusion of electrolysis. The anode was uniformly covered with a white deposit which was washed off before the final weighing. There was no detectable loss in weight of the magnesium cathode.

With magnesium iodide as electrolyte, a mean valence number significantly less than two was obtained. The anode started to turn dark at the beginning of electrolysis, and some black flakes fell from it during electrolysis. The black deposit was easily removed from the anode, leaving a shiny surface of magnesium. The black flakes on the bottom of the cell turned white when warmed to room temperature in the ammonia atmosphere. A non-persistent blue color developed at the cathode surface during electrolysis. There was no detectable loss in weight of the magnesium cathode.

With magnesium nitrate as the electrolyte, a mean valence number greater than two was obtained. However, in this instance, a black deposit developed on the anode and could not be removed, so that accurate weighing was impossible. The black flakes which fell to the bottom of the cell retained their color when warmed to room temperature in the ammonia atmosphere. No blue color developed at the cathode surface, and again, there was no detectable loss in weight of the magnesium cathode.

From these preliminary investigations it appears that the use of liquid ammonia as solvent might offer a possible means of isolating a black product free from magnesium hydroxide, although it might be contaminated with magnesium amide.

Summary and Conclusions

Magnesium dissolves anodically in aqueous salt solutions with an initial mean valence number significantly less than two. This behavior is accompanied by an evolution of hydrogen which quantitatively corresponds to the oxidation of the mean valence "state" to the dipositive state. These facts indicate that either metallic magnesium reacts non-electrolytically with water, or that an intermediate is formed as part of the anodic process. The intermediate in the oxidation of metallic magnesium to the dipositive state can only be unipositive magnesium.

When any of a variety of oxidizing agents is added to the electrolytic system, the amount of hydrogen evolved is decreased, and the added oxidizing species undergoes reduction. Appropriate control tests have indicated that these oxidizing species do not react non-electrolytically with metallic magnesium, although magnesium does react slowly with water in aqueous salt solutions. This type of behavior would indicate that an intermediate is formed which is capable of further oxidation in a competitive reaction with water and the added oxidizing species. Similar behavior, in varying degree, has been observed in the cases of aluminum, cadmium, and zinc.

The intermediate has been shown not to involve any product of the electrolyte used; the same general effect can be produced in a variety of electrolytes, such as sodium chloride, in which the anion is incapable of further reduction, and sodium sulfate, in which no reduced sulfate products or oxidized species (peroxy compounds) have ever been detected.

Further evidence that the observed behavior is not due to a non-electrolytically occurring reaction between metallic magnesium and an oxidizing species is provided by a "sweep" electrolytic method in which oxidizing species have been reduced by the anolyte at a short distance from the anodic surface. Without direct contact, there can be no possibility of a reaction between the added oxidizing species and the magnesium anode, regardless of whether or not the metallic magnesium becomes "activated" in some fashion by the current passage.

Data obtained with an intermittent direct current also have indicated that the hypothesis of activation of the anode while the current is flowing cannot be valid. Any activation would tend to be carried over into the part of the cycle when no current is flowing, and hence would result in a mean valence number lower than that obtained with a continuous direct current. The data obtained in this work,

however, have shown that essentially the same mean valence number is obtained whether an intermittent or a continuous direct current is used.

When the electrolyses were performed at room temperature, varying amounts, depending on the electrolyte, of a dark deposit were formed on the anode. When the electrolyses were carried out in an ice bath with sodium chloride as electrolyte, larger amounts of the dark material were formed, and, by the appropriate technique, quantities of black material adequate for analysis were isolated. This substance appeared to consist of a mixture of magnesium hydroxide and a black product which had reducing properties. It failed to undergo reactions characteristic of powdered magnesium metal. X-ray analysis gave a pattern characteristic of an amorphous substance, whereas a control analysis of a physical mixture of magnesium hydroxide and finely divided magnesium metal in proportions corresponding to the reducing power of the black material indicated that metallic magnesium could still be detected at this concentration in magnesium hydroxide. Although these results are not completely decisive, they strongly indicate that the black product does not contain finely divided metallic magnesium.

In summation, the evidence presented strongly indicates that unipositive magnesium ion is formed as part of the anodic process. This unipositive magnesium is ordinarily oxidized to the dipositive state either by water or by another oxidizing species, but under suitable conditions, it can enter into a black solid which can be isolated in an impure form. With the appropriate technique, the unipositive magnesium ion in solution may be removed a short distance from the anode, so that it may exhibit its reducing action away from the anode surface.

Part II

THE OXIDATION OF MAGNESIUM BY TRIIODIDE ION

Part II

THE OXIDATION OF MAGNESIUM BY TRIIODIDE ION

Introduction

Part I of this work has been concerned with evidence for the possible existence of unipositive magnesium ion, derived from studies of the anodic oxidation of magnesium. Other experiments have indicated, however, that valuable information might be gained also from studies of the chemical oxidation of magnesium. Thus, it was discovered in this laboratory that metallic magnesium is rapidly oxidized by an aqueous solution containing triiodide ion. This oxidation is accompanied by a vigorous evolution of hydrogen and by a pronounced liberation of heat. From the fact that hydrogen is evolved, it is evident that the reaction cannot be a simple oxidation-reduction reaction between metallic magnesium and iodine. Since there is at least a possibility that unipositive magnesium might be formed by chemical oxidation of metallic magnesium, this reaction between metallic magnesium and triiodide ion was subjected to further study.

Historical Review

In the course of the work to be described, evidence for the production of some form of magnesium polyiodide was obtained. Pure solid polyiodides of the alkaline earth metals have not been isolated; this fact is generally attributed to their high solubility in water. However, phase studies of the barium iodide-iodine-water system show that at 90° C. a solution saturated with respect to barium iodide and iodine contains these constituents in amounts corresponding to the formula $Ba(I_3)_2$ (25). No solid polyiodides were isolated.

The most common polyiodides are the triiodides, although higher order compounds are known (26). The stability of solid triiodides is apparently related to the cationic size. Cesium, the largest alkali metal, forms the most stable solid triiodide. The atomic sizes are still appreciable in the alkaline earth group, and these elements "show a tendency to form polyiodides" (27). Extensive studies of the alkali metal triiodides and other polyiodides have been made; this literature, however, need not be considered here. A complete discussion and bibliography is contained in Gmelin-Kraut (28).

In general, the polyhalides are water soluble, although "dissolution is often complicated by hydrolysis" (29). Iodine can be extracted from solid triiodides by means of carbon tetrachloride, although the amounts extracted are small and equilibrium is reached only very slowly (30).

The dissociation constant of triiodide ion in aqueous solution has been measured in a variety of ways. Gmelin (28) reports an average K value of 725 at 25° C. for the following expression:

$$K = \frac{[I_3^-]}{[I^-][I_2]}$$

From this, it is evident that conditions for equilibrium definitely favor the formation of triiodide ion, particularly when excess iodide ion is present.

Experimental Methods

The magnesium metal, of 99.8% purity, was furnished by the Aluminum Company of America through the courtesy of Dr. P. V. Paragher. All other chemicals were of C. p. or Reagent grades.

Two types of aqueous solutions containing triiodide ion were prepared; one consisted of a potassium iodide-iodine solution, the other of a magnesium iodide-iodine solution. With the potassium iodide-iodine system, the starting solution was 1 M with respect to potassium iodide and 0.5 M with respect to iodine. At this concentration of iodide ion, iodine would not dissolve in a quantity equivalent to the potassium iodide. However, in certain cases, it was desired to keep the solution saturated with respect to iodine throughout the course of the reaction. This was accomplished by the addition of excess iodine to the original solution. The magnesium iodide-iodine solution was 0.5 M with respect to magnesium iodide and also 0.5 M with respect to iodine. In this case, also, the solution could be kept saturated with iodine throughout the course of the reaction by the addition of excess iodine.

Since the reaction between magnesium metal and triiodide ion, if not controlled, proceeds very

vigorously, the constituents were mixed with caution. The general procedure for carrying out the reaction was as follows. Magnesium in the form either of rod or of filings was introduced into the appropriate triiodide solution. When magnesium filings were used, small quantities were added successively to the solution as a means of controlling the reaction. The reaction was allowed to proceed either until all the magnesium was used up, as evidenced by cessation of hydrogen evolution, or, in the instances in which it was desired to keep the solution saturated with iodine, until only a few crystals of solid iodine remained on the bottom of the reaction vessel. In some cases, the rate of the reaction was controlled by immersing the reaction vessel in an ice bath. At the conclusion of the reaction, the solution was filtered by means of a suction filter and the solid product was washed with distilled water until the washings were colorless.

In some cases, the wet product was analyzed directly in a manner to be described below. In other instances, the material was dried before analysis, either by heating at 110°C . or by prolonged evacuation at room temperature. The extraction experiments consisted of successive extractions of either the wet or the dry product with 100 ml. portions of carbon tetrachloride until the carbon tetrachloride was only slightly colored.

Methods of analysis. (a). Analysis of the wet product. The wet solid was dissolved in sufficient standard sulfuric acid solution to yield three 50 cc. aliquots. The three portions were withdrawn by means of a pipette. One of these portions was titrated directly with standard sodium thiosulfate solution to determine the free iodine content. In the second portion, the free iodine was reduced to iodide ion by sodium sulfite solution, and the resulting solution treated with an excess of standard silver nitrate solution. After titration of excess silver nitrate with standard potassium thiocyanate solution, total iodine was calculated. It was found that excess sulfite ion did not interfere with the silver nitrate titration. In the third portion, the free iodine was reduced by means of sodium thiosulfate, and the resulting solution was titrated with standard base to determine the hydroxide ion content. The sodium thiosulfate solution did not interfere with the hydroxide ion determination. The resulting solution was used for the magnesium determination by the pyrophosphate method.

(b). Analysis of the dried product. In those instances in which the product was dried according to one of the previously discussed procedures before analysis, the method of analysis was altered slightly.

A weighed sample of the material was dissolved in a known amount of standard sulfuric acid solution. The free iodine was titrated directly with standard sodium thiosulfate solution. The excess acid was then titrated with standard sodium hydroxide solution and the resulting solution used for the magnesium determination by the pyrophosphate method. A second weighed sample was dissolved in sulfuric acid solution and the free iodine was reduced by means of a sodium sulfite solution. The total iodine content was determined by titration with standard silver nitrate solution in the usual manner. Both of the above methods of analysis were checked against known solutions of iodine and iodide ion and were found to be satisfactory.

Results and Discussion

The qualitative characteristics of the reaction between metallic magnesium and triiodide ion in aqueous solution are rather striking. When a piece of magnesium rod is immersed in a solution of potassium iodide in water, there is a very slow evolution of gas which, as described in Part I, is characteristic of the behavior of magnesium in aqueous salt solutions. However, if solid iodine is added to this solution, the solution quickly becomes colored by the formation of triiodide ion, and a vigorous evolution of hydrogen commences. At the same time, the solution becomes quite warm. If an insufficient amount of iodine is added, the triiodide ion color eventually disappears from the solution, leaving a white solid. However, if iodine in excess of that required to react with the magnesium is added, the metal is soon used up. When the resulting solution is filtered, a dark brown to black solid is isolated.

The order of addition of the constituents is immaterial. If a piece of magnesium rod is immersed in a saturated solution of iodine in water, there is only a very slow reaction. However, as soon as potassium iodide is added, the reaction proceeds vigorously. The same general behavior is observed if

magnesium filings are used instead of the magnesium rod, although, in this case, the various reactions are somewhat more rapid.

Changes in pH were recorded during the course of the reaction between magnesium and an aqueous solution of triiodide ion. These changes are shown in Table IX, where they are compared with pH changes observed in reactions between magnesium metal with iodide ion and also with iodine solution.

Table IX

Measurements of pH

<u>Time</u> <u>(min.)</u>	<u>KI sol.</u> <u>(1 M)</u>	<u>I₂ sol.</u> <u>(sat'd)</u>	<u>KI₃ sol.</u> <u>(1 M KI, 0.5 M I₂)</u>
0.0	7.35	6.41	7.00
0.5	10.00	10.45	9.18
1.0	10.13	10.57	9.29
2.0	10.27	10.68	9.33
3.0	10.34	10.70	9.34
4.0	10.38	10.71	9.34
5.0	10.41	10.71	9.35

Distilled water - pH = 6.55

Sat'd solution of Mg(OH)₂ in distilled water - pH = 10.21

In each instance, an excess of magnesium filings was added to the solution. The pH values were constant after five minutes. With the iodine solution, the iodine color disappeared, but there was no detectable evolution of gas. In the case of the triiodide solution, there was a vigorous evolution of hydrogen and the solution became very hot. It is evident, from consideration of the pH of the initial solutions, that the evolution of hydrogen from the triiodide solution is not a function of the hydrogen ion concentration, since there was no detectable liberation of gas from the iodine solution which was more acidic than the triiodide solution. Moreover, the liberation of hydrogen from the triiodide solution continues unabated, even in the basic solution, so long as magnesium and triiodide ion are present. Therefore, the reaction cannot be a simple oxidation - reduction reaction between magnesium and iodine, but must involve an intermediate which is capable of liberating hydrogen from water. This intermediate is postulated to be the unipositive magnesium ion.

The rate of the reaction is apparently dependent on the concentration of the triiodide ion, as would be expected if the reaction involved this component. Whenever excess magnesium is present, the reaction in the triiodide solution gradually slows

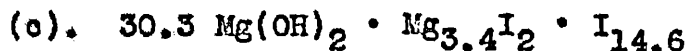
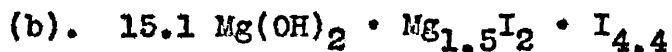
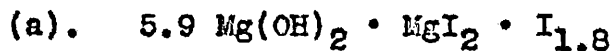
down. However, as soon as more solid iodine is added and the triiodide ion concentration thus increased, the reaction rate immediately increases. If solutions more concentrated in potassium iodide and iodine are used, the reaction proceeds almost violently. This same type of behavior was noted in the cases where magnesium iodide was used instead of potassium iodide.

As indicated previously, a dark brown to black solid was isolated from the solution after completion of the reaction between metallic magnesium and triiodide ion. This solid contained hydroxide ion, magnesium, iodide ion and titratable iodine. In some cases, the solid was subjected to prolonged evacuation and to heating at 110° C. without removal of appreciable titratable iodine. Carbon tetrachloride slowly extracts iodine from the solid, but as many as thirty-nine extractions have failed to remove all the iodine from the original solid. Therefore, this solid must contain some form of a magnesium polyiodide, since analysis has shown that, when the sample is dissolved in acid solution, free iodine is liberated. Experiments have shown also that repeated washing of the original solid with water will eventually decolorize the solid, particularly when the product is obtained from the magnesium iodide-iodine system. However, the washings are colorless and, when acidified, liberate

small quantities of iodine. This can be satisfactorily explained on the assumption that, in the washing process, the hydroxide ion reacts with iodine to form iodate ion, or a comparable species, and iodide ion. Indeed, evidence was found for the presence, in many of the solids, of some component which contains iodine in an oxidation state of +1 or higher. Unfortunately, this component, when present, interfered with the subsequent analyses for the remaining constituents of the solid. No satisfactory procedure was devised for the analysis of iodide ion and iodine in the presence of the component containing iodine in a positive oxidation state.

From consideration of the methods of analysis described in the section dealing with experimental methods, it is evident that the effect of the presence of the component containing iodine in a positive oxidation state would be to make both the hydroxide ion and the free iodine percentages higher than their true values. These effects were observed in the analyses of several of the solids obtained. Re-washing of the solids failed to remove the interfering component because the washing process regenerated the interfering component.

Some typical empirical compositions of the solid were as follows:



Sample (a) was obtained from a solution which was 1 M with respect to potassium iodide and 0.5M with respect to iodine. Magnesium filings were used in the reaction. The solid was not extracted with carbon tetrachloride and was analyzed according to the wet product analytical scheme described previously. It is evident that there is insufficient free iodine for the complete formation of magnesium triiodide and that there is no evidence for the presence of the interfering substance. Sample (b) was obtained from a solution which was 1M with respect to potassium iodide and saturated with respect to iodine. Magnesium filings were used in the reaction. The solid was extracted thirty-nine times with carbon tetrachloride and was analyzed according to the dried sample analytical scheme described previously. In this instance, the results indicate the presence of a small quantity of the component containing iodine in a positive oxidation state.

Sample (c) was obtained from a solution which was 1M with respect to magnesium iodide and saturated with respect to iodine. Magnesium rod was used in the reaction. The solid was dried by evacuation at room temperature. In this instance, the results indicate the presence of a considerable quantity of the interfering substance.

It is interesting to note the behavior of the dried samples upon dissolution in acid solution. The solution begins to turn brown as the solid dissolves. At first, the solution is clear, but, after a short time, the solution becomes turbid and fine, feathery particles of solid iodine separate. These particles do not dissolve until thiosulfate solution is added. The thiosulfate reduces some of the iodine to iodide ion, which is capable of causing the dissolution of more solid iodine by formation of the triiodide ion. These observations are in accord with the fact that, in dilute solutions of magnesium iodide, not even equimolar quantities of iodine will dissolve. Therefore, if the iodine is present in the solid as magnesium triiodide, much of the iodine will be precipitated when the polyiodide is brought in contact with water.

It is unfortunate that the solids obtained contained the hydroxide ion, the presence of which has

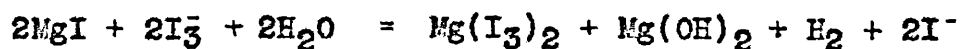
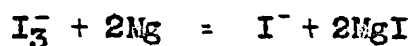
been indirectly responsible for the failure to obtain accurate quantitative analyses. Experiments were undertaken to provide conditions under which magnesium hydroxide would not be obtained. One such experiment consisted of keeping the solution definitely acidic throughout the course of the reaction. In this case, however, no solid product of any kind was obtained. Another experiment was performed in a saturated benzoic acid solution. Here, again, no solid product was obtained.

No reference dealing with phase studies of the magnesium iodide-iodine-water system has been found. However, it was determined that, at room temperature and in a solution saturated with respect to magnesium iodide and iodine, no solid triiodide was obtained. In fact, the solution does not even contain sufficient iodine to correspond to the formula $Mg(I_3)_2$. Therefore, from this consideration and from the results of the experiments carried out in acid solution, it is apparent that the hydroxide ion is necessary for the formation of the solid which has been described in this work. The exact function of the hydroxide ion has not been determined, but there is clearly no definite relationship between the hydroxide ion content and the iodine content.

A dark solid product was also obtained by the addition of carbonate-free sodium hydroxide solution to a triiodide solution containing magnesium ion. This product had properties similar to those of the product obtained as described above.

X-ray diffraction patterns were taken of two of the dried samples. No conclusive evidence regarding the structure of the solid was obtained. The patterns obtained gave no peaks corresponding either to magnesium hydroxide or to magnesium iodide. (No data on solid iodine were available.) The absence, from the observed pattern, of the most intense peak of magnesium hydroxide is especially noteworthy, and appears to confirm the hypothesis of the formation of a hitherto unknown compound.

On the basis of the evidence presented in this work, the reaction may be assumed to proceed according to some combination of the following sequence of reactions:



Preliminary investigations on the reaction between metallic magnesium and the magnesium bromide-bromine-water system have indicated that a phenomenon occurs which is similar to that observed in the iodide-iodine system. In this instance, a yellow solid, which contained titratable bromine, was obtained. Hydrogen was also liberated in the reaction. This reaction, however, was not further investigated.

Summary and Conclusions

An unusual reaction occurs between metallic magnesium and aqueous solutions containing the triiodide ion. The metallic magnesium dissolves with a vigorous evolution of hydrogen and a pronounced liberation of heat. The evolution of hydrogen is not dependent on the hydrogen ion concentration, since pH measurements have indicated that the initial solution containing the triiodide ion is less acidic than a solution containing iodine in which the above reaction does not occur. Moreover, although the solution becomes basic as a result of the liberation of hydrogen, the reaction still proceeds so long as both metallic magnesium and the triiodide ion are present. Therefore, the reaction must involve an intermediate which is capable of liberating hydrogen from water. This intermediate is postulated to be the unipositive magnesium ion.

The rate of the reaction has been found to be dependent on the concentration of the triiodide ion. This is evidenced by the fact that the reaction is slow in dilute solutions of triiodide ion and becomes almost violent in concentrated solutions.

A dark brown to black solid is formed during the course of the reaction. Analysis shows that this

solid, hitherto undescribed, contains magnesium ion, hydroxide ion, iodide ion and titratable iodine. This iodine cannot be removed to an appreciable extent by evacuation, by heating, or by extraction with carbon tetrachloride - facts which indicate that the iodine is chemically bound. Experiments indicate iodine in a positive oxidation state is also present in small quantities and interferes with the quantitative determinations of the various constituents of the solid. Attempts to free the solid from this interfering substance were unsuccessful. The presence of hydroxide ion appears to be essential to the formation of a solid product of this nature.

Although quantitative evidence for the exact structure of the solid obtained is lacking, the facts indicate that a magnesium polyiodide is formed along with the hydroxide. The reaction itself may be considered to involve the formation of unipositive magnesium as an intermediate. A possible mechanism has been postulated.

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