The Anodic Oxidation of Magnesium Metal: Evidence for the Existence of Unipositive Magnesium[1,2]

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When electrolysis of an aqueous solution of any one of several salts is carried out between magnesium electrodes in a divided cell, the metal dissolves anodically with an initial mean valence number appreciably lower than two. Such dissolution is accompanied by anodic evolution of hydrogen, in amount corresponding to oxidation from the measured mean valence state to the familiar dipositive magnesium ion. In the presence of any one of a variety of strong oxidizing agents, such as permanganate or chlorate ion, another reduction product in addition to gaseous hydrogen is observed in the electrolyte, and the quantity of anodic hydrogen is found to be decreased. No such reduction product, however, is observed at the magnesium cathode. When electrolyses are carried out in a cell in which electrolyte continually flows past the anode from a reservoir at a higher level, and the oxidizing agent is not permitted to come in contact with the anode, a reduction product is again observed in the vicinity of this electrode. All these facts may be explained in terms of a primary electrode reaction consisting in part of oxidation of magnesium to the unipositive state.

It has long been known that in the electrolytic oxidation of magnesium in aqueous salt solution, the dissolution of magnesium at the anode is accompanied by the evolution of hydrogen at or near the same electrode.[3] Although Turrentine[4] suggested, as an explanation of this phenomenon, the existence of a unipositive magnesium ion capable of but transitory existence, convincing evidence for the validity of this hypothesis hitherto has been lacking. It is interesting to note, however, that Gomberg,[5] in order to account for the reducing action of such mixtures as $Mg–MgI_2$, postulated the existence of halides of unipositive magnesium in ether–benzene solutions. In the present work, the anodic behavior of magnesium was studied from several different viewpoints. The results, it is believed, point strongly toward the conclusion that the primary reactions at a magnesium anode consist of the oxidation of the metal to both the unipositive and the dipositive state, the former of which, as a strong reducing agent, rapidly disappears in consequence of its oxidation either by the solvent or by some other reagent.

Experimental*

The 8-mm. magnesium rod, of 99.8% purity, from which all the electrodes used were cut, was furnished by the Aluminum Company of America.[6] The salts were of C.P. or reagent grade. The source of direct current was a full-wave mercury tube rectifier capable of supplying up to 1000 v. The quantity of electricity passing through the circuit was determined by means of a silver coulometer.

The first experiments were carried out in a divided cell similar to that described in a previous communication,[7] with compartments of a capacity of about 25 ml. each. An atmosphere of oxygen-free nitrogen was maintained over the solution in the anode compartment, while the cathode compartment was left open to the air.

When the amount of hydrogen liberated at the anode was to be determined, a sample of effluent gas from the anode compartment, measured after having been shaken for 30 minutes with chromium(II) sulfate solution for the removal of oxygen, was brought into contact, in a combustion chamber, with a platinum coil heated to dull redness. A measured excess of oxygen was then introduced into the chamber. After combustion, the gas was again shaken with chromium(II) sulfate solution. The hydrogen content could then be calculated by two semi-independent methods: either as two-thirds of the decrease in volume on combustion, or as the difference between the volumes of oxygen-free gas before combustion and after. For the experiments with flowing electrolyte, a different type of cell was used, which will be described later.

Results

Oxidation State Attained on Electrolysis.—It should be stated at the outset that the electrolytic solutions used became slightly basic during the course of the electrolysis, and direct non-electrolytic reaction between the magnesium and the electrolyte was negligible. In no instance was there a detectable loss in weight of the magnesium cathode. Further, although the electrolyte sometimes acquired a white turbidity, no trace of color ever appeared in it, so that there could have been no formation of colloidal magnesium by disintegration of the anode. Yet in every case the quantity of magnesium dissolved from the anode was greater than could be accounted for coulometrically on the assumption that magnesium is oxidized to the dipositive state. The extent of departure from normal current efficiency may conveniently be expressed by the initial mean valence number, V_i, of the magnesium ion formed, which was calculated, in conformity with our practice in previous communications,[7–9] by means of the equation

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

A series of typical initial mean valence numbers is shown in Table I. These electrolyses were carried out at room temperature, with a current density of about 0.05 amp. per sq. cm. Gas was liberated at both electrodes during the electrolysis, in smaller quantity, however, at the anode. The anode gas was found to contain no oxygen. In most cases, the anode acquired a superficial dark film which on drying turned white. This point will be discussed at greater length later. Since this film was too firmly adherent to be removed by gentle wiping, the measured decrease in weight of magnesium must have been slightly less than the

(1) From part of a thesis submitted by Roy L. Petty in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Kansas, 1953.

(2) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the Chicago Meeting, September 7, 1953.

(3) W. Beetz, *Phil. Mag.*, [4] **32**, 269 (1866).

(4) J. W. Turrentine, *J. Phys. Chem.*, **12**, 448 (1908).

(5) M. Gomberg, *Rec. trav. chim.*, **48**, 847 (1929).

(6) The authors hereby express their appreciation for this courtesy.

(7) W. E. Bennett, A. W. Davidson and J. Kleinberg, THIS JOURNAL, **74**, 732 (1952).

(8) A. W. Davidson and F. Jirik, *ibid.*, **72**, 700 (1950).

(9) A. D. McElroy, J. Kleinberg and A. W. Davidson, *ibid.*, **74**, 736 (1952).

actual loss by oxidation, and hence the recorded values of V_i are slightly too high.
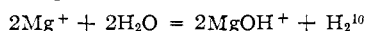
TABLE I

ANODIC OXIDATION OF MAGNESIUM IN VARIOUS AQUEOUS ELECTROLYTES

| Electrolyte	Initial concn. (g. per 100 ml. of water)	V_i
$MgSO_4$	2.5	1.38
$MgSO_4$	11.5	1.33
Na_2SO_4	7	1.41
NaCl	15	1.50
$KClO_3$	5	1.66
KI	20	1.54
$CaCl_2$	32	1.66

The maximum valence number obtained corresponds to a ratio of 1 unipositive to 2 dipositive ions, whereas the minimum value corresponds to 2 unipositive ions to 1 dipositive.

In a study, with magnesium sulfate as electrolyte, of the effect on V_i of concentration (2.5 and 11.5 g. per 100 ml. of water) and of current density (from 0.033 to 0.50 amp. per sq. cm.), slightly lower values were observed at low current densities, as shown in Table I, for the more concentrated solution. No significant trend of V_i values with current density was noted for the more dilute solution, nor for the concentrated solution up to 0.12 amp. per sq. cm. In the latter case, however, an abrupt increase in V_i took place between 0.12 and 0.16 amp. per sq. cm., and this change was accompanied by the occurrence, at the anode, of a peculiar cyclic phenomenon: the alternate appearance and dissolution, with gas evolution, of a superficial black deposit on the anode.

Anodic Evolution of Hydrogen.—In the experiments already described, it had been observed that, whereas gas evolution at the cathode (except for the minimal non-electrolytic reaction characteristic of magnesium in aqueous salt solutions) ceased with interruption of the current, yet vigorous evolution of gas at the anode continued for several minutes beyond this point. It was found, in fact, that approximately two-fifths of the total gas evolution at the anode occurred after the termination of electrolysis. This fact is in accord with the hypothesis of a primary anode product which is capable of further oxidation in a secondary reaction with the solvent, perhaps according to the equation

$$2Mg^+ + 2H_2O = 2MgOH^+ + H_2{}^{10}$$

The results of some typical experiments in which the amount of hydrogen evolved at the anode was determined are recorded in Table II, in which the volume of anodic hydrogen actually found is compared with that calculated from the initial mean valence number according to the schematic equation

$$Mg^{+V_i} + (2 - V_i)H^+ = Mg^{++} + \frac{2 - V_i}{2}H_2$$
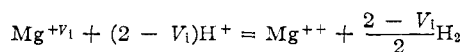
It will be noted that in the electrolysis of sodium sulfate solution, where hydrogen was the sole reduction product, although the calculated and the

(10) The use of the symbol Mg^+ for the hypothetical $Mg(I)$ ion may be regarded as an oversimplification. The formula Mg_2^{++}, analogous to that of mercurous ion, would perhaps represent a more probable entity.

TABLE II

ANODIC EVOLUTION OF HYDROGEN

Electrolyte	Wt. of Mg dissolved, g.	V_i	Volume of hydrogen (ml. at S.T.P.) Calcd.	Found
Na_2SO_4	0.0408	1.41	11.1	11.9
Na_2SO_4	.0470	1.39	13.2	14.2
Na_2SO_4	.0513	1.43	13.5	14.1
$KClO_3$	.0626	1.61	13.2	11.3
$KClO_3$	.0642	1.62	12.9	11.8

measured values are in fair agreement, the measured volume was always slightly greater than that calculated. (This difference appears to be due, at least in part, to the as yet unexplained liberation of a small quantity of hydrogen on the anode side of the porous disc separating anolyte from catholyte.) With potassium chlorate as electrolyte, however, the volume of hydrogen found was distinctly *less* than the calculated value. The difference between the results with the two electrolytes, too great to be attributed to experimental error, may readily be accounted for by the hypothesis that in the second case part of the unipositive magnesium formed during electrolysis was oxidized not by hydrogen ion from the solvent but by chlorate ion, perhaps according to the equation

$$6Mg^+ + ClO_3^- + 6H^+ = 6Mg^{++} + Cl^- + 3H_2O{}^{10}$$
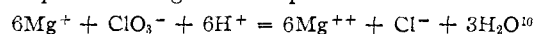
Strong support for the hypothesis is to be found in the fact that, although no reduction of chlorate ion by direct contact with metallic magnesium could be detected, yet a distinct qualitative test for chloride ion was obtained in the anolyte at the end of the electrolysis.

Anodic Reduction of Oxidizing Agents Other than Hydrogen Ion.—The appearance of chloride ion in the anolyte under the conditions mentioned in the preceding paragraph suggested the desirability of a more extended investigation of the phenomenon of "anodic reduction." Accordingly, a series of electrolyses were carried out with electrolytes containing oxidizing agents other than hydrogen ion. In some instance the reducible substance constituted the sole electrolyte, whereas in other cases it was added to a saturated solution of magnesium sulfate.[11] In each of these cases another reduction product, in addition to gaseous hydrogen, appeared in the anolyte, although, except in two instances, not in detectable concentration in the catholyte. In order to eliminate the possibility that such reduction might have been brought about by contact of the oxidizing agent with metallic magnesium, control tests were made by immersion of weighed pieces of magnesium rod in the oxidizing solution for several hours. In only one instance was there even the slightest evidence of chemical reaction, *i.e.*, either loss in weight of the magnesium or appearance of a reduction product in the solution. The results of these tests are summarized in Table III.

(11) It should be mentioned that in the electrolysis of magnesium sulfate solution between magnesium electrodes, no sulfite or other reduction product of sulfate ion has ever been detected in the anolyte. Neither have any peroxy compounds, such as peroxydisulfuric acid, ever been detected. Hence it appears extremely improbable that the reduction of an added oxidizing agent could be brought about either by a reduction product of sulfate ion, or by hydrogen peroxide formed by the action of water on peroxydisulfate ion.

TABLE III

REDUCTIONS AT A MAGNESIUM ANODE DURING ELECTROLYSIS

Electrolyte	Oxidizing agent	Reduction products obsd. during or after electrolysis		Control test
		In catholyte	In anolyte	
$MgSO_4$	MnO_4^-	None	MnO_2	Negative
$MgSO_4$	$Cr_2O_7^{--}$	None	Brown solid(CrO_2?)	Negative
$MgSO_4$	$Fe(CN)_6^{---}$	None	$Fe(CN)_6^{----}$	Trace of $Fe(CN)_6^{----}$
$Mg(NO_3)_2$	NO_3^-	NO_2^-	NO_2^-	Negative
$KClO_3$	ClO_3^-	Trace of Cl^-	Cl^-	Negative
$MgSO_4$	WO_4^{--}	None	Black deposit on anode	Negative
$MgSO_4$	VO_3^-	None	Black deposit on anode	Negative

It may be mentioned here that anodic reductions of this nature are not peculiar to magnesium, qualitatively similar effects of varying degree having been observed not only at a copper anode, but also with aluminum, zinc and cadmium. Some of these observations will be discussed in a future communication.

Reduction in a Solution Not in Contact with the Anode.—What appears to be the most convincing evidence of the existence of unipositive magnesium ion is to be found in the results of electrolyses carried out under conditions such as to preclude any possibility of direct contact between the substance to be reduced and the anode itself.

The apparatus used for these experiments is shown diagrammatically in Fig. 1. A reservoir R of 1.5-l. capacity, filled with the non-oxidizing electrolyte to be used, was supported at a level 3 to 4 feet higher than the cell. The rate of flow of electrolyte past the anode A could be controlled by means of the stopcock S. The solution of the oxidizing agent was contained in the beaker B. In order to prevent the entrance of any solid particles from the anode into B, the end of the delivery tube D was covered with a layer, G, of glass wool. Likewise, to prevent the contamination of the contents of B by any cathodic products, the cathode C was shielded by a porous cup P.

In the operation of this device, the beaker was filled with oxidizing solution to a level slightly below the end of D. The stopcock was then opened, and electrolysis was started when the level of solution in B had risen sufficiently to close the circuit. The flow of electrolyte and the passage of current were continued until the supply of electrolyte in R had been nearly exhausted. The solution in B was then filtered, and any solid products were examined. Although the amounts of reduction products obtainable by this technique were necessarily small, they nevertheless proved to be adequate for positive identification. The results of these experiments are listed in Table IV.

TABLE IV

ANODIC REDUCTIONS WITH FLOWING ELECTROLYTE

Electrolyte	Oxidizing agent	Observation
$Mg(NO_3)_2$	$AgNO_3$	Black finely divided subst.
Na_2SO_4	$AgNO_3$ (ammoniacal)	which gave qual. tests for metallic silver
Na_2SO_4	$KMnO_4$	Brown subst. which gave qual.
$NaCl$	$KMnO_4$	tests for manganese dioxide

These results, it is believed, can best be explained in terms of the hypothesis of a magnesium(I) ion,

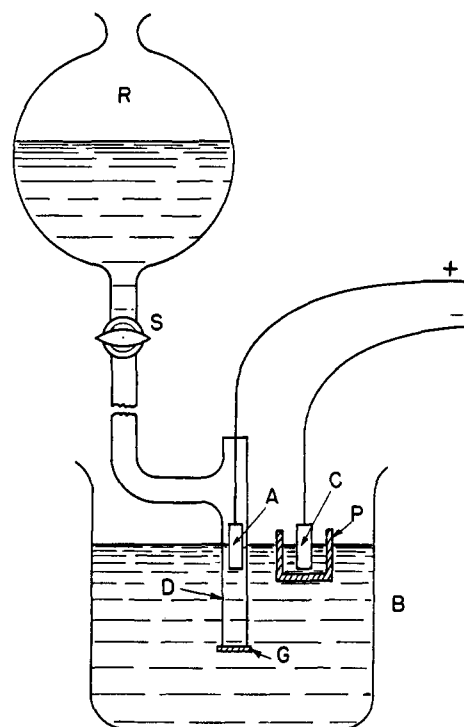sufficiently stable in solution so that it can be carried at least a short distance from the anode.

Fig. 1.—Apparatus for study of electrolysis with flowing electrolyte.

Additional Observations.—It has been suggested to the authors that the low initial valence numbers obtained by the oxidation of a magnesium anode might be due to some sort of anodic activation, that is, to non-electrolytic dissolution of the magnesium while it is acting as anode. In order to test this possibility, several electrolyses were carried out in which the rectifier was modified so as to yield an intermittent current; i.e., current flowed for periods of $1/120$ second separated by $1/120$ second intervals, so that the anode was subjected to the possibility of non-electrolytic corrosion for half the duration of the electrolysis. Such experiments, both with magnesium sulfate and sodium sulfate as electrolyte, did not yield unusually low initial valence numbers, but gave values of 1.37 to 1.40, essentially the same as those obtained with a continuous current.

The formation of an insoluble black product in the anodic oxidation of magnesium, previously reported by several workers,[3,12] was frequently ob-

(12) G. Baborovsky, Ber., 36, 2719 (1903).

served in the present work. The most favorable conditions found for the formation of this product were the use of sodium chloride as electrolyte, and the maintenance of a temperature of 0° during electrolysis. The product tended to turn white on drying, but if washed first with water and then several times with 95% ethanol at 0°, it remained dark gray to black even after it had been warmed to room temperature and allowed to dry in a desiccator.

This substance has marked reducing properties, liberating hydrogen from acid solution and react-

ing with potassium permanganate solution to yield manganese dioxide. Microscopic examination showed the product to be a mixture of a white and a black substance, which could not readily be separated. Chemical analysis showed the white component to be magnesium hydroxide. The black component did not appear to be metallic magnesium; persistent efforts, however, to identify it positively as a compound containing unipositive magnesium have thus far been unsuccessful.

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Studies of NaCl–KCl Solid Solutions. I. Heats of Formation, Lattice Spacings, Densities, Schottky Defects and Mutual Solubilities[1,2]

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Heats of formation, lattice spacings and densities of a series of NaCl–KCl solid solutions homogenized at 630° and quenched to room temperature are presented. Results of a redetermination of the solid state unmixing curve are also given. Data are included showing the number of Schottky defects in this system.

Introduction

Fontell in 1939 made[3] the first application of modern calorimetric techniques to the determination of the heat effects accompanying the formation of an alkali halide solid solution from its component salts. His measurements on the KCl–KBr system were later repeated and refined by Hovi.[4] At present there exist accurate heat of formation data for this and two additional systems, KCl–RbCl[5] and NaCl–NaBr.[6] The existence of this accurate body of thermal data and the obvious relationship to lattice theory has led to several attempts to account for the experimental heats of formation in terms of the lattice energies of the substances involved. Of these the two most recent—Wasastjerna[7] (1948) and Durham and Hawkins[8] (1951)—have been quite successful. Both treatments involved a novel feature. Instead of treating the lattice of the solid solution as uniform throughout, allowances were made for the fluctuations in interionic distances which result from the distribution of ions of unequal size over a common sublattice. Wasastjerna has, in addition, produced evidence suggesting the existence of local order in these solutions and has included in his treatment the effect of order on the calculated heats of formation.

In Wasastjerna's theory the heat of formation

(1) From a Thesis submitted by W. T. Barrett to the University of Pittsburgh in partial fulfillment of the requirements for the Ph.D. degree, February, 1952.

(2) This work was assisted by the Atomic Energy Commission and the Office of Naval Research.

(3) N. Fontell, Soc. Sci. Fennica, Commentationes Phys.-Math., 10, No. 6 (1939).

(4) V. Hovi, Ann. Acad. Sci. Fennicae, AI, No. 55, (1948).

(5) N. Fontell, V. Hovi and L. Hyvonen, ibid., IA, No. 65, (1949).

(6) M. A. Fineman and W. E. Wallace, THIS JOURNAL, 70, 4165 (1948).

(7) J. A. Wasastjerna, Soc. Sci. Fennica, Commentationes Phys.-Math., [XIV] 3, 1 (1948); ibid., [XIV] 7, 1 (1948); ibid., [XV] 3, 1 (1949). Cf. also V. Hovi, ibid., [XV] 12, 1 (1950).

(8) G. S. Durham and J. A. Hawkins, J. Chem. Phys., 19, 149 (1951).

is proportional to the quantity $(1/R)(\Delta R/R_0)^2$, where ΔR is the difference in lattice spacing for the components and R_0 is the lattice spacing of the solution. Designating $(10^3/R_0)(\Delta R/R_0)^2$ as δ, his theory indicates that the heat of formation vanishes as δ approaches zero and indeed all deviations from ideal solution behavior disappear when δ is sufficiently small. Examination of Wasastjerna's treatment indicates that the necessary simplifying assumptions become more valid as δ approaches zero so that in effect he has produced a limiting law in δ.[9] For the three systems studied to date δ has been small and has covered only a limited range—7.0, 7.3 and 9.8 for KCl–RbCl, KCl–KBr and NaCl–NaBr, respectively. (δ values are for the equimolal solution.) It is obviously of interest to examine a system having an appreciably larger δ.

For sufficiently large δ's, the solid solutions are so endothermal with respect to their constituent that even at temperatures approaching their melting points continuous solid solubility does not occur. To study the properties of solutions over the entire composition range in a single phase one is limited therefore to systems whose δ values are less than some maximal value. The NaCl–KCl system with $\delta = 18.3$ is a case where δ is nearly maximal for continuous solubility and therefore provides an excellent opportunity for examining Wasastjerna's theory at the upper limit of δ.

This paper contains an account of measurements of (1) heats of formation, (2) lattice spacings, (3) densities, (4) Schottky defects and (5) mutual solid solubility relationships for the NaCl–KCl system. The following paper is devoted to an examination of the experimental data in the light of Wasastjerna's theory, with particular emphasis on the entropy, since this aspect of Wasastjerna's theory has not been subjected to experimental test. If

(9) This is probably true of Durham and Hawkins' procedure also although it is less obvious in that case.