a solution of an oxidant contained in a separate vessel. In control experiments in which the only variation from these conditions consisted in the use of a platinum instead of an aluminum anode, there was no evidence of reduction. With the aluminum anode, although the quantities of reduction product obtained were small, they were nevertheless adequate for identification. The results are summarized in Table V.

TABLE V

ANODIC REDUCTIONS WITH FLOWING ELECTROLYTE

Electrolyte	Oxidizing agent	Observation
$NaNO_3$	Ammoniacal $AgNO_3$ soln.	Black finely divided substance: metallic Ag
NaCl	$K_3Fe(CN)_6$ and $FeCl_3$	Dark blue ppt.: Prussian blue
NaCl	$KMnO_4$	Dark brown ppt.: MnO_2

As in the case of magnesium, the formation of these reduction products provides further proof of the transitory existence of an anodic product with marked reducing properties.

TURKU, FINLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

Unipositive Beryllium as a Product of Anodic Oxidation

BY BARBARA D. LAUGHLIN, JACOB KLEINBERG AND ARTHUR W. DAVIDSON

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The electrolysis of an aqueous sodium chloride solution between beryllium electrodes in a divided cell results in the anodic conversion of the metal to both the uni- and dipositive oxidation states. The dissolution process is accompanied by anodic evolution of hydrogen; in electrolyses of short duration the quantity of hydrogen liberated corresponds to oxidation by the solvent of the unipositive beryllium formed, to the common dipositive state. During the course of longer runs metallic beryllium is deposited uniformly throughout the anolyte. The production of the metal can be accounted for only in terms of the disproportionation of unipositive beryllium: $2Be^+ = Be^{2+} + Be$. The product of the anodic oxidation of beryllium is capable of reducing permanganate ion to manganese dioxide, and silver ion to elementary silver, under conditions which do not permit the oxidizing agent to come directly in contact with the anode. These reductions offer further proof of the formation of +1 beryllium.

Strong evidence recently has been obtained to show that on the anodic oxidation of magnesium[1] and aluminum[2] in aqueous electrolytic solutions these metals are converted to oxidation states (*e.g.*, Mg^+ and Al^+) lower than those corresponding to complete removal of their valence electrons. The fact that no substance containing either magnesium or aluminum in a lower valence state could be isolated after electrolysis is not surprising; the chemistry of magnesium and aluminum is characterized by a notable scarcity of solid compounds in which the elements exhibit any oxidation state other than that corresponding to their number of valence electrons. The present communication is concerned primarily with the anodic behavior of beryllium in aqueous sodium chloride solution. Although no compound of lower valent beryllium has been isolated, data have been found which appear to show incontrovertibly that the metal is oxidized anodically to a mixture of uni- and dipositive states. In addition, some interesting information has been collected on the anodic oxidation of the metal in the presence of other inorganic electrolytes.

Experimental

The 0.25-in. beryllium rod, from which all the electrodes used were cut, was purchased from the Brush Beryllium Company and was described as "of highest purity." The other chemicals employed 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 cell was determined by means of a silver coulometer. Electrolyses were performed between beryllium electrodes in a divided cell similar to that described in a previous communication,[1] with compartments of a capacity of about 100 ml. each. In experiments where the hydrogen evolved at the electrodes during electrolysis was collected, an atmosphere of oxygen-free nitrogen was maintained over both anolyte and catholyte. In other electrolyses both compartments were left open to the air. After electrolysis, the anode was washed with water and dried in an oven at 120° before weighing.

When the amount of hydrogen liberated at the anode or at both electrodes was to be determined, the effluent gas, measured after having been shaken for 30 min. with chromium(II) sulfate solution, 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 in oxygen-free gas before and after combustion. It should be emphasized that in the experiments with sodium chloride as electrolyte the initial contact of the effluent gas with chromium(II) sulfate solution gave no decrease in volume, a fact which demonstrates that neither oxygen nor chlorine is formed in the electrolytic process.

For electrolyses with a flowing electrolyte, a cell like that previously described[1] was employed.

Results and Discussion

Anodic Oxidation of Beryllium in Aqueous Sodium Chloride.—The initial mean valence number, V_i, with which beryllium entered solution when anodically oxidized was calculated by means of the equation

$$V_i = \frac{\text{wt. of Ag deposited in coulometer} \times 9.02}{107.88 \times \text{wt. of Be lost from anode}}$$

A series of typical initial mean valence numbers obtained with sodium chloride as electrolyte is listed in Table I. These values have true electrochemical significance, since control experiments showed that direct non-electrolytic reaction between beryllium and electrolyte is negligible. The beryllium cath-

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[1] R. A. Petty, A. W. Davidson and J. Kleinberg, THIS JOURNAL, **76**, 363 (1954).

[2] E. Raijola and A. W. Davidson, *ibid.*, **78**, 556 (1956).

ode is unattacked during electrolysis. Moreover, a beryllium rod placed in the anolyte after electrolysis shows no detectable loss in weight. As electrolysis proceeds the anolyte becomes slightly more acidic; the initial *p*H is about 6 and the final value is a little above 5. This increase in acidity, which occurs despite the evolution of hydrogen at the anode, presumably comes from the hydrolysis of beryllium ion (Be^{2+}).

TABLE I

ANODIC OXIDATION OF BERYLLIUM IN AQUEOUS SODIUM CHLORIDE

(5–15 v. applied voltage; room temp.; 40 ml. of electrolyte in each compartment.)

Concn. of electrolyte, *M*	Current density, amp./sq. cm.	Time of electrolysis, min.	V_i
0.2	0.03	30	1.20–1.25(6 expt.)
0.2	.20	5	1.24
0.2	.003	140	1.27, 1.24
5.0	.03	30	1.19

The control experiments strongly indicate, first, that the initial valence numbers found for beryllium are reasonably explained on the basis of the anodic oxidation of this element to a mixture of the +1 and +2 states and, secondly, that the evolution of hydrogen from the anode results from the oxidation of unipositive beryllium by the solvent, presumably according to the equation

$$2Be^{+} + 2H_2O = 2BeOH^{+} + H_2$$

In the latter regard, it should be pointed out that whereas the evolution of cathodic hydrogen ceased as soon as the current was interrupted, liberation of gas at the anode continued for an additional five to ten minutes.

If oxidation of unipositive beryllium occurs as shown above, there should be a correlation between the initial valence number and the quantity of hydrogen evolved at the anode, on the assumption that all of the +1 beryllium is converted to the dipositive state. Accordingly, the gas evolved at the anode during and immediately after electrolysis was collected and analyzed. The results are given in Table II. It is apparent that there is excellent agreement between the volume of hydrogen evolved at the anode and that expected from the initial mean valence numbers.

TABLE II

CORRELATION OF V_i WITH HYDROGEN EVOLVED FROM ANODE

(Concn. of NaCl, 0.2 *M*; 75 ml. of electrolyte in each compartment)

V_i obsd.	H_2 obsd., ml. (S.T.P.)	V_i calcd. (from H_2 evolution)
1.23	10.7	1.28
1.27	10.9	1.28
1.18	16.6	1.11
1.20	16.3	1.20
1.16	12.3	1.21

During approximately the first 15 minutes of electrolysis with solutions of sodium chloride the anolyte remains clear and transparent. Beyond this time, however, there is slowly deposited from the anolyte a white gelatinous material ($Be(OH)_2$) and a black substance. The beryllium hydroxide first appears at the sintered glass disk separating anolyte and catholyte. *The black substance is formed uniformly throughout the anolyte.* Both this substance and the beryllium hydroxide are attacked by acids and alkalies. It was found, however, that the black material could be purified by treating the mixture (still suspended in the electrolyte) with a slightly ammoniacal aqueous suspension of acetylacetone, thus converting the hydroxide to the acetylacetonate, which was then dissolved in ethanol. The black material remaining was analyzed for beryllium by conversion to the oxide, and in three separate experiments gave values of 77, 79 and 81% beryllium. These values strongly suggest that the solid formed in the anolyte is metallic beryllium. This conclusion was confirmed by X-ray powder analysis, which showed the presence of *only* beryllium and beryllium oxide, the relative intensities of the peaks observed being in agreement with those recorded in the literature.[3,4] The formation of the metal *throughout the anolyte* can be accounted for only by the disproportionation of unipositive beryllium

$$2Be^{+} = Be^{2+} + Be$$

In electrolyses in which considerable beryllium is produced in the anolyte, the quantity of hydrogen liberated at the anode would be expected to be distinctly less than that calculated from the initial mean valence number, *i.e.*, from the oxidation by the solvent of the unipositive beryllium formed initially. In electrolyses with saturated sodium chloride as electrolyte this indeed proved to be the case. With dilute solutions of sodium chloride as electrolyte, however, the volumes of hydrogen evolved anodically were always greater than those calculated from the initial mean valence numbers. A reasonable explanation for these anomalous results would appear to be that the apparent initial valence numbers found for beryllium in these cases were too high, as a result of the formation of adherent beryllium hydroxide on the anode during the course of the relatively long time required for the production of elementary beryllium in the anolyte. In electrolyses with saturated sodium chloride solutions metallic beryllium appears in the anolyte before appreciable hydroxide is produced.

Reduction in a Solution Not in Contact with the Anode.—Additional confirmation of the formation of unipositive beryllium in the anodic oxidation of the metal in aqueous sodium chloride solutions comes from the demonstration that the product in the anolyte is capable of reducing certain oxidizing agents under conditions which preclude direct contact between such substances and the anode. Flow experiments similar to those previously reported for magnesium[1] were performed. Electrolyses were carried out in a cell in which 0.2 *M* sodium chloride solution was permitted to flow continually past a beryllium anode, from a reservoir at a higher level, into a solution of ammoniacal silver nitrate or dilute potassium permanganate in a separate vessel. In control experiments under identical conditions, except that no current was passed through the cell, no more than traces of reduction product

(3) L. W. McKeehan, *Proc. Nat. Acad. Sci.*, **8**, 270 (1922).

(4) H. E. Swanson and E. Tatge, J. C. Fel. Reports, N.B.S., 1951.

appeared in the solution of the oxidant. When electrolysis was taking place, on the other hand, appreciable quantities of metallic silver or of manganese dioxide were deposited and identified. Under these conditions it is scarcely conceivable that the reducing agent could be anything other than a lower valent beryllium species, which thus appears to be capable of at least transitory existence in aqueous solution.

Additional Observations.—The behavior of a beryllium anode in the presence of a number of other electrolytes was investigated, the conditions of electrolysis being similar to those described for sodium chloride. Results are tabulated below. No non-electrolytic attack on the anode was observed in any case.

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TABLE III

ELECTROLYSES WITH VARIOUS ELECTROLYTES

Electrolyte	V_i	Reduction product in anolyte	Remarks
$K_3Fe(CN)_6$	1.35	Prussian blue	
$KClO_4$	1.10	Cl^-	
$KClO_3$	0.83–0.90	Cl^-, ClO_2(?)	Some active intermediate capable of corroding Be must be formed
$NaClO_2$	1.05–1.27	Cl^-	Anolyte after electrolysis did not attack Be
$KMnO_4$	Passive		
$K_2Cr_2O_7$	Passive		
$NaNO_3$	Passive		Passivity destroyed by addition of small amount of chloride ion to anolyte

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES, K-25 PLANT, CARBIDE AND CARBON CHEMICAL COMPANY, UNION CARBIDE AND CARBON CORPORATION]

Vapor Pressure and Critical Constants of D_2O[1]

BY GEORGE D. OLIVER[2] AND J. W. GRISARD

RECEIVED JULY 18, 1955

The temperature and vapor pressure relations of normal and heavy water have been determined by means of a high pressure ebulliometer. Experimental observations were summarized in table form and represented by the following equations from 208 to 300°: $\log_{10} P_{D_2O}/P_{H_2O} = -3.4273 \times 10^{-2} + 2.1988 \times 10^{-4} t - 2.9329 \times 10^{-7} t^2$; from 300 to 370.6°: $\log_{10} P_{D_2O}/P_{H_2O} = 0.21516 \times 10^{-2} - 0.22949 \times 10^{-4} t + 1.1143 \times 10^{-7} t^2$. The boiling points of the two compounds are equal at 220.7° and 340.9 p.s.i.a., and differ as much as 2° at the critical point of D_2O. The critical temperature of D_2O, measured by means of the quartz tube method and the vapor pressure method, was 370.9 ± 0.1°. A critical pressure of 3170 ± 5 p.s.i.a. for D_2O was estimated from a plot of the vapor pressure data.

Previous work on heavy water has been limited to the region below the point where the vapor pressure of D_2O and H_2O are identical. Miles and Menzies[3] and Riesenfeld and Chang[4] almost simultaneously published their measurements of the vapor pressure of D_2O from 20 to 230°. Their data include the crossover point which was estimated by these workers as 224 and 225°, respectively. Lewis and MacDonald[5] were probably the first workers to compare the vapor pressure of heavy and normal water from 20 to 110° and to report the boiling and freezing points of D_2O. Riesenfeld and Chang[6] measured the critical temperature of D_2O by the quartz tube method in which normal water was used as a reference. They also estimated the critical pressure from the vapor pressure of H_2O at the critical temperature. In the present work the critical temperature has been measured by both the quartz tube method and an ebulliometric method. The latter also was used to measure the vapor pressure of D_2O, and the pressure difference of D_2O and H_2O between the crossover point and the critical point.

Experimental

Material.—The D_2O used in this investigation was prepared at the Consolidated Mining and Smelting Company of Canada, Limited, Trail, British Columbia, and had the following properties when sealed in a glass bottle: conductivity, 2.7×10^{-6} mhos; *p*H 6.5; weight % D_2O, 99.87. Heavy water from Trail normally contains about 0.3% of the O^{18} isotope.

The normal water was distilled from a permanganate solution contained in a glass distillation apparatus which had not more than two theoretical plates. Distilled water from a Barnstead distillation apparatus was used to prepare the permanganate solution.

Apparatus and Procedure.—Detailed description and diagrams of the apparatus have been published by the authors[7] consequently only a brief resumé will be included. Two metal boiling point tubes were connected to a common pressure system which contained the necessary valves, gages and helium supply. Each tube was constructed of one inch heavy-walled monel tubing and was surrounded by three concentric shields with the outermost one forming a vacuum jacket. Two thermocouples were used for control purposes, while the temperature was measured with a platinum resistance thermohm through a Mueller G-2 bridge and galvanometer. The boiling temperature of the test liquid in one tube was compared directly with the boiling tempera-

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(1) This work was done at the Oak Ridge Gaseous Diffusion Plant operated for the government by Union Carbide and Carbon Corporation.

(2) Monsanto Chemical Co., Texas City, Texas.

(3) F. T. Miles and A. W. C. Menzies, THIS JOURNAL, **58**, 1067 (1936).

(4) E. H. Riesenfeld and T. L. Chang, *Z. physik. Chem.*, **B33**, 120 (1936).

(5) G. N. Lewis and R. T. MacDonald, THIS JOURNAL, **55**, 3057 (1933).

(6) E. H. Riesenfeld and T. L. Chang, *Z. physik. Chem.*, **B28**, 408 (1935).

(7) G. D. Oliver and J. W. Grisard, *Rev. Sci. Inst.*, **24**, 204 (1953).