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

The Anodic Oxidation of Higher Members of the Aluminum Family in Liquid Ammonia[1]

BY ALBERT D. MCELROY, JACOB KLEINBERG AND ARTHUR W. DAVIDSON

The anodic oxidation of gallium, indium and thallium in a number of electrolytes in liquid ammonia solution has been studied. The results were found to vary widely from element to element, as well as from those previously reported for aluminum. It has been found that gallium is usually oxidized to an initial mean valence number between 2 and 3. In the case of ammonium nitrate–ammonium bromide mixtures as electrolyte, the valence number has been found to be a continuous function of the fraction of nitrate in the mixed solute, with a minimum value of 2.0 at about 17 mole % nitrate. It is believed that this value may be more plausibly interpreted in terms of the hypothesis of an equimolar mixture of unipositive and tripositive gallium ions, than as indicating the existence of a dipositive ion. Unlike the phenomenon observed in the case of aluminum, where no reducing power was detectable in the solution at the end of electrolysis, the product of electrolysis in the case of gallium is fairly stable, approximately 90% of the expected reducing power remaining in the anolyte. In the case of indium the results were more erratic; here also, however, initial valence numbers between 2 and 3 are obtained. With nitrate–bromide mixtures as electrolyte, the valence number does not appear to be a simple function of composition. The lower valent indium formed by electrolysis in ammonium bromide solution, and assumed to be unipositive, is subject not only to oxidation by the electrolyte, but also to rapid disproportionation to the free metal and the tripositive ion. Anodic oxidation of thallium in ammonia solutions of nitrates yields thallous ion exclusively. In ammonium bromide or potassium amide solutions, however, the anode product contains thallic as well as thallous ion. Both of these ions are stable throughout electrolysis, and can be identified in the product.

In a previous communication[2] dealing with the anodic oxidation of aluminum in a wide variety of electrolytes in liquid ammonia solution, evidence for the formation of unipositive aluminum was presented. The present paper reports the results of similar studies on gallium, indium and thallium, the higher members of the aluminum family. In every case, the initial mean valence number of the cations arising from electrolysis was appreciably lower than 3. The results, however, were found to vary widely from element to element, as well as from those which have been reported for aluminum.

Experimental

The simple and divided cell types, as well as the electrolytic techniques employed in the studies reported herein, have already been described.[2,3] The anodes consisted of C.P. metals from reliable sources. The metals were melted or pounded into rods of convenient dimensions. The current used was generally 0.05 to 0.1 amp.; the corresponding anode current densities were: gallium and indium, 0.015 to 0.03 amp. per sq. cm.; thallium, 0.008 to 0.016 amp. per sq. cm. A platinum cathode was employed when gallium was the anode; in experiments with indium and thallium anodes, an aluminum cathode was used. Gallium(III) iodide was prepared by a method essentially the same as that described for tin(IV) iodide.[4] Ammoniated zinc nitrate was obtained by treatment of a saturated aqueous solution of the hexahydrate with gaseous ammonia. Potassium amide was prepared as needed, by permitting a freshly cut sample of metallic potassium to react with liquid ammonia in the electrolytic cell in the presence of a few crystals of iron(II) ammonium sulfate. A number of other salts—ammonium bromide, ammonium chloride and sodium nitrate—were of C.P. quality and were used without further purification.

Results and Discussion

Gallium.—Metallic gallium does not react appreciably with liquid ammonia or its electrolytic solutions. The loss in weight of a gallium rod on immersion for 3.5 hr. in a solution containing 0.5 g. of ammonium bromide in 50 ml. of ammonia at −33° was only 0.0008 g. Upon the electrolysis of gallium(III) iodide solution between a gallium anode and a platinum cathode, metallic gallium was deposited on the cathode. This behavior is in sharp contrast to that observed during the electrolysis of aluminum iodide in liquid ammonia, where a blue solution of aluminum is formed at the cathode.[3]

On anodic oxidation in liquid ammonia solutions of ammonium bromide, gallium is found to go into solution with an initial mean valence number approximating 2.5. No measurable quantity of gas is evolved from the anode; the cathode reaction consists of the liberation of approximately 90% of the theoretical quantity of hydrogen. During electrolysis, a black substance, which proved to be soluble only in aqua regia, is formed at the cathode. At the end of electrolysis, about 90% of the reducing power expected on the basis of the initial mean valence number remains in the anolyte. A detailed description of the experimental procedure and calculations follows.

The electrolyses were carried out in the divided cell containing a sintered glass disk separating the anode and cathode compartments. After termination of electrolysis no gallium was detected in the catholyte; hence all the electrolytically dissolved metal must have remained in the anode compartment. The anolyte was filtered into a dry erlenmeyer flask and the ammonia permitted to evaporate. The grayish-white residue was dissolved in 100 ml. of a standard aqueous iodine solution containing 10 ml. of glacial acetic acid. The anode was washed with distilled water, the washings being added to the filtrate residue. The resulting solution was allowed to stand for 15 minutes, and the excess iodine was then titrated with standard sodium thiosulfate solution. The gallium, now completely oxidized to the tripositive state, was determined by precipitation with 8-hydroxyquinoline. A similar procedure was carried out on the grayish white insoluble material which remained in the anode compartment. The anode was then dried over calcium chloride and its loss in weight determined.

From the results so obtained, together with the coulometric data, the following pertinent quantities were calculated. (1) Initial mean valence number, V_i

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(1) Constructed from a portion of a thesis submitted by Albert D. McElroy in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1951.

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

(3) A. D. McElroy, J. Kleinberg and A. W. Davidson, *ibid.*, **72**, 5178 (1950).

(4) F. F. Fitzgerald, *ibid.*, **29**, 1693 (1907).

$$V_i = \frac{\text{faradays of electricity}}{\text{g.-atoms of Ga dissolved electrolytically}}$$

(2) Reducing power of each fraction of the anode products, and total reducing power, equal in each case to the appropriate quantity of iodine consumed, in equivalents.

(3) Mean valence number of the gallium in each of the fractions, and the mean valence number for the combined fractions

V_s = mean valence no. of Ga in anode solid
V_{fr} = mean valence no. of Ga in residue from evaporation of filtrate
V_f = mean valence no. of Ga in combined fractions

$$V_s,\ V_{fr},\ V_f = 3 - \frac{\text{equiv. of reducing power}}{\text{g.-atoms of Ga}}$$

(4) Theoretical quantity of reducing power corresponding to initial mean valence no., V_i, of Ga: theoretical reducing power = 3 × g.-atoms of Ga dissolved electrolytically—faradays of electricity.

The results of such calculations, for three expts. in which the concentration of ammonium bromide was 0.7 *M* and the temperature −70°, are given in Table I.

TABLE I

ANODIC OXIDATION OF GALLIUM IN LIQUID AMMONIA SOLUTIONS OF AMMONIUM BROMIDE

Current density, amp./sq. cm.	V_i	V_f	V_{fr}	V_s	Theoretical reducing power recovered, %
0.015	2.26	2.32	2.24	2.44	90
.030	2.23	2.29	2.12	2.56	91
.024	2.27	2.33	2.27	2.60	91

From these figures it is evident that the anode reaction consists of the oxidation of metallic gallium to a mixture of valence states, and that the lower oxidation state is relatively stable in liquid ammonia solutions of ammonium bromide.

In the earlier paper previously mentioned,[2] it was shown that the initial mean valence number of aluminum obtained in nitrate–halide electrolytes varied in a regular manner with the ratio of the concentrations of nitrate and halide. Similar experiments were carried out in a simple cell with gallium as anode and ammonium bromide–ammonium nitrate mixtures as electrolyte. In this case also, it was found that the initial mean valence number is a continuous function of the fraction of nitrate in the mixed solute, with a minimum value of 2.0 at about 17 mole % nitrate (Fig. 1). The fact that the minimum valence number obtained is 2.0 is not, however, regarded by us as evidence for the formation of dipositive gallium. It is believed that this value may be more plausibly interpreted in terms of the hypothesis of an equimolar mixture of unipositive and tripositive gallium ions.[5]

Indium.—Metallic indium is unattacked by liquid ammonia solutions of ammonium bromide. Mean valence numbers for indium varying from 2.01 to 4.72 were obtained in this medium in electrolyses carried out under conditions which differed little as to concentration of electrolyte, temperature and current density. Values greater than 3 can be interpreted only in terms of passivity of the anode, *i.e.*, as indicating the occurrence of some other anode reaction in addition to the oxidation of indium. Observations on electrolyses performed in a divided cell with metallic aluminum as a cathode showed: (1) the theoretical quantity of hydrogen, formed as a result of the reduction of ammonium ion, is evolved at the cathode; (2) metallic indium is precipitated in the anolyte; (3) some hydrogen is evolved in the anode compartment; (4) nitrogen is frequently liberated at the anode. The hydrogen evolved in the anode compartment presumably results from the reduction of the electrolyte by indium in a lower valence state

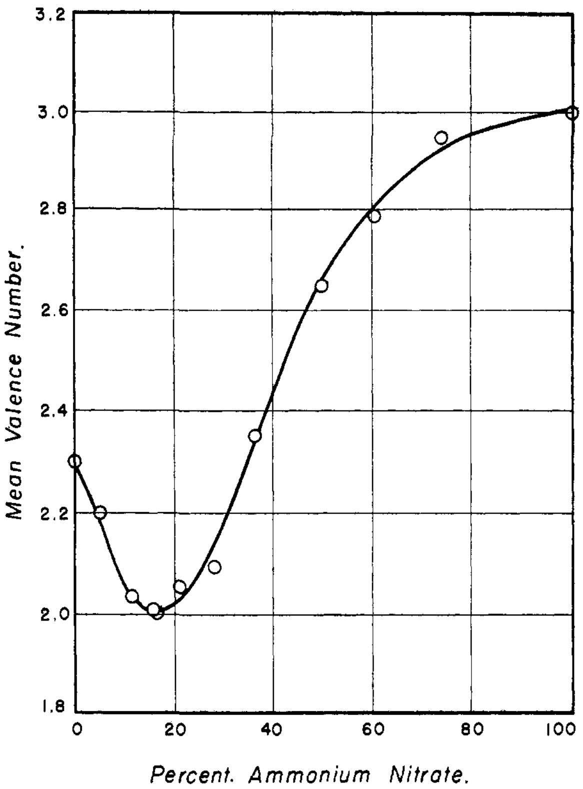

Fig. 1.—Variation of valence number of gallium with composition of electrolyte.

$$In^+ + 2NH_4^+ = 2NH_3 + H_2 + In^{+++}$$

while the nitrogen undoubtedly arises from a competing reaction involving the oxidation of ammonia (or amide ion)

$$3NH_2^- = {}^1/_2N_2 + 2NH_3 + 3e^-$$

A description of experiments designed to provide the necessary quantitative data follows, together with the pertinent methods of calculation. The cell and its contents, approximately 50 ml. of 0.7 *M* ammonium bromide solution, were cooled to −78°, and the liquid levels in anolyte and catholyte were adjusted to the same height, with the gas in each compartment at atmospheric pressure. A current sufficient to give an anode current density of 0.018 amp. per sq. cm. was passed through the solution for about two hours, the effluent gases being permitted to escape into the burets. The system was then re-equilibrated to the original conditions of temperature and pressure, with the liquid levels adjusted to the original positions as closely as possible. The stopcocks connecting the cell compartments to the burets were then closed, the effluent gases were washed free of ammonia in the dilute sulfuric acid in the scrubbers, and any

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(5) A. W. Davidson and F. Jirik, THIS JOURNAL, **72**, 1700 (1950).

volume changes were noted. The cooling bath was removed, each side of the cell was connected directly to the appropriate scrubber, and the liquid ammonia was permitted to boil. After about 10 minutes of boiling, during which the gases other than ammonia were driven from the cell, these fractions were added to those previously collected in the respective burets. The ammonia solution was then allowed to evaporate to dryness, any gases other than ammonia being trapped in the scrubbers. The gases were thus collected in three fractions, which presumably consisted of (1) hydrogen evolved at the cathode; (2) hydrogen and nitrogen liberated from the anode compartment during electrolysis; and, (3) hydrogen and any other gases evolved after electrolysis, during the evaporation process. Each of these three fractions was analyzed separately for hydrogen and nitrogen.

The residue in the cell after evaporation of ammonia usually consisted of metallic indium and a water-soluble material. After extraction of the latter, the metal was weighed, and the reducing power of the aqueous extract was determined by titration with standardized acid dichromate solution. When the quantity of indium was too small to be accurately weighed, it was combined with the aqueous extract and the mixture titrated with dichromate solution.

The following calculations were then made: (1) Mean valence number, V_i; calculated in the usual manner from loss in weight of anode and quantity of electricity.

(2) Reducing power of the residue; equal to equiv. of dichromate reduced +3 × g.-atoms of metallic In recovered from the residue.

(3) Mean valence number, V_r, of In in the residue:

$$V_r = 3 - \frac{\text{equiv. of reducing power}}{\text{g.-atoms of In dissolved from anode}}$$

(4) Quantity of gas evolved from anode compartment during electrolysis; equal to total moles of gas evolved − theoretical no. of moles of cathodic hydrogen.

(5) Moles of hydrogen in excess of cathodic hydrogen; equal to total moles of hydrogen, from analysis − theoretical no. of moles of cathodic hydrogen.

(6) Total reducing power; equal to reducing power of the residue, (2), +2 × (5), the reducing power corresponding to the excess hydrogen.

(7) Mean valence number from reducing power, $V_{\text{R.P.}}$

$$V_{\text{R.P.}} = 3 - \frac{\text{equiv. of total reducing power, (6)}}{\text{g.-atoms of In dissolved from anode}}$$

(8) Moles of nitrogen; equal to moles of anode gas, (4), − moles of hydrogen in anode fraction.

(9) Quantity of electricity required to liberate the nitrogen; equal to 6 × moles of nitrogen.

(10) Mean valence number, V_N, calculated on the basis of competing reactions at anode:

$$V_N = \frac{\text{total faradays} - \text{faradays in (9)}}{\text{g.-atoms of In dissolved from anode}}$$

The results of several such quantitative experiments are summarized in Table II.

It is evident from the data of Table II that in most cases there is fair agreement between the two valence numbers, V_N and $V_{\text{R.P.}}$; in cases in which no nitrogen is evolved at the anode the agreement between $V_{\text{R.P.}}$ and V_i is also satisfactory. Even when nitrogen evolution is taken into consideration, however, there is no consistency in the values of the mean valence numbers obtained in separate experiments under similar conditions.

TABLE II

ANODIC OXIDATION OF INDIUM IN LIQUID AMMONIA SOLUTIONS OF AMMONIUM BROMIDE

V_i	V_r	$V_{\text{R.P.}}$	V_N
2.60	2.75	2.62	No N_2
3.20	2.86	2.61	2.28
2.53	2.70	2.60	No N_2
2.75	2.80	2.32	2.27
2.72	2.89	2.10	1.98
2.92	2.94	2.15	1.89
2.82	2.92	2.58	2.30
2.01	2.22	2.16	No N_2
4.48	2.98	2.85	2.91

The results indicate that the indium is anodically oxidized to a mixture of oxidation states in such proportions that the mean valence number is always considerably less than 3, and that appreciable further oxidation occurs in solution during the period of electrolysis. The metallic indium formed in the anolyte is considered to result from the disproportionation of indous ion to indic ion and the metal, in a manner analogous to the previously reported disproportionation of this ion in aqueous and in acetic solutions[5]

$$3\text{In}^+ = 2\text{In} + \text{In}^{+++}$$

Experiments with ammonium nitrate–ammonium bromide mixtures as electrolyte showed that, unlike the case with gallium, the mean valence number of the indium appears not to be a simple function of electrolyte composition.

Thallium.—Unlike gallium and indium, thallium reacts fairly rapidly with anhydrous liquid ammonia; the reaction is even more rapid in the presence of certain dissolved salts. Although this non-electrolytic dissolution was taken into consideration in the calculation of the mean valence number of the electrolytically oxidized thallium, yet, since it cannot be stated unequivocally that the rate of non-electrolytic corrosion remains constant during electrolysis, the experiments with the thallium anode are to be regarded as semi-quantitative only. However, the individual experimental runs were completed in a relatively short time—1 hr. or less—and with a sufficiently high current so that a relatively large weight of thallium, 0.2 to 0.5 g., was dissolved; the quantity of non-electrolytically dissolved thallium was so small in comparison that it decreased the calculated valence number by no more than 0.03 to 0.04 valence unit.

Surprisingly, the anodic oxidation of thallium in ammonium bromide electrolyte yields thallic as well as thallous ion. The oxidizing power attributable to thallic ion was determined by treatment of the residue, remaining in the cell after evaporation of the liquid ammonia, with acidified potassium iodide solution, followed by titration of the liberated iodine with standard sodium thiosulfate solution. The results of a series of experiments in a divided cell with ammonium bromide as electrolyte are summarized in Table III, in which V_i = uncorrected mean valence number, V_c = mean valence number corrected for non-electrolytic corrosion, and V_{ox} = mean valence number calculated from oxidizing power. The temperature of the electrolyte was −70 to −75° in each case.

TABLE III

ANODIC OXIDATION OF THALLIUM IN LIQUID AMMONIA SOLUTIONS OF AMMONIUM BROMIDE

Molar concn. NH_4Br	Current density amp./sq. cm.	V_i	V_c	V_{ox}	Theoretical oxidizing power recovered, %
0.60	0.008	2.01	..	..	..
.70	.008	1.21	..	..	..
.70	.008	1.50	..	..	..
.35	.013	1.25	1.27	..	..
.35	.013	1.20	1.22	1.19	88.0
.60	.013	1.19	1.21	1.17	80.0

TABLE IV

ANODIC OXIDATION OF THALLIUM IN LIQUID AMMONIA SOLUTIONS OF VARIOUS SALTS

Electrolyte and molar concn.	Temp., °C.	V_i	V_c	Qualitative test for oxidizing power
1.0 NH_4NO_3	−50	0.92	0.95	......
0.8 $NaNO_3$	−75	.98	.99	Negative
0.25 $Zn(NO_3)_2$	−75	.98	.99	Negative
0.1 $Zn(NO_3)_2$	−70	.97	.99	Negative
0.8 NH_4Cl	−75	1.34	1.38	Negative
Satd. soln. of KNH_2	−60	2.33	2.41	Positive

Qualitative tests on the anolyte showed the presence of both thallous and thallic ions.

A few salts other than ammonium bromide were also used as electrolytes, with the results shown below. The current density in each of these experiments was 0.012 amp. per sq. cm. The solutions remaining after electrolysis were tested for oxidizing power.

One fact is outstanding: when the electrolyte consists of a nitrate, the corrected mean valence number is always approximately 1. With the other two electrolytes, ammonium chloride and potassium amide, however, values considerably higher than 1 are obtained. The negative test for oxidizing power when ammonium chloride is used as electrolyte is inconsistent with the value obtained for the mean valence number; a possible explanation is that the thallium anode may be partially passive in this case.

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Effect of Composition on Burning Velocities in Hydrogen–Bromine Mixtures[1]

BY STONE D. COOLEY, JAMES A. LASATER AND ROBBIN C. ANDERSON

Burning velocities (for flames in hydrogen–bromine mixtures) have been determined by using a Bunsen-type burner. The effects of the type of atmosphere, size of burner tube, position of burner, etc., have been investigated. The maximum burning velocity observed, for mixtures at 49° and atmospheric pressure was 32 cm./sec. at 41–44 mole % bromine. Absolute values of burning velocity depended somewhat upon experimental conditions, but the trend of variation with composition was not affected.

The reaction of hydrogen and bromine, $H_2 + Br_2 \rightarrow 2HBr$, offers interesting possibilities as a system for investigating and testing modern concepts of flame propagation. The work of Bodenstein, Christiansen, Polanyi and others[2] has shown that the reaction occurs by a chain mechanism which is simple compared to those occurring in ordinary combustion systems, particularly since chain-branching is not be be expected.

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\begin{aligned}
Br_2 &\rightleftarrows 2Br \\
Br + H_2 &\longrightarrow HBr + H \\
H + Br_2 &\longrightarrow HBr + Br \\
H + HBr &\longrightarrow H_2 + Br
\end{aligned}
$$

The heat of reaction is small but Ohmann,[3] Sagulin[4] and Kitagawa[5] showed that flames can be ignited in hydrogen–bromine mixtures. Earlier experiments in this laboratory[6] showed that such flames would propagate smoothly, though slowly, through straight tubes; and preliminary calculations of theoretical flame temperatures, etc., indicated no essential differences in mechanism of reaction to be expected in the flames as contrasted to ordinary conditions. Recently Kokochashvili[7] has reported further work on ignition of hydrogen–bromine mixtures.

Furthermore, in view of the question of diffusion of active particles as a factor in flame propagation, the hydrogen–bromine system is of interest because it involves only two such particles and these should differ appreciably in properties.

Experimental measurements of properties of hydrogen–bromine flames are, therefore, being made, for comparison with theoretical calculations. This report deals with results of measurements of burning velocities of mixtures of various compositions made using a bunsen-type burner.

Apparatus.—The burner itself consists of a monel metal jacket approximately 3 inches in diameter and two feet

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(1) Based partly upon a paper presented at sixth Southwest Regional Meeting, American Chemical Society, San Antonio, Texas, December, 1950.

(2) See, for example, N. Semenoff, "Chemical Kinetics and Chain Reactions," Chap. VI, Oxford Press, 1934; R. N. Pease, "Equilibrium and Kinetics of Gas Reactions," p. 112, Princeton University Press, 1942, p. 112.

(3) H. Ohmann, *Ber.*, **53**, 1429 (1920).

(4) A. B. Sagulin, *Z. physik. Chem.*, **1B**, 275 (1928).

(5) T. Kitagawa, *Rev. Phys. Chem. Japan*, **12**, 135 (1928).

(6) H. R. Garrison, J. A. Lasater and R. C. Anderson, "Third Symposium on Combustion, Flame and Explosion Phenomena," Williams and Wilkins Co., Baltimore, Md., 1949, p. 155.

(7) V. I. Kokochashvili, *J. Phys. Chem.* (*U. S. S. R.*), **23**, 15, 21 (1949); **24**, 268 (1950); *cf. C. A.*, **44**, 6707 (1951).