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

Anodic Oxidation of Elements of the Aluminum Sub-group in Anhydrous Acetic Acid

BY ARTHUR W. DAVIDSON AND FRANK JIRIK

In a previous paper from this Laboratory,[1] it was shown that a number of anhydrous acetates may readily be prepared by anodic oxidation of metals in an electrolyte consisting of a solution of an alkali metal acetate in anhydrous acetic acid. In later work,[2] as yet unpublished, dealing specifically with aluminum, remarkably high anodic current efficiencies were observed, the decrease in weight of the aluminum seldom being less than 120% of that calculated on the basis of Faraday's law.

The present work was undertaken with the initial object of preparing anhydrous acetates of gallium, indium and thallium. It soon became evident, however, that the pure triacetate could not in any case be obtained in this way; and attention was directed to the oxidation states of the ions formed during the electrolyses, in the hope also of throwing further light upon the anomalous behavior of the aluminum electrode. All of the electrolyses to be described were carried out in an oxygen-free atmosphere. Under these conditions, it was found that the mean oxidation state of the cations resulting from electrolysis was *in every instance* appreciably lower than 3.

Experimental

Materials.—The gallium, indium and thallium used in this work were C. P. samples from reliable sources. The m. p. observed for the gallium was within 0.1° of the value (29.8°) given in the literature. Since very pure aluminum sometimes exhibits a marked tendency toward anodic passivity in acetic acid,[2a] the sample selected for this work was of a commercial grade; analysis showed it to contain 99.6% aluminum. Pure anhydrous acetic acid and sodium acetate were prepared essentially as described in previous papers[3] from this Laboratory, while ammonium acetate solutions of the desired concentration were obtained by passage of anhydrous ammonia over anhydrous acetic acid.

Apparatus.—The power supply used in most of the work to be described was a variable transformer-rectifier, connected to a 110-volt a.c. source, by means of which direct current at any desired voltage from 30 to 680 could be obtained in the secondary circuit containing the electrolytic cell. In most instances, the voltage across the cell did not exceed 100.

Preliminary electrolyses were made in a simple cell, hereafter designated as Cell 1, of which the only special feature was an outlet in the bottom through which the electrolyte could be withdrawn under a solution of an appropriate oxidizing agent. When it became evident in the earlier experiments with a gallium electrode that a strong reducing agent was being produced in the electrolysis, it seemed desirable to construct a cell with separate anode and cathode compartments, in order that it might be possible to determine which electrode was the point of origin of the reducing substance. Accordingly, a U-

shaped cell, as illustrated in Fig. 1, was constructed of 2.5-cm. tubing; the vertical distance from the bottom of the U to the ground glass joints was 12.5 cm., and the outside width of the U, 10 cm. Electrical contact was made with the platinum cathode, C, and with the anode, A, by means of platinum wires dipping into mercury. Gas could be introduced at B and B', to pass out at E and E'. D was a disk of sintered glass separating the anolyte and catholyte, which could be separately withdrawn, after electrolysis, through the tubes F and F'. The diagram shows the arrangement used for a gallium anode, which consisted of a ring of the metal to which contact was made by a short piece of platinum wire, supported in a shallow glass cup, H, which was fused to the electrode tube at its center. This apparatus, to be referred to hereafter as Cell 2, was used for the greater part of the expts. to be described. Its only disadvantage lay in the difficulty of maintaining the same gas pressure in the two compartments, in order that electrolyte might not be forced through the disk.

Still another form of cell, which was used in some of the later expts., is illustrated in Fig. 2. Here the outer tube was about 5 cm. in diameter and 12 cm. high. The diagram shows a gallium anode, A, in place in the bottom of the tube; for an aluminum or an indium electrode, the lead wire was brought in through another hole in the rubber stopper. The cathode was a platinum wire, C, immersed in the electrolyte in the removable compartment, BE, the bottom of which consisted of the sintered glass disk, D, 1 cm. in diameter. Gas liberated at the cathode escaped at F, while the gas introduced at G, together with gas liberated in the anode compartment, passed out at H. This apparatus will be referred to hereafter as Cell 3.

Oxygen-free Atmosphere.—In the early experiments with Cell 2, an inert atmosphere was maintained by means of a current of nitrogen, previously passed through alkaline pyrogallol solution, dried with magnesium perchlorate, and finally bubbled through two successive vessels containing a solution of the same composition as the electrolyte. In expts. in which the amount of hydrogen evolved was to be determined, carbon dioxide was substituted for nitrogen, in order that substances other than hydrogen might readily be removed from the effluent gases by absorption in alkaline solution. Traces of oxygen in the commercial carbon dioxide used were removed by passage over heated copper turnings, after which the gas was dried and saturated with acetic acid vapor just as in the case of nitrogen.

Gas Analysis.—Although in almost every electrolysis (except with thallium as anode) there was visible gas evolution either in the anode compartment or at the surface of the sintered disk, the total quantity of anode gas was usually too small to permit of accurate recovery and analysis; better results were obtained by collecting the anode and cathode gas together[4] and determining the total quantity of hydrogen present; the amount liberated near the anode could then readily be determined by deducting from this total the amount known (from coulometric data) to have been liberated at the cathode.

For analysis, the effluent gas was collected over potassium hydroxide solution and transferred to the buret of a modified Orsat apparatus, where it was mixed with a measured excess of air. The mixture was then passed repeatedly through a tube containing palladium black deposited on asbestos, which was maintained at a temperature considerably below red heat by means of a gas flame held a few inches below the tube, until no further diminution in volume took place. The volume of hydrogen in the sample

(1) Adams and Davidson, *Trans. Kansas Acad. Sci.*, **38**, 129 (1935).

(2) (a) Kennedy, Master's Thesis, University of Kansas, 1937; (b) Kilpatrick, Master's Thesis, University of Kansas, 1942.

(3) Davidson and McAllister, THIS JOURNAL, **52**, 507, 519 (1930).

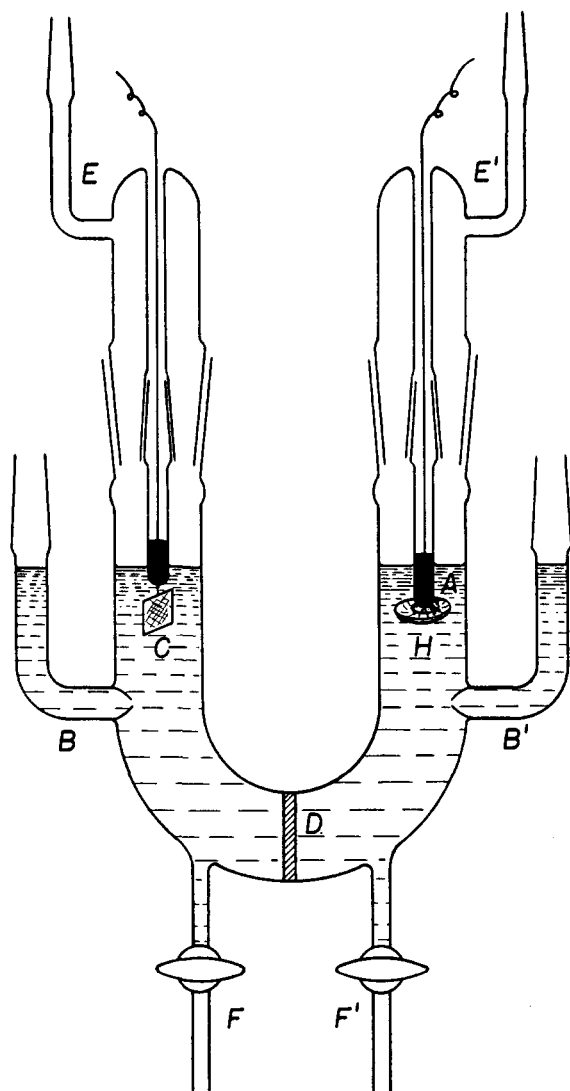(4) A preliminary analysis of the anode gas had shown it to consist of hydrogen alone.

Fig. 1.—Cell 2.

was then taken to be two-thirds of the total decrease in volume.

Procedure for a Typical Electrolysis.—The cell to be used, including the electrodes, was washed with acetone and thoroughly dried. After the electrodes had been weighed the electrolyte was introduced, and the assembled cell was immersed in a constant temperature bath and connected in series with the current source described above, a copper coulometer, and an ammeter. Oxygen-free gas was passed through the system until all the air had been displaced, after which the issuing gas was shunted to the collecting bottle. After electrolysis, during which the current was maintained constant by adjustment of the variable transformer, the cell was swept out with gas for an additional hour; the bottle was then sealed for analysis.

The cell contents were then either withdrawn into a known volume of standard iodine solution (Cell 2), or treated with such a solution introduced directly into the cell (Cell 3). The electrodes were removed, rapidly washed with distilled water (the washings being added to the electrolyte–iodine solution), dried, and weighed. The solution was titrated with sodium thiosulfate solution. In the case of indium, the coarse particles of free metal remaining in the solution after titration were filtered off, washed with acetone, dried and weighed.
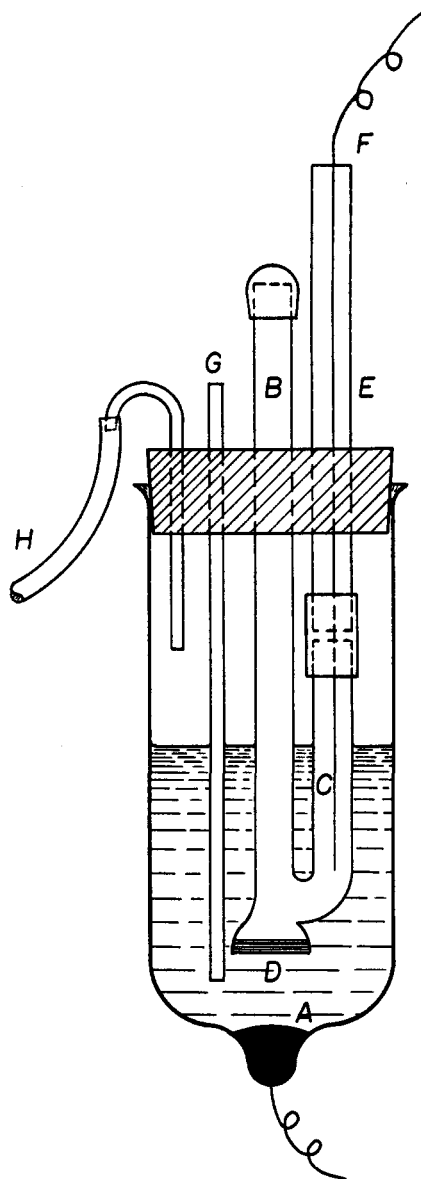

Fig. 2.—Cell 3.

Results

Thallium.—In the presence of air, metallic thallium reacts fairly rapidly with anhydrous acetic acid. In an atmosphere of nitrogen, the reaction, though slower, is still appreciable; thallium goes into solution as thallous acetate, with the liberation of hydrogen. Hence the electrolytic expts. with a thallium anode were semi-quantitative only. Three electrolyses were carried out in Cell 1, with a 3 mole % solution of sodium acetate as electrolyte; in one instance, the current density was in excess of 1 ampere per sq. cm. A black spongy deposit of metallic thallium appeared on the cathode shortly after the beginning of each electrolysis, but after the passage of current was discontinued this de-

posit slowly dissolved, with the liberation of hydrogen. Qualitative tests showed thallous ion (Tl^+) to be present in the solution in abundance, but no trace of thallic ion (Tl^{+++}) could be detected. The loss in weight of the anode, in every case, was from 60 to 100% greater than that corresponding (even on the hypothesis of oxidation to thallous ion alone) to the quantity of electricity which passed through the solution. This excess dissolution must be due to non-electrolytic oxidation. It may be safely concluded that the only product of anodic oxidation of thallium under these conditions is thallous ion. In view of the high oxidation potential of the Tl^+, Tl^{+++} electrode in aqueous solution ($E^0 = -1.25$ volts), this result is not surprising.

Gallium.—Unlike thallium, gallium does not react appreciably with solutions of sodium or ammonium acetate in anhydrous acetic acid. Nevertheless, preliminary expts. (Cell 1) showed that the quantity of metal that goes into solution from a gallium anode was always from 50 to 150% greater than that corresponding to uniform electrolytic oxidation to the gallic (Ga^{+++}) state. Although the cathode reaction in such electrolyses consisted predominantly in the liberation of hydrogen, minute quantities of supercooled liquid gallium occasionally appeared on the cathode.

In further electrolyses carried out in Cell 2, two additional phenomena were observed. First, there sometimes appeared in the neighborhood of the anode a distinct orange-brown color, which gradually spread throughout the entire anode compartment. Second, during the electrolysis, a small quantity of gas was given off as a stream of minute bubbles in the anode compartment, and especially in the neighborhood of the sintered disk. In one instance, a sample of the gas liberated in both compartments of the cell was subjected to a complete quantitative analysis, and was found to consist of hydrogen with no more than traces of hydrocarbons. No deposit of gallium was observed on the cathode. The freshly prepared anodic solution was found to have marked reducing power.[5] Thus, it rapidly decolorized acid permanganate, ferric thiocyanate complex, tetramminocupric ion, and free iodine in solution; it reduced auric chloride solution to a purple sol, and mercuric chloride to calomel, or, when the solution was warmed, to free mercury. The cathodic solution, on the other hand, showed no reducing properties.

These observations strongly suggest the hypothesis that the anode reaction does not consist exclusively in the oxidation of gallium to gallic ion, but that an ion of lower charge (probably +1), which we shall refer to as gallous ion, is formed simultaneously.

(5) This property was observed regardless of whether or not the solution was yellow in color. It may also be worthy of mention that it had previously been ascertained that no reducing substance is formed when sodium acetate solution is electrolyzed between platinum electrodes.

The most convenient means of expressing the mean oxidation state of the gallium ions formed at the anode is in terms of the number of faradays passed through the solution per gram-atomic weight of gallium lost from the anode. This number, which we shall designate as the initial mean valence number, X, of the gallium, may readily be calculated from the coulometric data by means of the equation

$$X = \frac{\text{wt. of Cu deposited in coulometer} \times 69.72}{31.77 \times \text{wt. of Ga lost from anode}}$$

The oxidation state of gallium in the electrolyte at the end of the electrolysis, which we shall designate as the final mean valence number, X', may be determined by subtracting from 3 the number of gram equivalents of iodine required, per gram-atomic weight of gallium in solution, for its complete oxidation to the tripositive state; in the form of an equation

$$X' = 3 - \frac{\text{wt. of I}_2 \text{ reduced} \times 69.72}{126.9 \times \text{wt. of Ga in solution}}$$

In every quantitative expt., $X' - X$, which we shall designate as $\Delta X_{obs.}$, had an appreciable positive value. Hence it is evident that non-electrolytic oxidation of gallous ion must occur in the course of the electrolysis. In the absence of air, the oxidizing agent most obviously available is hydrogen ion from the solvent, the reduction of which is indicated qualitatively by the evolution of bubbles of gas from the anolyte. This reaction may plausibly be supposed to proceed according to the equation

$$Ga^+ + 2H^+ = Ga^{+++} + H_2$$
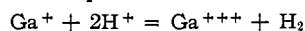
A quantitative measure of the hydrogen ion so reduced may be obtained from the excess of hydrogen, in the gas leaving the cell, over the quantity of cathodic hydrogen corresponding to the coulometric data. The increase in valence number of the gallium, ΔX_H, thus accounted for may readily be calculated as the number of equivalents of excess or anodic hydrogen per gram-atomic weight of gallium present; or, in the form of an equation

$$\Delta X_H = \left(\frac{\text{no. of ml. of H}_2 \text{ (S. T. P.) evolved}}{11200} - \frac{\text{wt. of Cu deposited}}{31.77} \right) \times \frac{69.72}{\text{wt. of Ga}}$$

TABLE I

ANODIC OXIDATION OF GALLIUM

Atmosphere, CO_2; temperature, 20°; time, 4 hr.; electrolyte, 6.5 mole % $NaC_2H_3O_2$ solution; area of anode, 0.5 sq. cm.; current, 0.028 amp.

Wt. of Cu deposited in coulometer, g.		0.1323
Wt. of Ga dissolved from anode, g.		.1898
Wt. of I_2 (by titration) reduced by gallous ion, g.		.2335
Vol. of H_2 liberated, ml. at S. T. P.		68.0
X	1.53	X' 2.32
$\Delta X_{obs.}$	0.79	ΔX_H 0.70
Oxidation unaccounted for $(\Delta X_{obs.} - \Delta X_H)$		0.09

The complete data for a typical quantitative expt. in Cell 2 are given in Table I.

Detailed data for other electrolyses need not be given, but some of the more significant results have been collected in Table II. Unless otherwise noted, the electrolyte was 6.5 mole % sodium acetate solution, and the temperature was 20°. In the first three electrolyses, an atmosphere of nitrogen was used, in the remainder, carbon dioxide.

TABLE II

SUMMARY OF RESULTS FOR GALLIUM ANODE

Current, amp.	Time, hours	X	X'	$\Delta X_{obs.}$	ΔX_H
0.013	14	1.25	2.00	0.75	..
.009	24	1.32	2.10	.78	..
.085[a]	1.5	1.27	1.49	.22	..
.026	4.5	1.68	2.35	.67	0.54
.028	4	1.53	2.32	.79	.70
.046	3	2.01	2.37	.36	.23
.010	6	1.82	2.36	.54	.48

[a] This electrolysis was carried out at 0°, with 18.6 mole % ammonium acetate solution as electrolyte. Note the relatively low value of ΔX in this case.

In numerous other electrolyses, the values of X varied from 1.12 to 1.55; no significant trend with varying current density could be discerned. While these results do not exclude the possibility of the existence of a bipositive gallium ion, neither do they lend any support to such a hypothesis; on the other hand, the fact that X is, in almost every case, lower than 2, may be regarded as strong evidence for the existence of a unipositive gallium ion. In any case, it seems probable that some gallium is oxidized directly to gallic ion.

Although numerous reports of compounds of bivalent gallium are to be found in the literature,[6] considerable uncertainty exists as to the structure of these compounds. Solid gallium dichloride, for instance, is diamagnetic,[7] and it has been suggested that its structure may best be represented by the formula $Ga^I[Ga^{III}Cl_4]$.[8] On the other hand, gallous oxide, Ga_2O,[9] and gallous sulfide, Ga_2S,[10] have been identified with certainty, and the existence of gallous ion, Ga^+, might readily be accounted for in terms of the loss by the element of its single $4 p$ electron.

Indium.—Unlike gallium, metallic indium is not completely inert in acetic acid solutions of acetates. The displacement reaction is much slower, however, than in the case of thallium, and the corresponding loss of indium was found to be negligible in comparison with the electrolytic oxidation to be discussed.

Preliminary expts. in Cell 1 showed the quantity of metal

leaving the electrode, with the sodium acetate solution as electrolyte, to be little greater than that corresponding to complete oxidation to indic ion, In^{+++}; with the more concentrated ammonium acetate solution, however, the quantity of metal dissolved was from 22 to 44% greater than this. In these expts., small quantities of indium were deposited on the cathode, and the amount of hydrogen liberated was slightly less than the cathodic hydrogen calculated from the coulometric data.

Further expts. were carried out in Cell 3, with ammonium acetate solution as electrolyte. As in the case of gallium, considerable evolution of gas was observed in the anode compartment, especially in the neighborhood of the disk. This again proved to be hydrogen, and the total quantity of hydrogen liberated exceeded the calculated cathodic hydrogen. As the electrolysis proceeded, the anolyte first showed a marked Tyndall effect, and then deposited a finely divided white precipitate which could only have been indic acetate. At the same time, dark gray metallic particles also appeared in the anolyte. In this cell, no metallic indium was deposited on the cathode and no more than a faint test for indium could be obtained in the catholyte.

All these phenomena may be satisfactorily accounted for in terms of the hypothesis that anodic oxidation results in the formation of both indic and indous, In^+, ion, and that the latter undergoes both oxidation by hydrogen ion and disproportionation according to the equation

$$3In^+ = In^{+++} + 2In$$
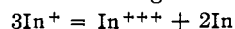
It may further be concluded that no indic ion migrates through the disk toward the cathode— a conclusion which seems especially probable in view of the insolubility in acetic acid of triacetates in general.

The initial mean valence number, X, of the indium was calculated from the coulometric data by means of the equation

$$X = \frac{\text{wt. of Cu deposited in coulometer} \times 114.8}{31.77 \times \text{wt. of indium lost from anode}}$$

Although the anolyte showed appreciable reducing power toward iodine solution, it seems probable that this was attributable to the finely divided indium metal[11] which it contained, rather than to indous ion. The validity of this hypothesis, however, is not involved in the calculation of the final mean valence number, X', which was carried out according to the equation

$$X' = 3 - \frac{(\text{wt. of } I_2 \text{ reduced} \times 114.8/126.9) + (3 \times \text{wt. of free In filtered off})}{\text{wt. of In lost from anode}}$$

In each of the quantitative experiments, X'

(6) See, for instance, Laubengayer and Schirmer, THIS JOURNAL, 62, 1578 (1940).

(7) Klemm and Tilk, Z. anorg. allgem. Chem., 207, 175 (1932).

(8) Emeléus and Anderson, "Modern Aspects of Inorganic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1938, p. 145.

(9) (a) Brukl and Ortner, Z. anorg. allgem. Chem., 203, 23 (1932); (b) Klemm and Schnick, ibid., 226, 353 (1936).

(10) Brukl and Ortner, Monatsh., 56, 358 (1930).

(11) Since some of the metallic indium in suspension was too fine to be filtered off, it was impossible to distinguish, by this method, between the reducing action of free indium and that of any indous ion which might conceivably still have been present. It was shown by expt., however, that finely divided indium is indeed oxidized by iodine solution sufficiently rapidly to account for the behavior of the solution during titration.

$-X$, or $\Delta X_{obs.}$, had a positive value, as did ΔX_H, calculated as in the case of gallium.

The complete data for a typical experiment in Cell 3 are given in Table III.

TABLE III

ANODIC OXIDATION OF INDIUM

Atmosphere, CO_2; temperature, 20°; time, 1.25 hr.; electrolyte, 18.6 mole% $NH_4C_2H_3O_2$ solution; area of anode, 6 sq. cm.; current, 0.068 amp.

Wt. of Cu deposited in coulometer, g.			0.1013
Wt. of In dissolved from anode, g.			.1744
Wt. of I_2 (by titration) reduced by In, g.			.0605
Wt. of free In recovered from solution, g.			.0143
Vol. of hydrogen liberated, ml. at S. T. P.			40.3
X	2.10	X'	2.44
$\Delta X_{obs.}$	0.34	ΔX_H	0.27
Oxidation unaccounted for $(\Delta X_{obs.} - \Delta X_H)$			0.07

Additional electrolyses, all carried out under similar conditions, with the current varying from 0.035 to 0.060 ampere, gave values of X ranging from 2.16 to 2.38; disproportionation to metallic indium and indic acetate occurred in every case.

These results do not, of course, exclude the possibility of the temporary existence in these solutions of bipositive indium ion, numerous compounds of which have been reported in the literature.[12] It is of interest to note, however, that indium dihalides have been observed to decompose, on contact with water, first to indous halide and halogen, then to indic halide and metallic indium. As was mentioned in the discussion of gallium, the existence of a unipositive ion might readily be accounted for in terms of the loss of a single electron, in this case from the 5 p subshell.

Aluminum.—Metallic aluminum, like gallium, is not acted upon by acetic acid solutions of acetates, even in the presence of air. Upon electrolysis, the behavior of an aluminum electrode was very similar to that described above for gallium. A yellowish-brown substance appeared in the immediate neighborhood of the anode, and gradually became dispersed throughout the solution. The quantity of metal dissolved was always from 20 to 30% greater than that corresponding to electrolytic oxidation to the tripositive aluminum ion. No metallic aluminum ever appeared at the cathode.

The amount of reducing agent remaining in the anolyte at the end of the reaction was in most cases very small, much less than in the case of gallium. In two instances, however, in which the electrolysis was carried out at 0°, the reducing power of the resulting solution was found to be appreciably higher (as in the case of gallium) than in the expts. at room temperature. A considerable amount of hydrogen was always liberated in the immediate neighborhood of the disk. The explanation of this is believed to be essenti-

ally the same as in the case of gallium, namely, that the hydrogen results, at least in part, from the reaction

$$Al^+ + 2HC_2H_3O_2 + C_2H_3O_2^- = Al(C_2H_3O_2)_3 \text{ (colloidal)} + H_2$$
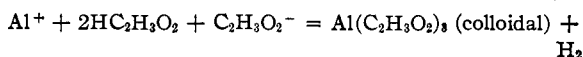
The values of the initial and final mean valence numbers, X and X', of the aluminum, and the increase in valence number corresponding to the excess hydrogen, ΔX_H, were calculated from the coulometric, iodimetric, and gasometric data by means of equations exactly analogous to those used for gallium.

Some typical results of electrolyses are presented in Table IV. Unless otherwise noted, the temperature was 20°. In the first three cases, the electrolyses were carried out in an atmosphere of nitrogen in Cell 2, the others in an atmosphere of carbon dioxide in Cell 3.

TABLE IV

SUMMARY OF RESULTS FOR ALUMINUM ANODE

Electrolyte	Current, ampere	Time, hours	X	X'	$\Delta X_{obs.}$	ΔX_H
9.7% NH_4OAc	0.042	4	2.36	2.94	0.58	..
18.6% NH_4OAc (40°)	.035	3	2.50	2.85	.35	..
26.6% NH_4OAc (40°)	.034	3	2.70	2.74	.04	..
6.5% $NaOAc$	.009	6	2.34	2.96	.62	0.32
6.5% $NaOAc$	.005	9.5	2.28	2.98	.70	.33
6.5% $NaOAc$	.024	3	2.45	2.96	.51	.48
6.5% $NaOAc$	.027	3	2.48	2.97	.49	.37

A number of other electrolyses were carried out under similar conditions, in which the values of X obtained varied from 2.38 to 2.54.

As indicated in the introduction, observation of "abnormally" high current efficiencies at an aluminum anode is by no means novel, although previous authors were extremely reluctant to interpret this phenomenon in terms of a lower valence state. Thus, Wöhler and Buff,[13] in the electrolysis of *aqueous* sodium chloride solutions, noted current efficiencies of 125%, corresponding to an initial mean valence of 2.40. These authors, indeed, did suggest (but only as, in their opinion, the far less plausible of two hypotheses) the possibility of the formation of an aluminum ion of charge less than $+3$ as the primary electrolytic reaction. Turrentine[14] reported the evolution of hydrogen at an aluminum anode in aqueous solutions. Sborgi and Marchetti,[15] in the electrolysis of acetone solutions of lithium chloride, and del Boca,[16] in the electrolysis of liquid ammonia solutions of cupric nitrate, again observed abnormally large current efficiencies at an aluminum anode. Del Boca, who found in one expt. an initial mean valence of as low as 1.5,[17] went

(12) See, for example, Thiel, *Z. anorg. allgem. Chem.*, **40**, 280 (1904); Hannebohn and Klemm, *ibid.*, **229**, 337 (1936).

(13) Wöhler and Buff, *Ann.*, **103**, 218 (1857).

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

(15) Sborgi and Marchetti, *Nuovo Cimento*, **22**, 151 (1921).

(16) del Boca, *Helv. Chim. Acta*, **16**, 565 (1933).

(17) This observation has been confirmed in unreported experiments in this Laboratory.

to considerable lengths to suggest alternative explanations of the phenomenon (including the cataphoresis of colloidal metallic aluminum, and the existence of complex ions such as $Al^{+++}Al_2$), which would avoid the hypothesis of a simple aluminum ion of charge lower than $+3$. On the other hand, abundant evidence is reported in the literature for the existence of such compounds as AlO[18] and AlF,[19] although at elevated temperatures only.

In the experiments here reported, both the excessive weight of aluminum dissolved from the anode during electrolysis and the liberation of hydrogen in the anolyte appear to leave small room for doubt that a singly or doubly charged aluminum ion does indeed exist, at least momentarily, in acetic acid solutions of acetates. The data do not point unequivocally either toward a unipositive or toward a bipositive ion, but analogy with the known behavior of other members of this family, as well as the electron structure of aluminum, with its single $3\,p$ electron, lends strong support to the former hypothesis.[20] If this supposition is correct, it must be concluded that aluminous ion, Al^+, is a considerably stronger reducing agent than gallous ion, Ga^+. For, in the first place, the amount of reducing agent remaining in the solution at the end of the electrolysis was always much smaller in the case of aluminum; and secondly, the amount of hydrogen liberated out of contact with the cathode was

(18) Coheur, *Bull. classe sci. Acad. roy. Belg.*, [5] **28**, 569 (1943).

(19) Klemm and Voss, *Z. anorg. allgem. Chem.*, **251**, 233 (1943).

(20) It may also be pointed out here that in later unpublished work in this laboratory (Mazzitelli, Master's Thesis, University of Kansas, 1949), initial mean valence numbers for aluminum in acetic acid solutions as low as 1.80 were obtained.

usually far less than sufficient to account for the oxidation of Al^+ to Al^{+++}. It seems not unlikely that acetate ion, which is, of course, present in the electrolyte in enormously higher concentration than hydrogen ion, may enter into the reaction also, and that such a reaction may account for the yellow color[21] observed in the electrolyte.

Summary

1. Anodic oxidation of thallium in acetic acid solution of an acetate yields thallous ion, Tl^+, exclusively.

2. In the anodic oxidation of gallium, indium, and aluminum in similar electrolytes, the loss of metal from the anode is always considerably greater than that corresponding to Faraday's law, if the product is assumed to be a triply charged cation; and free hydrogen is in every case evolved from the anolyte.

3. The behavior of the solutions resulting from such anodic oxidation of gallium, indium, and aluminum, as well as the coulometric data, may readily be explained in terms of the hypothesis that the primary anode product is in each case a mixture of a singly and a triply charged cation.

4. If this hypothesis is correct, it follows that gallous ion, Ga^+, and especially aluminous ion, Al^+, are to be regarded as very strong reducing agents; whereas indous ion, In^+, is subject not only to oxidation but to rapid disproportionation into indic ion, In^{+++}, and metallic indium.

(21) It was found possible to extract with ether, from an aqueous solution of the electrolyte after electrolysis, a minute amount of a yellow oil, obviously organic in nature.

Partition Systems for the Fractionation of Nitrocellulose with Respect to Molecular Weight[1,2]

BY MARVIN C. BROOKS AND RICHARD M. BADGER

Many studies of the molecular weight distribution of high polymers which would be of considerable interest are at present impracticable because of the limitations and tediousness of conventional fractionation procedures. The recent success of adsorption and partition methods in the separation of closely related chemical species has directed our attention to the possibility of applying such methods to the fractionation of high polymers. In this communication we describe a partition system applicable to the

(1) This paper is based on work supported by the Bureau of Ordnance and done under contract with the Office of Naval Research, Contract N6-ori-102, Task Order VI.

(2) Presented before the High Polymer Forum at the San Francisco meeting of the American Chemical Society, March 28, 1949.

fractionation of nitrocellulose with respect to molecular weight. Studies on adsorption systems are in progress and will be reported separately.

Partition separations depend upon differences in the way the solutes to be separated distribute themselves between immiscible phases. They have the great advantage that they can be brought about by the same convenient type of procedure used in ordinary chromatography, which automatically effects a repeated fractionation.[3] The method at present most commonly employed in fractionating high polymers, namely,

(3) Martin and Synge, *Biochem. J.*, **35**, 91, 1358 (1941). Partition chromatography has been applied with notable success to the separation of amino acids in protein hydrolysates, Stein and Moore, *J. Biol. Chem.*, **176**, 337 (1948).