this form. From the liquid poured off from the lead peroxide the copper was precipitated, after the excess of acid had been neutralized with ammonia.

		Electrolytically.			
Copper	2.70	2.70	2.74	2.76	2.75
Lead	12.66	12.60	12.50	12.67	12.66
Antimony	11.65	11.62	Determined in the liquid from which the Cu had been precipitated. The Sb was determined volumetrically, the Sn gravimetrically.[1]		
Tin	73.20	73.25			
	100.21	100.17			

From a dilute nitrohydrofluoric acid solution, copper can be separated from tungsten, and mercury and silver from tin and antimony. My assistant, Mr. N. H. Furman, finds that the results obtained in separating mercury from tin and antimony are fully as exact as those arrived at in separating copper from these metals. Attempts are being made to separate and determine other metals by means of the current when they are present in solutions containing hydrofluoric acid.

PRINCETON, N. J.

THE CONSTITUTION OF ALUMINATES. II.

BY EDWARD G. MAHIN.

Received August 18, 1914.

In a recent paper by Blum,[2] entitled "Constitution of Aluminates," criticism was made of an earlier paper bearing the same title[3] by Mahin, Ingraham and Stewart. Inasmuch as the author seems to have entirely misinterpreted a part of the experimental work described in the first paper, and the deductions therefrom, it seems necessary to correct these impressions.

Mahin, Ingraham and Stewart concluded that the hypothesis of aluminates having definite formulas had not been substantiated by any of the earlier work and that sufficient attention had not been given to the colloidal properties of aluminium hydroxide, as bearing upon its solubility in solutions of bases. Their supposition was that by adsorption of hydroxyl ions the aluminium hydroxide may be, to a considerable extent, maintained in a dispersed condition, molecular aggregates acquiring thereby a negative charge which has caused these aggregates to be mistaken for definite anions, because of their behavior when a current of electricity is passed through the solution of "aluminate."

This possibility seemed to be favored by the results of experiments upon the heat of solution of aluminium hydroxide in bases, upon the pre-

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[1] The metals were separated according to the method described in THIS JOURNAL, 31, 373 (1909).

[2] THIS JOURNAL, 35, 1499 (1913).

[3] *Ibid.*, 35, 30 (1913).

cipitation of aluminium hydroxide by reactions of ammonium nitrate with sodium aluminate and upon the electrolysis of aluminate solutions.

The reaction between ammonium nitrate and sodium aluminate was found to precipitate a proportionately *greater* quantity of aluminium hydroxide than would be indicated by the formula $NaAlO_2$, favored by most investigators. A substance of this formula could not produce more aluminium hydroxide than is indicated by the molecular proportion $Al_2O_3/NH_4NO_3 = 1/2$. In the experiments, however, the ratios $1/1.885$ and $1/1.930$[1] were obtained. This would indicate a substance having *less* sodium than that having the formula $NaAlO_2$ (see equations of former paper). Blum criticizes these deductions by saying that the theoretical ratio could not be expected because of incomplete hydrolysis of the aluminate, complete hydrolysis being possible only in case of absolute nonionization of ammonium hydroxide. This is certainly true, but Blum apparently overlooks the fact that incomplete hydrolysis would result in incomplete precipitation of aluminium hydroxide, with a consequent experimental ratio of Al_2O_3/NH_4NO_3 *less* than $1/2$, whereas Mahin, Ingraham and Stewart found ratios in two cases *greater* than $1/2$. In his reply (see following paper) Blum suggests that these ratios may have been obtained as a result of spontaneous decomposition of the aluminate solutions, the duration of the experiment not having been stated. Less than 15 minutes was required for these experiments and other portions of the aluminate solutions, not treated with ammonium nitrate, remained clear. Spontaneous decomposition is, therefore, extremely improbable.

A similar error was made by Blum in his discussion of the results of the electrolysis of aluminate solutions. The formula $NaAlO_2$ indicates the least alkali metal of all formulas that have been proposed for the alkali aluminates. Mahin, Ingraham and Stewart argued that electrolysis of such a substance could not produce a greater quantity of aluminium hydroxide, relative to oxygen liberated at the anode, than that indicated by the proportion $Al_2O_3/O_2 = 2/1$, while resolution of aluminium hydroxide in the basic solution at the anode was an unavoidable error that worked always toward diminishing the experimental ratio. The authors did not argue (although Blum so states) that failure to obtain a definite ratio for Al_2O_3/O_2 indicated absence of aluminates of definite formulas. They merely pointed out that the ratios obtained in three experiments showed, as in the ammonium nitrate reactions, that if aluminates as salts existed in the solutions their formulas must be different from any that have been proposed.

In the electrolysis of alkaline solutions of aluminium the difficulties encountered in the attempt to prevent resolution of aluminium hydroxide

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[1] In the original paper this ratio was given as $1/1.530$, as a result of a typographical error.

are practically insurmountable. Out of eighteen experiments reported in the original paper, three gave ratios of aluminium oxide precipitated to oxygen liberated at the anode, greater than 2/1. These were 2/0.9968, 2/0.8658, and 2/0.9174. Since that time, one of the authors (Mahin), working with Mr. O. M. Harrison, has obtained the ratios 2/0.8820 and 2/0.9524 in two experiments out of seven. If resolution could be entirely prevented the ratios would be still larger. If definite salts are present in the solutions they must be represented by such formulas as $Na_2Al_4O_7$, $NaAl_3O_5$, etc. The number of such formulas that might be invented is endless. (Blum suggests the possibility of spontaneous decomposition of the aluminate solutions in these experiments also. Such possibility was excluded by the fact that the experiments were watched very carefully, the electrolysis being stopped in each case whenever the least turbidity appeared in the main body of the solution.)

The evidence presented by Blum in his measurements of the amount of basic solution required to precipitate and redissolve aluminium hydroxide from aluminium chloride,[1] appears to be the most definite of any that has been presented. However, it may be pointed out that in his curve C,[2] if the third point of inflection is taken strictly as the curve indicates, it will fall at a point corresponding with $[H^+]$ = (nearly) $10^{-11.5}$ instead of $10^{-10.5}$. At this point the volume of basic solution is 28.5 cc. instead of 28 cc. In this case the ratio of base required to redissolve the precipitate, to that required to form it is $\frac{28.5 - 21.5}{21.5 - 4} = 0.4$, not 0.33. This would correspond with an aluminate containing more alkali metal than is indicated by the formula $KAlO_2$. In other words, this definite formula can be obtained from the curve only by a somewhat arbitrary selection of a point of inflection which is not indicated by the experiments.

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THE CONSTITUTION OF ALUMINATES.[3]

BY WILLIAM BLUM.

Received September 10, 1914.

In my discussion[4] of the evidence of Mahin, Ingraham and Stewart,[5] regarding the reaction between sodium aluminate and ammonium nitrate, stress was laid upon the uncertainty due to incomplete hydrolysis of the aluminate, which would lead to incomplete precipitation of the aluminium hydroxide, such as evidently occurred in Expt. 2 of Table I, where the ratio

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[1] *Loc. cit.*

[2] THIS JOURNAL, 35, 1500 (1913).

[3] Published by permission of the Director of the Bureau of Standards.

[4] THIS JOURNAL, 35, 1503 (1913).

[5] *Ibid.*, 35, 36 (1913).