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.

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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).

2.68/1 was obtained. The slight excess of aluminium hydroxide precipitated in the other two experiments may have been due to spontaneous decomposition of the aluminate solutions, even though the period of the reaction was only fifteen minutes, a phenomenon I have often observed with aluminate solutions saturated with aluminium hydroxide. It is at least interesting to note that the effect of any such error, if present, would be proportionally greater in Expts. 1 and 3, than in 2, owing to the smaller amounts of aluminium hydroxide involved in the former experiments. Indeed, if the molecular ratio NH_4NO_3/Al_2O_3 be calculated for the sum of the amounts involved in the three experiments, the ratio 2.39 is obtained; *i. e.*, the total error is in the direction expected, a deficient precipitation of aluminium hydroxide. In this connection, attention should be called to an error in calculating the result for Expt. 3 of Table I, where the molecular ratio NH_4NO_3/Al_2O_3 should be 1.93 (and not 1.53 as given).

Similarly, in the discussion of the electrolysis experiments, attention was called in my former paper to the probable spontaneous decomposition of the solutions during electrolysis; especially since "In every case the precipitated aluminium hydroxide possessed at first the appearance of a colloidal gel, changing to the crystalline modification as the experiment proceeded." Such an effect might have counteracted, or even counterbalanced, the admitted solvent action of the liberated alkali. The fact that in only three out of eighteen experiments described in his original paper and in only two out of seven mentioned in the second paper[1] Mahin obtained ratios indicating an excess precipitation of aluminium hydroxide, is certainly not conclusive evidence of the nonexistence of sodium aluminate with a formula, $NaAlO_2$, or some multiple.

The curve C in my paper, referred to by Mahin, represents the action of potassium hydroxide upon aluminium chloride, in which, as pointed out in the original article, great difficulty was experienced in obtaining a clear solution, owing to the above-mentioned spontaneous separation of crystalline aluminium hydroxide. Greater significance should therefore be given to curve B, representing the action of sodium hydroxide.

The above considerations, together with the failure of Hildebrand[2] to detect colloidal particles in aluminate solutions by means of the ultramicroscope, seem to justify the original conclusion that definite aluminates, having the formula $MAlO_2$ or some multiple of it, probably exist in aqueous solution.[3]

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[1] THIS JOURNAL, preceding paper.

[2] *Ibid.*, **35**, 864 (1913).

[3] My attention has been called to an article by Slade and Polack in *Trans. Faraday Soc.*, **10**, 150 (August, 1914), discussing the original paper by Mahin, Ingraham and Stewart, which came too late for consideration by the authors of these papers. [EDITOR.]