hard to observe. When the conditions were favorable, however, it was possible to find a field full of aggregations made up of a few particles only.

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THE CONSTITUTION OF ALUMINATES.[1]

BY WILLIAM BLUM.

Received August 8, 1913.

In a recent article by Mahin, Ingraham and Stewart upon the constitution of aluminates,[2] the authors conclude that the solubility of aluminium hydroxide in bases is due principally to its colloidal properties, and question the existence of aluminates as definit salts. Since, in a study now in progress to determin the conditions for the quantitative precipitation of aluminium hydroxide, results were obtained which indicated the existence of definit aluminates, a statement of these results, together with a discussion of the conclusions reached by Mahin and his co-workers seems desirable.

In the work at this Bureau the changes in hydrogen ion concentration taking place in a solution during the precipitation and re-solution of aluminium hydroxide by alkalis were determined by means of a hydrogen electrode, using an apparatus and method similar to that employed by Hildebrand and Harned[3] in the determination of magnesia in limestone. The method used here was briefly as follows: The solution to be titrated was maintained at about 25° in a beaker which was closed with a rubber stopper having suitable perforations for (*a*) the hydrogen electrode, (*b*) the connection with a cell containing saturated potassium chloride solution which was in turn connected to a calomel half-cell in 0.1 *N* potassium chloride solution, (*c*) the tip of the buret, and (*d*) an exit tube for the hydrogen. By this arrangement carbon dioxide was conveniently expelled from the original solution and excluded during the titration. The readings, made at ten-minute intervals, by means of a millivoltmeter and a capillary electrometer, are probably accurate to ±2 millivolts. The aluminium chloride solution, prepared from the recrystallized salt, was about decimolar (for $AlCl_3$) and contained some free hydrochloric acid; the sodium and potassium hydroxide solutions prepared from the metals, were about fifth normal. The initial volume of the titration was about 50 cc. The details of the method will be described in a later paper, in which the re-

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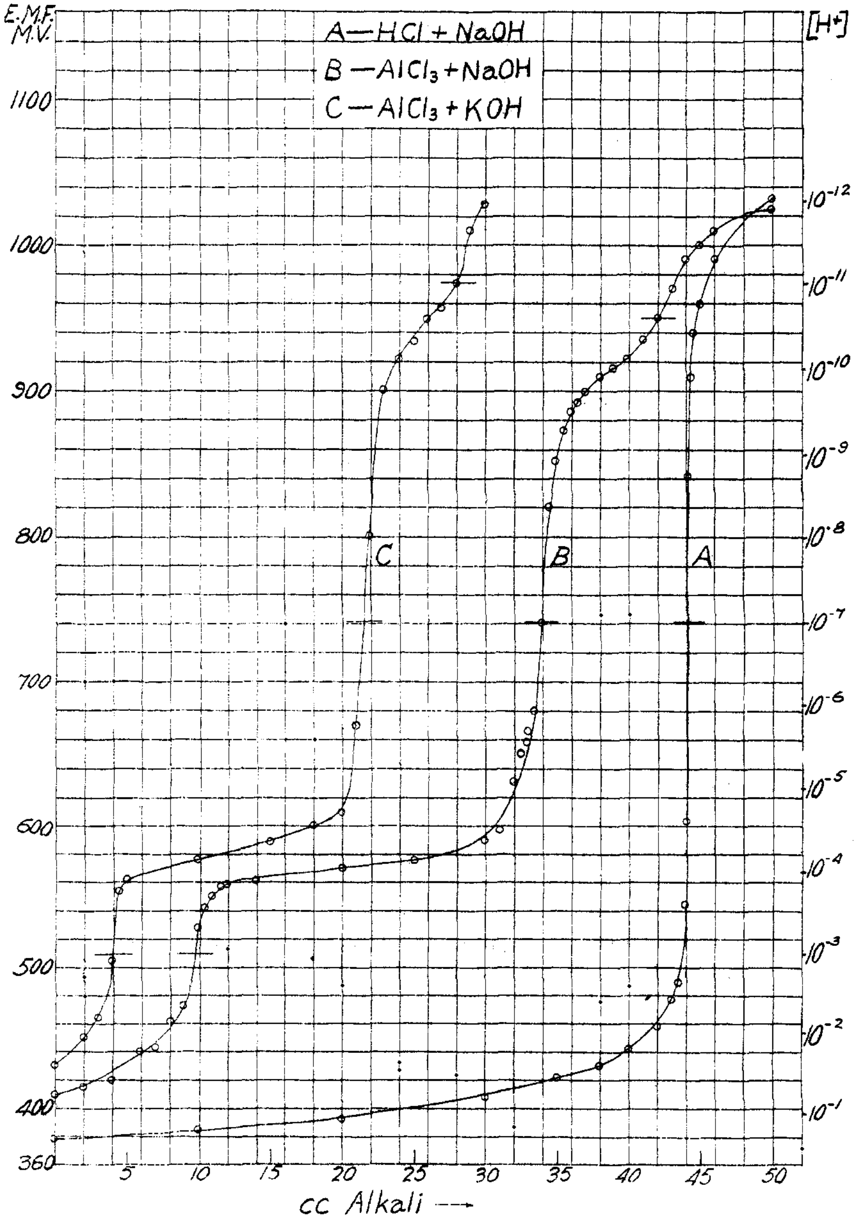
[1] Published by permission of the Director of the Bureau of Standards.

[2] THIS JOURNAL, 35, 30–9 (1913).

[3] *Orig. Com. 8th Intern. Congr. Appl. Chem.*, 1, 217–25 (1912). Consult also Joel H. Hildebrand, THIS JOURNAL, 35, 864 (1913), in which the curve for $Al_2(SO_4)_3$ + NaOH is shown, and attention called to the formation of $NaAlO_2$. This work though presented on March 25, 1913, in an address at the Milwaukee meeting, was not known to the author till its appearance in the July number of THIS JOURNAL, when the present article was being prepared for press.

lations of these results to the analytical chemistry of aluminium will be discussed.

The results are shown graphically in the figure in which the abscissas represent cubic centimeters of sodium or potassium hydroxide solution added, and the ordinates (as indicated on the left side) are the observed



E. M. F.'s expressed in millivolts. On the right side the value of the ordinates is expressed in hydrogen ion concentration, as calculated from the formula

$$\log \frac{1}{[H^+]} = \frac{\pi - 0.338}{0.058}$$

where π is the observed E. M. F. in volts.

The curve A for the neutralization of hydrochloric acid with sodium hydroxide is shown simply to indicate the normal course of such a reaction in the absence of any metals precipitable as hydroxides. It also furnished a means for determining the points of inflection in the precipitation curves, *i. e.*, the points of departure from a normal neutralization curve. From the curve B for the action of sodium hydroxide upon aluminium chloride, it may be noted that precipitation of aluminium hydroxide begins when $[H^+]$ is about 10^{-3}, and is complete before $[H^+]$ is 10^{-7}. The abscissa between these two points, *i. e.*, from 9.8 to 34.0 cc., or 24.2 cc., represents the volume of sodium hydroxide required to precipitate the aluminium present. The portion of the curve from $[H^+] = 10^{-7}$ to $[H^+] = 10^{-10.5}$ represents the dissolving of aluminium hydroxide in sodium hydroxide, the solution being almost entirely clear at the latter point. That the solution then contains a definit compound consisting of one atom of sodium to one of aluminium, is indicated by the fact that the volume of alkali from the neutral point to this point of inflection, or from 34.0 to 42.0 cc. is 8.0 cc., *i. e.*, almost exactly one-third of the volume (24.2 cc.) required to precipitate all the aluminium. This confirms the observation of Prescott[1] that one molecule of freshly precipitated aluminium hydroxide dissolves in exactly one molecule of sodium or potassium hydroxide. The same relation holds true in curve C for aluminium chloride and potassium hydroxide where the volumes of alkali required to precipitate and to redissolve the aluminium hydroxide are respectively, 17.5 cc. and 6.5 cc. The determination of the exact point of inflection when the aluminium hydroxide is all dissolved, is rendered difficult by the partial conversion of the colloidal form as first precipitated, to the "crystallin" variety, which is difficultly soluble even in great excess of alkali. On standing for several hours some "crystallin" aluminium hydroxide always separated from the alkalin solutions. The difficult solubility of the last traces of aluminium hydroxide, even with considerable excess of alkali, was more marked with potassium than with sodium hydroxide. No reason is advanced for this difference. Its effect upon the curve for potassium hydroxide and aluminium chloride was practically eliminated by first determining the precipitation portion of the curve, *i. e.*, to 20 cc. potassium hydroxide, and then starting with a fresh portion of solution, making a single addition of 20 cc. potassium hydroxide and completing the curve in 1 cc. intervals.

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[1] THIS JOURNAL, 2, 27 (1880).

By this means the time in which the aluminium hydroxide could change to the "crystallin," difficultly soluble variety, was reduced to such an extent that an almost perfectly clear solution was obtained at the point of inflection, *i. e.*, $[H^+] = 10^{-11}$.

Subsequent to the appearance of the paper by Hildebrand[1] the experiment shown in curve B was repeated and continued until considerable excess of alkali was present. No evidence was found, however, of another point of inflection corresponding with the second hydrogen of aluminic acid, the possibility of which was noted by Hildebrand.

The results of these experiments, therefore, indicate the existence of definit aluminates of the formulas $NaAlO_2$ and $KAlO_2$ (or multiples thereof) in solutions obtained by the action of the corresponding alkalies upon aluminium hydroxide. If this process of solution were due entirely, or even principally, to the colloidal properties of aluminium hydroxide there would probably be a reduction in the alkalinity of the solution, but it is improbable that it would be of such magnitude as has been shown here, much less that the maximum reduction in alkalinity would occur when the alkali was chemically equivalent to the aluminium hydroxide.

The conclusion of Slade[2] that aluminic acid is not a very weak monobasic acid, but has an ionization constant of at least 10^{-10}, is confirmed by the fact that in 0.06 *N* solution (the approximate concentration of the $NaAlO_2$ in experiment B when the aluminium hydroxide was entirely dissolved) $[OH^-]$ = about $10^{-3.5}$, corresponding with an ionization constant $K_a = [H^+][AlO_2^-]/[HAlO_2]$ between 10^{-8} and 10^{-9}.* It is recognized that this result is only a rough approximation, since we have no accurate data for the ionization of sodium aluminate nor for the true solubility of aluminium hydroxide, especially when the solid phase is colloidal. The fact that this value is considerably greater than that calculated by Slade is to be expected, since these solutions were in equilibrium with the colloidal and, therefore, more soluble form of aluminium hydroxide, while the values of Slade were derived from solutions in equilibrium with the crystallin variety. A high degree of hydrolysis of sodium alumi-

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[1] This Journal, **35**, 864 (1913).

[2] *Z. anorg. Chem.*, **77**, 457–60 (1912).

* Based on the following assumptions and equations:

$$NaAlO_2 \rightleftarrows Na^+ + AlO_2^-$$
$$AlO_2^- + HOH \rightleftarrows HAlO_2 + OH^-$$
$$K_a = [H^+][AlO_2^-]/[HAlO_2]$$
$$K_w = [H^+][OH^-] = 10^{-14}$$
$$[H^+] = 10^{-10.5}$$
$$c = \text{conc. of } NaAlO_2 = 0.06$$
$$\gamma = \text{ionization of } NaAlO_2 = 0.8 \text{ (assumed)}$$
$$[HAlO_2] = [OH^+] = 10^{-3.5}$$
$$[AlO_2^-] = \gamma c = 0.8 \times 0.06 = 0.05 = 10^{-1.3}$$
$$K_a = 10^{-10.5} \times 10^{-1.3}/10^{-3.5} = 10^{-8.3}$$

nate solutions, especially on long standing, does not necessarily indicate that the aluminic acid is a very weak acid, since progressive hydrolysis may take place owing to the slight solubility of the aluminic acid, which separates first in the colloidal, and later in the crystalloidal form and is thereby removed from the sphere of action. This explanation has been suggested by Dr. J. Johnston[1] to account for the abnormal alkalinity of alkali aluminate and silicate solutions, in view of the recent evidence that the corresponding aluminic and silicic acids are much stronger than has generally been supposed.

On the assumption of a maximum solubility of crystallin aluminium hydroxide in pure water of one milligram per liter, Slade calculated the concentration of the undissociated aluminic acid in neutral or alkalin solutions as approximately 10^{-5}, a value considerably smaller than the value ($[HAlO_2] = 10^{-3.5}$) employed in the above calculations. This discrepancy can also be accounted for by the fact that in the latter case the solid phase was almost entirely colloidal and must, therefore, have had a much greater solubility than the crystalloidal variety.

Consideration of the three methods employed by Mahin, Ingraham and Stewart in the study of this problem leads to the belief that none of them was such as to yield conclusive results. In a single experiment by these authors the heat of solution of aluminium hydroxide in sodium hydroxide was determined by dissolving a small amount of aluminium hydroxide in approximately one thousand times its equivalent of sodium hydroxide (if we assume $Al(OH)_3$ to be a monobasic acid). The entire rise in temperature of only 0.0065° was read on a rapidly rising curve. Dr. C. W. Kanolt,[1] of this Bureau has called attention to the fact that no account was taken of the heat of solution of aluminium hydroxide in water, which is probably negative. The analogous compound boric acid, has a negative molecular heat of solution of 10,790 cal. for $B_2O_3.3H_2O$.[2] It is doubtful, therefore, whether the calculated molecular heat of solution of 864 calories was determined with sufficient accuracy to indicate even the order of magnitude of this constant.

In a study of the action of ammonium nitrate upon sodium aluminate solutions, Mahin, Ingraham and Stewart state that if the formula $NaAlO_2$ represents the composition of sodium aluminate, the ammonium nitrate should precipitate aluminium hydroxide quantitatively in the proportion of one molecule of ammonium nitrate to one of aluminium hydroxide in accordance with the equations:

$$NH_4NO_3 + NaAlO_2 \longrightarrow NH_4AlO_2 + NaNO_3$$
$$NH_4AlO_2 + 2HOH \longrightarrow NH_4OH + Al(OH)_3$$

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[1] Private communication to the author.

[2] J. Thomsen, *Thermochemistry*, p. 47 (1908).

Such a conclusion is based upon the assumption that the ammonium aluminate first formed is entirely hydrolyzed, which could only be possible if the ammonium hydroxide thereby formed were entirely non-ionized, *i. e.*, the solution would no longer be alkalin. The experiments described in the first part of this paper indicate that, owing to the hydrolysis of aluminate solutions, the amount of aluminium hydroxide held in a given alkalin solution is a function of the alkalinity of the solution. Since ammonium hydroxide is much less ionized than sodium or potassium hydroxides, addition of ammonium nitrate to aluminate solutions will, of course, decrease the alkalinity and, therefore, cause partial precipitation of the aluminium hydroxide. The extent of such change in alkalinity, and, therefore, of the precipitation of aluminium hydroxide will depend upon the original alkalinity, and upon the amount of ammonium salt added, and will not bear any simple relation to either, owing to the complex nature of the resultant solutions. A small but appreciable amount of aluminium hydroxide was found to be dissolved in ammonium hydroxide even when the solution was just alkalin to phenolphthalein (when $[H^+] =$ about 10^{-9}). Simple calculation[1] shows that if an exact equivalent of ammonium nitrate were added to the approximately 0.5 N sodium aluminate solution used by these authors, and if as indicated in the above equations all the $Al(OH)_3$ were precipitated, the resultant solution would have a considerable alkalinity ($[H^+] < 10^{-11}$) and would therefore be capable of dissolving considerable aluminium hydroxide.

In the third method employed by Mahin, Ingraham and Stewart, *i. e.*, electrolysis of sodium aluminate solutions, their failure to obtain the calculated ratio of aluminium oxide to oxygen was considered evidence of the absence of definit aluminates in the solution. Their results were rendered uncertain, however, not alone from the re-solution of some of the precipitate in the alkali present in the anode section (which they state could not be entirely avoided) but also by the possible spontaneous decomposition of their aluminate solutions, especially after part of the precipitate had changed to the crystallin modification.

Their statement[2] that "no aluminate can be made to crystallize as such from a solution" fails to take into account the work of Allen and Rogers,[3] crystals of $K_2Al_2O_4.3H_2O$, though not of the corresponding sodium salt.

Though much work remains to be done upon the constitution of aluminates, and especially the factors influencing their decomposition, and upon the relations between the colloidal and so-called crystalloidal modifications

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[1] $[NH_4^+][OH^-]/[NH_4OH] = 1.8 \times 10^{-5}$

$[NH_4OH] = 0.5$

$[NH_4^+][OH^-] = [OH^-]^2 = 0.5 \times 1.8 \times 10^{-5} = 9 \times 10^{-6}$

$[OH^-] = 3 \times 10^{-3}$ and $[H^+] = 0.3 \times 10^{-11}$

[2] THIS JOURNAL, **35**, 31 (1913).

[3] *Am. Chem. J.*, **24**, 304–18 (1900).

of aluminium hydroxide, it is believed that the work described in this paper adds to the evidence in favor of the existence of definit aluminates in the solutions obtained by dissolving aluminium hydroxide in alkalis.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, NO. 217.]

THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE. XII. THE DROP WEIGHTS OF CERTAIN ORGANIC LIQUIDS AND THE SURFACE TENSIONS AND CAPILLARY CONSTANTS CALCULATED FROM THEM.[1]

BY J. LIVINGSTON R. MORGAN AND EDWARD C. STONE.

Received July 24, 1913.

Three tips were used in the course of this investigation, the benzene constants of which are given in the following table:[2]

CALIBRATION OF THE TIPS WITH BENZENE.

Tip.	t.	w = wt. 1 drop (mg.).	$w(M/d)^{2/3}$.	K_B.
1	30	29.307	587.86	2.3282
2	30	28.484	571.35	2.2628
3	30	28.464	570.91	2.2610

The density of benzene at 30° is 0.86824. K_B is calculated from the relationship

$$K_B = w(M/d)^{2/3}/(288.5-30-6),$$

where 288.5 is the critical temperature of benzene, and 6 is a constant.[3]

Since the surface tension is related to the weight of a falling drop according to the equation

$$\gamma = w \times 2.1148/K_B;$$

and the capillary constant (a^2, the height of ascension of a liquid in a tube of 1 mm. radius) is related to the drop volume (*i. e.*, the drop weight w, divided by the density, d) according to the equation

$$a^2 = 0.1837 \times 2.3502/K_B \times w/d;$$

it is now possible for us to calculate the constants by which the drop weight of any liquid must always be multiplied in order to give the surface tension of that liquid in dynes per centimeter at that temperature; and the constants by which drop volumes can be transformed into capillary

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[1] For other papers of this series see THIS JOURNAL, 30, 360–72, 1055–68; **33**, 349–62, 643–57, 657–72, 672–84, 1042–60, 1060–71, 1275–90, 1713–27; **35**, 1249–1262.

[2] In order to save space, only the means of several determinations of the drop weight will be given here, although in the actual work at least three determinations each of the 30 and of the blank of 5, were made, the differences never amounting to more than a few tenths of a milligram on these weights.

[3] For details of the calibration see THIS JOURNAL, **33**, 1714–16.