THE ELECTROMETRIC TITRATION OF SOME ALUMINIUM SOLUTIONS.

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The importance of aluminium hydroxide in soils, in water and sewage purification and in many other industrial operations has resulted in numerous investigations; but the satisfactory quantitative results that have been obtained are rather meager because of the uncertainties characteristic of many colloidal phenomena. One cause of the difficulty in getting satisfactory results may be attributed to the variable condition of the material separating out of molecular dispersion. Since time is a very important factor in determining the nature of the precipitate it must be carefully considered. In this investigation the time between the addition of reagent and the reading was one minute.

The first electrometric titration curve published was that by Hildebrand,(1)[1] who titrated aluminium sulfate with sodium hydroxide. Blum(2) next published curves for the titration of aluminium chloride with sodium and potassium hydroxides. These curves were found to be parallel for most of the way but are separated by about 8 cc. of hydroxide required for the same strength and amount of solution. Hildebrand's curve lies between the two but nearer Blum's sodium hydroxide curve. Greenfield with Buswell(3) published three curves with more dilute sulfate solutions titrated with sodium hydroxide. In all six of these curves an inflection starts at a ranging from 9 to about 10.5. This inflection is used to support the idea of the aluminium hydroxide going into a molecular dispersion in the shape of the alumination, A102, according to the reaction.

$$Al(OH)_3 + OH^- \lesseqgtr AlO_2^- + 2H_2O.$$

This contention has been further supported by evidence presented by Slade and Pollock.(4) Nevertheless the idea suggested by Mahin, Ingraham and Stewart(5) that the aluminium material changes into a colloidal solution through the peptizing action of the OH-ion must not be regarded as being impossible. The tendency of the opalescence to linger, as noted by Blum and observed in this investigation, together with the possibility of the formation of a sol so highly hydrated (like gelatine) that no Tyndall cone would be produced, is significant.

Solutions of aluminium chloride, nitrate or sulface of 0.1*N* concentration have been titrated with sodium, potassium and barium hydroxides, followed by back titration with hydrochloric, nitric or sulfuric acid, all 0.1*N* in concentration. Phosphoric acid (0.01*N*) were also used. The course of the reaction was followed with a hydrogen electrode, readings being taken with a Leeds and Northrup type K potentiometer. The electrodes were of fine platinum wire 0.5 mm. in

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[1] Numerals in parenthesis refer to the bibliography.

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diameter and 4 or 5 mm. in length covered with a thin coating of platinum black. They were tested by placing in 0.05*M* potassium acid phthalate solutions after the method of Clark.(6)

The aluminium solutions had been freed from all but a trace of iron by extracting a "C.P." concentrated chloride solution with a hydrogen chloride solution in ether or by recrystalizing an ammonium alum. The aluminium was precipitated by distilling ammonia into this solution followed by washing till free from chloride or sulfate. The hydroxide was then dissolved in redistilled acid. It happened that the aluminium hydroxide intended for the sulfate was allowed to stand for some length of time allowing crystallization to take place(7) so that excess acid was used. Nevertheless for complete solution several days on the steam bath were required. The pH of this solution was about 1.5 and the excess acid had to be neutralized before the aluminium hydroxide could start to precipitate. The alkali solutions used were free from carbonate. In making a titration 10 cc. 0.1*M* aluminium salt solution was used. It was stirred both by the hydrogen gas and by hand with the hydrogen electrode and suitable increments of base were added followed by active stirring and reading of the e. m. f. within one minute. Some pains was taken to make this time as uniform as possible. The temperature was that of the room, 22 2°. Occasionally an electrode became poisoned, probably by the faint trace of iron remaining. When this happened the points on the curve immediately preceding the poisoning were discarded. The course of the reaction was followed by means of a Tyndall cone secured by focusing a beam of light from an arc lamp in the solution. In this way the first appearance of an opalescence was observed as well as the point of final dissappearance of the cone. Similar points where visible turbidity appeared or disappeared were also noted.

The results obtained for all the titrations, except in the presence of the phosphate and sulfate ions, are given in the first figure, which includes observations made with the following combinations:

Titrations included in figure 1.

10cc.$A1C1_3$, (0.1*N*)	40cc.NaOH (0.1*N*)	50cc.HC1 (0.1*N*) 4 times
10cc.$A1C1_3$, (0.1*N*)	40cc.NaOH (0.1*N*)	50cc.H_2SO_4 (0.1*N*) once
10cc.$A1C1_3$, (0.1*N*)	40cc.KOH (0.1*N*)	50cc.H_2SO_4 (0.1*N*) twice
10cc.$A1(NO_3)_3$, (0.1*N*)	40cc.$Ba(OH)_2$ (0.1*N*)	50cc.HNO_3 (0.1*N*) twice
10cc.$A1(NO_3)_3$, (0.1*N*)	40cc.NaOH (0.1*N*)	50cc.HC1 (0.1N) once
10cc.$A1(NO_3)_3$, (0.1*N*)	40cc.NaOH (0.1*N*)	50cc.HNO_3 (0.1*N*) twice
10cc.$A1(NO_3)_3$, (0.1*N*)	40cc.KOH (0.1*N*)	50cc.HNO_3 (0.1*N*) twice
10cc.$NaA1O_2$, (0.033*N*)	50cc.HC1 (0.1*N*)	50cc.NaOH (0.1*N*) twice
10cc.$A1C1_3$, (0.01*N*)	40cc.$Ca(OH)_2$ (0.01*N*)	50cc.HC1 (0.01*N*) twice

On titrating the aluminate solution the curve was concave upwards instead of concave downward. When it was cut in two, however, the transposed parts coincided with the other curves and its data, transposed in this manner, are included in the figure.

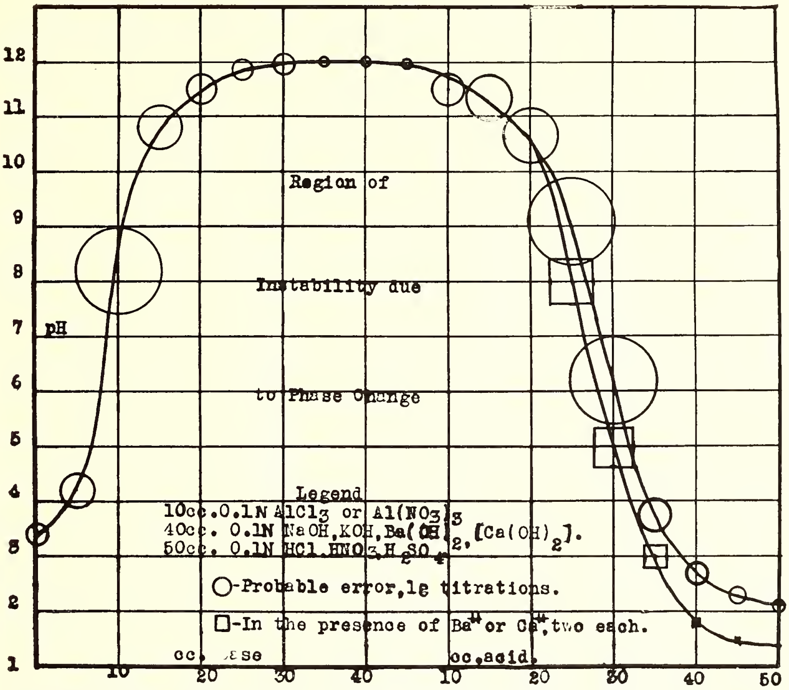

Fig. 1—The electrometric titration of aluminium chloride or nitrate with bases and the back titration with acids.

Titrations included in figure 2.

10cc.$Al_2(SO^4)_3$(0.1*N*)	40cc.NaOH (0.1*N*)	50ccHCl (0.1*N*) once
10cc.$Al_2(SO^4)_3$ (0.1*N*)	40cc.NaOH (0.1*N*)	50ccH_2SO^4 (0.1*N*) twice
10cc.$Al_2(SO^4)_3$ (0.1*N*)	50cc.KOH (0.1*N*)	50ccH_2SO^4 (0.1*N*) once

With the appearance and disappearance of opalescence and turbidity, especially in the steep part of the curve, we find a large probable error (shown in the figures by the radius of the circles.) P. P. Von Weimarn has studied the precipitation of colloids, corresponding in this investigation to turbidity formation, drawing the conclusion that, (8) "the duration of life of dispersoidal systems is determined by a large number of variables among which the electrical conditions are by no means always predominant. In fact, the influence of the electrolytes themselves is the resultant of quite a number of processes and consequently is far from being always so simple as sometimes represented." Apparently this conclusion can be extended with equal truth to the formation of colloidal aluminium hydroxide dispersion from the molecular condition as well as to the disappearance of both the turbidity and opalescence characteristic of mechanical and colloidal dispersions. The coincidence of the curves in the presence of several different combinations of ions tends to show that any specific effect of any of these univalent ions (or sulfate-ion during back titration) as carried out in this investigation, is apparently masked by some of the large number of variables referred to by Von Weimarn.

On the ascending curves summarized in figure 1 sufficient opalescence to form a Tyndall cone was observed at a pH ranging from 3.5 to 4.0. Turbidity was noted at 3.7 to 4.6. Its disappearance occurred at 7.4 to 10.5, while the opalescent material redissolved between 9.5 and 11.8. On the descending curve for the back titration the corresponding observations gave points in the ranges, 9.2 to 11.4, 6.8 to 9.8, 2.1 to 4.1 and 1.3 to 2.4, respectively. Obviously in a system with similar phase changes one can hardly say that aluminium hydroxide will precipitate at some definite pH. Even for a "precipitation range" the possibility of rather wide limits in the pH is to be anticipated.

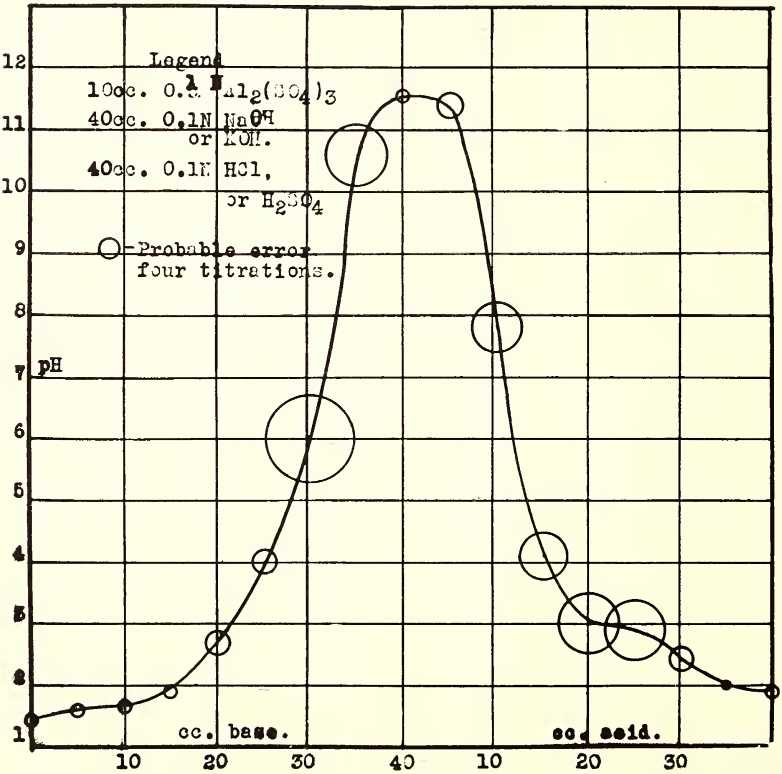

Fig. 2—The electrometric titration of aluminium sulfate with bases and back titration with acids.

The fact noted by Britton (9) that the aluminium is completely precipitated before adding the equivalent amount of base is confirmed in most of these titrations.

Divalent ions exert, apparently, effects differing slightly from those of univalent ions. During the titration of aluminium nitrate with barium hydroxide a turbidity was formed which persisted to the highest pH 12.0, and at the lowest, 1.4, on the back titration. At the end of the back titration in the presence of calcium ions, also, a turbidity persisted as low as 1.4. The results for the back titrations in the presence of these two divalents ions are indicated in figure 1 by squares, the side of the square giving the probable error. The coagulating effect of the two bivalent ions has slowed up the resolution of the precipitate very appreciably. The first ten cc. of acid should just combine with the aluminate to form the hydroxide. Further acid should cause re-solution with the production of aluminium ions and it is here that the pH is being lowered excessively because the hydroxide precipitated in the presence of these divalentions is probably too compact to redissolve very much during the time allowed for our titrations.

On titrating four sulfate solutions (fig. 2), the first opalescence appeared at pH 2.0, 2.2, 2.5, and 3.5 respectively. The first three values are unusually low. The average point of turbidity formation was 4.05 in the presence of sulfate as compared with 4.25 for the chlorides and 4.37 for the nitrates. The final disappearance of both turbidity and opalescence was nearly at the same point in all solutions except those containing barium and calcium ions.

A break similar to that noted by previous workers at a pH of 9 to 10.5 was observed in about one third of these experiments, for both parts of the curve. The method utilized here, of taking the reading just one minute after addition of the reagent, tended to obscure this inflection by allowing insufficient time for the reaction with its change in phase. Hence the failure to observe inflections cannot always be considered definite evidence against the existence of an action of this kind.(10)

Phosphoric acid is of different character from the other acids used in this investigation. It is quite weak but has three hydrogens which can usually be replaced one by one, although with increasing difficulty. With aluminium it forms three salts, mono-, di-, and tri-aluminium phosphates, (primary, secondary, or tertiary salts.) (11) On titrating phosphoric acid and sodium hydroxide against each other Davis, Oakes and Salisbury(12) obtained two points of inflection for primary and secondary salt formation only. Wendt and Clarke(13) obtained two clear points of inflection on adding saturated calcium hydroxide to phosphoric acid for the primary and the tertiary phosphates. They regarded the secondary phosphate as unstable. Hoffmann and Gortner(14) have titrated phosphoric acid with both sodium and calcium hydroxides. With sodium hydroxide breaks in the curves were obtained for primary and secondary phosphates while with calcium hydroxide only primary and tertiary salts were formed. A careful study of the published curves indicates that, while a valuable advance has been made, experimental work of much higher precision is needed to establish with any satisfactioon at all the second and third ionization constants for phosphoric acid. Thus, the third ionization constant has been given(15) as $3.6 \text{x} 10^{-13}$ or by Prideaux(16) as $3.0 \text{x} 10^{-12}$. Calculating from curves given by Davis, Oakes and Salisbury with conductivity water (their figures 8 and 9), the values 2.8 and $3.4 \text{x} 10^{-15}$ are obtained.

In figure 3 results are given for two titrations of aluminium chloride, to which phosphoric acid has been added, with sodium hydroxide. The points of inflection occur at pH 3.3-3.5, 5.3-5.8 and 8.2-8.7.

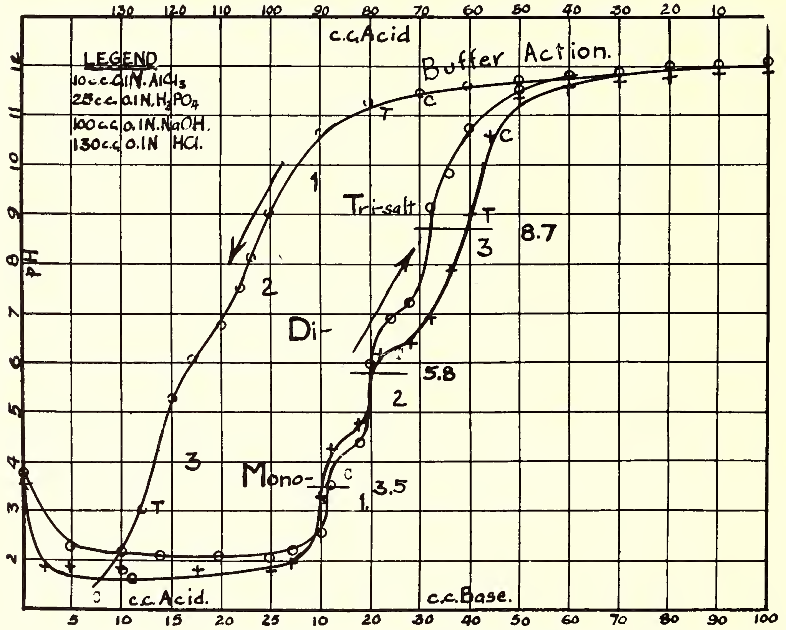

Fig. 3—The effect of the addition on the titration of aluminium chloride with sodium hydroxide and back titration with hydrochloric acid. Three points of inflection are observed, especially on the ascending curves.

On titrating back with hydrochloric acid the marked buffer action of the aluminium keeps the pH high. This curve is in direct contrast to that obtained by Hoffmann and Gortner on back-titrating calcium phosphate with hydrochloric acid. On our curve small deviations from a continuously smooth curve indicate points of inflection, but not decisively. The pH for the formation of the tertiary phosphate agrees with that observed by Wendt and Clarke for tricalcium phosphate and with the secondary sodium phosphate pH determined by Davis, Oakes and Salisbury. The pH of the primary salt is 3.3 or 3.5 for the ascending and about 4.7 for the descending curve. If one might take the mean of these, a value would be obtained similar to that taken from the curves of Wendt and Clarke or Hoffmann and Gortner or recorded by Davis, Oakes and Salisbury for monocalcium and monosodium phosphates. In the work of Wendt and Clarke some indication was obtained of a temporarily existing dicalcium phosphate. Two curves are given by them with points of nearly vertical slope at about pH 5.5 which is similar to the middle inflection point on the ascending curve in figure 3.

A back titration with phosphoric acid is given in figure 4. A curve for hydrochloric acid is given for comparison. The points of formation and dissolution of both opalescence (marked C) and turbidity (marked

T) are about the same as in the absence of phosphate. During the back titration the opalescence became visible on adding 10 cc. of acid insufficient, however, to neutralize the excess base. On adding 10 cc. more of the phosphoric acid a break was obtained in the curve corresponding to tertiary aluminium phosphate at this point with pH of 8.7. Another ten cc. resulted in a second break at 7.0 with the formation of the secondary salt. The next break occurred at pH 4.7 and required 20 cc. more acid. To neutralize the excess base and precipitate the hydroxide should have required 30 cc. This amount of acid brought the solution to the neutral point but the inflection at 8.7 indicates the formation of some tertiary salt while a similar inflection occurred at pH 7. From this point 10 cc. of acid should have been just sufficient to form the monoaluminium phosphate but 20 cc. was required for the next inflection because of the slow solubility of the higher salts.

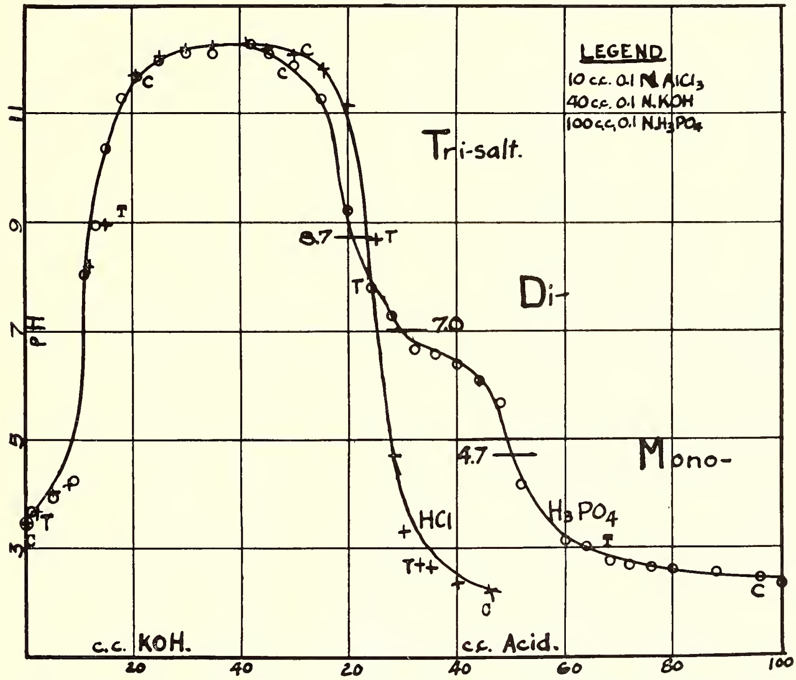

Fig. 4—Aluminium chloride titrated electrometrically with potassium hydroxide and titrated back with hydrochloric and phosphoric acids. The latter give three points of inflection corresponding to three aluminium phosphates.

The conclusion of H. T. S. Britton (17) that, "Hydrogen-ion concentrations, which are peculiar to the various hydroxides, are independent of both the a-ion and the precipitant and which only slightly influenced in dilute solutions by changes in concentrations of the metallic salts, have to be attained before any hydroxide can be precipitated," is not confirmed for aluminium hydroxides under the conditions used in these experiments.

Summary. Aluminium salts have been electrometrically titrated with sodium, potassium, barium or calcium hydroxides and back titrated with hydrochloric, nitric, sulfuric or phosphoric acid waiting just one minute after addition of the reagent before reading the e. m. f. In the presence of univalent ions similar curves are obtained but they show the minor variations characteristic of phase changes in systems where colloids are formed, precipitated or dissolved. It is, therefore, necessary to think in terms, not of points, but of ranges of precipitation and dissolution.

Calcium and barium ions slow up the rate of resolution of aluminium hydroxide formed from aluminate solutions by acid. In the presence of sulfate ion, the opalescence due to colloidal aluminium hydroxide may appear at a pH as low as 2.0. Turbidity, also, tends to be produced at low pH's. The sulfate ion has comparatively little effect on the back titration curve. Inflections have been obtained for three phosphates of aluminium at pH's about 4, 7 and 8.5 and the results have been compared with similar points for calcium and sodium phosphates.

On back titration of an alkaline aluminium phosphate solution with hydrochloric acid the buffer action maintains a high pH at first and only minor inflections for the three salts were observed.

BIBLIOGRAPHY.

1. Hildebrand. *J. Am. Chem. Soc.* **35**. 863 (1913)
2. Blum. *Ibid* 35. 1499 (1913)
3. Greenfield with Boswell, *Ibid* 44. 1435 (1922)
4. Slade and Pollock. *Trans. Faraday Soc.* **10**, 150 (1914)
5. Mahin, Ingraham and Stewart. *J. Am. Chem. Soc.* **35**, 1500 (1913)
6. Clark. "The Determination of Hydrogen Ions." Wilkens and Wilkens Co. 1923.
7. F. Haber. *Ber.* **55 B.** 1717 (1922)
8. *Chem. Reviews.* **2**, 231 (1925)
9. H. T. S. Britton. *J. Chem. Soc.* **127**, 2121 (1925) cf. also Williamson *J. Phys. Chem.* **27**, 284 (1923) and Miller. *U. S. Public Health Reports.* **38**, 1995 (1923) who had similar experiences.
10. Cit. 9 p. 2126. re. Na2 ZnO2
11. Mellor, "A Comprehensive Treatise of Inorganic Chemistry." V, 363. Longmans, Green & Co. (1922)
12. Davis, Oakes and Salisbury. *Ind. Eng. Chem.* 15, 184 (1923)
13. Wendt and Clarke. *J. Am. Chem. Soc.* **45**, 881 (1923)
14. Hoffmann and Gortner. *J. Phys. Chem.* **29**, 769-81 (1925)
15. Abbott and Bray. *J. Am. Chem.* **31**, 729-63 (1909)
16. Prideaux. "The Theory and Use of Indicators." Constable p. 287. (1917)
17. Cit. 9. p. 2120.