Oxygen was removed by a current of nitrogen, and a known weight of potassium iodide was added. The data for the cells made with these solutions are given in Table II. The reproducibility was better than for the first series; differences between duplicates were not larger than 0.09 mv., and the average was 0.03 mv.

The quantity ρ in Table II is the ratio of the molality of un-ionized acetic acid to the molality of acetate ion. The values for $E^{0'}_{25}$ were calculated by the equation[4d]

$$E^{0'}_{25} = E^0_{25} - \mathrm{f}(\gamma) = E_{25} + k \log\,[\mathrm{KI}] + k \log \rho + k \log K_{\mathrm{HOAc}}$$

in which K_{HOAc} is the ionization constant of acetic acid for which the value 1.754×10^{-5} was used.[6] The value of $\mathrm{f}(\gamma)$ is small and should become zero when $\mu = 0$. The relation of $E^{0'}_{25}$ to ionic strength is shown by Curve II of Fig. 2. Extrapolation to infinite dilution gives a value for E^0_{25} in good agreement with the value from the first series of cells, and $E^0_{25} = -0.0405$ v. can be taken as the best value.

Discussion. Combining $E^0_{25} = -0.0405$ v. with the electromotive force of the cell[3]

$$\mathrm{Pb(Hg)/PbI_2(sat.)/PbI_2\,(sat.),\ Hg_2I_2/Hg};\ E_{25} = 0.3175\ \mathrm{v.}$$

gives for the lead amalgam–lead iodide electrode the normal potential $E^0_{25} = 0.3580$. For this electrode Gerke[7] calculated 0.3579 v. while "International Critical Tables"[2] gives 0.3591 v.

Combination of the value $E^0_{25} = 0.3580$ v. with the electromotive force of the cell[4a]

$$\mathrm{Pb(Hg)/PbI_2\,(sat.),\ Pb(ClO_4)_2/Pb(ClO_4)_2,\ PbI_2(sat.),\ I_2/(Pt)};\ E_{25} = 0.8936\ \mathrm{v.}$$

gives $E^0_{25} = -0.5356$ v. for the normal potential of the iodine electrode. Jones and Kaplan[4c] found -0.5362 v., "International Critical Tables"[2] gives -0.5345 v. and Lewis and Randall[8] give -0.5357 v.

Summary

Measurements were made at 25° of the electromotive force of the cell $\mathrm{Hg/Hg_2I_2,\ HI/HI/H_2\,(Pt)}$, in which the hydriodic acid was furnished either by a solution of potassium iodide and hydrochloric acid or by a solution of potassium iodide, acetic acid and sodium acetate. The value of E^0_{25} was found to be 0.0405 v. From this value and data from the literature, normal potentials for the lead amalgam–lead iodide and iodine electrodes were calculated.

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(6) (a) Harned and Ehlers, THIS JOURNAL, **54**, 1356 (1932); (b) MacInnes and Shedlovsky, *ibid.*, **54**, 1438 (1932).

(7) Gerke, *Chem. Reviews*, **1**, 377 (1925).

(8) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Company, Inc., New York, 1923, p. 430.

DURHAM, N. C. RECEIVED APRIL 29, 1937

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

A Study of the Precipitation of Aluminum Basic Sulfate by Urea[1]

BY HOBART H. WILLARD AND NING KANG TANG[2]

In the separation of metals by precipitation as hydroxides, hydrous oxides or basic salts, the necessity for a careful control of *p*H is obvious. Sufficient attention has, however, not been given to the advantage of keeping the solution homogeneous with respect to *p*H. If the *p*H becomes too high locally, as, for example, by the addition of a base, even a weak one, the precipitation of some other hydroxide is facilitated, and if this occurs it may not dissolve when the solution is thoroughly mixed. Yet this is the usual method of precipitation. The best method of accomplishing this result is by the use of a substance which, dissolved in the solution, will slowly decompose so as to bring about neutralization of the acid. The following types of reagents have been used in an attempt to maintain the proper *p*H: buffers, such as acetic acid and acetate; insoluble oxides and carbonates, such as zinc oxide; weak bases, mostly organic, such as phenylhydrazine and pyridine; compounds which decompose with liberation of ammonia, such as hexamethylenetetramine and potassium cyanate; substances which decompose in hot solution with the formation of a volatile acidic constituent, such as sodium thiosulfate and ammonium nitrite; mixtures of halides, halates and halogen acids, such as iodate and iodide, bromate and bromide, bromate and chloride.[3]

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(1) Original manuscript received January 30, 1934.

(2) Rockefeller Foundation Fellow. From a dissertation presented by N. K. Tang in 1930 to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(3) For the sake of brevity a review of the literature has been omitted, but is given in the dissertation.

Although compounds and mixtures like those above possess certain advantages, none of them fulfils simultaneously the requirements of homogeneity of solution, slow precipitation and easy control of the final *p*H in an entirely satisfactory manner.

Precipitation by Means of Urea. Advantages.—The fact that urea decomposes into carbon dioxide and ammonia, when its solution is heated, has long been known. Since it is very soluble in water, and its rate of decomposition into ammonia and carbon dioxide, which is relatively slow, is dependent upon the temperature and duration of heating, a good control of the *p*H of the solution is possible, especially if it is buffered. The increase in *p*H can be stopped at any time by simply cooling, since no decomposition of urea takes place in the cold. The *p*H of the solution cannot rise very high and the more basic elements will not be precipitated, since the ammonia produced is driven from the hot solution if the *p*H is much above 7. The slow evolution of carbon dioxide, produced by the decomposition of the urea, effectively prevents bumping. In such a solution the change in *p*H will be uniform throughout, insofar as the temperature is the same, and no local excess of the reagent will be present at any point. No undesirable foreign ion will be introduced, except in some cases that of the buffer, and the excess of the precipitant can be decomposed easily. This greatly facilitates the use of the filtrate for further determinations if desired.

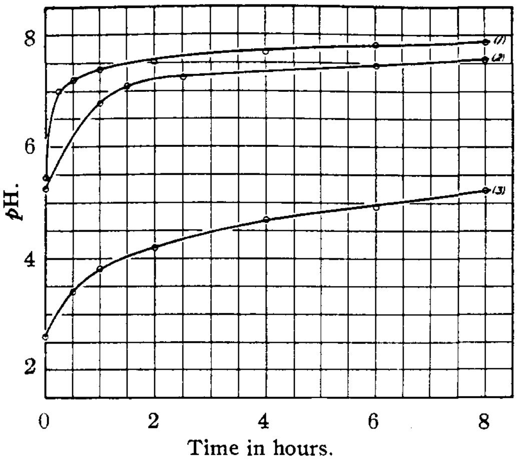

Fig. 1.—The effect of duration of heating on the *p*H of the solution: curve 1, solutions contained 4 g. of urea and 10 g. of ammonium chloride in 500 ml.; curve 2, solutions contained 4 g. of urea, 20 g. of ammonium chloride and 1 g. of ammonium sulfate in 500 ml.; curve 3, solutions contained 4 g. of urea, and 10 g. of ammonium chloride and 5 g. of succinic acid in 500 ml.

Consequently, if to an acid solution of an element, the hydroxide or basic salt of which is insoluble, urea is added and the mixture is heated, the hydroxide or basic salt should be precipitated slowly and uniformly throughout the solution. Precipitates formed in this manner should, in general, be more granular and less prone to show co-precipitation phenomena, thus giving better separations, a fact not previously emphasized.

The Effect of Duration of Heating on the *p*H of a Solution of Urea Containing Ammonium Salts and Succinic Acid.—The materials indicated were dissolved in 500 ml. of water and heated in an Erlenmeyer flask, covered with a watch glass, by immersion in boiling water. At intervals, samples were withdrawn, cooled in running water, and the *p*H in these and subsequent experiments determined by using a quinhydrone electrode for values below 8, and a hydrogen electrode for those above. The curves in Fig. 1 show the relationships obtained.

The Effect of the Concentration of Ammonium Ion on the Final *p*H Attained by Heating Solutions of Urea.—Two series of solutions were prepared, each containing 4 g. of urea, together with varying amounts of ammonium chloride in 500 ml. Series 1 also contained 1 g. of ammonium sulfate while series 2 contained 5 g. of succinic acid in addition to the ammonium chloride. These were heated for ten hours in the manner given above. They were then cooled and the *p*H determined. Curves 1 and 2, respectively, in Fig. 2 show the results obtained.

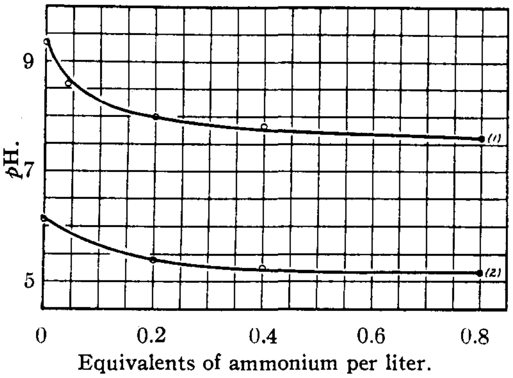

Fig. 2.—Effect of ammonium ion concentration on the *p*H of the solution: curve 1, solutions contained 4 g. of urea in 500 ml.; curve 2, solutions contained 4 g. of urea and 5 g. of succinic acid in 500 ml.

The Influence of Various Anions on the Character of the Precipitate Obtained with Aluminum Salts.—In previous work on the precipitation of basic salts and hydroxides, no attention has been paid to the importance of the anion present in affecting the physical character of the precipitate. In some cases attention has been called to the fact that solutions of different salts of a metal gave different results, but no systematic investigation of this subject has been made. In preliminary work it was noticed that when a solution containing alum was heated with urea, a dense precipitate was obtained. However, when the solution contained aluminum chloride instead of the alum, the precipitate was of the same gelatinous nature as that obtained by an ammonium hydroxide precipitation. A series of experiments was therefore made to determine the influence of various anions. Solutions containing aluminum chloride equivalent to 0.1 g. of aluminum, and 4 g. of urea in 500 ml. were prepared. Fifteen milli-equivalents of the anion, either as the alkali salt or the free acid, was added and the solution boiled gently over a free flame. Table I gives the results of the observations.

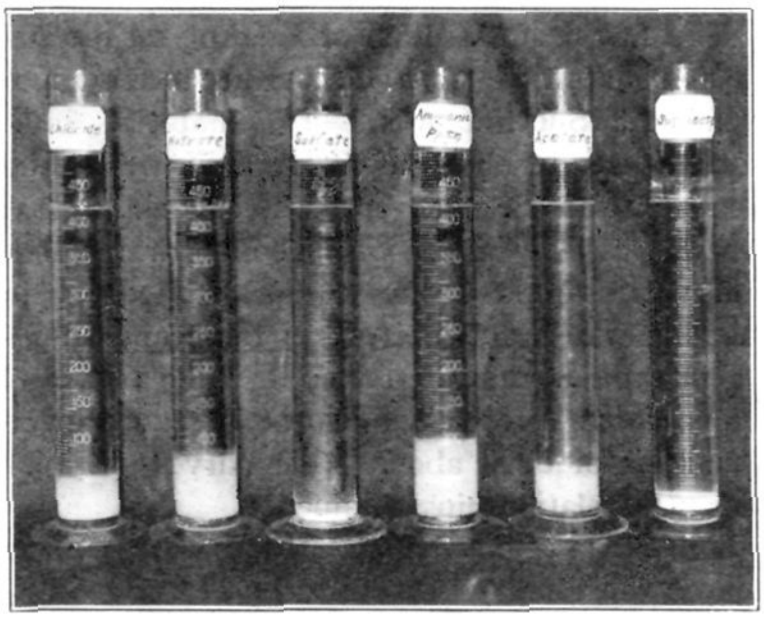

Fig. 3.—Effect of chloride, nitrate, sulfate, acetate and succinate on the precipitate obtained by urea, and of sulfate on precipitation by ammonia.

A similar series using 10 g. of ammonium chloride in addition to the above, to cause slower precipitation, gave precipitates which were slightly less voluminous but by no means dense, except as noted above. When the precipitation was carried out in the presence of organic anions, it was found necessary to use ammonium chloride and a larger concentration of the anion. Precipitates resulting in the presence of formate, oxalate, succinate, benzoate, and phthalate were dense, while that formed in the presence of acetate was flocculent. Figure 3 shows the effect of several of the above anions on the character of the precipitate.

TABLE I

EFFECT OF INORGANIC ANIONS ON THE CHARACTER OF THE PRECIPITATE

Anion	Character of prcippitate	Anion	Character of precipitate
Nitrate	Flocculent	Sulfate	Dense
Chloride	Flocculent	Selenite	Fairly dense
Chlorate	Flocculent	Selenate	Dense
Iodate	Flocculent	Tellurate	Flocculent
Perchlorate	Flocculent	Dithionate	Flocculent
Sulfite	Flocculent	Chromate	Flocculent

In the precipitation of aluminum it is evident that a slow diminution of the hydrogen ion concentration by the decomposition of urea does not necessarily produce a dense precipitate. The proper anion must be present and sulfate is particularly effective. But even this will not cause a dense precipitate unless the latter is formed by slow precipitation from a homogeneous solution. This is shown by the fourth cylinder in Fig. 3, in which sulfate was present. It seems therefore that the formation of a dense precipitate depends upon at least two factors.

A Study of the Dense Basic Sulfate Precipitate

Since the dense precipitate obtained by precipitation in the presence of certain anions is very different from the ordinary gelatinous one, a study of its physical properties and composition was made. The one formed in the presence of sulfate ion was selected for two reasons. (1) The precipitate could be obtained from solutions of widely different *p*H values. (2) The determination of the sulfate content of the precipitate could be made easily.

Effect of the Concentration of Sulfate Ion on the Quality of the Precipitate.—Solutions of 500-ml. volume, containing 0.1 g. (about 7 millimoles per liter) of aluminum, as chloride, 4 g. of urea and varying amounts of ammonium sulfate, were heated to about 90° on an electric hot-plate. The results of the observations are given in Table II.

An entirely satisfactory precipitate was not obtained until the solution contained 10 millimoles of sulfate ion per liter. This was an amount of sulfate which was practically equivalent to the quantity of aluminum present.

TABLE II

THE EFFECT OF THE CONCENTRATION OF SULFATE ION ON THE CHARACTER OF THE PRECIPITATE

Sulfate ion, mm. per liter	Quality of precipitate	Sulfate ion, mm. per liter	Quality of precipitate
0	Flocculent	1.5	Less flocculent
.02	Flocculent	2	Rather dense
.2	Less flocculent	10	Dense
1	Less flocculent	20	Dense

Microscopic and X-ray Examination.—A microscopic examination of the dense precipitate obtained in the presence of sulfate ion showed that it consisted of independent spherical granules of almost uniform size, with no sharp edges or angles characteristic of crystals. It was entirely different from the gelatinous precipitate obtained with ammonia, which consisted of large granules of no uniformity in size or shape.

An X-ray diffraction pattern obtained from a sample of a dense precipitate containing 59.73% Al_2O_3, 7.16% SO_3 and 33.11% H_2O showed only a few faint reflections corresponding to the monohydrate, $Al_2O_3 \cdot H_2O$. From a comparison of this pattern with similar ones obtained from precipitates produced by evaporation of a diethylamine aluminate solution and by an ordinary ammonia precipitation, it was concluded that the dense precipitate either contained very little crystalline material or consisted of a crystalline mixture of such complexity that the net result was similar to that which would be obtained from amorphous material.

The Determination of the Molar Ratio Aluminum to Sulfate.—Analyses of several precipitates showed that the sulfate content varied according to the conditions of precipitation, and there was not present a definite compound. Consequently the molar ratio, Al/SO_4, was determined in precipitates obtained under varying conditions, in order to ascertain the effect of *p*H and the concentration of sulfate ion on that ratio and also on the physical characteristics of the precipitate. Miller[4] studied in detail the composition of precipitates formed at different *p*H values. He added varying volumes of standard sodium hydroxide solution to known volumes of potassium alum solution, then determined the *p*H of the filtrates and the amounts of aluminum and sulfate in the precipitates. The results show that between *p*H 4.0 and 5.5, the molar ratio Al/SO_4 is practically constant. At higher *p*H values the sulfate content rapidly becomes smaller, and finally disappears completely. In the present work the Al/SO_4 ratio in the precipitates was studied over the *p*H range 6.5 to 9.4. The procedure was somewhat simpler than that of Miller,[4] since (1) a standard aluminum solution was used; (2) the precipitation was complete over the above range, neglecting the small solubility at the higher *p*H values; and (3) the precipitate, being dense, was easily filtered and washed.

A solution of aluminum chloride, equivalent to 2.0 g. of the metal per liter, was prepared by dissolving the metal (99.94%) in hydrochloric acid, evaporating off the excess acid and diluting to the required volume. Fifty milliliters of this solution was transferred to an Erlenmeyer flask, 4 g. of urea and 1 g. of ammonium sulfate (or an equivalent weight of potassium sulfate for *p*H values above 8.4) added. After diluting to 500 ml. the flask was covered and heated in a water-bath at the temperature of boiling water until the desired *p*H had been reached as estimated by the duration of heating. In order to obtain a *p*H higher than 9, the ammonium salt, formed during the precipitation of the aluminum hydroxide, had to be removed. This was accomplished by decanting the supernatant liquid, adding a fresh solution of urea and potassium sulfate, and heating for ten hours. Table III shows the correlation between the time of heating such a mixture and the *p*H attained.

TABLE III

INFLUENCE OF TIME OF HEATING ON THE *p*H

Duration of heating, hrs.	*p*H	Duration of heating, hrs.	*p*H
0.66	6.5	4	8.2
1.5	7.1	6	8.4
2	7.5	4–6[a]	8.6
2.5	7.8	10[a]	8.8–9.0
3	8.0		

[a] Potassium sulfate used instead of ammonium sulfate.

After heating, the flask was cooled in running water, the precipitate filtered off and washed fifteen times with hot, 1% ammonium chloride solution containing a trace of ammonium hydroxide. The *p*H of the filtrate was determined. The precipitate was dissolved in hydrochloric acid, the excess acid evaporated off and the solution diluted. It was neutralized to turbidity with sodium carbonate solution and cleared by the addition of a drop or two of hydrochloric acid. The sulfate was then determined gravimetrically by precipitation with barium chloride. The relationship between the *p*H and molar ratio Al/SO_4 is shown in Table IV and Fig. 4.

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(4) Miller, *U. S. Pub. Health Rep.*, **38**, 1995 (1923).

TABLE IV

MOLAR RATIO Al/SO$_4$ AT VARYING *p*H

Concentration of SO$_4$ 0.015 *M*

*p*H	Al/SO$_4$ ratio	*p*H	Al/SO$_4$ ratio	*p*H	Al/SO$_4$ ratio
6.53	5.40	7.77	12.3	8.60	33.9
7.03	8.11	7.95	14.5	8.64	32.5
7.07	8.18	7.97	14.8	8.69	36.7
7.19	8.47	8.02	15.3	8.71	46.5
7.38	9.84	8.05	15.4	8.88	69.8
7.48	9.95	8.05	14.9	8.93	70.9
7.50	10.2	8.17	18.0	9.00	82.4
7.71	10.7	8.22	16.2	9.36	190
7.77	12.2	8.28	19.2	9.43	210

From the results obtained it can be concluded that: (1) precipitates obtained at the same *p*H have a fairly constant composition; (2) with an increase in *p*H, the sulfate content of the precipitate decreases but does not disappear completely even at a *p*H of 9.4.

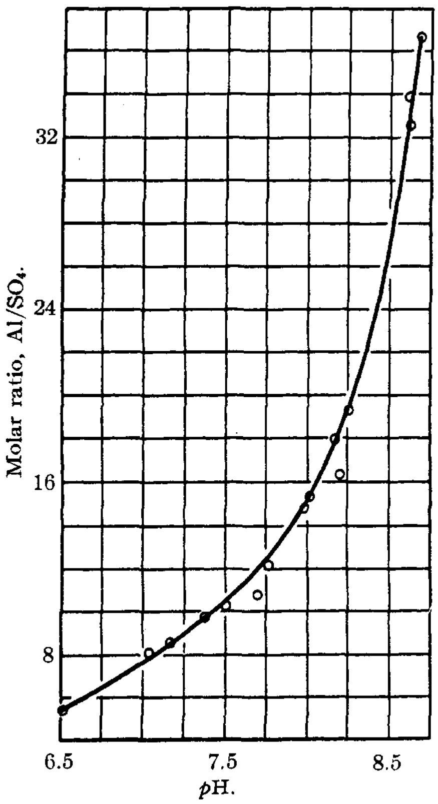

Fig. 4.—*Effect of pH on molar ratio Al/SO$_4$.*

The change in the Al/SO$_4$ ratio is accompanied by a change in the physical properties of the precipitates. Those which contain a larger proportion of sulfate, *i. e.*, obtained at a lower *p*H, are fine grained and more readily soluble in cold, dilute hydrochloric acid. Those which contain a smaller proportion of sulfate, *i. e.*, obtained at a higher *p*H, are coarser grained, less dense, and dissolve only upon prolonged digestion with fairly concentrated hydrochloric acid.

The Effect of Continuous Washing on the Composition of the Precipitate.—In order to ascertain what effect continuous washing with water would have on the dense precipitate obtained by heating with urea, a sample was prepared and washed with hot 1% ammonium chloride and air-dried. One portion of this was used to determine the Al/SO$_4$ ratio, and another extracted with cold water for several days in a Soxhlet extractor. This latter was again air-dried and the Al/SO$_4$ ratio determined. It was found that very little change had occurred during the extraction, either in the proportion of sulfate present, or in the physical character of the precipitate. It still retained its dense granular nature and showed absolutely no tendency to become colloidal and run through the extraction thimble.

The Influence of Sulfate Ion Concentration on the Al/SO$_4$ Ratio in the Precipitate.—The procedure was the same as before except that the concentration of sulfate ion was 0.15 *M* instead of 0.015 *M*. Table V shows the results, together with ratios obtained at the same *p*H with a sulfate ion concentration of 0.015 *M*.

TABLE V

THE EFFECT OF SULFATE ION CONCENTRATION ON THE COMPOSITION OF THE PRECIPITATE

SO$_4$ concn., moles/l.	*p*H	Al/SO$_4$ ratio
0.015	7.38	9.84[a]
.15	7.38	7.35
.15	7.38	7.28
.015	7.77	12.25[a]
.15	7.78	9.75
.15	7.79	9.77

[a] From data in Table IV.

From this it is seen that the proportion of sulfate present in the precipitate is a function of the sulfate ion concentration of the solution from which the precipitation is made. At a given *p*H, the higher the sulfate ion concentration, the smaller the Al/SO$_4$ ratio, or the greater the proportion of sulfate. This would be expected either on the basis of compound formation or of adsorption. Charriou[5] showed that when aluminum hydroxide was precipitated with ammonium hydroxide in the presence of varying amounts of ammonium sulfate, the absorption of sulfate by the precipitate followed Freundlich's law. The

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(5) Charriou, *J. chim. phys.*, **23**, 621 (1926).

phenomenon of adsorption of sulfate by hydrous oxides has also been investigated by Weiser and Porter.[6]

Approaching the Equilibrium from Both Sides.—Since the sulfate content of the precipitate varies with the *p*H of the solution, it seemed well to determine whether the sulfate present in a precipitate formed at low *p*H would be removed by digesting in a solution of higher *p*H and *vice versa.* A precipitate was prepared in a solution having a *p*H of approximately 7, in the manner already described. The supernatant liquid was decanted and the *p*H determined. To the precipitate in the flask, 4 g. of urea and 1.32 g. of potassium sulfate were added and the mixture diluted to 500 ml. After heating in a water-bath for about ten hours with occasional shaking, the precipitate was filtered off. The Al/SO_4 ratio in the precipitate and the *p*H of the filtrate were determined. The results obtained are given in Table VI.

TABLE VI

DECREASING THE PROPORTION OF SULFATE BY INCREASE IN *p*H

*p*H at which ppt. was prepd.	7.08	7.13
Ratio Al/SO_4 at original *p*H[a]	8.18	8.30
*p*H at which ppt. was digested	9.36	9.43
Ratio Al/SO_4 at final *p*H	190	210

[a] From curve in Fig. 4.

It is probable that this decrease in the proportion of sulfate occurs during all precipitations of aluminum by urea in the presence of sulfate. The precipitate is formed slowly at a relatively low *p*H and so contains a correspondingly large proportion of sulfate, or low Al/SO_4 ratio. As the digestion is continued and the *p*H increases, this sulfate is lost.

To investigate the reverse process, a precipitate prepared at a high *p*H as described above, was filtered off and the *p*H of the filtrate determined. The precipitate was returned to the flask, 4 g. of urea, 1 g. of ammonium sulfate and 20 g. of ammonium chloride (to maintain a low *p*H) were added. The mixture was diluted to 500 ml. and heated on a hot-plate for several days, while mechanically stirred. The solution was kept at a constant volume by the occasional addition of water. The precipitate was filtered off, the ratio Al/SO_4 in the precipitate, and the *p*H of the filtrate determined. The results are shown in Table VII.

TABLE VII

INCREASING THE PROPORTION OF SULFATE BY DECREASE IN *p*H

*p*H at which precipitate was prepared	9.14
Ratio Al/SO_4 at original *p*H[a]	123
*p*H at which precipitate was digested	6.50
Ratio Al/SO_4 at final *p*H found	34.2
Ratio Al/SO_4 at final *p*H[a] calcd.	5.40

[a] From curve in Fig. 4.

The reaction involving an increase in the proportion of sulfate at lower *p*H evidently proceeds much more slowly than the reverse reaction, several days being insufficient for equilibrium to be reached.

Slow Precipitation by Extremely Dilute Ammonium Hydroxide.—Since the dense precipitate obtained in the manner described does not contain urea, it should be possible to form a precipitate of the same dense nature by the very slow addition of an extremely dilute ammonium hydroxide solution to one containing aluminum chloride and sulfate ion. Five hundred milliliters of solution containing 0.1 g. of aluminum, as chloride, and 1 g. of ammonium sulfate was heated to about 80° in an Erlenmeyer flask. While this solution was being stirred mechanically, 0.002 *M* ammonium hydroxide was added dropwise from a buret, over a period of several days, until the solution reacted alkaline to methyl red. The precipitate was filtered off, washed with hot 1% ammonium chloride solution and the Al/SO_4 ratio determined. The precipitate was very dense and dissolved readily in cold dilute hydrochloric acid. It had an Al/SO_4 ratio of 8.0. This shows that the precipitation by urea is merely a process of slow precipitation, and that a precipitate of similar composition and dense character can be obtained by the very slow addition of extremely dilute ammonium hydroxide. With more concentrated ammonia the results were much less successful. The fact that the time required with ammonia is so enormously greater than that with urea is doubtless due to the homogeneity of the latter solution as already mentioned.

The Solubility of the Dense Precipitate at Various *p*H Values.—The amount of aluminum remaining in solution after an ammonium hydroxide precipitation has been determined by Blum[7] and by Jander and Weber.[8] The former found that as much as 6 mg. of aluminum oxide

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(6) Weiser and Porter, *J. Phys. Chem.*, **31**, 1383 (1927).

(7) W. Blum, THIS JOURNAL, **38**, 1282 (1916).

(8) Jander and Weber, *Z. anorg. allgem. Chem.*, **131**, 266 (1923).

per liter remained unprecipitated when the solution was just alkaline to *p*-nitrophenol (*p*H 6) while 2 mg. was left in solution when it was just alkaline to phenolphthalein (*p*H 9). The precipitation was complete in the presence of considerable ammonium chloride, at a *p*H of 6.5 to 7.5, which is approximately defined by the color change of methyl red. The latter authors reported that from 7.5 to 8.75 mg. of aluminum oxide per liter remained dissolved when ammonium hydroxide was added to a hot solution, containing 16 g. per liter of ammonium chloride, until alkaline to litmus. If the precipitation was made in the cold, only 5 mg. of aluminum oxide failed to precipitate.

In the present determination, for *p*H values between 6.5 and 7.5, 0.1 g. of aluminum as chloride in 500 ml. of solution, containing 4 g. of urea, 1 g. of ammonium sulfate and 20 g. of ammonium chloride was gently boiled until the desired *p*H had been attained. For *p*H values around 8.4, the ammonium salts were omitted and 1.0 g. of potassium sulfate added, while solutions which were taken to about *p*H 9, contained 0.5 g. of potassium sulfate and only 0.01 g. of aluminum. After digestion, the solution was cooled, the precipitate filtered off and the *p*H of the filtrate determined. The aluminum left in solution was determined colorimetrically by the method of Winter, Thrun and Bird[9] if 0.1 mg. or less was present. With larger quantities, the lake was filtered off, washed, ignited and the oxide weighed. The results are given in Table VIII.

TABLE VIII

SOLUBILITY OF THE DENSE BASIC SULFATE PRECIPITATE AT VARIOUS *p*H VALUES

*p*H	Al_2O_3, mg./l.	*p*H	Al_2O_3, mg./l.	*p*H	Al_2O_3, mg./l.
6.58	0.2	7.27	0.2	8.95	2.8
6.77	.2	7.50	.2	9.00	2.2
6.99	.2	8.43	.8	9.02	2.4
7.09	.2	8.85	2.6		

This shows that the solubility of the dense sulfate precipitate is of the same order as that of aluminum hydroxide obtained by Blum's method, and that most complete precipitation occurs at a *p*H of 6.5 to 7.5. This condition can be realized by gently boiling for two hours, the aluminum solution containing 4 g. of urea and 10 to 20 g. of ammonium chloride in 500 ml.

The advantages of urea as a reagent for the precipitation of aluminum may be summarized as follows. (1) It gives a homogeneous solution in which the increase in *p*H comes from within. (2) The final *p*H is attained slowly, without attention, and can be regulated accurately. (3) The slow evolution of carbon dioxide prevents bumping. (4) Urea is relatively inert to most reagents but can be removed easily if necessary. (5) It is cheap, easily obtained and readily soluble. The application of this precipitation process to the separation of aluminum from other metals will be described in a subsequent paper.

Summary

1. The slow decomposition of urea in hot solution into ammonia and carbon dioxide has been applied to the precipitation of aluminum in the presence of various anions and under varying conditions.

2. In the presence of sulfate, selenate and a number of organic anions such as succinate, formate, benzoate and phthalate, the precipitate was dense, in other cases, flocculent. Ammonia gives a flocculent precipitate in all cases unless it is extremely dilute and added over a period of several days.

3. The proportion of sulfate in the precipitate increased with decrease in *p*H and to a much smaller extent, with increase in sulfate concentration. At the same time there was an increase in the apparent density of the precipitate and in its solubility in acids. Washing with water had no effect.

4. Long digestion in a hot solution of different *p*H changed the proportion of sulfate in the direction to be expected.

5. The solubility of the basic sulfate is 0.2 mg. of aluminum oxide per liter at *p*H values between 6.5 and 7.5, but increases beyond those points.

6. The importance of a homogeneous solution is stressed and the advantages of urea are discussed.

ANN ARBOR, MICHIGAN RECEIVED APRIL 12, 1937

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[9] Winter, Thrun and Bird, THIS JOURNAL, **51**, 2730 (1929).