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

The Precipitation of Basic Gallium Sulfate by Means of Urea. I. A Study of the Precipitate Produced

BY HOBART H. WILLARD AND H. C. FOGG[1]

Introduction

The advantages of slow precipitation of basic salts in a homogeneous solution have been discussed by Willard and Tang.[2] They show that the decomposition of urea, by heating its aqueous solution, is exceedingly effective for causing a slow, uniform increase in *p*H and producing a dense precipitate of aluminum basic sulfate or succinate. Since the solution is homogeneous and the *p*H increases slowly, allowing the final value to be controlled by the duration of heating, they find it easy to obtain a much better separation of aluminum from the more basic elements than is possible using ammonium hydroxide as a precipitant.

Gallium, being closely related to aluminum chemically, would be expected to act in a somewhat similar manner when its solutions, containing ammonium chloride together with sulfate or succinate, are heated with urea.

Purification of Gallium Metal.—The metal was dissolved in hydrochloric acid and the 0.3 *N* acid solution saturated with hydrogen sulfide under slight pressure. The small precipitate was filtered off with the aid of paper pulp and the filtrate evaporated to small volume. This was taken up in 6 *N* hydrochloric acid, and extracted with cold ether previously shaken with the acid, in which gallium chloride is soluble.[3] The ether was evaporated off and the remaining solution diluted with water containing a little hydrochloric acid and filtered. This solution was heated and treated with sufficient sodium hydroxide to redissolve the gallium hydroxide. It was then heated practically to boiling, about 1 ml. of a 1% potassium permanganate solution added, and this followed by about the same volume of alcohol.[4] The heating was continued until the green color had disappeared and a brown precipitate of hydrated manganese dioxide had formed. Paper pulp was added and the precipitate filtered off.

The filtrate was acidified with hydrochloric acid, diluted to 1500–1800 ml., 20–25 g. of ammonium sulfate added, and the gallium precipitated by heating with urea until a *p*H of 4 to 5 had been reached. After filtering and washing, the precipitate was dissolved in hydrochloric acid and precipitated twice with ammonium hydroxide. The final precipitate was dissolved in perchloric acid, adding a little hydrochloric acid if the process was too slow, evaporated, and carefully heated on an air-bath to expel the excess of acid. Much care must be exercised to drive off the major part of the free acid and yet not decompose the gallium perchlorate. If the latter happens, incomplete solution will result when the salt is dissolved in water.

The gallium perchlorate was dissolved in water and electrolyzed with a current of about one ampere, using a platinum anode and a tungsten wire as a cathode. The globules of gallium which formed were allowed to fall into a small crucible placed below the electrode. Since the increase in the perchloric acid concentration during the electrolysis caused the deposition to decrease, the process was stopped after twenty-four to forty-eight hours and the liberated acid driven off as before. The gallium metal was washed with water, and the globules coalesced by adding a drop or two of hydrochloric acid. This acid was washed off with water and the latter removed by acetone.

A Study of the Dense Basic Sulfate Precipitate

It was found that when gallium solutions containing ammonium chloride, ammonium sulfate and urea were heated, the precipitate came down in a dense, granular, easily filterable form. A preliminary study of the influence of stirring and the rate of precipitation (rate of heating) on the composition of the precipitate showed that both had an appreciable effect on the ratio of gallium to sulfate. Precipitates obtained when the solutions were heated rapidly over a small flame had nearly one unit higher ratio than those formed when the precipitation was made slowly by heating in a water-bath. A precipitate formed in a solution that was gently stirred mechanically during the heating had a molar ratio of 11.18, while one from a solution which had been shaken only once or twice during the process showed a ratio of 7.43. The former precipitate, upon being rotated in contact with the original solution for twenty-four hours at room temperature, had only a slightly different ratio, *i. e.*, 11.38, while that of the latter had changed to 8.42. Stirring the solutions at greatly different rates, however, during the precipitation did not influence the composition of the precipitate to any appreciable extent. This indicates that the precipitate which settles on the bottom of the vessel does not come to equilibrium with the solution above it, and that equilibrium is reached if it is kept in suspension by even moderate stirring. The conditions, therefore, for obtaining comparable results which would most nearly represent equilibrium would be a uniform rate of heating of the solutions, accompanied by continuous stirring.

The Effect of *p*H on the Molar Ratio of Gallium to Sulfate.—Approximately 500 ml. of solution, 0.003 *M* with respect to gallium chloride, 0.02 *M* in ammonium

---

[1] Holder of the J. T. Baker Fellowship in Analytical Chemistry for the Midwestern Division during the academic year 1931–32. Present address, University of New Hampshire, Durham, N. H.

[2] H. H. Willard and N. K. Tang, THIS JOURNAL, **59**, 1190 (1937).

[3] E. H. Swift, *ibid.*, **46**, 2378 (1924).

[4] H. N. Stokes and J. R. Cain, *ibid.*, **29**, 409 (1907).

sulfate and containing 4 g. of urea was placed in a wide-mouthed Erlenmeyer flask. This was heated in a boiling water-bath with constant, mechanical stirring until the desired *p*H had been reached, as ascertained colorimetrically with indicators on test samples withdrawn at intervals. Much attention had to be exercised in obtaining the desired *p*H since it might change from less than 3 to around 7 in from ten to fifteen minutes. Nor could a definite time of heating be depended upon to bring the solution to a given *p*H, since some solutions required fifteen to twenty minutes longer than others to reach a given value. For *p*H values above 7.5, the flask was closed partially by a short-stemmed funnel through which the stirrer passed to prevent the escape of too much ammonia.

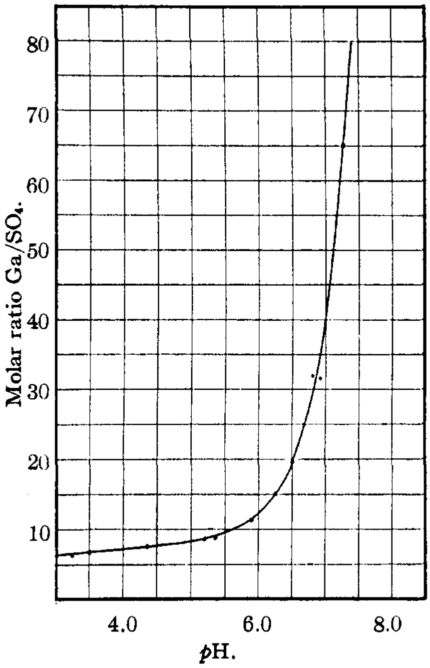

Fig. 1.—Relation between *p*H and ratio Ga/SO$_4$.

When the solution had attained the desired *p*H, it was cooled in running water, a sample removed and the *p*H determined, using a glass electrode[5] and vacuum tube potentiometer.[6] The precipitate was filtered off, using a porcelain filtering crucible, and washed 15 times with a 1% ammonium nitrate solution, the *p*H of which had been adjusted to approximately that of the filtrate. It was then dried at 110 to 120°. One portion of this precipitate was ignited directly to the oxide, while another was dissolved in hydrochloric acid and the sulfate determined gravimetrically as barium sulfate. It was found that precipitation of the sulfate directly, without prior removal of the major portion of the gallium, did not introduce an error of more than a few hundredths of a milligram, even when 30 to 40 mg. of barium sulfate was precipitated.

The concentration of the gallium in the filtrate from the basic sulfate precipitate was determined colorimetrically using quinalizarin, following the method described by Willard and Fogg.[7]

The individual results obtained are given in Table I, and the relationship between *p*H and the molar ratio shown graphically in Fig. 1.

TABLE I

RELATION BETWEEN *p*H, THE MOLAR RATIO Ga/SO$_4$, AND THE SOLUBILITY OF THE BASIC SULFATE

Concentration of Ga, 0.003 *M*; of $(NH_4)_2SO_4$, 0.02 *M*

No.	*p*H	Atoms of Ga/ moles of SO$_4$	Ga in filtrate, mg/liter
1	3.26	6.35	4.0
2	3.53	6.81	2.0
3	4.35	7.46	0.2
4	5.19	8.41	.06
5	5.36	8.33	.2
6	5.91	11.28	.8
7	6.24	14.90	2.0
8	6.53	19.51	2.7
9	6.80	32.10	3.3
10	6.91	31.58	1.0
11	7.28	64.93	7.0
12	7.36	1075	7.0
13	7.46	1628	
14	8.48	∝	

From the table and curve it can be seen that the *p*H of the solution has a very decided influence upon the amount of sulfate present in the precipitate. The ratio of gallium to sulfate shows only a small increase up to a *p*H of about 6, but after that it increases very rapidly. The sulfate content becomes practically negligible at 7.5, while at 8.5 the precipitate is pure hydroxide. The behavior of gallium is entirely different in this respect from that of aluminum[2] which shows a fairly uniform increase in the ratio, with increasing *p*H, with no abrupt change at any point. At the higher *p*H values the aluminum precipitate contains decidedly more sulfate.

Although the amount of gallium left in the filtrate shows many irregularities, there is no doubt about its being a minimum between the *p*H values of 4 and 5.5. This has been amply confirmed by many determinations of gallium in filtrates from actual quantitative precipitations made by urea.

Approaching the Equilibrium from Each Direction. The Replacement of Sulfate by Hydroxyl.—Since the sulfate content of a precipitate, removed from a solution of *p*H 7.5, or above, is so low, it would seem as if that which is present in a precipitate obtained at a low *p*H would be removed easily by digesting in a solution of higher *p*H. Accordingly, some precipitates were formed

---

(5) D. A. MacInnes and M. Dole, *Ind. Eng. Chem., Anal. Ed.*, **1**, 57 (1929); D. A. MacInnes and M. Dole, THIS JOURNAL, **52**, 29 (1930); **53**, 3315 (1931).

(6) S. E. Hill, *Science*, **73**, 529 (1931).

(7) H. H. Willard and H. C. Fogg, THIS JOURNAL, **59**, 40 (1937).

in the usual manner, the digestion being stopped when the *p*H was 5 or 6. After cooling and settling, the solution was decanted and replaced by a 0.02 *M* ammonium sulfate solution, the *p*H of which had been brought previously to about 7 by heating with 4 g. of urea. The mixture was heated and stirred as before for six and one-half hours. The precipitate was filtered off, the *p*H of the filtrate, and the molar ratio in the precipitate determined as before. With sample No. 3 the procedure was the same except that the mixture was placed in a bottle and rotated at room temperature for ninety-two hours, instead of being heated. The results are collected in Table II.

TABLE II

THE REPLACEMENT OF SULFATE BY HYDROXYL

Number	1	2	3
Original *p*H	5.89	4.80	5.89
Ratio Ga/SO_4 at orig. *p*H[a]	10.5	7.9	10.5
Final *p*H	7.61	7.68	7.34
Ratio Ga/SO_4 at final *p*H	1009	1219	399

[a] Values taken from Fig. 1.

These results show that sulfate in a basic gallium sulfate precipitate is so easily removed that agitation, even at room temperature, with a solution of higher *p*H will serve to take out a large proportion.

The Replacement of Hydroxyl by Sulfate.—A precipitate obtained from a solution of *p*H 8.68 was rotated in a bottle at room temperature for one hundred and eighty-six hours, in contact with 0.02 *M* ammonium sulfate solution which had a *p*H of approximately 3. At the end of this time the precipitate was filtered off and the ratio of gallium to sulfate in the precipitate, as well as the *p*H of the filtrate, determined.

SUMMARY OF DATA

Original *p*H	8.68
Ratio Ga/SO_4 at original *p*H	∝
Final *p*H	3.26
Ratio Ga/SO_4 at final *p*H	2997

This shows that the replacement of hydroxyl by sulfate in a precipitate of gallium hydroxide takes place very slowly.

The Effect of a Higher Concentration of Ammonium Sulfate on the Molar Ratio.—This effect was ascertained by the procedure described under the determination of the molar ratio, except that the solution was 0.2 *M* in ammonium sulfate. The data obtained are given in Table III.

TABLE III

THE EFFECT ON THE MOLAR RATIO OF VARYING THE CONCENTRATION OF AMMONIUM SULFATE

Number	1	2	3	4
*p*H	3.7	4.11	5.3	5.35
Ratio Ga/SO_4 with 0.02 *M* $(NH_4)_2SO_4$[a]	7.0	7.4	8.1	8.2
Ratio Ga/SO_4 with 0.2 *M* $(NH_4)_2SO_4$	7.49	7.93	9.09	8.94
Difference in ratio	+0.5	+0.5	+1.0	+0.7

[a] Values taken from Fig. 1.

The results show that increasing the concentration of sulfate ion present in the solution has only a slight influence in increasing the proportion of that radical to be found in the precipitate.

Summary

1. The composition of the dense gallium basic sulfate precipitated by urea from a solution containing sulfate varied from pure hydroxide at a *p*H of 8.5 to one containing a considerable portion of sulfate at a *p*H of 3.3.

2. Digestion in a solution of higher *p*H removed sulfate readily; the reverse process was extremely slow.

3. Precipitation of gallium with urea in 0.02 *M* ammonium sulfate solution is most complete at a final *p*H between 4 and 5.5; under these conditions about 0.2 mg. of gallium per liter remains in solution.

ANN ARBOR, MICH.

RECEIVED APRIL 12, 1937