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

# The Precipitation of Basic Gallium Sulfate by Means of Urea. II. The Separation and Determination of Gallium

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

**Introduction.**—It has been shown by Willard and Tang[2] that aluminum can be precipitated quantitatively by heating its solution with urea in the presence of ammonium chloride and ammonium sulfate or succinate. This method gives a much better separation of this element from the more basic elements such as zinc, nickel, cobalt, manganese, etc., than does an ammonium hydroxide precipitation. Willard and Fogg[3] found that a similar dense precipitate of basic sulfate was formed when gallium solutions were heated with urea, ammonium chloride and ammonium sulfate. In this latter instance, it was found that only about 0.2 mg. of gallium per liter remained dissolved if the final *p*H of the solution was 4 to 5.5, which is considerably less than the amount which remains when gallium is precipitated with ammonium hydroxide in the presence of ammonium salts.[4]

The common method of precipitating gallium hydroxide with ammonium hydroxide, followed by ignition to the oxide, has been investigated and discussed by Fricke and Meyring.[5] During careless ignition, the oxide may be reduced to the volatile metal by hot carbon, and such reduction always occurs if in contact with platinum.[4,5] Every trace of chloride must be washed out of the precipitate since ammonium chloride reacts with gallium oxide, even at 250°, to form volatile gallium trichloride.

## The Quantitative Precipitation of Gallium by Urea

**Preliminary Work.**—Preliminary work on the quantitative precipitation gave considerable information regarding some of the errors which would affect the accuracy of the results.

(a) It was found necessary to heat the gallium oxide to 1200° for one hour to obtain constant weight. No loss in weight resulted from this treatment. It was also found that great care must be used to avoid loss when the precipitate was ignited in the presence of paper.

(b) The presence of chloride in the solution from which the precipitation was made, always caused low results. This is doubtless due to some of the gallium precipitating as basic chloride, and volatilizing as the chloride, during ignition. When the metal was dissolved in hydrochloric acid, evaporated to *incipient* fuming with sulfuric acid, and the determination completed as described later, losses of 3 to 7 mg. occurred.

(c) Cold water was best for washing the precipitate of basic gallium sulfate, since it was more soluble in wash solutions containing ammonium salts.

(d) The amount of gallium remaining in solution after precipitation was much less if the cover glass was raised on hooks during the heating of the solution, so as to allow the escape of carbon dioxide. The weight of gallium, calculated as oxide, left in the filtrates after precipitation was found to be: with cover glass on beaker in usual manner, 0.70 mg./l. (average of 7); with cover glass raised on hooks, 0.33 mg./l. (average of 32).

(e) The most favorable *p*H for quantitative precipitation was found to be between 4 and 5.5.

(f) The precipitate was somewhat flocculent, but not at all gelatinous, and had an appreciable tendency to adhere to the beaker, regardless of whether the latter was of glass or of silica.

### Precipitation of Gallium from a Sulfate Solution

**Procedure.**—The sample of gallium metal purified as described by Willard and Fogg[3] was transferred to a 600-ml. beaker and dissolved by warming with 3 ml. of concentrated sulfuric acid on a hot-plate. After about twelve hours a little water was added, the solution evaporated and heated again, to make certain that all of the metal had been attacked; 150 to 200 ml. of water and 3 g. of urea, as a filtered solution, were added. After diluting to nearly 500 ml., redistilled ammonium hydroxide was added dropwise until the solution was almost permanently turbid. It was then heated to incipient boiling and kept at that temperature until a sample of the solution showed that the *p*H was between 4 and 5.5 (barely alkaline to methyl orange). When the desired *p*H had been reached the solution was filtered through a weighed porcelain filtering crucible, the precipitate washed with cold water and ignited at 850°. After weighing, most of the oxide was transferred to an unglazed porcelain crucible, ignited for one hour at 1200° and again weighed. From the loss in weight the corrected weight of the entire precipitate was calculated. This method was adopted because the filtering crucible could not be heated to this temperature, and it was desired to avoid any possibility of reduction by carbon.

The *p*H of the filtrate was determined by means of a set of approximately isohydric indicators.[6] The gallium which

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[1] Holder of the J. T. Baker Fellowship in Analytical Chemistry for the Mid-western Division during the academic year, 1931–1932. Present address: University of New Hampshire, Durham, N. H.

[2] H. H. Willard and N. K. Tang, *Ind. Eng. Chem., Anal. Ed.*, **9**, 357 (1937).

[3] H. H. Willard and H. C. Fogg, THIS JOURNAL, **59**, 1197 (1937).

[4] L. Moser and A. Brukl, *Monatsh.*, **50**, 181–192 (1928).

[5] R. Fricke and K. Meyring, *Z. anorg. allgem. Chem.*, **176**, 325–348 (1928).

[6] S. F. Acree and E. H. Fawcett, *Ind. Eng. Chem., Anal. Ed.*, **2**, 78 (1930).

remained in the filtrate and wash water, and which adhered to the beaker after as thorough removal as possible with a policeman, was determined colorimetrically by the method described by Willard and Fogg.[7] Table I shows the results obtained following the above procedure.

TABLE I

THE DETERMINATION OF GALLIUM BY PRECIPITATION AS BASIC SULFATE

Weight of gallium oxide taken, approximately 0.13 g.

| pH | Wt. $Ga_2O_3$ from filtrate and beaker, g. | Error $Ga_2O_3$, mg. |
|---|---|---|
| 6.1 | 0.00073 | −0.25 |
| 5.6 | .00088 | − .23 |
| 5.3 | .00078 | + .15 |
| 5.8 | .00096 | ± .00 |
| 6.1 | .00070 | − .25 |
| 5.0 | .00059 | − .21 |
| 4.3 | .00072 | − .18 |
| 4.4 | .00046 | − .21 |

**Discussion of Results.**—It can be seen that gallium can be determined quantitatively by precipitation from a sulfate solution by heating with urea. Although the precipitate is not quite as insoluble as could be desired, it is nevertheless much less soluble than the hydroxide. As a rule from 0.1 to 0.2 mg., calculated as oxide, remained in the 500 ml. of filtrate, and approximately 0.01 mg. was dissolved by 150 to 200 ml. of wash water. The most troublesome feature was the tendency of the precipitate to adhere to the beaker. From 0.1 to 0.6 mg. of oxide would remain even after a most thorough cleaning with a policeman.

**The Precipitation of Gallium from a Buffered Solution.**—Since so much difficulty was encountered in controlling the *p*H with no buffer in the solution, a number of determinations were made with varying amounts of succinate or acetate present. The above procedure was followed except that varying amounts of succinic acid or ammonium acetate, and 4 g. of urea, instead of 3, were added and the solutions heated for the time given. The results are shown in Table II.

TABLE II

THE DETERMINATION OF GALLIUM BY PRECIPITATION FROM A SOLUTION BUFFERED WITH ACETATE OR SUCCINATE

Weight of gallium taken, approximately 0.13 g.

| Ammonium acetate added, g. | Time of heating, hrs. | pH | Wt. $Ga_2O_3$ from filtrate and beaker, g. | Error $Ga_2O_3$ mg. |
|---|---|---|---|---|
| 3 | 3.5 | 4.7 | 0.00069 | −0.23 |
| 3 | 3.5 | 4.6 | .00078 | − .03 |
| 2 | 2.5 | 4.6 | .00088 | + .15 |
| 2 | 2.5 | 4.5 | .00081 | − .14 |
| Succinic acid added. | | | | |
| 5 | 2 | 4.0 | .00177 | − .08 |
| 2 | 2.5 | 4.1 | .00140 | − .06 |
| 1 | 2.5 | 5.5 | .00093 | − .32 |

**Discussion of Results.**—The amount of gallium recovered, using the two buffers, was in as good agreement with the quantity taken as when only sulfate was present. However, the concentration of gallium left in the filtrate was much greater than with sulfate, varying from 0.6 mg. to as much as 3.0 mg. per liter. This is not entirely obvious from the data listed, since in some instances the precipitation was made from a smaller volume.

## The Separation of Gallium from Other Elements by Precipitation from Sulfate Solution

**Separation from Calcium.**—The determination of gallium in gallium–calcium mixtures was made following the procedure first described. The calcium in the ignited oxide was determined by dissolving in hydrochloric acid and precipitating as oxalate in the usual manner. The results in Table III show that gallium can be separated from calcium by this method if there is not enough of the latter element present to exceed the solubility of calcium sulfate at the final *p*H. With approximately 500 ml. of solution, and 0.2 g. of calcium, less than 0.1 mg. was carried down, but if 0.3 g. is present, a considerable quantity accompanies the gallium.

TABLE III

THE DETERMINATION OF GALLIUM IN THE PRESENCE OF CALCIUM

Weight of gallium, approximately 0.13 g.

| pH | Ca taken, g. | $Ga_2O_3$ from filtrate and beaker, g. | Error $Ga_2O_3$, mg. |
|---|---|---|---|
| 3.9 | 0.05 | 0.00083 | −0.10 |
| 4.1 | .075 | .00066 | + .16 |
| 4.4 | .075 | .00035 | − .04 |
| 5.4 | .10 | .00037 | + .07 |
| 4.0 | .10 | .00039 | + .26 |
| 4.3 | .20 | .00072 | + .05 |
| 5.8 | .20 | .00037 | − .20 |

**Separation of Zinc.**—According to Britton[8] zinc begins to precipitate at a *p*H of 5.2. Even though this is not much higher than that required for the precipitation of basic gallium sulfate, a good separation is effected.

The results shown in Table IV were obtained by the method previously given. To determine

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

[8] H. T. S. Britton, "Hydrogen Ions," D. Van Nostrand Co., New York, 1932, p. 325; *J. Chem. Soc.*, **127**, [2] 2110–2159 (1925).

the zinc which accompanied the gallium, the final ignited oxide was dissolved by warming with concentrated hydrochloric acid and the zinc precipitated as sulfide from citric acid solution, using calcium citrate as a collector, as recommended by Bodansky.[9] It was then determined turbidimetrically with potassium ferrocyanide according to the method of Breyer.[10]

**Separation from Manganese.**—Since this element begins to precipitate at a *p*H of 8.5, it is readily separated from gallium by heating with urea. Table IV shows the results obtained, following the procedure already given. The manganese carried down by the gallium was determined colorimetrically.

TABLE IV

THE DETERMINATION OF GALLIUM IN THE PRESENCE OF ZINC AND MANGANESE

| *p*H | Zn taken, g. | In ppt., mg., ZnO | $Ga_2O_3$ from filtrate and beaker, g. | $Ga_2O_3$ taken, g. | Error $Ga_2O_3$ mg. |
|---|---|---|---|---|---|
| 4.5 | 0.01 | 0.05 | 0.00026 | 0.13496 | −0.20 |
| 4.5 | .015 | None | .00057 | .13268 | − .06 |
| 4.4 | .015 | 0.05 | .00022 | .13207 | − .15 |
| 4.2 | .025 | .15 | .00054 | .12750 | − .21 |
| 4.4 | .025 | .07 | .00025 | .13247 | + .01 |
| 4.5 | .05 | .60 | .00093 | .13832 | − .14 |
| 5.6 | .10 | 1.00 | .00055 | .13127 | − .07 |
| 4.4 | .25 | 0.63 | .00036 | .12703 | + .25 |
| 4.1 | .50 | 0.90 | .00075 | .13752 | − .02 |
| 4.7 | 1.00 | 2.00 | .00027 | .13214 | − .02 |
| 4.3 | 0.5 | 0.05 | .00033 | .03784 | + .14 |
| 4.6 | 0.5 | .07 | .00016 | .03475 | + .09 |
| 5.9 | 1.0 | .07 | .00090 | .01371 | − .43 |
| 5.7 | 1.0 | .25 | .00032 | .02178 | − .36 |
| 4.7 | 1.0 | .05 | .00022 | .01425 | + .12 |
| 5.9<br>4.0 | 1.0 | None[a] | .00182 | .13765 | + .07 |
| 4.6<br>5.6 | 1.0 | 0.05[a] | .00071 | .13711 | ± .00 |
| 5.1<br>4.2 | 1.0 | None[a] | .00127 | .13664 | − .17 |
| 5.6<br>4.7 | 1.0 | None[a] | .00123 | .13490 | − .27 |
|  | Mn | $Mn_3O_4$ |  |  |  |
| 4.8 | 0.5 | 0.05 | 0.00026 | 0.12307 | −0.01 |
| 4.2 | .5 | .07 | .00021 | .13416 | − .12 |
| 4.8 | .5 | .12 | .00021 | .13116 | + .08 |
| 4.7 | .5 | .11 | .00021 | .13419 | + .19 |
| 4.4 | 1.0 | .23 | .00095 | .13496 | − .11 |
| 5.2 | 1.0 | .32 | .00025 | .13429 | + .08 |
| 4.2 | 1.0 | .20 | .00024 | .13342 | − .13 |
| 4.4<br>4.3 | 1.25 | .01[a] | .00053 | .13220 | + .18 |
| 4.5<br>5.3 | 1.25 | .01[a] | .00044 | .13684 | − .15 |

[a] Two precipitations.

**Discussion of Results.**—Using a volume of about 500 ml., one precipitation will satisfactorily separate 0.1 g. of gallium from 0.02 g. of zinc or a few milligrams of gallium from 1 g. of the latter. If as much as 1 g. of zinc is present with the larger amount of gallium, a reprecipitation will remove all of it. Using 500 ml. of solution, 0.1 g. of gallium can be separated from as much as 0.5 g. of manganese by a single precipitation, with only 0.1 mg. of manganese oxide accompanying the precipitate. If 1.0 g. of manganese is present, somewhat more will be found with the gallium. A double precipitation gives complete separation, even when 1.25 g. is present. Undoubtedly an equally good separation would be obtained from magnesium, although this was not studied.

## Summary

Gallium can be precipitated quantitatively as basic sulfate by heating its sulfate solution, containing 3 g. of urea, until a *p*H of 4 to 5.5, or possibly 6, has been reached. If the solution contains acetate or succinate, more gallium remains in solution. Employing the procedure developed, it was found possible to separate gallium from 1 g. of zinc and manganese and 0.2 g. of calcium. Obviously weaker bases than these such as aluminum, chromium and iron will interfere. Magnesium should not interfere.

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(9) M. Bodansky, *Ind. Eng. Chem.*, **13**, 696 (1921).

(10) F. G. Breyer, in Scott, "Standard Methods of Chemical Analysis," 4th ed., D. Van Nostrand Co., New York, 1925, p. 607.