

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 43]

A NEW METHOD FOR THE SEPARATION OF GALLIUM FROM OTHER ELEMENTS

By ERNEST H. SWIFT

RECEIVED MAY 13, 1924

PUBLISHED NOVEMBER 5, 1924

Introduction

The method of extracting iron from hydrochloric acid solutions with ether proposed by Rothe¹ and developed by several other investigators² has become a standard quantitative procedure. It has also been applied to a system of qualitative analysis by Noyes, Bray and Spear,³ for separating iron and thallium from zirconium and titanium. In making provision for the presence of gallium in this same group it became necessary to determine whether it would be extracted by ether from a hydrochloric acid solution. This proved to be the case—a result that is in accord with the fact that gallium occurs in the same group with thallium and occupies the same position in the first period of eighteen elements as does thallium in the succeeding long period of thirty-two. It is interesting to note that indium, though it occurs in the same family as gallium and is the element analogous to it in the second period of eighteen, is not extracted by ether⁴ under the same conditions.

This research was carried out in connection with the system of qualitative analysis including the rare elements now being developed in this Laboratory by A. A. Noyes and W. C. Bray, to whom the author is indebted for many valuable suggestions. The author wishes especially to acknowledge his obligation to Professor Noyes for his assistance in preparing this paper for publication. The research was assisted on the financial side from a grant made to Professor Noyes by the Carnegie Institution of Washington. Thanks are also due to Professor T. W. Richards of Harvard University for his kindness in supplying the gallium that was used in this investigation.

Distribution of Gallium between Ether and Hydrochloric Acid Solutions

Preliminary experiments, carried out with small amounts of gallium in hydrochloric acid solutions of various concentrations, indicated that the extraction of the gallium by the ether was more nearly complete when the initial concentration of the hydrochloric acid was approximately 6 *N*. This is also the most favorable concentration for the extraction of iron.^{1, 2, 3} Accordingly, experiments were made with larger amounts of gallium in

¹ Rothe, *Stahl u. Eisen*, **12**, 1052 (1892); **13**, 333 (1893).

² (a) Langmuir, *THIS JOURNAL*, **22**, 102 (1900). (b) Kern, *ibid.*, **23**, 689 (1901). (c) Speller, *Chem. News*, **83**, 124 (1901).

³ Noyes, Bray and Spear, *THIS JOURNAL*, **30**, 515-516, 558-559 (1908).

⁴ Wada and Ato, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, **1**, 70 (1922).

order to determine somewhat more accurately the distribution of gallium between ether and solutions of hydrochloric acid of various concentrations.

The gallium solution used in these experiments was prepared as follows. Metallic gallium was dissolved in hydrochloric acid. The solution was tested for iron and thallium, and they were proved absent. The gallium was extracted from this solution with ether and thus separated from any other elements present. The ether extracts were evaporated to dryness on a steam-bath, and the salt was converted into nitrate by repeated moistening with 16 *N* nitric acid. The residue was dissolved in a small amount of 6 *N* nitric acid, transferred to a platinum dish, ignited to the oxide, and weighed as the trioxide, Ga₂O₃. This residue was dissolved in 12 *N* hydrochloric acid, the solution evaporated just to dryness, and then diluted so as to contain 10 mg. of gallium per cubic centimeter.

Ten-cc. portions of this solution were pipetted out and evaporated just to dryness on a steam-bath; the residues were dissolved in 50 cc. of standardized hydrochloric acid of various concentrations. These solutions were then treated in a graduated extraction flask with 50 cc. of ether. This had been previously shaken with three successive 100cc. portions of hydrochloric acid of the same concentration as that containing the gallium salt with which it was to be shaken, so as to decrease the heating effect upon mixing and to insure that the concentration of the hydrochloric acid remained fairly constant during the extraction of the gallium. The extraction flask was kept closed and cooled to 20° during the operations to avoid loss of ether. After the two layers had separated, they were drawn off into conical flasks and evaporated to dryness on a steam-bath; the residue was treated repeatedly with 16 *N* nitric acid until all chloride was destroyed, and then transferred to a platinum dish and ignited to constant weight.

The results are given in Table I.

Moles of HCl per liter (initial)	Volume after shaking		Ga ₂ O ₃ obtained from		Per cent. extracted	Millimoles of gallium per liter of		Distribution ratio
	Ether	Water	Ether Mg.	Water Mg.		Ether layer	Water layer	
1.97	45.0	54.5	3.3	135.1	2.4	0.78	26.40	0.029
3.07	43.2	55.8	20.5	118.1	14.8	5.05	22.60	0.223
3.80	42.8	56.2	110.2	27.5	80.0	27.30	6.22	5.23
4.90	40.0	59.0	134.4	4.5	96.7	35.70	0.81	43.8
5.45	39.0	60.0	131.7	2.7	97.9	35.90	0.48	74.7
5.91	37.0	61.5	132.6	4.2	96.9	38.1	0.73	52.2
6.92	28.0	70.0	113.8	24.1	82.5	43.2	3.67	11.8
7.92	13.0	84.0	35.2	102.6	25.5	28.8	13.0	2.21

It is seen from the table that by treating a 4.9–5.9 *N* solution of hydrochloric acid containing gallium with an equal amount of ether (previously shaken several times with hydrochloric acid of the same concentration) about 97% of the gallium is extracted. Hence, if such a solution contained 1 g. of gallium, three such extractions should leave only 0.03 mg. of it in the aqueous layer.

It will also be noted that the concentration of the gallium in the ether layer is at a maximum at about 7 *N* hydrochloric acid, but that the proportion of it extracted is much less because the volume of the ether layer is reduced by its increased solubility in the hydrochloric acid.

The distribution ratio of the gallium between the ethereal and aqueous layers for various initial concentrations of the hydrochloric acid is shown graphically in Fig. 1. This ratio (and also the percentage extracted) will be seen from this figure (or from the table) to have a maximum value at about 5.5 *N* hydrochloric acid.

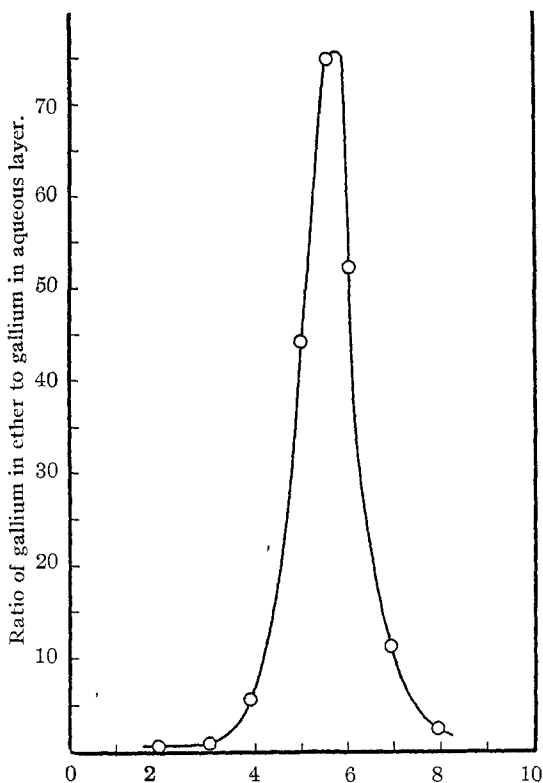


Fig. 1.—Moles of HCl per liter initially present in aqueous solution.

Non-Volatilization of Gallium on Evaporating Chloride Solutions

Statements are made in the literature⁵ that hydrochloric acid solutions of gallium cannot be evaporated without loss of that element. Since hydrochloric acid solutions of gallium were evaporated on a steam-bath in obtaining the data given above, the following experiments were performed to determine if there was any appreciable loss during this process. Samples of approximately 200 mg. of gallium as Ga_2O_3 were weighed into platinum dishes, dissolved in 20 cc. of 12 *N* hydrochloric acid, the solutions evaporated on a steam bath to dryness, the residues moistened with 1 cc. of 12 *N* hydrochloric acid, again evaporated to dryness and

⁵ Treadwell-Hall, 5th edition, vol. 1., John Wiley and Sons, 1921, p. 540.

allowed to remain on the steam-bath for one hour. The residues were dissolved in hydrochloric acid, transferred to conical flasks and treated with successive 5cc. portions of 16 *N* nitric acid until all chloride was removed, then again transferred to platinum dishes, evaporated to dryness and ignited. The weights of gallium trioxide taken were 0.2643 and 0.2655 g. The weights found after this treatment were 0.2655 and 0.2657 g., showing that there had been no loss.

Applicability of the Ether-Extraction Method to the Separation of Gallium from Other Elements

Gallium has been found to occur most frequently in iron and zinc ores, and in commercial aluminum. The other elements commonly occurring with it are lead, manganese, copper and indium.⁶ From all of these

TABLE II

BEHAVIOR OF VARIOUS ELEMENTS ON SHAKING A 6 NORMAL HYDROCHLORIC ACID SOLUTION WITH ETHER

Element	Per cent. extracted	Ref. No.	Element	Per cent. extracted	Ref. No.
Al	0	2c	Mo (MoO ₃)	80-90	9a
Sb (SbCl ₃)	6	7	Ni	0	2a
Sb (SbCl ₅)	81	7	Os	0	8b
As (AsCl ₃)	68	7	Pd	0	7
As (AsCl ₅)	2-4	8a	Pt	trace	7
Bi	0	8a	Rare earths	0	9b
Cd	0	8a	Rh	0	8b
Cr	0	2c	Se	trace	8a
Co	0	2c	Ag	0	7
Cu	trace	7	Te	34	7
Ga	97	8a	Th	0	9b
Ge	40-60	8a	Tl (TlCl ₃)	90-95	3
Gl	0	8c	Sn (SnCl ₄)	17	7
Au	95	7	Sn (SnCl ₂)	15-30	8a
In	trace	4	Ti	0	3
Ir	5	7	W (with PO ₄)	0	8c
Fe (FeCl ₃)	99	7	U	0	2b
Fe (FeCl ₂)	0	8a	V (V ₂ O ₅)	trace	8a
Pb	0	7	Zn	trace	7
Mn	0	2c	Zr	0	3
Hg	trace	7			

⁶ Kirkland, *Australian Assoc. Adv. Sci.*, Fourth Report, 1893, 266-267. Cornwall, *Am. Chem. J.*, 2, 44 (1880). Boulanger and Bardet, *Compt. rend.*, 157, 718-9 (1912); *Chem. News*, 108, 305 (1913). Hartley and Ramage, *J. Chem. Soc.*, (London) 71, 533 (1897).

⁷ Mylius and Hüttner, *Ber.*, 44, 1315 (1911).

⁸ (a) Swift, (b) Dalton, (c) Carter, unpublished experiments carried out in this Laboratory.

⁹ (a) Sammet, (b) Wada, unpublished experiments carried out at the Massachusetts Institute of Technology in collaboration with A. A. Noyes.

except iron, as well as from many other elements, gallium can be separated by shaking a 6 *N* hydrochloric acid solution with ether. The behavior of a large number of the elements under these conditions is given in Table II. The data for this table were obtained from the literature and from experiments made in connection with the rare-element system of qualitative analysis now being developed in this Laboratory. The values were in many cases obtained under different experimental conditions and are, therefore, often only approximate. The various sources are indicated in the table; the reference numbers ("Ref. Nos.") being those given in the footnotes to this article. Where the amount found in the ether layer is less than 1 or 2% it is indicated as a trace.

Separation of Gallium from Iron by Sodium Hydroxide

As iron is the only element occurring with gallium which in ordinary analyses is likely to pass into the ether extract along with it, the separation of these elements from each other was studied. The usual separation by sodium hydroxide is stated by Lecoq de Boisbaudran¹⁰ to require repeated precipitation, owing to the gallium being carried down by the ferric hydroxide precipitate. As it would seem probable that this effect might vary with the concentration of the sodium hydroxide, the following series of experiments was carried out to ascertain whether a complete separation at any concentration is possible. In these experiments, the results of which are given in Table III, to the amount of iron (as ferric nitrate) indicated in the first column, and of gallium (as chloride) indicated in the second column, contained in 25 cc. of solution, was added 6 *N* sodium hydroxide solution until, after precipitation of all the iron, an excess was present at the concentration indicated in the third column. The mixture was then boiled gently for two minutes, cooled, and filtered. To the filtrate 6 *N* hydrochloric acid was added until the solution was just neutral, and then 1 cc. more; the solution was diluted to 100 cc., treated with 5 cc. of 3 *N* ammonium acetate, boiled for two minutes, and the gallium precipitates were compared with standards as to quantity. The iron hydroxide precipitates were dissolved in hydrochloric acid, this solution was evaporated just to dryness, and the residue dissolved in 10–20 cc. of 6 *N* hydrochloric acid; this solution was then shaken with a large excess of metallic mercury until all the iron had been reduced. By treating this solution with ether the gallium was extracted and the ferrous iron remained in the aqueous layer. The ether extract was then evaporated just to dryness over a steam-bath and the gallium was precipitated with ammonium acetate as before, the precipitates being then compared with standards. The amount of gallium found in the filtrate is given in the fourth column; and that found in the ferric hydroxide precipitate, in the fifth column.

¹⁰ De Boisbaudran, *Compt. rend.*, 94, 1439, 1625 (1882).

TABLE III
SEPARATION OF GALLIUM FROM IRON BY SODIUM HYDROXIDE

Iron taken Mg.	Gallium taken Mg.	Normality of NaOH present in excess	Gallium found in	
			Filtrate Mg.	Precipitate Mg.
200	20	2.7	20	0
200	20	1.3	20	0
200	20	0.3	20	0
200	20	0.066	15-18	2-5
200	20	0.03	15-18	2-4
200	20	0.007	12-15	5-7
200	20	0.003	5-8	15-18
200	20	0 ^a	0	20
200	2	1	2 ^b	..
200	1	0.5	1 ^b	..
500	1	0.5	1 ^b	..
500	0	0.5	0	..

^a This filtrate required only 1 drop of 6 *N* NaOH to give a distinct alkaline reaction.

^b The size of these precipitates indicated no appreciable loss of gallium with the precipitate and confirmatory tests with potassium ferrocyanide were made in each case.

It is thus seen that it is possible to separate gallium completely from iron by one precipitation, provided the hydroxide concentration be kept above a certain minimum value, about 0.3 *N*. The amount of gallium carried out with the iron precipitate increases as the hydroxide concentration is decreased below this value, until in a neutral or very slightly acid solution complete precipitation of the gallium results. The fact that gallium is practically completely carried out by iron in the ammonium hydroxide precipitation is in agreement with these experiments, as the hydroxyl-ion concentration in such a solution is usually between 1×10^{-4} and 1×10^{-5} .

From the sodium hydroxide solution the gallium can be easily precipitated by carefully neutralizing the sodium hydroxide, adding 1 cc. excess of 6 *N* hydrochloric acid and 5 to 10 cc. of 3 *N* ammonium acetate solution for each 100 cc. of solution obtained, and boiling the solution for two to five minutes. Experiments have shown that under these conditions less than 1 mg. of gallium in 100 cc. of solution can be detected, but the ratio of acetic acid to acetate ion must be carefully regulated, and the total concentrations of these substances should not be greatly increased over those indicated.

The gallium can also be precipitated from the sodium hydroxide filtrate by diluting it so that the concentration of the sodium hydroxide is reduced to 0.2 *N* and completely saturating this solution with carbon dioxide gas.¹¹ It was found that when the sodium hydroxide concentration is initially above 0.3 *N* the precipitation of the gallium is incomplete.

¹¹ Porter and Browning, *THIS JOURNAL*, **43**, 111 (1921).

Procedure for the Detection of Gallium

The following procedure is based upon the facts established above. It is assumed that a sample consisting of not more than 5 g. of the original substance has been decomposed and brought into 15 to 30 cc. of solution just 6 *N* in hydrochloric acid.

Transfer the cold solution to a separating funnel, add to it an equal volume of ether (previously shaken with twice its volume of 6 *N* hydrochloric acid), shake vigorously, and then allow the two layers to separate completely. Draw off the water layer (preferably into another separating funnel), and treat it twice with ether as just described. Combine the ether extracts in a separating funnel, and wash them by shaking with 5 cc. of 6 *N* hydrochloric acid. Separate the two layers. Reject the two water layers. Evaporate the ether layers on a steam-bath almost to dryness. Dissolve the residue in 20 cc. of water, add 2 to 3 drops of phenolphthalein solution, and then 6 *N* sodium hydroxide solution until a red color results. Add just 2 cc. of 6 *N* sodium hydroxide solution in excess and boil the mixture for two minutes. Filter out and reject any precipitate. To the filtrate add 6 *N* hydrochloric acid until the color of the phenolphthalein just disappears, then 1 cc. more, dilute it to 100 cc., add 10 cc. of 3 *N* ammonium acetate, and heat just to boiling for five minutes. Any gallium present separates as an amorphous white precipitate. To confirm further the presence of gallium, collect the precipitate on a small filter, dissolve it by pouring repeatedly through the filter a 5cc. portion of warm 6 *N* hydrochloric acid, add to this solution 5 cc. of water and 3 cc. of 1 *N* potassium ferrocyanide solution and let the mixture stand for 5 to 10 minutes. A flocculent, white or bluish-white precipitate shows the presence of gallium.

This process can also be used for obtaining pure gallium preparations from natural materials.

Summary

A new method for the separation of gallium from most other elements has been presented. This is based upon the discovery that gallium trichloride is extracted almost completely by ether from 5 to 6 *N* hydrochloric acid solutions.

The distribution of gallium between ether and hydrochloric acid solutions, varying from 2 to 8 *N*, has been studied. The maximum distribution-ratio and the maximum percentage extracted were found at about 5.5 *N* hydrochloric acid.

The conditions for the separation of gallium and iron by sodium hydroxide solutions have been studied. A satisfactory separation results when the concentration of the excess of base is not less than 0.3 *N*.