[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY]

The Concentration of Gallium by Means of Adsorption on Hydrated Aluminum and Iron Oxides[1]

BY EUGENE WAINER

Introduction

Gallium has several properties in common with the other members of the third vertical group in the periodical table, such as the amphotericity and ease of hydrolysis of its salts, the flocculent voluminosity of the gelatinous precipitate formed in neutral or alkaline media in proper concentration, and many others. Usually, a corollary of the formation of precipitates in a gelatinous voluminous condition is that they easily adsorb, or drag down in some allied manner, otherwise unprecipitable substances, and in turn are easily adsorbed themselves under proper conditions.

The purpose of this investigation is to determine whether or not the last named property exists for hydrated gallium oxide with a view toward its application to the extraction of gallium from low grade ores.

Experimental

According to Moser and Brukl,[2] the solubility of $Ga(OH)_3$ in 0.01 molar ammonia is 0.0574 g. per liter; in pure water, 0.0010 g. per liter; and in the presence of ammonium salts, 0.0052 g. per liter.

Since the presence of ammonium salts is usual in water extracts of minerals containing gallium, due to neutralization of acids, a rough check was made on the figure for solubility in the presence of ammonium salts, with the exception that the temperature employed was 100°. Two solutions, made up as indicated in the table, were heated to boiling and carefully neutralized with dilute ammonia using methyl red as indicator[3] (Expts. 1 and 2, Table I). The first solution, held at just under the boiling temperature for one hour and filtered hot, washing the precipitate a few times with small portions of hot water, yielded 0.0036 g. of Ga_2O_3. The second solution, heated overnight, yielded 0.0044 g. of Ga_2O_3. Thus $Ga(OH)_3$ is incompletely precipitated by ammonia in neutral solution containing ammonium salts but a more complete precipitation is obtained on long standing.

TABLE I

RECOVERY OF GALLIUM

Ga_2O_3 used in each case, 0.0100 g.

Expt.	Al_2O_3 as sulfate, g.	Al_2O_3 pptd.,[a] g.	Fe_2O_3 as nitrate, g.	Fe_2O_3 pptd.,[b] g.	NH_4NO_3 g.	soln., l.	Ga_2O_3 recov., g.	Time heated before filtr.
1					10	1	0.0036	1 hour
2					10	1	.0044	Overnight
3	1	1			10	1	.0102	10 min.
4	0.1	0.1			10	1	.0085	10 min.
5	.1	.1			10	1	.0093	1 hour
6	.1	.1			10	1	.0099	2–3 hrs.
7	.1	.1			10	1	.0102	Overnight
8	.2	.2			10	1	.0104	10 min.
9	2	.1			10	1	.0046	1 hour
10	2	.1			10	1	.0056	Overnight
11	2	1			10	1	.0089	20 min.
12	2	1			10	1	.0097	Overnight
13[c]	2	1			10	1	.0101	20 min.
14	50	2			30	2	.0097	10 min.
15	50	2			30	2	.0106	Overnight
16			1	1	10	1	.0104	10 min.
17			0.1	0.1	10	1	.0099	10 min.
18			2	.2	10	1	.0096	Overnight
19			50	2	30	2	.0104	Overnight

[a] In Expt. 9–15, the values listed are approximate only.

[b] In Expt. 18–19, the values listed are approximate only.

[c] The amount of precipitated alumina was arrived at by initially complete neutralization followed by partial solution in sulfuric acid.

As a means of testing the adsorbability of hydrated gallium oxide, co-precipitation with hydrated iron and aluminum oxides was selected since, as a rule, these substances occur in the same minerals as does gallium. It had been noted previously that the filtrate from a solution containing gallium, from which the aluminum had been completely removed as hydroxide, contained no gallium.

In the subsequent experiments involving aluminum, the gallium was separated from the aluminum as follows: the gelatinous precipitate was dissolved in sufficient hot dilute sulfuric acid so that on dilution to 100 cc. a 2 N sulfuric acid

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

[3] Gallium oxide, designated as pure, was further purified by double electrolysis in 0.05 N HCl, between platinum electrodes at high current density. Spectroscopic examination of oxide prepared from this electrolyzed gallium, showed it to contain minute traces of iron, aluminum, and zinc in quantities insufficient to interfere with the subsequent investigation.

solution resulted. The solution was cooled to about 10° and the gallium precipitated with cupferron in the usual manner.[2] The precipitate was allowed to stand for five to ten minutes before filtration and was washed at room temperature with a mixture of 2 N sulfuric acid and 1.5 N cupferron. It was found that if the $Al_2O_3:Ga_2O_3$ ratio is greater than 200:1, a double precipitation with cupferron is necessary, especially if the solution be allowed to stand too long before filtration.

The results obtained and listed in Table I, Experiments 3–8, indicate that gallium is adsorbed by aluminum when the latter is completely precipitated with ammonia. The amount of Al_2O_3 necessary to carry down the 10 mg. of Ga_2O_3 completely lies between 0.1 and 0.2 g.

The determination was then made of the completeness of precipitation of the gallium in the presence of aluminum when an amount of ammonia insufficient to precipitate all the aluminum was added. In Experiment 13, Table I, the final weight of precipitated Al_2O_3 was arrived at by complete neutralization with ammonium hydroxide and subsequent partial solution with dilute sulfuric acid.

The results obtained and listed in Table I, Experiments 9–15, indicate that gallium is adsorbed by aluminum when the latter is incompletely precipitated with ammonia. The amount of precipitated Al_2O_3 necessary to carry down the 10 mg. of Ga_2O_3 completely lies between 1 and 2 g., the upper limit depending, to a certain extent, on the total amount of aluminum present.

In all cases where the Ga_2O_3 was separated from aluminum, spectroscopic traces of iron and aluminum were observed in the Ga_2O_3, estimated at a fraction of a per cent. of the total gallium content. In the last two runs (14 and 15) the Ga_2O_3 precipitate contained Fe_2O_3 estimated at 1% or more.

The substitution of iron for aluminum was then tried. Small amounts of gallium may be separated from considerable iron by means of Moser and Brukl's modification of Berzelius and Chancel's method for separating iron and aluminum,[4] giving a precipitate of gallium considerably contaminated with iron. Methods suggested by Moser and Brukl,[2] Papish and Hoag,[5] and others for removal of small amounts of iron were found to be laborious or inexact. It was found that the phenylhydrazine separation of iron and aluminum worked equally for iron and gallium concentrations such as are secured by Moser and Brukl's method. After solution of the last obtained iron–gallium precipitate in a $K_2S_2O_7$ fusion, the usual phenylhydrazine[6,7] procedure is then followed. Good separations are obtained in one operation with samples containing amounts of iron similar to that carried down by the previous gallium precipitates.

The results obtained and listed in Table I, Experiments 16–19, indicate that 0.1 g. of Fe_2O_3 is sufficient to carry down the 10 mg. of Ga_2O_3 when the iron is completely precipitated by ammonia, while 0.2–2.0 g. of Fe_2O_3 is necessary for the same purpose when the iron is incompletely precipitated, the upper limit depending, to a certain extent, on the amount of iron present in the solution. The final precipitates contained traces of iron and aluminum, while the aluminum content, in Expt. 19, amounted to an estimated value of one or two per cent.

Discussion

It may be seen from the values obtained that a more or less quantitative removal of gallium may be accomplished by means of co-precipitation of its gelatinous hydrated oxide with that of iron or aluminum. In the case of complete neutralization the $Al_2O_3:Ga_2O_3$ ratio should be at least 20:1 when aluminum alone is considered, and the $Fe_2O_3:Ga_2O_3$ ratio at least 10:1 when the iron alone is considered. In the case of incomplete precipitation the $Al_2O_3:Ga_2O_3$ ratio should be at least 100–150:1, while the $Fe_2O_3:Ga_2O_3$ ratio should be 20–50:1. It is expected that these last figures will vary with concentration and volume of solution.

Apparently, some increase in yield is obtained if complete precipitation is first carried out and then followed by partial solution of the gelatinous precipitate by means of acid. This is probably due to the condition in which these solids exist in neutral solution, that is, greater voluminosity and surface area, both properties making for increased adsorption, and acting in a manner analogous to irreversibility.

Summary

1. Hydrated gallium oxide possesses a measure of power of being adsorbed by or of adsorp-

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[4] L. Moser and A. Brukl, *Monatsh.*, **51**, 325 (1929); Chancel, *Compt. rend.*, **46**, 987 (1858); *Z. anal. Chem.*, **3**, 391 (1864); Scholler and Schrauth, *Chem.-Ztg.*, **37**, 1237 (1909).

[5] J. Papish and L. E. Hoag, THIS JOURNAL, **50**, 2118 (1928).

[6] Hess and Campbell, *ibid.*, **21**, 776 (1899).

[7] Allen, *ibid.*, **25**, 421 (1903).

tion of both gelatinous hydrated iron and aluminum oxides, that of iron being more efficient.

2. A method suitable for application to the extraction of gallium from low grade ores has been suggested.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Phenanthroline-Ferrous Ion. III. A Silver Reductor. The Direct Determination of Iron in the Presence of Vanadium[1]

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Our potential measurements at high acidities[2] have shown that the oxidimetric determination of ferrous ion using the phenanthroline-ferrous ion indicator will not be interfered with by the presence of tetravalent vanadium provided that the titration be made in the presence of 5 molar sulfuric acid. To make the fullest practical application of this knowledge it is extremely desirable to have a method of reducing iron to the ferrous state and vanadium to the tetravalent state without further reduction of the vanadium and without reduction of tetravalent titanium, which shall be highly precise and at the same time as rapid and convenient as the Jones reductor.

The Silver Reductor

We have therefore developed a silver reductor which not only satisfies all of these requirements but also appears to be the cheapest and most convenient reductor for the determination of iron yet devised. The use of silver as a reducing agent in the determination of iron has never become popular, although it has been suggested.[3,4] This is probably due as much to the difficulty caused in the subequent titration by the chloride ion necessarily present as it is to the feeling that silver must be too expensive a reagent. Chloride ion does not, however, interfere in the titration of iron with ceric sulfate using the phenanthroline ferrous indicator, and the cost of the silver for a reductor is very small since less than an ounce is required.

To obtain a sufficiently low oxidation potential with silver it must be used in contact with a solution containing an ion of a highly insoluble silver salt. When the reduction is carried out in one molar hydrochloric acid, a satisfactory acid concentration, the oxidation potential is given by the e. m. f. of the cell

$$\mathrm{Ag} \mid \mathrm{AgCl}\ 1\ M\ \mathrm{HCl} \parallel 1\ M\ \mathrm{HCl} \mid \mathrm{H_2(Pt)}$$

At 25° the potential[5] is 0.2329 volt, a value amply below that required for the quantitative reduction of ferric ion. We might expect, however, from a consideration of Fig. 1 of the previous paper[2] that in 1 M acid solution vanadium should be quantitatively reduced to V^{+++} at this potential (-0.53 volt referred to quinhydrone). Actually this reduction does not take place.[6] The reaction is probably very slow so that in the time required for the solution to pass through the silver reductor no measurable amount of the trivalent ion is formed.

Construction of the Reductor.—A reductor column of the usual Jones reductor type with an inside tube diameter of 2 cm. is recommended. Although the length of the column is immaterial it need be no longer than 12 cm. A reservoir bulb of 50–75 cc. capacity is most satisfactory. Approximately 18 g. of silver is precipitated from silver nitrate with copper. For this purpose a piece of electrolytic sheet copper about 10 cm. square is suspended in a solution of 29 g. of silver nitrate in 400 cc. of water to which has been added a few drops of nitric acid. The reaction is allowed to proceed with continuous vigorous mechanical stirring until a test shows the absence of silver ion in the solution. The silver is then washed by decantation with dilute sulfuric acid until most of the copper is removed. A small plug of glass wool is inserted in the lower end of the reductor column. The silver is suspended in water, the mixture poured into the reductor and the solution allowed to drain to the top of the silver column. The column is then rinsed with dilute sulfuric acid until a test shows the absence of copper in the wash liquid. Care should always be taken not to allow the liquid in the column to drain below the top of the silver.

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[2] THIS JOURNAL, **56**, 57 (1934).

[3] Hoenig, *Z. anal. Chem.*, **54**, 441 (1915).

[4] Edgar and Kemp, THIS JOURNAL, **40**, 777 (1918); Edgar, *ibid.*, **38**, 1297 (1916).

[5] Scatchard, *ibid.*, **47**, 641 (1925).

[6] In 6 M hydrochloric acid or in a solution five molar in sulfuric acid and also one molar in hydrochloric acid, there is partial reduction to the trivalent ion.