

5. An equation has been developed relating the free energy change referred to the solids to the potential in a given solution and the solubilities of the quinone and hydroquinone. The differences in the oxidation potential as measured in 2 different solvents can be thus calculated from the solubilities.

6. The discrepancy between our value for quinone and the one obtained by Haber and Russ has been traced to an invalid assumption made by these investigators.

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A NEW METHOD FOR THE GRAVIMETRIC DETERMINATION OF GERMANIUM

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Analytical procedure for the quantitative determination of germanium has not changed since the early investigations of Winkler¹ immediately following his discovery of the element in 1886; that is to say, germanium has always been weighed as sulfide or dioxide and no other compound has been reported which admits of direct application to quantitative estimation.

Weighing of the disulfide yields excellent results but is usually avoided on account of the required washing for the removal of free sulfur, as well as the inability of this salt to withstand ordinary ignition. In consequence, the sulfide is nearly always converted to dioxide by frequent evaporation with nitric acid and ignition to constant weight.

In many determinations it has been the writer's experience that the conversion of sulfide to oxide, aside from being time consuming, is subject to serious conflicting errors. First, the sulfide is violently attacked by even dil. nitric acid and yet must be thoroughly decomposed by this acid before much heat is applied to the residue. Second, after complete oxidation the removal of all of the sulfuric acid is very difficult, if indeed possible.

A slight loss of germanium through volatility of the unoxidized sulfide plus the mechanical loss in the escaping oxides of nitrogen tends to give low results, but on the other hand the tightly held sulfuric acid which clings to the ignited residue causes error in the other direction. These conflicting or balancing errors are practically beyond control of the analyst and have suggested to the writer the search for an altogether different method for the estimation of germanium.

The purpose of this communication is to describe a new method for the gravimetric determination of germanium, which is based upon the action

¹ Winkler, *J. prakt. Chem.*, [2] **34**, 177 (1886); **36**, 177 (1887).

of magnesia mixture upon solutions of germanic oxide in the presence of free ammonia.

It will be shown that, under proper conditions, the precipitate consists entirely of magnesium orthogermanate (Mg_2GeO_4), which hitherto unreported compound appears to possess all of the properties required for its use in this connection.

Reagents and Apparatus

The following reagents were employed throughout this work. A normal solution of magnesium sulfate, free from silica, iron, calcium. A 2*N* solution of ammonium sulfate, free from heavy metals and alkaline earths; ignition of a 5g. sample gave an inappreciable non-volatile residue.

Ammonium hydroxide, sp. gr. 0.89; this was freshly prepared by distillation from platinum and was preserved in vessels of the same material.

Hydrogen peroxide, a 30% solution, free from phosphoric acid and other non-volatile matter.

Germanic acid in aqueous solutions of different concentrations. The stock solution from which the other more dilute solutions were prepared contained 0.004308 g. of GeO_2 per cc. at 26°. These solutions were restandardized separately by evaporation of 50cc. samples and ignition of residual oxide to constant weight. The germanium dioxide was of the highest degree of purity and entirely free from arsenic.

Ordinary distilled water, freshly prepared, was used. The flasks and pipets were calibrated at 26°; the balance was a Troemner No. 10, with a sensibility of 0.00002 g.; the weights were recalibrated. Porcelain crucibles and Pyrex glassware were used throughout. All precipitates were collected upon ashless filter paper upon which the operation of drying and ignition was performed without disturbing the mass of precipitate.

Preliminary Experimental Work

One hundred cc. of an aqueous solution of germanic acid containing 0.4308 g. of germanium dioxide was treated with 25 cc. of *N* magnesium sulfate solution and 15 cc. of 2 *N* ammonium sulfate solution.

Upon addition of 20 cc. of conc. ammonium hydroxide, a bulky white precipitate immediately formed. The mixture was raised to boiling, allowed to cool and to stand for 12 hours. The filtrate and wash water were separately collected and examined for germanium as follows. Each was neutralized and then made approximately 6 *N* with sulfuric acid. The acid solutions were now saturated with hydrogen sulfide in the cold. Only a slight turbidity appeared in about an hour. In 24 hours each solution contained a small precipitate, which was converted to oxide in the usual way and weighed. The filtrate, measuring 140 cc., contained 0.0002 g. of germanium dioxide. The wash water, which was originally slightly ammoniacal, contained 0.0004 g. of germanium dioxide in 50 cc. This procedure was repeated several times and in no case was more than 0.0005 g. of germanium dioxide found in the combined filtrate and wash water.

Precipitation of the same quantity of germanium was carried out in the presence of a much larger excess of ammonium salt. The filtrate then contained an appreciable quantity of unprecipitated germanium, even after several days' standing. For example, 100 cc. of germanic acid solution treated with 50 cc. of 2 *N* ammonium sulfate solution, 20 cc. of *N* magnesium sulfate solution and 20 cc. of ammonium hydroxide gave a filtrate containing 0.0012 g. of germanium dioxide, although the solution was allowed to stand for several days before filtration.

A number of attempts to precipitate magnesium germanate completely with less than 5 or 6 hours' digestion in presence of the precipitant failed.

Elevation of the temperature to boiling point increases the rapidity of the precipitation and improves the condition of the precipitate for filtration and washing.

The chlorides of magnesium and ammonium cannot be substituted for the sulfates in the precipitation of magnesium germanate, because a small amount of ammonium chloride, invariably brought down with the magnesium salt, causes loss of germanium upon subsequent ignition of the precipitate, due to the volatility of germanium chloride.

Composition and General Properties of the Precipitate

The precipitates obtained in the above preliminary experiments were collected and analyzed as follows.

After ignition to constant weight by aid of a Meker burner and a blast lamp, the snow-white infusible mass was dissolved in a little dil. sulfuric acid, diluted to 50 cc. and then made approximately 6 *N* by addition of the measured quantity of conc. sulfuric acid. The acid solution was then saturated with hydrogen sulfide under pressure, and the germanium sulfide was converted to the dioxide in the usual manner and weighed. The magnesium content of the filtrate from the germanium sulfide was determined by the usual magnesium pyrophosphate method. The following table shows the results of four analyses of the magnesium salt.

TABLE I
ANALYSIS OF MAGNESIUM ORTHOGERMANATE

Wt. of salt taken G.	GeO ₂ found %	MgO found %
0.1186	56.72	43.17
0.2025	56.65	43.47
0.1348	56.30	43.20
0.3823	56.20	43.82
	Mean 56.47	Mean 43.42

From these results it may be seen that the salt precipitated from an aqueous solution of germanic acid by magnesia mixture is magnesium orthogermanate. Theoretically, this salt contains 56.45% germanium dioxide and 43.55% magnesia, which values are very close to the means obtained.

Magnesium orthogermanate is a pure white, amorphous substance which shows no definite crystalline structure under microscopic examination. It is infusible at the highest temperature obtainable in the blast lamp, and is non-volatile at a white heat. A large excess of ammonium salts retards its formation, but does not prevent quantitative precipitation unless present in greater concentration than that equivalent to 25 cc. of 2 *N* ammonium salt to each 100 cc. of germanic acid solution. The precipitate is very soluble in dilute solutions of all the mineral acids and is only slowly soluble in the same acids even after intense ignition. If the excess of ammonia be boiled off, the precipitate will pass into solution in the nearly neutral ammonium salt. Reprecipitation takes place upon addition of more ammonia.

Solubility of Magnesium Orthogermanate

An excess of the thoroughly washed salt was suspended in pure redistilled water in a platinum bottle in which it was allowed to remain for several weeks at 26°. The vessel was frequently shaken. After filtration through a dry filter, 25 cc. of the filtrate was evaporated to dryness and ignited in platinum. The residue of magnesium salt weighed 0.0004 g., representing a solubility of 0.000016 g. per cc. at this temperature.

The same procedure was carried out using 3 volumes of water and 2 volumes of ammonium hydroxide in place of the pure water. The solubility was only slightly different, 1 cc. containing 0.00002 g.

Another portion of the magnesium salt, suspended in a 10% ammonium sulfate solution rendered strongly alkaline with ammonia, and digested at room temperature for a week, showed upon filtration, evaporation and ignition of a 20cc. sample, a solubility of 0.00013 g. per cc.

It is evident that magnesium germanate is about 10 times as soluble in dil. aqueous ammonia containing 10% ammonium sulfate, as in pure water or dil. aqueous ammonia. The presence of an excess of magnesium ion, however, reduces this solvent action of the ammonium salt well within the limits required for a quantitative precipitation.

No advantage is obtained by addition of much ammonia to the wash water, as the precipitated magnesium salt shows nearly the same solubility in both water and dil. aqueous ammonia. In all of the described determinations the wash water contained 10 cc. of ammonium hydroxide, sp. gr. 0.89, to 90 cc. of water.

Final Determinations

In all of the final determinations which follow in tabular form, the germanic acid solutions were treated with the normal magnesium sulfate solution in excess, followed by at least an equal volume of 2 *N* ammonium sulfate solution. The ammonium hydroxide was always added last in amounts varying from 15 to 20 cc., for each 100 cc. of solution, while the solution was stirred vigorously, and the whole then raised to boiling for a few moments and allowed to cool and stand for 10 to 12 hours before it was filtered. The wash water, a mixture of 90 cc. of water and 10 cc. of ammonium hydroxide (sp. gr. 0.89) varied in volume with the quantity of precipitate, but did not exceed 50 cc. in any instance. Ash-free paper filters were used in every case, except Analyses 1 and 2, in which the bulky mass of precipitate was collected upon porcelain Gooch crucibles with asbestos mats. It was not necessary to remove precipitates from the filter paper. The precipitates were quickly dried and ignited with free access to air. Very little reduction takes place by action of the filter paper, and the slightly darkened surface of the ignited mass, produced by action of the carbon, rapidly oxidizes to the pure white germanate upon continued

ignition. Toward the end of each ignition the precipitate was heated over a blast lamp to constant weight.

Magnesium germanate may be ignited in platinum, if care be taken to avoid reducing gases. The presence of filter paper, however, makes this procedure rather unsafe.

Analytically, germanium is invariably met with as sulfide, but the determination as magnesium orthogermanate requires an ammoniacal solution of the oxide. The simplest method of treatment of the precipitated sulfide consists in the addition of a slight excess of ammonium hydroxide followed by an excess of hydrogen peroxide. Upon boiling, to destroy the excess of peroxide, the solution contains ammonium germanate and is ready for precipitation as the magnesium salt in the way described. It is scarcely necessary to remark that ordinary hydrogen peroxide often contains phosphoric acid and that such an impurity must be absent from the reagent used for this precipitation. Furthermore, hydrogen peroxide prevents the precipitation of magnesium germanate, so that it is essential that the excess of peroxide used to oxidize the ammonium thio-germanate be destroyed by long boiling before the precipitation of the magnesium salt.

When arsenic accompanies germanium the 2 sulfides may be separated through the solubility of germanium sulfide in hydrofluoric acid.² The solution of germanium fluoride, obtained by filtration, can then be evaporated with a little sulfuric acid to expel the hydrofluoric acid and may then be treated with magnesium sulfate and an excess of ammonium hydroxide. The presence of fluorides entirely prevents the precipitation of magnesium germanate.

It is necessary to lay emphasis upon the importance of controlling the concentration of the reagents used in the precipitation of magnesium germanate. For quantities of germanium dioxide varying between 0.5 and 0.2 g. in 100 cc. of solution, it was found best to add from 20 to 25 cc. of 2 *N* ammonium sulfate solution, together with the excess of magnesium salt (15 to 25 cc. of *N* solution). In a series of preliminary experiments it was found that lower concentrations of the ammonium salt resulted in the complete precipitation of the germanium content of the solution, but the analysis of the precipitate showed too high a content of magnesia, to correspond with the formula of the normal salt. On the other hand, a large excess of ammonium salt retards the precipitation to an unnecessary degree.

Obviously, two methods of procedure can be used to prevent this source of error: (1) add the proper excess of ammonium sulfate in quantity sufficient to prevent the separation of magnesia; (2) resort to a double precipitation of the magnesium germanate similar to that commonly carried out

² Müller, *THIS JOURNAL*, **43**, 2549 (1921).

in the quantitative estimation of magnesium pyrophosphate or arsenate; that is to say, the moist precipitate of magnesium germanate may be dissolved in dil. sulfuric acid and the solution then treated with excess of ammonia, the whole raised to boiling temperature and then allowed to cool before a slight excess of magnesium sulfate is added to complete the precipitation of the germanate.

TABLE II
FINAL DETERMINATIONS

GeO ₂ taken G.	Mg ₂ GeO ₄ found G.	GeO ₂ calculated from Mg salt G.	Vol. of soln. Cc.	GeO ₂ found in filtrate G.
0.4308	0.7623	0.4301	125	0.0006
0.2154	0.3823	0.2158	110	0.0002
0.0136	0.0248	0.0139	75	0.0004
0.0136	0.0244	0.0137	75	trace
0.1130	0.2036	0.1148	100	0.0006
0.0006	0.0013	0.0007	40	trace
0.0013	0.0027	0.0015	25	trace
0.0005	0.0011	0.0006	30	none
0.0011	0.0018	0.0010	50	none
0.0002	0.0003	0.0001	15	trace

The final results, Table II, show that the simpler method involving a single precipitation, allows the fairly accurate determination of germanium with the escape of almost negligible amounts of germanium in the filtrate and wash water. In the method of double precipitation, results were not obtained which were in any way superior to or more concordant than those resulting from a single precipitation in the presence of the above-mentioned excess of ammonium sulfate.

Summary and Conclusion

1. Magnesium orthogermanate, a compound not hitherto reported, has been prepared and its general properties described.
2. This salt is admirably adapted to the gravimetric determination of germanium in quantities ranging between 0.5 g. and 0.0002 g. The precipitation and ignition of this compound are not accompanied by change in composition or any loss by volatility.
3. Ordinary quantitative filter paper may be used and the precipitate quickly dried and ignited to constant weight.
4. The described method is considerably simpler than that of the determination as sulfide and, the writer believes, more accurate than the well-known conversion of the disulfide to dioxide.