(Fig. 3) obtained[3] through the use of this hypothesis is also wrong. The distance 1.440 ± 0.015 Å. determined by us is not completely outside of the range 1.45 to 1.58 Å. for A to O, which has been calculated to be necessary in order to account for the observed birefringence of ruby.[4]

## Summary

The crystal structures of hematite and corundum have been determined through the use of Laue and spectral photographs, interpreted with the aid of the theory of space groups. The unit of structure is a rhombohedron with $\alpha = 55°\ 17'$ and $a = 5.420 \pm 0.010$ Å. for hematite, and with $\alpha = 55°\ 17'$ and $a = 5.120 \pm 0.010$ Å. for corundum. The space group underlying the atomic arrangement is $D_{3d}^6$.

The data require that atoms of iron or aluminum be located at www, $\bar{w}\bar{w}\bar{w}$, $\frac{1}{2}-w\ \frac{1}{2}-w\ \frac{1}{2}-w$, $w+\frac{1}{2}\ w+\frac{1}{2}\ w+\frac{1}{2}$, and atoms of oxygen at $u\bar{u}0$, $\bar{u}0u$, $0u\bar{u}$, $\frac{1}{2}-u\ u+\frac{1}{2}\ \frac{1}{2}$, $u+\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}-u$, $\frac{1}{2}\ \frac{1}{2}-u\ u+\frac{1}{2}$, with $u = 0.292 \pm 0.007$ and $w = 0.1050 \pm 0.0010$ for hematite and $u = 0.303 \pm 0.003$ and $w = 0.1050 \pm 0.0010$ for corundum. These structures show that crystals of hematite and corundum consist of a compact arrangement of approximately but not exactly spherical ions, as shown in Fig. 3. The derived inter-atomic distances in Ångström units are as follows.

| | Hematite | Corundum |
|---|---|---|
| Smallest oxygen-oxygen distance............ | 2.545±0.060 | 2.495±0.025 |
| Metal-oxygen distance (B or C to A)........ | 2.060± .035 | 1.990± .020 |
| Metal-oxygen distance (D or E to A)........ | 1.985± .025 | 1.845± .015 |

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# GERMANIUM. X. THE DETERMINATION OF GERMANIUM

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Since the time of its discovery by Winkler, germanium has been determined by precipitating it as the disulfide, oxidizing the disulfide to the dioxide by means of nitric acid and weighing the dioxide.

Winkler[1] used this method, but he published no experimental results from which its accuracy might be judged. Indeed, he employed the method only once in the direct determination of germanium in argyrodite,[2] and he says that the result was obtained "unter Anwendung einer allerdings noch mangelhaften Methode."

Dennis and Papish, who give[3] the latest details for its application, also state that no great accuracy is claimed for the method.

It is evident that if the procedure is to give accurate results, the precipitation of the germanium as sulfide must be quantitative, and the oxidation of the sulfide to the dioxide must be complete and must be conducted in such manner as will avoid loss.

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[1] Winkler, *J. prakt. Chem.*, **142**, 228 (1886).

[2] *Ibid.*, **142**, 188 (1886).

[3] Dennis and Papish, THIS JOURNAL, **43**, 2131 (1921).

The oxidation of the sulfide to dioxide has hitherto been accomplished by the use of nitric acid. This procedure is open to several objections, chief among which are the violence of the reaction between germanium disulfide and nitric acid which takes place with rapid escape of oxides of nitrogen, the puffing up of the dry sulfide during oxidation, and the formation of free sulfur. The first two are apt to cause loss, and the oxidation of free sulfur by nitric acid is very slow. If the contents of the crucible in which the oxidation has been carried to partial completion is heated to a temperature at which the sulfur will be volatilized, there is every probability that some of the germanium dioxide will be reduced to the monoxide and loss will result through the comparatively easy volatilization of this latter compound.

The purpose of this paper is to show, (1) that the precipitation of germanium as sulfide is complete under the conditions which have usually been employed, and (2) that the oxidation of the sulfide to germanium dioxide and sulfuric acid can rapidly and quietly be effected, without loss of germanium, by the use of hydrogen peroxide.

The material employed in our study of the method was a portion of the germanium dioxide prepared by Dennis and Johnson.[4]

This product was placed in a small porcelain crucible and ignited to constant weight over a Meker burner.[3] Small samples of this dioxide were weighed out from the crucible. Each sample was dissolved in distilled water, the volume of water was brought up to 150 cc., and the contents of the flask was heated to boiling until the oxide had completely dissolved. Ignited germanium dioxide, if pure, is completely soluble in water, but passes into solution very slowly unless the water is heated to boiling. The solution was then allowed to cool, and 30 cc. of concd. sulfuric acid was added in order to bring the acid concentration to 6 *N*. The acidified solution was again cooled and hydrogen sulfide was passed in for 15 minutes. Some of the sulfide precipitated in this operation is deposited on the inlet tube. It can be removed by means of a rubber "policeman," but in these tests it was removed by dissolving it in a dilute solution of ammonium hydroxide. The small volume of ammoniacal solution so obtained was added to the precipitation flask. The flask was then tightly stoppered and allowed to stand for 48 hours.

At the end of the precipitating period of 15 minutes described above, the germanium sulfide which has come down is present in very finely-divided form giving the solution a milky, almost colloidal appearance. During the time of standing which is prescribed, however, this finely-divided precipitate agglomerates to flocculent form and settles, leaving a perfectly clear, supernatant liquid. It has been found that the length of standing may be reduced to 24 hours without affecting the accuracy of the result, but the time required for the filtration which follows is thereby made longer.

The germanium sulfide was then collected on a small filter paper and

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[4] Dennis and Johnson, This Journal, 45, 1391 (1923).

was washed thoroughly with 6 *N* sulfuric acid that had been saturated with hydrogen sulfide.

The funnel containing the filter was placed in the neck of a small Erlenmeyer flask and the precipitate was dissolved on the filter by adding several small portions of redistilled ammonium hydroxide. The concentration of the solution was about 10 *N*. Only a small volume of ammonium hydroxide is required for this operation, as the sulfide passes into solution very readily. This solution is yellow. Occasionally some sulfur which has been precipitated with the germanium sulfide by decomposition of the hydrogen sulfide remains behind on the filter, but no difficulty has been experienced in completely extracting the germanium sulfide from it. The filter was finally washed with small portions of water, the washing being continued until the filtrate came through colorless.

The germanium disulfide thus dissolved in ammonium hydroxide was oxidized by hydrogen peroxide. Since the final step in the analysis is the evaporation of this solution to dryness and the weighing of the residual germanium dioxide, it was obvious that a preparation of hydrogen peroxide which left no appreciable residue on evaporation must be employed. This was obtained by use of Perhydrol, which was diluted with water to a concentration of 3%.

The oxidation of the dissolved sulfide was first carried out in small Erlenmeyer flasks, and the resulting solution was evaporated to dryness in porcelain crucibles and the residue ignited and weighed. The results were in all cases too high. Examination of all of the reagents which were employed showed that the difficulty lay elsewhere. Contamination of the germanium dioxide must therefore have come from the glass in which the germanium disulfide had been precipitated or later oxidized. Trial of different kinds of "resistance" glass, including Pyrex, did not improve the results. The solution of the sulfide, when it was dissolved on the filter in ammonium hydroxide, was therefore received in a small, weighed, platinum dish, 20 cc. of diluted Perhydrol, 3%, was added, and the oxidation was allowed to proceed in the cold. The solution was then evaporated to dryness at a temperature of about 105°. When this residue was heated to drive off the ammonium sulfate which results from the oxidation of the ammoniacal solution of the sulfide, the latter salt sometimes decrepitated and caused loss. This decrepitation may be avoided by first moistening the dried residue with concd. sulfuric acid and then gently heating the contents of the dish with a Bunsen flame until the ammonium sulfate and sulfuric acid are driven off.

The residual germanium dioxide was finally ignited to constant weight. Of the results given below, the first nine were obtained without moistening the residue with sulfuric acid, while in the last five that procedure was employed.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $GeO_2$ taken, g. | 0.1789 | .2536 | .1699 | .1674 | .1791 | .1797 | .2757 |
| $GeO_2$ found, g. | 0.1785 | .2538 | .1701 | .1674 | .1786 | .1797 | .2745 |
| $GeO_2$ taken, g. | 0.2495 | .2654 | .1050 | .1093 | .1508 | .2016 | .2972 |
| $GeO_2$ found, g. | 0.2489 | .2640 | .1044 | .1092 | .1509 | .2013 | .2972 |

The method was then used in the determination of germanium in two different samples of germanium-bearing zinc oxide. The method of Dennis and Papish[3] was followed to the point of precipitation of the germanium sulfide. From there on, the procedure here described was employed. Three analyses of each sample were made.

ZINC OXIDE No. 1

| Crude oxide G. | $GeO_2$ found G. | $GeO_2$ found % |
|---|---|---|
| 100 | 0.1112 | 0.111 |
| 100 | .1116 | .112 |
| 105 | .1159 | .110 |

ZINC OXIDE No. 2

| Crude oxide G. | $GeO_2$ found G. | $GeO_2$ found % |
|---|---|---|
| 50 | .1054 | .211 |
| 60 | .1259 | .210 |
| 102 | .2150 | .211 |

## Summary

This article describes a method for the determination of germanium, in which the germanium is precipitated as the disulfide, the precipitate is oxidized with 3% hydrogen peroxide and the germanium is finally weighed as the dioxide.

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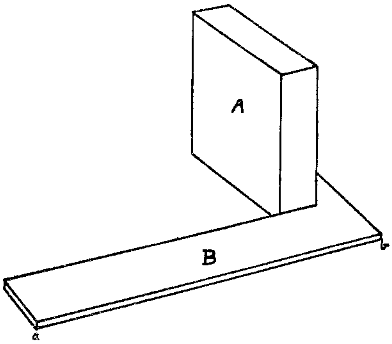
## NOTES

**A Simple Tangentimeter.**—It is often of the utmost importance to the physical chemist to know the slope of a plotted curve at any point. It was to satisfy such a need that the instrument shown in the figure and described below was constructed and used, after a search for, and trial of the various methods given in the literature. The essential feature of the device is copied from a mechanical differentiator constructed and described by A. Elmendorf.[1] In the figure, A is a mirror (a plane polished block of speculum metal in this case) mounted on one leg of the steel square B, so that the mirror face extends to the plane of the bottom of the square and is normal to the edge ab.



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[1] Elmendorf, *Sci. Am. Suppl.*, Feb. 12, 1916.