salt of magnesium, third, on an ammono salt of magnesium, and fourth on metallic magnesium itself.

The reactions studied were represented by the equations:

$$MgI_2 + 4KNH_2 = Mg(NHK)_2.2NH_3 + 2KI;$$

$$Mg(NO_3)_2 + 4KNH_2O = Mg(NHK)_2.2NH_3 + 2KNHO_3;$$

$$(CH_3CONH)_2Mg + 4KNH_2 = Mg(NHK)_2.2NH_3 + 2CH_3CONHK;$$

$$Mg + 2KNH_2 + 2NH_3 = Mg(NHK)_2.2NH_3 + 2H.$$

The compound may be formulated either as a salt with ammonia of crystallization, as has been done above, or as a molecular compound of magnesium amide and potassium amide, $Mg(NH_2)_2.2KNH_2$.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

A STUDY OF THE ACTION OF SULFUR MONOCHLORIDE ON CERTAIN MINERALS.

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Two fields in which sulfur monochloride is now proving a most helpful reagent are in the decomposition of minerals and in the preparation of anhydrous chlorides. Sulfur monochloride was first used for the decomposition of minerals by E. F. Smith,[1] in 1898, when it was employed with a number of naturally occurring sulfides and sulfarsenides. The minerals wolframite, columbite and scheelite were also decomposed. Anhydrous chlorides of arsenic, antimony and bismuth were prepared by Oddo and Serra[2] by the use of sulfur monochloride. Hall[3] repeated the decomposition of columbite, decomposed chromite and converted a number of metallic oxides to chlorides, notable among the latter being the preparation of the chlorides of columbium and tantalum. He also observed that the oxides of silicon and boron resisted the action of the reagent. Bourion[4] repeated the decomposition of the minerals scheelite and wolframite and prepared a number of anhydrous chlorides. Hicks,[5] working in this laboratory, employed sulfur monochloride in the decomposition of the minerals fergusonite, euxenite and samarskite and in the decomposition and analysis of aeschynite. By this means columbium, tantalum, titanium and tungsten were separated completely from silica and the rare earths.

Hicks had noticed that traces of silicates present in some of the minerals

[1] THIS JOURNAL, **20**, 289 (1898).
[2] *Gazz. chim. ital.*, [2] **29**, 355 (1899).
[3] THIS JOURNAL, **26**, 1243 (1904).
[4] *Ann. chim. phys.*, **20**, 547 (1910).
[5] THIS JOURNAL, **33**, 1492 (1911).

examined by him remained undecomposed. Bearing this in mind it was thought desirable to determin the action of this reagent upon certain other refractory minerals. Eleven minerals in all were treated with this reagent at elevated temperatures.

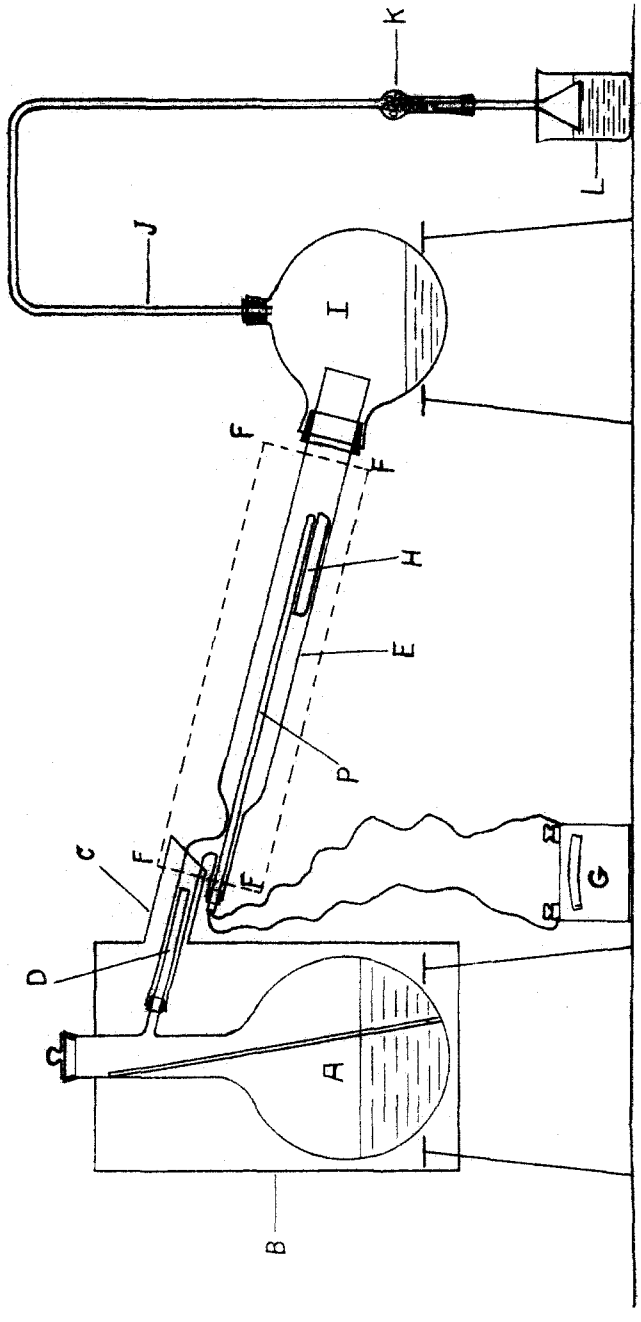
The mineral, except in cases noted, was ground in an agate mortar to pass through No. 25 bolting cloth. The sample to be subjected to the action of sulfur monochloride was then weighed in a fused silica boat and the boat and contents introduced into the apparatus illustrated in the drawing.

(A) represents a 500 cc. distilling flask, with ground glass stopper, surrounded by the asbestos jacket (B). The delivery tube fits rather closely into the tube (D), which connects with the Jena glass tube (E) in which the boat and contents (H) are heated. (P) represents a pyrometer element encased in a jacket of fused quartz, the two members insulated by a tube of quartz within. (G) is an Heraeus' direct reading galvanometer, graduated for use with the element used. The tube was so placed in a combustion furnace that the portion of the apparatus between the lines F. F. F. F. was within the furnace. The purpose of inclining the furnace was to allow the hot gases rising under the porcelain covers to pass up through the asbestos tube (C) and prevent condensation of the sulfur monochloride vapors in the tube (D). (J) represents an air condenser, (K) a tube filled with anhydrous calcium chloride, (L) a beaker containing a solution of caustic soda.

Although Hall had found silicon dioxide to be unacted upon by sulfur monochloride, it was thought best to determin whether the silica boat would resist action under the temperatures about to be employed. Accordingly, the boat was weighed and then subjected to the action of sulfur monochloride vapor at the maximum temperature of the furnace (780°) for a period of 6 hours. No change could be detected in the weight after cooling, washing with dilute hydrochloric acid and water and reweighing. In fact, the boat only suffered a loss of one-tenth of a milligram throughout the entire investigation.

The following minerals were subjected to the action of sulfur monochloride under the conditions noted in their respective paragraphs:

Feldspar, from Delaware County, Pa.
Garnet, from Delaware County, Pa.
Garnet (Pyrope), from Austria.
Zircon, from North Carolina.
Sphene, from Zilberthal.
Tourmaline, from Delaware.
Hornblende, from Roseville, N. J.
Pyroxene, from Franklin, N. J.
Spinel, from North Carolina.


K
L
J
I
F
F
H
E
P
C
F
F
G
D
A
B

Rhodonite, from Franklin, N. J.

Pyromorphite, from Davidson County, Pa.

Feldspar (Orthoclase).—The mineral was of great purity. A sample weighing 0.6027 gram was heated for 5 hours at a temperature of 650°. The boat was then removed from the reaction tube and the contents boiled with dilute hydrochloric acid (1 : 10). The residue, insoluble in acid, was filtered out and ignited to constant weight in a platinum crucible. This was thought to be as satisfactory a method as could conveniently be used to determin the per cent. of mineral decomposed. The residue in this case weighed 0.5782 gram, indicating a decomposition of 4.06%. The hydrochloric acid solution showed traces of iron and alumina but no calcium or magnesium.

Garnet, Delaware County.—This was a red garnet, containing considerable quartz. The sample taken weighed 0.6482 gram. The temperature of the furnace was slowly increased while passing a current of sulfur monochloride vapor over the mineral. At 450° traces of ferric chloride were noticed condensing in the tube in the cooler portions. It ceased after a time and the temperature was finally raised to 650° for 3 hours. After treating the residue with dilute hydrochloric acid, as indicated in the case of the feldspar, the residue was found to weigh 0.6017 gram, indicating a decomposition of 7.1%. Iron and magnesium were found in the hydrochloric acid solution.

Garnet (Pyrope).—This mineral was of gem quality and very pure. A sample weighing 0.7751 gram was slowly heated until 550° was reached. At this point ferric chloride was noticed in the condenser. This temperature was maintained for 4 hours. The residue after extraction weighed 0.3607 gram, showing a decomposition of 53.4%. The residue before ignition was pink in color. Iron, aluminium and calcium were found in the solution from the residue. A second sample ground to an impalpable powder was treated in a similar manner. The decomposition increased to 81.6%. A third sample of the impalpable mineral weighing 0.3116 gram was heated to 700° for 3 hours in a slow current of the vapors. After cooling, the boat was removed and the mineral stirred carefully with a platinum wire. It was then replaced and the heating continued for 4 hours longer. By stirring, fresh portions of the mineral were exposed. The residue weighed 0.0126 gram, indicating 95.96% decomposition. The residue was then treated with a mixture of hydrofluoric and sulfuric acids and ignited to constant weight. The residue from this treatment weighed 0.0048 gram, indicating that actually all but 1.54% of the mineral had been decomposed.

Zircon.—A sample weighing 1.1906 grams was heated for 5 hours at 700°. The residue weighed 1.1238 grams, indicating a decomposition of 5.6%. The residue, however, was white in color and on examination

failed to show the presence of iron. This method might therefore be employed as a means for removing iron in preparing pure zirconia from zircon.

Sphene.—No decomposition was noticed on heating in sulfur monochloride vapor up to 400°. From 550° to 600° the decomposition proceeded rapidly during 3 hours. The sample weighed 0.5233 gram. The residue after extraction weighed 0.0142 gram, indicating a decomposition of 97.29%. The residue after treatment with hydrofluoric acid weighed 0.0053 gram. Therefore, all but 1.7% of the mineral was decomposed. Calcium and traces of iron and titanium were found in the filtrate from the hydrochloric acid solution of the residue.

Spinel.—Decomposition began at 600°. From 600° to 750° it increased and the heating was continued at the latter temperature for 5 hours. 0.8495 gram gave a residue of 0.3941 gram, or 53.4% decomposition. After treatment with hydrofluoric acid, 0.3883 gram or 45.7% of the mineral remained undecomposed.

The residue reacted violently with dilute hydrochloric acid and the solution contained iron, aluminium, chromium and a trace of calcium.

Tourmaline.—This was a pure sample of the black variety and well crystallized. When the temperature of the furnace reached 600° ferric chloride began to sublime. The temperature was maintained between 690° and 700° for 5 hours. The original sample of 0.5944 gram gave a residue from solution in hydrochloric acid of 0.2446 gram—a decomposition of 58.9%. The lower layers of the residue in the boat seemed to have been unacted upon by the reagent. The hydrochloric acid solution from the residue showed traces of iron, calcium and magnesium. When the residue was treated with hydrofluoric acid and ignited the green color characteristic of boron was noticed in the burner flame. The residue from this treatment amounted to 0.1515 gram or 25.5% of the original sample.

Hornblende.—The finely ground mineral was light green in color. At 600° ferric chloride sublimed. A temperature of 700° was maintained for 4 hours. The residue in the boat was then brown in color, 0.6350 gram of mineral left a residue after treatment with hydrochloric acid of 0.1395 gram, indicating a decomposition of 78.1%. Evaporation with hydrofluoric and sulfuric acids and ignition to constant weight gave a residue of 0.1023 gram. Therefore 16.1% of the mineral remained undecomposed.

The hydrochloric acid solution showed traces of third group metals together with calcium and magnesium.

Pyroxene.—The mineral was brownish black in color and seemed free from other minerals. On raising the temperature slowly no decom-

position was noted until 700° was reached. After heating from 700° to 750° for 5 hours, 0.5783 gram of mineral gave a residue of 0.3812 gram, the decomposition representing 34.1%. The residue after treatment with sulfuric and hydrofluoric acids weighed 0.2834 gram, showing 49.0% of the mineral to be still undecomposed. This residue was then fused with sodium bisulfate. Analysis, on solution, showed the presence of iron, aluminium, chromium and a trace of magnesium.

Rhodonite.—The mineral was massive but quite pure. The temperature was raised to 780° without indication of change in the mineral or any sublimation being noticed. This temperature was continued for 5 hours. The sample of 0.6815 gram gave a residue after digestion with hydrochloric acid of 0.5636 gram. The decomposition, therefore, represented 17.2%. The hydrochloric acid solution showed manganese and calcium on examination. It is probable, therefore, that a higher temperature might possibly effect the decomposition of this mineral in a more satisfactory manner.

Pyromorphite.—The crystals were of a pale yellow color and very pure. On raising the temperature to 460° the mineral melted completely after a time, while the temperature was slowly increased to 550°. No sublimation was noticed during 3 hours. The boat and contents were then treated with a large volume of water, when all of the residue dissolved with the exception of 0.0320 gram, which was obtained from the decomposition of 1.4693 grams of mineral. The insoluble residue on examination proved to consist entirely of silica. Large crystals of lead chloride formed in the solution of the residue on cooling. After removing the lead present with hydrogen sulfide, phosphoric acid was found in the filtrate.

Summary.

Of the silicates examined, only those which contained a considerable quantity of elements whose chlorides are volatil in sulfur monochloride were acted upon to any marked extent.

Garnet (Pyrope) and sphene may be almost completely decomposed by heating in sulfur monochloride vapors.

Iron was completely removed from zircon by heating in sulfur monochloride vapor.

Pyromorphite may be completely decomposed by heating in sulfur monochloride vapor to a temperature of 450° to 550°. All is then soluble in dilute hydrochloric acid with the exception of any silica that may be present.

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