

XV.—Behavior of Natural Sulphides with Iodine and other Reagents.

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In a paper on the "Application of Organic Acids to the Examination of Minerals," presented to the Academy about a year ago,* we endeavored to show that citric (or tartaric) acid and potassium nitrite can be advantageously added to the usual list of dry reagents employed in the determination of minerals. Owing to the facility with which the latter reagent is decomposed by the former, nitric acid can be carried practically in the solid form; hydro-potassium sulphate, already in use†, furnishes sulphuric acid in a solid state; and it remains therefore to provide for hydrochloric acid, or chlorine. The alkaline chlorides, however, resist the action of organic acids; and a few experiments with easily decomposing sulphides yielded only negative results. Iodine, on the other hand, while less powerful than chlorine, possesses similar properties, and in aqueous solution it attacks many minerals, giving rise to characteristic phenomena.

The employment of bromine in analytical operations‡ has already demonstrated its power in decomposing natural sulphides; and it is precisely with these minerals that the most satisfactory results are obtained by the action of iodine.

The specimens named below are the same as those whose source and condition have been described in the paper referred to. The method of examination is exceedingly simple; the minerals in fine powder are placed in test tubes, a small quantity of pulverized iodine is added, and then water poured on; after standing in the cold for some hours (usually over

* *Annals N. Y. Acad. Sci.*, Vol. I, p. 1.† Distillation of Natural Sulphides by Bisulphate of Potassa; E. Jannetiaz (Transl. from *Compte Rendu*). *Am. Chem.*, IV, 450‡ P. Waage: *Zeitschr. anal. Chem.*, 1871.

night), the results are noted ; the contents of each tube are then heated to boiling, and the results again recorded. The solutions were tested by suitable reagents after expelling by heat the excess of iodine.

Stibnite, treated in the manner described, is strongly attacked ; and with excess of iodine the solution turns deep brown-red. On boiling the red solution, it loses color as the iodine volatilizes, and after the latter is completely expelled, suitable reagents demonstrate the presence of sulphuric acid and of antimony. The decomposition of this mineral is complete.

Molybdenite is not attacked either in the cold or on boiling.

Argentite is attacked in the cold, yielding a red solution and a yellowish-white precipitate. If an excess of iodine be present, the mineral is completely decomposed in the cold.

Galenite is decomposed in the cold, the liquid being completely decolorized. Lustrous, yellow crystals of plumbic iodide form on the surface of the mineral. On heating, the action is increased ; and the solution deposits, on cooling, large and abundant crystals.

Bornite is strongly attacked in the cold, the solution being brown-red and the residue yellowish-white. On heating, the decomposition is hastened, and a heavy precipitate of cuprous iodide forms.

Sphalerite is strongly attacked in the cold, the solution turning dark red and a crystalline precipitate forming. On heating, the decomposition is complete.

Chalcocite is strongly attacked in the cold, the solution with excess of iodine being brown-red. On the application of heat, the action is increased, but little (if any) cuprous iodide forms.

Cinnabar is feebly attacked in the cold. On heating, it is readily decomposed, with formation of small scarlet crystals of mercuric iodide.

Pyrrhotite is strongly attacked in the cold ; the solution is not completely decolorized, and becomes darker on heating.

Pyrite is decidedly attacked in the cold ; on boiling, the

action is increased, but the decomposition appears to be incomplete.

Niccolite is strongly attacked in the cold, yielding a green solution, which turns brown on heating with excess of iodine.

Smaltite is strongly attacked in the cold, forming a brown-red solution; heat increases the action.

*Chalcopyrite** yields a deep-red solution in the cold; the action is increased by boiling, but no precipitate forms.

Tetrahedrite, *ullmannite*, and *arsenopyrite* behave like chalcopyrite.

Bournonite yields a deep-red solution in the cold; and on heating, a heavy precipitate falls, which is evidently a mixture of plumbic iodide with yellowish-white cuprous iodide.

From the preceding notes, it appears that molybdenite is the only one of the seventeen sulphides examined which resists the action of an aqueous solution of iodine. The reactions of galenite and *Stannabar* are characteristic and beautiful; that of bournonite discloses its composition very satisfactorily. The difference of behavior between hornite and chalcocite is marked.

The results obtained with pyrite and pyrrhotite require some explanations. Professor Henry Wurtz,† in 1858, employed iodine-water to separate pyrrhotite from pyrite; he states that pulverized pyrite digested for 48 hours in the dark with a brown solution of iodine (pulverized and washed repeatedly to remove all free acid), "did not remove the brown color of the liquid, and the latter had dissolved but a trace of iron." We repeated this process, observing all the precautions mentioned, and found that pyrites (from Colorado, and from Saxony), was decidedly attacked. Possibly the discrepancy is only one of judgment as to the amount of decomposition which ensues, but under ordinary circumstances

* Meunel has studied the behavior of chalcopyrite with hydriodic acid; Ber. chem. Ges. III, 123; 1870.

† (In some improvements in the Preparation of Hard Minerals for Analysis, read before the A. A. S. at the Baltimore meeting. Am. J. Sci., [2] Vol. XXVI, p. 190.

we are confident that iodine (in excess) with water decomposes pyrite.

Besides the natural sulphides, we examined the behavior of a few minerals, belonging to various classes, with an aqueous solution of iodine. Limonite, hematite, magnetite, and the manganese oxides, as well as pyromorphite and calamine, are not attacked even on boiling the solution. Cuprite is completely decomposed in the cold, with formation of a bright green crystalline precipitate (CuIO_3 ?). Brucite, calcite, and natrolite, are decidedly attacked on boiling. Anglesite is feebly attacked in the cold, and strongly on heating; cerussite and vivianite appear to be slightly decomposed under the same circumstances. None of these reactions have special interest, except perhaps that of cuprite, which is quite characteristic.

Having continually in mind the possible application of methods to the examination of minerals in the field, and recognizing the impracticability of carrying iodine save in glass bottles, we were led to make another series of experiments with a view to providing iodine in a portable state. To this end, we took advantage of the ready decomposition of potassium iodide by organic acids. That even the weakest acids are able to set hydriodic acid free, in acting on the iodides of the alkaline metals, has been frequently noticed,* and we add the following observations:

When solid potassium iodide is added to strong acetic acid, in the cold, hydriodic acid is set free; and after standing for some time (24-48 hours), this acid decomposes, and the free iodine communicates to the solution a brownish-red color of varying intensity. With free access of air, the liberation of iodine begins at once, as shown by testing the mixture with carbon disulphide. This action is more marked in strong solutions than in weak.

* Dr. Rudolph Boehm, in his *Handbuch der Spec. Pathologie und Therapie*, vol. XV, p. 21, quotes Struve's discovery that even hydro-sodium carbonate decomposes potassium iodide in dilute aqueous solution. This power of carbonic acid has also been observed by Kammerer (*Virchow's Archiv*, LIX, 1874), and Binz (*ibid.*, LXII).

Tartaric and citric acids decompose potassium iodide in a similar manner.

A mixture of any of these organic acids with potassium iodide proves to be a powerful solvent of the natural sulphides. An examination of the seventeen sulphides already mentioned gave the following results:—

BEHAVIOR WITH POTASSIUM IODIDE AND CITRIC ACID.

Stibnite, *argentite*, *sphalerite*, *chalcocite*, *bornite*, and *ullmannite*, are attacked in the cold, with liberation of sulphuretted hydrogen; heat increases the action,—the gas coming off freely.

Galenite acts in the same manner, with formation of yellow crystalline flakes of plumbic iodide. On applying heat, the mineral is completely decomposed.

Cinnabar is also decomposed in the cold, with liberation of sulphuretted hydrogen. On boiling, the decomposition is complete, and crystals of mercuric iodide deposit on cooling,—provided no great excess of potassium iodide is present.

Arsenopyrite is decomposed in the cold, but no sulphuretted hydrogen appears to be set free. On boiling, the decomposition proceeds rapidly.

Pyrrhotite, *chalcopyrite*, and *bournonite* yield no sulphuretted hydrogen in the cold, but freely on heating. The latter is but feebly attacked.

Pyrite, *niccolite* and *smaltite*, give no sulphuretted hydrogen, either cold or hot, though they are strongly attacked on boiling the liquid.

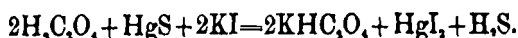
Tetrahedrite is attacked feebly in the cold; on heating, the action is increased.

Molybdenite resists the action of this mixture of reagents.

Similar results were observed with tartaric and oxalic acids, their decomposing power varying. *Cinnabar*, treated with a mixture of potassium iodide and oxalic acid, is decomposed with remarkable facility; the reaction sets in immediately and in the cold; on boiling, the decomposition continues with

violence; and on cooling, the solution deposits white crystals of hydro-potassium oxalate, mixed with scarlet crystals of mercuric iodide.

The probable nature of this reaction is shown in the following equation :



We examined the behavior of a few additional minerals with a mixture of potassium iodide and citric acid, with the results recorded below; but no special interest seems to be attached to this method of attack.

Magnetite is decidedly, and *franklinite* feebly, attacked in the cold, and strongly on heating. *Hematite* is feebly attacked, and *chromite* not at all.

Hausmannite, *pyrolusite*, and the other oxides of manganese, being attacked by citric acid alone, yield, as may be anticipated, deep brown-red solutions colored by the free iodine.

Anglesite and *pyromorphite* are completely decomposed in the cold, with formation of a yellow precipitate of plumbic iodide.

Cuprite is also completely decomposed in the cold, with formation of a yellowish-white precipitate of cuprous iodide, and a colorless solution. If, however, heat be applied at the outset, the same precipitate forms, while the solution is of a blue color.

We also examined the behavior of natural sulphides with a mixture of citric acid and potassium bromide. The latter does not, however, appear to be so easily decomposed as the iodide, and no characteristic phenomena were observed; nearly all the metallic bromides being soluble in water, no precipitates were obtained. In order to avoid repetition, we may briefly summarize the results by stating that, in general, the action of the bromide is less energetic than that of the iodide. Those minerals which yielded only with difficulty to the latter reagent, resist the former even on heating. Cinnabar, whose behavior with the iodide is so remarkable, is but fee-

bly attacked by the bromide. Argentite, galenite, sphalerite, chalcocite, pyrrhotite, pyrite, and chalcopyrite, are attacked in the cold, with or without liberation of sulphuretted hydrogen. Molybdenite resists this mixture of reagents, as well as the others previously mentioned.

In studying the behavior of minerals with organic acids, we obtained results which were embodied in a Table* exhibiting the eleven groups into which minerals are divided by the action of citric acid alone and with reagents. We are now able to add a twelfth group, viz: "minerals decomposed by heating with citric acid [and potassium iodide," and to transfer thereto, from the list of "minerals not decomposed by the above reagents," four species—cinnabar, magnetite, hematite, and franklinite.

Thus of the ninety minerals whose behavior with organic acids and reagents has been examined, only nine resist these methods of attack.

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* Ann. N. Y. Acad. Sci., Vol. I, p. 30.