Br_2 and Br_3^-, and the concentration of Br^- was calculated from the relation $(Br^-)(Br_2)/(Br_3^-) = 0.063$.

The results are arranged in the following table in order of increasing bromine concentration. The data in the last line refer to the saturated solution, the conductance and concentration being taken from the former article.

CONDUCTANCE AND HYDROLYSIS OF AQUEOUS BROMINE SOLUTIONS.

Spec. cond. $\times 10^6$.	Concentrations; Formula weights per liter $\times 10^3$. Total Br_2.	$(H^+)=(HBrO)$.	(Br^-).	(Br_3^-).	(Br_2).	$\frac{(H^+)(Br^-)(HBrO)}{(Br_2)}$.
261	31.4	0.616	0.415	0.201	30.6	5.2×10^{-9}
291	38.3	0.684	0.429	0.255	37.4	5.4×10^{-9}
287	38.5	0.675	0.423	0.252	37.4	5.2×10^{-9}
398	75.4	0.937	0.431	0.506	74.0	5.1×10^{-9}
503	115.8	1.184	0.422	0.762	113.8	5.2×10^{-9}
506	116.4	1.191	0.422	0.769	114.4	5.2×10^{-9}
545	125.1	1.283	0.434	0.849	123.0	5.8×10^{-9}
549	128.9	1.293	0.430	0.863	126.7	5.7×10^{-9}
727	210.0	1.71	0.40	1.31	207.0	5.7×10^{-9}

An examination of the table shows that the hydrolysis constant is

$$(H^+)(Br^-)(HBrO)/(Br_2) = 5.2 \times 10^{-9}.$$

The results are unexpectedly concordant, but the conductances in the second, seventh and eighth experiments appear to be one or two per cent. too high, and have been rejected, because the chief sources of error would lead to high values.

The increase of the hydrolysis constant with the concentration of bromine is probably due to the presence of a polybromide higher than HBr_3, since this would cause the concentrations (given in the table) of Br^- and Br_3^- in these solutions to be too large but would have practically no effect on the concentration of Br_2. Conversely, by assuming the hydrolysis constant to be 5.2×10^{-9}, the concentration of Br^- in the saturated bromine solution may be calculated. By assuming also that the higher polybromide is HBr_5 the composition of the saturated solution is found to be approximately as follows: Bromide, 0.37×10^{-3}; tribromide, 1.21×10^{-3}; pentabromide, 0.13×10^{-3} (sum, 1.71×10^{-3}); bromine as Br_2, 0.2068.

BOSTON.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE CONSTITUTION OF MARCASITE AND PYRITE.[1]

BY GEORGE W. PLUMMER.

Received July 22, 1911.

Attempts have been made at various times to ascertain the state of

---

[1] For the details of this study consult the author's doctoral thesis, 1910.

oxidation of the iron in these two minerals. The following experiments were made with the same object in view. In the first efforts equal quantities of the two minerals were exposed to the action of the vapors of carbon tetrachloride at 250° and then at 300°. The results showed that a large percentage of ferrous iron was present in each mineral. On heating weighed portions of the two minerals in sealed tubes at 250° with carbon tetrachloride, the results indicated that about $^3/_4$ of the iron in each mineral remained in the ferrous state. Sulfur monochloride was formed in each case and the inquiry arose as to whether during its formation reduction may not have occurred. It was, therefore, thought advisable to test the action of sulfur monochloride on iron salts. For this purpose 10 cc. of carbon tetrachloride, together with 0.5 cc. of sulfur monochloride and 0.2 gram of dry ferric oxide, were heated under pressure. The ferrous iron content of the ferric oxide had previously been determined by heating with sulfuric acid. It was found that about 2.5 per cent. of the ferric iron was reduced by the sulfur monochloride. Although the reducing action of sulfur monochloride is thus apparent, it is inappreciable in the experiments with marcasite and pyrite, so it may be said it is unlikely that the ferrous iron found in the two minerals was due to the sulfur monochloride. As a result of later work I am inclined to attribute the results obtained in this study of the behavior of carbon tetrachloride with the minerals to the establishment of an equilibrium between the several by-products. While the behavior of carbon tetrachloride is, at least, interesting in itself, it has thrown very little light upon the constitution of marcasite and pyrite.

Upon exposing portions of the two minerals to the action of a 10 per cent. cadmium sulfate solution at a temperature of 250° marcasite was decomposed to the extent of about 35 per cent. and pyrite to nearly 40 per cent. The relative amounts of ferrous and ferric iron were about the same for each mineral but the values were just the reverse of those obtained by the use of carbon tetrachloride, that is, about 20 per cent. of the iron was found to be in the ferrous state and 80 per cent. in the ferric state. It may be remarked that no trace of hydrogen sulfide, sulfurous acid or other reducing agents, nor indeed of any oxidizing agent, could be detected upon opening the tubes in which the experiments were carried out.

When portions of the two minerals were heated with solid ammonium chloride no difference in effect was apparent. The fact that all the iron was found to be in the ferrous state may be attributed to the reducing action of the ammonium sulfide and hydrogen sulfide which were produced.

On heating portions of the two minerals in a sealed tube with arsenic trichloride, little change was effected. Instead of obtaining yellow arsenic trisulfide, as was expected, the contents of the tube had a deep blue color when removed from the furnace. After filtering out the insoluble material the filtrate still retained its blue color in reflected light, but in transmitted light it was dark reddish brown. The color was probably occasioned by colloidal arsenic, although it was difficult to verify this, owing to the nature of the solvent in which it was present.

By far the most interesting results of this investigation were obtained by the use of bismuth chloride. An intimate mixture of bismuth chloride and the powdered mineral was placed in a porcelain boat which was then heated in a combustion tube, through which a stream of dry carbon dioxide was passed. It was noticed with marcasite that as soon as the melting point of the bismuth chloride was reached, a reaction occurred. The mass became brown in color, due to the formation of what was supposed to be bismuth sulfide, and upon subsequent treatment of the boat and its contents with water, large quantities of soluble iron were found in the solution, which according to qualitative tests appeared to be almost wholly in the ferrous condition. The gases issuing from the tube, however, contained some hydrogen sulfide, which was detected by passing them through an alkaline lead salt solution. Although the bismuth chloride had been heated to drive out all traces of moisture which it contained, during the operation of weighing the sample and preparing the mixture it must have taken up sufficient to account for the presence of the hydrogen sulfide.

The apparatus was accordingly changed to obviate this difficulty. The form decided upon was very simple. It consisted of a seven-inch test tube supported in an upright position and provided with a doubly perforated cork. A delivery and an exit tube were inserted in the cork, the former extending more than half way down the test tube. About 5 grams of bismuth chloride were placed in the test tube, the mouth being left open, and the salt was then heated until its greenish yellow vapors had mounted nearly to the top of the tube. The Bunsen burner flame was played over the whole of the tube to drive out all the water from the upper portions, and immediately upon removing the flame, the cork was inserted and while cooling, a rapid stream of carbon dioxide was passed through the apparatus. During the time required for cooling, the weighing bottle containing the mineral was tared. When room temperature was reached, the cork was removed for an instant and the quantity of the sample to be tested was dropped carefully down the center of the tube. The cork was replaced and the air which may have entered, again displaced by carbon dioxide while determining the weight of the sample by difference. The tube was then heated, as before, the flame being kept constantly in motion in order to prevent sputtering. Five minutes' fusion was sufficient to decompose both marcasite and pyrite completely. The product was allowed to cool in the atmosphere of carbon dioxide and the melt collected in the bottom of the tube in the form of a brown button. This was easily removed when cold and carefully crushed in a mortar to hasten the solution of the iron salts, then dissolved in cold water and washed into a flask of 250 cc. capacity. The tube was also washed several times with water and these washings transferred to the flask, which was subsequently filled to the mark.

By this procedure it was possible to effect the decomposition without the formation of the faintest trace of hydrogen sulfide. The reaction apparently was a simple transposition.

The liquid in the flask contained a precipitate of bismuth oxychloride in addition to the sulfide of bismuth, and in order to determin the iron in solution it was filtered as rapidly as possible through a dry filter and an aliquot part of the filtrate acidulated with sulfuric acid. The ferrous iron was then determined by titrating with potassium permanganate. It was necessary to filter before acidulating, because the quantity of sulfuric acid necessary to add in order to determin the ferrous iron in the presence of the chlorine ions evolved some hydrogen sulfide from the bismuth sulfide when added to the emulsion. The total iron was determined as in the previous experiments, by reducing with zinc and titrating.

The remarkable fact established upon making these titrations was that with both marcasite and pyrite all of the iron was found to be in the ferrous condition. The following table shows the results of some of the determinations made. Over 98 per cent. of the marcasite and over 96 per cent. of the pyrite were decomposed in each of these examples:

RESULTS OBTAINED WITH BISMUTH CHLORIDE.

Mineral.	Weight of sample.	Weight of total iron.	Weight of ferrous iron.
Marcasite	0.2220	0.1014	0.1014
Marcasite	0.3427	0.1579	0.1579
Pyrite	0.2416	0.1072	0.1072
Pyrite	0.2110	0.0955	0.0955

The original solution when acidulated and tested for ferric iron with potassium thiocyanate gave but the faintest pink color, but this may have been occasioned by oxidation during the manipulation.

In order to determin whether the ferrous iron so obtained can be considered as original ferrous iron in the minerals, it was next necessary to determin the quantity of sulfur existing as bismuth sulfide at the completion of the reaction. If all the sulfur were converted by a simple transposition into bismuth sulfide, the amount of hydrogen sulfide liberated from this by the action of hydrochloric acid should contain all the sulfur originally present in the mineral. Accordingly experiments were carried out to determin if such were the case. Since the melt obtained in making the fusion, when crushed, did not easily admit of the removal and collection of all the insoluble bismuth sulfide, and since it was not readily disintegrated by water alone, it was placed directly in the generating flask without removing the soluble ferrous chloride. Those parts of the test tube in which the fusion was made, which were coated with any deposit whatever, were likewise broken up and put in the flask with the melt. The sulfur determination was then made according to one of the common methods, *i. e.*, by pouring 1 : 1 hydrochloric acid upon the sulfide and collecting the hydrogen sulfide evolved in ammoniacal hydrogen peroxide. The sulfuric acid was then determined in this solution in the usual way. The results obtained are here appended:

Table Showing the Amount of Sulfur in Marcasite and Pyrite Converted into Bismuth Sulfide.

Mineral.	Weight of sample.	Weight of total sulfur.	Weight of sulfur in bismuth sulfide.	Pecentage of conversion.
Marcasite	0.1964	0.1045	0.0956	91.4
Marcasite	0.2182	0.1163	0.1060	91.2
Pyrite	0.2162	0.1152	0.1056	91.7
Pyrite	0.2222	0.1184	0.1093	92.4

The extent to which the mineral was decomposed was determined in each of these experiments by titrating the iron in the generating flask with a solution of potassium dichromate, 1 cc. of which was equivalent to 0.0047 gram of iron. Potassium permanganate could not be used for this purpose on account of the large excess of hydrochloric acid present. Complete decomposition had occurred in each case. The quantity of sulfur had already been determined in each mineral, and since the mean of several determinations was very close to the theoretical amount, 53.33 per cent., that value was used in calculating the total sulfur to be expected in the bismuth sulfide.

The fact that some of the sulfur was not in the form of bismuth sulfide, as is shown by a glance at the table, led to a closer study of the reaction, and it was found that some of it was evolved in the form of sulfur monochloride during the fusion. The fact would rather indicate the presence of some free sulfur in the reaction and possibly this may account for the presence of some of the ferrous iron. The 9 per cent. of sulfur, however, which is not converted into bismuth sulfide, would be insufficient to reduce as much as 20 per cent. of the iron present, even if it had an opportunity of acting upon ferric chloride. This is stated conditionally, because it is thought very probable that the sulfur does not reduce any ferric chloride, the reason being that on fusing free sulfur with bismuth chloride, the products obtained are bismuth sulfide and sulfur monochloride. It may be argued from this fact that since the quantity of bismuth chloride is always in large excess, any free sulfur would very likely be taken up by it to form the sulfur monochloride observed, simultaneously with, if not before, the formation of the chloride of iron. Hence the conclusion to be drawn as a result of the study of the behavior of marcasite and pyrite with bismuth chloride would be that each mineral contains its iron wholly in the ferrous state. The formula representing them would then have the following configuration: 

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE USE OF SULFUR MONOCHLORIDE IN THE DETERMINATION AND ANALYSIS OF THE RARE EARTH MINERALS.[1]

BY WILLIAM BROOKS HICKS.

Received July 22, 1911.

Many of the rare earth minerals contain columbium, tantalum and titanium as their acid components. The usual methods of decomposing such minerals are fusion with potassium bisulfate, bifluoride or by treatment with hydrofluoric acid. Each of these methods present difficulties. Fusion with potassium bisulfate is most generally used, but even when one fusion is sufficient to effect the decomposition the resulting mixture containing all the earths is difficult to handle, particularly when a quantitative separation of the metallic acids from the other constituents is desired. On the other hand, the fluoride methods lend themselves to cleaner and more rapid separations but are objectionable because they preclude the use of glass vessels. The present investigation introduces sulfur monochloride as a decomposing agent of such minerals and it is applied in their analysis. Smith,[2] who was the first one to use sulfur monochloride in the decomposition of minerals, showed that many naturally occurring sulfides, as well as rutile, wolframite, scheelite and columbite, were decomposed by this reagent. Oddo and Serra,[3] two Italian chemists, used it in the preparation of anhydrous chlorides of arsenic, antimony and bismuth, while Hall[4] applied it to the preparation of pentachloride of columbium. He also observed that it decomposed such minerals as chromite and columbite and that it converted many oxides into their corresponding chlorides, the notable exceptions being the oxides of boron and silicon. Bourion[5] has used sulfur monochloride in the preparation of anhydrous chlorides in general as well as for the decomposition and analysis of scheelite and wolframite. It, therefore, seemed probable to me that this reagent might decompose such minerals

---

[1] Details may be found in the author's inaugural thesis, Univ. of Penna., 1911.

[2] THIS JOURNAL, 22, 289 (1898).

[3] *Gaz. chim. ital.*, [2] 29, 355 (1899).

[4] THIS JOURNAL, 26, 1243 (1904).

[5] *Ann. chim. phys.*, 20, 547 (1910).