and *D*, are also triangular in shape, with edges parallel to the rhombohedral edges, and measure respectively, *C* four and five-tenths mm. by four and five-tenths by three mm., and for *D* three by three by two mm., both about five-tenths mm. thick.

These two cavities also contain oil with a globular space in the center, which can be seen to move about when the crystal is turned.

The cavities *E* and *F*, *F*, *F*, are quite small, but can be readily seen by the naked eye, and are full of oil with the exception of a minute globule of gas.

F, *F*, and *F* are the same cavity, being seen by refraction from the three faces.

The evidence of the character of the oil is not chemical, but yet sufficient to identify it.

It presents the appearance of petroleum in that it has the yellow green fluorescence. Some crystals from the same source were crushed in filter-paper, and the paper having absorbed the oil, showed the grease spot and gave the characteristic odor of petroleum and burned with a smoky flame.

Another evidence of the nature of the liquid is that petroleum occurs in the neighborhood where the crystals were found.

The specific gravity of crystal No. 2 is 2.6123.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 31.]

I. METAL SEPARATION BY MEANS OF HYDROBROMIC ACID GAS. II. INDIUM IN TUNGSTEN MINERALS.[1]

BY ELIZABETH ALLEN ATKINSON.

Received September 2, 1898.

INTRODUCTION.

THE application of hydrochloric acid gas as a means of separating metals has proved very successful. By means of this agent Moyer[2] volatilized the oxides of bismuth and antimony completely, separating bismuth from lead and copper, and antimony from copper and lead. In addition, this mode of analysis afforded him separations of arsenic from copper, lead, cadmium, silver, cobalt, and nickel.

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[1] From author's thesis presented for the degree of Doctor of Philosophy.

[2] This Journal, 18, 1029; Thesis.

Hibbs[1] had previously separated arsenic acid from phosphoric acid and tungstic acid, as well as molybdic acid from phosphoric acid, while Smith and Meyer,[2] in studying the action of haloid acids in gas form upon the salts of the elements of Group V, had observed many interesting facts, of which some have already been utilized in effecting separations, while others still remain for development.

It is natural to suppose that in these cases, when hydrochloric acid has been shown to be an effective and satisfactory separating agent, if it be replaced by hydrobromic acid gas, or any haloid acid gas, the results can almost be predicted. However, experiment alone can demonstrate the correctness or falsity of this assumption. To that end the experiments recorded in the following pages were instituted and carried out along lines almost exactly like those followed by Moyer[3] in order that a fair comparison could be made.

Meyer and Smith[4] had noticed that hydrobromic acid gas expelled arsenic and vanadic acids from their salts. Kelley and Smith[5] found that arsenic in the form of sulphide was also decomposed and volatilized in an atmosphere of hydrobromic acid gas. Antimony sulphide behaved similarly. It would be interesting to subject other metallic sulphides to this reagent, for it is very probable that some of them would be volatilized as readily as happens when they are exposed to heated hydrochloric acid gas. In this latter way, Smith and Field[6] succeeded in separating arsenic from vanadium, thus obtaining a most accurate and satisfactory mode of separating these two metals.

I. METHOD OF WORK.

Hydrobromic acid gas was generated by dropping bromine from a separatory funnel on anthracene contained in a liter flask. Five drops a minute will give a good steady flow of the gas. The flask was placed on a water-bath in which the water was kept very near to the boiling-point.

The gas was passed through a tube containing anthracene, to

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[1] This Journal, 17, 682.

[2] *Ibid.*, 17, 735.

[3] *Loc. cit.*

[4] *Loc. cit.*

[5] This Journal, 18, 1096.

[6] *Ibid.*, 18, 1051.

absorb any bromine that might be carried over, and then through a calcium-chloride tube, for absorption of moisture.

The substance to be acted upon was weighed out in a porcelain boat and placed in a combustion tube, which had been thoroughly dried. This tube was connected with the receiver by a bent tube provided with a stop-cock, which is necessary, as when the heat is removed there is danger of backward suction. The volatile substances were collected in water, with the exception of arsenic, in which case dilute nitric acid was used. The heat was obtained from a series of three fish-tail burners.

PREPARATION OF ANTIMONY TRIOXIDE.

Metallic antimony was ground in a mortar and treated with dilute nitric acid. The resulting metantimonic acid was dissolved in hydrochloric acid, and the oxychloride precipitated by an excess of water, washed thoroughly by decantation, dissolved in hydrochloric acid, and again precipitated. This procedure was repeated several times, and finally the antimony was precipitated by ammonium carbonate, filtered, washed, dried, and ignited to constant weight.

ACTION OF HYDROBROMIC ACID GAS ON ANTIMONY TRIOXIDE.

A slow current of the gas was passed over the oxide for one hour and a half. The first fifteen minutes in the cold; for an hour by heat given from a flame a half inch high, from three fish-tail burners placed two inches below the tube resting in an iron gutter.

At the end of the hour all the antimony had volatilized. The gas was then passed fifteen minutes in the cold, to insure the expulsion of all the volatilized bromide.

In the first experiments the tube containing the boat with the substance was run through holes in the ends of a drying oven. This oven was heated by means of a Bunsen burner. This method of heating had the advantage over that in which a direct flame was used, in that the exact temperature could be noticed by means of a thermometer.

After various experiments, I found it more satisfactory to be able to watch the reaction. The flow of gas and the heat could then be regulated so that the most satisfactory results could be obtained.

The volatilization of the antimony bromide could be somewhat hurried if a more rapid current of the gas was used, and a higher temperature allowed, but in view of the fact that this method was to be used as a means of separation from bromides of other metals that were slightly volatile at a high heat, I followed the above conditions.

PREPARATION OF LEAD OXIDE.

Pure lead acetate was ignited ; the residue was dissolved in nitric acid, evaporated to dryness, and ignited to constant weight.

ACTION OF HYDROBROMIC ACID GAS ON LEAD OXIDE.

Hydrobromic acid gas was passed over the oxide for two hours, using a slightly higher temperature than with the antimony. The tubes were washed into the receiver and the tests made for lead. It was not present, proving that lead had not volatilized.

An amount by weight of the oxide was treated as above. After allowing it to cool in an atmosphere of the gas, the boat and its contents were removed to a desiccator, and after standing a half hour they were weighed.

The results indicated that the residue remaining in the boat was not lead bromide, but evidently a mixture of lead oxide and bromide. The boat and its contents were returned to the tube, and the reaction with the gas continued for one hour, when the boat was allowed to cool, and again weighed. It had gained in weight, indicating that more of the oxide had been changed into bromide. This led me to suppose that if the action of the gas was continued long enough all the oxide could be converted into bromide. This proved to be erroneous, as the weights taken after the substance had been exposed to the gas for four hours and for five hours were the same.

The following series of seven results seem to show that the compound obtained has the formula $PbO.5PbBr_2$:

Experiment.	PbO taken. Gram.	$PbO.5PbBr_2$ obtained. Gram.	$PbO.5PbBr_2$ required. Gram.	Difference. Gram.
1	0.1059	0.1626	0.1624	0.0002
2	0.1209	0.1862	0.1859	0.0003
3	0.1314	0.2029	0.2016	0.0013
4	0.1649	0.2534	0.2530	0.0004
5	0.2046	0.3150	0.3139	0.0011
6	0.1475	0.2270	0.2263	0.0007
7	0.1145	0.1747	0.1756	0.0009

Moyer's experiments with hydrochloric acid gas on lead oxide indicated that all the oxide changed completely into chloride, in the cold, in two hours, and that this chloride slightly volatilized at a temperature above 225°. His chloride completely dissolved in hot water. My compound, on treatment with hot water, left a small black residue.

THE SEPARATION OF ANTIMONY FROM LEAD.

The oxides were thoroughly mixed in a boat and the hydrobromic acid gas passed over them for one hour and a half. The same conditions were observed as when antimony was treated alone.

In experiments 1 and 2 the antimony was estimated as oxide; in the third experiment as sulphide.

Experiment.	Sb_2O_3 taken. Gram.	Sb_2O_3 found. Gram.	Difference. Gram.
1	0.1248	0.1248	0.0000
2	0.1042	0.1032	0.0012
3	0.1180	0.1174	0.0006

In the third experiment the treatment with the gas was continued until a constant weight was obtained for the residue in the boat. The compound which resulted corresponded to the formula $PbO.5PbBr_2$.

Experiment.	PbO taken. Gram.	$PbO.5PbBr_2$ obtained. Gram.	$PbO.5PbBr_2$ required. Gram.	Difference. Gram.
1	0.1180	0.1808	0.1813	0.0005

In the other two experiments compounds were obtained that did not even approximate any definite formula.

By this method a clean separation of antimony from lead may be effected.

PREPARATION OF BISMUTH OXIDE.

Commercially pure bismuth nitrate was dissolved in nitric acid and the oxynitrate precipitated by an excess of water, washed by decantation, filtered, dissolved in nitric acid, and reprecipitated by water. This operation was repeated several times. Finally the oxide was dissolved in nitric acid and precipitated with ammonium hydroxide and ammonium carbonate from a boiling solution. The basic carbonate, ignited to constant weight, gave pure bismuth trioxide.

ACTION OF HYDROBROMIC ACID GAS ON BISMUTH TRIOXIDE.

Hydrobromic acid gas was passed over a weighed amount of bismuth oxide for two hours and a half, the first thirty minutes in the cold; it was then gradually heated until the last half hour, during which time a flame was used from a fish-tail burner a half inch high, placed two inches below the tube.

The bismuth bromide was not so volatile as the antimony salt, but at the end of two hours and a half it was all volatilized if the above conditions had been observed. It first sublimed above the boat and could then be easily driven out of the tube.

The bismuth collected in the receiver was evaporated to dryness, taken up with nitric acid, and placed in a weighed crucible, when the solution was evaporated to dryness and taken up with nitric acid. This operation must be repeated several times, or the oxybromide which may be formed, is not entirely broken up. It was finally weighed as bismuth trioxide.

The following results were obtained :

Experiment.	Bi_2O_3 taken. Gram.	Bi_2O_3 found. Gram.	Difference. Gram.
1	0.1954	0.1954	0.0000
2	0.1575	0.1577	0.0002
3	0.1529	0.1534	0.0005

THE SEPARATION OF BISMUTH FROM LEAD.

The two oxides were thoroughly mixed in a porcelain boat. The hydrobromic acid gas was passed over them for two hours and a half. The same conditions were maintained as for the volatilization of the bismuth alone.

The following results were obtained :

Experiment.	Bi_2O_3 taken. Gram.	Bi_2O_3 found. Gram.	Difference. Gram.
1	0.1002	0.1006	0.0004
2	0.1356	0.1360	0.0004

The lead compound in the boat contained no bismuth, and the volatile sublimate showed, on appropriate tests, that lead was absent.

This separation cannot be carried out as rapidly as the separation of antimony from lead, owing to the less volatility of bismuth.

Moyer met difficulties in the separation of bismuth from lead by means of hydrochloric acid gas, owing to the fact that a little of the lead chloride volatilized at a temperature as low as 180°.

In the experiments with hydrobromic acid gas, I did not notice that any of the lead volatilized at a temperature necessary to volatilize the bismuth, but a slow current of the gas was best, as otherwise some of the lead was mechanically driven out with the bismuth.

Moyer found that it took from seven to eight hours to volatilize all of the bismuth by means of hydrochloric acid gas. My results show that it can be done with hydrobromic acid gas in two hours and a half.

The residue in the boat was weighed, but in no case did it correspond to a definite compound.

THE PREPARATION OF COPPER OXIDE.

Copper nitrate was recrystallized several times, and was then ignited to constant weight.

ACTION OF HYDROBROMIC ACID GAS ON COPPER OXIDE.

The hydrobromic acid gas was passed over the pure, black oxide for two and one-half hours, the same conditions being observed as with bismuth. On testing the contents of the receiver, copper was found to be absent.

SEPARATION OF BISMUTH FROM COPPER.

Pure bismuth oxide and copper oxide were weighed and thoroughly mixed, and then exposed to the action of hydrobromic acid gas for two and one-half hours. The conditions noted under bismuth were observed here.

The volatile bismuth bromide was collected in a receiver containing water and estimated by the method already described.

The copper compound remaining in the boat had various colors, always green when hot and usually grayish white when cold; but its weight, whatever its color, always corresponded to the formula CuBr. The compound held tenaciously to hydrobromic acid gas, so it was necessary to allow it to stand over soda-lime for at least forty-five minutes before weighing. The first few experiments gave varying results, because the heat used was too low, and the major part of the copper compound remained as cupric bromide in beautiful iodine-like crystals; but when sufficient heat was applied to volatilize all of the bismuth, the higher copper bromide was decomposed, the bromine coming off in clouds.

Moyer found that at the temperature necessary to volatilize bismuth chloride the cupric chloride was not decomposed, and that it could be weighed directly as that salt.

The following results were obtained, using this method of separation:

Experiment.	Bi_2O_3 taken. Gram.	Bi_2O_3 found. Gram.	Difference. Gram.
1	0.1273	0.1277	0.0004
2	0.1111	0.1121	0.0010
3	0.1162	0.1170	0.0008

Experiment.	CuO taken. Gram.	CuBr found. Gram.	CuBr required. Gram.	Difference. Gram.
1	0.1103	0.2010	0.1996	0.0014
2	0.1318	0.2385	0.2394	0.0009

SEPARATION OF ANTIMONY FROM COPPER.

The same material was used as in the preceding experiments. The weighed oxides were thoroughly mixed. The antimony bromide was completely volatilized in one and a half hours, leaving cuprous bromide in the boat. The same care was exercised as in the separation of bismuth from copper, to insure the decomposition of the cupric bromide to cuprous bromide.

The volatile antimony bromide was collected in water.

At the close of the reaction the tubes and bulb were washed out with acidulated water, and the antimony precipitated with hydrogen sulphide water. The antimony sulphide was then filtered through a tared filter, the precipitate washed with alcohol, with carbon disulphide, again with alcohol, and finally with a mixture of alcohol and ether. It was then dried at from 105° to 110° in the air-bath, and weighed. The copper was weighed as cuprous bromide.

This bromide, as before mentioned, had various colors, running from a light gray through yellow and green to almost a black.

The copper bromide obtained contained no antimony, and the volatile antimony compound was entirely free from copper.

Experiment.	CuO taken. Gram.	CuBr found. Gram.	CuBr required. Gram.	Difference. Gram.
1	0.1025	0.1853	0.1855	0.0002
2	0.1218	0.2210	0.2204	0.0006
3	0.1137	0.2059	0.2058	0.0001

Experiment.	Sb_2O_3 taken. Gram.	Sb_2S_3 found. Gram.	Sb_2S_3 required. Gram.	Difference. Gram.
1	0.1250	0.1465	0.1458	0.0007
2	0.1181	0.1385	0.1377	0.0008

PREPARATION OF COPPER ARSENATE.

Commercial, chemically pure sodium arsenate was recrystallized three times and then gently ignited for one hour. Pyroarsenate resulted. Copper sulphate was recrystallized three times. A solution of this salt was mixed with a solution of the pure pyroarsenate, when green copper arsenate was precipitated. It was washed repeatedly and dried in an air-bath at 100°.

Salkowski[1] states that copper arsenate still contains water above 130°. Moyer worked with a salt with the composition $Cu_3As_2O_8.2H_2O$. My salt prepared by the same method had the same composition.

SEPARATION OF ARSENIC FROM COPPER.

The weighed copper arsenate was exposed to the action of the hydrobromic acid gas for two hours—fifteen minutes in the cold, one hour with the flame of three fish-tail burners a quarter of an inch high, a half an hour with flame an inch high from the same burners, and finally fifteen minutes in the cold.

The arsenic and water were driven out at the low heat. Higher heat decomposed the cupric bromide into cuprous bro-

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[1] *J. prakt. Chem.*, 104, 124.

mide and bromine. The cuprous bromide may be weighed in that condition after it has stood over soda-lime for forty-five minutes. Its color varied as it did in the other experiments already described.

The arsenic was washed out of the bulb into a beaker, warmed with nitric acid to insure oxidation, and precipitated from an ammoniacal solution with a magnesium solution. It was finally weighed as magnesium pyroarsenate.

The results follow :

Experiment.	$Cu_3As_2O_8 + 2H_2O$ taken. Gram.	CuBr obtained. Gram.	CuBr required. Gram.	Difference. Gram.
1	0.1227	0.1054	0.1046	0.0008
2	0.1238	0.1051	0.1055	0.0004
3	0.1137	0.0958	0.0969	0.0011

Experiment.	$Cu_3As_2O_8 + 2H_2O$ taken. Gram.	$Mg_2As_2O_7$ obtained. Gram.	$Mg_2As_2O_7$ required. Gram.	Difference. Gram.
1	0.1238	0.0766	0.0762	0.0004

PREPARATION OF SILVER ARSENATE.

The pure sodium pyroarsenate prepared as before described, was precipitated with silver nitrate. The nitrate was kept in excess. The reddish brown precipitate was washed with boiling water until the filtrate ceased to show the presence of silver when tested with hydrochloric acid. The silver arsenate was dried at 110°.

SEPARATION OF ARSENIC FROM SILVER.

Hydrobromic acid gas attacked the silver arsenate in the cold, forming yellow silver bromide. In the following experiments the salt was exposed to the action of the gas for one hour and a quarter. The reaction was allowed to take place for a half hour in the cold, and for thirty minutes a low heat was used. The resulting bromide was allowed to cool in the gas. Silver was not present in the receiver, and the silver bromide also proved to be free from arsenic.

The silver bromide was weighed as such. The arsenic was estimated as magnesium pyroarsenate.

Experiment.	Ag_3AsO_4 taken.	AgBr obtained.	AgBr required.	Difference.
	Gram.	Gram.	Gram.	Gram.
1	0.1783	0.2174	0.2171	0.0003
2	0.1990	0.2429	0.2424	0.0005
3	0.1677	0.2050	0.2042	0.0008

Experiment.	Ag_3AsO_4 taken.	$Mg_2As_2O_7$ obtained.	$Mg_2As_2O_7$ required.	Difference.
	Gram.	Gram.	Gram.	Gram.
1	0.1677	0.0561	0.0561	0.0000

PREPARATION OF CADMIUM ARSENATE.

Cadmium sulphate was recrystallized three times and then precipitated by a solution of sodium pyroarsenate. A white gelatinous salt was precipitated, which, upon stirring, became granular. The salt was washed thoroughly and dried at 110°.

Salkowski[1] had previously prepared this salt and observed that a red heat was necessary to completely dehydrate it. Moyer's salt contained two molecules of water. My salt also had the composition $Cd_3As_2O_8 + 2H_2O$.

SEPARATION OF ARSENIC FROM CADMIUM.

The hydrobromic acid gas was passed over the arsenate for one hour and a half, the same conditions being maintained as for the silver arsenate. The arsenic in the receiver showed no trace of cadmium. The cadmium in the boat was transformed into the white bromide, and was free from arsenic. It was weighed as cadmium bromide. The arsenic was determined as magnesium pyroarsenate.

Experiment.	$Cd_3As_2O_5 + 2H_2O$ taken.	$CdBr_2$ obtained.	$CdBr_2$ required.	Difference.
	Gram.	Gram.	Gram.	Gram.
1	0.1041	0.1294	0.1306	0.0012
2	0.1104	0.1378	0.1385	0.0007
3	0.1168	0.1471	0.1472	0.0001

Experiment.	$Cd_3As_2O_8+2H_2O$ taken.	$Mg_2As_2O_7$ obtained.	$Mg_2As_2O_7$ required.	Difference.
	Gram.	Gram.	Gram.	Gram.
1	0.1041	0.0485	0.0494	0.0009

PREPARATION OF COBALT ARSENATE.

A solution of pure cobalt nitrate was precipitated by a solution of pure sodium pyroarsenate. The purplish-pink salt having the formula $Co_3As_2O_8 + 2H_2O$ was precipitated. It was

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[1] *Loc. cit.*

thoroughly washed by decantation, and then gently ignited, until its weight was constant; the blue, anhydrous salt resulted.

SEPARATION OF ARSENIC FROM COBALT.

The hydrobromic acid gas attacks the cobalt arsenate in the cold, but the reaction takes place sooner if a low heat is applied. The blue arsenate is changed first to a pink bromide; this, on the application of heat changed to a dark green, anhydrous bromide. The low heat of 130° volatilized all the arsenic, leaving all of the cobalt in the boat. The arsenic was estimated in the usual manner.

The boat with its contents, after being cooled in a current of hydrobromic acid gas, and then standing in a desiccator for fifteen minutes, was weighed. Notwithstanding that it absorbs water rapidly, the weight was low if it was calculated as cobalt bromide.

In the first experiment the material taken was 0.1384 gram, the compound weighed 0.1640 gram. If the cobalt compound were cobalt bromide, it should weigh 0.2002 gram. The weight of the compound obtained, 0.1640 gram, is eighty-nine per cent. of the weight required.

In the second experiment, the cobalt arsenate taken was 0.1382 gram; the compound obtained weighed 0.1630 gram. If the cobalt compound were cobalt bromide it should have weighed 0.1999 gram. The weight of the compound obtained, 0.1630 gram, is only 81.5 per cent. of the required weight.

These results led to the conclusion that an oxybromide of indefinite composition is formed.

The next step was to heat the cobalt bromide in a stream of hydrogen, obtaining the metal.

The following satisfactory results were obtained:

Experiment.	$Co_3As_2O_8$ taken. Gram.	Co obtained. Gram.	Co required. Gram.	Difference. Gram.
1	0.1382	0.0525	0.0531	0.0006
2	0.1244	0.0475	0.0478	0.0003
3	0.1228	0.0473	0.0472	0.0001

Experiment.	$Co_3As_2O_8$ taken. Gram.	$Mg_2As_2O_7$ obtained. Gram.	$Mg_2As_2O_7$ required. Gram.	Difference. Gram.
1	0.1384	0.0943	0.0949	0.0006
2	0.1382	0.0945	0.0947	0.0002

PREPARATION OF IRON ARSENATE.

Chemically pure ferrous ammonium sulphate was dissolved in water and oxidized with nitric acid, and the ferric salt was crystallized from the solution. The best crystals were dissolved in water and precipitated by a solution of pure sodium pyroarsenate. The yellowish precipitate was washed by decantation, filtered, and the washing continued until the filtrate gave no precipitate with potassium ferrocyanide. The salt was then dried and gently ignited. It is necessary that this ignition should be carefully carried out, as there is danger of decomposing the salt.

SEPARATION OF ARSENIC FROM IRON.

The results were unsatisfactory. The acid gas acted very energetically on the arsenate. Even in the cold the bromide formed creeps over the sides of the boat, its contents becoming a reddish brown liquid. Unless the current of gas is very slow, and the heat applied very gently, the contents will spatter. The final product was a beautiful red compound, which took up water rapidly. It was dissolved in hydrochloric acid, oxidized with nitric acid, and the iron precipitated with ammonia. Several experiments were carried out; in every case the iron content was low. I was unable to account for this loss, as there was no iron present with the volatile arsenic in the receiver. The residue in the boat was free from arsenic.

BEHAVIOR OF MINERALS IN HYDROBROMIC ACID GAS.

Galenite.—A weighed amount of the mineral was placed in the boat and exposed to the action of the hydrobromic acid gas for two hours. For one hour of the time a temperature of 100° was maintained. Before the heat was applied hydrogen sulphide was evolved. After heating, the antimony in the galenite was volatilized and carried over into the receiver, where it was precipitated by the hydrogen sulphide that had been collected in the water, as the orange-colored sulphide of antimony. Tests were applied to the residue in the boat, and it was found to be free from antimony. The volatile products showed no lead, indicating a method for the decomposition and estimation of mineral sulphides that may prove more satisfactory than the present, often tedious, processes.

Smith and Hibbs[1] previous to this have shown that mimetite loses its arsenic quantitatively when heated in a stream of hydrochloric acid gas. Moyer found in his investigation that niccolite, exposed to the action of hydrochloric acid gas, was only slightly affected. If the niccolite was first dissolved in nitric acid and after evaporation to dryness, exposed to the gas, it was completely decomposed, giving a quantitative separation of the arsenic from the nickel.

SUMMARY.

A comparison of the results obtained in separating metals by means of hydrobromic acid gas, and those resulting through the action of hydrochloric acid gas, leads to the conclusion that those metals thus far studied that are volatile in one gas are volatile in the other, and that the same separations may be effected. The principal difference lies in the length of time which is required to make a separation.

The chlorides of antimony and bismuth require from six to eight hours for their complete volatilization. Antimony bromide can be entirely driven out in one hour and a half. The bismuth requires about an hour longer. In the case of arsenic, both the chloride and the bromide are volatilized in an hour and a half.

Some of those metals which do not form volatile compounds with the respective gases, have a tendency in the case of hydrobromic acid, to form oxybromides; the lead compound approximating the formula $PbO.5PbBr_2$, while the lead chloride can be weighed directly as $PbCl_2$. Cobalt also forms an oxybromide, while the chloride compound is probably free from oxygen.

After the reaction is finished between the hydrobromic acid gas and copper, cuprous bromide is the result; in the case of hydrochloric acid gas it remains as the cupric compound.

Silver is changed to the chloride and bromide by the action of the respective gases. Cadmium is also changed to a non-volatile chloride and bromide.

Unsatisfactory results were obtained by the use of both reagents in an attempt to separate arsenic from iron.

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[1] *Loc. cit.*

II. INDIUM IN TUNGSTEN MINERALS.

It was about the year 1866 that Hoppe-Seyler,[1] while engaged in the analysis of wolframite from Zinnwald, discovered that indium was present in it.

He obtained 0.028 gram of indium from 122.6 grams of the mineral. He believed that as the latter contained zinc, the indium was probably present in the zinc blende, inasmuch as the quantity of indium found by him was not very much greater than that contained in Freiberg zinc blende. Thinking that indium might possibly be a constant, regular constituent of tungsten-bearing minerals, I resolved to examine some of the latter for this interesting ingredient. The results are appended.

WOLFRAMITE FROM ZINNWALD.

Three hundred grams of wolframite from Zinnwald were ground and then treated with aqua regia. Several days were required for the complete decomposition of the mineral. The acid solution was then evaporated to dryness, and the residue moistened with dilute hydrochloric acid and taken up with water. The acid was neutralized with sodium carbonate; sodium acetate and a few drops of acetic acid were added. Hydrogen sulphide was then passed through this solution until it was thoroughly saturated with the gas. A yellowish brown precipitate at first came down, soon followed by a black precipitate. These were filtered, redissolved in hydrochloric acid, and the treatment outlined above repeated. It was found necessary to repeat several times before a pure yellow precipitate was obtained.

This yellow compound was dissolved in hydrochloric acid and when examined with the spectroscope gave the bright blue line of indium. The hydrochloric acid solution, upon treatment with ammonium hydroxide, precipitated a white gelatinous mass. This was filtered, dried, and ignited, when a yellow residue remained, which was the oxide of indium. Its weight was 0.0145 gram.

The filtrate from the indium hydroxide was evaporated to a small bulk, and treated with ammonium hydroxide. The solution was bright blue, and on treatment with ammonium sulphide

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[1] *Ann. Chem.* (Liebig), 140, 247.

gave a grayish, chocolate-colored precipitate. This all dissolved in dilute hydrochloric acid, with the exception of a black sediment. A copper bead was obtained with this insoluble portion.

Hydrogen sulphide when passed through the filtrate gave no precipitate, but after neutralizing with ammonium hydroxide and adding ammonium sulphide, a dirty white precipitate came down. This gave Rinman's green, an evidence of zinc.

WOLFRAMITE FROM CORNWALL, ENGLAND.

The mineral was an impure specimen. After it was broken into small pieces, the purest portions were ground up, and 300 grams were treated with aqua regia. The solution was poured off, the mineral again treated with acid, and the solution added to the first one. This treatment was continued until all of the mineral was decomposed.

The aqua regia solution was evaporated to dryness, taken up with hydrochloric acid and water, and after neutralization with sodium carbonate and addition of sodium acetate and acetic acid, was treated with hydrogen sulphide gas. The precipitate obtained was reddish brown in color. It dissolved in hydrochloric acid. When examined with the spectroscope, indium could not be discovered.

The hydrochloric acid solution was then examined as under the Zinnwald wolframite, but no zinc could be detected.

HÜBNERITE FROM COLORADO.

One hundred and fifty grams of hübnerite from Colorado were treated with aqua regia, and the further treatment for the isolation of indium, as already outlined, was carried out. Hydrogen sulphide caused a reddish precipitate, which dissolved in hydrochloric acid, and proved not to be indium. Zinc was also absent.

SCHEELITE FROM NEW ZEALAND.

Two hundred and fifty grams of this mineral were decomposed with aqua regia. There resulted the usual reddish precipitate with hydrogen sulphide in the acetate solution.

The hydrochloric acid solution when tested with the spectroscope gave a blue line, which at first was thought to be the indium line; but on closer examination it proved to be the strontium line. The indium and strontium lines lie close together. The line which I found had a wave-length of 4.61×10^{-5}, corresponding to the line Sr_ρ; whereas the indium lines are In_α 4.51×10^{-5} and In_β 4.10×10^{-5}.

The acid solution, neutralized with sodium carbonate, gave a white precipitate; on drying, a yellow powder was obtained, which proved to be calcium corbonate. Zinc was not present.

SCHEELITE FROM BOHEMIA.

A pure specimen of this mineral was subjected to the same treatment as has been described. The same results were obtained. No indium could be detected and the absence of zinc was proved.

The care exercised in the selection of material, and the large quantities employed, while working with every precaution, would seem to justify the conclusion that indium cannot be regarded as an associate of tungsten in its natural derivatives; that most probably the suspicion of Hoppe-Seyler in regard to its origin, *viz.*, blende, is correct, for it was only in the Zinnwald specimen that I could detect it.

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NEW BOOKS.

EXPLOSIVE MATERIALS. The Phenomena and Theories of Explosion and the Classification, Constitution, and Preparation of Explosives. BY 1ST LIEUT. JOHN P. WISSER, 1st Art., U. S. A. New York: D. Van Nostrand Company. 1898. Price, 50 cents.

This little book, which is issued as No. 70 in Van Nostrand's Science Series, bears the same leading title as the No. 70 of this series issued in 1883, but, while the contents of the 1883 edition consisted of a translation of "Berthelot's Lecture on Explosive Materials" by Dr. Marcus Benjamin, a translation of "Braun's Historical Sketch of Gunpowder" by Lieut. John P. Wisser, and a "Bibliography of Works on Explosives" by W. H. Farrington, the present edition contains an original essay by Lieut. Wisser only, which is based upon the lecture of Berthelot, but, which includes the more recently adopted theories, and much descriptive matter. Where considerable space is given to the display of graphic formulas of substances used in the manu-