VOL. XVIII. [DECEMBER, 1896.] NO. 12.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY. NO. 14.]

METAL SEPARATIONS BY MEANS OF HYDROCHLORIC ACID GAS.[1]

BY J. BIRD MOYER.

Received September 26, 1896.

INTRODUCTION.

THE action of gaseous haloid acids upon metallic oxides and their salts, is a field of investigation, which, though not of recent origin, has been but lately developed. It was Debray[2] who first called attention to the volatility of molybdic acid in a stream of hydrochloric acid gas, with the formation of $MoO(OH)_2Cl_2$.

E. Péchard[3] applied this and showed that molybdic acid was completely eliminated and separated from tungstic acid, by its volatility in a current of hydrochloric acid. Since that time nothing further has been done with single haloid acids, in gas form, until quite recently. Compounds have been decomposed, salts volatilized, and separations made, by means of other gases and mixtures, which may be as effective as hydrochloric acid, but are not devoid of trouble nor nearly so neat.

Smith and Oberholtzer[4] repeated and confirmed Péchard's

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[1] From author's thesis presented to the Faculty of the University of Pennsylvania for the degree of Doctor of Philosophy, 1896.

[2] *Compt. rend.*, **46** 1098, and *Ann. Chem.* (Liebig), **108**, 250.

[3] *Compt. rend.*, **114**, 173.

[4] *J. Am. Chem. Soc.*, **15**, 1.

work in regard to the separation of molybdic acid from tungstic acid, and in addition showed that gaseous hydrobromic, hydriodic, and hydrofluoric acids acted similarly. Later, Smith and Maas[1] made use of the volatilization of molybdic acid for a close atomic mass determination of molybdenum.

Smith and Hibbs[2] showed that vanadium behaved like molybdenum. Hydrochloric acid gas completely eliminates vanadic acid from sodium vanadate. A little later they investigated the action of hydrochloric acid upon the members of Group V of the periodic system.[3]

The sodium salts of nitric, pyrophosphoric, pyroarsenic and pyroantimonic acids were used. They found nitrogen, arsenic, and antimony to be volatile in gaseous hydrochloric acid, and made it the basis of a separation of phosphoric acid from nitric acid. Lead arsenate changed completely to chloride, the arsenic being volatilized, thus affording a good quick separation. Smith and Meyer[4] tried the action of all the haloid acids upon the elements of Group V of the periodic system. They worked with sodium salts and observed : I. That nitrogen was expelled completely by all the haloid acids. II. That phosphoric acid was not acted upon. III. That arsenic acid was fully expelled by hydrochloric, hydrobromic, and hydriodic acids, but only partially by hydrofluoric acid. IV. That antimony was completely volatilized by hydrochloric acid. There was no work done on bismuth. V. Vanadium went over completely in hydrochloric acid, but only partially in hydrobromic and hydrofluoric acids. VI. Columbium forms volatile products with hydrochloric and hydrobromic acids. No knowledge of didymium was obtained. VII. Tantalum is only slightly volatile in hydrochloric acid.

P. Jannasch and F. Schmidt[5] repeated some of the work of Smith and Hibbs, in which they confirmed the separation of arsenic from lead. They anticipated a slight portion of my work, and in addition separated arsenic acid from iron, tin from

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[1] *Ztschr. anorg. Chem.*, 5, 280.

[2] *J. Am. Chem. Soc.*, 16, 578.

[3] *Ibid.*, 17, 682.

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

[5] *Ztschr. anorg. Chem.*, 9, 274.

lead, tin from copper, and tin from iron, in a stream of hydrochloric acid gas.

The position of bismuth in the periodic system makes it natural to suppose that it too will be volatile in hydrochloric acid gas. This I have shown to be true, and was thus enabled to separate it from lead and copper. The action of hydrobromic acid on bismuth trioxide was also tried; it formed the bromide and then volatilized. It requires a higher temperature and longer action than with hydrochloric acid. Because of lack of time, I have been compelled to abandon the experiments instituted with a view of affecting separations, in atmospheres of hydrobromic acid and hydriodic acid gas and have confined my labors to hydrochloric acid gas.

METHOD OF WORK.

The hydrochloric acid gas was generated by dropping concentrated sulphuric acid from a separatory funnel, upon concentrated hydrochloric acid contained in a three liter flask. The gas evolved at the ordinary temperature was dried by passing it through two sulphuric acid drying bottles and then through a calcium chloride tower, when it was considered sufficiently dry for the purpose. The substance to be acted upon was weighed out in a porcelain boat and the latter was placed in a combustion tube of hard glass.

The tube had previously been rinsed with alcohol and then with ether, to remove all moisture. The ether was removed by drawing a current of dry air through the tube. This tube was connected to a two-necked bulb receiver containing about 300 cc. of distilled water. When working with arsenic ten cc. of nitric acid were added. The connecting tube from the combustion tube to the bulb receiver was made to enter the receiver and dip below the surface of the water, thus catching all volatile products, as well as taking up the hydrochloric acid gas. To insure safety from the loss of volatile products, a small flask containing water was attached to the bulb receiver. The apparatus was controlled at both ends by stop-cocks. This is necessary to prevent backward suction on disconnecting the apparatus. After the reaction was completed the boat was removed to a sulphuric acid desiccator from which the air could be exhausted. In general, the procedure was similar to that employed by Hibbs.[1]

I.—BEHAVIOR OF ANTIMONY TRIOXIDE.

Antimony oxide, labelled chemically pure, was dissolved in hydrochloric acid and precipitated with a large amount of water. After washing by decantation it was redissolved and reprecipitated. This procedure was repeated several times, when it was precipitated by ammonium carbonate, washed, and ignited. The pure oxide obtained in this manner was subjected to the action of hydrochloric acid gas and it was found to volatilize completely. In each trial a one-tenth gram of the oxide was acted upon. The temperature varied between 150° and 190° C. It was determined in the following way: The combustion tube was slipped through two holes made in the sides of a copper drying oven.

A very slow current of gas was used as the antimony seemed to volatilize more readily and completely, if the current was slow and the heat gentle. This I attribute, on reflection, to the fact that I ignited the oxide too strongly, (to a red heat) in its preparation. It dissolved with difficulty in concentrated hydrochloric acid. Lack of time prevented the repetition of this experiment and the separation of antimony from lead and copper, in which this substance was used. About eight hours was the time required for the volatilization; very probably a shorter time would be required if the oxide had been obtained by gentle ignition.

II.—BEHAVIOR OF LEAD OXIDE.

Pure lead oxide was obtained from recrystallized nitrate, by careful ignition. This oxide changed completely into chloride at the ordinary temperature and it was only necessary to apply a gentle heat to complete the change and entirely remove the water formed. No volatilization was noticed until a temperature of 225° was reached; at this point the lead chloride slightly volatilized.

I think it possible to estimate lead as chloride, if the temperature is kept under 200°. A weighed amount of lead oxide was

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[1] Thesis, 1896.

acted upon by hydrochloric acid gas in the cold, for two hours, and then heated sufficiently to remove all the water formed.

The boat was cooled in the gas, and then placed in a sulphuric acid desiccator and allowed to stand one-half hour. It was then weighed.

EXPERIMENTS.

	Lead oxide taken. Gram.	Lead chloride obtained. Gram.	Lead chloride required. Gram.	Difference. Gram.
Experiment I	0.1017	0.1267	0.1267	0.0000
" II	0.1015	0.1258	0.1265	—0.0007
" III.....	0.1169	0.1454	0.1447	+0.0007

The lead chloride dissolved in hot water without residue.

III.—THE SEPARATION OF ANTIMONY FROM LEAD.

The oxides were carefully weighed and thoroughly mixed in a porcelain boat. Hydrochloric acid gas was passed over them in the cold, until the lead oxide had been entirely changed to the chloride. It was then heated with the smallest flame obtainable from a fish-tail burner, placed about two inches below the tube.

	Antimony trichloride taken. Gram.	Lead chloride taken. Gram.	Lead chloride obtained. Gram.	Lead chloride required. Gram.
Experiment I	0.1015	0.1189	0.1470	0.1482
" II....	0.1090	0.1021	0.1266	0.1272
" III...	0.1350	0.0852	0.1057	0.1062
" IV ...	0.1250	0.1671	0.2069	0.2083

The time required was seven hours. The lead chloride was immediately weighed. It dissolved completely in hot water and this solution was tested by means of Marsh's apparatus for antimony, without finding the latter present. Experiment II was slightly varied by first moistening the oxides with a drop of hydrochloric acid.

IV.—BEHAVIOR OF BISMUTH OXIDE.

Bismuth nitrate, as pure as could be obtained, was dissolved in nitric acid and then thrown down with a large quantity of water. The precipitate was carefully washed by decantation. This operation was repeated several times.

It was then dissolved in acidulated water and precipitated with ammonium hydroxide and ammonium carbonate. This, on ignition, gave pure oxide, which, heated in a stream of hydrochloric acid gas, completely volatilized as chloride. Here the same treatment is necessary as obtained for antimony. A slow current of gas and a low heat were best adapted for the volatilization (a temperature of 130°, or roughly, the heat afforded by a fish-tail burner placed two inches below the combustion tube, with a flame an eighth of an inch high). The bismuth chloride sublimed nicely, forming a white crystalline mass beyond the boat, which could be readily driven along by a gentle heat.

V.—THE SEPARATION OF BISMUTH FROM LEAD.

The same material was used as in the preceding experiments. The weighed oxides were thoroughly mixed in a porcelain boat. Usually the gas was allowed to act in the cold for an hour, which changed the oxides completely to chlorides.

The same conditions prevailed as under bismuth oxide alone. If an attempt was made to hasten the reaction by heating higher than 180°, a little lead would volatilize. This sublimate, slightly yellow in color, would appear directly over the boat and could not be driven along the tube like bismuth, hence it was readily detected.

The separation of bismuth from lead requires much care, as it is not as sharp as could be desired. It is also difficult to tell exactly when the last traces of bismuth have been driven out of the boat, as there was no color change to indicate it, both metals forming white chlorides. The separation is complete in from six to seven hours. At the end of the separation the position of the boat was changed and the action continued; if no further sublimation occurred it was cooled and removed to a desiccator. The weight was taken after standing one-half hour over sulphuric acid. With care bismuth can be separated from lead in this manner.

	Lead oxide taken. Gram.	Bismuth trioxide taken. Gram.	Lead chloride obtained. Gram.	Lead chloride required. Gram.	Difference. Gram.
Experiment I	0.1014	0.2020	0.1261	0.1264	—0.0003
" II....	0.1006	0.0642	0.1252	0.1254	—0.0002
" III...	0.1038	0.1003	0.1294	0.1302	—0.0008
" IV ...	0.1412	0.1260	0.1759	0.1759	+0.0000

The chloride of lead dissolved completely in hot water. It showed no bismuth. The sublimate contained no lead.

VI.—BEHAVIOR OF CUPRIC OXIDE.

Pure copper nitrate was made by recrystallization. It was then ignited in a porcelain crucible at a dull red heat, until it became constant in weight. The pure black oxide was then subjected to the action of hydrochloric acid gas. In Experiment I, the boat containing the oxide was heated at the outset to 175°. It was taken out after two hours, placed over sulphuric acid for half an hour, and weighed. The weight showed that the copper oxide had hardly been acted upon. It had only been superficially changed to chloride. It was then moistened with two or three drops of hydrochloric acid, dried in a rapid current of the gas, and heated two hours longer. This resulted in the complete transformation into chloride. The anhydrous chloride thus obtained, liver brown in color, was placed in a desiccator from which the air was exhausted. This was done to remove all the gas that might be retained and prevented a too rapid absorption of moisture.

Copper chloride absorbs moisture but not so rapidly as to prevent weighing in this form :

	Copper oxide taken.	Copper chloride obtained.	Copper chloride required.	Difference.
	Gram.	Gram.	Gram.	Gram.
Experiment I	0.1011	0.1708	0.1713	—0.0005
" II....	0.1025	0.1726	0.1736	—0.0010
" III...	0.1034	0.1756	0.1752	+0.0004

In Experiment II, the change was completed in the cold by prolonged action through four hours. It was then heated about ten minutes at the end to drive out the moisture that had formed. In all the experiments cited, the copper chloride, after weighing, was found to dissolve completely in cold water.

VII.—THE SEPARATION OF ANTIMONY FROM COPPER.

The same material was used as in the preceding experiments. The weighed oxides were thoroughly mixed. The antimony was completely volatilized, leaving copper chloride which was weighed as such. The volatile antimony chloride was caught in the bulb receiver at the end of the tube. The bulb and tube were washed out with acidulated water into a beaker and the antimony thrown down with hydrogen sulphide. The antimony sulphide was filtered, thoroughly washed, and while moist dissolved in strong hydrochloric acid. The hydrogen sulphide evolved was conducted into bromine water and oxidized to sulphuric acid, which was estimated as usual and the antimony calculated.

The length of time required was eight hours. On several occasions the experiment was interrupted at the end of four hours, but invariably the separation was incomplete and on dissolving out the copper chloride formed, black copper oxide and white antimony oxide were plainly evident. In some cases the mixture of oxides was moistened with a couple of drops of hydrochloric acid and then evâporated down in a stream of acid gas, by heating the tube over a water-bath. This treatment seemed to facilitate matters but it is not altogether advisable, because the copper chloride has a tendency to creep over the sides of the boat. It is quicker in the end to separate them in the dry condition, allowing plenty of time for the reaction. The copper chloride obtained was perfectly soluble in cold water and contained no antimony. It could readily be changed to oxide and weighed if thought necessary.

	Antimony trioxide taken.	Copper oxide taken.	Copper chloride obtained.	Copper chloride required.	Difference.
	Gram.	Gram.	Gram.	Gram.	Gram.
Experiment I ..	0.1068	0.1040	0.1750	0.1745	+0.0005
" II ..	0.1062	0.1053	0.1774	0.1784	—0.0010
" III .	0.1022	0.1020	0.1726	0.1728	—0.0002
" IV .	0.1198	0.1020	0.1722	0.1728	—0.0006

	Antimony trioxide taken.	Antimony trioxide found.	Difference.
	Gram.	Gram.	Gram.
Experiment I	0.1068	0.1059	+0.0009

VIII.—THE SEPARATION OF BISMUTH FROM COPPER.

The pure oxides were mixed and treated as directed under bismuth and lead.

	Copper oxide taken.	Bismuth trichloride taken.	Copper chloride obtained.	Copper chloride required.	Difference.
	Gram.	Grams.	Grams.	Grams.	Grams.
Experiment I ..	0.1030	0.1069	0.1738	0.1745	—0.0007
" II..	0.1004	0.1077	0.1701	0.1713	—0.0012
" III.	0.1026	0.1060	0.1741	0.1738	+0.0003
" IV .	0.1019	0.1058	0.1718	0.1726	—0.0008

	Bismuth trioxide obtained.	Bismuth trioxide required.	Difference
	Gram.	Gram.	Gram.
Experiment I..............	0.1076	0.1069	+0.0007

The time required in each of these trials was seven hours. It seemed to be advantageous to raise the temperature and heat sharply for about ten minutes at the end, to insure the complete removal of the bismuth.

Moistening with acid helped the reaction but subjected it to the same danger of creeping as noted under antimony and copper.

The bismuth was estimated as follows: It was washed out of the tube and bulb with acidulated water and then precipitated as sulphide. The bismuth sulphide was filtered, washed, and dissolved in nitric acid. It was thrown out of the solution with ammonium hydroxide and ammonium carbonate, as hydrated oxide, and then filtered, dried, and ignited. It was weighed as oxide. The residue of copper chloride in the boat dissolved in cold water and showed no bismuth.

IX.—ACTION OF GASEOUS HYDROCHLORIC ACID ON SODIUM PYROARSENATE.

Hibbs[1] showed that arsenic was completely volatilized from sodium pyroarsenate, leaving weighable sodium chloride. In fact, so clean was the elimination of arsenic that he made it the basis of an arsenic atomic mass determination, with admirable success.

In working up the separation of arsenic from other metals it was necessary to start with the pure sodium salt. After purification I decided to test it, by weighing the salt produced by the action of the acid gas upon it. Several determinations gave close results, proving the salt pure.

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[1] See next paper, page 1044.

Chemically pure arsenate was procured. It was recrystallized and then ignited (not too strongly) for an hour. The pyroarsenate obtained was used in precipitating the various arsenates investigated.

	Sodium pyroarsenate taken. Gram.	Sodium chloride obtained. Gram.	Sodium chloride required. Gram.
Experiment I	0.2021	0.1330	0.1335
" II	0.1039	0.0691	0.0686

X.—THE SEPARATION OF ARSENIC FROM COPPER.

Pure sodium pyroarsenate was used to precipitate the copper salt.

Copper sulphate was recrystallized five times, a few good crystals were dissolved and the two solutions mixed. A green copper arsenate was precipitated. It was washed and dried at 100°. Salkowski[1] observes that copper arsenate still contains water above 130°. My salt had the composition $Cu_3As_2O_8 + 2H_2O$.

Hydrochloric acid gas completely changes it in the cold to chloride. A slight heat drives out the arsenic and water and leaves a brown anhydrous copper chloride, which can be weighed as such. Care was taken to remove all the acid gas before weighing.

The arsenic was washed out of the bulb into a beaker, this was warmed with nitric acid to insure oxidation, and then it was precipitated from an ammoniacal solution with " a magnesia mixture." It was weighed as $Mg_2As_2O_7$.

	Copper arsenate taken. Gram.	Copper chloride obtained. Gram.	Copper chloride required. Gram.	Difference. Gram.
Experiment I	0.1067	0.0850	0.0851	—0.0001
" II	0.1240	0.0998	0.0991	+0.0007
" III	0.1072	0.0860	0.0856	+0.0004
" IV	0.1155	0.0924	0.0923	+0.0001
" V	0.1042	0.0832	0.0833	—0.0001

Experiment I. As_2O_5 obtained, 0.0498 gram ; As_2O_5 required, 0.0487 gram.

The residue of copper chloride completely dissolved in water. It showed no arsenic when tested in a Marsh apparatus.

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[1] *J. prakt. Chem.*, 104, 129.

XI.—THE SEPARATION OF ARSENIC FROM SILVER.

Silver arsenate was made by precipitating silver nitrate with sodium arsenate. Care was taken to have the nitrate in excess. The reddish-brown arsenate of silver was washed with boiling water, until the washings no longer showed silver, when tested with hydrochloric acid. It was dried at 110°.

As was expected, the acid gas attacked it even in the cold. In fact the action was so vigorous that a couple of analyses were spoiled by spattering. The trouble arose from the fact that the arsenate was not finely powdered. Heat was generated in the reaction sufficiently to send over a portion of the water formed. Experiment I was run in the cold for one hour and then heated sharply, for a few minutes, to expel the arsenic and water. The result was only 0.46 per cent. too high, but indicated that the salt should be heated longer, and not necessarily as high to remove all the arsenic.

The succeeding experiments were heated from one to two hours at 150° with better results:

	Silver arsenate taken. Gram.	Silver chloride obtained. Gram.	Silver chloride required. Gram.	Difference. Gram.
Experiment I.....	0.2542	0.2381	0.2363	+0.0018
" II....	0.2325	0.2163	0.2161	+0.0002
" III...	0.2084	0.1952	0.1938	+0.0014
" IV...	0.2070	0.1927	0.1924	+0.0003

Experiment 1. Ag obtained = 70.45 per cent; Ag required = 69.99 per cent.

The residues in Experiments II, III, and IV were dissolved and tested for arsenic. None was found.

XII.—THE SEPARATION OF ARSENIC FROM CADMIUM.

Chemically pure cadmium sulphate was precipitated by a solution of sodium pyroarsenate. Stirring brought out a gelatinous arsenate, which changed by additional stirring to a granular salt. This was thoroughly washed and dried at 110°. It had the composition $Cd_3As_2O_8 + 2H_2O$. Salkowski[1] observes that a red heat is necessary to fully dehydrate this salt.

The moisture and arsenic were completely expelled at 150°,

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[1] *Loc. cit.*

leaving a uniform mass of cadmium chloride. It was weighed as such after standing over sulphuric acid for one-half hour. The arsenic was determined as usual.

	$Cd_3As_2O_8$ + $2H_2O$ taken. Gram.	Cadmium chloride obtained. Gram.	Cadmium chloride required. Gram.	Difference. Gram.
Experiment I	0.2359	0.1965	0.1977	—0.0012
" II ...	0.1166	0.0968	0.0968	—0.0000
" III...	0.1030	0.0857	0.0855	+0.0002
" IV ...	0.1138	0.0947	0.0946	+0.0001
" V	0.1043	0.0870	0.0867	+0.0003

	$Cd_3As_2O_8$ + $2H_2O$ taken. Gram.	As_2O_5 obtained. Gram.	As_2O_5 required. Gram.	Difference. Gram.
Experiment I	0.2359	0.0813	0.0822	0.0009

The cadmium chloride dissolved perfectly in water and showed no arsenic, when tested in a Marsh apparatus.

XIII.—THE ACTION OF HYDROCHLORIC ACID GAS ON FERRIC OXIDE.

Pure oxide of iron was heated in a stream of acid gas. The behavior of iron is rather peculiar, as it very readily changes into chloride, and then only partially volatilizes. On heating to 200° the greater part is driven over as flaky crystals of ferric chloride. The remainder consists of a white mass, which refuses to go over on prolonged action and also on raising the temperature.

This residue was soluble in water and did not react with potassium thiocyanate, but immediately gave a blue precipitate with ferricyanide. Reduction was therefore evident; this is also noted by Jannasch and Schmidt.[1] The temperature at which ferric chloride usually goes into the ferrous condition is above 1000°.

Care was taken to prepare perfectly pure hydrochloric acid gas. Chemically pure acids were used to this end. The action however was the same in all cases.

XIV.—THE SEPARATION OF ARSENIC FROM IRON.

Chemically pure ferrous ammonium sulphate was carefully

[1] *Loc. cit.*

oxidized with nitric acid, it was taken up in water, filtered and then crystallized several times. The best crystals were selected and a solution made to precipitate the arsenate. A white precipitate tinged with yellow was formed. It was washed by decantation and then filtered and washed until the washings no longer gave Prussian blue with ferrocyanide. It was then dried and gently ignited.

The acid gas acts on it quickly in the cold and it becomes a light green liquid. In evaporating off the moisture the chloride of iron was carried over with the arsenic.

In a second trial, with the temperature lower and occasionally removing the source of the heat altogether, when ebullition threatened to cause spattering, ferric chloride was obtained without loss. This was gradually heated a little higher to remove all the arsenic.

The chloride of iron was dissolved, oxidized, precipitated with ammonium hydroxide and estimated as usual. The result was fair and the product tested showed the absence of arsenic, but all succeeding experiments failed. Either the substance spattered or the iron went along with the arsenic.

Jannasch and Schmidt[1] separated arsenic from iron by placing their material in a large hard glass bulb and evaporating down to dryness with nitric acid, in an air current. This is not applicable when a porcelain boat is employed. They then volatilized the arsenic in hydrochloric acid gas at 120°.

XV.—SEPARATION OF ARSENIC FROM ZINC.

In some preliminary work zinc oxide was treated with acid gas at 200°. It completely changed to chloride and was not volatile. Pure zinc sulphate was used to precipitate the arsenate; it was washed, dried and ignited to 150°. The same difficulty appeared as was encountered under iron. Zinc arsenate melts down to a liquid mass as soon as the acid gas strikes it, which is extremely hard to evaporate without spattering. A small glass cover was placed over the boat, which tended to lessen the spattering, but did not entirely prevent it.

The zinc was estimated by taking the chloride up in a little

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[1] *Loc. cit.*

hydrochloric acid and running it down with pure mercuric oxide. It was then ignited and weighed as zinc oxide. One good result was obtained, but generally the residues of zinc contained arsenic and the results were far from being concordant.

XVI.—THE SEPARATION OF ARSENIC FROM COBALT AND NICKEL.

Cobalt and nickel were precipitated as arsenates in the usual manner, with a solution of pyroarsenate.

Cobalt nitrate, a Merck preparation, was carefully purified; considerable manganese was found and eliminated.

This gave the pink salt $Co_3As_2O_8 + 8H_2O$, which was ignited to the blue anhydrous compound.

Cobalt arsenate is very readily attacked by the acid gas in the cold, yielding a pink chloride. A slight heat, not much above 120°, changed it to the blue chloride and drove out the arsenic. At first it was quickly weighed as chloride, then it was taken up in a little hydrochloric acid and evaporated down with mercuric oxide. On ignition, black Co_3O_4 was obtained and weighed.

The arsenic was estimated as usual.

	Experiment I. Gram.	Experiment II. Gram.
$Co_3As_2O_8$ taken	0.1509	0.2029
$CoCl_2$ obtained	0.1309	....
$CoCl_2$ required	0.1293	....
Co_3O_4 obtained	0.0738	0.0969
Co_3O_4 required	0.0731	0.0983
Difference	+0.0007	—0.0014
As_2O_5 obtained	0.0770	....
As_2O_5 required	0.0764	....
Difference	+0.0006	....

On testing the cobalt residue by the Marsh test, no trace of arsenic was found. No cobalt was found in the sublimate. Some of the first experiments gave cobalt too low; it was thought that they had been heated too high, but testing showed no volatilized cobalt.

A temperature of 125° is sufficient to drive out all of the arsenic, and at this temperature there is no danger of volatilizing the cobalt.

In working with nickel, the green arsenate was simply dried in the first experiment. It therefore had the composition $Ni_3As_2O_8 + 8H_2O$.

Hydrochloric acid gas attacked it in the cold. A slight heat drives out the arsenic and moisture and leaves a salmon-colored chloride. The nickel chloride was changed to oxide by evaporating it with nitric acid and igniting.

	Experiment I. Gram.
$Ni_3As_2O_8 + 8H_2O$ taken	0.1502
NiO obtained	0.0554
NiO required	0.0561
Difference	—0.0007

In Experiments II and III the salt was made anhydrous by ignition.

	Experiment II. Gram.	Experiment III. Gram.
$Ni_3As_2O_8$ taken	0.1166	0.1040
NiO obtained	0.0577	0.0523
NiO required	0.0575	0.0513
Difference	+0.0002	+0.0010
As_2O_5 obtained	....	0.0515
As_2O_5 required	....	0.0526
Difference	....	—0.0011

The Marsh test showed no arsenic with the nickel.

XVII.—BEHAVIOR OF MINERALS IN HYDROCHLORIC ACID GAS.

Niccolite. One-half gram of the mineral was finely powdered and subjected to the action of acid gas for a day, at a temperature of 200° C. It was only very slightly affected.

A second portion was dissolved in nitric acid and evaporated down in a porcelain dish. It was then transferred to a boat and evaporated to dryness. To remove all the acid, it was heated in an oven to 110° for one-half hour. The dry substance was acted upon by the acid gas in the cold for five hours. It changed completely to chloride. A temperature of 150° for an hour removed all the moisture and arsenic.

The nickel chloride was evaporated down with nitric acid, ignited, and weighed as NiO. The arsenic was estimated as usual.

	Per cent.
Nickel found	43.79
Nickel calculated	43.60
Difference	0.19
Arsenic found	56.66
Arsenic calculated	56.40
Difference	0.26

Undoubtedly there is still a wide field open in regard to the behavior of hydrochloric acid gas upon mineral species. Smith and Hibbs[1] showed that mimetite lost its arsenic quantitatively, when heated in a stream of acid gas. In this laboratory others are being investigated with favorable indications. The direct employment of hydrochloric acid gas upon a powdered mineral would simplify many a tedious gravimetric process, leaving the separated elements in a desirable condition for further treatment.

In the case of a mineral such as niccolite, where it must first be decomposed with nitric acid and then transferred to a boat, the advantage is not so great. This, however, can be modified, so that the time factor is reduced and the advantage of the method still retained. Instead of using a boat, which has no advantage unless the non-volatile chlorides are to be weighed directly, a hard glass bulb can be substituted. The mineral is placed in the bulb, dissolved in nitric acid, and evaporated down by the aid of a current of air drawn through the bulb.

The residual oxides are then separated in a stream of hydrochloric acid gas as usual.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 15.]

THE ATOMIC WEIGHTS OF NITROGEN AND ARSENIC.[2]

BY JOSEPH GILLINGHAM HIBBS.

Received September 26, 1896.

THE atomic weight of the metal molybdenum had been determined by expelling molybdic acid from sodium molybdate with hydrochloric acid gas, then weighing the residual sodium chloride.

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[1] *Loc. cit.*

[2] From author's thesis presented to the Faculty of the University of Pennsylvania for the degree of Doctor of Philosophy, 1896.