At this point I was compelled to cease the experiments and have not since been able to renew the work, but I believe that if these observations could be extended they would prove fruitful not only in interesting but practical results. However, the observer must have had a large experience in explosive work and the effects of explosives, or he will frequently be deceived as to the nature of the results obtained.

THE ACTION OF THE HALOID ACIDS IN GAS FORM UPON MOLYBDIC ACID.

By Edgar F. Smith and Vickers Oberholtzer.

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Debray (*Compt. rend.*, **46,** 1098, and *Ann. Chem.* (*Liebig*) **108,** 250) first called attention to the fact that a very volatile, crystalline compound of the formula $MoO_3.2HCl$ resulted upon exposing molybdic acid heated from 150° to 200° to the action of hydrochloric acid gas. It is true that the constitution of this volatile product may also be represented by the formula $MoO(OH)_2Cl_2$, which would make it a molybdenum hydroxychloride. Dismissing the question of constitution for the present and considering the point of easy volatility, it seemed to us that this behavior might be utilized for the separation of molybdic acid from tungstic acid, as the latter apparently does not enter into volatile combination with hydrochloric acid gas. We therefore exposed weighed amounts of sublimed molybdic acid to the action of the acid gas, and succeeded in expelling the molybdic acid completely from the porcelain boats containing it. Applying the same treatment to what we considered pure tungstic acid we were greatly surprised to find that very appreciable quantities of a sublimate similar in every respect to that of molybdenum hydroxychloride were expelled from the boat. An examination of this product proved it to be the molybdic acid compound. In short our tungstic acid was not pure. We, however, continued to heat portions of it in hydrochloric acid gas until a sublimate was no longer obtained, when on mixing molybdic acid in known amount with the residual tungstic acid we discovered that we could completely expel the former acid from the latter. Our next step was to observe the effect of heating dry sodium molybdate in hydrochloric acid gas. The appended results show a quantitative conversion into sodium chloride, consequently a complete volatilization of the molybdic acid:

Na_2MoO_4.	NaCl.	NaCl req'd.
0.1302 gram gave at 150–200°	0.0738	0.0739
0.1832 " " " "	0.1038	0.1040
0.2046 " " " "	0.1159	0.1162
0.3845 " " " "	0.2186	0.2183

As we were on the point of applying the method to the quantitative separation of molybdic acid and tungstic acid, both present as sodium salts, a closer scrutiny of the existing literature relating to the subject revealed that E. Péchard (*Compt. rend.*, **114**, 173, and *Ztschr. anorg. Chem.*, **1**, 262) had already carried out the determination of molybdic acid and its separation from tungstic acid in this way with very evident success. Our own experiments confirm those of Péchard in every particular.

As previously observed, the tungstic acid that we considered pure contained molybdic acid. Traube (*Neues Jahrbuch für Mineralogie*, *Geologie and Paleontologie*, *Beilage*, *Band* **7**, 232) has demonstrated that natural calcium tungstate (scheelite) and commercial tungstic acid, obtained from the mineral wolframite, contain molybdic acid. E. Corleis (*Ann. Chem.* (*Liebig*,) **232**, 265) has shown that the latter acid is even present in the "*wolframsäure puriss*" of trade, while Friedheim (*Ztschr. anorg. Chem.*, **1**, 76) asserts that commercial sodium tungstate is strongly contaminated with sodium molybdate, and that even when exercising the greatest care in the process of purification the tungstate continued to show traces of molybdenum.

We found molybdic acid present in the purest sodium tungstate that we could get, and in the minerals scheelite and wolframite when these were exposed to the action of hydrochloric acid gas at a temperature not exceeding 400° C. We, therefore, are inclined to regard this method as excellently adapted for the detection of molybdic acid as well as for the purification of tungstic acid and tungstates containing molybdenum.

Our original purpose having been the study of the behavior of molybdic acid in atmospheres of all the gaseous haloid acids, we may now briefly recount our experience in those directions.

Action of Hydrobromic Acid, in Gas Form, upon Molybdic Acid.—The molybdic acid used by us was purified by converting the commercial acid into the ammonium salt, which was recrystallized a number of times and then ignited with access of air. The product was sublimed very carefully from a platinum crucible. The hydrobromic acid gas was prepared by dropping bromine from a separatory funnel upon crude anthracene contained in a half-liter flask. It passed through a hard glass tube six inches in length, filled with anthracene, then through the anthracene, then through two U tubes containing a paste of amorphous phosphorus and two U tubes provided with fused calcium chloride, while the sixth or last tube contained phosphoric anhydride. Having completed this circuit it was admitted to a perfectly dry combustion tube into which there had been introduced a porcelain boat filled with molybdic acid. The anterior end of the combustion tube was provided with a calcium chloride tube to exclude all moisture. The heat used in the experiment was applied from a combustion furnace. An ordinary thermometer was placed above the combustion tube; its bulb rested directly above the boat. In this manner we recorded the approximate temperature at which the reaction took place. As soon as the entire apparatus was filled with the gas, three burners of the furnace, directly under the boat, were lighted, and the heat raised gradually until it reached 200° C. A change took place almost instantly. Immediately beyond the boat appeared a heavy sublimate with a color resembling that of permanganate of potassium. Beyond this solid a brownish yellow colored liquid separated; on cooling it changed to long, beautiful, yellow needles. These proved to be very unstable, melting almost immediately when brought in contact with the air. At the expiration of an hour the passage of the hydrobromic acid gas was interrupted. The permanganate-colored sublimate was removed from the sides of the tube as completely as possible, introduced into a porcelain boat, and then carefully resublimed in a current of dry carbon dioxide.

The compound sublimed in fern-like aggregates of beautiful dark red or purple red, shining, overlapping plates, extending from side to side of the combustion tube. They dissolved in water with evolution of heat. Their aqueous solution was colorless, but upon standing became blue in color. The crystals also changed on prolonged exposure to the air. By bringing them into well corked bottles filled with carbon dioxide, they were preserved without undergoing decomposition. An examination of the crystals under a polarizing microscope showed them to be capable of polarizing light, and that they consisted of aggregations of perfectly square plates. After the resublimation portions of the substance were weighed off in closed weighing tubes and analzyed. For the determination of the bromine the material was dissolved in as little cold water as possible, dilute nitric acid added, and this followed immediately by the addition of silver nitrate. The resulting silver bromide was treated in the usual manner. In estimating the molybdenum the substance was brought into a weighed porcelain crucible and dilute nitric acid added. The solution was evaporated almost to dryness at a very gentle heat, when the crucible contents were treated with concentrated nitric acid, after which followed evaporation to perfect dryness. This operation was repeated, and a gentle but direct heat applied to the crucible for periods varying from one-half to one hour. This was done in order to completely oxidize the molybdenum to trioxide. To ascertain whether the new compound contained water, portions of it were mixed with freshly ignited litharge and heated in a current of dry air, using a perfectly dry combustion tube provided with a weighed calcium chloride tube. The weight of the latter showed no increase, so that we were safe in considering our substance free from hydrogen.

ANALYSIS.

Bromine determination:

		AgBr.	Per cent. Br.
No. 1.	0.1334 gram substance gave·····	0.1793 gram	59.19
No. 2.	0.3353 " " " ·····	0.4499 "	57.09
No. 3.	0.0680 " " " ·····	0.0908 "	56.82

The mean of these bromine percentages is 57.03 per cent.

Molybdenum determination:

		MoO_3.	Per cent Br.
No. 1.	0.2545 gram substance gave·····	0.12865 gram	33.69
No. 2.	0.2916 " " " ·····	0.1466 "	33.52
No. 3.	0.1115 " " " ·····	0.0559 "	33.42

The mean of the molybdenum percentages is 33.54 per cent. We experienced great difficulty in wholly eliminating the traces of "blue oxide" in all our determinations of the molybdenum, hence we look upon these results as low.

Regarding, then, our compound as consisting of molybdenum, bromine, and oxygen with the above percentages, taking the oxygen by difference, we deduce as the most probable formula: $MoO_2Br_2.MoOBr_2$ or $Mo_2O_3Br_4$—molybdenum sesquioxide tetrabromide. The theoretical requirements of this formula are 34.28 per cent. Mo, 57.14 per cent. Br, and 8.57 per cent. O.

The only existing molybdenum oxybromide until the present time has been MoO_2Br_2—molybdenyl bromide, discovered by Blomstrand in passing bromine vapor over the heated dioxide of molybdenum, or by heating a mixture of molybdic acid and borax with potassium bromide. It is mentioned as forming yellow deliquescent tablets. For the sake of comparison we prepared the compound of Blomstrand by the second method. We found that when it sublimed upon a previously heated portion of the tube, it separated in "mehr ausgebildeten Krystalltafeln auf; bei rascher Sublimirung in undeutlich krystallinischen Schuppen. Farbe schön gelbroth" (Blomstrand, *J. prakt. Chem.*, **82**, 439). Our compound, however, is formed simultaneously with that of Blomstrand when bromine vapors are conducted over heated molybdic acid. The tube in which this reaction was made was first freed from air by conducting bromine vapor through it, and heat was not applied until we were satisfied that bromine alone was present.

The brownish yellow liquid, formed at the same time with the purple red colored solid, was crystallized in the tube in which it was formed. The tube was then severed at a point between the yellow and red colored compounds. The yellow immediately liquefied on exposure to the air. The liquid was collected in a small beaker previously weighed. This was then placed in a sulphuric acid desiccator, and the air exhausted. At the expiration of two or three days the yellow needles had reformed. The beaker and its contents were then rapidly weighed. Water was poured on the needles. Their solution was colorless, or slightly yellow tinged. On standing, the liquid slowly acquired a deeper yellow, or reddish yellow hue, and after twenty-four hours a "blue oxide" of molybdenum had separated. The bromine and molybdenum were determined in this product in the same manner as in the purple colored solid. We, however, experienced no difficulty in obtaining perfectly white molybdic acid in all of our analyses.

ANALYSIS.

Bromine determination:

		AgBr.	Per cent. Br.
No. 1.	0.0950 gram substance gave.....	0.1403 gram	62.83
No. 2.	0.2523 " " "	0.3700 "	62.50
No. 3.	0.2709 " " "	0.3967 "	62.37
No. 4.	0.0250 " " "	0.0365 "	62.12

The mean of these determinations is 62.45 per cent. Br.

Molybdenum determination:

		AgBr.	Per cent. Br.
No. 1.	0.0946 gram substance gave.....	0.0346 gram	24.39
No. 2.	0.0946 " " "	0.0337 "	23.75
No. 3.	0.1892 " " "	0.0686 "	24.06

The mean percentage of molybdenum found is 24.03 per cent.

The formula that we deduce from these results is $MoO_3.3HBr$. It might be represented better, perhaps, as a trihydroxybromide, $Mo(OH)_3Br_3$. The theoretical requirements in either case are 62.02 per cent. Br and 24.80 per cent. Mo.

It is interesting to note that the long, yellow colored needles of this compound were also obtained upon passing hydrobromic acid gas over the oxybromide of Blomstrand at a gentle heat. This change may easily be conceived as occurring, if we grant the presence or production of water through the formation of secondary products:

$$MoO_2Br_2 + H_2O + HBr = MoO_3.3HBr.$$

As we were not in a position to ascertain the true composition of the residual substance or substances from scarcity of material, we offer the suggestion as a possible explanation for the appearance of the hydroxybromide in the manner above indicated.

Action of Hydriodic Acid, in Gas Form, upon Molybdic Acid.—A violent reaction occurred in the cold, upon passing the dry acid gas over molybdic acid. Much heat was evolved, and iodine was liberated. The non-volatile product that remained in the boat possessed a bright violet color. It was exposed for a period of two hours to a temperature ranging from 45°–50° C., during which time a continuous stream of dry and pure gas was conducted over it. Carbon dioxide was next introduced and passed for an equal period, while the temperature was maintained at 50° C. The results obtained from many analyses of this product pointed to the probable composition $MoO_3.HI$, but as the quantity of iodine varied according to the length of time during which the hydriodic acid acted, and with the temperature, we feel unable to assign any definite composition to the compound. It has seemed to us, from a careful study of the experimental results, that several derivatives were formed, but we were unable to separate them, and, indeed, by continuing the action of the gas for periods varying from six to eight hours, at the same time elevating the temperature to from 105°–120° C., iodine continued to separate. At last a violet blue colored product remained. This appeared to be homogeneous. Continued action of the gas was without further reduction, and, therefore, carbon dioxide was introduced to expel it. The blue colored product suffered no change on exposure to the air. We obtained what appeared to be the same substance by exposing the iodine-containing compound mentioned above to a temperature of 200° C., in an atmosphere of carbon dioxide. Indeed, mere exposure of the iodine-containing compound to the air for some days gave the blue colored derivative.

The same form of apparatus was used here that we have described with the oxybromides. The hydriodic acid gas was made from moist amorphous phosphorus and iodine. It was carefully dried.

An analysis of the blue colored residue resulted as follows. This was performed the same as under the bromine derivatives.

Molybdenum determination:

			MoO_3.	Per cent. Mo.
No. 1.	0.1099	gram substance gave	0.1053 gram	64.19
No. 2.	0.1017	" " "	0.0972 "	63.72
No. 3.	0.0807	" " "	0.0775 "	64.02
No. 4.	0.0959	" " "	0.0937 "	64.92
No. 5.	0.1386	" " "	0.1350 "	64.93

The mean percentage of Mo is 64.35 per cent.

Water determination:

		H_2O.	H_2O, per cent.	Mean.
No. 1.	0.1533 gram substance gave.....	0.0138 gram	9.00	
No. 2.	0.1673 " " "	0.0142 "	8.49	
				8.74

An intense red heat was required to fully expel the water content.

These figures would lead to an oxide of the formula $Mo_4O_{10}.3H_2O$, which would require 64.21 per cent. Mo and 9.03 per cent. H_2O. An examination of this violet blue colored oxide showed that iodine was absent. The dehydrated oxide left, upon igniting the blue oxide to a high heat in an atmosphere of carbon dioxide, was brown in color. Three determinations of its molybdenum content indicated it to be Mo_2O_6. As a result, then, of the action of hydriodic acid gas upon molybdic acid, we can point to no definitely iodated product, but to a "blue oxide," a product of reduction. In this connection, we may direct attention to the observation of Schulze (*J. prakt. Chem.*, **29**, N. F., 440), that molybdic acid sustains reduction when heated with potassium iodide, air being excluded. The resulting products possess variable composition, but by the use of four parts molybdenum trioxide, and one part potassium iodide, a definite product was prepared. It was proved to be a new oxide of molybdenum, steel blue in color, crystalline, and possessing metallic luster. Its analysis gave results agreeing with the formula Mo_4O_{11}. Our reduction compound is quite analogous to this; the product, while closely approximating that of Schulze, is hydrous, and contains a little less oxygen.

Action of Hydrofluoric Acid, in Gas Form, upon Molybdic Acid.—The hydrofluoric acid gas was evolved from fluor spar and sulphuric acid. It passed directly over the molybdic acid contained in a platinum boat, and the latter in a platinum combustion tube, from which a delivery tube led into a platinum flask, cooled by ice water. At a temperature ranging from 300°-400° C., all the molybdic acid was converted into a volatile product that collected upon the anterior portions of the platinum combustion tube in crystals, having a peculiar red color. On holding the tube, in which these crystals had been sublimed, towards the light, it appeared to be filled with violet vapors of iodine. This was due, however, to reflection of light from the sides of the flat, needle-like crystals. It is scarcely necessary to remark that before disconnecting the apparatus carbon dioxide was conducted through it to expel the hydrofluoric acid gas. The platinum flask also contained the volatile molybdenum product. Much hydrofluoric acid was with it. This was expelled by the introduction of carbon dioxide.

The new product, when removed from the vessels containing it, was found to be deliquescent, and gradually decomposed into a blue oxide of molybdenum. It attacked glass, was insoluble, or nearly insoluble, in water, but dissolved to a colorless liquid in hydrofluoric acid, and was left undecomposed on evaporation. Portions of it were weighed off as rapidly as possible in platinum crucibles, and the molybdenum determined as trioxide by evaporation with nitric acid, followed by gentle ignition.

ANALYSIS.

Molybdenum determination :

			MoO_3.	Per cent. Mo.
No. 1.	0.0526	gram substance gave	0.0479 gram	60.70
No. 2.	0.1066	" " "	0.0967 "	60.66
No. 3.	0.1166	" " "	0.1051 "	60.94
No. 4.	0.1265	" " "	0.1164 "	61.35

The mean of these determinations is 60.91 per cent.

Formed in the same manner as molybdenum sesquioxide tetrabromide, we find that these results agree very closely with an oxyfluoride of an analogous formula, $Mo_2O_3F_4$, which would require 60.76 per cent. of molybdenum.

In our experiments with the above oxyfluoride, we several times observed a slight quantity of a colorless liquid, which, upon careful evaporation with nitric acid, left a very appreciable amount of molybdic acid. In this compound of molybdenum, we may, perhaps, have an analogue of the very volatile $MoO_3.2HCl$, and the liquid, unstable $MoO_3.3HBr$. We endeavored to fix its composition, but experienced so much difficulty in obtaining material that we could regard as sufficiently pure, that we abandoned it entirely. The work attending its preparation is anything but pleasant, and the yield exceedingly uncertain.

Only one other oxyfluoride of molybdenum is known, namely that prepared by Schulze (*J. prakt. Chem.*, **21**, N. F., 442), by fusing metallic fluorides together with molybdic acid with the exclusion of air. It has the constitution expressed by the formula MoO_2F_2.

Reviewing, then, the action of the gaseous haloid acids upon molybdic acid, we find, first, that hydrochloric acid converts the acid into a solid, very volatile product, $MoO_3.2HCl$; second, that hydrobromic acid changes molybdic acid to a volatile brownish yellow liquid, $MoO_3.3HBr$, forming long yellow needles at low temperatures and under diminished pressure, and a beautifully crystallized solid of the formula $MoO_2Br_2.MoOBr_2$; third, that hydriodic acid reduces molybdic acid to a new oxide, $Mo_4O_{10}.3H_2O$; fourth, that hydrofluoric acid 'converts molybdic acid into at least one well formed, but volatile, product, having approximately the formula $MoO_2F_2.MoOF_2$ or $Mo_2O_3F_4$.

Püttbach (*Ann. Chem.*, (*Liebig*), **201**, 137) divides the known molybdenum oxychlorides into two classes:

Saturated	and	Unsaturated.
$MoOCl_4$		$Mo_3O_3Cl_7$
$Mo_2O_3Cl_6$		$Mo_2O_3Cl_4$
$Mo_3O_5Cl_8$		....
MoO_2Cl_2		....

But one oxybromide, already mentioned, is known. Its formula is MoO_2Br_2. Our experiments add to this the compound $Mo_2O_3Br_4$, which would correspond to $Mo_2O_3Cl_4$. The latter is light brown in color. Schulze's oxyfluoride would correspond to MoO_2Cl_2 and MoO_2Br_2, while that obtained by us corresponds to $Mo_2O_3Cl_4$ and $Mo_2O_3Br_4$. Püttbach's division presupposes the presence of a sexivalent molybdenum atom in the saturated members, while the unsaturated are regarded as derived from two molecules of $MoCl_5$ by the substitution of oxygen for equivalent amounts of chlorine. Our oxybromide $Mo_2O_3Br_4$ and oxyfluoride $Mo_2O_3F_4$ may be looked upon as possessing similar origin, although their corresponding pentabromide and pentafluoride are unknown.

The compound $MoO_3.3HBr$, like $MoO_3.2HCl$, presupposes the presence of a sexivalent molybdenum atom, and may be properly considered a hydroxybromide represented thus—$Mo(OH)_3Br_3$—a derivative of the unknown hexabromide.

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THE ELECTROLYTIC SEPARATION OF MERCURY FROM BISMUTH.

BY EDGAR F. SMITH AND J. BIRD MOYER.

The question as to whether mercury can be completely precipitated by the current in the presence of nitric acid has been frequently discussed and answered in the affirmative. We observe, too, that in electrolytic literature it is this solution of mercury which has been generally recommended for the separation of the latter metal from various other metals associated with it. Thus, in the latest edition (the third) of Classen's *Quantitative Analyse durch Elektrolyse*, p. 147, the author, in describing the analysis of an alloy containing tin, lead, bismuth, and mercury, writes as follows:

"Aus der saltpetersauren Lösung (the filtrate from the tin oxide) kann man nun zunächst das *Quecksilber* und einen Theil des Bleies als Superoxyd auf der positiven Elektrode fällen. Um die vollständige Abscheidung des Bleies zu bewirken unterwirft man die von Quecksilber befreite Lösung nochmals der Elektrolyse, indem man die Schale mit dem positiven Pol des Stromerzeugers verbindet, verdampft zur Bestimmung des *Wismuths* die bleifrei Lösung zur Trockne und verfährt nach S. 81," etc., etc.

These instructions would most certainly lead one to infer that mercury can be separated in the electrolytic way from bismuth in the presence of nitric acid. Trials, qualitative it is true, were made by one of us (S) years ago; these indicated a co-precipitation of the metals from a nitric acid solution, and therefore we find in Smith's *Electrochemical Analysis*,[1] p. 97, the statement that "mercury cannot be separated in the electrolytic way from silver and bismuth." The recent experience of Smith and Saltar[2] with

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[1] P. Blakiston, Son & Co., Philadelphia, Pa.

[2] *J. Anal. Appl. Chem.*, 7. 128.