but in addition to this there was quite a considerable amount of mercury in the form of drops so small as to be almost pulverulent. This rendered washing exceedingly difficult. The fluid contents of the dish, after the anode has been raised, are carefully decanted from the powder, boiling water added, allowed to flow around the dish, and again very carefully decanted. This was repeated six or seven times, never draining off the last drops to avoid loss of the mercury. If this care is taken there is no difficulty about good results, but the slightest haste results in the loss of mercury. Naturally when that much water remains on the mercury the evaporation from the heat of the hand is a most tedious, but the only safe, process.

Experiment 1.—The solution contained 0.0933 gram of mercury, 0.1009 gram of arsenic, 0.1024 gram of antimony, 0.1031 gram of tin, eight grams of tartaric acid, thirty cc. of ammonium hydroxide, and was diluted to 175 cc. The current gave 0.5 cc. of mixed gases per minute. It acted for sixteen hours and precipitated 0.0935 gram of mercury.

Experiment 2.—The conditions were the same as in the first experiment. The current gave 0.4 cc. of electrolytic gas per minute and precipitated 0.0933 gram of metallic mercury.

I made no attempt to separate lead from arsenic, antimony or tin.

In conclusion, I would acknowledge my indebtedness to Prof. Edgar F. Smith, at whose suggestion and under whose supervision the above studies were brought to completion.

UNIVERSITY OF PENNSYLVANIA,
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THE ACTION OF GASES UPON METALLIC MOLYBDENUM AND TUNGSTEN.

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HAVING prepared these two metals with care and believing them to possess a high degree of purity, we conceived that it might be of interest to observe their behavior when exposed, at more or less elevated temperatures, to the influence of different gases. We first studied their conduct in an atmosphere of carbon monoxide. The temperature was raised to a red heat, but no reaction whatever occurred. Again, both metals remained unaffected when heated to redness in a brisk current of dry ammonia gas. The period of time during which the gases mentioned were conducted over the heated metals was in each case one hour.

Our next step was to ascertain how each metal would deport itself in an atmosphere of carbonyl chloride ($COCl_2$). This compound was prepared by passing well-dried chlorine gas together with an excess of carbon monoxide through a hard glass tube filled with bone black, the latter being heated to redness. The air in the tube had been displaced by hydrogen and the metal ignited in this gas, after which carbon dioxide was introduced to displace the hydrogen, and the tube then connected with the apparatus from which the carbonyl chloride was evolved.

Action of Carbonyl Chloride upon Molybdenum.—The metal was contained in a porcelain boat. The reaction began at a temperature varying from 150 to 200° C. A dark red colored vapor was produced and condensed in drops in the cooler portions of the tube. The action of the gas was continued until no more molybdenum remained in the boat. As soon as the combustion tube had become perfectly cool the liquid in the anterior portion was quite stiff and jelly-like. On coming in contact with the air it immediately solidified, and its surface was covered with a light, white, woolly substance. This solid mass was subjected to sublimation in currents of carbon dioxide, carbon monoxide, and nitrogen with apparently no attendant decomposition, but we found that, after sublimation had occurred in an atmosphere of carbon monoxide, the boat contained a hard, black residue; its analysis revealed the presence of 32.79 per cent. of metallic molybdenum. The quantity of this material was so slight that we consumed much time in preparing a sufficient amount (0.0663 gram) for this single determination and we were forced to leave the examination for chlorine and carbon go by default. The jelly-like compound, mentioned above, melts below 100° C. Under certain conditions, not clearly understood by us, the product is solid from the very outset, is brittle and can be easily scraped from the sides of the tube upon which it had been deposited. It apparently is more stable, too, than the jelly-like mass. Both modifications decompose very energetically on coming in contact with water, carbonyl chloride or hydrochloric acid gas being simultaneously liberated. This behavior caused us much trouble in the estimation of the chlorine.

We analyzed both modifications, and give a few results obtained with the solid, non-crystalline and reddish-brown material.

Molybdenum Determination.

Per cent.

1.—0.1636 gram substance gave 0.0873 gram MoO_3 = 35.59
2.—0.1182 " " " 0.0626 " " = 35.29
3.—0.3867 " " " 0.2073 " " = 35.74

The jelly-like form contained a little less molybdenum, but approximated the figures just recorded.

The mean of these molybdenum percentages is 35.54 per cent.

Chlorine Determination:

Cl per cent.

1......... 0.0927 gram substance gave 0.2015 gram AgCl = 53.75
2......... 0.0321 " " " 0.0694 " " = 53.46
3......... 0.1864 " " " 0.3940 " " = 52.27

The mean of these results is 53.16 per cent. It may be well to add that in the third analysis a slight loss of chlorine was sustained when the material was brought in contact with water. Now, upon summing up the results we encounter a difference of 11.30 per cent., which perhaps may be due to oxygen. Granting that such is the case we then deduce an atomic ratio of one Mo, two O, and four Cl. This corresponds with no known molybdenum oxychloride, and we have further to add that, upon taking material which had been sublimed and re-sublimed in an atmosphere of nitrogen and which we had every good reason to presume was no longer accompanied with carbonyl chloride, and subjecting this apparently pure compound to analysis, viz., burning it in an atmosphere of oxygen and proceeding as in an ordinary combustion for the estimation of carbon, we several times obtained five per cent. of carbon monoxide. If the product under examination were a true and pure molybdenum carbonyl derivative, $Mo(CO)Cl_4$, we should have gotten about eleven per cent. of carbon monoxide. Qualitative tests, *e. g.*, burning of the compound in pure oxygen, and conducting the gases into lime water also revealed the presence of carbon monoxide. The product is not a pure carbonyl derivative, but we are firmly of the opinion that such a derivative is present in the mixture and that in all probability the contaminating or admixed substance is $MoOCl_4$, for we frequently noticed that the reddish-brown powder gradually assumed a greenish hue as traces of air came in contact with it. Assuming that what we analyzed was a mixture of a molecule of molybdenum oxychloride, $MoOCl_4$, and a molecule of molybdenum carbonyl, $Mo(CO)Cl_4$, we can get theoretical figures that closely approximate the results that we actually obtained by analysis. It is our purpose as time and opportunity allow, to follow this line of investigation further, and strive either to isolate the carbonyl derivative and prove its actual existence, or to show some reason for the peculiar results we have obtained in our present study. Abandoning, then, all further speculation as to the nature of our molybdenum product we may pass to the

Action of Carbonyl Chloride upon Tungsten.— The phosgene was prepared as before and the metal exposed just the same as in the case of the molybdenum. On raising the boat and its contents to a low red heat, at the same time conducting the gas in a rapid current through the tube, orange-red colored, needle-shaped crystals sublimed beyond the boat. In the course of an hour all the metallic tungsten had disappeared, leaving a black metallic residue in the boat. The combustion tube and its contents were allowed to cool. The orange-red colored sublimate was removed and sublimed in an atmosphere of nitrogen gas. An examination of the black residue contained in the boat proved it to be *pure carbon*. In appearance it resembled soot. The analyses of the purified orange-colored derivative show that it was tungsten oxytetrachloride.

Tungsten Determination:

				W per cent.
1	0.1076 gram	material gave	0.0729 gram WO_3	= 53.76
2	0.0300 "	"	0.0438 " "	= 54.30

Chlorine Determination:

				Cl per cent.
1	0.1120 gram	material gave	0.1935 gram AgCl	= 42.72
2	0.2114 "	" . "	0.3577 " "	= 41.25

In determining the chlorine we ignited the material in an air current and conducted the gases through a silver nitrate solution. The theoretical requirements of the compound $WOCl_4$ are 53.80 per cent. W and 41.52 per cent. Cl. These results leave little doubt as to the action of carbonyl chloride upon heated metallic tungsten and indicate, too, that an oxychloride could well be present in the molybdenum product that we have briefly described in the preceding paragraphs.

We next undertook the study of the deportment of the two metals when heated in the vapor of sulphur chloride (S_2Cl_2). To this end a small flask containing liquid chloride of sulphur was connected with a hard glass tube, about twenty inches long which terminated in a receiver. Carbon dioxide was first passed through the entire apparatus and when all the air had been expelled the flask containing the sulphur chloride was gently heated and the current of carbon dioxide continued. In this manner the vapor was brought in contact with the metals which were exposed in boats. The excess of sulphur chloride was condensed and collected in the receiver.

Action of Sulphur Chloride in Gas Form upon Molybdenum.—At a low temperature a yellowish-white, crystalline sublimate appeared, and sulphur separated. The crystalline product did not contain sulphur. As soon as it ceased forming it was removed, and the heat increased until the boat and its contents approached a red heat, when further reaction set in. A reddish-brown colored, and perfectly amorphous sublimate made its appearance. The slow current of carbon dioxide, passed continuously through the apparatus, carried off the excessive sulphur chloride. A white, very volatile and woolly product was produced simultaneously with the amorphous brown material; the latter was freed from the former by gently heating in a current of carbon dioxide. The amorphous product was heated several times in carbon dioxide, indeed as often as seemed necessary to eliminate any sulphur chloride that might be mixed with it. Sublimation in an atmosphere of carbon monoxide was tried, but partial decomposition ensued with the evident formation of a black mass resembling molybdenite very much in general appearance and behavior. The reddish-brown material proved to be rather stable in the air and insoluble in water and in the alkalies. Concentrated nitric acid dissolved it completely after standing for some time. The sulphur content was determined by heating a weighed quantity of the substance in a current of oxygen and passing the sulphur dioxide that resulted through hydrochloric acid containing bromine. The sulphur was finally weighed as barium sulphate.

ANALYSIS.

Molybdenum Determination :

			Mo per cent.
1	0.1009 gram substance gave	0.0680 gram MoO_3	= 44.93
2	0.0811 " " "	0.0556 " "	= 45.69
3	0.1094 " " "	0.0759 " "	= 44.78

The mean of these percentages is 45.13 per cent.

Chlorine Determination :

			Cl per cent.
1	0.1076 gram substance gave	0.1333 gram AgCl	= 30.63
2	0.1185 " " "	0.1422 " "	= 29.70

The mean of these results is 30.16 per cent. Cl.

Sulphur Determination :

			S per cent.
1	0.1090 gram substance gave	0.1945 gram $BaSO_4$	= 24.53
2	0.1855 " " "	0.3289 " "	= 24.37

The mean of results is 24.45 per cent. S.

The formula that may be deduced from these figures is $Mo_5S_8Cl_9$. Its theoretical requirements are 45.47 per cent. Mo, 24.25 per cent. S, and 30.27 per cent. Cl, with which our analytical results accord quite well. We must evidently regard this as an unsaturated molybdenum derivative, which can be explained by the assumption that sulphur has been substituted for equivalent amounts of chlorine in five molecules of molybdenum pentachloride.

The Action of Sulphur Chloride in Gas Form upon Tungsten.—A dark-red crystalline sublimate is produced when sulphur chloride vapors are conducted over gently heated tungsten.

This compound is readily volatilized and is soluble in sulphur chloride, from which it is rather difficult to free it. The first sublimate was sublimed and re-sublimed until only a crystalline product remained. This proved to be very unstable in the air, lost color and was decomposed quite energetically by water, liberating hydrogen sulphide and separating tungstic acid. The sulphur content was estimated in the same manner as with the preceding molybdenum derivative, while the tungsten and chlorine were determined in the ordinary way, care being exercised with the latter so that as little loss as possible would be sustained when the compound was brought in contact with water.

ANALYSIS.

Tungsten Determination :

								W per cent.
1	0.1157	gram	substance	gave	0.0618	gram	WO_3	= 42.38
2	0.0973	"	"	"	0.0510	"	"	= 41.59
3	0.1507	"	"	"	0.0814	"	"	= 42.19
4	0.1537	"	"	"	0.0838	"	"	= 42.19

The mean of these percentages is 42.12 per cent. W.

Sulphur Determination :

								S per cent.
1	0.1699	gram	substance	gave	0.3136	gram	$BaSO_4$	= 25.38
2	0.1737	"	"	"	0.5236	"	"	= 26.03

The mean percentage is 25.70.

Chlorine Determination :

								Cl per cent.
1	0.0631	gram	substance	gave	0.0734	gram	AgCl	= 31.93
2	0.0988	"	"	"	0.1274	"	"	= 31.88
3	0.1478	"	"	"	0.1867	"	"	= 31.24

The mean of these results equals 31.68 per cent.

Employing the means of the three determinations we deduce as the empirical formula of this new derivative, $W_2S_7Cl_8$, which we would express as follows: $W_2S_3Cl_4 + 2\ S_2Cl_2$ The theoretical requirements of this compound are 42.03 per cent. W, 25.57 per cent. S, and 32.42 per cent. Cl. Like the molybdenum derivative it may be viewed as an unsaturated sulphochloride derived from two molecules of the pentachloride by the substitution of sulphur for chlorine and in addition combined with sulphur chloride.

The study of the deportment of molybdenum and tungsten in atmospheres of other gases will be continued in this laboratory.

UNIVERSITY OF PENNSYLVANIA,
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