

three grams of potassium cyanide. It was heated to 65° and then electrolyzed for three and one-half hours with a current of $N.D_{100} = 0.04$ ampere. The precipitated silver weighed 0.1004 gram. No cadmium was found in it. The poles were separated two inches from each other.

Experiment 2.—Operating with conditions just like those in experiment 1, the deposit of silver weighed 0.0999 gram.

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THE ACTION OF PHOSPHORUS PENTACHLORIDE UPON MOLYBDENUM TRIOXIDE.

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THE action of phosphorus pentachloride upon the trioxides of tungsten and of molybdenum has been the subject of investigation by Schiff,¹ Teclu,² and Piutti.³ Schiff announced that with tungstic acid and the pentachloride the products were in the main phosphorus oxychloride and a brown colored tungsten oxychloride. Teclu, upon repeating Schiff's experiments, obtained phosphorus oxychloride and the *hexachloride of tungsten*. This was the result when working with one part of WO_3 and three parts of phosphorus pentachloride. The mixture was heated in sealed tubes. Piutti substituted molybdenum trioxide and hoped to get a corresponding molybdenum *hexachloride*. This he did not realize; instead, he obtained a compound which gave results on analysis that led to the formula $MoCl_4 \cdot POCl_3$. Along with the dark-green colored crystals of this compound there was a reddish-brown liquid. The tube, after being opened, and as soon as the liquid was removed, was connected with a Wouff bottle to which a drying tube was attached. The other end of the sealed tube was opened and connected with a carbon dioxide generator. The tube was next surrounded with water at 80° , and a current of carbon dioxide conducted through it, when the green colored crystals sublimed. They were carefully collected and gave the results from which was deduced the formula given above. We have repeated the experiment of Piutti under

¹ *Annalen der Chemie*, 102, 115.

² *Annalen der Chemie*, 187, 255.

³ *G. ch. italiana*, 9, 538.

slightly modified conditions. Thus, we exposed 1.5 grams molybdenum trioxide and ten grams of phosphorus pentachloride in a sealed tube, filled with chlorine, to a temperature of 175°C . The sides of the tube, on cooling, were covered with greenish-black crystals. One end of the tube was broken open, quickly connected with a dry flask, after which the other end was opened and attached to a delivery tube in union with a chlorine generator. As the chlorine gas was conducted through the tube a gentle heat was applied to the latter, when a colorless liquid distilled over and was carefully collected. Later the greenish-black crystals sublimed and were collected separately in a dry vessel. The analysis of the colorless liquid just mentioned indicated it to be phosphorus oxychloride. The greenish-black solid was rapidly weighed out in weighing bottles. The vessel containing the portion intended for the chlorine determination was, after weighing, uncorked under water and the substance allowed to gradually enter the water. The disengaged gases were thus wholly absorbed.

Chlorine Determinations.—(1) 0.3702 gram substance gave 1.0881 gram silver chloride, equal to 0.2720 gram chlorine, or 73.47 per cent. (2) 0.3103 gram substance gave 0.9074 gram silver chloride, equal to 0.2268 gram chlorine, or 73.14 per cent.

Phosphorus Determinations.—(1) 0.5610 gram substance gave 0.1375 gram magnesium pyrophosphate, equivalent to 6.84 per cent. phosphorus. (2) 0.7991 gram substance gave 0.1914 gram magnesium pyrophosphate, equal to 6.67 per cent. phosphorus.

Molybdenum Determination.—The substance was digested with ammonium sulphide, and from this solution hydrochloric acid precipitated the trisulphide, which was changed to disulphide and weighed as such. 0.2385 gram material gave 0.0457 gram, equal to 19.17 per cent. Mo.

From these figures we deduce an atomic ratio, which would point to our compound as being a union of one molecule of molybdenum pentachloride with one molecule of the phosphorus haloid— $\text{MoCl}_5 \cdot \text{PCl}_5$. The theoretical percentages in this case are:

$\text{Mo} = 19.91$ per cent., $\text{Cl} = 73.65$ per cent., $\text{P} = 6.43$ per cent.

Our compound is greenish-black in color and decomposes

quite easily. The conditions under which we operated being slightly different from those of Piutti, it is not surprising that our product should be different. We used an excess of the phosphorus haloid and took care that the tube in which the reaction occurred contained chlorine gas. Subsequently we also distilled out the phosphorus oxychloride in a current of chlorine, and did not use carbon dioxide until after the removal of the liquid, and not while the tube was exposed to a gentle heat. The reaction which occurred with us may be, perhaps, represented as follows:



With even a larger excess of the phosphorus haloid the same product was found, so that it is hardly probable that we can hope to arrive at the hexachloride of molybdenum through this reaction.

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SEPARATION OF TITANIUM FROM IRON.

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IN the recent literature which I have been able to consult, the separation of titanium from iron by means of sulphurous acid, has been confined to the sulphates of these two metals. This process is long and tedious and often unsatisfactory.

If a neutralized solution of titanium and iron chlorides, of not too great dilution, be boiled with an excess of sulphurous acid, the iron becomes deoxidized at once and a white flocculent precipitate of titanium settles out. By this means the titanium is obtained free from iron and requires no re-solution and second precipitation, as is frequently necessary for purification when precipitated from the sulphate. If the sulphate be changed into a chloride by precipitation with ammonium hydroxide and dissolving again in dilute hydrochloric acid and neutralizing the excess of acid with ammonium hydroxide, the separation is easily effected. The accuracy of the method is shown by the two following analyses:

	Found.	Used.
TiO ₂	0.0322	0.0308
TiO ₂	0.0317	0.0314