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AN ATTEMPT TO PREPARE MOLYBDENUM HEXACHLORIDE.

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It is well known that Teclu¹ obtained the hexachloride of tungsten by acting upon the trioxide of the metal with phosphorus pentachloride. The treatment of molybdenum trioxide in the same manner gave in one instance the compound $\text{MoCl}_5 \cdot \text{POCl}_3$, and in another, $\text{MoCl}_5 \cdot \text{PCl}_5$. In both of these derivatives the pentachloride of the metal is present. It would, therefore, seem that the metal is incapable of carrying the sixth chlorine atom. Reuter² heated both the trioxide of tungsten and that of molybdenum with silicon tetrachloride; his products, however, were not hexachlorides. Passing by his observations it was thought that if a partially chlorinated molybdic acid were exposed to chlorinating agents the residual oxygen might be removed and that then perhaps the hexachloride would be present in the reaction product. To this end molybdenyl chloride, MoO_2Cl_2 , was mixed with an equivalent quantity of phosphorus pentachloride and heated in a sealed tube in the presence of chlorine to a temperature of about 170°C . On cooling, it was found that the tube contained a mass of greenish-black crystals, which when carefully freed from adherent phosphorus oxychloride by distillation in an atmosphere of chlorine gave a product that on analysis yielded figures approximating the pentachloride more closely than the hexachloride.

Silicon tetrachloride was substituted for the phosphorus pentachloride and the experiment repeated. The resulting crystalline

¹ *Ann. Chem.*, (Liebig's), 187, 253.

² *Dissertation*, Tübingen, 1893.

product was quickly removed to a boat and carefully distilled in an atmosphere of carbon dioxide. Brown vapors were expelled from the boat, which finally contained nothing but white silica. The brown vapors quickly condensed in the colder portion of the tube, and upon analysis gave results varying between those required by the tetrachloride and pentachloride.

The conclusion to be drawn from these experiments then is that notwithstanding the molybdenum atom has already been partially chlorinated, and apparently is in a suitable condition to pass into the hexachloride, it yet does not do so, and we can hence only say that the molybdenum is either not sexivalent towards chlorine, or that at the elevated temperature at which these reactions took place, the hexachloride, if formed, cannot exist, but is dissociated into lower chlorinated derivatives.

On heating pure, finely divided molybdenum, intimately mixed with sugar-carbon, in an atmosphere of chlorine the invariable product was the pentachloride.

The temperature doubtless exerts a great influence in these reactions.

It has been observed in this laboratory that when metallic molybdenum acts upon an aqueous solution of ferric chloride rapid reduction of the ferric salt ensues with accompanying solution of the molybdenum. From a careful determination of the amount of iron thus reduced, the molybdenum evidently dissolves as a hexad, and it may be that if such solutions were allowed to evaporate slowly in desiccators, the hexachloride or some double salt, formed from it and ferrous chloride, might be found. Search will be made in this direction.

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THE ACTION OF HYDROCHLORIC ACID GAS UPON SODIUM VANADATE.

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THE reaction of Debray¹—the volatilization of molybdic acid by means of hydrochloric acid gas,—has suggested a number of experiments which of late have been tried in various

¹ *Compt. rend.*, 46, 1098.