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Abstract

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ON THE PREPARATION OF RHENIUM HEXAFLUORIDE BY FLUORINATION OF THE METAL WITH CHLORINE TRIFLUORIDE

(Presented by Academician N. V. Tananaev, 5 V 1960)

Rhenium hexafluoride—ReF_6—was first obtained by Ruff and Kwasnik (^{1}) by the action of fluorine on metallic rhenium at 125°. To avoid the formation of rhenium oxyfluorides, the fluorine must not contain oxygen; removal of the latter from fluorine gas was achieved by means of a silent discharge (in this process fluorine oxide—F_2O_2—is formed). The rhenium hexafluoride obtained by this method apparently still contained some quantities of oxyfluorides. A second report on obtaining rhenium hexafluoride by the same method dates to 1950. In that work the operation of purifying fluorine from oxygen was absent, but the product obtained was distilled in a stream of nitrogen in order to isolate pure ReF_6 (^{2}).

The chief difficulty in all cases of obtaining rhenium hexafluoride lies in the ready formation of oxyfluorides that contaminate the product (an analogous phenomenon was observed in the fluorination of molybdenum) (^{3}). For rhenium, the formation of oxyfluorides is still more characteristic owing to the possibility of oxidizing it to the heptavalent state. Consequently, when fluorine acts on oxygen-containing rhenium derivatives, oxyfluorides are formed, but not ReF_6.

The action of halogen fluorides—BrF_3 (^{4}) and IF_5 (^{5})—on perrhenates leads to the formation of complex oxyfluorides of the type $Me^I[ReO_2F_4]$ in the first case and to perrhenyl fluoride ReO_3F in the second. Rhenium hexafluoride is not formed in this process. It seemed of interest to investigate chlorine trifluoride in similar reactions as the most powerful fluorinating agent among all the halogen fluorides. We had previously established that metallic platinum is readily fluorinated by chlorine trifluoride to the tetravalent state (^{6}). This circumstance suggested the possibility of using this halogen fluoride for the fluorination of metallic rhenium. It turned out that liquid ClF_3 does not act on powdered rhenium, whereas with gaseous chlorine trifluoride at 300° a reaction is observed with a good yield of rhenium hexafluoride. For the experiments an apparatus was used, shown schematically in Fig. 1, consisting of a steel container **A** with chlorine trifluoride, a Teflon reactor **B** with powdered rhenium, previously ignited in a stream of hydrogen, and a Teflon receiver **V**, cooled with liquid nitrogen. To prevent atmospheric moisture from entering the apparatus,

Fig. 1

Figure 1: Fig. 1

a polyethylene throttle **G** with CCl_4 was placed at the outlet from the receiver.

At the beginning of the work the container **A** was cooled with dry ice, then a stream of nitrogen was turned on at such a rate that visible gas bubbles passed through the throttle **G**. The nitrogen was preliminarily dried with sulfuric acid, purified from oxygen with copper, and, for final drying, passed through a spiral immersed in liquid nitrogen. After all the air had been displaced from the system by nitrogen, heating of the reactor was turned on. At the same time the container **A** was also warmed to 0°. The reaction proceeded at a temperature of 300°, with 12 g of rhenium reacting in 6 hours. The collected

in the receiver the product was a yellow volatile liquid containing ReF_6 and an excess of ClF_3. To isolate pure ReF_6, it was crystallized from liquid hydrogen fluoride. For this purpose the product in the receiver was dissolved in hydrogen fluoride, and the solution was cooled with dry ice. On standing for 8-10 hours, large light-yellow crystals separated. The liquid then contained almost no rhenium. The crystals obtained were recrystallized from hydrogen fluoride. The yellow crystalline substance that precipitated from the solution in HF on cooling was apparently a solvate, $ReF_6 \cdot xClF_3$, since it contained chlorine trifluoride. It melts at about 0° and even in the liquid state is only sparingly soluble in hydrogen fluoride. Decomposition of this product in order to obtain pure ReF_6 was achieved by distillation in a stream of hydrogen at 50° in a platinum tube. The ReF_6 obtained as a result contained chlorine and hydrogen fluoride, from which it was purified by holding in vacuum at $-70°$ for 4 hours. Pure rhenium hexafluoride, under the microscope, consisted of large yellow crystals. For microscopic observations a Teflon cuvette was used, in which the substance was clamped between two films of the same material, 0.05 mm thick. The product was identified by melting point and chemical analysis. The capillary for determining the melting point was made of thin Teflon. The melting point of the ReF_6 obtained was $+18.7 \pm 0.1°$. According to the literature data, $+18.8°$ (^{1}) and $+19°$ (^{2}).

Fig. 1

The operations of taking samples for analysis were carried out in a dry box. The weighed portion was hydrolyzed in a tared quartz flask into which an excess of a titrated KOH solution had previously been poured, frozen by immersing the flask in liquid nitrogen. Under such cooling ReF_6 does not react with ice. The tightly closed flask with the stopper and alkali solution was warmed to room temperature and weighed. Then a neutral H_2O_2 solution was added to the hydrolysate, and the contents of the flask were boiled for 3 min with precautions against absorption of CO_2 from the air. After the solution was cooled, the excess alkali was titrated with hydrochloric acid. For the neutralization of 1 g of ReF_6

after hydrolysis and oxidation according to the equation

$$2ReF_6 + 14KOH + H_2O_2 = 2KReO_4 + 12KF + 8H_2O$$

0.233 equivalent of alkali is required. For 1 g of the ReF_6 obtained, 0.234 equivalent was consumed. In aliquot portions of the solution, rhenium was determined as nitron perrhenate, and fluorine by titration with $AlCl_3$ solution by the method of Kurtenacker and Jurenka ([7]).

Found, %: Re 62.4$\pm0.3; F 38.2\pm0.3; Cl'$—not detected.
Calculated, %: Re 62.04; F 37.96.

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Note: Figure translations are in progress. See original paper for figures.