

141. *Rhenium Oxychloride.*

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METALLIC rhenium when heated in pure dry chlorine gives first of all a trace of a brown, volatile, low-melting material and subsequently, and for the main part, a black crystalline compound recently shown to be the tetrachloride (Briscoe, Robinson, and Stoddart, J., 1931, 2263). In that communication, the brown material was described, and a photograph illustrating its typical crystalline form was given, but attempts then made to obtain it in quantities sufficient for investigation were unsuccessful. It has now been shown that one of the methods originally tried, without success, *viz.*, the addition of dry oxygen to the chlorine, does actually effect a quantitative conversion into the new compound. Synthetic experiments, analyses, and vapour-density measurements show that the substance is *rhenium oxychloride*, ReO_2Cl_2 .

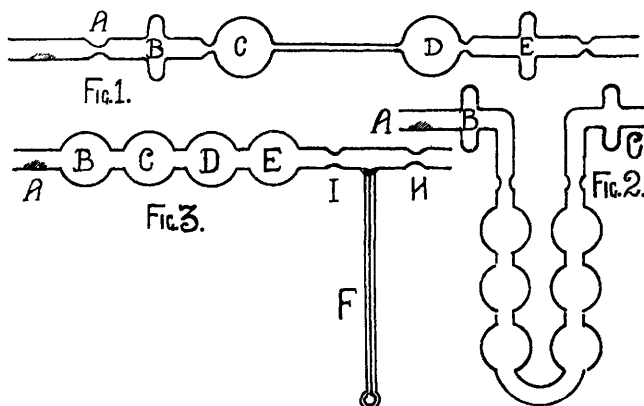
Preparation.—The oxychloride results on heating (*a*) the metal in dry mixtures of air and chlorine, (*b*) the tetrachloride in dry oxygen, or (*c*) the pentoxide (Briscoe, Robinson, and Rudge, J., 1931, 3087) in dry chlorine. Of these methods, the first proved most convenient and was generally used. Chlorine mixed with air over a certain minimum concentration and rigorously dried was passed over metallic rhenium in the apparatus (Fig. 1). The bulbs are used to reduce the gas velocity sufficiently to allow condensation of the oxychloride: in their absence its retention was incomplete. Most of the volatile brown material condensed in *B* and eventually solidified as a mass of dark crystals. When the reaction was over, the tube was sealed off at *A* and evacuated. In the preliminary experiments considerable difficulty was experienced at this stage through an occasional dissociation of the compound when pumping was commenced. It was suspected that this might be due to moisture, but greater precaution in the drying of apparatus and reagents failed to eradicate the trouble. It was finally discovered that if the material were melted in the preparative gas stream immediately after the completion of the preparation, it would not afterwards decompose in a vacuum. We have at present no idea why this should be the case.

Analysis.—The first analyses were made on material which had been distilled in a vacuum from bulb *B* into *C* and finally divided between bulbs *D* and *C*, where it was sealed off in two separate quantities. The contents of *D* and *C* were analysed by breaking the bulbs under water, the weight of the material being obtained by

collecting and weighing the fragments of glass, and allowing for the air displaced. In water the material is hydrolysed and yields some dioxide; this, together with the glass, was filtered off and weighed, after which the rhenium dioxide was dissolved in nitric acid, removed by washing, and the glass weighed alone. The chlorine in the filtrate from the dioxide and glass was estimated as silver chloride in the usual manner, and the results (below) show that it corresponds

Re, %	19.98	17.28	16.97	Mean	18.08
Cl, %	32.11	34.65	33.11	„	33.29
Total, %	52.09	51.93	50.08	„	51.37

closely with that required for ReO_2Cl_3 . At the same time, however, only about one-third of the rhenium had suffered precipitation as dioxide, and the filtrate containing the chlorine was found on being



tested to carry per-rhenate ion. In succeeding analyses, the rhenium in the filtrate was reduced with zinc and hydrochloric acid after the manner described by Briscoe, Robinson, and Stoddart (J., 1931, 666). Complete precipitation from these solutions was not attained, but the total rhenium accounted for in three different preparations was 52.95, 46.27, and 45.75% respectively, mean 48.32% (Found: Re, 48.32; Cl, 33.29. ReO_2Cl_3 requires Re, 57.32; Cl, 32.83%). It was believed that these results practically established the nature of the compound, and the synthetic experiments now to be described confirmed this view.

Rhenium was weighed out into the apparatus (Fig. 2), which had been previously cleaned, carefully dried, and weighed. The metal was treated with air and chlorine, and the product was collected in B and melted. The apparatus was closed by means of rubber at A and evacuated at C, the material distilled from B into the U-portion, and finally dry air was admitted at atmospheric pressure,

and the apparatus was closed at *B* by another rubber cap. In some experiments, the *U*-portion was cooled in a freezing mixture, but this did not appear to affect the results. These are given in Table I, where it will be seen that the proportion of rhenium differs from

TABLE I.

Expt.	Wt. of Re, g.	Product.		Re, %.
		Calc. for ReO_2Cl_3 , g.	Found, g.	
1	0.1671	0.2916	0.2938	56.87
2	0.2504	0.4368	0.3819	65.57
3	0.2278	0.3974	0.3991	57.07
4	0.1505	0.2625	0.2565	58.66
5	0.1173	0.2046	0.2051	57.19
6	0.0928	0.1619	0.1491	*62.23
7	0.1248	0.2177	0.2125	58.73
8	0.0871	0.1519	0.1540	56.56
		Mean		59.11
		Mean (excluding 2 and 6)		57.51

* Evident decomposition.

that calculated for ReO_2Cl_3 in two only of the eight experiments, and in one, at least, of these two cases some decomposition was observed.

Vapour Density.—This was determined by the method of Victor Meyer. Rhenium oxychloride prepared in the usual way was transferred to small bulbs, which were almost filled with the material and sealed off in an atmosphere of dry air. Immediately prior to the measurement, the top of the bulb was broken, and it was allowed to fall into the vaporising chamber of the apparatus, which was maintained at about 400° by means of an electric heater. The molecular weights obtained, *viz.*, 339.3 at 380° and 325.5 at 408° , mean 332.4, are in good agreement with that required by ReO_2Cl_3 , *viz.*, 324.5.

Liquid Density.—About 1.5 g. of rhenium were converted into oxychloride at *A* (Fig. 3). The apparatus was then evacuated and the compound distilled successively to *D*, *E*, and *F*, after which the bulbs were removed by being sealed off at *I*.

The height of the material in the stem of the density vessel *F* was measured by means of a cathetometer reading to 0.02 mm. at three distinct temperatures, and the volumes thus observed were subsequently determined by weight calibration with water. The density (g. per c.c.) was 3.359 at 35° , 3.320 at 47° , and 3.309 at 53° , giving a coefficient of expansion of 0.000840 between 35° and 53° .

Properties.—Rhenium oxychloride forms dark red-brown needle-shaped crystals which appear almost black in large masses and darken somewhat on keeping. The crystals melt very sharply at $23.9^\circ \pm 0.2^\circ$ to a yellowish-brown, rather viscous liquid (*d* 3.359 at

35°) which vaporises rapidly in a vacuum at a little below 300°, although the vapour pressure is evidently considerable at much lower temperatures. It is perfectly stable for long periods in a vacuum or in perfectly dry air, and may be heated at 260° with metallic rhenium without reaction. In the presence of the slightest trace of moisture it fumes, yielding hydrogen chloride, the residue at once darkening. With water it is decomposed, yielding in part rhenium dioxide. The reaction is complex, since about one-third of the rhenium appears in the bivalent and about two-thirds in the septavalent state.

Grateful acknowledgment is made to the Research Committee of Armstrong College for a grant which has defrayed the cost of the rhenium used in this investigation.

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[Received, February 18th, 1932.]
