The derived value is in excellent agreement with the figure 107.880 which has been accepted for many years by chemists. Although this outcome is just another way of showing that the results of our present series of analyses are consistent with the physical values for the atomic weights of fluorine and carbon, it is of particular importance because of the special position of the atomic weight of silver as the practical basis of the chemical atomic weight scale. The significance of this last point will be elaborated further in the section which follows.

The possibility of comparing fluorine and silver by the analysis of perfluorobutyryl chloride opens the way for a consideration of a number of questions. For one thing serious consideration can now be given to the adoption of fluorine as the basis of the chemical atomic weight scale. Some of the arguments in favor of the change may be noted here: The element is anisotopic[22] and hence, unlike oxygen, its chemical atomic weight is constant. Further to go from natural oxygen (16) to an assigned value of 19 for fluorine would mean an increase in the chemical atomic weight values of the other elements by less than 1 part in 20,000, a very minor change which should not present serious practical problems. Finally, since the atomic mass of fluorine can be established quite accurately on the physical scale by physical methods, fluorine could serve as a bridge between the two scales. Naturally, if fluorine were to be accepted as the basis of the chemical scale there would be need of further work to establish as accurately as possible the relationship between fluorine and silver. It would be desirable not only to repeat the analyses of perfluorobutyryl chloride and undertake the analyses of a pure sample of the corresponding bromide, but it would be important to explore the suitability of the acid halides of other perfluoroaliphatic acids for comparing the atomic weights of fluorine and silver.

In the latest "Report on Atomic Weights" Wichers[19] presents a most enlightening discussion of the "Problem of Two Scales" and raises the question of unifying the chemical and physical atomic weight scales. Of the various possibilities Wichers regards a common scale, based on fluorine with an assigned mass of 19, as the most attractive one. The fact that our work gives a comparison between the atomic weights of fluorine and silver (the practical basis of many chemical atomic weight values) lends support to Wicher's conclusion.

Acknowledgments.—This work on atomic weight of fluorine has received partial support from several grants to the senior author. Small grants from the Cyrus M. Warren Fund and the Permanent Science Fund of the American Academy of Arts and Sciences in 1937–38 were of great help; in fact a Troemner No. 10 balance, purchased at that time, was used in the present series of experiments. All the work on derivatives of trifluoroacetic acid carried out immediately following the war was supported by funds from an ONR Contract (onr #71600). A contract with the Division of Research, A.E.C., and a grant from the National Science Foundation, both primarily in support of other atomic weight projects, provided invaluable assistance at critical points in the present set of experiments. The senior author acknowledges gratefully all of this financial assistance.

PORTLAND, OREGON

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[22] This term has been proposed by H. E. Duckworth (private communication) as more correct etymologically than the older terms "monoisotopic" and "simple" to describe an element having only one atomic species. For further discussion of term "anisotopic," see footnote 46, ref. 19.

[CONTRIBUTION FROM THE RICHARD BENBRIDGE WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY]

The Preparation and Properties of Rhenium Oxychloride (ReO_3Cl)[1]

BY CLARENCE J. WOLF,[2] A. F. CLIFFORD AND W. H. JOHNSTON

RECEIVED APRIL 15, 1957

Rhenium oxychloride has been prepared in good yields by direct chlorination of rhenium trioxide. The gaseous infrared spectrum, the gas density and the vapor pressure were determined at room temperature. The general handling procedure and some properties of this compound are discussed.

Introduction

Rhenium oxychloride has been prepared by several investigators.[3–7] All of these preparations use essentially one of two procedures, either the reaction between rhenium(VII) oxide and rhenium tetrachloride ($ReCl_4$)[5] in a combustion tube or the oxidation of rhenium trichloride ($ReCl_3$). The present paper describes a direct procedure which gives a superior product which needs only be vacuum distilled to remove dissolved chlorine.

A limited number of physical properties of rhenium oxychloride have been reported. In 1932 Bruke and Ziegler[1] described it as a colorless liquid melting at 4.5°, boiling at 131°, and hydrolyzing immediately in air to perrhenic ($HReO_4$) and hydrochloric acids. In the following year Geilmann and Wrigge[5] reported it to be light sensitive, turning purple in sunlight and becoming colorless in the

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[1] This work was supported in part by the United States Atomic Energy Commission under Contract No. At(11-1)-166 with Purdue University

[2] Taken in part from research work done by Clarence J. Wolf for a thesis to be submitted to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] A. Bruke and K. Zielger, *Ber.*, **65**, 916 (1932).

[4] H. V. A. Brisco, P. L. Robinson and A. J. Rudge, *J. Chem. Soc.*, 2643 (1931).

[5] W. Geilmann and Fr. W. Wrigge, *Z. anorg. allgem. Chem.*, **214**, 248 (1933).

[6] O. W. Kolling, *Trans. Kansas Acad. Sci.*, **56**, 378 (1953).

[7] Rhenium tetrachloride is a mixture of the trichloride and the pentachloride.

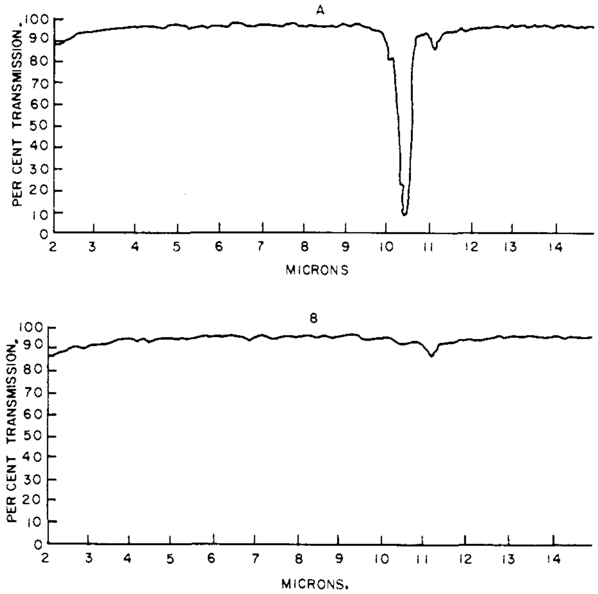

Fig. 1.—Infrared absorption spectrum of ReO_3Cl: upper (A), gaseous ReO_3Cl; lower (B), evacuated gas cell.

dark. In 1952 the microwave spectrum was studied by Amble, *et al.*,[8] who reported the structure as a symmetric top with an Re–Cl distance of 2.230 ± 0.004 Å., and Re–O distance of 1.761 ± 0.003 Å., and the Cl–Re–O angle as 108° 20′ ± 1°. Recently Eichhoff and Weigel[9] studied the Raman spectrum of rhenium oxychloride but encountered difficulty in photodecomposition of the sample. Some additional properties of this compound are reported in the present work.

Experimental

Rhenium(VII) oxide (Re_2O_7) readily is converted to rhenium(VI) oxide (ReO_3) by reduction with dioxane.[10] The reactions are

$$Re_2O_7 + xC_4H_8O_2 \longrightarrow Re_2O_7\cdot(C_4H_8O_2)_x$$

$$Re_2O_7\cdot(C_4H_8O_2)_x \xrightarrow{125-145^\circ} ReO_3 + \text{decomposition products}$$

The rhenium(VI) oxide is then allowed to react with chlorine in a dry combustion tube between 160 and 190°

$$2ReO_3 + Cl_2 \xrightarrow{160-190^\circ} 2ReO_3Cl$$

The yield obtained from these reactions is above 70%. The product is quite pure and is colored slightly yellow due to dissolved chlorine; this, however, may be removed readily by vacuum distillation leaving a clear colorless liquid boiling at 128° (uncor.). Analyses for chlorine were 12.74 and 12.71% as compared to the theoretical value of 13.14%. This slightly low value was caused by some hydrolysis in air during weighing.

Some precautions are necessary in the handling of this compound. Rhenium oxychloride reacts immediately with mercury and with ordinary stopcock grease; therefore, it must be trapped before reaching the diffusion pump. Furthermore, a special stopcock grease such as "Halocarbon grease" (Halocarbon Products Corporation) should be used to minimize the decomposition. Even this grease, however, caused some slight decomposition of the oxychloride leaving a purple colored substance, probably rhenium(VI) oxide (ReO_3).

To test the hypothesis that the purple color was due to this oxide, some ReO_3 was dissolved in a small amount of the oxychloride. It is interesting to note that a similar purple solution was formed.

The rhenium oxychloride can be kept without decomposition in a greaseless system of glass, Kovar and Monel. In this manner, we were able to keep the liquid colorless for several weeks.

Rhenium oxychloride is extremely reactive toward mercury, silver and a large number of organic compounds. Carbon tetrachloride, however, was found to be a good solvent, giving a clear, colorless, solution. The oxychloride does not appear to react with brass that has been first chlorinated, or with stainless steel.

The infrared spectrum of gaseous rhenium oxychloride was measured in a ten centimeter gas cell with potassium bromide windows, using a double beam Perkin–Elmer Recording Infrared Spectrometer Model 21. The spectrometer is shown in Fig. 1. Curve A is the absorption spectrum of the vapor in the cell and curve B is the absorption spectrum of the cell after removal of the oxychloride. The vapor pressure as measured with a Bourdon gage is 4.5 ± 0.5 mm. of mercury at room temperature. The vapor density of rhenium oxychloride at room temperature is 6.5×10^{-5} g./ml. (average of two determinations). Assuming the ideal gas law, the experimental molecular weight was 268 g. compared to a theoretical value of 270 g.

LAFAYETTE, INDIANA

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[8] E. Amble, S. L. Miller, A. L. Schawlow and C. H. Towner, *J. Chem. Phys.*, **20**, 192 (1952).

[9] H. J. Eichhoff and F. Weigel, *Z. anorg. allgem. Chem.*, **275**, 267 (1954).

[10] L. F. Audrieth, Editor-in-chief; "Inorganic Syntheses," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1950, p. 186.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

The Thermal Decomposition of Uranium Peroxide, $UO_4\cdot 2H_2O$

BY JAMES E. BOGGS AND MUNZIR EL-CHEHABI

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$UO_4\cdot 2H_2O$ decomposes slowly in the temperature range 90–195° to form a different peroxide, U_2O_7. The rate of this reaction has been followed and the properties of U_2O_7, which has not been isolated previously, have been investigated.

Uranium peroxide, $UO_4\cdot 2H_2O$, has been known since 1876[1] and has been subjected to intensive investigation in recent years. Nevertheless, its constitution is still unknown, some authors considering it to be a true peroxide hydrate, others a peroxy acid, and others an addition compound of uranium oxide, $UO_3\cdot H_2O_2\cdot H_2O$.

The existence of one other peroxide of uranium, U_2O_7, has been suggested. Evidence for a hydrated form of this substance was found by Hüttig and von Schroeder[2] in their experiments on the decomposition of hydrated UO_4. Later, Kraus[3] ob-

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[1] T. Fairley, *Chem. News*, **33**, 237 (1876).

[2] G. F. Hüttig and E. von Schroeder, *Z. anorg. allgem. Chem.*, **121**, 243 (1922).

[3] C. A. Kraus, Manhattan District Project Report A-281, Sept. 7, 1942.