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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF REED COLLEGE]

The Atomic Weights of Fluorine and Silver

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This is the first chemical determination of the atomic weight of fluorine by the Harvard method. Perfluorobutyryl chloride was prepared by the reaction between PCl_5 and carefully fractionated perfluorobutyric acid. The chloride was purified by fractional distillation in vacuum systems. Samples of the chloride were hydrolyzed in pyridine solution and the chloride was precipitated with a known amount of silver. The end-point was determined nephelometrically, the final adjustment being made after the precipitate had stood for two years. The atomic weight of fluorine is calculated to be 18.999 as the average result of six analyses. This new value is shown to be in excellent agreement with the best atomic weight values derivable from mass-spectrographic measurements and from nuclear reaction data. The question of unifying the chemical and physical atomic weight scales by assigning the value 19 to the mass of the anisotopic element F is discussed.

The present chemical value 19.00 of the atomic weight of fluorine is based upon a number of determinations[1] by two different methods: the chemical analysis of pure fluorine compounds; and the measurement of the gas density of fluorine compounds of carbon and silicon. In the case of this element the analytical determinations presented special difficulties and are generally regarded as inferior to those by the gas density method. By way of illustration of the status of the analytical determinations it may be noted that of the five determinations of this type the one which is given most weight is Smith and Van Haagen's[2] conversion of sodium fluoride to sodium sulfate, a determination which comprised only three experiments involving samples of sodium fluoride ranging in weight between 0.3 and 1.1 g. Obviously, this determination by Smith and Van Haagen leaves much to be desired in many respects. The atomic weight of fluorine derived from Smith and Van Haagen's measurements is 19.005.

The discovery of isotopes of oxygen by Giauque and Johnston in 1929 led to the acceptance by chemists and physicists of two different scales: chemists have continued to assign the value 16 to oxygen as found in nature, *i.e.*, to the naturally occurring mixture of isotopes; physicists, on the other hand, have consistently assigned the value 16 to the isotope O^{16}. The difference between these two scales is very small and conversions between them are readily made by means of a conversion factor (1.000275). However, following the discovery[3] that the isotopic composition of natural oxygen is not fixed and constant, the chemists are in the position of using an atomic weight scale based on a variable "constant." Although the variations in question are of no consequence with respect to present chemical atomic weight values, it has seemed desirable, for the sake of logic at least, to replace oxygen as the basis of the chemical scale by some anisotopic element.

Fluorine is a promising replacement for oxygen.[4] Its one serious disqualification is the simple fact that no strictly chemical atomic weight determination has been satisfactory, especially no determination relating fluorine to silver which, because of the part the latter plays in the Harvard atomic weight method, has become the "practical" basis of atomic weight values of a majority of the elements. The present investigation is the culmination of a series[5]

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[1] For a review of these determinations see A. F. Scott and M. Bettman, *Chem. Revs.*, **50**, 363 (1952).

[2] E. F. Smith and W. K. Van Haagen, Carnegie Inst. Pub. No. 267, 1918.

[3] By M. Dole in 1935. For references and discussion see review article by M. Dole, *Chem. Revs.*, **51**, 263 (1952).

[4] Dole, ref. 3, discusses this question. In 1936 he suggested protium and sodium as suitable replacements for oxygen; in his 1952 article his list includes fluorine as a third possibility.

[5] These studies have been senior projects under the Senior Thesis program of the College. The pioneering students were: Hilary B. Willis (1938); Robert W. Moen (1939); Joseph H. Gill and Arthur H. Livermore (1940); Chester Schink and Louis G. Stang, Jr.* (1941); Joseph F. Bunnett (1942); Edward L. Bennett* (1943); Dale C. Butner* (1948); Earl S. Scott* (1949). Theses by these students are on file in the College Library. Students who worked on the preparation and analysis of derivatives of trifluoroacetic acid are indicated by an asterisk.

of studies which has been carried out for the purpose of finding a fluorine compound suitable for the determination of the atomic weight of fluorine by the Harvard method.

The preliminary experiments involved the preparation, purification and analysis of trifluoroacetyl chloride, trifluoroacetyl bromide and silver trifluoroacetate; samples of the last two compounds were painstakingly analyzed. Although these compounds appeared rather promising, a final series of these experiments with them was not undertaken because pure perfluorobutyric (heptafluorobutyric) acid became available commercially, and its acid chloride appeared to have a number of advantages over trifluoroacetyl bromide. For example, the heptafluoro compound has the higher boiling point (39° *vs.* −5°) and the higher percentage of fluorine (57% *vs.* 32%).

A pathfinding preparation and study of perfluorobutyryl chloride and silver heptafluorobutyrate were carried out by Swanson[6] in this Laboratory. These experiments showed that the acid chloride was very promising for atomic weight purposes; these experiments also laid the groundwork for a new preparation and analysis of perfluorobutyryl chloride described in this article.

Preparation and Purification of Materials

After some trial experiments a final sample of perfluorobutyryl chloride was prepared as follows.[7] A two pound sample of perfluorobutyric acid obtained from Minnesota Mining and Manufacturing Co. was twice fractionated using a 20-plate Oldershaw column with an automatic vapor-dividing head. In the first distillation concentrated sulfuric acid was present as a drying agent. In both distillations one-third of the charge in the pot was equally divided between the head and tail fractions which were rejected. The purified acid (1.7 moles) was converted to the acid chloride by slowly adding it to reagent grade phosphorus pentachloride (3.8 moles). The all-glass reaction system consisted of three flasks provided with ball and socket joints, so that they could be joined together, or disconnected and capped as desired. The first or reaction flask carried a separatory funnel; the third flask was essentially a stillpot since it was sealed to a 10-plate Oldershaw column. Considerable pains were taken to remove all moisture from the glass system prior to use and to prevent admission of moist air at any time. The preparation of the acid chloride was carried out in the first flask. During the reaction the flask temperature was kept at 0°; at the end of the reaction the temperature was raised to 80°. The acid chloride condensed in the middle flask kept at −70°. When the reaction was completed the product was distilled into the third flask, and then the connecting tube was sealed off. The acid chloride product which was light yellow at this stage was refluxed for 4 hours, the cold finger in the head being maintained at −50 to −20°. During this refluxing operation a very small amount of distillate was condensed in a receiver at −60°. This distillate was yellow and was discarded; it apparently was the contaminant originally in the main product since the latter became colorless during the first hour of the refluxing operation.

Without changing the apparatus the acid chloride was distilled three times at atmospheric pressure. The first was simply a careful distillation from the preparation apparatus. In the second distillation the large middle fraction from the first step was fractionally distilled through a 20-plate Oldershaw column with a vapor dividing head. The middle fraction (about nine-tenths of the charge) was again distilled, the procedure and apparatus being the same as in the preceding step.

The middle fraction from this (third) distillation was fractionated further in a new apparatus which included a 10-plate Oldershaw column. Although great care had been taken in the previous distillations to remove and exclude moisture there was always the possibility that the acid chloride had come into contact with trace amounts of moisture which would result in the formation of hydrogen chloride. The new apparatus was designed to exclude moisture completely; and the preliminary part of the distillation was carried out so as to eliminate hydrogen chloride if any were present. Following this a small light fraction was removed and the bulk (*ca.* 100 ml.) of the acid chloride was distilled (reflux ratio 1:10 to 1:50) into a flask fitted with a capillary "valve" for subsequent distillation under vacuum. Once the middle fraction was collected the "valve" flask was sealed off from the distillation column, and then evacuated in a manner to cause the vapor of the acid chloride product to sweep out most of the air present. The tube connecting the evacuated "valve" flask to the pump was then sealed.

The acid chloride material was finally distilled a fifth and sixth time in evacuated systems. The general scheme of distillations of this type has been described many times.[8] In the present experiments, however, the apparatus and technique involved two new features. It was found possible without using ground-glass joints or grease, to incorporate a 10-plate Oldershaw column in the vacuum system and so improve the degree of fractionation obtainable. Also, the usual solenoid-hammer device for breaking the capillary "valve" was modified so that the hammer dropped vertically[9] rather than being moved horizontally and was moved by a small magnet.

In the first vacuum distillation small head and tail fractions were taken and the bulk of the material was collected in a capillary valve flask. There was some evidence of a small amount of air in the system.

The second distillation employed the same apparatus as the previous one, except that small sample bulbs (*ca.* 2 cm. in diameter) were included in the system for collecting the entire charge. The apparatus was pumped down to 0.001 mm. for several days and repeatedly flamed. Then the middle fraction from the previous vacuum distillation was transferred to the pot through the capillary valve, refluxed for one-half hour, and distilled. A very minute trace of air was apparently present in the system during the filling of the first three bulbs (#8, 9 and 10), and was successfully trapped in bulb #11. In filling the remaining bulbs (#12–18) the vapor literally rushed into the bulb the instant it was cooled, indicating the complete absence of air. All the acid chloride was collected by the time bulb #18 was filled. Seven of the samples collected in this distillation were subsequently analyzed.

The silver used in these analyses were prepared by Kurt H. Nelson.[10] The purification process[11] involved the electrolytic transport of the silver three times through a saturated silver nitrate solution contained in long quartz trays. The electrolytic crystals were fused into buttons of suitable size in a quartz furnace on a bed of pure lime in an atmosphere of slightly moist hydrogen. The fused buttons were etched several times with nitric acid, washed and dried at 100° in air, then at 400° *in vacuo*. The standard silver solution employed for fine adjustment of the weight of silver in the analyses was made with a small quantity of electrolytic crystals which also had been heated to 400°. Samples of these electrolytic crystals were examined spectrographically[12] and the only impurities detected were Al, Fe, Mg, Si and Cu. The percentage of each of the first four fell in the range 0.0001–0.001; that of Cu was less than 0.0001.

Water, nitric acid and pyridine were purified by distillation. Hydrogen was commercial tank gas which, after passing through a Deoxo unit to remove oxygen, was passed through a set of six all-glass Emmerling towers containing the following solutions in the order given: alkaline plumbite; 20% NaOH; concd. sulfuric acid; concd. sulfuric

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(6) John L. Swanson, Senior Thesis, 1951, Reed College.

(7) The details of this preparation appear in the Senior Thesis, 1953, of the junior author.

(8) See, for example: G. P. Baxter and A. F. Scott, *Proc. Am. Acad. Arts and Sci.*, **59**, 19 (1923); A. F. Scott and F. H. Hurley, THIS JOURNAL, **59**, 1905 (1937).

(9) This new arrangement has certain advantages over the older one. A note describing it will be submitted for publication shortly.

(10) Kurt H. Nelson, Senior Thesis, 1948, Reed College.

(11) G. P. Baxter and O. W. Lundstedt, THIS JOURNAL, **62**, 1829 (1940).

(12) For this test we thank the Metallurgical Division, Bureau of Mines, at the laboratory in Albany, Oregon.

acid; 20% NaOH; water. To adjust the aqueous vapor pressure in the hydrogen to the desired value[11] the gas was finally passed through two cold towers, the first kept at 0° and the second, at −18°.

Comparison[13] of the perfluorobutyryl chloride with silver followed conventional lines.[14] The scheme of this comparison can be presented briefly. A weighed sample bulb was placed in a thick-walled flask containing 25 ml. of pyridine and 50 ml. of water, and the flask was closed with a tight-fitting, ground glass stopper. After the flask was cooled to about 4° in the cold room the bulb was broken inside the flask by violent shaking and the perfluorobutyryl chloride was allowed to react with the aqueous pyridine. Due to the presence of the pyridine, the chloride samples were completely soluble in this mixture. Although the white fog formed upon breaking the bulb disappeared within one-half hour, the flask was allowed to stand for a day before opening. The solution was filtered through a Munroe platinum crucible using a specially designed filtering apparatus[15]; the filtrate was collected in a liter round-bottom flask and transferred from this to a 4-liter glass stoppered bottle.

After obtaining the weight of perfluorobutyryl chloride, the equivalent weight of silver was calculated. In the early analyses, for the purpose of this calculation, the atomic weight of fluorine was assumed to be slightly greater than 19.00; in the last few analyses it was assumed to be slightly less than 19.00. The silver, after being weighed out, was transferred to a flask fitted with a tower of bulbs, and dissolved in 50–100 ml. of 1:1 nitric acid. The quantity of acid used was such as to make the final analytical solution 0.2–0.3 M in nitric acid.

The precipitation of the chloride was carried out in a dark room by adding the dissolved silver to the pyridine solution of perfluorobutyryl chloride in small portions with constant agitation. After the quantitative addition of the silver solution, the amount added was immediately adjusted to the calculated value by the addition of silver nitrate or sodium chloride from carefully prepared solutions of the purified substances. These standard solutions contained approximately 0.1 mg. of silver or its equivalent per milliliter. The final volumes of the analytical solutions were between 2,000 and 3,000 ml. The solutions were shaken vigorously four or five times a day following precipitation and during the preliminary nephelometric tests. Following these tests the solutions were allowed to stand with occasional shaking for a period of two years before they were subjected to the final nephelometric tests and "crossing of the end-point."

Nephelometric tests of the silver and chloride concentrations in the analytical solutions were made with the usual precautions. The nephelometric test suspensions were prepared by the "uniform" precipitation device described by Scott and Hurley.[16] The opalescence of a test suspension was determined by use of a new Coleman Nephelocolorimeter. It may be recalled here that Scott and Hurley,[14] in connection with their analyses of benzoyl chloride, found that the presence of pyridinium nitrate in the analytical solution has no significant effect on the opalescences of nephelometric test suspensions.

Preliminary determinations (summer 1953) of the opalescence ratios for the seven analytical solutions, immediately after precipitating the chloride, were encouragingly close to unity. Nothing further could be established at the time because of other obligations. When it was realized that the determination would have to be put off for a period of time, suitable additions of silver nitrate or sodium chloride, in the form of the very dilute standard solutions, were made to the analytical solutions of analyses #1–#5 to make the amount of silver present in each solution equal to that calculated on the assumption that the atomic weight of fluorine is 19.000. These additions were all small. No additions were made to the analytical solutions of analyses #6 and #7, the silver for which was calculated on the assumption that the atomic weight of fluorine is 18.997. All seven analytical solutions were kept in a light-tight cupboard in a dark room from the summer of 1953 to the summer of 1955 when the analyses were completed. It is believed that this two year period was advantageous for several reasons. It certainly must have reduced the amount of colloidal silver in suspension; it also favored the aging of the precipitate and the establishment of equilibrium between the precipitate and mother liquor.

The final determination of the end-point was performed by Marvin H. Lehr.[17] To begin with the solutions were well shaken and then allowed to stand for several days. Next, on two consecutive days test samples were withdrawn from the analytical solutions, and the opalescence ratios determined by means of the Coleman nephelometer. These two measurements of the opalescence ratios, which were in very satisfactory agreement, all showed a slight excess of silver ion. It was estimated that in no case was this excess of silver greater than 0.15 mg.; and on this assumption chloride ion equivalent to 0.15 mg. of silver was added to each analytical solution in the form of very dilute standard solution. The solutions were then shaken repeatedly, and three measurements of the new opalescence ratios were made in the course of a week. The last two sets of measurements were in satisfactory agreement. These new ratios showed that the end-point had been crossed except in the case of analysis #5 in which case the ratio was 1.07. From the known values of the ratios before and after the addition of the chloride ion (equivalent to 0.15 mg. silver) and assuming that the variation in opalescence ratio with added chloride ion is linear, it is possible to estimate readily the amount of chloride necessary to bring the opalescence ratio to unity. This estimate was used in calculating the amount of silver added or subtracted in solution to give the exact end-point. In passing it is interesting to note that from this final series of nephelometric tests one can derive a new estimate of the sensitivity of the opalescence ratio. On the average it was found that a change of 0.01 in the opalescence ratio is caused by 0.006 mg. of silver ion or its equivalent in chloride ion.

Results of Analyses

The results obtained from the analysis of seven samples of the perfluorobutyryl chloride are given in Table I.[18] These samples formed a consecutive series and no accidents or mishaps occurred. All the weights in the table are corrected to the vacuum basis. The additions of silver tabulated in column 4 are those made *after* the nephelometric tests were begun.

TABLE I

RESULTS $C_4F_7OCl:Ag$

No. of analysis	Fraction of C_4F_7OCl	Wt. of C_4F_7OCl *in vacuo*, g.	Wt. of Ag added or subtracted in soln., g.	Cor. wt. of Ag *in vacuo*	Ratio C_4F_7OCl: Ag
1	8	6.37666	+0.00093	2.95871	2.15522
2	9	4.70614	− .00085	2.18369	2.15513
3	17	5.31133	+ .00311	2.46453	2.15511
4	18	1.70873	+ .00078	0.79279	2.15534
5	16	3.92030	+ .00812	1.81908	2.15510
6	11	3.86748	− .00099	1.79453	2.15516
7	12	4.24157	+ .00217	1.96816	2.15510
		Mean (A) (all analyses)			2.15517
		Mean (B) (excluding 4)			2.15513
		Mean (C) (excluding 1 and 4)			2.15512

Discussion of Results

With a series of analyses such as that reported above an important question is whether the variations in the results are due to differences in the samples analyzed or arise from the analytical operations. At first glance it is disturbing to find

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(13) These operations, up to the final nephelometric tests, were performed by the junior author, as a research associate, in the summer of 1953.

(14) For the important details of the weighing and analytical procedures see account given in article on analysis of benzoyl chloride by A. F. Scott and F. H. Hurley, THIS JOURNAL, **59**, 1905 (1937).

(15) A note describing this arrangement will be submitted for publication shortly.

(16) A. F. Scott and F. H. Hurley, THIS JOURNAL, **56**, 333 (1934).

(17) Reed College, 1954.

(18) The authors are greatly indebted to Marvin H. Lehr for his help in rechecking the calculations from beginning to end.

that the ratio values for the lightest (no. 8) and the heaviest (no. 18) fractions stand out as greater than the ratio values of the other five samples; for this might be an indication of a variation in the samples due to fractionation. This interpretation, however, appears to be contradicted by two lines of evidence. Most important is the fact that the results of adjacent fractions do not show any gradation in ratio values. Also significant is the fact that the most probable impurities (hydrogen chloride in the light fraction and phosphorus chloride or oxychloride in the heavy fraction) would result in low rather than high ratio values. Although the high ratio value of the lightest fraction (no. 8) presumably does not arise from the fractionation of the acid chloride material, it is conceivable that it is an indication of some impurity in the sample; for, as will be recalled, this fraction was the only one in the series which showed milkiness upon condensation of the sample, due possibly to a trace of air in the system.

If we assume the samples of acid chloride to have been uniform and the variations in the ratio values to have their origin in the analytical operations, we can treat the experimental data as follows. First, on the basis of the Pierce–Chauvenet criterion we find that the ratio value of analysis no. 4 most probably involves some mistake and can therefore be rejected as an aberrant measurement. Omitting no. 4 for the series we get the mean value "B" in Table I. If we also omit the result of analysis no. 1 on the ground that it is suspect because of the possible contamination with a trace of air as mentioned above, we get the mean value "C" of Table I. Information relating to the statistics of the experimental data is summarized in Table II.

TABLE II

INFORMATION PERTAINING TO THE PRECISION OF RATIO VALUES

Mean	No. of analyses in set	Mean value of ratio	Stand. dev.	Range of mean
A	7	2.15517	0.000081	
B	6	2.15514	.000043	±0.00004
C	5	2.15512	.000023	± .00002

The range of the mean represents the 90% confidence limits. As is evident, there is little difference between means B and C. Both values, however, will be carried along in the following discussion. It is of interest to note that the uncertainty of the mean values is 1–2 parts in 10^5.

First, following the traditional treatment we shall use the experimentally determined ratio C_4F_7OCl:Ag to calculate the atomic weight of fluorine. For this purpose we note first the necessary atomic weight values given in the most recent "Report on Atomic Weights"[19]

Oxygen	16
Chlorine	35.457
Silver	107.880
Carbon	12.011

There can be no question regarding the acceptability of the first three of these atomic weight values. They have been used in calculations of atomic weight determinations by the Harvard method for the past 30 years. Also there are no alternative values to consider.

Concerning the atomic weight of carbon the following notes are offered. The present accepted value for the chemical atomic weight of carbon 12.011 was derived from a combination of two physical measurements: mass determinations of C^{12} and C^{13} from observations of energy changes accompanying nuclear reactions; and mass spectrographic determinations of the relative abundance of the two isotopes. As a matter of fact, in the 1954 Report, the chemical atomic weight derivable from these physical measurements was estimated to range from 12.0113 and 12.0116, depending on the source of the carbon; and the value given (12.011) is a rounded-off figure. For our purposes we shall use the mean value 12.0114 as the best estimate of the chemical atomic weight of carbon. Finally, it may be noted that an uncertainty of 0.0002 unit in the atomic weight of carbon introduces an uncertainty of less than 0.0002 in the derived atomic weight of fluorine.

The atomic weight of fluorine calculated from the experimentally determined ratio C_4F_7COCl:Ag and the atomic weights of C, O, Cl and Ag given above are as follows, the last digit being of questionable significance.

Using mean ratio value	Atomic weight fluorine
"B"	18.9990
"C"	18.9987

These values can be compared with the value 18.9992 ± 0.0002 obtained by two physical methods. Nier[20] gives this figure as the best atomic weight value derivable from existing mass-spectrographic data; and exactly the same value is derived from the nuclear reaction data of Li, Whaling, Fowler and Lauritsen.[21] It is noteworthy, as Nier[20] points out, that the uncertainty in the physical values stems from the uncertainty in the conversion factor needed to convert from the physical to the chemical scale rather than from the physical measurements themselves. As is evident, the atomic weight of fluorine derived from our analyses of perfluorobutyryl chloride is in excellent agreement with the physical values. The evidence, therefore, is quite conclusive for revising the chemical atomic weight from the present value 19.00 to 18.999.

Since the chemical atomic weight of fluorine has been so well established by physical methods,[20,21] it is of interest to calculate the atomic weight of silver based on it. If we accept the usual values for Cl and O, and take F ± 18.9992 and C = 12.0114, we obtain from the results of our analyses of perfluorobutyryl chloride the following for the atomic weight of silver

Using mean ratio value	Atomic weight of silver
"B"	107.880
"C"	107.881

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[19] E. Wichers, THIS JOURNAL, **76**, 3235 (1956).

[20] A. O. Nier, *Science*, **121**, 737 (1955).

[21] C. W. Li, W. Whaling, W. A. Fowler and C. C. Lauritsen *Phys. Rev.* **83**, 512 (1951).

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

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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.