should be collected. Distillation must, however, not be pushed so far that less than 50 to 60 cc. of liquid remains in the flask. Reference to the table above and to the height of the barometer during the distillation shows the air weight of the constant-boiling mixture that contains 36.47 g. absolute or vacuum weight, of acid.

Summary

A set of precision measurements of the composition of the constant-boiling mixture of hydrogen chloride and water is given which shows the percentage of hydrogen chloride to be 20.245 if distillation is made at 750 mm. pressure.

It is shown that the rate of distillation affects the composition to a small extent.

Comparison is made with the results published in three other papers.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A REVISION OF THE ATOMIC WEIGHT OF TITANIUM. PRELIMINARY PAPER. THE ANALYSIS OF TITANIUM TETRACHLORIDE

BY GREGORY PAUL BAXTER AND GEORGE JOSEPH FERTIG

Received February 26, 1923

The atomic weight of titanium in use at the present time, 48.1, depends entirely upon the concordant analyses by Thorpe[1] of titanium tetrachloride and tetrabromide. Both these substances are very sensitive to moisture, and must therefore be purified in an atmosphere free from water vapor. Thorpe recognized this difficulty, and in preparing material for analysis took precautions to avoid it. There is some question, nevertheless, whether these precautions were entirely adequate, and whether the products of earlier exposure to air were removed from the material analyzed. Furthermore, the analytical procedure did not include many necessary modern refinements. His result is, therefore, subject to considerable uncertainty.

Recent work in this Laboratory involving the purification of volatile halides by fractional distillation[2] led us to investigate titanium tetrachloride in the same way. Since the atomic weight of titanium found as the result of the analysis of the purified material is distinctly lower than the generally accepted one, and since the experimental work has been interrupted for an indefinite period, it seems worth while to present the preliminary result at this time.

[1] Thorpe, *Ber.*, **16**, 3014 (1883); *J. Chem. Soc.*, **47**, 108 (1885).

[2] See especially Baxter, Weatherill and Scripture, *Proc. Am. Acad. Arts Sci.*, **58**, 245 (1923).

Purification of Materials

Titanium tetrachloride from a commercial source was employed. Although it had been rectified, it was obviously impure, since it was both cloudy and distinctly brown. It seemed reasonable to expect that it contained the products of hydrolysis, titanic and hydrochloric acids, and possibly the chlorides of carbon, silicon, vanadium and zirconium.

As can be seen from the following table, the boiling points of the various impurities are sufficiently different from that of titanium tetrachloride to offer reasonable hope that they could be eliminated by fractional distillation. Since the effect of impurities upon the observed atomic weight of titanium is in proportion to the difference between the equivalents of titanium and the element in question, very appreciable amounts of these substances are necessary to alter the atomic weight by an important amount.

	B. p.	Effect of 0.1% upon the at. wt. of Ti		B. p.	Effect of 0.1% upon the at. wt. of Ti
HCl	−83	−0.044	$TiCl_4$	136	.....
$SiCl_4$	58	−0.036	VCl_4	154	+0.003
CCl_4	78	−0.020	$ZrCl_4$	v. p. 8.2 mm. at 440°	+0.042

The experience gained by Baxter, Weatherill and Scripture in the distillation of silicon tetrachloride and tetrabromide was very valuable in the purification of titanium tetrachloride, and their paper[2] should be consulted for details concerning the construction of the apparatus. In brief the process was as follows. The original material (about 500 g.) was introduced into a large bulb which was exhausted while hot and then sealed. In this way nearly all the air was flushed out of the bulb by titanium tetrachloride vapor. In the course of the subsequent fractionation the material was never again exposed to the air. The original bulb, which terminated in a special sealed-in joint[3] which could be broken at will, was then attached through a fractionating column to a second bulb also terminating in a special joint as above. After the second bulb had been exhausted and sealed, connection was made between the bulb containing the tetrachloride and the exhausted bulb by breaking the joint, and the tetrachloride was distilled through the fractionating column from the first to the second bulb, leaving a semi-solid residue in the still.

During the distillation the still was heated to about 105° in a paraffin bath and the fractionating column was jacketed with asbestos paper and occasionally warmed to prevent choking. Refluxing appeared to be very efficient.

---

[3] See Bruner and Bekier, *Z. Elektrochem.*, **18,** 369 (1912). Briscoe and Little, *J. Chem. Soc.*, **105,** 1324 (1914). Baxter and Starkweather, THIS JOURNAL, **42,** 907 (1920).

The distillation was then many times repeated in such a way that one or two small most volatile fractions, as well as several least volatile fractions, could be collected in small bulbs which were sealed off as soon as filled. In all, 20 such fractionations were carried out, and the material resulting from the twentieth distillation was divided into 12 small fractions.

In the earlier distillations after the first a slight solid residue remained in the still, but this diminished with each distillation and after the fifteenth ceased to appear. Furthermore, at first the earlier portions of each distillate possessed a slight yellowish tint, but this also disappeared after the eighth distillation.

Fig. 1 illustrates the apparatus used in the later distillations. The exhausted bulb *A* containing the tetrachloride is connected with the bulb *B* which has been carefully exhausted and sealed at *C* by breaking the special joint *D*. After the two most volatile fractions have been distilled into Bulbs 1 and 2, the main portion is distilled into *B*. Then *B* is disconnected from *A* by sealing the capillary *E*. The residue in *A* is finally collected in Bulbs 3 and 4.

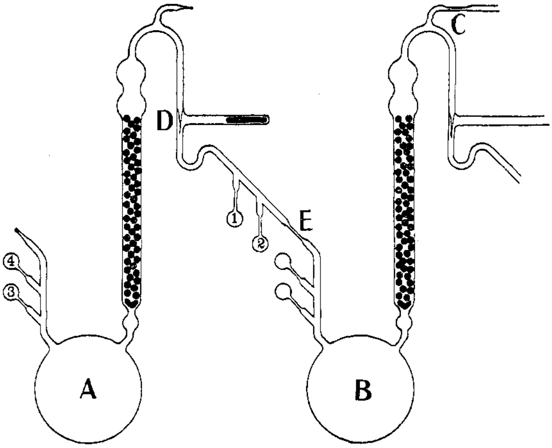

Fig. 1.

The whole process of fractionation is illustrated in Fig. 2. The large circles represent the separate distillations, the small circles the fractions removed. The fractions to the right are the more volatile ones, while the fractions to the left are the less volatile ones. The fractions analyzed, as well as the atomic weights found in the analyses, are indicated in the figure.

The residues from the first and ninth distillations were decomposed with water and the arc spectra of the resulting solids on pure graphite electrodes were examined in a Féry quartz spectrograph. No evidence of vanadium or zirconium could be discovered in either. Furthermore, Fraction *a* was decomposed with water in a platinum dish, and after evaporation the arc spectrum of the residue on copper electrodes was photographed. The lines of silicon were not visible in the photograph.

Water, nitric acid and silver were purified by the usual methods when extreme refinement is necessary.[4]

Method of Analysis

After being weighed, the bulb containing titanium tetrachloride was broken under nitric acid and the glass was collected and weighed. The solution was diluted to considerable volume and then was precipitated with a solution of a weighed nearly equivalent amount of pure silver. The point of exact equivalence between chloride and silver was then found with the assistance of a nephelometer.

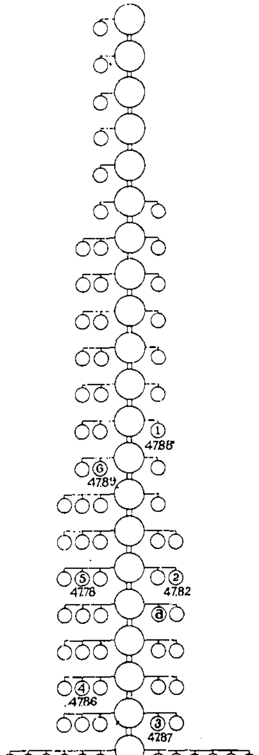

Fig. 2.

After cleansing with "cleaning solution" the bulb was soaked in distilled water for some time and then suspended in a platinum wire basket and weighed under water of known temperature. The weight of the basket alone, submerged in water, was also found. Next, the bulb was dried and left in a desiccator for at least 24 hours. Then it was weighed in air by substitution for weights, and at the same time the density of the air was found by weighing a sealed globe.[5]

The weighed bulb was now placed in a heavy-walled, glass-stoppered flask together with about 500 cc. of 2 *N* nitric acid and the bulb was broken by shaking the flask. At first fumes were visible in the flask, but these disappeared rapidly. Furthermore, titanic acid separated to a considerable extent, but this dissolved gradually, and ultimately the solution became clear. Hönigschmid[6] found that even 3 *N* nitric acid does not cause the loss of perceptible amounts of hydrochloric acid from potassium chloride. It is to be noted, too, that loss of hydrochloric acid would raise the apparent atomic weight of titanium. The solution was then filtered through a filter paper into a large glass-stoppered precipitating flask, and the glass fragments were washed by decantation with pure water and were transferred to the filter paper. Then the glass was further washed with *N* nitric acid and water before ignition of the filter paper and weighing. Blank experiments with empty bulbs gave evidence that this method of collecting the glass is not subject to important error.

The weight of the bulb was corrected to vacuum by computing the

---

[4] See for instance, Baxter and Grover, THIS JOURNAL, **37,** 1028 (1915).

[5] See Baxter, *ibid.*, **43,** 1317 (1921).

[6] Hönigschmid, *Z. Elektrochem.*, **26,** 403 (1920); *Ber.*, **54B,** 1873 (1921).

weight of air displaced by bulb and weights, and the weight of tetrachloride was found by subtracting the weight of glass, corrected to vacuum. From the weight of titanium tetrachloride the necessary amount of silver to combine with the chlorine was computed, and this quantity of the purest silver was weighed out and dissolved in nitric acid. After dilution until approximately 0.1 N, the silver solution was slowly added to the chloride and the mixture was thoroughly shaken and allowed to stand several days with occasional shaking. The clear, supernatant liquor was next tested for excess of chloride or silver in a nephelometer, and if a deficiency of either was found, a suitable amount of a 0.01 N solution of silver nitrate or potassium chloride was added and the shaking and testing were repeated. The process was continued until the amounts of chloride and silver were equivalent.

Vacuum corrections were applied as follows.

	Weights	Silver	Glass	Air
Density............	8.3	10.49	2.5	0.001293 (0° and 760 mm.)
Vac. corr. per g.....	...	−0.000031	+0.000335	.....

Weights were carefully standardized by the substitution method of Richards.[7]

THE ATOMIC WEIGHT OF TITANIUM

$TiCl_4$:4 Ag

Ag = 107.880 Cl = 35.458

Number of analysis	Fraction of $TiCl_4$	Wt. of $TiCl_4$ in vac. G.	Wt. of Ag in vac. G.	Wt. of Ag added or subtracted in solution G.	Corr. wt. of Ag in vac. G.	Ratio $TiCl_4$: 4 Ag	At. wt. of Ti
1	6	5.3314	12.1430	−0.0171	12.1259	0.43967	47.89
2	1	4.4803	10.2044	−0.0135	10.1909	0.43964	47.88
3	2	4.8304	10.9866	+0.0043	10.9909	0.43949	47.82
4	5	4.5808	10.4183	+0.0068	10.4251	0.43940	47.78
5	3	5.0843	11.5672	−0.0017	11.5655	0.43961	47.87
6	4	4.3018	9.7857	+0.0002	9.7859	0.43959	47.86
						Av. 0.43957	47.85

While the concordance of the results leaves much to be desired, the absence of any systematic trend is evidence that the irregularities are accidental. The most and least volatile fractions, 1 and 6, as well as the two middle portions, 3 and 4, give far more concordant results than the remaining two, and in view of the fact that the average of these four is 47.88, the rounded-off value 47.9 seems on the whole to represent the present outcome of this work.

As yet no results of the positive-ray analysis of titanium have been published. In view of the possible isotopic character of titanium the determination whether any of its isotopes have masses larger than 48

[7] Richards, THIS JOURNAL, **22**, 144 (1900); *Z. physik. Chem.*, **33**, 605 (1900).

will be of importance in the decision between the older value for the atomic weight and the one here presented.

This investigation will be continued by the analysis of additional fractions of the tetrachloride from those already prepared.

We are very greatly indebted to the Wolcott Gibbs and Bache Funds of the National Academy of Sciences for generous assistance in providing the necessary apparatus and materials.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN]

THE SOLUBILITIES OF CERTAIN METALLIC CHLORIDES IN SELENIUM OXYCHLORIDE[1]

BY CLARENCE R. WISE

Received February 26, 1923

This paper deals with the solubilities of a number of the more common chlorides in selenium oxychloride.

The observations of Lenher[2] have shown that when selenium oxychloride reacts with various substances its action in general is that of a chlorinating and oxidizing agent. As a part of the study of selenium oxychloride it has been deemed important to know the solubilities of the various reaction products in the reagent.

Materials

Reagent.—The selenium oxychloride used in this work was prepared by the method of Lenher.[3] It was purified by distillation[4] at reduced pressure and special precautions were taken to exclude moisture.

Metallic Chlorides.—Since selenium oxychloride is readily hydrolyzed, it is obvious that a solubility study necessitates the use of anhydrous chlorides as well as anhydrous reagent. It has been found convenient with many of the chlorides to dehydrate them by heating in a current of hydrogen chloride. Chlorides insoluble in water were prepared by the usual precipitation methods, while the volatile chlorides used were purified by sublimation or distillation. The purity of all of the chlorides used, as well as their freedom from moisture, was established by analysis.

Apparatus

All experiments were conducted in glass bottles provided with 2 well-fitting ground-glass stoppers which, in order to exclude moisture, were sealed with paraffin. These bottles containing the solvent and solute were shaken in a thermostat until equilibrium was reached. The temperature control was to within 0.05°.

---

[1] An abstract of a part of the thesis submitted to the Graduate School of the University of Wisconsin as a partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

[2] Lenher, THIS JOURNAL, **43,** 29 (1921); **44,** 1664 (1922).

[3] Lenher, *ibid.*, **42,** 2498 (1920).

[4] Lenher, Smith and Town, *J. Phys. Chem.*, **26,** 156 (1922).