Preparation of Titanium Tetrachloride of High Purity [1]

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A procedure is described for the preparation of titanium tetrachloride of high purity. Procedures are also given for determining the purity of titanium tetrachloride by cryoscopic, spectrochemical, and infrared absorption measurements.

The triple-point temperature of pure titanium tetrachloride was found to be 249.045° K, with an estimated uncertainty of ±0.010° K.

1. Introduction

Titanium tetrachloride is generally produced by the reaction of chlorine with an intimate mixture of a titanium-bearing ore (or titanium compounds) and carbonaceous material. The titanium tetrachloride so produced will consequently contain as impurities volatile chlorides formed from substances occurring in both the titaniferous and the carbonaceous materials. Among the possible impurities will be chlorides and oxychlorides of iron, vanadium, silicon, tin, and carbon, especially carbonyl chloride and other chlorinated organic compounds.

The usual methods for refining the crude tetrachloride consist of a preliminary treatment of the liquid and a subsequent distillation. Among the substances used for the preliminary treatment [2] are sulfur, hydrogen sulfide,[3] sulfuric acid, water, oleic and stearic acids, metallic soaps, and a number of metals, including copper. The particular functions of most of these substances have not been made clear. Copper, however, appears to be very suitable for removing vanadium.

Experience with these methods, as well as with variations of these methods, showed that none of them consistently yielded high-purity titanium tetrachloride. Much depends on the previous history of the so-called crude materials. In attempting to prepare titanium tetrachloride in as high a state of purity as possible, for use in determining its fundamental properties, it was found, by means of infrared spectroscopy, that organic material was the most persistent impurity. Emission spectroscopy showed that all metallic impurities except vanadium and tin were eliminated by a simple distillation of the tetrachloride. Vanadium was removed by treatment with copper and this element did not contaminate the tetrachloride. Tin was removed by means of a highly efficient still.

When it was realized that destruction and elimination of organic compounds in the tetrachloride was the major problem, attention was concentrated on this phase of the purification.

2. Destruction of Organic Matter and Elimination of Vanadium

It was found in this laboratory that organic matter was removed from the titanium tetrachloride by addition of chlorine to the refluxing tetrachloride. The destruction of organic matter was accomplished more rapidly if aluminum chloride hexahydrate and water were added as catalysts. It was found convenient and preferable to add the aluminum chloride hexahydrate as a slurry, with an equal amount of water. The total quantity of aluminum chloride hexahydrate and water added was about 2 percent of the mass of the titanium tetrachloride. A period of 2- to 6-hr refluxing under these conditions was sufficient to eliminate the organic impurities. Subsequent removal of the chlorine was accomplished by passing a stream of clean, dry air through the boiling tetrachloride, after which the tetrachloride was distilled. If the tetrachloride contained vanadium, the distilled product was colored yellow.

The apparatus in which the tetrachloride was chemically treated consisted of a round-bottom 3-necked Pyrex flask, a Vigreux column of 45 cm in height, a glass entrant tube for the introduction of chlorine, and a glass cap to close the third neck, through which material could be added to the flask. The Vigreux column had an outlet to direct escaping vapors into the suction opening of the hood.

The chlorine was dried by passing it through concentrated sulfuric acid contained in a 250-ml gas-washing bottle, the entrant tube of which was equipped with a fritted end to disperse the chlorine. A safety valve, consisting of a second 250-ml gas-washing bottle nearly filled with sulfuric acid but not having a fritted entrant tube, was connected by means of a T-tube between the first washing bottle and the flask containing the tetrachloride. As an added precautionary measure to prevent accident, the entrant tube leading the chlorine into the tetrachloride should be of a wide bore.

It was also found that organic matter can be destroyed by adding liquid bromine, equal to about one percent of the weight of the tetrachloride, and gently refluxing the resulting solution for several hours. After excess bromine is removed by a stream of clean, dry air, the tetrachloride is distilled. The distilled tetrachloride may have a yellow color, not attributable to vanadium, because of the formation of a small quantity of titanium tetrabromide, or, more properly, of a bromochloride. Treatment with

[2] Patents: British, 588,657; 600,003; 656,098; 674,315; German, 723,223; Swiss, 250,071; 255,404; 262,267; United States, 2,230,538; 2,289,327; 2,344,319; 2,370,525; 2,412,349; 2,416,191; 2,457,917; 2,463,396; 2,508,775; 2,512,807; 2,530,735; 2,533,021; 2,543,591; 2,555,361; 2,560,423; 2,560,424; 2,598,897; 2,598,898; 2,600,881.
[3] For use of hydrogen sulfide see C. Kerby and E. Pietz, Pilot Plant Distillation and Purification of Titanium Tetrachloride, U. S. Bur. Mines, Repts. Invest. No. 4153 (1947).

aluminum chloride and chlorine will decompose the bromo compound and cause the elimination of the small amount of resulting bromine.

To remove the vanadium, the tetrachloride previously freed from organic impurities was allowed to stand in contact with clean, greaseless copper turnings. The copper became blackened by the vanadium, and the tetrachloride became colorless. It was found that the vanadium was more efficiently removed if the organic matter was eliminated first. Refluxing the tetrachloride in contact with the copper hastened the deposition of the vanadium.

The tetrachloride may be decanted from the copper and distilled, or distilled directly from the copper. If the starting material contains unusually large amounts of both organic matter and vanadium, the distilled tetrachloride may have a slight yellow color or may turn yellowish on standing for several days. A second treatment with aluminum chloride hexahydrate, water, and chlorine, however, will complete the destruction of any remaining organic matter.

3. Preparation of Titanium Tetrachloride of High Purity

Although the objective of the refining operations was to produce titanium tetrachloride in as high a state of purity as possible, it was also of interest to ascertain the efficiency of simple chemical refining as applied to crude tetrachloride of various origins.

Experience showed that it was comparatively easy to prepare titanium tetrachloride with a purity of 99.99 percent, regardless of the source of the starting material. As a matter of fact, it was less troublesome to refine crude tetrachloride directly from the reactor than it was to purify commercial tetrachloride that had been partially refined before receipt.

Fifteen liters of titanium tetrachloride, obtained on the open market, was purified by the procedure involving aluminum chloride hexahydrate, water, chlorine, distillation, and copper as outlined in section 2. Seven of the 15 liters so treated was further purified by careful fractional distillation in a Podbielniak still. The column of the still was packed with a heligrid fabricated from an alloy composed of 5 percent of ruthenium and 95 percent of platinum. The heligrid occupied a space 1 in. in diameter and 37 in. in length. The apparatus for distilling and collecting the various fractions was assembled by means of both tapered and spherical joints. Teflon gaskets were used in the joints to prevent leakage. During distillation the tetrachloride was protected from the moisture of the outer atmosphere by guard tubes containing anhydrous magnesium perchlorate. The rate of return of liquid from the column to the still pot was maintained at about 32 ml/min, by automatic control of the voltage to the heaters. A reflux ratio of 70 to 1 was used. The distilling operation was completed in about 500 hr. The head fraction totaled 690 g, the middle fraction, 5,300 g, and the residual fraction, 40 g. In the final purification of the middle fraction the tetrachloride was placed in a reservoir and the process of freezing, pumping, and melting was repeated four times. To remove products of hydrolysis the tetrachloride was distilled in a high vacuum into the ampoules. The final product was found to have a purity of 99.999 mole percent. The tests for purity are described in the following section.

4. Examination for Purity

Three independent physical methods were used to establish the purity of the titanium tetrachloride prepared by the foregoing methods of refining.

4.1. Cryoscopic Measurement of Purity

To determine the degree of purity of the tetrachloride, 50 ml of the purified compound was transferred by means of high-vacuum distillation to a specially constructed iridioplatinum calorimeter. The material in the calorimeter was then frozen and gradually melted under equilibrium conditions. In this method it is possible to determine only those impurities that are insoluble in the crystalline phase but soluble in the liquid phase.

From the following observations by George T. Furukawa of the Thermodynamics Section of the Heat and Power Division, the triple-point of the pure substance was calculated as well as the mole percent of impurity in the tetrachloride. The observations obtained on the purest product [4] are given in table 1.

The plot of the observed results yielded a slope of 0.00052. Using 0.019 as the cryoscopic constant $(\Delta H_m/RT^2)$, calculated from the value of the heat of fusion $(\Delta H_m=12.5 \text{ cal/g})$ as determined in the course of these experiments, the mole fraction of solid insoluble-liquid soluble impurity becomes 0.000009_6. The mole percent purity then becomes 99.9990. The uncertainty of this figure is estimated to be ± 0.0002 mole percent.

TABLE 1. *Results obtained for the purity of titanium tetrachloride*

$1/F$ [a]	Observed T [b]
	°K
15.53	249.0369
6.32	249.0418
3.53	249.0429
2.45	249.0437
1.73	249.0444
1.14	249.0444
1	[c] 249.0445
0	[c] 249.0450

Triple-point temperature, 249.045° K, with an estimated uncertainty of ± 0.010° K.[d]
Thermometer used, L 15.
0° C = 273.16° K.

[a] F is fraction melted.
[b] The last two digits are significant only in the determination of small temperature differences.
[c] Extrapolated by means of a linear equation fitted to the data by the method of least squares.
[d] The uncertainties given in this paper were estimated by examining the imprecision of the measurements and all known sources of systematic error. The system was assumed to follow the ideal solution law and to form no solid solution with the impurities.

[4] This was the material distributed to the contractors participating in the Titanium Project administered by the Office of Naval Research, Department of the Navy, Washington 25, D. C.

The purity of the product obtained by simple chemical refining, without subsequent resort to the Podbielniak still, was calculated to be 99.992 mole percent. The uncertainty of this figure is estimated to be ±0.002 mole percent.

4.2. Spectrochemical Measurement of Impurities

To determine impurities in the titanium tetrachloride by spectrochemical means, experiments were made to ascertain the feasibility of diluting the tetrachloride with water, so that known quantities of certain elements could be added for control purposes. It was found that the tetrachloride could be slowly diluted with water at the temperature of melting ice without hydrolytic precipitation of titanium.

TABLE 2. *Limits of detection of impurities in titanium tetrachloride by spectrochemical means*

Element	Limit of detection	Element	Limit of detection
	ppm		ppm
Silver	0.2	Magnesium	0.05
Aluminum	1	Manganese	.1
Gold	1		
Boron	0.1	Molybdenum	10
Beryllium	.02	Nickel	1
		Lead	0.5
Calcium	.05	Antimony	2
Columbium (niobium)	40	Silicon	0.5
Cobalt	10		
Chromium	1	Tin	.2
Copper	<0.1	Tantalum	15
		Vanadium	2
Iron	.1	Tungsten	15
Gallium	.5	Zirconium	15
Hafnium	50		

The limits of detection of elements not listed in the table have not been established.
The values given are expressed in parts of the metallic impurity in one million parts of titanium tetrachloride.

TABLE 3. *Results of the spectrochemical examination of refined titanium tetrachloride*

Element	Material No. 1	Material No. 2	Material No. 3
	ppm	ppm	ppm
Silver	<0.5	0.2	0.2
Aluminum	—?	—	—
Gold	—	—	—
Boron	0.2	0.2	0.2
Beryllium	—	—	—
Calcium	0.2	0.1	0.2
Columbium (niobium)	—	—	—
Cobalt	—	—	—
Chromium	—	—	—
Copper	0.2	0.2	0.2
Iron	<0.5	2	1
Gallium	—	—	—
Hafnium	—	—	—
Magnesium	<0.1	<0.1	<0.1
Manganese	—	—	—
Molybdenum	—	—	—
Nickel	—	—	—
Lead	—	—	—
Antimony	—	—	—
Silicon	0.5	0.5	1
Tin	—	5	5
Tantalum	—	—	—
Vanadium	—	—	—
Tungsten	—	—	—
Zirconium	—	—	—

NOTE: <, means less than; —, means not detected; —?, means detection doubtful.

To prepare such an aqueous solution, take equal volumes of ice-cold titanium tetrachloride and ice-cold water. It is immaterial whether the water is added to the tetrachloride or the tetrachloride to the water. Add one to the other two drops at a time and allow the mixture to stand, between additions, in an ice bath until fumes that form dissolve in the mixture. The one-to-one mixture is a thick, syrupy yellow mass, which gradually becomes a yellow transparent solution. On further dilution with water, the solution may become slightly cloudy, but this cloudiness disappears on standing. It should be emphasized that the whole foregoing operation must be conducted slowly. Concentrations of 4, 8, and 12 g of elemental titanium in 100-ml volumes were successfully prepared. These diluted solutions were remarkably stable. Such a solution, containing 8 g of titanium in a volume of 100 ml, remained clear for more than 4 months at room temperature.

The spectrochemical analyses were performed by Martha Mayo Darr, of the Spectrochemistry Section of the Chemistry Division. Measured amounts of the titanium solutions were placed on graphite electrodes, and the electrodes dried at 105° C. The electrodes were then used as anodes in a 15-amp direct current arc. To determine the limit of detection of various foreign elements, known quantities of the elements in the form of their salts were added to the solutions of the titanium tetrachloride. The limits of detection of impurities in parts per million of titanium tetrachloride are given in table 2.

The results given in table 3 were obtained on the spectrochemical examination of (1) the tetrachloride of 99.9990 percent purity; (2) the tetrachloride of 99.992 percent purity; (3) a tetrachloride that was chemically refined from starting material intentionally contaminated with silicon, iron, lead, mercury, vanadium, copper, aluminum, sulfur, and various organic substances such as carbonyl chloride, ether, acetic acid, and chloroacetyl chlorides. The refining method used on material No. 3 was the same as that used on material No. 2, except that the final product was not vacuum-distilled.

4.3. Examination by Infrared Radiation

Infrared spectroscopy proved to be a valuable aid in detecting and determining those impurities in titanium tetrachloride not readily or easily determined by other means. A detailed discussion of this work has been given.[5] Some of the substances determinable by infrared absorption spectroscopy are listed in table 4.

No effort was made to ascertain the limits of detection for carbon dioxide or hydrolysis product, because both of these substances can be eliminated by a single careful distillation in an inert atmosphere or in a high vacuum. Whereas the sensitivity is not good for either vanadium oxytrichloride or silicon tetrachloride, vanadium and silicon can be determined by other methods. Vanadium oxytrichloride

[5] R. B. Johannesen, C. L. Gordon, J. E. Stewart, and R. Gilchrist, J. Research NBS 53, 197 (1954) RP2533.

TABLE 4. *Characteristic infrared absorption peaks and limits of detection of common impurities in titanium tetrachloride*

Impurity	Wavelength of peak	Limit of detection
	μ	ppm
Hydrogen chloride, HCl	3.53	2
Carbon dioxide, CO_2	4.30	?
Vanadium oxytrichloride, $VOCl_3$	4.84	40
Carbonyl chloride, $COCl_2$	5.51	ca. 2
Chloroacetyl chloride, $ClCH_2COCl$	5.55	0.5
Dichloroacetyl chloride, $Cl_2CHCOCl$	5.55	1
Trichloroacetyl chloride, Cl_3CCOCl	5.55	0.5
Silicon tetrachloride, $SiCl_4$	8.14	200
Hydrolysis product	8.45	?

produces a visible yellow color in low concentrations, and 1 ppm can be detected spectrophotometrically at 390 millimicrons if a 10-mm cell is used. As shown in table 2, silicon can be detected by spectrochemical means in a concentration as low as 0.5 ppm.

Infrared examination revealed that material No. 1 contained about 1 part of trichloroacetyl chloride in one million parts of the titanium tetracloride, material No. 2, 8 parts, and material No. 3, between 2 and 3 parts.

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