TITANIUM HALIDES

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TITANIUM HALIDES

By

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INTRODUCTION

I - INTRODUCTION

This study was concerned with certain chlorides and fluorides of titanium. The tetrafluoride is a solid under ordinary conditions, subliming at 284° C. The electronegativity difference for the Ti-F bond is 2.4 which corresponds to about 55% ionic character.[1] The thermal stability and non-solubility in organic solvents also indicate ionic character. The tetrachloride is a liquid, b.p. 136° C. The electronegativity difference for the Ti-Cl bond is 1.4 which corresponds to about 30% ionic character hence titanium tetrachloride is commonly recognized as a covalent type of compound. This study was undertaken to synthesize a compound intermediate between these two types, noting its properties, and perhaps observing something of the nature of the transition from ionic to the covalent type of compound. The possible intermediates are titanium trifluorochloride, titanium difluorodichloride, and titanium trichlorofluoride. A compound, approximately titanium trifluorochloride, has been reported by Ruff and Ipsen.[2] As yet titanium difluorodichloride and titanium trichlorofluoride have not been reported. It was proposed to prepare titanium trifluorochloride by chlorinating titanium trifluoride.

HISTORICAL

II - HISTORICAL

Two different mixed halides, titanium dichlorodibromide and titanium trichlorobromide were reported by Friedel and Guerin in 1896.[3] They are liquids boiling at 176° C. and 154° C. respectively. Raeder has shown by means of cryoscopic and ebullioscopic investigations that the properties of mixtures of titanium tetrachloride and titanium tetrabromide correspond to the properties of titanium dichlorodibromide and titanium trichlorobromide reported by Friedel and Guerin.[4] Therefore there is doubt that the mixed halides are individual compounds.

KNOWN COMPOUNDS WHICH COULD BE USED IN THE PREPARATION OF CHLOROFLUORIDES

III - KNOWN COMPOUNDS WHICH COULD BE USED IN THE PREPARATION OF CHLOROFLUORIDES

Titanium trichloride has been prepared in solution or in the anhydrous form in a number of ways. Titanous chloride solutions have been prepared by the action of a suitable reducing agent on a solution of the tetrachloride. Zinc has been used quite extensively for this purpose. The use of the zinc reductor in titanium analysis is an application of this reaction. Electrolytic reduction is another method of preparation.[5]

Two general methods have been used for the preparation of the anhydrous trichloride. Hydrogen gas will reduce titanium tetrachloride vapor in the furnace.[6] The second method employs metals such as antimony, aluminum, magnesium, zinc, arsenic, tin and silver which will reduce titanium tetrachloride at elevated temperatures to yield titanium trichloride and the chlorides of the metals used, a number of which are volatile.[7]

Titanium dichloride has been prepared by heating titanium trichloride in the furnace in a hydrogen atmosphere.[6]

Titanium trifluoride can be prepared by treating titanium trichloride with hydrogen fluoride, or by the reduction of potassium hexafluotitanate and leaching potassium fluoride from potassium pentafluotitanite.[8]

Titanium difluoride has been reported,[9] but this preparation has been refuted by further studies.

EXPERIMENTAL PROCEDURE

IV - EXPERIMENTAL PROCEDURE

The general method chosen for the preparation of the chlorofluorides of titanium was as follows:

1. Reduce titanium tetrachloride to titanium trichloride
2. Replace chloride ions with fluoride ions to obtain titanium trifluoride
3. Chlorinate titanium trifluoride with chlorine

Titanium tetrachloride obtained from the Stauffer Company was redistilled over copper turnings and calcium hydride to remove any excess chlorine, water and other impurities.

Titanium tetrachloride could not be used for reduction in pure water since it hydrolyzes readily. It can be dissolved in cold concentrated hydrochloric acid and then diluted to obtain a solution of titanium tetrachloride in hydrochloric acid and water.

A - PREPARATION OF TITANIUM TRICHLORIDE

The solution of titanium tetrachloride may be reduced by: (1) the use of zinc and hydrochloric acid; (2) a zinc reductor; (3) electrolytic reduction. The use of granulated zinc and hydrochloric acid tended to give excessive amounts of zinc salts as impurities in the titanium trichloride solution.

A zinc reductor was then constructed following directions in the text by Cumming and Kay.[10] A reducing column about one inch in diameter and ten inches high was used in some of the earlier preparations with considerable success. It had two drawbacks: (1) some zinc salts which would have to be removed later were always introduced into the solution; (2) the reduction was not complete unless the titanium tetrachloride solution was allowed to stand for quite some time in the reductor.

The last method used was electrolytic reduction, accomplished by an adaptation of the method given by Walton.[5] A two liter resin jar, with a four hole top was fitted with a large lead cathode, which had been amalgamated with mercuric chloride. The anode, a graphite electrode small enough to permit chlorine gas to excape around it easily, was placed inside a piece of 28 mm. Pyrex tubing. The end of the tubing was fitted to a coarse fritted glass filter funnel which had the lower portion of the apron removed. This prevented the chlorine gas liberated during the electrolysis from coming in contact with and re-oxidizing the titanium trichloride solution. The other two holes in the cover were utilized to provide an inert gas inlet, and an outlet tube for removing the titanium trichloride solution when the reduction was completed.

Two liters of 1.5 molar titanium tetrachloride solution were prepared by slowly adding 570 grams of titanium tetrachloride to 700 mls. of cold, (0 to 5° C.), concentrated hydrochloric acid. Cold water was slowly added to reach the desired volume. The clear solution was placed into the resin jar, and enough dilute (4 molar) hydrochloric acid was placed in the anode compartment to obtain good current flow. A current of 1 to 1 1/2 amperes was passed through the cell. The duration of the reduction was calculated by allowing

96,500 ampere-seconds for each mole of titanium tetrachloride to be reduced. Bubbles of hydrogen form at the cathode when the reduction is complete.

This method was considered to yield a superior product since there was no contamination with zinc or other reducing substances. The reduction could be carried to completion with a minimum of attention since the cell needed only periodic checking once the reduction was started.

The titanium trichloride prepared in this way served well for precipitation reactions but would not serve for the preparation of anhydrous titanium trichloride. Evaporation or vacuum distillation results in hydrolysis.

Anhydrous titanium trichloride was prepared by slowly passing a mixture of titanium tetrachloride vapor and hydrogen through a furnace at 660° C. The product is condensed on a cold finger. This method is very slow, gives small yields and involves a problem of protection from oxygen and moisture in transfer.[4]

The method of Billy and Brasseur[11] for the preparation of anhydrous titanium trichloride was then tried in which finely divided antimony is used as a reductant. The antimony is obtained from a solution of antimony trichloride by displacement with zinc metal. After purification and drying 4 grams of the antimony was placed into a Carius tube containing 30 grams of titanium tetrachloride. After being evacuated the tube was sealed and heated in a Carius furnace to 340° C. for several hours. Crystals of antimony trichloride indicated the reduction of titanium tetrachloride. Excess titanium tetrachloride was removed with anhydrous carbon tetrachloride and antimony trichloride was removed with anhydrous ether.

This method of purification is tedious, and difficult. It is hard to remove all impurities. The method was improved by evacuating the tube and heating to remove the impurities, because all of them were much more volatile than the titanium trichloride.

Antimony reduction in this manner gave small yields, and necessitated further transfer for fluorination. When the titanium trichloride was removed from the Carius tube for transfer it immediately began to fume. Within one minute it was red hot and oxidation was soon complete. Since the finely divided trichloride is oxidized very quickly on exposure to oxygen this method was discarded.

The use of powdered aluminum and aluminum chloride as a catalyst will give anhydrous titanium trichloride at a lower temperature than antimony.[5] Ruff's method was modified by using a copper autoclave for the reaction chamber, (Figure I). Sixty grams of titanium tetrachloride were placed in the bottom of the autoclave. Two grams of aluminum were ground with two grams of aluminum chloride in a mortar. The mixture was added to the titanium tetrachloride, after which the autoclave was assembled, evacuated and the valve was closed. Heat was applied so that the pressure rose to 120 pounds, and was maintained at that point for two hours by regulating the temperature. A large dry ice trap was attached to the sidearm of the autoclave. Suction was applied, and the trap was cooled in a dry ice-isopropyl alcohol mixture. The autoclave valve was opened so that the aluminum trichloride and excess titanium tetrachloride could be distilled out. The flume was maintained on the bottom of the autoclave for two hours

COPPER AUTOCLAVE

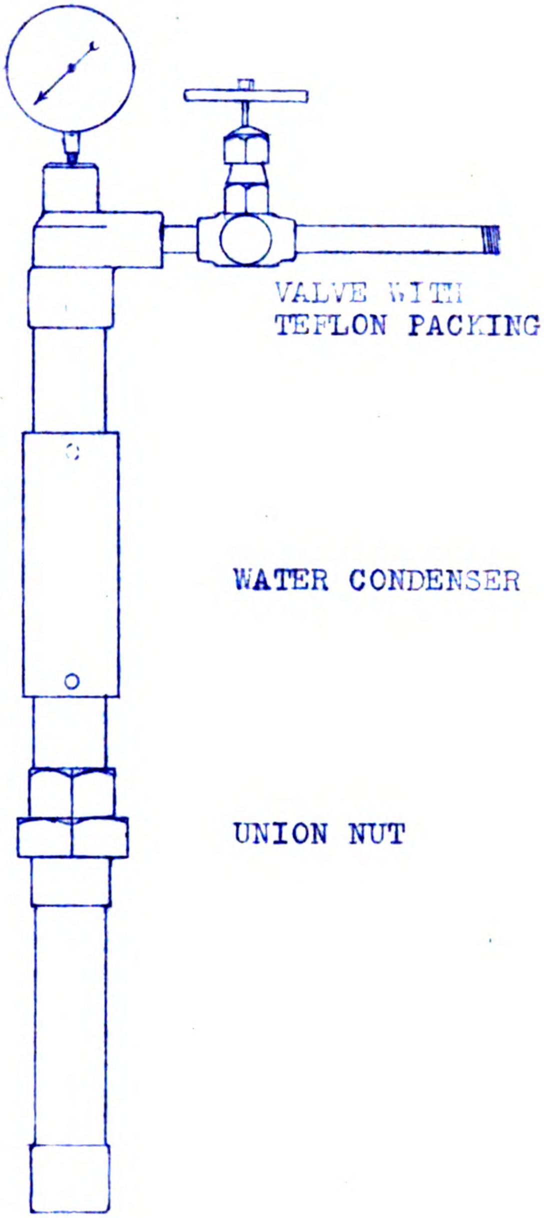


FIGURE I

to effect as complete a removal of aluminum trichloride as possible. The autoclave valve was then closed, and titanium trichloride remained, in the container ready for further treatment.

B - PREPARATION OF TITANIUM TRIFLUORIDE

The fluorination of titanium trichloride to produce titanium trifluoride can be carried out in several ways. For the titanium trichloride solution it was desirable to precipitate titanium trifluoride or some compound which could be easily converted to titanium trifluoride. For anhydrous titanium trichloride it would be desirable to treat with some reagent to leave pure anhydrous titanium trifluoride.

If a solution of titanium trichloride is treated with hydrogen fluoride no precipitate is formed. Evidently titanium trifluoride is quite soluble under these acid conditions. A precipitate will be formed on the addition of a solution of an alkali fluoride. Ammonium fluotitanites seem to be the least soluble. If ammonium fluoride solution is added to titanium trichloride solution a precipitate of ammonium pentafluotitanite is obtained.[12] If the order of addition is reversed ammonium hexafluotitanite is obtained.[12] It was hoped that ammonium fluotitanite could be heated in a combustion tube to remove ammonium fluoride by sublimation and leave titanium trifluoride.

A pH titration was carried out to learn more about the reaction of titanium trichloride with ammonium fluoride. The electrolytically prepared titanium trichloride solution was found to be 1.5 molar by titration with standard cerate. Concentrated ammonium fluoride (13 molar) was prepared by dissolving 117 grams in enough distilled water to make

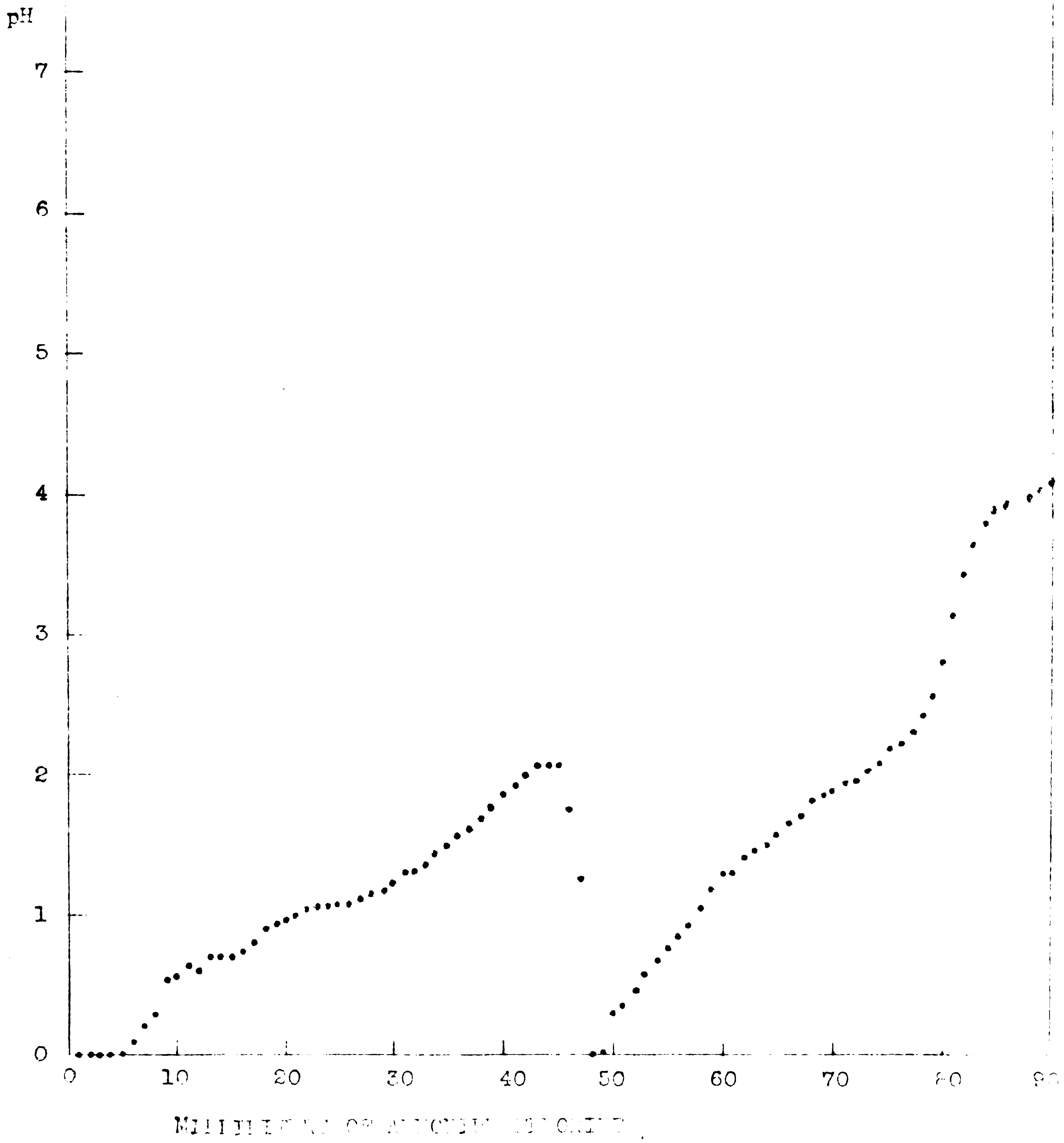
250 mls. of solution. The pH of the titanium trichloride solution was 0.0 or less as shown on a Beckman pH meter, while the pH of the ammonium fluoride solution was 7.5. Seventy mls. of titanium trichloride solution were placed in a beaker, and several drops of toluene were placed on top of the solution to prevent air oxidation. The ammonium fluoride was placed in a burette and added in 1.00 ml increments. A glass electrode and a calomel electrode were used with the pH meter, and the solution was agitated with a magnetic stirrer. The pH became stable after 15 to 30 seconds of stirring and readings were then taken. The data is plotted in Figure II.

The color of the solution changed during the titration so that certain parts of the curve are characterized by definite solution colors. At the beginning the trichloride solution was deep purple and slowly changed to a dark brown at the first peak. In the vicinity of the trough the solution changed from an almost opaque brown to a bright clear green color. No precipitate was visible up to this point, but upon the addition of more fluoride the color changed from green to a violet, and a precipitate formed.

After purification in a Soxhlet extractor with ethanol the ammonium fluotitanite was dried in an Abderhalden dryer at 100° C. for several hours. The material was then placed into a large tube and evacuated. Heat was applied in an attempt to drive off ammonium fluoride and leave titanium trifluoride. However the ammonium fluotitanite sublimed without decomposition to the trifluoride. Since the trifluoride could not be prepared in this way this method was discarded.

FIGURE II

TITRATION CURVE OF
TITANIUM TRICHLORIDE SOLUTION



The copper autoclave was utilized for the preparation of anhydrous titanium trifluoride. Titanium trichloride was prepared (page 7) and the autoclave was then attached to the manifold, (Figure III) and an excess of twice the necessary amount of anhydrous hydrogen fluoride was condensed on top of the titanium trichloride. After sealing the autoclave and removing it from the manifold, it was heated to about 100° C. to complete the reaction. Hydrogen chloride gas was allowed to escape slowly at 80 to 100 p.s.i. This method seems to leave some aluminum trifluoride in the titanium trifluoride.

Another method for producing titanium trifluoride is to make potassium hexafluotitanate, reduce it to potassium pentafluotitanite in the furnace at 600° C. with hydrogen and finally leach out potassium fluoride with water to leave the less soluble titanium trifluoride.[6] This method leaves some potassium fluoride in the titanium trifluoride.

C - PREPARATION OF TITANIUM TRIFLUOROCHLORIDE

The last step in the production of titanium trifluorochloride is the chlorination of titanium trifluoride. This has been done in the furnace and in test tubes heated, in an oil bath or with a bunsen burner.

Small amounts, about one gram, of titanium trifluoride were placed in test tubes arranged in series. Chlorine gas was passed through them and they were heated in an oil bath. At 220 to 225° C. a yellow sublimate covered the walls of the test tube above the titanium trifluoride.

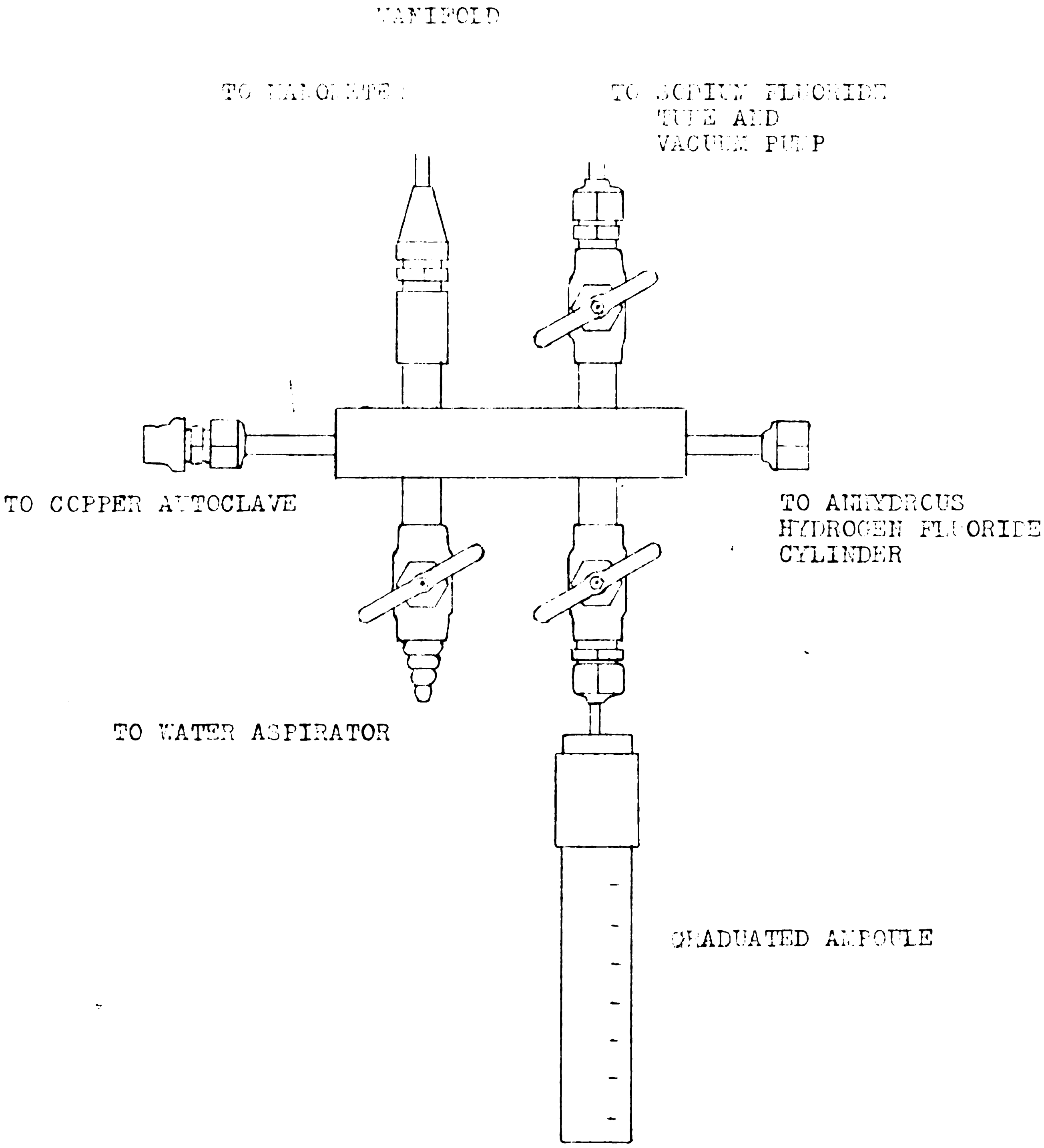

MANIFOLD
TO MANOMETER
TO SODIUM FLUORIDE TUBE AND VACUUM PUMP
TO COPPER AUTOCLAVE
TO ANHYDROUS HYDROGEN FLUORIDE CYLINDER
TO WATER ASPIRATOR
GRADUATED AMPOULE

FIGURE III

Qualitative tests indicated the presence of titanium, chlorine, and fluorine. Qunatitative analysis gives the following data:

	Per Cent			Average	Theoretical
Ti	35.4	34.8	34.4	34.9	34.1
F	36.4	34.8	34.9	35.4	40.6
Cl	26.8	28.7	27.2	27.6	25.3

Upon standing in the atmosphere titanium trifluorochloride changes from a yellow to a white solid. X-ray powder diffraction patterns indicate the product is titanium oxyfluoride. When weighed amounts of titanium trifluorochloride are allowed to stand in the air, and then are dried overnight the weight changes correspond to the change from titanium trifluorochloride to titanium oxyfluoride.

	Wt. of TiF_3Cl	Wt. of $TiOF_2$	Theoretical
I	.2120	.1549	.1539
II	.3406	.2270	.2473

When titanium trifluorochloride was placed in water it hydrolyzed vigorously, and dissolved completely leaving an acid solution.

D - PREPARATION OF TITANIUM TETRAFLUORIDE

The preparation of titanium tetrafluoride has been described by several workers. Usually titanium tetrachloride is treated with anhydrous hydrogen fluoride. The methods of treatment vary from one worker to the next. The method used for this work involved the use of the copper autoclave as a reaction chamber, (Figure I).

After cleaning and drying, the autoclave was attached to a manifold which was connected to a manometer, a vacuum pump, a cylinder of anhydrous hydrogen fluoride, and a semi-transparent graduated fluorethene ampoule, (Figure III).

The system was evacuated using the vacuum pump and then sealed off. The graduated ampoule was cooled in a mixture of dry ice and isopropyl alcohol. Anhydrous hydrogen fluoride was distilled into the ampoule until the desired quantity, about 50 mls., was obtained. The autoclave was then cooled, while the ampoule was warmed. In this way the quantity of hydrogen fluoride distilled into the autoclave was determined. The autoclave was evacuated after the transfer of hydrogen fluoride was complete.

About 50 grams of titanium tetrachloride was added on top of the hydrogen fluoride. The autoclave was removed from the manifold, and attached to the container of titanium tetrachloride. The lower part of the autoclave was kept cold in the dry ice and alcohol mixture. to retard the reaction. The vacuum inside the autoclave, and gravity were used to transfer the titanium tetrachloride. Hydrogen chloride gas which came from the reaction was allowed to bubble through the titanium tetrachloride until the transfer was complete. The autoclave valve was closed and the titanium tetrachloride transfer apparatus was removed. Then the autoclave was allowed to warm slowly. When the pressure reached 100 pounds the hydrogen chloride gas was allowed to escape slowly through the valve. Finally cold water was circulated through the condenser while the lower part of the autoclave was heated in a gas flame to complete the reaction.

The autoclave was cooled, evacuated and filled with dry nitrogen to a pressure of 10 p.s.i. The union nut was loosened just enough to permit removal with the hands. The positive pressure of the nitrogen prevented moisture from diffusing into the autoclave. The lower part of the autoclave was inserted in the dry box. A large one hole rubber stopper was placed around the autoclave just above the union nut. The outside edge of the rubber stopper fit tightly in a port in the dry box so that the lower part of the autoclave could be sealed in the dry box. After drying the autoclave was opened. At this stage the titanium tetrafluoride had a light tan color. Since the pure compound is white, this indicated impurities, and the product had to be resublimed.

The first attempts at resublimation were carried out in evacuated glass tubes. This gave a white product which would not resublime further. This material was titanium oxyfluoride. Evidently the titanium tetrafluoride attacked the glass and titanium oxyfluoride was obtained, rather than titanium tetrafluoride. A monel tube was substituted for the glass tube with satisfactory results. A white product which was solid along the walls of the tube, but similar to glass wool at the center, was obtained.

E - PREPARATION OF TITANIUM OXYFLUORIDE

This material was obtained when an attempt was made to resublime titanium tetrafluoride in a glass tube. Ruff and Ipsen reported that titanium tetrafluoride dihydrate can be obtained by dissolving titanium tetrafluoride in water and evaporating the solution. Solutions of titanium tetrafluoride could be produced by dissolving titanium dioxide in aqueous hydrogen fluoride. If the observations of Ruff and Ipsen were correct evaporation of these solutions should also yield titanium tetrafluoride dihydrate.

In an effort to determine what actually does happen two types of experiments were carried out. (1) The hydrolysis of a weighed amount of titanium tetrafluoride; (2) the reaction of a weighed amount of titanium dioxide with hydrogen fluoride.

(1) Several grams of titanium tetrafluoride were placed in a platinum crucible. Distilled water was added dropwise until the titanium tetrafluoride just dissolved. The material was placed in a covered container and allowed to dry in the oven at 120 to 140° C. A crust formed at the surface, while a pasty material remained below. The crust was periodically broken and the material allowed to dry. At the end of three weeks, the material was thoroughly dried.

Wt. of TiF_4	Wt. of $TiOF_2$	Theo. Wt.	Difference
4.6174 gms.	3.8040 gms.	3.7975 gms.	0.0065 gms.

Difference = 0.17%

(2) Titanium dioxide was dissolved in aqueous (50%) hydrofluoric acid and evaporated. The material was similar to that obtained by treating titanium tetrafluoride with water. It took two to three weeks to dry this material. X-ray powder diffraction patterns indicated that titanium oxyfluoride had been produced.

Finally titanium dioxide was placed in the copper autoclave. The autoclave was attached to the manifold used for the production of titanium tetrafluoride. The system was evacuated and an excess of anhydrous hydrogen fluoride was distilled into the autoclave. The autoclave was sealed off, removed from the manifold, and the lower portion heated in a steam bath. At 80 to 100 p.s.i. the excess hydrogen fluoride was allowed to escape slowly. Finally the top of the autoclave was wrapped with asbestos tape to provide insulation. The autoclave was evacuated with an aspirator and the lower part was then heated in a gas flame to drive off the last of the constant boiling hydrogen fluoride.

Wt. of TiO_2	Wt. of $TiOF_2$	Theo. Wt.	Difference
40.0 gms.	52.25 gms.	51.0 gms.	1.25 gms.

Difference = 2.5%

The material obtained gave powder diffraction patterns corresponding to titanium oxyfluoride. The color was not white but a light tan. Chlorine gas passed over the tan material in an eight inch Pyrex test tube with heating, gave a white product, and carried off volatile impurities.

Quantitative analysis yielded the following results:

	Per Cent		Average	Theoretical
Ti	47.10	47.18	47.14	47.01
F	36.11	36.33	36.22	37.29

The material is not very soluble in water, dilute acids or bases. A sodium carbonate fusion was used to put the material into solution.

The methods used in the analyses are given in the appendix.

X-RAY POWDER DIFFRACTION
STUDIES

V - X-RAY POWDER DIFFRACTION STUDIES

X-ray powder diffraction patterns were used extensively to check on the identity of the compounds prepared in this work. Data were not available for all of the compounds, and that which was published for titanium tetrafluoride was open to some question.[13]

Exposures were made with a North American Phillips X-ray unit. The cameras had a diameter of 11.459 cm., and the capillaries had a diameter of 0.5 mm. The copper K_α radiation was passed through a nickel filter for all exposures. The exposures were made at 35 kilovolts and 16 milliamperes for 4 to 6 hours. Relative line intensities were measured with a film strip made from a step tablet of the ratio one to the square root of two.

Some titanium trifluoride was carefully prepared to obtain high purity, and a diffraction pattern was obtained. The data is given in Table I. The structure was complex and no attempt at structural analysis was made.

Samples of titanium trifluorochloride were loaded into capillaries in the dry box. No patterns were obtained from four different samples which indicates that the particles are too fine.

Samples of titanium oxyfluoride gave patterns which indicated a cubic structure with a = 3.790 ± .005 Å. The density obtained using toluene in a pycnometer at 25° C. was 2.82. The calculated density is 3.10 which is in fair agreement since experimental densities are usually lower than those calculated from X-ray data. The diffraction data is given in Table II.

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR TITANIUM TRIFLUORIDE

d		I	I/I_o
4.23			1
3.84		100	100
3.57	Diffuse		45
3.11			10
2.71	Diffuse		25
2.31			6
2.08		100	100
1.92	Diffuse		45
1.80		85	85
1.72	Diffuse		45
1.62			1
1.57			1
1.36	Diffuse		4
1.28			50
1.089			45
1.042			20
.9033			6
.8287			20
.8074			15

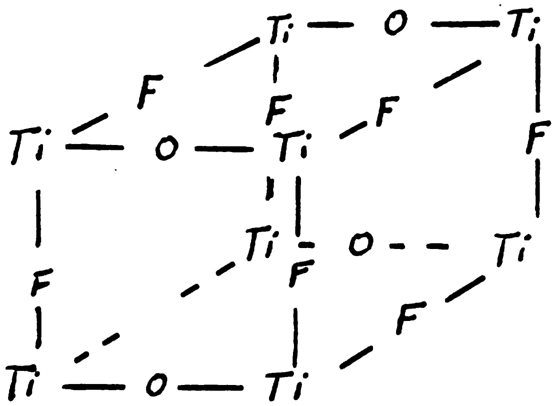
TABLE II

X-RAY POWDER DIFFRACTION DATA FOR TITANIUM OXYFLUORIDE

d	I	I/I_o	Plane_{hkl}
3.75	50	100	100
2.66		35	110
2.18		1	111
1.89	95	95	200
1.69	50	100	210
1.54		35	211
1.34		50	220
1.26		55	221 & 300
1.20		6	310
1.09		15	222
1.048		16	320
1.010		15	321
.947		2	400
.919		17	410 & 322
.893		6	411 & 330
.848		12	420
.827		18	421
.807		1	332

Structure factors were calculated using the equations given in the text by Bunn.[14] Values for each individual plane, (100, 010, 001) etc., were obtained and summed for the appropiate series of planes, (100, 010, and 001 calculated individually and summed for 100 series) etc.
The data is given in Table III.

It appears that the atoms are arranged with titanium at the corners of the cube. Eight fluorine atoms are located on the left and right sides halfway between the titanium atoms. Four oxygen atoms are located in the remaining spaces halfway between the titanium atoms.



A sample of titanium oxychloride was prepared by evaporating an aqueous hydrochloric acid solution of titanium tetrachloride, grinding the residue and drying in the oven at 120° C. for two days. This material gave no diffraction pattern. Therefore no comparisons could be made between the structure of titanium oxyfluoride and titanium oxychloride.

Diffraction patterns from titanium tetrafluoride which had been resublimed in a monel tube were measured. The comparison between the values obtained and those in the literature is given in Table IV.

TABLE III

STRUCTURE FACTORS FOR
TITANIUM OXYFLUORIDE

(Temperature factors and absorption coefficients omitted.)

Plane$_{hkl}$	$I_{calc.} \times 10^2$	$I_{obs.}$
100	1303	100
110	48	35
111	1	1
200	224	95
210	118	100
211	9	35
220	35	50
221 + 300	39	55
310	8	6
311	2	0
222	9	15
320	30	16
321	6	15
400	20	2
410 + 322	30	17
411 + 330	7	6
331	1	0
420	49	12
421	28	18
332	6	1

TABLE IV

X-RAY POWDER DIFFRACTION DATA FOR TITANIUM TETRAFLUORIDE

Observed Data			ASTM Data		
d	I	I/I_o	d	I	I/I_o
8.5		12	6.50		10
6.0		8	5.45		3
4.00	42	85	4.75		2
3.79		1	4.35		2
3.68	50	100	3.80	100	100
3.09		35	3.56		2
2.68		10	3.40		2
2.35		2	3.22		20
2.22		4	2.68		12.5
2.01		10	2.35		3
1.89	35	70	2.18		6
1.72		20	1.90	40	40
1.69		20	1.70	40	40
1.63		30	1.61		4
1.50		2	1.55		6
1.39		17	1.485		1
1.34		17	1.345		12.5
1.28		20	1.266		10
1.25		2	1.098		2
1.04		1	1.054		2
1.00		1	1.015		2
			.921		2

VI - MAGNETIC SUSCEPTIBILITY STUDIES

Magnetic susceptibility data on titanium compounds is limited. Measurements on the compounds used in this work were made to add to the existing data and to distinguish between possible types of bonding in titanium trifluorochloride.

A Gouy type magnetic susceptibility apparatus with a semi-micro balance was used. The 7 mm. Pyrex tube was calibrated at 1.80 c.c, with a mark which was 97 mm. from the septum. The elctromagnets were used at the following amperages which produced the fields given:

Amperes	3	5	8	11	15
Fields (oersted)	2,950	4,780	7,360	9,060	10,470

Klemm[15] measured the magnetic susceptibility of titanium trichloride and found it to be paramagnetic with a specific susceptibility of 7.18×10^{-6}.

Measurements on titanium trifluoride indicated a small amount of ferromagnetic impurity which did not permit an accurate value for the susceptibility but did show the trifluoride to be paramagnetic with a susceptibility of the order corresponding to one unpaired electron. A plot of $1/H$ versus χ was made to obtain the paramagnetic susceptibility without the effect of the ferromagnetic impurities. When $1/H$ was extrapolated to infinite field strength, $(1/H = 0)$, the value 7.5×10^{-6} was obtained for χ, which gave an effective Bohr magneton number of 1.40. The value of 1.73 would correspond to one unpaired electron.

The tetrafluoride contained a very minute trace of impurity but did give a specific diamagnetic susceptibility of -0.037×10^{-6} at 25° C.

The trifluorochloride gave a specific diamagnetic susceptibility of $(-0.060 \pm 0.020) \times 10^{-6}$ at 25° C. Within the limits of experimental error the values for the tetrafluoride and the trifluorochloride are about the same.

Measurements on titanium oxyfluoride indicated the presence of ferromagnetic impurities. A plot of $1/H$ versus χ gives $\chi = + (0.42 \pm 0.02) \times 10^{-6}$ at 22° C. which is slightly paramagnetic.

Data for magnetic susceptibility measurements is given on the following page.

TABLE V

MAGNETIC SUSCEPTIBILITY STUDIES

Titanium trifluoride

27° C.	Amperes	χ_{sp}
	3	$+ 17.1 \times 10^{-6}$
	11	10.7
	15	10.1

Titanium tetrafluorochloride

23° C.	Amperes	χ_{sp}
	0 - 11	No weight change detected
	15	-0.060×10^{-6}

Titanium tetrafluoride

25° C.	Amperes	χ_{sp}
	5	-0.006×10^{-6}
	11	-0.025
	15	-0.037

Titanium oxyfluoride
(prepared in the autoclave from C. P. titanium oxide and anhydrous hydrogen fluoride)

22° C.	Amperes	χ_{sp}
	5	$+ 0.476 \times 10^{-6}$
	8	0.471
	11	0.464
	15	0.460
-29.8° C.	5	$+ 0.623 \times 10^{-6}$
	8	0.596
	11	0.592
	15	0.576
-77.4° C.	5	$+ 0.760 \times 10^{-6}$
	8	0.759
	11	0.747
	15	0.738

DISCUSSION

VII - DISCUSSION

In the preparation of titanium trifluoride the main problem was that of protection from the moisture and oxygen of the atmosphere. Of the several methods tried the copper autoclave eliminated most of the problems since the reduction and fluorination could both be accomplished without transfer of the titanium compound.

Neither X-ray powder diffraction patterns nor magnetic susceptibility data was available for the trifluoride. The data obtained indicated that the structure is complex. Single - crystal X-ray analysis for further structural study was not possible since the product obtained was always a fine powder.

Magnetic susceptibility data indicated the presence of a ferromagnetic impurity, presumably from the iron in the pressure guage, valve, or pipe leading to the valve. A plot of χ versus 1/H extrapolated to infinite field strength gave an approximate value for . Since the points plotted did not lie directly on a straight line, an exact value cannot be claimed. However the value is close to that expected for a compound with one unpaired electron, and is relatively close to that obtained for the trichloride.

Chlorination of the trifluoride gave a yellow compound which sublimed at a lower temperature than the titanium tetrafluoride. The structure could not be determined since no X-ray powder diffraction patterns were obtained from the material. The diamagnetic susceptibility was close to that of the tetrafluoride. The trifluorochloride is insoluble in benzene and carbon tetrachloride, but it is somewhat soluble in chloroform. It reacts readily with water dissolving completely and leaving an acid solution. The addition of dilute sodium hydroxide yields a precipitate of titanium hydroxide. From this the following overall reaction is postulated:

$$TiF_3Cl +, 4OH^- \rightarrow Ti(OH)_4 + 3F^- + Cl^-$$

If the trifluorochloride is exposed to the atmosphere the yellow color slowly disappears and a white solid remains. The white solid gives a powder diffraction pattern for titanium oxyfluoride. From this the following equation is postulated:

$$TiF_3Cl + H_2O \rightarrow TiOF_2 + HF + HCl$$

The color of the trifluorochloride could not be explained on the basis of an unpaired electron, but may be ascribed to the polarization of the molecule. The difference in electronegativity of the fluoride and chloride is relatively large, and polarization effects would be encountered with a chlorofluoride that would not be found in either binary halide.

The titanium tetrafluoride which had been purified for X-ray analysis gave data which was similar to that in the literature. There was a difference for several lines indicating that some impurity possibly the oxyfluoride may have been present in the material for the original work.

Titanium oxyfluoride was obtained from the sublimation of titanium tetrafluoride in a glass tube, and from the reaction of titanium dioxide with aqueous or anhydrous hydrogen fluoride. In the evaporation of a solution of titanium tetrafluoride crystals of material corresponding to the formula $TiF_4 \cdot 2H_2O$ were not found. From this the following reactions are postulated:

$$TiF_4 + H_2O \rightarrow TiOF_2 + 2HF$$

$$TiO_2 + 2HF \rightarrow TiOF_2 + H_2O$$

Apparently the reaction:

$$TiO_2 + 4HF \rightarrow TiF_4 + 2H_2O$$

proceeds only when the system is swept continuously with hydrogen fluoride. If hydrogen fluoride is added to titanium dioxide as in the autoclave and heated the oxyfluoride will be produced. Evaporating an aqueous solution of titanium and fluoride ions will give the oxyfluoride, which suggests the existence of the titanyl ion rather than the monatomic tetravalent ion.

The magnetic susceptibility data indicates a slight amount of paramagnetism. This may be due to the different orbitals used for bonding, and to the different anions in the compound.

The structure of titanium oxyfluoride is apparently cubic. Since the ionic radii of the oxide and fluoride ions are almost the same this may be expected.

VIII - SUMMARY

Titanium trifluoride was prepared by the reduction of titanium tetrachloride and subsequent fluorination. X-ray powder diffraction data, which was not previously available was obtained.

Titanium trifluorochloride, not previously characterized, was prepared and some of its properties were observed. The properties of this substance are intermediate between those of the tetrafluoride and the tetrachloride.

Attempts to prepare titanium tetrafluoride dihydrate as reported by others always yielded the oxyfluoride. This compound results from either the hydrolysis of the tetrafluoride or the treatment of titanium dioxide with aqueous or anhydrous hydrogen fluoride, unless provision is made for the removal of water.

The oxyfluoride has a cubic structure, with $a = 3.790$ Å.

Magnetic susceptibility measurements were made on the tri- and tetrafluoride, the trifluorochloride and the oxyfluoride. The trifluorochloride and tetrafluoride are diamagnetic with similar values. The oxyfluoride is slightly paramagnetic and the trifluoride is paramagnetic with a value corresponding to approximately one unpaired electron.

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APPENDIX

The titanium oxyfluoride was fused with sodium carbonate, and dissolved in dilute nitric acid. Titanium was determined by precipitating the hydroxide with sulfur dioxide. Fluoride was determined as lead chlorofluoride.

Titanium trifluorochloride completely dissolved in water. Titanium hydroxide was precipitated upon the addition of sodium hydroxide, filtered at pH 5, washed and ignited. Chloride was determined from the filtrate using the gravimetric silver chloride method. Fluoride was then determined as lead chlorofluoride.

TITANIUM HALIDES

By

Karl S. Vorres

AN ABSTRACT

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Titanium trifluorochloride was prepared in an attempt to observe the transition from an ionic type of compound, characterized by titanium tetrafluoride, b.p. 284° C. to a covalent type of compound, titanium tetrachloride, b.p. 136° C. The trifluorochloride was prepared by reducing the tetrachloride with aluminum and aluminum chloride in a copper autoclave, fluorinating with hydrogen fluoride, and finally chlorinating with chlorine. The yellow compound sublimes readily at 220 to 225° C. The magnetic susceptibility is close to that obtained for titanium tetrafluoride. No X-ray powder diffraction patterns were obtainable.

Titanium oxyfluoride was prepared from the reaction of aqueous or anhydrous hydrogen fluoride with titanium dioxide. The oxyfluoride was also obtained from evaporating an aqueous solution of titanium tetrafluoride, and from the effect of atmospheric moisture on the trifluorochloride. X-ray powder diffraction patterns indicate a cubic structure for the oxyfluoride with $a = 3.79$ Å. Magnetic susceptibility measurements indicate a slight paramagnetism.

Titanium trifluoride gave complex X-ray powder diffraction patterns. The magnetic susceptibility corresponds to approximately one unpaired electron.

Titanium tetrafluoride was prepared in the copper autoclave by adding titanium tetrachloride to anhydrous hydrogen fluoride. Resublimation in a glass tube yielded the oxyfluoride. A monel tube eliminated the difficulty. The tetrafluoride obtained was used for X-ray powder diffraction data which indicated that the American Society for Testing Materials data for titanium tetrafluoride corresponds to a mixture of the tetrafluoride and oxyfluoride.