sonably explained in terms of a $Ga^{I}[Ga^{III}Cl_4]$ formulation.

TABLE II

THE ACTION OF H_2S ON $GaCl_2$ IN BENZENE

Formula of starting material	$\frac{\text{Ga in soln.}}{\text{Ga in solid}}$ Predicted	Found	Atomic ratio Cl:Ga remaining in soln.
$GaCl_{2.00}$	1.00	0.97	3.03
$GaCl_{2.02}$	1.04	1.05	3.03
$GaCl_{2.10}$	1.22	1.24	2.95
$GaCl_{2.14}$	1.33	1.25	3.00
$GaCl_{2.11}$	1.25	1.05	2.99
$GaCl^{a}_{2.05}$	1.11	1.01	..

[a] This material was prepared by the method described in reference 4a.

In a majority of the precipitations the ratio of gallium in the solid to that remaining in the benzene solution was close to the ratio expected from the formula of the starting material, on the assumption that the compound contained both Ga^{+1} and $[GaCl_4]^-$ and that the +1 gallium was precipitated. This point is brought out in Table II. In a number of cases the quantity of gallium in the solid exceeded appreciably that predicted from the formula of starting material. No explanation, beyond the possibility of coprecipitation, is offered for this.

Two additional significant facts came to light. First, as is seen from Table II, the chlorine: gallium atomic ratio in the benzene solution after precipitation was three, within experimental error, indicating that the gallium remaining was in the form of the trichloride. (It was noted in the Experimental section that appreciable chlorine was evolved as hydrogen chloride during precipitation. Moreover, as will be seen below, the precipitate contained chloride.) Second, only the precipitate possessed reducing power toward ammoniacal silver nitrate. Both these observations held even in situations where the precipitate contained more gallium than that expected from the formula of the starting compound.

The sulfide precipitate could not be characterized as a definite compound. The gallium content ranged from 33.4 to 51.3%; sulfide from 13.1 to 18.6%; and chloride from 13.2 to 20.0%. That the chloride was held quite firmly in the precipitate was demonstrated by the fact that neither extraction with benzene nor heating *in vacuo* to about 200° altered its content significantly.

Acknowledgment.—The authors are indebted to the Atomic Energy Commission for a grant in support of this investigation.

LAWRENCE, KANSAS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF BAYLOR UNIVERSITY]

Anion Exchange of Titanium(IV) in Hydrofluoric Acid

BY PATRICK H. WOODS[1] AND LEONE D. COCKERELL

RECEIVED AUGUST 22, 1957

The method of Fronaeus is used to show the existence of anionic fluoride complexes of titanium when the metal is dissolved in hydrofluoric acid. The color and oxidation state of the product has also been studied.

Introduction

Investigators reporting on the dissolution of titanium in hydrofluoric acid disagree as to the nature and color of the product formed. Glatzel[2] suggests the formation of TiF_4, whereas Straumanis[3] indicates that the dissolution proceeds according to the equation

$$2Ti + 6HF \longrightarrow 2TiF_3 + 3H_2$$

The color of the resulting solution is said to be purple[4] by some investigators and green[3] by others. In strongly acid solutions ($pH < 2$) the existence of the TiO^{++} ion usually is assumed.[5,6] As far back as 1908[7] the existence of $TiF_6^{=}$ ion has been suggested. More recently,[8] the failure to extract titanium salt with ether strongly suggests the possibility of an ionic product. If anionic complexes are formed, their existence can be shown by the method outlined by Fronaeus.[9] The purpose of the present investigation was to determine the color, oxidation state and nature of the product formed by the dissolution of titanium in hydrofluoric acid.

Experimental

Materials.—Reagent grade chemicals were used throughout the investigation. Titanium metal (purified by iodide method) was obtained from the Fisher Scientific Co. Purity is better than 99.9%.[10]

Amberlite IRA-400, a strongly basic quaternary ammonium type resin, was converted to the fluoride form with concentrated solutions of potassium fluoride. It was washed until the effluent would no longer give the zirconium-alizarin lake test for fluoride,[11] backwashed, column dried and finally air-dried before use. Its moisture content (18.54%) and ion capacity (1.472 meq./g.) were determined by accepted techniques.[12]

Preparation of Solutions.—The stock solution was made in a polyethylene bottle by dissolving titanium metal in hydrofluoric acid. When titanium metal was dissolved in

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[1] Taken from a thesis presented by Patrick H. Woods in partial fulfillment of requirements for the Doctor of Philosophy degree.

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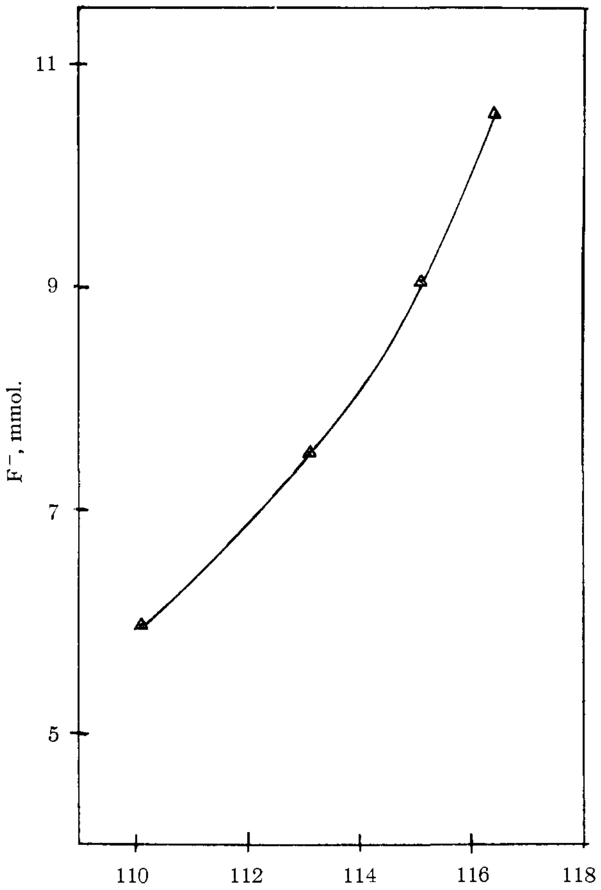

Fig. 1.—Correction curve for fluoride in coulometric titration of Ti^{+3} with Ce^{+4}.

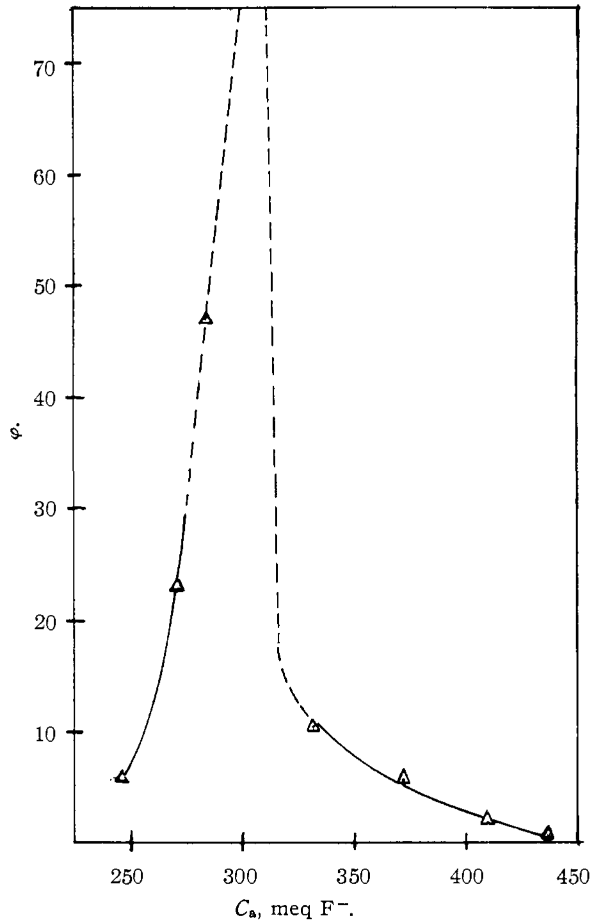

Fig. 2.—Distribution φ as a function of the ligand concentration C_a.

hydrofluoric acid in a glass container, a green solution formed (explained in Results and Discussion). The purple solution was oxidized to a colorless solution by bubbling oxygen gas through it.[3] Nitrogen was then bubbled through to remove excess oxygen. The titanium content was determined coulometrically[13] and the fluoride by the method of Geyer.[14]

A standard hydrofluoric acid solution was made by diluting 48% hydrofluoric acid with distilled water. The fluoride content was determined as above.

Apparatus.—For the coulometric titrations, an arrangement similar to that of Dilts and Furman[15] was used. The constant current source was a Lambda Model 25 Power Supply with 26,000 ohms resistance in the circuit. The milliammeter was calibrated with known solutions of titanium. Since the introduction of fluoride ion into a cerous-ceric system results in the precipitation of CeF_3,[16] a correction curve was made for this interference (Fig. 1). All time measurements were made with a Time-It precision timer from Precision Scientific Co. The sensitive amperometric end-point as developed by Cooke, Reilly and Furman[17] was used with the Sargent Ampot as the source of the impressed voltage.

Equilibration Technique.—One-half gram (0.736 meq.) of the fluoride resin was placed in a 130-ml. polyethylene bottle with a measured volume (polyethylene pipets which were prepared from polyethylene tubing and calibrated) of the stock solution and standard hydrofluoric acid solution. Water was added to make a total volume of 100 ml. This was agitated at 30° for approximately 18 hr. Preliminary runs had shown that equilibrium was attained between 12 and 16 hr.

Analytical.—The titanium content of the solution was determined from an aliquot that had been reduced with zinc amalgam spirals. Nitrogen gas was bubbled through the cerous sulfate solution and the aliquot for 1 hr. before analysis and during the analysis itself. From the known values of current and time and the value of the faraday (96,492 ± 3),[18] the equivalents of titanium in solution were determined. The concentration of metal on the resin was determined by difference. The influence of amine groups in the resin was neglected since the *p*H was less than one and rather high ligand concentrations were employed.[9]

Results and Discussion

The results of the ion-exchange study are shown in Fig. 2. φ is defined as the ratio of the concentration of metal ion in resin phase to that of the metal ion in solution after equilibration. The results show that anionic fluoride complexes of titanium exist in the concentration range studied. The maximum (representing quantitative absorption) indicates the formation of TiF_4 followed by the formation of TiF_5^- or higher complexes.

The dissolution of titanium in hydrofluoric acid in polyethylene bottles produces a purple solution which is oxidized rather rapidly by air. Oxygen, permanganate ion and ceric ion were found to

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(13) R. V. Dilts and N. H. Furman, *Anal. Chem.*, **27**, 1275 (1955).

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oxidize the purple solution to a colorless solution. Zinc amalgam spirals reduced the colorless solution back to a purple solution.

Dissolution of titanium in hydrofluoric acid in Pyrex test-tubes proceeds at a moderate rate to produce a purple solution. This reaction moderates, then proceeds vigorously to a green solution which is more stable to air than the purple, but also yields a colorless solution when in contact with oxygen, permanganate or ceric ions. The green solution is regenerated by placing zinc amalgam spirals in the colorless solution. Moreover, simply pouring some of the purple solution (from the polyethylene bottle) into a Pyrex test-tube produces the green solution. Quantitative oxidations with ceric ions show that both the green and purple solutions contain trivalent titanium while the colorless solutions contain tetravalent titanium. It appears that the green solution is a titanium–silicon–fluoride complex.

Acknowledgment.—The authors wish to thank the Research Corporation for financial assistance.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ANTIOCH COLLEGE]

Hydrothermal Reactions in the Na_2O–GeO_2 System[1]

BY ELWOOD R. SHAW, JAMES F. CORWIN AND JAMES W. EDWARDS

RECEIVED SEPTEMBER 9, 1957

The hydrothermal reactions between GeO_2 and water and water solutions containing sodium hydroxide have been studied at temperatures between 100 and 400°, and in the time range from 1 to 384 hours. The reaction of GeO_2 with water resulted in no new crystalline forms, but with solutions containing sodium hydroxide two crystalline forms having the proposed formulas $Na_3HGe_7O_{16}\cdot 4H_2O$ and $Na_2Ge_4O_9$ were prepared in such quantity that optical recognition and properties were easily established. The anhydrous material has heretofore been prepared by ignition only. On the basis of chemical analysis and *p*H determination mechanisms for the formation of these crystals are proposed.

Introduction

The early work[2,3] in the Na_2O–GeO_2 system consisted of studies of the melting point diagrams of mixtures. Eutectics were found at Na_2O–GeO_2 ratios of 1:1, 1:2 and 1:4 corresponding to compounds with the general formulas Na_2GeO_3, $Na_2Ge_2O_5$ and $Na_2Ge_4O_9$, respectively. The metagermanate and the tetragermanate have been prepared, but only the hydrated metagermanate has been characterized in the literature.[4–7]

Our studies of the products of hydrothermal reactions of NaOH–GeO_2 mixtures have shown that a condensed, anhydrous sodium germanate can be prepared in three crystalline habits and occurs as a single phase in the products of the reaction. Thus, the compound can be physically characterized and the structure determined.[8] By varying the conditions of the reaction the sodium hydrogen germanate described earlier by Nowotny and Wittmann[6] has been prepared in crystals of somewhat less regular habit. This hydrogen germanate is shown by X-ray studies to be the same compound precipitated at room temperatures from NaOH–GeO_2 mixtures containing NaCl. Infrared studies have shown the compound to be a definite hydrate so that the formula $Na_3HGe_7O_{16}\cdot 4H_2O$[6] is confirmed as preferable to $Na_2Ge_5O_{11}$.[9,10]

Ignition of this sodium hydrogen germanate at 900° caused a loss of 10.6% water and produced a compound with an identical X-ray pattern to that of the condensed anhydrous germanate synthesized hydrothermally from NaOH–GeO_2 mixtures and to that of a compound formed when a Na_2CO_3–GeO_2 mixture in the molar ratio 1:4 was fused at 900°.

From somewhat parallel reactions described by Nowotny and Wittmann,[6] and on the basis of Na_2O–GeO_2 analysis, the condensed germanate is identified as sodium tetragermanate.

By a similar hydrothermal reaction the ammonium and potassium hydrogen germanates were prepared; however the methods used for the hydrothermal conversion of sodium hydrogen germanate to the corresponding tetragermanate had no effect on the ammonium compound.

Hydrothermal runs in the GeO_2–H_2O system for purposes of familiarization with the products for optical identification confirmed the work of Laubengayer and Morton[11]; however new indices of refraction are proposed for the soluble form. Also, runs which were quenched produced birefringent, fibrous crystals with an average index of 1.66, close to that found for the commercial[12] GeO_2, 1.64–1.65, and to that reported in a handbook[13] for GeO_2, 1.65.

Experimental

Reagents.—Reagent grade chemicals were used in all cases unless otherwise described below. The germanium dioxide[12] was either in the form of a microcrystalline powder, 99.99% pure, or a fused glass in chunks of 5 mm. or less in

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under contract No. AF 18(600)1490. Reproduction in whole or in part is permitted for any purpose of the United States Government.

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