[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

The Thermal Decomposition of Ammonium Heptafluorozirconate(IV)[1]

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A study has been made of the thermal decomposition of ammonium heptafluorozirconate, $(NH_4)_3ZrF_7$, using the technique of differential thermal analysis. The decomposition proceeds in three distinct stages, $(NH_4)_3ZrF_7 \rightarrow (NH_4)_2ZrF_6 \rightarrow NH_4ZrF_5 \rightarrow ZrF_4$. The temperature of decomposition is a function of the pressure.

There are two reported ammonium fluorozirconates, the heptafluorozirconate, $(NH_4)_3ZrF_7$, and the hexafluorozirconate, $(NH_4)_2ZrF_6$. They were first prepared by deMarignac[2] and studied again by von Hevesy.[3] Hampson and Pauling[4] have given the complete structure of the cubic $(NH_4)_3ZrF_7$ and Gossner,[5] from crystallographic study, lists $(NH_4)_2ZrF_6$ as rhombohedral and hexagonal. Hartman[6] prepared zirconium(IV) fluoride by heating the heptafluorozirconate in nitrogen and Schulze[7] has reported the crystal form (monoclinic) and lattice for this product.

Study of these compounds offers the possibility of a comparison between a stepwise chemical reaction in the solid state and a set of accompanying crystallographic changes. The technique of differential thermal analysis[8,9] is effective in the study of decompositions of this type. The temperature differential between a decomposing sample and a stable referent is an indicator of the changes or transitions taking place.

Differential heating curves obtained on thermal decomposition of $(NH_4)_3ZrF_7$ at atmospheric pressure show three maxima, corresponding to the series

$$(NH_4)_3ZrF_7 \longrightarrow (NH_4)_2ZrF_6 \longrightarrow NH_4ZrF_5 \longrightarrow ZrF_4$$

cubic hexagonal (?) unknown monoclinic

The three maxima are also shown as breaks in the simple heating curve of the compound. There was consistent agreement between the decomposition temperatures obtained by these two methods. At lower pressures, the decomposition also proceeds in three distinct steps, at progressively lower temperatures as pressure decreases.

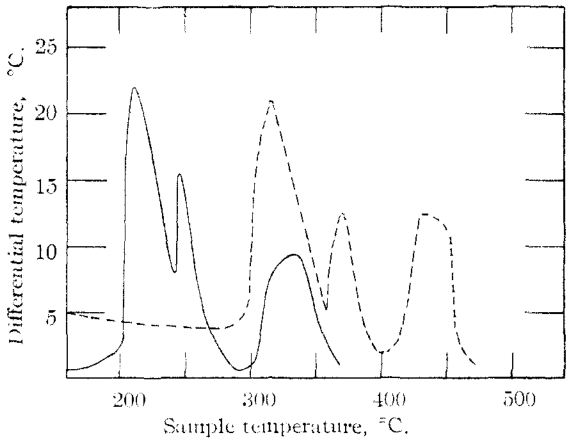

Fig. 1.—Thermal decomposition of $(NH_4)_3ZrF_7$: ——, at 20 mm.; - - - - -, at 760 mm.

The decomposition temperatures for the three successive decompositions are: 297, 357 and 410° at 760 mm.; 288, 355 and 404° at 515 mm.; 235, 288 and 380° at 120 mm.; and 203, 244 and 298° at 20 mm. Approximate values for heats of decomposition from these data are 21, 21 and 25 kcal., respectively. Equilibrium pressure measurements should be made for more precise values. Differential heating curves for the two limiting pressures are shown in Fig. 1.

The products of each stage have been identified analytically and by X-ray powder patterns. Samples were prepared by heating the heptafluorozirconate to a temperature only slightly above the proper decomposition temperature for several hours. The product of the first stage was $(NH_4)_2ZrF_6$, which was compared to a synthesized sample. Analysis showed the product of the second stage to be the new compound NH_4ZrF_5, with a distinctive X-ray pattern. The compound has been prepared by synthesis and has the same pattern. Work on the structure of this compound and of the hexafluoro compound is in progress. The final product is the fluoride, ZrF_4.

Experimental

The procedure outlined by Vold[9] was used with a few modifications. The two cells were of nickel, fitted with vacuum connections and Teflon gaskets. They were suspended in the air furnace and insulated with Lavite spacers. Single junction iron–constantan thermocouples were used. The temperature of the furnace and of the decomposing sample were measured separately by a Leeds and Northrup Speedomax recorder, calibrated with the melting points of tin and lead. The differential temperature, using calcium fluoride as the reference material and with a 3–5-g. sample of heptafluorozirconate, was followed with a Rubicon type B potentiometer. Pressure was controlled by a variable leak and was maintained at ± 5 mm. during each run.

X-Ray powder patterns were made with copper radiation, filtered by nickel, using a Philips 57.3-mm. powder camera. The samples were mounted on Pyrex fibers.

Ammonia was determined by distillation from strongly alkaline solution into boric acid followed by titration with standard hydrochloric acid. Zirconium was determined by digestion in platinum with sulfuric acid and subsequent ignition to the oxide.

Ammonium heptafluorozirconate was prepared by adding 100% excess ammonium fluoride (as a 30% solution) to a solution of zirconium dioxide in aqueous hydrofluoric acid, from which the excess acid had been driven off by repeated dilution and heating.[3]

Anal. Calcd. for $(NH_4)_3ZrF_7$: NH_4, 19.41; Zr, 32.78. Found: NH_4, 19.10, 19.36, 19.46; Zr, 32.50, 32.66.

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(1) This work is part of a program of research on inorganic fluorides supported by the Research Corporation and the Atomic Energy Commission.

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Ammonium hexafluorozirconate was prepared by adding the theoretical quantity of ammonium fluoride solution to a solution of oxide in hydrofluoric acid and evaporating to incipient crystallization.

Anal. Calcd. for $(NH_4)_2ZrF_6$: NH_4, 14.93; Zr, 37.80. Found: NH_4, 14.75, 14.84; Zr, 37.39, 37.78, 37.80.

The first decomposition product from the 515 mm. run was analyzed. Found: NH_4, 14.35, 14.05; Zr, 37.70, 37.97.

Ammonium pentafluorozirconate was prepared by adding 75% of the theoretical quantity of ammonium fluoride solution to a solution of the oxide in hydrofluoric acid and allowing the solution to crystallize slowly.

Anal. Calcd. for NH_4ZrF_5: NH_4, 8.82; Zr, 44.56. Found: NH_4, 8.58, 8.63, 8.67; Zr, 44.63, 44.13.

The product from the second decomposition at 515 mm. was analyzed. Found: NH_4, 8.80, 8.74, 8.74; Zr, 43.90, 43.95.

The zirconium(IV) fluoride used for comparison with the end product was prepared by fluorination of zirconium metal at 550°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Equilibria of Antimonous Oxide (Rhombic) in Dilute Solutions of Hydrochloric Acid and Sodium Hydroxide at 25°

BY KARL H. GAYER[1] AND A. B. GARRETT

The solubility of antimonous oxide has been determined in water and in dilute solutions of sodium hydroxide and hydrochloric acid. The equilibria in sodium hydroxide and in hydrochloric acid solutions indicate that the antimony is present in both cases as a monovalent ion. Values of the solubility of antimony oxide in water and for the acid and base constants of antimony trioxide have been obtained.

The purpose of this investigation was to obtain data on the equilibria of antimonous oxide in dilute hydrochloric acid and sodium hydroxide solutions. Previous work on antimonous oxide is incomplete in regard to solubility and equilibria values. The earliest reported work on the reactions of antimony was made by Terriel[2] who prepared sodium antimonite and studied some of its properties. Schulze[3] determined the solubilities of antimony trioxide in water at 15 and 100° and found them to be 5.5×10^{-5} and 3.4×10^{-4} mole per 1000 g. of water, respectively. Schuhmann[4] measured the solubility of antimony trioxide (probably the rhombic form) in several solutions of various concentrations of perchloric acid, and found a fairly constant value for the ratio of hydrogen ion concentration to antimony concentration, which led him to conclude that the SbO^+ ion exists in acid solutions.

Procedure

The general procedure was similar to that of Garrett and Heiks.[5]

Water.—Triply distilled water was boiled to free it from dissolved gases and then stored under nitrogen.

Antimony Trichloride.—Baker and Adamson Reagent antimony trichloride was used to prepare the rhombic antimonous oxide.

Antimony Metal.—Baker and Adamson Reagent antimony was used to prepare the colorimetric standards.

Sodium Carbonate.—Mallinckrodt anhydrous Analytical Reagent was used to precipitate the oxide.

Hydrochloric Acid.—Standard solutions for analysis and for the solubility measurements were prepared from C.P. hydrochloric acid and standardized gravimetrically.

Rhodamine B.—Eastman Kodak Co. practical grade was used to prepare the 0.2% water solution.

Rhombic Antimonous Oxide.—The antimonous oxide was prepared in an atmosphere of nitrogen. To a solution containing 30 g. of antimony trichloride per liter of water was added a saturated solution of sodium carbonate to precipitate the antimony oxide. The oxide was then washed with triple-distilled, boiled water until free of chloride and sodium ions. Fifteen one-liter washings sufficed. The identity of the rhombic form was obtained by X-ray analysis.[6]

Equilibration.—Two 180-ml. samples of the equilibrating mixture, contained in 200-ml. round bottom flasks, were prepared at each concentration of alkali or acid. One sample was agitated in a thermostat at 35° for a period of 5 to 7 days, then transferred to a thermostat at 25 ± 0.02° for an additional agitation period of seven days. The other one of each pair was placed directly in the 25° thermostat and agitated for seven days. By this means, equilibrium was approached from supersaturation and undersaturation. Both values were found to check within experimental limits.

Sedimentation.—After the completion of the agitation period, the flasks were clamped in an upright position in the 25° thermostat, and the oxide allowed to settle for seven days.

Filtration.—The flasks were opened and contents removed under an atmosphere of nitrogen through a covered, sintered glass funnel, and into a glass-stoppered bottle.

Measurement of Hydrogen Ion Concentration.—The *p*H values of the equilibrated samples were obtained by using a Beckman portable *p*H meter. The meter was calibrated with potassium acid phthalate–sodium hydroxide buffer at *p*H 4, and with boric acid–sodium hydroxide buffer at *p*H 10.

Analysis of Antimony.—The antimony analysis on the equilibrated samples was made with a Lumetron spectrophotometer using rhodamine B to produce the colored complex. The procedure for analysis was a modification of that described by Maren.[7] The analyses were reproducible to ± 3%.

The data are collected in Tables I and II and are shown graphically in Fig. 1. The rhombic form of

TABLE I

SOLUBILITY OF RHOMBIC Sb_2O_3 IN NaOH SOLUTIONS AT 25°

Initial mole NaOH/1000 g. H_2O	Gram atom of Sb/1000 g. H_2O $\times 10^5$	$K \times 10^3$
0.000	5.8	
.00505	9.8	7.9
.0101	14.8	8.9
.0202	23.8	8.9
.0404	42.8	9.2
.0400	37.8	8.0
.0749	75.8	9.3
.0998	99.8	9.4
		Av. 8.8

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[6] We are indebted to Dr. D. A. Vaughan of the Battelle Memorial Institute for the X-ray analysis of these samples.

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