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PRELIMINARY X-RAY INVESTIGATIONS
OF THE HYDRATES OF ZIRCONIUM TETRAFLUORIDE

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INTRODUCTION

In the studies of the dissolution of uranium-zirconium alloys used in nuclear reactor fuel elements, it was observed that insoluble salts were formed. A phase study of the zirconium-nitric acid-hydrofluoric acid system was undertaken by Chapman⁽¹⁾ and co-workers to investigate the chemistry of the formation of these salts.

Two of the numerous solid phases obtained in this study were tentatively identified as $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$ and $\text{ZrF}_4 \cdot \text{H}_2\text{O}$. It has been reported⁽²⁾ that the compound $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$ may have the formula $\text{H}_2\text{ZrOF}_4 \cdot 2\text{H}_2\text{O}$ or $\text{ZrOF}_2 \cdot 2\text{HF} \cdot 2\text{H}_2\text{O}$. Also, it would be possible to write the formula for $\text{ZrF}_4 \cdot \text{H}_2\text{O}$ as H_2ZrOF_4 or $\text{ZrOF}_2 \cdot 2\text{HF}$. The two hydrates were identified by comparing x-ray diffraction powder data with the data published by D'Eye and co-workers⁽³⁾. In order to obtain more knowledge of these hydrates a structural analysis by single crystal x-ray diffraction has been initiated.

PREPARATION AND ANALYSIS

Zirconium fluoride monohydrate single crystals were prepared from reactor grade zirconium metal in a mixture of concentrated nitric acid and 48 percent hydrofluoric acid, by the method described by Chapman⁽¹⁾. The trihydrated zirconium fluoride was prepared from the monohydrate⁽⁴⁾.

A saturated solution of the monhydrate in 6.0M nitric acid at 40-50 degrees Centigrade was allowed to cool and stand at room temperature for four to five days. The slow crystallization produced copious amounts of the trihydrate, from which single crystals could be separated.

Analyses on the two hydrates were obtained by x-ray diffraction and chemical methods, and they were found to be pure compounds.

(A) The x-ray diffraction data for identifying the hydrates were obtained with a Geiger Counter Powder Diffractometer using $\text{CuK}\alpha$ radiation. The powder data obtained were in agreement with that reported by D'Eye⁽³⁾.

(B) The chemical analyses for zirconium, fluorine and water were done in our analytical laboratories. The fluorine in the hydrates was determined by a volumetric titration of the pyrolyzed hydrogen fluoride⁽⁵⁾. The zirconium was determined by an amperometric titration with cupferron⁽⁶⁾. The water of hydration was obtained by difference after the preceding zirconium and fluorine analyses.

(C) Photomicrographs of crystals of the hydrates were taken by the Engineering Development and Metallurgy Section at the MTR. Figures 1 and 2 are representative of the trihydrate and monohydrate respectively, in polarized light and magnified thirty times.

X-RAY DIFFRACTION

Trihydrate

In 1860 DeMarignac⁽⁷⁾ did an optical crystallographic study of zirconium tetrafluoride trihydrate. He concluded that the trihydrate was

Figure I - Photomicrograph of Zirconium Tetrafluoride Crystals

Figure II - Photomicrograph of Zirconium Tetrafluoride Monohydrate Crystals

triclinic. Zachariasen and Plettinger⁽⁸⁾ reported in 1950 that the trihydrate was orthorhombic with unit cell dimensions $a = 6.64$ A, $b = 9.88$ A, and $c = 8.08$ A. In 1956 D'Eye⁽³⁾ published the powder diagram and the observed $\sin^2\theta$ data for the trihydrate, but he was not successful in indexing the data and obtaining lattice constants. D'Eye did not make a reference to the Zachariasen data, and it was not known if he tried to index his powder data on the basis of an orthorhombic cell.

A powder sample of the trihydrate was prepared and x-ray powder diffraction data were obtained using a 114.6 mm diameter camera, and copper radiation with a nickel filter. Comparison of the observed $\sin^2\theta$ values with that of D'Eye, showed that the two powder photographs were the same. It was then attempted to index the powder data on the basis of the cell dimensions given by Zachariasen. It was found that the powder data could not be indexed on this basis and obtain an agreement between observed and calculated $\sin^2\theta$ values.

An analytical method⁽⁹⁾ of indexing the powder data was then tried. Fairly good agreement between $\sin^2\theta$ values were obtained by using the equation $\sin^2\theta_c = (.00285)h^2 + (.00320)k^2 + (.00510)l^2$, which corresponds to an orthorhombic cell with $a = 14.40$ A, $b = 14.01$ A, and $c = 10.78$ A.

Since there was a discrepancy in the published data and the results from powder data taken in this laboratory, it was decided to further pursue this project by single crystal x-ray diffraction methods.

Three single crystals of zirconium tetrafluoride trihydrate were mounted in capillaries, in order to obtain Weissenberg photographs with three different rotation axes. The crystals used were approximately 0.75 mm in length and 0.5 mm in depth and width (See Fig. 1). A study of the crystals under magnification did not reveal any symmetry. The crystals were placed in capillaries because there is some decomposition upon standing in the atmosphere. One of the crystals was oriented assuming a rotation axis parallel to the long axis of the crystal. Two other crystals were placed in capillaries and oriented in such a position as to have rotation axes approximately 90° to the long axis in the first crystal. The crystals were aligned and zero level Weissenberg photographs were taken with copper radiation and a nickel filter. First, second, and third layer line photographs were also taken of the three crystals to aid in the choice of axes and the indexing. It was found to be impossible to choose axes and index the Weissenberg data on the basis of an orthorhombic unit cell. It was also impossible to choose axes so that the angles of the unit cell would fit the conditions for any crystallographic system other than triclinic. With this information and the observation of the absence of symmetry in the crystals, the data was tentatively indexed on the basis of a triclinic unit cell. The tentative unit cell dimensions and angles chosen were $a = 5.40$ Å, $b = 3.05$ Å, and $c = 4.87$ Å; with the angles of $\alpha = 105^\circ$, $\beta = 90^\circ$, and $\gamma = 68^\circ$.

Further work must be done to substantiate the above dimensions and angles, and because of the complexity of the problem, no further conclusive information is available at this time.

Monohydrate

Zachariasen and Plettinger⁽⁸⁾ reported in 1950 that the monohydrated zirconium tetrafluoride was tetragonal. In 1956 D'Eye⁽³⁾ published powder data on the monohydrate and his results were in agreement with Zachariasen's data in the latter report. Using only powder data D'Eye was able to arrive at lattice constants and give a tentative space group. Since single crystals were available in this laboratory, it was decided to work on the structure of zirconium tetrafluoride monohydrate, using single crystal data.

The monohydrate crystals used were in the form of octahedrons as shown in Figure 2. The crystal used was small with a length of approximately 0.2 mm. The crystal was mounted on a glass fiber with the rotation axes corresponding to the long axis of the crystal. Weissenberg photographs were taken of the zero, first, and second layer lines with the crystal in the above position. The photographs were taken with copper radiation and a nickel filter. The photographs were indexed and unit cell dimensions obtained corresponding to a body centered tetragonal cell. The unit cell dimensions obtained were $a = 7.71 \pm 0.01 \text{ \AA}$ and $c = 11.65 \pm 0.01 \text{ \AA}$, and the data was shown to be in agreement with the equation,

$$\sin^2 \theta \text{ (calculated)} = .009998(h^2 + k^2) + .004379 l^2.$$

On the basis of an experimental density of 3.24 g/cc, there were eight molecules per unit cell. On the basis of eight molecules per unit cell the calculated density was 3.42 g/cc, which is in good agreement with the experimental density.

For all observed indices the conditions for non-extinction were compatible with the space groups C_{4v}^{11} and D_{2d}^{12} as reported in the literature (3).

The complete structure determination of zirconium tetrafluoride monhydrate will involve the determination of many parameters. However, future work will be enhanced by the availability of single crystal data.

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