1.5° smaller, while if the observations were indeed in error due to contamination by TeO_2, the temperature should be 2° higher. Hence the boiling point of tellurium may be stated as 994 ±3°.

The use of (2) to compute the heat of vaporization is inaccurate at the lowest temperatures because of uncertainty of the data and inaccurate at the highest temperatures because of uncertainty in the value of C_2. At 600°, ΔH is computed from (1) and (2) to be 28.4 kcal. mole^{-1}; this value, together with $d\Delta H/dT = -9$ cal. mole^{-1} deg.$^{-1}$, probably gives heats of vaporization accurate within a few hundred calories per mole.

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[CONTRIBUTION FROM E. I. DU PONT DE NEMOURS AND CO., INC.]

Preparation and X-Ray Study of Some Tantalum Halides

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Tantalum penta-iodide and -bromide crystallize in the orthorhombic system. The pentaiodide was found to have a pycnometric density of 5.80 g. cc.$^{-1}$ and an X-ray density of 5.809 g. cc.$^{-1}$ with eight formula weights per unit cell. The pentabromide was found to have a pycnometric density of 4.99 g. cc.$^{-1}$ and an X-ray density of 5.238 g. cc.$^{-1}$ with eight formula weights per unit cell. Tantalum pentachloride crystallizes in the monoclinic system with an X-ray density of 3.761 g. cc.$^{-1}$, with twelve formula weights per unit cell. This is an excellent agreement with the pycnometric density of 3.68 g. cc.$^{-1}$. A compound corresponding to TaI_4 was prepared and characterized.

Introduction

There have been numerous reports on the preparation of the tantalum pentahalides.[1,2] The vapor pressures[3-5] and structures[6] of the gaseous species have been determined, but the X-ray diffraction and subsequent structural studies of the pure solid phases have not been made. The compound corresponding to TaI_4 was probably first isolated, although not characterized, by Körösy.[7]

Results and Discussion

Pure **tantalum pentaiodide** was prepared in the same manner as pure niobium pentaiodide.[8] Pure "iodide" tantalum was suspended in a Pyrex flask which contained only the vapor of resublimed iodine. The tantalum reacted to yield pentaiodide at about 300°, more rapidly at 340–370° (the previously reported[2] minimum value was 700°) and was prevented from reducing the pentaiodide to a lower iodide by maintaining a high partial pressure of iodine. The excess iodine was easily sublimed from the iodide. Tantalum was determined on freshly prepared samples by precipitation of tantalum hydroxide with ammonium hydroxide and igniting to the pentoxide (Ta_2O_5). Halogen, in this case iodine, was determined by the modified[9] Volhard technique. The results of chemical analyses are: 22.55, 22.26, 22.34% Ta; 77.95, 78.89, 77.95, 77.95% I; the theoretical values are 22.18% Ta and 77.82% I.

Samples of the powdered and hygroscopic material were hermetically sealed in 0.3 mm. Lindemann glass capillary tubes and exposed 24 hr. to the K-alpha radiation of copper (λ = 1.5418 Å.). The film, in a Phillips 114.6 mm. diameter camera, was covered with two nickel screens. In addition, a single crystal of the pure pentaiodide was hermetically sealed in a 0.3 mm. Lindemann glass capillary tube. The 0 and 1 levels were obtained with copper radiation by precession of the crystal about both the *b* and *c*-axis, the 2 and 3 level with molybdenum radiation by precession about the *b*-axis. The crystal was rotated also about the *a*-axis. As a result of this the crystal appears to be orthorhombic, D_{2h}^{16}-$P2_1/b\ 2_1/n\ 2_1/m$, with the lattice parameters of a_0 = 6.65Å., b_0 = 13.95 Å. and c_0 = 20.10 Å. The observed and calculated *d*-spacings (Å.) with the indices assignment and visually observed intensities determined as a result of this investigation were reported recently.[10]

The pycnometric density was determined at 26° by evacuating the pycnometer bulb containing the pure pentaiodide and then distilling, under vacuum, absolute carbon tetrachloride onto the solid sample. Values for three different samples were 5.791, 5.798 and 5.807 g. cc.$^{-1}$. The X-ray density was found to be 5.809 g. cc.$^{-1}$ as calculated with the above determined cell parameters and with eight formula weights per unit cell. It is interesting to observe that Körösy[2] found the density to be 4.68 g. cc.$^{-1}$ at 150° in carbon tetrachloride. This is obviously a misprint.

Tantalum pentaiodide is not isostructural with niobium pentaiodide.

Tantalum Pentachloride.—Tantalum pentachloride was prepared by the chlorination of a heated mixture of carbon and tantalum pentoxide and purified by sublimation in a current of purified chlorine. Results of chemical analyses are 50.88, 50.76, 50.68% Ta; 49.39, 48.97, 49.99% Cl; the theoretical values are 50.50% Ta and 49.50% Cl.

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(10) Copies of Document 5487 can be obtained at a cost of $1.25 from Chief, Photoduplication Service, ADI Auxiliary Publications Project, Library of Congress, Washington 25, D. C.

The powder diffraction photographs for the pure niobium[11] and tantalum pentachlorides, hermetically sealed in 0.3 mm. Lindemann glass capillaries, indicate that both compounds have the same crystal structure. The *d*-spacings observed as a result of this investigation were reported recently.[10] Assignment of indices was made by comparison with the reported[12] single crystal data for $NbCl_5$. Cell dimensions for monoclinic $NbCl_5$ are $a_0 = 18.23$ Å., $b_0 = 17.76$ Å., $c_0 = 5.86$ Å. with beta = 90.6°, and these values can be tentatively assumed for $TaCl_5$.

The X-ray density of 3.76 g. cc.$^{-1}$ as calculated with 12 formula weights per unit cell is in excellent agreement with the pycnometric[13] density of 3.68 g. cc.$^{-1}$. It should be noted that three lines, 4.11, 3.08 and 3.01 Å. were observed in the pattern for both the tantalum and niobium pentachloride but were not reported by Douglass.[12]

Tantalum Pentabromide.—Tantalum pentabromide was prepared by bromination of "iodide" tantalum at 450°–470° in the apparatus as described[14] for the preparation of $NbBr_5$. There was no problem with oxybromides although the initial product was a thin white to cream colored film. Results of chemical analyses are 31.22, 31.54, 31.44% Ta; 69.04, 68.55, 68.83% Br; the theoretical values are 31.15% Ta and 68.85% Br. The powder diffraction photographs for the pure niobium and tantalum pentabromide indicate that both compounds have the same crystal structure. Therefore, utilizing the single crystal data as determined[14] for orthorhombic $NbBr_5$, the observed powder diffraction lines for $TaBr_5$ were assigned indices with the cell dimensions of $a_0 = 6.125$ Å., $b_0 = 12.92$ Å. and $c_0 = 18.60$ Å. The complete X-ray data determined in this investigation were recently reported.[10]

The X-ray density of 5.238 g. cc.$^{-1}$ was calculated with eight formula weights per unit cell. The pycnometric density of the pentabromide was found to be 4.95, 4.99 and 5.04 g. cc.$^{-1}$ as determined in absolute carbon tetrachloride and can be compared to the reported[15] value of 4.67 g. cc.$^{-1}$. A better agreement between the X-ray and pycnometric densities may possibly have been achieved if well defined back reflections could be obtained and the lattice parameters refined by graphical methods.

Tantalum Subiodide.—A tantalum subiodide corresponding to the formula TaI_4 was prepared[16] in a "de Boer" type reaction bulb commonly used to refine transition metals. Gaseous iodine reacted with tantalum sheet to yield the pentaiodide which was then reduced with the excess tantalum to the lower iodide. This iodide completely dissolved in distilled water and gave clear, green aqueous solutions that became colorless with a white precipitate when permitted to stand in air. Some of the solid was permitted to remain for several days in closed weighing tubes stored over phosphorus(V) oxide before placing in distilled water. These samples gave a black aqueous solution with a black residue, and although this residue never disappeared, the black color changed to a colorless liquid over a white, flocculent precipitate. The analytical values of 26.65% Ta and 73.02% I for the green aqueous solution indicate the compound $TaI_{3.91}$. The total composition of 99.67% would account for some deviation from $TaI_{4.0}$ which contains 26.27% Ta and 73.73% I. Therefore, this deviation can be attributed to limitations of the analytical procedure rather than to the purity of the compound. It is interesting to note that Körösy,[7] in his study of the reaction between tantalum and iodine, prepared a material which produced a green aqueous solution and analyzed 26.7, 26.3% Ta; 73.3% I. He also could not unequivocally determine the oxidation state of the tantalum. Samples of the freshly prepared material ($TaI_{3.91}$) were pulverized in an agate mortar and hermetically sealed in 0.3 mm. Lindemann glass capillary tubes. They were exposed for 12 hr. to the K-alpha radiation of copper in a Phillips 114.6 mm. camera with a nickel port and a nickel screen over the film. The results of this investigation were recently reported.[10]

Samples of this material were independently studied[17]: it was found to contain 74.1% iodine, to give excellent agreement with the X-ray data reported here and to react with eight moles of liquid ammonia at −75°. In addition, it was found to be diamagnetic. If, as the above analyses indicate, this compound is tantalum tetraiodide, then it would be expected to have one unpaired electron and to be paramagnetic. Since the compound is diamagnetic, the one electron must be paired as would be expected for a dimer, or the solid may possibly consist of $Ta^{+3}Ta^{+5}I_8$. This latter compound, a tantalum iodotantalate, would also be diamagnetic.

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[11] Niobium pentachloride was prepared and purified by the technique given above for tantalum pentachloride.

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[17] I am grateful to Dr. George W. Watt, Professor of Chemistry at the University of Texas, Austin, Texas.