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THE EQUILIBRIUM PHASE DIAGRAMS FOR THE TANTALUM-TANTALUM BROMIDE AND TANTALUM-TANTALUM IODIDE SYSTEMS

by

James Claude Boatman

A Dissertation Submitted to the
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INTRODUCTION

There have been many tantalum halides reported in the literature up to now. These compounds include tantalum(V), tantalum(IV), tantalum(III), tantalum(II) and a water soluble halide with an apparent oxidation state of 2 1/3. The observations that have been made contradict one another and in some cases the reported data have not been of the highest quality. For the above reasons, it was felt that a systematic study of the tantalum halides was in order. It was the purpose of this work to make such a study of the tantalum bromide and tantalum iodide systems by means of an equilibrium phase diagram as a function of temperature and composition.

Reported Halide Compounds of Tantalum

Tantalum(V) halides

The tantalum(V) halides (chloride, bromide, and iodide) have been known since 1846 when Rose (1) prepared $TaCl_5$ by the chlorination of Ta_2O_5. Tantalum(V) bromide and iodide made their appearance in 1910 when Van Haagen (2) found that $TaBr_5$ was the resultant product when Ta_2O_5 and sugar carbon were heated to high temperatures and bromine passed over the mixture. At the same time he found that TaI_5 was formed by halogen exchange when $TaBr_5$ was heated in a stream of dry hydrogen iodide.

Since the first report of these compounds many variations of their preparation have been reported. The preparations of $TaCl_5$ (3,4,5, and 6), $TaBr_5$ (7 and 8), and TaI_5 (9,10,11, and 12) are well known and will not be discussed in detail.

The existence of the tantalum(V) halides was in no way contested since these compounds have been completely characterized.

Tantalum(IV) halides

Tantalum(IV) chloride has been well characterized primarily by Schäfer and his group in Germany. This compound was first reported by Ruff and Thomas (13) in 1922 when they reacted $TaCl_5$ with aluminum and $AlCl_3$ in sealed tubes for 2 to 3 hours at 300°C.

Schäfer and Grau (14) modified this method by excluding the $AlCl_3$ and reducing $TaCl_5$ with aluminum in a temperature gradient of 400° to 200°C. The volatile $TaCl_4$ was condensed at the 200°C. end of the reaction vessel. They found that $TaCl_4$ decomposed according to Reaction 1 when heated to 280° to 340°C. under nonequilibrium conditions.

$$2TaCl_4(s) = TaCl_3(s) + TaCl_5(g) \qquad (1)$$

In 1960, Schäfer and Kahlenberg (15) claimed to have improved the preparation of $TaCl_4$ by using tantalum metal as the reducing agent. In this procedure, $TaCl_5$ was reacted with tantalum metal in a temperature gradient of 630°C. at the end containing metal and 280°C. at the cool end of the quartz tube. This procedure was carried out under a vacuum of ca. 10^{-5} Torr. The temperature of 630°C was necessary to assure that reduction of $TaCl_5$ occurred, and the temperature of 280°C. maintained the vapor pressure of $TaCl_5$ at ca. three atmospheres. At the end of 6 days, 8 to 10 grams of $TaCl_4$ were obtained. In this same work they determined some thermodynamic properties of this compound.

In 1962, Shchukarev and Kurbanov (16) reported the aluminum reduction of $TaCl_5$ in sealed ampoules at 230°C. using an excess of $TaCl_5$. The resultant product was light green in color. When this experiment was repeated by this author, the best chloride to tantalum ratio that was obtained for the product was 3.93.

Gutmann and Tannenberger (17) first reported the formation of $TaBr_4$ by the reduction of $TaBr_5$ with hydrogen in an electrodeless electric discharge. According to their report, $TaBr_4$ disproportionated to $TaBr_3$ and $TaBr_5$ in a vacuum at

300°C. Their $TaBr_3$ was reported to be green, but they did not confirm its composition and only guessed that it was $TaBr_3$.

McCarley and Boatman (18) later obtained a pure sample of $TaBr_4$ by the reduction of $TaBr_5$ with tantalum metal in an evacuated, sealed Vycor tube in a temperature gradient of 630°C. at the metal end of the tube and 300°C. at the cool end of the tube. After a period of 14 days, _ca_. 1-2 grams of a dark brown crystalline material were obtained. It was found that temperatures above _ca_. 330°C. at the cool end of the apparatus resulted in compounds with a bromide to tantalum ratio of less than 4. As an alternate method this work also showed that $TaBr_4$ could be obtained by reducing $TaBr_5$ with aluminum foil. This was accomplished in sealed, evacuated Pyrex tubes in a temperature gradient of 500°C. at the aluminum end and 250°C. at the cool end of the tube. After 7 days 1-2 grams of the dark brown crystalline material were obtained.

Rolsten (19) first reported a subiodide of tantalum that corresponded to TaI_4 in 1958. This preparation was carried out in a "de Boer" type reaction bulb commonly used to refine transition metals. Gaseous iodine was reacted with sheet tantalum to yield TaI_5 which then was reduced with excess tantalum metal to the lower iodide. This iodide was reported to dissolve completely in distilled water giving a clear, green solution that slowly became colorless and precipitated a white solid on standing in air.

McCarley and Boatman (18, p. 548) reported two methods for the synthesis of TaI_4 in 1963. It had been noted in earlier work (20) that TaI_5 was reduced by pyridine to form the pyridine complex of TaI_4 and the iodine complex of pyridine as shown in Equation 2. The purified pyridine complex

$$2TaI_5 + 5C_5H_5N = 2TaI_4(C_5H_5N)_2 + C_5H_5NI_2 \qquad (2)$$

of TaI_4 was placed in a tube, which was fitted with a side arm condenser, evacuated and sealed. The tube containing the complex was heated for 2 days at 200°C. while the evolved pyridine was collected in the side arm at -78°C. The residue which was soluble in distilled water produced a brown solution but did not give a green solution as reported by Rolsten (19). A second method utilized the reduction of TaI_5 with aluminum foil in a temperature gradient of 500°C. (Al end) to 350°C. (ca. 16 mm. of TaI_5 pressure). After seven days, 5 grams of a lustrous gray crystalline deposit were found in a zone which was well separated from the excess TaI_5.

Anal. Calcd. for TaI_4: Ta, 26.29; I, 73.71. Found for pyridine reduced: Ta, 26.03; I, 73.43;

Found for Al reduced: Ta, 26.72; I, 74.31.

Lower tantalum halides

Attempts to prepare lower valent tantalum chlorides were initiated in 1907 by Chabriè (21) who reduced $TaCl_5$ with a 3% sodium amalgam at red heat under an aspirator vacuum. From the reduction mass a green solution was extracted with acidified water and evaporated to give a green crystalline powder. The formula $TaCl_2 \cdot 2H_2O$ was derived from a single analysis of the material obtained.

A series of studies was begun in 1922 by Lindner et al. (22,23,24,25,26) on the chlorides of divalent molybdenum, tungsten, and tantalum. A lower valent tantalum compound was obtained by the reduction of $TaCl_5$ with aluminum, zinc, or lead powder at 600°C in a stream of dry nitrogen. Excess $TaCl_5$ was removed by sublimation and the residue extracted with water in a refluxing vessel until only the insoluble portion remained. By evaporation of the solution under vacuum a black-green crystalline powder remained. This material was assigned the formula $H[Ta_3Cl_7 \cdot H_2O] \cdot 3H_2O$, indicating a water soluble tantalum(II) compound in agreement with Chabriè's tantalum(II) compound.

Also in 1922, Ruff and Thomas (27) reported the reduction of tantalum(V) chloride using powdered aluminum plus aluminum (III) chloride at 300°C. for 2 to 3 hours in an evacuated, sealed tube. Average composition of the residue, after heating at 200°C. to sublime $AlCl_3$ from the reaction zone followed by heating at 250°C., was found to correspond to $TaCl_4$. If the second heating were at 350° to 400°C., the residue was found to be approximately $TaCl_3$; at 500°C. it was between $TaCl_3$ and $TaCl_2$ with varying composition. At 600°C. tantalum(II) chloride was reported as an olive green powder. Reduction followed by heating at 680° to 700°C. produced a black compound, low in chlorine, whose chloride to tantalum ratio was 0.40. These data were interpreted according to the following reactions:

$$TaCl_3(\ell) + TaCl_5(\ell) \overset{250^{\circ}C.}{\rightleftarrows} 2TaCl_4(s) \qquad (3)$$

$$2TaCl_4(s) \overset{350^{\circ}-400^{\circ}C.}{\rightleftarrows} TaCl_3(s) + TaCl_5(g) \qquad (4)$$

$$3TaCl_3(s) \overset{500^{\circ}C.}{\rightleftarrows} 2TaCl_2(s) + TaCl_5(g) \qquad (5)$$

$$3TaCl_2(s) \overset{680^{\circ}-700^{\circ}C.}{\rightleftarrows} 2TaCl_3(s) + Ta(s) \qquad (6)$$

In air the materials formulated as $TaCl_3$ and $TaCl_2$ were stable; in water the trichloride dissolved to give an intensely green solution.

In 1952 Young and Brubaker (28) in attempts to synthesize tantalum(V) chloride by reaction of hydrogen chloride with tantalum metal at 600° to 700°C., noted that the formation of an olive green coat on the metal slowed the reaction. This green material, by properties and analysis, was similar to the tantalum(II) chloride reported by Ruff and Thomas (27). Reduction of $TaCl_5$ with tantalum metal in a gradient of 350° to 400°C. was ineffective; reduction at 475° to 500°C. yielded a green chloride, which was soluble in water to give a green solution. Oxidation of the green solution with Ce(IV) was interpreted as indicating that tantalum had an oxidation state of +3.29. Thus the compound was formulated Ta_3Cl_{10}.

Considerably less work has been done on the lower bromides of tantalum. The first mention of a green compound and solution was made by Van Haagen (2, p. 729) in 1910. While attempting to produce lower bromides of tantalum by reduction of $TaBr_5$ in a hydrogen stream, a metallic coat and a thin, greenish, almost black film were obtained at elevated temperatures in the reaction tube. The green material was soluble to give a remarkably intense green solution. Analysis of a small sample indicated a compound approaching $TaBr_3$.

His interest aroused by the similar properties of this compound and the chloride prepared by Chabrié (21), Chapin (29) in 1910 prepared 20 grams of this bromide compound from 200 grams of $TaBr_5$. Reduction of tantalum(V) bromide with 3% sodium amalgam was carried out at red heat under a water pump vacuum. The reduction products were extracted with hot aqueous HBr and the resultant green solution evaporated until the compound separated as a crystalline powder. From a solution of this material only one-seventh of the halogen could be precipitated with silver nitrate at 0°C. Molecular weight determinations in water and propanol indicated a value of 2275.

Anal. Found: Ta, 46.60; Br, 48.06; H_2O, 5.46. Calcd. for $TaBr_2 \cdot H_2O$: Ta, 48.01; Br, 42.44; H_2O, 9.55. Calcd. for $Ta_6Br_{14} \cdot 7H_2O$: Ta, 46.58; Br, 48.01; H_2O, 5.41.

On the basis of the bromide to tantalum ratio and the molecular weight data, the formulation $(Ta_6Br_{12})Br_2$ was given this material.

In earlier work[1] in this laboratory it was found that $TaBr_5$ was reduced with tantalum metal in a temperature gradient of 630°C. to a temperature of greater than 330°C. a

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[1] Boatman, J. C. Synthesis and reactions of some reduced tantalum halides. Unpublished M.S. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1962.

compound was formed with a bromide to tantalum ratio of ca. 2.5. This material was partially soluble in water to give an intensely green solution. It also was noted that there remained an insoluble residue. When this bromide was heated to 700°C. under a working vacuum for 24 hours a dark green material resulted having a bromide to tantalum ratio of 2.00. This material was also partially soluble in water to give an intense green solution. The material was only partially hydrolyzed in ca. a 50% sodium hydroxide solution, leaving a grey residue. Similar products could be obtained by using aluminum as the reducing agent, but much higher yields were obtained and a much shorter period of time for the reduction was required.

Young and Hastings (30) reported that $TaBr_3$ resulted when $TaBr_5$ and hydrogen were passed through a tube which was heated to 700°C. The unchanged $TaBr_5$ was removed by sublimation at 160°C. in a vacuum of 10^{-5} Torr. Eighteen grams of $TaBr_5$ only yielded one gram of the greyish green compound.

Anal. Calcd. for $TaBr_3$: Ta, 43.0; Br, 57.0.

Found: Ta, 43.3, 45.5; Br, 59.5, 58.3, 55.5.

It was their conclusion that the analyses indicated the formation of $TaBr_3$ mixed with higher and lower bromides. The tribromide was less hydroscopic than the pentabromide, but oxidized slowly in dry air, forming $TaOBr_3$ which was confirmed by Hönigschmid and Schlee (31). It was rapidly transformed in humid air to Ta_2O_5. Young and Hastings (30) measured the quantity of hydrogen evolved when $TaBr_3$ was reacted with water or hot alkali, in the absence of air, and found that the amount of hydrogen evolved corresponded to a change in oxidation state of tantalum from 3 to 4. The compound of the tantalum(IV) oxidation state was $TaO_2 \cdot 2H_2O$, which was slowly oxidized at room temperature to Ta_2O_5. The $TaBr_3$ was immediately oxidized to Ta_2O_5 when treated with an oxidizing agent such as concentrated nitric acid.

In 1939, Körösy (10) found that TaI_5 decomposed at the temperature necessary for volatilization to yield a black powder of varying iodide content. From this residue, only a deep green compound could be extracted into water. The residue from a sample of TaI_5, reduced with tantalum metal, similarly yielded a green solution. The iodide to tantalum ratio in that residue was an undetermined function of temperature and time. Analyses indicated that the iodide to tantalum ratios were 2.75 and 2.45. Although his valency determinations could best be represented by TaI_3, Körösy preferred emphasizing the analogy to $(Ta_6Br_{12})Br_2$ rather than depending upon his own data. He also proved that the ion giving the green solution must be positive because it traveled toward the cathode during electrolysis.

In 1960, Chizhikov and Rabinovich (32) reported that a lower tantalum iodide resulted when iodine was reacted with tantalum powder at 535°C. This product had an iodide to tantalum ratio of 2.8 to 3.0.

In recent work by Kuhn (33) it was demonstrated that the lower halides corresponding to $(Ta_6X_{12})X_2$ could be obtained by the reduction of excess tantalum(V) halide with aluminum foil in a temperature gradient. Gradients 400° to 200°C., 450° to 280°C., and 475° to 300°C. were used for the chloride, bromide and iodide respectively. After the reduction was complete, the tantalum(V) halide and the aluminum(III) halide were sublimed out of the reaction zone. Under optimum conditions the remaining material was heated at 550°C., 570°C., and 475°C. for the chloride, bromide, and iodide respectively. The products had the halide to tantalum ratios of 2.27 for the chloride, 2.26 for the bromide, and 2.31 for the iodide. It was found that high temperatures and long heating periods lowered the halide to tantalum ratio. Metal was found in the polynuclear tantalum bromide and it was indicated to be the major impurity in all the syntheses.

X-ray powder diffraction data were obtained for the three materials. In the iodide the x-ray data of mixtures varying in the iodide to tantalum ratio from 2.34 to 0.95 were compared, and the data were found to be invariant. Thus, the material was identified as a stoichiometric compound rather than a phase of variable composition. A similar observation made for the chloride indicated that all three polynuclear tantalum halides were compounds with constant composition.

Spectral investigations were made on the solid polynuclear tantalum halides and on the green aqueous solutions which appeared to be characteristic of the compounds. Excellent correlation of the solid and solution spectra was obtained for the bromide. Thus, it was concluded that the same molecular species was present in both the anhydrous solid and in the green solutions.

When a review of the literature has been accomplished, it becomes apparent that the higher halides of tantalum, i.e. the tantalum(V) and tantalum(IV) halides, have been quite thoroughly characterized. When the literature on the lower tantalum halides is considered it becomes apparent that there is great uncertainty as to which compounds actually exist. This uncertainty and the noticeable contradictions that exist were the main factors that brought about this systematic study of the equilibrium phases of the tantalum-tantalum halide systems.

EXPERIMENTAL

Equipment

Since either the reactants or the products of all of the synthetic reactions were sensitive to atmospheric moisture, the majority of the reactions were effected in evacuated glass systems. Materials were handled and stored in a dry box. The dry box contained an argon atmosphere which was maintained at a dew point of ca. -75°C. Sufficient drying of the argon was obtained by passing the gas over Linde 4A Molecular Sieves and maintaining an adequate supply of exposed magnesium perchlorate in the box.

Temperature gradient furnaces contained a split porcelain core each half of which was wound separately. Thus, the two ends of the furnace could be controlled at different temperatures. Use of an aluminum liner smoothed out the temperature gradient.

Materials

Tantalum metal

Tantalum powder obtained from the National Research Corporation was used in the preparation of all materials. Spectrographic analysis indicated the presence of the following elements: niobium, faint trace; chromium, faint trace;

iron, weak; oxygen, 1665 ppm; nitrogen, 220 ppm.

Aluminum metal

Aluminum as foil of *ca*. 99.9 per cent purity was used in the reductions. Spectrographic analysis indicated the following elements in trace of faint trace amounts: calcium, chromium, copper, iron, gallium, magnesium, manganese, nickel, silicon, and titanium.

Halogens

Reagent grade halogens were used. The bromine was dried over phosphorus(V) oxide for two days in an evacuated flask. Then the bromine was transferred to a clean flask from which it was vacuum distilled as needed for a synthesis.

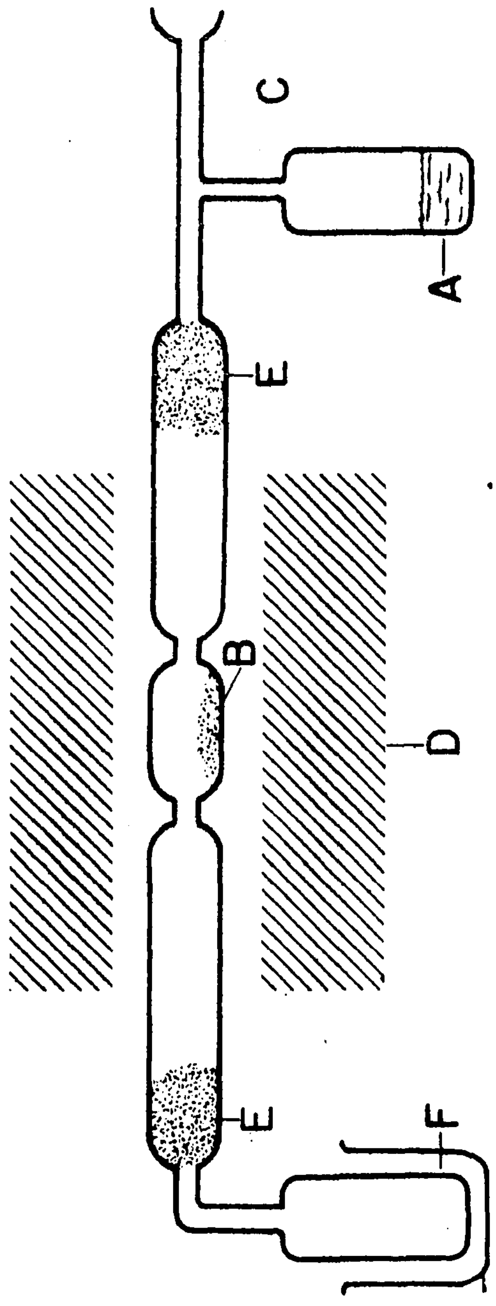
Synthesis

Tantalum(V) bromide

Tantalum(V) bromide was prepared in high yields by a reaction of the elements in a Pyrex glass reaction tube as shown in Figure 1. Twenty-three grams of tantalum metal were placed in the middle compartment, B, by means of a long funnel. The tube was connected to a vacuum system, flamed with the yellow flame of a torch to remove any adsorbed gases, and evacuated to *ca*. 10^{-5} Torr. Bulb A was placed in an ice-water bath, and a sufficient quantity of bromine was distilled into

Figure 1. Pyrex apparatus for the preparation of $TaBr_5$

A,F.	Bulbs for the liquid bromine
B.	Compartment for the metal
C.	Point at which the tube was sealed
D.	Furnace
E.	Compartments containing $TaBr_5$


C
A
E
B
D
E
F

it. The bromine was frozen with a Dry Ice-acetone bath and the entire apparatus pumped down to 10^{-5} Torr. The reaction tube then was sealed at point C.

As soon as the frozen bromine had melted away from the walls of the tube, the middle portion of the reaction tube was heated to between 400° and 450°C. in a split furnace. When bulb F was immersed in an ice-water bath bromine distilled readily over the heated tantalum powder forming tantalum(V) bromide which was deposited in compartments E as illustrated. Distillation of the bromine back and forth across the metal was continued until the reaction was completed. Conversion of the metal to pentabromide took 5 to 6 hours. An excess amount of bromine was used to prevent reduction by the metal to form lower bromides. This excess bromine was frozen with liquid nitrogen, and the reaction tube was sealed between the compartments. The pure yellow-orange crystalline tantalum(V) bromide was kept in these sealed, evacuated tubes until needed. The tubes then were opened and any extra material was stored in capped vials in the dry box.

Tantalum(V) iodide

Since iodine is not as easily distilled as bromine, a straight reaction tube was used in the synthesis of tantalum

(V) iodide. A small constriction one-third of the distance from one end formed two compartments in the Pyrex reaction tube. Usually _ca_. seven grams of tantalum metal powder with slightly less than a stoichiometric amount of iodine were placed in the tube which then was connected to a vacuum manifold, evacuated to _ca_. 10^{-5} Torr, sealed, and placed in a furnace with a 450^{o} to 180^{o}C. temperature gradient. At 450^{o}C. the metal was sufficiently reactive; the vapor pressure of iodine at 180^{o}C. was one atmosphere. In one or two days gold crystals of tantalum(V) iodide were obtained in the larger compartment of the tube. Subsequently, the product was resublimed at 350^{o}C. after transfer to another tube to insure the purity of the compound. The tube then was opened in the dry box and the material transferred to capped vials for storage.

Tantalum(IV) bromide

Since in this work large quantities of tantalum(IV) bromide were needed, the technique explained in earlier work (18, p. 547) was not adequate to supply the demand of material needed. After some exploratory work it was found that $TaBr_5$ could be reduced by aluminum at a temperature of 250^{o}C. In this procedure 0.2 grams of aluminum foil along with 15 grams of tantalum(V) bromide were placed in a Pyrex tube _ca_. 14

inches long and having a constriction about one-third of the distance from one end. The tube was taken from the dry box and connected to a vacuum manifold and evacuated to ca. 10^{-5} Torr and sealed. It then was placed in a temperature gradient furnace with the end containing the aluminum foil lower than the other end and both ends were heated to 250°C. At first the reaction was slow since it was a solid (Al)-gas ($TaBr_5$) reaction. After a short period of time enough aluminum(III) bromide was formed to dissolve the tantalum(V) bromide which definitely increased the rate of reaction. After seven days a dark crystalline material was formed. The excess tantalum (V) bromide and the aluminum(III) bromide that was formed during the reduction was sublimed away from the dark crystalline material at 225°C. for 16 hours. Analytical data for three different preparations are given below.

Anal. Calcd. for $TaBr_4$: Ta, 36.15; Br, 63.85.
Found for $TaBr_4$ (a): Ta, 36.27, 36.37; Br, 63.23, 63.18. $TaBr_4$ (b): Ta, 36.24, 36.23; Br, 63.42. $TaBr_4$ (c): Ta, 36.39, 36.38; Br, 63.52, 63.47.

The yields varied depending upon the amount of initial materials. The average yields were from 14 to 20 grams, or virtually quantitative based upon the amount of aluminum used.

The time required for the reduction was from 6 to 7 days regardless of the quantity used.

Tantalum(IV) iodide

The same demands for an adequate quantity of the tantalum(IV) iodide was also an important factor of this work. The same synthetic technique was used here as used for the tantalum(IV) bromide. The reduction temperature was 325°C. for a period of 6 days. Unfortunately it was not possible to easily sublime an excess of tantalum(V) iodide away from the products without decomposing the tantalum(IV) iodide. Therefore in this procedure carefully weighed stoichiometric amounts of aluminum foil and tantalum(V) iodide had to be used. In a typical reaction 0.25 grams of aluminum foil and 23.0 grams of tantalum(V) iodide were utilized. The yield was about 20 grams of tantalum(IV) iodide.

Anal. Calcd. for TaI_4: Ta, 26.29; I, 73.71.
Found: Ta, 26.10, 25.88; I, 73.78, 73.96;
I/Ta, 4.06.

Since the x-ray powder diffraction patterns of TaI_4 and TaI_5 are similar, the proof of TaI_4 was done chemically. When a sample of $TaI_{4.06}$ was added to distilled water a brown solution resulted and when ammonia was added a brown oxide

($TaO_2 \cdot XH_2O$) precipitated. If this material were a mixture of TaI_5 and $(Ta_6I_{12})I_2$, the solution would have been green, from $(Ta_6I_{12})I_2$, and white Ta_2O_5 would precipitate as the result of the hydrolysis of TaI_5. There has been no evidence of the existence of TaI_3 is this work, thus the $TaI_{4.06}$ must indeed be TaI_4.

Dodeca-μ-iodo-hexatantalum diiodide

Synthesis of the lower tantalum iodide, $(Ta_6I_{12})I_2$, was accomplished by aluminum reduction of an excess amount of tantalum(V) iodide after the method of Kuhn (33) and according to the general equation

$$18TaX_5 + 16Al \rightarrow 3(Ta_6X_{12})X_2 + 16AlX_3. \qquad (7)$$

A one gram excess of tantalum(V) iodide was added under an inert atmosphere to 0.15 grams of aluminum foil in a Pyrex reaction tube like the one previously described in the preparation of tantalum(V) iodide. The tube was evacuated to ca. 10^{-5} Torr and sealed. It then was placed in a 300° to 475°C. temperature gradient furnace such that the hot end was tilted downward. In this way a refluxing action of the liquid tantalum(V) iodide over the aluminum was obtained. Qualitatively it was found that the tantalum(V) iodide and aluminum(III) iodide mixture lowered the melting point and vapor pressure of each component. After ca. 2 days the reaction was stopped by pulling the tube half way out of the furnace. Sublimation of the volatile reaction products into the larger compartment of the tube was obtained at 300°C. The material left in the smaller compartment was heated at 300°C. for 24 hours; at this time and temperature no volatile products remained in the reaction zone. The black powdery material was analyzed and the remaining portion stored in the dry box until needed for further investigation.

Anal. Calcd. for $(Ta_6I_{12})I_2$: Ta, 37.93; I, 62.07.

Found: Ta, 38.37; I, 61.42; I/Ta, 2.28.

The composition of this material would vary slightly with the duration of the final heat treatment.

Dodeca-μ-bromo-hexatantalum dibromide

Synthesis of the lower tantalum bromide, $(Ta_6Br_{12})Br_2$, was analogous to that of the lower iodide. However, an additional heat treatment of the product was essential. Twenty-four grams of $TaBr_5$ were added to 0.8 grams of aluminum foil in a Vycor reaction tube. This amount of pentabromide constituted approximately one gram in excess (cf. Equation 7). The sealed, evacuated tube remained two days in a temperature gradient of 400° to 300°C. Again the hot end of the furnace was tilted downward to obtain a refluxing action. By pulling the tube part way out of the furnace the reaction was halted and the volatile tantalum(V) bromide and aluminum(III) bromide were sublimed at 280°C. to one end of the tube. The tube then was pulled slightly further from the furnace and the black, apparently non-volatile material remaining was heated to 560°C. for 15 hours to decompose any tantalum(IV) bromide formed. A bright green product was obtained. This product was transferred in the dry box from the reaction tube to capped vials for storage.

Anal. Calcd. for $(Ta_6Br_{12})Br_2$: Ta, 49.25; Br, 50.75; Br/Ta, 2.33. Found: Ta, 49.16, 49.39; Br, 50.63, 50.57; Br/Ta, 2.33, 2.34.

Analytical Procedures

Stability of the lower halides was such that transfer of the sample from a weighed vial to a beaker did not usually involve a loss of material as a result of atmospheric hydrolysis. However, with the higher halides some difficulty with this problem was encountered.

In the case of the lower halides the samples were placed in screw capped bottles in the dry box for weighing, and then transferred rapidly to beakers containing a dilute aqueous solution of ammonia for hydrolysis. The sample bottles were weighed initially with the sample under argon and finally the empty bottle was weighed filled with air. Since argon is heavier than air this negative bouyancy correction was applied to all samples. In the case of the higher halides, the weighed samples were transferred to a flask containing a vacuum tight cap fitted with a funnel and vacuum connection. This procedure was carried out in the dry box under argon. The flask then was placed on a vacuum manifold and evacuated slightly; the ammonia solution then was added by means of the funnel. This technique prevented loss of the halogen as hydrogen halide during vigorous hydrolysis.

Tantalum

Tantalum was determined gravimetrically as the oxide Ta_2O_5. After the samples were hydrolyzed in ammonia solution, they were heated on a hot plate to ensure complete hydrolysis and oxidation of TaO_2 to Ta_2O_5. The samples were cooled to room temperature and acidified with dilute nitric acid to pH 1. The precipitates then were filtered on medium retention filter paper and washed thoroughly with aqueous nitric acid. The paper and precipitates were dried at 110°C., the paper carefully burned away, and the oxide ignited at 750°C. in a muffle furnace.

Halogens

Both gravimetric precipitation of the silver halides, volumetric determinations using the Volhard method, or direct silver titration utilizing eosin as an indicator were used in ascertaining the halide content of the compounds. The amount of halide was determined in the solutions after the tantalum (V) oxide had been precipitated and removed by filtration.

Physical Measurements

X-ray diffraction

X-ray diffraction data were obtained with a 114.59 mm. Debye-Scherrer powder camera. Finely powdered samples were packed and hermetically sealed in 0.2 mm. Lindemann glass capillaries. These were exposed to Ni-filtered, $CuK\alpha$ radiation. Exposure time varied from 18 to 36 hours depending upon the sample.

Reflectance spectra

The reflectance spectrum of a mixture having the composition $TaBr_{3.02}$ was obtained with a Beckman Model DU spectrophotometer equipped with the Beckman 2580 reflectance attachment.

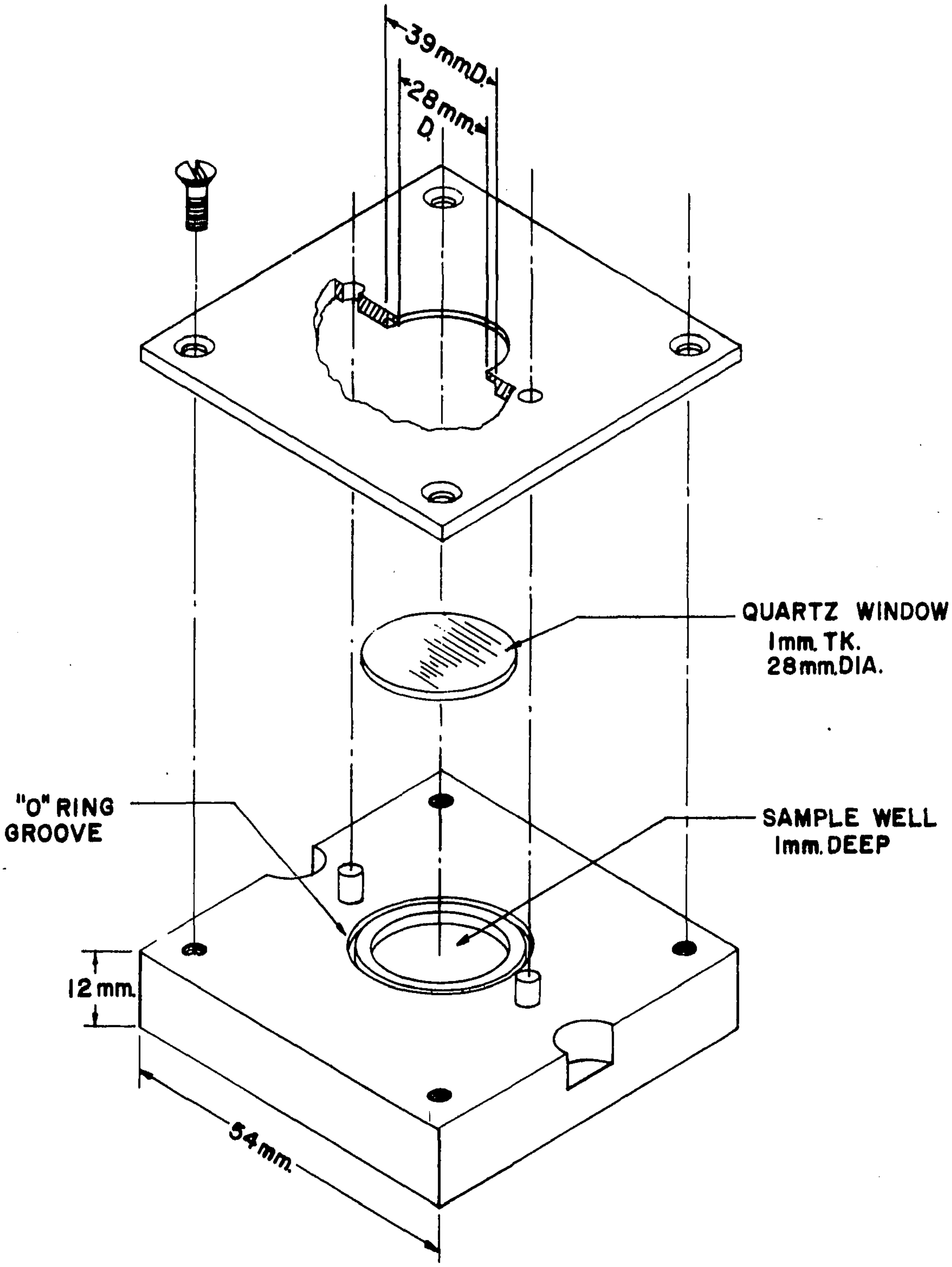
Since the spectrum was obtained on an anhydrous sample, special efforts were made to prevent exposure to air or moisture. B. A. Torp of this laboratory designed and developed the stainless steel cell shown in Figure 2. Specifications on this reflectance cell were such that it fit into the sample drawer of the Beckman reflectance attachment. The cell was sealed from moisture by the close fitting arrangement of a circular quartz disc which extended over both the sample well and the rubber "O" ring. The cell cover, which was countersunk to accomodate this piece of quartz, was aligned on the bottom plate with short dowel pins and secured with four screws.

Potassium bromide was used as a reference standard. The sample was diluted _ca_. twenty to one with potassium bromide which was dried at 110°C. for 12 hours under vacuum. The cell was packed under an argon atmosphere after it had been powdered to pass through a 100 mesh screen. The spectrum was obtained from 300 to 1000 mμ.

Differential Thermal Analysis

Since one of the better methods of determining an enthalpy change in a process is the use of heating and cooling data, the differential thermal analysis (DTA) technique was used with satisfying results. The apparatus used in this work is

Figure 2. Reflectance cell


39mmD.
28mm. D.
QUARTZ WINDOW
1mm. TK.
28mm.DIA.
"O" RING GROOVE
SAMPLE WELL
1mm. DEEP
12mm.
54mm.

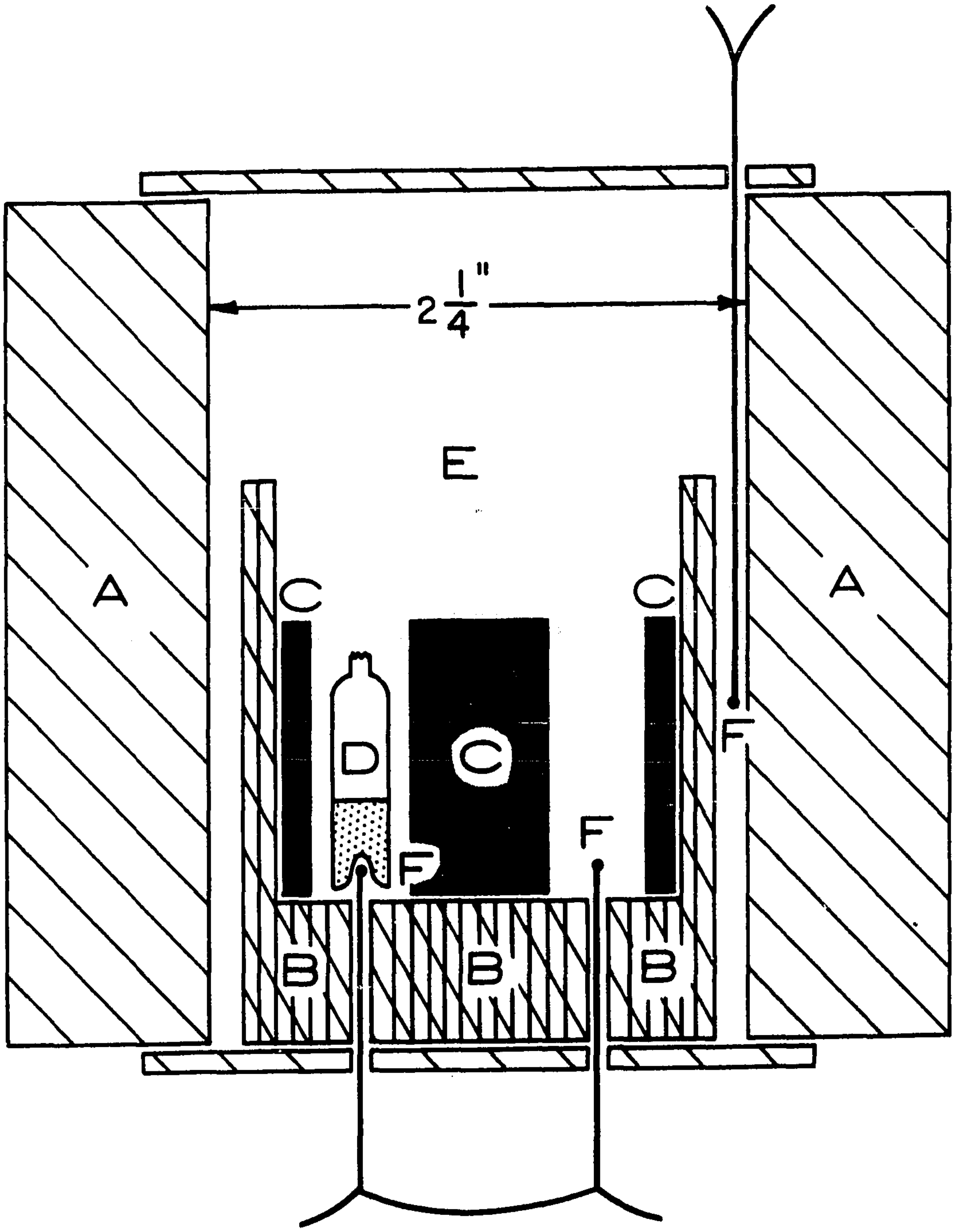
shown in Figure 3.

The furnace A was a 12 inch Marshall furnace fitted with transite covers over the ends to reduce heat loss. A copper block, B, six inches in length and two and one-quarter inches in diameter, was drilled three and one-half inches deep and two inches in diameter. This block was situated in the furnace so that the top was located essentially at the center of the furnace, hence keeping the top portion at a slightly higher temperature than the bottom. The primary function of this copper block was to smooth out temperature gradients and, due to its large mass, to prevent drastic temperature changes.

Fitted inside the copper block was a piece of insulating brick C which was three inches long and two inches in diameter. Two one-half inch holes were drilled into this brick to accomodate the samples and temperature sensing thermocouples. These holes were spaced equidistant from the center of the furnace tube so that an equivalent temperature gradient would be experienced by the thermocouples. The primary purpose of this insulating brick was to prevent rapid equilibration of the sample with the copper block, thus allowing a maximum time for the thermal process to occur before equilibration of the sample and block temperature.

Figure 3. Apparatus for differential thermal analysis

A. Furnace
B. Copper block
C. Insulating brick
D. Sample cell
E. Pyrex or quartz wool
F. Thermocouples


2 1/4"
E
A
A
C
C
C
D
F
F
F
B
B
B

The sample cells D were made from either 10 mm. Pyrex or Vycor depending upon the temperature requirements of the sample. They were made by sealing the tubing and rounding the bottom. While the bottom was still fluid a sharpened carbon rod was used to form a thermocouple well approximately one-fourth of an inch deep. The cell then was fitted with a vacuum joint. The cells were filled with either a pure sample or mixtures of materials of known composition by introducing a known weight by means of a funnel. This loading operation was done in an argon atmosphere. After loading, the cells were connected to a vacuum manifold and evacuated to 10^{-5} Torr and sealed so that they were from two and one-half to three inches in length. They then were introduced into the furnace so that the thermocouple was fitted into the thermocouple well. The total sample size was normally six to seven grams of material or *ca*. one-half inch deep in the cell to assure that the thermocouple well was completely covered, even after melting of the sample.

Three chromel-alumel thermocouples were utilized in this procedure. The thermocouples were standardized against a Pt-Pt(10% Rh) thermocouple that had been standardized by the National Bureau of Standards. This was accomplished by equilibrating the thermocouples in a copper block at temperatures from 300° to $700^{\circ}C$. The chromel-alumel thermocouples were also standardized against the melting point of lead. One was introduced into the top of the furnace and was placed in the center of the furnace between the copper block and the furnace. This thermocouple was connected to a Honeywell proportionating temperature controller. The other two thermocouples were introduced through the bottom of the furnace and up through one-eighth inch holes drilled into the copper block. They extended _ca_. one-half inch above the bottom of the block. They were connected chromel to chromel so that when a reading was taken across the couples on the two alumel leads a bucking voltage was recorded and under normal circumstances would be zero. When one of these couples was measuring the sample temperature and a process involving a heat change occurred a differential potential would be recorded.

The thermocouple leads were connected to a terminal block which in turn was connected to a Texas Instruments Incorporated "Servo Riter" two pen recording potentiometer. This potentiometer was designed so that one pen had a 2 millivolt full scale deflection; this channel was used for the differential temperature measurement. The second channel was supplied with a zero suppression circuit so that a full scale deflection of 1, 2, 5, 10, 20, 50, or 100 millivolts could be obtained anywhere on the scale from zero to 100 millivolts. For the most part a 2 millivolt full scale deflection between zero and 30 millivolts was used for this work. The differential circuit was passed through a double throw-double pull switch so that the differential leads could be switched with ease when heating and cooling data were being obtained.

After the sample was placed in the furnace, the space above the copper block was packed with Pyrex or quartz wool. The furnace was turned on and was heated by *ca*. 5.5 amps. This maintained a heating rate of from 2-3° per minute. The temperature of the sample and the differential temperature were recorded simultaneously on the recording potentiometer. The time corresponding to initiation of the thermal process was determined from the linear slope of the differential curve and the temperature at that time was obtained from the potential representing the sample temperature.

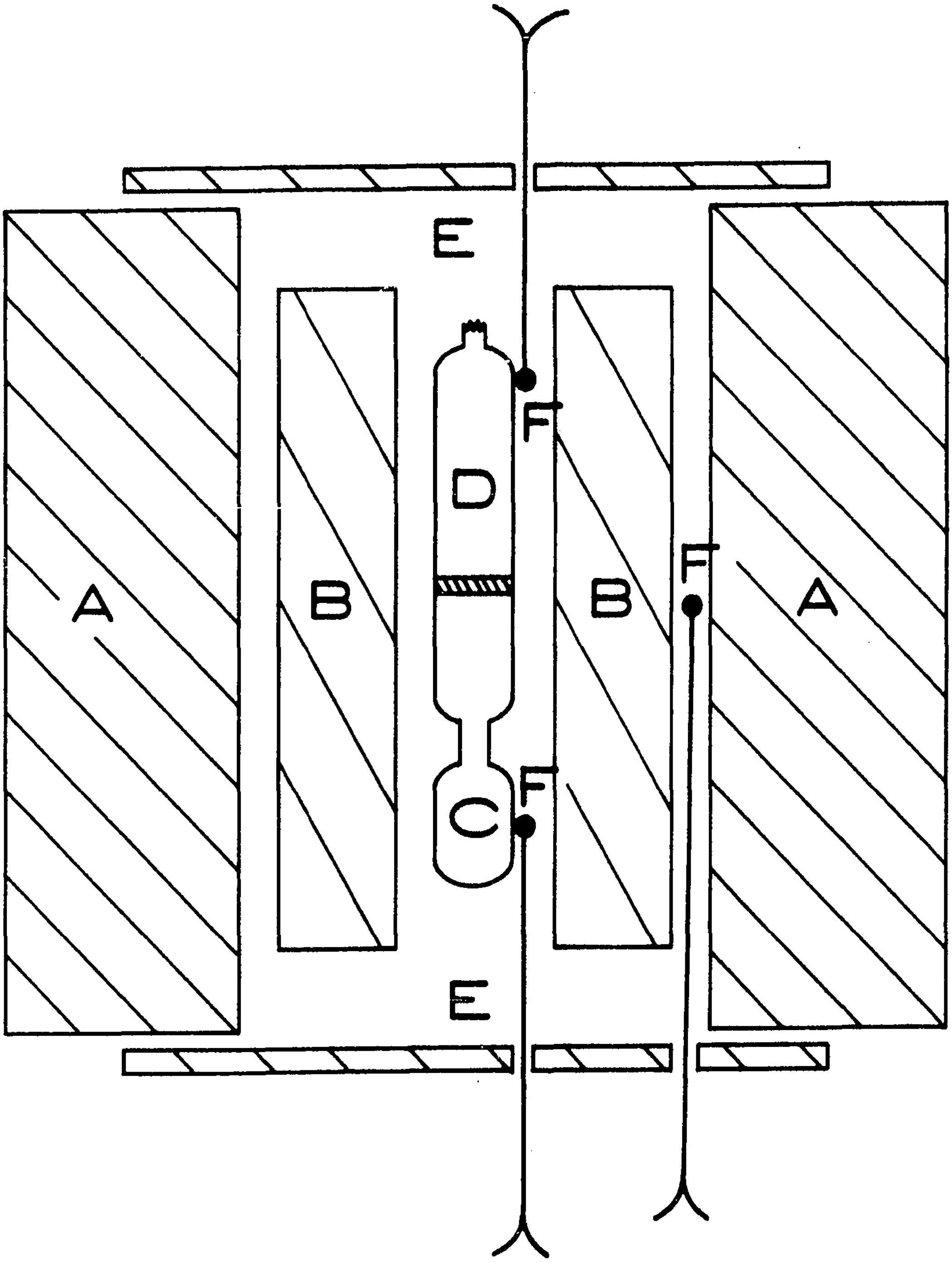
Solution studies

Since the liquidus lines could not be detected on heating and cooling curves a different technique was used to obtain these boundaries. The apparatus that was used for this study is shown in Figure 4. Furnace A was a 6 inch resistance wound furnace fitted with transite end plates to minimize heat loss and to maintain better equilibrium conditions. An insulating brick B was used as a liner, again to maintain better equilibrium conditions. The solution cell consisted of a dual compartment Pyrex tube with the compartments separated by means of a coarse fritted disc.

The purpose of this study was to ascertain to what extent $TaBr_4$ and $(Ta_6Br_{12})Br_2$ were soluble in $TaBr_5$ under the appropriate temperature conditions. The same type of information was needed for the equivalent iodide compounds. Thus the cell D was loaded with a mixture of the tantalum(V) halide and the lower halide in a slight excess under an argon atmosphere. The tube and its contents were evacuated to ca. 10^{-5} Torr and sealed. Thermocouples were attached to both ends of the tube and it then was wrapped with aluminum foil, which helped to smooth out any temperature gradients. The cell was placed in the furnace so that compartment D was located down and the furnace arranged so that the tube was in a vertical position. Both ends of the furnace were packed with Pyrex wool and the furnace heated to the desired temperature. The cell was positioned so that no more than a one degree temperature

Figure 4. Apparatus for solution studies

A. Furnace
B. Insulating brick
C,D. Compartments of the cell containing samples before and after filtration
E. Pyrex wool
F. Thermocouples


E
F
D
F
A
B
B
A
F
C
E

difference was obtained at the ends. The sample was allowed to equilibrate overnight at the desired temperature. After this temperature was recorded the furnace and its contents were rotated 180° which put compartment C in the down position. Since the equilibration temperature was above the eutectic temperature the equilibrated mixture was solid lower halide and liquid of the liquidus composition; thus the liquid filtered through the coarse frit. This process took *ca*. one hour. After this period of time the furnace was slow cooled to room temperature. The cool tube was taken into the dry box and carefully broken at the constriction. The compartment C and sample were weighed under argon and then transferred to a 95% ethanol solution which dissolved the sample without precipitation of tantalum oxides. Then C was dried and reweighed; from this the sample weight was obtained. The ethanol solution was made basic with aqueous ammonia which hydrolyzed the sample and precipitated Ta_2O_5. From this the composition of the liquidus was determined by standard analytical techniques.

Equilibration studies

Because of the character of the reduced halides it was impossible to completely determine the phase relationships by means of heating and cooling data, thus some equilibration studies were an important phase of this study. Most of the equilibration studies were carried out in evacuated, sealed Pyrex or Vycor tubes as the temperature requirement dictated. They were done in the furnace as illustrated in a previous section (cf. Figure 3). High temperature equilibration studies between tantalum metal and the lower halides, i.e. $(Ta_6Br_{12})Br_2$ and $(Ta_6I_{12})I_2$, were done in sealed tantalum tubes which were subsequently put in evacuated, sealed Vycor tubes.

RESULTS AND DISCUSSION

Since the two systems, tantalum-tantalum bromide and tantalum-tantalum iodide, exhibit some major differences they will be discussed separately. The major problems that were encountered during this study were perfection of the numerous syntheses, interpretation of x-ray powder diffraction data, and overcoming the slow kinetics involved in the equilibrium studies.

Tantalum-Tantalum Bromide System

Synthesis of tantalum(IV) bromide

Since large quantities of this material were essential to this study, a method of preparing high yields of $TaBr_4$ in a reasonable length of time became imperative. At first it was believed that $TaBr_4$ could be obtained by equilibrating tantalum metal with $TaBr_5$ at a temperature less than the equilibrium decomposition temperature of $TaBr_4$. When samples were equilibrated at $300^{\circ}C$. for varying time some $TaBr_4$ was formed, which was shown from heating and cooling data. When the samples were initially heated a thermal arrest occurred at the melting point of pure $TaBr_5$ but after equilibration both cooling and heating curves had thermal arrests at temperatures lower than that of the initial values. After several samples had been equilibrated for varying times the same result occurred for all, thus indicating that only token reduction of $TaBr_5$ had occurred. Thus this technique appeared to be unsatisfactory for preparation of either pure $TaBr_4$ or mixtures containing $TaBr_4$ and $TaBr_5$ in known ratios for securing subsequent heating and cooling data. Hence a search for a better method to produce $TaBr_4$ was initiated.

Since an aluminum reduction of $TaCl_5$ was fairly successful for Shchukarev and Kurbanov (16) in the preparation of $TaCl_4$, the method was considered as a starting point to solve this problem. The reduction of an excess of $TaBr_5$ with aluminum in a temperature gradient of 400° to 275°C. resulted in an inferior product, even after the sample was equilibrated with $TaBr_5$ at 280°C. for 7 days.

Anal. Calcd. for $TaBr_4$: Ta, 36.15; Br, 63.85.

Found: Ta, 37.42; Br, 62.48; Br/Ta, 3.78.

It then became evident that a direct reduction to $TaBr_4$ was the most desirable route since equilibration of $TaBr_5$ with lower bromides was extremely slow. Thus an equilibrium technique was used in which $TaBr_5$ was equilibrated with aluminum foil at temperatures of 300°, 275°, and 250°C. for 6 days in each case. It was found that equilibration at 250°C. with subsequent heating in vacuo at 225°C. to remove $AlBr_3$ and the excess $TaBr_5$ were the most satisfactory conditions. Since the temperature of 250°C. is lower than the melting point of pure $TaBr_5$ it was found that the addition of some $AlBr_3$ initiated the reduction by forming a low melting eutectic with $TaBr_5$. The products formed by this procedure were of sufficient purity for this work, but were not particularly suitable for work requiring extremely high purity material. When these products were added to water a very faint green solution resulted. The green solution was the result of the soluble $Ta_6Br_{12}^{2+}$ ion which has extinction coefficients of 10^3 to 10^4 liter mole^{-1} cm^{-1} (33) for the major absorption bands in the visible region of the spectrum. This ion can be detected visually when quantities as low as 10^{-5} moles are dissolved in water. Since the solutions that were used in the hydrolysis of $TaBr_4$ were only faintly green, the $TaBr_4$ was thought to be only slightly contaminated with this material. Moreover lines attributable to lower tantalum bromides were not found in the x-ray diffraction pattern of this material.

Differential thermal analysis

The samples of $TaBr_5$ were purified by two successive sublimations. This resublimed compound then was used for all samples involved in the thermal analyses. When heating and cooling curves were obtained on the pure $TaBr_5$ the average thermal arrest was found at 272 ± 1°C. This value is *ca.* 10°C. less than the value (280° ± 1°C.) reported by Alexander and Fairbrother (34) as determined from vapor pressure data.

Several mixtures having total Br/Ta > 4 were made by mixing weighed quantities of $TaBr_5$ and $TaBr_4$. Data for ten different mixtures in this composition range are shown in Table I. From these data it can be seen that $TaBr_5$ and $TaBr_4$ form a eutectic mixture which melted at 267°C. The eutectic composition must be greater than 4.84 because on heating a thermal arrest was found in mixtures up to that composition.

Table 1. Heating and cooling data of the tantalum bromide system between $TaBr_5$ and $TaBr_4$

Atom Ratio Br/Ta	Temperature °C Heating[a]	Temperature °C Cooling[a]
5.00	273	272
4.95	268,270	269,269
4.87	269,268	269,269
4.84	392	267
4.81	268,392	266
4.79	391	267
4.60	265,392	265
4.36	265,391	---
4.19	269,391	267
4.00	391	---

[a] Data obtained after equilibration of the mixture at temperatures in the range 271 to 300°C.

The heating curves on mixtures having Br/Ta in the range 4.00 to 4.84 exhibited weak thermal arrests at 392^o which indicated the peritectic melting of $TaBr_4$. Subsequent cooling of these mixtures which had been heated above 392^o gave no evidence of this thermal arrest. The absence of this thermal arrest on cooling must be a result of very sluggish reaction rates, as indicated by subsequent equilibration experiments, as discussed under Equilibrium Studies. Identification of the products of the peritectic decomposition of $TaBr_4$ also was established through equilibrium studies.

Although heating and cooling curves were obtained for mixtures having Br/Ta less than 4, no thermal arrests were detected.

Location of the liquidus line

Since the heating and cooling data did not provide evidence for the composition at the liquidus line a different technique had to be employed to locate this line. It became apparent that the composition at the liquidus varied only slightly with temperature. Since mixtures differing only slightly in their composition were difficult to compose, the solution technique as explained in the Experimental Section was used.

A mixture of $TaBr_5$ and $TaBr_4$ was equilibrated at 350°C. and filtered. After cooling the filtrate was removed from the cell and analyzed for tantalum and bromine. The composition

Anal. Found: Ta, 31.72; Br, 68.10; Br/Ta, 4.87.

of the eutectic mixture was thus fixed by extrapolating to the eutectic melting temperature from the temperature at this liquidus composition and the point representing the upper composition limit at the peritectic temperature.

The same type of experiment was carried out using a mixture of $(Ta_6Br_{12})Br_2$ and $TaBr_5$ whereby a sample was equilibrated at 420°C., filtered, and analyzed for tantalum. These data again indicated that the lower bromide was only slightly soluble in $TaBr_5$.

Anal. Found: Ta, 31.82; Br (by difference); Br/Ta, 4.85.

Equilibrium studies

To establish the composition of the next phase below $TaBr_4$ a series of equilibration experiments was performed. The results of these experiments can be seen in Table 2.

It has been noted previously that $TaBr_5$ could be separated from $TaBr_4$ by sublimation at 225°C. without destroying the lower phase. Thus samples of $TaBr_4$ were equilibrated at a temperature of 435°C. for periods of 1, 2, and 3 days, after

Table 2. Results of equilibration experiments on the tantalum-tantalum bromide system

Initial material	Equilibration temp., °C.	Time, days	Observations on products	Phases
$TaBr_4$	435	3	purplish-black & $TaBr_5$[a]	$TaBr_{2.83}$
$TaBr_4$	426	10	dark brown & $TaBr_5$[a]	$TaBr_{2.83}$
$TaBr_4$	453	1	dark brown & $TaBr_5$[a]	$TaBr_{2.83}$ + $TaBr_{2.5}$
$TaBr_4$	460	1	dark brown & $TaBr_5$[a]	$TaBr_{2.83}$ + $TaBr_{2.5}$
$TaBr_4$	470	1	dark brown & $TaBr_5$[a]	$TaBr_{2.83}$ + $TaBr_{2.5}$
$TaBr_4$	447	1	dark brown & $TaBr_5$[a]	$TaBr_{2.83}$
$TaBr_{2.33}$ + $TaBr_5$	375	10	dark brown	$TaBr_{2.83}$
$TaBr_{2.38}$[b]	500	4	dark green	$TaBr_{2.33}$
$TaBr_{2.52}$[b]	500	4	purple	$TaBr_{2.5}$
$TaBr_{2.75}$[b]	500	4	purple & $TaBr_5$[a]	$TaBr_{2.5}$

[a] The $TaBr_5$ was removed by sublimation at 225°C. prior to obtaining x-ray data.

[b] These mixtures were obtained by mixing weighed quantities of $TaBr_4$ and Ta_6Br_{14}.

Table 2. (Continued)

Initial material	Equilibration temp., °C	Time, days	Observations on products	Phases
$TaBr_{3.00}$[b]	500	4	purple & $TaBr_5$[a]	$TaBr_{2.5}$
$TaBr_4$ + (xs)Ta	600	2	black	$TaBr_{2.5}$, Ta
$TaBr_{2.5}$ + (xs)Ta	600	2	grey (large excess of Ta)	$TaBr_{2.5}$, Ta
$TaBr_{2.33}$ + Ta	605	5	dark green	$TaBr_{2.33}$, Ta
	815	4	dark green	Ta_2Si, Ta
$TaBr_{2.75}$ + (xs)Ta	600	2	dark brown	$TaBr_{2.5}$, Ta
$TaBr_{2.75}$ + Ta	684	1	dark green	$TaBr_{2.33}$
(tubing)	640	1	dark green	$TaBr_{2.33}$

which $TaBr_5$ was removed by sublimation. The sample tubes were opened and an analysis and an x-ray powder diffraction pattern were obtained. It was found that the Br/Ta ratio decreased as a function of time and reached an ultimate composition of $TaBr_{2.84}$. The analytical data are shown in Table 3. The x-ray powder diffraction data of the residue having the Br/Ta of 2.84 are shown in Table 9 of the Appendix.

Table 3. Composition of products from equilibrium decomposition of $TaBr_4$ at 435°C.

Sample	Time, days	% Ta	% Br	Br/Ta atom ratio
A	1	42.85	57.02	3.01
B	2	43.76	55.65	2.88
C	3	44.40	55.89	2.84

The x-ray powder diffraction pattern of this material was different than the patterns of lower tantalum bromides noted in earlier work in this laboratory, i.e. Ta_6Br_{14} (33) and $TaBr_{2.5}$ (18), thus the data indicated that this was a new phase in this system. When a larger sample of $TaBr_4$ was decomposed at 426°C. for 10 days the resultant product had an x-ray diffraction pattern identical to that of the residue $TaBr_{2.84}$. After sublimation of $TaBr_5$ at 225°C. the residue was analyzed and the average Br/Ta was calculated to be 2.82.

Anal. Found: Ta, 44.66, 44.39; Br, 55.18, 55.48;

Br/Ta, 2.80, 2.84.

These data indicated that the composition of this phase was apparently $TaBr_{2.83}$. This phase was also formed when a mixture of $TaBr_5$ and Ta_6Br_{14} was made having a Br/Ta of 3.50 and equilibrated at 375°C. for 10 days. The x-ray powder diffraction data were the same as the material having a Br/Ta of 2.84. Since there was $TaBr_5$ present after 10 days, it was removed by sublimation at 225°C. prior to analysis. Once again a

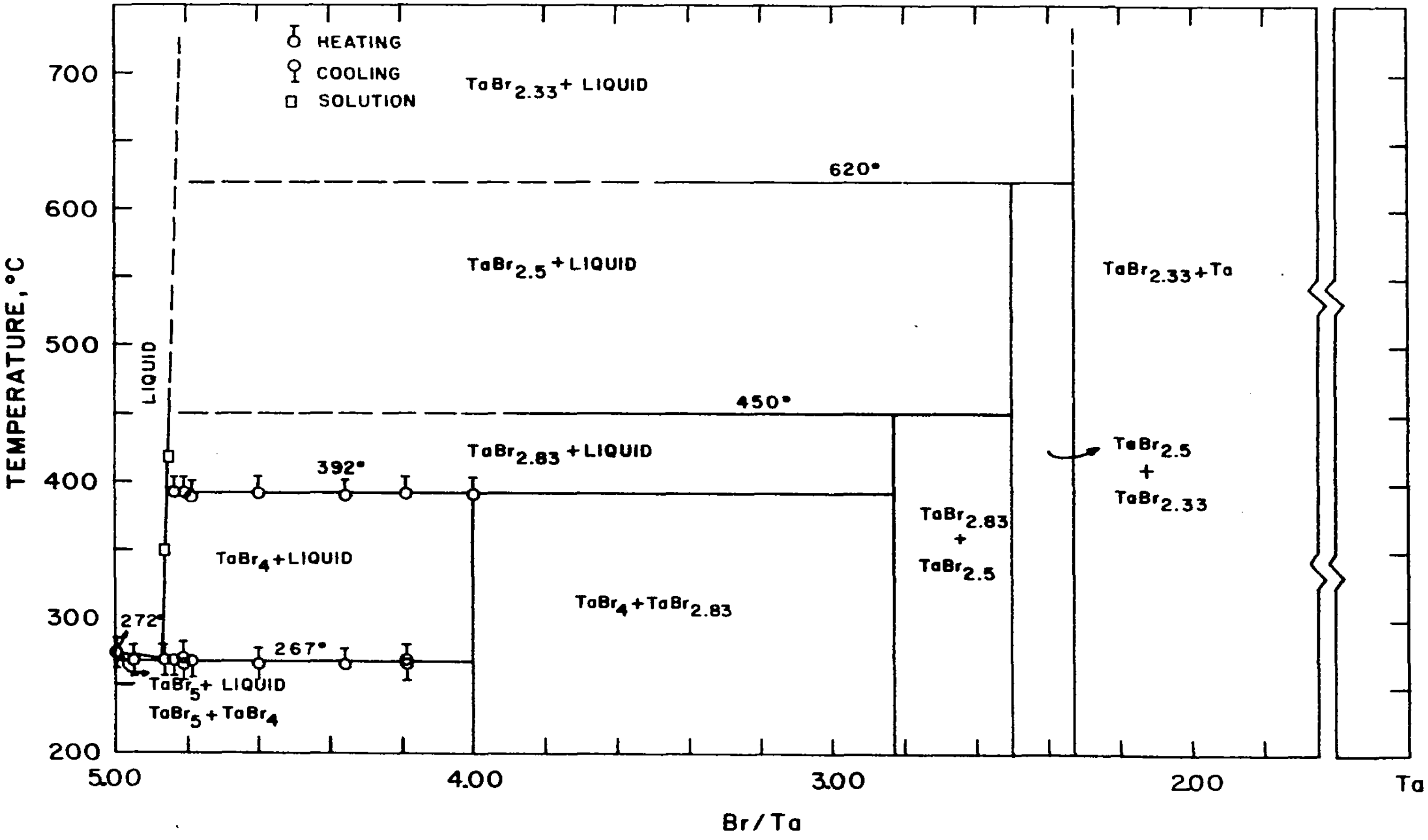
Anal. Found: Ta, 44.07; Br, 55.82; Br/Ta, 2.87.

Br/Ta of approximately 2.83 was obtained. From the above data it is suggested that upon decomposition of $TaBr_4$ the Br/Ta decreases with time until a value of 2.83 is obtained, thus indicating that the ultimate composition of this phase is $TaBr_{2.83}(Ta_6Br_{17})$.

To establish at what temperature this phase decomposed a series of equilibration experiments was performed. Small amounts (ca. 200 mg.) of $TaBr_4$ were sealed in evacuated 2 mm. capillary tubing and equilibrated at temperatures of 447°, 453°, 460°, and 470°C. for 1 day. The $TaBr_5$ formed during decomposition was removed by sublimation at 225°C. and x-ray powder diffraction patterns were obtained on the residue; the data for the residue resulting from the equilibration at 470°C. can be seen in Table 10 of the Appendix. All of these x-ray data showed that some $TaBr_{2.5}$ had formed during the equilibration. The intensities of the "d" spacings attributed to $TaBr_{2.5}$ increased with the increased equilibration temperature. The powder pattern obtained on the residue resulting from equilibration at 447°C. showed only 2 lines which could be attributed to $TaBr_{2.5}$. They were both of weak intensity but only one corresponded to a line of major intensity in the pattern of $TaBr_{2.5}$, the other corresponded only to a line of weak intensity. Hence it appears that the $TaBr_{2.5}$ phase, while forming at a slow rate, first occurs between 447 and 453°C. This temperature is designated as approximately 450° in Figure 5.

Decomposition of the phase having a Br/Ta of 2.83 resulted in the next phase, $TaBr_{2.5}$, and the unknown liquidus composition. The x-ray powder diffraction data of $TaBr_{2.5}$ can be seen in Table 11 in the Appendix. This phase was found to be stable up to 600°C. by means of a series of equilibration experiments. Mixtures having Br/Ta of 2.38, 2.52, 2.75, and 3.00 were obtained by mixing weighed quantities of

Figure 5. Phase diagram of the tantalum-tantalum bromide system


HEATING
COOLING
SOLUTION
TaBr$_{2.33}$+ LIQUID
620°
TaBr$_{2.5}$ + LIQUID
TaBr$_{2.33}$+Ta
LIQUID
450°
TaBr$_{2.83}$ + LIQUID
392°
TaBr$_{2.5}$ + TaBr$_{2.33}$
TaBr$_{2.83}$ + TaBr$_{2.5}$
TaBr$_4$+LIQUID
TaBr$_4$+TaBr$_{2.83}$
272°
267°
TaBr$_5$+ LIQUID
TaBr$_5$ + TaBr$_4$
TEMPERATURE, °C
700
600
500
400
300
200
5.00
4.00
3.00
2.00
Ta
Br/Ta

$(Ta_6Br_{12})Br_2$ and $TaBr_4$. After being sealed in evacuated Pyrex cells these mixtures were equilibrated at 500°C. for 4 days. The results of these experiments have been noted previously (cf. Table 2). In every case where the Br/Ta was greater than 2.5 the presence of $TaBr_{2.5}$ was indicated to be the major constituent of the mixture. However, it was believed that the reaction had not reached true equilibrium; this was evident from extraneous lines of $TaBr_{2.83}$ found in the x-ray diffraction pattern of the mixture having a Br/Ta of 3.00. Hence two more experiments were performed utilizing mixtures of $TaBr_4$ and $TaBr_{2.5}$ with excess tantalum metal. In both cases the mixtures were equilibrated at 600°C. for 2 days. X-ray powder diffraction patterns showed only "d" spacings of tantalum metal and $TaBr_{2.5}$, see Table 12 in the Appendix. Thus it was concluded that $TaBr_{2.5}$ was stable under equilibrium conditions up to a temperature of 600°C.

It was found by high temperature equilibration experiments that $TaBr_{2.5}$ decomposed at a temperature greater than 600°C. but less than 640°C. into $(Ta_6Br_{12})Br_2$ and the liquidus composition. These experiments were effected by packing a one-eighth inch tantalum tube with a mixture having a Br/Ta ratio of 2.75. Since the tantalum tube had been welded closed on one end prior to packing, it was crimped closed on the other end using pliers after packing. The tantalum tube then was placed in a Vycor tube which was subsequently sealed under an argon pressure of ca. 600 Torr, hence the pressure differential between the inside and the outside of the tantalum tube was insignificant. The Vycor tube and its contents then were placed in a furnace and heated to 684°C. for 1 day. After slow cooling the tube was opened and an x-ray powder diffraction pattern was obtained on the dark green residue; these data can be seen in Table 13 of the Appendix. These data showed conclusively that this material was $(Ta_6Br_{12})Br_2$. This same experiment was repeated at 640°C. with the same results. Hence at a temperature greater than 600°C. but less than 640°C. $TaBr_{2.5}$ reacts with tantalum metal forming $(Ta_6Br_{12})Br_2$.

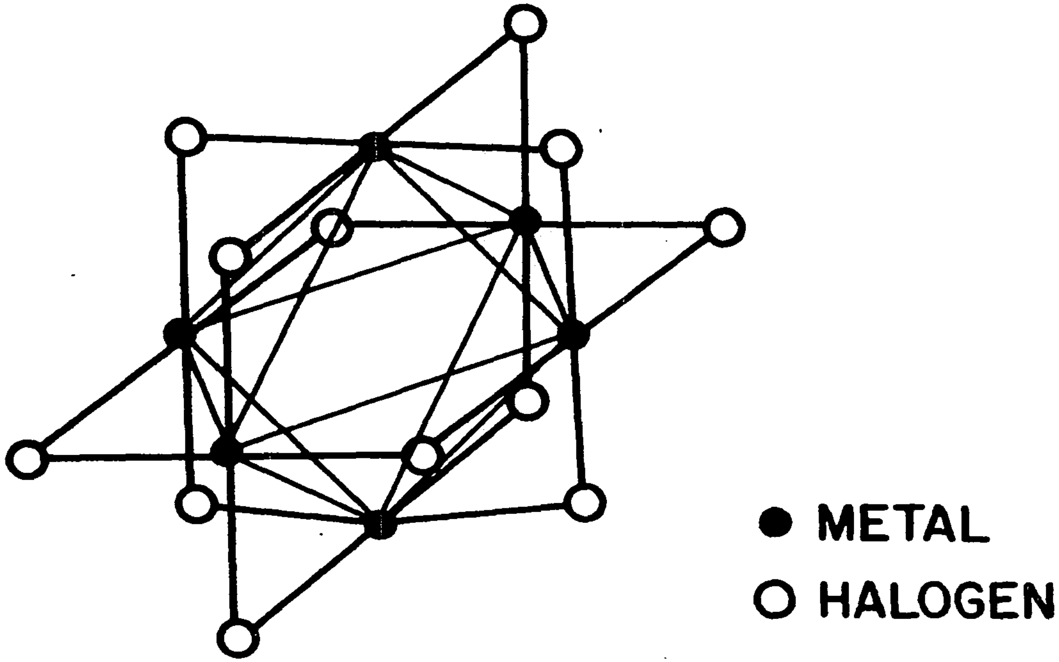
In order to account for the observation that $TaBr_{2.5}$ did not react with tantalum at 600°C. (2 days), but reacted completely at 640°C. (1 day) the peritectic decomposition of $TaBr_{2.5}$ at some temperature in the range 600-640°C. is suggested. The peritectic decomposition into $(Ta_6Br_{12})Br_2$ and liquid of higher composition would provide a mechanism for the relatively rapid equilibration and formation of only

$(Ta_6Br_{12})Br_2$ at 640°C. Below the peritectic temperature the equilibration may be very slow because both reactants are solids of low vapor pressure. Thus in Figure 5 the $TaBr_{2.5}$ phase is shown to decompose peritectically at about 620°C.

In attempts to determine if a lower phase was present in the phase diagram, high temperature equilibrations of $(Ta_6Br_{12})Br_2$ with tantalum were effected. A mixture of $(Ta_6Br_{12})Br_2$ and tantalum metal was sealed in an evacuated Vycor tube and heated to 605°C. for 5 days. The x-ray diffraction pattern of the dark green residue showed "d" spacings of $(Ta_6Br_{12})Br_2$ and tantalum metal. A second high temperature equilibration experiment was effected by placing a sample of $(Ta_6Br_{12})Br_2$ in tantalum tubing as explained above. In this case the equilibration was done in an evacuated Vycor tube and not under an argon atmosphere. Hence the large pressure differential between the inside and the outside of the tantalum tube was sufficient at 815°C. (ca. 4 atm.) to cause leakage of the higher tantalum halides, formed by decomposition of $(Ta_6Br_{12})Br_2$. These higher halides in turn reacted with SiO_2 causing the formation of Ta_2Si and Ta_2O_5 via the transport reaction reported recently by Schäfer et al. (35). Thus when the tantalum tube was opened and an x-ray diffraction pattern obtained the "d" spacings could be accounted for by either Ta_2Si (36, Card No. 6-0569) or tantalum metal. Therefore the experiment was inconclusive.

The phase diagram of the tantalum-tantalum bromide system can be seen in Figure 5. The phases other than $TaBr_5$ that were identified were $TaBr_4$, $TaBr_{2.83}$, $TaBr_{2.5}$, and $TaBr_{2.33}$. It was shown that $TaBr_4$ melted with decomposition at 392°C., $TaBr_{2.83}$ melted with decomposition at a temperature greater than or equal to 447°C. but less than 453°C., and that $TaBr_{2.5}$ decomposed at a temperature greater than 600°C. but less than 640°C. The temperature at which $(Ta_6Br_{12})Br_2$ decomposed was not detected. It was also observed that equilibrium was apparently very sluggish between these phases, especially when $(Ta_6Br_{12})Br_2$ was used in an equilibration reaction. This is not too surprising when the complex character of the cation, $Ta_6Br_{12}^{2+}$, is considered. The structure of this cation was determined by Vaughan _et_ _al_. (37) by visual and comparative interpretation of x-ray diffraction data of ethanol solutions. It was shown that the six metal atoms are arranged in an octahedran with the twelve bromine atoms located on the perpendicular bisectors of the edges of the metal octahedron, see Figure 6. This ion has O_h symmetry and there is no point where an

Figure 6. Structure of $Ta_6Br_{12}^{2+}$ ion



$M_6X_{12}^{++}$

electrophilic or nucleophilic attack can occur readily, hence reaction with higher halides might be expected to be slow.

As can be seen on the phase diagram no $TaBr_3$ was detected. A substance was obtained that analyzed $TaBr_{3.02}$ when

Anal. Calcd. for $TaBr_3$: Ta, 43.00; Br, 57.00.

Found: Ta, 42.87; Br, 57.35; Br/Ta, 3.02.

$TaBr_5$ was reduced with aluminum foil in a temperature gradient of 400° to 275°C. for 3 days with a subsequent heat treatment at 400°C. for 30 hours. It seemed peculiar that this material was essentially the same green as $(Ta_6Br_{12})Br_2$, thus a reflectance spectrum was obtained on this material. The results of this spectrum can be seen in Figure 7. This definitely showed that the green color was due to the presence of $(Ta_6Br_{12})Br_2$ (33). The x-ray diffraction pattern showed that it was a mixture of several substances. This material was placed in a modified Soxhlet extractor and washed first with acetonitrile and second with dry methanol. After drying under vacuum the residue that was left on the frit was analyzed for tantalum.

Anal. Found: Ta, 49.57, 49.39; Br, (by difference);

Br/Ta (ave.), 2.32.

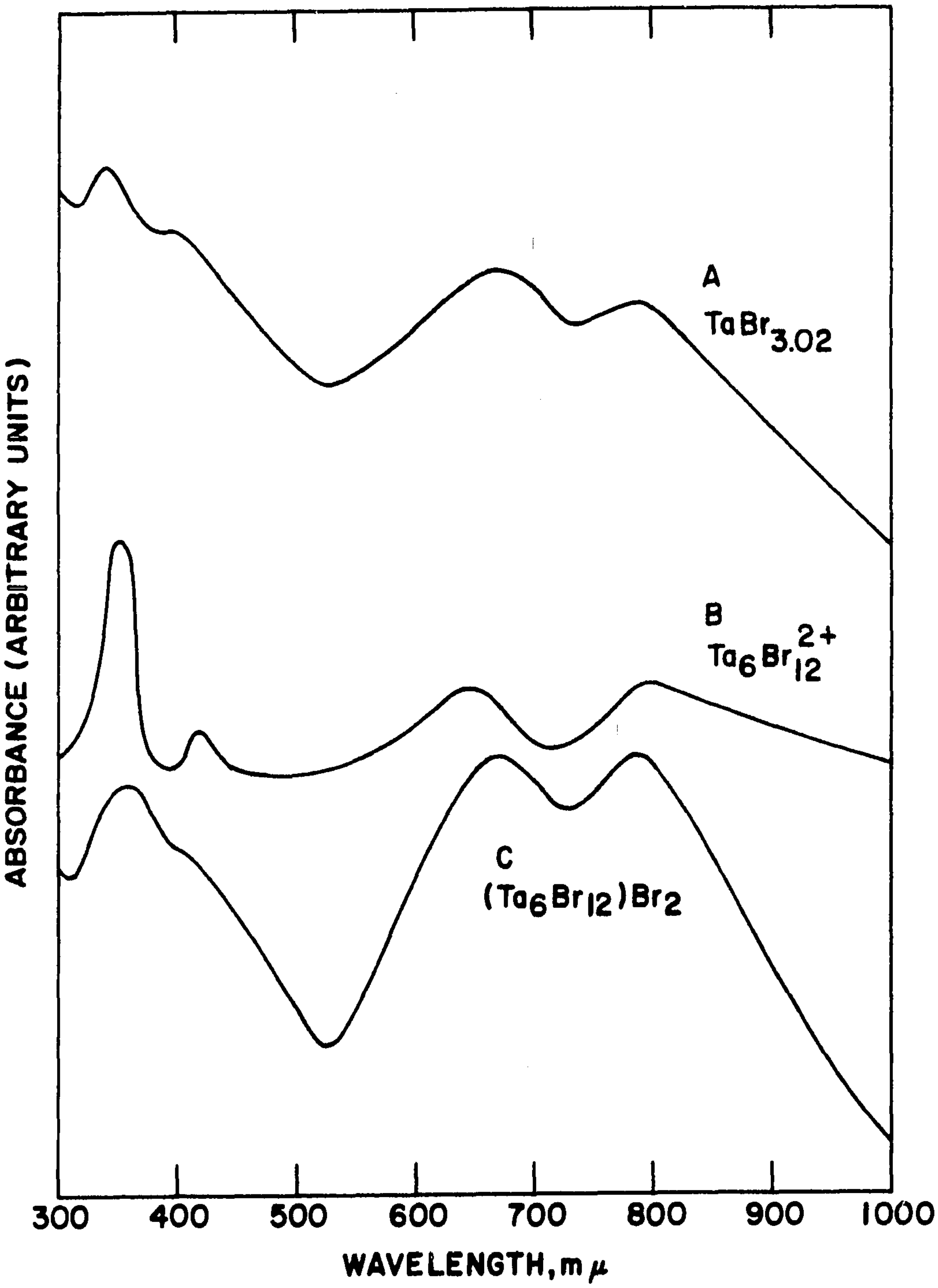
This again indicated that this substance having a Br/Ta of 3.02 was not a pure compound.

Figure 7. Spectra of some tantalum bromides

A. Reflectance spectrum of $TaBr_{3.02}$

B. Spectrum of $Ta_6Br_{12}^{2+}$ in H_2O

C. Reflectance spectrum of solid $(Ta_6Br_{12})Br_2$


ABSORBANCE (ARBITRARY UNITS)
A
TaBr$_{3.02}$
B
Ta$_6$Br$_{12}^{2+}$
C
(Ta$_6$Br$_{12}$)Br$_2$
300
400
500
600
700
800
900
1000
WAVELENGTH, mμ

The compositions of the nonstoichiometric phases were determined by various means. The composition of the phase having the Br/Ta of 2.83 was suggested when samples of $TaBr_4$ were equilibrated at temperatures less than the decomposition temperature of this phase for various lengths of time. A Br/Ta of 2.84 was obtained after equilibrating 3 days at 435°C. and a Br/Ta of 2.82 was obtained after equilibrating 10 days at 426°C. When a mixture of $(Ta_6Br_{12})Br_2$ and $TaBr_5$ were equilibrated at 375°C. a Br/Ta of 2.87 was obtained. The value of 2.83 was used since it gave a whole number formula of Ta_6Br_{17}. There was evidence that this phase is partially composed of the complex cation $Ta_6Br_{12}^{2+}$, i.e. the formation of green solutions when the material was added to H_2O for analysis.

The composition of $TaBr_{2.5}$ was demonstrated when this material was obtained via transport reaction when $TaBr_5$ was reduced with tantalum metal in a temperature gradient of 650°C. and 457°C. The composition of this phase has been

Anal. Found: Ta, 47.50; Br, 52.50; Br/Ta, 2.51.

verified recently by Schäfer[1].

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[1] Schäfer, H., Anorgaisch-Chemsihes Institut der Universität, Münster, Germany. On the lower phases of the tantalum chloride and the tantalum bromide systems. Private communication. 1964.

The composition of $(Ta_6Br_{12})Br_2$ was demonstrated primarily by chemical evidence. It has been shown that the spectrum of a H_2O solution of this phase and the reflectance spectrum of the anhydrous solid are essentially the same (cf. Figure 7). The green color of the solution was shown to result from a cation with a Br/Ta of 2.00[1] when it passed through an anion exchange column charged with sulfate ion. It was also shown at the same time that the $Ta_6Br_{12}^{2+}$ ion could be quantitatively oxidized to $Ta_6Br_{12}^{4+}$; subsequently the compounds $(Ta_6Br_{12})Br_4$ and $(Ta_6Br_{12})(SO_4)_2$ have been isolated and identified. Kuhn (33, p. 28) found that when the green colored solutions were slowly reduced in volume by boiling, a dark crystalline solid precipitated. When this solid was analyzed it showed a Br/Ta of 2.33. With these data and that

Anal. Found: Ta, 45.96, 46.48; Br, 47.23, 47.58;
Br/Ta, 2.33, 2.32; H_2O (by difference), 6.81, 5.94.

explained above, a good case has been presented to show that the lowest phase has indeed a Br/Ta of 2.33.

The tantalum-tantalum bromide system was in no way simi-

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[1] Hughes, B. G., Ames Laboratory, Ames, Iowa. Synthesis and properties of some reduced and oxidized polynuclear tantalum halides. Private communication. 1964.

lar to the niobium-niobium iodide system reported by Seabaugh (38). In the niobium-niobium iodide system the lowest phase was $NbI_{2.67}$ and apparently did not utilize the complex cation as the bases of its structure as did the tantalum-tantalum bromide lowest phase. It would be of immediate interest to look at the niobium-niobium bromide system under equilibrium conditions. Schäfer (39) has reported results of experiments utilizing transport reactions between niobium metal and $NbBr_5$ in temperature gradients. When a temperature gradient of 200° to 300°C. was used the resultant product was $NbBr_4$, but a temperature gradient of 450° to 400°C. resulted in a variable composition phase with a Br/Nb ranging from 3.03 to 2.67. There was no evidence given that indicated the formation of any of the lower phases found for the tantalum-tantalum bromide system.

Tantalum-Tantalum Iodide System

Synthesis of tantalum(IV) iodide

As in the case of the $TaBr_4$ the preparation of TaI_4 was a major problem. Small quantities could be obtained as explained in previous work (18, p. 548), but not sufficient amounts to be practical. Since an aluminum reduction of $TaBr_5$ was successful for the preparation of $TaBr_4$, the same type of technique was used to prepare TaI_4. The optimum conditions were found to be 325°C. for 6 days. When temperatures less than 325°C. were used the reduction was extremely slow, whereas when temperatures of greater than 325°C. were used an impure product resulted. A major difficulty arose from the fact that excess TaI_5 could not be removed effectively by sublimation without decomposing the TaI_4, hence stoichiometric quantities of the starting materials had to be used. When two preparations were effected utilizing the optimum conditions and stoichiometric amounts of TaI_5 and aluminum metal products of reasonable purity were obtained. A third preparation, when

Anal. Calcd. for TaI_4: Ta, 26.29; I, 73.71.
Found: Ta, 25.99; I, 73.92; I/Ta, 4.06.
Ta, 25.53; I, 74.19; I/Ta, 4.16.

reduced at 350°C., had a reasonable I/Ta, but there was evidence that the lower iodide, $(Ta_6I_{12})I_2$, was present in the residue. This was evident from the green solution that

Anal. Found: Ta, 26.13; I, 73.68; I/Ta, 4.03.

resulted when a sample of this material was added to water. Therefore the latter sample was not used and only the first two preparations were used in the experiments discussed below.

Differential thermal analysis

Heating and cooling data for this system were collected in the same manner as was described for the bromide system. In this system the decomposition of TaI_4 was sufficiently slow that a thermal arrest on heating was observed only for the compounds having I/Ta of 4.06 and 4.16. The heating and cooling data can be seen in Table 4. These data show that TaI_5 melts at 382°C., a value much lower than 496°C. obtained from vapor pressure data by Fairbrother and Alexander (40, p. 2475). A temperature of 365°C. is suggested as the eutectic melting point. The value of 365°C. was given by Körösy (10) as the melting point of TaI_5, but he was appar-

Table 4. Heating and cooling data of the tantalum-tantalum iodide system of mixtures between TaI_5 and TaI_4

I/Ta Atom ratio	Temperature, °C	
	Heating[a]	Cooling[a]
5.00	382,383	380,381
4.90	367	367
4.82	363	367
4.59	364	365
4.40	365	365
4.16	365,426	367
4.06	365,416	364
4.03	364	365

[a] Data obtained after equilibration of the mixture in the range of 380 to 390°C.

ently working with impure material. The data also show that thermal arrests were observed at 426°C. and 416°C. for the samples with I/Ta of 4.16 and 4.06 respectively. The high values can best be explained as super heating since the decomposition of TaI_4 was apparently sluggish. When a sample of Ta_6I_{14} was heated, no melting point was detected.

Location of the liquidus line

Since the heating and cooling curve data gave no indication of the eutectic composition, this composition was determined by the solution technique as was used for the tantalum-tantalum bromide system. The results of 3 experiments can be seen in Table 5. The liquidus line was found to be essentially a vertical line defining the eutectic composition at a I/Ta of 4.87.

Table 5. Results of the solution experiments for the tantalum-tantalum iodide system

Temperature of equilibration, °C.	% Ta	I/Ta Atom ratio[a]
390	22.59	4.88
400	22.76	4.84
420	22.53	4.90

[a] Ratio was calculated using iodide by difference.

Equilibrium studies

Since the equilibrium decomposition temperature of TaI_4 could not be found by heating and cooling data, this temperature was found using equilibration experiments. The x-ray powder diffraction pattern of $TaI_{4.06}$ was obtained and found to have no lines that could be attributed to $(Ta_6I_{12})I_2$. The x-ray powder diffraction pattern of $TaI_{4.06}$ can be seen in Table 8 of the Appendix.

Samples of $TaI_{4.06}$ were sealed in Pyrex cells, similar to the cells used for the differential thermal analysis experiments, and were placed in the furnace shown in Figure 3. The samples then were equilibrated at the desired temperature for 3 days after which they were slow cooled to room temperature. The temperatures that were used in this series of equilibration experiments were 395°, 402°, 406°, 421°, and 428°C. All of the x-ray diffraction patterns of the residue resulting from equilibration at temperatures of 402°C. or greater had a "d" spacing of minor intensity at 2.60. This "d" spacing does not occur in any of the known tantalum iodides except $(Ta_6I_{12})I_2$, see Table 16 in the Appendix, and in the x-ray diffraction patterns of this material it is the most intense line. However, it should be pointed out at this time that the x-ray powder diffraction patterns of the tantalum iodides are of poor quality. Since the powder patterns of the residues resulting from equilibration at 402°C. or greater are different than the powder diffraction patterns prior to equilibration it was indicated that $TaI_{4.06}$ had decomposed. The diffraction pattern of the sample of $TaI_{4.06}$ that had been equilibrated at 395°C. was the same before and after equilibration, hence it can be concluded that the $TaI_{4.06}$ had not decomposed at 395°C. Thus it must be assumed that TaI_4 melts with decomposition at about 398°C.

The next lower phase was thought to be $(Ta_6I_{12})I_2$. This was indicated when a sample of $TaI_{4.06}$ was equilibrated at 433°C. for 3 days. In this case the TaI_5 was removed by sublimation at 350°C. prior to procurement of an x-ray powder diffraction pattern. The resulting diffraction pattern was that of $(Ta_6I_{12})I_2$. Earlier equilibration experiments done in this laboratory (33) on mixtures with I/Ta of 3.0, 2.3, and 2.0 showed that the resultant phases were $(Ta_6I_{12})I_2$ and TaI_5 in the case of the I/Ta of 3.0. The results and conditions of these equilibration experiments can be seen in Table 6. These data indeed show that $(Ta_6I_{12})I_2$ is the stable phase between the temperatures of 550 and 650°C.

Table 6. Results and conditions of the high temperature equilibration experiments of the tantalum iodide system

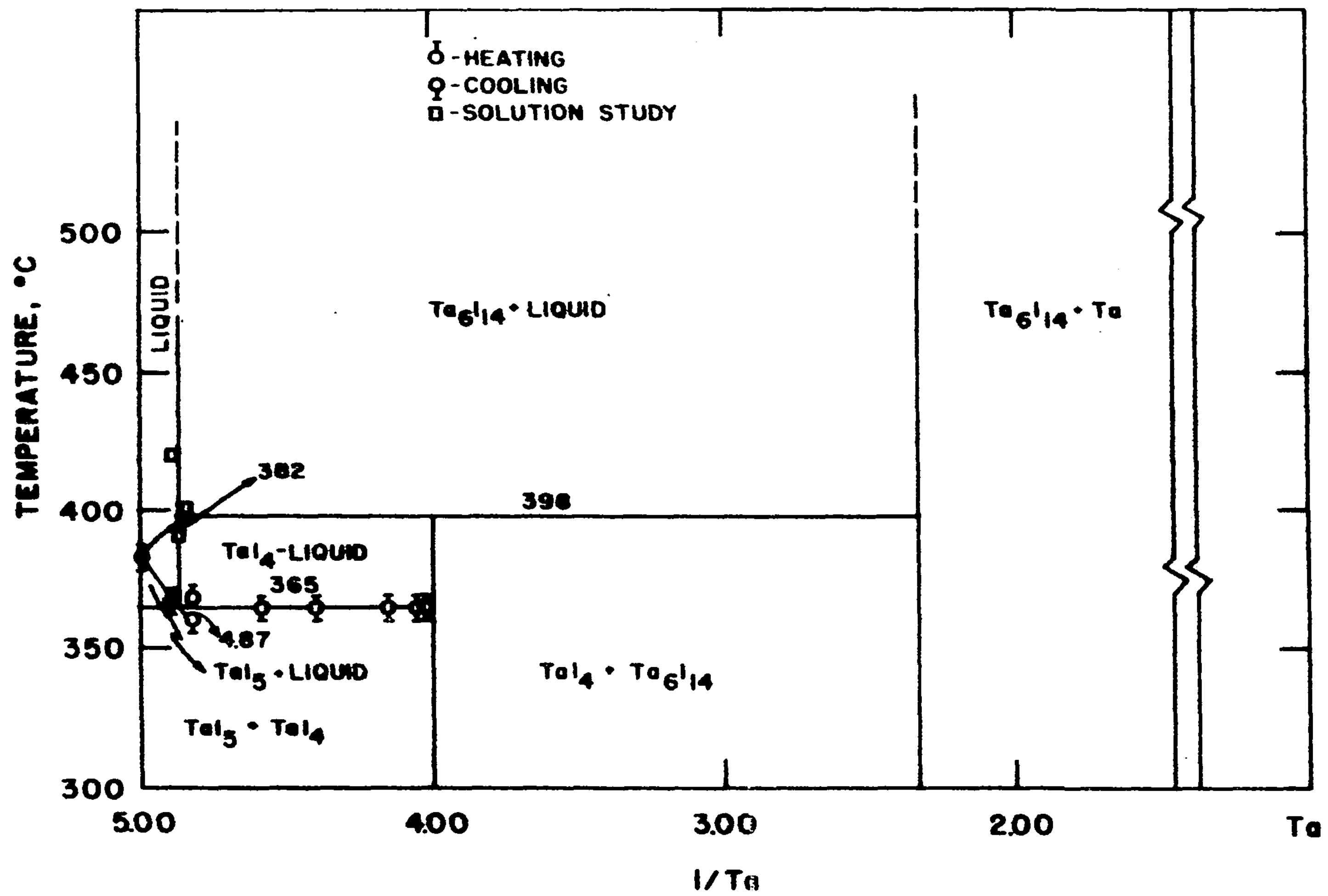
I/Ta atom[a] ratio	Temperature, °C.	Time, days	Phase present
3.00	550	3	$(Ta_6I_{12})I_2$, TaI_5
2.30	650	5	$(Ta_6I_{12})I_2$
2.00	650	5	$(Ta_6I_{12})I_2$, Ta

[a] These ratios were obtained by mixing weighed quantities of tantalum metal and iodine.

In an attempt to establish whether a lower phase, e.g. TaI_2, existed or not a high temperature equilibration experiment was effected. A sample of $(Ta_6I_{12})I_2$ was sealed into a one-eighth inch tantalum tube which subsequently was sealed into an evacuated Vycor tube. The tube was placed in the furnace shown in Figure 3 and heated to 815°C. for 4 days. After slow cooling to room temperature the Vycor tube was opened and the tantalum tube recovered. The tantalum tube had become brittle and cracked open. Located in the vicinity of this crack were small crystalline hexagonal rods which were scrapped off of the tube and powdered so that an x-ray powder diffraction pattern could be obtained. The data of this diffraction pattern can be seen in Table 17 of the Appendix. It was visually evident that the transport reaction reported by Schäfer (35) between SiO_2 and tantalum metal had indeed occurred. This was also evident since the "d" spacings of the material obtained by the high temperature equilibration could be accounted for by $(Ta_6I_{12})I_2$, Ta_2Si, β-Ta_2O_5, and tantalum metal. The impurities were obviously obtained when the crystalline product was scrapped off of the tantalum tube. Thus it appeared that a lower phase was not present in the tantalum-tantalum iodide system.

The diagram that can be constructed from the data thus far collected can be seen in Figure 8. From the data presented above it appears that TaI_3 or $TaI_{2.5}$ are not present in this phase diagram. There are indeed more equilibration experiments that can be effected to completely eliminate or substantiate the existence of phases other than those noted in this work. One of the interesting pieces of data from this work was proving the existence of $(Ta_6I_{12})I_2$, $(TaI_{2.33})$, whereas the lowest phase found for the niobium-niobium iodide system was the $NbI_{2.67}$ (38). The $(Ta_6I_{12})I_2$ structure utilizes the complex cation $Ta_6I_{12}^{2+}$ whereas the $NbI_{2.67}$ apparently does not. Another interesting observation was the apparent isomorphous character of $(Ta_6I_{12})I_2$ and

Figure 8. Phase diagram of the tantalum-tantalum iodide system


-HEATING
-COOLING
-SOLUTION STUDY
TEMPERATURE, °C
500
450
400
350
300
LIQUID
Ta6I14 + LIQUID
Ta6I14 + Ta
382
398
TaI4-LIQUID
365
4.87
TaI5 + LIQUID
TaI4 + Ta6I14
TaI5 + TaI4
5.00
4.00
3.00
2.00
Ta
I/Ta

$(Ta_6Br_{12})Br_2$. Evidence for this isomorphism was found by visual comparison of the x-ray diffraction patterns of the two compounds, which were very similar with a 1:1 correspondence between the positions of the most intense lines. Comparison of the data in Tables 15 and 16 shows that the "d" spacings, and hence the lattice constants of the $(Ta_6I_{12})I_2$ are shifted to higher values relative to those of $(Ta_6Br_{12})Br_2$.

SUMMARY

The tantalum-tantalum bromide and the partial tantalum-tantalum iodide equilibrium phase diagrams were obtained using a variety of techniques including differential thermal analysis, x-ray powder diffraction data, solution experiments, and equilibrium experiments.

The tantalum-tantalum bromide system was the more thoroughly studied system of the two. Four phases other than $TaBr_5$ were found in this system, i.e. $TaBr_4$, $TaBr_{2.83}$, $TaBr_{2.5}$ and $(Ta_6Br_{12})Br_2$. Tantalum(V) bromide was found to melt at 272°C. and $TaBr_4$ was found to melt with decomposition at 392°C. The phases having Br/Ta of 2.83 and 2.5 were found to melt with decomposition at a temperature of $447^\circ < T < 453^\circ$C. and $600^\circ < T < 640^\circ$C. respectively. The melting point of $(Ta_6Br_{12})Br_2$ was not detected. There was no evidence that $TaBr_3$ or $TaBr_2$ were equilibrium phases in this system.

The tantalum-tantalum iodide system was more difficult to investigate due to the fact that the x-ray powder diffraction patterns of the tantalum iodides were of poor quality. The only phases found other than TaI_5 were TaI_4 and $(Ta_6I_{12})I_2$. The TaI_4 was found to decompose at <u>ca</u>. 398°C. by means of equilibration experiments. No melting point was detected for

$(Ta_6I_{12})I_2$. There was no evidence based on the data collected during the course of this work that indicated any other phases should be included in this phase diagram. It is an interesting fact that the tantalum-tantalum iodide system is different than the niobium-niobium iodide system (38). The major difference is in the compositions of the lowest phases, i.e. $NbI_{2.67}$ as opposed to $TaI_{2.33}$. It was also interesting that the two compounds $(Ta_6I_{12})I_2$ and $(Ta_6Br_{12})Br_2$ were apparently isostructural.

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He also expresses his gratitude to the members of Metallurgy Group VI for their cooperation in the use of equipment and their free exchange of ideas concerning this project.

More than thanks to my wife Carolyn whose moral support and sacrifice made this possible.

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APPENDIX

Table 7 . X-ray diffraction data for $TaBr_4$[a]

Relative[b] intensity	Observed "d" spacing, Å	Relative intensity	Observed "d" spacing, Å
10	6.22	4	2.25
9	4.68	10	2.15
8	4.31	1	1.99
1	3.57	1	1.96
4	3.11	6	1.84
10	2.84	4	1.82
10	2.77	5	1.69
2	2.70	5	1.60
7	2.35	3	1.56

[a] Exposure time for this pattern was 14 hours.

[b] All intensities were measured visually relative to a value of 10 for the most intense line.

Table 8 . X-ray diffraction data for $TaI_{4.06}$[a]

Relative[b] intensity	Observed "d" spacing, Å	Relative intensity	Observed "d" spacing, Å
10	6.62	3	2.40
5	3.29	1	2.18
5	3.18	3	2.08
7	3.07	3	2.06
1	2.83	8	2.01
1	2.66	5	1.860
1	2.55	2	1.714
1	2.52		

[a] Exposure time of this pattern was 26 hours.

[b] All intensities were measured visually relative to a value of 10 for the most intense line.

Table 9. X-ray diffraction data for $TaBr_{2.83}$[a]

Relative[b] intensity	Observed "d" spacing, Å	Relative intensity	Observed "d" spacing, Å
10	9.38	4	1.963
10	6.59	1	1.892
4	5.60	3	1.870
4	5.32	2	1.834
5	4.65	1	1.799
5	4.23	5	1.777
5	4.11	4	1.709
1	3.89	1	1.659
2	3.75	3	1.619
8	3.57	1	1.579
3	3.34	2	1.557
3	3.24	1	1.531
3	3.17	2	1.448
4	3.11	1	1.418
7	2.97	1	1.401
1	2.92	1	1.387
2	2.86	1	1.374
3	2.80	1	1.361
3	2.77	2	1.332
4	2.70	2	1.323
10	2.61	2	1.314
9	2.55	1	1.290
9	2.44	2	1.273
9	2.40	1	1.252
8	2.33	1	1.243
8	2.27	2	1.221
8	2.25	2	1.211
6	2.11	3	1.196
6	2.04	3	1.161
7	2.02		

[a] Exposure time for this pattern was 19 hours.

[b] All intensities were measured visually relative to a value of 10 for the most intense line.

Table 10. X-ray data of residue resulting from decomposition of $TaBr_4$ at 453°, 460°, and 470°C.[a]

Relative[b] intensity	Observed "d" spacing, Å	Relative intensity	Observed "d" spacing, Å
10	9.29	3	2.40
10	7.51[c]	2	2.32
10	6.55	2	2.29[c]
1	5.57	2	2.27
1	5.31	1	2.24
2	4.64	2	2.19[c]
1	4.20	2	2.15[c]
2	4.11	1	2.10
5	3.57	1	2.09[c]
1	3.16	1	2.01
1	3.10	1	1.959
5	2.97	1	1.863
1	2.91	1	1.836
3	2.89[c]	1	1.812[c]
1	2.85	1	1.799
1	2.77	2	1.775
4	2.66[c]	1	1.737[c]
8	2.60	2	1.712
6	2.54	1	1.653
1	2.50[c]	1	1.642[c]
3	2.47[c]	1	1.616
4	2.43	1	1.601

[a] Exposure time on all three patterns was 18 hours.

[b] All intensities were measured visually relative to a value of 10 for the most intense line.

[c] These "d" spacings are the most intense lines of $TaBr_{2.5}$. All three patterns were the same except that the intensities of $TaBr_{2.5}$ were greater in the resultant product from the 470°C. heat treatment.

Table 11. X-ray diffraction data for TaBr$_{2.5}$[a]

Relative[b] intensity	Observed "d" spacing, Å	Relative intensity	Observed "d" spacing, Å
1	9.08	1	1.898
3	8.38	2	1.883
10	7.55	7	1.841
2	5.69	6	1.814
1	4.54	1	1.802
1	4.35	2	1.763
3	3.76	4	1.740
2	3.45	1	1.717
2	3.36	1	1.655
5	3.32	1	1.644
2	3.14	1	1.562
2	3.07	2	1.531
10	2.89	2	1.515
1	2.74	1	1.485
3	2.66	1	1.471
1	2.58	1	1.437
10	2.55	1	1.406
3	2.51	1	1.382
10	2.47	1	1.348
3	2.41	1	1.337
1	2.38	2	1.317
10	2.30	3	1.307
1	2.27	3	1.297
10	2.24	1	1.280
3	2.20	1	1.270
5	2.15	1	1.244
1	2.13	1	1.227
4	2.11	4	1.219
4	2.09	4	1.204
3	2.03	4	1.181
1	1.994		
2	1.961		
2	1.929		

[a] Exposure time for this pattern was 18 hours.

[b] All intensities were measured visually relative to a value of 10 for the most intense line.

Table 12. X-ray data of product when $TaBr_4$ was equilibrated with excess Ta at 600°C. for 2 days[a]

Relative[b] intensity	Observed "d" spacings, Å	Relative intensity	Observed "d" spacings, Å
1	8.37	2	2.11
10	7.51	2	2.09
1	5.64	1	2.03
1	3.76	1	1.961
1	3.44	1	1.932
1	3.36	1	1.841
3	3.29	4	1.815
5	2.90	3	1.765
1	2.67	2	1.740
1	2.58	3	1.717
4	2.55	1	1.657[c]
2	2.51	7	1.352[c]
4	2.47	10	1.318
10	2.34[c]	1	1.307
4	2.30	1	1.298
4	2.24	1	1.220
1	2.20	1	1.204
3	2.15	5	1.171[c]

[a] Exposure time for this pattern was 19 hours.

[b] All intensities were measured visually relative to a value of 10 for the most intense line.

[c] These high intensity lines are of tantalum metal. All the other "d" spacing can be attributed to $TaBr_{2.5}$.

Table 13. X-ray data of product resulting from reduction of $TaBr_{2.75}$ in tantalum tubing at 684°C. for 1 day[a]

Relative[b] intensity	Observed "d" spacing, Å	Relative intensity	Observed "d" spacing, Å
10	7.43	4	2.25
2	7.05	4	2.19
3	6.61	4	2.11
1	4.95	1	2.07
2	3.70	3	2.04
1	3.58	2	1.993
6	3.51	3	1.929
2	3.42	3	1.919
2	3.30	3	1.912
7	3.00	1	1.893
8	2.87	1	1.877
3	2.81	3	1.867
4	2.74	2	1.842
5	2.68	3	1.762
3	2.65	1	1.728
7	2.51	2	1.665
6	2.48	2	1.637
10	2.42	1	1.568
5	2.36	2	1.553
1	2.32	2	1.540

[a] Exposure time for this pattern was 19 hours.

[b] All intensities were measured visually relative to a value of 10 for the most intense line.

Table 14. X-ray data of product resulting from the equilibration of Ta_6Br_{14} with $TaBr_4$ at 500°C. for 4 days[a]

Relative[b] intensity	Observed "d" spacing, Å	Relative intensity	Observed "d" spacing, Å
3	9.10	5	2.29
3	8.45	1	2.27
10	7.52	5	2.24
3	7.33[c]	1	2.19
1	6.24[c]	4	2.15
1	5.69	1	2.13
1	5.33[c]	3	2.11
1	4.34	3	2.09
3	3.74	1	2.03
2	3.51[c]	2	1.958
2	3.45	2	1.926
1	3.36	1	1.896
5	3.28	1	1.882
1	3.20[c]	2	1.865[c]
2	3.13[c]	4	1.839[c]
2	3.07	4	1.810
2	3.01[c]	3	1.762
10	2.89	2	1.736
2	2.73	2	1.715
1	2.70[c]	2	1.651
3	2.64	2	1.642
7	2.62[d]	1	1.528
7	2.54	1	1.513
5	2.51	1	1.315
7	2.47	1	1.306
5	2.41	1	1.296

[a] Exposure time on this pattern was 15 hours.

[b] All intensities were measured visually relative to a value of 10 for the most intense line.

[c] These lines are lines of $TaBr_{2.5}$ but were not detected on the original diffraction pattern of $TaBr_{2.5}$.

[d] This line can not be explained.

Table 15. X-ray diffraction data for $(Ta_6Br_{12})Br_2$[a]

Relative[b] intensity	Observed "d" spacing, Å	Relative intensity	Observed "d" spacing, Å
10	7.39	4	2.12
6	7.03	1	2.07
8	6.59	3	2.04
2	5.76	1	1.998
1	4.45	5B	1.914
1	3.94	5B	1.866
2	3.70	5	1.760
2	3.57	3	1.729
10	3.51	5B	1.660
2	3.40	4	1.638
2	3.30	2	1.570
3	3.10	3	1.556
7	3.00	3	1.541
9	2.86	5	1.498
4	2.81	4B	1.439
5	2.74	2	1.363
6B	2.66	1	1.338
6B	2.49	4B	1.295
10	2.42	2	1.266
5	2.36	3	1.236
1	2.32	4	1.210
5	2.25	1	1.198
5	2.20		

[a] Exposure time on this pattern was 17 hours.

[b] All intensities were measured visually relative to a value of 10 for the most intense line. B = Broad.

Table 16. X-ray diffraction data for $(Ta_6I_{12})I_2$[a]

Relative[b] intensity	Observed "d" spacing, Å	Relative intensity	Observed "d" spacing, Å
10	8.02	2	1.908
1	7.26	3	1.886
1	3.78	1	1.873
1	3.27	3	1.817
3	3.23	2	1.796
8	3.14	3	1.776
5	2.95	2	1.710
2	2.74	1	1.638
10	2.61	5	1.618
1	2.44	3	1.572
1	2.41	1	1.415
3	2.37	1	1.326
3	2.29	3	1.308
3	2.22	2	1.289
3	2.09	1	1.264
3	2.06	3	1.246
3	2.04	3	1.207
4	2.01	1	1.189

[a] Exposure time for this pattern was 24 hours.

[b] All intensities were measured visually relative to a value of 10 for the most intense line.

Table 17. X-ray data of single crystal resulting from equilibration of Ta_6I_{14} in tantalum tubing at 815°C.[a]

Relative[b] intensity	Observed "d" spacing, Å	Relative intensity	Observed "d" spacing, Å
4	8.02	3	1.833
1	5.25[c]	3	1.799
3	4.34[d]	6	1.657[e]
10	3.89[c]	2	1.635
7	3.15[c]	1	1.577
7	3.09[d]	4	1.543[d]
1	2.95	1	1.458
1	2.87	8	1.438[d]
1	2.73	1	1.384[d]
1	2.68	1	1.355[e]
3	2.60	2	1.335
5	2.52[d]	2	1.321[c]
7	2.45	2	1.289
10	2.42[d]	4	1.263
4	2.34[e]	3	1.227
5	2.18[d]	1	1.215
1	2.01	3	1.201
9	1.947[d]		

[a] Exposure time on this pattern was 24 hours.

[b] All intensities were measured visually relative to a value of 10 for the most intense line.

[c] Those lines attributed to β-Ta_2O_5.

[d] Those lines attributed to Ta_2Si.

[e] Those lines attributed to tantalum metal. All others are "d" spacings of Ta_6I_{14}.