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A SUMMARY OF THE PROPERTIES,
PREPARATION, AND PURIFICATION OF THE
ANHYDROUS CHLORIDES AND BROMIDES OF
URANIUM. PART A. URANIUM CHLORIDES.
PART B. URANIUM BROMIDES

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ABSTRACT

A summary report is presented giving all available data on the properties, preparation, and purification of anhydrous uranium chlorides and uranium bromides. Data is given for UCl_3 , UCl_4 , UCl_5 , UCl_6 , $UOCl_2$, and UO_2Cl_2 in Part A. In Part B, data is given for UBr_3 , UBr_4 , $UOBr_5$, UO_2Br_2 , and the UBr_3 - UBr_4 system.

Part A.

A SUMMARY OF THE PREPARATION, PURIFICATION, AND
PROPERTIES OF ANHYDROUS CHLORIDES OF URANIUM

O. Johnson and T. Butler

I. Uranium Trichloride

Anhydrous UCl_3 can be conveniently prepared by the reaction of HCl gas on powdered uranium or uranium hydride at 250°C . (1) The UCl_3 produced in this way is an olive green powder which is hygroscopic but less so than other uranium chlorides. It turns a reddish-brown color upon heating to 350°C and to a purple color at 450°C , but returns to the green color upon cooling to room temperature.

The reduction of UCl_4 to UCl_3 with H_2 has been studied in detail. (2,3,4) There is little reduction below 525° and the initial reduction must be carried out at about 550° . As the amount of UCl_3 in the mixture becomes greater, the temperature can be raised to 650°C without causing sintering. Increased pressure of H_2 increases the rate of reduction, e.g., it requires 4 hours to reduce 20 grams of UCl_4 at 525° at 1 atm. of H_2 and only 1 hour at 7 atmospheres pressure. The UCl_3 is produced in this reduction as dark green crystals.

The density of UCl_3 , as measured in this laboratory by the displacement of CCl_4 , is 5.35 g/cc . (5) The density was reported in the literature as 5.44 g/cc . (6) The melting point of UCl_3 is $842 \pm 5^\circ$. (7) X-ray measurements (7a) show UCl_3 to have a hexagonal structure with the following constants:

$$A_0 = 7.428, C_0 = 4.312$$

$$\text{Density} = 5.51 \text{ g/cc}$$

A study (8) has been made of some of the thermal properties of UCl_3 in connection with the effusion method of measuring vapor pressures. There is appreciable decomposition at 850°C and the upper limit of the vapor pressure is 10^{-3} mm at 820°C . In a similar experiment (9) with several grams of UCl_3 , there was also found considerable decomposition at 850°C to produce UCl_4 , which sublimed to the cool portion of the tube. Some UCl_5 and UCl_6 were produced as colored bands in the upper part of the quartz tube. The quartz tube was attacked by the melt.

UCl_3 dissolves in water to give a momentary purple color but the solution soon turns green. This is accompanied by evolution of H_2 and formation of UO_2 . A wide green band and two sharp adjacent bands are observed (10) for the absorption spectrum of UCl_3 solutions and this was studied to show the mechanism of hydrolysis. UCl_3 dissolves in glacial acetic acid to give a red colored solution. It reacts with formamides and methyl alcohol. It is insoluble in carbon tetrachloride, acetone, chloroform and ether.

The reaction between UCl_3 and Cl_2 gas goes smoothly at 250°C (1) but becomes very vigorous at higher temperatures. UCl_3 reacts rapidly with oxygen at 150 – 200°C . (11) The products are UO_2Cl_2 and Cl_2 with some UO_2 resulting from overheating in the process of reacting.

Because of the relative ease of handling UCl_3 , the reduction of UCl_3 to uranium metal has been studied carefully. (12, 13, 14, 15) Sodium metal was usually used for the reduction

The following method has been used for producing kilogram lots of UCl_3 . The same apparatus as described for making UBr_3 in the bromide section of this report is used. About 700 grams of U turnings which have been cleaned with 1:1 HNO_3 are placed in the reaction tube. In the tube where reacting gasses enter, about 5 grams of uranium metal are placed. The gases used in the reaction pass through this section of the tube first and all impurities are removed. First the uranium is converted to hydride at 250°C by passing in H_2 . The hydride is then converted to UCl_3 by HCl gas. The tube must be rotated from time to time to prevent caking. The reaction is complete when the material is all a reddish-brown color. This becomes olive green when cooled to room temperature. The completion of the reaction can be determined by weighing the apparatus.

II. Uranium Tetrachloride

UCl_4 can be formed by the direct reaction of U and Cl_2 by the reaction of Cl_2 at red heat with UO_2 plus carbon, and of any of the uranium oxides with CCl_4 or S_2Cl_2 . (6) It had also been prepared in an autoclave by the reaction between UO_3 and CCl_4 at 150°C by extensive removal of Cl_2 from the mixture during the reaction. (15) UCl_4 is conveniently prepared by the reaction of powdered uranium with Cl_2 (diluted by an inert gas) at 250°C . This produces a light green powder. (1) UCl_4 is also produced by the dechlorination of UCl_5 (or mixtures of UCl_5 and UCl_6) by heating the higher chloride to 150° in a stream of inert gas or heating in vacuum. (13) In this process there is some loss of material as UCl_6 , but this can be minimized by progressive heating from the bottom of the tube to the top.

The red-brown vapors of UCl_4 condense either as a green powder or under suitable conditions as large green octahedral crystals. The density of UCl_4 has been found to be 4.88 g/cc . (16) The melting point is $588 \pm 4^\circ$. (7,9) It has been found that the addition of 10% UCl_3 lowers the melting point of UCl_4 by 14° . (See, however, 7). The boiling point of UCl_4 by direct measurement is 802°C . (17) Extrapolation from vapor pressure data gave 878°C as the boiling point at 760 mm.

The relative sensitivities of the uranium halides to moisture (18) are as follows: UCl_6 is extremely sensitive and reacts with minute traces of moisture. UCl_5 reacts with H_2O at partial pressures in N_2 as low as 0.007 mm . UCl_4 reacts as low as $2 \text{ mm H}_2\text{O}$ pressure. UCl_3 shows no reaction at 2 mm pressure of H_2O .

All of the halides fume in moist air and absorb enough H_2O to form a solution and, therefore, must be handled in a good dry box.

The X-ray study of UCl_4 crystals shows that UCl_4 has a tetragonal structure with the following lattice spacings: (19, 20)

$$A_0 = 8.296 \pm .009 \text{ \AA} \quad C_0 = 7.437 \pm .009 \text{ \AA} \quad D = 4.87 \text{ g/cc}$$

Crystals produced by sublimation at 600° , and which appeared to be single crystals, were used. However, a powder diagram was obtained in each case. This indicated that some crystal transformation had occurred in cooling. Such a solid phase transformation at about $545^\circ C$ has been found in measuring cooling curves of UCl_4 . (21)

UCl_4 is insoluble in ethyl ether, benzene, and carbon tetrachloride. It is soluble in acetone, ethyl acetate, ethyl benzoate. At temperatures up to $70^\circ C$, no solubility of UCl_4 was observed in the inorganic solvents PCl_3 , $POCl_3$, and $SnCl_4$. (22)

The corrosive action of UCl_4 solid and vapor on various materials of construction has been studied. In 3 hours at $465^\circ C$ there was no chemical action on graphite, fused quartz, refractory porcelain or alundum. (23) For metals under the same conditions, the loss in weight of W, Mo, and Nichrome was less than 1 mg/cm^2 . Ni, Ta, monel and stainless steel lost $1-2 \text{ mg/cm}^2$. Copper was badly attacked. There is excessive corrosion of stainless steel at $500^\circ C$. (24) Palladium plate has been shown to be unsatisfactory. (25) Corrosion tests have been performed on gold alloys, (26) nickel plated copper, (27) anodized aluminum. (28) Studies of corrosion on metals at different temperatures are also reported. (29, 30, 31) At $600^\circ C$, monel and chromel metals are least attacked. (16) The order of magnitude is indicated by the loss of weight of 5 mg/cm^2 in 5 hours. UCl_4 liquid and vapor attack both pyrex glass and quartz.

The vapor pressure of UCl_4 has been measured by two methods. The results, by the effusion method (32) are given in Table I and those by the transpiration method in Table II. (33) Both are included in Figure I.

TABLE I

Vapor Pressure of UCl_4 - Effusion Method (32)

<u>Temperature</u>	<u>Vapor Pressure</u>
330°C	2.14×10^{-4} mm of Hg
365	1.19×10^{-3}
380	2.5×10^{-3}
390	3.91×10^{-3}
400	6.4×10^{-3}
410	9.75×10^{-3}
420	1.5×10^{-2}
430	3.52×10^{-2}
440	3.4×10^{-2}
450	8.24×10^{-2}
460	7.4×10^{-2}
465	2.12×10^{-1}
480	1.5×10^{-1}
500	3.1×10^{-1}
520	1.03 mm

$$\Delta H_{\text{sublimation}} = 38,600 \text{ cal/mol.}$$

TABLE II

Vapor Pressure of UCl_4 - Transpiration Method (33)

<u>Temperature</u>	<u>Vapor Pressure</u>
450°C	0.9 mm
475	1.2
500	2.9
515	4.0
525	7.2
540	8.4
550	11.5
565	20.5
575	21.2
600	36.0
625	54.5
650	72.0
675	100.0

$$\text{Sublimation} \quad \log P = \frac{-7520}{T} + 10.22$$

$$\text{Vaporization} \quad \log P = \frac{-4755}{T} + 7.02$$

$$\Delta H_{\text{sublimation}} = 34,400 \text{ cal/mol}$$

$$\text{Troutons Constant} = 18.9$$

$$\Delta H_{\text{vaporization}} = 21,775 \text{ cal/mol}$$

Since the data on vapor pressures of UCl_4 were reported, the boiling point of UCl_4 at 740 mm was found to be 802°C by direct measurements. (64). Using this point on the liquid vapor pressure curve, the value $\Delta H = 27,300$ cal/mol is obtained, and Trouton's constant is 25.4 and the data can be represented by the equation:

$$\log P = \frac{-5965}{T} + 8.42$$

Phase diagrams of a number of complex salt of uranium halides with alkali and alkaline earth halides have been determined. (7) The following compounds are known: $2 \text{KCl} \cdot \text{UCl}_4$ (MP = 650°C), $2 \text{KCl} \cdot \text{UCl}_3$ (MP = 625°C), $2 \text{NaCl} \cdot \text{UCl}_4$ (MP = 430°C). Simple eutectic systems were found for UCl_4 and LiCl , UCl_4 and BaCl_2 , NaCl and UCl_3 , UCl_4 and CaCl_2 , and UCl_3 and CaCl_2 .

UCl_4 reacts with O_2 at $300\text{--}340^\circ$ to form anhydrous powdered UO_2Cl_2 . At higher temperatures UO_2 and Cl_2 are the products. At room temperature anhydrous UCl_4 absorbs dry NH_3 to form $\text{UCl}_4 \cdot 3 \text{NH}_3$ and the ammonia is retained in vacuum. At a temperature of 300°C , UCl_4 is reduced by NH_3 to UCl_3 with NH_4Cl as a product. (34) If the product is cooled in NH_3 a light green powder is obtained which contains several moles of NH_3 per mole UCl_3 . Flushing with N_2 or He eliminates most of the ammonia. No nitride is formed at 300° and although considerable nitride does form at 750°C , all the chlorine is not eliminated.

UCl_4 can be purified either by direct sublimation or by conversion to and sublimation of the higher chlorides followed by reconversion to UCl_4 . Direct sublimation in a stream of Cl_2 or inert gas at 600° gives large crystals of UCl_4 . (16) In the process the crude UCl_4 placed at one end of a pyrex tube in a furnace with a slow stream of gas passing over. The sublimate collects in the zone of the pyrex tube just outside the furnace where the temperature is about 400°C . In case Cl_2 is used as the carrier gas, some higher chlorides are produced but they sublime as a brown powder well past the zone in which UCl_4 deposits. Due to impurities present, some UOCl_2 and UO_2Cl_2 are produced in the process. Most of them remain in the residue and the small amount of UO_2Cl_2 that sublimes (in Cl_2) deposits in a hotter part of the tube than UCl_4 . Sublimation of UCl_4 at 1000°C has also been used as a method of purification. (35) A method which can be carried out without melting the UCl_4 involves sublimation in a stream of N_2 at 3-5 mm at $600\text{--}650^\circ\text{C}$. (36) Approximately 20 grams are completely volatilized in 6 min.

The purification from Fe, Cr, Cu, Mn, and Ni has been shown to be best if the sublimation is carried out at 550°C and the receiving flask is at 300°C . (37) Presence of water vapor lowers the sublimation rate of UCl_4 considerably. (38)

In the other method of purification, UCl_4 is converted to higher chlorides by passing Cl_2 over UCl_4 heated to $300\text{--}500^\circ\text{C}$. It has been found that the chlorine-uranium ratio of the sublimate changes with tem-

perature. (39) The advantage of this method is the relatively low temperature, which makes a glass apparatus possible. The disadvantage of the method is the fact that the higher uranium chlorides are fine powders and are difficult to handle. The final step of this method is the reconversion to UCl_4 , which is accomplished by heating the higher chlorides in a stream of inert gas at 150°C . (13,16) A method for converting 200 grams per hour of UCl_4 to UCl_5 has been worked out. (40)

III. Uranium Pentachloride

The preparation of UCl_5 from oxides of uranium by use of suitable chlorinating agents has been studied in considerable detail (3, 4, 41, 42, 43, 44, 45, 46). The method can be outlined as follows: 250 grams of UO_3 , 1000 cc CCl_4 and 100 grams UCl_5 (the coked material from a previous run) are placed in a stainless steel autoclave which is heated quickly to 115°C in an oil bath. CCl_4 and COCl_2 are bled out to keep the temperature at $100\text{--}102^\circ$ for 1 hour. Then the oil bath is heated to 160°C and reducing the pressure to fall to 100 psi. It is finally allowed to gradually drop to zero gauge pressure in 30 minutes. Excess CCl_4 is distilled out and the apparatus cooled and filled with dry CO_2 . The total time required is about five hours and the yield consists of 300 grams of very pure crystals of UCl_5 plus 150 grams of a caked material. This latter UCl_5 is used as a catalyst in subsequent reactions. The UO_3 used in the above process is best prepared (12, 41, 42) by calcining UO_4 at 350°C . It is finely ground and has a bulk density of about 1.

A similar method of preparation involves the refluxing of UO_3 with CCl_4 for 72 hours to give complete conversion to UCl_5 . (41) In repeat experiments very poor yields of UCl_5 were obtained by this method. (16)

Another method of preparing UCl_5 is the chlorination of UCl_4 . A continuously operating reactor for this chlorination has been used. (40, 47) UCl_4 is fed into the reacting chamber by a screw feed and at the temperature of the reactor (550°C) UCl_4 and Cl_2 react to form UCl_5 . The main portion of the UCl_5 collects in a 12 liter flask. This is followed by a Cottrell precipitator to stop fine UCl_5 dust. The Cl_2 is pumped through the system with about $\frac{1}{2}$ inch of CCl_4 pressure at the rate of 100-200 liters per hour. Material which analyses 99.8% UCl_5 is sublimed at the rate of 150-200 grams per hour. Maximum production depends on the maximum heat transfer to the UCl_4 , maximum surface of the UCl_4 and optimum Cl_2 velocity.

The Cl/U ratio in sublimates of higher chlorides has been found to change with temperature (39) and it appeared that UCl_5 did not act like a definite compound. However, in the experiments giving these results, the vapors of higher chlorides produced were not rapidly cooled and the UCl_5 may have decomposed during the experiments.

UCl_5 produced by the chlorination of UCl_4 is usually a fine brown powder. In a very slow stream of Cl_2 it sublimes as green crystals. It is produced as green crystals by the bomb reaction discussed above. The melting point has been estimated as 300°C . (6) The density of UCl_5 is

3.81 g/cc as measured by the displacement of benzene. (48) The extreme deliquescence of UCl_5 was discussed in the previous section. It fumes badly in moist air and immediately turns green. It is insoluble in benzene, xylene, and isopropyl ether. (5) It reacts immediately with formamide, dioxane, ethyl acetate and methyl alcohol. A slow reaction takes place with chloroform, acetophenone and chlorobenzene. Table III gives the solubilities of UCl_5 in CCl_4 . (49)

TABLE III

Solubility of UCl_5 in CCl_4

<u>Temperature</u>	<u>Solubility in g/100 g Soln.</u>
-16°C	0.29
0	0.45
22.8	0.94
25	1.04
70	5.3

UCl_5 is sparingly soluble in liquid Cl_2 and reacts with CCl_2F_2 , CClF_3 and $\text{C}_2\text{F}_3\text{Cl}_3$. (49)

The vapor pressure of UCl_5 at room temperature has been estimated as less than 10^{-7} mm from the fact that there is no sublimation to a liquid air trap in 4 hours. (50) Another study (51) sets the vapor pressure as much less than 0.01 mm. It also gives 0.01 mm as the partial pressure of Cl_2 over UCl_5 at 20°C in a N_2 atmosphere and 0.1 mm as the partial pressure of Cl_2 at 65°C. Water vapor appears to have no effect on the observed pressure. A study of the kinetics of decomposition of the UCl_4 - UCl_5 - UCl_6 system covers the following reactions: (50)

The disproportionation of UCl_5 according to reaction 2 begins at approximately 50°C. It was found that the decompositions of UCl_5 and UCl_6 occur in the solid phase and not in vapor state. There are indications of two forms of UCl_6 solid.

The constants are of the order of magnitude of 10^{-3} to 0.1 mm of Hg in the temperature interval 130-180°C and $K_1 > K_2 > K_3$. The activation energies from a plot of $\log K$ vs $1/T$ gives for (1) 40 K cal/mol and for (2) and (3), 28 K cal/mol.

Due to the hygroscopic nature of the halides, especially UCl_5 and UCl_6 , precaution must be taken to prevent loss of HCl before analysis. The technique of transferring samples in a dry box and then dissolving the solids in CCl_4 works well. The halide is extracted from CCl_4 with water and excess CCl_4 driven off by heating. Another technique (52) is to freeze 25 cc of dilute H_2SO_4 in a 500 cc glass stoppered Erlenmeyer, cool it in dry ice, transfer sample of UCl_x , stopper and then allow to warm up slowly. If water is added directly, there is violent fuming and considerable loss of HCl results.

IV. Uranium Hexachloride

UCl_6 was first prepared by the Berkeley group and reported in January 1943. (53) It is made by the disproportionation of UCl_5 when it is heated in a vacuum of less than 10^{-3} mm. The UCl_6 collects on a cold finger above the UCl_5 as fine black (or dark green) crystals. The density, as determined by displacement of benzene, is 1.56 g/cc. (54) The melting point is estimated as $177.5 \pm 2.5^\circ\text{C}$. (55) Stainless steel equipment is used in large scale production of UCl_6 from UCl_5 (56). The difficulty of fine powdered UCl_5 blowing into the receiving flask is eliminated by treating it with CCl_4 first. (56, 57) Molybdenum, Ni, monel and Au, as well as stainless steel, are resistant to UCl_6 at 100°C . Brass, Al, nichrome and Ta are slightly attacked. Cu, Ag and Hg are badly corroded. (58)

Another method of preparing UCl_6 involves the use of UO_3 , CCl_4 and UCl_5 . (45, 49, 59, 60, 61) One mole of UO_2 , 2 moles UCl_5 plus CCl_4 and Cl_2 react at 80 - 115°C to give UCl_6 as the main product, but yields are not always theoretical.

The following solubilities are reported for UCl_6 (49)

		CCl_4	-18°C	2.64 g/100 g sol.
		CCl_4	0°	4.9
		CCl_4	20°	7.8
6.8% Cl_2	93.4%	CCl_4	-20°	2.4
12.5% Cl_2	87.5%	CCl_4	-20°	2.23
"	"	CCl_4	0°	3.98
		Cl_2	-33°	2.20
		Benzene	B.P.	Insoluble
		Chloroform	-24°	1.16 (no reaction)
		$\text{C}_2\text{F}_3\text{Cl}_3$	45°	1.86 (no reaction)

The vapor pressure of UCl_6 has been measured by the click gauge method (62, 63) and by the transpiration method. (64) The results of the first method are given in Table IV. The p-T relation can be expressed by the equation

$$\log_{10} p = \frac{2422}{T} + 6.6337 \text{ and } \Delta H = 11,120 \text{ cal/mol.}$$

The report on these data gives no information about the magnitude of Cl_2 decomposition pressure which becomes appreciable above 50°C . It can be seen in Figure 2 that the results by this method are considerably higher than those by the transpiration method. This is probably due to their failure to take the Cl_2 decomposition pressure into account.

TABLE IV

Vapor Pressure of UCl_6 (62) (Calculated Values)

<u>T.</u>	<u>P.</u>	<u>T.</u>	<u>P.</u>
0°C	0.005 mm	120°C	2.95 mm
20	0.023	140	5.75
40	0.08	160	11.07
60	0.22	180	18.6
80	0.59	200	32.35
100	1.35		

The data from the transpiration method are given in Table V and can be represented by the equation

$$\log_{10} P = \frac{-3715}{T} + 9.32$$

$$\Delta H = 17,000 \text{ cal/mo.}$$

TABLE V

<u>T$^\circ\text{C}$</u>	<u>V.P. in mm</u>
75.5 $^\circ\text{C}$	0.054 mm
98.5	0.22
120	0.90
138	1.85

V. Uranous Oxychloride UOCl_2

In the sublimation of UCl_4 in a stream of Cl_2 gas at 600° , a residue of yellow feather-like crystals remains. The yellow crystals are stable in air and dissolve slowly in water to form a green solution. They have been assumed to be UOCl_2 . Preliminary x-ray data (64) show the spacings along the needle axis to be 3.32 Å as derived from layer line spacings. Layer line spacings normal to the needle axis are about 40 Å but are not very clear. The crystal is probably tetragonal or hexagonal.

An attempt to make UOCl_2 by the reaction between $\text{UO}_2 \cdot 2 \text{US}_2$ and Cl_2 , which is successful for the preparation of the corresponding bromide, resulted only in formation of UO_2Cl_2 along with the higher chlorides of uranium. (33)

Anhydrous UOCl_2 has been prepared (68) by the reaction between UO_2 and excess molten UCl_4 . The UO_2 is added in small increments to the molten UCl_4 in an open end pyrex tube in an atmosphere of dry N_2 . The melt is cooled and ground up in a dry box and the excess UCl_4 removed by sublimation at 450° in vacuo. The product is completely soluble in water and analyzes as UOCl_2 . It is stable at $450\text{--}500^\circ$ but disproportionates to UO_2 and UCl_4 at $550\text{--}600^\circ\text{C}$.

VI. Uranyl Chloride UO_2Cl_2

UO_2Cl_2 is prepared as a yellow deliquescent powder by the reaction between O_2 and UCl_4 at $300\text{--}350^\circ\text{C}$. (11) Special active UO_2 prepared by the reduction of UO_3 with methane (66) will react with Cl_2 to produce UO_2Cl_2 . (67) At reaction temperatures above 500°C , its vapors condense as yellow needle-like crystals. The following x-ray data have been determined for UO_2Cl_2 : (65)

Needles: $a_0 = 8.71 \pm .01 \text{ \AA}$ $b_0 = 8.39 \pm 0.01$ $c_0 = 5.72 \pm 0.01$

Powder: $a_0 = 8.67 \pm .01 \text{ \AA}$ $b_0 = 8.39 \pm 0.01$ $c_0 = 5.70 \pm 0.01$

The x-ray diagram of the needles is different from that of the powder form, the former showing many maxima which are absent in the powder diagram.

The density of UO_2Cl_2 has been measured by the displacement of benzene and found to be 5.28 g/cc . The value from x-ray determination was 5.43 g/cc .

UO_2Cl_2 decomposes to UO_2 and Cl_2 when heated in a vacuum or a stream of inert gas above 400°C . In a stream of Cl_2 it melts to a red-brown liquid at about 500°C and a small amount sublimes at 900° in Cl_2 . However, in Cl_2 at 900° , there is almost complete decomposition to an oxide.

UO_2Cl_2 is insoluble in CCl_4 , xylene and benzene. It is insoluble in, but reacts slowly with, ethers and chloroform. It dissolves in alcohols, acetophenone, pyridine, and dioxane, but reacts with all of them. At 18°C , 100 parts of water dissolve 746 parts of UO_2Cl_2 hydrates.

The intermediate oxychlorides, UOCl_4 and UOCl_3 , have been found at low temperature (65°C) in the reaction of CCl_4 and $^{238}\text{UO}_3$. (14) They decompose at 115° while UCl_5 , which is the main product of the reaction, is not decomposed until 125°C .

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Part B

A SUMMARY OF THE PREPARATION, PURIFICATION, AND
PROPERTIES OF THE ANHYDROUS BROMIDES OF URANIUM

Jack Powell and Robert Nottorf

I. Uranium Tribromide

Uranium tribromide is a dark-brown, crystalline compound, which has a greenish appearance in the molten state. Its density is ~ 5.98 $26^\circ/4^\circ$ (1) and its melting point has been reported as low as $\sim 733^\circ\text{C}$. (2) (3) More recent data, including the phase diagram $\text{UBr}_3\text{-UBr}_4$, shows the melting point to be nearer 760°C . (36) (37) The following vapor pressure data have been obtained, although there is some evidence of disproportionation into UBr_2 and UBr_4 at temperatures above 900°C . (2)

Gas Saturation Method: (2)

<u>Temperature ($^\circ\text{C}$)</u>	<u>$1000/T^\circ\text{K}$</u>	<u>Vapor Pressure (mm Hg)</u>
915	.842	0.30
1015	.776	1.9
1062	.749	3.1
1124	.716	6.6

Effusion Method: (3) (best values)

<u>Temperature ($^\circ\text{C}$)</u>	<u>$1000/T^\circ\text{K}$</u>	<u>Vapor Pressure (mm Hg)</u>
600	1.146	2×10^{-5}
650	1.083	1.6×10^{-4}
700	1.028	1.3×10^{-3}
750	0.976	8.0×10^{-3}
800	0.931	3.2×10^{-2}
850	0.890	1.6×10^{-1}
900	0.852	5×10^{-1}
950	0.818	1.6
1000	0.785	5.0

The heat of vaporization from these data is 68 kilocalories per mol.

It was found that the vapor pressure varied with different container materials. Molybdenum showed the least corrosion of all materials tested and probably gave the most reliable results. (3)

The tribromide is very hygroscopic and dissolves in water with the development of considerable heat and the evolution of hydrogen. (4) The solution is red-violet in color, but gradually turns green due to air-oxidation. When exposed to moist air, the compound rapidly loses HBr and deliquesces, turning first violet, then green, and eventually forming a dark green solution.

The solubility of UBr_3 has been examined to some extent. (5), (6), (7) In general, it can be said that UBr_3 dissolves in, forms stable solvates with, or in many cases reacts with, polar solvents including water, alcohol, acetone, acetic acid, ether, dioxane, nitrobenzene, formamide, and liquid ammonia. The solutions with water and dioxane are clear and relatively stable. The tribromide is essentially insoluble in non-polar organic solvents such as benzene, toluene, p-xylene, bromobenzene and ethyl bromide. It is also insoluble in such inorganic liquids as SnCl_4 , TiCl_4 and PCl_3 .

The methods of preparation are as follows:

The first method is said to give no compound lower than UBr_3 , (8), (9), but the most recent evidence shows some reduction below UBr_3 . (5), (10), (11) H_2 reduces UBr_4 at 500°C .

The second method requires that stoichiometric amounts of U and Br_2 be sealed in a glass tube and heated together. The Br_2 is kept frozen at one end while the metal in the other end is heated to 300 - 500°C . When the Br_2 is used up the whole tube is heated at 500 - 550°C .

The last and best method consists of passing HBr over hydride and proceeds very smoothly. The following procedure and apparatus is recommended by the authors for kilogram lots. The apparatus used is shown in Figure II.

Five hundred grams of clean U turnings are placed in Chamber A. Another 10-20 grams of U turnings are placed, with some loose glass-wool packing, in chamber C to remove any free Br_2 from the HBr. H_2 , purified by passing over U turnings at 600 - 800°C , is admitted at O after the chamber has been evacuated. The metal is converted to UH_3 at 250°C with stopcock J closed. The end of the reaction may be determined by visual inspection of the turnings, or by observing whether the pressure falls when stopcock V is closed. Stopcock M is then closed and D and G are evacuated. 600-700 grams of dry Br_2 are carefully added through Q after closing stopcocks V and W. Note: The manometer cannot be used with HBr and Br_2 . The hood tube is temporarily connected to O and H_2 is ad-

APPARATUS FOR PREPARING UBr_3 IN KILOGRAM LOTS

FIGURE II

- A. Reaction Chamber $7\frac{1}{2} \times 40$ cm.
- B. Glass wool plug held by indentations, or a sintered glass disc
- C. Scrubber chamber $3\frac{1}{2} \times 10$ cm.
- D. Platinized asbestos chamber maintained at $400-500^\circ C$
- E. Resistance furnace $400-500^\circ C$
- F. Hinged resistance furnace $200-300^\circ C$
- G. Bromine bubbler of 300 ml capacity
- H. H_2SO_4 bubbler and trap
- I. Rubber tubing joint
- J. 2-way stopcock - 2 mm.
- K. Fairly large standard taper joint
- L. Medium standard taper joint
- M. 2-way stopcock - 2 mm.
- N. Small standard taper joint
- O. H_2 inlet and vacuum pump connection
- P. 3-way stopcock - 2 mm.
- Q. Funnel for adding Br_2
- R. 3-way stopcock - 2 mm.
- S. H_2 inlet
- T. Outlet tube connected to hood
- U. Mercury filled manometer (may be omitted)
- V. 2-way stopcock - 2 mm.
- W. 2-way stopcock - 2 mm.
- X. Glass wool plugs

mitted through tube S and stopcock R. Stopcock V is opened to allow HBr to escape into the hood. After the HBr generator has been thoroughly flushed with hydrogen and furnace E is at 400°C, stopcock V is closed and stopcock M is opened to allow HBr to flow into the reaction chamber. The temperature of furnace F is raised to 300°C. When the pressure in A is greater than atmospheric, stopcock J is opened to permit the exit of H₂. The apparatus must be agitated occasionally to prevent packing and channeling. This may be done by closing stopcocks P, M, and J, and detaching the apparatus at N and I. The space between M and P is then evacuated before continuing the reaction. The end of the reaction may be ascertained by weighing the apparatus.

II. Uranium Tetrabromide

Uranium tetrabromide ranges in color from light tan to dark brown, depending on the size of its crystals. Its density, according to Richards and Merigold, (15) is 4.84 21°/4°. However, the density recently observed was 5.33 26°/4°. (1) It melts at 519 ± 2°C (16), (17) and boils at 765°C (34) with decomposition in N₂. The following vapor pressure data have been obtained.

Transpiration Method: (17) (from V.P. Curve)

<u>Temperature (°C)</u>	<u>1000/T°K</u>	<u>Vapor Pressure (mm Hg)</u>
450	1.383	0.30
475	1.338	0.95
500	1.294	2.85
525	1.253	9.15
550	1.215	13.5
575	1.180	24.0
600	1.146	40.8
625	1.113	70.1

A mathematical treatment of the vapor pressure data gives the following equations of state:

$$\text{For sublimation } \log P_{\text{mm}} = \frac{-10,900}{T} + 14.56$$

$$\text{For vaporization } \log P_{\text{mm}} = \frac{-7,060}{T} + 9.71$$

$$\Delta H_{\text{sublimation}} = 50,000 \text{ calories/mol.}$$

$$\Delta H_{\text{vaporization}} = 32,300 \text{ calories/mol.}$$

$$\Delta H_{\text{fusion}} = 17,700 \text{ calories/mol.}$$

$$\text{M.P. from graph} = 520^\circ\text{C}$$

$$\text{B.P. calculated} = 761^\circ\text{C}$$

$$\text{Trouton's constant } \Delta H/T_{\text{B.P.}} = 31.0$$

$$\text{Hildebrand's constant} = 32.8$$

In Hildebrand's constant, the boiling temperature is replaced by the temperature at which the equilibrium vapor concentration is 0.005 mols/l.

It is encouraging that the calculated melting and boiling points are in close agreement with the actual values.

Effusion Method: (18), (19), (35)

<u>Temperature (°C)</u>	<u>1000/T°K</u>	<u>Vapor Pressure (mm.Hg)</u>
300	1.745	1.08×10^{-4}
330	1.660	8.45×10^{-4}
		9.55×10^{-4}
350	1.605	3.08×10^{-3}
		3.24×10^{-3}
		3.33×10^{-3}
365	1.567	5.61×10^{-3}
375	1.543	1.27×10^{-2}
400	1.486	2.25×10^{-2}
	1.486	6.23×10^{-2}
450	1.383	2.9×10^{-1}

The tetrabromide is very hygroscopic and dissolves in water with the development of considerable heat. The resulting solution is emerald green. When exposed to moist air, the dry UBr_4 rapidly loses HBr and deliquesces, turning green on the surface and eventually forming a green solution.

The solubility of UBr_4 in various solvents has been studied to a considerable extent. (6), (7), (11), (15), (18), (20) In general, it may be said that UBr_4 dissolves in, forms stable solvates with, or in many cases reacts with, polar solvents. Notable examples are water, methyl alcohol, ethyl alcohol, isopropyl alcohol, phenol, aniline, n-butyl aniline, methyl acetate, ethyl acetate, amyl acetate, acetone, acetic acid, acetamide, dioxane, pyridine, nitrobenzene, nitromethane, diethyl ether, liquid ammonia, acetonitrile and benzonitrile. The solutions with water, methyl alcohol, ethyl alcohol, methyl acetate, ethyl acetate, acetic acid, acetamide, acetonitrile, benzonitrile and dioxane are clear and relatively stable. It neither reacts with nor dissolves to any appreciable extent in hydrocarbons and other non-polar organic solvents such as n-heptane, kerosene, benzene, toluene, p-xylene, tetralin, naphthalene, hexaethylbenzene, dimethylaniline, triethylamine and tetrabromide reacted with UBr_4 . (11) UBr_4 is also insoluble in a number of inorganic liquids, including PCl_3 , POCl_3 , SnCl_4 , TiCl_4 and Br_2 .

Uranium tetrabromide can be prepared by the following reactions:

- (1) $2 \text{ UBr}_3 + \text{Br}_2 = 2 \text{ UBr}_4$ (1), (21), (22)
- (2) $\text{UO}_2 + 2\text{C} + 2 \text{ Br}_2 = \text{UBr}_4 + 2 \text{ CO}$ (8), (9)
- (3) $\text{U}_3\text{O}_8 + 8\text{C} + 6 \text{ Br}_2 = 3 \text{ UBr}_4 + 8 \text{ CO}$ (8), (9)
- (4) $2 \text{ UH}_3 + 7 \text{ Br}_2 + 2 \text{ UBr}_4 + 6 \text{ HBr}$ (12)
- (5) $\text{UN}_2 + 2 \text{ Br}_2 + \text{UBr}_4 + \text{N}_2$ (17)
- (6) $\text{UC}_2 + 2 \text{ Br}_2 = \text{UBr}_4 + 2 \text{ C}$ (21)
- (7) $\text{US}_2 + 3 \text{ Br}_2 = \text{UBr}_4 + \text{S}_2\text{Br}_2$ (19), (21)
- (8) $\text{U}_3\text{O}_2\text{S}_4 + 6 \text{ Br}_2 = 2 \text{ UOBr}_2 + \text{UBr}_4 + 2 \text{ S}_2\text{Br}_2$ (17), (21), (23)
- (9) $2 \text{ UOBr}_2 + \text{heat} = \text{UBr}_4 + \text{UO}_2$ (21), (22), (23)
- (10) $\text{U} + 2 \text{ Br}_2 = \text{UBr}_4$ (23)

Methods 1 and 10 are recommended for the preparation of kilogram lots of UBr_4 and will be described in some detail. Methods 2-9 will be described only briefly.

(1) A kilogram of UBr_3 is prepared as described in the section on UBr_3 . The H_2 is replaced by N_2 which has been purified by passing over UN_2 at 600-700°C. Bubbler G is charged with 250 grams of Br_2 and flushed as previously described. The furnace E is allowed to cool. The mixture of N_2 and Br_2 is passed over the UBr_3 at 300°C with occasional shaking to prevent packing and channeling. The end of the reaction is determined by weighing the apparatus.

(2) and (3) UO_2 or U_3O_8 is mixed with excess carbon in a boat in a quartz tube and heated to a red heat. A stream of N_2 or other inert gas is bubbled through Br_2 and passed over the mixture. The UBr_4 condenses in a cooler portion of the tube.

(4) This method is not practical unless the UBr_4 is to be distilled as it forms. At lower temperatures, hot spots are developed which clog the apparatus. The reaction can be used in the quartz still, which will be described later.

(5) This reaction goes very smoothly at temperatures above 600°C. N_2 is used to carry in Br_2 and carry out the UBr_4 . This reaction can also be used in the quartz still.

(6) This reaction proceeds readily at 700-900°C in a stream of N_2 and Br_2 . However, it leaves a residue of fine C which may blow over and contaminate the product.

(7) This reaction goes smoothly above 200°C. The S_2Br_2 is carried off first and the UBr_4 formed can be distilled off by raising the temperature.

(8) and (9) U_3O_8 (27) (28) can be prepared from UO_2 or U_3O_8 by passing CS_2 and N_2 over it at 800-1000°C. This compound is heated to 400°C in a stream of Br_2 and N_2 . The S_2Br_2 distills out first. UBr_4 distills out at 600°C, leaving a residue of $UOBr_2$. At 800-1000°C the $UOBr_2$ decomposes into UO_2 and UBr_4 . The residue of UO_2 can be treated with CS_2 as before and recycled.

(10) Kilogram lots of UBr_4 can be prepared in a quartz still (Fig. IV) quite readily. 450 grams of clean U turnings are placed in bulb A. Joint G is sealed with "Apiezon W" and the system from H to N is evacuated. D is charged with 800 grams of Br_2 and flushed out through the hood tube P with He. The He should be purified by passing over U turnings at 600-800°C. After closing stopcock Q, stopcock N is opened to admit the He and Br_2 to the still. When the pressure in the still is greater than atmospheric and furnace F is at 650°C, stopcock H is opened. He is passed through the apparatus at the rate of 2 liters per minute for about 8 hours, or until all the Br_2 is used up. It is necessary to tap the still occasionally to prevent the plugging of tube R. The product consists of approximately one kilogram of fine brown crystals which condense in B and fall into C if the conditions are correctly adjusted.

The preparation of UBr_4 is confined almost entirely to glass or quartz apparatus, due to the corrosive properties of Br_2 and UBr_4 at high temperatures. Other materials tested (24, (25) include stainless steel, nickel, monel, chromel A, gold-plated nickel, gold-plated copper, platinum plated nickel and platinum plated copper. Of these, nickel, gold-plated nickel and gold-plated copper showed the least corrosion in UBr_4 .

III. Uranium Pentabromide

Uranium pentabromide has never been prepared in the pure state, if at all. An experiment has been described (8), (9) in which UBr_4 was heated at 230°C with excess Br_2 for a long time. No UBr_5 was formed. With temperatures up to 750°C no evidence of UBr_5 has been found in the distillation of UBr_4 with excess Br_2 . However, it has been reported in one instance (3) that UBr_5 may have been formed. UBr_3 containing some UBr_4 was distilled at 500-600°C in a vacuum. The material which collected in a region where the temperature was 50-100°C showed a Br/U ratio greater than 4. Under such conditions it appears unlikely that any free bromine could have remained adsorbed on the solid.

QUARTZ STILL FOR THE PREPARATION OF UF_4 IN KILOGRAM LOTS

FIGURE IV

- A. 500 ml quartz flask
- B. 1000ml quartz flask
- C. 1000 ml pyrex flask
- D. 300 ml bromine bubbler
- E. Nitrogen inlet
- F. 6 inch furnace --650°C
- G. "Apiezon W" seal between quartz and pyrex
- H. 2-way stopcock -- 2 mm
- I. Rubber or neoprene tube
- J. Cover -- remove for observation
- K. Aluminum foil reflector to insulate B
- L. Graded quartz to pyrex seal
- M. Small standard taper joint
- N. 2-way stopcock -- 2 mm
- O. 2-way stopcock -- 2 mm
- P. Hood outlet
- Q. H_2SO_4 bubbler to hood -- fairly large
- R. Opening which occasionally plugs up
- S. Glass wool plug to retain any fine powder

IV. Uranous Oxybromide (UOBr_2)

Uranous oxybromide consists of greenish yellow needles or a fine yellow to tan powder, depending upon its method of preparation. It is relatively air-stable and non-hygroscopic. It dissolves readily in water to give a clear green solution, which darkens gradually upon standing. X-ray data (22)(26) shows that it is a true compound and not a mixture of UO_2 and UBr_4 . Potentiometric titration of UOBr_2 with NaOH yields a curve very similar to the curve obtained when UBr_4 is titrated under the same conditions. Each mol of UOBr_2 requires two equivalents of NaOH while each mol of UBr_4 requires four equivalents of NaOH for neutralization. UOBr_2 (22) is stable and non-volatile when heated to 600°C in an inert atmosphere, but disproportionates at $800\text{--}1000^\circ\text{C}$ into UO_2 and UBr_4 . U_3O_8 is formed when it is heated in air.

The first UOBr_2 (22) was obtained as a feathery residue left behind during the distillation of crude UBr_4 . Later the compound was prepared as follows: (21)

The recommended procedure is to heat a boatful of $\text{U}_3\text{O}_2\text{S}_4$ at 600°C in a stream of N_2 and Br_2 , until no more S_2Br_2 or UBr_4 distills out. Upon cooling, the UOBr_2 is obtained as a tan or yellow powder. It is possible that UOBr_2 could be made from $\text{UO}_2 + \text{UBr}_4$ at the melting point of UBr_4 .

V. Uranyl Bromide (UO_2Br_2)

Previous references to the preparation of anhydrous UO_2Br_2 are open to some dispute. (8)(9) H. Hermann (29) and A. von Unruh (30) state that UO_2Br_2 is obtained simultaneously with UBr_4 by passing Br_2 vapor over a mixture of U_3O_8 and C. The work of Richards and Meri-gold, (15)(31) however, does not substantiate this fact. Likewise, anhydrous UO_2Br_2 is reported (8) as being yellow in color and more volatile than UBr_4 . Our own experience is that UO_2Br_2 is bright red, turning yellow when exposed to moisture, (16) and that it decomposes to UO_2 and Br_2 (32) when heated above $250\text{--}350^\circ\text{C}$ in an inert atmosphere. UO_2Br_2 is very hygroscopic and dissolves readily in water, ether and alcohol.

Several wet methods of preparing $\text{UO}_2\text{Br}_2 \cdot 7 \text{ H}_2\text{O}$ are known. (8)(9) It is reported (8)(9) that anhydrous UO_2Br_2 can be obtained by extracting the $\text{UO}_2\text{Br}_2 \cdot 7 \text{ H}_2\text{O}$ with ether and drying the solution with CaCl_2 and Na, or by treating with amyl alcohol and boiling.

UO_2Br_2 can be made by oxidizing UBr_4 with O_2 at 150°C . (16) The following data are submitted: (33)

	<u>Time (hrs.)</u>	<u>°C</u> <u>Temperature</u>	<u>Product</u>		<u>Based on Br-</u> <u>% UO₂Br₂</u>
			<u>% U</u>	<u>% Br</u>	
(1)	25	175	57.3	33.7	91
(2)	46	162	59.8	30.2	80
(3)	24	190-200	77.5	-	-
(4)	48	150-160	57.1	33.8	91
(5)	10	150-160	55.9	35.6	96
(6)	8	150-170 mols Br/mols U = 1.91			95½

With the exception of No. 3, the products were completely soluble in water, giving a clear yellow solution. This is a bit surprising in view of the fact that the difference between the analysis and 100% must be accounted for as an oxide of some sort. X-ray data showed no detectable UO₂, U₃O₈, UO₃ or UBr₄ to be present in the final product.

VI. UBr₃-UBr₄ System

The phase diagram (37) of the UBr₃-UBr₄ system is shown in Figure V. The data for this diagram were obtained from automatically recorded cooling curves of molten UBr₃-UBr₄ mixture. These data indicate a eutectic system with negligible solubility of UBr₄ in solid UBr₃, but appreciable solubility of UBr₃ in solid UBr₄. The data also indicate that the melting point of UBr₃ is near 760°C.

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