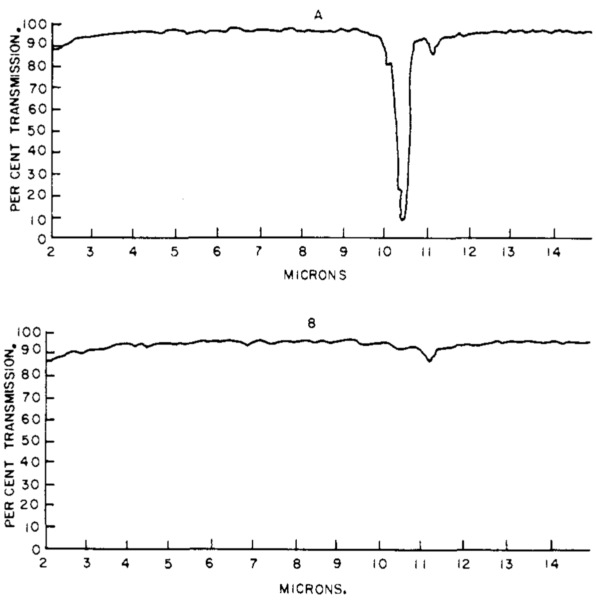

Fig. 1.—Infrared absorption spectrum of ReO_3Cl: upper (A), gaseous ReO_3Cl; lower (B), evacuated gas cell.

dark. In 1952 the microwave spectrum was studied by Amble, *et al.*,[8] who reported the structure as a symmetric top with an Re–Cl distance of 2.230 ± 0.004 Å., and Re–O distance of 1.761 ± 0.003 Å., and the Cl–Re–O angle as 108° 20′ ± 1°. Recently Eichhoff and Weigel[9] studied the Raman spectrum of rhenium oxychloride but encountered difficulty in photodecomposition of the sample. Some additional properties of this compound are reported in the present work.

Experimental

Rhenium(VII) oxide (Re_2O_7) readily is converted to rhenium(VI) oxide (ReO_3) by reduction with dioxane.[10] The reactions are

$$Re_2O_7 + xC_4H_8O_2 \longrightarrow Re_2O_7\cdot(C_4H_8O_2)_x$$

$$Re_2O_7\cdot(C_4H_8O_2)_x \xrightarrow{125-145^\circ} ReO_3 + \text{decomposition products}$$

The rhenium(VI) oxide is then allowed to react with chlorine in a dry combustion tube between 160 and 190°

$$2ReO_3 + Cl_2 \xrightarrow{160-190^\circ} 2ReO_3Cl$$

The yield obtained from these reactions is above 70%. The product is quite pure and is colored slightly yellow due to dissolved chlorine; this, however, may be removed readily by vacuum distillation leaving a clear colorless liquid boiling at 128° (uncor.). Analyses for chlorine were 12.74 and 12.71% as compared to the theoretical value of 13.14%. This slightly low value was caused by some hydrolysis in air during weighing.

Some precautions are necessary in the handling of this compound. Rhenium oxychloride reacts immediately with mercury and with ordinary stopcock grease; therefore, it must be trapped before reaching the diffusion pump. Furthermore, a special stopcock grease such as "Halocarbon grease" (Halocarbon Products Corporation) should be used to minimize the decomposition. Even this grease, however, caused some slight decomposition of the oxychloride leaving a purple colored substance, probably rhenium(VI) oxide (ReO_3).

To test the hypothesis that the purple color was due to this oxide, some ReO_3 was dissolved in a small amount of the oxychloride. It is interesting to note that a similar purple solution was formed.

The rhenium oxychloride can be kept without decomposition in a greaseless system of glass, Kovar and Monel. In this manner, we were able to keep the liquid colorless for several weeks.

Rhenium oxychloride is extremely reactive toward mercury, silver and a large number of organic compounds. Carbon tetrachloride, however, was found to be a good solvent, giving a clear, colorless, solution. The oxychloride does not appear to react with brass that has been first chlorinated, or with stainless steel.

The infrared spectrum of gaseous rhenium oxychloride was measured in a ten centimeter gas cell with potassium bromide windows, using a double beam Perkin–Elmer Recording Infrared Spectrometer Model 21. The spectrometer is shown in Fig. 1. Curve A is the absorption spectrum of the vapor in the cell and curve B is the absorption spectrum of the cell after removal of the oxychloride. The vapor pressure as measured with a Bourdon gage is 4.5 ± 0.5 mm. of mercury at room temperature. The vapor density of rhenium oxychloride at room temperature is 6.5×10^{-5} g./ml. (average of two determinations). Assuming the ideal gas law, the experimental molecular weight was 268 g. compared to a theoretical value of 270 g.

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[8] E. Amble, S. L. Miller, A. L. Schawlow and C. H. Towner, *J. Chem. Phys.*, **20**, 192 (1952).

[9] H. J. Eichhoff and F. Weigel, *Z. anorg. allgem. Chem.*, **275**, 267 (1954).

[10] L. F. Audrieth, Editor-in-chief; "Inorganic Syntheses," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1950, p. 186.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

The Thermal Decomposition of Uranium Peroxide, $UO_4\cdot 2H_2O$

BY JAMES E. BOGGS AND MUNZIR EL-CHEHABI

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$UO_4\cdot 2H_2O$ decomposes slowly in the temperature range 90–195° to form a different peroxide, U_2O_7. The rate of this reaction has been followed and the properties of U_2O_7, which has not been isolated previously, have been investigated.

Uranium peroxide, $UO_4\cdot 2H_2O$, has been known since 1876[1] and has been subjected to intensive investigation in recent years. Nevertheless, its constitution is still unknown, some authors considering it to be a true peroxide hydrate, others a peroxy acid, and others an addition compound of uranium oxide, $UO_3\cdot H_2O_2\cdot H_2O$.

The existence of one other peroxide of uranium, U_2O_7, has been suggested. Evidence for a hydrated form of this substance was found by Hüttig and von Schroeder[2] in their experiments on the decomposition of hydrated UO_4. Later, Kraus[3] ob-

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[1] T. Fairley, *Chem. News*, **33**, 237 (1876).

[2] G. F. Hüttig and E. von Schroeder, *Z. anorg. allgem. Chem.*, **121**, 243 (1922).

[3] C. A. Kraus, Manhattan District Project Report A-281, Sept. 7, 1942.

tained a red powder with the composition $UO_{3.14}$ to $UO_{3.38}$ by heating $UO_4 \cdot 2H_2O$ at 139° for 24 hours, then raising the temperature to 300°. Based on our experiments, this was probably a mixture of U_2O_7 and UO_3.

Hüttig and von Schroeder[2] studied the decomposition of $UO_4 \cdot xH_2O$ under 15 mm. water vapor pressure between 20 and 500°. They report that $UO_4 \cdot 4.5H_2O$ is stable up to about 55°, at which temperature water begins to be lost. At about 63°, one-half of the peroxide oxygen is lost, resulting in a composition corresponding to $U_2O_7 \cdot 6H_2O$. Between 63 and 162° the oxygen content remains unchanged while the water content gradually falls to $U_2O_7 \cdot 4H_2O$. At about 162°, water and oxygen are lost together, forming the hydrated oxide $UO_3 \cdot 0.5H_2O$. These results are very difficult to understand in view of the repeated success of many workers in preparing $UO_4 \cdot 2H_2O$ by drying freshly precipitated uranium peroxide at 100° for a short time.

More recently, Duval[4] has studied the decomposition of hydrated uranium peroxide, using a thermogravimetric balance. He concludes that water is smoothly driven off up to a temperature of 90°, at which point the composition corresponds to $UO_4 \cdot 2H_2O$. Between 90 and 180°, one molecule of H_2O_2 is lost, forming $UO_3 \cdot H_2O$. This is followed by the gradual loss of water, leaving anhydrous UO_3. From this he concludes that "uranium peroxide" must really be $UO_3 \cdot H_2O_2 \cdot H_2O$, although, as he points out, it is surprising that a substance containing a combined molecule of hydrogen peroxide is still relatively stable in the 100° region.

We have reinvestigated the decomposition of $UO_4 \cdot 2H_2O$ between 90 and 200° in a controlled atmosphere, making certain that the time of heating was adequate to ensure equilibrium.

Experimental

Materials.—Hydrated uranium peroxide was precipitated from $UO_2(NO_3)_2 \cdot 6H_2O$ (Calcd.: U, 47.4. Found: U, 47.5) purchased from Baker Chemical Co., using the procedure described by Watt, Achorn and Marley.[5] The resulting precipitate was washed with distilled water, dried at 100° for 4 hours, and stored over $CaCl_2$. (Calcd. for $UO_4 \cdot 2H_2O$: U, 70.4; peroxidic oxygen, 9.46. Found: U, 69.9; peroxidic oxygen, 9.25.)

Analytical Methods.—Uranium was determined either by ignition to U_3O_8[6] or by a volumetric method.[7] Peroxidic oxygen was determined by dissolving the compound in dilute sulfuric acid and titrating with potassium permanganate.

Experimental Method.—A tube furnace was constructed, the temperature of which could be regulated and maintained within ±0.5° by means of an automatic controller. A stream of oxygen or air was allowed to bubble through water at a controlled temperature, below the temperature of the room, in order to pick up a controlled quantity of water vapor, then passed over a sample of 2 to 2.5 g. of $UO_4 \cdot 2H_2O$ in a porcelain boat in the furnace. Samples of the decomposed uranium peroxide were removed periodically and analyzed for peroxidic oxygen. These analyses were checked at intervals by analysis for uranium and by determination of the total weight loss.

Results

The first experiments were performed by heating $UO_4 \cdot 2H_2O$ at a constant temperature in an atmosphere of oxygen containing 30 mm. water vapor pressure. Subsequent experiments showed that the same results were obtained using an atmosphere of air instead of oxygen and using water vapor pressures down to 8 mm. All of the experiments at temperatures up to 195° showed the slow decomposition of $UO_4 \cdot 2H_2O$ according to the equation

$$4UO_4 \cdot 2H_2O \longrightarrow 2U_2O_7 + O_2 + 8H_2O \qquad (1)$$

The reaction was followed to completion at temperatures of 130° and above. At lower temperatures, down to 90°, the reaction was still incomplete after a month of heating at constant temperature, but the resulting mixture showed the characteristic properties of U_2O_7.

Pure U_2O_7 (Calcd.: U, 80.96. Found: U, 80.72) was an orange hygroscopic solid which decomposed to UO_3 and oxygen gas in contact with water, and to uranyl salts and oxygen gas in contact with acids. The addition of U_2O_7 to acid permanganate solutions did not decolorize them, although oxygen was liberated. At higher temperatures U_2O_7 slowly loses oxygen to form UO_3. A weighed sample of U_2O_7 was added to dilute sulfuric acid and the oxygen released was collected. The volume obtained was 94% of that predicted from the equation

$$2U_2O_7 + 8H^+ \longrightarrow 4UO_2^{++} + 4H_2O + O_2$$

and the remaining 6% can be accounted for by solubility in the water.

U_2O_7 was pelleted with KBr and the infrared spectrum scanned between 2 and 16 μ on a Baird model 4–55 recording spectrophotometer. In addition to the usual absorption above 10 μ, which can be attributed to the U–O bond, U_2O_7 showed a sharp peak at 7.1–7.2 μ. This peak was not found in UO_3 or $UO_4 \cdot 2H_2O$.

The time required for reaction 1 to reach completion is very long. As an illustration, the data at 130° are presented in Table I. The $KMnO_4$ titration used in the analysis determined the peroxidic oxygen in the undecomposed $UO_4 \cdot 2H_2O$, but not that in the U_2O_7 produced. Even at 90°, reaction 1 occurred very slowly, as evidenced by the evolution of oxygen when $UO_4 \cdot 2H_2O$ which had been heated at this temperature for a long time

TABLE I

RATE OF CONVERSION OF $UO_4 \cdot 2H_2O$ TO U_2O_7 AT 130°

Time, hr.	$\%UO_4 \cdot 2H_2O$ remaining	$k \times 10^2$ (hr.$^{-1}$)
51	51.1	1.32
68	35.4	1.53
92	23.3	1.58
116	18.4	1.46
179	9.60	1.31
228	6.31	1.21
275	3.42	1.37
	Av.	1.40

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(4) C. Duval, *Anal. Chem. Acta*, **3**, 337 (1949).

(5) G. W. Watt, S. L. Achorn and J. L. Marley, THIS JOURNAL, **72**, 3341 (1950).

(6) W. W. Scott, "Standard Methods of Chemical Analysis," Vol. 1, 5th ed., D. Van Nostrand Co., New York, N. Y., 1939, p. 1022.

(7) U. S. Atomic Energy Commission Laboratory, New Brunswick, N. J., "Manual of Analytical Methods for the Determination of Uranium and Thorium in their Ores," U. S. Govt. Printing Office, Washington, D. C., 1955, p. 1.

was added to water. At temperatures of 200° and above, the decomposition of $UO_4 \cdot 2H_2O$ leads to UO_3 without the formation of U_2O_7.

The rate of decomposition of $UO_4 \cdot 2H_2O$ to U_2O_7 was found to give surprisingly good agreement with first-order kinetics, the rate of decomposition being proportional to the quantity of undecomposed peroxide. Table I shows the first-order rate constant calculated at 130°, the agreement being as good as could be expected from the accuracy of the measurements. In a similar manner the rate constant was found to be 4.4×10^{-4} hr.$^{-1}$ at 100°, 4.0×10^{-3} hr.$^{-1}$ at 120°, and 1.3×10^{-1} hr.$^{-1}$ at 150°. An Arrhenius plot of these data gives a very good fit to a straight line, from which the activation energy can be calculated to be 35 kcal./mole. It is questionable whether such good results would have been obtained if preparations of radically different crystal size had been used.

Discussion

The results obtained in this investigation are in striking disagreement with those reported by Duval[4] and in the earlier work by Hüttig and von Schroeder.[2] The explanation may lie in the extremely long time required for reaction 1 to reach completion. In the thermogravimetric method used by Duval, sufficient time for reaction 1 to reach completion could not possibly have been allowed, and Hüttig and von Schroeder do not state the length of time they heated their samples.

It may also be significant that both Hüttig and von Schroeder and Duval started with moist UO_4, containing an amount of water in excess of that required by the formula $UO_4 \cdot 2H_2O$, while in this investigation dried $UO_4 \cdot 2H_2O$ was employed.

On the basis of our experiments it may be concluded that $UO_4 \cdot 2H_2O$ decomposes to U_2O_7 in the temperature range between 90 and 195° and that the decomposition reaction does not give any evidence to support the formulation of uranium peroxide as $UO_3 \cdot H_2O_2 \cdot H_2O$.

AUSTIN 12, TEXAS

[CONTRIBUTION FROM THE LINCOLN LABORATORY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Hydrolysis of $A^{III}B^V$ Intermetallic Compounds[1]

BY J. A. KAFALAS, H. C. GATOS AND M. J. BUTTON

RECEIVED APRIL 3, 1957

$A^{III}B^V$ intermetallic compounds hydrolyze to a varying degree. Phosphides hydrolyze readily in acid media at room temperature with formation of phosphine. Arsenides and antimonides hydrolyze to a lesser extent.

Intermetallic compounds of the type $A^{III}B^V$ (InSb, GaAs, etc.) have become of considerable importance in recent years because of their semi-conducting properties.[2] During and after their preparation these compounds are generally brought into contact with aqueous media. They are usually prepared, for example, using an excess of constituent A; A is subsequently leached by an acid which does not appreciably attack the compound itself. Furthermore, for certain applications the crystal surfaces are treated with acid or basic solutions. The purpose of this study was to determine whether the above intermetallic compounds hydrolyze in aqueous media to form highly toxic hydrides of the type B^VH_3 (*viz.*, PH_3, AsH_3, SbH_3) according to the reaction

$$A^{III}B^V + 3H_2O \longrightarrow A^{III}(OH)_3 + B^VH_3$$

Preparation of Samples.—The representative intermetallic compounds used were InP, GaAs and GaSb, containing radioactive P, As and Sb, respectively. They were prepared as follows.

InP.—Elementary P, containing P^{32}, and In were placed in a quartz tube which was subsequently evacuated and sealed off. The mixture was then heated for one hour at 1050°.[3] The resulting sample was treated briefly with cold concentrated HNO_3 in order to remove the excess indium. An X-ray powder pattern confirmed the formation of InP. The radioactive P^{32} was obtained from $Ca_3(PO_4)_2$, containing P^{32}, by reduction with charcoal and SiO_2 at 1300°.

GaAs.—Elementary arsenic containing radioactive As^{73-74} together with non-radioactive GaAs was placed in a quartz tube which was then evacuated and sealed off. The end of the tube containing the GaAs was heated for several hours above the melting point (1280°) of GaAs. This treatment ensured homogeneous distribution of radioactive arsenic throughout the GaAs. The radioactive arsenic was obtained from radioactive $AsCl_3$ by reduction with H_3PO_2 and $SnCl_2$.

GaSb.—Radioactive Sb^{125} was homogeneously distributed in GaSb in the manner described for GaAs (m.p. of GaSb 725°). The radioactive antimony was obtained from $SbCl_3$ by reduction with iron and $SnCl_2$ in 16% HCl solution.

Experimental Technique.—The above compounds were crushed to coarse powders and were employed in this form. Measurements of the radioactive content of weighed fractions showed that the radioactive species were distributed homogeneously throughout the samples.

The apparatus employed in this study is shown in Fig. 1. The various coarse powders were placed on a fritted disk F in the reaction chamber S. A solution of known *p*H was added through the funnel P and a moderate stream of nitrogen was bubbled through the solution and through the adsorption traps T_1 and T_2 which contained an oxidizing solution of iodine, KI and $NaHCO_3$. The stream of nitrogen was employed for the purpose of stirring the reaction mixture and for carrying any SbH_3, AsH_3, PH_3 or other volatile hydrides formed into the adsorption traps as rapidly as possible. The reaction chamber S was designed so that no radioactivity was carried into the traps other than that associated with the gaseous products. Several blank tests were performed in which chamber S contained a radioactive solution, but not radioactive gases. In all cases, the nitrogen stream carried no detectable radioactivity into the traps.

Each sample of the intermetallic compounds was exposed to the solution for 16 hours. Upon completion of each run,

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(1) The research reported in this document was supported jointly by the Army, Navy and Air Force under contract with Massachusetts Institute of Technology.

(2) L. Pincherle and J. M. Radcliffe, *Advances in Phys.*, **5**, 271 (1956).

(3) Because the vapor pressure of free P is very high at this temperature one end of the quartz tube was kept at a lower temperature. In this way explosions were prevented. Similar precautions were taken in the preparation of arsenides.