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 $UO_3 \cdot H_2O_2 \cdot H_2O$.

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

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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 $B^{V}H_3$ (*viz.*, PH_3, AsH_3, SbH_3) according to the reaction

$$A^{III}B^{V} + 3H_2O \longrightarrow A^{III}(OH)_3 + B^{V}H_3$$

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.

liquid samples were withdrawn from the adsorption traps and counted by means of a cylindrical, well-type scintillation counter. All experiments were performed at room temperature.

Results.—The results obtained are summarized in Table I. It can be seen that InP reacts readily in acid solutions to form volatile hydrides of phosphorus. This result is to be expected in view of the fact that PH_3 is best prepared from AlP and H_2SO_4.[4] PH_3 prepared in this way usually contains traces of P_2H_4. It is of interest to note that InP reacts with HCl solutions, dilute or hot concentrated HNO_3, but it does not react with concentrated HNO_3 at room temperature. In this respect InP behaves like germanium which exhibits chemical passivity in concentrated HNO_3.[5] Similarities in crystalline structure and physical properties between the $A^{III}B^{V}$ intermetallic compounds and the Group IV_A elements are already known.[2] GaAs reacts to a lesser extent in acid solutions than does InP. AsH_3 is presumably formed in this reaction; it is the only known hydride of arsenic and its preparation from arsenides, such as Zn_3As_2, with H_2SO_4 is well known.[6] GaAs, like InP, becomes passive in concentrated HNO_3 at room temperature. GaSb reacts to an even lesser extent in acid solutions than does GaAs. The formation of SbH_3 is known to take place by the action of H_2SO_4 on Sb–Mg alloys.[7] Apparently, SbH_3 can be prepared in any appreciable amounts in the presence of excessive nascent hydrogen.

TABLE I

FORMATION OF VOLATILE HYDRIDES BY HYDROLYSIS OF $A^{III}B^{V}$ INTERMETALLIC COMPOUNDS IN CONTACT WITH AQUEOUS MEDIA FOR 16 HOURS

Inter-metallic compd.	Soln. used	Amt. of hydride recovered, expressed in γ per cm.² of $A^{III}B^{V}$	Hydride
InP	10 *N* NaOH	N.S.[a]	PH_3
	1 *N* NaOH	N.S.	
	0.1 *N* NaOH	N.S.	
	Dist. H_2O	N.S.	
	0.1 *N* HCl	0.35	
	1 *N* HCl	45.0	
	10 *N* HCl	Gross amounts (samples dissolve readily)	
GaAs	1 *N* NaOH	N.S.	AsH_3
	0.1 *N* NaOH	N.S.	
	0.01 *N* NaOH	N.S.	
	Dist. H_2O	N.S.	
	0.1 *N* HCl	0.35	
	1.2 *N* HCl	0.35	
	12.0 *N* HCl	0.35	
GaSb	Dist. H_2O	N.S.	SbH_3
	0.06 *N* HCl	0.01	
	1.8 *N* HCl	0.01	
	6.1 *N* HCl	N.S.	
	12 *N* HCl	N.S.	

[a] Not significant, <0.005 microgram.

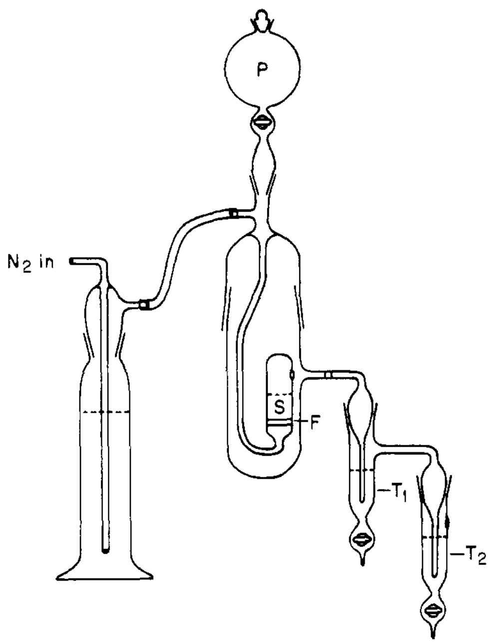

Fig. 1.—Apparatus for studying the hydrolysis of intermetallic compounds.

From the above it follows that InP and, in general, all $A^{III}P$ compounds should be considered as potential health hazards when in contact with acid solutions. Arsenides and antimonides also represent potential hazards in acid solutions but to a lesser degree than the corresponding phosphides.

It should be pointed out that the amounts of volatile hydrides recovered in the adsorption traps do not represent quantitatively the extent of hydrolysis of the above intermetallic compounds. Since the hydrides are rather unstable, particularly that of antimony, they undoubtedly undergo a certain amount of decomposition in the solution. In this study, however, we were concerned only with that portion of volatile products which persists in the gaseous phase and, thus, constitute a health hazard.

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(4) L. Moser and A. Brukl, *Z. anorg. Chem.*, **121**, 73 (1922).

(5) M. C. Cretella and H. C. Gatos, to be submitted for publication to the *J. Electrochem. Soc.*

(6) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Clarendon Press, Oxford, 1950, p. 760.

(7) Ref. 6, p. 761.