and more confidence should be put in this value for the total separation than in the others. The chlorine losses at the top of the column for a period of stable operation under conditions similar to those of experiments 2 and 3, amounted to only 0.1% of the chlorine refluxed and would not lessen the separation significantly.

Since the total separation was small, the single stage separation factor could only be estimated. It was assumed that the total separation obtained in the third experiment, which exhibited the most satisfactory column operation, was the best value, and that the 9 ft. exchange section had 8–20 stages. A single stage separation factor in the range 1.0024–1.006 is indicated, with the Cl^{37} concentrating in the gaseous chlorine.

Chloride ion is known to be relatively unhydrated and one would expect the Cl_2 to be the more "strongly bonded" state. This expectation is confirmed by the observed concentration of Cl^{37} in the gaseous phase. From spectroscopic data Urey[3] has calculated the separation factor between gaseous Cl_2 and free Cl atoms to be 1.0074, and the separation factor between gaseous Cl_2 and gaseous HCl to be 1.003 at 25°, with Cl^{37} concentrating in the Cl_2 molecules in both instances. In addition, Urey and co-workers[4] found a small enrichment of Cl^{37} in HCl gas for the system HCl(gas) *vs.* HCl (aqueous) indicating HCl gas to be more "strongly bonded" than Cl^-. Since Cl^- must interact to some extent with the solvent water it is reasonable to expect a lower separation factor for the present system than that between Cl_2 and the Cl atom, but one slightly larger than for the system Cl_2–HCl gas. Some work in this Laboratory indicated little if any isotopic fractionation between chlorine and its hydrolysis products (ClO^- and Cl^-). If this is the case, the separation factor between ClO^- and Cl_2 should be of the same magnitude as for the system Cl_2–Cl^- with Cl^{37} enriching in the ClO^- species.

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[3] H. C. Urey, *J. Chem. Soc.*, 574 (1947).

[4] H. C. Urey, A. Mills, I. Roberts, H. G. Thode and J. R. Huffman, *J. Chem. Phys.*, **7**, 138 (1939).

OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE

The Reported Oxychloride of Germanium, $GeOCl_2$

BY WALTER C. SCHUMB AND DONALD M. SMYTH

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Schwarz and Heinrich have reported the preparation of an oxychloride of germanium, $GeOCl_2$, by the exothermic reaction which results from the passage of trichlorogermane vapor over silver oxide in a vacuum system.[1] Analysis of the product, collected as droplets of oily liquid on the walls of the apparatus, indicated a composition close to $GeOCl_2$. The product was described, however, to exhibit several properties which are entirely unexpected in a compound of this type. The material was stated to be insoluble in all organic and inorganic solvents. This is not in accord with the high solubilities of the oxyhalides of silicon and that of the germanium oxychloride, Ge_2OCl_6. The product was said to undergo extremely rapid hydrolysis, but, instead of forming GeO_2, it yielded a precipitate of germanous hydroxide. This behavior is completely inconsistent with the assigned identity. Although germanium does have a well-defined oxidation state of two, it is obtained only by rather drastic conditions, and most certainly water alone is insufficient to effect a reduction of this type. The reported $GeOCl_2$ was non-volatile and underwent a slow, reversible decomposition at room temperature to give a citron-yellow solid and chlorine. The yellow solid was stated to be germanium monoxide, but the reasons for this identification are not obvious. Although a yellow form of GeO has recently been shown to exist,[2] it is unstable with respect to transformation into the more usual dark brown modification. Other properties of this product indicate further the peculiar tendency for it to be converted into divalent germanium and in each case the yellow solid product is reported to be GeO. A more obvious identity of this solid would seem to be that of germanium dichloride, which fits the reported properties much more closely than does GeO. In view of these peculiar properties it was felt that the material should be subjected to further examination.

The trichlorogermane for these experiments has been made most conveniently by the reaction of germanium monosulfide and hydrogen chloride at 50°. This reaction has been reported previously,[3] but the subsequent publication in "Inorganic Syntheses"[4] of a very simple preparation for GeS makes this reaction a much more convenient preparation for $GeHCl_3$ than those previously reported. It has been found, however, that the GeS prepared by the "Inorganic Syntheses" method is appreciably impure. Two separate lots were found to contain 10 and 20% chloride, respectively. Apparently this method does not lend itself to the preparation of GeS of high purity. Since the impurities did not react with HCl at the temperature required for the formation of $GeHCl_3$, the product was still useful for this preparation.

The reaction of $GeHCl_3$ with Ag_2O was carried out in a manner similar to that previously reported. The general observations were confirmed for the most part, and, in addition, it was found that insufficient product was usually formed for any identification. Several modifications of reaction technique were attempted and in every case the yield consisted of tiny droplets, widely scattered on the walls of the apparatus. Since it was impossible to collect enough of this material to weigh a sample for analysis, a more indirect approach was attempted. An apparatus was constructed and composed of two chambers, each of which contained a boat of Ag_2O and the reaction was allowed to proceed in the usual manner. As soon as the reaction ceased, the two sections were broken from the apparatus, the boats removed, and the tubes and the product which they contained were dropped into large erlenmeyer flasks fitted with ground glass stoppers. One of these contained standard iodine solution and the other distilled water. These were both allowed to stand for 48 hours to ensure complete reaction. The iodine solution was back-titrated with standard thiosulfate to determine divalent germanium and the total germanium content of the same sample was then determined

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[1] R. Schwarz and F. Heinrich, *Z. anorg. allgem. Chem.*, **209**, 273 (1930).

[2] W. L. Jolly and W. M. Latimer, THIS JOURNAL, **74**, 5751 (1952).

[3] L. M. Dennis and R. E. Hulse, *ibid.*, **52**, 3553 (1930).

[4] W. C. Fernelius, Editor, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 102.

by way of the sulfide, after a further oxidation with 3% H_2O_2. These two determinations indicated that the product had a divalent germanium-to-total germanium ratio of 1.04:1.00. The other sample was analyzed for chlorine as AgCl and germanium by way of the sulfide, and indicated a chlorine-to-germanium atomic ratio of 2.15:1.00.

These two ratios show clearly that the product of this reaction contains only divalent germanium and that sufficient chloride is present to satisfy all of the valence requirements of this germanium. The accuracy of the results is as good as can be expected since such small quantities were available for analysis. The evidence seems to indicate that the material is a new form of germanium dichloride, but whether this is a super-cooled liquid or a new structure has not been determined. The "decomposition" reported by Schwarz and Heinrich is apparently a transformation into the commonly observed form of $GeCl_2$, and this is borne out by the fact that no evolution of chlorine could be detected during the transformation, as would occur if it were $GeOCl_2$ decomposing into GeO and Cl_2.

The reaction of $GeHCl_3$ and oxygen also was studied. This reaction has been previously reported by Dennis, and the products were described as $GeCl_4$ and an unidentified clear, viscous oil which was present as a separate phase.[5] The reaction has been repeated by mixing trichlorogermane vapor, carried in a stream of dry helium, with dry oxygen in a reaction tube. The product consisted of two phases, as previously described, but only small quantities of the viscous oil were obtained. It was found to be insoluble in benzene and was separated from the $GeCl_4$ by an extraction with this solvent. An examination by the determination of the two ratios used above gave a divalent-to-total germanium ratio of 0.97:1.00 and a chlorine-to-germanium atomic ratio of 2.25:1.00. This is in close agreement with the results of the $GeHCl_3$–Ag_2O reaction and once again the product is most closely fitted by the formula $GeCl_2$.

The differences in the two reactions involving silver oxide and oxygen are few. The reaction of $GeHCl_3$ with oxygen was much slower and less vigorous as carried out here, but when pure oxygen reacts with liquid $GeHCl_3$ enough heat is liberated to cause the liquid to boil.[5] Since the reaction with silver oxide was highly exothermic, it is probable that the Ag_2O was decomposed to silver and oxygen rather rapidly. One very important function of the silver oxide is undoubtedly that of an acceptor for HCl. This reaction would give additional heat and aid in decomposing the $GeHCl_3$ to $GeCl_2$ and HCl by removing the HCl as it was formed.

Typical reactions which might occur in the two reactions studied are

$$2GeHCl_3 + 3Ag_2O \longrightarrow GeCl_4 + GeO_2 + 4Ag + 2AgCl + H_2O + \text{heat}$$

$$GeHCl_3 + \text{heat} \longrightarrow GeCl_2 + HCl$$

$$Ag_2O + 2HCl \longrightarrow 2AgCl + H_2O$$

$$2Ag_2O + \text{heat} \longrightarrow 4Ag + O_2$$

$$4GeHCl_3 + O_2 \longrightarrow 2GeCl_2 + 2GeCl_4 + 2H_2O$$

The second and fifth equations are the only ones of these which could occur during the reaction with oxygen gas and the last was used by Dennis to explain his results.[5] Dennis creates something of a paradox when he states that no HCl could be detected as a product of the oxygen reaction. It is not clear just how any reaction could occur without ultimately liberating HCl. It would appear that Dennis may have missed the HCl due to its extreme solubility in the germanium compounds.

The evidence presented here is in direct conflict with the previous claim for the preparation of $GeOCl_2$. The parallel nature of the reactions of trichlorogermane with silver oxide and with oxygen has been clearly exhibited, and it appears that the clear, viscous product of both reactions is a liquid modification of $GeCl_2$.

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DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE 39, MASSACHUSETTS

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On the Reaction of Europium Dichloride with Solutions of Hydrochloric Acid

BY C. T. STUBBLEFIELD AND L. EYRING

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Observations have been made for many years on the reactions of the rare earth dichlorides in acid solutions[1-4] In general, the previous investigations led to development of methods of separation of europium from the other rare earths and to determinations of oxidation potentials.

The purpose of the present study is to investigate the path of reaction of europium dichloride with various concentrations of hydrochloric acid saturated with hydrogen, oxygen or air.

Experimental Methods

Materials and Analysis.—The europium was obtained as 99.8% pure Eu_2O_3 from Research Chemicals. The dichloride was analyzed by a gravimetric chloride determination and was found to be pure $EuCl_2$.

Preparation of Dichloride.—Samarium and ytterbium trichlorides are prepared by the interaction of thionyl chloride vapor and the oxides at 400° for 24 hours in a simple and effective cycling system.[5] The same apparatus was used to prepare europium trichloride, but carbon tetrachloride replaced thionyl chloride as the chlorinator since the latter reactant produced some europium sulfide. The bright yellow trichloride thus prepared is rapidly and completely soluble in water without a trace of turbidity.

Europium dichloride was produced by hydrogen reduction of the trichloride in a quartz boat at 300° within six hours. The white $EuCl_2$ dissolves in dilute hydrochloric acid to give a slowly decomposing yellow solution.

Although a copious evolution of gas accompanies the solution of samarium or ytterbium dichloride in dilute hydrochloric acid, the volume of gas evolved when europium dichloride is dissolved depends upon the availability of dissolved oxygen gas and hydrogen ions.

Experimental Results.—The divalent europium ions may react by one of the paths

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