was boiled with reflux, the condenser being at −78°. The material decomposed slowly during this operation and the decomposition products were measured and analyzed. When attempts were made to conduct the distillation under atmospheric pressure, the material exploded. By conducting the distillation at pressures below 200 mm. (preferably below 100 mm.) it was possible to avoid an explosion. The decomposition was rapid enough, however, to permit the removal of products at a moderate rate. As the pentafluoropropionyl hypofluorite boiled with reflux, the temperature at the bottom of the still was measured with a thermocouple. In this manner pressure *vs.* boiling temperature measurements were made. Values are given in Table I. As the decomposition occurred successive cuts of the products were collected in small glass flasks.

TABLE I

VAPOR PRESSURE OF CF_3CF_2COOF

°C.	Mm.	°C.	Mm.	°C.	Mm.
−58.4	30	−44.5	79	−29.7	167
−54.9	37	−42.7	91	−28.6	177
−50.0	53	−41.9	96	−27.3	187
−46.8	67	−40.7	102	−25.4	208

The fluorine content of a middle cut from a distillation was determined by treating the gas with hot potassium and later titrating the fluoride ion in the reaction products. By this method a value of 62.4% fluorine was found. More extensive and complicated analyses of other samples permitted the fluorine content to be calculated. In one run the two middle cuts were found to contain 60.9% and 63.1% F and in another run 62.0% and 62.3% F (theoretical for C_2F_5-COOF, 62.6% F).

The more complex analysis involved the following steps: (1) measurement of the weight and volume of the sample, (a) as originally obtained, (b) after contact with and removal from air-free water, (c) after subsequent contact with and removal from sodium hydroxide solution; (2) titration of fluoride ion in the water and in the sodium hydroxide solutions resulting from this contact; (3) titration of the hydroxide ion and the carbonate ion remaining in the alkaline solution; (4) further examination of the part of the gas not absorbed by the water or caustic soda solution. These analyses led to the following conclusions: (1) The first and last fractions of decomposition products from a distillation contained some material, perhaps silicon tetrafluoride, which reacted with water to give fluoride ion. (2) Middle fractions contained only a little of this material and appeared to be uniform in composition, being composed of carbon dioxide (50% by volume) and a gas which was nearly all hexafluoroethane (50% by volume). (3) This fluorocarbon product had a density very close to 138 g. per G.M.V. Upon fractional distillation only hexafluoroethane was detected; however, small amounts of a less volatile fluorocarbon and of carbon tetrafluoride could have been present. When the vapor pressure of the whole fluorocarbon sample was measured using a static method, evidence was found for the presence of a small proportion of a material (probably CF_4) more volatile and less dense than hexafluoroethane. When the product boiled away the last part to distil had a density of 143. When the material was frozen and then allowed to warm slowly, it melted over a temperature range from −110 to −102° (melting point of C_2F_6, −100.1°).

A mass spectrometer was used to study the somewhat impure hexafluoroethane. Very strong peaks were found which corresponded to C_2F_8 and there were very weak lines at masses 150 and 169 which might have come from C_3F_8. Since the peaks due to CF_4 are also present in the mass spectrum of C_2F_6, no conclusion could be drawn about the presence or absence of a small amount of carbon tetrafluoride.

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WASHINGTON
SEATTLE 5, WASHINGTON

Some Physical Properties of the Deutero-germanes[1]

BY ALFRED H. ZELTMANN AND GEORGE C. FITZGIBBON

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Some deutero-germanes have been prepared in this Laboratory and a number of their physical properties measured. The results are summarized in Table I.

TABLE I

PHYSICAL PROPERTIES OF THE DEUTERO-GERMANES

Compound formula	M.p., °C.	B.p., °C.	$d^t{}_4$, g.	t, °C.	$-\Delta H$, cal./gram mole	B
GeD_4	−166.2	−89.2	1.684	−160.5	3744	7.327
Ge_2D_6	−107.9	28.4	2.184	−106.4	6483	7.579
Ge_3D_8	−100.3	110.5	2.618	− 99.9	7876	7.367

Experimental

Preparation.—The method of preparation was essentially that of Dennis, *et al.*,[2] used in the preparation of the ordinary germanes.

Deutero-hydrochloric acid, prepared[3a] by slowly adding D_2O to refluxing benzoyl chloride and diluted with D_2O to 4 *N*, was added dropwise to magnesium germanide, Mg_2Ge[2,3b] with frequent shaking. The resultant products were carried through a drying and purification train using dry helium gas.

Early runs indicated that thermal exchange of deuterium and hydrogen occurs between germanes and water. To prevent exchange heavy water was used in scrubbing towers which separated DCl and $GeDCl_3$ from the products. The products were then passed in succession over anhydrous calcium chloride and phosphoric acid anhydride to remove D_2O vapor. The products were collected in liquid nitrogen cold traps while the helium was allowed to escape. After collection the products were subjected to a fractionation in an all-glass vacuum system using Stock valves instead of stopcocks where possible.

Purified GeD_4 was prepared by maintaining a mixture of germanes at −155° with a Freon cold trap and then pumping a vacuum. While this method caused a loss of some GeD_4, it resulted in a purer product. The mixture of germanes was allowed to warm from −155 to −145° and maintained at this temperature where the vapor pressure of GeD_4 is about 10 mm. The distilled GeD_4 was collected in a bulb cooled with liquid nitrogen. This fractionation was repeated twice or until a satisfactory product resulted as shown by vapor pressure data.

Pure Ge_2D_6 was obtained by a similar procedure using the residual mixture of germanes. A vacuum was drawn while maintaining the mixture at −120° to remove any residual GeD_4. The mixture was then allowed to warm to −75° while surrounded by a $CHCl_3$-CCl_4 eutectic cooling mixture.[4] The distillate was collected in a bulb cooled with liquid nitrogen. This fractionation was also repeated several times.

Pure Ge_3D_8 was obtained by maintaining the mixture at −50° with a $CHCl_3$-CCl_4 bath while pumping a vacuum. A large portion of the product was lost, but this procedure was necessary in order to remove the last traces of Ge_2D_6. The temperature was allowed to increase to −20° and the Ge_3D_8 collected in a liquid nitrogen cold trap. This fractionation was repeated several times to yield a satisfactory product. An unidentified oily residue remained.

Mixtures of germanes were detected by taking vapor pressure data on a given sample before and after a fractionation. The fractionation procedure was repeated until separate fractions yielded identical results. Mass spectrometric

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[1] This document is based on work performed for the Atomic Energy Commission at Los Alamos Scientific Laboratory.

[2] L. M. Dennis, R. B. Corey and R. W. Moore, THIS JOURNAL, **46**, 657 (1924).

[3] (a) H. C. Brown and C. Groot, *ibid.*, **64**, 2223 (1942); (b) C. A. Kraus and E. S. Carney, *ibid.*, **56**, 765 (1934).

[4] Amer. Inst. of Physics, "Temperature, Its Measurement and Control," Reinhold Publ. Corp., New York, N. Y., 1941, p. 208.

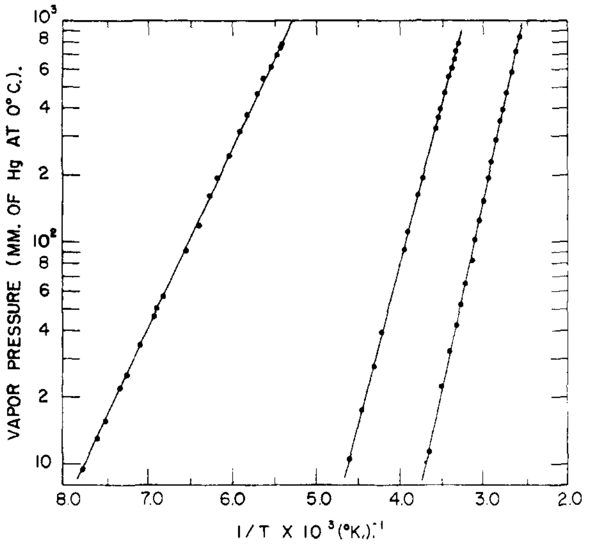

Fig. 1.

analyses showed that the deuterium isotope abundance was 99.58%.

Determination of Properties.—Low temperature measurements of vapor pressure were made using a cryostat with a constant liquid level device for the liquid nitrogen coolant. The cryostat was constructed according to details given by Scott and Brickwedde.[5] Temperature was controlled by maintaining the desired potential across a platinum resistance thermometer located inside the cryostat bath. When the temperature decreased, the resistance of the platinum thermometer also decreased and, therefore, the voltage across it was lowered. A 0–100 millivolt Brown Self-Balancing Electronik Strip Chart Recorder regulated heaters which controlled the temperature ±0.1°. The cryostat liquid bath was propane below −145° and Freon 12 or $CHCl_3$ above this temperature. Pressure was measured by means of an absolute mercury manometer, and all manometric pressures were corrected to 0° at sea level and 45° latitude. Measurements were carried out in a laboratory thermostated at 22°.

For temperatures 0° and above, either a bath of water or mineral oil was used and maintained at a constant temperature ±0.1°. The sample whose vapor pressure was being determined above 0° was sealed off in a tensiometer of the type described by Dennis, *et al.*[2] All temperatures were measured with a copper–constantan thermocouple which had been carefully standardized[6] at the following fixed points: oxygen boiling point, carbon dioxide sublimation point, and the freezing and boiling points of water.

Each vapor pressure plot is constructed from at least 20 individual measurements made between 10 mm. and 800 mm. pressure with results checked at selected points on separate samples. The data have been fitted by the least squares method to the equation

$$\log_{10} p = \frac{-\Delta H}{2.303RT} + B$$

where R = 1.987 calories per °C. per gram mole and ΔH is the latent heat of vaporization in calories per gram mole. The constants of this equation have been presented along with the other physical properties in Table I. From these equations the boiling points have been calculated.

Vapor densities were measured at room temperature and were found within experimental error to agree with the calculated values for GeD_4, Ge_2D_6 and Ge_3D_8 in which the deuterium isotopic abundance is 99.58%.

Melting points were measured using the drop ring method employed by Dennis, *et al.*[2] Triplicate determinations agreed within 0.2°.

Liquid density measurements were made as close to the melting point as was feasible because of the large temperature coefficient of expansion.

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LOS ALAMOS SCIENTIFIC LABORATORY
LOS ALAMOS, NEW MEXICO

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(5) R. B. Scott and F. G. Brickwedde, *Bureau of Standards J. Res.*, **6**, 401 (1931).

(6) Reference 4, p. 212.

The Chemistry of Thorium. VI.[1] Some Observations on the 5,7-Dihalo-8-quinolinol Chelates of Thorium

BY THERALD MOELLER AND M. VENKATA RAMANIAH

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In a previous communication,[1] it was pointed out that although the two thorium chelates with 8-quinolinol, $Th(C_9H_6NO)_4$ and $Th(C_9H_6NO)_4 \cdot C_9H_6NOH$, differ from each other in the solid state, they give absorption spectra differing only in intensities when dissolved in a variety of organic solvents. These data have been interpreted as indicating that the extra mole of 8-quinolinol in the 1 to 5 chelate is held by lattice forces. It has been of interest to extend these studies to the thorium chelates of several 5,7-dihalo-8-quinolinols. This extension has been prompted by desires to study other series of 8-quinolinol type addition compounds, previously limited to the simple 8-quinolinol derivatives of thorium,[1,2] uranium(VI),[2] plutonium(VI),[3] and scandium,[4] and to determine whether enhanced hydrolytic stabilities of the compound type in question could be achieved. Choice of 5,7-dihalo-8-quinolinols stemmed from an earlier observation of improvements in stabilities and extractabilities of tripositive rare earth metal chelates through use of the 5,7-dichloro material.[5] The investigation involved study of conditions for preparation of both 1 to 4 and 1 to 5 type chelates and measurements of absorption spectra in organic solvents.

Experimental

Materials Used.—The source of thorium ion was a sample of thorium nitrate 4-hydrate, obtained from the Lindsay Chemical Company and shown to be free from yttrium and the rare earth elements. Halogen substituted 8-quinolinols were reagent quality materials supplied by the Eastman Kodak Co. and the Matheson Co. They were recrystallized from acetone and ethanol prior to use. Reagent quality chloroform (containing *ca.* 1% ethanol by volume) and ethanol were used without treatment except as specified otherwise.

Thorium nitrate solutions were standardized gravimetrically by weighing as the oxide. The substituted 8-quinolinols were used as acetone solutions containing 3 g. of reagent per liter of solvent.

Apparatus.—All absorption spectra were measured at *ca.* 25° with a Cary Recording Spectrophotometer, using 5.0 cm. demountable cells with quartz windows. All *p*H measurements were made with a Beckman model G *p*H meter.

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(1) For the preceding communication in this series, see T. Moeller and M. V. Ramaniah, THIS JOURNAL, **75**, 3946 (1953).

(2) F. J. Frere, *ibid.*, **55**, 4362 (1933).

(3) B. G. Harvey, H. G. Heal, A. G. Maddock and E. L. Rawley, *J. Chem. Soc.*, 1010 (1947).

(4) L. Pokras and P. M. Bernays, THIS JOURNAL, **73**, 7 (1951).

(5) T. Moeller and D. E. Jackson, *Anal. Chem.*, **22**, 1393 (1950).