

[CONTRIBUTION NO. 639 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, AND FROM THE GEORGE FISHER BAKER LABORATORY OF CHEMISTRY OF CORNELL UNIVERSITY]

The Electron Diffraction Study of Digermane and Trigermane

BY LINUS PAULING, A. W. LAUBENGAYER AND J. L. HOARD

In order to obtain information about the covalent radius and bond angle of germanium we have prepared and analyzed electron diffraction photographs of digermane and trigermane, with the results described below.

Preparation and Purification of Substances.—

A mixture of the hydrides of germanium was prepared by the action of dilute hydrochloric acid on magnesium germanide which had been made from very pure germanium and magnesium.¹ This mixture of hydrides was then subjected to fractionation in a vacuum apparatus.² The sample was cooled with liquid air and all of the free hydrogen contaminating the hydrides was pumped off. The monogermane, GeH_4 , was removed by holding the hydrides at -130° and distilling off all of the material which was volatile at that temperature. The residue was warmed to -70° and the digermane, Ge_2H_6 , was distilled off. This fraction was found to possess the characteristic constants reported for digermane. The remaining material was freed of the last traces of digermane by distillation at -60° for several hours. The temperature was then raised to -20° and a fraction was collected. This fraction possessed the properties of pure trigermane, Ge_3H_8 .

Preparation of the Photographs.—The electron diffraction photographs were prepared in the usual manner.³ The sample of trigermane was allowed to vaporize into the evacuated apparatus for a minute or two at 0° to remove any residuum of digermane, and was then heated to about 20° for exposure of the photographs. The stopcock was held open for a few seconds before each exposure at this temperature. The entire sample of the substance was evaporated in the preparation of the series of photographs. About ten photographs were prepared and measured for each substance.

Analysis of the Photographs.—The photographs obtained for the two substances are closely similar in appearance. They show eight well-

defined rings, with the measured s_0 values and estimated intensity values given in Table I. The appearance of the rings does not differ greatly from that corresponding to a single $\sin ls/l_s$ curve; the intensity drop between the third ring and the fourth ring seems larger than for the other steps.

The radial distribution curve⁴ calculated for digermane with use of the c values given in the table, obtained from the estimated intensity values by multiplication by the factor $s^3e^{-As^2}$ as recommended by Schomaker and Degard,⁵ is given in Fig. 1. The curve shows a peak at 2.41 Å., representing the Ge-Ge distance. The other interatomic distances in the molecule are of less importance in the intensity function and are not apparent in the radial distribution curve.

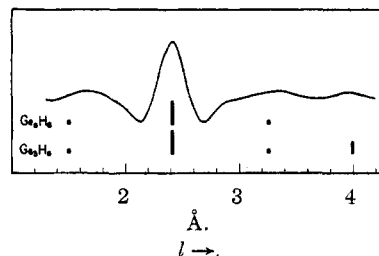


Fig. 1.

The simplified intensity curve corresponding to the model with Ge-Ge = 2.44 Å. and Ge-H = 1.52 Å. (the sum of single-bond covalent radii) and with all angles $109^\circ 28'$, shown in Fig. 2, agrees well with the photographs in appearance. The quantitative comparison given in Table I leads to the average value 2.40 Å. for the Ge-Ge distance, the first three s_0 values being ignored as unreliable.

The radial distribution curve for trigermane, for which the same I values were estimated as for digermane, is not appreciably different from that for the latter substance shown in Fig. 1, except that the Ge-Ge peak occurs at 2.42 Å. It is surprising that there is no definite indication of a Ge-Ge peak at 4.0 Å., corresponding to the distance between the two end germanium atoms. It

(1) L. M. Dennis, R. B. Corey and R. W. Moore, *THIS JOURNAL*, **46**, 658 (1924).

(2) A. W. Laubengayer and R. B. Corey, *J. Phys. Chem.*, **30**, 1043 (1926).

(3) See L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936),

(4) L. Pauling and L. O. Brockway, *THIS JOURNAL*, **57**, 2684 (1935).

(5) V. Schomaker and C. Degard, *ibid.*, to be published.

TABLE I
 ELECTRON DIFFRACTION DATA FOR DIGERMANE AND TRIGERMANE

Max.	Min.	l	c	Digermane			Trigermane		
				s_0	$s_0^{a^b}$	Ge-Ge	s_0	$s_0^{a^b}$	Ge-Ge
1	2	10	1	3.29	3.17	(2.35 Å.)	3.44	3.34	(2.37 Å.)
				4.59	4.43	(2.35)	4.52	4.31	(2.33)
2	3	9	5	5.97	5.80	(2.37)	5.91	5.68	(2.35)
				7.19	7.08	2.40	7.28	7.16	2.40
3	4	8	10	8.52	8.38	2.40	8.43	8.30	2.40
				9.83	9.60	2.38	9.80	9.41	2.34
4	5	6	10	11.13	10.84	2.38	11.11	11.03	2.42
				12.47	12.21	2.39	12.40	12.13	2.39
5	6	5	9	13.73	13.56	2.41	13.64	13.47	2.41
				15.00	14.88	2.42	14.93	14.94	2.44
6	7	4	6	16.29	16.10	2.41	16.20	16.03	2.42
				17.62	17.29	2.40	17.53	17.10	2.38
7	8	3	3	18.92	18.56	2.39	18.78	18.80	2.44
				20.24	20.00	2.41	20.11	19.97	2.42
8		2	1	21.56	21.34	2.42	21.25	21.24	2.44
Average						2.40 Å.			2.41 Å.
Radial distribution value						2.41 Å.			2.42 Å.

^a Calculated for the model with Ge-Ge = 2.44 Å., Ge-H = 1.52 Å., and all angles 109°28'. ^b Calculated for the model with Ge-Ge = 2.44 Å., Ge-H = 1.52 Å., angle Ge-Ge-Ge = 112°, angles H-Ge-Ge = 109°28'.

is possible that the bending frequency of the Ge-Ge-Ge chain is very low, and that in conse-

quence the longer Ge-Ge separation varies widely at room temperature, causing the peak to be flattened out.⁶ The possibility that the photographs obtained from the trigermane sample are really due to digermane has occurred to us. We

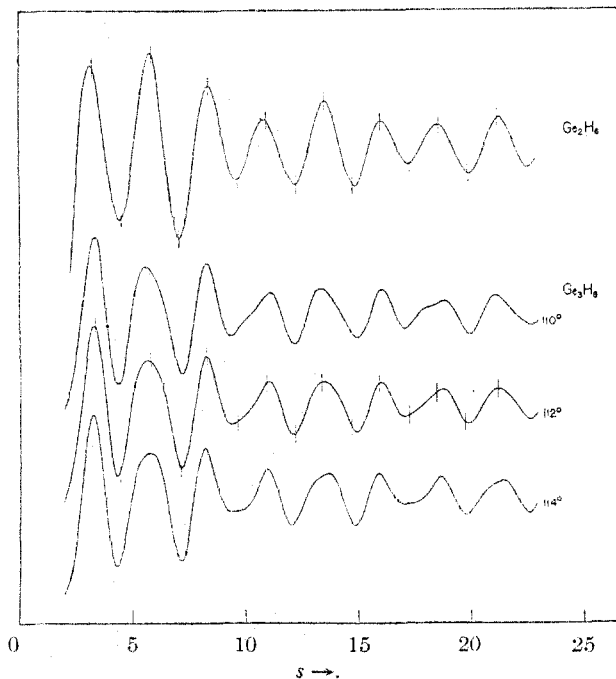


Fig. 2.

quence the longer Ge-Ge separation varies widely at room temperature, causing the peak to be flattened out.⁶ The possibility that the photographs obtained from the trigermane sample are really due to digermane has occurred to us. We

(6) Temperature effects of this kind will be discussed by Dr. V. Schomaker in a paper to be published soon.

believe, however, that the procedure followed was such as to make this unlikely. The radial distribution curve shows that the photographs cannot be used to evaluate the Ge-Ge-Ge bond angle reliably. Of the three simplified intensity curves shown in Fig. 2, calculated for the distances Ge-Ge = 2.44 Å. and Ge-H = 1.52 Å. and the angles H-Ge-Ge = 109°28' and Ge-Ge-Ge = 110, 112 and 114°, respectively, the 112° curve seems to resemble the photographs somewhat more closely than the others. The quantitative comparison with this curve leads to the value 2.41 Å. for the Ge-Ge distance.

Discussion of Results.—The investigation shows that the Ge-Ge bond distance in both digermane and trigermane is about 2.41 (± 0.02 Å.). There is some small evidence that the value for trigermane is 0.01 Å. larger than that for digermane; this difference is, however, less than the estimated probable errors of the values.

The Ge-Ge distance in elementary germanium, which crystallizes with the diamond structure, is 2.44 Å. This is the basis for the value 1.22 Å. assigned as the single-bond covalent radius of germanium.⁷ The decrease of about 0.03 Å. in interatomic distance observed for digermane and trigermane is probably real, and suggests that the covalent radius of germanium for use in compounds may be as low as 1.21 or 1.20 Å. The decrease may be due either to some

(7) L. Pauling and M. L. Huggins. *Z. Krist.*, **87**, 205 (1934).

interaction with the Ge-H bonds in the germanes or to partial metallic character (incomplete covalent character) of the element; in the former case the value 1.22 Å. for the radius would be the more generally applicable and in the latter case a smaller value. The uncertainty of 0.01 or 0.02 Å. in the radius is not of great significance.

The Ge-H bond distance in the substances is probably about 1.50 Å., and the bond angles are probably close to the tetrahedral value 109°28'; these values are, however, not de-

rived from the experimental data.

Acknowledgment.—We wish to thank Dr. K. S. Palmer and Dr. V. Schomaker for assistance in the preparation and measurement of the photographs.

Summary

The Ge-Ge bond distance in both digermane and trigermane is found by the electron diffraction method to be about 2.41 ± 0.02 Å.

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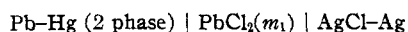
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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF NORTH CAROLINA]

The Activity Coefficients of Lead Chloride in Aqueous Solutions of Mannitol at 25°¹

BY H. D. CROCKFORD AND J. C. LOFTIN

An extensive study of the activity of lead chloride in aqueous solutions at 25° has been made by Carmody.² For this study he employed the following chemical cell



By the use of their extended Debye-Hückel equation La Mer, Gronwall and Greiff³ employed the data of Carmody to calculate the mean distance of closest approach of the ions of lead chloride. Crockford and Thomas⁴ and Crockford and Farr⁵ employed the same cell to determine the activity coefficients of lead chloride in aqueous solutions of cadmium nitrate and barium nitrate at 25°. The purpose of the work was to test the relationship proposed by Crockford and Thomas⁴ for the calculation of the \bar{a} parameter in solutions containing two electrolytes. In this paper are given the results of a series of studies designed to determine the effect of mannitol on the activity of lead chloride in aqueous solutions at 25°. From the data obtained has been calculated the mean distance of closest approach of the ions.

The chemical cell given above was used in the work. Four series of data were obtained: (I) constant molality of mannitol and varying concentrations of lead chloride; (II) constant ratio of lead chloride and barium nitrate and varying concentrations of mannitol; (III, IV) constant

molalities of lead chloride and varying concentrations of mannitol.

The mannitol used was the Pfanstiehl c. p. grade; it was dried and kept in a vacuum desiccator until used. For the purification of other materials, preparation of solutions, preparation of electrodes, and general experimental technique the same procedures as employed by Crockford and Farr⁵ were followed. Except for the very dilute solutions the e. m. f. values given are reproducible to 0.05 mv.

Results and Calculations

Tables I-IV give a summary of the experimental data and the calculated values for the activity coefficients and the a values.

The activity coefficients were calculated from the equation

$$E(\text{mv.}) + 88.7308 (0.200687 + \log m) = E_0(\text{mv.}) - 88.7308 \log f$$

this being the equation for a chemical cell without transference after the proper constants for a 1-2 salt at 25° have been introduced. The value $E_0 = 0.34320$ v. calculated by La Mer, Gronwall and Greiff³ from the data of Carmody² was used in the calculations.

TABLE I

Series I. Constant Molality of Mannitol 0.1000

	m_1, PbCl_2	$E, \text{v.}$	f	$a, \text{Å.}$
1	0.02109	0.50132	0.493	1.70
2	.01580	.50956	.532	1.62
3	.01056	.51970	.587	1.80
4	.00528	.54194	.688	1.58
5	.00262	.56592	.742	1.40

(1) From a thesis presented by Mr. Loftin to the faculty of the University of North Carolina as partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Carmody, *THIS JOURNAL*, **51**, 2905 (1929).

(3) La Mer, Gronwall and Greiff, *ibid.*, **58**, 2245 (1931).

(4) Crockford and Thomas, *ibid.*, **58**, 568 (1933).

(5) Crockford and Farr, *ibid.*, **58**, 87 (1936).