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 derived from the experimental data.

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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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[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

$$\text{Pb–Hg (2 phase)} \mid PbCl_2(m_1) \mid \text{AgCl–Ag}$$

By the use of their extended Debye–Hückel equation La Mer, Gronwall and Greiff[3] employed the data of Carmody to calculate the mean distance of closest approach of the ions of lead chloride. Crockford and Thomas[4] and Crockford and Farr[5] 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 Thomas[4] 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 Farr[5] 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 Greiff[3] from the data of Carmody[2] was used in the calculations.

TABLE I

Series I. Constant Molality of Mannitol 0.1000

	m_1, $PbCl_2$	E, v.	f	a, 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

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(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.*, **53**, 2245 (1931).

(4) Crockford and Thomas, *ibid.*, **55**, 568 (1933).

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

TABLE II

Series II. m_1/m_2 Constant

	m_1 PbCl$_2$	m_2 Ba(NO$_3$)$_2$	m_3 Mannitol	E, v.	f	$\bar{a}$, Å.
1	0.01090	0.02339	0.20698	0.52694	0.419	2.19
2	.01083	.02324	.15708	.52658	.498	2.26
3	.01076	.02308	.10002	.52606	.509	2.39
4	.01069	.02294	.05009	.52582	.515	2.46
5	.01063	.02281	.00000	.52558	.522	2.57

TABLE III

Series III. Constant Molality of PbCl$_2$ 0.01055

	m_3 Mannitol	E, v.	f	a, Å.
1	0.0000	0.51995	0.608	1.76
2	.1012	.52047	.600	1.60
3	.2897	.52166	.582	1.40
4	.5609	.52540	.528	1.44
5	.7313	.52702	.506	1.25

TABLE IV

Series IV. Constant Molality of PbCl$_2$ 0.023455

	m_3 Mannitol	E, v.	f	a, Å.
1	0.0000	0.49724	0.493	1.80
2	.0990	.49827	.480	1.71
3	.2899	.50000	.459	1.50
4	.5604	.50224	.433	1.30
5	.7304	.50470	.406	1.29

The ion size parameter values were calculated graphically according to the procedure outlined by La Mer, Gronwall and Greiff.[3] It is to be noted that the value for the dielectric constant varied with the concentration of mannitol. The values for the various solutions used can be calculated from the data of Åkerlöf,[6] who has made a thorough study of the dielectric constant of aqueous mannitol solutions. However, in the construction of the family of curves necessary for the determination of the a parameter the dielectric constant of pure water was used. The error so introduced is very small. But in the evaluation of the $10^{-8}K$ function for the various solutions the value for the dielectric constant obtained from the data of Åkerlöf was employed.

Discussion of Results

An inspection of the data in Series III and IV shows that the activity coefficient of the lead chloride decreases with increasing concentration of mannitol. Series I illustrates the same point when compared with the results of Carmody.[2] Series III and IV show that the a value decreases with increasing concentration of mannitol. In the solutions with zero concentration of mannitol the a values are close to the value of 1.75 Å. as calculated by La Mer, Gronwall and Greiff.[3] According to the equation of Crockford and Thomas[4] the $\bar{a}$ values in Series II should remain constant. Based on data given by Crockford and Farr[5] the value should be 2.53 Å., a value very close to that obtained in solution 6 which contains no mannitol. However, as in Series III and IV this value decreases with increasing concentration of mannitol.

We wish to acknowledge our indebtedness to the Rockefeller Foundation for financial aid in the original purchase of part of the equipment used.

Summary

The activity coefficients of lead chloride in aqueous solutions of mannitol at 25° have been determined. In Series I the molality of mannitol was kept constant. In Series II the ratio of lead chloride to barium nitrate was kept constant but the molality of the mannitol was varied. In Series III and IV the molality of lead was kept constant but the molality of mannitol was varied.

From the activity coefficients in Series I, III and IV the a parameter values for lead chloride were calculated. From Series II the mean $\bar{a}$ values for mixtures of lead chloride and mannitol were calculated.

The data obtained show that the activity coefficients and the a parameter values decrease with increasing concentrations of mannitol.

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(6) G. Åkerlöf, THIS JOURNAL, **54**, 4125 (1932).