

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

GERMANIUM. XXXVIII. THE PARACHORS OF CERTAIN COMPOUNDS OF GERMANIUM AND THE ATOMIC CONSTANT FOR GERMANIUM

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Introduction

From a consideration of the regularities in the differences between the parachors of neighboring elements in the periodic system, Sugden¹ predicted that the atomic parachor for germanium should be 36, but no experimental data have been available to verify the prediction. Metallic germanium melts at 958.5° and is easily oxidized, so that direct determination of its parachor is not readily accomplished. However, the element does form several compounds which are liquid under ordinary conditions and which lend themselves to such measurements.

In the present investigation carefully purified quantities of germanium tetrachloride, germanium tetrabromide, germanium tetraethyl and germanium tetraethoxyl were prepared, their densities and surface tensions were determined, and their parachors were calculated. By use of the accepted constants given by Sugden² for the other elements present in each compound the atomic parachor for germanium was calculated.

Experimental

A. Preparation and Purification of Materials

Benzene.—Thiophene-free benzene was purified by repeated freezing and by distillation over sodium. It melted at 5.4°. (All temperatures given are corrected.)

***m*-Xylene.**—Kahlbaum's "purest" *m*-xylene was distilled over sodium. The middle fraction selected distilled at 136–139°.

Germanium Tetrachloride, GeCl₄.—This was prepared from pure germanium dioxide and hydrochloric acid.³ The tetrachloride was allowed to stand over solid anhydrous sodium carbonate to remove traces of hydrogen chloride and was further purified by fractional distillation in a vacuum fractionation apparatus.⁴ The purified sample had a vapor tension at 0° of 25 mm. (24.3 mm. reported by Laubengayer and Tabern).⁵

Germanium Tetrabromide, GeBr₄.—The tetrabromide was prepared by the action of hydrobromic acid on pure germanium dioxide⁶ and was purified by fractional distillation. The middle fraction boiled at 186° (186.5° reported by Brewer and Dennis).⁷

¹ Sugden, "The Parachor and Valency," George Rutledge and Sons, Ltd., London, 1930, p. 184.

² Sugden, *ibid.*, p. 38.

³ Tabern, Orndorff and Dennis, *THIS JOURNAL*, **47**, 2039 (1925).

⁴ Laubengayer and Corey, *J. Phys. Chem.*, **30**, 1043 (1926).

⁵ Laubengayer and Tabern, *ibid.*, **30**, 1047 (1926).

⁶ Laubengayer and Brandt, *THIS JOURNAL*, **54**, 549 (1932).

⁷ Brewer and Dennis, *J. Phys. Chem.*, **31**, 1105 (1931).

Germanium Tetraethyl, $\text{Ge}(\text{C}_2\text{H}_5)_4$.—Germanium tetraethyl was prepared by the action of magnesium ethyl bromide on germanium tetrachloride⁸ and was purified by fractional distillation. The preparation that was used boiled at 162–163° (162.5–163° reported by Tabern, Orndorff and Dennis).⁸

Germanium Tetraethoxyl, $\text{Ge}(\text{OC}_2\text{H}_5)_4$.—This substance was obtained by the action of sodium ethylate on germanium tetrachloride.⁸ The sample boiled at 187° (185–187° reported by Tabern, Orndorff and Dennis).⁸

B. Measurement of Density.—The density determinations were made by a pycnometric method. Germanium tetrachloride, tetrabromide and tetraethoxyl are readily hydrolyzed by the moisture of the air and hence the ordinary type of pycnometer could not be used. One of special design was made by sealing a glass bulb of about 10-cc. capacity to a graduated capillary tube 5-cm. long which was connected through a stopcock to an interchangeable ground-glass slip joint so that the bulb could be fitted to the vacuum fractionation chain⁴ when the sample was to be transferred. This density bulb was calibrated with mercury at the temperature of the density determinations. The tared calibrated bulb was filled with the sample by distillation in dry air or *in vacuo*, eliminating all chance for hydrolysis and insuring high accuracy. A thermostat held constant within 0.1° provided proper temperature control. All weighings were corrected to vacuum.

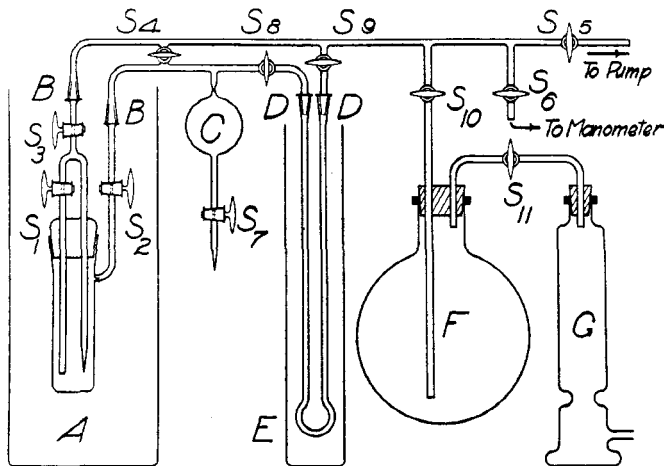


Fig. 1.

C. Measurement of Surface Tension.—The surface tension measurements were made by the maximum bubble pressure method described by Sugden.⁹ Since some of the substances investigated were very sensitive to moisture it was found necessary to modify the apparatus in order to prevent breakdown of the compound during transfer or while the measurements were in progress. Figure 1 shows the essential details. A is the bubbler tube constructed according to Sugden's directions. It is provided with stopcocks S_1 , S_2 and S_3 and the interchangeable ground glass slip joints B, B, and is immersed in the same thermostat that is used for the density determinations. C is a mercury aspirator bulb of about 150-cc. capacity. The manometer E is filled half full of purified xylene of known density and is immersed in a thermostatic bath

⁸ Ref. 3, p. 2043.

⁹ Ref. 1, p. 208.

held at $25 \pm 0.1^\circ$. Pressure differences are measured by means of a cathetometer reading to 0.01 mm. E is connected to the apparatus by the interchangeable slip joints D, D, through the stopcocks S_3 and S_9 . This construction makes it possible to remove the manometer, clean it, and refill it before each experiment, and if S_8 and S_9 are kept closed except when actual measurements are being made the chances for contamination of the manometric liquid are reduced to a minimum. F is a five-liter balloon flask containing phosphorus pentoxide and is used as a drying chamber and storage reservoir for the gas that is to be drawn through the bubbler. G is a calcium chloride tower for the preliminary drying of the gas. S_5 leads to an efficient vacuum pump and the system can be connected to a mercury manometer through S_6 .

When the surface tension of a sensitive liquid that has an appreciable vapor tension at room temperature is to be measured, the bubbler tube A is detached and connected to the vacuum fractionation chain⁴ containing the purified sample. A is then evacuated, dried and filled with the sample by low temperature vacuum distillation. If the liquid is not volatile at room temperature it may be purified and distilled into A in a current of dry inert gas. This procedure eliminates the possibility of breakdown of the sample during transfer. A is reattached to the surface tension apparatus and the entire system between S_2 , S_3 , S_7 and S_{10} is evacuated, S_4 , S_8 and S_9 being open. F is filled with a gas which does not react with the particular sample being investigated. S_{10} is opened slowly and the dry gas is admitted. S_8 , S_9 and S_{10} are closed and the apparatus is again evacuated to remove any traces of xylene vapor. Then S_2 and S_3 are opened, and dry gas from F is allowed to enter by opening S_{10} slowly. S_4 is closed and S_8 and S_9 are opened. The mercury aspirator is started and the procedure from this point on is that described by Sugden.

In order to allow evacuation of the apparatus it is necessary to use a lubricating grease on the stopcocks and slip joints, and some concern was felt about possible contamination of the sample. It was found, however, that if a good high-vacuum lubricant was applied sparingly, no contamination occurred, as was shown by the consistent results secured when benzene was used to calibrate the apparatus and by the fact that determinations of the surface tension of successive samples of the same substance always agreed well.

As a final test of the apparatus the parachor for pure benzene was determined at 30 and 50° . At 30° the value secured was 206.03 while at 50° it was 206.5. This showed that the apparatus described was satisfactory for the measurement of surface tension.

The apparatus was checked frequently during the course of the investigation by determining the surface tension of pure benzene.

D. Experimental Results.—The results found are given in Table I together with the molecular parachors [P], calculated according to the method of Sugden.¹⁰ The atomic parachor for germanium was obtained

TABLE I
EXPERIMENTAL RESULTS

Substance, germanium	Temp., °C.	Density	Surface tension	[P] observed	Σ [P]	Atomic parachor of germanium
Tetrachloride	30	1.8443	22.44	253.2	217.2	36.0
Tetrabromide	30	3.1002	35.51	308.9	272.0	36.9
Tetrabromide	50	3.0516	33.70	309.7	272.0	37.7
Tetraethyl	30	0.9850	22.96	419.5	380.4	39.1
Tetraethoxyl	30	1.1278	23.00	490.8	460.4	30.38

¹⁰ Ref. 1, p. 30.

in each case by subtracting the parachor increment, $\Sigma[P]$, due to all other atoms present in the molecule, from the molecular parachor.

Discussion of Results

The values obtained for the atomic parachor of germanium in the case of the tetrachloride, tetrabromide and tetraethyl are fairly consistent, and the average of these values, 37.4, is close to the 36 predicted by Sugden. Germanium tetraethoxyl gives a low value which probably may be accounted for by the difference in the type of compound. Simple alcohols give negative anomalies due to association, and the similarity in structure might lead one to expect that germanium tetraethoxyl should also show a negative anomaly.

The values for the germanium compounds are paralleled to some extent by the data reported for corresponding silicon compounds by Sugden and Williams.¹¹ The values for the methoxy and ethoxy compounds are lower than those reported for the tetraalkyls. Sugden and Williams also found that the parachors of silicon tetramethoxyl and silicon tetraethoxyl increase with the temperature while the tetraalkyls give a constant for silicon independent of temperature.

TABLE II
VALUES FOR SILICON COMPOUNDS

Substance, silicon	[P] obs.	$\Sigma[P]$	Atomic parachor of silicon
Tetraethoxyl	487.6	460.4	27.2
Tetramethoxyl	330.9	304.4	26.5
Tetraethyl	412.1	380.4	31.7
Tetrapropyl	565.3	536.4	28.9
Tetraphenyl	787.5	760.0	27.5

On the other hand it is remarkable that the borates show no corresponding anomaly, but give values¹² of the parachor of boron agreeing with that obtained from the trichloride.¹³

TABLE III
VALUES FOR BORON COMPOUNDS

Substance	[P] obs.	[P]	Atomic parachor of boron
Boron trichloride	178.8	162.9	15.9
Methyl borate	243.7	228.3	15.4
Ethyl borate	363.1	345.3	17.8

Summary

The molecular parachors of germanium tetrachloride, germanium tetrabromide, germanium tetraethyl and germanium tetraethoxyl have been

¹¹ Sugden and Williams, *J. Chem. Soc.*, 126 (1931).

¹² Etridge and Sugden, *ibid.*, 989 (1928).

¹³ Mills and Robinson, *ibid.*, 1823 (1927).

determined and the atomic parachor for germanium calculated. Good agreement with the value predicted by Sugden was observed. The anomaly obtained in the case of germanium tetraethoxyl is explained by the difference in structure.

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THE REACTION RATE OF POTASSIUM IODIDE WITH DIBROMIDES OF THE ETHYLENE BROMIDE TYPE

BY ROBERT T. DILLON

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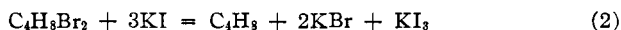
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Introduction

In a method for analyzing mixtures of the three normal butenes it was necessary¹ to utilize the specific reaction rate constants of the corresponding dibromobutanes with potassium iodide in methanol at 75°. The stoichiometric equation involved was expressed by equation (1)



Kinetically the reaction was readily followed by the titration of the iodine. It was pointed out in this article that the equation could equally well, and more probably should, have been expressed as follows



which differs from the first form only by equation (3)



In an aqueous solution this reaction of iodine with potassium iodide takes place completely; but in an alcoholic solution this is perhaps questionable and for this reason the first form of the dibromide reaction was used in the previous paper. In this article, however, are given calculations made from the experimental data of van Duin² which show that equation (3) is evidently complete even in alcoholic solutions and, therefore, that one mole of dibromide³ reacts with three moles of potassium iodide according to equation (2). Hence this stoichiometric equation should be the basis for the differential equations expressing the velocity of the reaction.

However, the use of either equation would not alter the result previously found, namely, that kinetically the reaction is one of the second order, the rate being proportional to the first power of the concentrations of both

¹ Dillon, Young and Lucas. *THIS JOURNAL*, **52**, 1953 (1930).

² Van Duin, *Rec. trav. chim.*, **43**, 341 (1924).

³ The term "dibromide" as used herein is understood to mean only ethylene bromide and its homologs, or their substituted derivatives.