oxygen gas. The two values are in almost exact agreement, showing that the triplet character of the oxygen molecule due to the unbalanced angular momentum of its two spinning electrons has contributed approximately *R* ln 3 to the entropy of gaseous oxygen, and also that the absence of alternate rotation levels in the oxygen molecule due to its homopolar nature results in an entropy of *R* ln 2 less than would be the case for a polar molecule of the same moment of inertia.

The entropy of oxygen gas at 298.1°K. was calculated by the "summation" method from the spectral data and found to be 49.03 calories per mole per degree. We believe that this is the best value for use in thermodynamic calculations.

It is also shown that the magnetons in the crystalline form of oxygen stable below 23.66°K. are not contributing appreciably to the entropy and must, therefore, be coupled in a non-random manner into what may be regarded as a magneton crystal within the ordinary molecular crystal lattice.

It is shown that the existing magnetic susceptibility data on solid oxygen are in agreement with the requirement of the third law of thermodynamics for zero entropy in magnetic systems, namely, that the temperature coefficient of the magnetic susceptibility should approach zero as the absolute zero of temperature is approached.

It is concluded that the large positive susceptibility of solid oxygen is due to the initial effect of a coupling breakdown induced by the applied field in analogy to the Paschen–Back effect in gaseous ions.

The general agreement of the various physical facts concerning the oxygen molecule in relation to the entropy and particularly the close agreement of the entropy as obtained by the two methods support our confidence that the third law of thermodynamics is an exact law.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

GERMANIUM. XXX. HALOGEN SUBSTITUTION PRODUCTS OF MONOGERMANE[1]

BY L. M. DENNIS AND P. R. JUDY

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Most of the possible halogen substitution products of methane and monosilane (SiH_4) of the types RHX_3, RH_2X_2 and RH_3X, have been prepared.[2] The purpose of the present investigation was the preparation and study of some of the analogous compounds of germanium.

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[1] This article is based upon part of the thesis presented to the Faculty of the Graduate School of Cornell University by P. R. Judy in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] See Landolt-Börnstein, "Physikalisch-chemische Tabellen," **1923**, Vol. I, p. 356.

Monochloromonogermane, GeH_3Cl, and Dichloromonogermane, GeH_2Cl_2.—These were prepared by the action of hydrogen chloride on monogermane in the presence of a catalyst.

Apparatus.—The apparatus was patterned after that of Laubengayer and Corey[3] and is shown in Fig. 1. Stock's[4] modification of his mercury float valve was used. The bulb B_1, which is used as the reaction chamber, has a capacity of about 500 cc. and there is attached to the bottom of the bulb a tube 14 mm. wide and about 15 cm. long which is closed at the lower end. A tube 7 mm. in diameter and about 6 cm. long, open at its further end, is fused at right angles to the upper tube of the bulb at C. Just before beginning an experiment, a short tube of the same diameter, closed at one end and containing about 0.1 gram of anhydrous aluminum chloride, is fused to the open end of this side tube and the aluminum chloride is then sublimed into the bulb B_1, whereupon the side tube is sealed off at the point marked C. Three smaller bulbs, B_2, B_3 and B_4, attached to the line as shown, are used for the fractionation of the gases. K is a manometer for measuring gas pressures and E is a bulb for the weighing of separate samples. The space between the stopcocks S_2 and S_4, which would be full of air after D is detached and again attached to the chain, can be exhausted through the stopcock S_3. The volumes of various portions of the apparatus are calibrated by the use of the Hempel buret F in the manner described by Laubengayer and Corey. H is a calibrated tube which is used for measuring the volumes of liquids and determining their melting points. The bulbs B_5 and B_6 are storage bulbs of about one liter capacity which carry at the bottom short tubes and small bulbs for the application of the cooling baths.

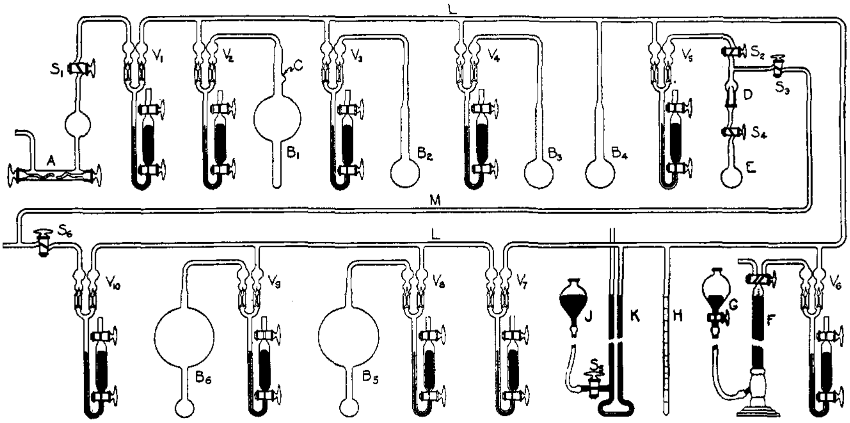

Fig. 1.

Before beginning an experiment the whole apparatus was freed from moisture by drawing through it air that had been purified by passage through soda lime, concentrated sulfuric acid and finally phosphorus pentoxide contained in the tube A.

Manipulation.—The monogermane that was used was a portion of the large sample of this gas that was prepared in 1923 for the study of the hydrides[5] of germanium. Determinations of the densities of two samples of this gas from different gas-holders gave

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[3] Laubengayer and Corey, *J. Phys. Chem.*, **30**, 1043 (1925), Fig. 1.

[4] Stock, *Z. Elektrochem.*, **23**, 33 (1917).

[5] Dennis, Corey and Moore, THIS JOURNAL, **46**, 657 (1924).

3.396 and 3.405, showing that the gas was quite pure and that it is very stable at room temperature over long periods of time. The gas was introduced through the stopcock S_6 into the bulbs B_5 and B_6.

Hydrogen chloride entirely free from air was introduced into the buret[3] F over mercury, where it could be measured.

The bulb B_1 was now evacuated, the catalyst was cautiously sublimed into it and the side tube was sealed by fusion at C. The change in the volume of the bulb which was thus caused was so small that recalibration of this part of the apparatus was unnecessary.

A known volume of monogermane, which was measured in the calibrated portion of the apparatus, was condensed in B_2 by means of liquid air. An amount of hydrogen chloride somewhat less than the theoretical volume required for the formation of monochloromonogermane was then drawn over into B_2 and condensed. The mixture of the two gases was then transferred to the reaction bulb, B_1, by cooling the tube attached to the bottom of the latter with liquid air and removing the refrigerant from around the bulb B_2. The valve V_2 was then closed.

Upon removing the liquid air from around the tube of B_1, the two liquids vaporized and reaction began at once. The application of heat was unnecessary. Equilibrium was reached in about thirty minutes.

After the reaction was complete, all gases other than hydrogen were frozen by liquid air and the hydrogen was measured.

In every experiment more hydrogen was evolved than corresponded to the formation of GeH_3Cl alone. Some dichloromonogermane was always simultaneously produced.

Fractionation.—After the hydrogen had been removed from the apparatus by the pump, the volatile residue in B_1 was transferred to B_2 to remove it from the catalyst. Unchanged monogermane (b. p. −90°) was distilled off at from −135 to −120° and condensed in B_4. Its volume was measured and it was then transferred to the storage bulbs. Hydrogen chloride (b. p. −83°) was then distilled off at from −120 to −90°, measured and removed.

The first slight rise in the manometer above −90° was at about −83°, at which temperature monochloromonogermane begins to come off. This was distilled over at −78°, and a quite pure product was usually obtained.

Dichloromonogermane began to come over at about −61° and distilled quite rapidly at −52°. Sharp separation of the two products was therefore possible on careful fractionation with the vacuum apparatus. The yield of the two compounds in the last experiment, after familiarity with the manipulation had been attained, was GeH_3Cl, 48%, and GeH_2Cl_2, 14%, of the GeH_4 that had reacted.

Analysis.—In the analysis of the corresponding compounds of silicon, Stock made use of the reaction with sodium hydroxide, in which hydrogen is quantitatively evolved. For example

$$SiH_3Cl + 3\,NaOH = Na_2SiO_3 + NaCl + 3\,H_2$$

This procedure was tried with the germanium compounds but when these were brought into contact with a solution of sodium hydroxide, germanium monoxide, not the dioxide, was formed, and the hydrogen set free was always considerably less than is called for in the equations

$$GeH_3Cl + H_2O = GeO + HCl + 2\,H_2$$
$$GeH_2Cl_2 + H_2O = GeO + 2\,HCl + H_2$$

Secondary reactions apparently take place, for even after prolonged treatment with sodium hydroxide, the odor of hydrides or chlorinated compounds of germanium could be detected.

The method of analysis that was finally adopted was to bring a known weight of the sample into the bulb *E*, close stopcock S_4, detach the bulb from *D*, cool *E* and then run into the bulb through the neck, first a dilute solution of potassium hydroxide, and then hydrogen peroxide. After decomposition of the sample and solution of the products were complete, the solution was acidified with nitric acid, the chlorine was precipitated by silver nitrate and after removal of the excess of silver from the filtrate, germanium was precipitated as the disulfide. The results of the analyses did not agree closely with the theoretical because of the unstable character of the compounds. They sufficed, however, to establish the identity of the monochloromonogermane and the dichloromonogermane and gave a ratio Ge:Cl of 1:1.03 in the first-named compound, and of 1:2.04 in the latter.

Properties of Dichloromonogermane and Monochloromonogermane.—Both substances are mobile, colorless liquids of peculiar, nauseating odor.

TABLE I

DICHLOROMONOGERMANE

Boiling point, 69.5°; melting point, −68°; density as liquid at −68°, 1.90; mol. wt., av. of four detns., 145.2; calcd., 145.54.

T, °C.	−54.7	−41.8	−31.5	−23.2	−11.5	−9.7	−3.5	0.4
P, mm.	1.3	2.1	5.9	9.3	19.3	21.6	30.6	36.9
T, °C.	2.5	8.4	13.8	20.7	26.4	31.3	35.8	40.2
P, mm.	41.1	58.1	72.2	110.0	142.1	176.3	214.2	258.2
T, °C.	44.3	48.5	53.5	58.0	61.6	65.3	68.7	71.2
P, mm.	304.9	358.8	431.2	511.7	588.2	660.6	739.4	802.3

The general equation derived from the above data is

$$\text{Log}_{10} P_{\text{mm.}} = -1742.7 \times \frac{1}{T} + 7.969$$

TABLE II

MONOCHLOROMONOGERMANE

Boiling point, 28°; melting point, −52°; density as liquid at −52°, 1.75; mol. wt., av. of seven detns., 110.92; calcd., 111.08.

T, °C.	−52	−44.2	−38.5	−32.8	−31.2	−24.6	−20.7
P, mm.	11.3	18.5	27.9	39.5	45.4	70.0	88.9
T, °C.	−14.8	− 9.4	− 5.0	2.1	5.5	8.8	
P, mm.	118.8	150.9	185.1	257.5	298.6	345.2	
T, °C.	11.9	16.3	20.7	24.6	27.6	29.5	
P, mm.	392.9	469.9	559.0	646.9	724.4	786.9	

The general equation derived from the above data is

$$\text{Log}_{10} P_{\text{mm.}} = -1527.4 \times \frac{1}{T} + 7.961$$

Both compounds fume when exposed to moist air, the walls of the container becoming coated with a film which is at first white and then becomes yellow, finally deepening to an orange tint. Considerable heat is liberated during this reaction. Water rapidly hydrolyzes the compounds and hydrogen is evolved. Absolute alcohol precipitates a white substance which dissolves to a yellow solution when an equal volume of water is added. Solutions of fixed alkali hydroxides precipitate an orange-colored compound, considerable hydrogen being set free. An alcoholic solution of potassium hydroxide yields a pale yellow precipitate, no hydrogen being evolved until water is added to the mixture.

Hydrogen chloride in the presence of aluminum chloride converts monochloromonogermane into dichloromonogermane with liberation of hydrogen. The dichloro compound does not further react with hydrogen chloride.

Ammonia acts instantly on both compounds, forming non-volatile, colored substances which decompose with explosive violence when heated in air.

Monochloromonogermane slowly breaks down at room temperature

$$2\,\mathrm{GeH_3Cl} = \mathrm{GeH_4} + 2\,\mathrm{HCl} + \mathrm{Ge}$$

Dichloromonogermane decomposes much more rapidly. Among the products that are formed there were detected Ge, $GeCl_2$, GeH_4, HCl, GeH_3Cl, $GeCl_4$ and traces of hydrogen.

Monobromomonogermane, GeH_3Br, and Dibromomonogermane, GeH_2Br_2.—The method of preparation of these compounds was essentially the same as for the chlorine substitution products, hydrogen bromide replacing hydrogen chloride and aluminum bromide being used as the catalyst.

Reaction between the monogermane and the hydrogen bromide took place as soon as they were brought together, considerable heat being evolved. When reaction was complete, the bulb was surrounded by liquid air and the hydrogen was pumped off. The excess of monogermane was then removed at about −120°. The separation of the bromination products by fractionation of the residue was difficult because of the instability of the compounds. This tendency to dissociate, even at quite low temperatures, rendered it impossible to obtain closely agreeing analytical results.

Properties of Dibromomonogermane and Monobromomonogermane.—Both compounds are colorless, mobile liquids of nauseating odor.

TABLE III

DIBROMOMONOGERMANE

Boiling point, 89°; melting point, −15°; density as liquid at 0°, 2.80

T, °C.	−26.6	− 5.6	0.6	5.9	15.5	21.7	27.4
P, mm.	1.2	3.7	6.5	9.6	15.7	28.3	36.1
T, °C.	34.1	35.2	38.9	43.2	49.5	57.2	
P, mm.	55.4	62.7	79.5	102.4	146.6	215.8	
T, °C.	63.9	69.2	75.3	79.2	81.1	82.3	
P, mm.	304.1	409.2	519.4	633.0	733.3	814.8	

The following general equation, derived from the above data, is accurate up to a temperature of 50°. At higher temperatures the pressure does not agree with the calculated values because of dissociation of the compound.

$$\mathrm{Log}_{10} P_{\mathrm{mm.}} = -2461.9 \times \frac{1}{T} + 9.798$$

Table IV

Monobromomonogermane

Boiling point, 52°; melting point, −32°; density as liquid at 29.5°, 2.34; mol. wt., 155.4; calcd., 155.54.

T, °C.	−44.6	−27.3	−16.4	− 7.8	− 3.3	4.8	10.9	15.4
P, mm.	8.1	22.2	43.0	59.2	73.8	107.7	145.4	176.6
T, °C.	19.1	24.5	29.4	35.2	40.5	45.3	49.0	52.5
P, mm.	212.9	265.1	321.9	401.4	496.3	592.6	687.5	776.1

The general equation derived from the above data is:

$$\mathrm{Log}_{10} P_{\mathrm{mm.}} = -1614.7 \times \frac{1}{T} + 7.851$$

The chemical behavior of the monobromo- and dibromomonogermane is quite similar to that of the corresponding chlorine compounds.

Mono-iodomonogermane, CH_3I, and Di-iodomonogermane, CH_2I_2.—The iodine derivatives of methane are not very stable. Iodoform sublimes at 110° and begins to dissociate at this temperature. Tri-iodomonosilane boils at about 220° and begins to decompose at 150°. Tri-iodomonogermane was found to be unstable[6] above 0°. It was therefore to be expected that GeH_3I and GeH_2I_2 would, if their syntheses were successful, prove to be considerably less stable than the corresponding bromine and chlorine compounds of germanium.

In the preceding experiments it was found that monogermane reacts quietly upon hydrogen chloride in the presence of a catalyst with only slight rise of temperature, whereas with hydrogen bromide the reaction is vigorous and considerable heat is evolved. When equal volumes of monogermane and hydrogen iodide were mixed and were brought into a bulb containing aluminum bromide, the two gases reacted energetically and the bulb became quite hot near the reaction zone. A gas was evolved and drops of a colorless liquid formed on the catalyst. This liquid almost immediately turned yellow and soon changed to a solid. After three hours, the hydrogen that had been liberated was pumped off, and the unattacked monogermane was removed at −78°. Attempts to isolate GeH_3I and GeH_2I_2 by careful distillation in the vacuum apparatus were unsuccessful, and although evidence of the formation of those two compounds in the first stages of the reaction was obtained, it appeared that they then reacted with the hydrogen iodide to yield GeI_2 as the final product.

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[6] Brewer and Dennis, *J. Phys. Chem.*, **31**, 1526 (1927).

$$\begin{aligned} GeH_3I + HI &= GeH_2I_2 + H_2 \\ GeH_2I_2 + HI &= GeHI_2 + H_2 \\ GeHI_3 &= GeI_2 + HI \end{aligned}$$

The formation of germanium di-iodide was established by first pumping off the hydrogen, monogermane and hydrogen iodide from the reaction bulb and then adding an excess of hydriodic acid to the yellow residue in the bulb. This dissolved the substance and the filtered solution deposited, on cooling, yellow, feathery crystals[6] of GeI_2. Some GeI_4 was also present, this being formed by the dissociation of some of the di-iodide

$$2\ GeI_2 = GeI_4 + Ge$$

The end-products of the reaction between monogermane and hydrogen iodide therefore appear to be germanium di-iodide, hydrogen and some germanium tetra-iodide.

Summary

This article deals with the preparation and properties of monochloromonogermane, dichloromonogermane, monobromomonogermane and dibromomonogermane. Evidence was obtained that indicated the formation of the corresponding iodo compounds which, however, could not be isolated because of their instability.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF PRINCETON UNIVERSITY]

POLARIZATION IN STANDARD CELLS

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Introduction

Experimental studies of the effects of withdrawing current from standard cells[1] have shown these cells to be subject to a considerable degree of polarization, even at relatively low currents. It has also appeared that the polarization is roughly proportional to the strength of current, and that the cells recover quite satisfactorily following polarization, provided it has not been too prolonged. The passage of a current in the reverse direction through the cells also causes polarization, which, from the published results, appears to be somewhat more severe and of longer duration than that produced by discharging.[1e,f]

In all of the work mentioned above the cell has been considered as a

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[1] (a) Rayleigh and Sidgwick, *Trans. Roy. Soc. London,* **175A**, 411 (1884); (b) Threlfall and Pollock, *Phil. Mag.*, **28**, 353 (1889); (c) Skinner, *ibid.*, **38**, 271 (1894); (d) Wulf, *Sitzb. Akad. Wiss. Wien,* Abt. IIa, **106**, 562 (1897); (e) Barnett, *Phys. Rev.*, **18**, 104 (1904); (f) Smith, *Trans. Roy. Soc. London,* **207A**, 393 (1908); (g) Wold, *Phys. Rev.*, **28**, 132 (1909); (h) Hackett and Feely, *Sci. Proc. Roy. Dublin Soc.*, **15**, 279 (1918).