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The Vapor Pressure of Silicobromoform

BY WALTER C. SCHUMB AND FRED A. BICKFORD

In a previous paper[1] the reaction of anhydrous hydrogen bromide with silicon at different temperatures was studied, and the optimum conditions for the preparation of silicobromoform (tribromosilane) were discussed. At that time the measurement of the vapor pressure was not undertaken, and since this property seems not to have been studied systematically hitherto, we have determined the vapor pressure of pure silicobromoform over the range 0 to 120°, and have also redetermined the freezing point. Search of the literature disclosed but a single value of the vapor pressure of this substance, at 0°, and this applied to a specimen admittedly contaminated with silicon tetrabromide.[2]

The sample chosen for these measurements was taken from some of the purest material afforded by the previous investigation, and was purified by fractional distillation according to the method of Guye.[3] The apparatus is sketched in Fig. 1.

A specimen of silicobromoform contained in a sealed glass tube was placed inside the vertical tube (a) upon a cushion of glass wool, with a magnetic hammer (a glass-enclosed iron rod) resting upon the tip of the sample tube. The apparatus was thoroughly evacuated by means of a mercury diffusion pump, backed by a Hyvac oil pump, and then filled with dry nitrogen. The sample was frozen by immersing tube (a) in liquid air; the nitrogen was then pumped out, and the sample tube was broken by operation of the solenoid (e). The system was again evacuated with (a) immersed in a carbon dioxide–alcohol mixture to remove any permanent gases released in breaking the sample tube, and the silicobromoform was then brought to 0° and the portion distilling at constant pressure (indicated on the manometer (f) was collected in bulb (b), such material as exhibited a higher or a lower vapor pressure being collected in (c). Care was taken to allow ample time for the system to reach equilibrium; the complete fractionation occupied about five hours. From bulb (b) the sample was distilled into the vapor pressure bulb (g), a small fraction first being rejected.

Since silicobromoform attacks mercury at elevated temperatures, it was necessary to employ one of the various types of gages designed for use with corrosive vapors.[4] A spiral manometer of the Johnson type[5] was chosen as best serving our purpose. Pyrex glass was found very satisfactory in its construction; the readings obtained we believe to be reliable to 0.1 mm. The inner spiral of the gage consisted of about 25 turns of thin, flat ribbon tubing (about 4 mm. wide), one end of which was connected to the vapor pressure bulb, the other, closed end being sealed to a glass stylus bearing a galvanometer mirror. The gage was used in conjunction with a Leeds and Northrup lamp and a scale about 2 meters from the mirror. The position of the image of the cross-hair was observed with a small telescope. The spiral withstood an unbalanced pressure of one atmosphere without rupture, and the point of rest remained unchanged on heating the gage to 125°. No hysteresis effect could be observed in the return to the original reading after deflection of the mirror.

The oil thermostat, of twenty liters' capacity, heavily insulated, provided control of the temperature to within 0.05° over the range studied. The 0.1° thermometer had been carefully compared with a standard thermometer.

In carrying out the vapor pressure measurements, the temperature of the oil-bath was raised 5° over a period of half an hour, and the temperature then maintained constant for another half hour to allow time for equilibrium to be established. This procedure was repeated over 5° intervals. Two separate samples were used, the pressure values obtained in the two cases agreeing within a few tenths of a millimeter. Data from the second run are shown in the table. The necessary corrections have been applied to all temperatures and pressures.

EXPERIMENTAL DATA

Temp., °C.	Pressure, mm.	Temp., °C.	Pressure, mm.	Temp., °C.	Pressure, mm.
0.00	8.8	54.41	114.2	90.03	397.7
27.01	35.1	59.97	140.3	94.82	461.3
29.95	39.6	66.04	176.1	99.83	539.6
34.99	49.2	70.42	206.4	105.36	627.7
40.00	62.2	74.98	242.8	110.36	720.7
45.00	76.9	79.88	286.1	115.26	822.5
49.92	94.9	84.94	339.5	120.16	940.8

The experimental data may be represented by the equation

$$\log P = -1819.5/T + 7.6079$$

with an average deviation of 0.3 mm. and a maximum deviation of 1.7 mm. The discrepancies show no trend.

The heat of vaporization, calculated in the usual manner, was found to be 8322 cal. per mole. Trouton's constant is 21.6. The boiling point at 760 mm. is 111.8°.

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(1) Schumb and Young, THIS JOURNAL, **52**, 1464 (1930).

(2) Stock and Somiesky, *Ber.*, **50**, 1739 (1917), reported a pressure of 7 mm. at 0°, which is definitely low.

(3) Guye, *Z. anorg. Chem.*, **64**, 25 (1909). *Cf.* Tiede and Richter, "Handbuch der Arbeitsmethoden in der anorganischen Chemie," Vol. II, p. 905.

(4) *Cf.* Daniels, THIS JOURNAL, **50**, 1115 (1928), for a discussion of a number of these gages.

(5) Johnson, *Z. physik. Chem.*, **61**, 457 (1907).

Analysis of Silicobromoform.—Additional evidence of the purity of the samples of silicobromoform used in the vapor pressure work is furnished by the determination of the hydrogen liberated by this substance when it reacts with a solution of an alkali.

$$SiHBr_3 + 5NaOH \longrightarrow 3NaBr + Na_2SiO_3 + H_2 + 2H_2O$$

This determination is to be preferred to the analysis for bromine or silicon, since a small quantity of the tetrabromide, if present, would not appreciably alter the percentage of bromine or of silicon.

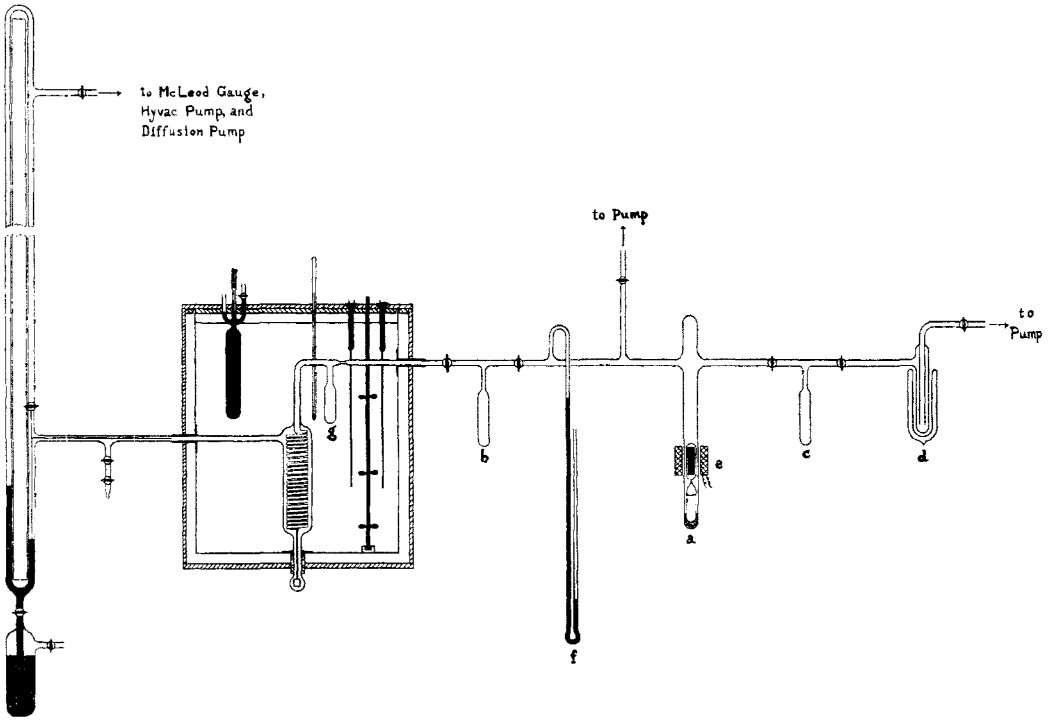

Fig. 1.

The hydrogen determination was carried out as follows. Samples of the silicobromoform were obtained by opening one of the sealed tubes containing the liquid in an evacuated system by means of a magnetic hammer and distilling small portions into capsules which were sealed off and weighed. The volume displaced by the capsule was also measured by immersion in a graduated cylinder partially filled with water and noting the increase in volume. The capsule was then broken under dilute sodium hydroxide solution by means of a magnetic hammer in a closed glass system, the hydrogen evolved being measured over mercury in a calibrated gas buret sealed to the evolution vessel. Time was allowed for the temperature of the system to become constant, and correction was made for the aqueous tension of the solution and for the vacuum space contained within the capsule. Two such analyses gave the following data, which furnish a satisfactory check on the purity of the substance.

	$SiHBr_3$, g.	Vol. of hydrogen, cc. Obs.	Calcd.
(1)	0.8588	71.4	71.6
(2)	.5882	49.5	49.0

The *melting point* of silicobromoform was redetermined by the method described in detail by Skau,[6] the apparatus, therefore, being in all essentials a duplicate of that employed by this investigator. From a heating curve obtained in this way with our preparation, the value found was −73.5°. The liquid exhibited a very great tendency to supercool.

Summary

1. The vapor pressure of silicobromoform has been determined from 0 to 120°; the data may be represented by the equation $\log P = -1819.5/T + 7.6079$. The 0° value is 8.8 mm., and a pressure of 760 mm. is reached at 111.8°.

2. The melting point of this substance was found to be −73.5°.

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[6] Skau, *Proc. Am. Acad. Arts Sci.*, **67**, 551 (1933).

3. The use of a Pyrex glass spiral manometer of the Johnson type as a null instrument in the measurement of vapor pressures of corrosive substances is discussed; constancy and reproducibility of readings, a lack of noticeable hysteresis and a degree of precision adequate for much work of this kind were noted with such an instrument.

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[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY, HARVARD UNIVERSITY]

The Atomic Weight of Uranium Lead from Great Bear Lake, N. W. T., Canada, Pitchblende

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Introduction

The recent discovery of extensive deposits of high-grade pitchblende ore at LaBine Point, Echo Bay, Great Bear Lake, North West Territories, Canada, has aroused wide-spread general interest. As one part of a complete investigation, the atomic weight of the uranium lead therein contained has been determined, to assist in the calculation of the geologic age of the deposit. Heartiest thanks are due to the Mines Branch, Department of Mines, of the Canadian Government, who generously have furnished ample material, and especially to Mr. Hugh S. Spence, Mining Engineer, Mineral Resources Division, Mines Branch, who personally obtained the samples used, and who furnished much valuable information.

The geological, mineralogical and engineering relations of the occurrence have been discussed by C. W. Knight,[2] D. F. Kidd,[3] J. A. Reid,[4] among others, and most fully by H. S. Spence,[5] and H. S. Robinson.[6] These references include partial analyses, which show the ore to be a very high-grade thorium-free siliceous pitchblende. This should offer a favorable opportunity to obtain an uranium lead of minimum atomic weight, provided "ordinary" lead is absent. Petrographic studies by H. J. Fraser, L. C. Graton, W. Lindgren, and W. H. Newhouse[7] indicate that galena is present in exceedingly small amounts, visible only under the microscope, in specimens taken from the same portion of the same vein as the sample used in this investigation. Spence, in a personal communication, states that no macroscopically visible galena has been found in that part of the vein system from which he selected our material, though it is found at other places in the general vein system. This would suggest very slight contamination, if any. If the galena is due to the alteration of radiogenetic lead by sulfide solutions, its presence should not affect the atomic weight, but if it has been derived from "common" lead, the atomic weight should be raised above the value for a "pure" uranium lead.

Purification of Reagents

Water, silver, nitric, hydrochloric, hydrofluoric and sulfuric acids, sodium carbonate, hydrogen chloride, nitrogen and air were purified as described in previous papers from this Laboratory.[8] The silver used was taken from several lots, each of which had been used in acceptable determinations of other atomic weights in this Laboratory. Especial care was taken to see that all reagents and apparatus were lead free.

Preparation and Purification of Lead Chloride

The method for extracting and purifying the lead was based on that used by Baxter and Bliss[8] on Wilberforce uraninite, modified by differences between the two minerals and by subsequent experience. Five different preparations were made, but only one—Sample E—was used in the series of definitive analyses. About 50 g. of the coarsely powdered pitchblende, as received, was extracted with nitric acid in a Pyrex dish, which was not attacked, filtered, silica removed with hydrofluoric acid, residual fluorides converted to nitrates, and a trace of insoluble matter filtered off and rejected. To this was added lead chloride recovered from preliminary tests. Lead, etc., were precipitated from the three combined dilute nitric acid solutions with hydrogen sulfide, drawn from a cylinder and washed with purest water. The sulfides were filtered on

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[1] Research Associate, Committee on the Measurement of Geologic Time, Division of Geology and Geography, National Research Council.

[2] C. W. Knight, *Can. Min. J.*, **51**, 964 (1930).

[3] D. F. Kidd, *ibid.*, **53**, 5 (1932); *Can. Min. and Met. Bull.* No. 245, p. 512 (1932).

[4] J. A. Reid, *Can. Min. J.*, **53**, 61 (1932).

[5] H. S. Spence, Section III of Investigations in Mineral Resources and the Mining Industry, Department of Mines, Mines Branch, 1931, p. 55, Ottawa (1932).

[6] H. S. Robinson, *Can. Min. and Met. Bull.*, No. 258, p. 609 (1933).

[7] Private communications; see also Report of Committee on the Measurement of Geologic Time, Washington, 1932, pp. 44–46.

[8] *Vide inter alia* G. P. Baxter and A. D. Bliss, THIS JOURNAL **52**, 4848, 4851 (1930).