NOTES

Vapor Pressure of Boron Triiodide and Silicon Tetraiodide[1]

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Vapor pressures of BI_3 and SiI_4 were measured in the 5–730 mm. range, using the static isoteniscope method of Smith and Menzies.[2]

Table I

BI_3: $\log P_{mm} = 24.3125 - (3{,}342.3/T,°K.) - 5.4058 \log T°K.$; (336–480°K.)

t, °C.	P_{mm} Obsd.	P_{mm} Calcd.	$P_{obsd.} - P_{calcd.}$
206.7	711.3	714.8	−3.1
189.8	485.9	483.2	+2.7
173.7	321.0	321.4	−0.4
153.7	183.8	183.7	+0.1
131.7	91.4	91.9	−0.5
113.6	49.2	48.3	+0.9
98.1	27.0	26.3	+0.7
80.9	12.7	12.1	+0.6
63.4	5.3	5.3	0

Calcd. b.p. at 760 mm., 209.5°. B.p. (ref. 3), 210°.

Table II

SiI_4: $\log P_{mm} = 23.3809 - (3.862.7/T,°K.) - 4.9934 \log T°K.$; (399–573°K.)

t, °C.	P_{mm} Obsd.	P_{mm} Calcd.	$P_{obsd.} - P_{calcd.}$
299.4	732.4	731.1	+1.3
285.2	559.4	558.3	+1.1
267.3	385.8	387.6	−1.8
244.6	232.3	233.5	−1.2
220.0	126.6	126.4	+0.2
201.9	77.3	76.6	+0.7
187.4	48.5	49.7	−1.2
169.4	26.9	27.7	−0.8
148.3	13.1	12.8	+0.3
126.4	5.3	5.3	0

Calcd. b.p. at 760 mm., 301.5°. B.p. (ref. 4), 290°.

Experimental

Temperatures were measured with a copper–constantan thermocouple and calibrations of the Bureau of Standards.[5] Pressures were measured with a mercury manometer–cathetometer and are corrected for temperature, latitude (elevation correction negligible) and difference in liquid level in the isoteniscope at moment of reading. This last correction required liquid density, which was determined on the SiI_4 as

$$\rho = 3.40 - 2.5 \times 10^{-3}(t - 120) \text{ g./cc. } t = °C.$$

The density of the BI_3 was assumed to be the same for this correction, which was always small. The equipment was filled with dry helium instead of air, to prevent hydrolysis and oxidation of the iodides. Mineral oil and molten salt constant temperature baths were used. Best reproducibility was achieved by measuring the vapor pressure at the highest temperature first and "boiling out" the last traces of contaminating volatiles, followed by measurement at the lower temperatures.

The SiI_4 was prepared by passing iodine and argon through ground silicon (30 × 80 mesh) held in a quartz reactor at 850°. The product was condensed and purified by distillation in a 4-step still at 200 mm. The white crystalline material had a melting point of 122–122.5° (m.p. 120.5°[6]). The BI_3 was prepared by the method of Schumb, Gamble and Banus[7] where sodium borohydride reacts with iodine and the resulting BI_3 is extracted by sublimation, dissolution and reduction of the excess iodide. About 15 g. of BI_3 was obtained from 1000 ml. of CS_2 liquor after reduction and removal of the iodine. The over-all material balance was 15 g. of BI_3 from 64 g. of sodium borohydride and 1054 g. of iodine. The BI_3 was resublimed twice before being deposited in the isoteniscope. The white crystalline solid had a melting point of 49.6° (m.p. 49.9 ± 0.5°[7]).

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The System Aluminum Triethyl–Ethyl Ether[1]

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Krause and Wendt[2] reported some three decades ago the formation of an etherate of aluminum triethyl to which they assigned the formula $4Al(C_2H_5)_3 \cdot 3(C_2H_5)_2O$. This formula is difficult to rationalize, particularly in view of the well known tendency for aluminum trimethyl to form 1:1 complexes with such Lewis bases such as dimethyl ether, trimethylamine, trimethylphosphine and dimethyl sulfide. The present study was undertaken to determine conclusively the composition of the etherate of aluminum triethyl by careful analysis and by cryoscopic studies of the binary system $Al(C_2H_5)_3$–$(C_2H_5)_2O$.

Preparation of Aluminum Triethyl.—The procedure used was an adaptation of that of Grosse and Mavity.[3] The process is represented essentially by the equations

$$2Al + 3C_2H_5Br \longrightarrow Al(C_2H_5)_2Br + Al(C_2H_5)Br_2$$

$$Al(C_2H_5)_2Br + Al(C_2H_5)Br_2 + 3Na \longrightarrow Al(C_2H_5)_3 + 3NaBr + Al$$

Granular aluminum (20 mesh) and Eastman Kodak ether-free ethyl bromide were used. The sodium was added directly to the mixture without previous distillation of the halides. The product was a colorless, clear liquid, b.p. 76° at 2.5 mm. and 69° at 1.5 mm. A hydrolyzed and acidified sample gave no precipitate with silver nitrate.

Purification of Ethyl Ether.—Anhydrous reagent grade ethyl ether was dried over sodium wire. Iron wire and copper powder were added to minimize peroxide formation. The ether was outgassed with nitrogen.

Apparatus for Cryoscopic Measurements.—Temperatures were measured with a recording potentiometer (Leeds and Northrup Micromax) using a copper–constantan thermo-

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[1] Taken from the Ph.D. dissertation of E. B. Baker, The Ohio State University, 1953.

[2] E. Krause and B. Wendt, *Ber.*, **56B**, 466 (1923).

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