Vapor Pressure of Deuterodiborane

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VAPOR PRESSURE data have been published for diborane (*1, 3, 4, 6*), but only scattered values are reported for deuterodiborane (of unknown deuterium content). In the course of studying the mass spectra of the deuterodiboranes (*2*), sufficient quantities of these materials were available for measurements of physical properties. Consequently, samples consisting of about a 0.5 ml. each of liquid deuterodiborane, B_2D_6, and diborane, B_2H_6, were prepared for vapor pressure measurements, the known values of B_2H_6 to be used as a check on the accuracy of the results. Mass spectrometric analyses indicated negligible impurities in both compounds; the deuterium content of the deuterated sample was determined to be 99.3%, corresponding to 95.9% B_2D_6 species, 4.1% B_2D_5H species, and negligible amounts of less deuterated species.

EXPERIMENTAL

Both compounds were kept in a common bath. Vapor pressures were measured with differential manometers, while bath temperatures were determined with calibrated vapor pressure thermometers (ethylene and carbon dioxide). All measurements were read with a cathetometer. The cold bath consisted of liquid Freon-12 in a 1-liter Dewar flask, which in turn was submerged in liquid nitrogen inside a larger Dewar flask. Temperature changes of Freon on standing under these conditions were practically negligible, and an electric heater had to be used to warm the Freon coolant between successive measurements. As an added control, however, the manometers could be isolated from the liquid reservoirs and be read at leisure after equilibrium conditions had been attained.

The vapor pressure data are shown in Table I. Included in the table are vapor pressures calculated from the following two equations, which are least squares representations of the experimental data:

$$B_2H_6 \log_{10}P_{mm.} = -974.156/T - 0.00653809\,T + 9.45290 \quad (1)$$

$$B_2D_6 \log_{10}P_{mm.} = -962.893/T - 0.00601480\,T + 9.31798 \quad (2)$$

Average per cent deviations are 0.69% for Equation 1 and 0.73% for Equation 2, while the extrapolated boiling points are 180.7° K. (−92.5° C.) for B_2H_6 and 179.8° K. (−93.4° C.) for B_2D_6. The vapor pressure data agree with those of Wirth and Palmer (*6*) within 1 to 2%, although present data are generally slightly higher than theirs. Their boiling point for B_2H_6 was 180.63° K.

When the Clapeyron equation for ideal gases is used in conjunction with Equations 1 and 2, the heats of vaporization of B_2H_6 and B_2D_6, at their boiling points, are calculated to be 3481 and 3516 cal. per mole, respectively, while the corresponding entropies of vaporization are 19.3 and 19.6 cal. per mole-degree. For B_2H_6 Wirth and Palmer, using critical pressure and temperature data, obtained 3413 cal. per mole for the heat of vaporization and 18.9 cal. per mole-degree for the boiling point entropy.

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Table I. Vapor Pressure of Diborane and Deuterodiborane

	Vapor Pressure, Mm.					
	B_2H_6			B_2D_6		
T° K.	Obsd.	Calcd.	Dev.	Obsd.	Calcd.	Dev.
118.2	2.7	2.7	0.0	2.5	2.9	+0.4
121.0	4.1	4.1	0.0	4.2	4.3	+0.1
124.3	6.5	6.4	−0.1	6.7	6.7	0.0
127.0	8.8	9.0	+0.2	9.1	9.4	+0.3
128.8	11.0	11.2	+0.2	11.5	11.7	+0.2
130.0	13.8	14.1	+0.3	14.3	14.8	+0.5
131.4	15.0	15.1	+0.1	15.7	15.8	+0.1
132.0	16.0	16.2	+0.2	16.7	17.0	+0.3
133.6	18.8	19.4	+0.6	19.9	20.3	+0.4
135.2	22.7	23.1	+0.4	23.7	24.1	+0.4
136.7	26.8	27.1	+0.3	28.1	28.3	+0.2
138.3	31.8	32.0	+0.2	33.2	33.4	+0.2
139.7	36.6	36.8	+0.2	38.6	38.5	−0.1
139.8	36.9	37.2	+0.3	38.7	38.9	+0.2
141.3	42.8	43.1	+0.3	44.8	45.0	+0.2
142.0	45.8	46.2	+0.4	48.1	48.2	+0.1
142.7	48.9	49.4	+0.5	51.3	51.5	+0.2
144.8	59.6	60.1	+0.5	62.2	62.7	+0.5
145.2	62.1	62.3	+0.2	65.3	65.0	−0.3
146.6	70.8	70.7	−0.1	73.7	73.8	+0.1
147.0	73.5	73.3	−0.2	76.6	76.5	−0.1
148.1	80.6	80.7	+0.1	84.5	84.2	−0.3
149.2	89.2	88.8	−0.4	93.2	92.7	−0.5
149.7	92.8	92.6	−0.2	96.8	96.7	−0.1
150.9	102.4	102.5	+0.1	107.0	107.0	0.0
152.3	115.1	115.0	−0.1	120.4	120.1	−0.3
156.2	156.5	156.7	+0.2	163.4	163.7	+0.3
158.4	185.6	185.1	−0.5	194.9	193.4	−1.5
159.7	203.6	203.6	0.0	212.8	212.8	0.0
161.4	232.5	230.1	−2.4	242.7	240.6	−2.1
163.0	259.3	257.5	−1.8	271.1	269.3	−1.8
164.7	292.0	289.3	−2.7	305.5	302.7	−2.8
166.0	319.3	315.6	−3.7	334.3	330.3	−4.0
167.8	357.3	355.1	−2.2	372.8	371.8	−1.0
169.8	402.8	403.3	+0.5	420.1	422.6	+2.5
171.1	438.8	437.3	−1.5	459.3	458.3	−1.0
173.2	497.0	496.6	−0.4	520.5	520.9	+0.4
175.1	554.8	555.5	+0.7	581.8	583.0	+1.2
177.1	622.3	622.9	+0.6	653.5	654.3	+0.8
178.3	663.7	666.2	+2.5	696.9	700.0	+3.1
178.5	670.2	673.6	+3.4	705.5	707.9	+2.4
179.2	699.7	700.1	+0.4	734.9	735.9	+1.0
180.8	760.3	763.5	+3.2			

Comparison of vapor pressure data of deuterated and protiated compounds reveals that the deuterated compound is the more volatile of the two; similar behavior was observed with the analogous pentaboranes (*5*).

LITERATURE CITED

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