hydroxide, an indicator with a color change above *p*H 7 cannot be used, because of the lability of the silane hydrogen in the presence of excess base. Satisfactory titrations were obtained using brom thymol blue (*p*H 6.0–7.6). However, equally good results were obtained without an added indicator; the first appearance of bubbles of hydrogen in the solution gave an accurate end-point.

Experimental

1,1,3,3-Tetrachlorodisiloxane.—To 70 ml. of anhydrous ethyl ether was added 47 g. (0.35 mole) of trichlorosilane (Anderson Laboratories). This solution was cooled to −78° in a Dry Ice–acetone-bath and stirred vigorously while 3.4 g. (0.19 mole) of water was added from a buret over a period of 30 minutes. The mixture was then stirred for several hours while it warmed to room temperature. Fractional distillation of the solution was carried out using a 50-cm. column packed with stainless steel helices. The product distilled at 99–100° (763 mm.); a trace of chlorine-containing material boiling at 145° was also found (probably hexachlorotrisiloxane). The yield was 3.2 g., or 8.5%. Yields from similar runs varied from 5 to 10%. The product was a colorless mobile liquid with n^{25}_{D} 1.4075 and d^{25}_{4} 1.347. The molecular weight by the vapor-density method was 222 (calcd. 216).

Anal. Calcd. for $H_2Si_2OCl_4$: Cl, 65.67. Found: Cl, 65.6, 65.7.

The infrared absorption spectrum of tetrachlorodisiloxane vapor was obtained using a cell of 3-cm. path length with KBr windows. The spectrum in the sodium chloride region was measured with a Baird automatic recording infrared spectrophotometer (Fig. 1); the region from 450 to 650 cm.$^{-1}$ was studied with a Perkin-Elmer spectrophotometer using a KBr prism. Strong absorption bands in this region were found centered at 533 and 604 cm.$^{-1}$. For most of the absorption bands, analogies are found in the spectrum of $HSiCl_3$.[4,5] However, the bands at 871, 912 and 1128 cm.$^{-1}$ have no counterparts in the $HSiCl_3$ spectrum.

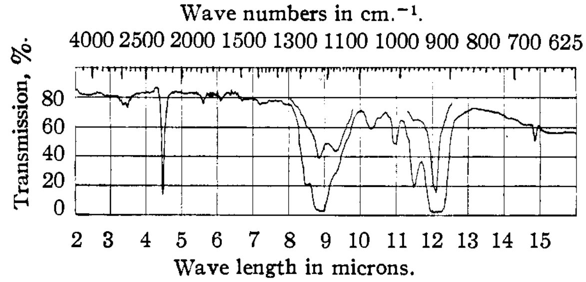

Fig. 1.—Infrared absorption spectrum of 1,1,3,3-tetrachlorodisiloxane. The lower line is at 40 mm., while the upper line is at 4 mm.

Partial Hydrolysis of Dichlorosilane.—The hydrolysis was carried out in the same way as that of trichlorosilane, except that *n*-propyl ether was used in place of ethyl ether. From 35 g. of dichlorosilane,[6] about 1 g. (4%) of product was obtained boiling over the range 70–81%. This material probably contained some *n*-propyl ether. Analysis gave 42.9% Cl; dichlorodisiloxane requires 48.2%.

In the course of this and other experiments with dichlorosilane, it was found that when a large quantity of the gas is vented in air, it inflames spontaneously and explosively. This is contrary to the findings of Stock,[7] who was working only with very small quantities. The liquid could be handled with relative safety if kept at −78°.

Partial Hydrolysis of Methyltrichlorosilanes.—The hydrolysis was performed in the same way as that of trichlorosilane. Only a trace of chlorine-containing material, boiling near 110°, was found.

Acknowledgment.—The author wishes to thank Dr. Eugene G. Rochow for his help and encouragement during the course of this work.

---

[4] T. C. Gibian and D. S. McKinney, THIS JOURNAL, **73**, 1431 (1951).

[5] C. A. Bradley, *Phys. Rev.*, **40**, 908 (1932).

[6] The dichlorosilane was a gift from the Linde Air Products Co., of Tonawanda, N. Y.

[7] A. Stock and C. Somieski, *Ber.*, **52**, 718 (1919).

MALLINCKRODT LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE 38, MASSACHUSETTS

COMMUNICATIONS TO THE EDITOR

THERMODYNAMIC AND KINETIC CONSTANTS FOR THE DIBORANE-BORINE EQUILIBRIUM

Sir:

We have succeeded in making a reliable estimate of the equilibrium constant for the dissociation of diborane into borine groups. The method is an indirect one. It is now clear why physical experiments designed to detect directly borine in diborane[1] have failed; at 155° and one atmosphere, the degree of dissociation of diborane as computed from the equilibrium constant given below is 1.63×10^{-5}, and at that temperature its general pyrolysis is fairly rapid.

The enthalpy change for the association reaction $2BH_3 = B_2H_6$ was deduced as follows. We measured the heats of reaction of trimethylamine with diborane and tetramethyldiborane, to produce the solid and liquid association products, respectively, using a precision vacuum ice calorimeter. These were corrected to the gas phase reactions and combined with the value given by Brown[2] for the heat of reaction of trimethylamine with boron trimethyl. Thus the three values (−17.3, −11.0, −17.6 kcal./mole of amine) demonstrate the effect of methyl substitution on the acidity of the boron unit, as well as on the strength of the (BH_2B) bridge. By making suitable corrections for inductive, steric and mesomeric contributions from the methyl groups as deduced from other data, we arrived at $\Delta H^{\circ}_{273} = -32 ^{+1}_{-2}$ kcal. per mole of diborane, for the above reaction.

The entropy change for the association of two borines was computed. Based on the structure of diborane as reported by Hedberg and Schomaker,[3] its translational plus rotational entropy is 53.70 ±

---

[1] A. Stock and E. Kuss, *Ber.*, **56B**, 789 (1923); G. C. Pimentel and K. S. Pitzer, *J. Chem. Phys.*, **17**, 882 (1949).

[2] H. C. Brown, H. Bartholomay and M. D. Taylor, THIS JOURNAL, **66**, 435 (1944).

[3] K. Hedberg and V. Schomaker, *ibid.*, **73**, 1482 (1951).

TABLE I

EQUILIBRIUM CONSTANTS AND EQUILIBRIUM PRESSURES OF BORINE, FOR THE REACTION $2BH_3 = B_2H_6$

T, °K.	K (at.$^{-1}$)	K (m./cc.$^{-1}$)	P_{BH_3} (at.)	P_{BH_3} (mm.)
273	1.73×10^{18}	3.88×10^{22}	$1.48 \times 10^{-9}\sqrt{P}_{at}$	$4.1 \times 10^{-8}\sqrt{P}_{mm}$
300	8.57×10^{15}	2.11×10^{20}	$2.16 \times 10^{-8}\sqrt{P}_{at}$	$6.0 \times 10^{-7}\sqrt{P}_{mm}$
373	2.34×10^{11}	7.16×10^{16}	$4.14 \times 10^{-6}\sqrt{P}_{at}$	$1.1 \times 10^{-4}\sqrt{P}_{mm}$
473	2.54×10^{7}	0.99×10^{12}	$1.99 \times 10^{-4}\sqrt{P}_{at}$	$5.5 \times 10^{-3}\sqrt{P}_{mm}$

0.1 e.u./mole, at 300°K. and one atmosphere. Using the frequency assignments for diborane as given by Anderson and Barker[4] we computed a vibrational contribution of 2.34 ± 0.1 e.u. A planar structure was assumed for BH_3, with a B–H distance equal to 1.16 Å. Badger's rule was then used to estimate the stretching force constant,[5] and various interpolations made to estimate the bending and interaction force constants. These led to a total entropy for BH_3 at 300°K. and one atmosphere of 44.9 ± 0.2 e.u. Thus for the association reaction, $\Delta S^\circ_{300} = -33.78$ e.u./mole of diborane. To the precision dealt with here one may neglect the specific heat correction and consider the enthalpy change independent of the temperature. Thus, $\log (K_{eq})_{atm} = -7.38_4 + (6995/T)$. Typical values for four temperatures are listed in the table. Clearly the equilibrium concentrations of borine are too small to be detected by the usual physical techniques.

We have also deduced an upper limit for the bimolecular rate constant (k') for the association of two borines. Burg[6] recently reported on the kinetics of the decomposition of borine carbonyl. He concluded that the mechanism of the reaction is as follows:

$$\text{(a)} \qquad BH_3CO = BH_3 + CO \quad K'_{eq}$$

$$\text{(b)} \qquad BH_3 + BH_3CO \longrightarrow B_2H_6 + CO \quad k$$

Hence, during the approach to equilibrium, both the inverse of (a), and step (b), must proceed faster than does the association:

$$\text{(c)} \qquad 2BH_3 \longrightarrow B_2H_6 \quad k'$$

That is, the correctness of Burg's mechanism implies the inequality

$$k'(BH_3)^2 < k(BH_3)(BH_3CO)$$

Using the equilibrium condition on the first step of the borine decomposition (a), this reduces to

$$k' < k(P_{tot}/K'_{eq})^{1/2}$$

ΔH° for (a) was obtained by combining the ΔH° for the over-all borine carbonyl decomposition as given by Burg with our value for the heat of dissociation of diborane. The entropy change for step (a) was obtained by subtracting the computed entropy of H_3BCO—as based on the structural data of Gordy[7] and spectral data of Cowan[8]—from the now known entropy of borine and carbon monoxide.[9] Thus K'_{eq} was computed. The resulting condition on the rate constant is

$$k' < 5 \times 10^9 \text{ cc./mole/sec.}$$

Such a value for a second order rate constant suggests an activation energy of about 5 kcal./mole. It is indeed very interesting to compare the following rate constants:

$$k \ = 1.98 \times 10^{6} \text{cc./mole/sec.}; \quad E_a \cong 6.8 \text{ kcal./mole}$$
$$k' < 5 \quad \times 10^9 \qquad E_a \sim 5$$
$$k'' = 6.4 \quad \times 10^9 \qquad E_a \cong 6$$

The last value is for the displacement reaction

$$BH_3 + B_2D_6 = BH_3BD_3 + BD_3 \quad k''$$

as reported by Koski.[10]

---

[4] W. E. Anderson and E. F. Barker, *J. Chem. Phys.*, **18**, 698 (1950).

[5] The force constant deduced is 3.38×10^5 dynes/cm. This compares with 3.21 and 3.42×10^5 reported for the B–H stretching force constant in H_3BCO and $B_3N_3H_6$, respectively.

[6] A. Burg, THIS JOURNAL, **74**, 3482 (1952).

[7] W. Gordy, H. Ring and A. Burg, *Phys. Rev.*, **78**, 512 (1950).

[8] R. D. Cowan, *J. Chem. Phys.*, **18**, 1101 (1950).

[9] H. L. Johnson and C. O. Davis, THIS JOURNAL, **56**, 271 (1934).

[10] W. S. Koski, private communication.

DEPARTMENT OF CHEMISTRY S. H. BAUER
CORNELL UNIVERSITY ALLAN SHEPP
ITHACA, NEW YORK ROBERT E. MCCOY

RECEIVED JANUARY 2, 1953

THERMODYNAMIC FUNCTIONS FOR SURFACES OF CRYSTALS

Sir:

Recently a method[1] was described for the determination of thermodynamic quantities of surfaces of solids which appears to be beautiful in its simplicity, and extremely general in its application. Besides the surface area, the measurements required are the differences in the heats of solution and in the heat capacities of a finely divided sample and one composed of very large crystals. It is regrettable that these authors omitted to call attention to an *essential pragmatic test* for the applicability of their method. Since the enthalpy, entropy and surface free energy are *extensive* properties their magnitudes per unit area should be *independent* of *crystallite size and shape.* The preliminary results quoted by Jura and Garland for magnesium oxide have not been subjected to this test. What, then, may we anticipate when a complete set of data becomes available for a well crystallized substance?

First let us assume that regardless of the temperature and crystallite size, the structure of the crystals is geometrically perfect,[2] and their surface is absolutely free of adsorbed gases. Nevertheless the thermodynamic functions for the surface for two samples with the same total area will differ *unless* they have the same proportions of area contributed by faces of different crystallographic indices. This is based on the established facts that faces with different indices have different characteristics for adsorption,[3] catalysis,[4] and reaction.[5]

---

[1] G. Jura and C. W. Garland, THIS JOURNAL, **74**, 6033 (1952).

[2] This is equivalent to the statement that such a structure is determined by the criterion of minimum enthalpy only.

[3] For example, T. N. Rhodin, Jr., THIS JOURNAL, **72**, 5691 (1950).

[4] O. Beeck, *Rev. Mod. Phys.*, **17**, 61 (1945).

[5] T. N. Rhodin, Jr., THIS JOURNAL, **73**, 3143 (1951).