η_0 the viscosity of solvent, Γ the ional concentration, $1/\kappa$ the mean radius of the ionic atmosphere, "a" the mean distance of approach of the ions and $\phi(\kappa a)$ the exponential integral function of the theory, values of which have been tabulated by Harned and Owen.[2,4] For calcium chloride at 25°, $\nu_1 = 2$; $\nu_2 = 1$; $z_1 = -1$; $z_2 = 2$; $\lambda_1^0 = 76.34$[3]; $\lambda_2^0 = 59.50$[3]; $\eta_0 = 8.949 \times 10^{-3}$; $D = 78.54$; $å = 4.944$ Å.[6]; and $T = 298.16$. Upon substitution of these values, equations (3) and (4) reduce to

$$\mathbf{D} = 24.9432 \times 10^{10}\, T\, (\overline{M}/c)(1 + c\, (\partial \ln y_{\pm}/\partial c)) \quad (5)$$

and

$$\left(\frac{\overline{M}}{c}\right) \times 10^{20} = 17.970 - \frac{4.3933\sqrt{c}}{(1 + 2.814\sqrt{c})} + 136.77c\, \phi(\kappa a) \quad (6)$$

The Debye and Hückel equation with an additional linear term, Bc, was employed to compute the activity coefficient term in equation (5). By introduction of the values of a and B given by MacInnes,[6] this function becomes

$$\left(1 + c\,\frac{\partial \ln y_{\pm}}{\partial c}\right) = 1 - \frac{2.0165\sqrt{c}}{(1 + 2.814\sqrt{c})^2} + 0.33854c - c\psi(d) \quad (7)$$

The density term $\psi(d)$ is negligible at low concentrations.

The results of this computation are given in the third column of Table II and both the observed and theoretical values are plotted in Fig. 1. The discrepancy between the observed and calculated results is very pronounced even at the lowest concentration of 0.001 molar. This fact is also supported by the diaphragm cell measurements of Hollingshead and Gordon,[7] which are represented by the dots in the figure.

Summary

1. The differential diffusion coefficient of calcium chloride in water at 25° has been determined at concentrations ranging from 0.001 to 0.005 molar. These results agree satisfactorily with those obtained from diaphragm cell measurement by Hollingshead and Gordon.

2. The observed differential diffusion coefficients do not agree with the theory of Onsager and Fuoss.

3. Since our results confirm the theory of Onsager and Fuoss for potassium chloride solutions, but differ widely from the theory for dilute calcium chloride solutions, we conclude that their estimate of the electrophoretic effect is either wrong or incomplete for this unsymmetrical type electrolyte.

NEW HAVEN, CONNECTICUT RECEIVED APRIL 2, 1949

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[6] MacInnes, "Principles of Electrochemistry," Reinhold Publishing Corporation, New York, N. Y., 1939, p. 164; Shedlovsky and MacInnes, THIS JOURNAL, **59**, 503 (1937). We have not recalculated the results by the equation for the activity coefficient with the more recent values of the universal constants but have used those given by MacInnes. Since $\partial \ln y_{\pm}/\partial c$ is required, this procedure makes no appreciable difference in the computations.

[7] Hollingshead and Gordon, *J. Chem. Phys.*, **9**, 152 (1941).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF CALIFORNIA]

Solutions of Diborane in Ammonia

BY GEORGE W. RATHJENS, JR., AND KENNETH S. PITZER

The nature of the addition compound of diborane and ammonia has been the subject of considerable discussion.[1-7] A review of the published data showed that evidence for the two boron formula $B_2H_6.2NH_3$ (as compared to $BH_3.NH_3$), was the tensiometric study of Stock and Pohland.[8] However, these data show a most peculiar increase in apparent molecular weight with dilution. Consequently, it seemed worthwhile to investigate this same system by determining the freezing point of ammonia in solutions containing diborane. The work of Schlesinger and Burg,[4,6] indicates that diborane–ammonia solutions which have never been hotter than the melting point of ammonia (195° K.) are reproducible and of simple and presumably definite molecular constitution as compared to similar solutions at higher temperatures.

Apparatus and Materials.—Commercial anhydrous ammonia was purified by distilling four times, including one distillation from a solution of sodium in the ammonia. The diborane was prepared from commercial lithium borohydride and boron trifluoride in ether solution. It was purified by repeated simple distillation.

The apparatus was of the same type as that used for heat capacity measurements in this Laboratory. A full description of this type of apparatus is given by Giauque and Egan.[9] Temperatures were measured with both a copper–constantan thermocouple and a gold resistance thermometer–heater. It is estimated that the temperature differences were measured to an accuracy of approximately 0.01°.

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[4] H. I. Schlesinger and A. B. Burg, THIS JOURNAL, **60**, 290 (1938).

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[7] L. Agronomov, *J. Gen. Chem.* (*U.S.S.R.*), **9**, 1389 (1939).

[8] A. Stock and E. Pohland, *Ber.*, **58**, 657 (1925).

[9] W. F. Giauque and C. J. Egan, *J. Chem. Phys.*, **5**, 45 (1937).

Procedure.—Diborane was distilled into the calorimeter containing solid ammonia at slightly above the melting point of diborane. The ammonia was melted a part at a time by supplying measured amounts of electrical energy through the resistance thermometer. The temperature was determined after each energy input during the melting and the fraction of ammonia melted calculated from the amount of energy supplied. From these data the mole fraction of diborane was calculated.

Although the apparatus used is excellently adapted for the thermal measurements, it does not permit stirring of the solutions. However, equilibrium was attained in about twenty-five minutes even with the two phase systems (as compared to six minutes for all solid or all liquid). Correction must be made for the heat leak between the calorimeter and the copper block surrounding it. Taking complete fusion as the base point, the uncertainty in the fraction melted is greater the smaller the amount melted. For this reason, the data are given only for fraction melted approximately 0.3 or greater.

Runs were made on pure ammonia to check both temperature and heat measurements. The data of Overstreet and Giauque[10] were used for pure ammonia.

Experimental Results.—Two series of runs were made with separate samples of ammonia and diborane. In the first series, two sets of temperature–fraction melted data were taken (shown as 1A and 1B in Table I). In the second series, three sets of data were obtained. Apparently on freezing and remelting to obtain a second set of data, a slight change in the resistance thermometer occurred. This is shown by the fact that the resistance thermometer ΔT's in set 1B are consistently smaller than in 1A for the same fraction melted and likewise as between sets 2B and 2C as compared to 2A. Furthermore, the observed resistance at the melting point of pure ammonia increased by 0.011 ohm (corresponding to 0.012°) between series 1 and series 2. Presumably this effect arose from a slight stretching of the calorimeter. The thermocouple would not be affected in this way but is hardly precise enough to verify the effect.

The experimental results are presented in Table I together with the theoretical ΔT values assuming the formula B_2H_6 and ideal solution behavior. Agreement is obtained on the assumption of a precision of about 0.05° for the thermocouple and the possibility of a shift of about 0.05° in the resistance thermometer between runs.

TABLE I

Series 1: 3.007 moles NH_3, 0.00437 mole B_2H_6
Series 2: 2.790 moles NH_3, 0.01636 mole B_2H_6

	Exptl. ΔT		
$N_{B_2H_6}$	T. C.	Resistance	Theoretical ΔT assuming B_2H_6
Series 1A			
0.00299	0.21	0.156	0.168
.00200	.15	.111	.112
.00154	.10	.087	.086
.00142		.079	.080
Series 1B			
0.00303	0.18	0.138	0.170
.00190	.09	.092	.106
.00173	.08	.087	.097
.00161	.06	.079	.090
.00142		.065	.080
Series 2A			
0.0203	1.17	1.17	1.14
.0120	0.71	0.69	0.67
.00844	.48	.48	.47
.00684	.38	.39	.38
.00583		.33	.33
Series 2B			
0.0223	1.33	1.24	1.25
.0141	0.80	0.76	0.79
.00929	0.56	.49	.52
.00583		.30	.33
Series 2C			
0.0211	1.35	1.26	1.18
.00943	0.60	0.49	0.53
.00727	0.46	.36	.41
.00583		.30	.33

Conclusion as to Molecular Species.—The data in Table I suffice to establish that B_2H_6 dissolves in ammonia at 195° K. as species with two boron atoms per molecule, *i. e.*, $B_2H_6 \cdot xNH_3$. Within the uncertainty of possibly 5%, there is no indication of either dissociation or association. In these dilute solutions no conclusions can be drawn concerning the amount of ammonia bound to a diborane molecule.

Most of the postulated formulas for this compound cited above are consistent with the present result. Thus the present result serves only to remove any remaining uncertainty that a one-boron formula, such as BH_3NH_3, might possibly apply under the conditions here investigated.

Heat of Reaction of Diborane with Ammonia.—We assumed and observations indicated that the diborane did not react rapidly with ammonia at 120° K. when it was distilled into the calorimeter. Then the total heat needed to warm up the system to a given fraction ammonia melted in the first run of a series should be less than the corresponding heat needed in later runs by the heat of reaction of the diborane. The data for the second series give 260 ± 20 cal. for this quantity which is quite uncertain because of large heat exchange corrections. (Series 1 with the smaller amount of diborane is not suited for this measurement at all.)

On a molal basis for B_2H_6 this heat becomes 15.9 ± 1.2 kcal. per mole; or

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(10) R. Overstreet and W. F. Giauque, THIS JOURNAL, **59**, 254 (1937).

$$B_2H_6(\text{liq.}) + xNH_3(s) = B_2H_6\cdot xNH_3(s);\ \Delta H = -15.9 \pm 1.2\ \text{kcal./mole.}$$

Summary

Freezing point depression measurements for diborane in ammonia (at approximately 195° K.) show the diborane to be present in a two boron formula, $B_2H_6\cdot xNH_3$. No sign of either dissociation or association was noted.

The heat evolved on reaction of diborane with solid ammonia is 15.9 ± 1.2 kcal, per mole of B_2H_6.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

The Rotational Configuration and Dipole Moments of 1,1,2-Trichloroethane and 1,1,2,2-Tetrachloroethane[1]

BY J. R. THOMAS[2] AND WILLIAM D. GWINN

The rotational configurations of 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane have been previously investigated. From the electron diffraction investigation of the former compound Beach and Turkevich[3] were able to show that the stable configurations were staggered rather than eclipsed. These authors suggested that the skew configuration formed by rotating one-half of the molecule 120° out of the *cis* position was the most important form. By similar means Schomaker and Stevenson[4] showed that 1,1,2,2-tetrachloroethane existed in staggered rather than eclipsed forms. They suggested that both possible configurations were relatively stable. Hassel and Viervoll,[5] however, interpreted the same type of data as showing that only the configuration oscillating about the *trans* position was of importance. From the number of Raman lines observed in the liquid spectrum it has been concluded that at least two configurations exist.[6,7] Langseth and Bernstein[7] from the Raman spectrum of the liquid and its variation with temperature concluded that the two forms differed in energy by 1100 cal./mole. These investigators assigned an eclipsed configuration to one of the forms, a possibility which is definitely excluded by the electron diffraction data. Mizushima and his co-workers[6] showed from the Raman spectrum that at least two forms probably existed in the solid state. From gaseous dipole moment determinations over a limited temperature range Smyth and McAlpine[8] showed a configuration other than the *trans* to be present. These authors also suggested that both staggered configurations existed and that the two were of comparable stability.

While the electron diffraction investigations show definitely that these compounds exist in staggered rather than eclipsed configurations, the method does not give reliable information about the relative abundance of the staggered forms. The Raman spectra of the liquid and solid states of 1,1,2,2-tetrachloroethane indicate that more than one configuration exists in these phases. However, the extrapolation of these data to the gaseous state seems questionable, since the intermolecular forces in condensed systems are comparable to the intramolecular forces determining the rotational configuration of an isolated molecule. While the gaseous dipole moment investigations of Smyth and McAlpine definitely show that 1,1,2,2-tetrachloroethane does not exist exclusively as the *trans* form, the restricted temperature range over which they were able to work prohibits any further conclusions.

In order to extend the information concerning the rotational configuration of these compounds, we have determined their gas dipole moments over an extended range of temperature. As an aid in the interpretation of these results the dipole moment of pentachloroethane also has been determined.

Experimental

The determinations of dielectric constants were made using the heterodyne beat method. A stainless steel gas cell with a capacity of 970 micromicrofarads was incorporated in the resonant grid circuit of a Hartley type electron coupled oscillator operating at 200 kc. An electron coupled crystal oscillator, operating at 100 kc., was used as a frequency standard. A high degree of frequency stability in both oscillators was obtained by proper choice of circuit elements and constructional details. In order to facilitate tuning, and to reduce inter-oscillator coupling, both oscillator tubes were followed by two wide band-pass buffer stages. The balance point was determined by applying the output of the two oscillators to the deflection plates of an oscilloscope tube and observing the ap-

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[1] Presented before the General, Physical and Inorganic Division of the American Chemical Society at Portland, Oregon, September 13, 1948. Abstracted from a thesis by J. R. Thomas, presented to the Graduate Division of the University of California in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1947.

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[6] S. Mizushima, Y. Morino and K. Kozima, *Sc. Pap. I. P. C. R. (Tokyo)*, **29**, 111 (1936).

[7] A. Langseth and H. J. Bernstein, *J. Chem. Phys.*, **8**, 1410 (1940).

[8] C. P. Smyth and K. B. McAlpine, THIS JOURNAL, **57**, 979 (1935).