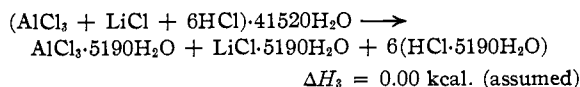
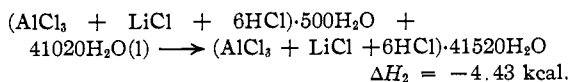
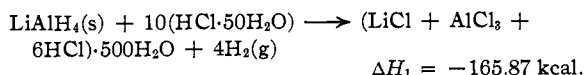
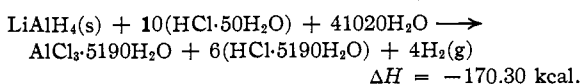


(3) **Lithium Aluminum Hydride.**—The reactions used to determine the heat of formation of this compound are expressed by the equations



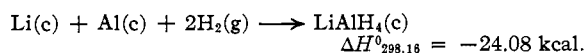
Summation of the above reactions gives



The following heats of formation,  $\Delta H_f^0$  in kcal., in addition to those listed previously were used to calculate the heat of formation of lithium aluminum hydride:  $\text{AlCl}_3\cdot 5190\text{H}_2\text{O}$ ,<sup>17</sup> -243.9;  $\text{LiCl}\cdot 5190\text{H}_2\text{O}$ , -106.41;  $\text{HCl}\cdot 5190\text{H}_2\text{O}$ ,<sup>17</sup> -39.973;  $\text{HCl}\cdot 50\text{H}_2\text{O}$ ,<sup>17</sup> -39.577.

The heat of formation of  $\text{LiCl}\cdot 5190\text{H}_2\text{O}$  was obtained by the same method used previously for  $\text{LiCl}\cdot 60\text{H}_2\text{O}$ .

The heat of formation of lithium aluminum hydride obtained was:



### Summary

A "bomb" calorimeter was used to determine the heats of reaction of sodium borohydride, lith-

ium borohydride, and lithium aluminum hydride with an excess of dilute hydrochloric acid. The heat effects were measured with a precision of 0.11, 0.35 and 0.20%, respectively. The specific heats and densities of the three hydrides were determined and, where significant, other thermal data were obtained so that the heats of formation of the hydrides at 25° could be calculated. The standard state chosen for boron was boron (solid, amorphous). The values for the standard heats of formation in kcal./mole were: sodium borohydride,  $-43.83 \pm 0.07$ ; lithium borohydride,  $-44.15 \pm 0.30$ ; lithium aluminum hydride,  $-24.08 \pm 0.35$ .

The values for the borohydrides, however, can be no more accurate than the least accurately known heat of formation used additively in their calculation.  $\Delta H_f^0$  for  $\text{H}_3\text{BO}_3 \cdot \infty \text{H}_2\text{O}$  was calculated from  $\Delta H_f^0$  for  $\text{B}_2\text{O}_3$  which is known only to about 1% or 3 kcal. Precise knowledge of the latter quantity will establish the above values with the accuracy indicated. An approximate allowance for impurities may be made by assuming them to be thermally inert in the reaction; the heats of formation may then be altered by an increment corresponding to the difference between the purities of the samples and 100%.

Methods were devised for increasing the purity of the crude hydrides to better than 99%. The purity of the compounds was determined by measuring the amounts of hydrogen liberated by their reaction with dilute acid with a precision and accuracy better than 0.1%.

PITTSBURGH, PENNSYLVANIA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

## The Differential Diffusion Coefficient of Calcium Chloride in Dilute Aqueous Solutions at 25°

BY HERBERT S. HARNED AND ARTHUR L. LEVY

Recent determinations of the diffusion coefficient of potassium chloride in water and at room temperatures have shown remarkable agreement with theory.<sup>1</sup> It is to be expected that this may not be the case for unsymmetrical type electrolytes, since the cation transference numbers of calcium and lanthanum chlorides do not appear to conform to the Onsager theory.<sup>2</sup> Indeed, the theory of electrophoresis as applied at present to unsymmetrical electrolytes will have to be modified if it can be shown that the behavior of the diffusion coefficient in dilute solutions of one of these salts exhibits a similar dis-

crepancy with the theory. In order to decide this question, we have determined the diffusion coefficient of calcium chloride in water in the concentration range 0.001 to 0.005 molal at 25°.

### Experimental Results

The determination of the diffusion coefficient was made by the conductance method as described in detail by Harned and Nuttall.<sup>1</sup> In this method the diffusion coefficient was determined by the equations

$$\ln(K_B - K_T) = -t/\tau + \text{constant} \quad (1)$$

and

$$D = \frac{a^2}{\pi^2} \times \frac{1}{\tau} \quad (2)$$

where  $D$  is the diffusion coefficient,  $K_B$  and  $K_T$  are the conductances at the bottom and top of the

(1) Harned and Nuttall, *THIS JOURNAL*, **67**, 736 (1947); **71**, 1460 (1949).

(2) See Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corporation, New York, N. Y., 1943, p. 164.

conductance cell, respectively,  $t$  is the time in seconds and " $a$ " is the depth of the cell. Equation (1) contains the assumption that, in the concentration ranges employed, the difference in conductances ( $K_B - K_T$ ) is proportional to the difference in concentrations at the bottom and top electrodes, or ( $c_B - c_T$ ). This assumption is proved to be valid for calcium chloride solutions within practical limits by examination of the data of Shedlovsky and Brown.<sup>3</sup> Their equation (2) with numerical coefficients computed by us becomes

$$\Lambda^0 \equiv \frac{\Lambda^0 + 109.8\sqrt{c}}{1 - 0.49074\sqrt{c}} = 135.84 + 404.48c + 102.36c \log c + 2604.4c^2 \quad (3)$$

which was found to agree with their observed values of  $\Lambda^0$  within very narrow limits. By use of this equation, values of  $\Lambda$  and subsequently, specific conductances,  $L$ , at the equivalent concentrations,  $c$ , were calculated. These are listed in Table I and from them the values of  $(L_1 - L_2)/(c_1 - c_2)$  at  $(c_1 + c_2) = 0.011$  given in the last column were computed.

TABLE I

SPECIFIC CONDUCTANCES OF CALCIUM CHLORIDE AT 25°

$c_1$	$L_1 \times 10^3$	$c_2$	$L_2 \times 10^3$	$(L_1 - L_2)/(c_1 - c_2)$
0.01	1.2036	0.001	0.13036	0.11925
.009	1.0890	.002	.25640	.11894
.008	0.97360	.003	.37986	.11875
.007	.85715	.004	.50136	.11860
.006	.73974	.005	.62125	.11850

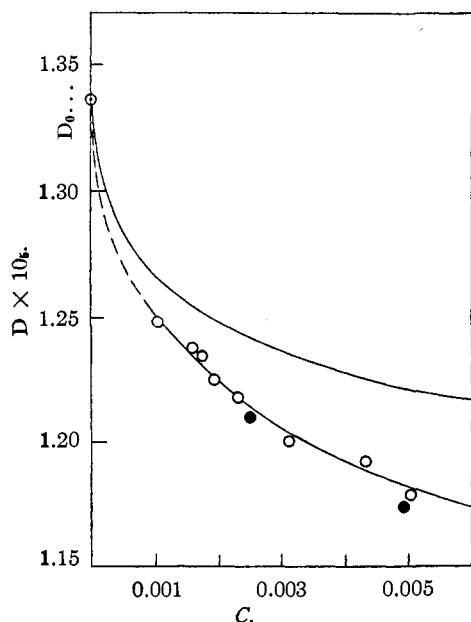


Fig. 1.—Observed and calculated differential diffusion coefficients of calcium chloride in dilute aqueous solutions at 25°: O, present results; ●, diaphragm cell measurements; upper curve, theoretical.

(3) Shedlovsky and Brown, *THIS JOURNAL*, **56**, 1066 (1934).

Although there is a small decrease in these concentration coefficients, the result is sufficiently constant to warrant the assumption involved in equation (1).

The diffusion coefficient was computed from the conductances by the procedure adopted previously for potassium chloride solutions. Twenty-four to thirty-six hours after diffusion was initiated, five readings per day at two-hour intervals were taken over a period of five days, and after thorough stirring the final conductances which determined the cell constant ratio between the top and bottom pairs of electrodes were recorded. The diffusion coefficient was then computed from  $1/\tau = -\Delta[\ln(K_B - K_T)]/\Delta t$  for each twenty-four-hour period. This method provides twenty determinations of  $D$  during the diffusion process and their mean is the value accepted for  $D$ . The measurements have the same consistency as those obtained with potassium chloride solutions, as illustrated by Table I given by Harned and Nuttall (ref. 1). The final results are listed in Table II.

TABLE II

OBSERVED AND CALCULATED ACTIVITY COEFFICIENTS OF CALCIUM CHLORIDE AT 25°

$c$ (moles l. <sup>-1</sup> )	$D \times 10^4$ (observed)	$D \times 10^4$ (theoretical)	$\Delta = \frac{D_{\text{theo.}}}{D_{\text{obs.}}}$
0.00000	...	1.3364	0.000
.00105	1.248	1.265	.017
.00173	1.235	1.254	.019
.00183	1.231	1.252	.021
.00193	1.225	1.251	.026
.00230	1.218	1.246	.028
.00309	1.199	1.237	.038
.00429	1.192	1.227	.035
.00501	1.179	1.222	.043

### Theoretical Calculations<sup>4</sup>

The theoretical equation of Onsager and Fuoss<sup>5</sup> for the diffusion coefficient of an electrolyte is

$$D = (\nu_1 + \nu_2) 1000 RT \left( \frac{\bar{M}}{c} \right) \left( 1 + c \frac{\partial \ln y_{\pm}}{\partial c} \right) \quad (3)$$

where

$$\frac{\bar{M}}{c} = 1.0748 \times 10^{-20} \frac{\lambda_1^0 \lambda_2^0}{\nu_1 |z_1| \Lambda^0} - \frac{(|z_2| \lambda_1^0 - |z_1| \lambda_2^0)^2 3.1322 \times 10^{-19}}{|z_1 z_2| (\nu_1 + \nu_2) \Lambda^{0.2}} \frac{\sqrt{\Gamma}}{\eta_0 (DT)^{1/2}} \frac{1}{(1 + \kappa a)} + \frac{(z_2^2 \lambda_1^0 + z_1^2 \lambda_2^0)^2 9.304 \times 10^{-13}}{\Lambda^0} \frac{c \phi(\kappa a)}{\eta_0 (DT)^2} \quad (4)$$

In the above,  $\nu_1$  is the number of anions,  $\nu_2$  the number of cations into which the electrolyte dissociates,  $z_1$ , and  $z_2$ , their valences and  $\lambda_1^0$  and  $\lambda_2^0$  their equivalent conductances at infinite dilution.  $\Lambda^0 = \lambda_1^0 + \lambda_2^0$ .  $R$  is the gas constant,  $T$  the absolute temperature,  $c$  is the concentration in moles per liter, and  $y_{\pm}$  is the activity coefficient or mean activity divided by the mean molar concentration.  $D$  is the dielectric constant,

(4) Ref. (2) and Harned, *Chem. Revs.*, **40**, 461 (1947).

(5) Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

$\eta_0$  the viscosity of solvent,  $\Gamma$  the ionic 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.<sup>2,4</sup> For calcium chloride at 25°,  $\nu_1 = 2$ ;  $\nu_2 = 1$ ;  $z_1 = -1$ ;  $z_2 = 2$ ;  $\lambda_1^0 = 76.34^3$ ;  $\lambda_2^0 = 59.50^3$ ;  $\eta_0 = 8.949 \times 10^{-2}$ ;  $D = 78.54$ ;  $\bar{a} = 4.944 \text{ \AA.}$ <sup>6</sup>; and  $T = 298.16$ . Upon substitution of these values, equations (3) and (4) reduce to

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

and

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

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,<sup>6</sup> this function becomes

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

(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.

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,<sup>7</sup> 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.

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

NEW HAVEN, CONNECTICUT RECEIVED APRIL 2, 1949

[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.<sup>1-7</sup> A review of the published data showed that evidence for the two boron formula  $B_2H_6 \cdot 2NH_3$  (as compared to  $BH_3 \cdot NH_3$ ), was the tensiometric study of Stock and Pohland.<sup>8</sup> 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,<sup>4,6</sup> 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.<sup>9</sup> 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°.

- (1) E. Wiberg, *Z. anorg. allgem. Chem.*, **173**, 219 (1928).
- (2) A. Stock and E. Wiberg, *Ber.*, **65**, 1711 (1932).
- (3) A. Stock, "The Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.
- (4) H. I. Schlesinger and A. B. Burg, *THIS JOURNAL*, **60**, 290 (1938).
- (5) H. I. Schlesinger, D. Ritter and A. B. Burg, *ibid.*, **60**, 2297 (1938).
- (6) H. I. Schlesinger and A. B. Burg, *Chem. Revs.*, **31**, 1 (1942).
- (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).