[CONTRIBUTION NO. 754 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Heats of Solution and Dilution of Orthoboric Acid at 25°[1]

BY JOE SMISKO AND L. S. MASON

This investigation was undertaken in conjunction with a program of study of thermochemical and thermodynamic properties of certain hydrides and metallo-borohydrides currently in progress in this Laboratory.[2] The heats of reaction of some of these compounds with dilute hydrochloric acid have been measured for the purpose of determining their heats of formation.[2a] Such calculations require a knowledge of the heats of formation of aqueous solutions of boric acid[3] which are formed when borohydrides react with water or dilute acids. Data on heats of solution and dilution obtained in this study, when combined with the heat of formation of crystalline boric acid, have made possible the calculation of the heats of formation of aqueous boric acid solutions from saturation (0.936 *m*) down to about 0.00035 *m*.

Previously reported values for the heat of solution of boric acid in kcal. per mole as tabulated by Bichowsky and Rossini[4] are as follows: 5.39 for $H_3BO_3{\cdot}400H_2O$[5]; 4.8 for $H_3BO_3{\cdot}200H_2O$[6]; 3.18 for H_3BO_3 dissolved to form a saturated solution.[7]

Experimental

C. P. Boric acid was recrystallized three times from twice distilled water and filtered through sintered glass. Samples were dried to constant weight over metaboric acid in a desiccator. Spectroscopic analysis[8] of the purified acid indicated that impurities did not exceed a few thousandths of 1%. The sample was found to have a purity of 100.0 ± 0.1% by titration with standard sodium hydroxide in the presence of mannitol using phenolphthalein as an indicator. Conditions recommended by Hollander and Rieman[9] for this analysis were carefully maintained.

The calorimeter[10] used in this study had a sensitivity of about 0.015 cal. per mm. deflection of the reading instrument. The heat of solution experiments were performed by sealing a weighed sample of boric acid in very thin-walled glass bulbs. These were crushed under water in the calorimeter. The heat developed by crushing the bulbs was negligible except in the case of the largest samples. In the latter cases a small correction was applied to the measured heats of solution. Solutions of boric acid contained in Monel metal pipets were diluted into one liter of water for the measurements of the heats of dilution. The volumes of the pipets were 6.788 and 6.755 ± 0.004 ml.

The densities of the boric acid solutions used in the heats of dilution experiments were required for the calculation of molalities from molarities. The densities were measured with calibrated 10-ml. pycnometers and were found to be d^{25}_4 1.016 and 1.008 for 0.936 *m* and 0.517 *m* solutions, respectively. The saturation concentration (0.936 *m*) was determined for carefully equilibrated solutions both by titration and by weighing the solid contained in a weighed quantity of the solution. This saturation concentration is slightly higher than the value of 0.928 *m* reported by Blasdale and Slansky.[11]

Results

In Table I each heat of solution value represents four or five experiments made by weighing separate samples of boric acid which when dissolved gave very nearly the same final concentrations. The heat effects represented by the small differences in the final concentrations were negligible. The heats of solution for the samples in a particular group were averaged and represented by one average final concentration. The heats of dilution were combined with the heats of solution values having the same final concentrations as the dilution experiments. Heats of solution to final concentrations from saturation to 0.00035 *m* were thereby obtained.

TABLE I

HEATS OF SOLUTION OF BORIC ACID AT 25°

Experiments	Average number of moles	Initial concentration moles/1000 g. water	Average final concentration moles/1000 g. water	ΔH (Experimental) cal./mole H_3BO_3	ΔH (from equation) cal./mole H_3BO_3
4	0.01024	Crystalline	0.01027	5277 ± 6[a]	5273
4	.00610	Crystalline	.00611	5273 ± 4	5273
5	.00224	Crystalline	.00225	5288 ± 7	5288
5	.000827	Crystalline	.000829	5355 ± 12	5357
5	.000351	Crystalline	.000352	5430 ± 12	5424
Heats of Dilution of Boric Acid at 25°					
4	0.00610	0.936	0.00612	49 ± 2	49
4	.00342	.517	.00343	31 ± 2	30

[a] Probable error of the mean.

The equation $\Delta H = Ae^{-km} + B - Cm$ was found to express the dependence of the molar heat of solution on the molality. *A*, *B*, *C* and *k* are constants having the values 234, 5273, 53 and 1230, respectively. The curve from 0.936 to 0.006 *m* is linear with a small slope (53 cal. per mole). From 0.006 to 0.00035 *m* the slope changes rapidly exponentially. It seems probable that heats of ionization contribute to the

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[2] (a) W. D. Davis, L. S. Mason and G. Stegeman, THIS JOURNAL, **71**, 2775 (1949); (b) C. C. Nathan, Thesis, University of Pittsburgh, 1948.

[3] Boric acid will mean ortho boric acid unless otherwise specified.

[4] F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

[5] J. Thomsen, "Thermochemische Untersuchungen," Vols. I–IV, 1882–1886.

[6] M. Berthelot, *Ann. Chim. Phys.*, **17**, 132 (1879).

[7] A. Ditte, *ibid.*, **13**, 67 (1878).

[8] Thanks are due to Dr. Mary E. Warga for this analysis.

[9] M. Hollander and W. Rieman, *Ind. Eng. Chem., Anal. Ed.*, **17**, 602 (1945).

[10] M. Fineman and W. E. Wallace, THIS JOURNAL, **70**, 4165 (1948).

[11] W. C. Blasdale and C. M. Slansky, *ibid.*, **61**, 917 (1939).

heats of solution in the low concentration range. The equation indicates that the heat of solution is 5507 cal. per mole at infinite dilution, but it seems inadvisable to give much weight to this extrapolated value in view of the large rate of change of ΔH with m at very low concentrations. Heats of solution at concentrations less than 0.00035 m were below the limit of measurement of the calorimeter used.

The heats of formation of crystalline boric acid and of aqueous boric acid solutions at rounded concentrations are shown in Table II. These values were calculated using a value of −303 kcal. per mole for the heat of formation of boric oxide reported recently by the National Bureau of Standards as a result of measurements of the heat of dissociation of diborane.[12] This value is in agreement with one obtained by Nathan and Stegeman[2b] by direct combustion of boron. The following two reactions were also used in the calculations

$$B_2O_3(c) + 3H_2O(l) + 1000H_2O = 2(H_3BO_3 \cdot 500H_2O)$$
$$\Delta H_{298°K} = -3.48 \text{ kcal./mole}$$
$$H_3BO_3(c) + 1000H_2O = H_3BO_3 \cdot 500H_2O$$
$$\Delta H_{298°K} = 5.27 \text{ kcal./mole}$$

The heat effect of the first reaction was reported by Southard[13] and the value for the second reaction was obtained in this study. The uncertainty of the tabulated values is probably of the order of 1% due to a similar uncertainty in the value of the heat of formation of boric oxide. The uncertainty in the differences between the values, however, is probably no greater than 0.01 kcal.

TABLE II

HEATS OF FORMATION OF BORIC ACID AND OF AQUEOUS BORIC ACID SOLUTIONS

State	Heat of formation, kcal./mole
H_3BO_3 crystalline	−260.98
H_3BO_3 in 59.3 H_2O (satn.)	−255.76
H_3BO_3 in 100 H_2O	−255.74
H_3BO_3 in 200 H_2O	−255.72
H_3BO_3 in 500 H_2O	−255.71
H_3BO_3 in 5000 H_2O	−255.71
H_3BO_3 in 20000 H_2O	−255.70
H_3BO_3 in 50000 H_2O	−255.65
H_3BO_3 in 100000 H_2O	−255.59
H_3BO_3 in 150000 H_2O	−255.56

Summary

The heats of solution and dilution of orthoboric acid have been determined in the range of concentrations from saturation (0.936 m) to 0.00035 m. An equation was found to express the data.

The heats of formation of crystalline boric acid and of aqueous solutions of boric acid from saturation $H_3BO_3 \cdot 59.3\ H_2O$ to $H_3BO_3 \cdot 150{,}000\ H_2O$ have been calculated.

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[12] E. J. Prosen, W. H. Johnson and F. A. Yenchius, National Bureau of Standards Technical Report on Project NA-onr-8-49 (1948).

[13] J. C. Southard, THIS JOURNAL, **63**, 3147 (1941).

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

The Activity Coefficients of $LaCl_3$, $CaCl_2$, KCl, NaCl and HCl in Dilute Aqueous Solutions

BY THEODORE SHEDLOVSKY

In this laboratory the activity coefficients of $LaCl_3$,[1] $CaCl_2$,[2] KCl,[2] NaCl[3] and HCl[4] for dilute solutions in water at 25° have been obtained from measurements on the e. m. f. of concentration cells, together with transference numbers by the method of the moving boundary.

All these salts, except $LaCl_3$, gave results which were in accord with the Debye–Hückel theory for strong electrolytes.

The apparent abnormal behavior of $LaCl_3$ as previously reported is, however, not real, but has been found to be due to an error in the computations which consisted in evaluating the integral of $Ed\delta$ instead of the required δdE by graphical means.[1] The corrected computations lead to results, given below, which show that the activity coefficient values for this tri-univalent salt are also in complete accord with the Debye–Hückel theory in sufficiently dilute aqueous solutions. I am indebted to Dr. R. H. Stokes, of the University of Western Australia, for suggesting the probability of error in the original calculations.

Since the publication of the papers mentioned above, there has been a significant revision of the most probable values of some of the constants involved in the Debye–Hückel equation for activity coefficients.[5] Accordingly, the data for all the five electrolytes have been recomputed on the newer basis and the results are reported in the present communication.

The familiar Debye–Hückel equation for ionic activity coefficients, f_R, in sufficiently dilute solutions is

$$-\log f_R = A\sqrt{C}/(1 + B\sqrt{C}) \qquad (1)$$

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[1] T. Shedlovsky and D. A. MacInnes, THIS JOURNAL, **61**, 200 (1939).

[2] T. Shedlovsky and D. A. MacInnes, *ibid.*, **59**, 503 (1937).

[3] A. S. Brown and D. A. MacInnes, *ibid.*, **57**, 1356 (1935).

[4] T. Shedlovsky and D. A. MacInnes, *ibid.*, **58**, 1970 (1936).

[5] R. T. Birge, *Rev. Mod. Phys.*, **13**, 233 (1941), R. T. Birge, *Rep. Prog. Phys.*, **8**, 90 (1941).