Heat of Solution of Boron Trifluoride in Water and Aqueous Hydrofluoric Acid

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The heat of solution of boron trifluoride in water and in dilute aqueous hydrofluoric acid was measured in a rotating bomb calorimeter. The heat of solution, ΔH_{298}, was −24.7 ± 0.5 kcal. mole^{-1} for both cases over the concentration range from 0.48 to 1.17 molal in boron trifluoride. The calculated heat of formation of $BF_3(OH)^-_{(aq.)}$ is −363.1 kcal. mole^{-1}.

RATHER LIMITED experimental data are available in the literature for the heat of solution of boron trifluoride in water. Hammerl (*1*) and Laubengayer and Finlay (*3*) report values which indicate the heat of solution to be independent of the final concentration over the range from 0.2 to 3 molal in boron trifluoride. We have obtained heat of solution values in reasonable agreement with the literature and have confirmed the absence of concentration dependence over the more limited range of 0.55 to 1.17 molal. The heat of solution has also been found to be unaffected by low concentrations of hydrofluoric acid over the range of 0.48 to 1.01 molal in boron trifluoride.

EXPERIMENTAL

Calorimeter. The rotating-bomb calorimeter was constructed from Argonne National Laboratory design CE-3986-A which is similar to that described by Hubbard (*2*). The bomb was made entirely of "A" nickel and had an internal volume of 350 cc. Temperature measurements were made with a calorimetric platinum resistance thermometer in conunction with a G-2 Mueller bridge and high-sensitivity galvanometer.

Calibration. The calorimeter was calibrated by combustion of standard benzoic acid, NBS 39h. Eight combustion experiments gave a mean energy equivalent for the standard calorimeter of 35,454 cal. ohm^{-1} with a standard deviation of the mean of ±34 cal. ohm^{-1}. All energies are expressed in terms of the defined calorie, equal to 4.184 (exactly) joules.

Materials. Boron trifluoride (Allied Chemical) was passed through a mercury bubbler into a high-vacuum system where non-condensables were removed. Infrared spectra showed no lines other than those for boron trifluoride. Hydrofluoric acid solutions were made up by dilution of ACS reagent 48% HF (Allied Chemical).

Procedures. Thin-walled Pyrex bulbs were filled with water, degassed, and sealed under vacuum. The bulbs, containing a weighed amount of water, were placed in the bomb. The bomb was evacuated and then pressurized with the desired amount of boron trifluoride, in the range from 0.9 to 1.9 atmospheres. After the usual equilibration period in the calorimeter, rotation of the bomb was started, breaking the glass bulb and initiating the solution reaction. Rotation of the bomb was continued throughout the remainder of the run.

Product Analyses. Completeness of solution was checked by infrared analysis of the vapor after solution, with no boron trifluoride being observed. Total boron and fluorine in solution were determined by decomposition of the fluoboric acids in the presence of calcium chloride. The F/B mole ratio obtained from the analyses was 3.00 ± 0.02. The boric acid was titrated in the presence of mannitol and the fluorine determined as the calcium fluoride precipitate. A small amount of nickel appeared in the solutions from the side reaction with the bomb surfaces. The amount varied from 2-4 mg., determined as the dimethylglyoxime complex. The nickel was removed by precipitation as the hydroxide before titration of the boric acid.

EXPERIMENTAL RESULTS

The experimental results of the solution of boron trifluoride in water are summarized in Table I. A correction was applied for the energy of vaporization of the water vaporized when the bulb was broken. Over the concentration range from 0.55 to 1.17 molal, there was no significant dependence of concentration. The mean value of ΔE from Table I gave, on conversion to constant pressure, a standard heat of solution, ΔH_{298}, of −24.7 ± 0.4 kcal. mole^{-1} BF_3^{-1}. The uncertainty interval was taken as twice the standard deviation of the mean.

The experimental data for the solutions of boron trifluoride in 0.32 molal hydrofluoric acid are summarized in Table II. The mean heat of solution, ΔH_{298}, and uncertainty interval are −24.7 ± 0.6. Again, there was no observed concentration dependence. In all of the experiments, correction for the nickel reaction was assumed to be negligible.

Table I. Boron Trifluoride–Water Solution Data

Exp. No.	Mass H_2O (Grams)	Mmoles BF_3	Final BF_3 Molality	$-\Delta E$ soln. (Kcal. Mole^{-1})
1	17.92	13.1	0.731	23.9
2	31.10	27.3	0.878	23.2
3	27.52	24.1	0.876	24.4
4	20.90	17.9	0.856	24.8
6	23.91	14.6	0.611	24.4
8	26.08	14.3	0.548	24.1
9	25.00	14.7	0.588	23.5
10	16.96	18.8	1.108	24.7
11	16.07	18.8	1.170	24.0
			Mean	24.1
			Std. Dev. of Mean	±0.2

Table II. Boron Trifluoride–Hydrofluoric Acid Solution Data

Exp. No.	Mass HF Soln. (Grams)	Mmoles BF_3	Final BF_3 Molality	$-\Delta E$ soln. (Kcal. Mole^{-1})
3	22.15	22.3	1.007	23.4
4	19.09	19.3	1.001	25.2
5	20.10	15.9	0.791	24.2
6	18.97	13.9	0.733	24.1
7	19.41	10.4	0.536	24.1
9	19.41	9.4	0.484	23.6
			Mean	24.1
			Std. Dev. of Mean	±0.3

DISCUSSION

The heat of solution of boron trifluoride in water observed in this work is slightly lower than that obtained by Hammerl (*1*) and Laubengayer and Finlay (*3*). Their results adjusted to 25° C. are −25.7 and −25.1 kcal. mole^{-1}, respectively.

Wamser (*6*) and Ryss and his coworkers (*4*) have studied the hydrolysis equilibria of BF_3 solutions. Wamser reports the initial rapid reaction of BF_3 with water to be:

$$BF_{3(g)} + (n+1)\,H_2O_{(l)} = HBF_3OH\cdot nH_2O_{(aq)} \qquad (1)$$

with further hydrolysis being much slower. Ryss and Elkenbard (*4*) have measured the heat of solution of KBF_3OH in water and aqueous NaOH. From these data, the heat of formation of $BF_3OH^-_{(aq)}$ has been derived as −363.1 kcal. mole^{-1}.

Assuming the solution reaction under the conditions of our study to be represented by Reaction 1, the heat of formation of $BF_3OH^-_{(aq)}$ may be derived as −363.1 kcal. mole^{-1}, using −270.1 kcal. mole^{-1} for the heat of formation of $BF_{3(g)}$ (*7*). The exact agreement with Ryss is undoubtedly fortuitous.

Our solution data in dilute HF indicate that, at low HF/BF_3 ratios (0.3-0.6), the heat of solution is unaffected by the presence of HF and the predominant species may still be assumed to be BF_3OH^-.

Wamser (*5*) has shown that higher HF/BF_3 ratios (> 3) drive the equilibrium toward formation of BF_4^- as the major species. We have measured a single heat of solution at an HF/BF_3 ratio of approximately 3. The observed heat of solution of −27.0 kcal. mole is in the direction one would expect, since the heat of formation of $BF_4^-{}_{(aq)}$ of −373.7, derived from the data of Ryss (*4*), gives a calculated heat for the reaction:

$$BF_{3(g)} + HF\cdot nH_2O_{(aq.)} = HBF_4\cdot nH_2O_{(aq.)} \qquad (2)$$

of −27.9 kcal. mole^{-1}.

The use of Equation 1 to represent the solution reaction in water is an oversimplification, since all of the possible acid species are present to some extent. This does not prevent, however, the discussion of the heat effects on solution as though they were produced only by the predominant species. HBF_3OH. Wamser (*6*) presents a more detailed hydrolysis scheme, but it is apparent from the results of the heat of solution measurements that the over-all heat balance of the complex equilibria is such that the measured heat is not significantly affected by minor changes in concentration of the various species.

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Equilibrium Diagram of the System Nb_2O_5-WO_3

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An equilibrium diagram of the Nb_2O_5–WO_3 system has been presented. The existence of two new compounds, Nb_2O_5–WO_3 and $Nb_2O_5\cdot 3WO_3$, has been postulated. The work of Kovba and Trunov on $Nb_2O_5\cdot 3WO_3$ (*a, b* = 12.190A, *c* = 3.934A.) has been verified. Experimental procedures included room temperature x-ray diffraction of previously annealed samples, high temperature x-ray diffraction, and differential thermal analysis. Some work was also done on the low temperature transformation of WO_3 and WO_3–Nb_2O_5 compounds.

AS PART of a project concerning the oxides of the refractory metals, the phase equilibrium of the system Nb_2O_5-WO_3 was investigated. The one published report on this system was done by Goldschmidt (*1*). His results indicated that WO_3 was soluble in Nb_2O_5 to the extent of 60 mole % WO_3. He also postulated the existence of a compound existing at the 25% Nb_2O_5-75% WO_3 composition.

EXPERIMENTAL

Sample Preparation. The oxide samples used in this investigation were prepared from materials obtained from A.D. Mackay and Co., Inc. The purities were 99.9+% for the Nb_2O_5 and 99.99% for the WO_3. Impurities detected spectroscopically in these materials were Si, Mg, Co, Zr, and Ni for Nb_2O_5 and Si, Al, and Mg for WO_3. Before mixing, the powders were prefired in air for 24 hours at 800° C. During this treatment and all subsequent annealing treatments, the samples were enclosed in platinum crucibles

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