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Heats of Solution of Crystalline and Amorphous Boron Oxide and Boric Acid

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The heats of hydrolysis for $B_2O_3(c) + 348\ H_2O \rightarrow 2(H_3BO_3) \cdot 345\ H_2O$; B_2O_3 (amorphous) + $372\ H_2O \rightarrow 2(H_3BO_3) \cdot 369\ H_2O$, and $H_3BO_3(c) + 504\ H_2O \rightarrow H_3BO_3 \cdot 504\ H_2O$ have been measured. From these data and accepting the value of -261.47 ± 0.2 kcal. per mole for the heat of formation of $H_3BO_3(c)$ as determined by Good and coworkers, the heats of formation for $H_3BO_3 \cdot 504\ H_2O$, $B_2O_3(c)$, and B_2O_3 (amorphous) were calculated. The energy of transformation from crystalline to amorphous B_2O_3 was also calculated.

THE heats of solution of crystalline and amorphous B_2O_3 and H_3BO_3 in water were calorimetrically measured. From these data and other pertinent auxiliary data, the heats of formation of $H_3BO_3 \cdot 504\ H_2O$, B_2O_3(c), and B_2O_3(amorphous) were determined.

EXPERIMENTAL

Calorimeter. The heats of solution were measured in a silvered Dewar-type reaction vessel containing 200 ml. of water. The lid was constructed to allow passage of the stirrer, heater, thermistor tube, and sample ampoule crushing rod. The assembled reaction vessel was submerged in a stirred water bath of 17 liters. The experiments were performed adiabatically whereby the bath temperature was held by a heater-relay system, at ±0.008° of the bath and calorimeter temperature (~25° C.). The final temperature was 0.25° or 0.5° C. higher, depending on the reaction studied.

Temperature measurements were made by employing a GB32P8 Fenwal thermistor of 2 kilohms in one arm of a Wheatstone bridge network and powered by one mercury battery of 1.35 volts. The bridge is kept balanced by manipulation of three 10-step decades totaling 11 ohms located in a second arm of the bridge. The output is amplified utilizing a Leeds and Northrup microvolt amplifier 9835-A.

The sensitivity of the system is $2.5 \times 10^{-5\circ}$ C., or 6×10^{-3} calorie. Operating under adiabatic conditions the thermal leak rate was approximately 0.003 to 0.045 calorie min.^{-1}.

Calibration. The calorimeter was electrically calibrated. The timing of the heating period was measured by a Model S-10 standard precision timer synchronized with the heater switch.

The reactions studied and the calibration runs created temperature increases of 0.25° and 0.5° C.

All experimental runs, including calibrations were initiated at a temperature between 25.0° and 25.1° C. The uncertainties listed throughout this work are twice the standard deviation.

Materials. The B_2O_3(amorphous) was from Fisher Scientific as 99.9+% pure; the B_2O_3(c) was synthesized in this laboratory from seeded H_3BO_3(c) which was obtained from U.S. Borax as 99.9+% pure.

The H_3BO_3(c) and B_2O_3(c) were identified by x-ray diffraction patterns. The boron compounds were spectrographically analyzed for 14 elements. The total impurities analyzed for in each were less than 300 p.p.m. No further analyses were made.

PROCEDURE

Two hundred milliliters of water were added to the Dewar reaction vessel. The sample contained in a glass ampoule was held in a submerged position by a three-pronged support. The Dewar was submerged in a stirred water bath maintained at 25.000±0.008° C. Upon initiating the reaction by breaking the sample ampoule, the bath temperature was simultaneously changed at the same rate as the solution temperature to effect an adiabatic measurement.

RESULTS

From the amounts of material used, the following equations represent the reactions studied and their heats of reaction.

	ΔH_{298}, Kcal./Mole	
$B_2O_3(c) + 3H_2O + 350\ H_2O \rightarrow$ $2(H_2BO_3 \cdot 175\ H_2O)$	-3.45 ± 0.03	(1)
$B_2O_3(\text{amorphous}) + 3H_2O + 369\ H_2O \rightarrow$ $2(H_3BO_3 \cdot 184\ H_2O)$	-7.78 ± 0.05	(2)
$H_3BO_3(c) + 504\ H_2O \rightarrow H_3BO_3 \cdot 504\ H_2O$	$+5.45 \pm 0.01$	(3)

From the results of Equation 3, and accepting the value of Good and coworkers (*3*) for the heat of formation of

Table I. Heat of Hydrolysis

	B_2O_3 (Crystalline)	B_2O_3 (Amorphous)	H_3BO_3
Mean ΔH_{298}	−3.45	−7.78	+5.45
Uncertainty	±0.03 or 1.15%	±0.05 or 0.65%	±0.01 or 0.34%
No. of runs	7	5	5

Table II. Comparison of Results with Existing Data

		ΔH
$H_3BO_3 + 504\ H_2O \rightarrow H_3BO_3 \cdot 504\ H_2O$		
Ditte (*2*)	1878	+3.2
Berthelot (*1*)	1879	+4.8
Stackelberg (*9*)	1937	+5.3
Roth-Borger-Bertram (*6*)	1937	+5.1 ± 0.05
Katz (*5*)	1949	+5.3
Smisko-Mason (*7*)	1960	+5.27
Van Artsdalen (*11*)	1951	+5.17 ± 0.04
This work	1964	+5.45 ± 0.02
B_2O_3(amorphous) $+ 3H_2O + 369\ H_2O \rightarrow 2(H_3BO_3 \cdot 369\ H_2O)$		
Berthelot (*1*)	1879	−7.3
Stackelberg (*9*)	1937	−8.0
Roth-Borger-Bertram (*6*)	1937	−7.85 ± 0.08
Southard (*8*)	1941	−7.839
Katz (*5*)	1949	−7.93
Van Artsdalen (*11*)	1951	−7.93 ± 0.03
This work	1964	−7.78 ± 0.05
$B_2O_3(c) + 3H_2O + 345\ H_2O \rightarrow 2(H_3BO_3 \cdot 345\ H_2O)$		
Southard (*8*)	1941	−3.477
Torgeson-Shomate (*10*)	1947	−3.3
Smisko-Mason (*7*)	1950	−3.48
This work	1964	−3.45 ± 0.04

No corrections were made to other data, such as standardizing to 25°, changes in atomic weights, or to final concentration.

H_3BO_3(c), −261.47 kcal. per mole, the heat of formation of $H_3BO_3 \cdot 504\ H_2O$ was calculated to be −256.02 kcal. per mole. From the work of Smisko and Mason (*7*), the difference (interpolated) in the heats of formation of $H_3BO_3 \cdot 345\ H_2O$ is 0.010 kcal. per mole. This correction was considered as negligible and was not applied to the $H_3BO_3 \cdot 504\ H_2O$ value.

From the results of Equations 1 and 2, and using the value of −256.02 kcal. per mole for the heat of formation of $H_3BO_3 \cdot (345\text{-}504\ H_2O)$, the heats of formation of B_2O_3(c) and B_2O_3(amorphous) were calculated. ΔHf H_2O (*1*) was taken as −68.32 kcal. per mole as taken from the Handbook of Chemistry and Physics (*4*).

Compound	ΔHf_{298}, Kcal./Mole
B_2O_3(c)	−303.63±0.42
B_2O_3(amorphous)	−299.30±0.43

The energy of transformation from crystalline to amorphous is therefore as follows:

$$B_2O_3(c) \rightarrow B_2O_3(\text{amorphous}) + 4.33\ \text{kcal./mole} \pm 0.06$$

The experimental results are shown in Table I. A comparison of existing data is given in Table II.

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NOMENCLATURE

ΔH_{298} = heat of solution or reaction at constant pressure and at 298° K., kcal./mole
ΔHf_{298} = heat of formation at 298° K., kcal./mole
q = electrical energy supplied to the calorimeter, calories
E_s = voltage drop across standard resistor, volts
R_s = 0.500 ohm standard wire-wound resistor
R_h = heater resistance = 23.96 ohms
t_{sec} = heating time, seconds
ΔR = change in the resistance of the thermistor
ϵ = energy equivalent, calories/ohm

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Heats of Combustion, Formation, and Isomerization of Nineteen Alkanols

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VERY few thermochemical investigations involving modern apparatus and techniques have been carried out on the simple alkanols in spite of their importance in science and industry. The present investigation reports experimental results of the heats of combustion, in the liquid state at 25° C., of 19 alkanols in the range C_1 to C_{10}: methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 3-methyl-1-butanol, 2-methyl-2-butanol, 3-methyl-2-butanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol. The values of the standard heats

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