ments from 80 to 298.16°K., which appear in the next three lines, were obtained by the usual methods directly from the experimental data. The results for the total entropy in calories per degree per mole are then given in the last line with the designation "S^0_{298}"; they are probably reliable to within 0.7 e. u. in an absolute sense and to 0.3 e. u. for comparative purposes.

Free Energy Data for the Decahydronaphthalenes

We have also calculated the free energies of formation of these isomers in the liquid state by means of the fundamental equation, $\Delta F = \Delta H - T\Delta S$. The essential thermal data are listed in Table IV.

TABLE IV

THERMAL DATA AT 298.16°K. FOR THE DECAHYDRONAPHTHALENE ISOMERS IN CALORIES PER MOLE; MOL. WT., 138.244

	cis	*trans*
ΔH°_f of liquid	−52,440	−54,560
ΔS°_f of liquid	−232.71	−231.77
ΔF°_f of liquid	16,940	14,550
ΔF°_f of vaporization	3,470	3,010
ΔF°_f of gas	20,410	17,560

The values for the ΔH° of formation of the liquid compounds were obtained by a revision of the combustion data of Davies and Gilbert[3] in terms of present-day standards,[7] and the use of 68,317.4 cal. and 94,051.8 cal.[8] for the heats of formation of water and carbon dioxide, respectively. The ΔS°_f values represent simply the differences between the S^0_{298} for each isomer and the corresponding values for the entropies of the elements contained therein. For this purpose we have used 31.211 e. u. for the entropy of hydrogen and 1.361 e.u. for carbon (β-graphite).[8] The resulting molal free energies for the liquids are probably reliable to ±400 calories in an absolute sense and to about one-half of this figure for the present comparative purposes.

The free energy changes for the vaporization of each liquid at 298.16° K. to yield a gas at the hypothetical fugacity of 1 atm. have been calculated by use of 2.19 and 4.73 mm. for the respective vapor pressures of the *cis*- and *trans*-compounds. These are values which we have deduced from a plot of Seyer's vapor pressure data.[2] Addition of the ΔF° of vaporization quantities to the free energies of the liquids then gives the tabulated free energies of formation for the gaseous state.

These data now yield for the free energy changes in the isomerization process

$$cis\ C_{10}H_{18} \longrightarrow trans\ C_{10}H_{18}$$

$$\Delta F^0_{298} \text{ (in liquid phase)} = -2390\ (\pm 280) \text{ cal.}$$

and

$$\Delta F^0_{298} \text{ (in gas phase)} = -2850\ (\pm 280) \text{ cal.}$$

Summary

1. The specific heats of *cis*- and *trans*-decahydronaphthalene have been measured between 78 and 298° K. The corresponding heats of fusion also have been measured.

2. The entropies (*cis*, 61.80 ± 0.7 e.u. and *trans*, 62.74 ± 0.7 e.u.) of these two isomers in the liquid state at 298.16°K. have been calculated from the foregoing heat capacity data.

3. The corresponding free energies for both the liquid and gaseous states have then been calculated from these entropies and other available data.

STANFORD, CALIFORNIA

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[7] R. S. Jessup, *J. Research Natl. Bur. Standards*, **29**, 247 (1942).

[8] D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer, and F. D. Rossini, *ibid.*, **34**, 143 (1945).

[CONTRIBUTION NO. 709 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Heats of Formation of Sodium Borohydride, Lithium Borohydride and Lithium Aluminum Hydride[1,2]

BY WILLIAM D. DAVIS,[3] L. S. MASON AND G. STEGEMAN

A number of metallo-borohydrides of the general formula $M(BH_4)_x$ and a number of metallic hydrides of unusual interest have been prepared and studied.[4] Reviews of the chemistry[5] and of the physical properties and structures[6,7] of the hydrides of boron and their derivatives have been published. Thermochemical information about these substances, however, is meager and in some cases uncertain. In the present study, the heats of formation of sodium borohydride, lithium borohydride, and lithium aluminum hydride have been determined by measuring calorimetrically the

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[1] This study is a part of a research project sponsored by the Office of Naval Research.

[2] This report is part of a thesis presented by William D. Davis in partial fulfillment of requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Pittsburgh, January, 1949.

[3] Present address: Knolls Atomic Power Laboratory, The General Electric Corporation, Schenectady, New York.

[4] (a) H. I. Schlesinger, R. T. Sanderson and A. B. Burg, THIS JOURNAL, **62**, 3421 (1940). (b) A. B. Burg and H. I. Schlesinger, *ibid.*, **62**, 3425 (1940). (c) H. I. Schlesinger and H. C. Brown, *ibid.*, **62**, 3429 (1940). (d) H. I. Schlesinger, H. C. Brown and G. W. Schaeffer, *ibid.*, **65**, 1786 (1943). (e) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *ibid.*, **69**, 1199 (1947).

[5] H. I. Schlesinger and A. B. Burg, *Chem. Revs.*, **31**, 1 (1942).

[6] S. H. Bauer, *ibid.*, **31**, 43 (1942).

[7] J. W. Smith, *Science Progress*, **35**, No. 139, 515 (1947).

heats of reaction of the compounds with dilute hydrochloric acid and applying the known heats of formation of the other reactants and products. A similar determination for aluminum borohydride is in progress. The entropies of the compounds are also being determined so that the free energies of formation may be calculated.

Experimental

Calorimeter.—The heats of reactions were determined in a bomb calorimeter conventionally used for measuring heats of combustion.[8] The rise in temperature of the calorimeter was observed while the temperature of the jacket was kept constant. Temperatures were measured with a calibrated platinum resistance thermometer, a G-2 Mueller bridge, and an HS galvanometer. The sensitivity of the system was 0.001° per mm. deflection, allowing an estimate to the nearest 0.0001°. The temperature rise was determined by the method developed for combustion calorimetry by Dickinson.[9] The interior of the bomb was protected from attack by the acid with a baked-on resin. To effect the reaction at the desired moment, a device was constructed which would fit inside the bomb and protect the sample from moisture until it was electrically released into the acid in the bomb (see Fig. 1). It was made entirely of copper and was varnished. The firing mechanism consisted of a short piece of iron fuse wire stretched between the two binding posts A and B, one of which was insulated and connected to the insulated terminal on the bomb while the other was grounded. A piece of nylon cord C was tied to this fuse wire and stretched taut over the bottom lid of the cylinder containing the sample by means of an adjustable post D on the opposite side. Both lids were well greased to make them air-tight. To start the reaction during a calorimetric run, about 18 volts was applied to the bomb terminals. This broke the fuse wire, released the nylon cord, and allowed the compressed spring in the upper lid of the cylinder to eject the perforated sample container, sample, and lower lid into the acid in the bomb.

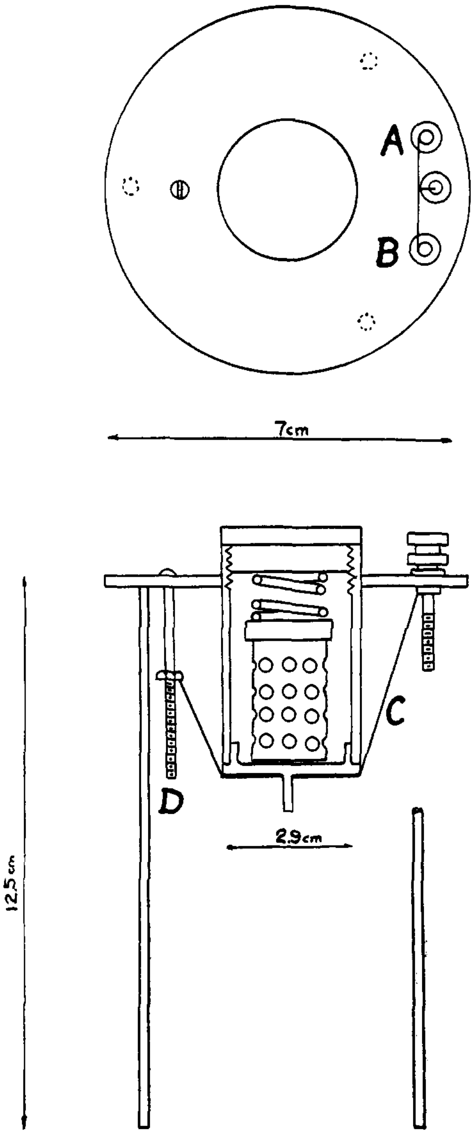

Fig. 1.

The heat capacity of the calorimeter system was determined by the combustion of Bureau of Standards Sample 39f benzoic acid in the empty bomb under established standard conditions.[10] Ten determinations during the course of this research gave an average value of 2732.9 cal. per degree, the unit of heat being the "defined" calorie (4.1833 international joules). The "precision error" of the standardization, as evaluated by the method of Rossini,[11] was 0.05%.

This measured heat capacity was the heat capacity of the system when the bomb contained only the nickel crucible and supports used for combustion work and had to be corrected to the conditions of the "heat of reaction" runs. This was done by subtracting the heat capacities of the nickel crucible and supports used for combustions from the measured heat capacity and adding the heat capacities of the copper sample holder, protecting varnish, and wiring associated with the determinations of the heats of reaction. These correcting heat capacities were determined by weighing the various materials and applying their known specific heats. The value of the heat capacity of the calorimeter system as used for determinations of the heats of reaction of the hydride was 2771.9 ± 1.4 calories per degree.

As a check on the precision of the calorimeter when used for measuring heats of reactions in solution, samples of magnesium ribbon were treated with $HCl\cdot 100H_2O$ using the same method employed for the hydrides. Two hundred milliliters of $HCl\cdot 100H_2O$ was used for each gram of magnesium. The values for the heat evolved per gram obtained from four samples of magnesium weighing one gram and one weighing 0.75 g. showed an average deviation of only 0.05%. The 0.75-g. sample gave a value which differed from the average by only 0.03%, indicating that the weight of the sample did not affect the final result.

The measured value for the heat of reaction at constant pressure was −110.5 kcal. per gram atom of magnesium. This value was not corrected to 25°, nor were corrections applied for the heats of dilution and mixing. An assessment of the accuracy of this value is precluded by the lack of agreement of published values for the reaction. The following values in kcal. have been reported for the heat of solution of one gram atom of magnesium in $2HCl(200)$: Richards, Rowe and Burgess,[12] −110.2; Biltz and Pieper,[13] −109.7; Sieverts and Gotta,[14] −112.1.

Materials.—The compounds were obtained in the impure state from outside sources. Their great reactivity, especially with water, made their purification difficult, and necessitated the design of special apparatus to achieve

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[8] G. Stegeman and T. H. Clarke, THIS JOURNAL, **61**, 1726 (1939).

[9] H. C. Dickinson, *Bull. Bur. Standards*, **11**, 187 (1915).

[10] E. W. Washburn, *NBS J. Research*, **10**, 525 (1933), RP546.

[11] F. D. Rossini, *Chem. Revs.*, **18**, 233 (1936).

[12] Richards, Rowe and Burgess, THIS JOURNAL, **32**, 1176 (1910).

[13] Biltz and Pieper, *Z. anorg. allgem. Chem.*, **134**, 13 (1924).

[14] Sieverts and Gotta, *Ann.*, **453**, 289 (1927).

reasonably good results. Almost all operations involving the samples were conducted in a large "dry box." The atmosphere within was kept dry by circulating the air with a small electric fan over two large trays of phosphorus pentoxide and keeping a small positive pressure of dry nitrogen inside the box. During periods of operation which involved the use of inflammable solvent vapors, the air inside the box was replaced by nitrogen. The atmosphere was tested by exposing samples of the hydrides for periods of one-half hour or more and noting if an appreciable gain in weight occurred. All procedures in purification, except those noted, were carried out in apparatus constructed entirely of glass, using sintered glass filters, ground glass joints and stopcocks. Closed systems were used and exposure of materials to the atmosphere was kept to a minimum, even when inside the drybox. Dry nitrogen pressure was used to effect filtration in most cases and the vacuum lines inside the drybox were protected against moisture diffusing back by suitable traps containing sodium hydride, magnesium perchlorate, and sodium hydroxide.

Methods of Analysis

(a) **Evolution of Hydrogen.**—The method of analysis which was thought to afford the best criterion of purity was a measure of the amount of hydrogen formed on treating the compounds with dilute acid. A pelletted and weighed sample was placed in a reaction vessel in the drybox. The vessel was removed and sealed to a vacuum system and the sample was allowed to react with dilute acid. The hydrogen evolved passed through cold traps and was transferred by means of a Sprengel pump to a calibrated, thermostatted liter bulb. The pressure of the hydrogen was measured with a cathetometer to within 0.1 mm. This was less than 0.02% of the total pressure. The volume of the bulb was known to 0.01%. The temperature of the bath was regulated to ±0.01°.

As a check on the over-all accuracy of the method, two samples of pure sublimed magnesium were allowed to react with dilute phosphoric acid in the apparatus. The weights of magnesium calculated from the determinations differed from the actual weights by +0.04 and +0.07%.

(b) **Titration with Acid and Base.**—Another indication of purity in the case of the borohydrides was titration with a standard solution of hydrochloric acid using methyl red as an indicator. The reaction which occurred was the same as that in the hydrogen analysis. The end-point was sharp and the results usually differed from each other by less than 0.1%.

The boric acid in the solution resulting from the titration with hydrochloric acid was titrated with a standard solution of sodium hydroxide in the usual manner using phenolphthalein indicator and mannitol. The precision of this method of analysis, however, was not as high as that of the titration with hydrochloric acid. Duplicate analyses differed by as much as 0.4%.

(c) **Gravimetric Analysis.**—Lithium aluminum hydride could not be titrated satisfactorily and gravimetric analysis for aluminum was substituted. The sample was dissolved in dilute hydrochloric acid and the aluminum precipitated by ammonia in the usual manner.

Purification

(a) **Sodium Borohydride.**—The crude material was obtained from Aerojet Engineering Corporation. The purity as determined by titration with hydrochloric acid was about 95%. About 115 g. of the original sample was dissolved in the minimum amount of water at 0° and filtered through a sintered glass Buechner funnel. The water in the clear solution was then pumped off using a dry ice trap and a mechanical vacuum pump. These operations were conducted in a cold room at 5°. The sample was then heated to about 80° under vacuum for several hours to remove water completely. The material was now free of water-insoluble impurities but presumably contained a considerable amount of sodium borate.

Isopropylamine was used as the solvent in all subsequent treatment of the sample. Commercial "anhydrous" isopropylamine was refluxed several days over sodium hydride, during which time a dark brown color developed. The amine was distilled onto fresh sodium hydride and the process repeated until a product was obtained which remained water white after prolonged refluxing over sodium hydride. The sodium borohydride was dissolved in the purified isopropylamine and the solution filtered from the undissolved sodium borate through a medium porosity sintered glass disk in a closed apparatus. The clear solution was crystallized by partial distillation of the solvent and decantation of the remaining solution from the purified crystals deposited in the distillation flask. The yield was increased by treating the remaining solution in a similar manner. The combined crops of purified sodium borohydride were pumped free of solvent and now presumably contained only a small amount of sodium borate from reaction with atmospheric moisture. The purified sodium borohydride was then heated in the drybox at 100° and 1 mm. pressure to remove any last traces of moisture. The sample was then dissolved in anhydrous isopropylamine distilled from sodium hydride in the dry-box directly onto the sample. The solution was filtered through a sintered glass disk and evaporated to dryness. The last traces of solvent were removed by heating at 100° and 0.1 mm. pressure for four hours. Analysis of the sample gave the following results expressed in per cent.: hydrogen analysis, 99.57, 99.65 (mean 99.61 ± 0.04); hydrochloric acid titration, 99.69, 99.66 (mean 99.67 ± 0.02); sodium hydroxide titration, 99.88, 99.44 (mean 99.66 ± 0.22).

(b) **Lithium Borohydride.**—The crude material was obtained from the Naval Research Laboratory in Washington, D. C. The purity was about 96%. All efforts at purification consisted of crystallization of the crude product from ether. All operations were carried out in the drybox. Altogether, about twelve attempts were made to increase the purity and the highest obtainable was 99.65%. This sample, however, was not large and no successful runs were obtained using it.

The sample used for the runs reported was purified by first dissolving the crude material in Mallinckrodt Analytical Reagent ether distilled from sodium hydride in the dry-box. The resulting cloudy solution was filtered twice through a medium porosity sintered glass filter and the clear solution cooled and crystallized by rapidly evaporating some of the ether by suction. The supernatant liquid was removed by suction from the mass of small needle-shaped crystals of lithium borohydride-etherate. This etherate was heated until only a few crystals remained and the resulting solution crystallized again as above. The remaining solution was drawn off and the ether removed from the crystals by pumping at about one mm. pressure and 100°. Analysis of this sample gave a purity of 99.2% by hydrogen analysis and 99.4% by titration with hydrochloric acid. To increase the purity, the process was repeated except that for the second crystallization, additional ether was added to dissolve the crystals of etherate resulting from the first crystallization. This enabled the solution to be filtered and crystallized as in the first crystallization. The ether was removed from the final product by suction alone, no heating being used. Analysis of this sample gave the following results for per cent. purity: hydrogen analysis, 99.43, 99.40, 99.38 (mean 99.40 ± 0.03); hydrochloric acid titration, 99.75, 99.58, 99.32 (mean 99.55 ± 0.15); sodium hydroxide titration, 99.9, 100.1, 99.8 (mean 99.9 ± 0.1).

However, satisfactory calorimetric runs were not obtained until approximately three months later and a new analysis at that time showed the purity to have decreased. Hydrogen analysis gave results of 98.72 and 98.75%. The reason for the decrease is not known, the sample having been protected inside a desiccator in the dry-box.

Two satisfactory calorimetric runs were obtained early in this research with a sample of lithium borohydride which by hydrogen analysis had a purity of 99.23% and by hydrochloric acid titration, 99.30%. The values of the heat of reaction obtained with this sample were only slightly higher than those obtained with the less pure sample. Considering this fact and the lack of precision obtained with the calorimetric determinations, no further effort was made to obtain a more satisfactory sample.

(c) **Lithium Aluminum Hydride.**—The crude material was obtained from Metal Hydrides, Incorporated. The approximate purity as determined by precipitation of the aluminum as the 8-hydroxyquinoline salt was 96%.

About 100 g. of the crude compound was dissolved in approximately 1500 ml. of Analytical Reagent anhydrous ether. As lithium aluminum hydride appears to dissolve in ether very slowly, the mixture had to be refluxed several days. The solution was filtered from the slurry of impurities by means of a large coarse sintered glass filter disk and the filtrate concentrated by distillation until about 400 ml. of sirupy solution remained. This was again filtered using a medium porosity sintered glass disk. Analytical Reagent benzene dried with sodium hydride was distilled into this clear solution until the total volume was approximately 1500 ml., causing lithium aluminum hydride to precipitate as fine white crystals. The solid was separated from the solution by means of the coarse filter and dissolved in the dry ether resulting from the earlier steps. The resulting solution was then introduced into the dry-box, filtered, and an approximately equal volume of dry benzene was distilled from sodium hydride into it. The precipitate of lithium aluminum hydride was separated from the remaining solution by suction and the ether pumped off at room temperature for about twelve hours at one mm. pressure.

Analysis of this sample gave a purity of only 98% but on dissolving it in ether, filtering the cloudy solution, and pumping off the ether as before, the following results were obtained: hydrogen analysis, 99.01, 99.04, 99.11 (mean 99.05 ± 0.04); gravimetric aluminum analysis, 99.42, 99.37 (mean 99.40 ± 0.03).

The last hydrogen analysis was obtained after the calorimetric runs, indicating that the sample did not decompose.

With lithium aluminum hydride, a satisfactory hydrogen analysis could not be obtained by the usual procedure. The lithium aluminum hydride reacted so violently with the water added that it became heated to incandescence, producing an insoluble gray residue. The final procedure consisted in adding ether instead of water to the sample in the reaction vessel and then adding ethyl alcohol to the resulting solution to decompose the lithium aluminum hydride. Dilute phosphoric acid was added finally to insure that all the lithium aluminum hydride had reacted.

Procedure.—The amounts of reactants were determined by the size of the sample that could be put in the copper container, the amount of acid that could be placed in the bomb (about 200 ml.), and the minimum temperature rise that could be measured accurately (about 0.5°). The acid was made as dilute as possible in order to minimize dilution corrections and an excess was used to insure a complete reaction. The amounts used gave these reactions

$$1\ \mathrm{LiBH_4} + 1.25(\mathrm{HCl\cdot200H_2O}) \longrightarrow (\mathrm{LiCl} + \mathrm{H_3BO_3} + 0.25\mathrm{HCl})\cdot247\mathrm{H_2O} + 4\mathrm{H_2}$$

$$1\ \mathrm{NaBH_4} + 1.25(\mathrm{HCl\cdot200H_2O}) \longrightarrow (\mathrm{NaCl} + \mathrm{H_3BO_3} + 0.25\mathrm{HCl})\cdot247\mathrm{H_2O} + 4\mathrm{H_2}$$

$$1\ \mathrm{LiAlH_4} + 10(\mathrm{HCl\cdot50H_2O}) \longrightarrow (\mathrm{LiCl} + \mathrm{AlCl_3} + 6\mathrm{HCl})\cdot500\mathrm{H_2O} + 4\mathrm{H_2}$$

The three molecules of water needed for the first two reactions came from the $\mathrm{HCl\cdot200H_2O}$.

The sample for a calorimetric determination was first formed into a pellet, weighed, and placed in the copper sample holder in the dry-box. The assembly was placed in the bomb, the wiring was attached to the binding posts, and the correct amount of dilute hydrochloric acid was pipetted into the bomb; the air inside the bomb was displaced by argon to prevent possible oxidation of the hydrogen formed. The actual calorimetric determination was very similar to an ordinary heat of combustion determination except that the temperature changes were slower.

In the reactions with lithium aluminum hydride, trouble was encountered in the formation of a small amount of insoluble gray residue. This appeared to be aluminum produced by thermal decomposition of the hydride dispersed within an insoluble form of aluminum oxide. The difficulty was traced to local looseness in the pellet which caused too rapid a reaction resulting in some thermal decomposition. A uniformly dense pellet, produced by an improvement in the pelleting technique, reacted to give a solution free of residue.

Results, Calculations, and Determinations of Required Additional Thermal Data

Evaluation of ΔE of Reaction at 25.00°.—The data obtained in the calorimetric measurements and the calculated value of ΔE of the reactions at 25.00° are listed in Table I. For each of the reactions ΔE at the final temperature was first calculated; this is the product of the heat capacity of the initial system and the temperature rise. ΔE of reaction at 25.00° was then calculated for sodium borohydride and lithium aluminum hydride from the equation

$$\Delta E_{298.2} = \Delta E_{t_f} - (C_f - C_i)(t_f - 25.00)$$

where t_f is the final temperature of the reaction and $C_f - C_i$ is the difference between the heat capac-

Table I

Experimental Values of ΔE of Reaction at 25.00°

Moles of hydride $\times 10^6$	Cor. temp. rise, °C.	Final temp., °C.	$-\Delta E$ at 25.00°C., kcal./mole
	A. Sodium Borohydride 99.61%[a]		
35605	0.8048	25.28	66.258
37189	0.8400	25.26	66.368
35103	0.7934	25.53	66.198
49795	1.1013	25.33	66.229
42637	0.9527	25.03	66.192
		Mean	66.249
		p. e.[b] =	0.11% or 0.071 kcal
	B. Lithium Borohydride[c] 98.74%		
5415	1.3385	25.32	74.49
3759	0.9571	25.20	74.84
3279	.8321	25.47	74.05
3367	.8586	25.63	74.51
3769	.9601	25.05	74.90
3719	.9405	25.29	74.30
		Mean	74.51
		p. e. =	0.35% or 0.26 kcal.
	C. Lithium Aluminum Hydride 99.05%		
26591	1.4939	25.49	168.74
21982	1.2467	25.23	168.05
19211	1.0979	25.23	167.97
24934	1.4009	25.20	167.92
19685	1.1272	25.26	168.53
		Mean	168.24
		p. e. =	0.20% or 0.34 kcal.

[a] Purity of samples as determined by hydrogen analysis.
[b] Precision error as evaluated by the method of Rossini.[11] The p. e. of standardization is incorporated in this value.
[c] ΔE values refer to the final temperature; correction to 25.00° was neglected.

ities of the products and reactants. In the case of lithium borohydride, the purity of the sample and the precision of the calorimetric measurements were too low to warrant this small correction from ΔE_{tf} to $\Delta E_{298.2}$.

In addition to the results listed in Table I, two experiments were performed on sodium borohydride, 99.34% pure, which gave a mean value of $-\Delta E$ at 25.00° of 66.110 kcal. (average deviation = 0.014 kcal.) and two experiments on lithium borohydride, 99.23% pure, which gave a mean value of $-\Delta E$ of 74.59 kcal. (average deviation = 0.014 kcal.).

For these calculations the following quantities had to be determined:

(1) **Densities of the hydrides** were determined at 25° by weighing the amount of inert fluid (toluene) that was displaced by a weighed amount of solid. The densities so determined were: sodium borohydride, 1.08 g./cc.; lithium borohydride, 0.681 g./cc.; lithium aluminum hydride, 0.917 g./cc.

The densities were used to determine the buoyancy corrections for the weights of samples taken.

(2) **Specific heats of the hydrides** were determined experimentally with a small "drop" calorimeter vessel made in the form a "U" from $^3/_8$ in. copper tubing. The open ends were fitted with caps which could be sealed tightly. The empty calorimeter was brought to 0° in an ice-bath and then quickly transferred to a 250-ml. Dewar flask containing 150 ml. of water at approximately 25°, a stirrer, and a Beckmann thermometer. The temperature change of this system was calculated from the initial and final temperature rates in the usual manner. This operation was repeated with the calorimeter vessel filled with distilled water and then with each hydride. The average specific heats of the hydrides over the range of 0 to 25° were calculated from these measured temperature changes and the specific heat of water. The results obtained in cal./g./deg. for the three hydrides were: sodium borohydride, 0.55 ± 0.01; lithium borohydride, 0.84 ± 0.01; lithium aluminum hydride, 0.48 ± 0.01.

(3) **The specific heats of $HCl\cdot 200H_2O$ and $HCl\cdot 50H_2O$** were calculated from the following equations[15]: $\bar{C}_{p_1} = 17.98 - 0.0842\ m^{1.5}$; $\bar{C}_{p_2} = -41 + 14\ m^{0.5}$; $C_p = n_1\bar{C}_{p_1} + n_2C_{p_2}$. The values obtained in cal./g./deg. were: $HCl\cdot 200H_2O$, 0.9778; $HCl\cdot 5OH_2O$, 0.9255.

(4) **The specific heats of the final solutions** were determined with a calorimeter similar to that used for determining the specific heat of the solid hydrides. The "U" tube was replaced by a solid block of copper having a heat capacity of approximately 24 cal. per degree. It was cooled to 0° and then quickly transferred to the Dewar vessel containing 150 g. of water at approximately 25°, the decrease in temperature of the water being noted. The process was repeated using 150 g. of the solution instead of water. Knowing the heat capacity of the copper and the water, the specific heat of the solution could be calculated. The following values in cal./g./deg. were obtained: resultant solution from sodium borohydride reaction, 0.975 ± 0.002; resultant solution from lithium aluminum hydride reaction, 0.929 ± 0.002.

(5) **The specific heat of hydrogen** at constant volume and 25° was taken as 4.89 cal./mole/deg.

Calculation of ΔH of Reaction at 25°.—In the equation $\Delta H = \Delta E + (\Delta n)RT$ Δn refers to four moles of hydrogen produced from one mole of hydride, and $(\Delta n)RT = 2369$ cal. The values of $\Delta H_{298.2}$ for the three reactions studied in kcal./mole are: sodium borohydride, −63.880; lithium borohydride, −72.14; lithium aluminum hydride, −165.87.

The Standard Heats of Formation

Required Additional Thermal Measurements: (1) **Heats of Mixing.**—To calculate ΔH_f^0 exactly for any one of the reactions studied, it would be necessary to determine the heat of mixing of the products of the reaction in the solution, that is, to determine the amount of heat required to separate the three components of the final solution of the reaction into three separate solutions of higher concentration whose individual heats of formation can be calculated or measured. However, the heats of mixing are small and only in the case of the final solution from the reaction of sodium borohydride was this correction deemed necessary. In the other two cases, the uncertainty in the heat of reaction was considered to be much larger than the heat of mixing. Accordingly, only the heat of mixing of the products of the reaction for the case of sodium borohydride was determined.

Separate solutions of sodium chloride, boric acid, and hydrochloric acid were prepared having concentrations such that after mixing the solutions in suitable proportions, the concentrations in the mixture corresponded to those in the final solution of the hydrolysis reaction. The heat of mixing of equal quantities of 0.925 *m* sodium chloride and 0.925 *m* boric acid was first determined. This heat of mixing was −26.4 cal. per mole of sodium chloride or boric acid. The heat of mixing of the above mixture with hydrochloric acid solution was then determined. A quantity of the sodium chloride–boric acid solution was mixed with an appropriate amount of 0.1093 *m* hydrochloric acid so that the final solution was composed of 0.225 *m* sodium chloride, 0.225 *m* boric acid, and 0.0562 *m* hydrochloric acid. These concentrations are identical with the end concentrations resulting from the reaction of the sodium borohydride. The heat of this mixing corresponded to 83.1 cal. per mole of sodium chloride or boric acid or to 332

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(15) M. Randall and W. D. Ramage, THIS JOURNAL, **49**, 93 (1928).

cal. per mole of hydrochloric acid. The measurement of these heats of mixing and of the heat of dilution of boric acid solution to be discussed later were performed in a twin differential calorimeter, the design and performance of which have been reported.[16]

(2) **Heat of Dilution of Boric Acid Solution.**—The heat of dilution of the 0.925 *m* boric acid solution was determined experimentally with the same calorimeter used for determining the heat of mixing. Boric acid (0.925 *m*) was diluted to a concentration of 0.006 *m*. The heat of this dilution was found to be 68.3 cal. per mole. This final concentration of 0.006 *m* was assumed to have the same heat content as the dilute aqueous solution of boric acid, the heat of formation of which is reported in the literature.

(3) **Heat of Dilution of Final Solution from Lithium Aluminum Hydride Reaction.**—In order to decrease the error involved in neglecting the heats of mixing and to allow the use of the values reported in the literature for the heat of solution of aluminum chloride, the heat of dilution of the solution resulting from the reaction of lithium aluminum hydride was determined. Approximately 13 g. of solution was diluted with a liter of water in the same calorimeter as was used for determining the heats of mixing. The mean value of two determinations was −4427 cal. per 9405 g. of solution (the result of the reaction of one mole of lithium aluminum hydride), the two individual values differing by 2.7%.

Calculation of Standard Heats of Formation: (1) **Sodium Borohydride.**—The reactions used to determine the heat of formation of sodium borohydride are expressed by the following equations and heats of reactions:

$$\mathrm{NaBH_4(c) + 1.25(HCl{\cdot}200H_2O) + [3H_2O(l)] \longrightarrow (NaCl + H_3BO_3 + 0.25HCl){\cdot}247H_2O + 4H_2(g)} \qquad \Delta H_1 = -63.880 \text{ kcal.}$$

$$\mathrm{NaCl{\cdot}60H_2O + H_3BO_3{\cdot}60H_2O \longrightarrow (NaCl + H_3BO_3){\cdot}120H_2O} \qquad \Delta H_2 = -0.026 \text{ kcal.}$$

$$\mathrm{(NaCl + H_3BO_3){\cdot}120H_2O + 0.25(HCl{\cdot}508H_2O) \longrightarrow (NaCl + H_3BO_3 + 0.25HCl){\cdot}247H_2O} \qquad \Delta H_3 = +0.083 \text{ kcal.}$$

$$\mathrm{H_3BO_3{\cdot}60H_2O + \infty H_2O \longrightarrow H_3BO_3{\cdot}\infty H_2O} \qquad \Delta H_4 = +0.068 \text{ kcal.}$$

Summation of the above reactions with due regard to sign gives

$$\mathrm{NaBH_4(c) + 1.25(HCl{\cdot}200H_2O) + [3H_2O(l)] + \infty H_2O \longrightarrow NaCl{\cdot}60H_2O + H_3BO_3{\cdot}\infty H_2O + 0.25(HCl{\cdot}508H_2O) + 4H_2(g)} \qquad \Delta H = -63.869 \text{ kcal.}$$

The three moles of water placed in brackets represent the water in the dilute acid that actually enters into the chemical reaction. This was done so that only the heat of formation of this amount of water needed to be taken into account. The heat of formation of sodium borohydride was calculated from the known heats of formation of the reactants and products of the final reaction. Values for ΔH_f^0 in kcal. are as follows: $\mathrm{HCl{\cdot}200H_2O}$,[17] −39.798; $\mathrm{HCl{\cdot}508H_2O}$,[17] −39.875; $\mathrm{NaCl{\cdot}60H_2O}$,[18] −97.428; $\mathrm{H_3BO_3{\cdot}\infty H_2O}$, −255; $\mathrm{H_2O(l)}$,[17] −68.3174.

The heat of formation of the dilute boric acid solution was obtained from the heat of hydrolysis and heat of decomposition of diborane at 25° reported by the Bureau of Standards.[19] In this same report, the heat of formation of boron oxide, $\mathrm{B_2O_3(c)}$, was calculated from the above heats of reaction and the heat of solution of boron oxide, $\mathrm{B_2O_3(c)}$, to give a value of −303 kcal. per mole. This agrees well with the value recently obtained by Stegeman and Nathan,[20] for the direct combustion of boron.

Using the above information, the heat of formation of sodium borohydride was calculated to be

$$\mathrm{Na(c) + B(solid,\ amorphous) + 2H_2(g) \longrightarrow NaBH_4(c)} \qquad \Delta H^0_{298.16} = -43.83 \text{ kcal.}$$

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

$$\mathrm{LiBH_4(c) + 1.25(HCl{\cdot}200H_2O) + [3H_2O(l)] \longrightarrow (NaCl + H_3BO_3 + 0.25HCl){\cdot}247H_2O + 4H_2(g)} \qquad \Delta H_1 = -72.14 \text{ kcal.}$$

$$\mathrm{LiCl{\cdot}60H_2O + H_3BO_3{\cdot}60H_2O + 0.25(HCl{\cdot}508H_2O) \longrightarrow (LiCl + H_3BO_3 + 0.25HCl){\cdot}247H_2O} \qquad \Delta H_2 = 0.00 \text{ kcal. (assumed)}$$

$$\mathrm{H_3BO_3{\cdot}60H_2O + \infty H_2O \longrightarrow H_3BO_3{\cdot}\infty H_2O} \qquad \Delta H_3 = 0.07 \text{ kcal.}$$

Summation of the above reactions with due regard to sign gives:

$$\mathrm{LiBH_4(c) + 1.25(HCl{\cdot}200H_2O) + [3H_2O(l)] + \infty H_2O \longrightarrow LiCl{\cdot}60H_2O + H_3BO_3{\cdot}\infty H_2O + 0.25(HCl{\cdot}508H_2O) + 4H_2(g)} \qquad \Delta H = -72.07 \text{ kcal.}$$

The heat of formation of $\mathrm{LiCl{\cdot}60H_2O}$ used to calculate the heat of formation of lithium borohydride was obtained by correcting to 25° the value listed by Rossini and Bichowsky[21] at 18° using the heat capacity data for lithium chloride solutions of Rossini.[22] The value obtained was −106.15 kcal. This combined with the other heat values gives the heat of formation of lithium borohydride.

$$\mathrm{Li(c) + B(solid,\ amorphous) + 2H_2(g) \longrightarrow LiBH_4(c)} \qquad \Delta H^0_{298.16} = -44.15 \text{ kcal.}$$

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

[17] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards.

[18] E. A. Gulbransen and A. L. Robinson, THIS JOURNAL, **56**, 2637 (1934).

[19] E. J. Prosen, W. H. Johnson and F. A. Yenchius, National Bureau of Standards Technical Report on Project NA-onr-8-47 (1948).

[20] G. Stegeman and C. C. Nathan, Thesis, University of Pittsburgh, 1948.

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

[22] F. D. Rossini, *J. Research Natl. Bur. Stds.*, **7**, 47 (1931), RP 331.

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

$$\mathrm{LiAlH_4(s)} + 10(\mathrm{HCl \cdot 50H_2O}) \longrightarrow (\mathrm{LiCl} + \mathrm{AlCl_3} + 6\mathrm{HCl})\cdot 500\mathrm{H_2O} + 4\mathrm{H_2(g)} \qquad \Delta H_1 = -165.87 \text{ kcal.}$$

$$(\mathrm{AlCl_3} + \mathrm{LiCl} + 6\mathrm{HCl})\cdot 500\mathrm{H_2O} + 41020\mathrm{H_2O(l)} \longrightarrow (\mathrm{AlCl_3} + \mathrm{LiCl} + 6\mathrm{HCl})\cdot 41520\mathrm{H_2O} \qquad \Delta H_2 = -4.43 \text{ kcal.}$$

$$(\mathrm{AlCl_3} + \mathrm{LiCl} + 6\mathrm{HCl})\cdot 41520\mathrm{H_2O} \longrightarrow \mathrm{AlCl_3 \cdot 5190H_2O} + \mathrm{LiCl \cdot 5190H_2O} + 6(\mathrm{HCl \cdot 5190H_2O}) \qquad \Delta H_3 = 0.00 \text{ kcal. (assumed)}$$

Summation of the above reactions gives

$$\mathrm{LiAlH_4(s)} + 10(\mathrm{HCl \cdot 50H_2O}) + 41020\mathrm{H_2O} \longrightarrow \mathrm{AlCl_3 \cdot 5190H_2O} + 6(\mathrm{HCl \cdot 5190H_2O}) + 4\mathrm{H_2(g)} \qquad \Delta H = -170.30 \text{ kcal.}$$

The following heats of formation, ΔH_f^0 in kcal., in addition to those listed previously were used to calculate the heat of formation of lithium aluminum hydride: $\mathrm{AlCl_3 \cdot 5190H_2O}$,[17] −243.9; $\mathrm{LiCl \cdot 5190H_2O}$, −106.41; $\mathrm{HCl \cdot 5190H_2O}$,[17] −39.973; $\mathrm{HCl \cdot 50H_2O}$,[17] −39.577.

The heat of formation of $\mathrm{LiCl \cdot 5190H_2O}$ was obtained by the same method used previously for $\mathrm{LiCl \cdot 60H_2O}$.

The heat of formation of lithium aluminum hydride obtained was:

$$\mathrm{Li(c)} + \mathrm{Al(c)} + 2\mathrm{H_2(g)} \longrightarrow \mathrm{LiAlH_4(c)} \qquad \Delta H^0_{298.16} = -24.08 \text{ kcal.}$$

Summary

A "bomb" calorimeter was used to determine the heats of reaction of sodium borohydride, lithium 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 ± 0.07; lithium borohydride, −44.15 ± 0.30; lithium aluminum hydride, −24.08 ± 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. ΔH_f^0 for $\mathrm{H_3BO_3 \cdot \infty H_2O}$ was calculated from ΔH_f^0 for $\mathrm{B_2O_3}$ 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 measing the amounts of hydrogen liberated by their reaction with dilute acid with a precision and accuracy better than 0.1%.

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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.[1] 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.[2] 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 discrepancy 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.[1] In this method the diffusion coefficient was determined by the equations

$$\ln (K_\mathrm{B} - K_\mathrm{T}) = -t/\tau + \text{constant} \qquad (1)$$

and

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

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

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[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.