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Lattice Energies and Related Thermodynamic Properties of the Alkali Metal Borohydrides and of the Borohydride Ion[1]

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A theoretical calculation has been made of the lattice energies of $NaBH_4$, KBH_4, $RbBH_4$ and $CsBH_4$. The lattice energy of $LiBH_4$ and the heats of formation of KBH_4, $RbBH_4$ and $CsBH_4$ have been estimated. The polarizability of BH_4^- in the solid state has been calculated to be 3.9 ± 0.1 Å.^{3} A heat of formation for BH_4^-(g) of −23 ± 5 kcal./mole has been obtained. The heat of the reaction $BH_3 + H^- \rightarrow BH_4^-$ is −75 ± 5 kcal./mole, while the heat of the reaction $^1/_2B_2H_6 + H^- \rightarrow BH_4^-$ is −61 ± 5 kcal./mole. The thermodynamic functions $C_p°$, $(H° - H_0°)/T$, $-(F° - H_0°)/T$, and $S°$ have been computed for BH_4^-(g) in the temperature range from 200 to 1000°K. Combining the above data with other entropy and free energy data available in the literature, an entropy and free energy of −25.7 cal./deg./mole and −67 kcal./mole have been calculated for the reaction $BH_3 + H^- \rightarrow BH_4^-$. The entropy and free energy have been calculated for the reaction $^1/_2B_2H_6 + H^- \rightarrow BH_4^-$ as −8.6 cal./deg./mole and −58 kcal./mole. The heat and entropy of hydration of BH_4^- have been found to be −72 ± 5 kcal./mole and −13 e.u., respectively.

The recent measurements of the lattice constants of the alkali metal borohydrides[2,3] make possible a theoretical calculation of the lattice energies of $NaBH_4$, KBH_4, $RbBH_4$ and $CsBH_4$. These lattice energies can be combined with the available thermochemical data to obtain the heats of formation of BH_4^-(g), of KBH_4(c), $RbBH_4$(c) and $CsBH_4$(c), and the lattice energy of $LiBH_4$. The heats of the gas reactions of the hydride ion with borane and diborane to form borohydride ion can also be evaluated. The thermodynamic functions, C_p°, $(H° - H_0^\circ)/T$, $-(F° - H_0^\circ)/T$ and $S°$, can be computed for BH_4^-(g) by the usual statistical thermodynamic methods. The entropies and free energies of the reactions of BH_3(g) and B_2H_6(g) with H^-(g) to form BH_4^-(g) can also be calculated. These various thermodynamic properties are obtained in the present investigation.

Since the compressibilities of the alkali metal borohydrides have not been reported, and the "main frequency" energy,[4] ϵ, is not known for BH_4^-, the lattice energies are calculated in part for a face-centered cubic lattice[2,3] (NaCl type) from the simple Born equation.[5]

$$U_0 = \frac{NAe^2}{r_0}(1 - 1/n)$$

where N is Avogadro's number, A is the Madelung constant, e is the electronic charge, r_0 is the smallest cation–anion distance and n is a constant for a particular ion type.

In the lattice energy calculations for the alkali metal borohydrides, the repulsive exponent n values are those employed formerly for the alkali metal fluorides.[6] These n values are chosen because the BH_4^- united atom (ion) is isoelectronic with F^- and is thus of the Ne ion type.[6]

In addition to the contributions from the coulombic and repulsion energy terms which are included in the Born equation, the van der Waals energy term must be included in at least an approximate manner. The van der Waals interactions in the crystal depend on the lattice type which is the same for the Na, K, Rb and Cs borohydrides as for the alkali metal halides (except CsCl, CsBr and CsI), on the polarizabilities of the ions, and the "main frequency" energies of the ions.

The polarizability of the borohydride ion may be

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[1] Presented (in part) before the Division of Physical and Inorganic Chemistry at the 127th meeting of the American Chemical Society, Cincinnati, Ohio, April, 1955.

[2] S. C. Abrahams and J. Kalnajs, *J. Chem. Phys.*, **22**, 434 (1954).

[3] A. M. Soldate, THIS JOURNAL, **69**, 987 (1947).

[4] J. E. Mayer, *J. Chem. Phys.*, **1**, 270, 327 (1933).

[5] M. Born, *Ber. deut. physik. Ges.*, **21**, 13 (1919).

[6] J. Sherman, *Chem. Revs.*, **11**, 93 (1932).

evaluated from the refractive indices[7] of $NaBH_4$, KBH_4, $RbBH_4$ and $CsBH_4$ by the method used by Tessman, *et al.*, to evaluate the polarizabilities of ions in crystals.[8] The polarizability of BH_4^- in the crystal is given in Table I along with the quantities $V_m = a^3/_4$, where a is the lattice constant, and $\alpha_m = 3V_m(n^2 - 1)/4\pi(n^2 + 2) = \alpha_{M^+} + \alpha_{BH_4^-}$.

TABLE I

POLARIZABILITY OF BH_4^-

Compd.	V_m, Å.^{3}	α_m, Å.^{3} (λ = Na$_D$)	α_{M^+}, Å.^{3} (λ = Na$_D$)[a]	$\alpha_{BH_4^-}$, Å.^{3} (λ = Na$_D$)[b]
$NaBH_4$	58.56	4.43	0.408	4.02
KBH_4	76.14	5.25	1.334	3.92
$RbBH_4$	86.82	5.96	1.979	3.98
$CsBH_4$	102.1	7.14	3.335	3.81
			Av.	3.9 ± 0.1

[a] Reference 8. [b] These values are in excellent agreement with the values for α obtained by Stockmayer, Rice and Stephenson, THIS JOURNAL, **77**, 1980 (1955).

The polarizability of BH_4^- of 3.9 Å.^{3} is only slightly smaller than the polarizability for Br^- of 4.158 Å.^{3} ($\alpha(Cl^-)$ = 2.960 Å.^{3}, $\alpha(I^-)$ = 6.431 Å.^{3}).

The polarizabilities of the alkali metal ions most applicable to crystal lattice calculations are those given by Tessman, *et al.*,[8] and listed in Table I. The "main frequency" energies of the alkali metal ions, ϵ_+, are taken as 0.9 of the second ionization potential of the elements.[4] The "main frequency" energy ϵ_- for BH_4^- is assumed to be close to the ϵ_- for Br^-.[9] The contribution from the dipole-dipole interactions, C/r_0^6, to the van der Waals energy can now be calculated by Mayer's method[4] using the above data. The quantities involved in the evaluation of the energy resulting from the dipole–dipole interactions are listed in Table II.

TABLE II

QUANTITIES INVOLVED IN EVALUATION OF VAN DER WAALS ENERGY FROM DIPOLE-DIPOLE INTERACTIONS IN LATTICE

	Ergs/molecule 10^{12}			
Compd.	C_{++}	C_{--}	C_{+-}	C
$NaBH_4$	8.6	160	27.9	336
KBH_4	60.6	..	83.4	749
$RbBH_4$	116	..	119	1036
$CsBH_4$	281	..	193	1671

The contributions from the dipole–quadrupole interactions, D/r_0^8, are approximated as $^2/_{15}$ the contributions from the dipole–dipole interactions. The fraction $^2/_{15}$ is chosen from the relative magnitudes of the two terms for the alkali metal halides.[4] The values of r_0 and n, the lattice energy contributions calculated from the Born equation, the total van der Waals energies, and the total lattice energies, $-U_T$, are listed in Table III.

The addition of the van der Waals energies to the coulombic and repulsion energies from the Born equation is an approximate procedure. Actually, all the terms in the energy equation should be minimized at the equilibrium distance. To estimate the uncertainty resulting from this approximation, the same approximate procedure was used for the alkali metal halides. The approximate lattice energies proved to be several kcal./mole higher than the very accurate lattice energies for the alkali metal halides calculated by Huggins.[10] The total uncertainty in the lattice energies for the alkali metal borohydrides resulting from the use of the Born equation, the approximate nature of the van der Waals energy calculations and the addition procedure, is estimated to be about ±5 kcal./mole.

TABLE III

LATTICE ENERGIES OF THE ALKALI METAL BOROHYDRIDES

Compd.	r_0,[a] Å.	n	$-U_c$ (Born eq.), kcal./mole	Van der Waals energy, kcal./mole	$-U_T$ kcal./mole
$NaBH_4$	3.082	7.0	161.4	6.3	168
KBH_4	3.364	8.0	150.9	8.4	159
$RbBH_4$	3.515	8.5	145.7	9.0	155
$CsBH_4$	3.715	9.5	139.9	10.4	150

[a] From the lattice constants a of reference 2.

The heat of formation of $BH_4^-(g)$ can now be calculated to be -23 ± 5 kcal./mole from a ΔH_f° (298°K.) for $NaBH_4(c)$[11] of -45.5 kcal./mole, ΔH_f° (298°K.) of $Na^+(g)$[12] of 146.0 kcal./mole and the lattice energy of 168 kcal./mole for $NaBH_4(c)$.

The lattice energy of $LiBH_4(c)$[13] can be calculated to be 186 kcal./mole from the heats of formation of $LiBH_4(c)$,[11] of $Li^+(g)$[12] and of $BH_4^-(g)$.

The heats of formation of $KBH_4(c)$, $RbBH_4(c)$ and $CsBH_4(c)$, may be estimated also from the reaction $MBH_4(c) \rightarrow M^+(g) + BH_4^-(g)$. The heats of these reactions are the lattice energies already calculated. The heat of formation of BH_4^- has been calculated in this paper and the heats of formation of $K^+(g)$, $Rb^+(g)$ and $Cs^+(g)$ are available.[12] From these data, the heats of formation of $KBH_4(c)$, $RbBH_4(c)$ and $CsBH_4(c)$ at 298°K. are estimated to be -58, -59 and -63 kcal./mole, respectively.

The heats of the reactions

$$BH_3(g) + H^-(g) \longrightarrow BH_4^-(g) \tag{1}$$

and

$$^1/_2B_2H_6(g) + H^-(g) \longrightarrow BH_4^-(g) \tag{2}$$

may now be calculated also. Using the heats of formation of $BH_3(g)$,[11,14] of $B_2H_6(g)$,[11] of $H^-(g)$[12] and of $BH_4^-(g)$, the heat of reaction for (1) is -75 ± 5 kcal./mole and the heat of reaction for (2) is -61 ± 5 kcal./mole.

The thermodynamic functions, C_p°, $(H^\circ - H_0^\circ)/T$, $-(F^\circ - H^\circ)/T$ and S° can be calculated by statistical thermodynamic methods for $BH_4^-(g)$. The B–H distance in BH_4^- has been obtained from nuclear magnetic resonance measurements on alkali metal borohydrides.[15] The r(B–H) in BH_4^- is

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(7) M. D. Banus, R. W. Bragdon and A. A. Hinckley, THIS JOURNAL, **76**, 3849 (1954).

(8) J. R. Tessman, A. H. Kahn and W. Shockley, *Phys. Rev.*, **92**, 890 (1953).

(9) If, instead of ϵ_- for BH_4^- being close to ϵ_- for Br^- it were actually close to ϵ for F^-, then the van der Waals energies would be increased by about 2 kcal./mole. Since the range from ϵ_- for Br^- to that for F^- probably represents the range of uncertainty in ϵ_- for BH_4, about ±2 kcal./mole would represent the uncertainty in the lattice energies resulting from this approximation.

(10) M. Huggins, *J. Chem. Phys.*, **5**, 143 (1937).

(11) D. D. Wagman, T. R. Munson, W. H. Evans and E. J. Prosen, NBS Report 3456 (Aug. 30, 1954).

(12) F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," NBS Circular 500, 1952.

(13) The $LiBH_4$ lattice is orthorhombic (P. M. Harris and E. P. Meibohm, THIS JOURNAL, **69**, 1231 (1947)) and a theoretical treatment leading to its lattice energy would be difficult.

(14) A. Shepp and S. H. Bauer, *ibid.*, **76**, 265 (1954).

(15) Private communication from Dr. R. E. Richards of Oxford. To be published in the *Discs. Faraday Soc.*

1.255 ± 0.02 Å.[15] Therefore, the moment of inertia, I, for BH_4^- is (7.03 ± 0.22) 10^{-40} g. cm.^{2}.

The BH_4^- ion is a spherical top with the observed vibrational frequencies,[16–18] ν_1 (1) = 2290 cm.$^{-1}$ [18]; ν_3 (3) = 2299 cm.$^{-1}$ [17]; ν_4 (3) = 1123 cm.$^{-1}$.[17] The frequency ν_2(2) has not yet been observed. This frequency, ν_2, can be approximated as 1180 cm.$^{-1}$ from the valence force field expression[19] for tetrahedral molecules, XY_4: $\nu_3\nu_4/\nu_1\nu_2 = [{}^2/_3 (1 + 4m_y/m_x)]^{1/2}$. However, for first row elements the values of $[{}^2/_3(1 + 4m_y/m_x)]^{1/2}$ are appreciably larger than the $\nu_3\nu_4/\nu_1\nu_2$ values. In particular, for the first row hydrides, XH_4, the calculated values average about 5% higher than the values obtained from $\nu_3\nu_4/\nu_1\nu_2$. Consequently, the vibrational frequency values for ν_2 obtained from the valence force field equation has been corrected by 5% to give a value for ν_2 of 1240 ± 50 cm.$^{-1}$. From the combination band $\nu_2 + \nu_4 = 2398$ cm.$^{-1}$ [17] a value for ν_2 of 1275 cm.$^{-1}$ is obtained. The average of these two values, $\nu_2 = 1260$ cm.$^{-1}$ is used in calculating the thermodynamic functions.

The thermodynamic functions as calculated by the rigid rotator–harmonic oscillator approximation are given below for BH_4^- in the ideal gaseous state at one atmosphere pressure.

TABLE IV

THERMODYNAMIC FUNCTIONS FOR BH_4^- IN THE IDEAL GASEOUS STATE AT ONE ATMOSPHERE PRESSURE (IN CAL./DEG./MOLE)

T, °K.	$C_p°$	$\frac{H° - H_0°}{T}$	$\frac{F° - H_0°}{T}$	$S°$
200	8.11	8.00	33.84	41.84
250	8.49	8.06	35.62	43.69
298.16	9.08	8.18	37.05	45.23
300	9.11	8.19	37.10	45.29
400	10.76	8.63	39.50	48.13
500	12.55	9.24	41.48	50.72
600	14.26	9.94	43.22	53.16
700	15.78	10.67	44.80	55.47
800	17.12	11.40	46.27	57.67
900	18.27	12.10	47.65	59.75
1000	19.24	12.77	48.96	61.73

The uncertainties in the moment of inertia, I, and the vibrational frequencies, along with the use of the rigid rotator–harmonic oscillator approximation, limit the accuracy of C_p° to ±0.2 unit and the accuracy of $(H° - H_0°)/T$, $-(F° - H_0°)/T$ and $S°$ to ±0.1 unit at 300°K. and below and to ±0.2 unit at higher temperatures. Near 1000°K. the neglect of the effects of anharmonicity may decrease the accuracy of the thermodynamic functions even more than is estimated.

The entropies and free energies can now be evaluated for reactions (1) and (2). The entropy of BH_3(g) at 300°K. is 44.9 cal./deg./mole,[14] while the entropy of B_2H_6(g) is 55.5 cal./deg./mole.[11] The entropy of H^-(g) from the Sackur equation is 26.04 cal./deg./mole, and the entropy of BH_4^-(g) at 300°K. is 45.23 cal./deg./mole. Consequently, the entropy of reaction (1) is −25.7 cal./deg./mole and that of reaction (2) is −8.6 cal./deg./mole. Using the heat of reaction for reaction (1) of −75 ± 5 kcal./mole with its entropy of reaction, one obtains a free energy for (1) of −67 ± 5 kcal./mole. Similarly, for reaction (2) the free energy of the reaction is −58 ± 5 kcal./mole. Thus, both reactions at standard state conditions will tend to result in borane and diborane reacting with hydride ion almost completely to form borohydride ion.

The heat of formation, ΔH_f°(aq) and the entropy, $\bar{S}°$, for the aqueous borohydride ion have recently been reported.[20] These values, $\Delta H_f^\circ(\text{aq}) = 12.4$ kcal./mole and $\bar{S}° = 25.5 \pm 1$ e.u., can be combined with the heat of formation and the entropy of the gaseous borohydride ion given above to calculate the heat and entropy of hydration of the BH_4^- ion. The heat of hydration, $-\Delta H_{\text{hyd.}}$, of BH_4^- is 72 ± 5 kcal./mole. The entropy of hydration (corrected for the entropy change resulting from volume contraction, 6.35 e.u.) is −13 e.u. The heat of hydration of BH_4^- is about the same as $\Delta H_{\text{hyd.}}$ for a halide-like ion of the same size (2.03 Å.) which would be about 77 kcal./mole.[21] The entropy of hydration of BH_4^-, −13 e.u., $(-\Delta S_{\mathrm{H}^+ = 0})$ is only slightly more negative than the $\bar{S}°$ for a halide-like ion of the same size which would be −11 e.u.[21]

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(16) W. C. Price, *J. Chem. Phys.*, **17**, 1044 (1949).

(17) T. H. Walnut, Jr., Ph.D. Thesis, Brown Univ., 1951.

(18) W. J. Lehmann, Ph.D. Thesis, St. Louis Univ., 1954.

(19) G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, pp. 181–183.

(20) W. H. Stockmayer, D. W. Rice and C. C. Stephenson, THIS JOURNAL, **77**, 1980 (1955).

(21) W. M. Latimer, *J. Chem. Phys.*, **23**, 90 (1955).