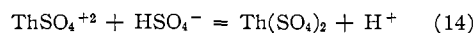


A final summary of the thermodynamic quantities for the sulfate complexes of thorium and the association of bisulfate ion is presented in Table VI. The values for the second complex correspond to the more conventional stepwise form of the reaction



Acknowledgments.—The author is indebted to Dr. James C. Hindman for the initial suggestion of

this research and many critical discussions throughout the entire work. Dr. Darrell W. Osborne provided helpful advice on the calorimetry problems and also made available the equipment for precision electrical heating. The technical assistance of Mr. Willard G. Greenhow in programming the majority of the least squares analyses for the GEORGE electronic digital computer was invaluable.

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[CONTRIBUTION FROM THE THERMAL LABORATORY, THE DOW CHEMICAL COMPANY]

The Chemical Thermodynamic Properties of Calcium Hydroxide

BY W. E. HATTON, D. L. HILDENBRAND, G. C. SINKE AND D. R. STULL

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The heat capacity of crystalline calcium hydroxide was measured from 19 to 330°K. and the entropy at 298.15°K. calculated as 19.93 ± 0.10 cal. deg.⁻¹ mole⁻¹. The heat of dissociation was calculated from dissociation pressures by third law methods. The result is in excellent agreement with calorimetric values, indicating no residual entropy at 0°K. Selected best values for the heat and free energy of formation at 298.15°K. are -235.71 and -214.77 ± 0.10 kcal. mole⁻¹, respectively.

Introduction

Although an accurate value is available for the heat of dissociation of calcium hydroxide,¹ the entropy listed by Kelley² is based on fragmentary data. The free energy of formation calculated from dissociation pressures indicates Kelley's value to be too low. The entropy of calcium hydroxide therefore was determined by measurement of the heat capacity from 19 to 330°K.

Experimental

Calcium hydroxide was prepared by calcining Mallinckrodt Analytical Reagent calcium carbonate and treating the resulting oxide with a stoichiometric amount of water. Analysis indicated the sample to be 99.75% calcium hydroxide with the remainder calcium carbonate and water. The purity was considered adequate for heat capacity purposes. An X-ray diffraction pattern indicated the sample to be crystalline.

Heat capacity measurements were made over the range 19 to 330°K. with an automatically operated adiabatic calorimeter that has been described previously.^{3,4} A sample weighing 39.010 g. corrected to vacuum, was sealed in a nickel-plated copper calorimeter under one atmosphere pressure of helium gas at room temperature. The filling and sealing operation were done under anhydrous, CO₂-free conditions so as to avoid contamination of the sample. The experimental heat capacity data are given in Table I. Temperatures and temperature differences were measured with a platinum resistance thermometer ($R_0 = 96$ ohms) calibrated by comparison with an N.B.S. calibrated platinum thermometer. Temperature rises were approximately 10% of the absolute temperature below 50°K. and 5 to 7% at higher temperatures. Corrections for curvature were not applied, nor should they be necessary with intervals of this size. The heat capacities are believed to be accurate to within 0.2 to 0.3% above 50°K. and to within 1% at lower temperatures. The accuracy estimates are based on the results of a series of check measurements on a heat capacity standard, as well as on the results of several inter-laboratory comparisons. Results are given in terms of the defined thermochemical calorie, equal to 4.1840 abs. joules. The ice point

TABLE I

THE HEAT CAPACITY OF CALCIUM HYDROXIDE, CAL. MOLE⁻¹ DEG.⁻¹

T, °K.	C _p	T, °K.	C _p	T, °K.	C _p
Series I					
18.85	0.177	159.46	13.63	136.07	11.60
21.27	.268	170.25	14.35	140.62	12.02
23.76	.352	175.35	14.83	145.06	12.50
26.49	.505	181.34	15.17	150.42	12.74
29.81	.671	188.21	15.64	156.65	13.39
33.26	.887	194.92	16.08	162.67	13.83
36.90	1.185	201.50	16.47	168.52	14.29
41.26	1.466	207.98	16.86	174.24	14.68
45.79	1.867	214.36	17.17	179.86	15.17
50.04	2.211	Series II			
54.28	2.677	22.91	0.312	190.82	15.84
59.05	3.158	25.92	.448	196.84	16.21
63.93	3.677	28.95	.608	203.44	16.54
68.30	4.257	32.02	.862	209.94	17.00
71.72	4.477	35.24	1.029	216.35	17.33
76.89	5.040	38.77	1.310	222.68	17.68
83.03	5.814	42.84	1.577	228.92	18.08
88.65	6.492	47.54	1.944	247.18	18.85
93.92	6.975	52.61	2.378	253.17	19.15
98.89	7.778	57.84	2.952	259.09	19.41
103.61	8.205	63.33	3.623	264.96	19.63
108.15	8.699	69.12	4.263	270.78	19.88
112.52	9.171	75.18	4.856	276.55	20.07
116.75	9.587	81.01	5.590	282.28	20.31
120.86	10.03	87.22	6.322	287.96	20.54
124.85	10.40	93.77	7.054	294.16	20.75
130.01	10.93	105.78	8.440	300.86	21.06
136.27	11.62	111.30	9.108	307.87	21.35
142.33	12.09	116.59	9.630	315.18	21.61
148.22	12.62	121.69	10.13	322.43	21.80
153.93	13.16	126.62	10.67	329.62	22.10
		131.41	11.11		

(1) K. Taylor and L. S. Wells, *J. Research Natl. Bur. Standards*, **21**, 133 (1938).

(2) K. K. Kelley, U. S. Bur. Mines Bull. 477, 1950.

(3) D. R. Stull, *Anal. Chim. Acta*, **17**, 133 (1957).

(4) D. L. Hildenbrand, W. R. Kramer, R. A. McDonald and D. R. Stull, *THIS JOURNAL*, **80**, 4129 (1958).

was taken as 273.15°K. and the molecular weight of calcium hydroxide as 74.096.

The entropy, free energy and heat content functions of crystalline calcium hydroxide, obtained by graphical integration of the heat capacity data, are listed at even tempera-

TABLE II
THERMODYNAMIC PROPERTIES OF CALCIUM HYDROXIDE,
CAL. MOLE⁻¹ DEG.⁻¹

T, °K.	C _p ^o	S ^o	$-(F^o - H_0^o)$	
			T	T
20	0.220	0.070	0.017	0.053
25	.418	.139	.034	.105
30	.673	.237	.059	.178
35	.990	.363	.093	.270
40	1.360	.520	.138	.382
45	1.783	.703	.189	.514
50	2.248	.915	.251	.664
55	2.748	1.152	.322	.830
60	3.268	1.414	.402	1.012
70	4.339	1.999	.589	1.410
80	5.460	2.651	.805	1.846
90	6.614	3.360	1.048	2.312
100	7.777	4.117	1.317	2.800
110	8.897	4.911	1.607	3.304
120	9.962	5.730	1.916	3.814
130	10.97	6.568	2.242	4.326
140	11.91	7.416	2.582	4.834
150	12.80	8.268	2.932	5.336
160	13.62	9.121	3.293	5.828
170	14.39	9.970	3.660	6.310
180	15.10	10.812	4.034	6.778
190	15.77	11.646	4.412	7.234
200	16.39	12.472	4.795	7.677
210	16.98	13.286	5.180	8.106
220	17.52	14.089	5.567	8.522
230	18.03	14.879	5.955	8.924
240	18.51	15.656	6.342	9.314
250	18.97	16.422	6.731	9.691
260	19.41	17.174	7.118	10.056
270	19.82	17.914	7.504	10.410
280	20.22	18.642	7.888	10.754
290	20.60	19.358	8.271	11.087
298.15	20.91	19.934	8.583	11.351
300	20.98	20.063	8.653	11.410
310	21.34	20.757	9.033	11.724
320	21.70	21.440	9.410	12.030
330	22.04	22.114	9.785	12.329

Results and Discussion

The heat capacities of Table I and the high temperature values of Kobayashi⁶ can be connected by a smooth curve which was extrapolated to 800°K. Free energy functions for calcium hydroxide were calculated from this curve and the measured entropy at 298°K. Free energy functions for calcium oxide were obtained from data listed by Kelley^{2,7} and for water from values given by Friedmann and Haar.⁸ The change in free energy function, $\Delta[(F^o - H_{298}^o)/T]$, for the dissociation reaction was calculated as 33.92 cal. deg.⁻¹ mole⁻¹ at 600°K., 33.56 at 700°K., and 33.18 at 800°K. Intermediate values were derived by interpolation.

The heat of dissociation of calcium hydroxide was computed using these free energy functions and the dissociation pressures measured by Halstead and Moore,⁹ Tamaru and Siomi¹⁰ and Johnston.¹¹ Results are given in Table III. The data of Hal-

TABLE III
THE HEAT OF DISSOCIATION FROM DISSOCIATION PRESSURES

Investigators	Temp. range, °K.	No. of expts.	ΔH_{298} kcal. mole ⁻¹
Halstead and Moore ⁹	635-777	14	26.02 ± 0.10
Tamaru and Siomi ¹⁰	694-775	8	26.18 ± .06
Johnston ¹¹	663-804	7	27.04 ± .17

stead and Moore and Tamaru and Siomi are in good agreement and give an average heat of dissociation of 26.10 ± 0.10 kcal. mole⁻¹. Pressures measured by Johnston are too low due to failure to reach true equilibrium. Taylor and Wells¹ measured the heat of dissociation from heats of solution in hydrochloric acid as 15.57 ± 0.08 kcal. mole⁻¹ and by direct hydration of calcium oxide as 15.43 ± 0.09 kcal. mole⁻¹. Taking the average and combining with the heat of vaporization of water listed by the National Bureau of Standards¹² gives the heat of dissociation as 26.02 ± 0.10 kcal. mole⁻¹. The excellent agreement indicates there

TABLE IV
CHEMICAL THERMODYNAMIC PROPERTIES OF CALCIUM HYDROXIDE

T, °K.	Cal. deg. ⁻¹ mole ⁻¹			Kcal. mole ⁻¹ deg. ⁻¹			Log K _p
	C _p	S ^o	$-(F^o - H_{298}^o)/T$	H ^o - H ₂₉₈ ^o	ΔH^o_t	ΔF^o_t	
298.15	20.91	19.93	19.93	0	-235.71	-214.77	157.421
300	20.98	20.06	19.93	0.39	-235.71	-214.64	156.354
400	23.52	26.47	20.79	2.28	-235.52	-207.63	113.440
500	24.76	31.88	22.48	4.70	-235.21	-200.70	87.719
600	25.58	36.47	24.44	7.22	-234.86	-193.83	70.598
700	26.25	40.46	26.45	9.81	-234.50	-187.02	58.387
800	26.75	44.00	28.43	12.46	-234.40	-180.22	49.232
900	27.20	47.18	30.34	15.16	-234.07	-173.47	42.122
1000	27.55	50.06	32.17	17.90	-233.79	-166.76	36.444

tures in Table II. Heat capacities are also included. The equation

$$C_p = 2.64 \times 10^{-5} T^3$$

fits the experimental points from 19 to 30°K. very well and was used in extrapolating the heat capacity below 20°K. At 298.15°K., the entropy of solid calcium hydroxide was derived as 19.93 ± 0.10 cal. mole⁻¹ deg.⁻¹, as compared to the value 17.4 ± 1.0 cal. mole⁻¹ deg.⁻¹ given by Kelley,² based on the incomplete data of Nernst and Schwers.⁵

(5) W. Nernst and F. Schwers, *Sitzb. Konig. preuss. Akad. Wiss.*, 355 (1914).

is no residual entropy in calcium hydroxide at absolute zero.

(6) K. Kobayashi, *Sci. Repts. Tohoku Univ. First Ser.*, 34, 153 (1950).

(7) K. K. Kelley, U. S. Bur. Mines Bull. 476, 1949.

(8) H. S. Friedmann and L. Haar, *J. Chem. Phys.*, 22, 2052 (1954).

(9) P. E. Halstead and A. E. Moore, *J. Chem. Soc.*, 3873 (1957).

(10) S. Tamaru and K. Siomi, *Z. physik. Chem.*, 161A, 421 (1932).

(11) J. Johnston, *ibid.*, 62, 330 (1908).

(12) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circ. 500, 1952.

A recent determination¹³ of the heat of formation of calcium oxide is in good agreement with the value listed by the National Bureau of Standards.¹² Taking an average of -151.85 kcal. mole⁻¹, the heat of formation of water as -57.80 kcal. mole⁻¹, and an average heat of dissociation of 26.06 kcal. mole⁻¹ gives the standard heat of formation at 298°K. of calcium hydroxide as -235.71 ± 0.10 kcal. mole⁻¹. With entropies of the elements

(13) E. J. Huber, Jr., and C. E. Holley, Jr., *J. Phys. Chem.*, **60**, 498 (1956).

listed by Stull and Sinke,¹⁴ the standard free energy of formation at 298°K. is -214.77 ± 0.10 kcal. mole⁻¹. The chemical thermodynamic properties from 298.15 to 1000°K. have been calculated using these selected values and are given in Table IV. These values lead to a calculated dissociation pressure of one atmosphere at 784°K.

(14) D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," Advances in Chemistry Series No. 18, American Chemical Society, 1956.

MIDLAND, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE UNIVERSITY OF KANSAS]

Precise Lattice Parameters of Selected Rare Earth Tetra- and Hexa-borides¹

BY HARRY A. EICK AND PAUL W. GILLES

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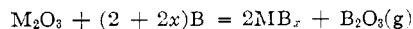
The refractory tetraborides and hexaborides of seven of the rare earth elements have been prepared by heating intimate mixtures of the sesquioxide and boron in a high vacuum in tantalum, molybdenum or graphite crucibles. The samples were analyzed by chemical and X-ray diffraction procedures. Precise lattice parameters, obtained by analytical extrapolation using a digital computer, indicate a pronounced difference between the tetraborides and the hexaborides in the trends of their lattice parameters. The former show a nearly linear decrease in lattice parameters through the series, while the latter show an irregular decrease. The results generally confirm earlier values of Post, Moskowitz and Glaser.

The rare earths form two groups of refractory borides. The tetraborides are gray and have a tetragonal structure belonging to space group $D_{4h}^5-P_4/mbm$. The hexaborides are blue with a cubic structure, space group $O_h^1-Pm\bar{3}m$.

Many investigators²⁻⁷ have examined various facets of the rare earth-boron systems. The crystal structure and lattice parameters of CeB_4 were reported by Zalkin and Templeton,³ while the lattice parameters of PrB_4 , Gd_2B_6 , SmB_6 and YbB_6 were reported by Post, *et al.*⁶ Neshpor and Samsonov⁷ have recently published lattice parameters for the hexa- and tetraborides of Dy, Ho and Lu which differ drastically from the values that would be predicted from the data of Post, *et al.*⁶ This investigation was undertaken to determine which of the reported values were correct and to establish more nearly accurate parameters for the compounds.

Materials.—99.9% pure Nd_2O_3 and Sm_2O_3 were obtained from Ames Laboratories, Ames, Iowa. Similar purity Sm, Gd, Tb, Dy, Ho, Er and Yb sesquioxides were obtained from Heavy Minerals Corporation, Chattanooga, Tennessee. The 99.11% boron containing 0.5% Fe and 0.2% C was obtained from Fairmont Chemical Company, Inc., Newark 5, New Jersey.

Preparation.—Samples were prepared in the form of wafers $1/8''$ to $1/4''$ high and $1/4''$ in diameter by pressing at about 500 p.s.i. mixed powders of sesquioxide and boron in the proportions to give MB_4 or MB_6 according to the equation



(1) Data included herein were presented at the 134th meeting of the American Chemical Society at Chicago, September, 1958.

(2) J. M. Lafferty, *J. Appl. Phys.*, **22**, 299 (1951).

(3) M. V. Stackelberg and F. Neumann, *Z. physik. Chem.*, **19B**, 314 (1932).

(4) P. Blum and F. Bertaut, *Acta Cryst.*, **7**, 81 (1954).

(5) A. Zalkin and D. H. Templeton, *ibid.*, **6**, 269 (1953).

(6) (a) B. Post, D. Moskowitz and F. W. Glaser, *THIS JOURNAL*, **78**, 1800 (1956); (b) E. J. Felten, I. Binder and B. Post, *ibid.*, **80**, 3479 (1958).

(7) (a) V. S. Neshpor and G. V. Samsonov, *Dopovidi Akad. Nauk Ukr. R.S.R.*, 478 (1957); (b) V. S. Neshpor and G. V. Samsonov, *Zhur. Fiz. Khim.*, **32**, 1328 (1958).

The wafers were heated separately by induction from 5 min. to 12 hr. at 1000 to 2100°.

Considerable care was taken to obtain pure samples; to reveal any possible reaction with crucible materials, graphite, Mo and Ta were used. The wafers were placed on edge to minimize contact. Samples obtained from all types of crucibles were identical in all respects, thus indicating freedom from contamination.

At temperatures of about 1400° a deposit which was primarily iron, an impurity in the boron, sublimed from the samples, indicating in effect that the boron probably could now be considered as greater than 99.6% pure. After the heating, the sample was carefully broken and examined visually and by X-ray diffraction for homogeneity. Many preparations were reheated when two-phase regions were apparent.

Although enough boron was added to form B_2O_3 , it is not known whether this was the actual species evolved at the temperatures of the reaction. Possibly some $B_2O_3(g)$ was formed, and, if so, the product was deficient in boron. Such a situation was not harmful because the excess sesquioxide could be removed easily.

An X-ray powder diffraction study made of the products which resulted when Sm_2O_3 and boron were heated at various temperatures in a graphite and a Mo crucible indicated that the reaction proceeded first to give SmB_6 plus an unknown phase "Y"; then phase "Y" subsequently reacted with SmB_6 to form SmB_4 . This phase was not the same as that reported by Post, *et al.*⁶

The tetraborides free from diffraction lines of other phases were prepared both in graphite and Ta despite unsuccessful previous attempts.⁶ With Gd, Tb, Dy, Ho and Er, one hr. at 1900–2100° was required, while with Nd and Sm, 2–12 hr. at 1600° was required. All attempts to produce YbB_4 yielded YbB_6 and Yb.

The hexaborides of Nd, Sm and Yb were prepared in 1–6 hr. at 1800–1900°, but for Gd, Tb, Dy and Ho, 15–60 min. at less than 1500° were satisfactory. Ho and Tb hexaboride were never prepared free from the tetraboride, and the results are necessarily for metal saturated material. Erbium hexaboride could not be prepared in any manner, perhaps because too much boron was lost during the heating. A new, unidentified phase appeared in preparations designed to give HoB_6 and ErB_6 .

X-Ray and Analytical Procedures.—When X-ray examination revealed that a pure sample had been prepared, it was ground carefully in an Alundum mortar and washed twice with concentrated HCl to remove the sesquioxide. Unreacted boron presumably was not removed. The incompletely reacted sample was quite hard, but the final