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THE THERMOCHEMICAL AND THERMOPHYSICAL FUNCTIONS OF SOLID $Sr(OH)_2$ AND β-$Ba(OH)_2$

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ABSTRACT

Low-temperature heat capacities from 5 to 350 K by adiabatic calorimetry and high-temperature enthalpy increments above 450 K by drop calorimetry of high-purity $Sr(OH)_2$ and β-$Ba(OH)_2$ have been measured. From the results, smoothed thermochemical and thermophysical functions of the two compounds have been tabulated at selected temperatures.

INTRODUCTION

Surprisingly, the thermodynamics of the alkaline-earth hydroxides are poorly known at present, and data for solid $Sr(OH)_2$ and $Ba(OH)_2$ are particularly scarce. Heat capacity data for both compounds were reported only by Powers and Blalock [1], who measured enthalpy increments above 298.15 K of the solid and the liquid phases in a drop calorimeter. Their results, however, are suspect: (1) the data are extremely scattered, suggesting poor reproducibility, (2) the total alkalinity of the $Sr(OH)_2$ sample decreased considerably during the measurements, and (3) the crystalline form of the starting $Ba(OH)_2$ sample is not reported.

Calorimetric determinations of the enthalpies of formation of $Sr(OH)_2$ and the low-temperature β-modification of $Ba(OH)_2$ have been reported recently by the present authors [2]. The same high-purity samples have been used to measure the low-temperature heat capacities at the University of Michigan and the enthalpy increments at the Netherlands Energy Research Foundation; the results are reported here. The nature and thermodynamics of the α–β transformation in $Ba(OH)_2$ will be discussed in a forthcoming paper [3].

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EXPERIMENTAL DETAILS

The preparation and characterization of the $Sr(OH)_2$ and β-$Ba(OH)_2$ samples were described in a previous paper [2].

The low-temperature heat capacities were measured in an adiabatic calorimetric cryostat (laboratory designation Mark XIII) over the temperature range 5 to 350 K using a gold-plated calorimeter made of high conductivity, oxygen-free copper. The temperature of the calorimeter was measured with a Leeds & Northrup platinum encapsulated platinum resistance thermometer in an entrant well. The thermometer was calibrated by the U.S. National Bureau of Standards (NBS) against IPTS-48 [4] and is judged to reproduce thermodynamic temperatures within 0.03 K from 5 to 300 K. Determinations of mass, current, voltage and time are referred to standardizations and calibrations performed at NBS. For a more detailed description of the technique and apparatus see refs. 5 and 6.

For the measurements, 16.863 g of $Sr(OH)_2$ or 9.7346 g of β-$Ba(OH)_2$ was loaded into the calorimeter (laboratory designation W-139 or W-99, respectively). The loading and unloading of the calorimeter were performed in an argon-filled glove box. To facilate thermal contact between sample and calorimeter, 2.7 kPa (at 300 K) of helium was added after evacuation.

The enthalpy increments above 298.15 K were measured in an isothermal diphenyl ether drop calorimeter, which is a modified version of the Bunsen-type ice calorimeter. For the measurements, the samples were enclosed in spherical silver ampoules with a volume of approximately 4 cm^3. The ampoules were heated in a furnace whose temperature was measured with calibrated Pt–(Pt + 10 mass% Rh) thermocouples to ±0.1 K. After a thermal equilibration the ampoule was dropped into the calorimeter, where the energy of the ampoule plus the sample melted diphenyl ether in equilibrium with its liquid in a closed system. The resulting volume increase of the ether was determined by weighing the displaced mercury. The ratio of heat input to mass of mercury making up the volume increase is a constant for the apparatus, and is obtained by calibration with NBS standard reference material (No. 720) synthetic sapphire, Al_2O_3. Details of the calorimeter, calibration and performance are given in ref. 7.

For the present measurements, 5.341 22 g of $Sr(OH)_2$ or 6.802 44 g of β-$Ba(OH)_2$ was enclosed in ampoules of weight 4.028 55 g and 2.902 16 g, respectively. Loading of the ampoules was performed in an argon-filled glove box, and all masses were corrected for weighing in argon. A correction was made to account for the difference in enthalpy between the final calorimeter temperature (300.06 K) and the standard reference temperature, using C_p (298.15 K) values from the present low-temperature measurements.

TABLE 1

Experimental heat capacities of $Sr(OH)_2$ and β-$Ba(OH)_2$

T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})
$Sr(OH)_2$							
6.92	0.069	40.65	9.805	120.12	47.89	236.70	78.92
7.59	0.086	43.13	10.99	125.35	49.92	239.85	79.47
8.39	0.119	45.81	12.28	130.59	51.86	242.87	80.00
9.17	0.163	48.50	13.61	135.85	53.67	249.06	81.09
9.98	0.216	51.40	15.07	141.11	55.44	255.24	82.13
10.90	0.278	54.49	16.66	146.39	57.15	261.42	83.20
11.96	0.360	57.60	18.31	151.68	58.79	267.60	84.31
13.02	0.458	60.92	20.08	156.97	60.36	273.79	85.38
14.09	0.581	64.44	21.95	162.28	61.88	279.98	86.41
15.17	0.735	67.99	23.80	167.59	63.36	286.17	87.40
16.38	0.937	71.75	25.73	173.26	64.91	292.36	88.37
17.70	1.195	75.72	27.77	179.30	66.51	298.55	89.25
19.03	1.494	79.71	29.82	185.33	68.05	301.19	89.62
20.38	1.834	83.95	32.00	191.37	69.50	304.74	90.13
21.76	2.215	88.45	34.24	197.41	70.91	310.92	90.94
23.27	2.677	92.96	36.38	203.46	72.28	313.58	91.26
24.90	3.219	97.71	38.53	209.52	73.62	317.12	91.65
26.56	3.802	102.67	40.71	215.57	74.85	319.79	91.92
28.23	4.431	107.64	42.83	221.64	76.05	326.01	92.64
30.05	5.145	109.96	43.82	224.45	76.61	332.21	93.45
32.00	5.948	112.73	44.93	227.71	77.27	338.41	94.22
33.99	6.795	114.91	45.80	230.52	77.81	343.59	94.83
38.37	8.748	117.95	47.02	233.78	78.41	346.41	95.13
						347.74	95.29
β-$Ba(OH)_2$							
6.98	0.152	42.13	16.16	112.80	50.61	221.44	76.76
7.55	0.201	44.89	17.76	117.65	52.20	227.61	77.79
8.35	0.278	47.68	19.41	122.51	53.70	233.79	78.87
9.15	0.377	50.67	21.17	127.38	55.14	239.20	79.80
10.87	0.668	53.86	23.03	132.26	56.56	239.98	79.96
11.91	0.885	57.08	24.88	137.14	57.98	246.17	80.94
12.97	1.144	60.55	26.86	142.04	59.35	252.35	81.95
14.04	1.448	62.15	27.75	147.24	60.77	258.53	83.02
15.12	1.806	64.27	28.89	152.74	62.18	264.72	84.08
16.34	1.820	65.84	29.73	158.26	63.55	270.92	85.05
17.67	2.807	68.02	30.88	163.79	64.90	277.10	86.05
19.03	3.400	69.23	31.53	169.32	66.19	283.29	86.95
20.40	4.048	71.94	32.96	174.85	67.41	289.73	87.87
23.55	5.660	76.10	35.10	180.39	68.62	296.42	88.76
25.21	6.550	79.70	36.89	185.94	69.76	303.10	89.74
26.89	7.472	83.45	38.75	191.49	70.95	309.78	90.90
28.71	8.492	87.23	40.54	197.04	72.12	316.45	92.14
30.67	9.600	91.01	42.24	202.60	73.24	323.12	93.27
32.65	10.74	95.01	43.95	208.16	74.22	329.83	94.28
34.82	11.98	99.23	45.63	214.08	75.30	336.56	92.22
37.18	13.33	103.45	47.25	214.14	75.35	343.28	96.25
39.55	14.68	107.98	48.93	220.36	76.50		

RESULTS AND DISCUSSION

The results of the low-temperature heat capacity measurements of $Sr(OH)_2$ and β-$Ba(OH)_2$ in the temperature range 5–350 K are given in Table 1. The individual measurements are plotted in Fig. 1 as a function of the temperature. No phase transitions were observed in the heat capacity of the two alkali hydroxides: the heat capacity curves rise monotonically to 350 K. Smoothing and integration of the experimental data using the FITAB computer program [8] give the following values at 298.15 K

$$C_p[\mathrm{Sr(OH)_2}] = (89.22 \pm 0.09)\ \mathrm{J\ mol^{-1}\ K^{-1}},$$

$$S^{\ominus}[\mathrm{Sr(OH)_2}] = (94.99 \pm 0.07)\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

and

$$C_p[\beta\text{-}\mathrm{Ba(OH)_2}] = (89.08 \pm 0.09)\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

$$S^{\ominus}[\beta\text{-}\mathrm{Ba(OH)_2}] = (107.28 \pm 0.07)\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

The results of the enthalpy increment measurements are given in Table 2. The results have been fitted by the least-squares method, using $[H^{\ominus}(T) - H(298.15\ \mathrm{K})] = 0$ at 298.15 K and the $C_p(298.15\ \mathrm{K})$ values given above as boundary conditions, to give for $Sr(OH)_2$

$$[H^{\ominus}(T) - H^{\ominus}(298.15\ K)] = 78.9922T + 35.2860 \times 10^{-3}T^2 + 9.61225 \times 10^{6}T^{-1} - 29912.2$$

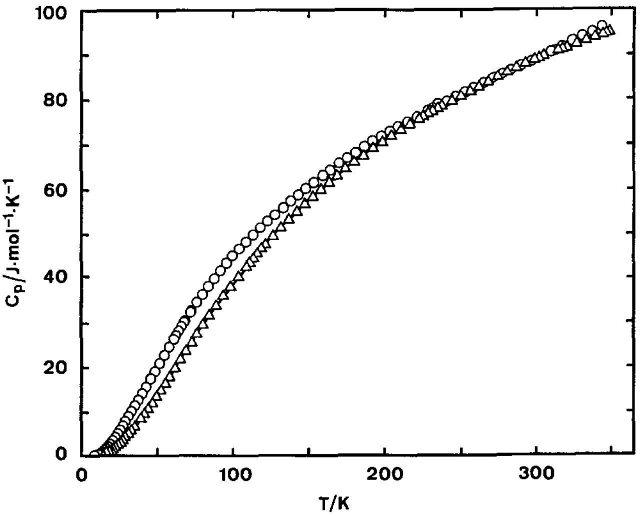

Fig. 1. Low-temperature heat capacities of $Sr(OH)_2$ and β-$Ba(OH)_2$: ○, $Ba(OH)_2$; △, $Sr(OH)_2$.

TABLE 2

Experimental enthalpy increment values of $Sr(OH)_2$ and β-$Ba(OH)_2$

T (K)	$[H^\ominus(T) - H^\ominus(298.15\ K)]$ (J mol^{-1}) Exp.	Calc.	Deviation (%)
$Sr(OH)_2$			
449.6	14813	14873	−0.40
464.1	16471	16419	0.32
479.1	18018	18039	−0.12
508.7	21285	21292	−0.03
523.5	22927	22947	−0.09
538.4	24629	24631	−0.01
553.2	26366	26322	0.17
568.4	28154	28087	0.27
588.4	30349	30417	−0.22
598.4	31592	31598	−0.02
613.7	33435	–	–
648.9	37594	–	–
668.7	39914	–	–
699.3	43530	–	–
β-$Ba(OH)_2$			
440.0	14125	14191	−0.47
444.8	14728	14726	0.01
449.6	15251	15264	−0.09
459.2	16380	16351	0.18
468.8	17433	17453	−0.11
479.0	18655	18638	0.09
488.8	19799	19793	0.03
498.6	21069	20962	0.51
508.5	22539	–	–

and for β-$Ba(OH)_2$

$$\left[H^\ominus(T) - H^\ominus(298.15\ K)\right] = 42.9863T + 77.2995 \times 10^{-3}T^2 - 19687.8$$

For $Sr(OH)_2$ only the enthalpy data below 600 K have been used for the least-squares fit, since above this temperature the change in enthalpy decreases rapidly (Fig. 2). This effect can be attributed to some dissociation of $Sr(OH)_2(s)$ to $SrO(s)$ and $H_2O(g)$. This effect has no influence on the measurements for β-$Ba(OH)_2$, since the dissociation pressures of $Ba(OH)_2$ are considerably lower than for $Sr(OH)_2$ [9–11] and the upper limit of the measurements is lower also.

A good agreement exists between the low-temperature heat capacity measurements and the high-temperature enthalpy increment measurements for both compounds, as is demonstrated in Fig. 2 in a plot of the apparent heat capacity. The data sets join smoothly at 298.15 K. The results of Powers and Blalock [1] for $Sr(OH)_2$ and $Ba(OH)_2$ are not shown in this figure, but deviate significantly from the present results. Part of the difference and scatter of their results for $Sr(OH)_2$ may arise from dissociation effects, since the measurements were made at considerably higher tempera-

TABLE 3

Low-temperature thermophysical functions of $Sr(OH)_2$ and β-$Ba(OH)_2$

T (K)	C_p° (J mol^{-1} K^{-1})	$S^\ominus$ (J mol^{-1} K^{-1})	FEF [a] (J mol^{-1} K^{-1})	$[H^\ominus(T) - H^\ominus(0\ \mathrm{K})]$ (J mol^{-1})
$Sr(OH)_2$				
10	0.106	0.075	0.022	0.532
20	1.729	0.572	0.146	8.531
40	9.513	3.927	1.071	114.3
60	19.56	9.639	2.926	402.8
80	30.01	16.71	5.467	899.2
100	39.54	24.45	8.483	1596.8
120	47.85	32.41	11.81	2472.6
140	55.06	40.34	15.32	3503.6
160	61.26	48.11	18.93	4668.3
180	66.67	55.64	22.60	5948.6
200	71.51	62.92	26.27	7331.2
220	75.77	69.94	29.92	8804.9
240	79.50	76.70	33.54	10358.2
260	82.98	83.20	37.11	11974.8
280	86.40	89.48	40.63	13677.1
300	89.48	95.54	44.09	15437.0
273.15	85.25	87.35	39.43	13089.2
298.15	89.22	94.99	43.77	15271.6
β-$Ba(OH)_2$				
10	0.506	0.175	0.052	1.231
20	3.851	1.367	0.351	20.32
40	14.95	7.352	2.207	205.8
60	25.53	15.61	5.263	621.1
80	37.07	24.72	8.980	1259.0
100	45.95	33.98	13.05	2092.9
120	52.91	43.00	17.30	3084.1
140	58.79	51.61	21.59	4202.1
160	63.97	59.81	25.86	5431.0
180	68.54	67.60	30.06	6757.1
200	72.68	75.05	34.20	8169.7
220	76.43	82.15	38.24	9661.3
240	79.93	88.96	42.18	11225.3
260	83.29	95.48	46.03	12858.2
280	86.42	101.78	49.79	14556.0
300	89.35	107.84	53.46	16312.9
273.15	85.39	99.65	48.51	13967.4
298.15	89.08	107.28	53.12	16148.2

[a] FEF $= -[G^\ominus(T) - H^\ominus(0\ \mathrm{K})]/T$.

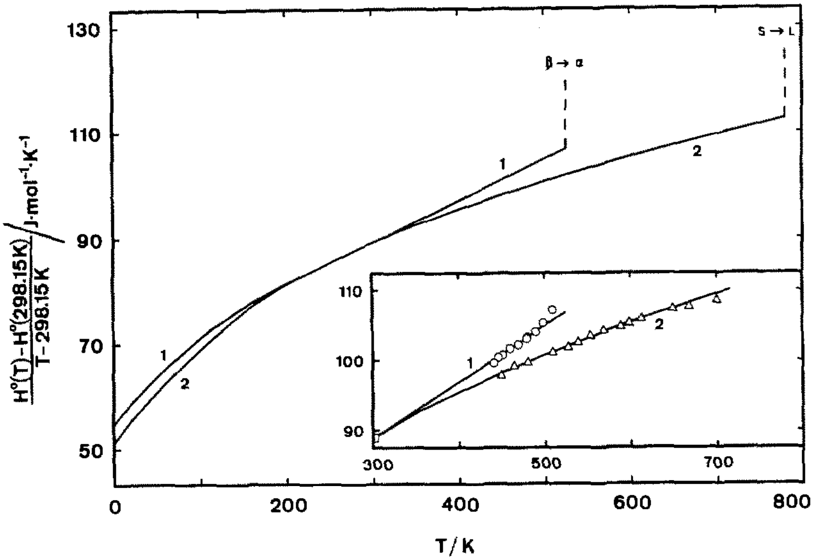

Fig. 2. Reduced enthalpy increment functions of $Sr(OH)_2$ and β-$Ba(OH)_2$: 1, $Ba(OH)_2$; 2, $Sr(OH)_2$.

TABLE 4

High-temperature thermochemical functions of $Sr(OH)_2$ and β-$Ba(OH)_2$

T (K)	$C_p^{\ominus}$ (J mol^{-1} K^{-1})	$S^{\ominus}$ (J mol^{-1} K^{-1})	FEF [a] (J mol^{-1} K^{-1})	$[H^{\ominus}(T) - H^{\ominus}$ (298.15 K)] (J mol^{-1})	$\Delta_f H^{\ominus}(T)$ (J mol^{-1})	$\Delta_f G^{\ominus}(T)$ (J mol^{-1})
$Sr(OH)_2$						
298.15	89.220	94.990	94.990	0	−963900	−875554
300	89.484	95.543	94.992	165	−963892	−875005
400	101.213	122.988	98.655	9734	−962929	−845494
500	110.433	146.591	105.935	20328	−961144	−816327
600	118.665	167.462	114.482	31788	−958703	−787585
700	126.431	186.342	123.420	44046	−955672	−759296
794.7 [b]	133.554	202.828	131.912	56357	−952290	−732974
β-$Ba(OH)_2$						
298.15	89.080	107.280	107.280	0	−940200	−853491
300	89.366	107.832	107.282	165	−940195	−852953
400	104.826	135.658	110.972	9875	−939602	−823941
500	120.286	160.710	118.450	21130	−938077	−795179
526.0 [c]	124.305	166.909	120.692	24310	−937524	−787937

[a] FEF $= -[G^{\ominus}(T) - H^{\ominus}(298.15\text{ K})]/T$.

[b] Melting point.

[c] Transition point to α-$Ba(OH)_2$ [3].

tures than in the present study. Differences for $Ba(OH)_2$ may arise from the use of different starting materials. As already mentioned, the crystalline form of the $Ba(OH)_2$ sample of Powers and Blalock [1] was not reported; probably it was the alpha-modification, since no alpha-to-beta phase transition was observed.

The smoothed thermochemical and thermophysical functions at selected temperatures are listed in Tables 3 and 4. The formation properties above 298.15 K were calculated from the enthalpies of formation as reported by Konings et al. [2], which have been rounded to

$$\Delta_f H^{\ominus}[\mathrm{Sr(OH)_2(s)},\ 298.15\ \mathrm{K}] = -(963.9 \pm 1.0)\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta_f H^{\ominus}[\beta\text{-}\mathrm{Ba(OH)_2(s)},\ 298.15\ \mathrm{K}] = -(940.2 \pm 1.8)\ \mathrm{kJ\ mol^{-1}}$$

Auxiliary data for the reference states of strontium, barium, oxygen and hydrogen were taken from Glushko et al. [12].

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