[CONTRIBUTION FROM THE CHEMISTRY DIVISION, RESEARCH DEPARTMENT, U. S. NAVAL ORDNANCE TEST STATION]

High Temperature Heat Content and Entropy of Lithium Oxide and Lithium Hydroxide

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The high temperature heat contents of lithium oxide and lithium hydroxide were measured in a "drop" calorimeter. Both materials were enclosed in sealed gold capsules. Measurements on lithium oxide were carried to 1050°K., and lithium hydroxide to 900°K. The heat of fusion of lithium hydroxide was determined to be 5010 cal./mole at 744.3°K.

Very few high temperature thermodynamic data have been reported for inorganic hydroxides, and for oxides of the alkali metals. This paper presents such data for lithium oxide and lithium hydroxide.

Method.—The high-temperature heat contents were measured by the "drop" method, in which the sample, contained in a capsule of known heat content, was heated in a furnace to a measured temperature, and then dropped into a copper calorimeter whose heat capacity had been previously measured. The rise in temperature of the calorimeter thus measured the difference in heat content of the sample at the furnace temperature and at the final calorimeter temperature.

The apparatus was similar in design to one originally described by Southard,[1] and later more completely described by Kelley, Naylor and Shomate.[2] Several significant changes, designed to improve the accuracy or ease of operation of the apparatus, were made. For example, in order to increase the length of the furnace isothermal zone, the length of the furnace was increased to 24 inches. Also, the furnace was not wound uniformly, but a graduated winding, heavier at the ends, was employed. The particular geometrical winding configuration finally used was the best from several of such windings tested. The length of the zone isothermal to 1° was 7.8 cm. at 800°, and 4.0 cm. at 1200°. The capsules containing the samples were slightly longer than those employed by Southard, being 2.5 cm., while the diameters were the same, 2.0 cm. Since a number of compounds were being considered which strongly attacked platinum at elevated temperatures, capsules of the same dimensions were also fabricated from gold.

The calorimeter resistance thermometer was a transposed bridge arrangement of two copper and two manganin resistances, previously described by Maier.[3] The thermometer winding covered about half the cylindrical surface of the copper block and was protected by a copper sleeve. The e.m.f. developed by the thermometer was 11,140 μv. at 25.00°, with a temperature coefficient of about 2662 μv./deg. The energizing current was 5 milliamperes.

The water jacket consisted of a spirally wound copper tube around the furnace plus special jackets for enclosing the ends. Both the furnace water-cooled gate and the calorimeter gate were split, spring-actuated, circular gates.

All weighings were reduced to vacuum. The results are expressed in defined calories (1 cal. = 4.1840 abs. joules).

Materials. Lithium Oxide.—This compound was prepared from pure (99.9%) Li_2O_2, whose preparation has previously been described.[4] Lithium peroxide was loaded into a gold capsule used in the heat content measurements, and heated in a stream of dry helium, the temperature gradually being raised to 550° during a 24-hour period. Heat content measurements on this material disclosed that 5.8 mg. of water had been absorbed during the preparation of the sample and the sealing of it in the gold capsule, resulting in a 0.8% lithium hydroxide impurity, for which correction was made.

Lithium Hydroxide.—Carefully cleaned lithium ribbon, obtained from the Metalloy Corporation, Minneapolis, Minnesota, was dissolved in distilled water. The concentrated solution was evaporated by placing it in a vacuum desiccator and pumping for several days. The resultant moist crystals of $LiOH \cdot H_2O$ were heated in platinum boats in a dry, CO_2-free helium stream, the temperature gradually being raised over a 24-hour period to 350°. All operations were carried out in a helium-filled dry-box, or under conditions where absorption of carbon dioxide would be minimized. Analysis of the product showed only a trace of carbonate, and no corrections were made in the results for any impurities.

Results.—In order to check the operation of the apparatus, measurements were made on a sample of synthetic sapphire (Al_2O_3) supplied by the Bureau of Standards. Table I lists the heat content results, the maximum deviation from a smooth curve through the experimental points being 0.11%. The results are slightly lower than those of Ginnings and Furukawa,[5] the difference ranging from less than 0.1% below 800°K. to 0.5% at 1200°K. (the highest temperature to which Ginnings and Furukawa report their results). The mean deviation in the range 700–1200°K. is 0.26%.

TABLE I

MOLAL HEAT CONTENT ABOVE 298.16°K. OF Al_2O_3 (MOL. WT. = 101.96)

T, °K.	$H_T - H_{298.16}$, cal.	T, °K.	$H_T - H_{298.16}$, cal.
707.0	10,122	1140.8	22,775
802.4	12,847	1282.0	27,026
919.0	16,189	1361.3	29,424
1098.8	21,510		

The experimentally determined heat contents above 298.16°K. of lithium oxide and lithium hydroxide are given in Tables II and III. Three samples of lithium hydroxide were used, the measurements on each being carried to a temperature where the capsule developed a leak. The one sample of lithium oxide was carried only to a temperature considered safe in respect to the melting of the small amount of gold alloy solder used in fabricating the gold capsules.

TABLE II

MOLAL HEAT CONTENT ABOVE 298.16°K. OF Li_2O (MOL. WT. = 29.88)

T, °K.	$H_T - H_{298.16}$, cal.	T, °K.	$H_T - H_{298.16}$, cal.
424.7	1836	684.1	6,291
437.3	2025	690.6	6,403
449.5	2227	752.0	7,556
480.5	2726	754.6	7,576
484.1	2781	823.8	8,925
515.0	3303	883.9	10,103
530.7	3557	954.4	11,529
558.9	4048	1019.8	12,871
592.1	4620	1045.1	13,376
625.2	5208		

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(1) J. C. Southard, THIS JOURNAL, **63**, 3142 (1941).

(2) K. K. Kelley, B. F. Naylor and C. H. Shomate, Bur. Mines Tech. Paper 686, p. 12 (1946).

(3) C. G. Maier, *J. Phys. Chem.*, **34**, 2860 (1930).

(4) A. J. Cohen, THIS JOURNAL, **74**, 3762 (1952).

(5) D. C. Ginnings and G. T. Furukawa, *ibid.*, **75**, 522 (1953).

TABLE III

MOLAL HEAT CONTENT ABOVE 298.16°K. OF LiOH (MOL. WT. = 23.948); (p) = premelting.

T, °K.	$H_T - H_{298.16}$, cal.	T, °K.	$H_T - H_{298.16}$, cal.
418.3	1577	671.3	5,556
447.3	1991	690.8	5,855
456.5	2128	724.6(p)	6,652
468.2	2297	725.1(p)	6,632
516.8	3032	731.5(p)	6,900
532.0	3272	748.5	11,914
595.6	4281	751.2	11,930
599.0	4345	767.5	12,264
633.2	4883	814.3	13,222
657.5	5330	878.6	14,612
662.1	5383		

Lithium hydroxide exhibited a sharp fusion at 744.3°K., with a heat of fusion of 5,010 cal./mole. The fusion temperature was determined by a separate experiment in which the capsule containing lithium hydroxide was drawn up into the furnace whose temperature was only slightly greater than the fusion temperature. Approximately six hours were required to melt the sample completely. Under these conditions it was felt that the thermocouple, placed adjacent to the junction of the neck and the top surface of the capsule, recorded a temperature close to that of the material within the capsule.

The following heat content, specific heat and entropy equations were derived by the method of Shomate[6] to fit the experimental data

Lithium Oxide

$$H_T - H_{298.16} = 14.939T + 0.00304T^2 + 338{,}000T^{-1} - 5858$$
$$C_p = 14.939 + 0.00608T - 338{,}000T^{-2}$$
$$S_T - S_{298.16} = 34.398 \log T + 0.00608T + 169{,}000T^{-2} - 88.830$$

Lithium Hydroxide (crystals)

$$H_T - H_{298.16} = 11.988T + 0.00412T^2 + 226{,}700T^{-1} - 4701$$
$$C_p = 11.988 + 0.00824T - 226{,}700T^{-2}$$
$$S_T - S_{298.16} = 27.603 \log T + 0.00824T + 113{,}350T^{-2} - 72.035$$

Lithium Hydroxide (liquid)

$$H_T - H_{298.16} = 20.74T - 3638 \text{ (744–900°K.)}$$
$$C_p = 20.74$$
$$S_T - S_{298.16} = 47.76 \log T - 116.859$$

Shomate's method[7] also was used to obtain the smoothed values of the heat content and entropy of lithium oxide and lithium hydroxide compiled at 50° intervals in Table IV. The entropy was calculated directly from the smoothed heat content values by the following relationship

$$S_{T_2} - S_{T_1} = \frac{H_{T_2} - H_{298.16}}{T_2} - \frac{H_{T_1} - H_{298.16}}{T_1} + \int_{T_1}^{T_2} \frac{H_T - H_{298.16}}{T^2}\, dT$$

The integral in this equation is easily evaluated by means of Simpson's rule. In addition to the endpoint values of $(H_{T_2} - H_{298.16})/T_2^2$ and $(H_{T_1} - H_{298.16})/T_1^2$, usually only one other point was necessary, *i.e.*, the value at $^1/_2(T_1 + T_2)$, which could be readily evaluated from the Shomate-function[7] curve.

TABLE IV

HEAT CONTENTS (CAL./MOLE) AND ENTROPIES (CAL./DEG. MOLE) ABOVE 298.16°K.

T, °K.	$H_T - H_{298.16}$	$S_T - S_{296.16}$	$H_T - H_{298.16}$	$S_T - S_{298.16}$
	Li_2O		LiOH	
400	1,447	4.159	1,320	3.794
450	2,229	6.000	2,032	5.471
500	3,047	7.723	2,778	7.042
550	3,893	9.335	3,554	8.521
600	4,765	10.852	4,356	9.916
650	5,661	12.286	5,183	11.240
700	6,577	13.644	6,031	12.496
744.3			6,802(c)	13.564
744.3			11,812(1)	20.296
750	7,513	14.935	11,923	20.444
800	8,469	16.169	12,927	21.740
850	9,439	17.345	13,983	23.020
900	10,428	18.476	15,090	24.285
950	11,434	19.563		
1000	12,457	20.613		
1050	13,493	21.624		

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[6] C. H. Shomate, THIS JOURNAL, **66**, 928 (1944).

[7] C. H. Shomate, *J. Phys. Chem.*, **58**, 368 (1954).