[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Low Temperature Heat Capacities of Inorganic Solids. IV. Heat Capacities and Entropies of Lithium Hydroxide and of Lithium Hydroxide Monohydrate from 15 to 300°K. Third Law Check on the Entropies Through the Reaction LiOH + H_2O (Gas) = $LiOH \cdot H_2O$[1]

BY THOMAS W. BAUER, HERRICK L. JOHNSTON AND EUGENE C. KERR

Introduction

No previous measurements of low-temperature heat capacities have been reported in the literature for either LiOH or $LiOH \cdot H_2O$. However, Kelley[2] has recalculated a value for the entropy of LiOH at 25° from cell data obtained by Ueda[3] for the cell

Li (amalgam, 0.035%) $LiOH \cdot H_2O$ (saturated) HgO, Hg

and obtained the value 12.8 cal. per mole per degree. It appeared desirable to check this value calorimetrically and also to obtain the entropy of the monohydrate.

Apparatus and Materials

Relatively pure lithium hydroxide, obtained from the Metalloy Corporation of Minneapolis, was purified by recrystallization of the monohydrate from triple-distilled water, and the monohydrate was then decomposed at 150° to LiOH in a stream of carbon-dioxide free air. Spectrographic analyses showed that the purified material contained less than 0.001% Si, Mg, Fe, Al, Cu, Na, Ni and Ca, and therefore no correction was applied for these impurities. Titration with hydrochloric acid gave a purity of 99.9 ± 0.2%.

Pure lithium hydroxide monohydrate for use in the calorimeter was prepared from the recrystallized monohydrate by desiccating over anhydrous lithium hydroxide to remove excess moisture; this method was necessary since vacuum drying or air drying causes appreciable dissociation.[3] Titration of the desiccated material with standard hydrochloric acid yielded 0.9993 ± 0.0027 for the molal ratio H_2O/LiOH. Spectrographic analysis showed that the desiccated material contained 0.01% Si and less than 0.001% of Mg, Fe, Al, Cu, Ni and Ca.

Experimental Data and Results

The calorimetric data were obtained with calorimeter No. 3, whose construction and operation have been described in a previous paper[4] from this Laboratory. Measurements were made with the calorimeter filled with 31.069 g. (1.2973 moles) of LiOH and, later, with 54.541 g. (1.2997 moles) of $LiOH \cdot H_2O$.

The experimental values of the molal heat capacities, in defined thermochemical calories, are given in Tables I and II.

TABLE I

MOLAL HEAT CAPACITY OF LITHIUM HYDROXIDE. LiOH

Mol. wt. 23.94; 1.2973 moles

Temp., °K.	C_p, cal./deg./mole
15.91	0.090
18.66	.131
20.89	.181
22.97	.244
25.82	.315
28.86	.396
30.71	.457
33.39	.554
36.55	.667
40.06	.798
44.04	.938
44.75	1.000
48.95	1.142
54.20	1.335
58.94	1.550
61.10	1.654
66.23	1.856
71.92	2.098
77.62	2.360
84.08	2.677
90.52	3.000
96.76	3.322
103.34	3.682
109.49	4.014
116.96	4.446
124.56	4.883
132.86	5.328
141.97	5.829
149.04	6.216
162.75	6.904
177.01	7.592
191.45	8.257
206.75	8.872
230.43	9.857
239.44	10.137
248.88	10.398
257.38	10.733
275.93	11.316
283.83	11.526
292.32	11.725
302.85	11.956

TABLE II

MOLAL HEAT CAPACITY OF LITHIUM HYDROXIDE MONOHYDRATE. $LiOH \cdot H_2O$

Mol. wt. 41.96; 1.2977 moles

Temp., °K.	C_p, cal./deg./mole
15.81	0.064
18.49	.121
20.76	.198
23.34	.281
26.00	.385
29.95	.544
32.93	.760
36.45	1.005
40.73	1.288
44.64	1.647
49.81	2.088
55.29	2.573
60.16	3.024
64.53	3.388
70.39	3.911
77.65	4.604
84.42	5.210
91.14	5.784
97.85	6.367
104.40	6.907
111.83	7.494
118.39	8.041
127.23	8.767
135.96	9.408
144.53	10.057
153.76	10.708
163.99	11.422
175.44	12.217
186.58	12.984
198.00	13.687
209.88	14.360
220.19	14.923
229.77	15.472
239.38	15.973
248.80	16.533
258.04	16.999
267.76	17.511
277.29	17.970
284.81	18.411
286.53	18.459
295.31	18.890
301.63	19.140

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[1] This was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

[2] K. K. Kelley, U. S. Bureau of Mines Bull. No. 434 (1941).

[3] Y. Ueda, *J. Chem. Soc. Japan*, **52**, 740 (1931); *Sci. Reports, Tohoku Imp. Univ.*, [1] **22**, 448 (1933).

[4] H. L. Johnston and E. C. Kerr, THIS JOURNAL, **72**, 4733 (1950).

Smoothed values of the thermodynamic functions, obtained from the heat capacity data by graphical means, are entered in Tables III and IV. The heat capacities are believed accurate to within 0.2% above about 45° K., but may be in error by as much as 0.5% at 20° K. The molal entropies at 298.16° K. are 10.23 ± 0.05 cal. per degree for LiOH and 17.07 ± 0.05 cal. per degree for $LiOH \cdot H_2O$. Of these amounts 0.03 E. U. was contributed to each substance by Debye extrapolations below the respective temperatures of 15 and 14° K. where θ equals 285 for LiOH and 277 for $LiOH \cdot H_2O$.

TABLE III

THERMODYNAMIC FUNCTIONS OF LITHIUM HYDROXIDE BASED ON THE SMOOTH CURVE OF HEAT CAPACITY

Temp., °K.	C_p, cal./deg./mole	$H° - H°_0$, cal./mole	$(H° - H°_0)/T$ cal./deg./mole	$S°$, cal./deg./mole	$-((F° - H°_0)/T)$, cal./deg./mole
16	0.085	0.340	0.021	0.028	0.007
25	.290	1.945	.078	.105	.027
50	1.173	19.632	.392	.560	.167
75	2.251	62.189	.829	1.235	.405
100	3.491	133.49	1.335	2.047	.712
125	4.889	238.10	1.905	2.975	1.070
150	6.253	277.61	2.517	3.989	1.471
175	7.506	549.94	3.413	5.049	1.906
200	8.617	751.73	3.759	6.125	2.366
225	9.603	979.72	4.354	7.198	2.844
250	10.494	1231.2	4.925	8.257	3.332
275	11.277	1503.6	5.468	9.295	3.827
298.16	11.849	1771.7	5.942	10.231	4.228
300	11.888	1793.5	5.979	10.304	4.325

TABLE IV

THERMODYNAMIC FUNCTIONS OF LITHIUM HYDROXIDE MONOHYDRATE BASED ON THE SMOOTH CURVE OF HEAT CAPACITY

Temp., °K.	C_p, cal./deg./mole	$H° - H°_0$, cal./mole	$(H° - H°_0)/T$, cal./deg./mole	$S°$, cal./deg./mole	$-((F° - H°_0)/T)$, cal./deg./mole
16	0.090	0.359	0.022	0.030	0.007
25	0.343	2.139	.086	.114	.028
50	2.109	30.352	.607	.825	.218
75	4.353	110.97	1.480	2.102	.622
100	6.539	247.47	2.475	3.658	1.183
125	8.590	436.89	3.495	5.340	1.845
150	10.486	675.67	4.505	7.103	2.599
175	12.233	959.89	5.485	8.825	3.340
200	13.792	1285.4	6.427	10.562	4.135
225	15.214	1648.2	7.325	12.270	4.945
250	16.561	2045.5	8.182	13.943	5.761
275	17.858	2475.9	9.003	15.583	6.580
298.16	19.001	2902.9	9.736	17.073	7.337
300	19.100	2938.0	9.293	17.190	7.397

Thermodynamic Calculations

Third Law Check on the Entropies Through the Dissociation Pressure of $LiOH \cdot H_2O$.—Ueda[3] measured dissociation pressures of $LiOH \cdot H_2O$ between 20 and 40° by a tensimeter method and also determined heats of solution of both LiOH and $LiOH \cdot H_2O$ in sufficient water to form 0.13889 *M* LiOH solutions. He obtained 3.90 mm. for the dissociation pressure at 25° with an apparent precision of ±0.02 mm. The integral heats of solution, to form solutions containing one mole of LiOH in 400 moles of water, were 4887 cal. and 867 cal. for LiOH and $LiOH \cdot H_2O$, respectively. The heat of solution data correspond to the reaction

$$LiOH \cdot H_2O \text{ (cryst.)} = LiOH \text{ (cryst.)} + H_2O \text{ (liq.)} \quad (1)$$
$$\Delta H°_{25} = 4020 \pm 20 \text{ cal.}$$

which agrees with de Forcrand's[5] calorimetric value for the same reaction, when corrected to 25°. These several data, combined with the value selected by Wagman and collaborators[6] as the best value for the molal heat of vaporization of water at 25°, namely, 10,520 ± 3 calories, yield for the reaction

$$LiOH \cdot H_2O\text{(cryst.)} = LiOH\text{(cryst.)} + H_2O\text{(gas)} \quad (2)$$
$$\Delta F°_{25} = 3124 \pm 3 \text{ cal.}$$
$$\Delta H°_{25} = 14.540 \pm 23 \text{ cal.}^7$$
$$\Delta S°_{25} = 38.29 \pm 0.09 \text{ cal. per degree}$$

Using Gordon's[8] accurate spectroscopic value of the entropy of water vapor, namely, $S°_{25}$ equals 45.10 E. U., we obtain 6.81 ± 0.1 E. U. for the difference between the molal entropies of $LiOH \cdot H_2O$ (crystalline) and LiOH (crystalline). This difference agrees accurately with the difference between our own "Third Law" entropies, namely, 6.84 ± 0.1 E. U., and confirms the application of the Third Law to both LiOH and $LiOH \cdot H_2O$.

Summary

Heat capacities of lithium hydroxide and of its monohydrate have been measured from 15 to 300° K. Integration of the heat capacity curves yields molal entropy values, at 298.16° K. of 10.23 ± 0.05 E. U. for lithium hydroxide and 17.07 ± 0.05 E. U. for lithium hydroxide monohydrate.

The change in entropy at 25° for the reaction $LiOH \cdot H_2O\text{(cryst.)} = LiOH\text{(cryst.)} + H_2O\text{(gas)}$ obtained from Ueda's[3] data for dissociation pressures of the hydrate and for heats of solution of the two crystals, combined with the value 10,520 ± 3 calories for the molal heat of vaporization of water, is in excellent agreement with $\Delta S°_{25}$ for the same reaction computed from our own experimental entropies for the crystals and with the spectroscopic value for the entropy of steam.[8] The two values agree to within 0.03 E. U., which is well within the experimental error limits of

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(5) de Forcrand, *Ann. chim. phys.*, [8] **15**, 474 (1908).

(6) D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

(7) A value for $\Delta H°_{25}$ can also be computed from Ueda's measurement of the temperature coefficient of the dissociation pressure. This value is 14,270 cal. per mole but, as recognized by Ueda, is considerably more uncertain than the calorimetric value.

(8) A. R. Gordon, *J. Chem. Phys.*, **2**, 65 (1934).

±0.2 E. U., and confirms the application of the Third Law to the calorimetric entropies of both LiOH and LiOH·H_2O.

COLUMBUS 10, OHIO RECEIVED MAY 19, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, FACULTY OF SCIENCE, TOKYO UNIVERSITY]

Chemical Reaction in the Torch Discharge in Carbon Monoxide and Carbon Dioxide

BY SAN-ICHIRO MIZUSHIMA, YONEZO MORINO, HISAO HIRAO HIRABAYASHI, KOJI KAKIHARA AND YOJIRO MIZUSHIMA

At high frequencies the discharge from a single electrode can take place in the form of a flame and is called a "Torch Discharge."[1] The present paper deals with the spectroscopic observation of such a discharge in carbon monoxide and in carbon dioxide and the consideration of chemical reactions taking place in the discharge vessel. The vessel is shown in Fig. 1, where F is the quartz window and E a single electrode connected to a resonance circuit coupled with an oscillator of 7 m. wave length (output 1.5 kw.). The emission spectra of different parts of the flame were photographed with two spectrographs, one having glass optics and the other quartz optics. The height of the three prisms used in the former amounted to 12–15 cm. and the focal length of the camera lens to 150 cm.

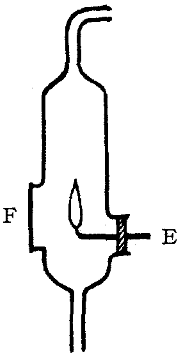

Fig. 1.—The discharge vessel.

At ordinary pressures the discharge takes place in the form of a flame as shown in Fig. 1. However, as pressure is lowered, the contour of the flame becomes more diffuse until the luminous part covers the whole vessel. In the case of discharge in carbon monoxide a considerable amount of carbon was produced, while no such reaction was observed in the case of carbon dioxide.

The observed bands are shown in Table I. Appearance of CN and OH bands is due to a small quantity of air and water vapor contained in the sample of carbon monoxide and their intensities could be made weaker by more careful preparation of the sample.

TABLE I

THE BAND SPECTRA OBSERVED IN THE DISCHARGE VESSEL

	Carbon monoxide, bands	
	Ordinary press.	Low press.
Electrode	CO ångström	CO ångström
	CO 3rd positive	CO 3rd positive
	CO 4th positive	
	C_2 Swan	
	CN red and violet	
	OH	
	Cu atomic lines	
Flame	C_2 Swan	CO ångström
	CN red and violet	
	OH	
	Carbon dioxide, bands	
	Ordinary press.	Low press.
Electrode	CO Ångström	CO ångström
	CO 3rd positive	
	CO 4th positive	
	OH	
	Cu atomic lines	
Flame	Continuous	CO ångström
	OH	

We see that at ordinary pressures there appear in the vicinity of the electrode the bands whose excitation requires high energy, while in the general part of the flame, only those of low excitation energy are observed. At lower pressures the bands of higher excitation energy can also appear (see Fig. 2). These would be due to the fact that at ordinary pressures electrons with high kinetic energy are only found in the vicinity of the electrode, where the electric field is intense, while under low pressure even the electrons in the general part of the flame would have sufficient kinetic energy to excite the higher energy bands owing to the increase in the mean free path and to the change of intensity distribution of the field.

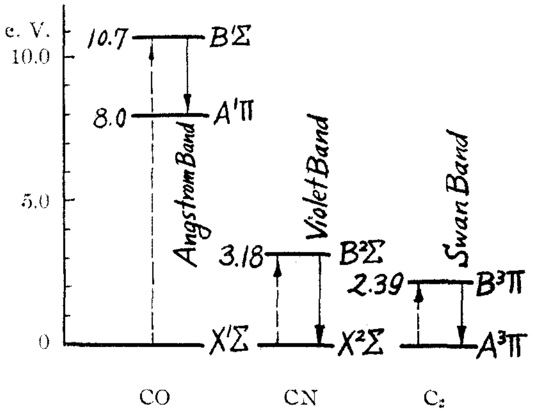

Fig. 2.—Energy diagram for the observed bands.

The remarkable difference in the torch discharge between carbon monoxide and dioxide is that free carbon was produced and C_2 Swan bands were observed in the former substance, but not in the latter. This may be explained by assuming in the first place that the chemical reaction in carbon monoxide proceeds as

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[1] K. N. Mochalov, *C. R. Acad. Sci. U. R. S. S.*, **18**, 329 (1938); **20**, 297 (1938).