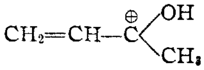
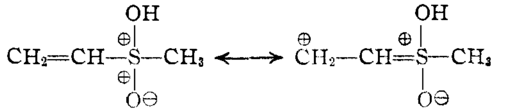
The second wave would again result from the reduction of the double bond. Thus, the nonreduction of the sulfone group could be attributed to the difficulty of forming appreciable concentrations of the conjugate acid of the sulfone (II) due to the inability of structures such as II-b to contribute proportionately to the resonance hybrid. It is, of course, possible that the conjugate acid reduces



I



IIa IIb

with great difficulty and that this accounts for the difference in ease of reduction. The absence of acid catalysis in halogen addition to methyl vinyl sulfone[8] can also be ascribed to the absence of conjugation involving structures such as IIb.

[8] I. R. C. McDonald, R. M. Milburn and P. W. Robertson, *J. Chem. Soc.*, 2836 (1950).

DEPARTMENT OF CHEMISTRY
POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN 2, NEW YORK

Low Temperature Heat Capacities of Inorganic Solids. XIII. Heat Capacity of Lithium Borohydride[1]

BY NATHAN C. HALLETT AND HERRICK L. JOHNSTON

RECEIVED MAY 24, 1952

Introduction

The only measurements of thermodynamic interest thus far reported on lithium borohydride are the heats of formation by Davis, Mason and Stegeman.[2] As part of the Cryogenic Laboratory program of measuring the thermodynamic properties of the boron hydrides and of the metallo borohydrides the heat capacity of solid lithium borohydride has been measured from 15 to 303°K.

Apparatus and Material

The heat capacity measurements were made in calorimeter No. 1, one of a group of seven calorimeters for the measurements of the heat capacity of solid materials. This calorimeter has been described in an earlier paper.[3]

The sample of lithium borohydride was obtained through the courtesy of the General Electric Research Laboratory at a reported purity of approximately 95%. The sample was purified and analyzed by the method of Davis, Mason and Stegeman,[2] except that all handling of the sample, including purifying, filling, sealing and emptying the calorimeter was done under an anhydrous nitrogen atmosphere in a dry-box. The resulting purity was found to be 99.7%. The calorimeter contained 9.9290 g. (0.4556 mole) of lithium borohydride.

Experimental Results

The experimental heat capacity data, summarized in Table I, follow a normal S-shaped curve.

TABLE I

MOLAR HEAT CAPACITY OF LITHIUM BOROHYDRIDE ($LiBH_4$)

Mol. wt. 21.79; 0.4556 mole

Mean *T*, °K.	C_p, cal./mole/deg.	Mean *T*, °K.	C_p, cal./mole/deg.
15.72	0.1781	225.36	15.65
19.37	.2484	231.97	15.96
21.76	.3369	238.75	16.30
23.64	.3981	244.35	16.59
25.39	.4723	249.53	16.74
27.40	.5546	250.48	16.83
30.71	.7642	254.66	17.02
34.28	.9532	255.97	17.12
38.04	1.226	259.50	17.28
42.41	1.585	260.63	17.353
46.88	2.027	262.14	17.45
51.67	2.374	264.87	17.63
56.55	2.854	266.59	17.70
61.06	3.310	267.60	17.73
62.08	3.384	269.11	17.94
67.12	3.892	270.41	17.96
72.79	4.390	272.45	18.07
78.65	5.072	272.82	18.21
84.98	5.755	272.96	18.24
86.23	5.894	274.47	18.24
92.82	6.516	277.65	18.44
99.93	7.168	278.32	18.50
107.76	7.895	278.71	18.53
115.93	8.618	280.25	18.75
124.42	9.324	283.77	18.87
132.35	9.975	284.15	18.90
140.02	10.49	284.76	18.95
147.33	11.08	288.74	19.10
155.32	11.631	288.75	19.12
164.09	12.21	289.20	19.18
172.37	12.67	293.43	19.48
180.82	13.13	294.27	19.50
188.84	13.63	296.95	19.62
196.83	14.06	298.50	19.74
204.66	14.50	299.20	19.74
212.05	14.91	299.47	19.80
218.86	15.28	302.88	20.02

Table II gives the heat capacity and derived thermodynamic functions for lithium borohydride at selected integral values of the temperature.

TABLE II

THERMODYNAMIC FUNCTIONS FOR LITHIUM BOROHYDRIDE ($LiBH_4$)

Temp., °K.	C_p, cal./mole/deg.	S^0, cal./mole/deg.	$(H^0_0 - H^0)/T$, cal./mole/deg.	$-(F^0 - H^0_0)/T$, cal./mole/deg.
15	0.152	0.0874	0.0515	0.0359
25	0.451	0.225	.144	.0811
50	2.235	1.013	.692	.322
75	4.709	2.373	1.606	.766
100	7.188	4.077	2.700	1.376
125	9.371	5.919	3.820	2.099
150	11.246	7.799	4.906	2.892
175	12.832	9.655	5.929	3.726
200	14.250	11.462	6.881	4.581
225	15.617	13.221	7.777	5.444
250	16.802	14.930	8.622	6.308
275	18.254	16.595	9.428	7.168
298.16	19.733	18.131	10.226	7.904
300	19.847	18.252	10.230	8.022

---

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

[2] W. Davis, L. Mason and G. Stegeman, Thermal Properties of Some Hydrides, Univ. of Pittsburgh, ONR Contract Number N6ORI-43, Task Order No. 1, Technical Report, Dec 1, 1948.

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

The entropy at 298.16°K. is 18.13 ± 0.03 e.u. of which 0.03 e.u. was contributed by the extrapolation below 15°K.

Acknowledgment.—We wish to acknowledge the assistance of Mr. W. D. Wood who assisted in the calculations.

CRYOGENIC LABORATORY AND DEPT. OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO

Catalytic Activity of Lanthanum and Strontium Manganite

BY G. PARRAVANO

RECEIVED JUNE 20, 1952

Recent work of Jonker and van Santen[1] and Volger[2] has shown that compounds of the general formula $(La_{1-\delta}\,Sr_\delta)\,(Mn^{+3}_{1-\delta}\,Mn^{+4}_\delta)O_3$ can be prepared from a mixture of the corresponding oxides or carbonates. Strontium up to $\delta = 0.7$ can be introduced in the $LaMnO_3$ phase without changing its perowskite structure. These compounds have a magnetic Curie temperature which is dependent on the amount of strontium added, and the temperature coefficient of the electrical resistivity shows anomalous behavior; it is positive for the ferromagnetic state and negative above the Curie point. It was therefore considered interesting to investigate the possibility of a relationship between the anomalous behavior of the temperature coefficient of the resistivity of these compounds and the activity of the solid surface to catalyze a chemical reaction. The compound $La_{0.65}Sr_{0.35}MnO_3$ was chosen for this investigation because it possesses the highest Curie point (~373°K.) of the series, and because it was found that at that temperature the oxidation of carbon monoxide on the above compound proceeded at rates which could be experimentally detected.

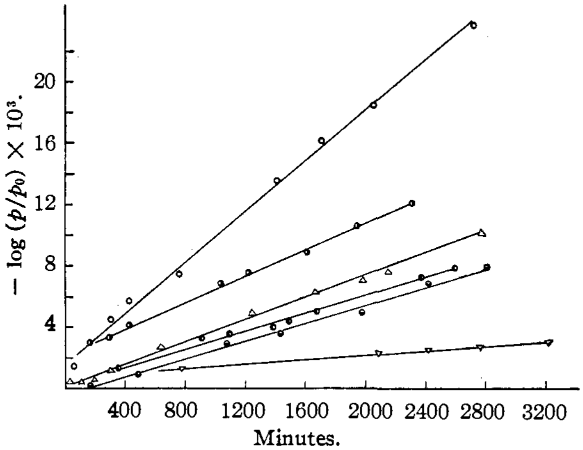


Fig. 1.—Oxidation of carbon monoxide on $La_{0.65}Sr_{0.35}MnO_3$ (2.139 g.): $CO/O_2 = 2/1$; $P_0 = 280$ mm.: ▽, 50°; ◐, 81.5°; ◒, 88°; △, 96°; ◑, 100°; ○, 105°.

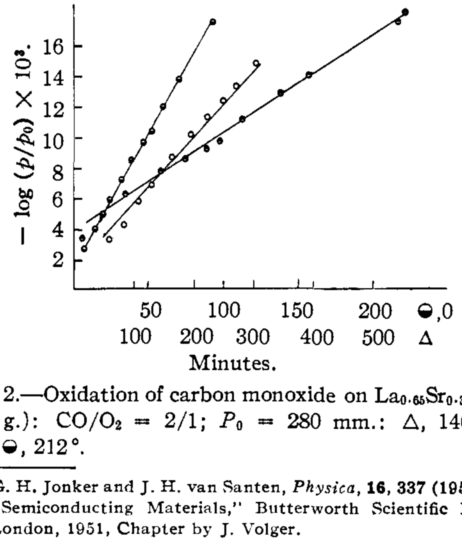


Fig. 2.—Oxidation of carbon monoxide on $La_{0.65}Sr_{0.35}MnO_3$ (2.139 g.): $CO/O_2 = 2/1$; $P_0 = 280$ mm.: △, 140°; ○, 183°; ◒, 212°.

$La_{0.65}Sr_{0.35}MnO_3$ was prepared by ball milling a mixture of stoichiometric amounts of C.P. manganese carbonate, strontium oxide and lanthanum oxalate for 1 hour. The mixture was then fired in a platinum crucible in air at 850° for 5 hours, milled again for 1 hour and finally heated at 900° for an additional 3 hours.

Purification of gases and apparatus used for the catalytic experiments have already been described.[3] It was found that the experimental data on the oxidation reaction could be fitted quite well to a first-order equation (Figs. 1, 2). Values for the velocity constant, k(min.$^{-1}$, g^{-1}), at different temperatures are presented in the following table and in Fig. 3, where they are plotted according to the Arrhenius equation, from which an over-all activation energy of 10.6 kcal./mole could be derived.

TABLE I

OXIDATION OF CARBON MONOXIDE ON $La_{0.65}Sr_{0.35}MnO_3$

$CO/O_2 = 2/1$, $p_0 = 280$ mm.

t, °C.	$k \times 10^6$, min.$^{-1}$, g^{-1}	t, °C.	$k \times 10^6$, min.$^{-1}$, g^{-1}
50	0.34	105	3.83
81.5	1.45	140	11.8
88	1.37	183	49.0
95	1.69	212	82.0
100	2.17		

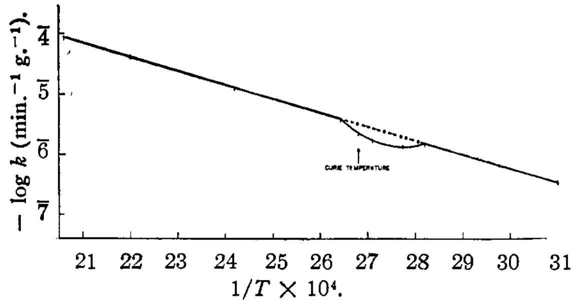


Fig. 3.—Oxidation of carbon monoxide on $La_{0.65}Sr_{0.35}MnO_3$. Arrhenius plot.

From the experimental data it is clear that the oxidation reaction shows the same activation energy below and above the Curie point of the catalyst. This is in disagreement with the magneto-catalytic effect studied by Hedvall.[4] According to this effect the temperature coefficient of the activity of a catalyst is markedly different below and above its

---

[1] G. H. Jonker and J. H. van Santen, *Physica*, **16**, 337 (1950).

[2] "Semiconducting Materials," Butterworth Scientific Publications, London, 1951, Chapter by J. Volger.

[3] G. Parravano, THIS JOURNAL, **74**, 1448 (1952).

[4] For a review on this effect see: Schwab, "Handbuch der Katalyse," Vol. 6, Springer, Verlag Wien, 1943, chapter by J. A. Hedvall.