TABLE II

THERMODYNAMIC FUNCTIONS FOR DECABORANE, $B_{10}H_{14}$

T, °K.	C_p cal./mole/°K.	S^0 cal./°K.	$H^0 - H^0_0$ cal./mole	$(H^0 - H^0_0)/T$	$(F^0 - H^0_0)T$
14	0.810	0.270[a]	2.835[a]	0.203	0.067
25	3.350	1.352	24.714	0.989	0.363
50	8.135	5.381	176.86	3.537	2.207
75	11.135	9.300	421.08	5.614	3.686
100	13.325	12.799	726.47	7.265	5.534
125	16.30	16.074	1094.8	8.758	7.316
150	20.03	19.365	1547.5	10.317	9.048
175	24.62	22.790	2104.3	12.025	10.765
200	29.82	26.414	2784.3	13.922	12.423
225	35.30	30.241	3597.9	15.991	14.250
250	41.02	34.254	4551.3	18.205	16.049
275	47.13	38.448	5652.7	20.555	17.893
298.16	52.42	42.475	6806.9	22.830	19.645
300	52.78	42.798	6903.7	23.012	19.786

[a] Debye extrapolation: $C_p = 2D\,(145/T)$.

Since the above equation fits the experimental data to within 0.5% throughout most of the range, only that portion under the hump is shown (dotted line) in the figure. The area between the experimental curve and the Debye–Einstein curve correspond to an entropy of 0.210 e.u.

Standard thermodynamic functions have been calculated from the experimental data and are given at integral temperature values in Table II. The entropy at 298.16 is 42.48 ± 0.1 e.u.

Summary

The heat capacities of decaborane have been measured in the range 14 to 305°K. and the derived thermodynamic functions have been calculated and tabulated at integral values of the temperature over this range. The entropy at 298.16°K. is 42.48 ± 0.1 e.u.

COLUMBUS 10, OHIO RECEIVED JULY 5, 1950

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

Low Temperature Heat Capacities of Inorganic Solids. VII. Heat Capacity and Thermodynamic Functions of Li_2O. Thermodynamics of the Li_2O–H_2O System[1]

BY HERRICK L. JOHNSTON AND THOMAS W. BAUER

Introduction

No previous measurements of the heat capacity of lithium oxide have been reported in the literature.

Apparatus and Material

The calorimetric data were obtained with our calorimeter No. 3, whose construction and operation have been described in a previous paper[2] from this Laboratory.

Relatively pure lithium hydroxide, obtained from the Metalloy Corporation of Minneapolis, was purified by recrystallization from triply distilled water. The $LiOH \cdot H_2O$ formed was decomposed to Li_2O in a nickel boat, in a stream of purified hydrogen gas, first at about 150° to LiOH and then at about 800°. Difficulty was experienced due to the extreme wetting properties of the fused LiOH. The fused material showed a tendency to creep out of the boat and attacked the monel furnace tube even in a reducing atmosphere of hydrogen. Titration with normal HCl gave a purity of 99.4% when all the base present was calculated as Li_2O. A spectroscopic analysis of the purified sample showed that some calcium was present as an impurity and that faint traces of less than 0.001% aluminum, magnesium, silicon, sodium and nickel were also present.

The lithium oxide was further purified by heat treatment in a nickel crucible at temperatures ranging from 1000 to 1300°. The crucible was supported inside a water-cooled Pyrex condenser through which hydrogen circulated, and was heated by induction heating.

Heating the sample for 3 to 5 hours increased its purity to 99.90 ± 0.10%, on the basis of an hydrochloric acid titration of Li_2O; further heating did not change the purity. Nickel contamination did not rise above 0.001%. We assumed that the 0.50% increase in purity must have represented removal of the last traces of water, and possibly CO_2, and that any remaining impurity must be CaO. After correcting for CaO, on the basis of the 99.90% Li_2O titration, the composition of the final purified sample was 99.74% Li_2O, the remaining 0.26% being CaO.

The measured values of the heat capacity were corrected for the small amount of CaO present by use of the data of Nernst and Schwers[3] and of Parks and Kelley.[4] This correction was less than 0.07%.

Results

Measurements were made with the calorimeter filled with 43.088 g. (1.4420 moles) of Li_2O and with 0.112 g. (0.0020 mole) of CaO.

The experimental values of the molal heat capacity are given in Table I in defined thermochemical calories.[5] The heat capacity of the empty calorimeter amounts to almost 90% of the total heat capacity below 30°K.

Smoothed values of the thermodynamic functions obtained by graphical means from the heat capacity are entered in Table II. The smoothed values are accurate to within 0.2% above 45°K., but might be in error as much as 2% at 20°K. The values at the lowest temperatures are less accurate than other data[6] obtained at this Laboratory, due to the very low heat capacity of Li_2O in this region. The molal entropy of Li_2O at 298.16°K. is 9.06 ± 0.03 e.u., with only 0.003 e.u. contributed by a Debye extrapolation ($\theta = 559$) below 16°K.

Thermodynamic Calculations

Third Law Check on the Entropies Through the Dissociation Pressure of LiOH.—Johnston[7]

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

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

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TABLE I

HEAT CAPACITY OF 1.4420 MOLES OF LITHIUM OXIDE, Li_2O. MOLECULAR WEIGHT 29.880

$T_{av.}$, °K.	ΔT, °K.	C_p, cal.(deg. mole)$^{-1}$	$T_{av.}$, °K.	ΔT, °K.	C_p, cal.(deg. mole)$^{-1}$
17.06	2.699	0.0198	127.38	9.896	4.326
20.68	1.685	.0288	137.49	10.381	5.006
23.03	1.673	.0316	146.97	9.109	5.649
25.01	1.560	.0358	155.73	8.410	6.222
27.23	2.303	.0448	164.96	10.015	6.805
29.87	2.739	.0531	174.90	9.022	7.415
32.81	3.115	.0670	184.52	9.574	8.029
36.59	4.476	.102	194.17	9.526	8.596
41.04	4.393	.154	204.23	10.499	9.110
46.44	6.363	.240	208.11	8.833	9.303
52.12	4.976	.365	214.43	9.677	9.584
58.05	6.849	.522	227.44	11.294	10.254
64.51	6.064	.715	238.53	10.467	10.729
68.01	6.723	.838	248.71	9.792	11.149
74.26	5.903	1.086	258.38	9.472	11.542
81.75	6.119	1.448	268.63	10.454	11.954
88.90	8.188	1.830	279.01	9.846	12.313
97.03	9.236	2.316	288.74	9.325	12.655
107.30	11.177	2.962	298.89	10.389	12.938
117.64	9.520	3.669			

TABLE II

MOLAL HEAT CAPACITY AND DERIVED THERMODYNAMIC FUNCTIONS OF LITHIUM OXIDE, Li_2O

T, °K.	C^0_p, cal./deg.	$H^0 - H^0_0$, cal.	$(H^0 - H^0_0)/T$, cal./deg.	S^0, e. u.	$-(F^0 - H^0_0)/T$, cal./deg.
16	0.009	0.044	0.003	0.003	0.000
25	.024	0.206	.008	.008	.000
50	.316	3.566	.071	.090	.019
75	1.119	20.303	.271	.372	.101
100	2.497	64.289	.643	.868	.225
125	4.157	147.25	1.173	1.660	.482
150	5.844	272.25	1.815	2.644	.829
175	7.439	438.51	2.506	3.589	1.083
200	8.892	643.24	3.216	4.680	1.464
225	10.120	881.45	3.918	5.801	1.883
250	11.216	1148.5	4.594	6.925	2.331
275	12.173	1441.1	5.241	8.040	2.799
298.16	12.927	1732.2	5.810	9.056	3.246
300	12.980	1756.0	5.853	9.135	3.282

measured dissociation pressures of LiOH between 500 and 924°. A least squares fit of his data yields

$$\log p = 1.214415 + 1.216868(1000/T) + 3.204257(1000/T)^2 \quad (1)$$

where p is in mm. and T is the absolute temperature. Differentiation of this equation yields, for the heat of dissociation in calories,

$$\Delta H^0 = 29{,}323(1000/T) - 5568 \quad (2)$$

Equations 1 and 2 do not apply below 500°. However, we have derived a general expression for ΔH, for the reaction

$$2LiOH(\text{crystalline}) = Li_2O(\text{crystalline}) + H_2O(\text{gas}) \quad (3)$$

by the method of Shomate[8] and obtained an equation applicable between 1000° and room temperagure. This equation is

$$\Delta H^0 = 35{,}186 - 0.501T - 0.010835T^2 - 373.56(1000/T) \quad (4)$$

To obtain equation 4, we have employed de Forcrand's[9] calorimetric values for the heats of solution of both LiOH and Li_2O, which we have corrected to 25° and to the currently accepted atomic weight of lithium. The molal heat of vaporization of water at 25° was taken as 10,520 ± 3 cal.[10] and the ΔC_p of the dissociation reaction at 25° as -2.76 cal./deg. The latter is based on our data[6] for the heat capacities of LiOH and of Li_2O and on Gordon's[11] spectroscopic value for steam. In applying Shomate's method, equation 2 was used to get preliminary values of ΔH^0 at temperatures above 500°.

From equation 4, we have derived the useful relationships

$$\Delta C^0_p = -0.501 - 0.02167T + 0.37356(1000/T)^2 \quad (5)$$

$$\Delta F^0/T = 35{,}186/T + 1.1536 \log T + 0.010835\,T + 0.18678(1000/T)^2 + I \quad (6)$$

and evaluated the integration constant I from Johnston's[7] dissociation pressure points above 700°. The calculation yielded an average value of I of -45.758.

By combining equations 4 and 6 with the relation of entropy to heat content and free energy, we obtain

$$2LiOH(\text{crystalline}) = Li_2O(\text{crystalline}) + H_2O(\text{gas})$$

$$\Delta H^0_{25} = 32{,}821 \pm 113 \text{ cal.}$$

$$\Delta F^0_{25} = 22{,}731$$

$$\Delta S^0_{25} = 33.85 \text{ e.u.}$$

The value of ΔS^0 at 25° was also computed, by use of the Third Law of Thermodynamics, from our calorimetric entropies of Li_2O (9.06 e.u.) and of LiOH[6] (10.23 e.u.) and from Gordon's[11] spectroscopic value for water vapor (45.10 e.u.). This third law calculation yielded

$$S\Delta^0_{25} = 33.70 \pm 0.12 \text{ e.u.}$$

a value which is in close agreement with that computed from the dissociation equilibrium. The excellent agreement is much closer than could be anticipated in view of the 500° extrapolation of dissociation heat, and establishes the validity of the ordinary use of the Third Law in application to both Li_2O and LiOH. This result confirms our previous conclusion regarding LiOH[6] and is consistent with the X-ray diffraction data for Li_2O,[12] which indicate an ionic lattice of the fluorite type, with no opportunity for random entropy of lattice disorder.

Heat and Free Energy of Formation of LiOH.—The most reliable value of the heat of solution of lithium metal is that of Moers,[13] who determined the heat of solution, in the presence of a large excess of water, at 9.8, 12.2 and 18.2°. Disregarding the 9.8° value, which was less accurate than the others because a very small amount of lithium was employed, we have used Rossini's values[14,15] for the integral heats of dilu-

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[12] J. M. Bijvoet and A. Karsen, *Rec. trav. chim.*, **43**, 680 (1924).

[13] K. Moers, *Z. anorg. allgem. Chem.*, **113**, 179 (1920).

[14] F. D. Rossini, *J. Research Natl. Bur. of Standards*, **6**, 791 (1931).

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tion of LiOH at 18° and for the partial molal heat capacities of LiOH and of H_2O to convert Moers' 12.2 and 18.2 results to the reaction process

$$\text{Li(crystalline)} + 401\text{H}_2\text{O (liquid)} = \text{LiOH}\cdot 400\ \text{H}_2\text{O (solution)} + {}^1/_2\text{H}_2\text{(gas)} \qquad (7)$$

for which we obtained

$$\Delta H_{12.2} = -52{,}517\ \text{cal.};\ \Delta C_p = -51.50\ \text{cal./deg.}$$
$$\Delta H_{18.2} = -52{,}826\ \text{cal.};\ \Delta H_{15.0} = -52{,}661\ \text{cal.}$$

In using Moers' data, a correction of −11 cal. has been applied to each of his measured ΔH's to convert his data to the defined thermochemical calorie.[5]

The value of ΔC_p for reaction 7 can also be calculated from the difference in the heats of solutions of LiOH at 15 and at 25°, as measured by de Forcrand[9,16] and by Ueda,[17] respectively, used in conjunction with the heat capacities of Li,[18] of LiOH,[6] of H_2O (liquid),[19] and of H_2.[20] This treatment yields a ΔC_p of -50 ± 4 cal./deg., a value which is in good agreement with the value −51.50 cal./deg. determined directly from Moers' data. It fixes the accuracy of ΔH_{15} obtained from Moers' heats of solution at about 50 cal.

Combining ΔH_{15} for equation 7 with de Forcrand's[9] corrected value for the reaction

$$\text{LiOH(crystalline)} + 400\text{H}_2\text{O(liquid)} = \text{LiOH}\cdot 400\text{H}_2\text{O(solution)} \qquad (8)$$

namely

$$\Delta H^0_{15} = -4474 \pm 30\ \text{cal.}$$

and with ΔH^0_{25} and ΔC^0_p for the reaction

$$\text{H}_2\text{(gas)} + {}^1/_2\text{O}_2\text{(gas)} = \text{H}_2\text{O(liquid)} \qquad (9)$$
$$\Delta H^0_{25} = -68{,}317 \pm 10\ \text{cal.}^{10}$$
$$\Delta C^0_p = 7.60\ \text{cal./deg.}^{19,20,21}$$

yields

$$\text{Li(crystalline)} + {}^1/_2\text{H}_2\text{(gas)} + {}^1/_2\text{O}_2\text{(gas)} = \text{LiOH(crystalline)} \qquad (10)$$
$$\Delta H^0_{15} = -116{,}580 \pm 90\ \text{cal.}$$
$$\Delta C^0_p = -0.86\ \text{cal./deg.}$$
$$\Delta H^0_{25} = -116{,}589 \pm 90\ \text{cal.}$$

By use of the entropies of Li,[18] H_2,[22] O_2[21] and LiOH,[6] the following further relationships appropriate to equation 10 are obtained

$$\Delta S^0_{25} = -36.60 \pm 0.13\ \text{e. u.}$$
$$\Delta F^0_{25} = -105{,}676 \pm 130\ \text{cal./mole}$$

Heat and Free Energy of Formation of LiOH·H_2O.—From calorimetric measurements of heats of solution of both LiOH and LiOH·H_2O in sufficient water to form a 0.13889 *M* LiOH solution, Ueda[17] found that

$$\text{LiOH(crystalline)} + \text{H}_2\text{O(liquid)} = \text{LiOH}\cdot\text{H}_2\text{O(crystalline)} \qquad (11)$$
$$\Delta H^0_{25} = -4020 \pm 20\ \text{cal.}$$

Combining this value with ΔH^0_{25} for the formation of H_2O (liquid),[10] with ΔH^0_{25} for equation 10, and with the entropy of LiOH·H_2O[6] gives

$$\text{Li(crystalline)} + 3/2\text{H}_2\text{(gas)} + \text{O}_2\text{(gas)} = \text{LiOH}\cdot\text{H}_2\text{O(crystalline)} \qquad (12)$$
$$\Delta H^0_{25} = -188{,}926 \pm 120\ \text{cal.}$$
$$\Delta S^0_{25} = -85.49 \pm 0.15\ \text{e.u.}$$
$$\Delta F^0_{25} = -163{,}437 \pm 160\ \text{cal.}$$

Heat and Free Energy of Formation of Li_2O. From de Forcrand's corrected values[9,16] for the heats of solution of both Li_2O and LiOH in water, we obtained

$$2\text{LiOH(crystalline)} = \text{Li}_2\text{O(crystalline)} + \text{H}_2\text{O (liquid)} \qquad (13)$$
$$\Delta H^0_{25} = 22{,}301 \pm 110\ \text{cal.}$$

Combining this value with those of ΔH^0_{25} for equations 9 and 10 and with entropies of Li,[18] Li_2O and O_2[21] yields

$$2\text{Li(crystalline)} + {}^1/_2\text{O}_2\text{(gas)} = \text{Li}_2\text{O(crystalline)} \qquad (14)$$
$$\Delta H^0_{25} = -142{,}567 \pm 160\ \text{cal.}$$
$$\Delta S^0_{25} = -28.85 \pm 0.13\ \text{e. u.}$$
$$\Delta F^0_{25} = -133{,}965 \pm 210\ \text{cal.}$$

Entropy and Heat and Free Energy of Formation of the Lithium Ion.—The free energy of solution of lithium hydroxide to form lithium and hydroxide ions in their standard states is obtained by combining the processes

(a) LiOH·H_2O(crystalline) = LiOH·H_2O(satd. solution)
$$\Delta F_a = 0\text{(at equilibrium)}$$

(b) LiOH(crystalline) + H_2O(liquid) = LiOH·H_2O (crystalline)
$$\Delta F_b = -1070 \pm 3\ \text{cal.}^{23}$$

(c) H_2O(satd. solution) = H_2O(liquid)
$$\Delta F_c = -RT \ln a_1\text{(satd.)} = 103\ \text{cal.}^{24}$$

(d) LiOH·H_2O(satd. solution) = Li^+ (standard state solution) + OH^- (standard state solution) + H_2O (satd. solution)
$$\Delta F_d = -RT \ln a_2\text{(satd.)} = -1049 \pm 30\ \text{cal.}^{25}$$

Addition of reactions (a) to (d) yields

$$\text{LiOH(crystalline)} = \text{Li}^+\text{ (standard state)} + \text{OH}^-\text{ (standard state)} \qquad (15)$$
$$\Delta F^0_{25} = -2016 \pm 40\ \text{cal.}$$
$$\Delta H^0_{25} = -5076 \pm 30\ \text{cal.}^{26}$$
$$\Delta S^0_{25} = -10.26 \pm 0.23\ \text{e.u.}$$

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[21] H. L. Johnston and M. K. Walker, *ibid.*, **55**, 172 (1933).

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[23] Computed from Ueda's[17] determination of the dissociation pressure of LiOH·H_2O at 25° (3.90 mm.) in conjunction with the vapor pressure of pure water at 25° (23.76 mm.) by the relationship $\Delta F = -RT \ln p$.

[24] Computed from Ueda's[11] determination of the vapor pressure of water from the saturated solution at 25° (19.97 mm.) in conjunction with the vapor pressure of pure water, since $a_1 = p_1/p_1^0$.

[25] The activity of LiOH in the saturated solution, at 25°, (a_2, satd.) is computed as the square of the product of the molality (5.159[17]) and the activity coefficient γ. The latter value, 0.470 ± 0.010, is obtained by extrapolating the data of Harned and Swindells for compositions up to 4 *M*. *Cf.* H. S. Harned and F. E. Swindells, THIS JOURNAL, **48**, 126 (1926).

[26] Obtained by combining Ueda's[17] calorimetric determination of the heat of solution of LiOH to form a 0.13889 *M* solution with Rossini's[14,15] values of the heat of dilution and the partial molal heat capacities of LiOH and H_2O.

When we combine the value of ΔS^0 obtained from equation 15 with our value[6] for the entropy of LiOH (10.23 ± 0.05 e.u.) and with that of Latimer, Pitzer and Smith[27] for the entropy of the hydroxyl ion (−2.49 ± 0.06 e.u.) the standard state entropy of the lithium ion is

$$S^0_{25}\,(\mathrm{Li}^+) = 2.46 \pm 0.34 \text{ e.u.} \qquad (16)$$

This result compares with that, 4.7 ± 1.0 e.u., obtained by Brown and Latimer[28] from measurements of Li_2CO_3. Most of the discrepancy may have been due to Brown and Latimer being forced to use the heat of dilution of Li_2SO_4, in their computations, rather than that of Li_2CO_3, which was not available.

We can compute the heat and free energy of formation of the lithium ion in its standard state by combining the ΔH values of reactions 10 and 15 with those of the heat of formation of water[10] and the heat of ionization of water,[29] in conjunction with the standard entropies of Li,[18] Li^+ and H_2.[20] The following results are obtained

$$\mathrm{Li(crystalline)} + \mathrm{H^+(aqueous)} = \mathrm{Li^+(aqueous)} + {}^1/_2\mathrm{H_2(gas)} \qquad (17)$$

$$\Delta H^0_{25} = -66{,}706 \pm 100 \text{ cal.}$$

$$\Delta S^0_{25} = 11.37 \pm 0.40 \text{ e.u.}$$

$$\Delta F^0_{25} = -70{,}096 \pm 220 \text{ cal.}$$

In the above computations, the heat and free energy of formation of the hydrogen ion in its standard state are taken as zero, in accordance with the usual convention.

Finally, we can compute the standard oxidation potential of lithium from its standard free energy of formation. This computation yields

$$E^0 = 3.0383 \pm 0.0010 \text{ int. volts}$$

Summary

The heat capacity of Li_2O has been measured over the temperature range 16 to 304°K. Graphical integration of the heat capacity curve yields 9.06 ± 0.03 cal./mole/deg. for the entropy at 25°. When the entropies of LiOH and of steam are also considered, the curve yields a ΔS° of 33.70 ± 0.12 e.u. for the dissociation reaction $2LiOH = Li_2O + H_2O(gas)$. This latter value is in good agreement with the value, 33.85, obtained from the dissociation equilibrium and confirms the application of the third law of thermodynamics to Li_2O.

A table of thermodynamic functions for Li_2O has been prepared for smoothed values of temperature.

Heats and free energies of formation have been computed for LiOH, $LiOH{\cdot}H_2O$ and Li_2O, by combining their entropies with heat of solution and vapor pressure data.

The standard state entropy of the lithium ion at 25°, has been calculated as 2.46 ± 0.34 e.u. and the standard electrode potential of lithium as 3.0383 ± 0.0010 int. volts.

COLUMBUS 10, OHIO RECEIVED JULY 5, 1950

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[CONTRIBUTION NO. 1409 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

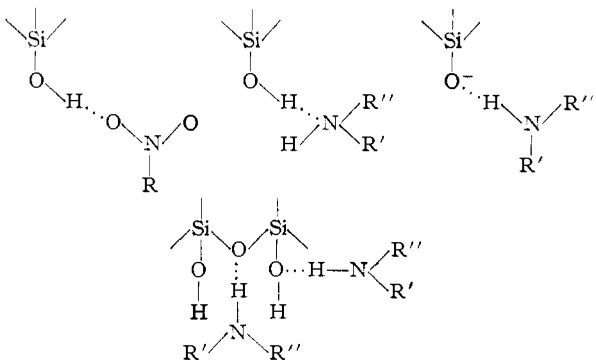
Hydrogen Bonding and Relative Adsorption Affinities on Silicic Acid of Certain Derivatives of Diphenylamine and N-Ethylaniline[1]

BY W. A. SCHROEDER

Introduction

The chromatographic investigations[2,3,4] of the products which are formed from diphenylamine and centralite (1,3-diethyl-1,3-diphenylurea) during their action as stabilizers of double base smokeless powder have resulted in the assembling of a detailed body of information on the chromatographic behavior on silicic acid of their nitro and nitroso derivatives and of those of N-ethylaniline. Consideration of the relative adsorption affinities of these compounds showed, however, that there was little evident regularity of behavior and that, for example, increase in the number of substituent or potential "anchoring" groups[5] was not necessarily accompanied by an increase in adsorption affinity as is so often the case, for instance, in the chromatography of the carotenoids.[6]

If one considers the structure of silicic acid, hydrogen bonding between it and amino and nitro compounds might be expected to take place in many ways such as



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[1] Presented before the symposium on "The Specificity of Adsorbents," Division of Colloid Chemistry, Houston Meeting of American Chemical Society, March 28, 1950.

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