[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heat Capacity of Lithium Carbonate from 16 to 300°K. The Entropy and Heat of Solution of Lithium Carbonate at 298°K. The Entropy of Lithium Ion

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The heat capacity of lithium carbonate has been determined from 16 to 300°K. in order to evaluate more accurately the entropy of lithium ion in aqueous solution.

Material.—A c. p. grade of lithium carbonate was shaken with distilled water saturated with carbon dioxide. The solution was filtered through sintered glass and the filtrate boiled to precipitate lithium carbonate. This procedure was repeated with the product thus obtained. The final product was dried at 110° and for a short time at 200°. The carbonate was definitely crystalline, and analysis by titration with weight burets, using sulfuric acid standardized against sodium carbonate, showed 99.82, 99.82 and 99.79% lithium carbonate.

Heat Capacity Measurements.—The measurements were made with a calorimeter and cryostat similar to that previously described.[1] One calorie was assumed equal to 4.1833 int. joules. The molecular weight of lithium carbonate was taken as 73.88. Measurements were made on a sample of 61.814 g. (weight *in vacuo*). The heat capacity measurements are summarized in Table I, and are plotted as a function of temperature in Fig. 1.

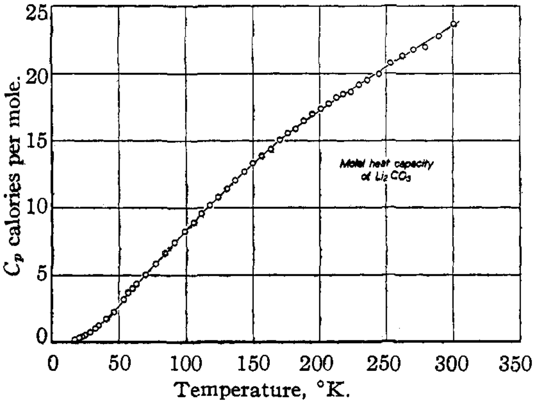

Fig. 1.—Molal heat capacity of lithium carbonate.

Entropy of Lithium Carbonate.—The entropy at 298.1°K. was obtained by graphical integration of the integral $S = \int C_p d \ln T$ between 16.68 and 298.1°K. combined with an extrapolation from 16.68 to 0°K. using the Debye specific heat equation. The calculation is summarized in Table II.

TABLE I

MOLAL HEAT CAPACITY OF LITHIUM CARBONATE

T, °K.	C_p cal./mole/deg.	T, °K.	C_p cal./mole/deg.
16.68	0.16	136.89	12.02
20.10	.25	143.65	12.66
22.30	.33	149.97	13.31
24.77	.44	156.44	13.83
28.59	.67	163.38	14.44
32.35	.94	170.12	15.04
35.04	1.18	176.09	15.52
40.49	1.74	181.98	15.98
46.56	2.32	187.97	16.48
49.33	2.73	194.44	17.00
53.58	3.24	200.85	17.40
56.96	3.70	206.78	17.74
60.16	4.03	212.47	18.21
63.18	4.35	217.84	18.48
69.90	5.03	223.23	18.64
76.94	5.83	229.21	19.16
83.96	6.61	235.84	19.50
91.32	7.41	244.66	19.94
98.90	8.21	253.68	20.73
105.47	8.92	262.21	21.31
111.32	9.53	270.72	21.76
117.68	10.16	279.51	21.96
123.83	10.74	289.58	22.76
130.59	11.40	300.20	23.69

TABLE II

ENTROPY OF LITHIUM CARBONATE

0–16.68°K.	Debye extrapolation	0.05
16.68–298.1°K.	Graphical from data	21.55 ± 0.05
	Entropy at 298.1°K.	21.60 E. U.

Heat of Solution of Lithium Carbonate.—The heat of solution of lithium carbonate was determined with the calorimeter previously described.[2]

The integral heat of solution of one mole of lithium carbonate in 1900 moles of water at 298.1°K. was found to be −3371 and −3395 cal. The average value −3383 cal. was corrected for the heat of hydrolysis of carbonate ion and extrapolated to infinite dilution on the assumption that the heat of dilution was the same as for lithium sulfate. In this way the theoretical heat of solution of lithium carbonate in an infinite amount of water with no hydrolysis was found to be −4200

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[1] Latimer and Greensfelder, THIS JOURNAL, **50**, 2202 (1928).

[2] Brown, Smith and Latimer, *ibid.*, **58**, 1758 (1936).

cal./mole. The probable error resulting from these corrections is difficult to estimate, but may be as high as 200 cal.

Entropy of Solution of Lithium Carbonate.—Seyler and Lloyd[3] measured the solubility of lithium carbonate at 298.1°K., in water solutions containing various amounts of carbon dioxide. They measured the total carbonate and bicarbonate by titration. By plotting the reciprocal of the mean molality of lithium ion and carbonate ion against the square root of the ionic strength, a fairly good straight line was obtained, from which the activity coefficient of lithium carbonate at saturation was found to be 0.59. The calculation is not of high accuracy but fortunately this does not affect greatly the free energy of solution. For example, a change of 10% in the activity coefficient would change the free energy of solution only about 180 cal., which corresponds to 0.3 E. U. in the entropy of lithium ion. The solubility of lithium carbonate in pure water is 0.169 *M* according to the same authors, so that $\Delta F^\circ = 3280$ cal./mole.

The entropy change when the solid salt dissolves to form a hypothetical one molal solution is given by the expression

$$\Delta S^\circ = (\Delta H - \Delta F^\circ)/T = (-4200 - 3280)/298.1 = -25.1 \text{ E. U.}$$

Entropy of Lithium Ion.—The entropy of carbonate ion[4] is -12.7 E. U., so that the entropy of lithium ion is given by the expression

$$S^\circ_{\mathrm{Li^+}} = {}^1/_2(\Delta S^\circ + S^\circ_{\mathrm{Li_2CO_3}} - S^\circ_{\mathrm{CO_3^{--}}}) = {}^1/_2(-25.1 + 21.6 + 12.7) = 4.6 \text{ E. U.}$$

Because of the absence of calorimetric data on lithium compounds, the entropy of lithium ion previously has been calculated from the entropy change of the lithium electrode reaction, even though the uncertainties were quite large.[5] The value thus obtained (-1.8 E. U.) differs by 6.4 E. U., or about 1900 calories, from the value calculated above. Since we believe the possible uncertainty introduced into the entropy of solution of lithium carbonate by the troublesome corrections for hydrolysis are not greater than one E. U. in $S^\circ_{\mathrm{Li^+}}$, we must conclude that the discrepancy is due to errors in the entropy change of the electrode reaction.

Summary

The heat capacity of lithium carbonate has been measured from 16 to 300°K. The entropy of lithium carbonate at 298.1°K. obtained from these data is 21.60 E. U. The heat of solution in water at 298.1°K. has been determined. The entropy of lithium ion calculated from these and other data has been found to be 4.6 E. U.

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[3] Seyler and Lloyd, *J. Chem. Soc.*, **111**, 994 (1917).

[4] Latimer, Schutz and Hicks, *J. Chem. Phys.*, **2**, 82 (1934).

[5] Latimer, *Chem. Rev.*, **18**, 351 (1936).

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[CONTRIBUTION FROM VALENCIA HIGH SCHOOL]

The Boyle Temperature and a General Equation of State

BY GEORGE WOOLSEY

If a general equation of state is possible the Boyle temperature, the temperature at which $\left(\frac{\partial PV/T}{\partial P}\right)_T = 0$, at zero pressure must be either the same temperature or a function of RT_c/p_cv_c (n in my notation) for all pure non-associating and non-dissociating substances. Empirically the older data seem to indicate that the Boyle temperature, T_B (reduced), is a function of n. For example, taking T_B as the temperature for which the second virial coefficient equals zero, Holborn and Otto[1] found

Substance	Ne	He	H_2	O_2	A	N_2
T_B	3.00	3.65	3.21	2.72	2.73	2.56
n	3.254	3.261	3.282	3.423	3.424	3.428

Recomputing the values for oxygen and argon, using more recent values for critical temperatures, gives 2.74 and 2.72, respectively. These figures seem to indicate quite definitely that T_B is a function of n.

However, using data compiled by Beattie and Bridgeman,[2] approximate values of T_B are obtained which indicate that the other possibility, that T_B is a constant, is the correct one.

Substance	Ne	H_2	O_2	A	N_2	CH_4
T_B	<2.77	Between 3.7 and 2.5	>2.4	2.5	Between 2.56 and 2.33	2.48
n	3.245	3.282	3.423	3.424	3.428	3.448

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[1] Holborn and Otto, *Z. Physik*, **33**, 9 (1925); **38**, 365 (1926).

[2] Beattie and Bridgeman, "A New Equation of State for Fluids," *Proc. Am. Acad. Arts Sci.*, **63**, No. 5 (1928).