The data obtained included only two values which deviated as much as this from what seemed to be the best curve passed through these data and those of Parks, Huffman and Barmore in the neighboring temperature region. Check measurements of the heat capacity of water over this same temperature region gave values which agreed with those accepted by Dorsey[7] within these limits.

In an earlier series of measurements on a different sample of sucrose values were obtained which scattered widely. In making these earlier measurements the sucrose had been exposed to temperatures near 90° for more than two weeks by the time the final measurements were made. By this time the value of the heat capacity of sucrose at 20° had increased to a value about 15% higher than the values obtained earlier or those reported by Parks, Huffman and Barmore. When the sample container was opened it was found that the sucrose had caramelized to a solid brown mass.

It is of interest that the sucrose caramelized at temperatures well below the decomposition value of 186° given in the handbook.[8]

When the measurements reported here were made only three determinations were carried out above 45° and these in the shortest possible time. After completion of the measurements a check determination of the heat capacity at room temperature gave a value in agreement with the other values within the estimated uncertainty of the measurements. When the sample container was opened it was found that the sucrose was still powdery and white and that there was no visible evidence of decomposition.

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(7) N. E. Dorsey, "Properties of Ordinary Water Substance," Reinhold Publishing Corp., New York, N. Y., p. 613 and 616.

(8) "Handbook of Chemistry and Physics," 29th edition, Chemical Rubber Publishing Co., p. 1019; see, however, Circular C440 (*loc. cit.*) p. 398.

M. W. KELLOGG CO.
JERSEY CITY 3, N. J.

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The Heat of Solution of Sucrose in Water at 25°[1]

BY HOWARD HIGBIE[2] AND GEBHARD STEGEMAN[3]

Measurements of the quantities needed for a thermal description of the system sucrose–water are being made in this Laboratory.[4] This paper presents measurements of the heat of solution of sucrose in water at 25° and an evaluation of the heat of solution at infinite dilution at this temperature.

Experimental

The sucrose was Standard Sample 17 prepared by the National Bureau of Standards.[5] This was received in a highly purified condition and was used without further treatment. Distilled water was used as the solvent.

The apparatus and operating techniques have been described.[6] The apparatus was a twin Joule solution calorimeter holding about a liter of water in each side and having sensitivity limits of about ± 0.02 cal on the basis of the sensitivity limits of the 25 junction thermel–galvanometer combination.

The values obtained for the heat of solution of sucrose in water at 25° are tabulated below. The heat of solution at infinite dilution was evaluated from the relation

$$\overline{H}_2^0 - H_2^s = Q/n_2 - 55.51L_1/m - L_2$$

where $\overline{H}_2^0 - H_2^s$ is the heat of solution at infinite dilution, Q/n_2 is the heat absorbed per mole of sucrose dissolved, m is the molality of the final solution and $\overline{L}_1$ and $\overline{L}_2$ are the relative partial molal heat contents of the water and sucrose in solution. The values of $\overline{L}_1$ and $\overline{L}_2$ at the indicated molalities were obtained from the empirical expressions given by Gucker, Pickard and Planck.[7]

Sucrose dissolved, mole	Concn. of final soln., molality	Heat absorbed, cal./mole^{-1}	$H_2 - H_2$, cal./mole
0.008214	0.008237	1453	1452
.008555	.008579	1462	1461
.007921	.007943	1448	1447
.008103	.008126	1468	1467
.007671	.007692	1447	1446
		Mean value	1455 ± 5

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(1) This work was supported by a grant to the University of Pittsburgh from The Sugar Research Foundation Inc. and is a portion of the dissertation presented by Howard Higbie to the Graduate School of the University of Pittsburgh in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) The M. W. Kellogg Co., Jersey City 3, N. J.

(3) Deceased September 5, 1949.

(4) Anderson, Higbie, and Stegeman, THIS JOURNAL, **72**, 3798 (1950).

(5) Circular C 440, U. S. Department of Commerce, National Bureau of Standards, page 392.

(6) Fineman and Wallace, THIS JOURNAL, **70**, 4165 (1948).

(7) Gucker, Pickard and Planck, *ibid.*, **61**, 459 (1939).

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The Preparation and Structure of Lanthanum Cobaltic Oxide

BY FRED ASKHAM,[1] I. FANKUCHEN AND ROLAND WARD[2]

The existence of the perowskite-like compound of approximate composition $BaFeO_{2.63}$[3] suggests that it might be possible to prepare a similar compound of cobalt. Since no such compound was found, the substitution of lanthanum for barium was tried. Naray-Szabo[4] has prepared $LaMnO_3$ and $LaFeO_3$ by heating oxides of manganese and iron with lanthanum oxide and has shown that the products were of the perowskite type. Hedvall,[5] however, reported that no compounds were formed when lanthanum and cobaltous oxides were heated together at 1100 to 1300°.

Experimental

Intimate mixtures of the hexahydrates of lanthanum and cobaltous nitrates were heated in a tube furnace in a stream

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(1) Abstracted from a thesis submitted to the Graduate School of the Polytechnic Institute of Brooklyn by Fred Askham in partial fulfillment of the Master of Science degree 1950.

(2) Department of Chemistry, University of Connecticut, Storrs, Connecticut.

(3) M. Erchak, Jr., I. Fankuchen and R. Ward, THIS JOURNAL, **68**, 2085 (1946).

(4) I. Naray-Szabo, *Naturwissenschaften*, **31**, 466 (1943).

(5) J. A. Hedvall, *Z. anorg. allgem. Chem.*, **93**, 313 (1915).

of air. The temperature was raised gradually (to prevent spattering of the melt) to a fixed temperature at which it was held constant for twelve to twenty-four hours. The products were periodically removed from the furnace, ground in a mortar and again heated. Products obtained over the range 150 to 1020° were examined by X-ray analysis and the diffraction patterns of several unidentified phases were obtained. From the mixture in which the ratio La/Co = 1, an essentially homogeneous product was obtained between 800 and 970°. It appeared to be contaminated by a small amount of lanthanum oxide. Chemical analysis showed that the valence of cobalt in this product is 3. Subsequent study of the diffraction patterns of the 700° products from mixtures in which the ratio La/Co ranged from 0.5 to 3, showed the presence of the same phase strongly contaminated with other phases. From these results it is reasonable to conclude that the composition of the persistent phase is $LaCoO_3$. Further justification for this conclusion was obtained by the determination of the structure.

The diffraction pattern (given in Table I) resembled that of a perowskite structure except that many lines appeared as doublets and a few as triplets. This was taken as an indication that the structure was slightly distorted from the cubic. A tentative value (3.82 Å.) was obtained for the pseudo-cubic unit cell dimension by assuming that the innermost reflection was due to the 100 plane. Upon this basis, the other lines of the pattern were indexed. It was found that reflections corresponding to the 100, 200, 300 and 400 planes were all single lines while those due to such planes as 110, 111, 210, 221, etc., were doublets or triplets. This points to a rhombohedral unit cell the interplanar spacings for which can be calculated from the equation

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + hl + kl)(\cos^2\alpha - \cos\alpha)}{a^2(1 - 3\cos^2\alpha + 2\cos^3\alpha)}$$

where α is the interaxial angle.

TABLE I

X-RAY DIFFRACTION PATTERN OF $LaCoO_3$

I = Intensity; VS = Very strong; S = Strong; M = Medium; W = Weak; VW = Very weak; VVW = Extremely weak

d	I	$h^2 + k^2 + l^2$
3.82	M	1
2.721	VS	2
2.681	VS	
2.213	M	3
2.178	W	
1.911	S	4
1.719	VVW	5
1.701	VVW	
1.568	S	6
1.545	M	
1.360	M	8
1.343	M	
1.275	VVW	9
1.213	M	10
1.204	M	
1.154	VW	11
1.143	VW	
1.108	W	12
1.091	VW	
1.068	VVW	13
1.055	VVW	
1.027	M	14
1.021	W	
1.013	W	
0.956	W	16
0.906	VW	18
0.896	VW	
0.860	VW	20
0.851	VW	
0.820	VW	22
0.806	VW	
0.786	W	24
0.782	W	

The value for α was found to be 90°42′. The obtuse angle was chosen on the basis of the relative intensities of pairs of reflections when compared with the number of equivalent reflections that could be obtained from a set of planes. Table II gives the computed and observed values of d^* ($d^* = \lambda/d = 2\sin\theta$). Since excellent agreement was obtained, the unit cell dimension was recalculated using the equation given above. It was found to be 3.82 ± 0.01 Å.

TABLE II

A COMPARISON OF VALUES OF $d^*_{obs.}$ AND $d^*_{calcd.}$

Plane	d^* obs.	d^* calcd.
100	0.403	0.403
$\bar{1}10$	.566	.567
110	.574	.574
$\bar{1}11$	.695	.695
111	.707	.707
200	.806	.806
$\bar{2}10$	.896	.897
210	.905	.906
$\bar{2}11, 2\bar{1}1$	.982	.983
211	.997	.997
$\bar{2}20$	1.133	1.133
220	1.147	1.147
300	1.208	1.209
$\bar{3}10$	1.270	1.270
310	1.279	1.279
$\bar{3}11, 3\bar{1}1$	1.335	1.334
311	1.347	1.347
$\bar{2}22$	1.390	1.391
222	1.412	1.413
$\bar{3}20$	1.442	1.445
320	1.460	1.461
$\bar{3}21, 3\bar{2}1$	1.500	1.501
$32\bar{1}$	1.508	1.510
321	1.520	1.522
400	1.611	1.612
$\bar{3}30, \bar{4}11$	1.700	1.701
330, 411	1.719	1.720
$\bar{4}20$	1.795	1.794
420	1.812	1.811
$\bar{3}32, 33\bar{2}$	1.883	1.884
332	1.913	1.912
$\bar{4}22$	1.959	1.962
422	1.970	1.970

The density of $LaCoO_3$ was found to be 7.2 g./c.cm. which corresponds to one formula weight per unit cell.

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7-Isopropylpodocarpinol

BY MANUEL M. BAIZER, MARILYN KARNOWSKY AND W. G. BYWATER

Campbell and Todd[1] have shown that 6-hydroxydehydroabietic acid (I) differs from

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[1] Campbell and Todd, THIS JOURNAL, 64, 928 (1942).