

pinacol. Neither of these workers mentioned the yields obtained.

Takaki³ treated *p*-hydroxybenzaldehyde with ammonium amalgam and from the mixture of products obtained a very small yield of the hydrobenzoin.

The preparation of 4,4'-dihydroxyhydrobenzoin was carried out by electrolytic reduction at controlled cathode potential with resultant high yield of the desired hydrobenzoin. The tetraacetate was also prepared and characterized.

Experimental⁴

4,4-Dihydroxyhydrobenzoin.—The apparatus used in this preparation is the same as that previously described.^{5,6} Twelve grams of *p*-hydroxybenzaldehyde dissolved in 100 ml. of 2 *N* sodium hydroxide was placed in the cathode chamber. A 2*N* sodium hydroxide solution was introduced into the anode chamber. At a cathode potential of -2.0 volts and a temperature of 30° the initial current was 4.1 amperes. After thirty-four minutes of electrolysis a current plateau of 0.5 ampere was reached which indicated the completion of the reaction. The catholyte was filtered and acidified. The precipitate was washed lightly with cold water and cold ethanol, yield 11.5 g. (95.2%), m. p. 214.5°. Recrystallization from methanol gave white prisms, m. p. 215.5°.

4,4-Dihydroxyhydrobenzoin Tetraacetate.—Five grams of the hydrobenzoin was suspended in 75 ml. of acetic anhydride and a few drops of concentrated sulfuric acid added. The mixture was shaken until all the hydrobenzoin was in solution and then poured on ice. The solid was recrystallized from 70% ethanol and dried over phosphorus pentoxide, yield 4.99 g. (78.4%), m. p. 121.5–122.5°.

Anal. Calcd. for C₂₂H₂₂O₈: C, 63.76; H, 5.35. Found: C, 63.57; H, 5.52.

A sample of the tetraacetate was saponified and the resulting product gave no depression in melting point when mixed with a sample of 4,4'-dihydroxyhydrobenzoin.

- (3) Takaki, *J. Pharm. Soc. Japan*, **58**, 156 (1938).
 (4) All melting points reported are corrected.
 (5) Allen, *J. Org. Chem.*, **15**, 435 (1950).
 (6) Allen, *Ind. Eng. Chem., Anal. Ed.*, **22**, 804 (1950).

ENDOCRINOLOGY SECTION
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The Heat Capacity of Sucrose from 25 to 90°¹

BY G. L. ANDERSON, JR., HOWARD HIGBIE² AND GEBHARD STEGEMAN³

In recent years this laboratory has been engaged in a program to secure thermal data on biologically active compounds. Measurements are now being made to evaluate the quantities required for a thermal description of the system sucrose-water from 0 to 90°. Heat capacity values for solid sucrose from -179 to 24° are available,⁴ and

(1) This work was supported by a grant to the University of Pittsburgh of 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) Parks, Huffman and Barmore, *THIS JOURNAL*, **55**, 2733 (1933).

this paper presents the results of measurements covering the temperature range from 24 to 90°.

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.

The heat capacity measurements were made in an adiabatic calorimeter of the type described by Southard and Brickwedde.⁶ Only the important differences between the Southard and Brickwedde apparatus and that used in this investigation are noted here. In the present case a copper resistance thermometer was wound on the outside of the sample container and was calibrated by comparison with a platinum resistance thermometer bearing a certificate of calibration from the National Bureau of Standards. The heater was centrally located in a re-entrant tube in the sample container. The cable carrying the electrical leads to the calorimeter heater, thermometer and to the difference thermocouples between the shield and sample container was cemented on the outside of the radiation shield heater. The heat capacity values obtained in this investigation along with the values reported by Parks, Huffman and Barmore in the neighboring temperature region are tabulated below. The calculated values were obtained from the equation

$$C_p = A + B(t - 25^\circ) + C(t - 25^\circ)^2$$

where $A = 101.7 \text{ cal. mole}^{-1} \text{ degree}^{-1}$

$B = 0.394 \text{ cal. mole}^{-1} \text{ degree}^{-2}$

$C = 5.1 \times 10^{-4} \text{ cal. mole}^{-1} \text{ degree}^{-3}$

Temp., °C.	Heat capacity of solid sucrose (cal. mole ⁻¹ degree ⁻¹)	
	Measured	Calculated
2.6	93.1 ^a	93.2
8.9	95.5 ^a	95.6
16.7	98.2 ^a	98.4
23.2	102.7	101.0
23.8	101.0 ^a	101.2
23.9	101.3	101.3
26.4	102.3	102.2
28.2	102.3	103.0
29.8	103.4	103.6
40.0	107.5	107.7
47.3	110.6	110.8
69.4	120.8	120.2
89.7	129.4	129.3
26.8 ^b	103.4 ^b	102.4

^a Values reported by Parks, Huffman and Barmore.
^b Check determination.

The principal source of uncertainty in these measurements was the measurement of the temperature rise of the sample container. From observations of the rate of temperature drift while adiabatic conditions were being maintained as well as possible it was estimated that the uncertainty in the value of heat capacity of sucrose was ≈2%.

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

(6) Southard and Brickwedde, *THIS JOURNAL*, **55**, 4378 (1933).

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 Dorsey⁷ 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.

(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.

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

BY HOWARD HIGBIE² AND GEBHARD STEGEMAN³

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.

(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).

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

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

where $\bar{H}_2^0 - H_2^s$ 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 L_1 and L_2 are the relative partial molal heat contents of the water and sucrose in solution. The values of L_1 and 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	$H_2 - H_2^s$, 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 \pm 5

(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 WARD²

The existence of the perovskite-like compound of approximate composition $\text{BaFeO}_{2.63}$ 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-Szabo⁴ 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 perovskite 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

(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.

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(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).