individual measurements from a smooth curve drawn through the plotted data was 0.3%. The values of the entropy for each of the compounds have the usual uncertainty arising from the extrapolated portion of the heat capacity curve.

The molal entropy of β-lactose at 298.16°K. was found to be lower by 4.3 e. u. than the value previously determined in this Laboratory.[11] This discrepancy is caused by errors in the calibration of the calorimeter thermometer, as a result of a poor reference scale for the lower temperatures.

Summary

1. The heat capacity has been measured for three disaccharides from 60 to 298°K.

2. From these and other data, the entropy and free energy of formation at 298.16°K. have been calculated for each sugar.

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[11] Furtsch and Stegeman, THIS JOURNAL, **58**, 881 (1936).

[CONTRIBUTION NO. 432 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Heat Capacities and Entropies of Two Monosaccharides

BY GEORGE W. JACK[1,2] AND GEBHARD STEGEMAN

In this paper are presented heat capacity data from 60° to 298°K., for *l*-sorbose and *α-d*-galactose. From these and other thermal data the entropies and free energies of formation have been computed. The case of *l*-sorbose is of particular interest in that it displays a transition of the type shown by ammonium chloride.

Preparation of Materials.—The *l*-sorbose was obtained from the Chas. Pfizer Chemical Co. This sugar was used without special preparation other than drying to constant weight. Combustion studies in this Laboratory[3] have shown that the particular sample of *l*-sorbose used required no further treatment.

The *α-d*-galactose used was obtained from the Pfanstiehl Chemical Co. and was purified in a manner similar to that described by Hudson and Yanovsky.[4] This consisted in solution of the sugar in pure water, filtration to remove insoluble impurities, and reduction of the water by evaporation *in vacuo* to the amount required for the proper water–alcohol mixture to ensure the presence of the desired solid isomer. The water–alcohol mixture was formed by adding the proper quantity of anhydrous ethyl alcohol. The precipitated sugar was allowed to stand in the alcohol solution for one week; it was then filtered, and vacuum dried over anhydrous calcium chloride at 45°.

The initial and final rotations of the purified *α-d*-galactose were $[\alpha]^{20}_{D}$ 80.3° and $[\alpha]^{20}_{D}$ 144.0°, respectively. These compare favorably with Hudson's values[4] of 80.5 and 144.0°.

The Heat Capacity Measurements.—The apparatus and method have been described.[5] In the region of transition of *l*-sorbose, numerous measurements of the heat capacities were made in order to determine as accurately as possible the shape of the heat capacity–temperature

TABLE I

MOLAL HEAT CAPACITIES OF *α-d*-GALACTOSE

T, °K.	C_p, cal./°K.	T, °K.	C_p, cal./°K.
63.92	11.32	185.77	32.93
68.52	12.17	194.63	34.71
74.03	13.42	195.08	34.97
79.42	14.54	201.46	35.60
86.81	16.08	204.82	36.52
93.86	17.42	213.78	38.11
103.48	19.20	226.39	39.88
113.18	20.98	234.71	41.21
124.08	22.79	243.69	42.71
133.16	24.44	253.78	44.74
142.40	26.08	263.88	46.55
152.41	27.76	272.54	48.41
161.33	29.18	280.37	49.43
169.45	30.54	288.28	50.26
176.06	31.57	296.86	52.71

TABLE II

MOLAL HEAT CAPACITIES OF *l*-SORBOSE

T, °K.	C_p, cal./°K.	T, °K.	C_p, cal./°K.
64.02	11.48	194.30	44.25
69.51	12.56	196.11	48.91
76.03	13.99	198.30	75.36
82.39	15.29	198.70	98.10
88.36	16.55	198.83	122.49
99.00	18.58	200.03	125.03
105.04	19.74	200.98	56.28
115.51	21.85	202.27	39.48
124.17	23.48	204.86	39.39
132.36	25.27	207.74	39.75
141.29	27.37	213.96	40.30
151.59	29.48	224.44	42.36
160.10	31.26	235.18	43.97
170.95	34.07	245.68	45.53
181.93	37.01	257.47	47.84
182.70	37.38	268.04	49.80
187.59	39.40	276.05	51.13
190.45	41.34	284.02	52.12
192.50	42.61	292.85	53.76
192.92	42.84	295.86	54.64
193.34	43.02		

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[1] From a thesis presented to the Graduate School of the University of Pittsburgh in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] The author is indebted to the Buhl Foundation of Pittsburgh for a grant which facilitated this work.

[3] Clarke and Stegeman, THIS JOURNAL, **61**, 1726 (1939).

[4] Hudson and Yanovsky, *ibid.*, **39**, 1013 (1917).

[5] Anderson and Stegeman, *ibid.*, **63**, 2119 (1941).

curve throughout this range. In addition, measurements of the energy input necessary to carry the sample completely through the transition region were made.

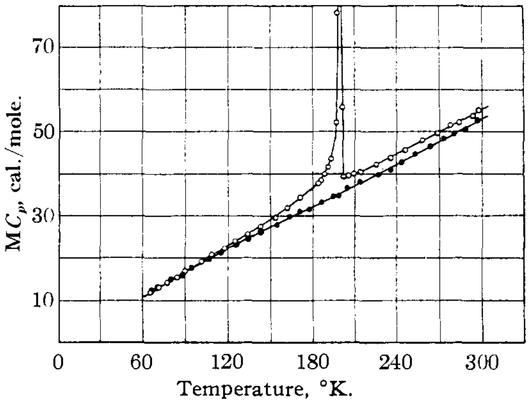

Fig. 1.—○, *l*-Sorbose; ●, *α*-*d*-galactose.

The molal heat capacities are listed in Tables I and II and plotted in Fig. 1. The energies of transition are reported in Table III.

TABLE III

TRANSITION ENERGY OF *l*-SORBOSE

T, °K.	Heat absorbed, cal./mole
195.70–202.94	479.63
195.76–202.19	444.03

Entropy from Thermal Data.—The entropy of *α*-*d*-galactose from 90 to 298°K. was evaluated in the usual manner by determining the area under the C_p *versus* ln T curve. The entropy from 0 to 90°K. was obtained by an application of the extrapolation method of Kelley, Parks and Huffman.[6] In this case the equation $C_p = (1.04614 + 0.0076248T)C_p^0$, was found to fit the experimental curve from 60 to 90°K. The "standard heat capacity" for aliphatic compounds was used. The entropy calculations are summarized in Table IV.

TABLE IV

ENTROPY OF *α*-*d*-GALACTOSE

	E. u./mole
0–90°K. (extrapolation)	11.7
90–298.16°K. (graphical)	37.40
Entropy, 298.16°K.	49.1

The major portion of the entropy of *l*-sorbose from 90 to 298°K. was evaluated in the usual manner. To evaluate the entropy in the region of transition, the method outlined by Giauque and Wiebe[7] for hydrogen bromide was followed. In this case, heat capacities up to 48 cal./°K. mole were plotted against ln T and the area under the curve determined. Since the transition took place over a narrow temperature range, a single temperature, corresponding to a true transition temperature, was chosen by the center of gravity method of Giauque and Wiebe. The part of the entropy not determined from the C_p *versus* ln T plot (the area above 48 cal./°K. mole defined by the curve) was evaluated by determining the energy involved in this region, and dividing this energy by the estimated transition temperature. The energy was evaluated from a C_p *versus* T plot with the aid of measurements which included the entire region of transition. As in the case of *α*-*d*-galactose, the entropy of *l*-sorbose from 0 to 90°K. was evaluated by extrapolation. The equation $C_p = (1.14213 + 0.0066503T)C_p^0$ was found to fit the experimental curve from 60 to 90°K. The "standard heat capacity" used was again that for aliphatic compounds. The computations are summarized in Table V.

TABLE V

ENTROPY OF *l*-SORBOSE

	E. u./mole
0–90°K. (extrapolation)	12.0
90–298.16°K. (graphical)	40.05
199.22°K. (transition), 143.7/199.22	0.721
Entropy, 298.16°K.	52.8

Entropy and Free Energy of Formation.—The entropies of formation of *l*-sorbose and *α*-*d*-galactose were calculated using 1.36, 15.615, and 24.515 as the entropies of carbon, hydrogen and oxygen, respectively.

The uncertainty in the entropy values of the compounds measured appears to be determined principally by the influence of the extrapolated portion of the heat capacity curve.

The values of the heats of formation necessary for the free energy calculations were obtained by Clarke and Stegeman.[3] The essential data are shown in Table VI.

TABLE VI

ENTROPY AND FREE ENERGIES OF FORMATION

Compound	ΔS 298.16°K. E. u./mole	ΔH^0 298.16°K. cal./mole	ΔF^0 298.16°K. cal./mole
l-Sorbose	−289.8	−303,500	−217,100
α-*d*-Galactose	−293.5	−307,100	−219,600

Summary

1. The heat capacities from 60 to 298°K. of *l*-sorbose and *α*-*d*-galactose have been measured.

2. From these and other thermal data the free energies of formation of these compounds have been computed.

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[6] Kelley, Parks and Huffman, *J. Phys. Chem.*, **33**, 1802 (1929).

[7] Giauque and Wiebe, THIS JOURNAL, **50**, 2193 (1928).

3. One of the compounds measured, *l*-sorbose, has been shown to possess a transition of the type displayed by ammonium chloride.

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The Rate and Mechanism of the Hydrolysis of Hydroxylamine Disulfonate Ion

BY SAM NAIDITCH AND DON M. YOST

Neutral or dilute acid solutions of potassium hydroxylamine disulfonate hydrolyze at a measurable rate at room temperature to give potassium hydroxylamine monosulfonate and potassium bisulfate, the hydrolytic reaction being, in ionic form

$$HON(SO_3)_2^= + H_2O = HONHSO_3^- + H^+ + SO_4^= \qquad (1)$$

The hydroxylamine monosulfonate ion is relatively stable and does not hydrolyze in dilute acid solution except at higher temperatures. Wagner[1] made a single measurement on the rate of hydrolysis of the disulfonate and found it to be proportional to the concentrations of $HON(SO_3)_2^=$ and H^+. The present paper describes the results of a detailed study of the rate and mechanism of this hydrolysis.

Preparation of the Materials. Experimental Procedure

Potassium hydroxylamine disulfonate was prepared according to the method described by Rollefson and Oldershaw[2] in which an ice-cold, acetate-buffered solution of potassium nitrite is treated with sulfur dioxide. The moist salt obtained was washed with ice-cold water and used directly, or it was washed repeatedly with absolute alcohol, and, after drying by evaporation, it was placed in a vacuum desiccator over concentrated sulfuric acid or phosphorus pentoxide and kept at about 5°. The anhydrous salt thus prepared, $K_2HON(SO_3)_2$, could be kept for more than a month without decomposition.

In the first 35 runs the freshly prepared, moist salt was washed repeatedly with ice-cold water, and then portions of it were dissolved rapidly in a thermostated volumetric flask nearly filled with a mixture of water and a measured quantity of hydrochloric acid; time was counted from solution of the salt upon shaking after filling the flask to the mark. For the remainder of the measurements the alcohol-washed salt was used, accurately weighed amounts being dissolved in water in a volumetric flask as before. For those experiments in which acid was added initially, hydrochloric acid was used.

The reaction was followed by determining the acid concentration of the reaction mixture at measured intervals. Samples of 25 or 50 ml. were pipetted into an excess of standard sodium hydroxide to stop the reaction, and the excess base was back-titrated with standard hydrochloric acid, using phenolphthalein as an indicator. Consistent results were not obtainable when the back-titration was postponed for more than about fifteen minutes.

All solutions used for the rate runs were carbonate-free, and all flasks were flushed free of carbon dioxide before use. The samples withdrawn from the reaction mixtures were pipetted by means of nitrogen under pressure. During the titration of the mechanically stirred samples, carbon dioxide-free air was passed into the flasks used.

That the alcohol-washed, anhydrous $K_2HON(SO_3)_2$ was pure is shown by the following experiments, in which accurately weighed amounts of the salt were dissolved in pure water and, after several days, the acid formed was determined by the same procedure as that used for the rate determinations.

$K_2HON(SO_3)_2$ taken, g.	Final acid concn. found, mole/l.	Final acid concn., calcd., mole/l.	Diff., %
0.6076	0.00453	0.00451	0.4
.5630	.00417	.00418	.2

It is believed that the present preparations of the pure, anhydrous potassium hydroxylamine disulfonate are the first that have been reported.

Results of the Rate Experiments

At ionic strengths from about 0.01 to 0.4 *m* the rate of hydrolysis in acid solution at 25° is adequately represented by the rate equation

$$-d(\Sigma Ds^=)/dt = k(\Sigma Ds^=)(\Sigma H^+) = k(a - x)(b + x) \qquad (2)$$

where $(\Sigma Ds^=)$ is the total concentration of hydroxylamine disulfonate at the time t, and a is its initial concentration in mole/l.; b is the initial normality of acid, and x is the normality produced by the hydrolysis of the disulfonate during the time t. This equation may be integrated to give

$$\log \frac{b + x}{a - x} = \frac{a + b}{2.303}kt + \text{const.} \qquad (3)$$

The specific reaction rate constants, k, were obtained from the slopes of the plots of $\log (b + x/a - x)$ against t. Apparently the acids H_3O^+, HSO_4^-, $HON(SO_3)_2H^-$, and $HONHSO_3H$, when present in appreciable concentrations, are equally

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[1] Wagner, *Z. physik. Chem.*, **19**, 678 (1896).

[2] Rollefson and Oldershaw, THIS JOURNAL, **54**, 977 (1932).