

measured from 15 to 300°K. A maximum occurs in the heat capacity at  $216.1 \pm 0.5^\circ\text{K}$ . The heat of transition is  $220 \pm 15 \text{ cal. mole}^{-1}$  and the corresponding entropy change is  $1.02 \pm 0.07 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ . The entropy of crystalline  $\text{NH}_4\text{-}$

$\text{H}_2\text{AsO}_4$  at  $298.19^\circ\text{K}$ . is  $41.12 \pm 0.10 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ . The transition is attributed to a rearrangement of the hydrogen bonds in the crystal.

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## The Heat Capacity of Silver Trihydrogen Paraperiodate from 15 to 300°K. The Anomaly at the Curie Temperature

BY C. C. STEPHENSON AND H. E. ADAMS<sup>1</sup>

The application of the third law of thermodynamics to compounds containing hydrogen bonds is a complicated problem. A residual entropy associated with a random orientation of the hydrogen bonds may persist to the lowest attainable temperatures, as in ice,<sup>1a</sup> heavy ice<sup>2</sup> and sodium sulfate decahydrate.<sup>3</sup> If the crystal structure of the compound is known in detail this residual entropy may be calculated, and Pauling<sup>4</sup> has discussed a number of such cases. The experimental data required to confirm the predictions of theory have been obtained only for water and heavy water. However, in the compounds  $\text{KH}_2\text{-PO}_4$ ,<sup>5</sup>  $\text{KH}_2\text{AsO}_4$ ,<sup>6</sup> and  $\text{NH}_4\text{H}_2\text{PO}_4$ ,<sup>7</sup> the transition from the random to an orientated arrangement of the hydrogen bonds occurs at easily attainable temperatures and the entropy of transition may be measured directly. This entropy change may be calculated by Pauling's method or by the alternative method of Slater<sup>8</sup>; the two calculations give the same result for the total entropy change from the ordered to the disordered state. The good agreement between the theoretical and experimental values found in these cases justifies the application of the theory to other systems containing hydrogen bonds.

The structure<sup>9</sup> of  $(\text{NH}_4)_2\text{H}_3\text{IO}_6$  is very similar to the structure of  $\text{KH}_2\text{PO}_4$  in so far as the hydrogen bonds are concerned, except that the octahedral  $\text{IO}_6$  group is linked to neighboring paraperiodate groups by six hydrogen bonds, while the tetrahedral phosphate group has only four hydrogen bonds. In both cases the hydrogen bonds are unsymmetrically arranged around the central group and a preferred orientation of the hydrogens is possible at not too low a temperature. The

expected transition was found<sup>10</sup> in  $(\text{NH}_4)_2\text{H}_3\text{IO}_6$  at  $254^\circ\text{K}$ ., but the compound loses water and ammonia too rapidly to permit measurements on a sample of well-defined composition. The structurally similar salt,  $\text{Ag}_2\text{H}_3\text{IO}_6$ , was more suitable for accurate measurements from this point of view.

The heat capacity of silver trihydrogen paraperiodate has been measured from 15 to 300°K. The entropy of transition of this salt, estimated from the anomalous portion of the heat capacity curve, agrees satisfactorily with the predicted value of  $3/4 R \ln 3$ ; this agreement is particularly gratifying as a test of the hydrogen bond theory in view of the comparatively large amount of entropy involved.

**Material.**—A number of silver periodates ( $\text{Ag}_5\text{IO}_6$ ,  $\text{Ag}_2\text{H}_3\text{IO}_6$ ,  $\text{Ag}_3\text{IO}_6$ ,  $\text{Ag}_2\text{HIO}_6$ ,  $\text{AgIO}_4$ , and perhaps others) exist, and the preparation of pure  $\text{Ag}_2\text{H}_3\text{IO}_6$  requires a careful control of temperature and concentration. As a starting point,  $\text{Na}_3\text{H}_2\text{IO}_6$  is prepared by the oxidation of  $\text{NaIO}_3$  with chlorine in a basic solution.<sup>11</sup> This salt is dissolved in dilute nitric acid and treated with a silver nitrate solution in the ratio of two moles of  $\text{AgNO}_3$  to one of  $\text{Na}_3\text{H}_2\text{IO}_6$ . A finely divided greenish-yellow precipitate of  $\text{Ag}_2\text{H}_3\text{IO}_6$  is formed, but this precipitate usually changes into the red  $\text{Ag}_2\text{HIO}_6$  with loss of water on standing for a day or more. A solution of 5*N* nitric acid is saturated with the salt at  $80^\circ$  (at this temperature all of the yellow salt is converted into  $\text{Ag}_2\text{HIO}_6$ ), filtered at  $40^\circ$  to remove any  $\text{AgIO}_3$  which has formed, and allowed to crystallize in an ice-bath. The solution is not heated above  $80^\circ$  because a white precipitate, presumably silver iodate, forms in larger amounts and the color of the solution turns to a deep brown. The solution can be filtered at  $40^\circ$  to remove this white precipitate since no more of it is formed at lower temperatures. The  $\text{Ag}_2\text{H}_3\text{IO}_6$  forms so slowly that none starts to crystallize at this temperature, and it is usually necessary to allow the solution to crystallize for

(1) Present address, Armstrong Cork Company, Lancaster, Pennsylvania.

(1a) W. F. Giaque and J. W. Stout, *THIS JOURNAL*, **58**, 1144 (1936).

(2) E. A. Long and J. D. Kemp, *ibid.*, **58**, 1829 (1936).

(3) K. S. Pitzer and L. V. Coulter, *ibid.*, **60**, 1310 (1938).

(4) L. Pauling, *ibid.*, **57**, 2680 (1935).

(5) C. C. Stephenson and J. G. Hooley, *ibid.*, **66**, 1397 (1944).

(6) C. C. Stephenson and A. C. Zettlemoyer, *ibid.*, **66**, 1402 (1944).

(7) C. C. Stephenson and A. C. Zettlemoyer, *ibid.*, **66**, 1405 (1944).

(8) J. C. Slater, *J. Chem. Phys.*, **9**, 16 (1941).

(9) L. Helmholtz, *THIS JOURNAL*, **59**, 2036 (1937).

(10) C. C. Stephenson, *J. Chem. Phys.*, **9**, 379 (1941).

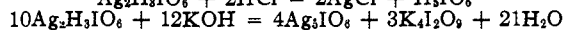
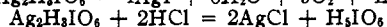
(11) "Inorganic Syntheses," H. S. Booth, Editor-in-Chief, McGraw-Hill Book Company, Inc., New York, 1930, Vol. I, p. 169.

twenty-four hours to ensure complete crystallization. The yields are about twenty grams of salt per liter of solution from the greenish-yellow precipitate, and considerably less from the red  $\text{Ag}_2\text{HIO}_6$  or the black  $\text{Ag}_3\text{IO}_6$  which eventually forms when the red salt is repeatedly heated with the acid solution. If the concentration of the nitric acid is increased, orange-yellow crystals of the tetragonal  $\text{AgIO}_4$  are formed with a larger amount of the white silver iodate.

The silver trihydrogen paraperiodate crystallizes in beautifully formed yellow rhombohedra which sometimes grow to several millimeters on an edge. Some batches of the crystals were stable in air at room temperature for long periods of time, while other batches decomposed overnight into  $\text{Ag}_2\text{HIO}_6$ , but all of the batches remained undecomposed when kept in a refrigerator. The crystals dried rapidly in air and were further dried in vacuum for two hours without any signs of decomposition. Immediately after drying the salt in vacuum, the calorimeter was loaded and cooled below  $0^\circ$  within a few hours. The calorimeter was never allowed to rise above  $0^\circ$  until the final high temperature heat capacity measurements were made. The crystals were then removed from the calorimeter and examined for evidence of decomposition; the absence of any discoloration showed that no decomposition had occurred.

The rhombohedral angle for  $\text{Ag}_2\text{H}_3\text{IO}_6$  is given by Groth<sup>12</sup> as  $67^\circ 38'$ . The angle found for this preparation was  $67^\circ$ .<sup>13</sup>

The salt was analyzed quantitatively by three methods represented by the following equations:



After heating  $\text{Ag}_2\text{H}_3\text{IO}_6$  to constant weight at  $400^\circ$ , the loss in weight found in three experiments was 22.45, 22.44, and 22.43%; theoretical, 22.42%. When the salt was treated with 6*N* nitric acid and hydrochloric acid, the decrease in weight on conversion to silver chloride was found to be 35.25, 34.98, and 35.01%; theoretical, 35.10%. When the salt was treated with potassium hydroxide and allowed to stand for five days, the decrease in weight on conversion to  $\text{Ag}_3\text{IO}_6$  in two trials was 30.98 and 31.00%; theoretical, 30.97%. On the basis of these results, the sample used for the calorimetric measurements was 99.9% pure.

All of the measurements were made on a single loading of 464.227 g. in vacuum, or 1.0510 moles. These figures have been corrected for the presence of 0.053 weight per cent. of 10 mole per cent. nitric acid solution, as explained below. The molecular weight of  $\text{Ag}_2\text{H}_3\text{IO}_6$  is taken as 441.704.

The density of the salt was needed to determine

(12) Groth, "Handbuch der kristallographisch-physikalischen Chemie," Leipzig, 1881, Vol. II, p. 181.

(13) We wish to thank Dr. T. R. P. Gibb, Jr., Analytical Division of the Chemistry Department, M. I. T., for measuring this angle.

the volume of helium gas introduced into the calorimeter for heat conduction. The density of silver trihydrogen paraperiodate, found by displacement of water in a pycnometer, is 5.68 at  $25-26^\circ$ .

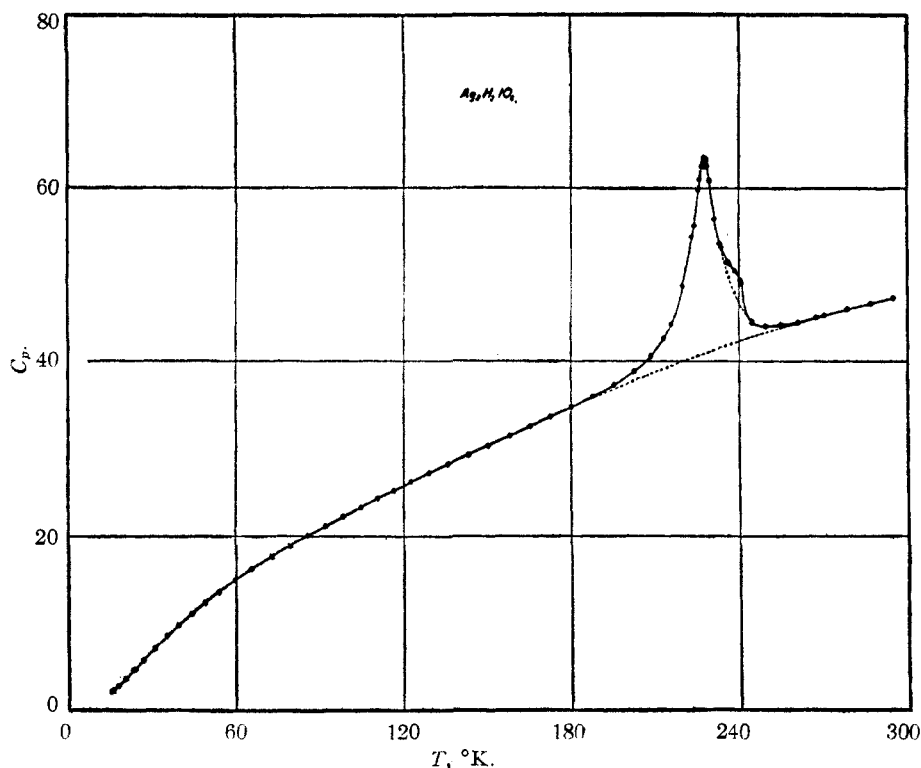
**Apparatus and Method.**—The cryostat used for these measurements has been described.<sup>14</sup> This cryostat was adapted to calorimetric work by Dr. R. W. Blue. The calorimeter was the same as the one employed in the determination of the heat capacity of  $\text{MnF}_2$ .<sup>15</sup> The temperatures and

TABLE I  
THE HEAT CAPACITY OF SILVER TRIHYDROGEN  
PARAPERIODATE  
Molecular weight, 441.704;  $0^\circ\text{C.} = 273.19^\circ\text{K.}$

$T, ^\circ\text{K.}$	$\Delta T$	$C_p,$ cal. deg. <sup>-1</sup> mole <sup>-1</sup>	$T, ^\circ\text{K.}$	$\Delta T$	$C_p,$ cal. deg. <sup>-1</sup> mole <sup>-1</sup>
Series I					
215.86	4.339	44.35	150.59	7.217	30.44
220.03	3.999	48.73	157.97	7.535	31.55
223.13	2.189	54.38	165.35	7.226	32.64
225.23	2.021	59.80	172.83	7.523	33.74
227.20	1.919	63.46	180.20	7.224	34.84
229.15	1.976	60.96	187.68	7.732	36.00
231.18	2.096	56.36	195.24	7.402	37.34
233.32	2.186	53.24	202.45	7.020	38.87
235.91	2.987	51.30	208.49	5.048	40.63
236.90	3.005	50.88	213.17	4.320	42.72
240.31	3.820	49.36	Series IV		
244.66	4.916	44.59	233.10	2.526	53.64
249.60	4.963	43.96	235.67	2.599	51.45
255.02	5.880	44.15	238.28	2.626	50.50
261.09	6.266	44.50	240.93	2.679	48.99
267.53	6.622	45.01	243.05	1.564	45.23
Series II			244.62	1.583	44.42
223.70	2.867	55.67	Series V		
225.74	1.212	61.03	15.31	0.644	2.086
226.43	0.176	62.55	16.19	1.150	2.342
226.61	0.176	62.62	17.84	2.335	2.839
226.78	0.176	62.43	20.09	2.563	3.566
226.99	0.234	63.00	22.94	3.153	4.557
227.28	0.349	63.49	26.70	4.377	5.792
227.71	0.518	63.36	31.10	4.330	7.245
228.28	0.628	62.62	35.26	3.991	8.562
229.01	0.838	60.78	39.43	4.335	9.800
Series III			44.13	5.076	11.12
72.82	6.861	17.74	49.01	4.673	12.45
79.39	6.256	18.95	54.08	5.484	13.68
85.75	6.482	20.12	59.68	5.713	14.99
92.02	6.043	21.23	65.45	5.822	16.27
98.19	6.297	22.31	Series VI		
104.60	6.520	23.37	23.46	2.865	4.725
110.68	5.648	24.37	26.61	3.616	5.743
116.54	6.058	25.31	Series VII		
122.77	6.414	26.29	270.32	8.245	45.25
129.34	6.733	27.27	278.49	8.091	45.96
136.22	7.015	28.29	286.74	8.432	46.61
143.35	7.258	29.35	295.08	8.242	47.29

(14) R. W. Blue and J. F. G. Hicks, *THIS JOURNAL*, **59**, 1962 (1937).

(15) J. W. Stout and H. E. Adams, *ibid.*, **64**, 1535 (1942).

Fig. 1.— $\text{Ag}_2\text{H}_3\text{IO}_6$ .

energy inputs were measured by means of a platinum-rhodium resistance thermometer-heater having the laboratory designation R222. The ice-point resistance of this thermometer, which had been calibrated with a helium gas thermometer,<sup>14</sup> agreed with the original calibration.

The calorie was taken to be 4.1833 international joules. The absolute temperature of the ice point was taken as 273.19°K.

**Heat Capacity Measurements.**—The results of the heat capacity measurements, obtained in seven series, are summarized in Table I, and presented graphically in Fig. 1. The correction for heat leak at the higher temperatures has been greatly reduced by the use of an adiabatic shield. Above 30°K., all of the experimental values fall within 0.1% of a smooth curve through the data except the very short runs in the transition region and one point which included the ice point. This value, at 270.32°K., was 0.60% high due to the condensation of water on the outside of the calorimeter. The cryostat developed a leak between Series VI and VII, and water condensed on the calorimeter in spite of a liquid nitrogen trap in the system. All of the values for this last Series VII have been corrected for 0.04 g. of water; the other measurements are, of course, unaffected. This correction amounts to 0.08% of the total heat capacity.

The peculiar shape of the heat capacity curve indicates the presence of two transitions superimposed upon each other. The short dotted

curve in Fig. 1 is an attempt to differentiate these two transitions. The secondary anomaly is undoubtedly caused by a small amount of nitric acid solution retained in the crystals in spite of the high vacuum to which they were subjected. According to the phase diagram for water and nitric acid,<sup>16</sup> the melting of  $\text{H}_2\text{O}$  and  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$  of a composition (10 mole %  $\text{HNO}_3$ ) corresponding to that used for the recrystallization of the  $\text{Ag}_2\text{H}_3\text{IO}_6$  would give an irregularity similar to that observed. It is unfortunate that the eutectic temperature of this mixture, 231°K., falls in the most interesting temperature range of these experiments. However, the changes in heat content and entropy for this secondary transition, estimated from the portion of the curve above the short dotted line in Fig. 1, are only 17.0 cal. mole<sup>-1</sup> and 0.07 cal. mole<sup>-1</sup> deg.<sup>-1</sup>, respectively. This corresponds to 0.053% by weight of nitric acid solution impurity. Recently Forsythe and Giauque<sup>17</sup> have published an extensive thermal study of nitric acid and its hydrates. Using their data on the heat capacity of  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ , combined with the data on the heat capacity of  $\text{H}_2\text{O}$ ,<sup>18</sup> it has been possible to correct our measurements for the presence of the nitric acid solution. The impurity was assumed to be composed of 0.00109 mole of  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$  and 0.00654 mole

(16) "Gmelin's Handbuch der anorganischen Chemie," Systemnummer 4, Stickstoff, 8th edition, Berlin, 1936, p. 969.

(17) W. R. Forsythe and W. F. Giauque, *THIS JOURNAL*, **64**, 48 (1942).

of  $H_2O$ . The total correction amounted to 0.09–0.16% of the total heat capacity below the melting temperature range and 0.38–0.35% above the melting temperature range.

The results given in Table I are the original values of the heat capacity and have not been corrected for the presence of the nitric acid solution. However, the values at even temperatures listed in Table II were taken from a smooth curve through the data and have been corrected for the presence of the impurity. These values represent the true differential heat capacity and are believed to be accurate to 0.2% above 35°K., to 1% at 20°K., and to 5% at 15°K.

TABLE II  
THE HEAT CAPACITY OF SILVER TRIHYDROGEN  
PARAPERIODATE

Values from a smooth curve through the observations.

$T$ , °K.	$C_p$ , cal. deg. <sup>-1</sup> mole <sup>-1</sup>	$T$ , °K.	$C_p$ , cal. deg. <sup>-1</sup> mole <sup>-1</sup>
15	2.000	150	30.31
20	3.540	160	31.79
25	5.216	170	33.28
30	6.879	180	34.76
35	8.469	190	36.33
40	9.955	200	38.24
45	11.36	210	41.17
50	12.68	215	43.70
55	13.88	220	48.61
60	15.04	224	56.33
65	16.13	227.25	63.5 (max.)
70	17.15	230	58.89
75	18.12	234	52.04
80	19.05	238	48.08
85	19.95	242	45.37
90	20.84	245	44.17
95	21.72	250	43.79
100	22.57	260	44.26
110	24.23	270	45.05
120	25.80	280	45.90
130	27.33	290	46.71
140	28.82	300	47.48

**Transition Temperature.**—The abnormally high heat capacities from 180.0 to 268.5°K. are caused by the re-orientation of the hydrogen bonds in the solid. Although the transition occurs over a wide range of temperatures, it is customary to define the transition temperature as the temperature at which the heat capacity reaches a maximum. The maximum occurs at 227.25 ± 0.20°K.; this temperature is somewhat difficult to locate because the heat capacity curve is apparently dome-shaped near the peak.

**Heat and Entropy of Transition.**—The change in heat content, derived from the heat capacity curve, uncorrected for the presence of  $HNO_3$  solution, is 3943.0 cal. mole<sup>-1</sup> from 180.0 to 268.5°K. The change in heat content from 180.0 to 268.5°K., assuming "normal" heat capacities in this temperature region, is 3567.9 cal. mole<sup>-1</sup>. The heat of transition is then 375.1 ± 20.0 cal. mole<sup>-1</sup>.

Corresponding figures for the entropy changes are: experimental, 17.65 e. u. from 180.0 to 268.5°K.; calculated for "normal" heat capacities, 15.98 e. u. from 180.0 to 268.5°K. The entropy change for the transition is then 1.67 ± 0.10 cal. deg.<sup>-1</sup> mole<sup>-1</sup>.

If, however, the proper corrections for the presence of the nitric acid solution are made, the heat of transition and the entropy change for the hydrogen bond anomaly are then 358.1 ± 20.0 cal. mole<sup>-1</sup> and 1.60 ± 0.10 cal. mole<sup>-1</sup> deg.<sup>-1</sup>.

**Entropy of  $Ag_2H_3IO_6$  at 298.19°K.**—The entropy of the salt was determined by graphical integration of  $\int C_p d \ln T$  from 15 to 298.19°K. The entropy from 0 to 15°K. was obtained by means of a Debye function,  $2D(112.2°K.)$  per mole of  $Ag_2H_3IO_6$ . Table III is a summary of the calculation. The correction due to the presence of the  $HNO_3$  impurity is subtracted separately.

TABLE III  
THE ENTROPY OF  $Ag_2H_3IO_6$

0–15°K., Debye extrapolation	0.71
15–298.19°K., graphical integration	58.95
	59.66
Minus entropy due to $HNO_3$ impurity	0.22
	59.44 ± 0.10 cal. deg. <sup>-1</sup> mole <sup>-1</sup>

This entropy value should be of use in determining the entropy of the periodate ions when the additional thermodynamic data are available.

**Nature of the Transition.**—The entropy change for the transition in  $Ag_2H_3IO_6$  may be calculated if the reasonable assumption is made that the hydrogen bond arrangement is similar to that in the corresponding ammonium salt. The octahedral  $IO_6$  ion is linked to neighboring paraperiodate groups by six hydrogen bonds: that is, one hydrogen lies along each oxygen–oxygen line connecting the  $IO_6$  groups and this hydrogen is closer to one oxygen than to the other. These bonds are not symmetrically ordered about the central group as in the case of ice, and hence the bonds are not of equal energy. A rearrangement of the hydrogen bonds to some preferred orientation of lowest energy is therefore possible at not too low a temperature. The total number of protons adjacent to a paraperiodate group is restricted to three by electrostatic considerations.

The entropy change from an oriented to a random arrangement of the hydrogens may be calculated by the method used by Pauling<sup>4</sup> for ice. If  $W$  is the number of accessible configurations,  $\Delta S = Nk \ln W$ . In a mole of  $Ag_2H_3IO_6$  there are 3  $N$  hydrogens, and if each hydrogen had a possibility of two positions, the total number of configurations would be  $2^{3N}$ . However, many of these configurations are forbidden by the restriction that only three hydrogens may be near a paraperiodate ion. This reduces the total number of accessible configurations to  $(20/64)^N 2^{3N}$  or  $(5/2)^N$

and the theoretical entropy change,  $\Delta S$ , is  $R \ln 5/2 = 1.82 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$ .

If, however, the method of Slater<sup>8</sup> or Onsager<sup>18</sup> is followed, which takes into account the fact that all the allowed positions of the hydrogen atoms do not have the same energy, the following partition function for the states above the Curie point can be set up

$$Z = 2^{3N} \left[ \frac{2}{64} e^{-0/kT} + \frac{18}{64} e^{-\epsilon/kT} \right]^N = \left( \frac{1}{4} + \frac{9}{4} e^{-\epsilon/kT} \right)^N$$

In this equation, the twenty allowed states of the sixty-four are distinguished by assuming that eighteen have an energy  $\epsilon$  higher than the two of zero energy. Below the Curie point all the dipoles are assumed to be parallel to the axis, hence  $Z = 1$ . The theoretical entropy change,  $\Delta S$ , calculated in this manner, is  $3/4 R \ln 3$  or 1.64 e. u., and at infinite temperatures  $\Delta S = R \ln 5/2$ , in agreement with the value obtained by employing Pauling's method. Thus the results of this research seem to indicate an entropy change associated with the transition of  $3/4 R \ln 3$ , which makes itself evident in a relatively small temperature range around the transition temperature. This entropy change probably increases slowly with increasing temperature until it reaches the value  $R \ln 5/2$  at high temperatures.

TABLE IV

Substance	Transition temperature, $T$ , °K.	$\Delta H$ , cal. mole <sup>-1</sup>	$\Delta S$ , cal. deg. <sup>-1</sup> mole <sup>-1</sup>
KH <sub>2</sub> PO <sub>4</sub>	121.97 ± 0.05	87 ± 6	0.74 ± 0.06
KH <sub>2</sub> AsO <sub>4</sub>	95.57 ± 0.05	84 ± 4	0.90 ± 0.05
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	147.9 ± 1.0	154 ± 5	1.05 ± 0.04
NH <sub>4</sub> H <sub>2</sub> AsO <sub>4</sub>	216.1 ± 0.5	220 ± 15	1.02 ± 0.07
Ag <sub>2</sub> H <sub>3</sub> IO <sub>6</sub>	227.25 ± 0.2	358 ± 20	1.60 ± 0.10

For convenience, the entropy changes, heats of transition and transition temperatures for the five similar substances are summarized in Table IV. The theoretical entropy change for the dihydrogen

(18) Onsager, presented at Conference on Dielectrics, New York Academy of Sciences, May, 1939.

phosphates and arsenates is 0.69 increasing to a total change of 0.81 cal. deg.<sup>-1</sup> mole<sup>-1</sup>. These results agree as well as can be expected with the predictions of theory, and justify the assumptions of the hydrogen bond theory. In view of the fact that the entropy calculation is made for constant pressure rather than constant volume, and that an arbitrary "normal" heat capacity is assumed, the results cannot be used to determine whether the total theoretical entropy change occurs in a relatively narrow temperature interval. In the case of silver trihydrogen paraperiodate the calculations following the method of Slater and Onsager give better agreement. The higher results for the ammonium salts may be explained by an entropy contribution above the theoretical value caused by abnormal volume changes at the transition.

The calculated entropies of transition have been confirmed in these cases, and the same theory may be applied with confidence to other substances when the hydrogen bond arrangement is known in sufficient detail. In addition, these results may be considered as additional evidence for the interpretation of the residual entropies of ice and heavy ice, where the transition is not observed.

### Summary

The heat capacity of silver trihydrogen paraperiodate has been measured from 15 to 300°K. A region of abnormally high heat capacity occurs between 180 and 270°K., and the maximum in the heat capacity curve is at 227.25 ± 0.20°K. The change in heat content for this non-isothermal transition is 358.1 ± 20.0 cal. mole<sup>-1</sup> and the corresponding entropy change is 1.60 ± 0.10 cal. mole<sup>-1</sup> deg.<sup>-1</sup>.

The entropy change agrees within the limits of error with the calculated value of  $3/4 R \ln 3$  or 1.64 cal. mole<sup>-1</sup> deg.<sup>-1</sup>, based on a hydrogen bond theory of the transition.

The entropy of crystalline Ag<sub>2</sub>H<sub>3</sub>IO<sub>6</sub> at 298.19°K. is 59.44 ± 0.10 cal. deg.<sup>-1</sup> mole<sup>-1</sup>.

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## Enzymatically Synthesized Crystalline Sucrose

BY W. Z. HASSID, M. DOUDOROFF AND H. A. BARKER

Doudoroff, *et al.*,<sup>1,2</sup> have shown recently that the bacterium *Pseudomonas saccharophila* Doudoroff contains a sucrose phosphorylase catalyzing the reaction: sucrose + inorganic phosphate → glucose-1-phosphate + fructose. Evidence was obtained indicating the reaction to be reversible: in the presence of purified phosphorylase, fructose and glucose-1-phosphate react to give inorganic phos-

phate and a carbohydrate having certain properties of sucrose. The data previously reported are not, however, sufficient to justify the conclusion that the product of the reverse reaction is identical with natural sucrose. Further work was, therefore, undertaken to isolate and positively identify the synthetic product. The results here reported show conclusively that the synthetic product is sucrose.

There is some uncertainty as to whether or not sucrose has been previously synthesized. Pictet

(1) M. Doudoroff, N. Kaplan and W. Z. Hassid, *J. Biol. Chem.*, **148**, 67 (1943).

(2) M. Doudoroff, *ibid.*, **151**, 351 (1943).