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The Heat Capacity of KH_2AsO_4 from 15 to 300°K. The Anomaly at the Curie Temperature

BY C. C. STEPHENSON AND A. C. ZETTLEMOYER[1]

The heat capacity of potassium dihydrogen arsenate has been investigated. This salt, which is isomorphous with KH_2PO_4, is spontaneously polarized[1a] at a temperature somewhat lower than the corresponding temperature for the phosphate. The entropy increase associated with the transition from the polarized to the non-polarized configuration has been determined for KH_2PO_4[2] and found to be in agreement with the theoretical value derived from a consideration of the arrangement of the hydrogen bonds in the crystal.[3] The same theory applies to KH_2AsO_4, and the experimental entropy change reported in this paper is also in agreement with the predicted value.

The measurements given by Busch show that the maximum spontaneous polarization is reached in a smaller temperature region for the dihydrogen arsenate than for the dihydrogen phosphate. The anomalous heat capacities were accordingly expected, and found by experiment to occur, over a smaller temperature interval than for KH_2PO_4. An improved calculation of the entropy change of the transition (relating to the case for KH_2PO_4) was possible with the arsenate.

Material.—The KH_2AsO_4 was of reagent quality and contained, other than water, less than 0.03% impurities.[4] The salt was dried *in vacuo* to constant weight. The regularity of the heat capacities in the neighborhood of the ice-point demonstrated the absence of water. The crystal size, although not completely uniform, was approximately 1.5 × 0.2 × 0.2 mm.

TABLE I

HEAT CAPACITY OF POTASSIUM DIHYDROGEN ARSENATE

Molecular weight, 180.02; 0°C. = 273.19°K.

T, °K.	ΔT	C_p, cal. deg.$^{-1}$ mole^{-1}	Series	T, °K.	ΔT	C_p, cal. deg.$^{-1}$ mole^{-1}	Series	T, °K.	ΔT	C_p, cal. deg.$^{-1}$ mole^{-1}	Series
16.07	3.048	0.728	I	94.59	0.346	29.93	II	146.94	5.192	19.92	I
18.19	2.896	0.990	I	94.93	.293	39.47	II	151.97	5.073	20.39	I
20.84	3.014	1.389	I	95.07	.560	53.07	I	157.01	4.947	20.74	I
23.67	2.966	1.863	I	95.16	.172	59.36	II	160.08	5.187	21.07	I
26.52	3.230	2.302	I	95.32	.152	71.07	II	165.55	5.568	21.57	I
29.92	3.317	3.057	I	95.47	.133	85.16	II	171.24	5.435	21.96	I
33.48	3.572	3.883	I	95.59	.470	68.68	I	177.23	5.332	22.35	I
37.21	3.735	4.693	I	95.61	.145	76.35	II	182.39	5.229	22.84	I
41.68	4.841	5.647	I	95.81	.251	30.79	II	185.62	5.160	23.02	I
46.88	5.239	6.815	I	96.09	.304	19.88	II	190.85	5.056	23.44	I
52.13	5.238	7.917	I	96.29	.937	18.36	I	195.98	4.969	23.72	I
57.40	5.286	8.942	I	96.41	.327	16.16	II	200.97	5.350	24.12	I
62.58	5.218	9.919	I	96.80	.438	15.62	II	206.33	5.228	24.52	I
67.84	5.121	10.885	I	97.24	.437	15.47	II	208.89	5.152	24.65	I
73.13	5.531	11.83	I	97.27	.986	15.58	I	214.02	5.083	25.01	I
78.83	5.833	12.86	I	97.79	.651	15.48	II	220.86	4.989	25.45	I
83.11	3.005	13.74	II	98.30	.979	15.64	I	225.90	4.838	25.80	I
84.45	5.326	14.01	I	98.59	.953	15.55	II	231.17	5.475	26.15	I
85.57	1.919	14.35	II	99.29	.971	15.50	I	237.06	5.908	26.55	I
87.47	1.862	14.99	II	99.53	.941	15.67	II	240.31	5.870	26.70	I
89.30	1.800	15.62	II	100.52	1.047	15.64	II	246.43	5.862	27.12	I
89.58	4.869	15.76	I	102.71	5.796	15.83	I	252.81	6.312	27.51	I
91.24	1.735	16.57	II	108.51	5.517	16.38	I	259.38	6.229	27.96	I
92.49	0.980	17.88	I	114.02	5.289	16.90	I	265.62	6.122	28.42	I
92.73	1.913	17.93	II	119.50	5.588	17.49	I	271.62	6.014	28.69	I
93.46	0.941	19.40	I	124.68	5.384	17.98	I	277.59	5.931	28.84	I
93.69	.682	19.92	II	130.30	5.683	18.39	I	283.89	5.830	29.35	I
94.22	.379	24.16	II	136.02	5.494	18.99	I	290.27	6.172	29.86	I
94.36	.831	25.69	I	141.62	5.340	19.46	I	296.78	6.140	30.28	I

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(1a) G. Busch, *Helv. Phys. Acta*, **11**, 269 (1938).

(2) C. C. Stephenson and J. G. Hooley, THIS JOURNAL, **66**, 1397 (1944).

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

(4) Prof. S. G. Simpson, Analytical Division of the Chemistry Dept., M. I. T., kindly performed the quantitative analysis.

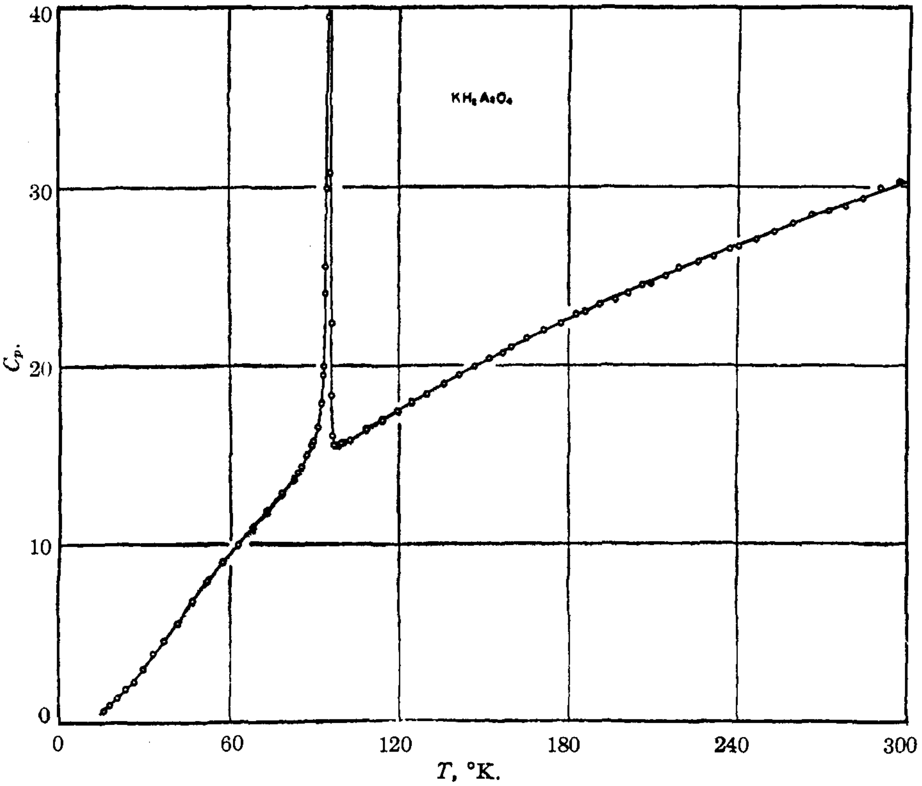

Fig. 1.—KH_2AsO_4.

All measurements were made on a single calorimeter loading of 110.711 g. *in vacuo*, or 0.61499 mole. The molecular weight of KH_2AsO_4 was taken to be 180.02.

Apparatus and Method.—The temperatures and energy inputs were measured by means of a platinum-rhodium resistance thermometer-heater having the laboratory designation R197. The ice-point resistance was remeasured and was found to check the original calibration.

The apparatus and method of measurement have been previously described.[5] Reference has recently been made to the redetermination of the heat capacity of the empty calorimeter.[2]

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

Heat Capacity Measurements.—The heat capacity measurements were made in two series. They are summarized in Table I and plotted as a function of temperature in Fig. 1. The average deviation of the points from a smooth curve is: from 15 to 30°K., 1.00%; from 30 to 200°K., 0.17%; and, from 200 to 300°K., 0.13%. Results near the transition temperature are excluded from these averages. Because of the small temperature intervals of these runs, they are less accurate.

Table II lists values taken from the smooth curve through the experimental values of Table I. From 90 to 100°K. the values in Table II were taken as the slopes of a heat content versus temperature curve. In this region the heat capacity varies too greatly for values to be obtained directly. However, the heat content is known accurately.

TABLE II

HEAT CAPACITY OF POTASSIUM DIHYDROGEN ARSENATE

Values from a smooth curve through the data

T, °K.	C_p, cal. deg.$^{-1}$ mole^{-1}	T, °K.	C_p, cal. deg.$^{-1}$ mole^{-1}
15	0.611	105	16.04
20	1.246	110	16.52
25	2.073	120	17.51
30	3.077	130	18.44
35	4.188	140	19.34
40	5.312	150	20.21
45	6.398	160	21.07
50	7.480	170	21.87
55	8.478	180	22.63
60	9.441	190	23.35
65	10.37	200	24.05
70	11.28	210	24.73
75	12.16	220	25.40
80	13.08	230	26.07
85	14.21	240	26.72
90	15.78	250	27.34
92	17.1	260	27.96
94	22.4	270	28.58
95.57	Maximum	280	29.19
96	21.3	290	29.80
98	15.5	300	30.40
100	15.62		

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(5) J. F. G. Hicks, THIS JOURNAL, **60**, 1000 (1938).

In runs made near the maximum in the anomaly in the heat capacity curve, thermal equilibrium, before and after supplying heat to the sample, was lacking. For KH_2PO_4 this was accounted for, at least in part, by a marked decrease in the thermal conductivity. For KH_2AsO_4 no such change was indicated.

Total energy inputs through the transition region were measured between temperatures at which equilibrium was easily attained. Such values allowed a more exact calculation of the total entropy change associated with the transition.

The heat capacity of potassium dihydrogen arsenate was reported by W. Bantle and P. Scherrer.[6] Their values were reported graphically and are considerably higher than the values reported here.

Transition Temperature.—The temperature at which the heat capacity reaches a maximum, the transition temperature, was studied by measuring rates of cooling and warming. Within the limits of accuracy of the observations there was no isothermal absorption of heat. Figure 2 shows a differential cooling and a warming curve. From several curves of this kind, the transition temperature was found to be 95.57 ± 0.05°K. The cooling and warming rates were measured under non-ideal conditions. For these measurements the vacuum in the apparatus was partially broken: but not to the same extent for each set of measurements. However, if any hysteresis occurred it must have been less than 0.04°K.

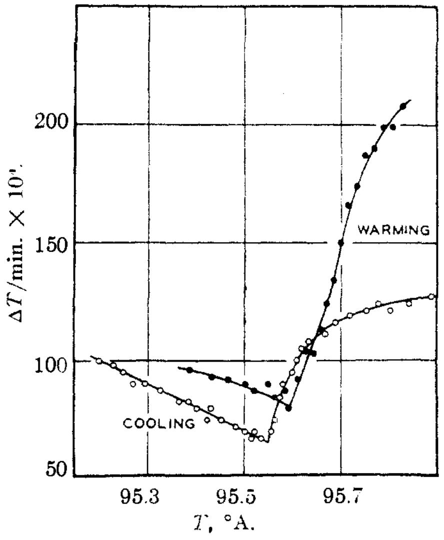

Fig. 2.

Cooling curves were also made from measurements taken in a simple cooling-curve apparatus using a copper–constantan thermocouple. Transition temperatures were determined for the same sample used for the calorimetric measurements and for another sample which had been powdered. The values were 95.58 ± 0.1°K., in good agreement with the more accurate value above.

Bantle and Scherrer[6] found maxima in the heat capacity curve at about 95.5 and 97°K. They claim that the position of the maximum, as well as the shape of the curve, depends upon the size of the crystal used. However, they have not labeled the two curves appearing in their diagram, nor do they show enough points to produce reliable results. Furthermore, one of their heat capacity curves displays a double maximum. No evidence of such an effect could be found. Busch[1] found that the spontaneous polarization occurs at 91°K. His temperature scale is probably unreliable.

Heat of Transition.—Since the transition occurs over approximately forty degrees, the determination of values for the heat effect and entropy change associated with the transition is difficult. An interpolated "normal" heat capacity curve allows the summation of the "normal" heat change over the transition region. This "normal" value subtracted from the total heat content obtained for this region from the heat capacity data gave the desired value for the heat effect associated with the transition itself.

In single increments, the energy required to increase the temperature from 90.088 to 101.297°K. was found to be 240.6 cal. per mole, from 89.552 to 101.385°K., 250.4 cal. per mole, and from 88.667 to 101.732°K., 269.8 cal. per mole. These end-point temperatures are well outside the region of thermal instability. These data combined with the heat capacity data gave 701.8, 701.8, and 701.6 cal. per mole for the change in heat content from 65 to 110°K. These values are to be compared with 699.9 and 698.4 cal. per mole, obtained by integrating the heat capacity data of Series I and II between 65 and 110°K. Because a smaller number of energy increments were required and because thermal instability was avoided in obtaining the former values, they are more accurate. The best value was taken to be 701.7 ± 0.5 cal. per mole.

Two values, 614.9 and 621.2 cal., were found for the "normal" heat content between 65 and 110°K. These values are obtained from the lowest and the highest reasonable interpolated "normal" curves drawn on a large scale plot of the heat capacity data. The assumption was made that a single smooth curve represents the "normal" heat capacity between the low and high temperatures.

Subtraction of these "normal" heat contents from the best value of the total heat content for the transition gave 87 and 81 cal. per mole for limiting values of the heat of the transition.

Entropy of the Transition.—The total entropy change, $\int C_p \, d \ln T$, for the transition region was found by summation. For better accuracy in the region near the maximum in the anomaly, small increments of $\Delta H/T$ were used. The total en-

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[6] W. Bantle and P. Scherrer, *Helv. Phys. Acta*, **13**, 214 (1940).

tropy change was found to be 7.98 ± 0.01 cal. per mole per deg. from 65 to 110°K.

Entropy changes corresponding to the two "normal" curves were found to be 7.05 and 7.12 cal. per mole per deg. The entropy change of the transition is then 0.90 ± 0.05 entropy unit.

The transition is of the same nature as the transition which occurs in KH_2PO_4, and the same theory[3] may be used. The entropy of transition is associated with an order-disorder transformation of the $H_2AsO_4^-$ dipoles: the total entropy change from the oriented to the random configuration is $R \ln 3/2 = 0.81$ entropy unit. The observed entropy change, which is slightly higher, agrees as well as can be expected with the theoretical value.

Abnormal volume changes in the transition region would contribute to the experimentally observed entropy change, but at these low temperatures this effect is probably small. The uncertainty in the estimation of the "normal" heat capacity over the transition region also makes a comparison of theoretical and experimental results difficult. Nevertheless, the agreement is good enough to supply convincing evidence for the theory that the hydrogen bonds are responsible for the transitions in crystals of this type.

Entropy of KH_2AsO_4 at 298.19°K.—The entropy was determined graphically from 15 to 298.19°K., and combined with an extrapolation by a Debye function to 0°K. The third law entropy value thus found is 37.08 ± 0.1 cal. deg.$^{-1}$ mole^{-1} at 298.19°K.

Summary

The heat capacity of KH_2AsO_4 has been measured from 15 to 300°K. A maximum occurs in the heat capacity at 95.57 ± 0.05°K. The heat of transition is 84 ± 4 cal. per mole and the entropy change is 0.90 ± 0.05 cal. deg.$^{-1}$ mole^{-1}. The entropy of crystalline KH_2AsO_4 at 298.19°K. is 37.08 ± 0.1 cal. deg.$^{-1}$ mole^{-1}. The experimental entropy change of the transition affords further evidence for the hydrogen bond theory of transitions in crystals of this type.

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The Heat Capacity of Ammonium Dihydrogen Phosphate from 15 to 300°K. The Anomaly at the Curie Temperature

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In order to study the effect of hydrogen bonds on the thermal properties of solids, the heat capacity of ammonium dihydrogen phosphate has been determined. This salt is isomorphous with potassium dihydrogen phosphate and potassium dihydrogen arsenate; the heat capacities of the latter salts[2] have been investigated previously. A transition analogous to the transitions in KH_2PO_4 and KH_2AsO_4 was expected. Furthermore, Klug and Johnson[3] have reported an ammonium-type transition at 18.9 ± 2.5°C. The hydrogen bond transition was found, but there is no evidence for an ammonium-type transition.

Material.—The $NH_4H_2PO_4$ was of reagent quality and was recrystallized from water three times. The crystal size was approximately 2.0 × 1.0 × 1.0 mm. The salt was dried in vacuum for more than twenty-four hours, but this treatment was found to be inadequate.

An irregularity in the heat capacity near the ice-point (Table I, Series I) showed the presence of water. Another series (Series IV, Table I) of measurements was taken through this temperature range. The excess heat input for the one point of Series I above the normal curve was found to be 11.707 cal. per mole of $NH_4H_2PO_4$. This value combined with the heat of fusion of ice indicated 0.147 mg. of H_2O, or 0.128% by weight of the total sample taken. The second series of runs through the region (Series IV) gave a smaller amount of H_2O. It is believed that the latter series is in error because the sample was not cooled to a temperature low enough to preclude hysteresis and supercooling. The value taken was from a series of runs beginning at liquid nitrogen temperatures. The correction to the heat capacities amounted to approximately 0.2% below and 0.4% above the eutectic point.

Brown, Smith and Latimer[4] have applied a correction for water impurity in potassium permanganate in a similar manner. They found the heat capacities corrected in this way checked exactly the heat capacities determined on a dry sample.

After the heat capacities were determined, the salt was further dried in vacuum for 60 hrs. with a loss of only 8 mg., or only 6% of the total water.

All measurements were made on a single calorimeter loading of 102.339 g. of wet $NH_4H_2PO_4$ *in vacuo*, or 102.262 g. *in vacuo* of dry $NH_4H_2PO_4$. This corresponds to 0.88896 mole of $NH_4H_2PO_4$.

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(2) (a) C. C. Stephenson and J. G. Hooley, THIS JOURNAL, **66**, 1397 (1944); (b) C. C. Stephenson and A. C. Zettlemoyer, *ibid.*, **66**, 1402 (1944).

(3) H. P. Klug and W. W. Johnson, *ibid.*, **59**, 2061 (1937).

(4) O. L. I. Brown, W. V. Smith, and W. M. Latimer, *ibid.*, **58**, 2144 (1936).