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

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

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).

TABLE I

HEAT CAPACITY OF AMMONIUM DIHYDROGEN PHOSPHATE

Molecular weight, 115.04; 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
18.06	1.971	0.749	III	142.59	1.647	20.32	II	159.13	4.937	21.49	I
19.99	2.120	0.997	III	144.03	2.563	20.51	I	163.42	4.818	21.90	I
22.35	2.658	1.335	III	144.22	1.628	20.57	II	168.44	5.124	22.42	I
25.28	2.905	1.767	III	145.49	0.912	20.84	II	173.50	5.010	22.86	I
28.40	2.940	2.241	III	146.19	1.620	21.24	I	178.46	4.886	23.45	I
31.64	3.178	2.772	III	146.33	0.902	21.09	II	183.31	4.779	23.93	I
35.10	3.569	3.389	III	147.13	0.705	21.82	II	188.24	5.064	24.47	I
38.86	3.849	4.049	III	147.68	0.388	22.44	II	193.90	4.394	24.96	I
43.24	4.629	4.818	III	147.71	1.388	27.53	I	198.55	4.780	25.42	I
48.19	5.003	5.711	III	148.02	0.286	25.57	II	203.36	4.680	25.87	I
53.39	5.261	6.594	III	148.25	.181	33.97	II	208.45	5.511	26.24	I
58.77	5.459	7.527	III	148.40	.138	48.44	II	214.01	5.609	26.81	I
64.07	5.187	8.468	III	148.51	.104	69.20	II	219.93	6.593	27.29	I
69.01	4.642	9.333	III	148.60	.080	93.50	II	227.22	7.805	27.95	I
73.75	4.827	10.134	III	148.62	.392	140.12	I	235.27	8.215	28.64	I
78.64	4.943	10.87	III	148.66	.062	124.62	II	243.41	8.001	29.33	I
82.54	4.701	11.47	I	148.71	.049	161.84	II	251.47	7.822	30.06	I
83.61	5.030	11.60	III	148.75	.063	205.27	II	259.52	8.153	30.75	I
87.33	4.819	12.23	I	148.80	.051	203.18	II	263.60	1.587	31.19*	IV
92.22	4.925	12.99	I	148.86	.088	273.84	II	265.47	2.237	32.11*	IV
97.22	5.022	13.73	I	148.93	.236	242.09	I	267.40	7.728	32.75	I
102.32	5.147	14.50	I	148.98	.180	167.19	II	267.81	2.452	32.17*	IV
107.35	4.894	15.28	I	149.22	.313	90.27	II	275.32	8.275	32.08	I
112.38	5.136	15.95	I	149.49	.891	51.74	I	270.12	2.250	31.32*	IV
117.42	4.908	16.66	I	150.00	1.125	25.47	II	272.42	2.447	31.55*	IV
122.23	4.718	17.30	I	150.75	1.623	20.65	I	283.56	8.084	32.80	I
126.69	4.966	17.92	I	151.21	1.264	20.59	II	288.93	4.164	33.25	I
131.61	4.791	18.61	I	152.63	1.569	20.84	II	292.68	3.420	33.56	I
136.61	4.990	19.33	I	152.83	2.475	20.85	I	296.04	3.390	33.65	I
140.97	3.717	20.01	I	154.35	4.606	21.04	I	299.34	3.360	33.93	I

The molecular weight of $NH_4H_2PO_4$ was taken as 115.04.

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 accuracy of the results was improved by the use of a lighter calorimeter. It is to be compared with the calorimeter described by Hicks.[5] The new calorimeter is a similar annular cylinder 4 in. high and 1.75 in. in diameter, having a volume of 114.2 cc. The R197 thermometer-heater is frozen into thermal contact with the calorimeter in the inner space by stopcock grease. Metal vanes have been eliminated in this calorimeter. Loading and unloading is through a $^1/_4$ in. long by $^3/_8$ in. diameter super nickel tube on the bottom of the calorimeter. A small copper disk may be easily soldered onto the tube as a stopper. The outside surface of the calorimeter was gold plated. The empty calorimeter weighed 152.456 g.; as calibrated with the thermometer-heater, 199.637 g.

The remaining parts of the apparatus and the method of measurement have been previously described.[5]

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 capacities were measured in four series. They are summarized in Table I. The "starred" values represent the series of runs, Series IV, made to confirm the presence of water, but not used to determine the amount of water present. Except for Series IV, the heat capacities are plotted in Fig. 1. The heat of fusion of the ice has been eliminated for the run of Series I through the eutectic point. The average deviation of the points from a smooth curve is: 0.1% from 15 to 30°K.; 0.14% from 30 to 200°K.; and, 0.11% from 200 to 300°K. Results obtained near the ice-point and through the transition are excluded from these averages. Because of the small temperature intervals of these runs, they are less accurate.

Table II lists values taken from a smooth curve through the experimental values of Table I.

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

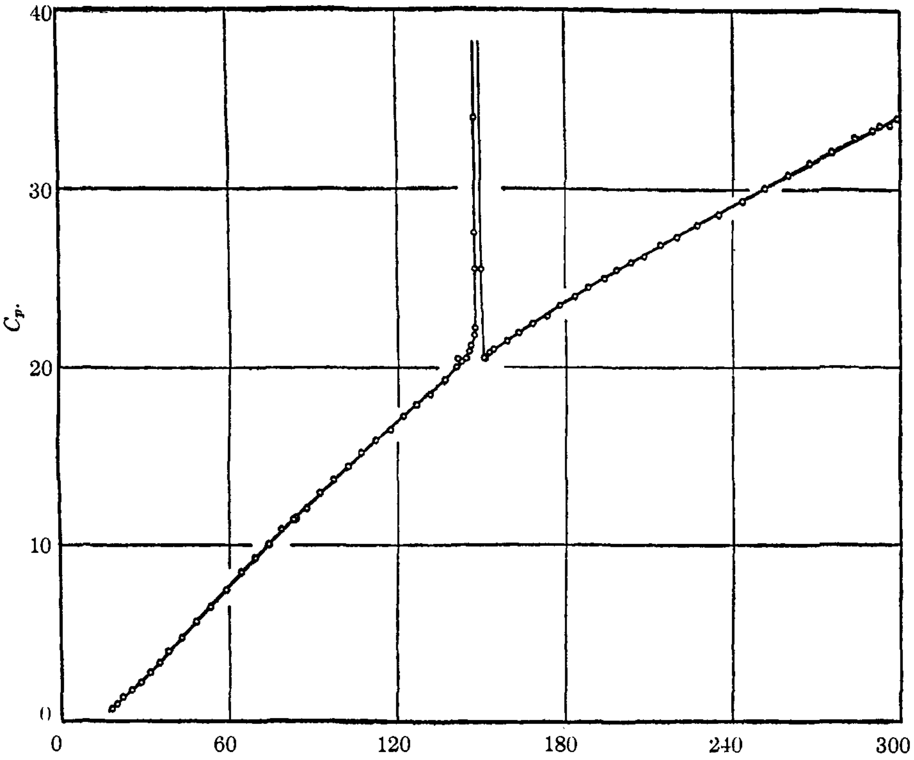

Fig. 1.—$NH_4H_2PO_4$.

From 146 to 150°K. inclusive, 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 AMMONIUM DIHYDROGEN PHOSPHATE

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	0.410	146	20.9
20	0.999	147	22.0
25	1.722	148	29.0
30	2.494	148.87	Maximum
35	3.360	149	114.2
40	4.248	150	31.5
45	5.122	151	20.63
50	6.000	155	21.06
55	6.883	160	21.56
60	7.780	170	22.58
65	8.654	180	23.60
70	9.492	190	24.60
75	10.31	200	25.56
80	11.12	210	26.41
85	11.89	220	27.30
90	12.65	230	28.18
95	13.40	240	29.07
100	14.16	250	29.93
110	15.62	260	30.78
120	17.00	270	31.64
130	18.38	280	32.49
140	19.86	290	33.32
145	20.69	300	34.17

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. As for KH_2AsO_4 but unlike KH_2PO_4, this could not be accounted for by a change in the thermal conductivity.

No anomaly of the type and at the temperature (18 ± 2.5°C.) Klug and Johnson[3] described could be found: cooling and warming curves taken over the region from the ice-point to room temperature showed no disturbances; the heat capacities showed no anomaly in this temperature range. Any ammonium-type anomaly must be less than 0.5%. Their findings cannot be reconciled with these data.

Transition Temperature.—The transition temperature was studied by measuring rates of cooling and warming as described previously.[2] Figure 2 shows two cooling curves and one warming curve. The transition temperature on warming obtained by this method accurately checks the temperature indicated by the heat capacity data. The hysteresis which occurs at this transition was not observed in KH_2PO_4 and KH_2AsO_4. The transition temperature is taken as 147.9 ± 1.0°K.

Heat of Transition.—In single increments, the energy required to increase the temperature from

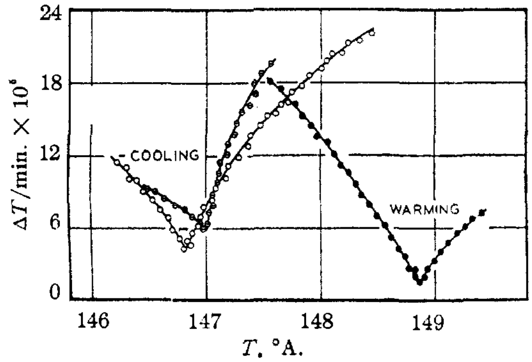

Fig. 2.

145.342 to 151.846°K. was found to be 274.3 cal. per mole and from 145.393 to 151.296°K., 261.7 cal. per mole. These end-point temperatures were well outside the region of thermal instability. These data combined with the heat capacity data gave 1413.2 and 1413.0 cal. per mole for the change in heat content between 95 and 165°K. By summing the energy inputs of Series I and Series II between 65 and 110°K., the values of 1409.5 and 1394.0 cal. per mole were obtained. The last value is less accurate because very short temperature intervals were taken for each run. Because thermal instability was avoided and a smaller number of increments are involved in the summation, the values of 1413.2 and 1413.0 cal. per mole are more reliable. The best value was taken to be 1413.1 ± 0.7 cal. per mole.

For the lowest and highest reasonable, interpolated "normal" heat capacity curves, values of 1254.0 and 1264.4 were found. These "normal" curves were determined as previously described.[2a]

Subtraction of these values from the best total heat content gave 159.1 and 148.7 cal. per mole as limiting values of the heat of transition. It is possible, in this case, to conceive a "normal" curve hugging the heat capacity curve until very near the transition and then having an abrupt change of slope. Such a "normal" curve, the highest it is possible to draw, gave a "normal" heat content from 95 to 165°K. of 1272.6 cal. per mole and a heat of transition of 140.5 cal. per mole.

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 entropy change was found to be 10.76 ± 0.01 cal. per mole per deg. from 95 to 165°K.

Entropy changes corresponding to the two "normal" curves were found to be 9.67 and 9.75 cal. per mole per deg., and for the "normal" curve with the change of slope at the transition temperature, 9.82 cal. per mole per deg. The most probable value for the entropy of transition is then 1.05 ± 0.04 cal. deg.$^{-1}$ mole^{-1} and the lowest value which can be obtained by any reasonable "normal" curve is 0.94 cal. deg.$^{-1}$ mole^{-1}. The total entropy change predicted by the hydrogen bond theory[6] is $R \ln {}^3/_2 = 0.81$ cal. deg.$^{-1}$ mole^{-1}; this entropy increase is associated with the rearrangement of the hydrogen bonds in the crystal. The slight increase in the experimentally determined entropy over $R \ln {}^3/_2$ is attributed to an interaction of the hydrogen bonds with the crystal lattice itself. The agreement is close enough to afford satisfactory evidence for the hydrogen bond theory of the transition.

Entropy of $NH_4H_2PO_4$ 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. to give 36.32 ± 0.1 cal. deg.$^{-1}$ mole^{-1} at 298.19°K.

Summary

The heat capacity of crystalline $NH_4H_2PO_4$ has been measured from 15 to 300°K. A maximum occurs in the heat capacity at 148.9°K. on warming or at 147.0°K. on cooling. The transition temperature is 147.9 ± 1.0°K. The heat of transition is 154 ± 5 cal. mole^{-1} and the entropy of transition is 1.05 ± 0.04 cal. deg.$^{-1}$ mole^{-1}. Of this, 0.81 cal. deg.$^{-1}$ mole^{-1} is attributed to a rearrangement of the hydrogen bonds and the remainder to the crystal lattice. The entropy of $NH_4H_2PO_4$ at 298.19°K. is 36.32 ± 0.1 cal. deg.$^{-1}$ mole^{-1}.

Cambridge, Mass. Received April 21, 1944

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[6] J. C. Slater, *J. Chem. Phys.*, **9**, 16 (1941).