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

BY C. C. STEPHENSON AND H. E. ADAMS[1]

The heat capacities of potassium dihydrogen phosphate,[2] potassium dihydrogen arsenate[3] and ammonium dihydrogen phosphate[4] have been determined previously. In order to complete this interesting series of isomorphous salts, the heat capacity of ammonium dihydrogen arsenate has been measured from 15 to 300°K.

The heat capacity curves of all the above salts exhibited a maximum and a maximum was expected in the heat capacity curve of $NH_4H_2AsO_4$. This was found at 216.1° K., the highest transition temperature of this series. This anomalous increase in the heat capacity is caused by a rearrangement of the hydrogen bonds, as in the other isomorphous salts.

Material.—The $NH_4H_2AsO_4$ used for the heat capacity measurements was prepared[4a] by adding stoichiometric amounts of ammonia to C. P. As_2O_5. The blue color of the resulting solution was attributed to copper. This and other heavy metals present in the As_2O_5 were removed by adding ammonium sulfide and filtering off the resulting sulfides. The solution was then boiled to remove the excess ammonium sulfide and ammonia. Upon the addition of a small amount of As_2O_5 to make the solution slightly acid, the $NH_4H_2AsO_4$ started to crystallize. This salt was twice crystallized from water. After appropriate drying the salt was analyzed for NH_3. The analysis gave 11.22% NH_3 compared to the theoretical 10.71%. A small amount of $(NH_4)_2HAsO_4$ was probably present. This salt was again recrystallized twice from water and dried over phosphorus pentoxide for twenty-two hours. After drying in vacuum for more than twenty-four hours, the analysis[5] gave 10.64, 10.69, and 10.67% NH_3.

An irregularity in the heat capacity was found near the ice-point. If this is due to the fusion of ice it would correspond to 0.36% by weight of water in the sample. A similar situation was experienced for $NH_4H_2PO_4$.[3] In the case of $NH_4H_2AsO_4$ it is impossible to heat the salt to drive off the water because it decomposes slowly at 100° giving off both water and ammonia. The heat capacities have been corrected for this amount of water impurity. The correction amounted to approximately 0.5% below and 1.0% above the eutectic point.

All measurements were made on a single calorimeter loading of 95.860 g. of wet $NH_4H_2AsO_4$ *in vacuo*, or 95.516 g. *in vacuo* of dry $NH_4H_2AsO_4$. This corresponds to 0.60086 mole of $NH_4H_2AsO_4$. The molecular weight of $NH_4H_2AsO_4$ was taken as 158.966.

Apparatus and Method.—The calorimeter used has been described by Zettlemoyer and Stephenson.[4] The rest of the apparatus and method of measurement have been previously described.[6]

Energy was introduced and the temperatures measured by means of the platinum–rhodium resistance thermometer of laboratory designation R197. The thermometer had previously been calibrated against a helium gas thermometer.[7] During the present measurements the ice-point resistance was remeasured and was found to check 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.

The Heat Capacity of Ammonium Dihydrogen Arsenate.—The heat capacity measurements are presented in Table I and represented graphically in Fig. 1. They were measured in four series. The measurements of Series I extend from 90 to 300°K. The runs of this series near the transition are exploratory runs; consequently, the $\Delta H/\Delta T$ for some of these runs does not give true differential heat capacities. Series II consists of measurements with small temperature increments extending through the region of the transition, thus affording a better idea of the true heat capacities through this region. In Series I the heat of fusion of the ice has been eliminated for the two runs at 260.39 and 269.54°K. Series III and IV extend the measurements down to 15°K. The maximum deviation of the points from a smooth curve is 0.5% from 15 to 30°K.; 0.1% from 30 to 200°K.; and 0.5% from 200 to 300°K., with the exception of the results obtained near the ice-point and through the transition.

Values of the heat capacity read from a smooth curve through the experimental values of Table I are listed in Table II.

The same lack of thermal equilibrium was experienced in those measurements taken through the transition as was found in the case of the other isomorphous salts.[1,2,3]

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[1] Present address, Armstrong Cork Company, Lancaster, Pennsylvania.

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

[3] C. C. Stephenson and A. C. Zettlemoyer, *ibid.*, **66**, 1402 (1944).

[4] C. C. Stephenson and A. C. Zettlemoyer, *ibid.*, **66**, 1405 (1944).

[4a] We express our appreciation to Dr. A. C. Zettlemoyer, who assisted in the preparation of the ammonium dihydrogen arsenate.

[5] Prof. S. G. Simpson of this Laboratory kindly performed all the quantitative analyses of this salt.

[6] J. F. G. Hicks, THIS JOURNAL, **60**, 1000 (1938).

[7] R. W. Blue and J. F. G. Hicks, *ibid.*, **59**, 1962 (1937).

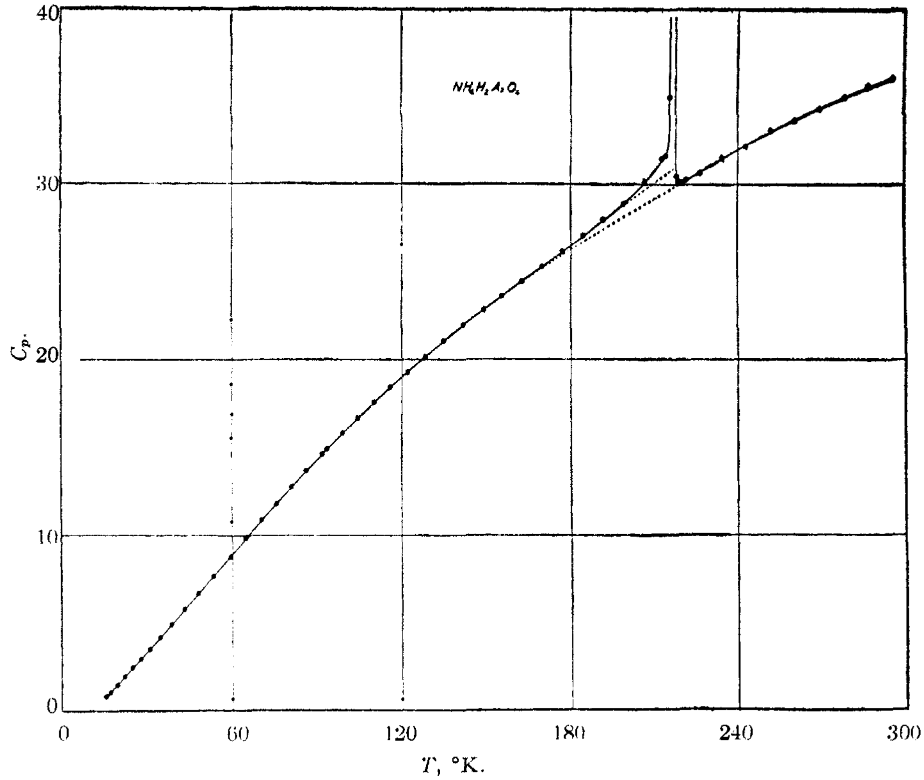

Fig. 1.—$NH_4H_2AsO_4$.

TABLE I

THE HEAT CAPACITY OF AMMONIUM DIHYDROGEN ARSENATE

Molecular weight, 158.966; 0°C. = 273.19°K.

T, °K.	ΔT	C_p, cal. deg.$^{-1}$ mole^{-1}	T, °K.	ΔT	C_p, cal. deg.$^{-1}$ mole^{-1}
	Series I			Series II	
93.54	5.413	14.94	214.01	2.349	31.65
98.93	5.381	15.81	215.58	0.771	34.97
104.43	5.649	16.68	216.12	0.324	236.4
110.18	5.878	17.59	216.45	0.399	279.4
115.89	5.595	18.43	217.14	1.127	47.57
121.90	6.441	19.28	217.85	0.527	30.47
128.26	6.297	20.15	218.50	0.937	30.18
134.83	6.785	21.04	221.43	5.109	30.27
141.85	7.224	21.96		Series III	
148.95	6.942	22.80	65.05	5.733	9.874
155.25	7.386	23.59	70.39	5.100	10.93
162.59	7.255	24.43	75.69	5.207	11.82
169.73	7.006	25.28	80.90	5.237	12.78
177.03	7.520	26.15	86.28	5.539	13.70
184.49	7.277	27.05	91.92	5.783	14.67
191.68	7.051	27.95		Series IV	
199.02	7.521	28.87	15.47	1.977	0.837
206.45	7.251	30.11	17.10	2.013	1.087
212.60	5.091	31.47	19.39	2.179	1.488
215.78	1.295	135.5	22.05	2.376	1.981
221.37	9.888	36.43	24.76	2.854	2.451
226.27	7.720	30.64	27.72	3.151	2.966
234.40	8.212	31.48	30.98	3.457	3.558
243.08	8.746	32.15	34.49	3.540	4.221
251.76	8.484	33.05	38.43	4.226	4.941
260.39	8.918	33.62	43.12	5.040	5.832
269.54	9.199	34.32	47.99	4.732	6.749
278.40	8.651	35.00	53.27	5.802	7.699
286.94	8.220	35.65	59.50	5.361	8.839
295.61	8.919	36.10	65.09	5.687	9.906

Transition Temperature.—The exact value of the transition temperature is rather difficult to determine due to the fact that the transition exhibits a definite hysteresis effect. Cooling and warming curves with varying thermal heads were taken. Two of these curves are shown in Fig. 2. It is to be noted that there is no definite break in the rate of cooling or warming. This effect was not experienced in the cooling or warming curves taken on the other salts. The transition temperature determined from the warming curve accurately checks the temperature indicated by the heat capacity data. The transition temperature was taken as 216.1 ± 0.5°K.

A cooling curve was determined from measurements taken in a simple cooling-curve apparatus. A much faster rate of cooling was used and the transition temperature was lowered to 214.1 ± 0.2°K.

Heat and Entropy of Transition.—Although the region of anomalous heat capacity occurs over a very narrow temperature range, it is practically impossible to draw a smooth curve representing the "normal" curve through the transition temperature range and have it join

TABLE II

THE HEAT CAPACITY OF AMMONIUM DIHYDROGEN ARSENATE

Values from a smooth curve through the observations.

T, °K.	C_p, cal. deg.$^{-1}$ mole^{-1}	T, °K.	C_p, cal. deg.$^{-1}$ mole^{-1}
15	0.780	160	24.14
20	1.584	170	25.30
25	2.483	180	26.48
30	3.392	190	27.70
35	4.315	200	29.02
40	5.247	205	29.82
45	6.173	210	30.74
50	7.100	211	30.94
55	8.034	212	31.15
60	8.963	213	31.38
65	9.897	214	31.64
70	10.82	216.5	Maximum
75	11.73	218	30.37
80	12.62	219	30.14
85	13.48	220	30.12
90	14.34	230	31.05
95	15.18	240	31.94
100	15.98	250	32.78
110	17.56	260	33.59
120	19.02	270	34.35
130	20.38	280	35.04
140	21.71	290	35.66
150	22.95	300	36.24

smoothly to both of the experimental curves above and below the transition. The two dotted curves in Fig. 1 represent an attempt to draw the highest plausible "normal" curve and the lowest "normal" curve. In calculating the heat and entropy of the transition, the heat content and entropy derived from these interpolated "normal" heat capacity curves are subtracted from the total heat content and entropy obtained from the experimental heat capacity measurements.

In single increments, the energy required to increase the temperature of one mole of $NH_4H_2AsO_4$ from 213.985 to 219.818°K. was found to be 376.96 cal. and from 213.610 to 219.430°K., 377.40 cal. These end-point temperatures are well outside the region of thermal instability. Using the heat capacity data, corrections have been applied in order to convert the two measurements to a common temperature interval for comparison. Thus the two values for the change in heat content between 213.5 and 219.5°K. are 382.7 and 383.0 cal. mole^{-1}. The accepted value was taken as 382.8 ± 0.4 cal. mole^{-1}. These data combined with the heat capacity data gave 1834.9 cal. per mole for the change in heat content between 162.50 and 221.00°K. From the "normal" heat capacity curves described above, values of 1628.6 and 1602.6 were found for the same temperature interval. Hence the two values of the heat of transition corresponding to the two "normal" curves are 206.3 and 232.3 cal. mole^{-1}.

Correspondingly, the total entropy change was

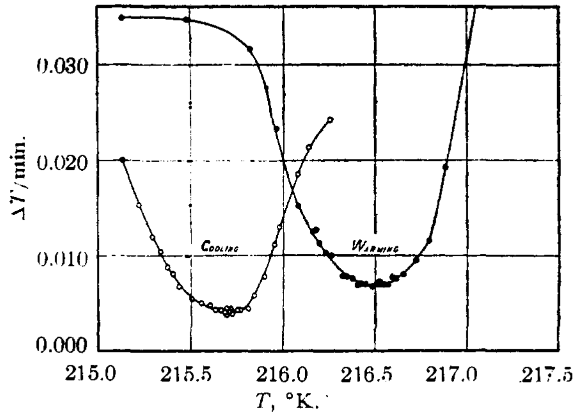

Fig. 2.

found by graphical integration of $\int C_p \, d \ln T$. The change in entropy in the region near the maximum in the anomaly was obtained by dividing the change in heat content 382.8 cal. mole^{-1} between 213.5°K. and 219.5°K. by the average temperature 216.50°K. The total entropy change between 162.50°K. and 221.00°K. was found to be 9.45 ± 0.01 cal. per mole per deg. Entropy changes corresponding to the two "normal" curves are 8.51 and 8.38 cal. per mole per deg. The most probable value of the entropy of transition is then 1.08 ± 0.05 cal. deg.$^{-1}$ mole^{-1}, and the lowest value that can be obtained by a reasonable "normal" curve, is 0.95 cal. deg.$^{-1}$ mole.$^{-1}$

This is to be compared with the entropy change of $R \ln 3/2 = 0.81$ cal. deg.$^{-1}$ mole^{-1}, predicted by the hydrogen bond theory.[8] The excess entropy change over that predicted by the theory is probably due to abnormal volume changes. In addition, it must be remembered that it is quite arbitrary what kind of curve is assumed for the "normal" heat capacities through the transition region. Thus it is felt that the experimental entropy change agrees well enough with the theoretical value to supply good evidence that hydrogen bonds are responsible for the transition in $NH_4H_2AsO_4$.

Entropy of $NH_4H_2AsO_4$ 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 4/3 D (137.2°K.) per mole of $NH_4H_2AsO_4$.

Table III is a summary of the calculations.

TABLE III

THE ENTROPY OF $NH_4H_2AsO_4$

0–15°K. Debye extrapolation	0.28
15–298.19°K. Graphical integration	40.84
	41.12 ± 0.10 cal. deg.$^{-1}$ mole^{-1}

Summary

The heat capacity of $NH_4H_2AsO_4$ has been

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

measured from 15 to 300°K. A maximum occurs in the heat capacity at 216.1 ± 0.5°K. The heat of transition is 220 ± 15 cal. mole^{-1} and the corresponding entropy change is 1.02 ± 0.07 cal. deg.$^{-1}$ mole^{-1}. The entropy of crystalline $NH_4H_2AsO_4$ at 298.19°K. is 41.12 ± 0.10 cal. deg.$^{-1}$ 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[1]

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,[1a] heavy ice[2] and sodium sulfate decahydrate.[3] If the crystal structure of the compound is known in detail this residual entropy may be calculated, and Pauling[4] 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 KH_2PO_4,[5] KH_2AsO_4,[6] and $NH_4H_2PO_4$,[7] the transition from the random to an orientated arrangement of the hydrogen bonds occurs at easily attainable temperatures and the entropy of transiton may be measured directly. This entropy change may be calculated by Pauling's method or by the alternative method of Slater[8]; 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[9] of $(NH_4)_2H_3IO_6$ is very similar to the structure of KH_2PO_4 in so far as the hydrogen bonds are concerned, except that the octahedral 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[10] in $(NH_4)_2H_3IO_6$ at 254°K., but the compound loses water and ammonia too rapidly to permit measurements on a sample of well-defined composition. The structurally similar salt, $Ag_2H_3IO_6$, 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 (Ag_5IO_6, $Ag_2H_3IO_6$, Ag_3IO_5, Ag_2HIO_5, $AgIO_4$, and perhaps others) exist, and the preparation of pure $Ag_2H_3IO_6$ requires a careful control of temperature and concentration. As a starting point, $Na_3H_2IO_6$ is prepared by the oxidation of $NaIO_3$ with chlorine in a basic solution.[11] This salt is dissolved in dilute nitric acid and treated with a silver nitrate solution in the ratio of two moles of $AgNO_3$ to one of $Na_3H_2IO_6$. A finely divided greenish-yellow precipitate of $Ag_2H_3IO_6$ is formed, but this precipitate usually changes into the red Ag_2HIO_5 with loss of water on standing for a day or more. A solution of 5N nitric acid is saturated with the salt at 80° (at this temperature all of the yellow salt is converted into Ag_2HIO_5), filtered at 40° to remove any $AgIO_3$ which has formed, and allowed to crystallize in an ice-bath. The solution is not heated above 80° 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° to remove this white precipitate since no more of it is formed at lower temperatures. The $Ag_2H_3IO_6$ forms so slowly that none starts to crystallize at this temperature, and it is usually necessary to allow the solution to crystallize for

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