A Calorimetric Study of Ammonium, Rubidium, and Potassium Hexafluophosphate

By L. A. K. Staveley, N. R. Grey, and M. J. Layzell

The Inorganic Chemistry Laboratory, Oxford University

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Dedicated to Prof. Dr. K. Clusius *on his sixtieth birthday*

Measurements have been made of the heat capacities of ammonium, rubidium, and potassium hexafluophosphate from ~ 20 °K to ~ 300 °K. The heat capacity curve of the ammonium salt shows two anomalous regions, and an order-disorder change also occurs in the rubidium salt. The potassium salt, however, undergoes a first-order transition with a large entropy change. The heat capacity of the ammonium and rubidium salts in the neighbourhood of room temperature (but not that of the potassium salt) is altered by cooling to low temperatures. In certain ranges of temperature it was unusually difficult with the rubidium salt to obtain reproducible heat capacity values. The results show that the rotation of the ammonium ion is not completely free, but they are consistent with almost free rotation in one degree of freedom and partially restricted rotation in the other two. The possible significance of the entropy changes of the various transitions is briefly discussed.

Although it is now known that free or almost free rotation of polyatomic ions or molecules in crystal lattices is a more rare occurrence than was at one time supposed, there is evidence that in particular cases the barrier hindering the rotation of a symmetrical ion such as the ammonium ion (at least for rotation about one axis) may be very low. For example, in the high-temperature (face-centred cubic) form of ammonium iodide the preferred orientation of the cation is that in which one N-H bond is directed towards a neighbouring iodide ion, and the barrier to rotation about this axis is so low (<100 cal./gm. ion) that at room temperature rotation in this degree of freedom is virtually free, while about the other two axes the ion executes torsional oscillations [1].

One of the methods by which the rotational or torsional movement of the ammonium ions in a lattice can be investigated is by measuring the molar heat capacity difference ΔC_p, where

$$\Delta C_p = C_p(\mathrm{NH_4X}) - C_p(\mathrm{MX}) - C_{\mathrm{int}}\,.$$

In this equation, $C_p(\mathrm{NH_4X})$ is the molar heat capacity of a particular ammonium salt, $C_p(\mathrm{MX})$ that of the *isomorphous* alkali metal salt with the lattice dimension nearest to that of the ammonium salt (which is usually the rubidium salt), and C_{int} is the calculable contribution from the internal vibrations of the ammonium ion. (Even at room temperature, C_{int} is quite small). It is reasonable to suppose that almost identical contributions to the molar heat capacity of each salt at a given temperature are made by (a) $C_p - C_v$, (b) the intramolecular vibrations of the anion, (c) the torsional oscillations of the anion. At temperatures sufficiently high for the lattice vibrations to make almost their maximum contribution to C_p (a condition which should be reached well below room temperature, especially if the anion is relatively large), ΔC_p will then be the contribution of the heat capacity from the torsional or rotational oscillations of the ammonium ion. For free three-dimensional rotation of these ions, ΔC_p will be $3\,R/2$: for fully excited simple-harmonic torsional oscillations it will be $3\,R$: while for an intermediate state of affairs, ΔC_p will increase with rising temperature to a maximum and then decrease asymptotically to the value for free rotation, the height and temperature of the maximum depending on the height of the barrier opposing rotation. One would expect to find the smallest barriers in those ammonium salts which have anions which are large but not highly charged and whose structure is such that the ammonium ions have very symmetrical environments. Two salts which meet these conditions and to which we have already applied the heat capacity method just outlined are ammonium stannichloride, $(\mathrm{NH_4})_2\mathrm{SnCl_6}$, and ammonium stannibro-

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[1] R. C. Plumb and D. F. Hornig, J. Chem. Phys. **21**, 366 [1953].

mide[2], $(NH_4)_2SnBr_6$. This investigation showed that the barriers to the rotation of the ammonium ion in these salts are quite low (~1000 cal./gm. ion), and from this it was possible to draw semi-quantitative conclusions about the charge distribution in the stannihalide ions.

In this paper we give results for ammonium fluophosphate, NH_4PF_6, and the corresponding rubidium and potassium salts. In these compounds, which are isomorphous at room temperature, the cations and the phosphorus atoms at the centres of the octahedral anions are arranged on a sodium chloride type lattice, but the anions are tilted with respect to the cubic axes. There is a similarity between the environment of the ammonium ion in ammonium fluophosphate and that in the high-temperature face-centred cubic form of ammonium iodide, in which, as has been stated, one-dimensional rotation of the ammonium ion is almost free. Moreover, the atoms which form the nearest neighbours of the ammonium ions, namely the fluorine atoms, cannot individually carry charges much in excess of $e/6$. For these reasons, NH_4PF_6 seemed to be an interesting salt to which to apply the heat capacity method used for the stannichlorides and stannibromides. However, unexpected complications were encountered. The ammonium salt was found to have two regions of anomalous heat capacity. Rubidium hexafluophosphate also showed a region of abnormal heat capacity, and the approach to thermal equilibrium was often so laborious that it was exceptionally difficult to obtain reliable heat capacity values. Experiments were therefore carried out on the potassium salt, although it was expected from the work of Bode and Clausen[3] that a transition would be encountered at about -25 °C which would limit the range available for comparison with the ammonium salt. In fact, the transition in the potassium salt occurs at $+0.7$ °C so that the comparison could only be made over a still more restricted temperature range. It has therefore not been possible to reach such definite conclusions about the torsional or rotational movement of the ammonium ions in NH_4PF_6 as was hoped, but at least the investigation has added to our knowledge of the physical properties of these interesting salts.

Experimental

The heat capacities of the three salts were measured from ~ 20 °K to ~ 300 °K, using the calorimeter described by Davies and Staveley[4].

Ammonium hexafluophosphate obtained from the Ozark-Mahoning Co., U.S.A., was twice recrystallized from water in a platinum dish. The rubidium salt was prepared by adding rubidium chloride solution to a solution of once recrystallized ammonium hexafluophosphate, and recrystallizing the product.

A sample of the potassium salt obtained from the Ozark-Mahoning Co. was twice recrystallized and then subjected to a complete analysis. The potassium was estimated as the tetraphenylboron salt. To determine the phosphorus and fluorine content, a weighed sample of the salt was fused with sodium hydroxide (diluted with fusion mixture) under conditions which minimized the possible escape of phosphorus pentafluoride. To determine the phosphorus content of the product, the phosphate was separated from the fluoride as silver phosphate, then precipitated twice as magnesium ammonium phosphate, and finally weighed as magnesium pyrophosphate. To estimate the fluoride, the product after fusion was distilled with sulphuric acid and the fluoride in the distillate (after suitable dilution) determined by titration with thorium nitrate solution using sodium alizarin red as indicator. The thorium nitrate solution was standarized against a solution of sodium fluoride. The analytical results were K, 21.20% (theory, 21.25); F, 62.23% (theory, 61.93); P, 16.88% (theory, 16.82).

Results

Ammonium fluophosphate

Our previous work on the stannichlorides and stannibromides revealed an unusual phenomenon, in that the heat capacities of these salts at higher temperatures (from roughly 150 °K to room temperature) proved to be affected by the thermal history of the sample[5]. At these higher temperatures the C_p values were found to have decreased after the sample had been cooled to the temperature of liquid nitrogen or below, and only after repeated cooling were reproducible values over the whole temperature range obtained. Each of the three salts studied in the present investigation was examined to see if it showed similar behaviour, which may possibly be connected with the presence of defects in the lattice, and it was found that for the ammonium and

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[2] R. G. S. Morfee, L. A. K. Staveley, S. T. Walters, and D. L. Wigley, J. Phys. Chem. Solids **13**, 132 [1960].

[3] H. Bode and H. Clausen, Z. anorg. Chemie **265**, 230 [1951].

[4] T. Davies and L. A. K. Staveley, Trans. Faraday Soc. **53**, 19 [1957].

[5] R. G. S. Morfee and L. A. K. Staveley, Nature, Lond. **180**, 1246 [1957].

rubidium salts C_p in the neighbourhood of room temperature was indeed altered by cooling the solid, while the potassium salt showed no detectable change in heat capacity after such treatment. The magnitude of the effect found with ammonium fluophosphate is shown in Fig. 1. The C_p values tabulated for this salt in Table 1 are the final reproducible values. Smoothed C_p values at regular temperature intervals are given in Table 2. The precision of the heat capacity measurements was 0.15% between 90° and 300 °K, and 0.7% between 20° and 90 °K.

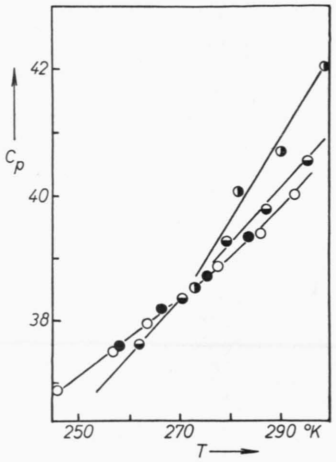

Fig. 1. Plot of the molar heat capacity C_p of ammonium fluophosphate against temperature, showing the change in the C_p values at higher temperatures after cooling the salt to low temperatures. The half-shaded circles are for two series of measurements made before the salt had been cooled below 255 °K. The full and open circles show the reproducible results obtained after cooling the sample to liquid air temperatures.

The ammonium salt was found to have two regions of anomalous heat capacity, as may be seen from the plot of C_p against temperature in Fig. 2. The upper anomaly is a characteristic λ-type transition with C_p reaching very high values. By making heat capacity measurements with suitably short heating periods, the temperature at which C_p reaches its maximum was found to be 191.8 °K. At the lower heat capacity anomaly the maximum C_p value was relatively low. In assessing the heat content and entropy changes associated with these two anomalies, a freehand curve was drawn joining up with the C_p curve below the lower anomaly and the C_p curve above the λ-point. The "extra" heat capacity above 148 °K was taken to belong to the λ-type anomaly, and that below it to the low-temperature anomaly.

Temp. (°K)	C_p	Temp. (°K)	C_p	Temp. (°K)	C_p
21.01	3.94	117.20	30.94	189.23	47.92
22.67	4.47	120.65	32.13	190.53	55.60
25.09	5.37	123.98	33.72		
28.73	6.47	127.85	36.21	197.54	33.93
34.35	8.39	129.55	37.51	203.61	33.93
41.15	10.42	131.22	37.45	216.91	34.63
47.79	12.61	134.22	35.67	224.18	35.18
54.10	14.29	139.50	31.71	231.96	35.88
60.49	16.45	142.04	31.20	238.94	36.37
65.70	18.02	145.31	30.82	246.16	36.91
70.36	19.16	147.65	30.95	257.28	37.51
75.10	20.54	151.15	31.01	258.44	37.60
80.04	22.05	153.37	31.17	263.97	37.94
84.98	23.35	159.64	32.10	266.74	38.19
89.89	24.61	162.00	32.30	270.35	38.58
94.72	25.66	167.82	33.42	275.25	38.71
99.24	26.59	170.31	34.01	277.72	38.84
102.14	27.15	174.31	34.95	283.94	39.32
103.55	27.45	183.58	37.80	286.40	39.39
106.10	27.92	186.18	40.62	291.85	39.86
114.09	29.82	………	…….	293.67	40.02

Table 1. Molar heat capacity C_p, in cal. deg.$^{-1}$ mole^{-1}, of ammonium hexafluophosphate. 1 cal. = 4.1840 abs. joules.

The entropy increase ΔS_t associated with the lower anomaly was obtained graphically from the plot of the "extra" C_p/T against T. For the upper, λ-type transition, the entropy increase from the onset of the transition to 10° below the transition temperature was obtained in the same way, and the remaining, major part of ΔS_t was assumed to be given by the ratio of the measured "extra" heat input on completing the transition from this stage and the transition temperature (taken as the temperature of maximum heat capacity). The division of the entropy into the "normal" contribution and that associated with the anomalies is rather arbitrary, but should not seriously affect the estimate of the total

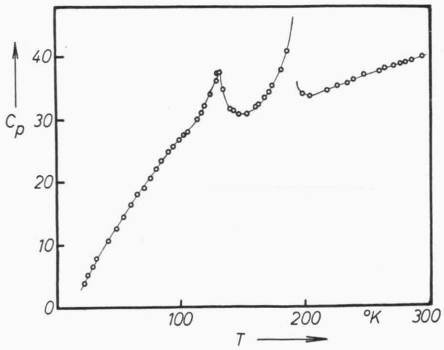

Fig. 2. Plot of the molar heat capacity C_p of ammonium hexafluophosphate against temperature.

entropy of the salt at 25 °C, which should be accurate to 0.2%. The entropy increase from 0 °K to 20 °K was estimated using a Debye function of the form $A\,D(\Theta/T)$, where the coefficient A and the parameter Θ were chosen to give the best fit with the experimental C_p values at 20°, 25°, and 30 °K.

Rubidium hexafluophosphate

As already mentioned, great difficulty was experienced in obtaining reproducible C_p values with this salt. As with the ammonium salt, the heat capacity in the neighbourhood of room temperature was affected by cooling to low temperatures, but this time in rather a different way. After loading the calorimeter and thoroughly evacuating the space around it, it was cooled to about 255 °K and a set of C_p measurements made up to ~300 °K. These showed no abnormality and could be reproduced on cooling the salt again to ~255 °K. (This temperature lies above the region of the major heat capacity anomaly.) After the salt had been repeatedly cooled to liquid air temperatures or below, and finally left to stand at room temperature for several days, a repetition of the C_p measurements from 255 °K to 300 °K gave a curve with a small but definite and reproducible hump (Fig. 3). This was taken to represent the normal behaviour of this salt in evaluating the final smoothed C_p values given in Table 2.

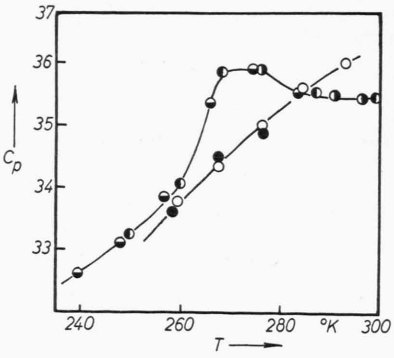

Fig. 3. Plot of the molar heat capacity of rubidium hexafluophosphate against temperature, showing the change in the heat capacity C_p at higher temperatures after cooling the salt to low temperatures. The full and open circles are for two series of measurements made before the salt had been cooled below 255 °K. The half-shaded circles show the reproducible results obtained in three series of measurements made after the sample had been cooled to liquid air temperatures.

Temp. (°K)	$C_p(NH_4PF_6)$	$C_p(RbPF_6)$	$C_p(KPF_6)$
20	3.63	4.04	2.56
25	5.27	5.98	4.17
30	6.96	7.91	5.62
35	8.56	9.58	7.05
40	10.09	10.95	8.60
45	11.64	12.00	10.03
50	13.15	12.92	11.00
55	14.69	13.83	12.12
60	16.24	14.7	13.12
65	17.71	15.55	13.96
70	19.17	16.35	14.55
75	20.63	17.05	15.20
80	22.04	17.7	15.79
85	23.37	18.2	16.44
90	24.63	18.74	17.07
95	25.73	19.20	17.59
100	26.74	19.63	18.10
105	27.75	20.03	18.65
110	28.79	20.41	19.29
115	30.03	20.77	19.85
120	31.73	21.46	20.43
125	34.36	22.30	21.10
130	37.70	23.08	21.68
135	33.90	23.77	22.21
140	31.57	24.42	22.78
145	30.87	25.12	23.50
150	30.94	25.83	24.00
155	31.34	26.56	24.65
160	32.07	27.33	25.24
165	32.94	28.13	25.80
170	33.94	28.98	26.41
175	35.00	29.89	26.98
180	36.36	30.87	27.52
185	38.87	32.04	28.06
190	—	33.43	28.61
195	—	35.13	29.13
200	—	37.52	29.64
205	33.60	—	30.13
210	34.03	—	30.67
215	34.46	30.70	31.11
220	34.90	31.08	31.60
225	35.32	31.48	32.18
230	35.71	31.87	32.76
235	36.08	32.36	33.29
240	36.43	32.63	33.84
245	37.76	32.95	34.41
250	37.09	33.22	35.03
255	37.41	33.65	35.60
260	37.73	34.26	36.19
265	38.06	35.24	35.06
270	38.38	35.94	36.94
275	38.71	35.86	37.31
280	39.03	35.68	37.56
285	39.36	35.56	37.65
290	39.67	35.50	37.70
295	40.00	35.46	37.81
300	40.33	35.44	37.89

Table 2. Smoothed values of the Molar Heat Capacity C_p, in cal. deg.$^{-1}$ mole^{-1}, of Ammonium, Rubidium, and Potassium Hexafluorophosphates.

The heat capacity measurements below 250 °K were complicated by a very slow change at temperatures between 60° and 90 °K. If the salt was cooled to and held at a temperature in this range, there was a spontaneous evolution of heat at a rate which was always very slow, which was a maximum at about

80 °K, and which decreased considerably over periods of the order of one hour. Although the change responsible for these effects appeared to involve only small amounts of heat, it nevertheless had a marked effect on the heat capacity measurements at higher temperatures, for once the salt had been cooled below 90 °K the C_p values at higher temperatures were irreproducible. However, so long as the sample was not cooled below 115 °K, reproducible heat capacity values were obtained which are recorded in Table 3, and which have been used to give the smoothed values of Table 2. In the experiments which gave the reproducible values above 115 °K there was a region of anomalous heat intake with the characteristics given in Table 4, which were also quite reproducible. (If, however, the sample was cooled to 60° to 90 °K and then heated, the anomaly was less marked and the temperature at which the heat capacity reached a maximum was displaced upwards by about 8°.) It proved possible to get reproducible C_p values from 20° to 60 °K by holding the salt at ~65 °K for about twelve hours and then cooling to 20 °K. From 65° to 115 °K, however, there is some uncertainty in the smoothed C_p values which may amount to as much as 3 per cent.

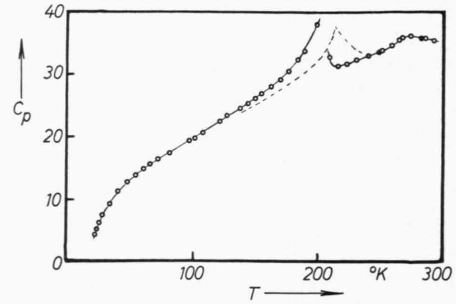

Fig. 4. Plot of the molar heat capacity C_p of rubidium hexafluophosphate against temperature. The dotted curve shows the course taken by the heat capacity after keeping the sample for some time between 60 and 90 °K.

Temp. (°K)	C_p	Temp. (°K)	C_p	Temp. (°K)	C_p
21.21	4.49	117.04	20.83	223.36	31.35
22.74	5.00	122.80	21.92	231.36	31.97
25.07	6.00	127.25	22.75	239.35	32.60
28.36	7.30	132.73	23.48	247.81	33.09
33.20	9.00	138.11	24.18	250.85	33.20
39.72	10.89	143.49	24.93	256.30	33.83
46.77	12.34	149.31	25.77	259.54	34.06
53.61	13.60	155.10	26.56	265.37	35.35
60.04	14.66	163.19	27.89	268.66	35.84
66.34	15.8	169.86	29.00	274.13	35.88
72.84	16.1	176.57	30.07	275.44	35.85
79.48	17.0	183.20	31.70	283.24	35.51
92.01	18.2	190.27	33.54	285.20	35.52
97.08	19.17	192.39	34.00	....	....
102.09	19.61	200.75	37.93	296.19	35.46
107.06	20.19	209.71	34.40	296.51	35.43
112.27	20.66	215.91	30.80		
116.58	20.87	216.80	30.91		

Table 3. Molar heat capacity C_p, in cal. deg.$^{-1}$ mole^{-1} of rubidium hexafluophosphate.

The estimates of the heat and entropy of the gradual transition culminating at 207 °K and of the total entropy of the salt at 25 °C which are given in Table 4 were made in the same way as the corresponding quantities for the ammonium salt.

Potassium hexafluophosphate

For this salt, the heat capacity was not dependent on its thermal history. C_p values from −40 °C to room temperature, made before the salt had been

	NH_4PF_6		$RbPF_6$		KPF_6	
Transition temp. ΔS_t	(191.8 ± 0.05) °K 2.23	gradual λ-point	(207 ± 0.5) °K 2.42	gradual	(273.87 ± 0.02) °K 6.87 ± 0.02	first order
Transition temp. ΔS_t	131.3 ± 0.1 °K 2.48	gradual	— —		— —	
ΔS, 0° − 20 °K	1.40 ± 0.03		1.55 ± 0.03		0.93 ± 0.03	
ΔS, 20° − 298.16 °K, (less entropy of transitions).	54.38		49.05		45.74	
Total ΔS, 0° − 298.16 °K	60.49 ± 0.12		53.02 ± 0.13		53.54 ± 0.13	

Table 4. Entropy results for ammonium, rubidium, and potassium hexafluophosphates. (All entropy values in cal. deg.$^{-1}$ mole^{-1}. ΔS_t = entropy of transition.)

cooled below $-40°$, were identical within the precision of the measurements in this range ($\pm 0.1\%$) with the values obtained after the salt had been kept at -180 °C for a fortnight. The observed and smoothed C_p values are recorded in Tables 5 and 2 respectively.

Temp. (°K)	C_p	Temp. (°K)	C_p	Temp. (°K)	C_p
21.62	2.97	122.29	20.70	238.57	33.69
24.50	3.91	129.29	21.48	244.65	34.29
28.74	5.285	135.85	22.32	246.53	34.50
34.90	7.29	141.42	23.00	248.37	34.79
43.90	9.80	147.89	23.76	252.11	35.14
53.53	11.84	154.20	24.53	255.04	35.44
61.39	13.58	159.34	24.96	261.97	35.48
67.66	14.23	165.50	25.87	264.33	35.64
72.61	14.83	171.72	26.46	268.60	37.18
76.87	15.75	184.31	27.88	277.88	37.52
82.02	15.99	190.69	28.67	282.30	37.71
87.63	16.81	197.59	29.29	283.15	37.43
93.10	17.44	205.33	30.06	286.39	37.70
98.37	17.82	205.71	30.13	288.32	37.69
103.98	18.48	213.54	30.92	290.93	37.74
109.89	19.17	221.14	31.74	293.55	37.73
115.83	19.94	229.69	32.89		

Table 5. Molar heat capacity C_p of potassium hexafluophosphate.

The transition temperature of the phase change, which from the work of BODE and CLAUSEN was expected to be about -25 °C, was in fact found to be 273.87 °K ± 0.01 °K. The transition is first order, and the transition temperature was measured by the usual method of measuring the equilibrium temperature attained at successive stages of the change from the low-temperature to the high-temperature form. After each heating, equilibrium was established in about an hour. The heat content and entropy increase associated with the transition are considerable (Table 4).

Discussion

The analysis of the heat capacity of the ammonium salt, with the object of elucidating the movement of the ammonium ion, is handicapped by the limited temperature range available for comparison with either of the other two salts. Owing to the variability in the heat capacity of the rubidium salt and to the lower transition in the ammonium salt, it is only in the range 215° to 245 °K that reasonable reliance can be placed on the values of ΔC_p, where

$$\Delta C_p = C_p(NH_4PF_6) - C_p(RbPF_6) - C_{\text{int}}.$$

In this limited temperature range, ΔC_p has an almost constant value of 3.7 to 3.8 cal. deg.$^{-1}$ (gm. ion.)$^{-1}$. [C_{int}, which amounts to 0.39 cal. deg.$^{-1}$ (gm. ion)$^{-1}$ at 25 °C was estimated from the interionic vibration frequencies given by WAGNER and HORNIG [6].] This value of ΔC_p is too large for free three-dimensional rotation of the ammonium ion, but could mean either that rotation about all three axes is restricted by a fairly low barrier, or else that rotation about one axis is almost free and in the other two degrees of freedom is to some extent restricted. The latter interpretation is the more probable. In NH_4PF_6, ammonium ions and hexafluophosphate ions are arranged on a face-centred cubic lattice. The N-F distance of 3.10 Å is considerably larger than the corresponding distance in ammonium fluoride (2.66 Å). Since in NH_4PF_6 the fluorine atoms must carry a considerably smaller charge than the fluorine ions in NH_4F, any hydrogen bonding is probably so weak as to be insignificant. Indeed, an NMR study on NH_4BF_4 showed that in this salt any hydrogen bonds are exceptionally weak, even though the N-F distance of about 2.83 Å is less than that in NH_4PF_6 [7]. In the face-centred cubic form of ammonium iodide, one N-H bond is directed towards an iodide ion, and rotation about this axis at room temperature is almost free, the energy barrier hindering rotation being <100 cal. In the other two rotational degrees of freedom the ammonium ions execute torsional oscillations. It is very likely therefore that the ammonium ion behaves similarly in NH_4PF_6, with one N-H bond directed at the phosphorus atom at the centre of an anion, and that there is even less hindrance to rotation about this bond than for the same motion in NH_4I. If in fact rotation in this degree of freedom is virtually free, then for a total rotational heat capacity of 3.7 to 3.8 cal. deg.$^{-1}$ (gm. ion)$^{-1}$ the average contribution for each of the other two degrees of freedom is ~ 1.4 cal. deg.$^{-1}$ (gm. ion)$^{-1}$, consistent with an energy barrier in these degrees of freedom of about 1000 cal.

Useful comparison of C_p for the ammonium and potassium salts is limited to the 25° or so above

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[6] E. L. WAGNER and D. F. HORNIG, J. Chem. Phys. **18**, 296 [1950].

[7] D. PENDRED and R. E. RICHARDS, Trans. Faraday Soc. **51**, 468 [1955].

the first order transition in the latter salt. In this range ΔC_p is surprisingly low, rising from ~ 1.3 cal. deg.$^{-1}$ mole^{-1} at the transition to ~ 2.0 cal. deg.$^{-1}$ mole^{-1} at 300 °K. It is of course not unknown for the persistence of local order in an order-disorder transition to lead to heat capacity values in the high temperature form which are above the "normal" values, and though the transition in the potassium salt is a first order phase change the rate of change of C_p with temperature above the transition is rather small, consistent with C_p immediately above the transition temperature being increased by a contribution which falls off rapidly with rising temperature. No reliable conclusions can therefore be drawn about the ammonium salt by comparison with the potassium salt, though this might be possible if the heat capacity measurements on both salts were extended to higher temperatures.

It remains to comment on the transitions found in the hexafluophosphate. In view of the very symmetrical nature of the anion, it is pertinent to ask to what extent the entropy increase on the passage of a low-temperature to a high-temperature form can be attributed to a number of distinguishable orientations or configurations of equal or nearly equal energy becoming available to the PF_6 ions. (Such a correlation has been sought for transitions in molecular crystals by Guthrie and McCullough [8] by considering the symmetry of the molecule in relation to that of the lattice.) The most striking transition is the first-order change in the potassium salt with its large entropy of transition ΔS_t of 6.87 e.u., which happens to be almost exactly equal to $R \ln 32$. It is likely that the high-temperature form of this salt is a more open structure than the low-temperature form (cf. the volume increase when an ammonium halide passes from a simple cubic to a face-centred cubic lattice), and that above the transition temperature the PF_6 ions can readily change from one orientation to another. Bode and Clausen concluded that at room temperature the anions in KPF_6 oscillate about cube diagonals so that the P-F bonds make maximum angles of 17° with these diagonals. Since four sets of cube diagonals pass through a phosphorus atom at a cube corner, a linear F-P-F grouping might choose any one of these four diagonals about which to oscillate, but this in itself could not account for the large ΔS_t. It is possible however that an X-ray diffraction study would not readily distinguish between the situation envisaged by Bode and Clausen and one in which the PF_6 ions oscillate not about the cube diagonals but randomly about axes making a small angle with these diagonals. For a PF_6 ion with one F-P-F grouping aligned in a particular direction further distinguishable orientations might be possible by virtue of this fourfold symmetry axis. It is also worth noting that Bode and Clausen report that associated with the vibrational movement of the PF_6 ions is a loss of their centre of symmetry by the rotation with respect to each other of the two groups of three fluorine atoms within any one anion. If there is more than one way of realising this for any one set of vibrational axes it would of course contribute to the entropy of transition.

Although NH_4PF_6 and $RbPF_6$ have no first-order phase change like KPF_6, the upper order-disorder transition in the former ($\Delta S = 2.23$) occurs over much the same temperature range as that in the latter ($\Delta S = 2.42$ e.u.), and it would seem that both are probably associated with the PF_6 group. Possibly here in the larger unit cells (as compared with the potassium salt) the PF_6 ions at room temperature do in fact oscillate about the cube diagonals. Utilisation of the set of four of these by any one ion could account for an entropy increase of $R \ln 4 = 2.75$ e.u. It may be noted that there are other instances of structural differences between a potassium salt on the one hand and the corresponding rubidium and ammonium salts on the other. Thus, while Rb_2SnBr_6 and $(NH_4)_2SnBr_6$ are isomorphous with the anti-fluorite structure, K_2SnBr_6 is said to be tetragonal [9], while K_2SnCl_6 shows a λ-point whereas the ammonium and rubidium salts do not [2].

Finally, if the upper transition in NH_4PF_6 is associated with randomization of the orientation of the anions, the lower, more gradual transition may be due to a similar type of disorder affecting the ammonium ions. Unfortunately, nothing is known at present in detail about the structure of the ammonium salt at low temperatures, and it is in any case difficult to assess the uncertainty in the estimate of 2.48 e.u. for the transition entropy.

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