On the Thermal Transition in Solid Deuterio-Ammonium Sulphate, $(ND_4)_2SO_4$.

By Isamu NITTA and Katsuji SUENAGA.

(Received December 28, 1937.)

In a previous paper⑴ it has been reported that deuterio-ammonium chloride, ND_4Cl, shows like ordinary one the phenomenon of excessive specific heat with a discontinuity at about -24°C., this being roughly by six degrees higher than the corresponding transition temperature of ordinary ammonium chloride. The work had been carried out in an attempt to get some closer informations concerning the nature of such peculiar kind of thermal transitions, which, according to the rather qualitative explanation of Pauling,⑵ are due to the onset of rotations of the atomic groups in crystals. As a continuation of the investigation, thermal and dilatometrical measurements of the transition of deuterio-ammonium sulphate, $(ND_4)_2SO_4$, have now been made, of which an account will be given in the present paper.

The material used in the present experiment was prepared in the following way. The starting substances of the preparation were deuterium oxide from Norsk Hydro-Electrisk Kvaelstofaktieselskab, magnesium metal from Schering-Kahlbaum A. G., potassium nitrite, ammonium chloride and sulphur trioxide, the last three being pure chemicals of E. Merck. Using magnesium powder and chemical nitrogen from potassium nitrite and ammonium chloride, magnesium nitride, Mg_3N_2, was first produced. By the reaction of this nitride with deuterium oxide, heavy ammonia, ND_3, was then obtained and this was led into heavy sulphuric acid, D_2SO_4, from D_2O and SO_3, to produce the final material $(ND_4)_2SO_4$, the whole procedure being carried out in an evacuated system. The sample thus obtained was determined to contain 93.5 per cent of deuterium. A Debye-Scherrer photograph of this sample showed that the crystal structure is the same as that of ordinary ammonium sulphate, having the unit of practically the same dimensions.

By use of a micro-dilatometer of ordinary type, measurements were made with ordinary and heavy sulphates in a temperature range from

---

(1) I. Nitta and K. Suenaga, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **32** (1937), 83. See also A. Smits and C. J. Muller, *Nature*, **139** (1937), 804.

(2) L. Pauling, *Phys. Rev.*, **36** (1930), 430.

-55 to -40°C. Carbon disulphide was chosen as the dilatometer liquid for the reason that the molecule of this compound contains no hydrogen atom. It is found from the measurements that both salts show quite similar volume-temperature curves and the transitions are accompanied by abrupt contraction of their volumes as the temperature is being raised, the relative change $\Delta V/V$ being approximately a half per cent for both salts. In the case of the ordinary salt the sudden change in volume occurs at -50.3°C. when the temperature is being lowered and -49.5°C. when raised. For the heavy salt the corresponding temperatures are -49.8 and -49.0°C. *From these, the dilatometrical values of the transition* temperatures are determined to be -49.9°C. for $(NH_4)_2SO_4$ and -49.4°C. for $(ND_4)_2SO_4$. Besides carbon disulphide, toluene was also used, in another dilatometer, to study the transition of ordinary ammonium sulphate with higher precision, and the result is given in Fig. 1. In spite of the early report that R. Ewald⁽³⁾ failed to find out dilatometrically the transition of $(NH_4)_2SO_4$, it is certain from the present experiment that it really exists and can be observed by use of a dilatometer, if the temperature intervals are chosen small enough.

In order to confirm these obtained values for the transition points and, at the same time, to determine the heats of transition, cooling and heating curve measurements were also carried out with the aid of the same calorimeter as that used for the specific heat determination, which will be described below. The amount of sample taken was 8.35 g. in the case of the ordinary salt and 8.58 g. in the other. The heating curves were prepared with the energy supply of about 2 calories per minute. The obtained curves are shown in Fig. 2. Ordinary ammonium sulphate exhibits an arrest at -49.5°C. on heating and it shifts to -50.7°C. on cooling. The corresponding temperatures for the heavy ammonium sulphate are -48.9 and -50.2°C. Taking the mean of the both arrests on heating and cooling curves, the transition temperatures are given to be -50.1°C. for $(NH_4)_2SO_4$ and -49.6°C. for $(ND_4)_2SO_4$ in good agreement with the dilatometric values obtained above. From the data of the heating curves the heats of transition were determined for both ordinary and heavy salts. They are 210 at -49.5°C. for the former and 225 at -48.9°C. for the latter in calories per gram-ion of ammonium. These values are very remarkable in such a respect that Crenshaw and Ritter⁽⁴⁾ gave from their specific heat measurement as the heat of transition of ordinary ammonium sulphate the value 485 cal./gram-ion, which is more

---

(3) R. Ewald, *Ann Physik*, **44** (1914), 1223.

(4) J. L. Crenshaw and I. Ritter, *Z. physik. Chem.*, B, **16** (1932), 143.

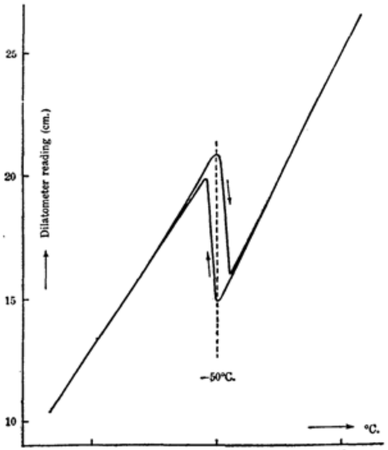

Fig. 1. Dilatometric curve of $(NH_4)_2SO_4$.
The liquid : toluene.
Sample taken : 8.02 g.

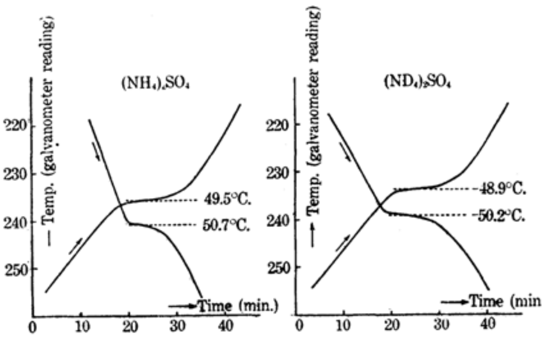

Fig. 2. Cooling and heating curves.

than double as large as the present value 210. This great disagreement seems to be due partly to the difficulty in computation of the heat of transition from the specific heat data and partly to their obtained data themselves, which are always somewhat too high as compared with the values of the present specific heat measurement (Table 1), and also judging from the molecular heat 44.80 cal. at 29°C. obtained by R. Ewald.⁽³⁾

The specific heats of ordinary and heavy ammonium sulphates were measured in the range from −180 to +25°C., using an improved vacuum calorimeter of the Nernst type. This calorimeter is made of copper and nickel-plated, its dimensions being 2 cm. in diameter and 4 cm. in height. There are six radial vanes, about 0.2 mm. thick, welded on the inside wall of this calorimeter in order to secure quick and effective conduction of heat into the crystalline sample. Being surrounded by a copper vessel, which is also nickel-plated and whose temperature can be controlled electrically, the calorimeter is put into an enclosed glass system to be evacuated. The samples taken were the same as those used for the cooling and heating curve measurements, viz. 8.35 g. of $(NH_4)_2SO_4$ and 8.58 g. of $(ND_4)_2SO_4$. In each measurement 5 to 20 calories of energy were supplied electrically to the calorimeter and the temperatures were measured by means of copper-constantan thermocouples. The obtained molecular heats C_p are shown in Tables 1 and 2. They are also plotted in form of the molecular heat-temperature curves in Fig. 3. The general features of the curves are similar to those of ordinary and heavy ammonium chlorides. The discontinuous fall of specific heat begins at −50°C. in the case of ordinary ammonium sulphate and at −49.5°C. in the other. These temperatures of transition agree very well with those found on the volume-temperature and thermal analysis curves. As in the case of deuterio-ammonium chloride, the anomalous rise of the specific heat curve of the heavy sulphate begins at a relatively lower temperature as compared with that of the ordinary one. However, it is not certain whether this is characteristic of ND_4 ions, or due to the presence of lighter

Table 1. Molecular heat of $(NH_4)_2SO_4$.

t°C.	Mol. heat	t°C.	Mol. heat	t°C.	Mol. heat
−180	19.5	−90	38.0	−47.5	42.3
−170	20.9	−80	43.0	−45	40.4
−160	22.6	−70	47.2	−40	40.9
−150	25.2	−60	55.2	−30	42.2
−140	26.8	−55	63.4	−20	43.3
−130	29.2	−52.5	70.7	−10	44.4
−120	31.4	−51.0	80.1	0	44.8
−110	33.6	−50.5	103.	+10	45.5
−100	36.4	−49	53.8	+20	46.0

Table 2. Molecular heat of $(ND_4)_2SO_4$.

t°C.	Mol. heat	t°C.	Mol. heat	t°C.	Mol. heat
−180	23.0	−90	47.2	−47.5	45.9
−170	25.2	−80	50.6	−45	44.8
−160	27.8	−70	54.2	−40	45.8
−150	30.2	−60	60.2	−30	45.9
−140	33.0	−55	67.8	−20	46.4
−130	34.2	−53	75.9	−10	47.2
−120	37.6	−51	92.3	0	48.3
−110	39.6	−50.5	107	+10	49.8
−100	43.2	−48.5	50.2	+20	50.6
				+25	51.5

components. Besides this peculiarity the curve for the heavy compound lies always higher than that for the ordinary one.

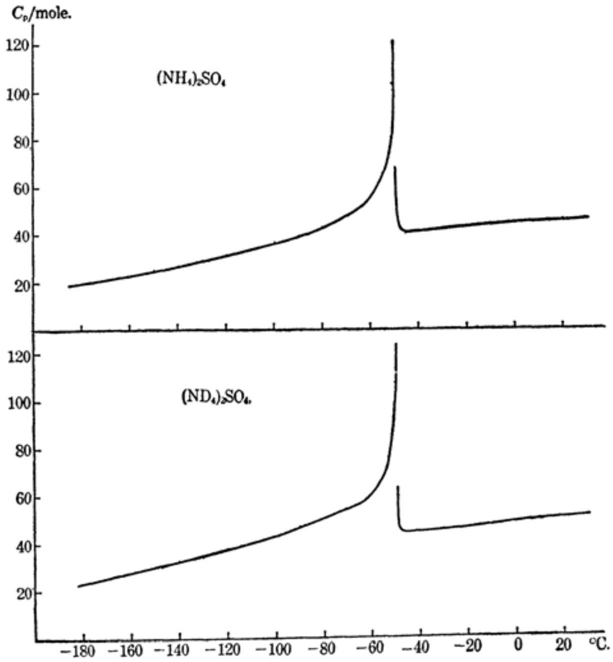

Fig. 3. Molecular heat-temperature curves.

For the reason of analogy, it would be natural from the observations on ordinary and heavy ammonium chlorides to expect that the transition point of heavy ammonium sulphate would be at least a few degrees higher than that of the ordinary sulphate. In the actual case, there was found a temperature shift of not more than a half degree. Perhaps this suggests that the phenomena of such transitions would not be so simple, if one tries to give a quantitative explanation of them. From the point of view of Pauling and Fowler,(5) it seems not impossible to imagine that, in the case of an oxy-acid, the interaction between deuterio-ammonium ion and the surrounding oxygen atoms would be weaker than that in the ordinary ammonium salt and that such effect would cancel out the opposing tendency of raising the transition temperature due to the doubling of the moment of inertia, brought about by the substitution of deuterium

---

(5) L. Pauling, *loc. cit.*; R. H. Fowler, *Proc. Roy. Soc.* (London), A, **149** (1935), 1; A, **151** (1935), 1; see further his book, "Statistical Mechanics," 2nd Ed., 789 (1936).

in the rotating ammonium ion. Further discussion will be reserved until the investigation is extended to other deuterio-ammonium salts. Only it will be added that, though there are structurally two kinds of ammonium ions in the crystal lattice, the one is surrounded by nine and the other by ten oxygen atoms, there was found single transition point without any observable fine structure in the volume-temperature, thermal analysis, and molecular heat-temperature curves.

In conclusion, we wish to express our thanks to Mr. M. Koizumi for the determination of deuterium content and also to the Hattori Hôkôkwai for a grant.

Laboratory of Physical Chemistry, Faculty of Science,
Osaka Imperial University.