with various reagents, such as silver oxide in benzene, potassium hydroxide in ether, aqueous potassium hydroxide, in an attempt to eliminate hydrogen chloride and form a cyclic ketimine. No reaction occurred in anhydrous media, and aqueous alkali decomposed the compound to give benzilic acid.

NOTRE DAME, INDIANA RECEIVED AUGUST 9, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF IDAHO]

Thermal Transitions in Ammonium Compounds[1]

BY HAROLD P. KLUG[2] AND WAYNE W. JOHNSON[3]

The phenomenon of molecular rotation in crystalline solids has been treated theoretically by several investigators.[4] Systematic investigations of those groups of compounds in which molecular rotation might be expected to occur have not as yet been made. In fact most of the experimental data on this phenomenon thus far have come as more or less incidental findings of studies with other ends in view. An exception would be the dielectric constant studies on solids.[5] We have been interested in the systematic investigation of these compounds for the purpose of locating the transitions where molecular rotation sets in. The purpose of this paper is to report some results of the investigation of a series of ammonium compounds for thermal transitions which might be interpreted as molecular rotation transitions.

By means of the method of differential temperatures we have investigated the warming curves of these substances over the temperature range from −70 to +40°. The ammonium halides had been observed to show such transitions in the temperature range between −45 and −30°.[6] As pointed out by Pauling,[4a] the temperature at which rotation sets in may be expected to decrease with increase in the size of the anion. Other hindrances to rotation, however, may be present and exert their influence, thus preventing the inception of rotation until a somewhat higher temperature if at all. At the beginning of this study it was anticipated that crystals of most ammonium compounds would show such rotational transitions, and at temperatures below −30°. The studies in this paper were limited on the low temperature side by the refrigerant available, solid carbon dioxide. Further studies in the future will take these investigations down to liquid air temperatures.

Experimental

The experimental procedure and equipment were similar to those used in the studies of thermal transitions in hydrates.[7] The copper block for the sample and neutral body was gold plated so that the materials might be placed directly in it without glass protecting tubes. Both single and triple junction copper–constantan differential thermocouples were used. The temperature thermocouples (of same material) were calibrated at the melting points of sodium sulfate decahydrate, carbon tetrachloride, mercury, and chloroform. They were used with a deviation curve and the standard calibration table of the "I. C. T."[8] A photographic recording device[9] was available, during the latter part of the investigation, for the automatic and continuous recording of the differential curves. Using the triple junction differential thermocouple with this device, a temperature difference of 0.01° between its junctions gave a deflection of approximately 7.25 cm. on the photographic paper.

The ammonium compounds used were Mallinckrodt "Analytical Reagent" or Baker "C. P. Analyzed" salts. No further purification was deemed necessary for this study. Where possible they were ground to pass through a 100-mesh sieve, otherwise they were ground as fine as could readily be attained. The neutral body was sodium chloride, Baker "C. P. Analyzed Special Crystals," ground to 100 mesh.

Since ammonium chloride and bromide had had the most work done on them in the past, they were chosen for investigation as a check on our method. Other ammonium compounds which had been studied previously were investigated to obtain a more accurate value for their transition temperatures. In the above cases the entire tem-

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(4) (a) Pauling, *Phys. Rev.*, **36**, 430 (1930); (b) Stern, *Proc. Roy. Soc.* (London), **A130**, 551 (1931); (c) Nielsen, *J. Chem. Phys.*, **3**, 189 (1935); (d) Frenkel, Tode and Ismailow, *Acta. Phys. U. R. S. S.* **1**, 97 (1934); (e) Frenkel, *ibid.*, **3**, 23 (1935); (f) Fowler, *Proc. Roy. Soc.* (London), **A149**, 1 and **A151**, 1 (1935); (g) Devonshire, *ibid.*, **A153**, 601 (1936).

(5) Smyth, *Chem. Rev.*, **19**, 329 (1936). A large list of references on the subject accompanies this article.

(6) Crenshaw and Ritter, *Z. physik. Chem.*, **B16**, 143 (1932).

(7) Taylor and Klug, *J. Chem. Phys.*, **4**, 601 (1936).

(8) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, Vol. I, 1926, p. 58.

(9) Klug, *Northwest Science*, **11**, 36 (1937).

TABLE I

TRANSITIONS IN AMMONIUM COMPOUNDS

Compound	Number of determinations	Transition pcint, °C.			
		This study	Previously reported		
NH_4Cl	7	−30.54 ± 0.10	-30.4^6	−30.52	-30.79^{10}
NH_4Br	5	−38.12 ± .10	-38.0^6	−38.78	-38.81^{11}
NH_4I	6	−41.65 ± .20	-42.5^6		
$(NH_4)_2SO_4$	5	−49.71 ± .20	-50.7^6		
$(NH_4)_3AsO_4{\cdot}3H_2O$	5	−56.02 ± .10	....		
$(NH_4)_2Cr_2O_7$	5	− 2.40 ± .20	....		
$NH_4H_2PO_4$	5	+18.9 ± 2.5	....		

perature range, −70 to 40°, was not investigated, merely the range in the vicinity of the known transitions. Compounds not previously studied were examined first over the entire temperature range. If evidence for a transition was found, the compound was given a detailed study over the range in this vicinity.

Results and Discussion

The change of slope of the temperature–time curve in most cases is not sharp enough (Figs. 1 and 2) to be used for locating the transition temperature, because the heat of transition is usually small. Hence, the temperature of the transition, in every case, was taken as the maximum on the differential curve. This has been the customary practice in locating these transitions in ammonium compounds, since most of them show a gradual change in specific heat (see Fig. 1 for ammonium bromide) over a considerable temperature range below the transition. Of those compounds studied only ammonium arsenate shows an abrupt break before the maximum, Fig. 2.

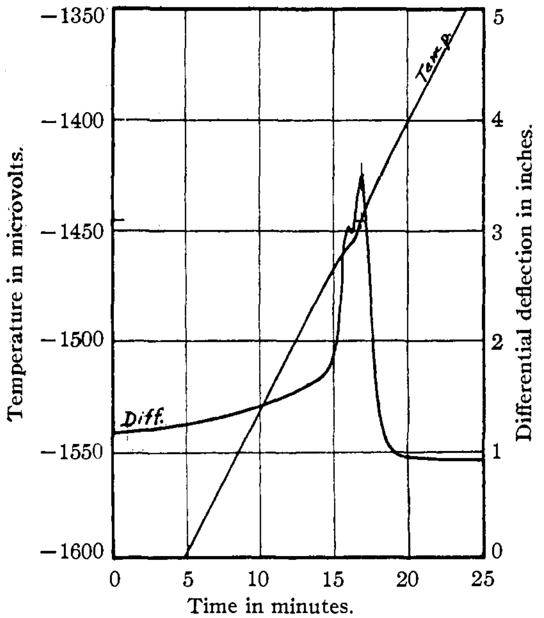

Fig. 1.—Typical warming curves (traced from the photographic record) for the ammonium bromide transition. Note the inflection on the left side just below the maximum.

In Table I are the tabulated results for those compounds which showed transitions.

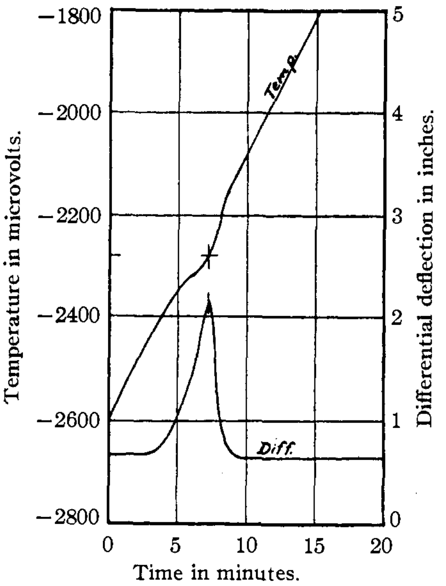

Fig. 2.—Typical warming curves (traced from the photographic record) for the ammonium arsenate transition.

The value found for the transition in ammonium chloride is in very good agreement with that, −30.52°, reported by Smits and MacGillavry[10] on heating. Their other value, −30.79°, was obtained on cooling. The values reported by Smits, Ketelaar, and Muller[11] for the ammonium bromide transition are lower than our value and are more nearly in agreement with the inflection point reported below. The above results, however, were considered to constitute a satisfactory check on our method. The values we report for the iodide and sulfate are believed to be better than those of earlier workers.

The curves for ammonium bromide (Fig. 1)

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[10] Smits and MacGillavry, *Z. phsyik. Chem.*, **A166**, 97 (1933).

[11] Smits, Ketelaar and Muller, *ibid.*, **A175**, 359 (1936).

are of particular interest since they seem to indicate a fine structure for the transition. All curves show the inflection on the left side just below the maximum, at a temperature of −38.53 ± 0.10°. That this point has not been observed before is no doubt due to the fact that it would be extremely difficult to detect by any means other than photographic. Its significance is not quite clear. Pauling has suggested[4a] that possibly molecular rotation sets in first about one directional axis in the crystal, and then later about other axes. This seems to be the case for hydrogen bromide which shows three transitions at −184.1, −160.1, and −156.1°. It is possible that this inflection marks the inception of rotation of the NH_4^+ ion about one axis, and that the maximum at −38.12 ± 0.10° marks the inception of rotation about all possible axes.

The transition observed for ammonium arsenate falls in the expected temperature range for rotation of the ammonium ion. The transitions in the dichromate and primary phosphate do not fall in the expected temperature range, and further that of the phosphate is somewhat more gradual than the others observed. If they are due to rotation of the ammonium ion, other factors must be at work in these cases which hinder the motion until higher temperatures are reached. The rotation of an atom group in a crystal may be blocked by its size, or the presence of other atom groups.[5] The possibility of hydrogen bond formation in the case of ammonium compounds of the oxy acids also presents itself as a factor in hindering rotation. Investigation of this factor is underway.

The following ammonium salts were also studied but no transitions were observed in them: chromate, borate, carbonate, nitrate, oxalate, persulfate, secondary phosphate, and tartrate. Crenshaw and Ritter[6] also report no transition for the oxalate, but found a well defined one for ammonium nitrate at −60.4°. Our failure to locate the ammonium nitrate transition we feel to be due to our inability to cool the sample far enough below the transition to be certain to freeze out the molecular rotation. This will be investigated further.

Acknowledgment.—We are indebted to the Northwest Scientific Association for a grant which made possible the building of the photographic recording device.

Summary

A series of ammonium compounds has been investigated in the temperature range −70 to +40° for thermal transitions which might be due to rotation of the ammonium ion. The following transitions were observed: chloride, −30.54 ± 0.10°; bromide, −38.12 ± 0.10°; iodide, −41.65 ± 0.20°; sulfate, −49.71 ± 0.20°; arsenate, −56.02 ± 0.10°; dichromate, −2.40 ± 0.20°; and primary phosphate, +18.9 ± 2.5°. The transition in the bromide seems to show a fine structure. The following exhibited no transitions: borate, carbonate, chromate, nitrate, oxalate, persulfate, secondary phosphate, and tartrate.

MOSCOW, IDAHO RECEIVED JUNE 16, 1937

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF THE STATE UNIVERSITY OF IOWA]

The Potential of the Silver–Silver Thiocyanate Electrode

BY J. N. PEARCE AND LOTHROP SMITH

Any slightly soluble salt of a metal may form, potentially, a good electrode, provided the electrode is perfectly reversible and the metallic salt is stable in solution. In this paper we present briefly the results obtained from a study of the silver–silver thiocyanate electrode.

Materials and Apparatus.—The silver thiocyanate was prepared by mixing dilute solutions of silver nitrate and potassium thiocyanate in the dark. The product was washed thoroughly and stored under conductivity water.

All solutions of potassium thiocyanate were prepared on the weight molal basis, free from dissolved oxygen, and were stored under hydrogen.

The silver crystals were prepared in the manner described by Pearce and Wirth.[1]

All other materials were purified by approved methods.

The electrodes were prepared by a method similar to that described by Linhart.[2] Each half-cell contained either four or five individual electrodes. As a reference, a second cell of each type was kept in the thermostat under exactly parallel conditions. Immediately before and after each determination of electromotive force, the electrodes used were checked against those of the reference cells. All electrodes checked within 0.01 mv. in every case.

A large oil thermostat regulated at 25° was used, and

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[1] Pearce and Wirth, THIS JOURNAL, **55**, 3569 (1933).

[2] Linhart, *ibid.*, **41**, 1175 (1919).