327. *The Effect of Particle Size and Deuterium Substitution on the λ-Point in Ammonium Chloride.*

By D. G. Thomas and L. A. K. Staveley.

The final stages of the λ-points in ammonium chloride, monodeutero-ammonium chloride, and trideuterammonium chloride have been examined dilatometrically with temperature control to ~ ±0·002°. The transitions in the partly deuterated salts, like that in ammonium chloride, reach completion almost isothermally, and hysteresis is associated with the nearly vertical part of the volume–temperature curves. This is in contrast to the transition in tetradeuterammonium chloride which is known to be continuous throughout and free from hysteresis.

The salts examined were prepared by reaction of equimolecular quantities of the component gases. The products were found by electron-microscope examination to consist of very small crystals. The hysteresis loop for these small crystals of ammonium chloride was appreciably narrower than that for larger crystals, but the mean transition temperature was almost unchanged.

A careful dilatometric investigation by Smits and his co-workers of the λ-point transitions in ammonium chloride and tetradeuterammonium chloride revealed interesting qualitative differences [Smits and MacGillavry, *Z. physikal. Chem.*, 1933, *A*, **166**, 97 (NH_4Cl); Smits, Muller, and Kröger, *ibid.*, 1937, *B*, **38**, 177(ND_4Cl)]. Whereas the transition in the tetradeuter-salt is completely continuous and without hysteresis, that in ammonium chloride is discontinuous (*i.e.*, isothermal) in its closing stages, with a hysteresis loop ~0·3° wide. The object of the experiments described in this paper was to discover whether there is a gradual change in these characteristics between the extremes of ammonium chloride and tetradeuterammonium chloride, or whether on replacement of hydrogen by deuterium the discontinuity in the transition and the hysteresis disappear before substitution is complete. Ideally, such experiments would be performed on the salts, mono- and tri-deuterammonium chloride, each containing one kind of cation only, *i.e.*, such that every cation in the first salt, for example, would be NH_3D^+. An attempt was made to prepare such samples of mono- and tri-deuterammonium chloride by slow reaction of equimolecular quantities of ammonia and deuterium chloride, and tri-deuterammonia and hydrogen chloride, respectively, in a dry atmosphere at 0°, though without a spectroscopic investigation there is no guarantee that isotopic redistribution did not occur during the preparation.

Crystals of ammonium chloride, prepared in this way from ammonia and hydrogen chloride, were shown by the electron microscope to be extremely small. Since little is known of the effect of crystal size on gradual transitions, it was thought worth while to compare the behaviour of this product with that of much larger crystals obtained from it by sublimation. The same comparison of the small with the sublimed crystals was also carried out with mono- and tri-deuterammonium chloride. Here, sublimation not only increases the crystal size, but almost certainly brings about as well some isotopic redistribution.

Experimental.

For the investigation of hysteresis effects a dilatometric method is undoubtedly the best, since the measurements are made isothermally, and volume changes can be determined with great precision. Each transition was studied in this way over a range of a few degrees. The nature of the problem is such that it demands (*a*) a high degree of temperature control, (*b*) extreme purity of the materials. With the thermostat described below, the temperature was controlled to within ±0·002°.

Dilatometers.—For the investigation of a salt, two similar dilatometers were used, one for the small crystals, and one for the large ones obtained from them by sublimation. The bulb had a capacity of 7—8 c.c. and held about 3 g. of salt; the calibrated portion of the vertical capillary in which volume changes were observed had a length of 36 cm. and a cross section of 0·002 sq. cm. In a preliminary investigation of the small crystals in ammonium chloride a modified dilatometer was used in which the graduated capillary was in a horizontal position and mercury was used as the confining fluid. The magnitude of the volume change accompanying the transition as found with this apparatus was appreciably greater than that recorded by Smits *et al.* (*loc. cit.*); furthermore, it was observed that when the pressure on the mercury surface was increased by about an atmosphere there was an apparent volume change in the dilatometer of the order of 1 c.c. That this was not due to gas in the dilatometer (an extremely unlikely contingency in view of the thorough evacuation of the salt before admission of mercury), was shown by the fact that the volume changes consequent upon the progressive increase in pressure did not conform to those predicted by the gas laws. Electron-microscope photographs (see below) showed that the crystals were extremely small, and these curious volume changes were ascribed to the effect of pressure in forcing the mercury, which presumably does not wet ammonium chloride, into the many minute crevices that must have been present between such small crystals. This appears to be a serious drawback to the use of mercury as a dilatometric fluid when examining small particles; otherwise it has much to recommend it (Bekkedahl, *J. Res. Nat. Bur. Stand.*, 1949, **43**, 145). It was accordingly decided to use carbon disulphide as the confining fluid, and in order to examine the effect, if any, of crystal size on the nature of the transition, samples of large and small crystals were compared simultaneously in two dilatometers, the large crystals being made from the small by sublimation.

The dilatometers were filled with salt through a tube joined on to the bulb which was subsequently sealed off, the weight of salt being obtained by difference. This operation involved exposure of the salts to the atmosphere for a short time. The dilatometers were then sealed on to the vacuum system, and thoroughly evacuated through both the capillary tube and a wider tube joined directly to the bulb which was later sealed off. Carbon disulphide, purified by shaking with mercury and fractionation, was poured into a trap system, with mercury cut-offs (Shapiro, *Analyt. Chem.*, 1949, **21**, 888) in place of greased taps, dried with phosphoric oxide, and carefully degassed, after which it was distilled into the evacuated dilatometers.

After adjustment of the amount of fluid so that the transition occurred when the meniscus was near the centre of the capillary, the tops of the dilatometers were sealed off.

Variations due to changes in the room temperature of the volume of carbon disulphide which was not in the thermostat, were approximately corrected for by observing the variations in a " dummy " capillary similar to those of the dilatometers, but terminating just above the thermostat fluid.

The work of Smits *et al.* (*loc. cit.*) and others has indicated that the hysteresis effects cannot be eliminated or materially altered by waiting for periods of time of the order of a day. We have accepted this and have carried out no further investigations of the point. Above or below the nearly vertical limbs of the hysteresis loops the volume became constant almost at once; on the limbs themselves the volumes became virtually constant after one or two hours.

Thermostat, Temperature Control, and Measurement.—The thermostat used was similar to that described by Scott and Brickwedde (*J. Res. Nat. Bur. Stand.*, 1931, **6**, 401), except that the heating current was controlled by a vapour-pressure regulator which was filled with methyl chloride. Solid carbon dioxide was used as the refrigerant.

Methyl chloride was obtained from a cylinder and purified by distillation in a low-temperature column (Clusius and Riccoboni, *Z. physikal. Chem.*, 1938, *B*, **38**, 81). A small bulb in the thermostat contained about ½ c.c. of liquid methyl chloride, and the pressure of its vapour supported a column of mercury; the meniscus on the evacuated side of this column could make contact with a pointed wire and open and close a circuit operating a relay which controlled the heating current. Such a regulator, having a small heat capacity, responds very rapidly to changes of temperature. Methyl chloride was chosen because it has a suitable vapour pressure (½—1¼ atm.) over the temperature range under investigation. The mercury column was surrounded by a jacket through which water from a thermostat was pumped. The temperature at which the regulator operated was changed by altering the quantity of mercury in it by means of a mercury reservoir and a system of taps; fine adjustment was obtained by running mercury into or out of a capillary tube.

The temperature of the thermostat was measured with a methyl chloride vapour-pressure thermometer. The pressures were read to ±0·01 mm. on a steel scale which had been compared with a Geneva glass scale. The corresponding temperatures were calculated from Messerly and Aston's data (*J. Amer. Chem. Soc.*, 1940, **62**, 886). The absolute accuracy of the temperature measurements was checked with a platinum resistance thermometer: at an arbitrary temperature it read $-30{\cdot}67°$, while the vapour-pressure thermometer gave $-30{\cdot}67_2°$.

Preparation of Materials.—Ammonia. Synthetic ammonia was passed through a dust trap and over potassium hydroxide pellets. For final drying it was condensed over clean sodium and kept in contact with it as a liquid overnight; it was then submitted twice to fractional sublimation, and finally the middle fraction was stored in a globe.

Trideuterammonia was prepared by reaction of 99·7% deuterium oxide with magnesium nitride. The nitride was made by passing cylinder nitrogen over hot copper, through a liquid-air trap, and then over magnesium at red heat; immediately before the reaction with deuterium oxide vapour it was degassed *in situ* at 400°. The crude trideuterammonia contained much deuterium oxide, and was therefore passed back and forth several times over the nitride, which was heated in the final stages. After being kept in contact with more nitride, and then dried with sodium, the trideuteroammonia was finally purified in the low-temperature fractionating column from a bath of boiling " Freon."

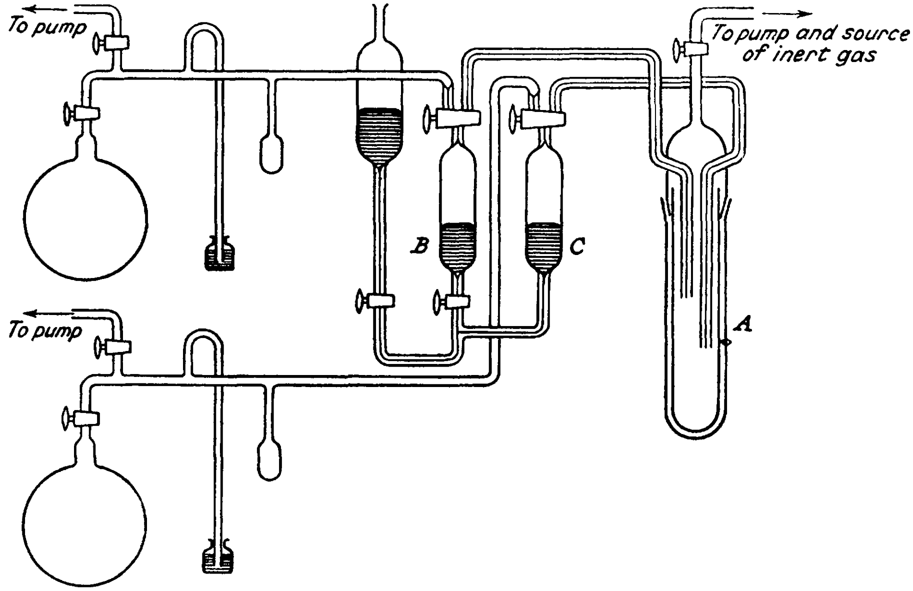
Hydrogen and deuterium chlorides. These were prepared respectively from water and 99·7% deuterium oxide, by the method described by Brown and Groot (*J. Amer. Chem. Soc.*, 1942, **64**, 2223). Both gases were finally purified by fractionation at −78°.

Preparation of salts. The salts were prepared from the component gases in the apparatus shown in Fig. 1: *B* and *C* are two similar vessels, 20 cm. long and of 2·8 cm. internal diameter, one of which contained ammonia or trideuterammonia at a pressure a little below atmospheric, the other hydrogen chloride or deuterium chloride at an equal pressure. By admitting mercury into these vessels simultaneously the two gases were slowly forced into the reaction chamber *A*, which contained nitrogen at approximately the same pressure as that of the reacting gases. These were led into *A* by capillary tubes, that conducting the lighter gas terminating below the other. All the salt collected in the inner tube in *A*, which was 27 cm. long and 2·5 cm. in diameter, and by disconnection of the cone and socket, the salt could easily be transferred to another vessel. *A* was surrounded by ice, to minimise any local heating of the gases or product and hence to reduce the chance of isotopic redistribution. Each charge was introduced during 10—15 minutes. Usually about 20 charges could be admitted before the apparatus became blocked; the reaction of the gases did not seem to be complete, probably partly owing to diffusion effects and partly to the fact that exactly equivalent proportions of the reactants were not used, as the pressure in *A* slowly increased. The salt was finally thoroughly evacuated to remove any unreacted gases.

The salt so formed consisted of a powder made up of minute crystals (see below). In order to obtain larger crystals, about half of the product ($\sim$3 g.) was sublimed, by placing it at the bottom of a tube 2·8 cm. in diameter, filling this with dry nitrogen at 0·5 cm. pressure, and immersing the lower portion of the tube in an oil-bath at 250°. The salt sublimed to form a hard crust on the glass just above the liquid level; it was scraped off and finally crushed in a mortar. The crystals were perhaps 0·1 mm. long.

FIG. 1.

Apparatus used for the preparation of ammonium chlorides.



Experimental Results.—The powders made by mixing the gases were examined with an electron microscope. We are much indebted to Dr. K. Little and to the Diffraction Group at the Atomic Energy Research Establishment, Harwell, for taking these photographs for us. The ammonium chloride was found to consist of crystals beyond the limit of resolution of the instrument. Shadowing with gold vapour revealed particles with linear dimensions between 120 and 20 A.; it would not be possible to detect particles smaller than 20 A. The monodeuterammonium chloride consisted mostly of similar particles though some appeared to be cubes with sides between 200 and 1000 A., and occasionally as large as 4000 A. Unfortunately, it was not possible to disperse the trideuterio-compound, and poor photographs were obtained; but again it appeared that the particles were very small.

It is possible that crystals larger by several powers of ten were present, but were not included in the sample examined by the electron microscope; however, this seems unlikely, as the conditions of formation were kept as uniform as possible.

The results of the dilatometric investigations are presented as molar volumes at different temperatures. The relative accuracy of the molar volumes is of course much higher than the absolute accuracy.

Briefly, the molar volumes were calculated as follows. The mass of salt is known; from the volume changes just above the transition, the coefficient of expansion of all the salts being assumed to be the same as that found by Simon and Bergmann for ammonium chloride at this temperature (*Z. physikal. Chem.*, 1930, *B*, **8**, 255), the quantity of fluid in the dilatometer may be approximately calculated. Hence it is possible to assess the volume changes due to the salt itself. An approximate value of the molar volume at a particular point was taken to be absolutely correct and so the molar volumes at the remaining points were calculated.

Figs. 2—7 show the plots of *V*, the molar volume, against *T*, the temperature, for the large and small crystals of the three salts examined. Selected points from the graphs are given in Table I.

FIG. 2.
NH_4Cl, *small crystals.*

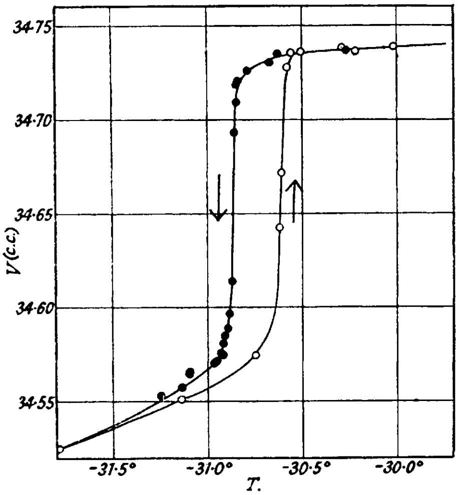


FIG. 3.
NH_4Cl, *sublimed crystals.*

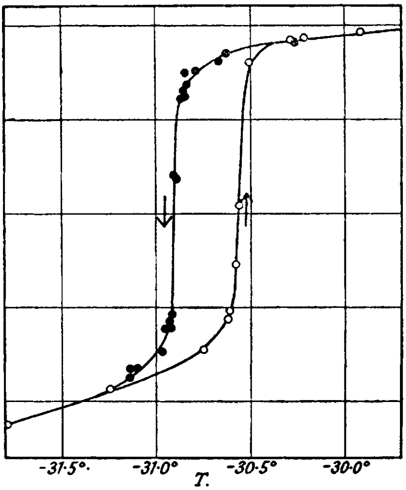


FIG. 4.
NH_3DCl, *small crystals.*

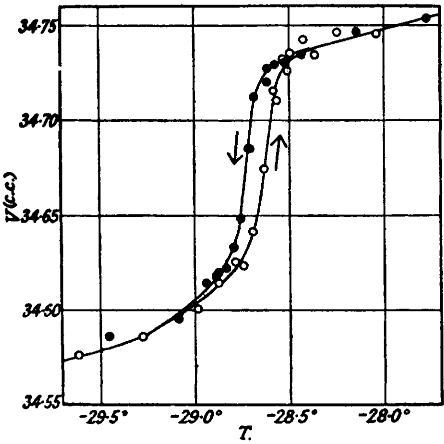


FIG. 5.
NH_3DCl, *sublimed crystals.*

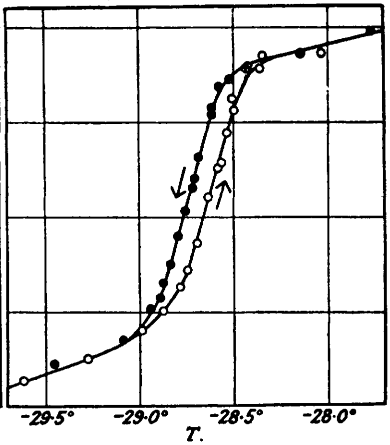


FIG. 6.
ND_3HCl, *small crystals.*

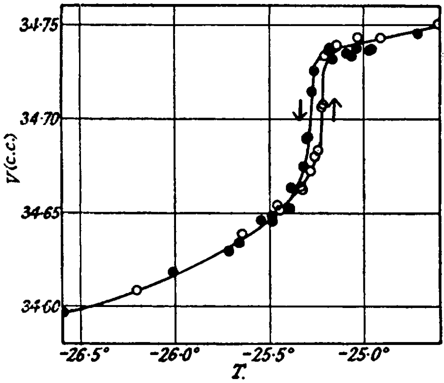
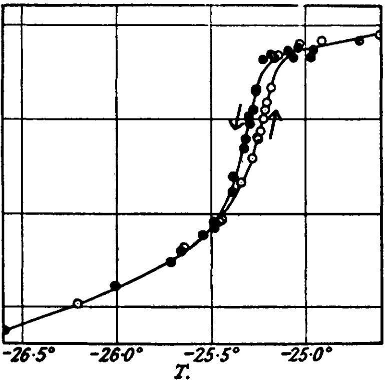


FIG. 7.
ND_3HCl, *sublimed crystals.*



FIGS. 2—7.

Variation with temperature (in ° C.) of the molar volume of ammonium chloride and partly deuterated ammonium chlorides. The open circles relate to runs for ascending temperatures, the full circles to those for descending temperatures.

TABLE I.

Small crystals.				Large crystals.			
Ascending temp.		Descending temp.		Ascending temp.		Descending temp.	
V.	*T.*	*V.*	*T.*	*V.*	*T.*	*V.*	*T.*
NH_4Cl.							
34·5251	−31·781°	34·7406	−29·615°	34·5379	−31·781°	34·7414	−30·262°
34·5510	−31·138	34·7353	−30·628	34·5623	−31·138	34·7262	−30·788
34·5740	−30·745	34·7264	−30·788	34·5774	−30·745	34·7113	−30·867
34·6429	−30·617	34·7191	−30·842	34·5940	−30·617	34·7037	−30·880
34·6718	−30·607	34·7092	−30·846	34·6230	−30·575	34·6705	−30·903
34·7283	−30·575	34·6164	−30·867	34·6543	−30·556	34·6683	−30·890
34·7367	−30·219	34·5968	−30·880	34·7309	−30·505	34·5966	−30·912
		34·5760	−30·925	34·7429	−30·289	34·5764	−30·962
		34·5571	−31·133	34·7465	−30·018	34·5568	−31·241
NH_3DCl.							
34·5764	−29·618	34·7537	−27·777	34·5632	−29·618	34·7477	−27·777
34·5861	−29·277	34·7306	−28·521	34·5901	−28·984	34·7283	−28·432
34·6238	−28·742	34·7273	−28·616	34·6132	−28·783	34·7190	−28·576
34·6412	−28·691	34·7126	−28·684	34·6365	−28·691	34·7040	−28·611
34·6745	−28·632	34·6855	−28·704	34·6788	−28·561	34·6702	−28·704
34·7105	−28·561	34·6852	−28·717	34·7062	−28·497	34·6535	−28·754
34·7159	−28·580	34·6488	−28·754	34·7350	−28·248	34·6155	−28·873
34·7260	−28·506	34·6332	−28·792			34·5860	−29·089
34·7457	−28·039	34·6227	−28·832				
		34·5955	−29·089				
ND_3HCl.							
34·6083	−26·203	34·7451	−24·713	34·6014	−26·203	34·7418	−24·713
34·6380	−25·645	34·7319	−25·165	34·6313	−25·645	34·7340	−25·187
34·6729	−25·284	34·7253	−25·261	34·6661	−25·348	34·7153	−25·261
34·6806	−25·255	34·7147	−25·279	34·6790	−25·284	34·7048	−25·279
34·6804	−25·259	34·6903	−25·299	34·6933	−25·241	34·6972	−25·299
34·6938	−25·241	34·6898	−25·301	34·7048	−25·219	34·6843	−25·326
34·7062	−25·223	34·6750	−25·320	34·7162	−25·181	34·6695	−25·385
34·7079	−25·219	34·6639	−25·385	34·7338	−25·143	34·6455	−25·486
34·7376	−25·181	34·6456	−25·483	34·7413	−24·911	34·6109	−26·010
34·7504	−24·609						

Our results for ammonium chloride may be compared with those of Smits and MacGillavry (*loc. cit.*). For the limits of the hysteresis loop they give −30·79° and −30·52°, mean −30·65°, which is about 0·07° higher than our value for the mean temperature for the larger crystals. We do not believe our values for the absolute temperatures to be in error by as much as this in view of the satisfactory check already noted carried out with a platinum-resistance thermometer. Smits gives 0·27° as the width of the hysteresis loop, whereas we found 0·35° and 0·25° for the large and small crystals, respectively. It may be that Smits's method of preparation of ammonium chloride, which involved sublimation at low temperatures, gave smaller crystals than those obtained by us by sublimation; this might account for the difference between his and our values for the loop width.

DISCUSSION.

It is hoped to consider these results with others of the same kind in a later paper, in which the possibility of formulating a comprehensive theory of hysteresis in phase transitions will be examined; the present discussion will therefore be brief.

Perhaps the most interesting observation in our study of the ammonium chlorides is the contraction of the hysteresis loop in ammonium chloride as the crystals become very small. Hitherto, there has been little work on the effect of particle size in this connection. Attempts have been made to vary the size of crystals of condensed gases displaying transitions, but the hysteresis remains unaltered (Eucken and Bartholomé, *Göttingen Nachr.*, Math.-Phys. Kl. II, 1936, 2, 53; Clusius and Weigand, *Z. Elektrochem.*, 1938, **44**, 679), but it is doubtful if really small crystals can be obtained in these circumstances. Dinichert (*Helv. Physica Acta*, 1944, **17**, 400), however, found by dielectric-constant measurements that, in agreement with our experiments, the hysteresis loop is narrower for finely ground crystals of ammonium chloride than for single crystals. But he also reported, contrary to our findings, that the transition in the smaller crystals was more diffuse. Nevertheless, it follows from what we have found that if in ideal crystals of uniform size the final part of a transition is an isothermal process, in a sample consisting of crystals of widely differing sizes the closing stages would appear to be diffuse.

The more important of our quantitative results are summarised in Table II. Those so Smits *et al.* (*loc. cit.*) on tetradeuterammonium chloride are included for comparison; T_w if the temperature at which, on warming, dV/dT is a maximum, and T_c the corresponding temperature on cooling; T_m is the mean of T_w and T_c. ΔT is the width of the hysteresis loop approximately half-way up the almost vertical part of the curves. ΔV is that part of the molar-volume change which occurs comparatively abruptly, though it is difficult to assess this with any accuracy, particularly for the sublimed samples of the partly deuterated salts.

TABLE II.

Summary of the transition characteristics in ammonium chlorides.

	NH_4Cl.		NH_3DCl.		ND_3HCl.		
	Small.	Large.	Small.	Large.	Small.	Large.	ND_4Cl
T_w	−30·61°	−30·55°	−28·61°±0·03°	−28·55°±0·05°	−25·22°±0·03°	−25·21°±0·04°	−23·4°
T_c	−30·86°	−30·90°	−28·72°±0·03°	−28·68°±0·05°	−25·27°±0·01°	−25·28°±0·05°	−23·4°
T_m	−30·735°	−30·725°	−28·665°	−28·62°	−25·245°	−25·245°	−23·4°
ΔT	0·25°	0·35°	0·10°	0·12°	0·06°	0·07°	0°
ΔV	0·15	0·15	0·10	0·11	0·06	0·07	0

The transition temperature (as assessed by T_w, T_c, or T_m) varies almost, but not exactly, linearly with deuterium content. Thus, T_m for the large crystals of mono- and tri-deuterammonium chloride, calculated on the assumption of a linear variation from ammonium to tetradeuterammonium chloride, would be −28·895° and −25·23°, as compared with the experimental figures of −28·62° and −25·245°. The discrepancy for the monodeuterio-salt is small, but we consider real. Linear variation of transition temperature with deuterium content in mixed crystals of isotopic molecules has been found for the systems HBr–DBr (Clusius, *Z. Naturforsch.*, 1946, **1**, 142) and CH_4–CD_4 (Bartholomé, Drikos, and Eucken, *Z. physikal. Chem.*, 1938, *B*, **39**, 371).

The experiments with ammonium chloride show that the change in crystal size brought about by sublimation does not in itself make the final volume change any less abrupt. However, on sublimation of the partly deuterated salts, the closing stages of the transitions certainly become more diffuse; this can therefore be ascribed to some isotopic redistribution occurring during sublimation, so that the salt virtually becomes a mixed crystal of the five possible ammonium chlorides. The comparative sharpness of the completion of the transitions in the original samples suggests that the cations in any one of these are mainly of one kind. Nevertheless, the mean temperatures of the transitions in mono- and tri-deuterammonium chloride are scarcely altered by sublimation. This is in harmony with the observation that the transition temperature of mixed crystals of 75% of methane and 25% of tetradeuteriomethane is the same as that of pure monodeuteriomethane (Bartholomé, Drikos, and Eucken, *loc. cit.*).

The figures in Table II show that there is a rough correspondence between the widths of the hysteresis loops and the magnitudes of the comparatively abrupt volumes changes. It seems that these quantities are altered most by the initial introduction of deuterium into ammonium chloride or of hydrogen into tetradeuterammonium chloride.

Although in the transitions we have examined part of the volume change occurs within a very small temperature range, it is not true to say that a discontinuous volume change occurs at any particular temperature. Impurities, however, undoubtedly tend to make sharp transitions diffuse [cf. the observations on ammonium bromide (Smits, Ketelaar, and Muller, *Z. physikal. Chem.*, 1936, *A*, **175**, 359) and the effect of isotopic redistributions commented on above]; strains in crystals may have the same effect, and our own observations show that the transition temperature is a function of crystal size. These factors will combine to make somewhat diffuse a volume change which would occur discontinuously in pure, unstrained crystals of uniform size. We therefore agree with Smits's conclusion that ideally the final part of the transition in ammonium chloride occurs isothermally, and we consider that this is also true for mono- and tri-deuterammonium chloride. It therefore appears from the experiments on "light" and "heavy" ammonium chloride, bromide, and iodide that, as Smits has implied, hysteresis only occurs when part of the transition is sharp, but that hysteresis is absent when the transition is completely continuous. We hope in a later paper to consider whether or not this generalization can be applied to transitions in other substances.

We thank Prof. K. Clusius for a gift of heavy water, and Dr. B. Lambert for constructing some of the glass apparatus.

THE INORGANIC CHEMISTRY LABORATORY, OXFORD. [*Received, January 23rd*, 1951.]