526. *Studies of Gradual Transitions in Mixed Crystals. Part I. The System Ammonium Chloride–Ammonium Bromide.*

By C. J. Mandleberg and L. A. K. Staveley.

The volume–temperature relationships for mixed crystals of ammonium chloride and ammonium bromide have been determined between room temperature and *ca.* −110° with the object of investigating the effect of mixed-crystal formation on the gradual transitions (λ-points) in these two salts. The λ-point for pure ammonium chloride (242·5° K.) is depressed by the replacement of chloride by bromide ions, the temperature of the transition falling off increasingly rapidly and reaching 212·2° K. at 11·6 moles % of bromide. At about 8 moles % of bromide an upper transition appears, similar to that in pure ammonium bromide, in that it involves a contraction when the crystal is heated. For a range of a few units % of ammonium bromide, therefore, the mixed crystals display two successive transitions, but above 15 moles % of this salt, the lower can no longer be detected. Thereafter, the temperature of the bromide-like transition rises to a maximum at about 50 moles % of ammonium bromide, and then falls to the value for the pure salt. These results are considered in the light of existing knowledge of the nature of transitions in ammonium halides, the gradual transitions in which are regarded as representing changes from a state in which the cations undergo torsional oscillations, to one in which, while this motion continues to be predominantly of the same kind, they can occasionally change from one orientation to another. This type of motion we have called quasi-rotation. Reasons are given for believing that in the mixed crystals the N–H · · · Br interaction gives rise to a stronger orienting force on the ammonium ions than do the N–H · · · Cl interactions, and that the phenomenon displayed by the mixed crystals is due essentially to the decreased symmetry of the field of force acting on a cation, compared with that in the pure salts. In particular, it is suggested that in the region of composition where the system displays two transitions, the cations achieve quasi-rotational freedom in two stages, first about the N–H · · · Br axes at low temperatures, and finally in three degrees of freedom at the upper temperature.

Although many of the gradual transitions (λ-points) occurring in pure solids have been carefully investigated, relatively little work has so far been carried out on binary mixed crystals in which one or both of the components exhibit such a transition. Since mixed-crystal formation involves an alteration in the molecular or ionic environment in the lattice, which must necessarily have repercussions on what are essentially co-operative phenomena, it would seem that studies of such binary systems should provide one useful experimental line of attack on the problem of the nature and causes of these gradual transitions. Interesting results have in fact been obtained from the very few complete investigations of this kind which have already been carried out, such as those on the systems methane–krypton (Eucken and Veith, *Z. physikal. Chem.*, 1936, *B*, **34**, 275) and methane–tetradeuteriomethane (Bartholomé, Drikos, and Eucken, *ibid.*, 1938, *B*, **39**, 371).

In this paper are presented the results of what, it is hoped, will be the first of a series of investigations on solid solutions of two components of which one or both possess a λ-point. The system ammonium chloride–ammonium bromide was chosen as the first subject for study since there already exists a considerable amount of information about the transitions in these salts, and because they form a complete series of mixed crystals. The only previous observation relating to transitions in mixed crystals of these two salts seems to be that of Crenshaw and Ritter (*ibid.*, 1932, *B*, **16**, 143), who found by heat-capacity measurements that there is a gradual transition in a mixed crystal of approximately equimolecular proportions which lies at a higher temperature than the λ-points in the two pure compounds.

Experimental.

A dilatometric method is perhaps best suited to exploratory investigations of gradual transitions, since it lends itself both to the accurate determination of their temperatures, and to the investigation of any attendant hysteresis. Moreover, the particular system ammonium chloride–ammonium bromide has the additional interest that the volume changes occurring at the transition in the pure substances have opposite signs.

Smits and his co-workers have carried out very careful dilatometric studies on pure ammonium halides, in an apparatus designed for the intensive examination of any one salt (Smits and MacGillavry, *ibid.*, 1933, *A*, **166**, 97). Since an investigation of one given system of mixed crystals involves the successive study of several mixtures, we have used a simpler apparatus which permits of more rapid working over a range of temperature much wider than that investigated by Smits, at the expense of a slight loss in accuracy. It could in fact be emptied of one mixture, cleaned, and refilled with another in two days, and used for continuous observations between room temperature and −110°.

The dilatometer (Fig. 1) consisted of a bulb of about 50 c.c. capacity sealed to a calibrated capillary 120 cm. long, of internal cross-sectional area 1·1 × 10^{-2} sq. cm., terminating in a small tap. The bulb, in which the salt under observation was contained together with the indicator liquid, had a thin-walled re-entrant glass tube, in which a thermocouple was placed. A side arm from the capillary led to a three-way tap through which the whole could be evacuated, or alternatively filled with liquid.

The thermostat consisted essentially of a cylindrical block of magnesium, 25 cm. long and 6 cm. in diameter, at the base of which was a small spike 1 cm. long. The dilatometer rested in a cavity in this block, and the block was suspended well inside a deep Dewar vessel containing liquid oxygen. This Dewar vessel was mounted on a platform the height of which could be varied with precision. To cool the block, matters were so arranged that the spike was either immersed in, or held just above, the liquid-oxygen surface. The block was wound with a heating coil, connected to the mains through a variable resistance. It could be held at a steady temperature by striking a balance between the current in the heating coil, and the height of the spike above the liquid oxygen surface.

The central cavity in the block, within which rested the bulb, had three vertical grooves disposed equiangularly in its side to receive copper tubes containing thermocouples. These grooves extended ⅓, ⅔, and the whole of the depth of the cavity, respectively. The block was suspended by a cord from three hooks, also equiangularly disposed, screwed into its upper face. One of the low-freezing non-inflammable mixtures recommended by Kanolt (*Sci. Papers Bur. Stand.*, 1924—1926, **20**, 619) was used to improve thermal contact between the bulb and the block.

When the dilatometer bulb was in position in the magnesium block, the capillary, which was etched with reference marks, lay flush against a steel metre scale which had previously been calibrated against a standard. The meniscus in the capillary was observed through an eyepiece.

To fill the dilatometer, it was inverted, and a weighed amount of solid introduced *via* a tube sealed to the base of the bulb. The tube was then drawn off 1 cm. from the bulb. The dilatometer was next turned right way up, and connected to a high-vacuum pump through the three-way tap which was lubricated with a dextrose–mannitol–glycerol grease. After being thoroughly evacuated, the dilatometer was filled with the degassed indicator fluid through the other limb of the tap. Toluene was first used as the indicator fluid, but in order to extend the experiments below −90°, it was discarded in favour of carbon disulphide (f. p. −111°). The liquids were purified by fractional distillation and dried over phosphoric oxide, and the dissolved air was boiled out.

The liquid level in the capillary could be adjusted by turning the three-way tap so that the liquid drained out, or by blowing more liquid into the capillary through the three-way tap by means of a hand bellows.

Temperature was measured with copper–constantan thermocouples, which were calibrated at the m.p.s of mercury, chloroform, *n*-heptane, and carbon disulphide, and also in liquid air (the temperature of which was measured with a carbon monoxide vapour-pressure thermometer). A calibration curve was constructed from these results and the data of Southard and Andrews (*J. Franklin Inst.*, 1929, **207**, 323). It was considered that these thermocouples then gave an absolute accuracy of temperature measurement of 0·1°, while temperature changes of a few degrees were estimated to 0·01°.

Three thermocouples were employed. One, in the re-entrant glass tube, was considered to give the temperature in the centre of the bulb. Another, in the groove extending ⅔ of the way down the magnesium cylinder, gave the temperature of the block opposite the centre of the bulb. The third could be placed at various depths in the block, and used differentially to give information about the temperature gradient.

The apparatus was operated by placing the dilatometer in the block, reading on the scale the position of one of the reference marks on the capillary, and placing the Dewar vessel round the block. The mouth of the Dewar vessel was heavily lagged both inside and outside. (Such lagging was essential to the establishment of temperature uniformity through the magnesium block. Temperature differences between the ends of the block were, in fact, not more than 0·1°.) The indicator fluid was then pumped to the top of the capillary. The position of the liquid-air level relative to the block, and the heating current, were adjusted until the reading of the thermocouple in the block was steady. The readings of the thermocouple in the re-entrant tube, and of the meniscus in the capillary, were recorded when they became constant. The tap at the top of the capillary was momentarily opened before each reading to equalise the pressure within and without; otherwise it was kept shut to prevent loss from evaporation. The heating current was switched off, the block allowed to cool, and the process repeated at a suitable lower temperature. When, after several such readings, the liquid level approached the bottom

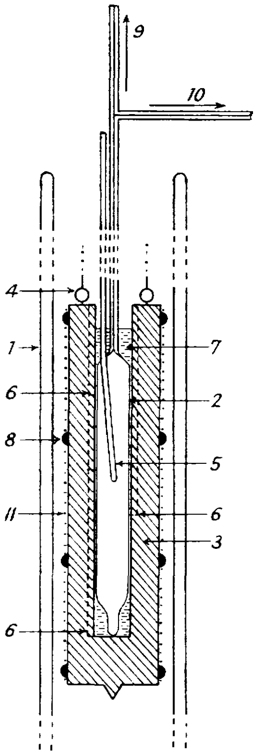


FIG. 1.

Dilatometer and thermostat : (1) *Dewar vessel,* (2) *dilatometer,* (3) *magnesium block,* (4) *hook and cord suspension,* (5) *thin-walled glass tube for thermocouple,* (6) *grooves in block, at different depths, for thermocouples,* (7) *low-freezing liquid,* (8) *asbestos string for protection of Dewar vessel,* (9) *to calibrated capillary,* (10) *to three-way tap, connecting to pump and reservoir of dilatometer fluid,* (11) *heating coil.*

FIGS. 2—11.

Variation with absolute temperature of the molar volume of the pure salts and mixed crystals. The quantity plotted as ordinate is $V_T - V_0$, *where* V_T *is the volume in c.c. at* T° K. *of one mole of solid of composition specified, and* V_0 *is the volume of the same quantity at the ice-point. The open circles relate to runs in which the salt was being heated, the full circles to those in which it was being cooled.*

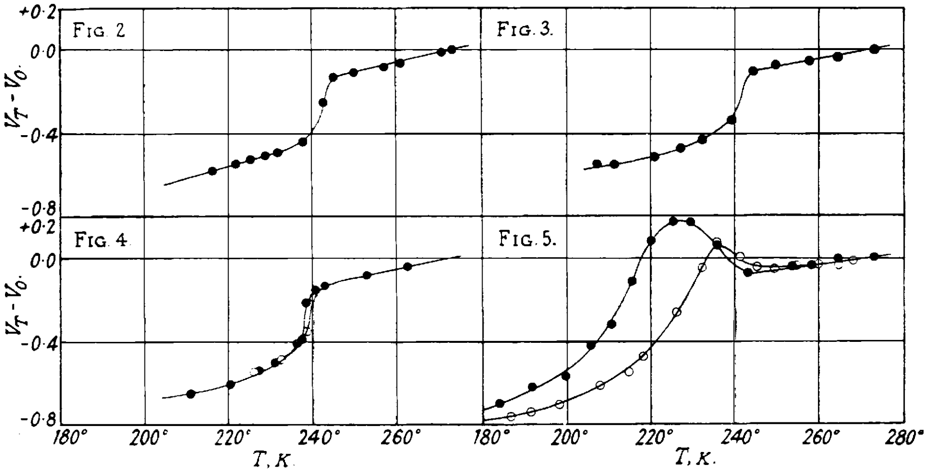


FIG. 2. *Pure* NH_4Cl. FIG. 3. 1·5 *Moles % of* NH_4Br. FIG. 4. 3·5 *Moles % of* NH_4Br. FIG. 5. 8·5 *Moles % of* NH_4Br.

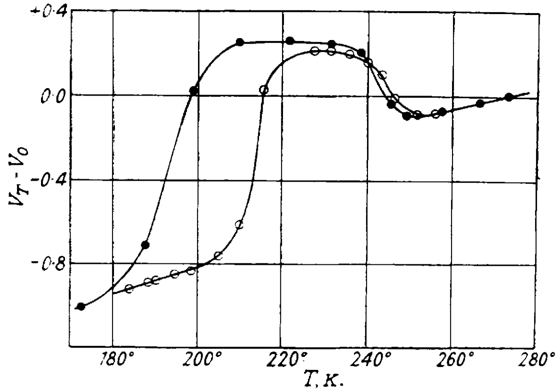


FIG. 6. 11·6 *Moles % of* NH_4Br.

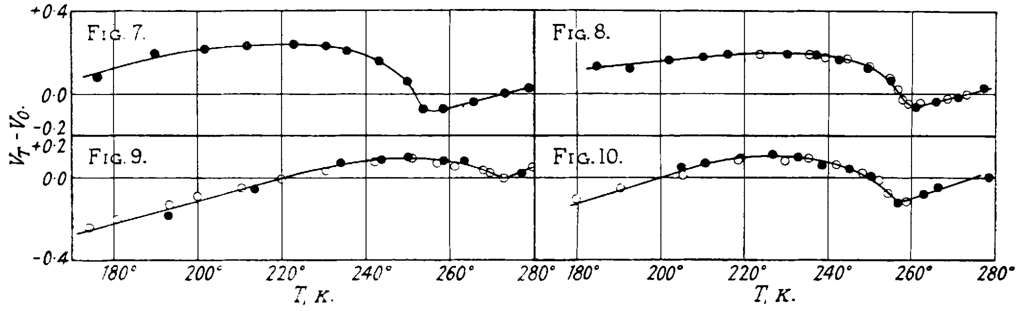


FIG. 7. 15·4 *Moles % of* NH_4Br. FIG. 8. 21·3 *Moles % of* NH_4Br.
FIG. 9. 59·8 *Moles % of* NH_4Br. FIG. 10. 84·8 *Moles % of* NH_4Br.

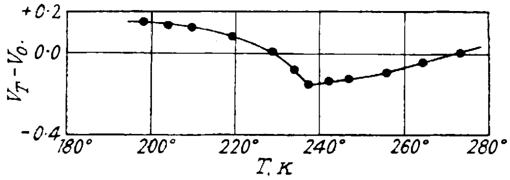


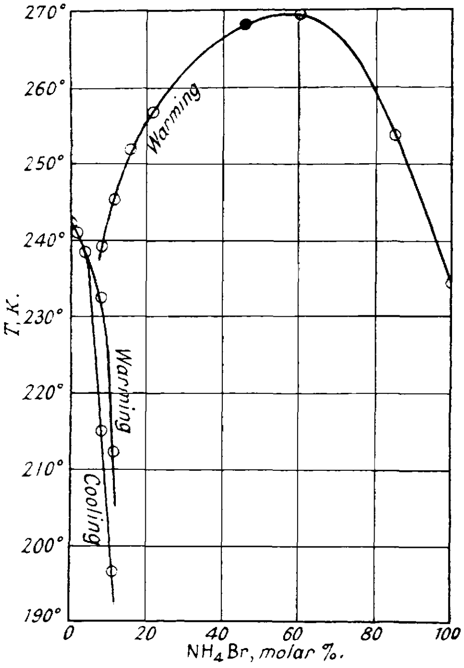
FIG. 11. *Pure* NH_4Br.

of the scale, the temperature was held constant while a reading was taken as described above, the liquid was pumped to the top of the capillary, and a second reading taken at the same temperature. When the lowest desired temperature had been attained, the procedure was reversed, and a heating run was carried out. When several such runs had been undertaken on each sample investigated, the dilatometer was removed from the block, the drawn-off tube cut off, the bulb emptied, and a new tube sealed on, before it was cleaned and refilled.

" AnalaR " ammonium chloride was used without further purification, and ammonium bromide was obtained by twice recrystallising the purest sample available. The mixed crystals were made by slow recrystallisation from solutions containing various proportions of the two salts. After being dried at 120° (cf. Crenshaw and Ritter, *loc. cit.*), they were heated in a sealed tube at 180° for 10—12 hours to ensure their homogeneity. The evidence for believing that this treatment does in fact give homogeneous mixed crystals is as follows : (1) Crenshaw and Ritter found that mixed crystals made by this method behaved in their calorimetric experiments identically with those which had been kept in the mother-liquor under isothermal conditions long enough to achieve equilibrium. (2) Havighurst and Mack (*J. Amer. Chem. Soc.*, 1925, **47**, 29) reported that their *X*-ray diffraction patterns of mixed crystals made by this method were those of homogeneous crystals. (3) The transitions in crystals containing more than 20% of ammonium bromide were no more diffuse than those in the pure salts; the behaviour of the chloride-rich mixtures is discussed below. (4) A sample mixed crystal was progressively dissolved after being subjected to the above thermal treatment : there was no change in the chloride/bromide ratio of the residue after each dissolution.

FIG. 12.

Variation with composition of the temperatures of transitions in mixed crystals of NH_4Cl *and* NH_4Br. *The full circle gives the transition temperature found by Crenshaw and Ritter* (loc. cit.) *in the one mixture which they studied calorimetrically.* (0° C. ≡ 273·10° K.)



There was, moreover, no indication that there was any tendency towards a separation of the components when a mixed crystal was cooled to low temperatures. That the homogeneity persisted was shown by (1) the perfect reproducibility of the results on every sample right from the first run ; (2) the examination of *X*-ray powder photographs of two samples of mixed crystals with 8·5% of ammonium bromide, one of which had never been cooled below room temperature whereas the other had been cooled to −90°. These two photographs (which were kindly taken for us by Mr. H. M. Powell) were indistinguishable.

The mixed crystals were analysed by titrating portions of solutions of known strength with standard silver nitrate. There is a linear relation between the molar percentage of any one halide and the ratio of the weight concentration of a solution of the mixed crystals to the titre of standard silver nitrate for a fixed volume of this solution.

In order to find the variation with temperature of the volume of the salt, it is necessary to know as accurately as possible the volume of the fluid in the bulb at one temperature. As the bulb had to be opened and resealed for the investigation of each sample, its internal volume varied somewhat from one set of experiments to another. For this reason, and also because of the difficulties inherent in any method of finding directly the volume of fluid introduced into the bulb, this was estimated as follows. The volume of the solid was derived from its known mass and its density, which for the mixed crystal was calculated on the basis of Havighurst and Mack's statement (*loc. cit.*) that the side of the cubic unit cell in this system varies linearly with composition. Careful measurements were made of the rate of change of volume of the salt plus fluid in the neighbourhood of room temperature, *i.e.*, above the region of the transitions. That part of the expansion due to the salt was assessed for pure ammonium chloride and bromide from Simon and Bergmann's coefficient of expansion data (*Z. physikal. Chem.*, 1930, *B*, **8**, 255), and for the mixed crystals on the assumption that the coefficient of expansion is a linear function of composition. From the rate of volume change due to the fluid alone, its volume was determined, using for toluene the density data of Timmermans (*Sci. Proc. Roy. Dublin Soc.*, 1912, **13**, 310) and for carbon disulphide the coefficient of expansion results of Seitz, Alterthum, and Lechner (*Ann. Physik*, 1916, **49**, 85). The expansion effects due to the fluid are relatively so large that in calculating, by what is essentially the reverse of the procedure just described, the change in volume of the salt below 0°, allowance must be made for the fact that the latter changes slightly the volume of fluid in the bulb.

The results are shown graphically in Figs. 2—11. These have been plotted from a representative selection of a large number of experimental points, and show the variation with absolute temperature T of the quantity $V_T - V_0$, where V_T is the volume in c.c. at T° K. of one mole of solid of composition specified, and V_0 the volume of the same quantity at the ice point.

Although a study of hysteresis was not a primary object of the investigation, and although the measurements were not sufficiently precise for the examination of very small effects of this kind, it may be stated that in the mixed crystals containing more than about 20% of ammonium bromide, the hysteresis accompanying the transition was not markedly greater than that for the pure salts. On the other hand, in the two mixtures which were found to undergo two transitions (*i.e.*, those containing 8·5 and 11·6% of NH_4Br; Figs. 5 and 6, respectively) there was very pronounced hysteresis. There was nothing to suggest that in these regions of large hysteresis the establishment of equilibrium was unusually slow; on reaching a particular temperature the dilatometer reading soon settled down to a steady value which showed no alteration after a period of 3 or 4 hours. It is interesting that for mixed crystals containing 8·5 and 11·6% of ammonium bromide the volume which a given mass of the solid occupies at 0° can be reproduced at no less than four lower temperatures.

The transition temperatures have, as usual, been regarded as those at which dV/dT is a maximum or a minimum. In order to determine them as accurately as possible, runs were carried out with small temperature increments or decrements (usually about 0·1° or 0·2°), and the transition temperature taken as the mean value of the temperatures for the interval showing the maximum or minimum dV/dT values. The transition temperatures are summarised in the Table. The figures for the two pure salts are in close agreement with the accurate values of Smits and his co-workers (NH_4Cl, Smits and MacGillavry, *loc. cit.*; NH_4Br, Smits, Ketelaar, and Muller, *Z. physikal. Chem.*, 1936, *A*, **175**, 359). In Fig. 12 the transition temperatures are plotted against the molar percentage of bromide. It will be seen that the transition temperature for the one mixed crystal studied calorimetrically by Crenshaw and Ritter is completely consistent with our own results.

Transition temperatures (K.) *of the pure salts and of mixed crystals of ammonium chloride and and ammonium bromide* (0° C. ≡ 273·10° K.).

NH_4Br,	Expansion :		Contraction :		NH_4Br,	Expansion :		Contraction :	
moles %.	cooling.	warming.	cooling.	warming.	moles %.	cooling.	warming.	cooling.	warming.
0·0	242·2(3)°	242·5(5)°	—	—	15·4	—	—	250·5°	251·8°
1·3	240·8	241·1	—	—	21·3	—	—	256·7	256·7
3·5	238·1	238·6	—	—	59·8	—	—	269·1	269·5
8·5	215	232·5	238·5°	239·1°	84·8	—	—	253·7	253·8
11·6	196·6	212·2	244·0	245·2	100·0	—	—	234·3(0)	234·4

DISCUSSION.

Although the available information about these transitions has been recently reviewed (Staveley, *Quart. Reviews*, **1949**, **3**, 65) we shall restate briefly the essential facts about the λ-points in the pure salts before attempting to explain the observations made on the mixed crystals.

At room temperature and normal pressure, the stable forms of ammonium chloride and ammonium bromide both have body-centred cubic lattices. (These forms are designated II, since at higher temperatures they both change into a modification I each with face-centred cubic lattices.) On passing into the form III stable below the λ-point, the chloride retains its simple cubic lattice but becomes piezoelectric, so that III is in some way a less symmetrical structure than II (Hettich, *Z. physikal. Chem.*, 1934, *A*, **168**, 353). Ammonium bromide-III, however, has a tetragonal lattice, though of such dimensions that only slight changes in the relative positions of the ions are involved in the transformation II ⟶ III (Weigle and Saini, *Helv. Phys. Acta*, 1936, **9**, 515).

Menzies and Mills (*Proc. Roy. Soc.*, 1935, *A*, **148**, 407) showed that the transformation II ⟶ III is accompanied in the chloride, but not in the bromide, by the appearance of a Raman line of low frequency, which they attributed to asymmetric lattice vibrations. Since the positive charge on an ammonium ion is no doubt largely localised on the hydrogen atoms, it is highly probable that the energetically preferred orientation of such an ion with respect to its halide neighbours is that in which each of the four hydrogen atoms is as near as possible to a neighbouring anion. In a simple cubic lattice there are eight halide ions cubically grouped round each nitrogen atom, and such a preferred orientation of the tetrahedral cation will then obtain when each diagonal of the cube is perpendicular to a face of the tetrahedron. Menzies and Mills suggested that in the low-temperature form of the chloride, the lattice was built up by the simple translation of the elementary cube, so that all ammonium ions (when in the mean position) are in all respects parallel to one another. The chloride ions, however, are now not symmetrically placed with respect to the ammonium ions, so that the existence of the low-frequency Raman line is explained. They further suggested that, in the bromide in the III-form, the ammonium cations in two adjacent elementary cubes are anti-parallel to each other, so that the nearest *edges* of these two tetrahedra are now *parallel* to one another and not *perpendicular* as in the chloride.

If, in the chloride, the ammonium ions acquire mutually disordered orientations, or commence to rotate, or if the amplitude of the torsional oscillations increases sufficiently, the lattice gains in symmetry, and both the low-frequency Raman line and also the piezoelectric properties disappear. A further consequence of this change in motion of the cations, however, is that it will tend to reduce the average distance between the hydrogen atoms of adjacent ammonium ions, and since these ions carry similar charges and thus tend to repel one another, the inter-ammonium repulsion will be thereby enhanced, and the lattice accordingly constrained to expand. A similar change in the bromide, however, involves a decrease in the average distance which separates the hydrogen atoms of neighbouring cations and hence results in a contraction of the lattice in virtue of the decreased inter-ammonium repulsion. In this way Menzies and Mills accounted for the striking fact that, although the gradual transitions in ammonium chloride and bromide are in many respects very similar, they differ in that the volume changes which accompany them are in opposite directions. It is important to stress that it is not necessary to postulate that in these salts the ammonium ions freely rotate in form II, for more recent evidence indicates that, for the chloride at least, cations do *not* in fact gain rotational freedom in the neighbourhood of the λ-point. The c_v values for ammonium chloride are only consistent with a librational or rocking movement of the ions both above and below the λ-point (Lawson, *Physical Rev.*, 1940, **57**, 417), and this conclusion is supported by nuclear magnetic resonance experiments (Bitter *et al.*, *ibid.*, 1947, **61**, 738).

We shall therefore suppose that in the III-forms of both salts the ammonium ions are constrained to librate with small amplitudes about ordered axes, the orienting forces being provided by the N–H · · · Hal interactions, and the mean position in each salt being that in which any one hydrogen atom is collinear with a nitrogen and a halogen ion. Furthermore, it will be assumed that in the form of the pure salts stable above the λ-points the torsional oscillation of the cations now occurs about disordered axes, that the amplitude of the oscillation is somewhat increased, and that occasionally an ammonium ion changes from one to the other of its two possible equilibrium positions within an elementary cube. (It may be noted that at transitions in molecular crystals composed of polar molecules, the change to the high-temperature form is often accompanied by a considerable increase in dielectric constant, showing that the molecules gain considerably in orientational freedom though they need not necessarily rotate in the high-temperature form.) Since the properties of forms II are in many ways what would be expected if the cations had the spherical symmetry which free rotation would give them, we shall speak of the motions of these ions as quasi-rotational.

The gradual transitions must therefore be regarded as essentially co-operative phenomena arising from a gradual change from purely librational to quasi-rotational motion, the region of temperature in which they are observed to occur depending primarily on the strength of the orienting forces. Since the transitions in the chloride and the bromide reach completion at temperatures only a few degrees apart, it would seem that the orienting forces in the two lattices are very nearly of the same strength, in spite of the fact that the distance of closest approach of a nitrogen and a bromine atom in the bromide (3·505 A. at room temperature) is greater than that of a nitrogen and a chlorine atom in the chloride (3·34 A.). Now Havighurst and Mack's *X*-ray studies (*loc. cit.*) established that the length of the side of the unit cell in mixed crystals of the two salts varies linearly with the composition. In any mixed crystal, therefore, the minimum N · · · Br distances are less, and the N · · · Br interactions stronger than in the pure bromide, while the minimum N · · · Cl distances must be greater and therefore the N · · · Cl interactions weaker than in the pure chloride. Accordingly, any NH_4 ion in a mixed crystal of these two substances is in a less symmetrical field of force than a cation in either of the pure salts. In particular, there is a preference for the N–H bonds to be aligned in the direction of bromide rather than chloride ions, and we consider that this is fundamentally responsible for the phenomena we have observed in the mixed crystals.

If we start with the pure bromide, and replace some of the anions by chloride ions, the orienting forces on any one cation are strengthened in some directions and weakened in others. Up to 50 moles % of chloride it seems that the net effect is an increased restriction on the torsional freedom of the cations, since the transition temperature rises until this composition is reached. On further replacement, the decrease in the number of bromide ions is no longer outweighed by the increasing strength of the N–H · · · Br interactions and the transition temperature falls. So long, however, as each cation has at least two bromide ions among the eight nearest anion neighbours, its orientation in the unit cube will be determined by its interaction with the bromide ions. In mixed crystals containing more than about 25 moles % of bromide we should therefore expect that the preferred mutual orientations of neighbouring tetrahedra will be similar to that in the pure bromide, and hence that the transition II ⟶ III will be bromide-like in the sense that it will involve a contraction, as is indeed the case. It is noteworthy that this transition in the mixed crystal is not appreciably any more diffuse than in the pure bromide. At very low bromide concentrations, however, the rate at which the transition is depressed by increasing the proportion of bromide is about the same as that at which the transition temperature for ammonium bromide is raised by introducing a little chloride. When the bromide content is very small, the majority of cations still have eight chloride ions as nearest neighbours, and presumably endeavour to retain the relationship which prevails in the pure chloride, so that the depression of the transition temperature is probably largely caused by the slight increase in the lattice dimensions which the introduction of the bromide ions produces. In the region of 5—12 moles % of bromide, however, the temperature of the (lower) transition falls much more rapidly as the substitution of bromide for chloride proceeds. This rapid change in behaviour, coinciding with the appearance of the upper transition (and, incidentally, with an enormous increase in the hysteresis associated with the lower transition), suggests that it is in this region that a fundamental alteration takes place in the type of inter-ammonium ion relationship which prevails in the lattice.

The situation in this range of composition is perhaps most readily apprehended if we consider a mixed crystal containing 12½ moles % of ammonium bromide, and which is ideal in the sense that the distribution of chloride and bromide ions throughout the whole lattice is as uniform as possible. Although such uniformity cannot prevail in a real mixed crystal, this idealised model serves to throw light on the most probable interionic relationships.

Any one ammonium ion has then seven chloride ions and one bromide ion as its nearest anion neighbours. It is convenient here to visualise as the unit, a group of eight elementary cubes with one central bromide ion in common. Owing to the strong N–H · · · Br interaction, it is reasonable to suppose that the preferred orientation of the eight tetrahedra of the group will be that in which each has an apex directed towards the bromide ion. This group of eight tetrahedra, with cubic symmetry, recalls the arrangement which Menzies and Mills (*loc. cit.*) postulated for the pure bromide, and suggests that even at these comparatively low bromide concentrations, the transition characteristics of the mixed crystals should begin to show some resemblance to those of ammonium bromide. There is, however, the difference that the bases of the tetrahedra opposite to those apices which are nearest to the bromide ions, are, as it were, less firmly anchored than the apices themselves. It is thus possible in principle for the tetrahedra to undergo limited quasi-rotational movement about the N–H · · · Br axis, while preserving the same relationship with regard to the bromide ion. This partial quasi-rotation will be opposed by the N–H · · · Cl interaction, but as these are weaker than in the pure chloride, the quasi-rotation should set in at a lower temperature than it does in the pure chloride. It is suggested, therefore, that the low-temperature transition in that range of mixed crystals where there are two gradual transitions is, in fact, a manifestation of the acquisition by the ammonium ions of quasi-rotational freedom about one axis only. The upper transition is considered to result from the extension of this quasi-rotational movement to all axes when the temperature has become sufficiently high for the strong N–H · · · Br interaction to be overcome.

We now consider the volume changes at these successive transitions. Since tetrahedra in adjacent elementary cubes with a common face have their nearest edges parallel, any increase in the amplitude of oscillation about the N–H · · · Br axis increases the separation of these pairs of hydrogen atoms, and thereby reduces their mutual repulsion, and encourages contraction. On the other hand, this increase in inter-hydrogen separation will not be as great as that produced by an enhancement of the oscillational freedom about an axis, say, at right angles to the N–H · · · Br direction. Furthermore, if we regard the idealised 12½ moles % of bromide solid as being formed by the simple translation of a cube which consists of eight elementary cubes with a bromide ion at the centre of the group, then along the cube diagonals the arrangement of the tetrahedra is :

–face–apex–apex–face–face–apex–apex–face–

In addition, the hydrogen atoms of any two consecutive faces in the series (whether separated by two apices or not) are " staggered." Quasi-rotation of the tetrahedra about these diagonals (*i.e.*, about the N–H · · · Br axes) will diminish the average separation of these hydrogen atoms, and encourage an expansion of the lattice. Pending a detailed quantitative treatment, we may therefore say that limited quasi-rotation of the kind described is not necessarily inconsistent with a net expansion of the solid. The contraction at the upper transition presumably depends, like that in the pure bromide, on the marked increase in the distance between hydrogen atoms of the tetrahedral edges adjacent and parallel to the face diagonals of the elementary cubes.

The change to full quasi-rotational motion (which produces the last effect) will also cause a separation of the eight hydrogen atoms at the apices of the eight tetrahedra which are directed towards a bromide ion, and the diminished repulsion between these hydrogen atoms will likewise contribute towards a shrinking of the lattice.

If the distribution of the two sorts of halogen ion throughout the lattice of a mixed crystal were always as uniform as possible the interpretation we have placed on the experimental evidence would require that all signs of a low-temperature chloride-like transition should vanish when the bromide concentration reaches 25 moles %. Although we were unable to follow it to the point of its disappearance, the experiments give the impression that at least it is not likely to persist to higher bromide concentrations. At the highest bromide concentration which it was positively detected in the dilatometric experiments, its temperature is falling rapidly with increasing percentage of bromide. In addition, cooling curves were obtained for the samples containing up to 21·3 moles % of bromide down to 135° K. While these showed the presence of low-temperature transitions in the mixtures containing up to 11·6 moles % of bromide, there was no sign of this in the curves for the crystals with 15·4% and 21·3% of bromide. Accordingly, if it still persists in these crystals, the transition occurs at a temperature below 135° K., or else it has become very diffuse, or the heat effects associated with it have become very small.

THE INORGANIC CHEMISTRY LABORATORY,
SOUTH PARKS ROAD, OXFORD.

[*Received, May* 11*th*, 1950.