

# IONIC AND MOLECULAR ROTATION IN AMMONIUM SALTS AND CLATHRATE COMPOUNDS

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It was at one time rather widely believed that certain ions and molecules could rotate virtually freely in the lattice containing them. It now appears that such almost free rotation, in the literal sense, is probably rare. The solids which have been most thoroughly investigated are ammonium chloride, bromide, and iodide. It has been established beyond doubt that in the simple cubic forms of these salts the ammonium ions do not rotate, being prevented from doing so by energy barriers of 6410, 4645 and 4100 cal/g-ion, respectively<sup>1</sup>. It is to be noted, however, that there is a considerable decrease in this energy barrier as the lattice dimensions increase, and the possibility must still be considered that in ammonium salts where the anion is large, symmetrical, and not too highly charged, the barrier is small enough for the ammonium ion to undergo something approaching free rotation at room temperature. Another circumstance which will be favourable to free rotation is if the disposition of the anions about the ammonium ion is such as to give only a slight energetic preference for one orientation rather than another. This happens, for example, in the high-temperature face-centred cubic form of ammonium iodide, where the tetrahedral cation is surrounded octahedrally by six anions. Each ammonium ion directs one N—H bond towards one of the anions. The barrier to one-dimensional rotation about this bond is, however, then so small ( $< 100$  cal/g-ion) that the ammonium ions must at room temperature undergo almost free rotation about one N—H bond<sup>2</sup>.

With these considerations in mind we have studied the motion of the ammonium ion in several selected ammonium salts by attempting to estimate the contribution made to the heat capacity  $C_p$  of the salts by the rotational or torsional movements of the ammonium ions. All the salts investigated have isomorphous rubidium salts, and the lattice dimensions of the ammonium and rubidium salts differ by less than 1 per cent. It is therefore reasonable to suppose that, for a given pair of such salts, the quantity  $(C_p - C_v)$  and the contribution to  $C_p$  from the torsional oscillations of the *anion* will be almost equal. Consequently, at temperatures high enough for the lattice vibrations to make effectively their maximum and hence identical contributions to  $C_p$ , the quantity  $\Delta C_p = C_{p, \text{NH}_4 \text{ salt}} - C_{p, \text{Rb salt}} - C_{\text{int}}$  should give the contribution made by the torsional oscillations (or rotations) of the ammonium ions ( $C_{\text{int}}$  is the relatively small contribution from the internal vibrations of the ammonium ion). We may distinguish, for convenience, between three possibilities for  $\Delta C_p$  (expressed per g-ion) as a function of temperature.

(1) If the barrier to rotation is sufficiently high,  $\Delta C_p$  will rise to a limiting value of  $3R$ . This may not be reached at room temperature. An example of this is given by ammonium chloride, in which the torsional oscillation frequency of the ammonium ion is high ( $360\text{ cm}^{-1}$ ) and  $\Delta C_p$  at  $25^\circ\text{C}$  is still only  $\sim 4.7\text{ cal }^\circ\text{C}^{-1}\text{ g-ion}^{-1}$ .

(2) If the barrier is so small that the ammonium ions virtually rotate freely,  $\Delta C_p$  will be  $\frac{3}{2}R$ .

(3) With barriers of intermediate height, the ammonium ions will behave as restricted rotators, and with rising temperature  $\Delta C_p$  will rise to a maximum and then decrease, approaching  $\frac{3}{2}R$  asymptotically.

So far in this laboratory, the following salts have been investigated by this comparative method: ammonium tetraphenylboron<sup>3</sup>,  $\text{NH}_4\text{B}(\text{C}_6\text{H}_5)_4$ ; ammonium stannichloride,  $(\text{NH}_4)_2\text{SnCl}_6$ ; ammonium stannibromide<sup>4</sup>,  $(\text{NH}_4)_2\text{SnBr}_6$ .

$\Delta C_p$  for ammonium tetraphenylboron provides another example of case (1) above. At room temperature,  $\Delta C_p$  is only  $\sim 5\text{ cal }^\circ\text{C}^{-1}\text{ g-ion}^{-1}$  and still rising. So, in spite of the large size of the anions the ammonium ions do not even approach free rotation. A crystallographic study of this salt<sup>5</sup> showed that the tetraphenylboron ions are arranged in parallel columns, with an ammonium ion trapped between two neighbouring anions in one and the same column. The unoccupied space in the lattice is chiefly that between the columns and is therefore not available to the ammonium ions. On the other hand  $\Delta C_p$  for ammonium stannichloride rises to a maximum of  $4.8\text{ cal }^\circ\text{C}^{-1}\text{ g-ion}^{-1}$  at  $180^\circ\text{K}$  and by  $25^\circ\text{C}$  has declined to a value of  $4.1\text{ cal }^\circ\text{C}^{-1}\text{ g-ion}^{-1}$ , which is roughly half-way between the extreme values of  $3R$  and  $\frac{3}{2}R$ . For the stannibromide the position is much the same; at  $25^\circ\text{C}$ ,  $\Delta C_p$  is  $4.3\text{ cal }^\circ\text{C}^{-1}\text{ g-ion}^{-1}$  and is decreasing. The ammonium ion in these two salts therefore behaves as a restricted rotator (case (3)). Ammonium stannichloride and stannibromide both have antiferroite structures. Each octant of the unit cell has an ammonium ion at its centre which is surrounded by four stannihalide ions. The tin-halogen bonds lie along or parallel to the axes of the unit cell, and each ammonium ion is surrounded by four tin atoms and by twelve equidistant halogen atoms. Although the height of the energy barrier restricting free rotation cannot be precisely estimated from the  $\Delta C_p$  values, it must be considerably less than in the ammonium halides in their simple cubic forms. From quantitative considerations of the interaction between the ammonium ion and the neighbouring stannihalide ions it appears that this can only be so if the charge distribution in the stannihalide ion does not differ very much from zero charge on the tin atom and an effective charge of  $-\frac{1}{3}$  located at the centre of each halogen atom. It is worth noting that if, by refining the analysis of  $C_p$ , it becomes possible to make reasonably reliable estimates of the potential barrier restricting ammonium ion rotation in salts with complex anions, then with the aid of sufficiently accurate crystallographic data it should be possible to draw conclusions about the charge distribution within the complex ion, since that within the ammonium ion is already known from Hornig's work<sup>6</sup>.

The discovery of clathrates (or inclusion compounds) has made it possible to study the behaviour of small isolated molecules trapped in cavities in

lattices of almost fixed size. The best known clathrates are those formed by quinol. This substance can crystallize in an unstable  $\beta$ -modification, in which there are approximately spherical cavities regularly dispersed throughout the lattice. There is one cavity to three quinol molecules. By producing the  $\beta$ -form in the presence of a given kind of small molecule, e.g. by carrying out the crystallization in the presence of, say, argon under pressure, the resultant crystals contain small molecules trapped individually in the cavities. The proportion of holes filled can vary from a few per cent to almost 100 per cent in favourable cases, and the molecules which can be so trapped include those of argon, krypton and xenon, numerous diatomic molecules, methane, sulphur dioxide, and even molecules as large as methyl alcohol and acetonitrile. In a sense, clathrates provide idealized examples of the cell model which has played such a large part in recent theories of pure liquids and solutions, and it is therefore of interest to investigate the motion of the small molecules in the cavities. We have recently made such a study of the methane clathrates by measuring the contribution made to  $C_p$  per mole of methane. In principle this can be done by measuring  $C_p$  for any one clathrate of known composition and also for the pure  $\beta$ -quinol itself, but although this can be prepared, it is rather unstable and it is better to make measurements on two or preferably more samples of different composition. In order to decide whether the methane molecules are rotating within the cavities, it is necessary to assess  $C_{vib}$ , the contribution made to the heat capacity by the vibrational or translational movement (the "rattling", as it were) within the cavity. This may be done with the help of a statistical theory of clathrates due to J. H. van der Waals<sup>7</sup> (which uses the cell model approach of Lennard-Jones and Devonshire), which enables  $C_{vib}$  to be calculated using, *inter alia*, data on the intermolecular potential energy parameters for pairs of the small molecules. To check the reliability of the  $C_{vib}$  values calculated in this way, we have made a careful study of the argon clathrates, where the whole of the contribution of the argon molecules to  $C_p$  is of course  $C_{vib}$ , and we find reasonably good agreement between the observed and calculated values<sup>8</sup>. An analysis of the results for the methane clathrates on this basis shows that the contribution to be attributed to the rotational or torsional motion of the molecules is from  $\sim 150^\circ\text{K}$  upwards constant at  $\frac{3}{2}R$  within  $0.3 \text{ cal } ^\circ\text{C}^{-1} \text{ mole}^{-1}$ , thus leaving no doubt that in this range these molecules rotate virtually as freely as gaseous molecules. Only an approximate analysis of the heat capacity can be made at lower temperatures, since the treatment of J. H. van der Waals then no longer applies, but it seems that the course taken by the rotational heat capacity of the methane molecules does not differ much from that calculated for gaseous methane.

A similar conclusion has been reached in a different way about the oxygen clathrates by Meyer, O'Brien and Van Vleck<sup>9</sup>, who, from a study of the magnetic properties of the clathrate at low temperatures concluded that rotation of the oxygen molecule is impeded by a barrier of only 127 cal/mole of  $\text{O}_2$ , so that here again at higher temperatures the rotation will be virtually free. It may therefore be expected that this situation prevails with several clathrates with sufficiently small molecules. On the other hand, it is known that the inclusion of larger molecules such as acetonitrile and methyl alcohol appreciably changes the lattice dimensions of the  $\beta$ -quinol and therefore

deforms the hole, so that it may be doubted whether these molecules can undergo free rotation within the cavities, at least in all their degrees of freedom.

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