THE CRYSTAL STRUCTURE AND POLYMORPHISM OF HYDROGEN HALIDES

IN a previous letter to NATURE (July 19, 1930, p. 97) I communicated some preliminary results upon the crystal structure of hydrogen iodide. I have now repeated, with greater accuracy the X-ray examination of this substance, in order to investigate the discrepancies previously observed in certain values of the lattice dimensions, and have also examined solid hydrogen chloride and bromide at different temperatures, using, for X-ray examination, the same apparatus as previously described (NATURE, Mar. 22, 1930, vol. 125, p. 457; *Rend. Acc. Lincei*, vol. 11, p. 679).

The results obtained for hydrogen chloride agree, in the main, with those of Simon and Simson (*Zeitschrift f. Physik*, vol. 21, p. 168), with the exception that the a constant of the cubic modification, stable over 98° abs., has been found to be smaller than that obtained by them, namely, $a = 5.44 \pm 0.01$ A. at the transition temperature (instead of 5.54 at 103° abs. by Simon and Simson). The volume of the elementary cell is then 161×10^{-24} c.c.; the density, for a cell containing 4 molecules, is 1.49, which is in better agreement with the experimental density (1.47) than their calculated results.

The modification of hydrogen chloride stable at lower temperature was examined by cooling the capillary of the spectrograph with liquid nitrogen. The photogram taken at 85° abs. shows numerous lines, of which only a certain number correspond to the tetragonal system for an axial ratio $c/a = 1.10$, and for one side of the base of the elementary prism $a = 5.27$ A. Most likely this modification of hydrogen chloride possesses a lower symmetry, perhaps rhombic, with axial ratios near those belonging to the tetragonal system.

Hydrogen bromide, like the chloride, is dimorphous. The modification, stable at high temperature, shows at 100° abs. a face-centred cubic structure. The side of the elementary cell is $a = 5.77$ A., the volume 192×10^{-24} c.c., the density, for a cell of 4 molecules, 2.78.

The low temperature stable modification shows tetragonal symmetry, with an axial ratio $c/a = 1.10$, and with a basic side $a = 5.55$ A., or perhaps a pseudo-tetragonal structure with ratios very little different from those of a tetragonal one. The volume of the cell is 188×10^{-24} c.c. at 90° abs.

Various photograms of hydrogen iodide have been taken, cooling in succession the capillary of the spectrograph with liquid hydrogen chloride (188° abs.), methane (112°), oxygen (90°), nitrogen (77°). Hydrogen iodide was prepared by the action of

iodine upon red phosphorus. I have succeeded in getting much better defined photograms than before. They contain many lines which cannot be ascribed to iodine impurities originating from photochemical decomposition of hydrogen iodide, as I thought at first, and which cannot be arranged in a cubical structure. On the other hand, following this hypothesis, some divergences could be observed between the calculated and the experimental lattice distances. I have thus come to the conclusion that hydrogen iodide does not show, as I had previously considered, a face-centred cubic structure, but a face-centred tetragonal structure with an axial ratio not much differing from the cubic one. As a matter of fact, all lines of the photogram can be assigned to a face-centred tetragonal structure, with an axial ratio $c/a = 1.08$ and a side of the elementary cell $a = 6.10$ A. at 100° abs. The volume of the cell is 245×10^{-24} c.c., and the density, for a cell of 4 molecules, 3.45. (The present values do not differ much from those previously calculated for a cubic structure.)

From the lattice constants of the cubic modifications of hydrogen chloride and bromide the ionic radii of chlorine and bromine can be calculated, assuming the ions to be tangential in the face-centred cubic lattice : the new values are somewhat higher than Goldschmidt's values calculated from the alkaline halogenides (" Geoch. Verteilungsgesetze d. Elem.", *Norsk. Vid. Ak.*, 7 ; 1926), but they are perfectly consistent, as previously pointed out by Nasini and myself (NATURE, Mar. 22, p. 457 ; June 14, p. 889; 1930: *Rend. Acc. Lincei*, vol. 11, p. 1009 ; vol. 12, p. 141 ; 1930), with the atomic radii of the inert gases having the same number of external electrons, as the following table shows :

$Cl^- = 1.81$ (Goldschmidt), 1.92 (Natta)		$A = 1.92$ (Simon-Simson)
$Br^- = 1.96$,, 2.04 ,,		$Kr = 2.04$ (Nasini-Natta)
$I^- = 2.20$,, 2.21 ,,		$X = 2.18$ (Natta-Nasini)

The 2.21 value of the iodine ion is obtained from the ratio of the volumes of the elementary cells of the isomorphous modifications of hydrogen iodide and hydrogen bromide, assuming as the bromine ionic radius that calculated from the cubic modification of hydrogen bromide. We might also assume for the iodine ion a non-spherical form, as has already been suspected from the structure of other iodides.

I cannot agree with Simon and Simson's hypothesis as to hydrogen chloride, and I assume that hydrogen halides show ionic structure and not molecular lattices as supposed by them. This is proved by the agreement observed between the ionic radii of the free hydrogen halides and those of the alkaline halides. The contraction suffered by the anion in the lattice of the latter must be ascribed to polarisation forces due to the alkali cation.

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