THE SIGNIFICANCE OF THE EXPERIMENTALLY DETERMINED CRYSTAL STRUCTURES OF THE ALKALI POLYHALIDES

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Communicated, March 3, 1923

By means of a new and powerful method of X-ray analysis the crystal structures of some of the alkali polyhalides have just been determined by the writer in association with Professor William Duane. Both the details of the method and of the analyses have been presented in other notes.[2] It is the purpose of this note to bring the new experimental data to bear upon the great uncertainty concerning the real constitution of these unique compounds which has prevailed since their discovery 30 years ago by Wells and. Wheeler.[3]

Few experimental facts concerning the alkali polyhalides have been known up to the present time, except that solutions of cesium iodide, for example, are able to dissolve iodine, or bromine or chlorine, and produce crystals whose chemical analyses may be expressed by the empirical formulas CsI_3, CsI_5, $CsIBr_2$, $CsBrI_2$, $CsICl_2$, $CsIBrCl$, etc. Wells and Penfield[4] found that the trihalides crystallize similarly and may even be isomorphous. Stability measurements by the writer and by Ephraim[5] show that the trihalides form a remarkable continuous series, in which maximum dimensions of the atoms are favorable to stability: thus CsI_3 is most stable, while $CsCl_3$, KBr_3 or NaI_3 do not exist; and KI_3, $RbBrI_2$ and $CsBr_3$ are all equally stable. These measurements also indicate very clearly that all salts which contain iodine form one stability and crystallographic series, and those containing bromine in the absence of iodine another; in other words, the heaviest halogen atom has a defining influence, so that such a formula as $CsBrI_2$ might more properly be written $CsI.BrI$.

It has been suggested that in the alkali polyhalides the metal may have a higher primary valence, as is true of gold (which is in the same periodic group as the alkali metals) in the known reaction $Au^+Cl + Cl_2 = Au^{+++}Cl_3$. Again, it has been advocated by Remsen,[6] Wells and Penfield,[4] McCombe and Reade[7] (in February, 1923), and others, that one or more of the halogen atoms have a higher valence than is true in the simple halides. Several experimental facts disprove these contentions. Freezing point and conductivity experiments show that the ions in a solution of CsI_3, for example, are Cs^+ and $I_3{}^-$. This means that in a molecule of the trihalide the single primary valence bond which holds cesium and iodine together in CsI is unchanged, but that the iodide ion is able to associate with itself two additional atoms of iodine, or a halogen *molecule* capable of independent existence, and form complexes. In solution the equilibrium $I^- + I_2 \rightleftarrows I.I_2{}^-$

is very definitely established. Besides the complex anions of the halogens, those of sulfur, $S.S^{--}$, S_2S^{--}, S_3S^{--}, S_4S^{--} and S_5S^{--}, have been identified by Küster,[8] and those of tellurium, $TeTe^{--}$ and Te_3Te^{--} in the beautiful work of Kraus.[9] These are all manifestations of secondary valence just as truly as the combinations of water with salts to form hydrates or of ammonia to form ammines (cationic complexes) are secondary valence phenomena. These experiments, however, cannot explain the structure and the real nature of these complex groups, and they cannot be interpreted so as to give concrete knowledge of secondary valence. The actual crystal structures give this information unmistakably, and in addition answer many questions which are confronting chemists, such as whether or not the identity of the single chemical molecule is retained in the space lattice of a solid.

The crystal structures of four alkali polyhalides have now been more or less completely determined. The results are as follows:

KI_3 monoclinic $d_{100} = 4.70 \times 10^{-8}$ cm.

CsI_3 orthorhombic $d_{100} = 4.49$, $d_{010} = 6.43$, $d_{001} = 7.02 \times 10^{-8}$ cm.

$CsIBr_2$ orthorhombic $d_{100} = 4.26$, $d_{010} = 5.91$, $d_{001} = 6.90 \times 10^{-8}$ cm.

$CsICl_2$ rhombohedral hexagonal d (Cs to I along trigonal axis) = 6.102×10^{-8} cm.

Of these the first three have been studied by the writer[2] and the last by Wyckoff.[10] In spite of the fact that three crystallographic systems are represented, the exceedingly interesting result comes out that all four crystal structures present precisely the *same* relative arrangement of atoms in the unit parallelopipeda, if these unit cells are properly oriented so as to include one molecule. It is of secondary importance for the purpose in hand that the unit cell planes may be perpendicular or inclined to each other, or that the axes may be equal or unequal in length. This arrangement is as follows: metal atoms at the corners of the cell, and halogen atoms inside the cell *in a line* on the body diagonal, with the heaviest halogen atom at the center and the other two on the diagonal on either side equidistant from the center (if they are alike). In CsI_3 and $CsIBr_2$ the distance from the center along the diagonal of the two iodine or two bromine atoms is half that from the center to the corner; hence the coördinates are $(a/4, b/4, c/4)$ and $(-a/4, -b/4, -c/4)$, where a, b, and c are the edge lengths of the unit cell in three directions at right angles. In $CsICl_2$ the chlorine atoms have a parameter of .19 of the total length of the diagonal on either side of the central iodine atom, so that the unit cell is a rhombohedron instead of a rectangular parallelopiped. It is an interesting conjecture whether the orthorhombic variety of $CsICl_2$, if it does exist, is produced by a displacement of the chlorine atoms farther along the diagonal from the center. The only other possibility would be that a chlorine atom occupies a central position instead of the iodine, but this should be very

much less stable than the other arrangement.   There is no doubt but that
the normal tendency of the compound is to form the rhombohedral hex-
agonal form.

In KI_3 the unit cell is a monoclinic prism which has been formed by the
slight deformation of a cube.   The parameter of the two non-central iodine
atoms on the body diagonal is slightly less than .25 (approximately .23)
of the total length of the diagonal.

Thus in every case experimentally observed the three halogen atoms are
closely associated together in a line, and constitute a singly acting group in
the space lattice just as truly as they do in the formation of complex anions
in solution, and just as truly as the identity of the complex cation [Ni
$(NH)_6]^{++}$ is perfectly maintained in the space lattice of crystals, as proven
by the crystal structures of nickel halide and nitrate hexammoniates de-
termined by Wyckoff.[11]   There is every reason to believe that the facts
discovered for the four typical polyhalides are also true of all other poly-
halides; since they are so closely related crystallographically and chemi-
cally.   At least it is practically certain that the relative arrangement of
atoms in the unit cells is the same.   The experimental proof that the heav-
iest halogen atom is central in the halogen group is entirely compatible
with the facts also experimentally observed that salts containing iodine
form one stability and crystallographic series and bromine another.   Dif-
ferences in the polyhalides therefore arise only in the size and shape of
the crystal unit cell, and in most cases even the latter is the same.

While it is clear that the secondary valence group of the polyhalides, as
well as those of ammines and hydrates, maintains its individuality in the
crystal space lattice, it is still a question whether the whole molecule of KI_3,
for example, exists as such in the space lattice.   It has been clearly demon-
strated that the simple chemical molecule Na-Cl as it is found in vapor does
not exist as such in the crystal lattice, since every sodium atom is sur-
rounded at the corners of an octahedron by chlorine atoms, and every
chlorine atom similarly by six sodium atoms.   On the other hand Bragg[12]
has shown conclusively that the single molecules of organic substances, and
perhaps of some inorganic compounds, are retained intact in the lattice,
and that the actual symmetry of single molecules is the determining factor
of crystallographic symmetry.   Thus a single completely asymmetrical
molecule in a unit cell can produce only the asymmetrical triclinic system;
the higher symmetry of the monoclinic and orthorhombic systems is at-
tained by placing 2 or 4 or 8 whole asymmetrical molecules in the unit
cell properly oriented about planes or centers of symmetry.   As a sort of
middle ground between the lattices of sodium chloride and of organic
compounds, there may be cited the examples of the hexammoniates of the
nickel halides[11] and the hexahydrate of zinc bromate.[13]   In the single mole-
cule of $Ni(NH_3)_6Cl_2$, six molecules of ammonia are bound to the nickel atom

by secondary valence forces, and the two chlorine atoms by primary valence bonds. In the crystal lattice each nickel atom is still surrounded symmetrically by six ammonia molecules, but there are not two but *eight* equidistant chlorine atoms in the same way that there are six chlorine atoms around each sodium atom in sodium chloride. The compound $Zn(H_2O)_6$-BrO_3 is exactly analogous.

It cannot be denied that the forces which hold organic molecules fixed in crystal lattices, or which enable very long molecules lying parallel to form liquid crystals, or which cause the molecules of almost all organic substances to become very definitely oriented in surfaces, are the same kind of forces which hold electrically neutral molecules of ammonia or water to metal atoms, either in the single molecule or in the crystal lattice. Now it has been proven that precisely the same thing is true of the halogen groups in polyhalides, even though the forces are holding together three atoms, or even more, of the same chemical nature, instead of grouping neutral atoms or molecules around a central atom of greatly different nature.

If planes are drawn through the lattices of the four experimentally studied trihalides so as to enclose $1/2$ instead of one molecule, then the metal atoms and the heaviest (previously body-centered) halogen atoms appear alternately at the corners of the new unit, while one atom of iodine in KI_3 or CsI_3, one atom of bromine in $CsIBr_2$, or one atom of chlorine in $CsICl_2$ lies on the body diagonal at .46 or .50 or .38 of its length from a corner iodine atom. Hence the structures are remarkably closely related to the simple halide unit cubes. A halogen atom in the latter case is replaced by a polyhalide group. Dimensions are changed and perfect cubic symmetry destroyed, but every metal atom is surrounded by six complex halogen groups, each acting as a single point in the lattice. The single primary valence bond of the chemical molecule is split in the lattice, but the secondary valence group within itself is retained intact.

It has already been stated that the stability of the alkali polyhalides depends upon the metal—as a matter of fact relative stabilities are directly proportional to the atomic volumes of the metals. This is now easily explained. The size of the metal atom in the lattice determines the dimensions of the unit cell, or the interplanar distances, other things being equal. The smaller the dimensions the more difficult it is for three halogen atoms to lie on a straight line within the cell with any degree of stability. Halides of potassium are just able to form polyhalides; as a matter of fact only the iodide is able to form such compounds sufficiently stable to isolate. The size of the potassium atoms and the interplanar distances are such that upon the formation of KI_3 the string of iodine atoms predominates, the frame-work of the potassium atoms is distorted unequally in different directions, and the resultant properties approximate those of elementary iodine crystals. The compound NaI_3 does not exist because, even if the

I_3 groups were compressed in the lattice, the attraction of two iodine atoms under these circumstances far outweighs the ability of the sodium atom to hold three iodine atoms in spatial distribution.   The equilibrium expression $I^- + I_2 \rightleftarrows I.I_2^-$ holds just as truly in the formation of solid crystal lattices as it does in ionized solution.   Hence even in the very stable CsI_3 the reaction is easily sent from right to left by the application of mechanical compression or by increasing kinetic energies of vibration by means of heat.

The newly determined crystal structures of the trihalides present interesting evidence bearing upon the general question of the additivity of atomic radii.   In the case of CsI_3, for example, the diagonal along which lie 1 atom of cesium and 3 atoms of iodine has a length of 10.6×10^{-8} cm. This is appreciably smaller than the sum of 1 cesium diameter plus 3 iodine diameters as evaluated under different assumptions by Bragg, Richards, Davey and others.[14]   Hence the I_3 group must be very considerably compressed so that the atoms may be pictured as flattened in the direction parallel to the crystal cell diagonal into a shape something like that of red blood corpuscles.   The experimental results are further proof of the validity of the conception of compressible atoms so long advanced by Professor T. W. Richards and of the incorrectness of the hypothesis of constant atomic radii.[15]

It is interesting to note that it is possible to prepare CsI_5. Wells and Penfield[4] claim that the crystals are triclinic.   If this is true it may be safely predicted upon the basis of the present analyses, that the lines joining the two iodine atoms on each side of the center to the central iodine atom *will intersect at an angle.*

Finally, it may be asked whether any formula can express the constitution of the alkali polyhalides.   It is obvious that none can express all the facts.   The X-ray data gives the only absolute picture of the constitution of the solid state.   The nearest approach to a mechanical formulation would express the empirical formula $CsICl_2$ as Cs$-- --$I .   The dotted lines

$$\begin{array}{c} {}^{\nearrow}\text{Cl} \\ \text{Cs}{\scriptstyle\diagup}\!-\!-\!-\!\text{I} \\ {}_{\searrow}\text{Cl} \end{array}$$

mean not an increase in the number of primary valences for cesium, but a split one.   The expression shows the halogens bound together by secondary valences, with the heaviest halogen at the center, so that a singly acting unit is produced; and yet each single halogen atom also comes under the direct influence of the metal atom.   Otherwise it would be difficult to explain the mechanism whereby $CsICl_2$, prepared by passing chlorine into a solution of CsI, should decompose into CsCl and ICl.   It is of course perfectly natural that the strongest halogen should remain bound to the

metal.   Furthermore, by a simple consideration of balance the formula

shows why Cs—I should be, and is, more stable even than Cs—I .
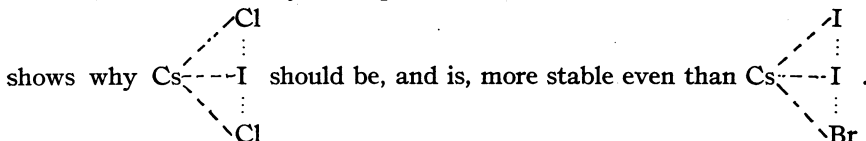
Even with these advantages, however, the formula falls far short of expressing correctly all the facts which crystal structure determinations have revealed.

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[2] Clark and Duane, these PROCEEDINGS, **8**, 90 (1922); *Ibid.*, April, 1923.

[3] Wells and Wheeler, *Zs. anorg. Chem.*, **1**, 442 (1892).

[4] Wells and Penfield, *Amer. J. Sci.*, **43**, 21, 475 (1892).

[5] Ephraim, *Ber. deut. chem. Ges.*, **50**, 1069 (1917).

[6] Remsen, *Amer. Chem. J.*, **11**, 291.

[7] McCombe and Reade, *J. Chem. Soc.* (London), **123**, 141 (Feb., 1923).

[8] Küster, *Zs. anorg. Chem.*, **43**, 53 (1905); **44**, 431 (1905); **46**, 113 (1905).

[9] Kraus, *J. Amer. Chem. Soc.*, **44**, 1216 (1922).

[10] Wyckoff, *Ibid.*, **42**, 1100 (1920).

[11] Wyckoff, *Ibid.*, **44**, 1239, 1260 (1922).

[12] Bragg, *J. Chem. Soc.* (London), **121**, 2766 (Dec., 1922).

[13] Wyckoff, *Amer. J. Sci.*, **4**, 188 (1922).

[14] Clark, *Science*, **55**, 401 (1922).

[15] Cf. also Wyckoff, these PROCEEDINGS, **9**, 33 (Feb., 1923).   The radius of the chlorine atom calculated from $CsICl_2$ is unusually small as it should be since it is measured along the diagonal in the direction of greatest compressing forces.   For this reason the direct application of this dimension to other chlorine compounds has little meaning.

THE CRITICAL AND DISSOCIATION POTENTIALS OF HYDROGEN

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When electrons collide with gas molecules the collisions are elastic, or nearly so, until the electrons acquire a definite velocity.   This velocity is characteristic of the gas.   The potential through which the electrons must fall to attain this velocity is called a critical potential.   The determination of the critical potentials of hydrogen has been the object of many investigations during the last ten years, but considerable uncertainty still attaches to their exactness.   Thus the potential ascribed to the dissociation of the hydrogen molecule and the ionization of one of the resultant atoms was found by Franck, Knipping and Krueger[1] to be 17.1 volts, whereas Boucher[2] reports 15.6 volts for the same phenomenon.   Recently