STRUCTURES OF INTERHALOGEN COMPOUNDS AND POLYHALIDES

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I. Introduction

In spite of their unusual composition, many of the interhalogen compounds and polyhalides are easily prepared; some of them are known almost as long as the halogens themselves. The first interhalogens, ICl and ICl_3, were discovered by Davy (*27*) and by Gay-Lussac (*41*) in 1814, the first crystalline polyhalide, strychnine triiodide, was prepared by Pelletier and Caventou (*77*) in 1819.

The two classes of compounds have in common that they are, or contain, complexes of halogen atoms; the interhalogen compounds are electrically neutral polyhalogen complexes, the polyhalides contain negatively charged polyhalide ions. Recently also some positive polyhalogen complexes have been discovered, for instance BrF_2^+, ICl_2^+ and IF_4^+; these will be included in our discussion of the polyhalogen complexes.

The formulas of the polyhalogen compounds were not well understood from the point of view of the classical valence rules; they are a challenge for the application of the modern theories of valency. During the last years many of the structures of polyhalogen complexes have been elucidated

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and theoretical interpretations of them have been proposed. This work will be the main subject of the present review. In Section II a survey will be given of the existing polyhalogen complexes. Their chemical and physical properties will be discussed only in outline, but a fairly complete account will be given of their stability and structures. In Section III the various theoretical interpretations of these structures will be compared.

II. Survey of the Structures and Properties of Polyhalogen Complexes

A. INTERHALOGEN COMPOUNDS

1. *Classification of the Interhalogens*

In composition all interhalogen compounds belong to one of the classes AB, AB_3, AB_5 or AB_7 (Table I). This means that if they consist of molecules these molecules must contain an even number of atoms, and hence, an even number of electrons. Ternary or quaternary interhalogens are not known; attempts to isolate ternary compounds of iodine, bromine, and chlorine proved to be unsuccessful (*19, 44*).

TABLE I
MOLECULAR FORMULAS OF THE INTERHALOGEN COMPOUNDS

AB	AB_3	AB_5	AB_7
IF[a] (*30*)	BrF_3 (*59, 80*)	IF_5 (*67*)	IF_7 (*88*)
BrF (*87*)	ClF_3 (*90*)	BrF_5 (*91*)	
ClF (*86*)	I_2Cl_6 (*41*)		
ICl (*41*)			
IBr (*3*)			
BrCl (*3*)			

[a] IF is observed only in flames obtained when iodine or substances containing iodine are brought into contact with fluorine. It was identified by its emission spectrum (*30*).

All interhalogens are found to be molecular compounds; indeed, their molecular formulas have been determined from measurements of vapor densities and freezing points of solutions or, in the case of I_2Cl_6, which is only known in the solid state, from X-ray diffraction. In Table I the molecular formulas are listed. It is seen that, with the exception of I_2Cl_6, the molecules contain only one A atom.

Table I shows that in the group AB all conceivable representatives are known, whereas in the other groups many combinations are lacking. Apparently the occurrence of compounds in these latter groups is confined to those for which halogen A is larger than B. Whether or not a conceivable interhalogen can be prepared depends on its stability with respect to the elements from which it is composed and with respect to other interhalogens of the elements considered (see Section II,A,*3*).

2. Properties of the Interhalogens

a. Preparation. The interhalogens are prepared from the elements; the type of compound being obtained depends on the conditions under which the reaction is carried out. Because of the great reactivity of fluorine and some of its interhalogens, copper, nickel, or fluorothene reaction vessels are used for the preparation of the interhalogens of fluorine (*50, 96*). The interhalogens ClF_3 and BrF_3 are produced on a technical scale (*60, 79*).

b. Reactivity. In general the chemical properties of the interhalogen compounds are similar to those of the halogens themselves. Still, the use of interhalogens instead of the halogens is of advantage in some halogenation reactions. Fluorinations, for instance, which would take place too vigorously with fluorine itself, can easily be performed when ClF_3, BrF_3 or IF_5 are used as fluorinating agents (*4, 31, 75, 79, 89, 100*). Conversely, the application of an interhalogen compound is sometimes useful in cases where the substitution of a halogen takes place too slowly when the halogen itself is used as a reactant. For instance, iodinations in organic chemistry can in some cases be performed more easily by ICl than by iodine itself (*20, 120*).

c. Physical properties. ICl, IBr, and ICl_3 are solids at room temperature; BrF_3, BrF_5, and IF_5 are liquids, whereas the other interhalogens are gases. The electrical conductivity is very small in the solid state; in the liquid state some of the interhalogens show a small conductivity, which has been explained by the assumption that these liquids are ionized to a small extent; for instance:

$$2ICl \rightleftharpoons I^+ + ICl_2^-$$

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

$$2IF_5 \rightleftharpoons IF_4^+ + IF_6^-$$

In all cases, however, the electrical conductivity is much smaller than for instance that of fused salts; the interhalogens can therefore be considered as molecular compounds.

3. Stability of the Interhalogens

Some information about the nature of the bonds in the interhalogens can be obtained from a study of the thermodynamical data. In Table II, ΔH°, ΔG° and ΔS° represent the standard enthalpy, free enthalpy and entropy of formation. These data have been derived from heats of reaction, spectroscopic heats of dissociation, equilibrium constants, and statistically calculated entropy values. They can be corrected for the virtual transformation to the gaseous state of those halogens and interhalogens which are

TABLE II

THERMODYNAMIC DATA AND DIPOLE MOMENTS OF INTERHALOGEN COMPOUNDS AND HALOGENS[a]

Substance	State under standard conditions	ΔH°	ΔG°	ΔS°	$\Delta H^\dagger$	$\Delta G^\dagger$	$\Delta S^\dagger$	$-D$	μ (in debyes)
IF	g	−22.7	−28.1	18.3	−30.1	−30.4	1.1	−66.2	
BrF	g	−14.7	−18.3	12.4	−18.4	−18.7	1.2	−59.4	1.29 (*104*)
ClF	g	−13.4	−13.8	1.2	−13.4	−13.8	1.2	−60.3	0.88 (*43*)
ICl	s	−7.67	−3.36	−14.5	−3.35	−3.76	1.4	−49.6	0.63[b] (*62, 110*)
IBr	s				−1.42	−1.83	1.4	−41.9	1.26[b] (*97, 98*)
BrCl	g	3.46	−0.24	12.5	−0.21	−0.62	1.4	−51.5	
BrF_3	l	−75	−57	−60	−67.1	−54.9	−40.9	−144.9	
ClF_3	g	−38.8	−29.5	−31.3	−38.8	−29.5	−31.3	−122.4	0.554 (*63*)
ICl_3	s	−21.1	−5.36	−52.9					
IF_5	l	−205.3	−180.3	−84.0	−202.6	−180.6	−73.6	−312.1	
BrF_5	l	−127.5	−101.9	−86.0	−124.0	−101.9	−74.0	−238.5	
IF_7	g	−224.3	−194.3	−100.8	−231.7	−196.6	−118.0	−378.0	
F_2	g	0	0	0	0	0	0	−36.7	
Cl_2	g	0	0	0	0	0	0	−57.08	
Br_2	l	0	0	0	7.34	0.751	22.2	−45.46	
I_2	s	0	0	0	14.88	4.63	34.4	−35.54	

[a] ΔH, ΔG and D are given in kcal/mole, ΔS in cal/degree/mole; the data were taken or calculated from (*36*), (*85*), and (*107*).

[b] Average of different values from the literature.

liquids or solids under standard conditions. In this way the quantities $\Delta H\dagger$, $\Delta G\dagger$ and $\Delta S\dagger$ are obtained, which thus refer to the formation of gaseous AB_n from gaseous A_2 and B_2 at 25°C and 1 atm pressure.

We first consider the available data for the group AB. From the $\Delta G°$ values listed it is seen that the stability of the interhalogens AB relative to the elements at standard conditions decreases in the order IF > BrF > ClF > ICl > IBr > BrCl. The same holds for their stability relative to the gaseous elements at 25°C and 1 atm pressure, as appears from the values of $\Delta G\dagger$.

As is to be expected, the entropy change connected with the reaction

$$\tfrac{1}{2}A_2(g) + \tfrac{1}{2}B_2(g) = AB(g)$$

is small, since from two diatomic molecules, two other diatomic molecules are formed. The small increase in entropy $\Delta S\dagger$ of about 1.3 cal/degree, which is observed for all these reactions, may be interpreted as the difference in entropy per mole between an asymmetric and a symmetric diatomic molecule:

$$\Delta S = R \ln 2 = 1.4 \text{ cal/degree.}$$

Since the $\Delta S\dagger$ values are small, and equal for all interhalogens AB, the stability of these compounds relative to the gaseous elements is practically determined by the heats of formation $\Delta H\dagger$, and the order of the stabilities depends entirely on them. These $\Delta H\dagger$ values represent the bond energy of the A—B bond relative to half of the sum of the bond energies A—A and B—B; they are negative, which means that the bond A—B is stronger than the arithmetic mean of the bonds A—A and B—B.

It is interesting to compare the observed order of stability IF > BrF > ClF > ICl > IBr > BrCl, corresponding to the order in which the relative bond energies A—B decrease, with the difference in electronegativity of the constituting halogen atoms. These differences in electronegativity amount to 1.5; 1.2; 1.0; 0.5; 0.3 and 0.2 respectively (*76*). Apparently a large difference in electronegativity of the constituents corresponds to a strong bond and a larger stability of the interhalogen relative to the elements. The gain in energy with the formation of an interhalogen AB may thus be ascribed to the polar character of the A—B bond formed. The polarity of the bonds appears from the dipole moments μ shown in Table II. The order in which these dipole moments decrease corresponds to the order of decreasing stability, except in the case of IBr. The dipole moment of IBr, however, has been determined in solution, whereas those of the other interhalogens refer to the vapor phase. There are reasons to expect that the dipole moment of IBr in the gas phase will be considerably smaller than that in solution (*46*).

Although IF is the most stable of the AB interhalogens, it has been shown to exist only in small quantities under extreme conditions (*30*). This will be due to the tendency of IF to disproportionate into $I_2 + IF_5$, and to a small extent into $I_2 + IF_7$. For these reactions $\Delta G^\circ = -39.8$ and $+2.4$ kcal respectively per mole of IF_5 or IF_7 formed. For an analogous reason, the synthesis of pure BrF is difficult because of its tendency to disproportionate into a mixture of Br_2, BrF_3, and BrF_5. The standard free enthalpies for disproportionation into $Br_2 + BrF_3$ and $Br_2 + BrF_5$ are -2.1 and -10.4 kcal, respectively. The existence of the interhalogens AB is thus closely connected with the stability of the compounds AB_3, AB_5, and AB_7. The data listed for ClF and ClF_3 show that ClF is more stable than BrF with respect to disproportionation into A_2 and AB_3, since $\Delta G^\circ = +11.9$ kcal for the reaction $3ClF = Cl_2 + ClF_3$. For the disproportionation of ICl into I_2 and ICl_3, a ΔG° value of $+4.7$ kcal/mole of ICl_3 is calculated.

The stability of interhalogens of the type AB_3 relative to the elements decreases in the order $BrF_3 > ClF_3 > ICl_3$, which appears from the ΔG° values listed in Table II. As in the case of the AB interhalogens, the stability thus decreases with decreasing difference of electronegativity of the constituents.

Not only is the stability of AB_3 relative to the elements of importance, but also the stability with respect to the dissociation products $AB + B_2$, and, for BrF_3, that with respect to disproportionation into Br_2 or $BrF + BrF_5$. Bromine trifluoride has been shown to disproportionate to a small extent into BrF and BrF_5 (*105*), for which reaction $\Delta G^\circ = -6$ kcal/mole of BrF_5. The standard free enthalpy for disproportionation into $Br_2 + BrF_5$, is -6.9 kcal/mole of BrF_5 formed. For the dissociation reactions $AB_3 = AB + B_2$ we find in the cases of BrF_3, ClF_3, and ICl_3 respectively, $\Delta G^\circ = +38.7$, $+15.7$ and $+2.0$ kcal. Since the ΔH° values for these reactions are positive, the dissociation will increase at higher temperatures. The ΔG° values show that ICl_3 dissociates completely at relatively low temperatures, whereas ClF_3 and BrF_3 are quite stable with respect to dissociation.

In the group AB_5 we notice that IF_5 is more stable relative to the elements than is BrF_5. The standard free enthalpies for the dissociation and disproportionation reactions are as follows:

	ΔG°
$IF_5 \rightleftharpoons 2F_2 + IF$	+ 152.2 kcal
$BrF_5 \rightleftharpoons 2F_2 + BrF$	+ 83.6 kcal
$BrF_5 \rightleftharpoons F_2 + BrF_3$	+ 45 kcal
$\frac{7}{5}IF_5 \rightleftharpoons \frac{1}{5}I_2 + IF_7$	+ 58.1 kcal
$\frac{3}{2}IF_5 \rightleftharpoons \frac{1}{2}IF + IF_7$	+ 62.1 kcal

Both compounds are thus rather stable with respect to dissociation and, in the case of IF_5, with respect to disproportionation.

IF_7 is stable with respect to dissociation into $F_2 + IF$, but dissociates at higher temperatures into $F_2 + IF_5$:

	$\Delta G°$
$IF_7 \rightleftharpoons 3F_2 + IF$	+ 166.2 kcal
$IF_7 \rightleftharpoons F_2 + IF_5$	+ 14.0 kcal

We shall now compare the bond energies A—B in the interhalogens AB_n with those in AB. For this purpose we need the heats of dissociation into atoms, *D*, which are also collected in Table II. Part of these *D* values have been derived from the spectra of the interhalogens, others have been calculated from $\Delta H\dagger$ and the heats of dissociation of the halogens. When we anticipate the results of the structure determinations of the interhalogens (Section II,A,*4*), from which it appears that the molecules AB_3, AB_5, and AB_7 contain three, five, and seven A—B bonds respectively, the D values listed in Table II show, that the average energy per bond AB in the interhalogens AB_n is smaller than the bond energy A—B in the simple interhalogens AB. The difference is about 5% in the case of IF_5, 20% for IF_7, BrF_3, and BrF_5, and 30% for ClF_3. This may indicate a change of bond type, the influence of steric hindrance in AB_n, or both.

A reaction of the type $A_2 + nB_2 = 2AB_n$ will only be possible if $\Delta H\dagger$ has a rather large negative value, since the entropy decreases appreciably as a consequence of the decrease in the number of molecules. This will be the case if the energies of the bonds in AB_n are of the same order of magnitude as the bond energies in A_2 and B_2, because the total number of bonds in $2AB_n$ is larger than that in $A_2 + nB_2$. If, however, the bonds in AB_n are appreciably weaker than in A_2 and B_2, the interhalogen AB_n will not be stable. It is to be expected, therefore, that the interhalogens AB_n will only be stable if A is sufficiently larger than B for steric hindrance to be small.

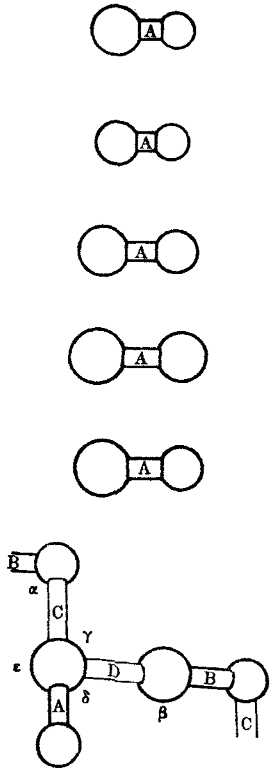
From the values listed in Table II, we can make estimates of the average bond energies in hypothetical interhalogens AB_n and of their entropies of formation. The interhalogens IF_3, ClF_5, and BrF_7 are then expected to be stable relative to the elements, although these compounds have not been observed.* It can be shown, however, that IF_3 would probably disproportionate into $I_2 + IF_5$ and that BrF_7 and ClF_5 are likely to dissociate into $F_2 + BrF_5 + BrF_3$ and into $F_2 + ClF_3$ respectively.

* *Note added in proof:* The interhalogen IF_3 has been prepared recently by M. Schmeisser and E. Scharf, *Angew. Chem.* **72,** 324 (1960). It is a yellow powder which decomposes very fast into I_2 and IF_5 at room temperature.

4. Structure of the Interhalogens

As appears from Figs. 1, 3, 4, and 5, the structures of almost all interhalogens are now known; the only exceptions are IF, which has only been obtained in small concentrations in the gas phase, and IF_5, for the structure of which only indications are available.

The atomic distances in the diatomic molecules AB in the vapor phase have been determined with great precision by spectroscopic methods and by electron diffraction; in Fig. 1 the mean values of these determinations are given as found in ref. *108*. When these distances are compared with the sum D_c, of the covalent radii of the constituting halogens (Table III), it is observed that the distance A—B is smaller than D_c by an amount which increases when the difference in electronegativity of the halogens



BrF(g)
ref. (*108*)
$A = 1.756\ (0.001)$
$D_c = 1.851$

ClF (g)
ref. (*108*)
$A = 1.628\ (0.001)$
$D_c = 1.703$

BrCl (g)
ref. (*108*)
$A = 2.138\ (0.005)$
$D_c = 2.136$

IBr (g)
(ref. *92*)
$A = 2.470\ (0.005)$
$D_c = 2.475$

ICl (g)
ref. (*108*)
$A = 2.321\ (0.001)$
$D_c = 2.327$

α-ICl (s)
ref. (*7*)
$A = 2.37\ (0.04)$
$B = 2.44\ (0.04)$
$C = 3.00\ (0.04)$
$D = 3.08\ (0.02)$
$\alpha = 102\ (2)$
$\beta = 179\ (2)$
$\gamma = 85\ (2)$
$\delta = 94\ (2)$
$\epsilon = 179\ (2)$
$D_c(\text{I—Cl}) = 2.327$
$D_c(\text{I—I}) = 2.667$
$D_W(\text{I} \cdots \text{Cl}) = 3.95$
$D_W(\text{I} \cdots \text{I}) = 4.30$

FIG. 1. Structure of the interhalogens AB. The standard error, where possible to estimate, is given in parentheses. Distances are in Å, angles in degrees.

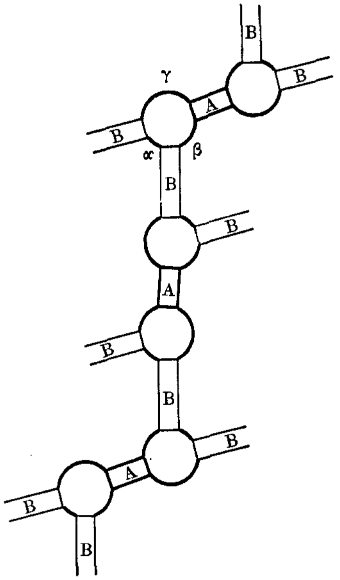
increases. This is in accordance with the rule found in Section II,A,*3*, that the bond strengths increase with the electronegativity difference.

TABLE III

COVALENT RADII (r_e) AND VAN DER WAALS RADII (r_W) OF THE HALOGENS

Substance	r_e (Å) (*108*)	r_W (Å) (*76*)
F_2	0.709	1.35
Cl_2	0.994	1.80
Br_2	1.142	1.95
I_2	1.333	2.15

The structure of one of the interhalogens AB has also been studied in the solid state. In this structure, the α modification* of ICl, the molecules are arranged in puckered zigzag chains. The intermolecular distances indicate clearly that a strong interaction between the molecules exists, because these intermolecular distances are far smaller than the sum D_W of the Van der Waals radii (Table III) of the elements in contact. On the other hand, the atomic distances in the molecules are a little larger than observed in ICl vapor. To a smaller extent the same phenomena are observed in solid



I_2 (s)
refs. (*49, 58*)
$A = 2.68$
$B = 3.56$
$\alpha = 76$
$\beta = 109$
$\gamma = 175$

FIG. 2. Crystal structure of iodine. The molecules lie in parallel layers, the arrangement in one layer is shown.

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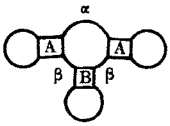
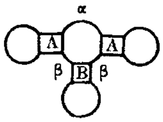
* Very similar interatomic distances have been observed in β-ICl (G. B. Carpenter, private communication).

iodine (Fig. 2), where the intermolecular distances are also smaller than the sum of the Van der Waals radii. In this case the intramolecular distance is not significantly larger, however, than the distance observed in iodine vapor.

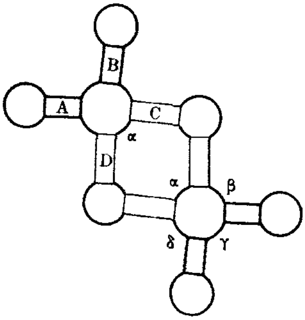
In the group AB_3 (Fig. 3) the structure of ClF_3 has been determined in the vapor as well as in the solid state, with essentially the same results. Since the accuracy of the microwave method, according to which the structure in the vapor phase has been determined, is greater than the accuracy of the X-ray diffraction study of the solid, the results of the former have been given in Fig. 3. The atomic distances in BrF_3 and ClF_3 indicate that two of the three bonds in these molecules are weaker than in BrF and ClF respectively, whereas the third might be slightly stronger. In contrast to the results obtained for solid ICl no strikingly small intermolecular distances are observed in solid ClF_3. The structure of ICl_3 is exceptional in this respect, that molecules I_2Cl_6 have been found. These molecules are separated from each other by normal Van der Waals distances. It appears



BrF_3 (g)
ref. (*64*)
A = 1.810 (0.005)
B = 1.721 (0.005)
α = 187.58 (0.2)
β = 86.21 (0.2)



ClF_3 (g)
refs. (*14*, *103*)
A = 1.698 (0.005)
B = 1.598 (0.005)
α = 185.0 (0.2)
β = 87.5 (0.2)

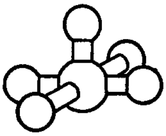


I_2Cl_6 (s)
ref. (*8*)
A = 2.38 (0.02)
B = 2.39 (0.02)
C = 2.68 (0.02)
D = 2.72 (0.02)
α = 84 (1)
β = 91 (1)
γ = 94 (1)
δ = 90 (1)

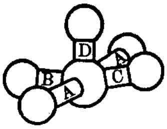
Fig. 3. *Structure of the interhalogens* AB_3.

from the intramolecular distances that the bonds in the molecule are of two different types.

The structures of IF_5 and BrF_5 (Fig. 4) are known from spectroscopic studies of the vapors and from X-ray diffraction. The spectroscopic work only indicates the symmetry of the molecules and gives only a rough estimate of the bond lengths; the X-ray diffraction study gives reasonably reliable bond lengths and angles for BrF_5. As in the case of BrF_3, one of the bonds (D) is, probably significantly, smaller than the other ones.



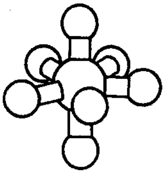
IF_5 (g)
ref. (*61*)
Bond lengths ≈ 1.75



BrF_5 (s)
refs. (*16*, *17*, *106*)
$A = 1.75$
$B = 1.82$
$C = 1.81$
$D = 1.68$
$\angle DA = 85.4$
$\angle DB = 86.5$
$\angle DC = 80.5$

FIG. 4. Structure of the interhalogens AB_5.

The structure of IF_7 (Fig. 5) is only fairly accurately known. Spectroscopic studies indicated a pentagonal bipyramid as the most probable shape of the molecule; this model was confirmed by electron diffraction studies, and it was found that the two I—F distances in the direction of the pentagonal axis (1.94 Å) were larger than those in the equatorial plane (1.83 Å). An X-ray diffraction study of solid IF_7 finally showed that in the solid the pentagonal bipyramid may be somewhat distorted. The average I—F distance was found to be 1.80 Å. The accuracy of the X-ray diffraction study leaves something to be desired, however, because of the difficulty of



IF_7 (g,s)
refs. (*5*, *13*, *15*, *28*, *61*)
Bond lengths ≈1.80 (≈0.04)
Bond angles ≈72 and ≈90
$D_c = 2.042$

FIG. 5. Structure of IF_7.

obtaining a sufficiently large number of accurate diffraction intensities for this highly reactive compound. The reported I—F distance of 1.80 Å shows a considerable contraction compared with the sum of the covalent radii of iodine and fluorine (2.04 Å).

B. POLYHALIDES

1. *Classification of the Polyhalides*

Polyhalides can, according to the number of atoms in their ions, be divided into trihalides, pentahalides, heptahalides etc. In Table IV are listed crystalline polyhalides which are obtainable with univalent cations without inclusion of solvent or other molecules. In most cases it is clear from the formulas that the polyhalide ion must contain an even number of electrons; the lowest possible formula weight of the polyhalide ion contains an odd number of atoms and hence, because of its charge, an even number of electrons. Only the formulas of the group of "even" polyhalides do not allow this conclusion to be drawn. On the contrary, if the ion in, say, CsI_4 had the formula I_4^-, the number of electrons would be odd, and the substance would be paramagnetic (*56*). From the diamagnetism of this compound it can be concluded that the formula should at least be doubled.

Polyhalides with dipositive or tripositive cations are known to be formed only with large complex cations; examples are $Ni(NH_3)_4I_n$ with $n = 4, 6, 10$, and 14 and, from tripositive cobalt, $Co(NH_3)_6I_9$ (*35*). The only exceptions to this rule are $Ba(IF_4)_2$ (*96*) and Ba $(BrF_4)_2$ (*32*).

Many crystalline polyhalides contain molecules of the solvent or other foreign molecules which are apparently essential for the stability of the compound, because the whole substance decomposes into a monohalide and halogen or interhalogen when these foreign molecules are removed. Examples of these "solvated" polyhalides are $KI_3 \cdot H_2O$, $KI_3 \cdot 2H_2O$, $KI_7 \cdot H_2O$ (*10*); $CsI_{10} \cdot 2C_6H_6$ (*38*); and $Be(ICl_4)_2 \cdot 8H_2O$ (*113*). In this way even some crystalline polyhalogen *acids* have been prepared, viz.: $HI_3 \cdot 4C_6H_5CN$ (*65*) and $HICl_4 \cdot 4H_2O$ (*18*).

Many of the polyhalide ions exist, or are assumed to exist, also in solution (Section II,B,*2*,*c*).

When we compare the compositions of the polyhalide ions with those of the uncharged interhalogen complexes, striking differences are noticed. First of all, while no ternary interhalogens exist, some ternary polyhalides are found in Table IV; secondly, many polyhalide ions are known consisting of only one species of halogen atom, whereas no uncharged complexes of more than two halogen atoms of the same kind have been described, unless crystalline iodine is considered an example of such a complex.

TABLE IV

COMPOSITIONS OF NONSOLVATED POLYHALIDES WITH UNIVALENT CATIONS

Trihalides	Ref.	Pentahalides	Ref.	Heptahalides	Ref.	Other odd polyhalides	Ref.	Even polyhalides	Ref.
NH_4I_3	(*9*)	$N(CH_3)_4I_5$	(*116, 117*)	$N(C_2H_5)_4I_7$	(*42*)	$N(CH_3)_4I_9$	(*42*)	CsI_4	(*11, 82*)
CsI_2Br	(*114*)	$N(CH_3)_4I_4Br$	(*21*)	$N(CH_3)_4I_6Br$	(*21*)	$N(CH_3)_4I_{11}$	(*39*)	$N(CH_3)_4I_{10}$	(*39*)
$N(C_2H_5)_4I_2Cl$	(*21*)	$N(CH_3)_4I_4Cl$	(*21*)	KIF_6	(*32*)	$N(CH_3)_4Br_9$	(*37*)		
$KIBr_2$	(*24*)	$NaICl_4$	(*83*)	$N(C_2H_5)_4Br_6Cl$	(*21*)				
$KIBrCl$	(*24*)	$KICl_3F$	(*6*)						
$CsIBrF$	(*24*)	$C_6H_5N(CH_3)_3Br_5$	(*40*)						
$KICl_2$	(*24*)	$AgBrF_4$	(*96*)						
NH_4Br_3	(*2*)	KIF_4[a]							
$RbBr_2Cl$	(*115*)								
$RbBrCl_2$	(*115*)								
$N(CH_3)_4Cl_3$	(*21*)								

[a] *Added in proof.* [From G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.* p. 2373 (1960).]

2. Chemical Properties of the Polyhalides

a. Preparation. It has long been known that iodine, although slightly soluble in water, readily dissolves in solutions of iodides because of the formation of triiodide. In an analogous way other polyhalides can be prepared. Examples are:

$$CsI + Br_2 \rightarrow CsIBr_2$$
$$CsBr + IBr \rightleftharpoons CsIBr_2$$
$$CsBr + 2ICl \rightarrow CsICl_2 + IBr$$
$$KCl + ICl_3 \rightleftharpoons KICl_4$$

In many cases the crystalline polyhalides can be obtained from the solution by evaporation of the solvent or by cooling. Also reactions between gaseous halogen or interhalogen and solid monohalides, without solvent, can be used for the synthesis of crystalline polyhalides.

b. Dissociation of solid polyhalides. All polyhalides decompose to some extent into a halogen or interhalogen compound and a lower halide. In many cases the dissociation pressure is already appreciable at room temperature. The chemical reactions of the polyhalides are mostly those of the dissociation products.

The stability of the polyhalides with respect to dissociation and the nature of the dissociation products will be further discussed in Section II,B,*3*.

c. Polyhalides in solution. The existence of polyhalide ions in solutions of the polyhalides in polar solvents has been adequately proved for all trihalide ions consisting of iodine, bromine, and/or chlorine atoms. The evidence was obtained from measurements of freezing point depressions, electrical conductivities, distribution equilibria with nonpolar solvents, absorption spectra, exchange of radioactive isotopes between halide ions and halogen molecules, oxidation-reduction potentials, and reactions of the polyhalide ions in solution.

For the more complex polyhalides only the existence of ICl_4^- in solution has been established; other polyhalide ions probably also exist in concentrated solutions, but their composition is not certain.

The ions in solution are in dissociative equilibrium with halide ions and halogen or interhalogen (see Section II,B,*3*).

3. Stability of the Polyhalides

It was pointed out in Sections II,B,*2*,*b* and II,B,*2*,*c* that the polyhalides are not stable with respect to dissociation into a monohalide and halogen or interhalogen compound. It is found that the dissociation always takes place in such a way that the halogen or interhalogen molecules formed contain the heaviest halogen atoms. For instance, $CsICl_2$ dissociates into $CsCl + ICl$ and not into $CsI + Cl_2$; similarly, in solution the ICl_2^- ion dissociates into $Cl^- + ICl$.

For the crystalline trihalides the order of stability has been determined by measuring the temperature at which the dissociation pressure reached one atmosphere (*34*). When the stabilities of trihalides containing the same trihalide ion but *different cations* were compared, it appeared, irrespective of the anion, that the stability of a trihalide with respect to dissociation is greater when the cation is larger and more symmetrical. This rule was also established by bringing the solid polyhalide into contact with carbon tetrachloride at 25°C, after which the equilibrium concentration of the halogen or interhalogen in this solvent was measured (*25*). Furthermore, for other types of crystalline polyhalides this relationship was derived from measurements of the dissociation pressures. In Table IV the polyhalides with the smallest unipositive cations have therefore been listed: it follows from the above rule that, in general, the corresponding polyhalides with larger cations also exist. From the fact that polyhalides with dipositive or tripositive cations are found to exist only when these cations are very large, it may be inferred that polyhalides are less stable when the charge of the cation is higher.

It is tempting to explain the dependence of the stability of a crystalline polyhalide on the nature of its cation from the fact that the lattice energy of the monohalide formed in the dissociation reaction will be large for small, highly charged and asymmetrical cations. It is difficult to prove, however, that this will be the dominating factor. The standard free enthalpy of dissociation also depends on the lattice energy of the polyhalide, and on the difference in entropy between the solid polyhalide and the monohalide. Even if the influence of the entropy is neglected, the difference between the lattice energies of different polyhalides cannot be expected to be negligible, especially when their crystals are not isomorphous.

We shall now compare the stabilities of trihalides containing the same cation but *different trihalide ions,* which have been determined from measurements of dissociation pressures as well as from measurements of the equilibrium concentration of the halogen or interhalogen formed in carbon tetrachloride. In this case the order of stability obtained by the two methods was different, which is not surprising, because in the second method the interaction between halogen or interhalogen and the solvent plays a role. Again, a somewhat different order of stability may be expected when the degrees of dissociation of different trihalide ions in (aqueous) solution are compared. The results of the three types of experiments are collected in Table V.

All three methods confirm the regularity, already mentioned, that, on dissociation, the monohalide formed contains the lightest halogen atom.

We may try to explain this regularity in a way similar to that attempted for the explanation of the dependence of the stability on the nature of the cation. It may then be ascribed to the large lattice energy of the monohalide formed when this monohalide contains the small halide ion. Here, however, a further complication arises, because for the different ways of dissociation of the polyhalide which are possible *a priori*, the halogen or interhalogen formed is also different. In addition to the lattice energies and entropies, the energy and entropy change in the reaction: trihalide ion = monohalide ion + halogen or interhalogen, is important. In Section III,C we shall find an indication that the formation of the smallest halide ion is also favored in the latter reaction.

TABLE V

TRIHALIDES OF THE SAME CATION LISTED IN ORDER OF DECREASING STABILITY

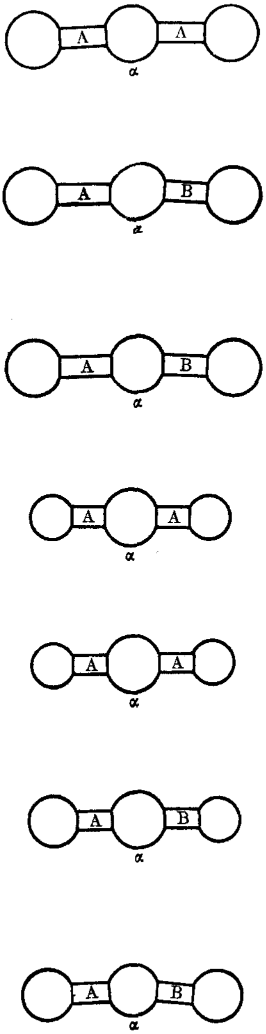
Dissociation pressure (*34*)	CCl_4 method (*25*)	Dissociation in H_2O (*66*)
I_3^-	ICl_2^-	I_3^-
IBr_2^-	IBr_2^-	IBr_2^-
ICl_2^-	I_3^-	$BrCl_2^-$
I_2Br^-	$IBrCl^-$	ICl_2^-
Br_3^-		Br_3^-
$BrCl_2^-$		I_2Br^-
Br_2Cl^-		I_2Cl^-
		Cl_3^-

An explanation of the method of dissociation of polyhalides in solution may be given along the same lines, if lattice energy is replaced by energy of hydration.

4. Structures of the Polyhalides

Our present knowledge of the structures of the polyhalides is entirely due to the application of X-ray diffraction to the crystalline compounds. The structures are now known of one or more compounds of each of the different categories of polyhalides listed in Table IV. Many of these have been established rather recently, but a number of them are due to spectacular early examples of the application of X-ray diffraction in the field of inorganic chemistry. Most of this earlier work was done by Mooney, who investigated a number of trihalides and tetrachloromonoiodides. In Figs. 6 to 10 a survey is given of the polyhalide structures known at present, only the polyhalogen complex being represented.

In the group of the trihalides (Fig. 6) some triiodides have been investi-



$As(C_6H_5)_4I_3$
ref. (*72*)
$A =$ 2.90 (0.02)
$\alpha =$ 176 (1)

NH_4I_3
ref. (*68*)
$A =$ 3.10
$B =$ 2.82
$\alpha =$ 177

CsI_3
ref. (*109*)
$A =$ 3.03 (0.015)
$B =$ 2.83 (0.015)
$\alpha =$ 176 (0.5)

$N(CH_3)_4ICl_2$
ref. (*71*)
$A =$ 2.34 (0.03)
$\alpha =$ 180

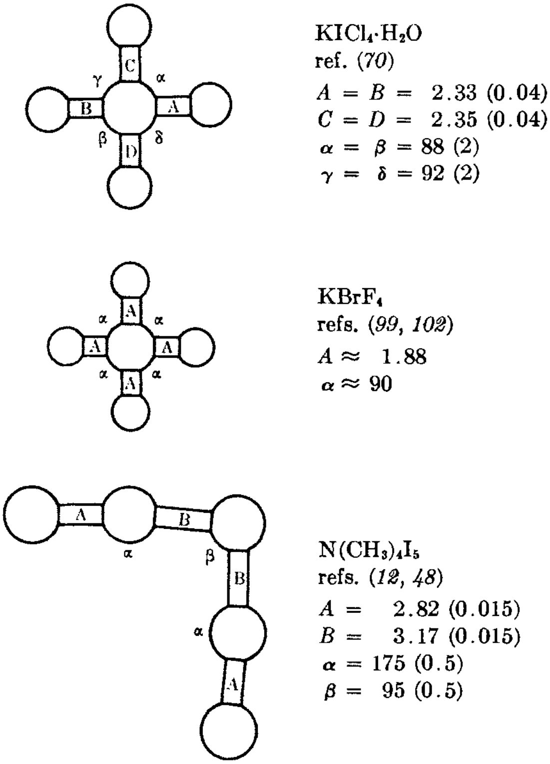
$[PCl_4][ICl_2]$
ref. (*121*)
$A =$ 2.36 (0.06)
$\alpha =$ 180

NH_4BrICl
ref. (*69*)
$A =$ 2.50 (0.04)
$B =$ 2.38 (0.05)
$\alpha =$ 179 (3)

$[N(CH_3)_3H^+]_2Br^-Br_3^-$
ref. (*84*)
$A =$ 2.54
$B =$ 2.53
$\alpha =$ 171

FIG. 6. Structure of trihalide ions.

gated. The structures observed for the triiodide ion are interesting in that symmetrical as well as asymmetrical triiodide ions have been found to exist in the solid triiodides. A recent example of the first category is the triiodide ion in tetraphenylarsonium triiodide; the triiodide ions in $N(C_2H_5)_4I_7$ (Fig. 8) may be added to this group because this heptaiodide is essentially a network of cations, centrosymmetrical triiodide ions, and iodine molecules. The most accurately investigated asymmetrical triiodide ion is that in CsI_3, where a difference in the two bond lengths of 0.20 Å, and a bond angle of 176°, are observed; these deviations from a centrosymmetrical ion are certainly significant. The average of the two bond lengths does not differ much from the bond length found in the symmetrical ions. It is 0.26 Å larger than the I—I distance in an isolated iodine molecule.



$KICl_4 \cdot H_2O$
ref. (*70*)
$A = B = 2.33\ (0.04)$
$C = D = 2.35\ (0.04)$
$\alpha = \beta = 88\ (2)$
$\gamma = \delta = 92\ (2)$

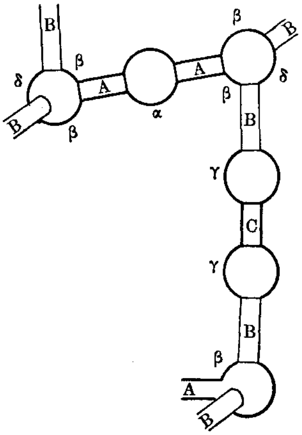
$KBrF_4$
refs. (*99*, *102*)
$A \approx 1.88$
$\alpha \approx 90$

$N(CH_3)_4I_5$
refs. (*12*, *48*)
$A = 2.82\ (0.015)$
$B = 3.17\ (0.015)$
$\alpha = 175\ (0.5)$
$\beta = 95\ (0.5)$

FIG. 7. Structure of pentahalide ions.

Among the other trihalides we find centrosymmetrical $Cl—I—Cl^-$ ions in $N(CH_3)_4ICl_2$ and $PICl_6$, in which the bond lengths are not significantly larger than the sum of the covalent radii of I and Cl or the atomic distance in the ICl molecule. Neither is the I—Br bond length in $Br—I—Cl^-$ significantly larger than the sum of the covalent radii of iodine and bromine. In the tribromide ion, however, the Br—Br distance seems to be appreciably longer again than the bond length in the bromine molecule; the difference, 0.25 Å, is probably significant, even though the structure of $[N(CH_3)_3H^+]_2Br^- \cdot Br_3^-$ has not yet been refined to the greatest possible accuracy.

In the group of the pentahalides (Fig. 7) two different types of structure have hitherto been observed. The first is the square planar structure of the ICl_4^- ion, to which structure type the BrF_4^- ion also seems to belong, although the available X-ray data hardly serve to distinguish between the square configuration and a tetrahedral one. The bond lengths correspond closely to the sum of the covalent radii of iodine and chlorine, and of bromine and fluorine, respectively. The configuration of the atoms in the I_5^- ion is entirely different; this is L-shaped and the bond lengths are appreciably greater than in the iodine molecule; they are similar to the atomic distances in the triiodide ion.

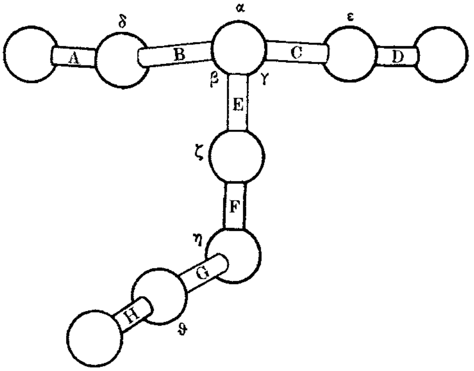


$N(C_2H_5)_4I_7$
at −175°C
ref. (*53*)
$A =$ 2.904 (0.003)
$B =$ 3.435 (0.003)
$C =$ 2.735 (0.003)
$\alpha =$ 180 (0.2)
$\beta =$ 80.5 (0.2)
$\gamma =$ 176.3 (0.2)
$\delta =$ 80.3 (0.2)

FIG. 8. Structure of $N(C_2H_5)_4I_7$. Ions I_3^- and iodine molecules form a three-dimensional array in which no I_7^- ions can be distinguished.

One representative of the group of heptahalides (Fig. 8) has been studied. It has already been mentioned that in this structure no separate I_7^- ions can be distinguished. In the structure of $N(C_2H_5)_4I_7$ centrosymmetrical I_3^- ions and I_2 molecules form a three-dimensional pattern in which each I_3^- ion is surrounded by four I_2 molecules and each iodine molecule by two I_3^- ions. Efforts have been made to prove that the symmetrical shape of the I_3^- ions is not simulated by a statistical distribution of triiodide ions, in themselves asymmetrical. The formula of tetraethylammoniumheptaiodide is more correctly written as $N(C_2H_5)_4I_3 \cdot 2I_2$. The distances between the I_3^- ions and I_2 molecules are far smaller than the Van der Waals distance of two iodine atoms, and even smaller than the intermolecular spacings in crystalline iodine; this indicates a rather strong interaction between the I_3^- ions and the iodine molecules.

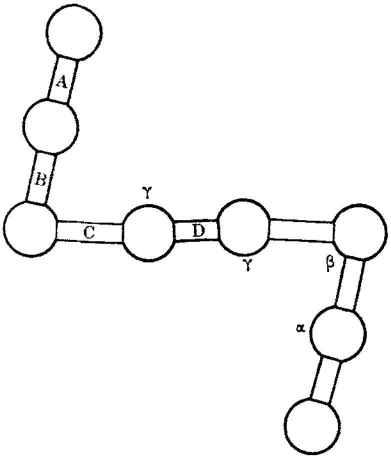
In the group of the other polyhalides with an odd number of atoms in the polyhalide ion, the structure of $N(CH_3)_4I_9$ (Fig. 9) was found to contain groups of iodine atoms which might be considered to form I_9^- ions. However, one of the atomic distances in this I_9^- unit (3.43 Å) is hardly smaller than the smallest distance between iodine atoms of different I_9^- complexes (3.49 Å). Therefore the structure can also be considered as I_7^- complexes in strong interaction with iodine molecules and with each other.



$N(CH_3)_4I_9$
ref. (*57*)
A = 2.67 (0.03)
B = 3.43 (0.03)
C = 3.24 (0.03)
D = 2.67 (0.03)
E = 3.18 (0.03)
F = 2.90 (0.03)
G = 3.24 (0.03)
H = 2.91 (0.03)
α = 156 (2)
β = 85 (2)
γ = 89 (2)
δ = 168 (2)
ε = 178 (2)
ζ = 175 (2)
η = 87 (2)
ϑ = 169 (2)

FIG. 9. Structure of $N(CH_3)_4I_9$. A complex I_9^- is shown in which the nearest approaches between iodine atoms are observed. Some distances between atoms of different I_9^- complexes are, however, as small as 3.49 Å.

A far more distinct complex is observed in the crystal structure of CsI_4 (Fig. 10). As was mentioned in Section II,B,*1*, the absence of paramagne-



CsI_4
ref. (*52*)
A = 2.85 (0.015)
B = 3.00 (0.015)
C = 3.42 (0.015)
D = 2.80 (0.015)
α = 177 (0.5)
β = 81 (0.5)
γ = 175 (0.5)

FIG. 10. Complexes $I_8^=$ in the crystal structure of CsI_4.

tism indicates a doubling of the formula of this compound. The result of the structure determination of CsI_4 shows, indeed, that I_4^- complexes do not occur in this substance, but that instead planar $I_8^=$ complexes may be distinguished. From the interatomic distances in these complexes it appears that they consist of two asymmetrical I_3^- ions of approximately the same dimensions as observed in CsI_3, and one iodine molecule. There is a rather strong interaction between the I_3^- ions and the I_2 molecule, much stronger than the interaction between different $I_8^=$ complexes, the closest inter-anionic approach being 3.88 Å.

C. Positive Polyhalogen Complexes

1. Chemistry of the Compounds Containing Positive Polyhalogen Complexes

Compounds containing positive polyhalogen ions are relatively rare. They are listed in Table VI. The BrF_2^+ ion was discovered by Emeléus and his co-workers when they studied the electrolysis of BrF_3; they later prepared a number of compounds of this cation which are given in Table VI.

TABLE VI
Compounds Containing Positive Polyhalogen Ions

Cation	Anion	Reference
BrF_2^+	SbF_6^-	(*33, 119*)
	NbF_6^-	(*47*)
	TaF_6^-	(*47*)
	BiF_6^-	(*47*)
	SnF_6^{2-}	(*119*)
	PtF_6^{2-}	(*95*)
	TiF_6^{2-}	(*94*)
	AuF_4^-	(*93*)
IF_4^+	SbF_6^-	(*118*)
ICl_2^+	$SbCl_6^-$	(*112*)
	$AlCl_4^-$	(*112*)

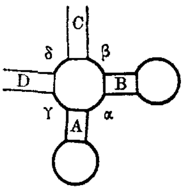
Emeléus provided strong evidence for the existence of BrF_2^+ ions by experiments in which the ion was titrated conductometrically with BrF_4^- ions. The reaction that takes place during the titration is of the following type:

$$BrF_2^+SbF_6^- + Ag^+BrF_4^- \rightarrow AgSbF_6 + 2BrF_3$$

A compound like $BrF_2^+SbF_6^-$ can be prepared from BrF_3 and SbF_5. In a similar fashion $IF_4^+SbF_6^-$ can be prepared from IF_5 and SbF_5. Compounds containing ICl_2^+ ions were recently prepared by Vonk from ICl_3 and $SbCl_5$ or $AlCl_3$. The existence of these ions could not be proved by titration reactions analogous to those with the BrF_2^+ compounds because no suitable solvent was found, but was established by X-ray diffraction studies of $ISbCl_8$ and $IAlCl_6$.

2. Structures of Positive Polyhalogen Complexes

X-ray diffraction studies have only been made of two compounds containing positive polyhalogen ions, namely $ISbCl_8$ and $IAlCl_6$. They both contain the ICl_2^+ ion and the dimensions determined for this ion in the two compounds are essentially the same. It is seen from Fig. 11 that, unlike the ICl_2^- ion, the ICl_2^+ ion is not linear but rectangular. It appears from the atomic distances that each ICl_2^+ ion interacts rather strongly with two Cl atoms of the anions in these compounds. The latter chlorine atoms lie in the plane of the ICl_2^+ ions, the four chlorine atoms constituting a distorted square. The I—Cl distances in the ICl_2^+ ion are within the limits of error equal to the sum of the covalent radii of iodine and chlorine; the other two I—Cl distances in the square are very much larger than the sum of the covalent radii, but far smaller than the sum of the Van der Waals radii.



$ISbCl_8$, $IAlCl_6$
ref. (*111*)
$A = B = 2.29\ (0.04)$
$C \approx D \approx 2.89$
$\alpha = 95\ (2)$
$\beta \approx \gamma \approx 90\ (2)$
$\delta = 85\ (2)$

FIG. 11. Structure of the ICl_2^+ ion in the crystals of $ISbCl_8$ and $IAlCl_6$. There is a strong interaction between the ICl_2^+ ion and two Cl atoms of the $SbCl_6^-$ or $AlCl_4^-$ ion.

We have now given a survey of all structures of polyhalogen complexes hitherto investigated; in the next section we shall compare these structures and try to formulate some of the characteristics they have in common.

D. SUMMARY OF THE CHARACTERISTIC FEATURES OF THE STRUCTURES OF POLYHALOGEN COMPLEXES

We shall first give a summary of the atomic distances in these complexes. In Tables VII and VIII they are compared with the bond lengths in the simple interhalogens AB or in the halogens. It is found that only in IF_7, IF_5, BrF_3, and ClF_3 are the distances, or some of the distances, significantly smaller than the corresponding spacing in AB; in all other cases the atomic distances in the polyhalogen complex are somewhat larger. For the large iodine complexes some distances are even considerably larger than the I—I bond length in the iodine molecule.

Concerning the valency angles, it is a striking feature of the polyhalogen complexes that the bond angles are close to 90° or 180°. The only notable exception is the approximately pentagonal configuration in the equatorial plane of the IF_7 molecule, while in the I_9^- conformation one angle (156°) differs appreciably from 180°.

TABLE VII

Atomic Distances in Interhalogen Compounds, Compared with the Corresponding Distances in the Simple Interhalogens AB or Halogens A_2

Compound	A—B A—A (Å)	A—B in AB A—A in A_2 (Å)	Δ (Å)
IF_7 (s)	≈1.80	(1.92)	−0.12
IF_5 (g)	≈1.75	(1.92)	−0.17
BrF_5 (s)	1.68	1.76	−0.08
	1.75		−0.01
	1.81		+0.05
	1.82		+0.06
BrF_3 (g)	1.72	1.76	−0.04
	1.81		+0.05
ClF_3 (g)	1.60	1.63	−0.03
	1.70		+0.07
I_2Cl_6 (s)	2.38	2.32	+0.06
	2.39		+0.07
	2.68		+0.36
	2.72		+0.40
ICl (s)	2.37	2.32	+0.05
	2.44		+0.12
	3.00		+0.68
	3.08	2.68	+0.41

An adequate theory of the chemical bond in the polyhalogen complexes will have to explain the above-mentioned characteristics of the bonds. In Section III we shall discuss the different attempts which have been made to achieve this end.

III. Theoretical Interpretations of the Structures of Polyhalogen Complexes

Three types of interpretation have been given of the nature of the bonds in polyhalogen complexes. The first attempts were made on a non-quantum-mechanical basis and will be indicated by "electrostatic." A second effort to explain the increased valency of the halogen atoms in the complexes was the assumption of promotion of one or more electrons from *s*- or *p*-orbitals to *d*-orbitals, after which the shape of the complexes formed was explained by hybridization of *s*-, *p*-, and *d*-orbitals to form strongly directed, localized covalent bonds. In the third type of theory, delocaliza-

TABLE VIII

ATOMIC DISTANCES IN POLYHALIDE IONS AND ICl_2^+, COMPARED WITH THE CORRESPONDING DISTANCES IN THE SIMPLE INTERHALOGEN AB OR HALOGEN A_2

Ion	A—B A—A (Å)	A—B in AB A—A in A_2 (Å)	Δ (Å)
I_3^-	2.90	2.67	+0.23
ICl_2^-	2.35	2.32	+0.03
$BrICl^-$	2.50	2.47	+0.03
	2.38	2.32	+0.06
Br_3^-	2.53	2.28	+0.25
	2.54		+0.26
ICl_4^-	2.33	2.32	+0.01
	2.35		+0.03
BrF_4^-	1.88	1.76	+0.12
I_5^-	2.82	2.67	+0.15
	3.17		+0.40
I_7^-	2.74	2.67	+0.07
	2.90		+0.23
	3.44		+0.77
I_9^-	2.67	2.67	0.00
	2.90		+0.23
	2.91		+0.24
	3.18		+0.51
	3.24		+0.57
	3.43		+0.76
$I_8^{=}$	2.80	2.67	+0.13
	2.85		+0.17
	3.00		+0.33
	3.42		+0.75
ICl_2^+	2.29	2.32	−0.03

tion of the *p*-electrons of the halogen atoms has been considered as the energetic cause of the stability of the polyhalogen complexes. We shall discuss the merits of these different points of view in the following sections.

A. ELECTROSTATIC INTERACTION

Electrostatic interactions were first put forward by van Arkel and de Boer in 1928 (*1*) to account for the existence of trihalide ions. The bond in these ions was described as an ion-dipole interaction between the halide ion and a point dipole induced by it in the associated halogen molecule; in this way the relative stability of the trihalides as a function of the polarizability and radius of the three constituent halogen atoms was discussed. Davies and Gwynne (*26*) showed that electrostatic interaction may lead to the correct order of magnitude for the energy of formation of an I_3^- ion from its constituents I^- and I_2. A more detailed electrostatic estimate by Havinga (*51*) in which, in addition to ion-dipole attraction and Born repulsion, Van der Waals attraction was also included, confirmed that electrostatic interaction leads to the right order of magnitude for the energy of formation and showed that this interaction may also produce a rather appreciable reduction of the ion-molecule distance, the calculated distance being about 3.2 Å. The value of these calculations is questionable, however, since they involve the very crude approximation of an induced *point* dipole, which is certainly far from valid in the case considered, and the use of several empirical constants. Havinga also showed that electrostatic interaction may result in an L-shaped I_5^- ion and an $I_8^{=}$ ion of the shape observed, when these units are considered as an electrostatic complex of one I^- ion and two I_2 molecules, and of two I^- ions and three I_2 molecules respectively. The structure of the I_9^- complex may be interpreted as an electrostatic interaction between an I^- ion and four I_2 molecules, three of which are directly linked to the ion, the fourth linked indirectly via the dipole induced in one of the first three molecules.

Electrostatic interaction between an I^- ion and an iodine molecule will result in an *asymmetrical* I_3^- ion, because in this theory the two bonds in the triiodide ion are essentially nonequivalent. Therefore the centrosymmetric triiodide ion, as observed in $As(C_6H_5)_4I_3$ and $N(C_2H_5)_4I_7$, cannot be explained by an electrostatic theory, unless the bonds are considered as an electrostatic interaction between an I^+ ion and two I^- ions. Similarly, the only means of explaining the existence of polyhalide ions like the symmetrical ICl_2^- and ICl_4^- ions electrostatically, would be as follows:

$$\mathrm{Cl^-I^+Cl^-} \qquad \begin{array}{c} \mathrm{Cl^-} \\ \mathrm{Cl^-I^{3+}Cl^-} \\ \mathrm{Cl^-} \end{array}$$

There are, however, arguments against the validity of these interpretations, such as the diamagnetism of the ICl_2^- ion (*45*) and the planar configuration of the ICl_4^- ion.

For the angular, positively charged complex ICl_2^+, a plausible electrostatic model cannot be given, and the same holds for the uncharged complexes, the interhalogens.

Summarizing, we may say that only in some special cases, such as the asymmetrical I_3^- ion, and the I_5^-, $I_8^{=}$, and I_9^- ions, does the electrostatic interaction provide a more or less satisfactory explanation of the structure observed; in all other cases, including the interhalogens, the ICl_2^+ ion, and the symmetrical polyhalide ions, an electrostatic theory is not useful. In the majority of instances the explanation of the bonds will have to be based on a covalent type of bonding.

B. Localized Covalent Bonds

The covalent interpretation of the interhalogens AB and of the ICl_2^+ ion does not present problems. The bonding in the compounds AB can be ascribed to the sharing of a *p*-electron of each of the two halogen atoms, in a way similar to that in the molecules A_2. The bonds in ICl_2^+ can be formed by sharing the two *p*-electrons with uncompensated spins of the I^+ ion with the valence *p*-electron of each of the two chlorine atoms; this explains the bond angle of about 90° at the I^+ ion.

In all other polyhalogen complexes the number of bonds formed by some of the halogen atoms is larger than its number of electrons with free spin. The most obvious way to account for the increased covalency of these atoms is to suppose that *d*-orbitals can participate in the bond formation. As the promotion of an electron to a *d*-orbital in these atoms requires a very large amount of energy (*78*), it has to be assumed that this loss of energy can be more than compensated for by the energy furnished by the formation of strongly directed hybridized bonds, and by the improved separation of the charge clouds of the lone pair electrons, when they go into the hybrid orbitals. Polarization of the *d*-orbitals by the electronegative ligands may be an important factor (*23*).

The promotion of *one* electron to a *d*-orbital makes it possible to share three electrons with electrons from other halogen atoms. It thus provides the possibility of the formation of three bonds in interhalogen compounds, or the accommodation of an excess electron and the formation of two bonds in the polyhalide ions. In order to account for the observed shape of the molecules or ions, sp^3d hybridization has been assumed (*55*, *76*). This hybridization results in orbitals directed to the corners of a trigonal bipyramid. Two of these hybrid orbitals have to be used for the accommodation of two lone pairs, the other three are available for bond formation or the accommodation of an excess electron of a negative ion. In this way the structures of ClF_3, BrF_3, and the trihalide ions have been interpreted as shown in Fig. 12. The observed shapes are understood to a certain extent if it is assumed that lone pair – lone pair repulsions are stronger than lone pair – bond pair repulsions, and the latter stronger than bond pair – bond pair repulsions. These assumptions are in agreement with the experience for a number of molecules outside the domain of the polyhalogen complexes.

The T-shaped AB_3 molecule will be more stable than a triangular one because the second model would contain six lone pair – bond pair angles of 90°, while the first has only four lone pair – bond pair angles of 90°, and two of 120°. The orientation of the lone pairs relative to each other, however, would be more favorable in the second model. The observed deviation of the bond angles B—A—B from 90° is elegantly explained by the assumed large repulsion between the lone pairs and bond pairs (*55*).

In the trihalide ions a linear symmetrical model is obtained when the three lone pairs occupy the equatorial orbitals, in which their mutual repulsion is probably at a minimum, and the bond pairs go into the remaining orbitals. Deviation from a symmetrical structure, such as is observed in the triiodide ions in many cases, must in this picture be due to secondary causes, probably to the influence of the environment in the crystal.

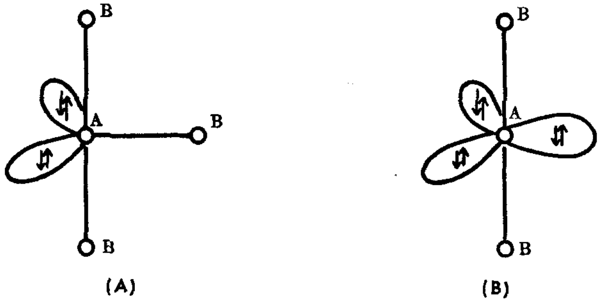


FIG. 12. Disposition of bonds and lone pairs when sp^3d hybridization is assumed (a) in ClF_3 or BrF_3, and (b) in trihalide ions.

Promotion of *two* electrons to *d*-orbitals is required in order to explain by localized covalent bonds the structure of the interhalogens AB_5 or that of the polyhalide ions ICl_4^- and BrF_4^-, in which 5 or 4 bonds respectively originate from one halogen atom. The assumption of octahedral sp^3d^2 hybridization leads to the structures represented in Fig. 13 (*55, 70, 76*).

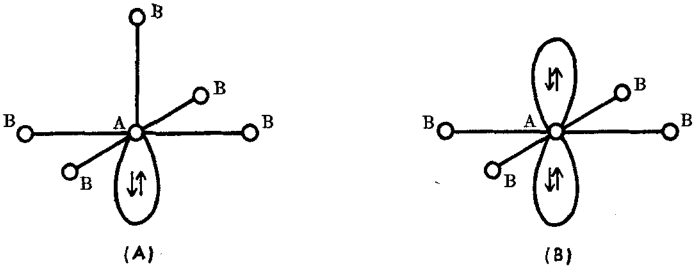


FIG. 13. Disposition of bonds and lone pairs when sp^3d^2 hybridization is assumed (a) in IF_5 or BrF_5, and (b) in ICl_4^- or BrF_4^-.

Again, the repulsion between lone pair and bond pairs explains the observed bond angles F—Br—F in BrF_5 which are slightly smaller than 90° between the vertical bond and the equatorial ones. In the AB_4^- ions the proposed structure is similar to that of the AB_5 interhalogens, except that the second lone pair replaces the vertical bond pair in the interhalogens.

The structure of IF_7, finally, can be interpreted by sp^3d^3 hybridization, requiring the promotion of *three* electrons to *d*-orbitals. This hybridization can result in bonds pointing to the corners of a pentagonal bipyramid, in which the bonds perpendicular to the equatorial plane are different from the in-plane bonds (*29*). In this model all valence electrons of the iodine atom are used in bond formation.

Depending on the mixing proportion of *s*-, *p*- and *d*-orbitals, equivalent or nonequivalent bonds can be obtained. Probably the hybridized orbitals are not all equivalent to each other, judging from the different bond lengths in the molecules or ions. Thus, in BrF_3 and ClF_3 the two vertical bonds in Fig. 12a are longer than the in-plane bond. This may be explained for instance by assuming that the vertical bonds are essentially *pd*-hybrids, whereas the equatorial ones are formed out of the remaining one *s*- and two *p*-orbitals, which again need not be equivalently hybridized. Similarly the vertical bond in BrF_5 (Fig. 13a) is probably significantly smaller than the in-plane bonds, which can be explained by assuming either the vertical bonds to be *pd*-hybrids and the horizontal ones square plane sp^2d-hybrids, or by assuming the vertical bonds to be formed by *sp*-hybrids and the equatorial ones by square plane p^2d^2 hybrids.

We have now seen that a covalent interpretation involving localized bonds can be given for the interhalogen molecules AB, for the ICl_2^+ ion, and, if the promotion of one or more electrons to *d*-orbitals is accepted as energetically possible, also for the interhalogens BrF_3, ClF_3, IF_5, BrF_5, IF_7, and the polyhalide ions ABC^-, ICl_4^- and BrF_4^-. There remain a number of structures which have not yet been considered in this Section, namely those of solid ICl and I_2Cl_6 and those of I_5^-, I_7^-, I_9^-, and $I_8^=$. Characteristic of these structures is the fact that, judging from the bond lengths, they contain bonds between the same atoms which are very different from each other. In α-ICl, for instance, we find two I—Cl bonds of about 2.4 A, while one other I—Cl bond is 3.0 Å. In I_2Cl_6 two different types of bonds are observed, one with a length of 2.4 Å and one with a length of 2.7 A. Similarly, in the polyhalide ions mentioned, the I—I bonds vary in length from 2.67 to 3.43 A. It seems unlikely that these differences in bond lengths are due to influences of the crystal environment on localized bond pairs. We saw in Section III,A that for the structure of asymmetric I_3^- ions and for that of the complexes I_5^-, I_9^- and $I_8^=$, an electrostatic explanation is possible to a certain extent; the electrostatic theory cannot account, however, for the observed distances in I_2Cl_6 and α-ICl.

C. NONLOCALIZED ORBITALS

It is well known from examples like the π-electrons in benzene, that delocalization of valence electrons may result in a gain of energy. Similarly it has been assumed (*48, 78*) that the bonds in the I_3^- ion, for instance, are the result of a delocalization of the 5*p*-electrons of the iodine atoms;* i.e., in the valence bond representation, a resonance between the structures:

$$I^- \quad I—I \quad \text{and} \quad I \cdots I \quad I^-$$

Since the interaction integral will be much larger for *p*-orbitals overlapping in the direction of their axes than for a lateral overlap of *p*-orbitals, the delocalization energy will be mainly due to the overlap of the *p*-orbitals extending in the direction of the bonds. Whether an equilibrium state with equivalent or nonequivalent bonds is obtained will depend on the nature of the system, on the magnitude of the interaction integrals, and on the way they change with the interatomic spacings.

The interaction integrals can have an appreciable value only if the atoms are sufficiently close together. In this respect there is an important difference between the well-known examples of resonance in organic chemistry and the polyhalogen complexes we are considering now. A molecule like benzene already contains a framework of σ-bonds by which the atoms are kept together; on this framework additional delocalized bonds are superimposed. On the other hand, in a case like I_3^-, the I^- ion must first be brought close to the I_2 molecule before an appreciable resonance energy can be gained.

In the system $H + H_2$, which is similar to that of $I^- + I_2$ to a certain extent, the Born repulsion will keep the H atom and the H_2 molecule a great distance apart, because the Van der Waals attraction between the two particles is very weak. The combined action of these forces will lead to an extremely loose complex, in which delocalization energy is of practically no importance. We have seen in Section III,A, however, that in the case of the I_3^- ion a relatively strong Van der Waals attraction and electrostatic interaction tend to bring the I^- ion quite close to the I_2 molecule. Furthermore, we there consider the overlap of *p*-functions, which will start at relatively larger interatomic spacings than that of the less extended *s*-functions which play a role in the system $H + H_2$. We may therefore expect that the I_3^- ion formed is appreciably stabilized by delocalization energy. Because of the complexity of the system, however, it is not possible to predict theoretically whether the bonds between the iodine atoms will be equivalent or not.

Slater (*101*), in his discussion of the structure of the I_3^- ion, assumes this ion to be asymmetrical when it is not subjected to external constraints.

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* Complexes such as the I_3^- ion were described by Mulliken (*73, 74*) as special cases of charge-transfer complexes. The stability of these complexes is also essentially due to delocalization energy.

From this point of view a symmetrical I_3^- ion is obtained only if external influences, namely the surroundings in the crystal, push the atoms of the I_3^- ion nearer to each other; below a certain critical distance of the extreme atoms resonance will result in the formation of a symmetrical ion, just as a symmetrical H_3 molecule is calculated to be formed when the distance of the extreme H atoms is below a certain limit. It is supposed that in $As(C_6H_5)_4I_3$, where a symmetrical I_3^- ion is observed, the large positive ions exert a pressure on the I_3^- ions.

Hach and Rundle (*48*) and Pimentel (*78*) take the other point of view and assume that resonance in the I_3^- ion results in a centrosymmetrical system. Asymmetrical I_3^- ions are, in this theory, due to an asymmetric surrounding in the crystal, disturbing the equivalence of the relatively weak bonds. Havinga and Wiebenga (*54*) applied a similar but somewhat extended treatment to the structure of all polyhalogen complexes, including the interhalogen compounds. We shall summarize the method followed in this paper and the results which are obtained. Most of these results are contained in (*54*) and (*51*).

The method followed is a simple LCAO—MO treatment, in which the molecular orbitals are represented by a linear combination of the outermost *p*-orbitals of the halogen atoms. Overlap integrals are neglected and all interaction integrals are taken to be zero, except those involving orbitals of adjacent atoms in the bond direction, to all of which the same value β is assigned. The calculations are made in two approximations: (*a*) as a zero approximation all Coulomb integrals α are supposed to have the same value, regardless of the nature of the halogen atoms and their formal charge; (*b*) in a first approximation different Coulomb integrals are assigned to different atoms and to equal atoms with different formal charges, according to the following rules. (i) For I, Br, Cl, and F the values α, $\alpha + 0.2\beta$, $\alpha + 0.4\beta$, and $\alpha + 1.0\beta$ are taken respectively; the assumed differences in these values are approximately proportional to the differences in electronegativities of the atoms, with a proportionality constant of $\frac{2}{3}\beta$. (ii) A formal charge Q, calculated for an atom in zero approximation, is supposed to increase the absolute value of its Coulomb integral by $\frac{2}{3}\beta \times \frac{3}{10}Q = \frac{1}{5}Q\beta$. This means that, following Pullman and Pullman (*81*), a charge Q is taken to be equivalent to an increase of electronegativity of $\frac{3}{10}Q$.

Because of the arbitrariness of the factor $\frac{2}{3}$ in assumption (i) the calculations in first approximation give no quantitative results, but indicate only the *direction* in which the results obtained in zero approximation are changed.

The LCAO—MO method described leads to the following results.

(*a*) Bond angles in polyhalogen complexes should be equal to 90° or 180°, since only then the *p*-functions of different atoms overlap satisfactorily. This is in agreement with the valence angles observed, except in the case of IF_7 (see Section II,D).

(*b*) The delocalization energy was calculated for different possible configurations of a given number of halogen atoms. It was shown that, in all cases considered, the configuration with the lowest calculated energy corresponds with the configuration actually observed for the interhalogen compound or polyhalide ion concerned. For instance, the energy of a linear trihalide ion was calculated to be lower than that of an angular one, whereas the reverse was found for a positive trihalogen ion. The energy of the linear $IBrCl^-$ ion was shown to have the lowest value when the I atom takes the central position. For the pentahalide ion it was shown that of the arrangements represented in Fig. 14, configuration (a) has the lowest energy in the first approximation when the halogen atoms are identical (I_5^-). For the ICl_4^- ion, on the contrary, configuration (c), with the I atom in the central position, has the lowest energy. However, in the latter case the energy of (b), with three bonds at the iodine atom, is almost equal to that of (c).

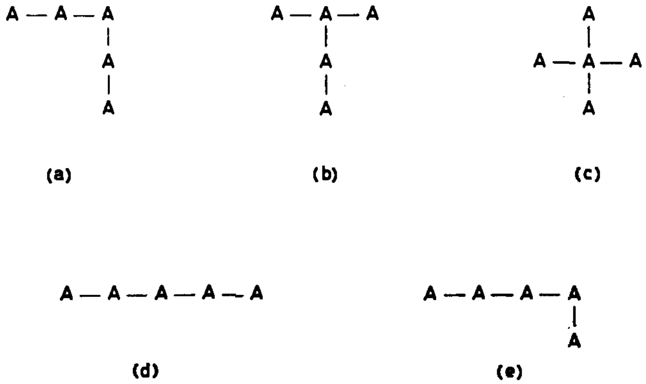

FIG. 14. Tentative shapes for a pentahalide ion.

A well-known difficulty of the simple LCAO—MO method, namely the extra stability obtained when more atoms are added to a complex, was also observed in the case of the polyhalogen complexes. Thus the calculated energy per unit ClF_3 is lower for the hypothetical molecule Cl_2F_6 in the configuration found for I_2Cl_6, than for the T-shaped molecule actually observed. Therefore it should be emphasized that it is not possible to predict, by the method followed, the number of atoms in a complex; only the configuration of a *given number* of atoms can be calculated. Probably closely connected with the extra stability of large complexes in this type of calculation is the fact that stability seems to be predicted for some complexes which do not exist, but which would be analogous to existing polyhalogens. For instance, when the interaction integral is indicated by β, and β is taken to be negative, the energy of a molecule I_4 of a shape analogous to that of the ClF_3 molecule is calculated, in zero approximation, to be -0.83β lower than that of two I_2 molecules. This gain of energy is just as high as that calculated in zero approximation for the formation of ClF_3 and for the formation of an I_3^- ion from an iodide ion and an iodine molecule. Yet the complexes ClF_3 and I_3^- can exist, whereas a complex I_4 is not observed. The discrepancy is partially removed when the calculations are repeated in the first approximation. The gain of energy on formation of an I_3^- ion, a ClF_3 molecule, and a hypothetical I_4 molecule, is then calculated to be -0.96β, -0.66β, and -0.58β, respectively. It must then be assumed that the first two reaction energies are sufficient to compensate for the loss of entropy connected with the formation of the complex, while the last one is not.

(*c*) For all interhalogen compounds and polyhalide ions the bond orders of the different bonds and the formal charges on the atoms were calculated. It appears that in all cases the sequence of the calculated bond orders agrees with the sequence of the observed bond lengths. For this comparison of bond orders and bond lengths we may refer to (*54*). The asymmetry of the triiodide ions in CsI_3 and NH_4I_3 is ascribed to the asymmetric environment of this ion in the crystal. One of the extreme iodine atoms of the complex is surrounded by cations at shorter distances than are the other two iodine atoms. When this is taken into account in the first approximation, by assigning a somewhat larger (negative) value to the Coulomb integral for this atom, a qualitative agreement between bond orders and bond lengths is again obtained. It is to be expected that the I_3^- ion will show a more pronounced deviation from a symmetrical shape in compounds with small cations than in those with larger cations, and that the deviation will disappear when the surroundings of the triiodide ion are symmetrical or nearly so. This has been observed in the compounds $As(C_6H_5)_4I_3$ and $N(C_2H_5)_4I_7$.

The formal charges appear to be quite different for the different atoms in polyhalogen complexes, even when they consist of only one kind of halogen atoms. In the triiodide ion, for instance, the formal charge of the two extreme atoms is approximately -0.5, whereas that of the central atom is about zero. In ICl_2^-, the formal charges on the Cl atoms are -0.55 and that on the I atom $+0.11$. In ICl_4^-, the Cl atoms carry a charge of -0.52 and the I atom one of $+1.07$. The results for the latter two ions seem to be in agreement with measurements of nuclear quadrupole coupling for these ions, that suggest a bonding scheme in which the electron distribution is shifted outward toward the chlorine atoms (*22*).

(*d*) We have seen in Section II,B,*3* that compounds containing a $BrICl^-$ ion decompose into a monochloride and BrI. This was partially ascribed to the high lattice energy of the crystalline monochloride formed, as compared with the energy of the corresponding bromide or iodide. In this connection it is interesting to calculate the reaction energy ΔE for the three possible decompositions of the free $BrICl^-$ ion:

$$BrICl^- \rightarrow Cl^- + BrI \tag{1}$$

$$BrICl^- \rightarrow Br^- + ICl \tag{2}$$

$$BrICl^- \rightarrow I^- + BrCl \tag{3}$$

It is found that the values of ΔE for the reactions (1), (2), and (3) are -0.82β, -1.00β, and -1.22β respectively. The fact that the calculated dissociation energy is the smallest for the first reaction may be an additional explanation for the experimentally observed method of dissociation.

(*e*) Qualitative agreement between theory and experiment is obtained when the energies of formation calculated in first approximation for simple interhalogens AB are compared with the experimental values (Table IX).

TABLE IX

Calculated and Observed Heats of Formation of the Interhalogens AB in the Gas Phase

Reaction	ΔE calc.	ΔH† obs. (kcal/mole)
$\frac{1}{2}I_2 + \frac{1}{2}F_2 = IF$	0.24β	−30.1
$\frac{1}{2}Br_2 + \frac{1}{2}F_2 = BrF$	0.15β	−18.4
$\frac{1}{2}Cl_2 + \frac{1}{2}F_2 = ClF$	0.09β	−13.4
$\frac{1}{2}I_2 + \frac{1}{2}Cl_2 = ICl$	0.04β	− 3.35
$\frac{1}{2}I_2 + \frac{1}{2}Br_2 = IBr$	0.01β	−1.42
$\frac{1}{2}Br_2 + \frac{1}{2}Cl_2 = BrCl$	0.01β	−0.21

These results demonstrate the role of the difference in electronegativity of the constituents, which was emphasized in Section II.

D. CONCLUSION

We may summarize the merits of the different approaches to an explanation of the nature of the bonds in polyhalogen complexes by stating that the pure electrostatic theory is of very limited importance for a complete understanding of these bonds. However, both the concept of localized covalent bonds and that of delocalized orbitals seem to be applicable in many cases, although they fail in particular instances. Localized bonds do not easily account for complexes like the L-shaped I_5^- ion; delocalized molecular orbitals composed from *p*-functions are attractive insofar as they do not require the use of *d*-orbitals of high energy, but they are not able to account for the structure of IF_7. In the latter case, however, the assumption of hybrids in which *d*-orbitals participate is less objectionable than in other cases, because all hybrid orbitals are used in bond formation, so that no lone pairs have to go into hybrid orbitals of high energy.

Note added in proof: A refinement of the structure of $KICl_4 \cdot H_2O$ shows that the average bond length I—Cl in the ICl_4^- ion is about 0.14 Å larger than the sum of the covalent radii of I and Cl. This long average bond length and the observed relationship between the environment of the individual Cl atoms in the crystal and their distances to the central I atom, seem to support the view that the bonds in ICl_4^- are due to electrons in delocalized molecular orbitals. The average bond order calculated on this basis (*54*) is approximately 0.7.

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