QUARTERLY REVIEWS

INTERHALOGEN COMPOUNDS AND POLYHALIDES

By A. G. Sharpe, M.A., Ph.D.
(Fellow of Jesus College, Cambridge, and University Demonstrator in Chemistry)

The existence of compounds formed by union of the halogens with one another has been recognised for more than a hundred years, and eleven such substances are now known. These are tabulated below. No ternary compound is yet known.[1]

	Type AX.	Type AX_3.	Type AX_5.	Type AX_7.
M.p. .	ClF − 156°	ClF_3 − 83°	BrF_5 − 61°	IF_7 + 5° (2 atm.)
B.p. .	− 100	+ 12	+ 40	+ 4 (v.p. = 1 atm.)
M.p. .	BrF − 33	BrF_3 + 9	IF_5 + 8	
B.p. .	+ 20	+ 127	+ 97	
M.p. .	BrCl − 66	ICl_3 + 101 (decomp.)		
B.p. .	+ 5			
M.p. .	ICl α + 27·2 β + 13·9			
B.p. .	+ 97·4			
M.p. .	IBr + 36			
B.p. .	+ 116			

All the interhalogen compounds may be (and almost invariably are) obtained by direct combination of the elements. The chlorides of iodine were discovered by Gay Lussac and by Davy in 1814. Balard first made iodine bromide in 1826; he also noticed that when bromine is mixed with chlorine the intensity of the colour is much diminished, but it was not until a century later that spectroscopic evidence established beyond doubt the existence of bromine chloride.[2] Iodine pentafluoride may have been obtained by G. Gore [3] in 1871, but its preparation from iodine and fluorine and its properties were first described by H. Moissan [4] in 1902. P. Lebeau [5] and E. B. R. Prideaux [6] independently discovered bromine trifluoride in 1905, and observed its great reactivity. The remaining compounds were first prepared by O. Ruff and his collaborators at Breslau between 1925

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[1] A. N. Campbell and L. W. Shemilt, *Trans. Roy. Soc. Canada*, 1946, **40,** III, 17.

[2] For the history of bromine chloride, see ref. (12).

[3] *Phil. Mag.*, 1871, **41,** 309.

[4] *Compt. rend.*, 1902, **135,** 563.

[5] *Ibid.*, 1905, **141,** 1015.

[6] *J.*, 1906, **89,** 316.

and 1933. Chlorine monofluoride [7] and trifluoride [8] were made from chlorine and fluorine at 250° ; the unstable bromine monofluoride [9] was prepared from the elements at 10° ; and bromine pentafluoride [10] and iodine heptafluoride [11] were obtained by fluorination of bromine trifluoride at 200° and iodine pentafluoride at 280°, respectively.

The most recent general review of the interhalogen compounds is by N. V. Sidgwick ; [12] the halogen fluorides, however, have been the subject of a separate review by H. S. Booth and J. T. Pinkston,[13] who have assembled nearly all the relevant information published before 1947. This consists mainly of methods of preparation and descriptions of physical properties, such as melting and boiling points, vapour pressures, and densities ; [13a] the sections of the review which deal with chemical properties emphasise how much is known about the reactivity of these compounds, and how little about their reactions.

Recent work on the chlorine fluorides, bromine trifluoride, and iodine pentafluoride has done something to remedy this defect, and it is with these compounds that this Review is most concerned. Investigation of the chemistry of bromine trifluoride has shown, however, how closely the chemistry of the interhalogen compounds is related to that of the polyhalides. These substances have not been reviewed for many years ; and this Review therefore deals in turn with aspects of current interest of the chemistry of iodine chlorides and bromide, polyhalides (up to 1947), recent work on halogen fluorides and related substances, the thermochemistry of the interhalogen compounds, the uses of these substances in organic chemistry, and, finally, the stereochemistry of the interhalogen ions and molecules.

The Iodine Chlorides and Iodine Bromide.—Relatively little work on the older interhalogen compounds has been reported during the last twenty years. Convenient methods for the preparation of iodine monochloride and trichloride have been given by J. Cornog and R. A. Karges [14] and by H. S. Booth and W. C. Morris,[15] respectively. The monochloride has a Trouton constant of 27·5.[16] Its polymorphism [17, 18] remains unexplained, no investigation of the structure of the solid substance ever having been made. Reactions of iodine monochloride with a number of salts have been studied : [19] the chlorides of potassium, ammonium, rubidium, and cæsium

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[7] O. Ruff and E. Ascher, *Z. anorg. Chem.*, 1928, **176**, 258.

[8] O. Ruff and H. Krug, *J.*, 1930, **190**, 270.

[9] O. Ruff and A. Braida, *ibid.*, 1933, **214**, 81.

[10] O. Ruff and W. Menzel, *ibid.*, 1931, **202**, 49.

[11] O. Ruff and R. Keim, *ibid.*, 1930, **193**, 176.

[12] *Ann. Reports*, 1933, **30**, 128.

[13] *Chem. Reviews*, 1947, **41**, 421.

[13a] A. A. Banks and A. J. Rudge (*J.*, 1950, 191) have given further physical properties of ClF_3.

[14] " Inorganic Syntheses ", Vol. I, 1939, p. 165.

[15] *Ibid.*, p. 167.

[16] J. Cornog and R. A. Karges, *J. Amer. Chem. Soc.*, 1932, **54**, 1886.

[17] W. Stortenbecker, *Z. physikal. Chem.*, 1889, **3**, 11.

[18] J. R. Partington, " General and Inorganic Chemistry ", 1946, p. 816.

[19] J. Cornog, H. W. Horrabin, and R. A. Karges, *J. Amer. Chem. Soc.*, 1938, **60**, 429.

are soluble in the molten substance, forming polyhalides, whilst those of lithium, sodium, silver, and barium are only very slightly soluble ; cyanates and thiocyanates react to form iodine tricyanate, $I(CNO)_3$, and iodine trithiocyanate, $I(CNS)_3$. The chemistry of such halogen–pseudohalogen compounds, and indeed that of the pseudohalogens themselves, has been little investigated and deserves further attention.[20]

Fused iodine monochloride was found by Faraday and many later investigators to conduct electricity, and it is now certain that the conductivity, which approaches that of some fused salts, is not due to impurities. The most recent values for the specific conductivity are $4{\cdot}58 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$ and $4{\cdot}52 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$ (both at 35°) by Cornog and Karges,[16] and by Y. A. Fialkov and O. I. Shor.[21] Fialkov and Shor also studied the variation of specific conductivity with temperature ; they found an extended maximum in the range 50—70°, and above that temperature a steady decrease which they attributed to thermal dissociation. H. J. Emeléus and N. N. Greenwood [22] have confirmed their results, and noted in addition that there is no decomposition potential. The electrolysis of the fused substance, however, still awaits detailed investigation. On electrolysis of iodine monochloride in nitrobenzene [23] or acetic acid,[24] both iodine and chlorine appear at the anode ; their determination by the use of silver electrodes indicates that about 1·5 equivalents of chlorine and less than one equivalent of iodine per Faraday are liberated at the anode, and seems to indicate dissociation according to the equation $2ICl = I^+ + ICl_2^-$.

Electrolytic studies [23] on the system $ICl{-}AlCl_3{-}Ph{\cdot}NO_2$ have indicated the existence of a compound $IAlCl_4$. F. Fairbrother [25] found the dipole moments of iodine monochloride in carbon tetrachloride and *cyclo*hexane solution (1·49 and 1·47 D., respectively) to be about twice the dipole moment in the vapour phase, and suggested that in solvents of higher dielectric constant free ions should be formed ; his suggestion thus appears to be correct, though the chloride ion is probably solvated, yielding $(ICl_2)^-$.

Few data for the conductivity of iodine trichloride are available. Solutions of the compound in nitrobenzene,[26] acetic acid,[27] and bromine [28] have been shown to conduct, and fused iodine trichloride in a closed vessel is a good conductor,[22] the specific conductivity at the melting point (101°) being $8{\cdot}4 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$—nearly twice the value for iodine monochloride at 35°. It increases up to 111° and then decreases. No decomposition potential has been found, but for iodine trichloride (unlike the monochloride and the bromide) the conductivity of the solid at the melting point is of the same order of magnitude as that of the liquid.

The specific conductivity of iodine bromide [29] is $6{\cdot}4 \times 10^{-4}$ ohm^{-1} cm.$^{-1}$

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[20] For a review, see P. Walden and L. F. Audrieth, *Chem. Reviews*, 1928, **5**, 339.

[21] *J. Gen. Chem. Russia*, 1948, **18**, 14.

[22] *J.*, 1950, 987.

[23] Y. A. Fialkov and K. Y. Kaganskaya, *J. Gen. Chem. Russia*, 1948, **18**, 289.

[24] C. Sandonnini and N. Borghello, *Atti R. Accad. Lincei*, 1937, **25**, 46.

[25] *J.*, 1936, 847.

[26] V. Finkelstein, *Z. physikal. Chem.*, 1925, **115**, 303.

[27] B. P. Bruns, *ibid.*, 1925, **118**, 89.

[28] W. A. Plotnikov, *Chem. and Ind.*, 1923, **42**, 750.

[29] Y. A. Fialkov and N. I. Goldman, *J. Gen. Chem. Russia*, 1941, **11**, 910.

at 45° and has a maximum value at 65° No recent measurements on the conductivity of iodine bromide solutions have been reported, though solutions in nitrobenzene, liquid sulphur dioxide, and arsenic trichloride are known to be conductors.[26]

The reaction $H_{2(g)} + 2ICl_{(g)} = 2HCl_{(g)} + I_{2(g)}$ has attracted some attention. The thermal reaction at temperatures between 205° and 240° was followed iodometrically by W. D. Bonner, W. L. Gore, and D. M. Yost,[30] who obtained a value of 33·9 kcals. for the activation energy of the slower reaction in a suggested mechanism :

$$H_2 + ICl = HI + HCl \quad \text{(slow)} \quad . \quad . \quad . \quad . \quad (1)$$

$$HI + ICl = HCl + I_2 \quad \text{(fast)} \quad . \quad . \quad . \quad . \quad (2)$$

Activation energies for these reactions were calculated by A. Sherman and N. Li [31] to be 39 and 41 kcals., respectively. This would make (2) the slower reaction, and Sherman and Li therefore suggested an alternative mechanism, of lower overall activation energy, to replace reaction (2). The hydrogen–iodine monochloride photochemical reaction has also been studied ; [32] the primary process is dissociation of the interhalogen compound into iodine and chlorine atoms.

Polyhalides.—The solubility of iodine in potassium iodide solution, and the formation of compounds between the alkali-metal halides and the chlorides and bromide of iodine, attracted early attention to the polyhalides, and there is a considerable nineteenth and early twentieth century literature on them. H. W. Cremer and D. R. Duncan made a careful and thorough re-examination of the methods of preparation,[33] physical properties,[34] and reactions in solution [35] and in the solid state,[36] of the polyhalides ; and their systematic survey summarises most of the work done before 1931 and adds a considerable amount of fresh material.

The general method for the preparation of polyhalides is direct combination between metallic halide and interhalogen compound (or, for polyiodides, iodine). This may be brought about by mixing solutions of the reactants in a suitable solvent, by exposing the halide to the vapour of the interhalogen compound, or by producing the interhalogen compound and effecting combination *in situ*. Cremer and Duncan described the preparation of compounds of the types $MIBr_2$, $MIClBr$, $MICl_2$, and $MICl_4$, and confirmed the existence of the cæsium polyhalides $CsBr_3$, CsI_3, $CsBr_2Cl$, $CsBrCl_2$, and CsI_2Br. Indications of the existence of polyhalides of sodium were obtained, but none was prepared pure and anhydrous. Methods for the determination of the dissociation pressures of the polyhalides (into the halide containing the most electronegative halogen present and an interhalogen compound) were reviewed critically, and the general order of magnitude of the dissociation pressures for series of polyhalides containing the ions I_3^-, IBr_2^-, $IBrCl^-$, and ICl_2^- was established as $Na \gg K > NH_4 > Rb > Cs$. A cæsium polyhalide containing fluorine, CsIBrF, was prepared.[34] Poly-

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[30] *J. Amer. Chem. Soc.*, 1935, **57**, 2723.

[31] *Ibid.*, 1936, **58**, 690.

[32] L. J. E. Hofer and E. O. Wiig, *ibid.*, 1945, **67**, 1441.

[33] *J.*, 1931, 1857.

[34] *Ibid.*, p. 2243.

[35] *J.*, 1932, 2031.

[36] *J.*, 1933, 181.

halides of large organic cations were described, and those of symmetrical cations were found to be the most stable.[34]

Polyhalides are, like typical ionic compounds, insoluble in liquids of low dielectric constant (such as carbon tetrachloride) but are decomposed by them to an extent which depends on the dissociation pressure of the compound under consideration. An example of the importance of the dissociation pressure in influencing reactivity is provided by the reactions of the dibromoiodides (dibromohypoiodites) with ammonia : those which have a dissociation pressure greater than about 0·005 mm. react (*via* the interhalogen compound) to yield nitrogen tri-iodide ; those of lower dissociation pressure merely form addition products.[36]

Potassium, rubidium, and cæsium compounds of the type $MICl_3F$ have been made from the fluorides and iodine trichloride ; they exhibit the usual mode of thermal decomposition and order of stability.[37] The existence of a compound of empirical formula CsI_4 was established in a study [38] of the system $CsI–I_2–H_2O$; this substance was later found [39] to be diamagnetic and was therefore allotted the formula Cs_2I_8. The isomorphism of the thallium compound TlI_3 and the tri-iodides of rubidium and cæsium [40] suggests that TlI_3 is a thallous compound, though from a study of its reactions in solution the formulation as thallic iodide is said to be supported.[41] Its preparation from thallous iodide and iodine, however, shows it to be a thallous compound, since it is clear from consideration of the appropriate standard redox potentials that iodine will not oxidise thallous thallium to the tervalent state. The relation between thallous tri-iodide and the iodothallates, such as $KTlI_4$, which it forms with solutions of iodides, requires further study.

The anhydrous acids from which the polyhalides are derived have not been prepared, but $HICl_4,4H_2O$ has been obtained by passing chlorine through a suspension of iodine in concentrated hydrochloric acid,[42] and conductivity and transference experiments [43] on solutions of iodine monochloride in hydrochloric acid prove that the interhalogen compound is present as $(H_3O)^+(ICl_2)^-$. This accords with the well-known fact that at the end of an Andrews titration (*i.e.*, by iodate in presence of *ca.* 5N-hydrochloric acid) the iodine monochloride is in the aqueous layer. The use of an organic liquid as indicator in this titration may be avoided, incidentally, by employing certain organic dyestuffs (such as Brilliant Ponceau 5R) as irreversible redox indicators, oxidised by the $(IO_3)^-$ but not by the $(ICl_2)^-$ ion.[44]

The structures of the polyhalide anions caused much speculation until

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[37] H. S. Booth, C. F. Swinehart, and W. C. Morris, *J. Amer. Chem. Soc.*, 1932, **54**, 2561.

[38] T. R. Briggs and S. S. Hubard, *J. Physical Chem.*, 1941, **45**, 806.

[39] S. S. Hubard, *ibid.*, 1942, **46**, 227.

[40] H. L. Wells and S. L. Penfield, *Z. anorg. Chem.*, 1894, **6**, 312.

[41] A. J. Berry, T. M. Lowry, and R. R. Goldstein, *J.*, 1928, 1748.

[42] V. Caglioti, *Atti R. Accad. Lincei*, 1929, **9**, 563.

[43] J. H. Faull and S. Baeckström, *J. Amer. Chem. Soc.*, 1932, **54**, 620.

[44] G. F. Smith and C. S. Wilcox, *Ind. Eng. Chem.* (*Anal.*), 1942, **14**, 49.

X-ray studies of $CsICl_2$ by R. W. G. Wyckoff,[45] of CsI_3 and $CsIBr_2$ by R. M. Bozorth and L. Pauling,[46] and, especially, of $(NH_4)I_3$,[47] $(NH_4)IClBr$,[48] $KICl_4$,[49] $(NMe_4)ICl_2$,[50] $(NMe_4)I_3$,[51] and other polyiodides,[52] by R. C. L. Mooney, led to the general conclusion that in such anions the heaviest halogen is multivalent and the others are distributed symmetrically around it. The ions containing three atoms are linear, and the $(ICl_4)^-$ ion is planar ; in all of them the interatomic distances are very nearly equal to the sums of the single-bond covalent radii of the appropriate halogens. In a series of polyiodides of organic bases, the crystal symmetry varies according to the size of the cation, and the stability increases with increasing cation size.[52] The relation between the electron configuration and the stereochemistry of these ions is discussed below.

The Halogen Fluorides.—The preparation of chlorine trifluoride on a semi-technical scale has been described by H. R. Leech,[53] W. Kwasnik,[54] and R. W. Porter.[55] Leech's description of a German process using nickel reaction vessels may be taken as typical : chlorine monofluoride is first formed (at 200°) and is converted into the trifluoride at 280° ; this is condensed and stored in steel vessels. Kwasnik [54] has also described the preparation of bromine trifluoride from bromine and fluorine at 80—100° in iron apparatus, whilst A. G. Sharpe and H. J. Emeléus [56] have reported a modification of the laboratory method used by O. Ruff and A. Braida.[57] A convenient apparatus for the laboratory preparation of iodine pentafluoride has also been described.[58] This compound has been shown [59] to be a product of the reaction between fluorine and iodine pentoxide at 250°.

Some examples of the uses of halogen fluorides prepared in Germany during the war as fluorinating agents in inorganic chemistry have been given. Thionyl chlorofluoride, SOClF, is obtained from thionyl chloride and bromine trifluoride or iodine pentafluoride ; [60] sulphuryl bromofluoride, SO_2BrF, from sulphur dioxide, bromine trifluoride, and bromine in an autoclave at ordinary temperatures.[61] The preparations of carbonyl chlorofluoride, COClF, from carbon monoxide and chlorine monofluoride, of carbonyl bromofluoride, COBrF, from carbon monoxide and bromine trifluoride, and of carbonyl iodofluoride, COIF, from carbon monoxide and iodine pentafluoride, have also been reported.[62]

Sharpe and Emeléus investigated the action of liquid bromine trifluoride on the chlorides, bromides, and iodides of a number of metals ; the general reaction was found to be fluorination to the highest known fluoride of the

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[45] *J. Amer. Chem. Soc.*, 1920, **42,** 1100.
[46] *Ibid.*, 1925, **47,** 1561.
[47] *Z. Krist.*, 1935, **90,** 143.
[48] *Ibid.*, 1938, **98,** 324.
[49] *Ibid.*, p. 377.
[50] *Ibid.*, 1939, **100,** 519.
[51] *Physical Rev.*, 1938, **53,** 851.
[52] *Ibid.*, 1943, **64,** 315.
[53] *Quart. Reviews*, 1949, **3,** 22.
[54] F.I.A.T. Review of German Science (1939—1946), Inorganic Chemistry, Pt. I, 1948, p. 168.
[55] *Chem. Eng.*, 1948, **55,** No. 4, 102.
[56] *J.*, 1948, 2135.
[57] *Z. anorg. Chem.*, 1932, **206,** 62.
[58] R. N. Haszeldine, *J.*, 1949, 2856.
[59] G. H. Rohrback and G. H. Cady, *J. Amer. Chem. Soc.*, 1948, **70,** 2603.
[60] J. Söll, ref. (54), p. 192.
[61] W. Kwasnik and co-workers, *ibid.*, p. 193.
[62] *Idem*, *ibid.*, p. 243.

element (silver provided an exception), though the formation of reagent-insoluble fluoride films on the surface often prevented the reaction from going to completion. Plumbous, thallous, and cobaltous halides, for example, yielded mixtures of lower and higher fluorides. When the product was volatile (*e.g.*, uranium hexafluoride) or soluble in the reagent (*e.g.*, the fluorides of the alkali metals) conversion into the fluoride was quantitative. Sodium, potassium, rubidium, cæsium, silver(I), and barium fluorides were found to be soluble in bromine trifluoride, and removal of the solvent by distillation *in vacuo* at room temperature yielded solid polyhalides of a new type. Four such compounds, the bromotetrafluorides (tetrafluorobromites) of sodium, potassium, silver, and barium, were isolated ; those of rubidium and cæsium were found to be relatively unstable.

Potassium bromotetrafluoride, $KBrF_4$, the most closely studied of the new compounds, is a white crystalline solid, very much less reactive than bromine trifluoride, but immediately decomposed by water. It neither reacts with, nor dissolves in, any of the common organic solvents. Thermal decomposition, which is slow at temperatures below 200°, yields potassium fluoride and bromine trifluoride. Lack of reactivity, thermal stability, analogy with $KICl_4$, and the combination of two (BrF_4) units with the invariably bivalent barium ion indicate the existence of the $(BrF_4)^-$ ion in these new polyhalides. *X*-Ray powder photography of $KBrF_4$ shows it to possess a cubic or pseudocubic unit cell,[63] but it is not yet possible to give a full description of the structure.

The small dissociation pressures of the alkali-metal bromofluorides have not been measured, but their stabilities *in vacuo* show that amongst these compounds the order of stability is $K > Na > Rb > Cs$. In this respect, therefore, and also in the formation of a stable silver polyhalide, the bromotetrafluorides differ from all other known series of polyhalides ; this is attributed to the relatively small size of the $(BrF_4)^-$ ion. A structure similar to that of $(ICl_4)^-$ being assumed, the $(BrF_4)^-$ ion should be a square of side 4·84 A., compared with 6·66 A. for the former ion. A fuller discussion of the relation between ionic size and stability must, however, await the determination of detailed structures.

The preparation of a polyhalide KIF_6 (potassium iodohexafluoride, or hexafluoroiodate) from potassium fluoride and iodine pentafluoride has also been described ; [64] in its ready hydrolysis by water and its method of thermal decomposition, this resembles the bromotetrafluoride and must be formulated $K^+(IF_6)^-$. Chlorine trifluoride does not yield similar polyhalides,[56] and the validity of G. Beck's claim [65] to have made a compound K_2ClF_7 or $KF,KClF_6$ has been disputed.[64]

Bromine trifluoride reacts with many uranium compounds, converting them quantitatively into the hexafluoride.[56, 66] This led to an investigation of its action on other naturally occurring radio-elements and their

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[63] F. J. T. Harris, unpublished.

[64] H. J. Emeléus and A. G. Sharpe, *J.*, 1949, 2206.

[65] *Z. anorg. Chem.*, 1937, **235**, 77.

[66] A. A. Banks, Thesis, Cambridge, 1948.

compounds.[67] It was found that only radon accompanies uranium on treatment of radioactive mixtures with bromine trifluoride, and this process therefore provides a new and rapid method for the removal of uranium from U-X_1 (thorium) and U-X_2 (protoactinium) preparations.

The electrical conductivities of chlorine trifluoride, bromine trifluoride, and iodine pentafluoride have been measured by A. A. Banks, H. J. Emeléus, and A. A. Woolf.[68] Values obtained for the specific conductivities (in ohm^{-1} cm.$^{-1}$) of these substances are: ClF_3, $< 10^{-6}$ at 0°; BrF_3, $8{\cdot}0 \times 10^{-3}$ at 25°; IF_5, 2×10^{-5} at 25°. The temperature coefficient of conductivity is negative for bromine trifluoride in the range 15—60°, and positive for iodine pentafluoride in the range 10—40°. Ohm's law is obeyed by bromine trifluoride but not by iodine pentafluoride. Direct-current electrolysis of the former compound produces no evolution of gas, but the liquid round the cathode becomes brown whilst the colour of that round the anode is unchanged. The suggested explanation of this is: bromine trifluoride is partly dissociated into $(BrF_2)^+$ and $(BrF_4)^-$ ions; $(BrF_2)^+$ is discharged at the cathode, and disproportionates to pale yellow BrF_3 and brown BrF; $(BrF_4)^-$, discharged at the anode, disproportionates giving BrF_3 and colourless BrF_5. The negative temperature coefficient is attributed to thermal instability of the ions, this factor outweighing in effect the decreased viscosity of the medium. In view of the very great reactivity of bromine trifluoride, the precautions taken in making such measurements are especially important. These included the use of all-quartz apparatus, the direct distillation of the liquid into the conductivity cell *in vacuo*, and the investigation of the possible effects of reaction with the quartz or the presence of bromine on the conductivity. Consistent values were obtained, and it may therefore be taken that the observed results were not due to impurities.

The reactions of bromine trifluoride with oxides and oxy-salts have been examined by H. J. Emeléus and A. A. Woolf.[69] The degree of completion of the reactions (determined by measuring the oxygen evolution with a Töpler pump) varied in the manner described for the halides. From compounds of the alkali metals, however, even when all the oxygen present was liberated, bromotetrafluorides were not always formed. Metaphosphates, for example, yielded hexafluorophosphates, whilst orthophosphates gave mixtures of hexafluorophosphates and bromofluorides in molecular proportions 1 : 2. In the latter instance, the formation of a mixture clearly originates in the 3 : 1 atomic ratio for metal : phosphorus in an orthophosphate. Investigation of the action of bromine trifluoride on sodium and potassium salts of the oxy-acids of sulphur showed that the perdisulphates and pyrosulphates yield only fluorosulphonates, that the pyrosulphites, thiosulphates, and sulphates yield 1 : 1 mixtures of fluorosulphonate and bromotetrafluoride, and that the hydrosulphites (dithionites) and sulphites yield only bromofluorides. Here, the amount of oxygen available for the formation of $(SO_3F)^-$ ions is as important as the metal : sulphur ratio. The mechanism of such reactions is discussed below.

[67] H. J. Emeléus, A. G. Maddock, G. A. Miles, and A. G. Sharpe, *J.*, 1948, 1991.

[68] *J.*, 1949, 2861.

[69] *J.*, 1950, 164.

The most interesting result of the study of the action of bromine trifluoride on oxides, however, was the isolation of a stable compound of antimony pentafluoride and bromine trifluoride. This substance, antimony bromo-octafluoride, $SbBrF_8$, gave conducting solutions in bromine trifluoride; conductometric titration of such solutions with silver bromotetrafluoride in bromine trifluoride indicated a minimum conductivity when the $SbBrF_8 : AgBrF_4$ ratio was 1 : 1, and on removal of the solvent silver fluoroantimonate, $AgSbF_6$, remained.[70]

This experiment provides strong evidence for the existence of an ionic equilibrium

$$2BrF_3 = (BrF_2)^+ + (BrF_4)^-$$

in liquid bromine trifluoride. Adopting the definitions of acid and base given by H. P. Cady and H. M. Elsey,[71] a substance which gives rise to $(BrF_2)^+$ ions (the cation characteristic of the solvent) is an acid, and a substance which gives rise to $(BrF_4)^-$ ions, a base. The reaction which takes place during the titration is then represented by the equation

$$[BrF_2]^+[SbF_6]^- + Ag^+[BrF_4]^- = Ag[SbF_6] + 2BrF_3$$

There is also evidence for the existence of a compound between one molecule of stannic fluoride and two molecules of bromine trifluoride. A solution of this substance in bromine trifluoride has been titrated conductometrically with potassium bromotetrafluoride; the minimum conductivity corresponds to one molecule of the tin compound and two of the bromotetrafluoride, and the product of the reaction is potassium fluorostannate, K_2SnF_6. The tin compound therefore reacts in solution as $(BrF_2)_2SnF_6$, difluorobromonium fluorostannate.

A third example of a neutralisation reaction has been described.[72] Gold dissolves in warm bromine trifluoride, and evaporation of the solution yields a compound of empirical formula $AuBrF_6$; a solution of this substance in bromine trifluoride gives with silver bromotetrafluoride in the same solvent an immediate precipitate of silver fluoroaurate, $AgAuF_4$. Instantaneous reactions in solution are usually reactions between oppositely charged ions, for which the activation energies are negligible, and this reaction must therefore be represented by the equation

$$[BrF_2]^+[AuF_4]^- + Ag^+[BrF_4]^- = Ag^+[AuF_4]^- + 2BrF_3$$

Decomposition of $[BrF_2][AuF_4]$ at 180° produces the hitherto unknown auric fluoride, the properties of which are described elsewhere.[72]

Further recent work by H. J. Emeléus and V. Gutmann[73] has shown that two more acids of the bromine trifluoride system may be isolated in the solid state. These are compounds formed by bromine trifluoride with niobium and tantalum pentafluorides, $[BrF_2][NbF_6]$ and $[BrF_2][TaF_6]$, respectively. With bromotetrafluorides they yield hexafluoroniobates and hexafluorotantalates. A bismuth acid, $[BrF_2][BiF_6]$, also exists.

For the preparation of complex fluorides by neutralisation reactions in

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[70] A. A. Woolf and H. J. Emeléus, *J.*, 1949, 2865.

[71] *J. Chem. Educ.*, 1928, 1425.

[72] Sharpe, *J.*, 1949, 2901.

[73] *J.*, 1950, 1046.

bromine trifluoride it is not, however, necessary to prepare the acid and the base separately. The action of an excess of bromine trifluoride on a mixture of equivalent quantities of gold and silver, for example, followed by removal of the excess, yields nearly pure silver fluoroaurate.[72] It therefore seems likely that, as suggested by Emeléus and Woolf, an ionic reaction mechanism involving the unstable acid $[BrF_2]^+[PF_6]^-$ is involved in the conversion of potassium metaphosphate into the hexafluorophosphate. A similar mechanism has been suggested for the preparation of potassium hexafluorovanadate, KVF_6, by treating potassium chloride and vanadium trichloride with bromine trifluoride.[74] Some of the new complex fluorides obtained by the use of bromine trifluoride are unstable even in 40% hydrofluoric acid, and a useful method for their preparation in a non-aqueous system has therefore been developed.[74a] It should be mentioned, however, that they are not always obtained in a pure condition, and that retention of the elements of bromine trifluoride often occurs to some extent.[70, 72] This has been attributed [72] to solvolysis by bromine trifluoride, but experimental confirmation of this suggestion is still required.

Other solvents for which ionic equilibria not involving the proton have been suggested include dinitrogen tetroxide,[75] sulphur dioxide,[76] and iodine.[77] In view of the relationship between the bromotetrafluorides and bromine trifluoride, it seems very likely that some, at least, of the other polyhalides may be bases in as yet unknown acid–base systems in other interhalogen compounds; and the extension of the work described here to these substances appears to be a promising field for future investigation.

Thermochemistry of the Interhalogen Compounds.—The thermodynamic properties of bromine chloride,[78] iodine monochloride,[79] iodine trichloride,[80] and iodine bromide [81] have been measured by Yost and his collaborators, who have also given data for iodine monochloride, iodine bromide, and bromine chloride in carbon tetrachloride solution.[82] For iodine monochloride and -bromide their results are in agreement with those obtained spectroscopically by other workers.[83, 84]

The thermochemistry of the chlorine fluorides has recently received considerable attention, and the heat of formation of the monofluoride is

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[74] Emeléus and Gutmann, *J.*, 1949, 2979.

[74a] Emeléus and Woolf (*J.*, 1950, 1050) have prepared nitronium complex fluorides such as $(NO_2)(BF_4)$, $(NO_2)(PF_6)$, and $(NO_2)(AuF_4)$ from dinitrogen tetroxide; Woolf (*ibid.*, p. 1053) has made similar nitrosyl salts from nitrosyl chloride.

[75] C. C. Addison and R. Thompson, *J.*, 1949, S211.

[76] G. Jander and K. Wickert, *Z. physikal. Chem.*, 1936, *A*, **178**, 57; see also, however, L. C. Bateman, E. D. Hughes, and C. K. Ingold, *J.*, 1944, 243.

[77] G. Jander and K. H. Bandlow, *Z. physikal. Chem.*, 1943, *A*, **191**, 321

[78] C. M. Beeson and D. M. Yost, *J. Amer. Chem. Soc.*, 1939, **61**, 1432.

[79] J. McMorris and D. M. Yost, *ibid.*, 1932, **54**, 2247.

[80] N. P. Nies and D. M. Yost, *ibid.*, 1935, **57**, 306.

[81] McMorris and Yost, *ibid.*, 1931, **53**, 2625.

[82] C. M. Blair and D. M. Yost, *ibid.*, 1933, **55**, 4489.

[83] G. E. Gibson and R. C. Ramsperger, *Physical Rev.*, 1927, **30**, 598.

[84] W. G. Brown, *ibid.*, 1932, **42**, 355.

now important in fixing the heat of dissociation of fluorine. O. Ruff and F. Laass[85] measured the heat of the reaction $ClF + H_2 = HCl + HF$, and from their results O. Ruff and W. Menzel,[86] taking the heat of formation of hydrogen fluoride as 64·0 kcals., calculated that of chlorine monofluoride to be 27·4 kcals. H. Schmitz and H. J. Schumacher[87] determined the heats of the smooth and rapid reactions

$$NaCl + ClF = Cl_2 + NaF \quad . \quad . \quad . \quad . \quad (1)$$

$$NaCl + \tfrac{1}{2}F_2 = \tfrac{1}{2}Cl_2 + NaF \quad . \quad . \quad . \quad . \quad (2)$$

as 24·5 ± 0·1 and 39·5 ± 0·5 kcals., respectively, and from them found the heat of formation of chlorine monofluoride to be 15·0 ± 0·5 kcals. at 18°. The reaction

$$3NaCl + ClF_3 = 3NaF + 2Cl_2 \quad . \quad . \quad . \quad . \quad (3)$$

was found to be exothermic to the extent of 76·5 kcals., leading to values of 27·0 ± 1·5 kcals. for the heat of the reaction

$$ClF + F_2 = ClF_3 \quad . \quad . \quad . \quad . \quad (4)$$

and 42 ± 2 kcals. for the heat of formation of chlorine trifluoride from chlorine and fluorine.

The heat of reaction (4) at 300° was determined by investigating the variation of K_p with temperature in a coated nickel or magnesium vessel, using, however, a quartz manometer. The results were moderately consistent and indicated a value of 25 ± 2 kcals. This agreement with the calorimetric determination, and the fact that the result for reaction (2) was in very close agreement with a previous determination[88] suggest that Schmitz and Schumacher's value for the heat of formation of chlorine monofluoride is correct at least to within a few kilocalories. Another recent determination of the heat of formation, by E. Wicke,[89] who used a direct calorimetric method, led to a value of 11·6 ± 0·4 kcals. at 20°, which, considering the difficulties created by the reactivity of the substance under examination, is in fair agreement with Schmitz and Schumacher's result.

A. L. Wahrhaftig[90] and Schmitz and Schumacher[91] have independently examined the absorption spectrum of chlorine monofluoride in the visible and the ultra-violet region. Some of the experimental details given by the latter authors are interesting: the sample was contained at a pressure of 1·5 atm. in a 380-cm. long iron tube fitted with fluorspar windows; and two methods for the preparation of the chlorine monofluoride, from chlorine and fluorine and from chlorine trifluoride and chlorine, were used. A weak band system in the visible region was found, and from the extrapolated series limit the heat of dissociation of chlorine monofluoride was calculated. Wahrhaftig, assuming the products of dissociation to be excited chlorine and normal fluorine atoms, evaluated the energy required for dissociation

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[85] *Z. anorg. Chem.*, 1929, **183**, 214.

[86] *Ibid.*, 1931, **198**, 375.

[87] *Z. Naturforsch.*, 1947, **2a**, 362.

[88] H. v. Wartenberg and O. Fitzner, *Z. anorg. Chem.*, 1926, **151**, 313.

[89] *Nachr. Akad. Wiss. Göttingen, Math.-physik. Klasse*, 1946, 89.

[90] *J. Chem. Physics*, 1942, **10**, 248.

[91] *Z. Naturforsch.*, 1947, **2a**, 359.

into two normal atoms as 60·3 kcals., and, taking the dissociation energy for chlorine to be 57·2 kcals., deduced that

$$D_{(F_2)} + 2Q_f(\mathrm{ClF}) = 63{\cdot}4 \text{ kcals.}$$

where $D_{(F_2)}$ is the dissociation energy of fluorine and $Q_f(\mathrm{ClF})$ the heat of formation (thermochemical) of chlorine monofluoride. Schmitz and Schumacher obtained for the dissociation energy of chlorine monofluoride into normal atoms values of 58·9 kcals. (assuming production of excited chlorine and normal fluorine) and 60·3 kcals. (assuming normal chlorine and excited fluorine). These values lead to 60·6 and 63·4 kcals., respectively, for $D_{(F_2)} + 2Q_f(\mathrm{ClF})$. If, therefore, the heat of formation of chlorine monofluoride lies between 12 and 15 kcals., the dissociation energy of fluorine should be 35—40 kcals.

Such a value is much lower than that suggested by H. von Wartenberg, G. Sprenger, and J. Taylor,[92] *viz.*, 63·3 kcals. This was obtained from the absorption spectrum of fluorine, and involved an extrapolation from the properties of the other halogens for which there was no theoretical justification.[93] A lower value for the dissociation energy of fluorine has not been universally accepted, however, and Wicke [94] has criticised the spectroscopic work on chlorine fluoride and has produced fresh evidence in favour of a high dissociation energy. Meanwhile, A. D. Caunt and R. F. Barrow,[95] from the ultra-violet absorption spectra of rubidium and cæsium fluorides and thermochemical data for these compounds, have suggested a value of 50 ± 6 kcals.; and whether the source of the disagreement between different results lies in the interpretation of the spectrum of chlorine monofluoride, or the value for the heat of formation of chlorine monofluoride, or the thermochemical data (especially the heats of sublimation) for the alkali-metal fluorides, is not yet known.

Examination of the absorption spectrum of bromine monofluoride [96] led to values for the dissociation energy of 59·9 and 50·3 kcals., fluorine and bromine respectively being taken to be the excited atom. The ultra-violet absorption spectra of chlorine trifluoride,[97] bromine trifluoride,[98] and iodine pentafluoride [98] have also been studied, but no band structures have been found. The heats of formation of the bromine and iodine fluorides are all unknown, though methods for the determination of some of them have been suggested.[69]

The deviation of chlorine trifluoride from the perfect-gas laws at pressures of 300—800 mm. was studied tensimetrically by Schmitz and Schumacher,[99] who showed that the results obtained could be explained by dimerisation, the heat of the reaction $2\mathrm{ClF}_3 = (\mathrm{ClF}_3)_2$ being 3·3 ± 0·5 kcals. in the tem-

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[92] *Z. physikal. Chem.*, 1931, Bodenstein Festband, 61.

[93] R. S. Mulliken, *J. Chem. Physics*, 1934, **2**, 792.

[94] *Z. Elektrochem.*, 1949, **53**, 212.

[95] *Nature*, 1949, **164**, 753.

[96] P. Brodersen and H. J. Schumacher, *Z. Naturforsch.*, 1947, **2a**, 358.

[97] Schmitz and Schumacher, *ibid.*, p. 363.

[98] C. F. White and C. F. Goodeve, *Trans. Faraday Soc.*, 1934, **30**, 1049.

[99] *Z. Naturforsch.*, 1947, **2a**, 363.

perature range 9—24°. The degree of association at 20°, calculated from their results, is 0·054.

Interhalogen Compounds in Organic Chemistry.—Iodine monochloride in acetic acid (Wijs's solution) has long been used for the estimation of the " iodine value " of unsaturated compounds,[100] and this reagent is now also important for the iodination of aromatic compounds. That the attacking entity in this reaction is the I^+ ion is suggested by the conversion of compounds containing groups which activate the aromatic nucleus into *o*- and *p*-iodo-compounds : acetanilide, for example, yields *p*-iodoacetanilide,[101] and salicylic acid gives 2-hydroxy-3 : 5-di-iodobenzoic acid.[102] Under similar conditions, however, iodine bromide effects bromination : phenol in carbon tetrachloride forms *p*-bromophenol, and α-naphthol in acetic acid gives 4-bromo-1-naphthol.[103] The bromide is dissociated more than the chloride into its elements, and, since bromination by bromine is a much faster reaction than iodination by the I^+ ion, the bromide is a brominating agent even in nitrobenzene ; the chloride chlorinates phenol only in the absence of a solvent.[103a] The kinetics of the reactions of iodine monochloride with acetanilide and anisole in acetic acid solution have been studied by L. J. Lambourne and P. W. Robertson,[104] who found the reaction to be of the first order with respect to the concentration of the aromatic compound and of the second order with respect to that of the iodinating agent. The hydrogen chloride formed in the reaction competes with the aromatic compound for the remaining iodine monochloride (with which it forms $HICl_2$), and the rate falls off rapidly as the reaction proceeds.

The first published account of a controlled fluorination with bromine trifluoride was the conversion of carbon tetrachloride into a mixture of chlorofluoromethanes.[105] This work was later amplified by A. A. Banks, H. J. Emeléus, R. N. Haszeldine, and V. Kerrigan,[106] who also showed that bromine trifluoride reacts with carbon tetraiodide, forming carbon tetrafluoride and bromofluoromethanes. By the action of bromine trifluoride on hexachlorobenzene, E. T. McBee, V. V. Lindgren, and W. B. Ligett [107] obtained products corresponding in composition to approximately $C_6Br_2Cl_4F_6$; and the same authors,[108] by successive treatment of hexachlorobenzene with bromine trifluoride, antimony pentafluoride, and zinc dust and alcohol, prepared perfluoro*cyclo*hexadiene.

Iodine pentafluoride is only moderately reactive, and it appears to be a mild fluorinating agent which will replace iodine, but not hydrogen, by fluorine. From the slow reaction between iodine pentafluoride and carbon tetrachloride O. Ruff and R. Keim [109] obtained trichlorofluoromethane and a little dichlorodifluoromethane. J. H. Simons, R. L. Bond, and R. E.

[100] A. D. Mitchell, " Sutton's Volumetric Analysis ", J. and A. Churchill, London, 1935, p. 411.

[101] F. D. Chattaway and A. B. Constable, *J.*, 1914, **105**, 124.

[102] G. H. Woollett and W. W. Johnson, *Org. Synth.*, Coll. Vol. II, 1943, p. 343.

[103] W. Militzer, *J. Amer. Chem. Soc.*, 1938, **60**, 256.

[103a] F. W. Bennett and R. G. Sharpe, *J.*, 1950, 1383.

[104] *J.*, 1947, 1167.

[105] H. S. Nutting and P. S. Petrie, U.S.P. 1,961,622 (1934).

[106] *J.*, 1948, 2188.

[107] *Ind. Eng. Chem.*, 1947, **39**, 378.

[108] U.S.P. 2,432,997 (1947).

[109] *Z. anorg. Chem.*, 1931, **201**, 245.

McArthur [110] identified fluoroform as the principal product of the reaction between iodine pentafluoride and iodoform ; this reaction was carried out in a copper apparatus, and the authors reported that under similar conditions carbon tetraiodide yielded hexafluoroethane. Banks, Emeléus, Haszeldine, and Kerrigan, however, showed that in glass carbon tetraiodide and iodine pentafluoride yield iodotrifluoromethane ; [106] and it has been found that even in copper apparatus, using the technique employed by Simons, Bond, and McArthur, iodotrifluoromethane is still the main product of the reaction.[111] Iodine pentafluoride has also been found to react with carbon tetrabromide, forming bromofluoromethanes, and with tetraiodoethylene, forming iodopentafluoroethane.[106] Further properties of iodotrifluoromethane and iodopentafluoroethane have recently been described.[58, 112] An addition compound of iodine pentafluoride and dioxan, $C_4H_8O_2,IF_5$, has been made ; [113] this is analogous to similar compounds obtained from iodine, iodine monochloride, and iodine bromide.[114]

Information concerning the reactions of the other halogen fluorides with organic compounds is scanty, and no controlled reactions of chlorine monofluoride, bromine monofluoride and pentafluoride, and iodine heptafluoride with organic substances have yet been described. R. W. Porter [55] and R. le G. Burnett and A. A. Banks [110a] have reported that the controlled reaction of chlorine trifluoride with organic compounds results in the introduction of both chlorine and fluorine ; and R. N. Haszeldine,[111] by the vapour-phase fluorination of benzene and toluene, has obtained evidence for the formation of chlorofluoro-addition and -substitution products. In view of the relatively low cost of chlorine it seems that it is in this field that discoveries of future industrial importance are most likely to be made.

The Structural Chemistry of Interhalogen Molecules and Ions.—Reference has already been made to the electrical conductivities of certain interhalogen compounds and to *X*-ray data for ions. Other structural information is scanty. H. Braune and P. Pinnow [115] studied iodine pentafluoride by the electron-diffraction method ; they concluded that the I–F distances are all equal, but when a trigonal bipyramidal shape was assumed the bond length was calculated to be 2·56 A. The sum of the covalent radii for iodine and fluorine is only 1·97 A., and Braune and Pinnow's result did not meet with general acceptance. Investigation of the infra-red absorption spectrum of the vapour and the Raman spectrum of the liquid led to the conclusion that the molecule has the shape of a tetragonal pyramid.[116] Similar investigations on iodine heptafluoride, the only known AB_7 molecule, suggested

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[110] *J. Amer. Chem. Soc.*, 1940, **62**, 3477.

[110a] Communicated at the Chemical Society Symposium on Fluorine Chemistry, Nov. 30, 1949.

[111] R. N. Haszeldine, private communication.

[112] H. J. Emeléus and R. N. Haszeldine, *J.*, 1949, 2948.

[113] A. F. Scott and J. F. Bunnett, *J. Amer. Chem. Soc.*, 1942, **64**, 2727.

[114] H. Rheinboldt and R. Boy, *J. pr. Chem.*, 1931, **129**, 273.

[115] *Z. physikal. Chem.*, 1937, *B*, **35**, 239.

[116] R. C. Lord, M. A. Lynch, jun., W. C. Schumb, and E. J. Slowinski, jun., *J. Amer. Chem. Soc.*, 1950, **72**, 522.

that this compound is pentagonal bipyramidal in configuration, a structure previously unknown. The I–F distance in IF_5 is 1·75 A.

The Raman spectrum of liquid chlorine trifluoride and the infra-red absorption spectrum of the gas have been studied by E. A. Jones, T. F. Parkinson, and R. B. Murray,[117] using fluorothene (polychlorotrifluoroethylene) apparatus. Their results suggested either an unsymmetrical structure for chlorine trifluoride or association in the liquid. From consideration of the orbitals likely to be involved in bonding, anything but a planar structure for the single ClF_3 molecule seems unlikely ; and in view of Schmitz and Schumacher's investigation on the gas,[99] a high degree of association in the liquid phase appears probable. The infra-red spectrum of chlorine monofluoride has also been examined ; the location of the centre of the fundamental band at 772 $cm.^{-1}$ is in agreement with the calculated position from the ultra-violet absorption spectrum of the molecule.[118]

The electrical conductivity of a number of the interhalogen compounds raises the problem of their structures in the solid state. Absence of a decomposition potential is usually a characteristic of electronic conduction ; this, however, normally differs little in magnitude in the solid and the liquid state, and must be ruled out for iodine monochloride [118a] and bromine trifluoride,[68] since for these compounds the conductivity of the solid is very much less than that of the liquid. The discovery of the ionic structures of solid phosphorus pentachloride [119] and phosphorus pentabromide [120] suggests that some of the interhalogen compounds may also be found to possess ionic lattices.

A wide range of molecules and ions is now available for use in the discussion of the relation between electronic configuration and stereochemistry. These include IF_7 ; $(IF_6)^-$; IF_5 and BrF_5 ; $(ICl_4)^-$ and $(BrF_4)^-$; ICl_3, BrF_3, and ClF_3 ; $(ICl_2)^-$, etc. ; ClF, ICl, etc. ; $(BrF_2)^+$, and, perhaps, $(ICl_2)^+$. The observed configurations of the $(ICl_4)^-$ and $(ICl_2)^-$ ions are usually described [49, 121, 122] by saying that the valency shells of the iodine atoms in these ions contain twelve and ten electrons, respectively, and that the structures result from the occupation by unshared electron pairs of two *trans*-positions in an octahedron and of three equatorial positions in a trigonal bipyramid, respectively. It has been suggested in a similar way that the structure of iodine pentafluoride may be derived from an octahedron by postulating occupation of one position by an unshared electron pair.[121, 122] It may be pointed out, however, that from G. Kimball's systematic calculations of bond type and electronic configuration,[123] the observed shapes of $(ICl_4)^-$, $(ICl_2)^-$, and IF_5 may be derived by allotting to the iodine atoms valency configurations of $5p^45d^4$, $5p^25d^2$, and $5p^65d^4$, since p^2d^2, pd, and

[117] *J. Chem. Physics*, 1949, **17**, 501.

[118] T. F. Parkinson, E. A. Jones, and A. H. Nielsen, *Physical Rev.*, 1949, **76**, 199.

[118a] N. N. Greenwood, unpublished.

[119] D. Clark, H. M. Powell, and A. F. Wells, *J.*, 1942, 642.

[120] Clark and Powell, *Nature*, 1940, **145**, 971.

[121] L. Pauling, " The Nature of the Chemical Bond ", Cornell, 1940.

[122] A. F. Wells, " Structural Inorganic Chemistry ", Oxford, 1945.

[123] *J. Chem. Physics*, 1940, **8**, 194.

p^3d^2 bonds are calculated to give planar, linear, and tetragonal pyramidal configurations, respectively. On the basis of either method of approach $(BrF_2)^+$, unlike $(ICl_2)^-$, is expected to be angular. What influence then has an " inert pair " of electrons on the stereochemistry of an ion or molecule ? From the discussion of this question by N. V. Sidgwick and H. M. Powell [124] it is evident that for most molecules it matters little if we assume that " the mean positions of the electron pairs are the same whether they are shared or not ", though the observed bond angle in hydrogen sulphide (92°) does appear to require pure *p*-bonding in this compound. With valency groups of twelve or less electrons, symmetrical configurations, easily reconciled with one and often with more than one reasonable combination of orbitals, are available ; and they frequently bear simple relationships to other symmetrical structures, *e.g.*, the octahedron to the square.

For atoms with valency shells containing more than twelve electrons the position seems to be different. In the ions $(SeCl_6)^{--}$, $(SeBr_6)^{--}$, and $(TeCl_6)^{--}$, which have a central atom with a valency shell of fourteen electrons but only six-fold co-ordination, the configuration is octahedral, but the observed bond lengths [125, 126] are unexpectedly high by about 0·25 A. J. Y. Beach [127] has made the suggestion that such an increase in bond length is to be correlated with the existence of the 4*s* orbital (in the case of selenium) as a separate energy level, the bonding orbitals in $(SeCl_6)^{--}$ being $4p^34d^25s$ orbitals. The $(IF_6)^-$ ion would be effectively isoelectronic with $(TeCl_6)^{--}$, and it has therefore been suggested [64] that this ion (unless it differs from all other known finite complex six-co-ordination ions by not being octahedral) should have an interhalogen distance appreciably greater than the sum of the covalent radii.

The structure of IF_7 then has to be considered separately ; in this compound the iodine atom would possess no inert electron pair, and there is no reason to predict a long bond here. The observed symmetrical configuration of iodine heptafluoride lies beyond the scope of Kimball's treatment, but it is not to be expected that the structures of IF_7 and $(IF_6)^-$ will be simply related. It now appears that the $(ZrF_7)^{---}$ and $(NbF_7)^{--}$ ions,[128, 129] and the IF_7 molecule, which might have been expected to be similar, all have different structures.

The technical difficulties in the way of further structural investigations on the substances under discussion are considerable, chemical reactivity and differences in the scattering powers of the halogens being especially important. If, however, these difficulties can be overcome, the determination of the structures of the series of interhalogen ions and molecules seems likely to provide results of considerable theoretical significance.

The author thanks Dr. W. G. Palmer and Dr. P. Gray for reading through this Review and making a number of helpful suggestions.

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[124] *Proc. Roy. Soc.*, 1940, *A*, **176**, 153.
[125] G. Engel, *Z. Krist.*, 1935, **90**, 341.
[126] J. L. Hoard and B. N. Dickinson, *ibid.*, 1933, **84**, 436.
[127] Quoted in ref. (121), p. 184.
[128] G. C. Hampson and L. Pauling, *J. Amer. Chem. Soc.*, 1938, **60**, 2702.
[129] J. L. Hoard, *ibid.*, 1939, **61**, 1252.