

$MF_n < MCl_n < MBr_n < MI_n$ . By contrast for less-ionic halides with significant non-coulombic lattice forces (e.g. Ag) solubility in water follows the reverse sequence  $MI_n < MBr_n < MCl_n < MF_n$ . For molecular halides solubility is determined principally by weak intermolecular van der Waals' and dipolar forces, and dissolution is commonly favoured by less-polar solvents such as benzene,  $CCl_4$  or  $CS_2$ .

Trends in chemical reactivity are also apparent, e.g. ease of hydrolysis tends to increase from the non-hydrolysing predominantly ionic halides, through the intermediate halides to the readily hydrolysable molecular halides. Reactivity depends both on the relative energies of  $M-X$  and  $M-O$  bonds and also, frequently, on kinetic factors which may hinder or even prevent the occurrence of thermodynamically favourable reactions. Further trends become apparent within the various groups of halides and are discussed at appropriate points throughout the text.

### 17.2.3 Interhalogen compounds<sup>(65-67)</sup>

The halogens combine exothermically with each other to form interhalogen compounds of four stoichiometries:  $XY$ ,  $XY_3$ ,  $XY_5$  and  $XY_7$  where X is the heavier halogen. A few ternary compounds are also known, e.g.  $IFCl_2$  and  $IF_2Cl$ . For the hexatomic series, only the fluorides are known ( $ClF_5$ ,  $BrF_5$ ,  $IF_5$ ), and  $IF_7$  is the sole example of the octatomic series. All the interhalogen compounds are diamagnetic and contain an even number of halogen atoms. Similarly, the closely related polyhalide anions  $XY_{2n}^-$  and polyhalonium cations  $XY_{2n}^+$  ( $n = 1, 2, 3$ ) each have an odd

number of halogen atoms: these ions will be considered in subsequent sections (pp. 835, 839).

Related to the interhalogens chemically, are compounds formed between a halogen atom and a pseudohalogen group such as CN, SCN,  $N_3$ . Examples are the linear molecules  $ClCN$ ,  $BrCN$ ,  $ICN$  and the corresponding compounds  $XSCN$  and  $XN_3$ . Some of these compounds have already been discussed (p. 319) and need not be considered further. A microwave study<sup>(68)</sup> shows that chlorine thiocyanate is  $CISCN$  (angle  $Cl-S-C$   $99.8^\circ$ ) rather than  $CINCS$ , in contrast to the cyanate which is  $CINCO$ . The corresponding fluoro compound,  $FNCO$ , can be synthesized by several low-temperature routes but is not stable at room temperature and rapidly dimerizes to  $F_2NC(O)NCO$ .<sup>(69)</sup> The chemistry of iodine azide has been reviewed<sup>(70)</sup> — it is obtained as volatile, golden yellow, shock-sensitive needles by reaction of  $I_2$  with  $AgN_3$  in non-oxygen-containing solvents such as  $CH_2Cl_2$ ,  $CCl_4$  or benzene: the structure in the gas phase (as with  $FN_3$ ,  $ClN_3$  and  $BrN_3$  also) comprises a linear  $N_3$  group joined at an obtuse angle to the pendant X atom, thereby giving a molecule of  $C_s$  symmetry.

### Diatomic interhalogens, $XY$

All six possible diatomic compounds between F, Cl, Br and I are known. Indeed,  $ICl$  was first made (independently) by J. L. Gay Lussac and H. Davy in 1813–4 soon after the isolation of the parent halogens themselves, and its existence led J. von Liebig to miss the discovery of the new element bromine, which has similar properties (p. 794). The compounds vary considerably in thermal stability:  $ClF$  is extremely robust;  $ICl$  and  $IBr$  are moderately stable and can be obtained in very pure crystalline form at room temperature;  $BrCl$  readily dissociates reversibly into its

<sup>65</sup> Ref. 23, pp. 1476–1563, see also D. M. MARTIN, R. ROUSSON and J. M. WEULERSSE, in J. J. LAGOWSKI (ed.), *The Chemistry of Nonaqueous Solvents*, Chap. 3, pp. 157–95, Academic Press, New York, 1978.

<sup>66</sup> A. I. POPOV, Chap. 2, in V. GUTMANN (ed.), *MTP International Review of Science: Inorganic Chemistry Series* 1, Vol. 3, pp. 53–84, Butterworths, London, 1972.

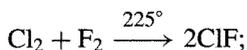
<sup>67</sup> K. O. CHRISTE, *IUPAC Additional Publication 24th Int. Congr. Pure Appl. Chem.*, Hamburg, 1973, Vol. 4. *Compounds of Non-Metals*, pp. 115–41, Butterworths, London, 1974.

<sup>68</sup> R. J. RICHARDS, R. W. DAVIS and M. C. L. GERRY, *J. Chem. Soc., Chem. Commun.*, 915–6 (1980).

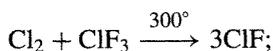
<sup>69</sup> K. GHOLIVAND and H. WILLNER, *Z. anorg. allg. Chem.* **550**, 27–34 (1987).

<sup>70</sup> K. DEHNICKE, *Angew. Chem. Int. Edn. Engl.* **18**, 507–14 (1979).

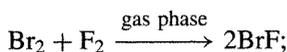
elements; BrF and IF disproportionate rapidly and irreversibly to a higher fluoride and Br<sub>2</sub> (or I<sub>2</sub>). Thus, although all six compounds can be formed by direct, controlled reaction of the appropriate elements, not all can be obtained in pure form by this route. Typical preparative routes (with comments) are as follows:



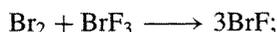
must be purified from ClF<sub>3</sub> and reactants



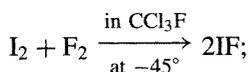
must be purified from excess ClF<sub>3</sub>



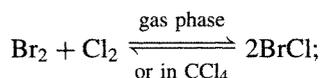
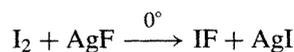
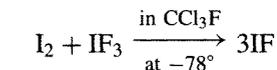
disproportionates to Br<sub>2</sub> + BrF<sub>3</sub> (and BrF<sub>5</sub>)  
at room temp



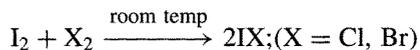
BrF favoured at high temp



disproportionates rapidly to I<sub>2</sub> + IF<sub>5</sub>  
at room temp



compound cannot be isolated free from  
Br<sub>2</sub> and Cl<sub>2</sub>



purify by fractional crystallization of  
the molten compound

In general the compounds have properties intermediate between those of the parent halogens, though a combination of aggressive chemical reactivity and/or thermal instability militates against the determination of physical properties such as mp, bp, etc., in some instances. However, even for such highly dissociated species as BrCl, precise molecular (as distinct from bulk) properties can be determined by spectroscopic techniques. Table 17.12 summarizes some of the more important physical properties of the

**Table 17.12** Physical properties of interhalogen compounds XY

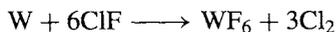
Property	ClF	BrF	IF	BrCl	ICl	IBr
Form at room temperature	Colourless gas	Pale brown (Br <sub>2</sub> )	Unstable	Red brown gas	Ruby red crystals	Black crystals
MP/°C	-155.6	ca. -33 Disprop <sup>(a)</sup>	— Disprop <sup>(a)</sup>	ca. -66 Dissoc <sup>(a)</sup>	27.2(α) 13.9(β)	41 Some dissoc
BP/°C	-100.1	ca. 20	—	ca. 5	97-100 <sup>(b)</sup>	~116 <sup>(b)</sup>
ΔH <sub>f</sub> <sup>o</sup> (298 K)/kJ mol <sup>-1</sup>	-56.5	-58.6	-95.4	+14.6	-35.3(α)	-10.5 (cryst)
ΔG <sub>f</sub> <sup>o</sup> (298 K)/kJ mol <sup>-1</sup>	-57.7	-73.6	-117.6	-1.0	-13.95(α)	+3.7(gas)
Dissociation energy/ kJ mol <sup>-1</sup>	252.5	248.6	~277	215.1	207.7	175.4
d(liq. T°C)/g cm <sup>-3</sup>	1.62(-100°)	—	—	—	3.095(30°)	3.762(42°)
r(X-Y)/pm	162.81	175.6	190.9	213.8	232.07	248.5
Dipole moment/D	0.881	1.29	—	0.57	0.65	1.21
κ(liq. T°C)/ ohm <sup>-1</sup> cm <sup>-1</sup>	1.9 × 10 <sup>-7</sup> (-128°)	—	—	—	5.50 × 10 <sup>-3</sup>	3.4 × 10 <sup>-4</sup>

<sup>(a)</sup>Substantial disproportionation or dissociation prevents meaningful determination of mp and bp; the figures merely indicate the approximate temperature range over which the (impure) compound is liquid at atmospheric pressure.

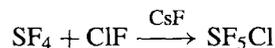
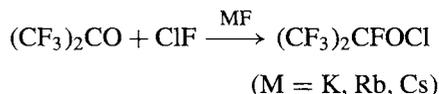
<sup>(b)</sup>Fused ICl and IBr both dissociate into the free halogens to some extent: ICl 0.4% at 25° (supercooled) and 1.1% at 100°C; IBr 8.8% at 25° (supercooled) and 13.4% at 100°C.

diatomic interhalogens. The most volatile compound, ClF, is a colourless gas which condenses to a very pale yellow liquid below  $-100^\circ$ . The least volatile is IBr; it forms black crystals in which the IBr molecules pack in a herringbone pattern similar to that in  $I_2$  (p. 803) and in which the internuclear distance  $r(\text{I}-\text{Br})$  is 252 pm, i.e. slightly longer than in the gas phase (248.5 pm). ICl is unusual in forming two crystalline modifications: the stable ( $\alpha$ ) form crystallizes as large, transparent ruby-red needles from the melt and features zigzag chains of molecules (Fig. 17.6) with two different ICl units and appreciable interchain intermolecular bonding. The packing is somewhat different in the yellow, metastable ( $\beta$ ) form (Fig. 17.6) which can be obtained as brownish-red crystals from strongly supercooled melts.

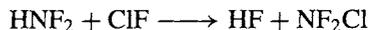
The chemical reactions of XY can be conveniently classified as (a) halogenation reactions, (b) donor-acceptor interactions and (c) use as solvent systems. Reactions frequently parallel those of the parent halogens but with subtle and revealing differences. ClF is an effective fluorinating agent (p. 820) and will react with many metals and non-metals either at room temperature or above, converting them to fluorides and liberating chlorine, e.g.:



It can also act as a chlorofluorinating agent by addition across a multiple bond and/or by oxidation, e.g.:



Reaction with OH groups or NH groups results in the exothermic elimination of HF and the (often violent) chlorination of the substrate, e.g.:



Lewis acid (fluoride-ion acceptor) behaviour is exemplified by reactions with NOF and MF to give  $[\text{NO}]^+[\text{ClF}_2]^-$  and  $\text{M}^+[\text{ClF}_2]^-$  respectively (M = alkali metal or  $\text{NH}_4$ ). Lewis base (fluoride ion donor) activity includes reactions with  $\text{BF}_3$  and  $\text{AsF}_5$ :

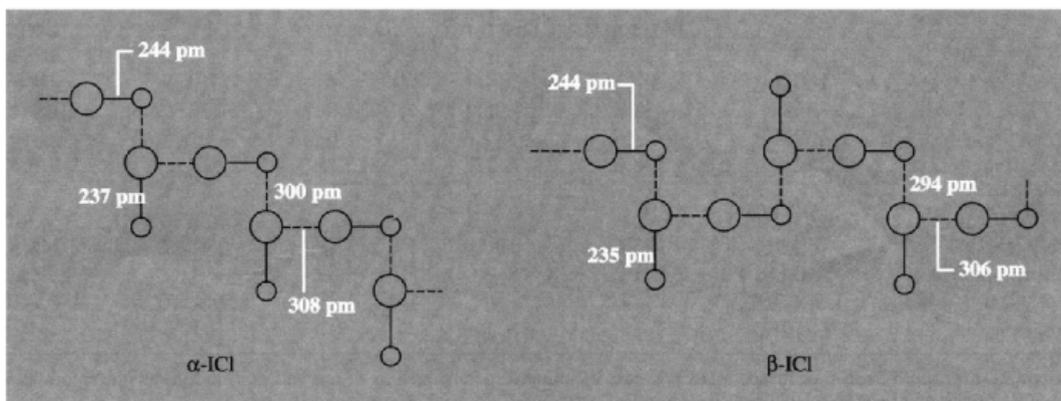
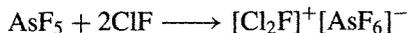


Figure 17.6 Structures of  $\alpha$ - and  $\beta$ -forms of crystalline ICl.



The linear polyhalide anion  $[\text{F}-\text{Cl}-\text{F}]^-$  and the angular polyhalonium cation  $[\text{F} \begin{array}{c} \text{Cl} \\ \diagup \quad \diagdown \\ \text{Cl} \end{array}]^+$  are members of a more extensive set of ions to be treated on pp. 835ff. ClF is commercially available in steel lecture bottles of 500-g capacity but must be handled with extreme circumspection in scrupulously dried and degreased apparatus constructed in steel, copper, Monel metal or nickel; fluorocarbon polymers such as Teflon can also be used, but not at elevated temperatures.

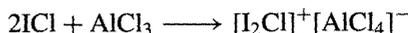
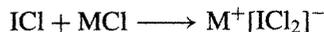
The reactivity of ICl and IBr, though milder than that of ClF is nevertheless still extremely vigorous and the compounds react with most metals including Pt and Au, but not with B, C, Cd, Pb, Zr, Nb, Mo or W. With ICl, phosphorus yields  $\text{PCl}_5$  and V conveniently yields  $\text{VCl}_3$  (rather than  $\text{VCl}_4$ ). Reaction with organic substrates depends subtly on the conditions chosen. For example, phenol and salicylic acid are chlorinated by ICl *vapour*, since homolytic dissociation of the ICl molecule leads to chlorination by  $\text{Cl}_2$  rather than iodination by the less-reactive  $\text{I}_2$ . By contrast, in  $\text{CCl}_4$  solution (low dielectric constant) iodination predominates, accompanied to a small extent by chlorination: this implies heterolytic fission and rapid electrophilic iodination by  $\text{I}^+$  plus some residual chlorination by  $\text{Cl}_2$  (or ICl). In a solvent of high dielectric constant, e.g.  $\text{PhNO}_2$ , iodination occurs exclusively.<sup>(71)</sup> Likewise BrF, in the presence of EtOH, rapidly and essentially quantitatively monobrominates aromatics such as PhX: when X = Me, Bu', OMe or Br, substitution is mainly or exclusively *para*, whereas with deactivating substituents (X =  $-\text{CO}_2\text{Et}$ ,  $-\text{CHO}$ ,  $-\text{NO}_2$ ) exclusively *meta*-bromination occurs.<sup>(72)</sup> A similar interpretation explains why IBr almost invariably brominates rather than iodates aromatic compounds due to its appreciable dissociation into  $\text{Br}_2$  and  $\text{I}_2$  in

solution and the much greater rate of reaction of bromination by  $\text{Br}_2$  compared with iodination by iodine.

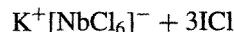
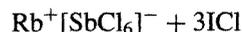
Both ICl and IBr are partly dissociated into ions in the fused state, and this gives rise to an appreciable electrical conductivity (Table 17.12). The ions formed by this heterolytic dissociation of IX are undoubtedly solvated in the melt and the equilibria can be formally represented as



The compounds can therefore be used as nonaqueous ionizing solvent systems (p. 424). For example the conductivity of ICl is greatly enhanced by addition of alkali metal halides or aluminium halides which may be considered as halide-ion donors and acceptors respectively:



Similarly pyridine gives  $[\text{pyI}]^+ [\text{ICl}_2]^-$  and  $\text{SbCl}_5$  forms a 2:1 adduct which can be reasonably formulated as  $[\text{I}_2\text{Cl}]^+ [\text{SbCl}_6]^-$ . By contrast, the 1:1 adduct with  $\text{PCl}_5$  has been shown by X-ray studies to be  $[\text{PCl}_4]^+ [\text{ICl}_2]^-$ . Solvoacid-solvobase reactions have been monitored by conductimetric titration; e.g. titration of solutions of  $\text{RbCl}$  and  $\text{SbCl}_5$  in ICl (or of  $\text{KCl}$  and  $\text{NbCl}_5$ ) shows a break at 1:1 molar proportions, whereas titration of  $\text{NH}_4\text{Cl}$  with  $\text{SnCl}_4$  shows a break at the 2:1 mole ratio:



The preparative utility of such reactions is, however, rather limited, and neither ICl or IBr has been much used except to form various mixed polyhalide species. Compounds must frequently

<sup>71</sup> F. W. BENNETT and A. G. SHARPE, *J. Chem. Soc.* 1383-4 (1950).

<sup>72</sup> S. ROZEN and M. BRAND, *J. Chem. Soc., Chem. Commun.*, 752-3 (1987).

be isolated by extraction rather than by precipitation, and solvolysis is a further complicating factor.

### Tetra-atomic interhalogens, $XY_3$

The compounds to be considered are  $ClF_3$ ,  $BrF_3$ ,  $IF_3$  and  $ICl_3$  ( $I_2Cl_6$ ). All can be prepared by direct reaction of the elements, but conditions must be chosen so as to avoid formation of mixtures of interhalogens of different stoichiometries.  $ClF_3$  is best formed by direct fluorination of  $Cl_2$  or  $ClF$  in the gas phase at 200–300° in Cu, Ni or Monel metal apparatus.  $BrF_3$  is formed similarly at or near room temperature and can be purified by distillation to give a pale straw-coloured liquid. With  $IF_3$ , which is only stable below –30° the problem is to avoid the more facile formation of  $IF_5$ ; this can be achieved either by the action of  $F_2$  on  $I_2$  suspended in  $CCl_3F$  at –45° or more elegantly by the low-temperature fluorination of  $I_2$  with  $XeF_2$ :



$I_2Cl_6$  is readily made as a bright-yellow solid by reaction of  $I_2$  with an excess of liquid chlorine at –80° followed by the low-temperature evaporation of the  $Cl_2$ ; care must be taken with this latter operation, however, because of the very ready dissociation of  $I_2Cl_6$  into  $ICl$  and  $Cl_2$ .

Physical properties are summarized in Table 17.13. Little is known of the unstable

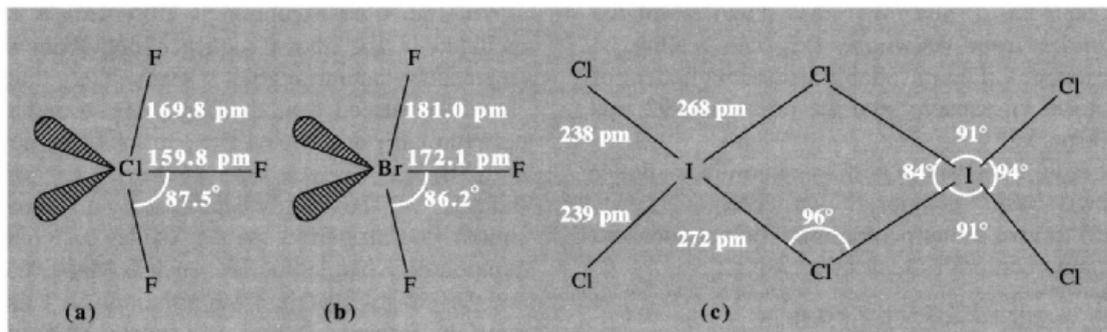
$IF_3$  but  $ClF_3$  and  $BrF_3$  are well-characterized volatile molecular liquids. Both have an unusual T-shaped structure of  $C_{2v}$  symmetry, consistent with the presence of 10 electrons in the valency shell of the central atom (Fig. 17.7a,b). A notable feature of both structures is the slight deviation from colinearity of the apical F–X–F bonds, the angle being 175.0° for  $ClF_3$  and 172.4° for  $BrF_3$ ; this reflects the greater electrostatic repulsion of the nonbonding pair of electrons in the equatorial plane of the molecule. For each molecule the X–F<sub>apical</sub> distance is some 5–6% greater than the X–F<sub>equatorial</sub> distance but the mean X–F distance is very similar to that in the corresponding monofluoride. The structure of crystalline  $ICl_3$  is quite different, being built up of planar  $I_2Cl_6$  molecules separated by normal van der Waals' distances between the Cl atoms (Fig. 17.7c). The terminal I–Cl distances are similar to those in  $ICl$  but the bridging I–Cl distances are appreciably longer.

$ClF_3$  is one of the most reactive chemical compounds known<sup>(73)</sup> and reacts violently with many substances generally thought of as inert. Thus it spontaneously ignites asbestos, wood, and other building materials and was used in incendiary bomb attacks on UK cities during the Second World War. It reacts explosively with water and with most organic substances, though

<sup>73</sup> L. STEIN, in V. GUTMANN (ed.), *Halogen Chemistry*, Vol. 1, pp. 133–224, Academic Press, London, 1967.

**Table 17.13** Physical properties of interhalogen compounds  $XY_3$

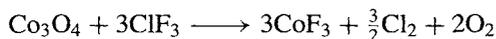
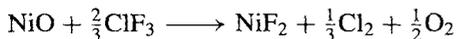
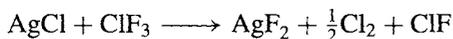
Property	$ClF_3$	$BrF_3$	$IF_3$	$I_2Cl_6$
Form at room temperature	Colourless gas/liquid	Straw-coloured liquid	Yellow solid (decomp above –28°)	Bright yellow solid
MP/°C	–76.3	8.8	—	101 (16 atm)
BP/°C	11.8	125.8	—	—
$\Delta H_f^\circ(298\text{ K})/\text{kJ mol}^{-1}$	–164 (g)	–301 (l)	ca. –485 (g) calc	–89.3 (s)
$\Delta G_f^\circ(298\text{ K})/\text{kJ mol}^{-1}$	–124 (g)	–241 (l)	ca. –460 (g) calc	–21.5 (s)
Mean X–Y bond energy of $XY_3/\text{kJ mol}^{-1}$	174	202	ca. 275 (calc)	—
Density( $T^\circ\text{C}$ )/ $\text{g cm}^{-3}$	1.885 (0°)	2.803 (25°)	—	3.111 (15°)
Dipole moment/D	0.557	1.19	—	—
Dielectric constant $\epsilon(T^\circ)$	4.75 (0°)	—	—	—
$\kappa(\text{liq}, T^\circ\text{C})/\text{ohm}^{-1}\text{cm}^{-1}$	$6.5 \times 10^{-9}(0^\circ)$	$8.0 \times 10^{-3}(25^\circ)$	—	$8.6 \times 10^{-3}(102^\circ)$



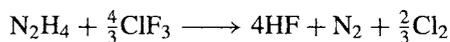
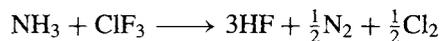
**Figure 17.7** Molecular structures of (a)  $\text{ClF}_3$  and (b)  $\text{BrF}_3$  as determined by microwave spectroscopy. An X-ray study of crystalline  $\text{ClF}_3$  gave slightly longer distances (171.6 and 162.1 pm) and a slightly smaller angle ( $87.0^\circ$ ). (c) Structure of  $\text{I}_2\text{Cl}_6$  showing planar molecules of approximate  $D_{2h}$  symmetry.

reaction can sometimes be moderated by dilution of  $\text{ClF}_3$  with an inert gas, by dissolution of the organic compound in an inert fluorocarbon solvent or by the use of low temperatures. Spontaneous ignition occurs with  $\text{H}_2$ , K, P, As, Sb, S, Se, Te, and powdered Mo, W, Rh, Ir and Fe. Likewise,  $\text{Br}_2$  and  $\text{I}_2$  enflame and produce higher fluorides. Some metals (e.g. Na, Mg, Al, Zn, Sn, Ag) react at room temperature until a fluoride coating is established; when heated they continue to react vigorously. Palladium, Pt and Au are also attacked at elevated temperatures and even Xe and Rn are fluorinated. Mild steel can be used as a container at room temperature and Cu is only slightly attacked below  $300^\circ$  but the most resistant are Ni and Monel metal. Very pure  $\text{ClF}_3$  has no effect on Pyrex or quartz but traces of HF, which are normally present, cause slow etching.

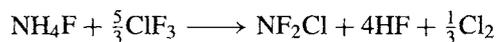
$\text{ClF}_3$  converts most chlorides to fluorides and reacts even with refractory oxides such as  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MnO}_2$ ,  $\text{Ta}_2\text{O}_5$  and  $\text{MoO}_3$  to form higher fluorides, e.g.:



With suitable dilution to moderate the otherwise violent reactions.  $\text{NH}_3$  gas and  $\text{N}_2\text{H}_4$  yield HF and the elements:

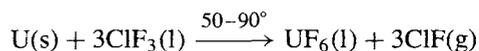


At one time this latter reaction was used in experimental rocket motors, the  $\text{ClF}_3$  oxidizer reacting spontaneously with the fuel ( $\text{N}_2\text{H}_4$  or  $\text{Me}_2\text{N}_2\text{H}_2$ ). At low temperatures  $\text{NH}_4\text{F}$  and  $\text{NH}_4\text{HF}_2$  react with liquid  $\text{ClF}_3$  when allowed to warm from  $-196$  to  $-5^\circ$  but the reaction is hazardous and may explode above  $-5^\circ$ :



The same products are obtained more safely by reacting gaseous  $\text{ClF}_3$  with a suspension of  $\text{NH}_4\text{F}$  or  $\text{NH}_4\text{HF}_2$  in a fluorocarbon oil.

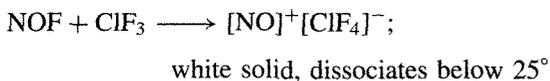
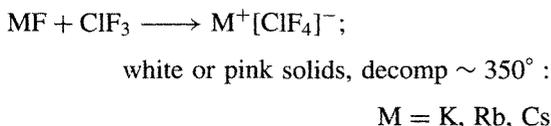
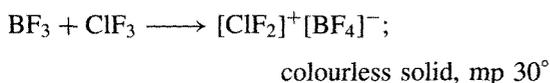
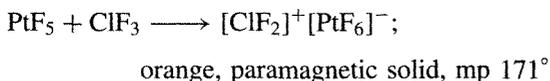
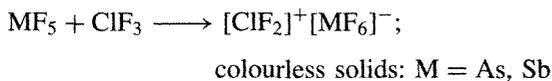
$\text{ClF}_3$  is manufactured on a moderately large scale, considering its extraordinarily aggressive properties which necessitate major precautions during handling and transport. Production plant in Germany had a capacity of  $\sim 5$  tonnes/day in 1940 ( $\sim 1500$  tonnes pa). It is now used in the USA, the UK, France and Russia primarily for nuclear fuel processing.  $\text{ClF}_3$  is used to produce  $\text{UF}_6(\text{g})$ :



It is also invaluable in separating U from Pu and other fission products during nuclear fuel reprocessing, since Pu reacts only to give the (involatile)  $\text{PuF}_4$  and most fission products

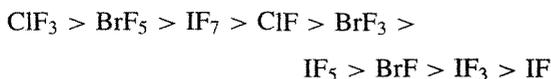
(except Te, I and Mo) also yield involatile fluorides from which the UF<sub>6</sub> can readily be separated. ClF<sub>3</sub> is available in steel cylinders of up to 82 kg capacity and the price in 1992 was \$100 per kg.

Liquid ClF<sub>3</sub> can act both as a fluoride ion donor (Lewis base) or fluoride ion acceptor (Lewis acid) to give difluorochloronium compounds and tetrafluorochlorides respectively, e.g.:



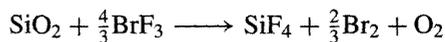
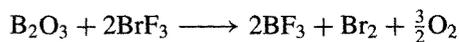
Despite these reaction products there is little evidence for an ionic self-dissociation equilibrium in liquid ClF<sub>3</sub> such as may be formally represented by  $2\text{ClF}_3 \rightleftharpoons \text{ClF}_2^+ + \text{ClF}_4^-$ , and the electrical conductivity of the pure liquid (p. 828) is only of the order of  $10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$ . The structures of these ions are discussed more fully in subsequent sections.

Bromine trifluoride, though it reacts explosively with water and hydrocarbon tap greases, is somewhat less violent and vigorous a fluorinating agent than is ClF<sub>3</sub>. The sequence of reactivity usually quoted for the halogen fluorides is:

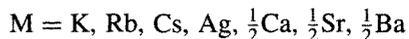
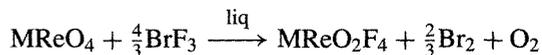


It can be seen that, for a given stoichiometry of XF<sub>n</sub>, the sequence follows the order Cl > Br > I and for a given halogen the reactivity of XF<sub>n</sub> diminishes with decrease in n, i.e. XF<sub>5</sub> > XF<sub>3</sub> >

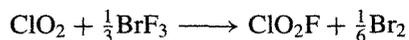
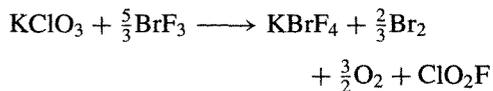
XF. (A possible exception is ClF<sub>5</sub>; this is not included in the above sequence but, from the fragmentary data available, it seems likely that it should be placed near the beginning — perhaps between ClF<sub>3</sub> and BrF<sub>5</sub>.) BrF<sub>3</sub> reacts vigorously with B, C, Si, As, Sb, I and S to form fluorides. It has also been used to prepare simple fluorides from metals, oxides and other compounds: volatile fluorides such as MoF<sub>6</sub>, WF<sub>6</sub> and UF<sub>6</sub> distil readily from solutions in which they are formed whereas less-volatile fluorides such as AuF<sub>3</sub>, PdF<sub>3</sub>, RhF<sub>4</sub>, PtF<sub>4</sub> and BiF<sub>5</sub> are obtained as residues on removal of BrF<sub>3</sub> under reduced pressure. Reaction with oxides often evolves O<sub>2</sub> quantitatively (e.g. B<sub>2</sub>O<sub>3</sub>, Tl<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, GeO<sub>2</sub>, As<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, SeO<sub>3</sub>, I<sub>2</sub>O<sub>5</sub>, CuO, TiO<sub>2</sub>, UO<sub>3</sub>):

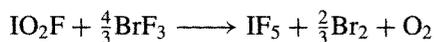
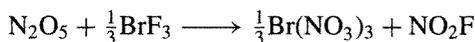


The reaction can be used as a method of analysis and also as a procedure for determining small amounts of O (or N) in metals and alloys of Li, Ti, U, etc. In cases when BrF<sub>3</sub> itself only partially fluorinates the refractory oxides, the related reagents KBrF<sub>4</sub> and BrF<sub>2</sub>SbF<sub>6</sub> have been found to be effective (e.g. for MgO, CaO, Al<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, NiO, CeO<sub>2</sub>, Nd<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, ThO<sub>2</sub>). Oxygen in carbonates and phosphates can also be determined by reaction with BrF<sub>3</sub>. Sometimes partial fluorination yields new compounds, e.g. perrhenates afford tetrafluoroperrhenates:



Likewise, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and Ag<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> yield the corresponding MCrOF<sub>4</sub> (i.e. reduction from Cr<sup>VI</sup> to Cr<sup>V</sup>). Other similar reactions, which nevertheless differ slightly in their overall stoichiometry, are:



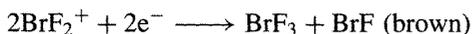


As with  $\text{ClF}_3$ ,  $\text{BrF}_3$  is used to fluorinate U to  $\text{UF}_6$  in the processing and reprocessing of nuclear fuel. It is manufactured commercially on a multitonne scale and is available as a liquid in steel cylinders of varying size up to 91 kg capacity. The US price in 1992 was ~\$80 per kg.

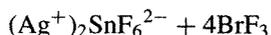
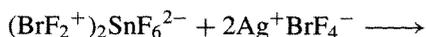
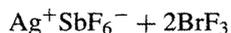
In addition to its use as a straight fluorinating agent,  $\text{BrF}_3$  has been extensively investigated and exploited as a preparative nonaqueous ionizing solvent. The appreciable electrical conductivity of the pure liquid (p. 828) can be interpreted in terms of the dissociative equilibrium



Electrolysis gives a brown coloration at the cathode but no visible change at the anode:

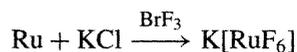
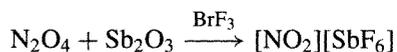
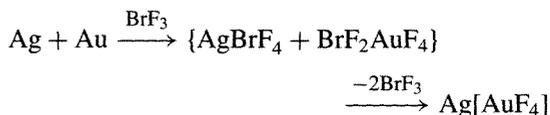


The specific conductivity decreases from  $8.1 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$  at  $10^\circ$  to  $7.1 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$  at  $55^\circ$  and this unusual behaviour has been attributed to the thermal instability of the  $\text{BrF}_2^+$  and  $\text{BrF}_4^-$  ions at higher temperatures. Consistent with the above scheme  $\text{KF}$ ,  $\text{BaF}_2$  and numerous other fluorides (such as  $\text{NaF}$ ,  $\text{RbF}$ ,  $\text{AgF}$ ,  $\text{NOF}$ ) dissolve in  $\text{BrF}_3$  with enhancement of the electrical conductivity due to the formation of the solvobases  $\text{KBrF}_4$ ,  $\text{Ba}(\text{BrF}_4)_2$ , etc. Likewise,  $\text{Sb}$  and  $\text{Sn}$  give solutions of the solvoacids  $\text{BrF}_2\text{SbF}_6$  and  $(\text{BrF}_2)_2\text{SnF}_6$ . Conductimetric titrations between these various species can be carried out, the end point being indicated by a sharp minimum in the conductivity:



Other solvoacids that have been isolated include the  $\text{BrF}_2^+$  compounds of  $\text{AuF}_4^-$ ,  $\text{BiF}_6^-$ ,  $\text{NbF}_6^-$ ,

$\text{TaF}_6^-$ ,  $\text{RuF}_6^-$  and  $\text{PdF}_6^{2-}$  and reactions of  $\text{BrF}_3$  solutions have led to the isolation of large numbers of such anhydrous complex fluorides with a variety of cations.<sup>(73)</sup> Solvolysis sometimes complicates the isolation of a complex by evaporation of  $\text{BrF}_3$  and solvates are also known, e.g.  $\text{K}_2\text{TiF}_6 \cdot \text{BrF}_3$  and  $\text{K}_2\text{PtF}_6 \cdot \text{BrF}_3$ . It is frequently unnecessary to isolate the presumed reaction intermediates and the required complex can be obtained by the action of  $\text{BrF}_3$  on an appropriate mixture of starting materials:



In these reactions  $\text{BrF}_3$  serves both as a fluorinating agent and as a nonaqueous solvent reaction medium.

Molten  $\text{I}_2\text{Cl}_6$  has been much less studied as an ionizing solvent because of the high dissociation pressure of  $\text{Cl}_2$  above the melt. The appreciable electrical conductivity may well indicate an ionic self-dissociation equilibrium such as

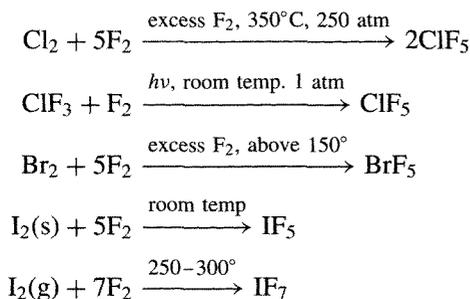


Such ions are known from various crystal-structure determinations, e.g.  $\text{K}[\text{ICl}_2] \cdot \text{H}_2\text{O}$ ,  $[\text{ICl}_2][\text{AlCl}_4]$  and  $[\text{ICl}_2][\text{SbCl}_6]$  (p. 839).  $\text{I}_2\text{Cl}_6$  is a vigorous chlorinating agent, no doubt due at least in part to its ready dissociation into  $\text{ICl}$  and  $\text{Cl}_2$ . Aromatic compounds, including thiophen,  $\text{C}_4\text{H}_4\text{S}$ , give chlorosubstituted products with very little if any iodination. By contrast, reaction of  $\text{I}_2\text{Cl}_6$  with aryl-tin or aryl-mercury compounds yield the corresponding diaryliodonium derivatives, e.g.:

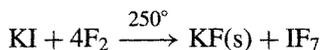
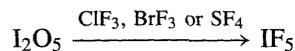
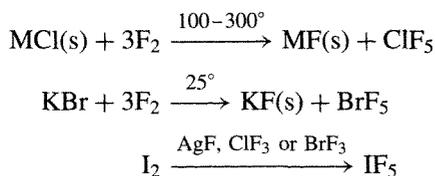


Hexa-atomic and octa-atomic interhalogens,  $\text{XF}_5$  and  $\text{IF}_7$

The three fluorides  $\text{ClF}_5$ ,  $\text{BrF}_5$  and  $\text{IF}_5$  are the only known hexa-atomic interhalogens, and  $\text{IF}_7$  is the sole representative of the octa-atomic class. The first to be made (1871) was  $\text{IF}_5$  which is the most readily formed of the iodine fluorides, whereas the more vigorous conditions required for the others delayed the synthesis of  $\text{BrF}_5$  and  $\text{IF}_7$  until 1930/1 and  $\text{ClF}_5$  until 1962. The preferred method of preparing all four compounds on a large scale is by direct fluorination of the element or a lower fluoride:



Small-scale preparations can conveniently be effected as follows:



This last reaction is preferred for  $\text{IF}_7$  because of the difficulty of drying  $\text{I}_2$ . ( $\text{IF}_7$  reacts with  $\text{SiO}_2$ ,  $\text{I}_2\text{O}_5$  or traces of water to give  $\text{OIF}_5$  from which it can be separated only with difficulty.)

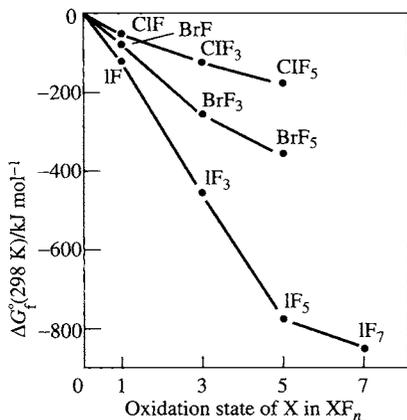
$\text{ClF}_5$ ,  $\text{BrF}_5$  and  $\text{IF}_7$  are extremely vigorous fluorinating reagents, being excelled in this only by  $\text{ClF}_3$ .  $\text{IF}_5$  is (relatively) a much milder fluorinating agent and can be handled in glass apparatus: it is manufactured in the USA on a scale of several hundred tonnes pa. It is available as a liquid in steel cylinders up to 1350 kg capacity (i.e.  $1\frac{1}{3}$  tonnes) and the price in 1992 was *ca.* \$50 per kg. All four compounds are colourless, volatile molecular liquids or gases at room temperature and their physical properties are given in Table 17.14. It will be seen that the liquid range of  $\text{IF}_5$  resembles that of  $\text{BrF}_3$  and that  $\text{BrF}_5$  is similar to  $\text{ClF}_3$ . The free energies of formation of these and the other halogen fluorides in the gas phase are compared in Fig. 17.8. The trends are obvious; it is also clear from the convexity (or concavity) of the lines that  $\text{BrF}$  and  $\text{IF}$  might be expected to disproportionate into the trifluoride and the parent halogen, whereas  $\text{ClF}_3$ ,  $\text{BrF}_3$  and  $\text{IF}_5$  are thermodynamically the most stable fluorides of Cl, Br and I respectively. Plots of average bond energies are in Fig. 17.9: for a

Table 17.14 Physical properties of the higher halogen fluorides

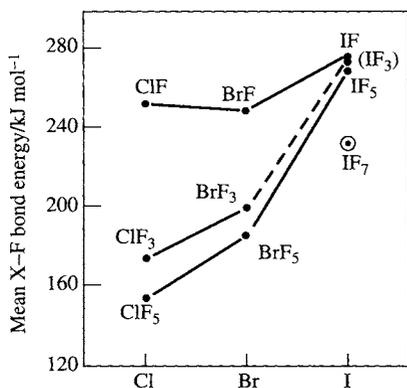
Property	$\text{ClF}_5$	$\text{BrF}_5$	$\text{IF}_5$	$\text{IF}_7$
MP/ $^\circ\text{C}$	-103	-60.5	9.4	6.5 (triple point)
BP/ $^\circ\text{C}$	-13.1	41.3	104.5	4.8 (subl 1 atm)
$\Delta H_f^\circ(\text{gas}, 298 \text{ K})/\text{kJ mol}^{-1}$	-255	429 <sup>(a)</sup>	-843 <sup>(b)</sup>	-962
$\Delta G_f^\circ(\text{gas}, 298 \text{ K})/\text{kJ mol}^{-1}$	-165	-351 <sup>(a)</sup>	-775 <sup>(b)</sup>	-842
Mean X-F bond energy/ kJ mol <sup>-1</sup>	154	187	269	232
$d_{\text{liq}}(T^\circ\text{C})/\text{g cm}^{-3}$	2.105 (-80°)	2.4716 (25°)	3.207 (25°)	2.669 (25°)
Dipole moment/D	—	1.51	2.18	0
Dielectric constant $\epsilon(T^\circ\text{C})$	4.28 (-80°)	7.91 (25°)	36.14 (25°)	1.75 (25°)
$\kappa(\text{liq at } T^\circ\text{C})/\text{ohm}^{-1} \text{ cm}^{-1}$	$3.7 \times 10^{-8}$ (-80°)	$9.9 \times 10^{-8}$ (25°)	$5.4 \times 10^{-6}$ (25°)	$<10^{-9}$ (25°)

<sup>(a)</sup>For liquid  $\text{BrF}_5$ :  $\Delta H_f^\circ(298 \text{ K}) -458.6 \text{ kJ mol}^{-1}$ ,  $\Delta G_f^\circ(298 \text{ K}) -351.9 \text{ kJ mol}^{-1}$ .

<sup>(b)</sup>For liquid  $\text{IF}_5$ :  $\Delta H_f^\circ(298 \text{ K}) -885 \text{ kJ mol}^{-1}$ ,  $\Delta G_f^\circ(298 \text{ K}) -784 \text{ kJ mol}^{-1}$ .



**Figure 17.8** Free energies of formation of gaseous halogen fluorides at 298 K.

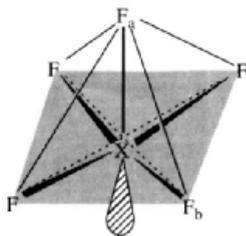


**Figure 17.9** Mean bond energies of halogen fluorides.

given value of  $n$  in  $\text{XF}_n$  the sequence of energies is  $\text{ClF}_n < \text{BrF}_n < \text{IF}_n$ , reflecting the increasing

difference in electronegativity between X and F. ClF is an exception. As expected, for a given halogen, the mean bond energy decreases as  $n$  increases in  $\text{XF}_n$ , the effect being most marked for Cl and least for I. Note that high bond energy (as in BrF and IF) does not necessarily confer stability on a compound (why?).

The molecular structure of  $\text{XF}_5$  has been shown to be square pyramidal ( $C_{4v}$ ) with the central atom slightly below the plane of the four basal F atoms (Fig. 17.10). The structure is essentially the same in the gaseous, liquid and crystalline phases and has been established by some (or all) of the following techniques: electron diffraction, microwave spectroscopy, infrared and Raman spectroscopy,  $^{19}\text{F}$  nmr spectroscopy and X-ray diffraction analysis. This structure immediately explains the existence of a small permanent dipole moment, which would be absent if the structure were trigonal bipyramidal ( $C_{3v}$ ), and is consistent with the presence of 12 valence-shell electrons on the central atom X. Electrostatic effects account for the slight displacement of the four  $\text{F}_b$  away from the lone-pair of electrons and also the fact that  $\text{X}-\text{F}_b > \text{X}-\text{F}_a$ . The  $^{19}\text{F}$  nmr spectra of both  $\text{BrF}_5$  and  $\text{IF}_5$  consist of a highfield doublet (integrated relative area 4) and a 1:4:6:4:1 quintet of integrated area 1: these multiplets can immediately be assigned on the basis of  $^{19}\text{F}-^{19}\text{F}$  coupling and relative area to the 4 basal and the unique apical F atom respectively. The molecules are fluxional at higher temperatures: e.g. spin-spin coupling disappears in  $\text{IF}_5$  at  $115^\circ$  and further heating leads to broadening and coalescence of the two signals, but a sharp singlet could not be attained at still



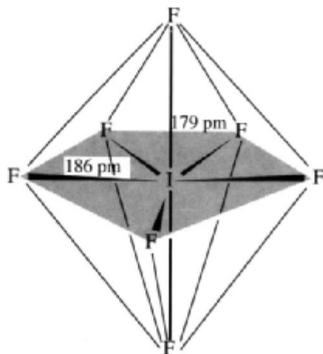
	$\text{ClF}_5$		$\text{BrF}_5$		$\text{IF}_5$	
	(gas)	(gas)	(cryst)	(gas)	(cryst)	(gas)
$\text{X}-\text{F}_b/\text{pm}$	~172	177.4	178	186.9	189	
$\text{X}-\text{F}_a/\text{pm}$	~162	168.9	168	184.4	186	
$\angle \text{F}_a-\text{X}-\text{F}_b$	~ $90^\circ$ (assumed)	$84.8^\circ$	$84.5^\circ$	$81.9^\circ$	$80.9^\circ$	

**Figure 17.10** Structure of  $\text{XF}_5$  (X = Cl, Br, I) showing X slightly below the basal plane of the four  $\text{F}_b$ .

higher temperatures because of accelerated attack of  $\text{IF}_5$  on the quartz tube.

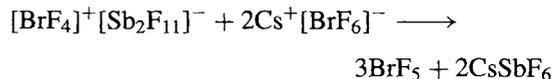
The structure of  $\text{IF}_7$  is generally taken to be pentagonal bipyramidal ( $D_{5h}$  symmetry) as originally suggested on the basis of infrared and Raman spectra (Fig. 17.11). Electron diffraction data have been interpreted in terms of slightly differing axial and equatorial distances and a slight deformation from  $D_{5h}$  symmetry due to a  $7.5^\circ$  puckering displacement and a  $4.5^\circ$  axial bending displacement. An assessment of the diffraction data permits the Delphic pronouncement<sup>(74)</sup> that, on the evidence available, it is not possible to demonstrate that the molecular symmetry is different from  $D_{5h}$ .

The very great chemical reactivity of  $\text{ClF}_5$  is well established but few specific stoichiometric reactions have been reported. Water reacts vigorously to liberate HF and form  $\text{FClO}_2$  ( $\text{ClF}_5 + 2\text{H}_2\text{O} \longrightarrow \text{FClO}_2 + 4\text{HF}$ ).  $\text{AsF}_5$  and  $\text{SbF}_5$  form 1:1 adducts which may well be ionic:  $[\text{ClF}_4]^+[\text{MF}_6]^-$ . A similar reaction with  $\text{BrF}_5$  yields a 1:2 adduct which has been shown by X-ray crystallography to be  $[\text{BrF}_4]^+[\text{Sb}_2\text{F}_{11}]^-$  (p. 841). Fluoride ion transfer probably also occurs with  $\text{SO}_3$  to give  $[\text{BrF}_4]^+[\text{SO}_3\text{F}]^-$ , but adducts with  $\text{BF}_3$ ,  $\text{PF}_5$  or  $\text{TiF}_4$  could not be formed. Conversely,  $\text{BrF}_5$  can act as a fluoride ion acceptor (from  $\text{CsF}$ ) to give  $\text{CsBrF}_6$  as a white, crystalline solid stable



**Figure 17.11** Approximate structure of  $\text{IF}_7$  (see text).

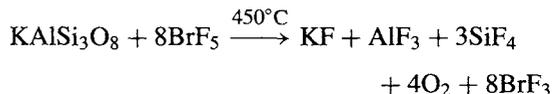
to about  $300^\circ$ , and this solvobase can be titrated with the solvoacid  $[\text{BrF}_4]^+[\text{Sb}_2\text{F}_{11}]^-$  according to the following stoichiometry:



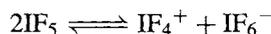
$\text{BrF}_5$  reacts explosively with water but when moderated by dilution with MeCN gives bromic and hydrofluoric acids:



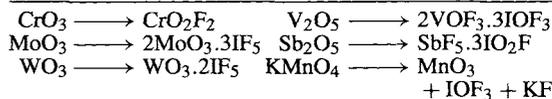
The vigorous fluorinating activity of  $\text{BrF}_5$  is demonstrated by its reaction with silicates, e.g.:



The chemical reactions of  $\text{IF}_5$  have been more extensively and systematically studied because the compound can be handled in glass apparatus and is much less vigorous a reagent than the other pentafluorides. The (very low) electrical conductivity of the pure liquid has been ascribed to slight ionic dissociation according to the equilibrium



Consistent with this, dissolution of  $\text{KF}$  increases the conductivity and  $\text{KIF}_6$  can be isolated on removal of the solvent. Likewise  $\text{NOF}$  affords  $[\text{NO}]^+[\text{IF}_6]^-$ . Antimony compounds yield  $\text{ISbF}_{10}$ , i.e.  $[\text{IF}_4]^+[\text{SbF}_6]^-$ , which can be titrated with  $\text{KSbF}_6$ . However, the milder fluorinating power of  $\text{IF}_5$  frequently enables partially fluorinated adducts to be isolated and in some of these the iodine is partly oxygenated. Complete structural identification of the products has not yet been established in all cases but typical stoichiometries are as follows:



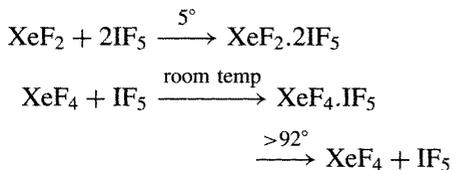
Potassium perhenate reacts similarly to  $\text{KMnO}_4$  to give  $\text{ReO}_3\text{F}$ . Similarly, the mild fluorinating

<sup>74</sup> J. D. DONOHUE, *Acta Cryst.* **18**, 1018–21 (1965).

action of  $\text{IF}_5$  enables substituted iodine fluorides to be synthesized, e.g.:



$\text{IF}_5$  is unusual as an interhalogen in forming adducts with both  $\text{XeF}_2$  and  $\text{XeF}_4$ :



It should be emphasized that the reactivity of  $\text{IF}_5$  is mild only in comparison with the other halogen fluorides (p. 830). Reaction with water is extremely vigorous but the iodine is not reduced and oxygen is not evolved:



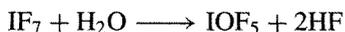
$$\Delta H = -92.3 \text{ kJ mol}^{-1}$$



$$\Delta H = -497.5 \text{ kJ mol}^{-1}$$

Boron enflames in contact with  $\text{IF}_5$ ; so do P, As and Sb. Molybdenum and W enflame when heated and the alkali metals react violently. KH and  $\text{CaC}_2$  become incandescent in hot  $\text{IF}_5$ . However, reaction is more sedate with many other metals and non-metals, and compounds such as  $\text{CaCO}_3$  and  $\text{Ca}_3(\text{PO}_4)_2$  appear not to react with the liquid.

$\text{IF}_7$  is a stronger fluorinating agent than  $\text{IF}_5$  and reacts with most elements either in the cold or on warming. CO enflames in  $\text{IF}_7$  vapour but NO reacts smoothly and  $\text{SO}_2$  only when warmed.  $\text{IF}_7$  vapour hydrolyses without violence to  $\text{HIO}_4$  and HF; with small amounts of water at room temperature the oxyfluoride can be isolated:



The same compound is formed by action of  $\text{IF}_7$  on silica (at  $100^\circ$ ) and Pyrex glass:



$\text{IF}_7$  acts as a fluoride ion donor towards  $\text{AsF}_5$  and  $\text{SbF}_5$  and the compounds  $[\text{IF}_6]^+[\text{MF}_6]^-$  have

been isolated. Few complexes with alkali metal fluorides have been isolated but  $\text{CsF}$  and  $\text{NOF}$  form adducts which have been characterized by X-ray powder data, and formulated on the basis of Raman spectroscopy as  $\text{Cs}^+[\text{IF}_8]^-$  and  $[\text{NO}]^+[\text{IF}_8]^-$ .<sup>(75)</sup>

### 17.2.4 Polyhalide anions

Polyhalides anions of general formula  $\text{XY}_{2n}^-$  ( $n = 1, 2, 3, 4$ ) have been mentioned several times in the preceding section. They can be made by addition of a halide ion to an interhalogen compound, or by reactions which result in halide-ion transfer between molecular species. Ternary polyhalide anions  $\text{X}_m\text{Y}_n\text{Z}_p^-$  ( $m + n + p$  odd) are also known as are numerous polyiodides  $\text{I}_n^-$ . Stability is often enhanced by use of a large counter-cation, e.g.  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{NR}_4^+$ ,  $\text{PCl}_4^+$ , etc.; likewise, for a given cation, thermal stability is enhanced the more symmetrical the polyhalide ion and the larger the central atom (i.e. stability decreases in the sequence  $\text{I}_3^- > \text{IBr}_2^- > \text{ICl}_2^- > \text{I}_2\text{Br}^- > \text{Br}_3^- > \text{BrCl}_2^- > \text{Br}_2\text{Cl}^-$ ). The structures of many of these polyhalide anions have been established by X-ray diffraction analysis or inferred from vibrational spectroscopic data and in all cases the gross stereochemistry is consistent with the expectations of simple bond theories (p. 897); however, subtle deviations from the highest expected symmetry sometimes occur, probably due to crystal-packing forces and residual interactions between the various ions in the condensed phase.

Typical examples of linear (or nearly linear) triatomic polyhalides are in Table 17.15;<sup>(67,76)</sup> the structures are characterized by considerable variability of interatomic distances and these distances are individually always substantially greater than for the corresponding diatomic interhalogen (p. 825). Note also that for

<sup>75</sup> C. J. ADAMS, *Inorg. Nuclear Chem. Letters* **10**, 831–5 (1974).

<sup>76</sup> Ref. 23, pp. 1534–63 (Polyhalide anions) and references therein.

Table 17.15 Triatomic polyhalides  $[X-Y-Z]^-$ 

Polyhalide	Cations	Structure	Dimensions $x/\text{pm}$ , $y/\text{pm}$	Angle
$\text{ClF}_2^-$	$\text{NO}^+$ $\text{Rb}^+$ , $\text{Cs}^+$	$[\text{F}^{\Delta}\text{Cl}^{\Delta}\text{F}]^-$ $[\text{F}-\text{Cl}-\text{F}]^-$	$x = y$ $x \neq y$	$\sim 180^\circ$
$\text{Cl}_3^-$	$\text{NEt}_4^+$ , $\text{NPr}_4^+$ , $\text{NBu}_4^+$	$[\text{Cl}-\text{Cl}-\text{Cl}]^-$	$x = y$	$\sim 180^\circ$
$\text{BrF}_2^-$	$\text{Cs}^+$	$[\text{F}-\text{Br}-\text{F}]^-$		
$\text{BrCl}_2^-$	$\text{Cs}^+$ , $\text{NR}_4^+$ ( $\text{R} = \text{Me}$ , $\text{Et}$ , $\text{Pr}^n$ , $\text{Bu}^n$ )	$[\text{Cl}-\text{Br}-\text{Cl}]^-$	$x = y$	$\sim 180^\circ$
$\text{Br}_2\text{Cl}^-$		$[\text{Br}-\text{Br}-\text{Cl}]^-$	$x \neq y$	
$\text{Br}_3^-$	$\text{Me}_3\text{NH}^{+(a)}$ $\text{Cs}^+$ (and $\text{PBr}_4^+$ )	$[\text{Br}-\text{Br}-\text{Br}]^-$ $[\text{Br}-\text{Br}-\text{Br}]^-$	$x = y = 254$ 244(239) 270(291)	$171^\circ$ $177.5^\circ$ ( $177.3^\circ$ )
$\text{IF}_2^-$	$\text{NEt}_4^+$	$[\text{F}-\text{I}-\text{F}]^-$		
$\text{IBrF}^-$		$[\text{F}-\text{I}-\text{Br}]^-$		
$\text{IBrCl}^-$	$\text{NH}_4^+$	$[\text{Cl}-\text{I}-\text{Br}]^-$	291 251	$179^\circ$
$\text{ICl}_2^-$	$\text{NMe}_4^+$ (and $\text{PCl}_4^+$ ) piperazinium <sup>(b)</sup> triethylenediammonium <sup>(c)</sup>	$[\text{Cl}-\text{I}-\text{Cl}]^-$ $[\text{Cl}-\text{I}-\text{Cl}]^-$ $[\text{Cl}-\text{I}-\text{Cl}]^-$	$x = y = 255$ 247 269 254(253) 267(263)	$180^\circ$ $180^\circ$ $180^\circ$ ( $180^\circ$ )
$\text{IBr}_2^-$	$\text{Cs}^+$	$[\text{Br}-\text{I}-\text{Br}]^-$	262 278	$178^\circ$
$\text{I}_2\text{Cl}^-$		$[\text{Cl}-\text{I}-\text{I}]^-$		
$\text{I}_2\text{Br}^-$	$\text{Cs}^+$	$[\text{Br}-\text{I}-\text{I}]^-$	291 278	$178^\circ$
$\text{I}_3^-$	$\text{AsPh}_4^+$ $[\text{PhCONH}_2]_2\text{H}^+$ $\text{NEt}_4^+$ (form I) (form II) $\text{Cs}^+$ (and $\text{NH}_4^+$ )	$[\text{I}-\text{I}-\text{I}]^-$ $[\text{I}-\text{I}-\text{I}]^-$ $[\text{I}-\text{I}-\text{I}]^-$ $[\text{I}-\text{I}\cdots\text{I}]^-$	$x = y = 290$ 291 295 293 294 283(282) 303(310)	$176^\circ$ $177^\circ$ $180^\circ$ $180^\circ$ (& $178^\circ$ ) $176^\circ$ ( $177^\circ$ )

<sup>(a)</sup>In the compound  $[\text{Me}_3\text{NH}]^+\text{Br}^-\text{Br}_3^-$ ; same dimensions for  $\text{Br}_3^-$  in  $\text{PhN}_2\text{Br}_3$  and in  $[\text{C}_6\text{H}_7\text{NH}]_2[\text{SbBr}_6][\text{Br}_3]$ . Other known values summarized in ref. 77

<sup>(b)</sup>piperazinium,  $[\text{H}_2\text{NC}_4\text{H}_8\text{NH}_2]^{2+}$ .

<sup>(c)</sup>triethylenediammonium,  $[\text{HN}(\text{C}_2\text{H}_4)_3\text{NH}]^{2+}$ : compound contains 2 non-equivalent  $\text{ICl}_2^-$  ions.

$[\text{Cl}-\text{I}-\text{Br}]^-$  the I-Cl distance is greater than the I-Br distance, and in  $[\text{Br}-\text{I}-\text{I}]^-$  I-Br is greater than I-I. On dissociation, the polyhalide yields the solid monohalide corresponding to the smaller of the halogens present, e.g.  $\text{CsICl}_2$  gives  $\text{CsCl}$  and  $\text{ICl}$  rather than  $\text{CsI} + \text{Cl}_2$ . Likewise for  $\text{CsIBrCl}$  the favoured products are  $\text{CsCl}(\text{s}) + \text{IBr}(\text{g})$  rather than  $\text{CsBr}(\text{s}) + \text{ICl}(\text{g})$  or  $\text{CsI}(\text{s}) + \text{BrCl}(\text{g})$ . Thermochemical cycles have been developed to interpret these results.<sup>(76)</sup>

Penta-atomic polyhalide anions  $[\text{XY}_4]^-$  favour the square-planar geometry ( $D_{4h}$ ) as expected for species with 12 valence-shell electrons on the central atom. Examples are the  $\text{Rb}^+$  and  $\text{Cs}^+$  salts of  $[\text{ClF}_4]^{-1}$ , and  $\text{KBrF}_4$  (in which Br-F is 189 pm and adjacent angles F-Br-F are  $90^\circ$  ( $\pm 2^\circ$ ). The symmetry of the anion is slightly

lowered in  $\text{CsIF}_4(\text{C}_{2v})$  and also in  $\text{KICl}_4 \cdot \text{H}_2\text{O}$  (in which I-Cl is 242, 247, 253, and 260 pm and the adjacent angles Cl-I-Cl are  $90.6^\circ$ ,  $90.7^\circ$ ,  $89.2^\circ$  and  $89.5^\circ$ . Other penta-atomic polyhalide anions for which the structure has not yet been determined are  $[\text{ICl}_3\text{F}]^-$ ,  $[\text{IBrCl}_3]^-$ ,  $[\text{I}_2\text{Cl}_3]^-$ ,  $[\text{I}_2\text{BrCl}_2]^-$ ,  $[\text{I}_2\text{Br}_2\text{Cl}]^-$ ,  $[\text{I}_2\text{Br}_3]^-$ ,  $[\text{I}_4\text{Br}]^-$  and  $[\text{I}_4\text{Cl}]^-$ . Some of these may be "square planar" but the polyiodo species might well be more closely related to  $\text{I}_5^-$ : the tetramethylammonium salt of this anion features a planar V-shaped array in which two  $\text{I}_2$  units are bonded to a single iodide ion, i.e.  $[\text{I}(\text{I}_2)_2]^-$  as in Fig. 17.12. The V-shaped ions are arranged in a planar array which bear an interesting relation to a (hypothetical) array of planar  $\text{IX}_4^-$  ions.

Hepta-atomic polyhalide anions are exemplified by  $\text{BrF}_6^-$  ( $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  salts) and  $\text{IF}_6^-$  ( $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{NMe}_4^+$  and  $\text{NEt}_4^+$  salts). The

<sup>77</sup>F. A. COTTON, G. E. LEWIS and W. SCHWOTZER, *Inorg. Chem.* **25**, 3528-9 (1986).

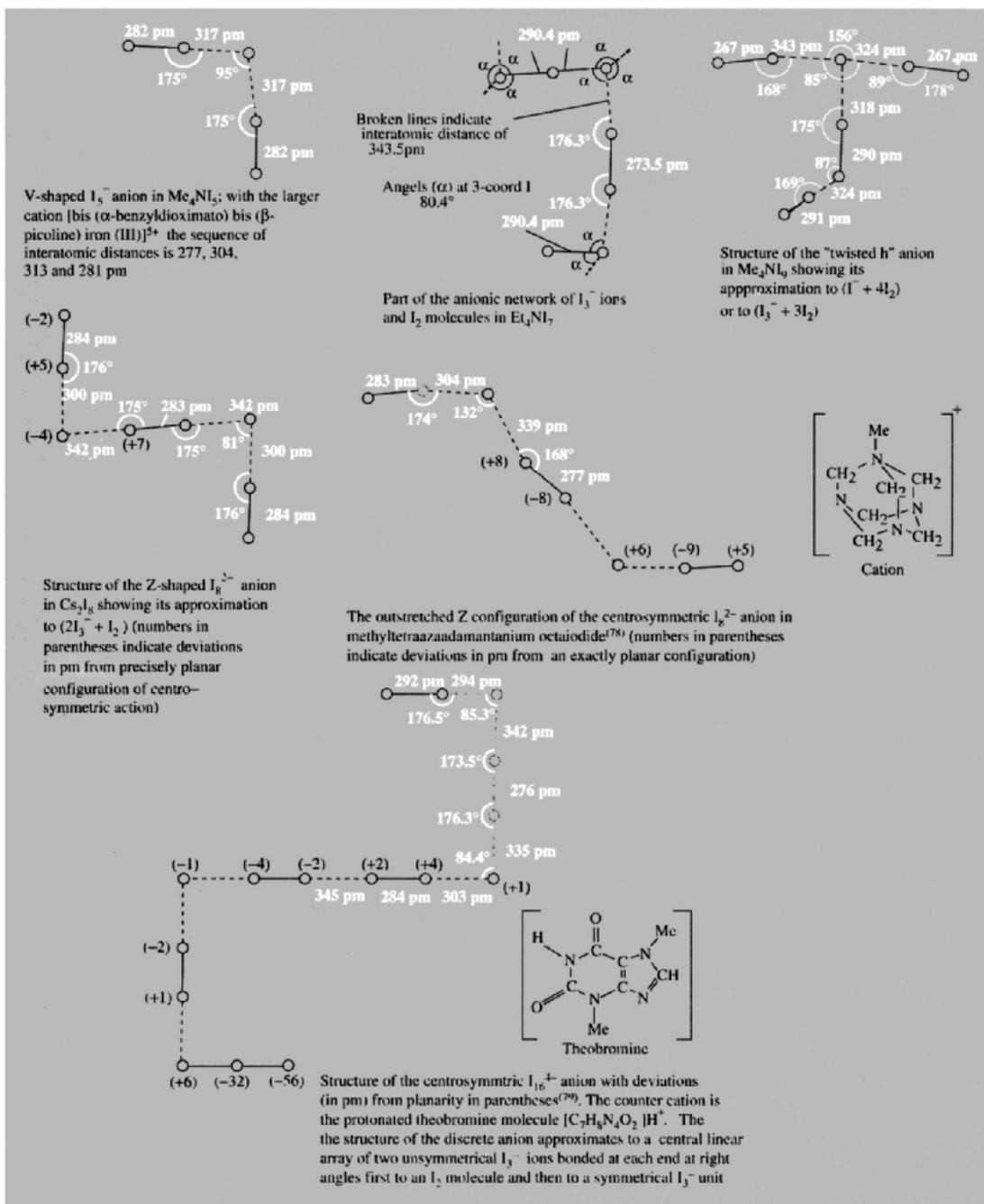


Figure 17.12 Structure of some polyiodides.

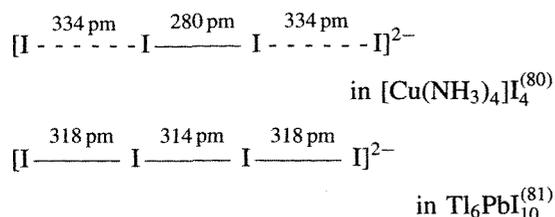
<sup>78</sup> P. K. HON, T. C. M. MAK and J. TROTTER, *Inorg. Chem.* **18**, 2916–7 (1979) and references therein.

<sup>79</sup> F. H. HERSTEIN and M. KAPON, *J. Chem. Soc., Chem. Commun.*, 677–8 (1975).

anions have 14 valence-shell electrons on the central atom and spectroscopic studies indicate non-octahedral geometry ( $D_{3d}$  for  $\text{BrF}_6^-$ ). Other possible examples are  $\text{Br}_6\text{Cl}^-$  and  $\text{I}_6\text{Br}^-$  but these have not been shown to contain discrete hepta-atomic species and may be extended anionic networks such as that found in  $\text{Et}_4\text{NI}_7$  (Fig. 17.12).

$\text{IF}_7$  has been shown to act as a weak Lewis acid towards  $\text{CsF}$  and  $\text{NOF}$ , and the compounds  $\text{CsIF}_8$  and  $\text{NOIF}_8$  have been characterized by X-ray powder patterns and by Raman spectroscopy; they are believed to contain the  $\text{IF}_8^-$  anion.<sup>(75)</sup> A rather different structure motif occurs in the polyiodide  $\text{Me}_4\text{NI}_9$ ; this consists of discrete units with a "twisted h" configuration (Fig. 17.12). Interatomic distances within these units vary from 267 to 343 pm implying varying strengths of bonding, and the anions can be thought of as being built up either from  $\text{I}^- + 4\text{I}_2$  or from a central unsymmetrical  $\text{I}_3^-$  and  $3\text{I}_2$ . (The rather arbitrary recognition of discrete  $\text{I}_9^-$  anions is emphasized by the fact that the closest interionic  $\text{I} \cdots \text{I}$  contact is 349 pm which is only slightly greater than the 343 pm separating one  $\text{I}_2$  from the remaining  $\text{I}_7^-$  in the structure.)

The propensity for iodine to catenate is well illustrated by the numerous polyiodides which crystallize from solutions containing iodide ions and iodine. The symmetrical and unsymmetrical  $\text{I}_3^-$  ions (Table 17.15) have already been mentioned as have the  $\text{I}_5^-$  and  $\text{I}_9^-$  anions and the extended networks of stoichiometry  $\text{I}_7^-$  (Fig. 17.12). The stoichiometry of the crystals and the detailed geometry of the polyhalides depend sensitively on the relative concentrations of the components and the nature of the cation. For example, the linear  $\text{I}_4^{2-}$  ion may have the following dimensions:



(Note, however, that the overall length of the two  $\text{I}_4^{2-}$  ions is virtually identical.) Again, the  $\text{I}_8^{2-}$  anion is found with an acute-angled planar  $Z$  configuration in its  $\text{Cs}^+$  salt but with an outstretched configuration in the black methyltetraazaadamantanium salt (Fig. 17.12). The largest discrete polyiodide ion so far encountered is the planar centro-symmetric  $\text{I}_{16}^{4-}$  anion; this was shown by X-ray diffractometry<sup>(79)</sup> to be present in the dark-blue needle-shaped crystals of (theobromine) $_2 \cdot \text{H}_2\text{I}_8$  which had first been prepared over a century earlier by S. M. Jorgensen in 1869.

The bonding in these various polyiodides as in the other polyhalides and neutral interhalogens has been the subject of much speculation, computation and altercation. The detailed nature of the bonds probably depends on whether F is one of the terminal atoms or whether only the heavier halogens are involved. There is now less tendency than formerly to invoke much d-orbital participation (because of the large promotion energies required) and Mössbauer spectroscopic studies in iodine-containing species<sup>(82)</sup> also suggest rather scant s-orbital participation. The bonding appears predominantly to involve p orbitals only, and multicentred (partially delocalized) bonds such as are invoked in discussions of the isoelectronic xenon halides (p. 897) are currently favoured. However, no bonding model yet comes close to reproducing the range of interatomic distances and angles observed in the crystalline polyhalides.<sup>(76)</sup> There has also been much interest in the bis(ethylenedithio)tetrathiafulvalene layer-like compounds with polyhalide anions. For example,  $[(\text{BEDT-TTF})(\text{ICl}_2)]$  is a one-dimensional metal down to  $\sim 22 \text{ K}$  at which temperature it transforms to an insulator. The  $[\text{BrICl}]^-$  salt is similar, whereas with the larger

<sup>80</sup> E. DUBLER and L. LINOWSKY, *Helv. Chim. Acta* **58**, 2604-9 (1978).

<sup>81</sup> A. RABENAU, H. SCHULZ and W. STOEGER, *Naturwissenschaften* **63**, 245 (1976).

<sup>82</sup> N. N. GREENWOOD and T. C. GIBB, *Mössbauer Spectroscopy*, pp. 462-82, Chapman & Hall, London, 1971.