into infinite chains (Fig. 17.3d, e), whereas with methanol, the additional possibility of hydrogen bonding permits further association into layers (Fig. 17.3f). The structure of $C_6H_6.Br_2$ is also included in Fig. 17.3(g). In all these examples, the lengthening of the $X-X$ bond from that in the free halogen molecule is notable.

The intense blue colour of starch-iodine was mentioned on p. 790.

17.2 Compounds of Fluorine, Chlorine, Bromine and Iodine

17.2.1 Hydrogen halides, HX

It is common practice to refer to the molecular species HX and also the pure (anhydrous) compounds as hydrogen halides, and to call their aqueous solutions hydrohalic acids. Both the anhydrous compounds and their aqueous solutions will be considered in this section. HCl and hydrochloric acid are major industrial chemicals and there is also a substantial production of HF and hydrofluoric acid. HBr and hydrobromic acid are made on a much smaller scale and there seems to be little industrial demand for HI and hydriodic acid. It will be convenient to discuss first the preparation and industrial uses of the compounds and then to consider their molecular and bulk physical properties. The chemical reactivity of the anhydrous compounds and their acidic aqueous solutions will then be reviewed, and the section concludes with a discussion of the anhydrous compounds as nonaqueous solvents.
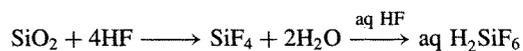
Preparation and uses

Anhydrous HF is almost invariably made by the action of conc H_2SO_4 ($\geq 95\%$) on "acid grade" fluorspar ($\geq 98\%$ CaF_2):

$$CaF_2(s) + H_2SO_4(l) \longrightarrow CaSO_4(s) + 2HF(g)$$
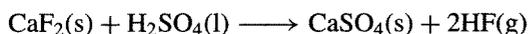
As the reaction is endothermic heat must be supplied to obtain good yields in reasonable

time (e.g. 30–60 min at 200–250°C). Silica is a particularly undesirable impurity in the fluorspar since it consumes up to 6 moles of HF per mole of SiO_2 by reacting to form SiF_4 and then H_2SiF_6. A typical unit, producing up to 20 000 tonnes of HF pa, consists of an externally heated, horizontal steel kiln about 30 m long rotating at 1 revolution per minute. The product gas emerges at 100–150°C and, after appropriate treatment to remove solid, liquid and gaseous impurities, is condensed to give a 99% pure product which is then redistilled to give a final product of 99.9% purity. The technical requirements to enable the safe manufacture and handling of so corrosive a product are considerable.[2,13] In principle, HF could also be obtained from the wet-processing of fluorapatite to give phosphoric acid (p. 521) but the presence of SiO_2 preferentially yields SiF_4 and H_2SiF_6 from which HF can only be recovered uneconomically.

$$Ca_5(PO_4)_3F + 5H_2SO_4 \longrightarrow 5CaSO_4 + 3H_3PO_4$$
$$+ HF$$

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O \xrightarrow{\text{aq HF}} \text{aq } H_2SiF_6$$

Some of the H_2SiF_6 so produced finds commercial outlets (p. 810), but it has been estimated that ~500 000 tonnes of H_2SiF_6 is discarded annually by the US phosphoric acid industry, equivalent to ~1 million tonnes of fluorspar — enough to supply that nation's entire requirements for HF. Production figures and major uses are in the Panel.

Hydrogen chloride is a major industrial chemical and is manufactured on a huge scale. It is also a familiar laboratory reagent both as a gas and as an aqueous acid. The industrial production and uses of HCl are summarized in the Panel on p. 811. One important method for synthesis on a large scale is the burning of H_2 in Cl_2: no catalyst is needed but economic sources of the two elements are obviously required. Another major source of HCl is as a by-product of the chlorination of hydrocarbons (p. 798). The traditional "salt-cake" process of treating NaCl with conc H_2SO_4 also remains an important industrial source of the acid. On a small laboratory scale, gaseous HCl can be made by treating concentrated aqueous hydrochloric acid

Production and Uses of Hydrogen Fluoride

Anhydrous HF was first produced commercially in the USA in 1931 and in the UK from about 1942. By 1992 some eighteen countries were each producing at least 3000 tonnes pa with North America accounting for some 330 000 tonnes of the estimated annual world production of about 875 000 tonnes. A further 205 000 tonnes was used captively for production of AlF_3. Price in 1990 was about \$1.50/kg for the anhydrous acid and somewhat less for 70% acid. The primary suppliers ship HF in tank-cars of 20–91-tonne capacity and the product is also repackaged in steel cylinders holding 8.0–900 kg (2.7–635 kg in the UK). Lecture bottles contain 340 g HF. The 70% acid is shipped in tank-cars of 32–80-tonne capacity, tank trucks of 20-tonne capacity, and in polyethylene-lined drums holding 114 or 208 l.

The early need for HF was in the production of chlorofluorocarbons for refrigeration units and pressurizing gases. The large increase in aluminium production in 1935–40 brought an equivalent requirement for HF (for synthetic cryolite, p. 219) and these two uses still account for the bulk of HF produced in North America (comprising the single market of USA, Canada and Mexico), namely 53.0% and 24.3%, respectively. Other outlets are petroleum alkylation catalysts and steel pickling (3.8% each) and the nuclear industry (3.0%). The remaining 12.1% is distributed amongst traditional uses (such as glass etching and the frosting of light bulbs and television tubes, and the manufacture of fluoride salts), and newer applications such as rocket-propellant stabilizers, preparation of microelectronic circuits, laundry sours and stain removers.

Probably about 50 000 tonnes of HF are used worldwide annually to make inorganic compounds other than UF_4/UF_6 for the nuclear industry. Prominent amongst these products are:

NaF: for water fluoridation, wood preservatives, the formulation of insecticides and fungicides, and use as a fluxing agent. It is also used to remove HF from gaseous F_2 in the manufacture and purification of F_2.

SnF_2: in toothpastes to prevent dental caries.

HBF_4 (aq) and metal fluoroborates: electroplating of metals, catalysts, fluxing in metal processing and surface treatment.

H_2SiF_6 and its salts: fluoridation of water, glass and ceramics manufacture, metal-ore treatment.

The highly corrosive nature of HF and aqueous hydrofluoric acid solutions have already been alluded to (pp. 792, 797) and great caution must be exercised in their handling. The salient feature of HF burns is the delayed onset of discomfort and the development of a characteristic white lesion that is excruciatingly painful. The progressive action of HF on skin is due to dehydration, low pH and the specific toxic effect of high concentrations of fluoride ions: these remove Ca^{2+} from tissues as insoluble CaF_2 and thereby delay healing; in addition the immobilization of Ca^{2+} results in a relative excess of K^+ within the tissue, so that nerve stimulation ensues. Treatment of HF burns involves copious sluicing with water for at least 15 min followed either by (a) immersion in (or application of wet packs of) cold $MgSO_4$, or (b) subcutaneous injection of a 10% solution of calcium gluconate (which gives rapid relief from pain), or (c) surgical excision of the burn lesion.[4] Medical attention is essential, even if the initial effects appear slight, because of the slow onset of the more serious symptoms.

with conc H_2SO_4. Preparation of DCl is best effected by the action of D_2O on $PhCOCl$ or a similar organic acid chloride; PCl_3, PCl_5, $SiCl_4$, $AlCl_3$, etc., have also been used.

Similar routes are available for the production of HBr and HI. The catalysed combination of H_2 and Br_2 at elevated temperatures (200–400°C in the presence of Pt/asbestos, etc.) is the principal industrial route for HBr, and is also used, though on a relatively small scale, for the energetically less-favoured combination of H_2 and I_2 (Pt catalyst above 300°C). Commercially HI is more often prepared by the reaction of I_2 with H_2S or hydrazine, e.g.:

$$2I_2 + N_2H_4 \xrightarrow{H_2O} 4HI + N_2 \text{ (quantitative)}$$

Reduction of the parent halogen with red phosphorus and water provides a convenient

laboratory preparation of both HBr and HI:

$$2P + 6H_2O + 3X_2 \longrightarrow 6HX + 2H_3PO_3$$

$$H_3PO_3 + H_2O + Br_2 \longrightarrow 2HBr + H_3PO_4$$
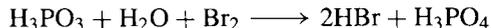
The rapid reaction of 1,2,3,4-tetrahydronaphtha-lene (tetralin) with Br_2 at 20° affords an alternative small-scale preparation though only half the Br_2 is converted, the other half being lost in brominating the tetralin:

$$C_{10}H_{12} + 4Br_2 \longrightarrow 4HBr + C_{10}H_8Br_4.$$
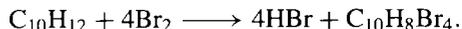
The action of conc H_2SO_4 on metal bromides or iodides (analogous to the "salt-cake" process of HCl) causes considerable oxidation of the product HX but conc H_3PO_4 is satisfactory. Dehydration of the aqueous acids with P_2O_5 is a viable alternative. DBr and DI are obtained by reaction of D_2O on PBr_3 and PI_3 respectively.

Industrial Production and Uses of Hydrogen Chloride[35]

World production of HCl is of the order of 10 million tonnes pa, thus making it one of the largest volume chemicals to be manufactured. Four major processes account for the bulk of HCl produced, the choice of method invariably being dictated by the ready availability of the particular starting materials, the need for the co-products, or simply the availability of by-product HCl which can be recovered as part of an integrated process.

1. The classic salt-cake method was introduced with the Leblanc process towards the end of the eighteenth century and is still used to produce HCl where rock-salt mineral is cheaply available (as in the UK Cheshire deposits). The process is endothermic and takes place in two stages:

$$NaCl + H_2SO_4 \xrightarrow{\sim 150°} NaHSO_4 + HCl; \text{ and } NaCl + NaHSO_4 \xrightarrow{540-600°} Na_2SO_4 + HCl$$

2. The Hargreaves process (late 19th C) is a variant of the salt-cake process in which NaCl is reacted with a gaseous mixture of SO_2, air and H_2O (i.e. "H_2SO_4") in a self-sustaining exothermic reaction:

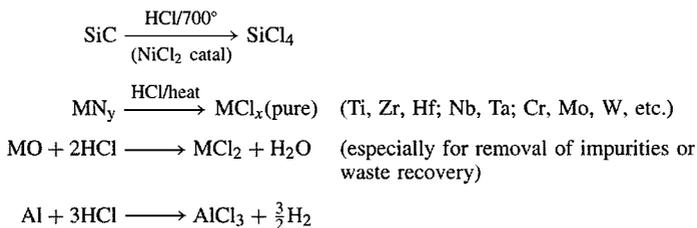$$2NaCl + SO_2 + \tfrac{1}{2}O_2 + H_2O \xrightarrow{430-450°} Na_2SO_4 + 2HCl$$
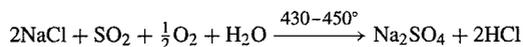
Again the economic operation of the process depends on abundant rock-salt or the need for the by-product Na_2SO_4 for the paper and glass industries.

3. Direct synthesis of HCl by the burning of hydrogen in chlorine is the favoured process when high-purity HCl is required. The reaction is highly exothermic (~ 92 kJ/mol HCl) and requires specially designed burners and absorption systems.
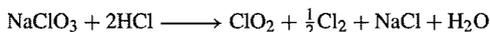
4. By-product HCl from the heavy organic-chemicals industry (p. 798) now accounts for over 90% of the HCl produced in the USA. Where such petrochemical industries are less extensive this source of HCl becomes correspondingly smaller. The crude HCl so produced may be contaminated with unreacted Cl_2, organics, chloro-organics or entrained solids (catalyst supports, etc.), all of which must be removed.

Most of the byproduct HCl is used captively, primarily in oxyhydrochlorination processes for making vinyl chloride and chlorinated solvents or for Mg processing (p. 110). The scale of the industry is enormous; for example, 5.2 million tonnes of HCl per annum in the US alone (1993). HCl gas for industrial use can be transmitted without difficult over moderate distances in mild-steel piping or in tank cars or trailers. It is also available in cylinders of varying size down to laboratory scale lecture bottles containing 225 g. Aqueous hydrochloric acid consumption (1993) was 1.57 Mt (100% basis). Price for anhydrous HCl is $\sim$\$330/tonne and for 31.4% aqueous acid $\sim$\$73/tonne (1993) depending on plant location and amount required.

Industrial use of HCl gas for the manufacture of inorganic chemicals includes the preparation of anhydrous NH_4Cl by direct reaction with NH_3 and the synthesis of anhydrous metal chlorides by reaction with appropriate carbides, nitrides, oxides or even the free metals themselves, e.g.:

$$SiC \xrightarrow[\text{(NiCl}_2 \text{ catal)}]{HCl/700°} SiCl_4$$

$$MN_y \xrightarrow{HCl/heat} MCl_x(\text{pure}) \quad (\text{Ti, Zr, Hf; Nb, Ta; Cr, Mo, W, etc.})$$

$$MO + 2HCl \longrightarrow MCl_2 + H_2O \quad \begin{array}{l}(\text{especially for removal of impurities or} \\ \text{waste recovery})\end{array}$$

$$Al + 3HCl \longrightarrow AlCl_3 + \tfrac{3}{2}H_2$$

HCl is also used in the industrial synthesis of ClO_2 (p. 846):

$$NaClO_3 + 2HCl \longrightarrow ClO_2 + \tfrac{1}{2}Cl_2 + NaCl + H_2O$$

The reaction is catalysed by various salts of Ti, Mn, Pd and Ag which promote the formation of ClO_2 rather than the competing reaction which otherwise occurs:

$$NaClO_3 + 6HCl \longrightarrow 3Cl_2 + NaCl + 3H_2O$$
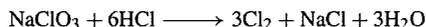
Panel continues

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[35] *Kirk–Othmer's Encyclopedia of Chemical Technology*, 4th Edn., Vol. 13, pp. 894–925 (1995).

HCl is also used in the production of Al_2O_3 (p. 242) and TiO_2 (p. 959), the isolation of Mg from sea water (p. 110), and in many extractive metallurgical processes for isolating or refining metals, e.g. Ge, Sn, V, Mn, Ta, W and Ra.

Aqueous HCl is also produced on a vast scale (e.g. 1.57 Mt/yr in the USA, 1993). Most of this is made and consumed captively at the site of production, predominantly for brine acidification prior to electrolysis in Cl_2/alkali cells. The largest merchant market use is for pickling steel and other metals to remove adhering oxide scale, and for the desulfurization of petroleum. It is also used in pH control (effluent neutralization, etc.), the desliming of hides and chrome tanning, ore beneficiation, the coagulation of latex and the production of aniline from $PhNO_2$ for dyestuffs intermediates. The manufacture of gelatine requires large quantities of hydrochloric acid to decompose the bones used as raw materials — high purity acid must be used since much of the gelatine is used in foodstuffs for human consumption. Another food-related application is the hydrolysis of starch to glucose under pressure: this process is catalysed by small concentrations of HCl and is extensively used to produce "maple syrup" from maize (corn) starch. At higher concentrations of HCl wood (lignin) can be converted to glucose.

Other uses of HCl are legion and range from the purification of fine silica for the ceramics industry, and the refining of oils, fats and waxes, to the manufacture of chloroprene rubbers, PVC plastics, industrial solvents and organic intermediates, the production of viscose rayon yarn and staple fibre, and the wet processing of textiles (where hydrochloric acid is used as a sour to neutralize residual alkali and remove metallic and other impurities).

Anhydrous HBr is available in cylinders (6.8-kg and 68-kg capacity) under its own vapour pressure (24 atm at 25°C) and in lecture bottles (450-g capacity). Its main industrial use is in the manufacture of inorganic bromides and the synthesis of alkyl bromides either from alcohols or by direct addition to alkenes. HBr also catalyses numerous organic reactions. Aqueous HBr (48% and 62%) is available as a corrosive pale-yellow liquid in drums or in large tank trailers (15 000 l and 38 000 l).

There seem to be no large-scale uses for HI outside the laboratory, where it is used in various iodination reactions (lecture bottles containing 400 g HI are available). Commercial solutions contain 40–55 wt% of HI (cf. azeotrope at 56.9% HI, p. 815) and these solutions are thermodynamically much more stable than pure HI as indicated by the large negative free energy of solution.

Physical properties of the hydrogen halides

HF is a colourless volatile liquid and an oligomeric H-bonded gas $(HF)_x$, whereas the heavier HX are colourless diatomic gases at room temperature. Some molecular and bulk physical properties are summarized in Table 17.10. The influence of H bonding on the (low) vapour pressure, (long) liquid range and (high) dielectric constant of HF have already been discussed

(pp. 53–5). Note also that the viscosity of liquid HF is lower than that of water (or indeed of the other HX) and this has been taken to imply the absence of a three-dimensional network of H bonds such as occurs in H_2O, H_2SO_4, H_3PO_4, etc. However, it should be remembered that the viscosity of HF is quoted for 0°C, i.e. some 80° above its mp and only 20° below its bp; a more relevant comparison might be its value of 0.772 centipoise at −62.5° (i.e. 19° above its mp) compared with a value of 1.00 centipoise for water at 20°. Hydrogen bonding is also responsible for the association of HF molecules in the vapour phase: the vapour density of the gas over liquid HF reaches a maximum value of ~86 at −34°. At atmospheric pressure the value drops from 58 at 25° to 20.6 at 80° (the limiting vapour density of monomeric HF is $\frac{20.0063}{2.0159} = 9.924$). These results, together with infrared and electron diffraction studies, indicate that gaseous HF comprises an equilibrium mixture of monomers and cyclic hexamers, though chain dimers may also occur under some conditions of temperature and pressure:

$$6HF \rightleftharpoons (HF)_6; \quad 2HF \rightleftharpoons (HF)_2$$

The crystal structure of HF shows it to consist of planar zigzag chain polymers with an $F-H\cdots F$ distance of 249 pm and an angle at F of 120.1°.

The other HX are not associated in the gaseous or liquid phases but the low-temperature forms of crystalline HCl and HBr both feature weakly

Table 17.10 Physical properties of the hydrogen halides

Property	HF	HCl	HBr	HI
MP/°C	−83.5	−114.2	−88.6	−51.0
BP/°C	19.5[(a)]	−85.1	−67.1	−35.1
Liquid range (1 atm)/°C	103.0	29.1	21.5	15.9
Density(T°C)/g cm^{-3}	1.002(0°)[(b)]	1.187(−114°)	2.603(−84°)	2.85(−47°)
Viscosity(T°C)/centipoise	0.256(0°)	0.51(−95°)	0.83(−67°)	1.35(−35.4°)
Dielectric constant, ε	83.6(0°)[(c)]	9.28(−95°)	7.0(−85°)	3.39(−50°)
Electrical conductivity (T°C)/ohm^{-1} cm^{-1}	∼10^{-6}(0°)	∼10^{-9}(−85°)	∼10^{-9}(−85°)	∼10^{-10}(−50°)
ΔH_f°(298°)/kJ mol^{-1}	−271.12	−92.31	−36.40	26.48
ΔG_f°(298°)/kJ mol^{-1}	−273.22	−95.30	−53.45	1.72
S°(298°)/J mol^{-1}K^{-1}	173.67	186.80	198.59	206.48
$\Delta H_{\mathrm{dissoc}}$(H−X)/kJ mol^{-1}	573.98	431.62	362.50	294.58
r_e(H−X)/pm	91.7	127.4	141.4	160.9
Vibrational frequency ω_e/cm^{-1}	4138.33	2990.94(H^{35}Cl) 2988.48(H^{37}Cl)	2649.65	2309.53
Dipole moment μ/D	1.86	1.11	0.788	0.382

[(a)]Vapour pressure of HF 363.8 mmHg (48.50 kPa) at 0°.
[(b)]Density of liquid HF 1.23 g cm^{-3} near melting point. [(c)]Dielectric constant ε(HF) 175 at −73°C.

H-bonded zigzag chains similar to those in solid HF. At higher temperatures substantial disorder sets in.

The standard heats of formation ΔH_f° of gaseous HX diminish rapidly with increase in molecular weight and HI is endothermic. The very small (and positive) value for the standard free energy of formation ΔG_f° of HI indicates that (under equilibrium conditions) this species is substantially dissociated at room temperature and pressure. However, dissociation is slow in the absence of a catalyst. The bond dissociation energies of HX show a similar trend from the very large value of 574 kJ mol^{-1} for HF to little more than half this (295 kJ mol^{-1}) for HI.

Chemical reactivity of the hydrogen halides

Anhydrous HX are versatile and vigorous reagents for the halogenation of metals, non-metals, hydrides, oxides and many other classes of compound, though reactions that are thermodynamically permissible do not always occur in the absence of catalysts, thermal initiation or photolytic encouragement, because of kinetic factors. For example,[(36)] reaction of HX(g) with elements (M) can thermodynamically proceed according to the equation

$$\mathrm{M} + n\mathrm{HX} = \mathrm{MX}_n + \tfrac{1}{2}n\mathrm{H}_2$$
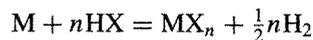
providing that ΔG for the reaction [i.e. $\Delta G_f^\circ(\mathrm{MX}_n) - n\,\Delta G_f^\circ$ (HX, g)] is negative. From the data in Table 17.10 this means that M could be oxidized to the n-valent halide MX_n if:

for the fluoride $\Delta G_f^\circ(\mathrm{MF}_n)$ is $< -274n$ kJ mol^{-1}
for the chloride $\Delta G_f^\circ(\mathrm{MCl}_n)$ is $< -96n$ kJ mol^{-1}
for the bromide $\Delta G_f^\circ(\mathrm{MBr}_n)$ is $< -54n$ kJ mol^{-1}
for the iodide $\Delta G_f^\circ(\mathrm{MI}_n)$ is $<{\sim}0$ kJ mol^{-1}

Using tables of free energies of formation it is clear that most metals will react with most HX. Moreover, in many cases, e.g. with the alkali metals, alkaline earth metals, Zn, Al and the lanthanide elements, such reactions are extremely exothermic. It is also clear that Ag should react with HCl, HBr and HI but not with HF, and

[36] T. C. WADDINGTON, in V. GUTMANN (ed.), *Main Group Elements: Group VII and Noble Gases*, MTP International Review of Science: Inorganic Chemistry Series 1, Vol. 3, pp. 85–125, Butterworths, London, 1972.

Cu should form CuF_2 with HF but not CuX_2 with the other HX. Iron should give $FeCl_3$ but in practice the reaction only proceeds to $FeCl_2$. TiX_4 can be made, but only at high temperatures. Reactions of Si to form SiX_4 are very favourable for X = F, Cl, Br, but only HF reacts at room temperature. With As, reaction with HF to give AsF_3 is thermodynamically favourable but reactions with the other HX are not. Similar, though more complicated, schemes can be worked out for the reactions of HX with oxides, other halides, hydrides, etc.

HF is miscible with water in all proportions and the phase diagram (Fig. 17.4a) shows the presence of three compounds: $H_2O.HF$ (mp $-35.5°$), $H_2O.2HF$ (mp $-75.5°$) and $H_2O.4HF$ (mp $-100.4°$, i.e. $17°$ below the mp of pure HF). Recent X-ray studies have confirmed earlier conjectures that these compounds are best formulated as H-bonded oxonium salts $[H_3O]F$, $[H_3O][HF_2]$, and $[H_3O][H_3F_4]$ with three very strong H bonds per oxonium ion and average $O \cdots F$ distances of 246.7, 250.2

and 253.6 pm respectively.[37] More recently, the low-temperature crystal structure of $Me_4NF.5HF$ (decomp. $-76°C$) has revealed the presence of $H_5F_6^-$, i.e $[(FH)_2FHF(HF)_2]^-$, with four terminal $F-H \cdots F$ of 248.4 pm and a very strong central $F-H \cdots F$ of 226.6 pm. $Me_4NF.7HF$ was also identified (decomp. $-110°C$).[38] Another significant crystal structure, that of tris(ethylenediamine)zinc(II) fluoride dihydrate reveals the strongly H-bonded difluoride cluster $[F_2(H_2O)_2]^{2-}$ which adopts a diamond-shaped cyclic structure $\overline{F \cdots HOH \cdots F \cdots HOH \cdots}^{2-}$ with $O-H \cdots F$ distances of 258.6 and 267.9 pm and non-bonded distances across the lozenge of $O \cdots O$ 335 pm and $F \cdots F$ 406 pm.[39] Such H bonds are very relevant to the otherwise surprising observation that, unlike

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[37] D. MOOTZ, *Angew. Chem. Int. Edn. Engl.* **20**, 791 (1981). See also J. EMSLEY and D. A. JOHNSON, *Polyhedron* **5**, 1109–10 (1986).
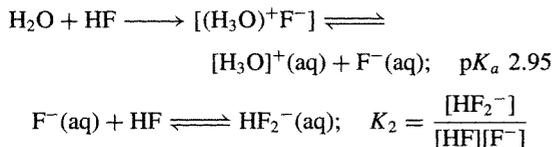
[38] D. MOOTZ and D. BOENIGK, *Z. anorg. allg. Chem.* **544**, 159–66 (1987).

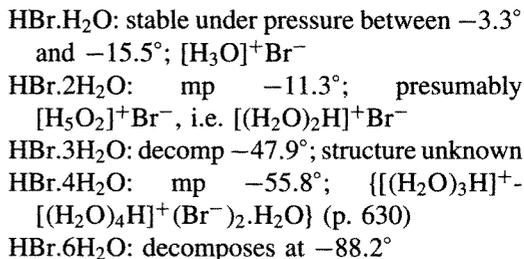[39] J. EMSLEY, M. ARIF, P. A. BATES and M. B. HURSTHOUSE, *J. Chem. Soc., Chem. Commun.*, 738–9 (1989).
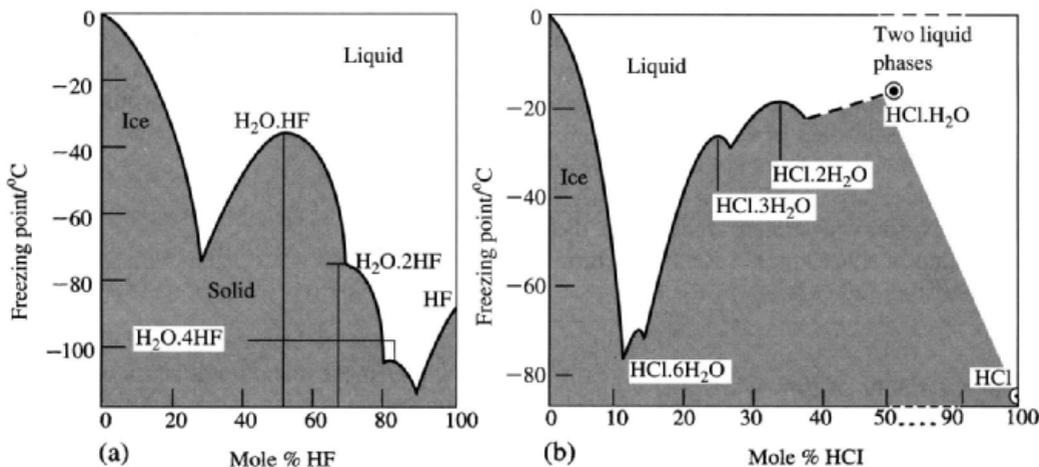
Figure 17.4   The phase diagrams of the systems (a) HF/H_2O and (b) HCl/H_2O. Note that for hydrofluoric acid all the solvates contain $\geq 1HF$ per H_2O, whereas for hydrochloric acid they contain $\leq 1HCl$ per H_2O. This is because the H bonds $F-H \cdots F$ and $F-H \cdots O$ are *stronger* than $O-H \cdots O$, whereas $Cl-H \cdots Cl$ and $Cl-H \cdots O$ are *weaker* than $O-H \cdots O$. Accordingly the solvates in the former system have the crystal structures $[H_3O]^+F^-$, $[H_3O]^+[HF_2]^-$ and $[H_3O]^+[H_3F_4]^-$, whereas the latter are $[H_3O]^+Cl^-$, $[H_5O_2]^+Cl^-$ and $[H_5O_2]^+Cl^-$. H_2O. The structures of $HCl.6H_2O$ and the metastable $HCl.4H_2O$ are not known.

the other aqueous hydrohalic acids which are extremely strong, hydrofluoric acid is a very weak acid in aqueous solution. Indeed, the behaviour of such solutions is remarkable in showing a dissociation constant (as calculated from electrical conductivity measurements) that *diminishes* continuously on dilution. Detailed studies reveal the presence of two predominant equilibria:[40]

$$H_2O + HF \longrightarrow [(H_3O)^+F^-] \rightleftharpoons$$

$$[H_3O]^+(aq) + F^-(aq); \quad pK_a \ 2.95$$

$$F^-(aq) + HF \rightleftharpoons HF_2^-(aq); \quad K_2 = \frac{[HF_2^-]}{[HF][F^-]}$$

The dissociation constant for the first process is only $1.1 \times 10^{-3}\,\mathrm{l\,mol^{-1}}$ at 25°C; this corresponds to pK_a 2.95 and indicates a rather small free hydrogen-ion concentration (cf. $ClCH_2CO_2H$, pK_a 2.85) as a result of the strongly H-bonded, undissociated ion-pair $[(H_3O)^+F^-]$. By contrast, $K_2 = 2.6 \times 10^{-1}\,\mathrm{l\,mol^{-1}}$ (pK_2 0.58), indicating that an appreciable number of the fluoride ions in the solution are coordinated by HF to give HF_2^- rather than by H_2O despite the very much higher concentration of H_2O molecules.

Numerous hydrates also occur in the HCl/H_2O system (Fig. 17.4b), e.g. $HCl.H_2O$ (mp $-15.4°$), $HCl.2H_2O$ (mp $-17.7°$), $HCl.3H_2O$ (mp $-24.9°$), $HCl.4H_2O$ and $HCl.6H_2O$ (mp $-70°$). The system differs from HF/H_2O not only in the stoichiometry of the hydrates but also in separating into two liquid phases at HCl concentrations higher than 1:1. The weakness of the $O-H\cdots Cl$ hydrogen bond also ensures that there is very little impediment to complete ionic dissociation, and aqueous solutions of HCl (and also of HBr and HI) are strong acids; approximate values of pK_a are HCl -7, HBr -9, HI -10. The systems HBr/H_2O and HI/H_2O also show a miscibility gap at high concentrations of HX and also numerous hydrates which feature hydrated oxonium ions:

$HBr.H_2O$: stable under pressure between $-3.3°$ and $-15.5°$; $[H_3O]^+Br^-$

$HBr.2H_2O$: mp $-11.3°$; presumably $[H_5O_2]^+Br^-$, i.e. $[(H_2O)_2H]^+Br^-$

$HBr.3H_2O$: decomp $-47.9°$; structure unknown

$HBr.4H_2O$: mp $-55.8°$; $\{[(H_2O)_3H]^+-[(H_2O)_4H]^+(Br^-)_2.H_2O\}$ (p. 630)

$HBr.6H_2O$: decomposes at $-88.2°$

The compound $HI.H_2O$ does not appear as a stable hydrate in the phase diagram, but the vibrational spectra of frozen solutions of this composition indicate the formulation $[H_3O]^+I^-$. Higher hydrates appear at $HI.2H_2O$ (mp $\sim -43°$), $HI.3H_2O$ (mp $\sim -48°$), and $HI.4H_2O$ (mp $-36.5°C$).

Just as the solid/liquid phase equilibria in the systems HX/H_2O show several points of interest, so too do the liquid/gas phase equilibria. When dilute aqueous solutions of HX are heated to boiling the concentration of HX in the vapour is less than that in the liquid phase, so that the liquid becomes progressively more concentrated and the bp progressively rises until a point is reached at which the liquid has the same composition as the gas phase so that it boils without change in composition and at constant temperature. This mixture is called an azeotrope (Greek $\acute{\alpha}$, without; ζείη, *zein*, to boil; τροπή, *trope*, change). The phenomenon is illustrated for HF and HCl in Fig. 17.5. Conversely, when more concentrated aqueous solutions are boiled, the concentration of HX in the vapour is greater than that in the liquid phase which thereby becomes progressively diluted by distillation until the azeotropic mixture is again reached, whereupon distillation continues without change of composition and at constant temperature. The bps and azeotropic compositions at atmospheric pressure are listed below, together with the densities of the azeotropic acids at 25°C:

[40] L. G. SILLÉN and A. E. MARTELL, *Stability Constants of Metal-Ion Complexes*, Special Publication No. 17, pp. 256–7, The Chemical Society, London, 1964; *Supplement No. 1* (Special Publication No. 17), pp. 152–3 (1971). See also P. McTIGUE, T. A. O'DONNELL and B. VERITT, *Aust. J. Chem.* **38**, 1797–807 (1985).

Azeotrope	HF	HCl	HBr	HI
BP (1 atm)/°C	112	108.58	124.3	126.7
g(HX)/100 g soln	38	20.22	47.63	56.7
Density(25°)/g cm^{-3}	1.138	1.096	1.482	1.708
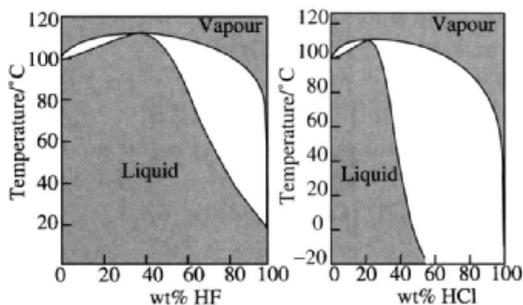
Figure 17.5 Liquid/gas phase equilibria for the systems HF/H$_2$O and HCl/H$_2$O showing the formation of maximum boiling azeotropes as described in the text.

Of course, the bp and composition of the azeotrope both vary with pressure, as illustrated below for the case of hydrochloric acid (1 mmHg = 0.1333 kPa):

P/mmHg	50	250	500	700
BP/°C	48.72	81.21	97.58	106.42
g(HX)/100 g soln	23.42	21.88	20.92	20.36
Density(25°)/g cm^{-3}	1.112	1.104	1.099	1.097

P/mmHg	**760**	800	1000	1200
BP/°C	**108.58**	110.01	116.19	122.98
g(HX)/100 g soln	**20.222**	20.16	19.73	19.36
Density(25°)/g cm^{-3}	**1.0959**	1.095$_5$	1.093	1.091$_5$

The occurrence of such azeotropes clearly restricts the degree to which aqueous solutions of HX can be concentrated by evaporation. However, they do afford a ready means of obtaining solutions of precisely known concentration: in the case of hydrochloric acid, its azeotrope is particularly stable over long periods of time and has found much use in analytical chemistry.

The hydrogen halides as nonaqueous solvents

The great synthetic value of liquid NH$_3$ as a nonaqueous solvent (p. 424) has encouraged the extensive study of the other neighbour of H$_2$O in the periodic table, namely, HF.[36,41-44] Early studies were hampered by the aggressive nature of anhydrous HF towards glass and quartz,

but the pure acid can now be safely handled without contamination using fluorinated plastics such as polytetrafluoroethylene. The self-ionic dissociation of the solvent, as evidenced by the residual electrical conductivity of highly purified HF, can be represented as HF $\rightleftharpoons$ H$^+$ + F$^-$; however, since both ions will be solvated it is more usual to represent the equilibrium as

$$3HF \rightleftharpoons H_2F^+ + HF_2^-$$
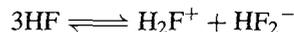
The fluoride ion has an anomalously high conductance, λ_∞, as shown by the following values obtained at 0°:

Ion	Na$^+$	K$^+$	**H$_2$F$^+$**	BF$_4^-$	SbF$_6^-$	**HF$_2^-$**
λ_∞/ohm^{-1} cm^2 mol^{-1}	117	117	**79**	183	196	**273**

As the specific conductivity of pure HF is ~10^{-6} ohm^{-1} cm^2 at 0°, these values imply concentrations of H$_2$F$^+$ = HF$_2^-$ $\simeq$ 2.9 × 10^{-6} mol l^{-1} and an ionic product for the liquid of ~8 × 10^{-12} mol^2 l^{-2} (cf. values of ~10^{-33} for NH$_3$ and ~10^{-14} for H$_2$O).

The high dielectric constant, low viscosity and long liquid range of HF make it an excellent solvent for a wide variety of compounds. Whilst most inorganic fluorides give fluoride ions when dissolved (see next paragraph), a few solutes dissolve without ionization, e.g. XeF$_2$, SO$_2$, HSO$_3$F, SF$_6$ and MF$_6$ (M = Mo, W, U, Re and Os). It is also probable that VF$_5$ and ReF$_7$ dissolve without ionizing. Perhaps more surprisingly liquid HF is now extensively used in biochemical research: carbohydrates, amino acids and proteins dissolve readily, frequently with only minor chemical consequences. In particular, complex organic compounds that are potentially

[41] H. H. HYMAN and J. J. KATZ, Chap. 2 in T. C. WADDINGTON (ed.), *Nonaqueous Solvent Systems*, pp. 47–81, Academic Press, London, 1965.

[42] M. KILPATRICK and J. G. JONES, Chap. 2 in J. J. LAGOWSKI (ed.), *The Chemistry of Nonaqueous Solvents*, pp. 43–99, Vol. 2, Academic Press, New York, 1967.

[43] T. A. O'DONNELL, Chap. 25 in *Comprehensive Inorganic Chemistry*, Vol. 2, pp. 1009–106, Pergamon Press, Oxford, 1973.

[44] R. J. GILLESPIE and J. LIANG, *J. Am. Chem. Soc.* **110**, 6053–7 (1988).

capable of eliminating the elements of water (e.g. cellulose, sugar esters, etc.) often dissolve without dehydration. Likewise globular proteins and many fibrous proteins that are insoluble in water, such as silk fibroin. These solutions are remarkably stable: e.g. the hormones insulin and ACTH were recovered after 2 h in HF at 0° with their biological activity substantially intact.

Many of the ionic fluorides of M^I, M^{II} and M^{III} dissolve to give highly conducting solutions due to ready dissociation. Some typical values of the solubility of fluorides in HF are in Table 17.11: the data show the expected trend towards greater solubility with increase in ionic radius within the alkali metals and alkaline earth metals, and the expected decrease in solubility with increase in ionic charge so that $MF > MF_2 > MF_3$. This is dramatically illustrated by AgF which is 155 times more soluble than AgF_2 and TlF which is over 7000 times more soluble than TlF_3.

With inorganic solutes other than fluorides, solvolysis usually occurs. Thus chlorides, bromides and iodides give the corresponding fluorides with evolution of HX, and fluorides are also formed from oxides, hydroxides, carbonates and sulfites. Indeed, this is an excellent synthetic route for the preparation of anhydrous metal fluorides and has been used with good effect for TiF_4, ZrF_4, UF_4, SnF_4, VOF_3, VF_3, NbF_5, TaF_5, SbF_5, MoO_2F_2, etc. (Note, however, that AgCl, $PdCl_2$, $PtCl_4$, Au_2Cl_6 and ICl are apparently exceptions.[42]) Less-extensive solvolysis occurs with sulfates, phosphates and certain other oxoanions. For example, a careful cryoscopic study of

solutions of K_2SO_4 in HF (at $\sim -84°C$) gave a value of $\nu = 5$ for the number of solute species in solution, but this increased to about 6 when determined by vapour-pressure depressions at 0°. These observations can be rationalized if un-ionized H_2SO_4 is formed at the lower temperature and if solvolysis of this species to unionized HSO_3F sets in at the higher temperatures:

$$K_2SO_4 + 4HF \xrightarrow{-80°} 2K^+ + 2HF_2^- + H_2SO_4$$

$$H_2SO_4 + 3HF \xrightarrow{0°} H_3O^+ + HSO_3F + HF_2^-$$
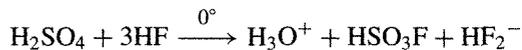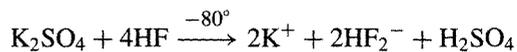
Consistent with this, the ^{19}F nmr spectra of solutions at 0° showed the presence of HSO_3F, and separate cryoscopic experiments with pure H_2SO_4 as the sole solute gave a value of ν close to unity.

Solvolysis of phosphoric acids in the system $HF/P_2O_5/H_2O$ gave successively H_2PO_3F, HPO_2F_2 and $H_3O^+PF_6^-$, as shown by ^{19}F and ^{31}P nmr spectroscopy. Raman studies show that KNO_3 solvolyses according to the reaction

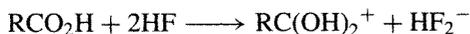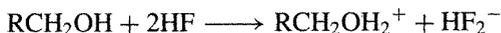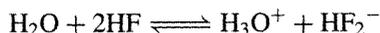$$KNO_3 + 6HF \longrightarrow K^+ + NO_2^+ + H_3O^+ + 3HF_2^-$$
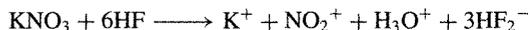
Permanganates and chromates are solvolysed by HF to oxide fluorides such as MnO_3F and CrO_2F_2.

Acid–base reactions in anhydrous HF are well documented. Within the Brønsted formalism, few if any acids would be expected to be sufficiently strong proton donors to be able to protonate the very strong proton-donor HF (p. 51), and this is borne out by observation. Conversely, HF can protonate many Brønsted bases, notably water,

Table 17.11 Solubility of some metal fluorides in anhydrous HF (in g/100 g HF and at 12°C unless otherwise stated)

LiF	NaF(11°)	NH_4F(17°)	KF(8°)	RbF(20°)	CsF(10°)	**AgF**	**TlF**
10.3	30.1	32.6	36.5	110	199	**83.2**	**580**
Hg_2F_2	BeF_2(11°)	MgF_2	CaF_2	SrF_2	BaF_2	**AgF_2**	CaF_2
0.87	0.015	0.025	0.817	14.83	5.60	**0.54**	0.010
HgF_2	CdF_2(14°)	ZnF_2(14°)	CrF_2(14°)	FeF_2	NiF_2	PbF_2	
0.54	0.201	0.024	0.036	0.006	0.037	2.62	
AlF_3	CeF_3	**TlF_3**	MnF_3	FeF_3	CoF_3	SbF_3	BrF_3
0.002	0.043	**0.081**	0.164	0.008	0.257	0.536	0.010

alcohols, carboxylic acids and other organic compounds having one or more lone-pairs on O, N, etc.:

$$H_2O + 2HF \rightleftharpoons H_3O^+ + HF_2^-$$

$$RCH_2OH + 2HF \longrightarrow RCH_2OH_2^+ + HF_2^-$$

$$RCO_2H + 2HF \longrightarrow RC(OH)_2^+ + HF_2^-$$

Alternatively, within the Lewis formalism, acids are fluoride-ion acceptors. The prime examples are AsF_5 and SbF_5 (which give MF_6^-) and to a lesser extent BF_3 which yields BF_4^-. A greater diversity is found amongst Lewis bases (fluoride-ion donors), typical examples being XeF_6, SF_4, ClF_3 and BrF_3:

$$MF_n + HF \longrightarrow MF_{n-1}^+ + HF_2^-$$
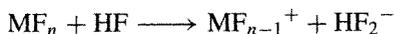
Such solutions can frequently be "neutralized" by titration with an appropriate Lewis acid, e.g.:

$$BrF_2^+HF_2^- + H_2F^+SbF_6^- \longrightarrow BrF_2^+SbF_6^- + 3HF$$
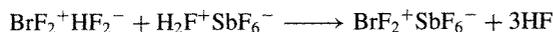
Oxidation-reduction reactions in HF form a particularly important group of reactions with considerable industrial application. The standard electrode potentials $E°(M^{n+}/M)$ in HF follow the same sequence as for H_2O though individual values in the two series may differ by up to ± 0.2 V. Early examples showed that CrF_2 and UF_4 reduced HF to H_2 whereas VCl_2 gave VF_3, 2HCl and H_2. Of more significance is the very high potential needed for the anodic oxidation of F^- in HF:

$$F^- \rightleftharpoons \tfrac{1}{2}F_2 + e^-; \quad E°(F_2/2F^-) = 2.71 \text{ V at } 0°C$$
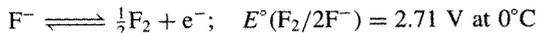
This enables a wide variety of inorganic and organic fluorinations to be effected by the electrochemical insertion of fluorine. For example, the production of NFH_2, NF_2H and NF_3 by electrolysis of NH_4F in liquid HF represents the only convenient route to these compounds. Again, CF_3CO_2H is most readily obtained by electrolysis of CH_3CO_2H in HF. Other examples of anodic oxidations in HF are as follows:

| Reactant	Products	Reactant	Products
NH_4F	NF_3, NF_2H, NFH_2	NMe_3	$(CF_3)_3N$
H_2O	OF_2	$(MeCO)_2O$	CF_3COF
SCl_2,SF_4	SF_6	SMe_2, CS_2	CF_3SF_5, $(CF_3)_2SF_4$
$NaClO_4$	ClO_3F	$MeCN$	CF_3CN, $C_2F_5NF_2$

The other hydrogen halides are less tractable as solvents, as might be expected from their physical properties (p. 813), especially their low bps, short liquid ranges, low dielectric constants and negligible self-dissociation into ions. Nevertheless, they have received some attention, both for comparison with HF and as preparative media with their own special advantages.[36,45,46] In particular, because of their low bp and consequent ease of removal, the liquid HX solvent systems have provided convenient routes to BX_4^-, BF_3Cl^-, $B_2Cl_6^{2-}$, NO_2Cl, $Al_2Cl_7^-$, R_2SCl^+, $RSCl_2^+$, PCl_3Br^+, $Ni_2Cl_4(CO)_3$ (from nickel tetracarbonyl and Cl_2) and $Ni(NO)_2Cl_2$ (from nickel tetracarbonyl and NOCl). Solubilities in liquid HX are generally much smaller than in HF and tend to be restricted to molecular compounds (e.g. NOCl, PhOH, etc.) or salts with small lattice energies, e.g. the tetraalkylammonium halides. Concentrations rarely attain 0.5 mol l^{-1} (i.e. 0.05 mol/100 g HF). Ready protonation of compounds containing lone-pairs or π bonds is observed, e.g. amines, phosphines, ethers, sulfides, aromatic olefins, and compounds containing $-C\equiv N$, $-N=N-$, $>C=O$, $>P=O$ etc. Of particular interest is the protonation of phosphine in the presence of BX_3 to give $PH_4^+BCl_4^-$, $PH_4^+BF_3Cl^-$, and $PH_4^+BBr_4^-$. $Fe(CO)_5$ affords $[Fe(CO)_5H]^+$ and $[Fe(\eta^5-C_5H_5)(CO)_2]_2$ yields $[Fe(\eta^5-C_5H_5)(CO)_2]_2H^+$. Solvolysis is also well established:

$$Ph_3SnCl + HCl \longrightarrow Ph_2SnCl_2 + PhH$$

$$Ph_3COH + 3HCl \longrightarrow Ph_3C^+HCl_2^- + H_3O^+Cl^-$$

[45] M. E. PEACH and T. C. WADDINGTON, Chap. 3 in T. C. WADDINGTON (ed.), *Nonaqueous Solvent Systems*, pp. 83–115, Academic Press, London, 1965.

[46] F. KLANBERG, Chap. 1 in J. J. LAGOWSKI (ed.), *The Chemistry of Nonaqueous Solvents*, Vol. 2, pp. 1–41, Academic Press, New York, 1967.

Likewise ligand replacement reactions and oxidations, e.g.:

$$Me_4N^+HCl_2^- + BCl_3 \longrightarrow Me_4N^+BCl_4^- + HCl$$

$$PCl_3 + Cl_2 + HCl \longrightarrow PCl_4^+HCl_2^-$$
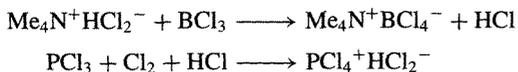
The preparation and structural characterization of the ions HX_2^- has been an important feature of such work.[36] As expected, these H-bonded ions are much less stable than HF_2^- though crystalline salts of all three anions and of the mixed anions HXY^- (except $HBrI^-$) have been isolated by use of large counter cations, typically Cs^+ and NR_4^+ (R = Me, Et, Bu^n) — see pp. 1313–21, of ref. 23 for further details. Neutron and X-ray diffraction studies suggest that $[Cl–H\cdots Cl]^-$ can be either centrosymmetric or non-centrosymmetric depending on the crystalline environment. An example of the latter mode involves interatomic distances of 145 and 178 pm respectively and a bond angle of $\sim 168°$ ($Cl\cdots Cl$ 321.2 pm).[47]

17.2.2 Halides of the elements

The binary halides of the elements span a wide range of stoichiometries, structure types and properties which defy any but the most grossly oversimplified attempt at a unified classification. Indeed, interest in the halides as a class of compound derives in no small measure from this very diversity and from the fact that, being so numerous, there are many examples of well-developed and well-graded trends between the limiting cases. Thus the fluorides alone include OF_2, one of the most volatile molecular compounds known (bp $-145°$), and CaF_2, which is one of the least-volatile "ionic" compounds (bp 2513°C). Between these extremes of discrete molecules on the one hand, and 3D lattices on the other, is a continuous sequence of oligomers, polymers and extended layer lattices which may be either predominantly covalent [e.g. ClF, $(MoF_5)_4$,

$(CF_2)_\infty$, $(CF)_\infty$, p. 289] or substantially ionic [e.g. Na^+F^-(g), $(SnF_2)_4$, $(BeF_2)_\infty$ (quartz type), SnF_4, NaF (cryst)], or intermediate in bond type with secondary interactions also complicating the picture. The problems of classifying binary compounds according to presumed bond types or limiting structural characteristics have already been alluded to for the hydrides (p. 64), borides (p. 145), oxides, sulfides, etc. Such diversity and gradations are further compounded by the existence of four different halogens (F, Cl, Br, I) and by the possibility of numerous oxidation states of the element being considered, e.g. CrF_2, Cr_2F_5, CrF_3, CrF_4, CrF_5 and CrF_6, or S_2F_2, SF_2, SF_4, S_2F_{10} and SF_6.

A detailed discussion of individual halides is given under the chemistry of each particular element. This section deals with more general aspects of the halides as a class of compound and will consider, in turn, general preparative routes, structure and bonding. For reasons outlined on p. 805, fluorides tend to differ from the other halides either in their method of synthesis, their structure or their bond-type. For example, the fluoride ion is the smallest and least polarizable of all anions and fluorides frequently adopt 3D "ionic" structures typical of oxides. By contrast, chlorides, bromides and iodides are larger and more polarizable and frequently adopt mutually similar layer-lattices or chain structures (cf. sulfides). Numerous examples of this dichotomy can be found in other chapters and in several general references.[48−52] Because of this it is convenient to discuss fluorides as a group first, and then the other halides.

47 W. KUCHEN, D. MOOTZ, H. SOMBERG, H. WUNDERLICH and H.-G. WUSSOW, *Angew. Chem. Int. Edn. Engl.* **17**, 869–70 (1978).

48 V. GUTMANN (ed.), *Halogen Chemistry*, Academic Press, London, 1967; Vol. 1. 473 pp.; Vol. 2, 481 pp; Vol. 3, 471 pp.

49 R. COLTON and J. H. CANTERFORD, *Halides of the First Row Transition Elements*, Wiley, London, 1969, 579 pp.; *Halides of the Second and Third Row Transition Elements*, Wiley, London, 1968, 409 pp.

50 Ref. 43, pp. 1062–1106; ref. 23, pp. 1232–80.

51 A. F. WELLS, *Structural Inorganic Chemistry*, 5th edn. pp. 407–44, Oxford University Press, Oxford, 1984.

52 B. MÜLLER, *Angew. Chem. Int. Edn. Engl.* **26**, 1081–97 (1987).

Fluorides

Binary fluorides are known with stoichiometries that span the range from C_4F to IF_7 (or even, possibly, XeF_8). Methods of synthesis turn on the properties of the desired products.[50,53-57] If hydrolysis poses no problem, fluorides can be prepared by halide metathesis in aqueous solution or by the reactions of aqueous hydrofluoric acid with an appropriate oxide, hydroxide, carbonate, or the metal itself. The following non-hydrated fluorides precipitate as easily filterable solids: LiF, NaF, NH_4F; MgF_2, CaF_2, SrF_2, BaF_2; SnF_2, PbF_2; SbF_3. Gaseous SiF_4 and GeF_4 can also be prepared from aqueous HF. Furthermore, the following fluorides separate as hydrates that can readily be dehydrated thermally, though an atmosphere of HF is required to suppress hydrolysis except in the case of the univalent metal fluorides:

$KF.2H_2O$	$CuF_2.4H_2O$	$AlF_3.H_2O$
$RbF.3H_2O$	$ZnF_2.4H_2O$	$GaF_3.3H_2O$
$CsF.1\frac{1}{2}H_2O$	$CdF_2.4H_2O$	$InF_3.3H_2O$
$TlF.2HF.\frac{1}{2}H_2O$	$HgF_2.2H_2O$	$LnF_3.xH_2O$
$AgF.4H_2O$	$MF_2.6H_2O$	(Ln = lanthanide
	(M = Fe,	metal)
	Co, Ni)	

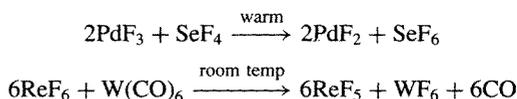By contrast $BeF_2.xH_2O$, $TiF_4.2H_2O$ and $ThF_4.4H_2O$ cannot be dehydrated without hydrolysis.

When hydrolysis is a problem then the action anhydrous HF on the metal (or chloride) may prove successful (e.g. the difluorides of Zn, Cd, Ge, Sn, Mn, Fe, Co, Ni; the trifluorides of Ga, In, Ti and the lanthanides; the tetrafluorides of Ti, Zr, Hf, Th, U; and the pentafluorides of Nb and Ta). However, many higher fluorides require the use of a more aggressive fluorinating agent or even F_2 itself. Typical of the fluorides prepared by oxidative fluorination with F_2 are:

difluorides:	Ag, Xe
trifluorides:	Cl, Br, Mn, Co
tetrafluorides:	Sn, Pb, Kr, Xe, Mo, Mn, Ce, Am, Cm
pentafluorides:	As, Sb, Bi, Br, I, V, Nb, Ta, Mo
hexafluorides:	S, Se, Te, Xe, Mo, W, Tc, Ru, Os, Rh, Ir, Pt, U, Np, Pu
heptafluorides:	I, Re
octafluorides:	Xe(?)

Wherever possible the use of elementary F_2 is avoided because of its cost and the difficulty of handling it; instead one of a graded series of halogen fluorides can often be used, the fluorinating power steadily diminishing in the sequence: $ClF_3 > BrF_5 > IF_7 > ClF > BrF_3 > IF_5$. Other "hard" oxidizing fluorinating agents are AgF_2, CoF_3, MnF_3, PbF_4, CeF_4, BiF_5 and UF_6. When selective fluorination of certain groups in organic compounds is required, then "moderate" fluorinating agents are employed, e.g. HgF_2, SbF_5, $SbF_3/SbCl_5$, AsF_3, CaF_2 or KSO_2F. Such nucleophilic reagents may replace other halogens in halohydrocarbons by F but rarely substitute F for H. An electrophilic variant is ClO_3F. Most recently XeF_2, which is available commercially, has been used to effect fluorinations via radical cations: it can oxidatively fluorinate CC double bonds and can replace either aliphatic or aromatic H atoms with F. Even gentler are the "soft" fluorinating agents which do not cause fragmentation of functional groups, do not saturate double bonds, and do not oxidize metals to their highest oxidation states; typical of such mild fluorinating agents are the monofluorides of H, Li, Na, K, Rb, Cs, Ag and Tl and compounds such as SF_4, SeF_4, COF_2, SiF_4 and Na_2SiF_6.

The fluorination reactions considered so far can be categorized as metathesis, oxidation or substitution. Occasionally reductive fluorination is the preferred route to a lower fluoride. Examples are:
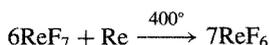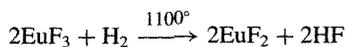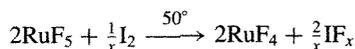
$$2PdF_3 + SeF_4 \xrightarrow{\text{warm}} 2PdF_2 + SeF_6$$

$$6ReF_6 + W(CO)_6 \xrightarrow{\text{room temp}} 6ReF_5 + WF_6 + 6CO$$

[53] E. L. MUETTERTIES and C. W. TULLOCK, Chap. 7 in W. L. JOLLY (ed.), *Preparative Inorganic Reactions*, Vol. 2, pp. 237–99 (1965). R. J. LAGOW and L. J. MARGRAVE, *Prog. Inorg. Chem.* **26**, 161–210 (1979). M. R. C. GERSTENBERGER and A. HAAS, *Angew. Chem. Int. Edn. Engl.* **20**, 647–67 (1981).

[54] J. PORTIER, *Angew. Chem. Int. Edn. Engl.* **15**, 475–86 (1976).

[55] R. D. PEACOCK, *Adv. Fluorine Chem.* **7**, 113–45 (1973).

[56] B. ZEMVA, K. LUTAR, A. JESIH, W. J. CASTEEL and N. BARTLETT, *J. Chem. Soc., Chem. Commun.*, 346–7 (1989).

[57] G. A. OLAH, G. K. S. PRAKASH and R. D. CHAMBERS (eds.), *Synthetic Fluorine Chemistry*, Wiley, Chichester, 1992, 416 pp.
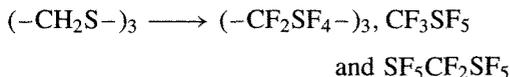
$$2RuF_5 + \tfrac{1}{x}I_2 \xrightarrow{50°} 2RuF_4 + \tfrac{2}{x}IF_x$$

$$2EuF_3 + H_2 \xrightarrow{1100°} 2EuF_2 + 2HF$$

$$6ReF_7 + Re \xrightarrow{400°} 7ReF_6$$

Further examples of this last type of reductive fluorination in which the element itself is used to reduce its higher fluoride are:

Product	ClF	CrF$_2$	GeF$_2$
Reactants	Cl$_2$/ClF$_3$	Cr/CrF$_3$	Ge/GeF$_4$
$T/°C$	350	1000	300
Product	MoF$_3$	UF$_3$	IrF$_4$	TeF$_4$
Reactants	Mo/MoF$_5$	U/UF$_4$	Ir/IrF$_6$	Te/TeF$_6$
$T/°C$	400	1050	170	180

The final route to fluorine compounds is electrofluorination (anodic fluorination) usually in anhydrous or aqueous HF. The preparation of NF$_x$H$_{3-x}$ ($x = 1, 2, 3$) has already been described (p. 818). Likewise a reliable route to OF$_2$ is the electrolysis of 80% HF in the presence of dissolved MF (p. 638). Perchloryl fluoride has been made by electrolysing NaClO$_4$ in HF but a simpler route (p. 879) is the direct reaction of a perchlorate with fluorosulfuric acid:

$$KClO_4 + HSO_3F \longrightarrow KHSO_4 + ClO_3F$$

Electrolysis of organic sulfides in HF affords a variety of fluorocarbon derivatives:

$$Me_2S \text{ or } CS_2 \longrightarrow CF_3SF_5 \text{ and } (CF_3)_2SF_4$$

$$(-CH_2S-)_3 \longrightarrow (-CF_2SF_4-)_3, CF_3SF_5$$
$$\text{and } SF_5CF_2SF_5$$

$$R_2S \longrightarrow R_fSF_5 \text{ and } (R_f)_2SF_4$$

where R$_f$ is a perfluoroalkyl group.

The application of the foregoing routes has led to the preparation and characterization of fluorides of virtually every element in the periodic table except the three lightest noble gases, He, Ne and Ar. The structures, bonding, reactivity, and industrial applications of these compounds will be found in the treatment of the individual elements and it is an instructive exercise to gather this information together in the form of comparative tables.[2,50,53−62]

One important postscript can be added — the achievement by K. O. Christe in 1986 of synthesizing fluorine itself by chemical means alone, a goal that had eluded chemists for at least 173 years.[63] In this context, the term *chemical synthesis* excludes techniques such as electrolysis, photolysis, discharge, etc., or the use of F$_2$ in the synthesis of any of the starting materials. It is well known that high oxidation states can often be stabilized by complex-ion formation. Christe's ingenious strategy was to treat just such a complex fluoride with a strong fluoride-ion acceptor, thus liberating the unstable metal fluoride which then spontaneously decomposed to a lower oxidation state with the liberation of F$_2$. He chose to use K$_2$MnF$_6$ and SbF$_5$, both of which can be readily prepared from HF solutions without the use of F$_2$ itself:

$$K_2MnF_6 + 2SbF_5 \longrightarrow 2KSbF_6 + [MnF_4]$$
$$\longrightarrow MnF_3 + 1/2F_2$$

The reaction was carried out in a passivated Teflon-stainless steel reactor at 150°C for 1 hour, and the yield was >40%. Fluorine pressures of more than 1 atm were generated in this way.

Chlorides, bromides and iodides

A similar set of preparative routes is available as were outlined above for the fluorides, though the range of applicability of each method and the products obtained sometimes vary from halogen to halogen. When hydrolysis is not a problem

[58] A. J. EDWARDS, *Adv. Inorg. Chem. Radiochem.* **27**, 83–112 (1983).

[59] P. HAGENMÜLLER (ed.), *Inorganic Solid Fluorides*, Academic Press, N.Y., 1985, 628 pp.

[60] J. F. LIEBMAN, A. GREENBERG and W. R. DOLBIER (eds.), *Fluorine-containing Molecules: Structure, Reactivity, Synthesis and Applications*, VCH Publishers, N.Y. 1988, 350 pp.

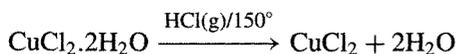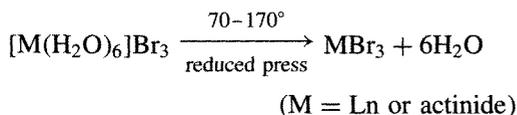[61] A. E. COMYNS (ed.), *Fluoride Glasses*, Wiley, Chichester, 1989, 219 pp.

[62] J. S. THRASHER and S. H. STRAUSS (eds.) *Inorganic Fluorine Chemistry Towards the 21st Century*, ACS Symposium Series **555**, 1994, 437 pp.

[63] K. O. CHRISTE, *Inorg. Chem.* **25**, 3721–2 (1986). See also *C & E News*, March 2, pp. 4–5 (1987) for discussion of the implications.

or when hydrated halides are sought, then wet methods are available, e.g. dissolution of a metal or its oxide, hydroxide or carbonate in aqueous hydrohalic acid followed by evaporative crystallization:

$$Fe + 2HCl\ (aq) \longrightarrow [Fe(H_2O)_6]Cl_2 + H_2$$

$$CoCO_3 + 2HI\ (aq) \longrightarrow [Co(H_2O)_6]I_2 + H_2O$$
$$+ CO_2$$
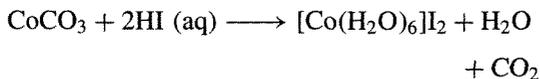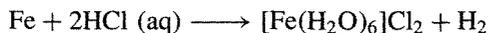
Dehydration can sometimes be effected by controlled removal of water using a judicious combination of gentle warming and either reduced pressure or the presence of anhydrous HX:

$$[M(H_2O)_6]Br_3 \xrightarrow[\text{reduced press}]{70-170°} MBr_3 + 6H_2O$$

$$(M = Ln\ or\ actinide)$$

$$CuCl_2.2H_2O \xrightarrow{HCl(g)/150°} CuCl_2 + 2H_2O$$

Hydrated chlorides that are susceptible to hydrolysis above room temperature can often be dehydrated by treating them with $SOCl_2$ under reflux:

$$[Cr(H_2O)_6]Cl_3 + 6SOCl_2 \xrightarrow{79°} CrCl_3 + 12HCl$$
$$+ 6SO_2$$
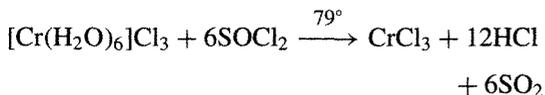
Alternative wet routes to hydrolytically stable halides are metathetical precipitation and reductive precipitation reactions, e.g.:

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl$$

$$Cu^{2+}(aq) + 2I^-(aq) \longrightarrow CuI + \tfrac{1}{2}I_2$$
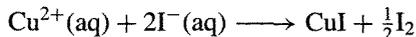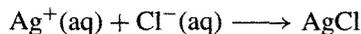
More complex is the hydrolytic disproportionation of the molecular halogens themselves in aqueous alkali which is a commercial route to several alkali-metal halides:
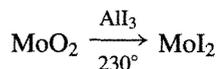
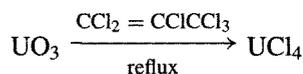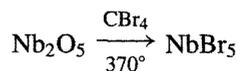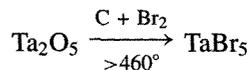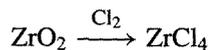$$3X_2 + 6OH^- \longrightarrow 5X^- + XO_3^- + 3H_2O$$
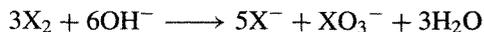
When the desired halide is hydrolytically unstable then dry methods must be used, often at elevated temperatures. Pre-eminent amongst these methods is the oxidative halogenation of metals (or non-metals) with X_2 or HX; when more than one oxidation state is available X_2 sometimes gives the higher and HX the lower, e.g.:
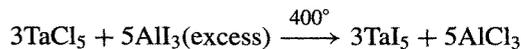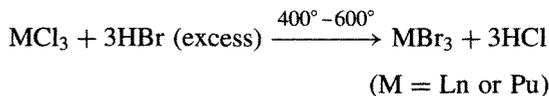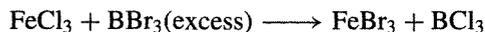
$$Cr + \tfrac{3}{2}Cl_2 \xrightarrow{600°} CrCl_3$$

$$Cr + 2HCl(g) \xrightarrow{\text{red heat}} CrCl_2 + H_2$$
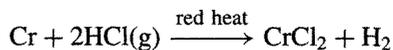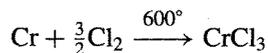
Similarly, Cl_2 sometimes yields a higher and Br_2 a lower oxidation state, e.g. $MoCl_5$ and $MoBr_3$.
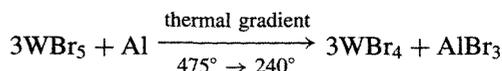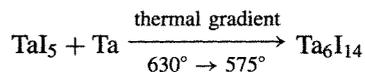
Other routes include the high-temperature halogenation of metal oxides, sometimes in the presence of carbon, to assist removal of oxygen; the source of halogen can be X_2, a volatile metal halide CX_4 or another organic halide. A few examples of the many reactions that have been used industrially or for laboratory scale preparations are:

$$ZrO_2 \xrightarrow{Cl_2} ZrCl_4$$

$$Ta_2O_5 \xrightarrow[>460°]{C\ +\ Br_2} TaBr_5$$

$$Nb_2O_5 \xrightarrow[370°]{CBr_4} NbBr_5$$

$$UO_3 \xrightarrow[\text{reflux}]{CCl_2\ =\ CClCCl_3} UCl_4$$

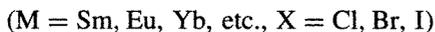$$MoO_2 \xrightarrow[230°]{AlI_3} MoI_2$$

The last two of these reactions also feature a reduction in oxidation state. A closely related route is halogen exchange usually in the presence of an excess of the "halogenating reagent", e.g.:

$$FeCl_3 + BBr_3(\text{excess}) \longrightarrow FeBr_3 + BCl_3$$

$$MCl_3 + 3HBr\ (\text{excess}) \xrightarrow{400°-600°} MBr_3 + 3HCl$$
$$(M = Ln\ or\ Pu)$$

$$3TaCl_5 + 5AlI_3(\text{excess}) \xrightarrow{400°} 3TaI_5 + 5AlCl_3$$

Reductive halogenation can be achieved by reducing a higher halide with the parent metal, another metal or hydrogen:

$$TaI_5 + Ta \xrightarrow[630° \to 575°]{\text{thermal gradient}} Ta_6I_{14}$$

$$3WBr_5 + Al \xrightarrow[475° \to 240°]{\text{thermal gradient}} 3WBr_4 + AlBr_3$$

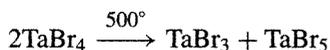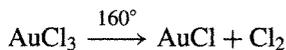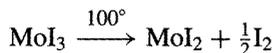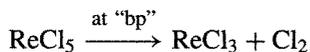$$MX_3 + \tfrac{1}{2}H_2 \longrightarrow MX_2 + HX$$

$$(M = Sm, Eu, Yb, etc., X = Cl, Br, I)$$
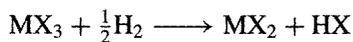
Alternatively, thermal decomposition or disproportionation can yield the lower halide:

$$ReCl_5 \xrightarrow{\text{at ``bp''}} ReCl_3 + Cl_2$$

$$MoI_3 \xrightarrow{100°} MoI_2 + \tfrac{1}{2}I_2$$

$$AuCl_3 \xrightarrow{160°} AuCl + Cl_2$$

$$2TaBr_4 \xrightarrow{500°} TaBr_3 + TaBr_5$$

Many significant trends are apparent in the structures of the halides and in their physical and chemical properties. The nature of the element concerned, its position in the periodic table, the particular oxidation state, and, of course, the particular halogen involved, all play a role. The majority of pre-transition metals (Groups 1, 2) together with Group 3, the lanthanides and the actinides in the +2 and +3 oxidation states form halides that are predominantly ionic in character, whereas the non-metals and metals in higher oxidation states ($\geq$ +3) tend to form covalent molecular halides. The "ionic-covalent transition" in the halides of Group 15 (P, As, Sb, Bi) and 16 (S, Se, Te, Po) has already been discussed at length (pp. 498, 558, 772) as has the tendency of the refractory transition metals to form cluster halides (pp. 991, 1021, etc.). The problems associated with the ionic bond model and its range of validity were considered in Chapter 4 (p. 79). Presumed bond types tend to show gradual rather than abrupt changes within series in which the central element, the oxidation state or the halogen are systematically varied. For example, in a sequence of chlorides of isoelectronic metals such as KCl, $CaCl_2$, $ScCl_3$ and $TiCl_4$ the first member is predominantly ionic with a 3D lattice of octahedrally coordinated potassium ions; $CaCl_2$ has a framework structure (distorted rutile) in which Ca is surrounded by a distorted octahedron of 6Cl; $ScCl_3$ has a layer structure and $TiCl_4$ is a covalent molecular liquid.

The sudden discontinuity in physical properties at $TiCl_4$ is more a function of stoichiometry and coordination number than a sign of any discontinuous or catastrophic change in bond type. Numerous other examples can be found amongst the transition metal halides and the halides of the post-transition elements. In general, the greater the difference in electronegativity between the element and the halogen the greater will be the tendency to charge separation and the more satisfactory will be the ionic bond model. With increasing formal charge on the central atom or with decreasing electronegativity difference the more satisfactory will be the various covalent bond models. The complexities of the situation can be illustrated by reference to the bp (and mp) of the halides: for the more ionic halides these generally follow the sequence $MF_n > MCl_n > MBr_n > MI_n$, being dominated by coulombic interactions which are greatest for the small F^- and least for the large I^-, whereas for molecular halides the sequence is usually the reverse, viz. $MI_n > MBr_n > MCl_n > MF_n$ being dictated rather by polarizability and London dispersion forces which are greatest for I and least for F. As expected, intermediate halides are less regular as the first sequence yields to the reverse, and no general pattern can be discerned. Physical techniques such as $^{35,37}Cl$ nmr spectroscopy and nuclear quadrupole resonance spectroscopy are being increasingly used to probe such trends.[64]

Similar observations hold for solubility. Predominantly ionic halides tend to dissolve in polar, coordinating solvents of high dielectric constant, the precise solubility being dictated by the balance between lattice energies and solvation energies of the ions, on the one hand, and on entropy changes involved in dissolution of the crystal lattice, solvation of the ions and modification of the solvent structure, on the other: [ΔG(cryst$\rightarrow$saturated soln) $= 0 = \Delta H - T\Delta S$]. For a given cation (e.g. K^+, Ca^{2+}) solubility in water typically follows the sequence

64 T. L. WEEDING and W. S. VEEMAN, *J. Chem. Soc., Chem. Commun.*, 946–8 (1989).

$MF_n < MCl_n < MBr_n < MI_n$. 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 [65-67]

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[68] shows that chlorine thiocyanate is ClSCN (angle $Cl-S-C$ 99.8°) rather than ClNCS, in contrast to the cyanate which is ClNCO. The corresponding fluoro compound, FNCO, can be synthesized by several low-temperature routes but is not stable at room temperature and rapidly dimerizes to $F_2NC(O)NCO$.[69] The chemistry of iodine azide has been reviewed[70] — 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

[65] 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.

[66] 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.

[67] 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.

[68] R. J. RICHARDS, R. W. DAVIS and M. C. L. GERRY, *J. Chem. Soc., Chem. Commun.,* 915–6 (1980).

[69] K. GHOLIVAND and H. WILLNER, *Z. anorg. allg. Chem.* **550**, 27–34 (1987).

[70] K. DEHNICKE, *Angew. Chem. Int. Edn. Engl.* **18**, 507–14 (1979).