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The Halogens: Fluorine, Chlorine, Bromine, Iodine and Astatine

17.1 The Elements

17.1.1 Introduction

Compounds of the halogens have been known from earliest times and the elements have played a particularly important role during the past two hundred years in the development of both experimental and theoretical chemistry.[1] Some of this early history is summarized in Table 17.1. The name "halogen" was introduced by J. S. C. Schweigger in 1811 to describe the property of chlorine, at that time unique among the elements, of combining directly with metals to give salts (Greek $\dot{\alpha}\lambda\varsigma$, sea salt, plus the root -$\gamma\varepsilon\nu$, produce). The name has since been extended to cover all five members of Group 17 of the periodic table.

Fluorine

Fluorine derives its name from the early use of fluorspar (CaF_2) as a flux (Latin *fluor*, flowing). The name was suggested to Sir Humphry Davy by A.-M. Ampère in 1812. The corrosive nature of hydrofluoric acid and the curious property that fluorspar has of emitting light when heated ("fluorescence") were discovered in the seventeenth century. However, all attempts to isolate the element either by chemical reactions or by electrolysis were foiled by the extreme reactivity of free fluorine. Success was finally achieved on 26 June 1886 by H. Moissan who electrolysed a cooled solution of KHF_2 in anhydrous liquid HF, using Pt/Ir electrodes sealed into a platinum U-tube sealed with fluorspar caps: the gas evolved immediately caused crystalline silicon to burst into flames, and Moissan reported the results to the Academy two days later in the following cautious words: "One can indeed make various hypotheses on the nature of the liberated gas; the simplest would be that *we are in the*

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[1] M. E. WEEKS, *Discovery of the Elements*, 6th edn., Journal of Chemical Education, Easton, 1956, Chap. 27, 'The halogen family', pp. 729–77.

Table 17.1   Early history of the halogens and their compounds

3000 BC	Archaeological evidence for the use of rock-salt
~400 BC	Written records on salt (ascribed to Herodot)
~200 BC	Use of salt as part payment for services (salary)
~21 AD	Strabo described dyeworks for obtaining tyrian purple (dibromoindigo) in his *Geographica*
~100	Use of salt to purify noble metals
~900	Dilute hydrochloric acid prepared by Arabian alchemist Rhazes
~1200	Development of *aqua regia* (HCl/HNO_3) to dissove gold — presumably Cl_2 was also formed
1529	Georgius Agricola described use of fluorspar as a flux
~1630	Chlorine recognized as a gas by Belgian physician J. B. van Helmont (see Scheele, 1774)
1648	Concentrated HCl prepared by J.L. Glauber (by heating hydrated $ZnCl_2$ and sand)
1670	H. Schwanhard (Nürnberg) found that CaF_2 + strong acid gave acid vapours (HF) that etched glass (used decoratively)
1678	J. S. Elsholtz described emission of bluish-white light when fluorspar was heated. Also described by J. G. Wallerius, 1750; the name "fluorescence" was coined in 1852 by G. G. Stokes
1768	First chemical study of fluorite undertaken by A. S. Marggraf
1771	Crude hydrofluoric acid prepared by C. W. Scheele
1772	Gaseous HCl prepared over mercury by J. Priestley
1774	C. W. Scheele prepared and studied gaseous chlorine (MnO_2 + HCl) but thought it was a compound
1785	Chemical bleaching (eau de Javel: aqueous KOH + Cl_2) introduced by C.-L. Berthollet
1787	N. Leblanc devised a technical process for obtaining NaOH from NaCl (beginnings of the chemical industry)
1798	Bleaching powder patented by C. Tennant (Cl_2 + slaked lime) following preparation of bleaching liquors from Cl_2 and lime solutions by T. Henry (1788)
1801	W. Cruickshank recommended use of Cl_2 as a disinfectant (widely used in hospitals by 1823; notably effective in the European cholera epidemic, 1831, and in the outbreak of puerperal fever, Vienna, 1845)
1802	Fluoride found in fossil ivory and teeth by D. P. Morichini (soon confirmed by J. J. Berzelius who found it also in bones)
1810	H. Davy announced proof of the elementary nature of chlorine to the Royal Society (15 November) and suggested the name "chlorine" (1811)
1811	B. Courtois isolated iodine by sublimation (H_2SO_4 + seaweed ash)
1811	The term "halogen" introduced by J. S. C. Schweigger to denote the (then) unique property of the element chlorine to combine directly with metals to give salts
1812	A.-M. Ampère wrote to H. Davy (12 August) suggesting the name *le fluore* (fluorine) for the presumed new element in CaF_2 and HF (by analogy with *le chlore*, chlorine). Adapted by Davy in 1813
1814	Starch/iodine blue colour-reaction described by J.-J. Colin and H.-F. Gaultier de Claubry; developed by F. Stromeyer in the same year as an analytical test sensitive to 2–3 ppm iodine
1814	First interhalogen compound (ICl) prepared by J.L. Gay Lussac
1819	Potassium iodide introduced as a remedy for goitre by J.-F. Coindet (Switzerland), the efficacy of extracts from kelp having been known in China and Europe since the sixteenth century
1823	M. Faraday showed that "solid chlorine" was chlorine hydrate ($Cl_2.\sim10H_2O$ using present-day nomenclature). He also liquefied Cl_2 (5 March) by warming the hydrate in a sealed tube
1825	First iodine containing mineral (AgI) identified by A. M. del Rio (Mexico) and N.-L. Vauquelin (Paris)
1826	Bromine isolated by A.-J. Balard (aged 23 y)
1835	L. J. M. Daguerre's photographic process (silver plate sensitized by exposure to iodine vapour)
~1840	Introduction of (light sensitive) AgBr into photography
1840	Iodine (as iodate) found in Chilean saltpetre by A. A. Hayes
1841	First mineral bromide (bromyrite, AgBr) discovered in Mexico by P. Berthier — later also found in Chile and France
1851	Diaphragm cell for the electrolytic generation of Cl_2 invented by C. Watt (London) but lack of electric generators delayed exploitation until 1886–90 (Matthes and Weber of Duisberg)
1857	Bromide therapy introduced by Lacock as a sedative and anticonvulsant for treatment of epilepsy
1858	Discovery of Stassfurt salt deposits opened the way for bromine production (for photography and medicine) as a by-product of potash
1863	Alkali Act (UK) prohibited atmospheric pollution and enforced the condensation of by-product HCl from the Leblanc process
1886	H. Moissan isolated F_2 by electrolysis of KHF_2/HF (26 June) after over 70 y of unsuccessful attempts by others (Nobel Prize for Chemistry 1906 — he died 2 months later)
1892–5	H. Y. Castner (US/UK) and C. Kellner (Vienna) independently developed commercial mercury-cathode cell for chlor-alkali production

Table 17.2   Halogens in the twentieth century

~1900	First manufacture of inorganic fluorides for aluminium industry
1902	J. C. Downs (of E. I. du Pont de Nemours, Delaware) patented the first practical molten-salt cell for Cl_2 and Na metal
1908	HCl shown to be present in gastric juices of animals by P. Sommerfeld
1909	P. Friedländer showed that Tyrian Purple from *Murex brandaris* was 6,6'-dibromoindigo (previously synthesized by F. Sachs in 1904)
1920	Bromine detected in blood and organs of humans and other animals and birds by A. Damiens
1928	T. Midgley, A. L. Henne and R. R. McNary synthesized Freon (CCl_2F_2) as a non-flammable, non-toxic gas for refrigeration
1928	ClF made by O. Ruff *et al.* ($Cl_2 + F_2$ at 250°)
1930	IF_7 made by O. Ruff and R. Keim (IF_5 having been made in 1871 by G. Gore)
1930+	H. T. Dean *et al.* put the correlation between decreased incidence of dental caries and the presence of fluoride ions in drinking water on a quantitative basis
1931	First bulk shipment of commercial anhydrous HF (USA)
1938	R. J. Plunket discovered Teflon (polytetrafluoroethylene, PTFE)
1940	Astatine made via $^{209}Bi(\alpha,2n)$ by D. R. Corson, K. R. Mackenzie and E. Segré
1940–1	Industrial production of $F_2(g)$ begun (in the UK and the USA for manufacture of UF_6 and in Germany for ClF_3)
1950	Chemical shifts for ^{19}F and nmr signals for ^{35}Cl and ^{37}Cl first observed
1962	ClF_5 (the last halogen fluoride to be made) synthesized by W. Maya
1965	LaF_3 crystals developed by J. W. Ross and M. S. Frant as the first non-glass membrane electrode (for ion-selective determination of F^-)
1965	Perchlorate ion established as a monodentate ligand (to Co) by X-ray crystallography, following earlier spectroscopic and conductimetric indications of coordination (1961)
1968	Perbromates first prepared by E. H. Appelman
1967	First example of $\mu(\eta^1,\eta^1)$-ClO_4^- as a bidentate bridging ligand (to Ag^+); chelating η^2-ClO_4^- identified in 1974
1971	HOF first isolated in weighable amounts (p. 856)
1986	First chemical synthesis of F_2 gas (p. 821)

presence of fluorine, but it would be possible, of course, that it might be a perfluoride of hydrogen or even a mixture of hydrofluoric acid and ozone. ...." For this achievement, which had eluded some of the finest experimental chemists of the nineteenth century [including H. Davy (1813–14), G. Aimé (1833), M. Faraday (1834), C. J. and T. Knox (1836), P. Louyet (1846), E. Frémy (1854), H. Kammerer (1862) and G. Gore (1870)], and for his development of the electric furnace, Moissan was awarded the Nobel Prize for Chemistry in 1906.

Fluorine technology and the applications of fluorine-containing compounds have developed dramatically during the twentieth century.[2,3] Some highlights are included in Table 17.2 and will be discussed more fully in later sections.

Noteworthy events are the development of inert fluorinated oils, greases and polymers: Freon gases such as CCl_2F_2 (1928) were specifically developed for refrigeration engineering; others were used as propellants in pressurized dispensers and aerosols; and the non-stick plastic polytetrafluoroethylene (PTFE or Teflon) was made in 1938. Inorganic fluorides, especially for the aluminium industry (p. 219) have been increasingly exploited from about 1900, and from 1940 UF_6 has been used in gaseous diffusion plants for the separation of uranium isotopes for nuclear reactor technology. The great oxidizing strength of F_2 and many of its compounds with N and O have attracted the attention of rocket

compounds, pp. 267–466; Organic fluorine compounds, pp. 467–729.

³ R. E. BANKS, D. W. A. SHARP and J. C. TATLOW (eds.), *Fluorine: the First Hundred years*, Elsevier, New York, 1987 399 pp.

² *Kirk–Othmer Encyclopedia of Chemical Technology*, 4th edn., Vol. 11, 1994: Fluorine pp. 241–67; In- organic fluorine

engineers and there have been growing large-scale industrial applications of anhydrous HF (p. 810).

The aggressive nature of HF fumes and solutions has been known since Schwanhard of Nürnberg used them for the decorative etching of glass. Hydrofluoric acid inflicts excruciatingly painful skin burns (p. 810) and any compound that might hydrolyse to form HF should be treated with great caution.[4] Maximum allowable concentration for continuous exposure to HF gas is 2–3 ppm (cf. HCN 10 ppm). The free element itself is even more toxic, maximum allowable concentration for a daily 8-h exposure being 0.1 ppm. Low concentrations of fluoride ion in drinking water have been known to provide excellent protection against dental caries since the classical work of H. T. Dean and his colleagues in the early 1930s; as there are no deleterious effects, even over many years, providing the total fluoride ion concentration is kept at or below 1 ppm, fluoridation has been a recommended and adopted procedure in several countries for many years (p. 810). However, at 2–3 ppm a brown mottling of teeth can occur and at 50 ppm harmful toxic effects are noted. Ingestion of 150 mg of NaF can cause nausea, vomiting, diarrhoea and acute abdominal pains though complete recovery is rapid following intravenous or intramuscular injection of calcium ions. The deliberate fluoridation of domestic water supplies has been a controversial, even polemical subject for several decades, though it is important to separate out the biological and toxicological aspects from the moral and philosophical aspects concerning the "right" of individuals to drink untreated water if they wish.[5–7]

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[4] A. J. FINKEL, Treatment of hydrogen fluoride injuries, *Adv. Fluorine Chem.* **7**, 199–203 (1973).

[5] G. L. WALDBOTT (with A. W. BURGSTAHLER and H. L. MCKINNEY, *Fluoridation: The Great Dilemma*, Coronado Press, Lawrence, Kansas, 1978, 423 pp.

[6] B. HILEMAN, Fluoridation of Water: A Special Report, *C & E News* August 1, 26–42 (1988). See also B. HILEMAN, *C & E News* February 25, 6–7 (1991).

[7] B. MARTIN, *Scientific Knowledge in Controversy: The Social Dynamics of the Fluoridation Debate*, State University of New York Press, Albany, N.Y. 1991, 256 pp.

Chlorine

Chlorine was the first of the halogens to be isolated and common salt (NaCl) has been known from earliest times (see Table 17.1). Its efficacy in human diet was well recognized in classical antiquity and there are numerous references to its importance in the Bible. On occasion salt was used as part payment for the services of Roman generals and military tribunes (salary) and, indeed, it is an essential ingredient in mammalian diets (p. 68). The alchemical use of *aqua regia* (HCl/HNO$_3$) to dissolve gold is also well documented from the thirteenth century onwards. Concentrated hydrochloric acid was prepared by J. L. Glauber in 1648 by heating hydrated ZnCl$_2$ and sand in a retort and the pure gas, free of water, was collected over mercury by J. Priestley in 1772. This was closely followed by the isolation of gaseous chlorine by C. W. Scheele in 1774: he obtained the gas by oxidizing nascent HCl with MnO$_2$ in a reaction which would now formally be written as:

$$4NaCl + 2H_2SO_4 + MnO_2 \xrightarrow{\text{heat}} 2Na_2SO_4$$
$$+ MnCl_2 + 2H_2O + Cl_2$$
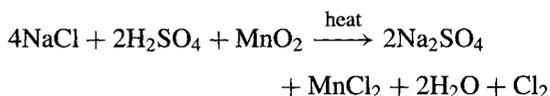
However, Scheele believed he had prepared a *compound* (dephlogisticated marine acid air) and the misconception was compounded by C.-L. Berthollet who showed in 1785 that the action of chlorine on water releases oxygen: [Cl$_2$(g) + H$_2$O $\longrightarrow$ 2HCl(soln) + $\frac{1}{2}$O$_2$(g)]; he concluded that chlorine was a loose compound of HCl and oxygen and called it oxymuriatic acid.[†]

[†] *Muriatic* acid and *marine* acid were synonymous terms for what is now called hydrochloric acid, thus signifying its relation to the sodium chloride contained in brine (Latin *muria*) or sea water (Latin *mare*). Both names were strongly criticized by H. Davy in a scathing paper entitled "Some reflections on the nomenclature of oxymuriatic compounds" in *Phil. Trans. R. Soc.* for 1811: "To call a body which is not known to contain oxygen, and which cannot contain muriatic acid, oxymuriatic acid, is contrary to the principles of that nomenclature in which it is adopted; and an alteration of it seems necessary to assist the progress of the discussion, and to diffuse just ideas on the subject. If the great discoverer of this substance (i.e. Scheele) had signified it by any simple name it would have been proper to have referred to it; but

The two decades from 1790 to 1810 were characterized by two major advances in chemical theory: Lavoisier's demolition of the phlogiston theory of combustion, and Davy's refutation of Lavoisier's contention that oxygen is a necessary constituent of all acids. Only when both these transformations had been achieved could the elementary nature of chlorine and the true composition of hydrochloric acid be appreciated, though some further time was to elapse (Dalton, Avogadro, Cannizaro) before gaseous chlorine was universally recognized to consist of diatomic molecules, Cl_2, rather than single atoms, Cl. The name, proposed by Davy in 1811, refers to the colour of the gas (Greek χλωρός, *chloros*, yellowish or light green — cf. chlorophyl).

The bleaching power of Cl_2 was discovered by Scheele in his early work (1774) and was put to technical use by Berthollet in 1785. This was a major advance on the previous time-consuming, labour-intensive, weather-dependent method of solar bleaching, and numerous patents followed (see Table 17.1). Indeed, the use of chlorine as a bleach remains one of its principal industrial applications (bleaching powder, elemental chlorine, hypochlorite solutions, chlorine dioxide, chloramines, etc.).[8] Another all-pervading use of chlorine, as a disinfectant and germicide, also dates from this period (1801), and the chlorination of domestic water supplies is now almost universal in developed countries. Again, as with fluoride, higher concentrations are toxic to humans: the gas is detectable by smell at 3 ppm, causes throat irritation at 15 ppm, coughing at 30 ppm, and rapid death at 1000 ppm. Prolonged exposure to concentrations above 1 ppm should be avoided.

Sodium chloride, by far the most abundant compound of chlorine, occurs in extensive evaporite deposits, saline lakes and brines, and in the ocean (p. 795). It has played a dominant role in the chemical industry since its inception in the late eighteenth century (p. 71). The now defunct Leblanc process for obtaining NaOH from NaCl signalled the beginnings of large-scale chemical manufacture, and NaCl remains virtually the sole source of chlorine and hydrochloric acid for the vast present-day chlorine-chemicals industry.[8] This embraces not only the large-scale production and distribution of Cl_2 and HCl, but also the manufacture of chlorinated methanes and ethanes, vinyl chloride, aluminium trichloride catalysts and the chlorides of Mg, Ti, Zr, Hf, etc., for production of the metals. Details of many of these processes are to be found either in other chapters or in later sections of the present chapter. About 15 000 chlorinated compounds are currently used to varying degrees in commerce. Of these, the environmental and health hazards posed by certain polychlorinated hydrocarbons is now well established, though not all such compounds are dangerous: focused selective restrictions rather than a blanket banning of all organochlorine compounds is advocated.[9] The rôle of chlorofluorocarbons in the depletion of stratospheric ozone above the polar regions has already been mentioned (p. 608).

Bromine

The magnificent purple pigment referred to in the Bible[10] and known to the Romans as Tyrian purple after the Phoenician port of Tyre (Lebanon), was shown by P. Friedländer in 1909 to be 6,6'-dibromoindigo. This precious dye was extracted in the early days from the small purple snail *Murex brandaris*, as many as 12000 snails being required to prepare 1.5 g of dye. The element itself was isolated by A.-J. Balard in 1826 from the mother liquors remaining after the crystallization of sodium chloride and sulfate from the waters of the Montpellier salt marshes;

'dephlogisticated marine acid' is a term which can hardly be adopted in the present advanced area of the science. After consulting some of the most eminent chemical philosophers in the country, it has been judged most proper to suggest a name founded upon one of its most obvious and characteristic properties — its colour, and to call it *Chlorine*."

[8] J. S. SCONCE, *Chlorine: Its Manufacture, Properties and Uses*, Reinhold, New York, 1962, 901 pp.

[9] B. HILEMAN, *C & E News*, April 19, 11–20 (1993). See also B. HILEMAN, J. R. LONG and E. M. KIRSCHNER, *C & E News*, November 21, 12–26 (1994).

[10] Holy Bible, Ezekiel **27**:7, 16.

the liquor is rich in $MgBr_2$, and the young Balard, then 23 y of age, noticed the deep yellow coloration that developed on addition of chlorine water. Extraction with ether and KOH, followed by treatment of the resulting KBr with H_2SO_4/MnO_2, yielded the element as a red liquid. Astonishingly rapid progress was possible in establishing the chemistry of bromine and in recognizing its elemental nature because of its similarity to chlorine and iodine (which had been isolated 15 y earlier). Indeed, J. von Liebig had missed discovering the element several years previously by misidentifying a sample of it as iodine monochloride.[1] Balard had proposed the name *muride*, but this was not accepted by the French Academy, and the element was named bromine (Greek βρῶμος, stink) because of its unpleasant, penetrating odour. It is perhaps ironic that the name fluorine had already been pre-empted for the element in CaF_2 and HF (p. 789) since bromine, as the only non-metallic element that is liquid at room temperature, would pre-eminently have deserved the name.

The first mineral found to contain bromine (bromyrite, AgBr) was discovered in Mexico in 1841, and industrial production of bromides followed the discovery of the giant Stassfurt potash deposits in 1858. The major use at that time was in photography and medicine: AgBr had been introduced as the light-sensitive agent in photography about 1840, and the use of KBr as a sedative and anti-convulsant in the treatment of epilepsy was begun in 1857. Other major uses of bromine-containing compounds include their application as flame retardants and as phase-transfer catalysts. The scale of the present-day production of bromine and bromine chemicals will become clear in later sections of this chapter.[11]

Iodine

The lustrous, purple-black metallic sheen of resublimed crystalline iodine was first observed by the industrial chemist B. Courtois in 1811, and the name, proposed by J. L. Gay Lussac in 1813, reflects this most characteristic property (Greek ἰωδης, violet-coloured). Courtois obtained the element by treating the ash of seaweed (which had been calcined to extract saltpetre and potash) with concentrated sulfuric acid. Extracts of the brown kelps and seaweeds *Fucus* and *Laminaria* had long been known to be effective for the treatment of goitre and it was not long before J. F. Coindet and others introduced pure KI as a remedy in 1819.[12] It is now known that the thyroid gland produces the growth-regulating hormone thyroxine, an iodinated aminoacid: p-(HO)-$C_6H_2(I)_2$-O-$C_6H_2(I)_2$-$CH_2CH(NH_2)CO_2H$.

If the necessary iodine input is insufficient the thyroid gland enlarges in an attempt to garner more iodine: addition of 0.01% NaI to table salt (iodized salt) prevents this condition. Tincture of iodine is a useful antiseptic.

The first iodine-containing mineral (AgI) was discovered in Mexico in 1825 but the discovery of iodate as an impurity in Chilean saltpetre in 1840 proved to be more significant industrially. The Chilean nitrate deposits provided the largest proportion of the world's iodine until overtaken in the late 1960s by Japanese production from natural brines (pp. 796, 799).

In addition to its uses in photography and medicine, iodine and its compounds have been much exploited in volumetric analysis (iodometry and iodimetry, p. 864). Organoiodine compounds have also played a notable part in the development of synthetic organic chemistry, being the first compounds used in A. W. von Hofmann's alkylation of amines (1850), A. W. Williamson's synthesis of ethers (1851), A. Wurtz's coupling reactions (1855) and V. Grignard's reagents (1900).

Astatine

From its position in the periodic table, all isotopes of element 85 would be expected to

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[11] D. PRICE, B. IDDON and B. J. WAKEFIELD, *Bromine Compounds: Chemistry and Applications*, Elsevier, Amsterdam 1988, 422 pp.

[12] E. BOOTH, *Chem. Ind. (Lond.)* 31 and 52–5 (1979).

be radioactive. Those isotopes that occur in the natural radioactive series all have half-lives of less than 1 min and thus occur in negligible amounts in nature (p. 796). Astatine (Greek $\overset{\prime}{\alpha}\sigma\tau\alpha\tau$-$o\varsigma$, unstable) was first made and characterized by D. R. Corson, K. R. Mackenzie and E. Segré in 1940: they synthesized the isotope ^{211}At ($t_{\frac{1}{2}}$ 7.21 h) by bombarding ^{209}Bi with α-particles in a large cyclotron:

$$^{209}_{83}\text{Bi} + {}^{4}_{2}\text{He} \longrightarrow {}^{211}_{85}\text{At} + 2{}^{1}_{0}n$$
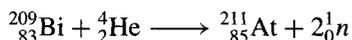
In all, some 27 isotopes from ^{194}At to ^{220}At have now been prepared by various routes but all are short-lived. The only ones besides ^{211}At having half-lives longer than 1 h are ^{207}At (1.80 h), ^{208}At (1.63 h), ^{209}At (5.41 h), and ^{210}At (8.1 h): this means that weighable amounts of astatine or its compounds cannot be isolated, and nothing is known of the bulk physical properties of the element. For example, the least-unstable isotope (^{210}At) has a specific activity corresponding to 2 curies per μg, i.e. 7×10^{10} disintegrations per second per μg. The largest preparations of astatine to date have involved about 0.05 μg and our knowledge of the chemistry of this element comes from extremely elegant tracer experiments, typically in the concentration range 10^{-11}–10^{-15} M. The most concentrated aqueous solutions of the element or its compounds ever investigated were only $\sim 10^{-8}$ M.

17.1.2 Abundance and distribution

Because of their reactivity, the halogens do not occur in the free elemental state but they are both widespread and abundant in the form of their ions, X$^-$. Iodine also occurs as iodate (see below). In addition to large halide mineral deposits, particularly of NaCl and KCl, there are vast quantities of chloride and bromide in ocean waters and brines.

Fluorine is the thirteenth element in order of abundance in crustal rocks of the earth, occurring to the extent of 544 ppm (cf. twelfth Mn, 1060 ppm; fourteenth Ba, 390 ppm; fifteenth Sr, 384 ppm). The three most important minerals are

fluorite CaF_2, cryolite Na_3AlF_6 and fluorapatite $Ca_5(PO_4)_3F$. Of these, however, only fluorite is extensively processed for recovery of fluorine and its compounds (p. 809). Cryolite is a rare mineral, the only commercial deposit being in Greenland, and most of the Na_3AlF_6 needed for the huge aluminium industry (p. 219) is now synthetic. By far the largest amount of fluorine in the earth's crust is in the form of fluorapatite, but this contains only about 3.5% by weight of fluorine and the mineral is processed almost exclusively for its phosphate content. Despite this, about 7% of the domestic requirement for fluorine compounds in the USA was obtained from fluorosilicic acid recovered as a by-product of the huge phosphate industry (pp. 476, 520). Minor occurrences of fluorine are in the rare minerals topaz $Al_2SiO_4(OH,F)_2$, sellaite MgF_2, villiaumite NaF and bastnaesite $(Ce,La)(CO_3)F$ (but see p. 1229). The insolubility of alkaline-earth and other fluorides precludes their occurrence at commercially useful concentrations in ocean water (1.2 ppm) and brines.

Chlorine is the twentieth most abundant element in crustal rocks where it occurs to the extent of 126 ppm (cf. nineteenth V, 136 ppm, and twenty-first Cr, 122 ppm). The vast evaporite deposits of NaCl and other chloride minerals have already been described (pp. 69, 73). Dwarfing these, however, are the inconceivably vast reserves in ocean waters (p. 69) where more than half the total average salinity of 3.4 wt% is due to chloride ions (1.9 wt%). Smaller quantities, though at higher concentrations, occur in certain inland seas and in subterranean brine wells, e.g. the Great Salt Lake, Utah (23% NaCl) and the Dead Sea, Israel (8.0% NaCl, 13.0% $MgCl_2$, 3.5% $CaCl_2$).

Bromine is substantially less abundant in crustal rocks than either fluorine or chlorine; at 2.5 ppm it is forty-sixth in order of abundance being similar to Hf 2.8, Cs 2.6, U 2.3, Eu 2.1 and Sn 2.1 ppm. Like chlorine, the largest natural source of bromine is the oceans, which contain $\sim 6.5 \times 10^{-3}$%, i.e. 65 ppm or 65 mg/l. The mass ratio Cl:Br is $\sim$300:1 in the oceans, corresponding to an atomic ratio

of ~660:1. Salt lakes and brine wells are also rich sources of bromine, and these are usually proportionately richer in bromine than are the oceans: the atom ratio Cl:Br spans the range ~200–700. Typical bromide-ion concentrations in such waters are: Dead Sea 0.4% (4 g/l), Sakskoe Ozoro (Crimea) 0.28% and Searle's Lake (California) 0.085%.

Iodine is considerably less abundant than the lighter halogens both in the earth's crust and in the hydrosphere. It comprises 0.46 ppm of the crustal rocks and is sixtieth in order of abundance (cf. Tl 0.7, Tm 0.5, In 0.24, Sb 0.2). It occurs but rarely as iodide minerals, and commercial deposits are usually as iodates, e.g. lautarite, $Ca(IO_3)_2$ and dietzeite, $7Ca(IO_3)_2.8CaCrO_4$. Thus the caliche nitrate beds of Chile contain iodine in this form (~0.02–1 wt% I). These mine workings soon replaced calcined seaweeds as the main source of iodine during the last century, but have recently been themselves overtaken by iodine recovered from brines. Brines associated with oil-well drillings in Louisiana and California were found to contain 30–40 ppm iodine in the 1920s, and independent subterranean brines were located at Midland, Michigan, in the 1960s, and in Oklahoma (1977), which is now the main US source. Natural brine wells in Japan (up to 100 ppm I) were discovered after the Second World War, and exploitation of these now ensures Japan first place among the world's iodine producers. The concentration of iodine in ocean waters is only 0.05 ppm, too low for commercial recovery, though brown seaweeds of the *Laminaria* family (and to a lesser extent *Fucus*) can concentrate this up to 0.45% of their dry weight (see above).

The fugitive radioactive element astatine can hardly be said to exist in nature though the punctillious would rightly point to its temporary participation in the natural radioactive series. Thus ^{219}At ($t_{\frac{1}{2}}$ 54 s) occurs as a rare and inconspicuous branch (4×10^{-3}%) of another minor branch (1.2%) of the ^{235}U ($4n + 3$) series (see scheme). Another branch (5×10^{-4}%) at ^{215}Po yields ^{215}At by β emission before itself decaying by α emission ($t_{\frac{1}{2}}$ 1.0×10^{-4} s); likewise ^{218}At ($t_{\frac{1}{2}}$ ~ 72 s) is a descendant of the ^{238}U ($4n + 2$) series, and traces have been detected of ^{217}At ($t_{\frac{1}{2}}$ 0.0323 s) and ^{216}At ($t_{\frac{1}{2}}$ 3.0×10^{-4} s). Estimates suggest that the outermost kilometre of the earth's crust contains no more than 44 mg of astatine compared with 15 g of francium (p. 69) or the relatively abundant polonium (2500 tonnes) and actinium (7000 tonnes). Astatine can therefore be regarded as the rarest naturally occurring terrestrial element.

17.1.3 Production and uses of the elements

The only practicable large-scale method of preparing F_2 gas is Moissan's original procedure based on the electrolysis of KF dissolved in anhydrous HF; (see however p. 821). Moissan used a mole ratio KF:HF of about 1:13, but this has a high vapour pressure of HF and had to be operated at $-24°$. Electrolyte systems having mole ratios of 1:2 and 1:1 melt at ~72° and ~240°C respectively and have much lower vapour pressures of HF; accordingly
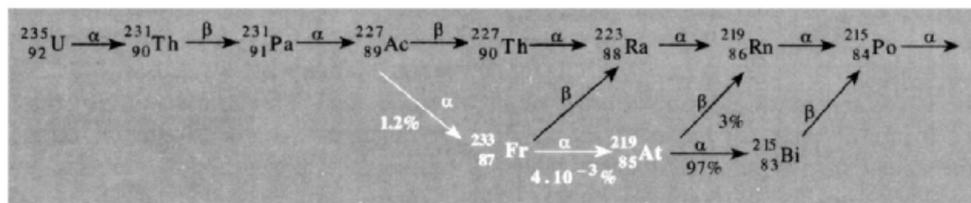
these compositions were subsequently favoured. Nowadays, medium-temperature cells (80–100°) are universally employed, being preferred over the high-temperature cells because (a) they have a lower pressure of HF gas above the cell, (b) there are fewer corrosion problems, (c) the anode has a longer life and (d) the composition of the electrolyte can vary within fairly wide limits without impairing the operating conditions or efficiency. The highly corrosive nature of the electrolyte, coupled with the aggressive oxidizing power of F_2, pose considerable problems of handling, and these are exacerbated by the explosive reaction of F_2 with its co-product H_2, so that accidental mixing of the gases must be prevented at all costs. Scrupulous absence of grease and other flamable contaminants must also be ensured since they can lead to spectacular fires which puncture the protective fluoride coating of the metal containers and cause the whole system to enflame. Another hazard in early generators was the formation of explosive graphite-fluorine compounds at the anode (p. 289). All these problems have now been overcome and F_2 can be routinely generated with safety both in the laboratory and on a large industrial scale.[2,13] A typical generator (Fig. 17.1) consists of a mild-steel pot (cathode) containing the electrolyte KF.2HF which is kept at 80–100°C either by a heating jacket when the cell is quiescent or by a cooling system when the cell is working. The anode consists of a central rod of compacted, ungraphitized carbon, and the product gases are kept separate by a skirt or diaphragm dipping below the electrolyte surface. The temperature is automatically controlled, as is the level of the electrolyte by controlled addition of make-up anhydrous HF. Laboratory generators usually operate at about 10–50 A whereas industrial production, employing banks of cells, may operate at 4000–6000 A and 8–12 V. An individual cell in such a bank might typically be $3.0 \times 0.8 \times 0.6$ m and hold 1 tonne of electrolyte; it might have 12 anode
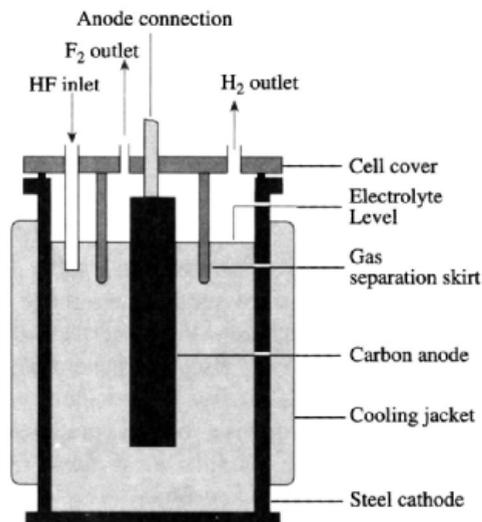

Figure 17.1   Schematic diagram of an electrolytic fluorine-generating cell.

assemblies each holding two anode blocks and produce 3–4 kg F_2 per hour. A large-scale plant can produce *ca.* 9 tonnes of liquefied F_2 per day. The total annual production in the USA and Canada exceeds 5000 tonnes, and similar though somewhat smaller amounts are produced in several European countries (UK, France, Germany, Italy, Russia). Production in Japan approaches 1000 tpa.

Cylinders of F_2 are now commercially available in various sizes from 230-g to 2.7-kg capacity; 1993 price ~$110–260 per kg depending on cylinder size. The gas pressure is 2.86 MPa (~28 atm.) at 21°C. Liquid F_2 is shipped in tank trucks of 2.27 tonnes capacity, the container being itself cooled by a jacket of liquid N_2 which boils 8° below F_2. Alternatively, it can be converted to ClF_3, bp 11.7°C (p. 828), which is easier to handle and transport than F_2. In fact, about 70–80% of the elemental F_2 produced is used captively for the manufacture of UF_6 for nuclear power generation (p. 1259). Another important use is in the production of SF_6 for dielectrics (p. 687). The captive use to manufacture the versatile fluorinating agents ClF_3, BrF_3 and IF_5 is a third important outlet. Fluorination of W and Re to

[13] H. C. FIELDING and B. E. LEE, in R. THOMPSON (ed.), *The Modern Inorganic Chemicals Industry*, pp. 149–67, Chemical Society Special Publication No. 31, 1977.

their hexafluorides is also industrially important since these volatile compounds are used in chemical vapour deposition of W and Re films on intricately shaped components. Most other fluorinations of inorganic and organic compounds avoid the direct use of F_2. The former demand for liquid F_2 as a rocket-fuel oxidizer has now ceased.

Chlorine is rarely generated on a laboratory scale since it is so readily available in cylinders of all sizes from 450 g (net) to 70 kg. When required it can also be generated by adding concentrated, air-free hydrochloric acid (d 1.16 g cm^{-3}) dropwise on to precipitated hydrated manganese dioxide in a flask fitted with a dropping funnel and outlet tube: the gas formation can be regulated by moderate heating and the Cl_2 thus formed can be purified by passage through water (to remove HCl) and H_2SO_4 (to remove H_2O). The gas, whether generated in this way or obtained from a cylinder, can be further purified if necessary by passage through successive tubes containing CaO and P_2O_5, followed by condensation in a bath cooled by solid CO_2 and fractionation in a vacuum line.

Industrial production of Cl_2 and chlorine chemicals is on a vast scale and comprises a major section of the heavy chemical industry.[8,9,14,15] Some aspects have already been discussed on p. 793, and further details are in the Panel.

Bromine is invariably made on an industrial scale by oxidation of bromide ion with Cl_2. The main sources of Br$^-$ are Arkansas brines (4000–5000 ppm) which account for most of US production, various brines and bitterns in Europe, the Dead Sea (4000–6000 ppm), and ocean waters (65 ppm). Following the oxidation of Br$^-$ the Br_2 is removed from the solution either by passage of steam ("steaming out") or air ("blowing out"), and then condensed and purified. Although apparently simple, these unit operations must deal with highly reactive and corrosive materials, and the industrial processes have been ingeniously developed and refined

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[14] R. W. PURCELL, The chor-alkali industry, in ref. 13, pp. 106–33. A. CAMPBELL, Chlorine and chlorination, *ibid.*, pp. 134–48.
[15] *Kirk–Othmer Encyclopedia of Chemical Technology*, 4th edn., **1**, 938–1025 (1991).

Industrial Production and Uses of Chlorine

The large-scale production of Cl_2 is invariably achieved by the electrolytic oxidation of the chloride ion. Natural brines or aqueous solutions of NaCl can be electrolysed in an asbestos diaphragm cell or a mercury cathode cell, though these latter are being phased out for environmental and other reasons (p. 1225). Electrolysis of molten NaCl is also carried out on a large scale: in this case the co-product is Na rather than NaOH. Electrolysis of by-product HCl is also used where this is cheaply available. World consumption of Cl_2 in 1987 exceeded 35 million tonnes. Production is dominated by the USA, but large tonnages are produced in all industrial countries: USA 30%, Western Europe 29%, Eastern Europe 15%, Japan 8.5%, Asia/Pacific 6.8%. Cl_2 was ranked eighth among the large-volume chemicals manufactured in the USA during 1996. Diaphragm cells predominated though there is a growing interest in membrane cells in which the anolyte and catholyte are separated by a porous Nafion membrane (Nafion is a copolymer of tetrafluoroethylene and a perfluorosulfonylethoxy ether and the membrane is reinforced with a Teflon mesh).[15] In addition to cylinders of varying capacity up to 70 kg, chlorine can be transported in drums (865 kg), tank wagons (road: 15 tonnes; rail 27–90 tonnes), or barges (600–1200 tonnes).

The three main categories of use for Cl_2 are:

(a) Production of organic compounds by chlorination and/or oxychlorination using a fluidized bed of copper chloride catalyst (pre-eminent amongst these are vinyl chloride monomer and propylene oxide which in the USA alone are produced on a scale of 9.0 and 2.0 million tonnes respectively). Production of chlorinated organic compounds accounts for about 63% of the Cl_2 produced.

(b) Bleaches (for paper, pulp and textiles) sanitation and disinfection of municipal water supplies and swimming pools, sewage treatment and control. These uses account for about 19% of the Cl_2 produced.

(c) Production of inorganic compounds, notably HCl, Cl_2O, HOCl, $NaClO_3$, chlorinated isocyanurates, $AlCl_3$, $SiCl_4$, $SnCl_4$, PCl_3, PCl_5, $POCl_3$, $AsCl_3$, $SbCl_3$, $SbCl_5$, $BiCl_3$, S_2Cl_2, SCl_2, $SOCl_2$, ClF_3, ICl, ICl_3, $TiCl_3$, $TiCl_4$, $MoCl_5$, $FeCl_3$, $ZnCl_2$, Hg_2Cl_2, $HgCl_2$, etc. (see index for page references to production and uses). About 18% of Cl_2 production is used to manufacture inorganic chemicals.

to give optimum yields at the lowest possible operating costs.[16,17]

World production of Br_2 in 1990 was about 438 000 tonnes pa, i.e. about one-hundredth of the scale of the chlorine industry. The main producing countries are (tonnes): USA 177 000, Israel 135 000, Russia 60 000, UK 28 000, France 18 000 and Japan 15 000. The production capacity of Israel has recently increased almost threefold because of expanded facilities on the Dead Sea. Historically, bromine was shipped in individual 3-kg (net) bottles to minimize damage due to breakage, but during the 1960s bulk transport in monel metal drums (100-kg capacity) or lead-lined tanks (24 or 48 tonnes) was developed and these are now used for transport by road, rail and ship. The price of Br_2 in tank-car lots was $975/kg in 1990.

The industrial usage of bromine has been dominated by the single compound ethylene dibromide which has been (with ethylene dichloride) a valuable gasoline (petrol) additive where it acts as a scavenger for lead from the anti-knock additive $PbEt_4$. Environmental legislation has dramatically reduced the amount of leaded petrol produced and, accordingly, ethylene dibromide, which accounted for 90% of US bromine production in 1955, declined to 75% a decade later and now represents a mere 16% of the total bromine consumption in the USA (1990). Fortunately this decline has been matched by a steady increase in other applications and the industry worldwide has shown a modest growth. Most of these large-volume applications involve organic compounds, notably MeBr, which is one of the most effective nematocides known (i.e. kills worms) and is also used as a general pesticide (herbicide, fungicide and insecticide). Ethylene dibromide and dibromochloropropane are also used as pesticides. Bromine compounds are extensively used as fire retardants, especially for fibres, carpets, rugs and plastics; they are about 3–4 times as effective (weight for

weight) as chlorocompounds which gives them a substantial cost advantage.

Other uses of bromo-organics include high-density drilling fluids, dyestuffs and pharmaceuticals. Bromine is also used in water sanitation and to synthesize a wide range of inorganic compounds, e.g. AgBr for photography, HBr, alkali metal bromides, bromates, etc. (see later sections). An indication of the overall pattern of use (USA, 1990) is as follows: flame retardants 29%, ethylene dibromide 16%, agrochemicals 16% drilling fluids 11% inorganic bromides 5.5%, water treatment chemicals 5.5%, other 17%.

The commercial recovery of iodine on an industrial scale depends on the particular source of the element.[18] From natural brines, such as those at Midland (Michigan) or in Russia or Japan, chlorine oxidation followed by air blow-out as for bromine (above) is much used, the final purification being by resublimation. Alternatively the brine, after clarification, can be treated with just sufficient $AgNO_3$ to precipitate the AgI which is then treated with clean scrap iron or steel to form metallic Ag and a solution of FeI_2; the Ag is redissolved in HNO_3 for recycling and the solution is treated with Cl_2 to liberate the I_2:

The newest process to be developed oxidizes the brine with Cl_2 and then treats the solution with an ion-exchange resin: the iodine is adsorbed in the form of polyiodide which can be eluted with alkali followed by NaCl to regenerate the column. About 65% of the iodine consumed in the world comes from brines.

Recovery of iodine from Chilean saltpetre differs entirely from its recovery from brine since it is present as iodate. $NaIO_3$ is extracted from the caliche and is allowed to accumulate in the mother liquors from the crystallization of $NaNO_3$

[16] R. B. McDONALD and W. R. MERRIMAN, pp. 168–82 of ref. 13.
[17] Ref. 2, Vol. 4 (1992), Bromine, pp. 536–60; Bromine compounds, pp. 560–89.

[18] Ref. 2, Vol. 14 (1995), Iodine and Iodine compounds, pp. 709–37.

until its concentration is about 6 g/l. Part is then drawn off and treated with the stoichiometric amount of sodium hydrogen sulfite required to reduce it to iodide:

$$IO_3^- + 3HSO_3^- \longrightarrow I^- + 3SO_4^{2-} + 3H^+$$

The resulting acidic mixture is treated with just sufficient fresh mother liquor to liberate all the contained iodine:

$$5I^- + IO_3^- + 6H^+ \longrightarrow 3I_2\downarrow + 3H_2O$$

The precipitated I_2 is filtered off and the iodine-free filtrate returned to the nitrate-leaching cycle after neutralization of any excess acid with Na_2CO_3.

World production of I_2 in 1992 approached 15 000 tonnes, the dominant producers being Japan 41%, Chile 40%, USA 10% and the former Soviet Union 9%. Crude iodine is packed in double polythene-lined fibre drums of 10–50-kg capacity. Resublimed iodine is transported in lined fibre drums (11.3 kg) or in bottles containing 0.11, 0.45 or 2.26 kg. The price of I_2 has traditionally fluctuated wildly. Thus, because of acute over-supply in 1990 the price for I_2 peaked at \$22/kg in 1988, falling to \$12/kg in 1990 and \$9.50/kg in 1992. Unlike Cl_2 and Br_2, iodine has no predominant commercial outlet. About 50% is incorporated into a wide variety of organic compounds and about 15% each is accounted for as resublimed iodine, KI, and other inorganics. The end uses include catalysts for synthetic rubber manufacture, animal- and fowl-feed supplements,

stabilizers, dyestuffs, colourants and pigments for inks, pharmaceuticals, sanitary uses (tincture of iodine, etc.) and photographic chemicals for high-speed negatives. Uses of iodine compounds as smog inhibitors and cloud-seeding agents are small. In analytical chemistry $KHgI_3$ forms the basis for Nessler's reagent for the detection of NH_3, and Cu_2HgI_4 was used in Mayer's reagent for alkaloids. Iodides and iodates are standard reagents in quantitative volumetric analysis (p. 864). Ag_2HgI_4 has the highest ionic electrical conductivity of any known solid at room temperature but this has not yet been exploited on a large scale in any solid-state device.

17.1.4 Atomic and physical properties

The halogens are volatile, diatomic elements whose colour increases steadily with increase in atomic number. Fluorine is a pale yellow gas which condenses to a canary yellow liquid, bp $-188.1°C$ (intermediate between N_2, bp $-195.8°$, and O_2, bp $-183.0°C$). Chlorine is a greenish-yellow gas, bp $-34.0°$, and bromine a dark-red mobile liquid, bp $59.5°$: interestingly the colour of both elements diminishes with decrease in temperature and at $-195°$ Cl_2 is almost colourless and Br_2 pale yellow. Iodine is a lustrous, black, crystalline solid, mp $113.6°$, which sublimes readily and boils at $185.2°C$.

Atomic properties are summarized in Table 17.3 and some physical properties are in Table 17.4.

Table 17.3 Atomic properties of the halogens

Property	F	Cl	Br	I	At
Atomic number	9	17	35	53	85
Number of stable isotopes	1	2	2	1	0
Atomic weight	18.998 4032(9)	35.4527(9)	79.904(1)	126.90447(3)	(210)
Electronic configuration	$[He]2s^22p^5$	$[Ne]3s^23p^5$	$[Ar]3d^{10}4s^24p^5$	$[Kr]4d^{10}5s^25p^5$	$[Xe]4f^{14}5d^{10}6s^26p^5$
Ionization energy/kJ mol^{-1}	1680.6	1255.7	1142.7	1008.7	[926]
Electron affinity/kJ mol^{-1}	332.6	348.7	324.5	295.3	[270]
ΔH_{dissoc}/kJ mol$(X_2)^{-1}$	158.8	242.58	192.77	151.10	—
Ionic radius, X$^-$/pm	133	184	196	220	—
van der Waals radius/pm	135	180	195	215	—
Distance X–X in X_2/pm	143	199	228	266	—

Table 17.4 Physical properties of the halogens

Property	F_2	Cl_2	Br_2	I_2
MP/°C	−219.6	−101.0	−7.25	113.6[a]
BP/°C	−188.1	−34.0	59.5	185.2[a]
d (liquid, T°C)/g cm^{-3}	1.516(−188°)	1.655(−70°)	3.187 (0°)	3.960[b] (120°)
ΔH_{fusion}/kJ mol$(X_2)^{-1}$	0.51	6.41	10.57	15.52
ΔH_{vap}/kJ mol$(X_2)^{-1}$	6.54	20.41	29.56	41.95
Temperature (°C) for 1% dissoc at 1 atm	765	975	775	575

[a] Solid iodine has a vapour pressure of 0.31 mmHg (41 Pa) at 25°C and 90.5 mmHg (12.07 kPa) at the mp (113.6°).

[b] Solid iodine has a density of 4.940 g cm^{-3} at 20°C.

As befits their odd atomic numbers, the halogens have few naturally occurring isotopes (p. 3). Only one isotope each of F and I occurs in nature and the atomic weights of these elements are therefore known very accurately indeed (p. 17). Chlorine has two naturally occurring isotopes (^{35}Cl 75.77%, ^{37}Cl 24.23%) as also does bromine (^{79}Br 50.69%, ^{81}Br 49.31%). All isotopes of At are radioactive (p. 795). The ionization energies of the halogen atoms show the expected trend to lower values with increase in atomic number. The electronic configuration of each atom (ns^2np^5) is one p electron less than that of the next succeeding noble gas, and energy is evolved in the reaction X(g) + e$^-$ $\longrightarrow$ X$^-$(g). The electron affinity, which traditionally (though misleadingly) is given a positive sign despite the negative enthalpy change in the above reaction, is maximum for Cl, the value for F being intermediate between those for Cl and Br. Even more noticeable is the small enthalpy of dissociation for F_2 which is similar to that of I_2 and less than two-thirds of the value for Cl_2.[19] In this connection it can be noted that N–N single bonds in hydrazines are weaker than the corresponding P–P bonds and that O–O single bonds in peroxides are weaker than the corresponding S–S bonds. This was explained (R. S. Mulliken and others, 1955) by postulating that partial pd hybridization imparts some double-bond character

to the formal P–P, S–S and Cl–Cl single bonds thereby making them stronger than their first-row counterparts. However, following C. A. Coulson and others (1962), it seems unnecessary to invoke substantial d-orbital participation and the weakness of the F–F single bond is then ascribed to decreased overlap of bonding orbitals, appreciable internuclear repulsion and the relatively large electron–electron repulsions of the lone-pairs which are much closer together in F_2 than in Cl_2.[20] The rapid diminution of bond-dissociation energies in the sequence $N_2 \gg O_2 \gg F_2$ is, of course, due to successive filling of the antibonding orbitals (p. 606), thus reducing the formal bond order from triple in N≡N to double and single in O=O and F–F respectively.

Radioactive isotopes of the halogens have found use in the study of isotope-exchange reactions and the mechanisms of various other reactions.[21,22] The properties of some of the most used isotopes are in Table 17.5. Many of these isotopes are available commercially. A fuller treatment with detailed references

[19] J. BERKOWITZ and A. C. WAHL, *Adv. Fluorine Chem.* **7**, 147–74 (1973). A. A. WOOLF, *Adv. Inorg. Chem. Radiochem.* **24**, 1–55 (1981). J. J. TURNER, *MTP International Review of Science: Inorganic Chemistry Series* 1, Vol. 3, pp. 253–91, Butterworths, London. 1972.

[20] P. POLITZER, Anomalous properties of fluorine, *J. Am. Chem. Soc.* **91**, 6235–7 (1969); Some anomalous properties of oxygen and nitrogen, *Inorg. Chem.* **16**, 3350–1 (1977).

[21] M. F. A. DOVE and D. B. SOWERBY, in V. GUTMANN (ed.), *Halogen Chemistry*, Vol. 1, pp. 41–132, Academic Press, London, 1967.

[22] R. H. HERBER (ed.), *Inorganic Isotopic Syntheses*, W. H. Benjamin, New York, 1962; Radio-chlorine (B. J. MASTERS), pp. 215–26; Iodine-131 (M. KAHN), pp. 227–42. See also G. ANGELINI, M. SEPERANZA, C.-Y. SHIUE and A. P. WOLF, *J. Chem. Soc., Chem. Commun.*, 924–5 (1986) for radio fluorine (^{18}F).

Table 17.5   Some radioactive isotopes of the halogens

Isotope	Nuclear spin and parity	Half-life	Principal mode of decay (E/MeV)	Principal source
^{18}F	1+	109.77 min	β^+ (0.649)	^{19}F(n,2n)
^{36}Cl	2+	3.01×10^5 y	β^- (0.714)	^{35}Cl(n,γ)
^{38}Cl	2−	37.24 min	β^- (4.81, 1.11, 2.77)	^{37}Cl(n,γ)
^{80m}Br	5−	4.42 h	γ (internal trans) (0.086)	^{79}Br(n,γ)
^{80}Br	1+	17.68 min	β^- (2.02, 1.35)	^{80m}Br (IT)
^{82}Br	5−	35.30 h	β^- (0.44)	^{81}Br (n,γ)
^{125}I	$\frac{5}{2}+$	60.2 d	Electron capture (0.035)	^{123}Sb(α,2n), ^{124}Te(d,n), or ^{125}Xe(β^-)
^{128}I	1+	24.99 min	β^- (2.12, 1.66)	^{127}I(n,γ)
^{129}I	$\frac{7}{2}+$	1.57×10^7 y	β^- (0.189)	U fission
^{131}I	$\frac{7}{2}+$	8.04 d	β^- (0.806)	^{130}Te(n,γ), U or Pu fission

of the use of radioactive isotopes of the halogens, including exchange reactions, tracer studies of other reactions, studies of diffusion phenomena, radiochemical methods of analysis, physiological and biochemical applications, and uses in technology and industry is available.[23] Excited states of ^{127}I and ^{129}I have also been used extensively in Mössbauer spectroscopy.[24]

The nuclear spin of the stable isotopes of the halogens has been exploited in nmr spectroscopy. The use of ^{19}F in particular, with its 100% abundance, convenient spin of $\frac{1}{2}$ and excellent sensitivity, has resulted in a vast and continually expanding literature since ^{19}F chemical shifts were first observed in 1950.[25] The resonances for ^{35}Cl and ^{37}Cl were also first observed in 1950.[26] Appropriate nuclear parameters are in Table 17.6. From this it is clear that the ^{19}F resonance can be observed with high receptivity

at a frequency fairly close to that for ^{1}H. Furthermore, since $I < 1$ there is no nuclear quadrupole moment and hence no quadrupolar broadening of the resonance. The observed range of ^{19}F chemical shifts is more than an order of magnitude greater than for ^{1}H and spans more than 800 ppm of the resonance frequency.[27,28] The signal moves to higher frequency with increasing electronegativity and oxidation state of the attached atom thus following the usual trends. Results are regularly reviewed.[29] For other halogens, as seen from Table 17.6, the nuclear spin I is greater than $\frac{1}{2}$ which means that the nuclear charge distribution is non-spherical; this results in a nuclear quadrupole moment, and resonance broadening due to quadrupolar relaxation severely restricts the use of the technique except for the halide ions X^- or for tetrahedral species such as ClO_4^- which have zero electric field gradient at the halogen nucleus. The receptivity is also much less

[23] A. J. DOWNS and C. J. ADAMS, in J. C. BAILAR, H. J. EMELÉUS, R. S. NYHOLM and A. F. TROTMAN-DICKENSON, *Comprehensive Inorganic Chemistry*, Vol. 2, pp. 1148–61 (Isotopes), Pergamon Press, Oxford, 1973.

[24] N. N. GREENWOOD and T. C. GIBB, *Mössbauer Spectroscopy*, pp. 462–82, Chapman & Hall, London, 1971. R. V. PARISH in G. J. LONG (ed.), *Mössbauer Spectroscopy Applied to Inorganic Chemistry*, Vol. 2, Chap. 9, 391–428 (1987). Plenum Press, New York.

[25] W. C. DICKENSON, *Phys. Rev.* **77**, 736–7 (1950). H. S. GUTOWSKY and C. J. HOFFMAN, *Phys. Rev.* **80**, 110–11 (1950).

[26] W. G. PROCTOR and F. C. YU, *Phys. Rev.* **77**, 716–7 (1950).

[27] J. W. EMSLEY, J. FEENEY and L. H. SUTCLIFFE, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Vols. 1 and 2, Pergamon Press, Oxford, 1966, Chap. 11, Fluorine-19, pp. 871–968.

[28] C. J. JAMESON in J. MASON (ed.) *Multinuclear NMR*, Plenum Press, New York, 1987. Fluorine, pp. 437–46. See also J. H. CLARK, E. M. GOODMAN, D. K. SMITH, S. J. BROWN and J. M. MILLER, *J. Chem. Soc., Chem. Commun.*, 657–8 (1986).

[29] *Annual Reports on NMR Spectroscopy*, Vol. 1 (1968)–Vol. 10b (1980) (Fluorine).

Table 17.6 Nuclear magnetic resonance parameters for the halogen isotopes

Isotope	Nuclear spin quantum no. I	NMR frequency rel to ^{1}H(SiMe$_4$) = 100.000	Relative receptivity $D_p^{(a)}$	Nuclear quadrupole moment Q/ (e 10^{-28} m^2)
^{1}H	1/2	100.000	1.000	0
^{19}F	1/2	94.094	0.8328	0
^{35}Cl	3/2	9.809	3.55×10^{-3}	-8.2×10^{-2}
^{37}Cl	3/2	8.165	6.44×10^{-4}	-6.5×10^{-2}
(^{79}Br)$^{(b)}$	3/2	25.140	3.97×10^{-2}	0.33
^{81}Br	3/2	27.100	4.87×10^{-2}	0.27
^{127}I	5/2	20.146	9.34×10^{-2}	-0.79

$^{(a)}$Receptivity D is proportional to $\gamma^3 NI(I+1)$ where γ is the magnetogyric ratio, N the natural abundance of the isotope, and I the nuclear spin quantum number; D_p is the receptivity relative to that of the proton taken as 1.000.
$^{(b)}$Less-favourable isotope.

Table 17.7 Interatomic distances in crystalline halogens (pm)

X	X–X	X···X Within layer	X···X Between layers	X···X Ratio ——— X–X
F	149	324	284	(1.91)
Cl	198	332, 382	374	1.68
Br	227	331, 379	399	1.46
I	272	350, 397	427	1.29

than for ^{1}H or ^{19}F which accordingly renders observation difficult. Despite these technical problems, much useful information has been obtained, especially in physicochemical and biological investigations.[30,31] The quadrupole moments of Cl, Br and I have also been exploited successfully in nuclear quadrupole resonance studies of halogen-containing compounds in the solid state.[32]

The molecular and bulk properties of the halogens, as distinct from their atomic and nuclear properties, were summarized in Table 17.4 and have to some extent already been briefly discussed. The high volatility and relatively low enthalpy of vaporization reflect the diatomic molecular structure of these elements. In the solid state the molecules align to give a layer lattice: F_2 has two modifications (a low-temperature, α-form and a higher-temperature, β-form) neither of which resembles the orthorhombic layer lattice of the isostructural Cl_2, Br_2 and I_2. The layer lattice is illustrated below for I_2 the I–I distance of 271.5 pm is appreciably longer than in gaseous I_2 (266.6 pm) and the closest interatomic approach between the molecules is 350 pm within the layer and 427 pm between layers (cf the van der Waals radius of 215 pm). These values are

[30] B. LINDMAN and S. FORSEN, Chap. 13 in R. K. HARRIS and B. E. MANN (eds.), *NMR and the Periodic Table*, pp. 421–38, Academic Press, London, 1978. B. LINDMAN and S. FORSEN, Physicochemical and biological applications, Vol. 12 of P. DIEHL, E. FLUCK and R. KOSFELD (eds.), *NMR Basic Principles and Progress*, Springer-Verlag, Berlin, 1976, 365 pp.
[31] J. W. AKITT, in ref. 28, The quadrupolar halides Cl, Br and I, pp. 447–61.
[32] T. P. DAS and E. L. HAHN, *Nuclear Quadrupole Resonance Spectroscopy*, Academic Press, New York, 1958, 223 pp; E. A. C. LUCKEN, *Nuclear Quadrupole Coupling Constants*, Academic Press, London, 1969, 360 pp.

compared with similar data for the other halogens in Table 17.7 from which two further features of interest emerge: (a) the intralayer intermolecular distances $Cl \cdots Cl$ and $Br \cdots Br$ are almost identical, and (b) the differences between intra- and inter-layer $X \cdots X$ distances decreases with increase in atomic number. (Fluorine is not directly comparable because of its differing structure.)

As expected from their structures, the elements are poor conductors of electricity: solid F_2 and Cl_2 have negligible conductivity and Br_2 has a value of $\sim 5 \times 10^{-13}$ ohm^{-1} cm^{-1} just below the mp. Iodine single crystals at room temperature have a conductivity of 5×10^{-12} ohm^{-1} cm^{-1} perpendicular to the *bc* layer plane but this increases to 1.7×10^{-8} ohm^{-1} cm^{-1} within this plane; indeed, the element is a two-dimensional semiconductor with a band gap $E_g \sim 1.3$ eV (125 kJ mol^{-1}). Even more remarkably, when crystals of iodine are compressed they become metallic, and at 350 kbar have a conductivity of $\sim 10^4$ ohm^{-1} cm^{-1}.[33] The metallic nature of the conductivity is confirmed by its negative temperature coefficient.

The ease of dissociation of the X_2 molecules follows closely the values of the enthalpy of dissociation since the entropy change for the reaction is almost independent of X. Thus F_2 at 1 atm pressure is 1% dissociated into atoms at 765°C but a temperature of 975°C is required to achieve the same degree of dissociation for Cl_2; thereafter, the required temperature drops to 775°C for Br_2 and 575°C for I_2 (see also next section for atomic halogens).

17.1.5 Chemical reactivity and trends

General reactivity and stereochemistry

Fluorine is the most reactive of all elements. It forms compounds, under appropriate conditions, with every other element in the periodic table except He, Ar and Ne, frequently combining

directly and with such vigour that the reaction becomes explosive. Some elements such as O_2 and N_2 react less readily with fluorine (pp. 639, 438) and some bulk metals (e.g. Al, Fe, Ni, Cu) acquire a protective fluoride coating, though all metals react exothermically when powdered and/or heated. For example, powdered Fe (0.84 mm size, 20 mesh) is not attacked by liquid F_2 whereas at 0.14 mm size (100 mesh) it ignites and burns violently. Perhaps the most striking example of the reactivity of F_2 is the ease with which it reacts directly with Xe under mild conditions to produce crystalline xenon fluorides (p. 894). This great reactivity of F_2 can be related to its small dissociation energy (p. 801) (which leads to low activation energies of reaction), and to the great strength of the bonds that fluorine forms with other elements. Both factors in turn can be related to the small size of the F atom and ensure that enthalpies of fluorination are much greater than those of other halogenations. Some typical average bond energies (kJ mol^{-1}) illustrating these points are:

X	XX	HX	BX$_3$	AlX$_3$	CX$_4$
F	159	574	645	582	456
Cl	243	428	444	427	327
Br	193	363	368	360	272
I	151	294	272	285	239

The tendency for F_2 to give F^- ions in solution is also much greater than for the other halogens as indicated by the steady decrease in oxidation potential ($E°$) for the reaction X_2(soln) $+ 2e^- \rightleftharpoons 2X^-$ (aq):

X_2	F_2	Cl_2	Br_2	I_2	At_2
$E°$/V	2.866	1.395	1.087	0.615	~ 0.3

The corresponding free energy changes can be calculated from the relation $\Delta G = -nE°F$ where $n = 2$ and $F = 96.485$ kJ mol^{-1}. Note that $E°$($F_2/2F^-$) is greater than the decomposition potential for water (p. 629). Note also the different sequence of values for $E°$($X_2/2X^-$) and for the electron affinities of X (g) (p. 800). A similar "anomaly" was observed (p. 75) for $E°$ (Li$^+$/Li) and the ionization energy of Li(g), and

[33] A. S. BALCHIN and H. G. DRICKAMER, *J. Chem. Phys.* **34**, 1948–9 (1961).

Chemical reactivity and trends

in both cases the reason is the same, namely the enhanced enthalpy of hydration of the smaller ions. Other redox properties of the halogens are compared on pp. 853–6.

It follows from the preceding paragraph that F_2 is an extremely strong oxidizing element that can engender unusually high oxidation states in the elements with which it reacts, e.g. IF_7, PtF_6, PuF_6, BiF_5, TbF_4, CmF_4, $KAg^{III}F_4$ and AgF_2. Indeed, fluorine (like the other first-row elements Li, Be, B, C, N and O) is atypical of the elements in its group and for the same reasons. For all 7 elements deviations from extrapolated trends can be explained in terms of three factors:

(1) their atoms are small;
(2) their electrons are tightly held and not so readily ionized or distorted (polarized) as in later members of the group;
(3) they have no low-lying d orbitals available for bonding.

Thus the ionization energy I_M is much greater for F than for the other halogens, thereby making formal positive oxidation states virtually impossible to attain. Accordingly, fluorine is exclusively univalent and its compounds are formed either by gain of 1 electron to give F^- $(2s^2 2p^6)$ or by sharing 1 electron in a covalent single bond. Note, however, that the presence of lone-pairs permits both the fluoride ion itself and also certain molecular fluorides to act as Lewis bases in which the coordination number of F is greater than 1, e.g. it is 2 for the bridging F atoms in $As_2F_{11}^-$, $Sb_3F_{16}^-$, Nb_4F_{20}, $(HF)_n$ and $(BeF_2)_\infty$. The coordination number of F^- can rise to 3 (planar) in compounds with the rutile structure (e.g. MgF_2, MnF_2, FeF_2, CoF_2, NiF_2, ZnF_2 and PdF_2). Likewise, fourfold coordination (tetrahedral) is found in the zinc-blende-type structure of CuF and in the fluorite structure of CaF_2, SrF_2, BaF_2, RaF_2, CdF_2, HgF_2 and PbF_2. A coordination number of 6 occurs in the alkali metal fluorides MF (NaCl type). In many of these compounds F^- resembles O^{2-} stereochemically rather than the other halides, and the radii of the 2 ions are very similar (F^- 133, O^{2-} 140 pm, cf. Cl^- 184, Br^- 196 pm).

The heavier halogens, though markedly less reactive than fluorine, are still amongst the most reactive of the elements. Their reactivity diminishes in the sequence $Cl_2 > Br_2 > I_2$. For example, Cl_2 reacts with CO, NO and SO_2 to give $COCl_2$, NOCl and SO_2Cl_2, whereas iodine does not react with these compounds. Again, in the direct halogenation of metals, Cl_2 and Br_2 sometimes produce a higher metal oxidation state than does I_2, e.g. Re yields $ReCl_6$, $ReBr_5$ and ReI_4 respectively. Conversely, the decreasing ionization energies and increasing ease of oxidation of the elements results in the readier formation of iodine cations (p. 842) and compounds in which iodine has a higher stable oxidation state than the other halogens (e.g. IF_7). The general reactivity of the individual halogens with other elements (both metals and non-metals) is treated under the particular element concerned. Reaction between the halogens themselves is discussed on p. 824. In general, reaction of X_2 with compounds containing M–M, M–H or M–C bonds results in the formation of M–X bonds (M = metal or non-metal). Reaction with metal oxides sometimes requires the presence of C and the use of elevated temperatures.

The stereochemistry of the halogens in their various compounds is summarized in Table 17.8 and will be elucidated in more detail in subsequent sections.

Reactivity is enhanced in conditions which promote the generation of halogen atoms, though this does not imply that all reactions proceed via the intermediacy of X atoms. The reversible thermal dissociation of gaseous $I_2 \rightleftharpoons 2I$ was first demonstrated by Victor Meyer in 1880 and has since been observed for the other halogens as well (p. 804). Atomic Cl and Br are more conveniently produced by electric discharge though, curiously, this particularly method is not successful for I. Microwave and radiofrequency discharges have also been used as well as optical dissociation by ultraviolet light. At room temperature and at pressures below 1 mmHg, up to 40% atomization can be achieved, the mean lives of the Cl and Br atoms in glass apparatus being of the order of a few milliseconds. The

Table 17.8   Stereochemistry of the halogens

CN	Geometry	F	Cl	Br	I
0	—	$F^\bullet$(g), F^- (soln)	$Cl^\bullet$(g), Cl^- (soln)	$Br^\bullet$(g), Br^- (soln)	$I^\bullet$(g), I^- (soln)
1	—	F_2, ClF, BrF_3, BF_3, RF	Cl_2, ICl, BCl_3, RCl	Br_2, IBr, BBr_3, RBr	I_2, IX, PI_3, RI
2	Linear	Nb_4F_{20}, NbF_3(ReO$_3$-type)	ClF_2^-, YCl_3(ReO$_3$-type)	Br_3^-, $(MeCN)_2Br_2$, $CrBr_3$(ReO$_3$-type)	I_3^-, ICl_2^-, $BrICl^-$, Me_3NI_2, BiI_3(ReO$_3$-type)
	Bent	$(BeF_2)_\alpha$, $(HF)_n$, Sn_4F_8	ClO_2, ClO_2^-, Al_2Cl_6, $[Nb_6Cl_{12}]^{2+}$, ClF_2^+ $BeCl_2$ (polym), $PdCl_2$	BrF_2^+, Al_2Br_6	IR_2^+, Al_2I_6, AuI(polymeric)
3	Trigonal pyramidal		ClO_3^-, $CdCl_2$, $[Mo_6Cl_8]^{4+}$	BrO_3^-, $MgBr_2$	HIO_3, IO_3^-, CdI_2
	T-shaped		ClF_3	BrF_3	$RICl_2$
	Planar	MgF_2 (rutile)			
4	Tetrahedral	CaF_2 (fluorite), CuF (blende)	$SrCl_2$ (fluorite), ClO_4^-, $FClO_3$, CuCl	BrO_4^-, $FBrO_3$, CuBr BrF_4^-	IO_4^-, CuI
	Square planar				ICl_4^-, I_2Cl_6
	See-saw (C_{2v}, or C_s)		F_3ClO, $[F_2ClO_2]^-$	F_3BrO, $[F_2BrO_2]^-$	$[F_2IO_2]^-$, IF_4^+
5	Square pyramidal		ClF_5, $[F_4ClO]^-$	BrF_5, $[F_4BrO]^-$	IF_5, $[(F_5TeO)_4IO]^-$
	Trigonal bipyramidal		F_3ClO_2		IO_5^{3-} (?)
6	Octahedral	NaF	NaCl	NaBr	IO_6^{5-}, F_5IO, NaI, IF_6^+
	Distorted octahedral			BrF_6^-	IF_6^- (?)
7	Pentagonal bipyramidal				IF_7
	Hexagonal pyramidal		$C_6H_6.Cl_2$	$C_6H_6.Br_2$	
8	Cubic		CsCl, TlCl	CsBr, TlBr	CsI, TlI, $Zr(IO_3)_4$
	Square antiprismatic				

reason for the slow and relatively inefficient reversion to X_2 is the need for a 3-body collision in order to dissipate the energy of combination: $X^\bullet + X^\bullet + M \longrightarrow X_2 + M^*$. A fuller account of the production, detection and chemical reactions of atomic Cl, Br and I is on pages 1141–8 and 1165–72 of reference 23.

Solutions and charge-transfer complexes [34]

The halogens are soluble to varying extents in numerous solvents though their great reactivity sometimes results in solvolysis or in halogenation of the solvent. Reactions with water are discussed on pp. 855ff. Iodine is only slightly soluble in water (0.340 g/kg at 25°, 4.48 g/kg at 100°). It is more soluble in aqueous iodide solutions due to the formation of polyiodides (p. 835) and these can achieve astonishing concentrations; e.g. the solution in equilibrium with solid iodine and $KI_7.H_2O$ at 25° contains 67.8 wt% of iodine, 25.6% KI and 6.6% H_2O. Iodine is also readily soluble in many organic solvents, typical values of its solubility at 25°C being (gI/kg solvent): Et_2O 337.3, EtOH 271.7, mesitylene 253.1, *p*-xylene 198.3, CS_2 197.0, toluene 182.5, benzene 164.0, ethyl acetate 157, EtBr 146, EtCN 141,

[34] Ref. 23, pp. 1196–220.

$C_2H_4Br_2$ 115.1, Bu^iOH 97, $CHBr_3$ 65.9, $CHCl_3$ 49.7, cyclohexane 27.9, CCl_4 19.2, *n*-hexane 13.2, perfluoroheptane 0.12.

The most notable feature of such solutions is the dramatic dependence of their colour on the nature of the solvent chosen. Thus, solutions in aliphatic hydrocarbons or CCl_4 are bright violet (λ_{max} 520–540 nm), those in aromatic hydrocarbons are pink or reddish brown, and those in stronger donors such as alcohols, ethers or amines are deep brown (λ_{max} 460–480 nm). This variation can be understood in terms of a weak donor–acceptor interaction leading to complex formation between the solvent (donor) and I_2 (acceptor) which alters the optical transition energy. Thus, referring to the conventional molecular orbital energy diagram for I_2 (or other X_2) as shown in Fig. 17.2, the violet colour of I_2 vapour can be seen to arise as a result of the excitation of an electron from the highest occupied MO (the antibonding π_g level) into the lowest unoccupied MO (the antibonding σ_u level). In non-coordinating solvents such as aliphatic hydrocarbons or their fluoro- or chloro-derivatives the transition energy (and hence the colour) remains essentially unmodified.
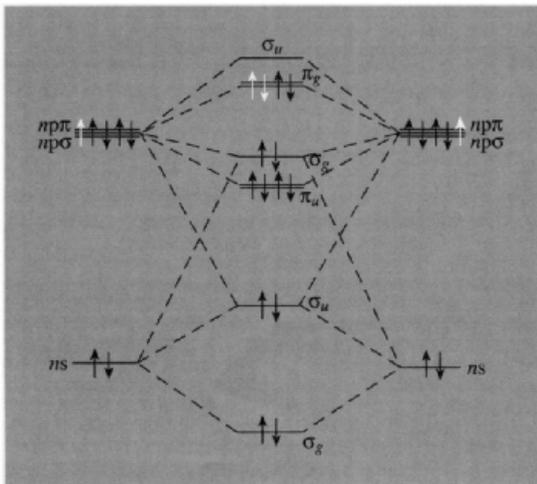

Figure 17.2   Schematic molecular orbital energy diagram for diatomic halogen molecules. (For F_2 the order of the upper σ_g and π_u bonding MOs is inverted.).

However, in electron-donor solvents, L, the vacant antibonding σ_u orbital of I_2 acts as an electron acceptor thus weakening the I–I bond and altering the energy of the electronic transitions:

$$\sigma_g^2 \pi_u^4 \pi_g^3 \sigma_u^1 (^3\Pi_u \text{ and } ^1\Pi_u) \leftarrow \sigma_g^2 \pi_u^4 \pi_g^4 (^1\Sigma_g^+)$$
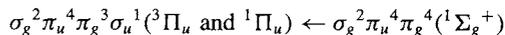
Consistent with this: (a) the solubility of iodine in the donor solvents tends to be greater than in the non-donor solvents (see list of solubilities), (b) brown solutions frequently turn violet on being heated, and brown again on cooling, due to the ready dissociation and reformation of the complex, and (c) addition of a small amount of a donor solvent to a violet solution turns the colour brown. Such donor solvents can be classified as (i) weak π donors (e.g. the aromatic hydrocarbons and alkenes), (ii) stronger σ donors such as nitrogen bases (amines, pyridines, nitriles), oxygen bases (alcohols, ethers, carbonyls), and organic sulfides and selenides.

The most direct evidence for the formation of a complex L→I_2 in solution comes from the appearance if an intense new charge-transfer band in the near ultraviolet spectrum. Such a band occurs in the region 230–330 nm with a molar extinction coefficient ε of the order of $5 \times 10^3 - 5 \times 10^4 \, l \, mol^{-1} \, cm^{-1}$ and a half-width typically of 4000–8000 cm^{-1}. Detailed physico-chemical studies further establish that the formation constants of such complexes span the range $10^{-1} - 10^4 \, l \, mol^{-1}$ with enthalpies of formation 5–50 kJ mol^{-1}. Some typical examples are in Table 17.9. The donor strength of the various solvents (ligands) is rather independent of the particular halogen (or interhalogen) solute and follows the approximate sequence benzene < alkenes < polyalkylbenzenes ≈ alkyl iodides ≈ alcohols ≈ ethers ≈ ketones < organic sulfides < organic selenides < amines. Conversely, for a given solvent the relative acceptor strength of the halogens increases in the sequence Cl_2 < Br_2 < I_2 < IBr < ICl, i.e. they are class b or "soft" acceptors (p. 909). Further interactions may also occur in polar solvents leading to ionic dissociation which

Table 17.9   Some iodine complexes in solution

Donor solvent	Formation constant $K(20°C)/1\ mol^{-1}$	$-\Delta H_f/$ $kJ\ mol^{-1}$	Charge-transfer band		
			λ_{max}/nm	ε_{max}	$\Delta\nu_{\frac{1}{2}}/cm^{-1}$
Benzene	0.15	5.9	292	16 000	5100
Ethanol	0.26	18.8	230	12 700	6800
Diethyl ether	0.97	18.0	249	5 700	6900
Diethyl sulfide	210	32.7	302	29 800	5400
Methylamine	530	29.7	245	21 200	6400
Dimethylamine	6 800	41.0	256	26 800	6450
Trimethylamine	12 100	50.6	266	31 300	8100
Pyridine	269	32.6	235	50 000	5200

renders the solutions electrically conducting, e.g.:

$$2pyI_2 \rightleftharpoons [py_2I]^+ + I_3^-$$
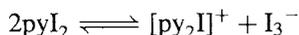
Numerous solid complexes have been crystallized from brown solutions of iodine and extensive X-ray structural data are available. Complexes of the type L→I–X and L→I–X←L

(L = Me$_3$N, py, etc.; X = I, Br, Cl, CN) feature a linear configuration as expected from the involvement of the σ_u antibonding orbital of IX (Fig. 17.3a, b, c). When the ligand has two donor atoms (as in dioxan) or the donor atom has more than one lone-pair of electrons (as in acetone) the complexes can associate
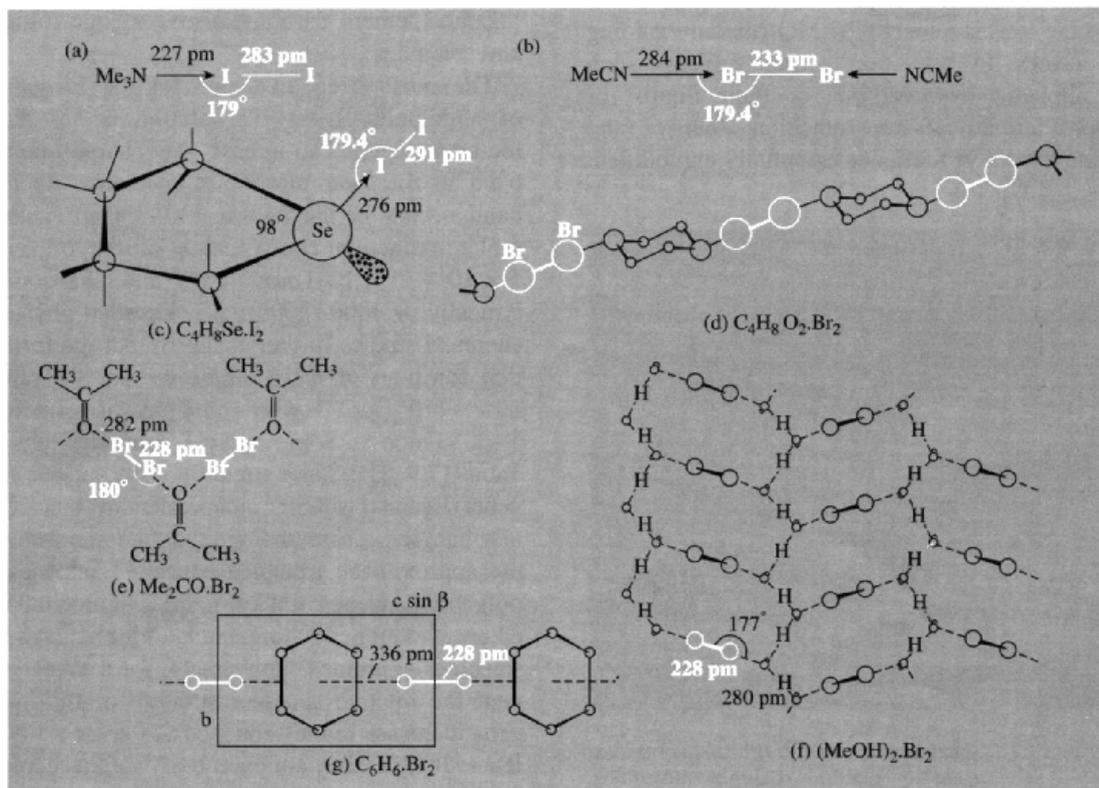

Figure 17.3   Structures of some molecular complexes of the halogens.

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):

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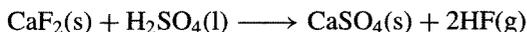
As the reaction is endothermic heat must be supplied to obtain good yields in reasonable

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.

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

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O \xrightarrow{aq\ HF} aq\ H_2SiF_6$$
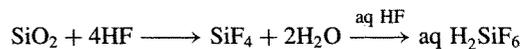
Some of the H_2SiF_6 so produced finds commercial outlets (p. 810), but it has been estimated that $\sim$500 000 tonnes of H_2SiF_6 is discarded annually by the US phosphoric acid industry, equivalent to $\sim$1 million tonnes of fluorspar — enough to supply that nation's entire requirements for HF. 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