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Chapter 1

ISOLATION OF FLUORINE BY MOISSAN: SETTING THE SCENE

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What is fluorine?

The lightest halogen [1]

FLUORINE (symbol F), the most electronegative[1] of all the chemical elements and easily the most reactive, stands at the head of the *halogen* family in Group VII of the Periodic Table of the Elements.[2] Its fellow 'salt-formers' (Greek *hals*, sea salt; *gennao*, I beget) are chlorine, bromine, iodine, and — the heaviest of the bunch — astatine, a fugitive radioactive element of incredible rarity.[3] Fluorine's atoms are small,[4] light (atomic weight 18.99 840), stable,[5] mononuclidic ($^{19}_{9}F$)[6] like iodine's,[7] possess

IVB	VB	VIB	VIIB	0
				2 He
6 C	7 N	8 O	9 F	10 Ne
4	15 P	16 S	17 Cl	18 Ar
	33 As	34 Se	35 Br	36 Kr
		52 Te	53 I	54 Xe
		84 'o	85 At	86 Rn
			17	18

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[1] That is, a fluorine atom *in a molecule* attracts electrons to itself more powerfully than an atom of any other element. On a modern Pauling scale of electronegativities, fluorine (value 4.0) lies well above the next two elements, oxygen (3.4) and chlorine (3.2).

[2] Group 17 in the controversial new format [2].

[3] Astatine is the only halogen without stable isotopes (natural or synthetic), so its name, which is derived from the Greek word for unstable (*astatos*) is very apt. Each of the four isotopes belonging to natural radioactive decay chains has a half-life of less than 1 min, hence the amount of astatine present in the Earth's crust at any one time is estimated not to exceed 50 mg. This easily makes astatine the rarest element.

[4] Radii for fluorine = 71 (covalent), 133 (ionic), 135 (van der Waals) pm [*cf.* chlorine = 99 (Cl), 181 (Cl^-), 180 (vdW) pm; hydrogen = 37 (H), 120 (vdW) pm] (1 pm = 0.01 Å) [3].

[5] Five artificial isotopes have been prepared: $^{x}_{9}F$, $x = 17, 18, 20, 21, 22$. All are radioactive, and the longest lived, fluorine-18, is a positron emitter ($^{18}_{9}F \rightarrow {}^{18}_{8}O + \beta^+$) with a half-life of 109.72 ± 0.06 min [4].

[6] The atomic weight of fluorine [3] can be determined with such great accuracy because the element is monoisotopic.

[7] Halogen isotopes found naturally are (abundances/% in parentheses): ^{19}F (100); ^{35}Cl (75.53), ^{37}Cl (24.47); ^{79}Br (50.54), ^{81}Br (49.46); ^{53}I (100) [3].

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the electronic configuration $1s^2 2s^2 2p^5$, and are strictly univalent, forming compounds with other elements either by sharing one electron in covalent bonds or by gaining one to produce fluoride ions $\{F\cdot([He]2s^2 2p^5) \rightarrow F^-([He]2s^2 2p^6)\}$. In stark contrast to the situation with the other halogens, therefore, the chemistry of fluorine is characterised by a unique oxidation state of −1.

When released from bondage in compounds, fluorine atoms pair up to form molecular fluorine, F_2, a very pale greenish-yellow gas (see p. 46), which is highly toxic; fortunately, its penetrating odour reminiscent of hypochlorous acid or ozone[8] is so intense that the nose can detect it at concentrations in air well below the recommended [6] safe working level (TLV) of 0.1 ppm.[9] When cooled to −188.14 °C, gaseous fluorine condenses to a straw-coloured liquid, which solidifies at −219.62 °C [3].

The ultimate combiner

Fervid Fluorine, though just Nine,
Knows her aim in life: combine!
In fact, of things that like to mingle,
None's less likely to stay single.[10]

The bond energy in molecular fluorine (*i.e.* the enthalpy for the dissociation $F_2 \rightarrow 2\,F\cdot$) has the remarkably low value of 158.8 kJ mol^{-1}, which is much lower than the value for Cl_2 [$\Delta H_{\mathrm{dissoc}}$/kJ mol$(X_2)^{-1}$ = 242.58 (X = Cl), 192.77 (Br), 151.10 (I)]. This phenomenon, which bears vitally on the relative reactivities of fluorine and chlorine, is generally attributed mainly to greater repulsion between lone-pair electrons of the component atoms of F_2, the smaller molecule. In fact, fluorine is not only the most reactive halogen but easily the most reactive element known: *under appropriate conditions* it forms compounds with all other elements except the lighter noble gases helium, neon and argon, often combining directly and violently even at ambient temperature. This outstanding characteristic stems from the surprising weakness of the F—F link (which leads to low activation energies of reaction) and from the great strengths of the bonds fluorine forms with other elements, be they ionic or covalent. The latter factor, like

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[8] Fluorine reacts rapidly with moisture to give hydrogen fluoride and hypofluorous acid, and thence oxygen difluoride, so the actual odour detected may be that of OF_2 rather than F_2 — as pointed out by Cady and Burger [5]. Under certain conditions, however, ozonised oxygen may also be produced (see ref. 8, p. 55).

[9] Threshold limit values (TLV) in parts per million (ppm; volume per million volumes of air for airborne contamination) averaged for a normal working day (8 h) refer to healthy adults showing no special sensitivity to the chemical in question [6]. Fluorine is said to be detectable by smell at concentrations in air as low as 20 parts per billion (ppb; 10^9) [3].

[10] This quatrain, 'Mistress Fluorine' is reproduced by permission of Vernon C. J. Newton from his very clever collection of verses entitled *Adam's Atoms: Making Light of the Elements*, Viking press, New York, 1965 (now out of print).

the first, stems from fluorine's small size, which ensures good overlap of atomic orbitals (hence bonds are short and strong) and allows high coordination numbers to be achieved in molecular fluorides.

Regrettably the name *fluorine* stems from the occurrence of element number 9 as native calcium fluoride (CaF_2; *fluor*, *fluorspar*, *fluorite*[11]) and conveys no hint of its aggressive nature. By contrast, the names chlorine, bromine, iodine (Greek *chloros*, greenish-yellow; *bromos*, a stench; *ioeides*, violet) [7] and astatine[3] do reveal obvious characteristics.

Natural occurrence as fluorides

In view of its reactivity, fluorine is not an element one expects to find free in Nature; traces have been reported to occur, however, in fluoride minerals damaged by radiation emanating from radioactive geological neighbours [7, 8]. Otherwise, fluorine as fluoride ion (F^-) is very widely disseminated in Nature being — to some people's surprise — more abundant in the mineral kingdom than chlorine (as Cl^-) if the hydrosphere is discounted. Virtually all foods contain traces of fluoride, and it is also present in most fresh groundwaters [6]. Sea water contains very little fluoride, approximately 1.4 mg l^{-1} [3].

Fluorine normally ranks 13th (*cf.* chlorine, 20th) in most tables of abundance of the elements in the Earth's crustal rocks. Its average concentration approaches 0.1% by weight, so it is more abundant than combined chlorine by a factor of about seven. The reverse is overwhelmingly true for sea water, of course, in which the F/Cl ratio is $(6.75 \pm 0.03) \times 10^{-5}$ [9]. Considering *all* accessible halogen reservoirs (continental crust, oceanic crust, hydrosphere, sediments), chlorine is about 2.7-times more abundant than fluorine (48×10^{18} kg *versus* 18×10^{18} kg), whereas speculations concerning whole-Earth contents indicate that fluorine is the dominant halogen [$<66 \times 10^{18}$ kg(Cl) based on an estimate of $\sim 10 \times 10^{19}$ kg(F)] [10]. The world's main resources of fluorine are locked up in two ores, *i.e.* *fluorspar* and *phosphate rock*; these contain the minerals fluorite and fluorapatite [$Ca_5(PO_4)_3F$] which, with cryolite (Na_3AlF_6) and topaz [$Al_2SiO_4(F, OH)_2$], are the most familiar of the numerous (more than 100) fluorine-containing minerals present in the lithosphere [11]. The radii of fluoride and oxide ions [$r(F^-) = 133$, $r(O^{2-}) = 140$ pm] are almost identical, hence the ability of fluorine to replace oxygen (as hydroxide) geologically in a wide variety of minerals and so extend the range available.

Fluorspar has always been, and remains, the most important primary source of fluorine and its compounds (*fluorochemicals* — inorganic and organic [11 - 16]). Total world demonstrated and identified reserves stand at 135 and 262 Mt respectively, and about 5 Mt are produced worldwide per

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[11] The name *fluor* is seldom used nowadays; *fluorite* is reserved for the pure mineral; and *fluorspar* is the commercial name for products consisting mainly of fluorite [common associative minerals are quartz (SiO_2), calcite ($CaCO_3$), galena (PbS), barytes ($BaSO_4$) and sphalerite (ZnS)].

annum [14, 15]. About 40% of the fluorspar being mined is utilised as a metallurgical flux, mainly in the steel industry, and most of the remainder is treated with concentrated sulphuric acid to provide hydrogen fluoride [$CaF_2 + H_2SO_4(>98\%) \rightarrow 2\ HF + CaSO_4$], the principal manufactured derivative of fluorine.[12] Pure calcium fluoride melts at 1402 °C and has a very poor solubility in water ($0.015\ g\ l^{-1}$ at 25 °C).

Hydrogen fluoride — beware!

Hazards

Aptly called the life blood of the modern fluorochemicals industry [16], hydrogen fluoride is also the most important compound of fluorine from the historical viewpoint: it may have been used to etch glass (decoratively) as early as the 17th century, and subsequent investigations of its chemistry are inextricably associated with the discovery and isolation of fluorine. Crucial amongst events prior to Moissan's entry to the field of fluorine chemistry in 1884 were the deduction (*ca.* 1813) of the chemical nature of hydrogen fluoride and, more than 40 years on, mastery of the preparation of anhydrous samples. In no small measure was progress towards the goal so admirably reached by Moissan in 1886 — *unquestionable isolation of fluorine* — hampered by the hazards associated with hydrogen fluoride. It is apposite at this stage, therefore, to be reminded that *considerably* more care needs to be exercised when working with hydrogen fluoride, aqueous (hydrofluoric acid) or anhydrous (AHF), than with any other mineral acid because of the unique and notorious damage it inflicts on the skin, underlying tissues, and even bone in serious cases [17]. Sadly, early pioneers of fluorine chemistry endured much suffering before this was fully realised, and many shortened their lives[13] — some drastically — through breathing 'vapours of hydrofluoric acid'. No wonder the history of fluorine's isolation has been called tragic [19].

Voluntary acute exposure to AHF vapour (anhydrous hydrogen fluoride boils at 19.5 °C) or fumes evolved by its concentrated aqueous solutions (at ambient temperature, serious inhalation hazard arises for solutions containing >60% HF w/v) should never occur because such severe irritation is associated with inhalation of 'HF vapours'. Symptoms of exposure include a burning sensation of the eyes (with lachrimation), an intolerable burning sensation in the mouth, nose and throat (with cough and hoarseness), and a deep substernal pain; in severe cases coughing up of blood and lung congestion may occur. Fortunately, the presence of HF vapour in the atmosphere is detectable by smell at sub-harmful levels. A maximum TLV[9] of 3 ppm or less is recommended [6, 14].

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[12] Hydrogen fluoride also occurs naturally in effluvia from volcanic vents [7, 8, 11].

[13] According to Alfred Stock [18], Moissan himself remarked: "Le fluor aura raccourci ma vie de dix ans".

Liquid AHF, and, to a lesser degree, its vapour produce serious skin burns. Aqueous HF (hydrofluoric acid) can also harm the skin, underlying tissues and — in extreme cases — the bone; the more concentrated the acid and the longer the exposure time and the thinner the skin, the more rapidly do lesions appear and the more severe are the subsequent pains and white necrosis. Case histories and treatments for HF burns are well documented [17].[14]

As emphasised by O'Donnell [20], eye or skin contact with many fluorides — organic as well as inorganic — must be regarded as contact with hydrogen fluoride because body moisture hydrolyses them to this compound. The same problem arises with elemental fluorine, which attacks skin (causing a thermal burn) and moisture,[8] liberating hydrogen fluoride in both cases. In general, ingestion of fluorides must be controlled[15] owing to toxicity problems (*fluorosis*, fluoride poisoning) [6, 21]. The fatal dose of fluoride in humans is usually unknown; however, it has been deduced that the lethal dose for a 70-kg man probably lies in the range 5 - 10 g of sodium fluoride [6]. A TLV for airborne particulate fluoride (as F^-) of 2.5 mg m^{-3} (8-h day, 40-h week) seems acceptable [6, 14].

Clearly great vigilance and strict adherence to safety precautions need to be practised by all those who work with fluorine and its compounds; above all, sensible adequate prior arrangements must be made for medical treatment [17, 22, 23].

The silica problem

To be fair to the pioneers of fluorine chemistry, anhydrous hydrogen fluoride is not easy to prepare, purify and manipulate even in a modern laboratory because of its volatility (it boils at room temperature or there-

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[14] The severe pain, attributable to immobilisation of tissue calcium as insoluble CaF_2, can be rapidly relieved by injecting a sterile 10% solution of calcium gluconate into and around the burn; this treatment has been criticised, however, and topical application of iced alcoholic or aqueous solutions of quaternary ammonium compounds [22] or of a calcium gluconate gel [23] recommended instead.

[15] Deliberate addition of fluoride ion in low concentration to drinking water [*water fluoridation* — an emotive topic (see *Fluoridation: The Great Dilemma,* by G. L. Waldbott *et al.*, Coronado, KA, 1978)] and the use of toothpaste containing fluoride additives (see pp. 208, 209) are widely recommended as modern health procedures to counteract tooth decay in humans. Fluoride ion replaces hydroxide (OH^-) from tooth enamel — hydroxyapatite, $Ca_5(PO_4)_3OH$ — producing fluorapatite crystals; it seems that this reduces the solubility of enamel in mouth acids and also exerts an anti-enzymatic effect on plaque bacteria, thus reducing susceptibility to caries formation. The U.K. Water Fluoridation Bill, brought from the House of Commons on 7th March, 1985, instructs that only the compounds H_2SiF_6 and Na_2SiF_6 may be added to public water supplies in mainland Britain to secure, "so far as is reasonably practicable", that the concentration of fluoride is maintained at 1 mg l^{-1}.

abouts[16]), its great affinity for water (hence the white mist its vapour forms in moist air) and its corrosive action on glass or other siliceous apparatus. The last property stems from the well-known reaction $4\ HF + SiO_2 \rightarrow SiF_4 + 2\ H_2O$, which lies behind the old school test for metal fluorides or silicates [24] and the commercial 'frosting' of electric light bulbs [13]. Formation of silicon tetrafluoride (a gas) in this manner occurs during the manufacture of AHF because even specially purified *acid grade* fluorspar (>96.5% CaF_2) contains some silicon dioxide (silica, quartz); and additional complications arise through the formation of water, carbon dioxide ($CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$), sulphur dioxide and/or hydrogen sulphide from carbonate and sulphide minerals also present [13, 14]. Silicon tetrafluoride dissolves in water, producing hexafluorosilicic acid and gelatinous silica (*simply:* $3\ SiF_4 + 4\ H_2O \rightarrow H_4SiO_4 + 2\ H_2SiF_6$). Hexafluorosilicic acid [25], often referred to as fluosilicic acid and sold as a 30 - 35% aqueous solution, should be handled as if it were hydrofluoric acid.

Nowadays, of course, AHF is rarely made in the laboratory because samples of very high quality (not less than 99.8% HF) can be purchased. It comes in mild steel cylinders, from whence it is easily transferred via a flexible copper tube to chilled receptacles or reaction vessels constructed (as appropriate to temperature etc.) from suitable thermoplastics [e.g. poly(ethylene), poly(tetrafluoroethylene)] and/or metals [mild steel, nickel or its alloys] [20, 26, 27]. All this is a far cry from storage of AHF in platinum bottles, as recommended [7] in the early 1920s and still being mentioned in 1941 [28], a decade after commercial production began (in America [26, 29]).

'Bottled' fluorine is also available commercially now. Made by an adaptation of Moissan's electrolytic method, it is packaged and shipped as a compressed gas (with or without nitrogen as diluent) in special steel cylinders and used — always respectfully — to effect reactions in carefully designed apparatus [20] built from fluoropolymer, metal and, sometimes, glass or silica components. Some researchers still prefer to generate their own fluorine, using it directly as produced by small laboratory fluorine 'cells' (electrolytic generators). These too are descendants of Moissan's apparatus, the background to the development of which will now be addressed.

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[16] The boiling point of anhydrous hydrogen fluoride (19.54 °C; *cf.* HCl, −84.9 °C) is anomalously high as a result of extensive molecular association via hydrogen bonding, which persists even in the vapour phase; the other hydrogen halides are not associated in either the gaseous or liquid phases. Hydrogen bonding in fluorine compounds is a familiar phenomenon and is associated with the high electronegativity of the bound element (see footnote 1 on p. 3).

Pre-Moissan history of fluorine[17]

The master problem

Excluding astatine — a special case[18] — all of the halogens must be isolated from natural compounds because their reactivity as a class virtually precludes access to native samples. Despite determined efforts by distinguished 19th century chemists, fluorine is adjudged not to have been isolated until 112 years after chlorine, the fellow halogen it resembles most in terms of chemical reactivity, physical properties, history, natural abundance and length of man's awareness of its principal ore [*cf.* fluorspar (CaF_2) and common salt (rock salt, halite — NaCl)]. In short, as succintly put by Partington [33],[19] "the isolation of fluorine was long one of the master problems of inorganic chemistry". The root of the delay was that fluorine is the most powerful oxidising agent known, and cannot, like the other halogens,[20] be liberated directly from its compounds via simple chemical means; though indicated in 1810, electrochemical oxidation of fluoride ion — as used to this day — took nearly 80 years to demonstrate successfully because of fluorine's extreme reactivity and the 'HF problem'.

The order in which the non-radioactive halogens were isolated runs chlorine (K. W. Scheele, 1774), iodine (B. Courtois, *ca.* 1811), bromine (A. J. Balard, 1824), and fluorine (F. F. H. Moissan,[21] 1886), all but the first falling to French chemists. Alchemists in the 13th century must have encountered the corrosive, suffocating, greenish-yellow gas we call chlorine when they used mixtures of concentrated hydrochloric acid and nitric acid (*aqua regia*) to dissolve gold. However, credit for chlorine's isolation goes to the remarkable Swedish apothecary and phlogistonist Scheele (1742 - 86), [34] who oxidised concentrated hydrochloric acid (marine or muriatic acid;

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[17] Information relating to the history of fluorine's isolation was gleaned initially by consulting the literature cited under ref. 30. Primary sources of information actually examined are referenced in the text. General historical facts were taken from refs. 7 (all the halogens with the exception of astatine) and 31.

[18] Astatine is excluded from this discussion for obvious reasons (see footnote 3 on p. 3). It was discovered in 1940 by Corson *et al.* [32] at the University of California, where a large cyclotron was used to effect the synthesis ${}^{209}_{83}Bi + {}^{4}_{2}He \rightarrow {}^{211}_{85}At + 2\,{}^{1}_{0}n$.

[19] J. R. Partington (1886 - 1965), the famous British historian of chemistry, who was born six days before Moissan isolated fluorine.

[20] Values [3] of standard reduction potentials (E°/V at 25 °C) in acidic aqueous solutions indicate a steadily decreasing oxidising power in the sequence $F_2(+2.87) > Cl_2(+1.3583) > Br_2(+1.087) > I_2(+0.535)$. Since fluorine reacts with water (see footnote 8 on p. 4), no direct measurement of E° for the half-reaction $\frac{1}{2} F_2 + e^- \rightleftharpoons F^-$ is possible; the value quoted above has been calculated from thermochemical data.

[21] Note that the initials of Moissan's forenames (Ferdinand Frédéric Henri) nicely befit the man who mastered the isolation of fluorine.

Latin *muria*, brine)[22] with manganese dioxide and called the greenish-yellow gas evolved dephlogisticated marine acid — a name subsequently changed to *oxymuriatic acid* (Berthollet, 1785; Lavoisier, 1789).

Convincing proof that oxymuriatic acid contained no oxygen became available in 1810 through the research work of Humphry Davy which demolished Lavoisier's contention that all acids contain oxygen — including muriatic (hydrochloric) and fluoric (hydrofluoric). Davy chose the term chlorine for the new element (Greek *chloros*: greenish-yellow) — "founded upon one of the obvious properties of the gas" — to help dispel the hypothesis advertised by the term oxymuriatic acid that oxidation of muriatic acid produces a compound of oxygen. Lavoisier (1743 - 94), famous for his demolition of the phlogiston theory of combustion, was guillotined during the Reign of Terror in France, whereas his tenet that acids always contain oxygen lingered on even after Davy's work on chlorine. In particular, J. J. Berzelius (1779 - 1848), the great Swedish chemist, was loath to discard it completely until about 1820, when finally he started to use the name chlorine. Thus, in his seminal essay on the cause of chemical proportions, in the section (III) entitled *On the Chemical Signs*, etc. [35], Berzelius referred to the muriatic radical M; in the second edition (1825 - 31) of his great *Lärbok* [36], however, he listed chlorine, iodine and fluorine as *Corpora Halogenia*, abbreviated to Cl, I and F, respectively. The symbol F for *fluoric radical (fluoricum)* was used first in the article published in 1814 [35].

Once bromine and iodine had been isolated, their elementary natures and their relationship to each other and to chlorine were quickly recognised by the French school. Balard wished to have his smelly, dark-red, liquid halogen called *muride*, since it was derived from Montpellier brines by removing salt and treating the residual bromide-containing liquors with chlorine water; to avoid confusion with muriatic entities, however, the name bromine (Greek *bromos*, a stench) was adopted. Gay-Lussac named Courtois' halogen *iode* [iodine (Davy); Greek *ioeides*, violet] after the impressive colour of the vapour produced when this blackish-grey solid element is heated.

By contrast with chlorine, bromine and iodine, fluorine — the superhalogen — was so named *prior* to its isolation and according to *source-based* nomenclature. The originator of the name, surprisingly perhaps, was the French physicist and mathematician A.-M. Ampère (1775 - 1831), whose

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[22] The well-known Bavarian iatro-chemist J. R. Glauber (1604 - 68) taught how to prepare concentrated hydrochloric acid from rock salt and oil of vitriol (sulphuric acid), and the simple chemistry involved formed the basis of the famous salt-to-soda process which was invented by Nicholas Leblanc (1742 - 1806) and lay at the heart of the emerging British chemical industry in the 19th century: $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$; $NaCl + NaHSO_4 \rightarrow Na_2SO_4$ (salt-cake) $+ HCl(+H_2O \rightarrow$ hydrochloric acid); $Na_2SO_4 + CaCO_3 + 2\,C \rightarrow Na_2CO_3 + CaS + 2\,CO_2$ (black-ash mixture). Hydrogen chloride (b.p. -84.9 °C) is a gas under normal conditions and was first collected in 1771 by Joseph Priestley (over mercury), who called it *marine acid air*.

interest in chemistry led him to deduce that hydrofluoric acid is analogous to hydrochloric acid. His opinions were communicated to Humphry Davy in two letters [37] sent from Paris to London during the Napoleonic war; note that the first one, dated 1st November, 1810, contained a suggestion that the unknown substance combined with hydrogen in hydrofluoric acid might be isolable via electrolysis of the anhydrous acid using (as in modern fluorine cells!) a carbon anode:

> "Reste à savoir si l'électricité ne décomposerait pas l'acide hydrofluorique sous sa forme liquide, lorsqu'on en aurait écarté l'eau le plus possible, en portant l'hydrogène d'un côté et l'oxy-fluorique de l'autre ...... Peut-être aucun métal ne pourrait se refuser à cette combinaison. Mais, en supposant que l'oxy-fluorique fût, comme l'oxy-muriatique, incapable de se combiner avec le charbon, ce dernier corps serait peut-être assez bon conducteur pour être employé avec succès comme tel dans cette expérience."

In Ampère's second letter (25th August, 1812), the term oxy-fluorique was replaced by *fluorine*, which was coined to harmonise with the then recently adopted name chlorine. Davy approved publicly on 8th July, 1813 [38], and the element — putative until 1886 — has been called fluorine in English ever since. Fluor or a derived name has, in fact, been adopted almost universally [e.g. French *le fluor* (*fluore* originally [39]); German, *das Fluor*; Italian, *il fluòro*]. But note that since 1832 (F.S. Beudant), fluorite (fluorspar) has been called *la fluorine* (le spath fluor) in France.

Ampère himself, however, soon decided to abandon the term *le fluore* in favour of *le phtore* (Greek *phthoros*, destructive) on etymological grounds [39]: "..... j'ai choisi le nom de *phtore*, de l'adjectif grec φθόριοζ (on dit aussi φθόροζ, qui se prend dans les deux sens substantif et adjectif) *délétère, qui a la force de ruiner, de détruire, de corrompre*" [37]. Although the name *phtorine* (or *phthorine* [40]) stemmed from the agressive natures of fluorine (then perceived) and hydrofluoric acid (only too well known) and thereby conformed with halogen nomenclature, it did not displace *fluorine*. The influential editor of *Annals of Philosophy* at the time, Thomas Thomson, who brought the word chloride (hence fluoride) into use, clearly was not amused by Ampère's proposal when he cautioned [40]: "There would be no end to new names if every person at pleasure could coin new ones." This did not prevent G. H. Hess (1802 - 50), who was born in Geneva but spent most of his life in Russia and is best known for his law of constant heat summation, from designating element number 9 фтор (*ftor*) when he wrote his important book *Osnovaniya Obshchei Khimii* (1831); thanks to that, Russian chemists adopted the nomenclature preferred by Ampère. Greek chemists are completely in line with Ampère, too, for they write φθόριον when referring to the lightest halogen.

Sparry fluor — the flux behind the name fluorine

Writing "of fluorine" in 1831 [40], the eminent British chemist and historian of chemistry Thomas Thomson (1773 - 1852) commented:

"The mineral called *flour* (sic![23]) *spar*, and in this country frequently distinguished by the name of Derbyshire spar, is so common in lead mines, and is so beautiful in consequence of its transparency, its fine colours, and the large size of its cubic crystals, that it must have early attracted the attention of mankind. There can be little doubt that it is mentioned both by Theophrastus and Pliny under the name of *false emerald* ... In the time of Agricola it was employed as a flux for ores, and is mentioned by him under the name of fluor."

Partington was more explicit in 1923 when he reviewed the somewhat involved early history of hydrofluoric acid [41]:

"The old German miners of the 16th century called this mineral *fluss*, obviously a German word, like *fliessen*, derived from the Latin *fluo*, 'I flow'. This name was given to it on account of its easy fusibility, and its use as a flux. George Agricola (a Latinised form of Bauer or Landsmann), in his *Bermannus, sive de re metallica*, first published, according to Hoover, in 1530 by Frobenius at Basle, calls it *fluor.*"

Georgius Agricola (Glaucha, 1494 - Chemnitz, 1555), a contemporary of the famous Paracelsus and a physician by trade, promoted applied chemistry during the iatro-chemical period through his deep interest in the flourishing mining and smelting industry of Saxony.

By the end of the 18th century, the terms *fluor*, *fluorspar* and *fluorite* were being used synonymously for the mineral soon to be designated calcium fluoride. Nowadays, the name *fluorite* — which conforms with the 'suffix *ite*' guideline of modern mineralogical nomenclature [42] — is normally reserved for the 'pure' mineral; in commercial circles, fluorspar signifies ores rich in fluorite [14, 43, 44]. The affix spar (Old English: *spaerstan*, *spar stone*) occurs in old common names for many minerals which, like fluorite, are vitreous, crystalline and easily cleavable [42]. Derbyshire spar is a case in point, and, as remarked by Thomson, certainly cannot be overlooked: particularly the beautiful and unique purplish-blue and white banded fluorite known worldwide by the vulgar name *Blue John* (originally *Blew John* [45]), removal of which from the Treak Cliff reef knoll at Castleton, Derbyshire (U.K.) for ornamental purposes (e.g. Adam fireplaces, Boulton ormolu work, Vallance vases) began in the mid-1700s [45] (see Fig. 1.1)).

Worldwide, fluorite occurs in almost every colour of the rainbow (see Fig. 1.2), and material quite similar to Blue John, but possibly from Persia, seems to have been used in Roman times to make goblets [*vasa murrina* (Pliny)] [45, 46]. Commonly, it is transparent or translucent, but mainly opaque; and ordinarily is white, tan, yellowish or green with attached and admixed mineral impurities.[11] Coloured variations are produced by certain impurities and by radiation damage, which causes release of fluorine [7, 8] and 'colloidal' calcium (colour-centre aggregates) [47]. Because of rare-earth

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[23] This is an early example of a familiar spelling error. Strangely, even the most diligent of proof-readers sometimes overlook examples.

Fig. 1.1. Antique Blue John bowl (12 cm in diameter) from the Braithwaite collection of fluorite specimens. (Photograph reproduced by permission of Dr. R. S. W. Braithwaite.)

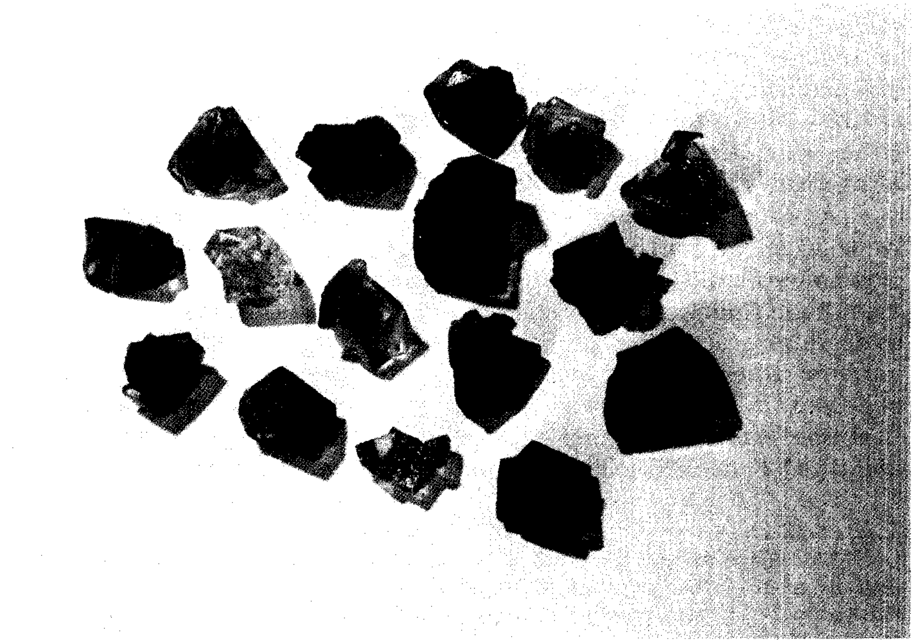

Fig. 1.2. A collection of small specimens of fluorite from different locations, showing some of the various colours encountered. (Photograph by courtesy of Dr. R. S. W. Braithwaite.)

impurities, some fluorites fluoresce when exposed to UV light — the phenomenon being named after the mineral by G. G. Stokes in 1852 [48]:

> "I am also inclined to coin a word, and call the appearance fluorescence, from fluor-spar, as the analogous term opalescence is derived from the name of a mineral."

The fact that "some varieties of fluor phosphoresce when raised to a temperature less than that of boiling water" [49] seems first to have been noted by J. L. Elsholtz of Vienna in 1676 [41].

Scheele's acid of fluor

The systematic study of fluorine chemistry began in 1764 when the important German phlogistonist A. S. Marggraf (1709 - 82) attempted to ascertain the composition of fluorspar by heating it with sulphuric acid in a glass retort attached to a receiver containing water; he obtained [40] "a white saline sublimate", and remarked, with surprise, that "the retort was corroded into holes in several places". In 1771, the gifted Swedish pharmacist K. W. Scheele (1742 - 1786) repeated Marggraf's experiment and concluded that sulphuric acid liberated a peculiar acid (*Flusssäure* — fluor acid) which is united with lime in fluorspar (*flusssäure Kalk*); he was perplexed, however, by the separation of 'earth' (silica) when the gas evolved from fluorspar–sulphuric acid mixtures contacted water in his glass receivers [$SiO_2 + 4\,HF \rightarrow SiF_4 + 2\,H_2O$; $3\,SiF_4 + 2\,H_2O \rightarrow SiO_2 + 2\,H_2SiF_6$].[24] Other chemists (notably Joseph Priestley, J. C. F. Meyer, C. F. Wenzel, J. C. Wiegleb and C. F. Buchholz) began to experiment with fluorspar and sulphuric acid, and soon the formation of silica and fluorosilic acid was traced to the use of glass apparatus. The most impressive work was carried out independently by the German chemists Meyer (1733 - 1811) and Wenzel (1732 - 1800), the former adapting a gun barrel for use as a retort and the latter using lead apparatus; their work was published in 1781 and 1783 respectively, before Scheele mentioned his use of a tin retort (1786).

A detailed account of the researches of Meyer (in particular) and Wenzel can be found in Partington's review [41], which describes how the first ammonium fluoride ("Flusspath Salmiaks") was made and converted into "synthetic fluorspar" with lime water. The first fairly pure sample of aqueous hydrofluoric acid was probably prepared by Meyer when he heated ammonium fluoride with concentrated sulphuric acid in his iron retort and collected the vapour evolved in a lead receiver containing water. When Lavoisier wrote his *Traité Elémentaire de Chimie* (published in 1789) he identified Scheele's acid of fluor (*l'acide fluorique*) as an oxide of an un-

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[24] The common assertion that Heinrich Schwanhardt of Nuremberg discovered accidentally in 1670 that glass can be etched with acidified fluorspar has been questioned by Partington [41], who thought it likely that an unknown English glassworker first prepared crude hydrofluoric acid around 1720, and that Schwanhardt etched his 'soft' glass spectacles with *aqua fortis* (concentrated nitric acid). For a recent review of the history of acid-etching of glass, see ref. 50.

specified radical; he was, of course, similarly ignorant of the composition of muriatic acid.

Recognition of fluorine: enter Humphry Davy

Almost 30 years after Meyer and Wenzel published their work, the distinguished French duo J. L. Gay-Lussac (1778 - 1850) and L. J. Thénard (1777 - 1857) reported (on 23rd January, 1809 [51]) how they had prepared tolerably pure and highly concentrated hydrofluoric acid by heating a mixture of virtually silica-free white fluorspar (*fluate de chaux*) with concentrated sulphuric acid in lead apparatus and condensing the vapours evolved at 0 °C.[25] Their product fumed strongly in air, rapidly dissolved glass, possessed a great affinity for water, and — a phenomenon they described in some detail — caused extraordinary burns on contact with the skin [51]:

"A peine la touche-t-il, que déjà elle est désorganisée. Un point blanc se manifeste aussitôt, et une douleur, se fait bientôt sentir; les parties voisines du point touché ne tardent point à devenir blanches et douloureuses, et peu après il se forme une cloche, dont les parois sont une peau blanche très épaisse et qui contient du pus."

Gay-Lussac and Thénard elucidated the action of hydrofluoric acid on silica and also discovered boron trifluoride (*le gaz acide fluo-borique*) through heating fluorspar with boric oxide in an iron tube. This forestalled John Davy's claim (1812) concerning the synthesis of *silicated fluoric acid gas* (SiF_4) and *fluoboracic acid gas* (BF_3) from powdered glass and boric oxide, respectively, via treatment of each with HF formed *in situ* from fluorspar and concentrated sulphuric acid [53]. John Davy (1790 - 1868), then a medical student and later a British Army surgeon, worked on fluorine compounds at the request of his famous elder brother, Humphry, who became involved with Scheele's acid of fluor in 1808. According to John [54]:

"His researches relative to fluoric acid, which were commenced at the same time as those we have just been considering relative to the muriatic acid, did not make the same rapid progress, nor were the results equally successful."

By mid-1813 (8th July), however, Humphry, having failed to isolate fluorine but shown *inter alia* that [55]:

"The action of potassium upon fluate of ammonia is precisely similar to its action upon muriate of ammonia, in which as I have found, by numerous experiments, ammonia and hydrogen to each other in volume as two to one are disengaged, and muriate of potassa (*potassane*) formed." [In modern terms: $2\ NH_4X + 2\ K \rightarrow 2\ KX + 2\ NH_3 + H_2$ ($X = Cl$ or F).]
was ready to pronounce [55]:

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[25] A modern version of this experiment was used 50 years ago by members of the chemistry class at Williamson Central School, New York, to prepare 'home-made hydrofluoric acid' for etching (glass) purposes [52].

"From the general tenor of results that I have stated, it appears reasonable to conclude that there exists in the fluoric compounds a peculiar substance, possessed of strong attractions for metallic bodies and hydrogen, and which combined with certain inflammable bodies forms peculiar acids, and which, in consequence of its strong affinities and high decomposing agencies, it will be very difficult to examine in a pure form, and, for the sake of avoiding circumlocution, it may be denominated *fluorine*, a name suggested to me by M. Ampère."

At the same time, he fully acknowledged Ampère's remarkable original contribution [55]:

"During the period I was engaged in these investigations, I received two letters from M. Ampère of Paris, containing many ingenious and original arguments in favour of the analogy between the muriatic and fluoric compounds. M. Ampère communicated his views to me in the most liberal manner; they were formed in consequence of my ideas on chlorine, and supported by reasonings drawn from the experiments of MM. Gay-Lussac and Thénard.

In the second hypothesis, that which I have alluded to in the beginning of this paper, and that adopted by M. Ampère, the silicated fluoric acid is conceived to consist of a peculiar undecompounded principle, analogous to chlorine and oxygen, united to the basis of silica, or *silicum*; the fluo-boric acid of the same principle united to boron; and the pure liquid fluoric acid as this principle united to hydrogen."

Davy did not state categorically that fluorine is an element, and this he made perfectly clear in a paper read on 13th February, 1814 [56]:

"In the views that I have ventured to develop, neither oxygen, chlorine, or fluorine, are asserted to be elements; it is only asserted, that, as yet, they have not been decomposed."

This paper contained details of new experiments on "fluoric compounds", including the first determinations of fluorine's "combining proportion" (atomic weight),[26] and a reasoned attack on Berzelius and other critics of his declaration that chlorine is not a compound of oxygen.

Publication of the Ampère–Davy hypothesis in 1813 was a crucial watershed in the history of fluorine chemistry. It dispelled ambiguity about the nature of hydrofluoric acid and, harnessed to the general advance of inorganic chemistry in the early part of the 19th century, resulted in the synthesis and study of many common metallic fluorides. Analogies between compounds of fluorine and those of chlorine, iodine and — subsequently — bromine soon strengthened to the point where no one seriously doubted

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[26] Davy found, for example, that treatment of 100 grains of "very pure white [powdered] Derbyshire spar" with sulphuric acid gave 175.2 grains of calcium sulphate; therefore "supposing the number representing calcium to be 40, the number representing fluorine will be 34.2, and fluor spar must be supposed to be composed of 40 calcium and 34.2 fluorine." (Using modern data, this result corresponds with an atomic weight of 18.8 for fluorine.)

the existence of the fourth halogen. What did remain uncertain was that chemists would ever succeed in isolating it! Even the preparation of pure anhydrous hydrogen fluoride was not achieved until the 1850s.

Pure AHF at last, via Frémy's salt (KHF_2)[27]

Edmond Frémy (1814 - 1894), the well-known French chemist who numbered Moissan amongst his pupils, maintained in his *Recherches sur Les Fluorures* (1856) [57] that HF furnished by the Gay-Lussac/Thénard method always contains water, sulphuric acid, sulphurous acid, hexafluorosilicic acid, etc. After failing to purify and dehydrate such material, he treated it with potassium fluoride to cause precipitation of potassium hydrogen fluoride, which he recrystallised several times to remove potassium hexafluorosilicate, dried carefully and then heated strongly in platinum apparatus to produce the first pure sample of anhydrous hydrogen fluoride: $KHF_2 \rightarrow KF + HF$ (condensed at ice–salt temperatures). Although Berzelius had discovered the so-called acid fluorides MHF_2 (M = Li, Na, K)[28] of the alkali metals about 30 years earlier, the potassium compound became known as Frémy's salt in honour of the Frenchman's achievement;[27] he called it *le fluorhydrate de fluorure de potassium*, and represented it by a formula with Fl symbolising fluorine not Berzelius' F, *i.e.* FlH,FlK [57]. Frémy's method remains an excellent means of acquiring *small* known quantities of AHF in the laboratory; the salt, which melts at 239 °C, is simply heated slowly to *ca.* 500 °C in a copper tube attached to a refrigerated receiver. Frémy described his product thus [57]:

"L'acide fluorhydrique anhydre obtenu par cette méthode est gazeux à la température ordinaire, mais condensable par un mélange de glace et de sel en un liquide très fluide, agissant sur l'eau avec une grande énergie, et répandant à l'air des fumées blanches dont l'intensité ne peut être comparée qu'à celles du fluorure de bore."

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[27] N.B. This trivial name for potassium bifluoride (potassium hydrogen difluoride) tends to be reserved for the persistent inorganic nitroxide $(KO_3S)_2NO\cdot$ (potassium nitrosodisulphonate), which Frémy discovered in 1845 and ought now to be called Frémy's radical.

[28] The ability of hydrogen fluoride to combine with its alkali metal salts (MF) to form readily isolable mono-acid halides (MHF_2) stable at ordinary temperatures makes it unique amongst the hydrogen halides [58]. Powerful hydrogen bonding occurs in the hydrogen difluoride (bifluoride) anion, $F—H\cdots F^-$, the energy value for which (experimental range, 150 - 250 kJ mol^{-1}; calculated, 217 - 234 kJ mol^{-1}; *cf.* HCl_2^-, 75 and 67 kJ mol^{-1}, respectively [58]) was believed at one time to represent the upper limit of H-bond strength; fairly recently, however, the calculated value of the dissociation energy of the hydrogen bond between formic acid and fluoride ion, $HCO_2H\cdots F^-$, has been found to lie within the range 245 - 250 kJ mol^{-1} (see Greenwood and Earnshaw for a discussion of these matters and for the appropriate references [1]).

During the next decade (1860 - 9), the superb British experimentalist George Gore[29] determined the boiling point ("67° FAHR."), vapour pressure and liquid density of AHF prepared by Frémy's method during his thorough study of hydrofluoric acid; this was conducted with the aid of an impressive collection of platinum apparatus, some lent by Messrs. Matthey & Co, joints on which were sealed with molten sulphur or paraffin wax mixed with lampblack [60]. Both Frémy and Gore confirmed Davy's claim that hydrofluoric acid contains no combined oxygen [Gore, for example, made a quantitative study of the reaction $2AgF + H_2 \rightarrow$ (at red heat) $2Ag + 2\,HF$], and both stressed the difficulties of working with AHF; to quote Gore [60]:

> "The low boiling-point, the extremely dangerous and corrosive nature of the acid, and its great affinity for water, illustrate the very great difficulty of manipulating with it and retaining it in a pure state; nevertheless by the contrivance described and placing the [platinum] bottles containing it in a cool cellar (never above a temperature of 60° FAHR.), the author has succeeded in keeping the liquid acid perfectly, without loss, and unaltered through the whole of the recent hot summer."

The starting material for Gore's work was crude aqueous hydrofluoric acid ("ordinary hydrofluroic acid") manufactured in England chiefly for glass-etching and related purposes by heating fluorspar with sulphuric acid in iron retorts attached to water-containing leaden receivers [*i.e.* Meyer's method (see p. 14)];[30] he purified such material on a *multi-gallon* scale by chemical treatment, followed by distillation from a leaden retort attached to a Liebig condenser containing a sizeable platinum tube.[31]

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[29] George Gore [22nd January, 1826 (Bristol) - 20th December, 1908 (Birmingham)] was a remarkable self-taught Victorian electro-metallurgist and chemist who, from 1880 onwards conducted private research at the Institute of Scientific Research, Easy Row, Birmingham, which was also his home; his previous occupations included cooper (in Bristol), practitioner in medical galvanism, analytical chemist at a phosphorus factory, and lecturer in chemistry and physics at King Edward's School (in Birmingham). His wide-ranging and prolific contributions to British science and industry earned him the offer of a knighthood, which he declined, and election to the Fellowship of the Royal Society [59].

[30] For a late 19th century American review of commercial aqueous hydrofluoric acid, see Stahl's article [61]. This records that crude commercial hydrofluoric acid was stored or shipped in lead or (for small quantities) guttapercha vessels when it contained 40 - 52% HF, and wooden barrels (short-term only) when less strong (*ca.* $\leqslant$35%); so-called C.P. (chemically pure) aqueous HF required ceresine wax (used in the U.S.) or platinum (Europe) bottles. [Nowadays, of course, high-quality commercial hydrofluoric acid ($\leqslant$70% HF) is shipped and stored in poly(ethylene) drums with steel overpacks or stout poly(ethylene) bottles).] Fehr places the manufacture of aqueous hydrofluoric acid (30 - 60%) in the United States as "prior to 1876" [26].

[31] Gore wrote [60]:

> "The tube employed by me was 6 feet long and ½ inch diameter, and was kindly lent to me by Messrs. Matthey and Co. ...... Hot junctions in the distillatory apparatus are best made gas-tight by vulcanized indiarubber washers, or by binding them round with ribbon of the thinnest and best quality of vulcanized rubber secured by tarred string."

Great care must always be taken when heating KHF_2 (starting at the apparatus design stage), because the molten salt tends to foam badly; hence spray containing KF is readily carried forward by the HF released, and not infrequently blocks the condenser system. The Americans Mathers and Humiston, who invented the first practical high-temperature fluorine cell (for the electrolysis of fused KHF_2 with a graphite anode and a copper cathode), experienced two explosions when a copper tube leading to a condenser became blocked in this manner [62].

Gore re-distilled his AHF in platinum apparatus to remove entrained potassium fluoride before embarking on his wide-ranging studies of its properties. Amongst other things, he observed the action of AHF on numerous organic materials, using viewing chambers comprising platinum cups cooled to temperatures in the range −7 to −18 °C (ice–$CaCl_2$) and sometimes covered with plates of transparent fluorite.[32] That paper, cotton-wool, or calico were "instantly converted into glutinous substances and dissolved" [60] led eventually to use of the rate of dissolution of filter paper as a test for the quality (absence of water) of HF produced via Frémy's method [63] and to industrial involvement around 1930 in Germany with so-called HF-saccharification of lignocellulosics [64] — biomass conversion technology which has been re-discovered recently [65].

A detailed investigation of AHF production via Frémy's method was mounted about 60 years ago by Karl Fredenhagen and Gustav Cadenbach, who required considerable quantities of the acid for work on its properties as a solvent. At that time, Fredenhagen made important contributions to knowledge of HF burns and their treatment, and, with H. Wellman [17], suggested that calcium gluconate therapy[14] be tried. According to Stahl's pre-1900 review,[30] workers involved in the manufacture of hydrofluoric acid were advised to wear rubber gloves and, should acid come into contact with the skin, to wash it off at once with water and aqueous ammonia or another alkali. Use of an alkaline wash and creams was recommended in 1811 by Gay-Lussac and Thénard [51], who were the first investigators to describe the salient features of HF burns (see p. 15); they suffered from accidental burns and also observed what happened when concentrated hydrofluoric

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[32] In many ways, fluorite was the equivalent of today's poly(tetrafluoroethylene) to the pioneers of fluorine chemistry. For example, the Knox brothers [66] (see later) used it to construct reaction vessels and electrolytic cells for use in their attempts to liberate fluorine; Moissan employed it to make inert insulating stoppers to carry platinum–irridium electrodes in his first successful fluorine cell; and Gore's laboratory was equipped with vessels, plates and stoppers "of fluor-spar" obtained [60] from "Mr J. Tym, Speedwell Mine, Castleton, Derbyshire". Paraffin wax, which is still thus used on occasion, was much prized by Gore as a material unaffected by HF under normal circumstances. He wrote [60]:

> "Paraffin answers admirably for resisting hydrofluoric acid when heat is not applied; it may easily be formed into stoppers, cups, plates, rods, and almost any desired shape; it is, however, liable to become full of cracks when suddenly immersed in a freezing mixture. Temporary stoppers were conveniently made by melting paraffin in a test-tube, and then breaking the tube."

acid (six drops) was applied to the skin of a small dog or (on the point of a needle) to their own skins (to make a comparison with sulphuric and nitric acids). Presumably, subsequent pioneers of fluorine chemistry followed their advice, which included that small blisters should be drained of pus. Gore, who (like Frémy) lived to be an octagenarian, did not mention HF-burn treatment in his lengthy paper [60] on hydrofluoric acid; clearly he was a careful experimentalist. Stahl's 1896 review [61] of commercial hydrofluoric acid describes how plant operatives protected themselves against HF fumes with respirators or, preferably, by tying a handkerchief over nose and mouth and coating unprotected parts of the face with lanolin![33]

Pre-Moissan attempts to isolate fluorine

The initial attempts to prise fluorine out of its compounds were made by Humphry Davy about 70 years before that long-awaited moment on 26th June, 1886, in Paris when Moissan made chemical history by becoming the first to produce the gaseous element in appreciable quantity. Using facilities, techniques, equipment and materials judged to be hopelessly inadequate by today's standards, Davy examined, for example, the action of chlorine on red-hot metal fluorides ("fluates of silver, mercury, potassa and soda") and the electrolysis of hydrofluoric acid [55, 56]; nothing worked, and the manner in which his health must have suffered as he strove for success can be judged from the following passage, which appears in the famous paper published in 1813 [55]:

"I applied the power of the great Voltaic batteries of the Royal Institution to the liquid fluoric acid, so as to take sparks in it. In this case, gas appeared to be produced from both the negative and the positive surfaces; but it was probably only the undecompounded acid rendered gaseous, which was evolved at the positive surface, for during the operation the fluid became very hot, and speedily diminished. The manner in which the surrounding atmosphere became filled with the fumes of the fluoric acid, rendered it, indeed, very difficult to examine the results of any of these experiments; the dangerous action of these fumes have been described by MM. Gay-Lussac and Thénard, and I suffered considerable inconvenience from their effects during this investigation. By mere exposure to them in their uncondensed state, my fingers became sore beneath the nails, and they produced a most painful sensation, which lasted for some hours, when they came in contact with the eyes."

Worse was to befall some others treading in Davy's footsteps: two Irishmen, the Knox brothers (Thomas and George J.), suffered appallingly in the 1830s through inhaling vapour evolved by concentrated hydrofluoric acid (George apparently lost his voice permanently), and the Belgian P. Louyet (1818 - 50) and F. J. Nicklès of Nancy (died 1869) are said to have

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[33] See ref. 67 for an informative account of the professional treatment of hydrofluoric acid burns in the 1930s. This is illustrated with the case histories of 12 patients involved in industrial incidents, and some photographs are included.

died from the effects of breathing HF fumes. As pointed out by Rudge [12], there exists no better or more graphic illustration of the failure by early workers to take adequate precautions than a quotation from a paper written by Louyet a few years before his death:

> "En terminant mon Mémoire, j'ai fait remarquer qu'il est nécessaire de prendre les plus grandes précautions pour se préserver de l'atteinte des vapeurs fluorhydriques, quand on voudra répéter ces expériences; car elles agissent avec la plus grande énergie sur l'économie animale. Tous les chimistes qui se sont occupés du fluor l'ont appris à leurs dépens; MM. Gay-Lussac et Thénard ont fortement insisté sur ses dangereux effets; outre les douleurs aiguës sous les ongles, l'inflammation momentanée des yeux, la fatigue de la vue, on est atteint de maux de poitrine, d'irritation prolongée du larynx, de crachements épais et parfois sanglants et il faut beaucoup de temps pour se rétablir. Il est rare que ses effets soient instantanés et rapides. Le révérend Th. Knox a failli en mourir; le mal n'a disparu qu'en faisant usage de l'acide cyanhydrique pendant six mois. M. George Knox en a ressenti les effets pendant trois années, et a dû aller à Naples pour se rétablir. Quant à moi ma santé en a été profondément altérée, et j'ai craché le sang à plusieurs reprises."

Such events discouraged activity in the area; but note that Bohuslav Brauner [68] of Prague was foolhardy enough in the 1890s to test for fluorine in gases evolved by the hot acid salt K_3HPbF_8 by inhaling a sample and noting whether "fumes of hydrofluoric acid issued from the nose" during exhalation![34]

All of the pioneers, of course, including Moissan faced not only the demanding task of how to deal with hydrogen fluoride (prepare, purify, maintain free from water, and contain; avoid contact with; dispose of; treat burns caused by), but how to devise experiments so that any fluorine generated would not be lost prior to detection and examination via its attack on apparatus, sealants, electrical insulators, reagents or adventitious moisture.

The struggle to isolate fluorine beyond doubt (*i.e.* liberate, collect and characterise) has been reviewed in scientific vein by Mellor [7] (in detail) and, more recently, by Emeléus (concisely) [73]. Weeks and Leicester [19] have covered the events from an historical viewpoint. Reasonable strategies (chemical and electrochemical oxidation of fluorides; thermal or electrical decomposition of metallic and non-metallic fluorides) were adopted — with an eye always for methods analogous to those successful in the case of chlorine. To quote the famous British fluorine chemist H. J. Emeléus (born 1903): "a few of these experiments were probably partially successful, and

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[34] Brauner, who also thought that he might have produced fluorine by heating materials of composition $CeF_4.H_2O$ and $3KF.2CeF_4.2H_2O$ [69], later could not repeat his experiment with the lead tetrafluoride complex [70], neither could the famous German fluorine chemist Otto Ruff confirm the original conclusions [71]. Unsatisfactory accounts exist of claims by American workers to have obtained small amounts of fluorine by Brauner's method [62, 72].

the apparent failure was due to difficulties in isolating the gas, rather than to a wrong choice of reactions." For the record, Mellor refers to "unsuccessful" work by the following fluorine-seekers: H. Davy (published in 1813, 1814), G. Aimé (1833), M. Faraday (1834), C. J. and T. Knox (1836), A. Baudrimont (1836), P. Louyet (1846), E. Frémy (1854, 1856), T. L. Phipson (1861), H. Kammerer (1862), J. P. Prat (1867), P. Cillis (1868), G. Gore (1869, 1870, 1871), L. Varenne (1880), O. Loew (1881), B. Brauner (1881), H. B. Dixon and H. B. Baker (1883), and H. Moissan (1884).

Ampère's suggestion (see p. 10) that electrolysis of hydrofluoric acid might yield fluorine was followed up vigorously by Davy (see p. 20), G. J. Knox [66], Faraday [74] and Gore [60, 75], but they only succeeded in decomposing water. AHF is virtually a non-conductor of electricity,[35] and Gore showed that traces of adventitious water greedily picked up by AHF (thus providing conductivity: $H_2O + 2\ HF \rightleftharpoons H_3O^+ + HF_2^-$) can be removed by electrolysis.[36] In addition to testing numerous anode materials (platinum, palladium, silver, gold and numerous types of carbon) in would-be fluorine cells made from cathodic platinum cups [60, 75], Gore worked hard trying to displace fluorine from silver monofluoride with the other halogens, principally chlorine [75, 76]. Would Gore have produced a steady flow of fluorine, one wonders, if, like Moissan on 26th June, 1886 [18], he had electrolysed AHF derived from Frémy's salt but not freed from entrained potassium fluoride? He certainly had no success with molten Frémy's salt (platinum electrodes) [60], the electrolyte employed for fluorine generation by Mathers *et al.* during World War I (see p. 19) [62]; neither did one of ICI's experts, A. J. Rudge [12], much more recently ("..... platinum anode. The anode was attacked very rapidly and no free fluorine could be detected.").

Frémy seems not to have thought [77] of turning to potassium bifluoride (m.p. 239 °C) as an electrolyte when he encountered technical problems and vicious destruction of platinum anodes by nascent fluorine at the temperature required to keep potassium fluoride (m.p. 846 °C) molten. Despite the difficulties, however, it appears that he was able to produce a small quantity of fluorine prior to 1856 via electrolysis of molten potassium fluoride in a cylindrical platinum crucible (the cathode) fitted with a stout wiry anode of the same metal; in his own words [57]:

"Il se dégage, par le col de la cornue de platine, un gaz odorant qui décompose l'eau en produisant de l'acide fluorhydrique, et qui déplace l'iode contenu dans les iodures: ce gaz me parait être le fluor."

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[35] The electrical conductivity of re-distilled commercial AHF at −15 °C is 1.4×10^{-5} Ω^{-1} cm^{-1} (dielectric constant 84 at 0 °C [58]; *cf.* H_2O, 5.7×10^{-8} Ω^{-1} cm^{-1} at 20 °C and 78, respectively).

[36] This trick is still used today, *e.g.* for drying commercial AHF after it has been transferred from commercial cylinders to Simons' electrofluorination cells (see p.) and, inevitably, picked up moisture en route [78].

Enter Moissan

At the time of Frémy's frustration, the man who eventually succeeded where so many eminent chemists had failed was but a child. He rose to achieve the highest distinction as an inorganic chemist, the 'isolation' of fluorine being but part of his massive contribution to the subject as a whole. As Sir William Ramsay remarked in his Moissan Memorial Lecture delivered on 29th February, 1912 [79], Henri Moissan "contributed to turn the tide which had set so long in favour of organic research". "In the domain of chemistry", declared Ramsay, "many names of illustrious Frenchmen suggest themselves; Lavoisier, Guyton de Morveau, Berthollet, Gay-Lussac, Dumas, and Berthelot stand out among a crowd of others hardly less distinguished ..... it is my duty tonight to ask you to listen to a brief discourse on a contemporary of Bethelot, who, though cut off by fate at a comparatively early age, stood only second to him among the representatives of chemistry in France in his time". Others might well have ranked Moissan higher.

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