SOME GENERAL ASPECTS OF THE INORGANIC CHEMISTRY OF FLUORINE

By A. G. Sharpe, M.A., Ph.D.
(University Chemical Laboratory, Cambridge)

Recent advances in the descriptive inorganic chemistry of fluorine and its compounds have been the subject of several reviews,[1] but their correlation and interpretation in terms of measurable physical properties have rarely been discussed. The aim of this Review is to describe briefly some of the principal properties of the fluorine molecule, the fluorine atom, and the fluoride ion, and to show how a knowledge of these properties can help in the understanding of the chemistry of fluorine and its relationship to the other halogens.

The Physical Properties of Fluorine.—*Interatomic Distance.* The values obtained by the electron diffraction [2] and the Raman spectroscopic [3] method (1·435 and 1·418 Å respectively) are in good agreement, and the covalent radius of fluorine (the bond being assumed to be of unit order—see p. 50) may be taken as 0·71 Å. Since the corresponding radii for chlorine, bromine, and iodine are 0·99, 1·14, and 1·33 Å, the volume of a fluorine atom in the combined state is only one-third of that of a chlorine atom and less than one-sixth of that of an atom of iodine.

Dissociation Energy. This quantity (the energy absorbed when a gaseous molecule is converted into two atoms in the ground state) has been the subject of much controversy. Fluorine does not show banded absorption in the visible or ultraviolet region (presumably because of the instability of the excited state) and spectroscopic determination of $D(F_2)$ is therefore impossible. Older values for the dissociation energy were usually based, explicitly or implicitly, on extrapolation of those for chlorine, bromine, and iodine (58·0, 46·1, and 36·1 kcal., respectively), and were of the order of 60—70 kcal. In 1950, however, Evans, Warhurst, and Whittle,[4] on the basis of recent work on the thermochemistry and absorption spectrum of chlorine monofluoride, suggested that the true value was 37 ± 8 kcal. Most later investigations support this lower figure; the following determinations may be taken as representative.

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[1] (*a*) Simons, Editor, " Fluorine Chemistry ", Academic Press Inc., New York, Vol. I, 1950; Vol. II, 1954; (*b*) Haszeldine and Sharpe, " Fluorine and its Compounds ", Methuen and Co., Ltd., London, 1951; (*c*) Gutmann, *Angew. Chem.*, 1950, **62,** 312; (*d*) Sharpe, *Quart. Rev.*, 1950, **4,** 115; (*e*) Leech, *Research*, 1952, **5,** 108, 449; (*f*) Emeléus, *J.*, 1954, 2979; (*g*) Klemm, *Angew. Chem.*, 1954, **66,** 470; (*h*) Rudge, *Chem. and Ind.*, 1956, 504; (*i*) Mellor, " A Comprehensive Treatise on Inorganic and Theoretical Chemistry ", Suppl. II, Part I, Longmans, Green and Co., Ltd., London, 1956.

[2] Rogers, Schomaker, and Stevenson, *J. Amer. Chem. Soc.*, 1941, **63,** 2610.

[3] Andrychuk, *Canad. J. Phys.*, 1951, **29,** 151.

[4] Evans, Warhurst, and Whittle, *J.*, 1950, 1524.

(i) Doescher [5] studied the pressure–temperature relationship for fluorine in a pre-treated nickel vessel, over the temperature range 759—1115° K, by comparing the pressure with that of nitrogen at the same temperature, using a differential manometer containing a fluorocarbon oil. His results indicate a value for $D(F_2)$ at 25° of $37{\cdot}4 \pm 0{\cdot}4$ kcal.

(ii) From observation of the rate of effusion of fluorine at low pressures through a small hole (a method which permitted the use of relatively low temperatures, 500—650° K), Wise [6] found $D(F_2) = 39{\cdot}9 \pm 0{\cdot}8$ kcal.

(iii) Barrow and Caunt [7] determined the dissociation energies of the potassium, rubidium, and cæsium halides spectroscopically, and combined their results with independently obtained thermochemical data for these substances and the alkali metals:

$$\tfrac{1}{2}D(F_2) = D(MF) + L(MF) - L(M) - Q(MF)$$

where $Q(MF)$ is the heat of formation of a solid fluoride MF from solid M and gaseous F_2, and $L(MF)$ and $L(M)$ are the heats of sublimation of the fluoride and of the alkali metal respectively. They obtained $D(F_2) = 37{\cdot}6 \pm 3{\cdot}5$ kcal.

In this Review the dissociation energy is henceforth taken to be 38 kcal.

This low value is generally ascribed to the repulsion of non-bonding electrons in the F_2 molecule, but it has also been suggested that for chlorine, bromine, and iodine hydridisation of *p*- and *d*-valence shell orbitals strengthens the bonding.[4, 8] The nice distinction between the bond in fluorine being abnormally weak and the bonds in the other halogens being abnormally strong is essentially a theoretical matter. It should, however, be pointed out that the N–N and O–O bond energies (21 and 35 kcal. in N_2H_4 and H_2O_2 respectively [9]) are also low, and that here, too, repulsion of non-bonding electrons of small atoms may well be the cause.

Thermodynamic Properties. The usual thermodynamic functions for atomic and molecular fluorine have been calculated [10] from the interatomic distance,[2] the fundamental vibration frequency,[3] and Doescher's value [5] for $D(F_2)$. Two important points may be noted. First, fluorine is dissociated into atoms to a greater extent than chlorine at the same temperature, and since reactions of atomic fluorine are strongly exothermic the great reactivity of the element may be attributed to the weakness of the bond in the F_2 molecule. Secondly, since the standard entropies of molecular and atomic fluorine (48·6 cal. mole^{-1} deg.^{-1} and 37·9 cal. g.-atom^{-1} deg.^{-1}) differ but little from those of molecular and atomic chlorine (53·3 and 39·5 entropy units [11]), differences between the two halogens are due to heat effects (*e.g.*, the strengths of bonds) rather than to entropy effects. This generalisation holds, in fact, for all the halogens.

Ionisation Potential. The energy required for removal of an electron

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[5] Doescher, *J. Chem. Phys.*, 1952, **20**, 330.

[6] Wise, *ibid.*, p. 927.

[7] Barrow and Caunt, *Proc. Roy. Soc.*, 1953, *A*, 219, 120.

[8] Mulliken, *J. Amer. Chem. Soc.*, 1955, **77**, 884.

[9] Cottrell, " The Strengths of Chemical Bonds ", Butterworths Scientific Publications, London, 1954.

[10] Cole, Farber, and Elverum, *J. Chem. Phys.*, 1952, **20**, 586.

[11] Nat. Bur. Stand. Tables, Circular No. 500.

from atomic fluorine is 401 kcal./g.-atom.[12] This figure, combined with that for $D(F_2)$, leads to a standard heat of formation of the gaseous F^+ ion of 420 kcal./g.-ion. Such a high value (those for Cl^+, Br^+, and I^+ are 327, 301, and 268 kcal., respectively [11]) suggests that even solvated fluoronium ions are unlikely to be encountered in chemical investigations; there is, in fact, at the present time no evidence of any kind for the existence of "positive fluorine".

Electron Affinity. The classical method for determining the heat liberated, E, when gaseous halogen atoms combine with electrons, giving gaseous halide ions, is by the Born cycle:

$$E(\mathrm{X}) = Q(\mathrm{MX}) + L(\mathrm{M}) + I(\mathrm{M}) + \tfrac{1}{2}D(\mathrm{X}_2) - U(\mathrm{MX})$$

where $I(\mathrm{M})$ is the first ionisation potential of the alkali metal M, and $U(\mathrm{MX})$ the lattice energy of the solid halide MX (the heat liberated when one formula weight is produced from gaseous M^+ and X^- ions). U may be calculated from the interionic distance, r, in solid MX (determined by *X*-ray analysis) and the compressibility of the solid by an expression of the type

$$U = NMz_1z_2e^2(1 - 1/n)/r$$

where M, the Madelung constant, is a geometrical constant for a particular type of structure, z_1 and z_2 are the charges on the ions, e the electronic charge, N the Avogadro number, and n a constant (about 9) which takes account of interionic repulsion arising from the finite size of the ions.

This method when applied to fluorine yields $E(\mathrm{F}) = 84 \pm 2$ kcal./g.-atom,[13] a value intermediate between those for chlorine and bromine (88 and 82 kcal./g.-atom, respectively). This somewhat surprising result is, as was first pointed out by Evans, Warhurst, and Whittle,[4] an inescapable consequence of the low value of $D(F_2)$; it must, however, be remembered that additional factors are always involved in determining the stability of compounds containing fluoride ions.

The Valency of Fluorine.—The electronic configuration of the fluorine atom is $1s^22s^22p^5$, and expansion of the valency shell beyond $2s^22p^6$ is impossible. It is known from the atomic spectrum of fluorine that promotion of an electron to the $3s$, $3p$, or $3d$ level is a highly endothermic process; this, of course, provides no direct evidence concerning the possibility of promotion in a stable molecule, but comparison with other first-row elements strongly suggests that fluorine should be exclusively univalent.[14] With the possible exception of the difluorides and trifluorides of the alkali metals [15] (*e.g.*, RbF_3, obtained by the action of fluorine on rubidium chloride at 150°) this generalisation seems valid for all fluorine compounds. Rubidium trifluoride must obviously contain multivalent rubidium or multivalent fluorine; the structure $Rb^{3+}F_3$ is inadmissible on energy considerations, but a decision between structures such as $Rb^+F_3^-$ and $Rb^+(RbF_6)^-$ is at present impossible.

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[12] Nat. Bur. Stand. Tables, Circular No. 467.

[13] Pritchard, *Chem. Rev.*, 1953, **52**, 529.

[14] Gillespie, *J.*, 1952, 1002.

[15] Bode and Klesper, *Z. anorg. Chem.*, 1951, **267**, 97. For a discussion of the structure of RbF_2 see also Sharpe, Ref. 1(*a*), Vol. II p. 2.

The Physical Properties of the Fluoride Ion.—*Ionic Radius.* *X*-Ray structure determinations yield information about atomic positions, and for the division of interionic distances into ionic radii the introduction of certain hypotheses is necessary. The simplest of these is that in the lithium halides the anions are in contact; this and a variety of other more elaborate methods[16] lead to the values F^-, 1·36; Cl^-, 1·81; Br^-, 1·95; I^-, 2·16 Å.

The fluoride and oxide ions are of almost identical size [$r(O^{2-}) = 1{\cdot}40$ Å], and thence arises the similarity in structure which is often found between oxides and fluorides of the same formula type (*e.g.*, MgO and NaF); fluorides and chlorides of the same metals, however, often have quite different structures (*e.g.*, CdF_2 and HgF_2 both crystallise with the fluorite structure, but $CdCl_2$ has a layer lattice in which the Cd^{2+} ion has co-ordination number six, and $HgCl_2$ has a molecular lattice). The crystal chemistry of both simple and complex fluorides is admirably discussed by Wells.[17]

Heat and Entropy of Hydration. When an ionic crystal dissolves in water, the sum of the heats of hydration of the ions must equal the lattice energy of the solid plus the heat of solution. Two principal difficulties attend the assignment of individual heats of hydration: uncertainty over the values for ionic radii in solution [which would enable approximate values to be calculated from Born's expression $Ne^2(1 - 1/D)/2r$, where D is the dielectric constant of the medium], and the absence of any precise knowledge of the structure of hydrated ions. Differences in heats of hydration, however, are not subject to the same uncertainty: *e.g.*, the heats of solution of sodium fluoride and sodium chloride are both very small, and since their lattice energies at 25° are 215·4 and 183·5 kcal. respectively, the heat of hydration of F^- must be 32 kcal. greater than that of Cl^-. The absolute values are estimated[18] to be F^-, 123; Cl^-, 89 kcal.; these lead to standard heats of formation of the hydrated ions of 188 and 148 kcal.*

A similar position exists with regard to entropies of hydration, which have to be obtained from entropies of solid salts, entropy changes attending dissolution, and entropies of gaseous ions calculated by statistical mechanics; the estimated values[18] for fluoride and chloride ions (F^-, -29; Cl^-, -15 cal. g.-ion^{-1} deg.$^{-1}$) are, however, so similar that (as with molecules and atoms) entropy changes in fluoride–chlorine substitutions may almost be neglected in comparison with the big difference in heats of hydration: the standard free energies of hydration are F^-, -114; Cl^-, -84 kcal.

The Standard Potential of the Fluorine–Fluoride Ion Electrode.[19] An

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[16] Pauling, " The Nature of the Chemical Bond ", 2nd edn., Cornell Univ. Press, Ithaca, New York, 1940.

[17] Wells, " Structural Inorganic Chemistry ", 2nd edn., Oxford Univ. Press, 1950; *Quart. Rev.*, 1954, **8**, 380.

[18] Latimer, Pitzer, and Slansky, *J. Chem. Phys.*, 1939, **7**, 108.

[19] Latimer, " The Oxidation States of the Elements and their Potentials in Aqueous Solutions ", 2nd edn., Prentice-Hall, Inc., New York, 1952.

* It should be noted that these are absolute values; the National Bureau of Standards values[11] are based on a standard heat of formation of the hydrated hydrogen ion of zero. This practice is more convenient in thermochemistry, because of the uncertainty in the magnitude of the hydration energy of the proton

indirect calculation of E^0 for the $\frac{1}{2}F_2/F^-_{(aq)}$ electrode from related thermochemical data leads to a value of +2·8 v (relative to E^0 for the $\frac{1}{2}H_2/H^+_{(aq)}$ electrode as zero). The corresponding value for chlorine is +1·36 v. The figure for fluorine expresses the fact that it is the most powerful oxidising agent known, and explains why the element can be prepared only by thermal decomposition of a few higher fluorides (such as cobalt trifluoride) or by electrolysis of solutions of fluorides in media (such as hydrogen fluoride) in which no other anion is present.

The factors which determine the oxidation potential of a halogen may be seen by considering the following sequence :

$$\tfrac{1}{2}X_{2(g)} \longrightarrow X_{(g)} \longrightarrow X^-_{(g)} \longrightarrow X^-_{(aq)}$$

The first stage involves absorption of energy equal to one-half of the dissociation energy, the second stage the liberation of the electron affinity, and the third stage the liberation of the hydration energy. Although, therefore, the electron affinity of fluorine is lower than that of chlorine, the weaker bond in the F_2 molecule and the higher hydration energy of the smaller fluoride ion make fluorine the more powerful oxidising agent.

The Electronegativity of Fluorine.[16, 20]—All of the quantities mentioned hitherto, however difficult their measurement may be, are easily defined. The concept of electronegativity, however, calls for some comment. The strength of trifluoroacetic acid, the absence of basic properties in the fully fluorinated amine $(CF_3)_3N$, and the retardation of attack by electrophilic reagents in aromatic substitution when the CH_3 group of toluene is replaced by CF_3, all suggest that fluorine in such molecules attracts electrons. This " power of an atom in a molecule to attract electrons to itself " [16] is what most chemists mean by electronegativity, but unfortunately this quantity is not susceptible to direct experimental measurement. (It is, indeed, an assumption that each element has a numerically expressible electronegativity which remains constant through its compounds.)

Three principal methods for the assessment of electronegativity have been suggested. Mulliken proposed taking the mean of ionisation potential and electron affinity ; in this context, however, it is the ionisation potential of the element in its valency state (which has to be estimated) that is required. Malone related electronegativity to dipole moments ; unfortunately, *bond* dipole moments (as distinct from molecular moments) are not in general measurable, since the effect of unshared pairs of electrons on the moment is considerable. This is clearly illustrated by the fact that nitrogen trifluoride, although having a pyramidal structure with $\angle FNF = 102°$ and N–F = 1·37 Å, has a dipole moment of only 0·2 D. Pauling's scale rests on a number of unproven assumptions, but does have the advantage of being related to molecular properties. The energy of a normal single covalent bond between two elements A and B (*e.g.*, H_2 and F_2) is taken to be the mean of the bond energies in A_2 and B_2. The difference in electronegativity of A and B, $x_A - x_B$, is then taken as

$$x_A - x_B = 0{\cdot}208[E_{AB} - (E_{AA} + E_{BB})/2]^{\frac{1}{2}}$$

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[20] Pritchard and Skinner, *Chem. Rev.*, 1955, **55**, 745.

where E_{AB} is the actual bond energy in AB (in kcal.), and the expression in square brackets is regarded as " extra " bond energy arising from the partial ionic nature of the A–B bond. This relationship does lead to a fairly self-consistent set of electronegativities, and if x_H is arbitrarily taken to be 2·1 (in order to make all values of x positive) x_F is found to be 4·0, making fluorine easily the most electronegative element. Bond energies in fluorine compounds are discussed again later.

Some Properties of Inorganic Fluorine Compounds

The Dissociation of Hydrogen Fluoride in Aqueous Solution.—The large dipole moment of hydrogen fluoride (1·9 D at pressures so low that association is negligible [21]) shows the bond in this compound to be strongly polar, and the chain structure in the solid [22] (the other hydrogen halides have close-packed structures) arises from dipole–dipole interaction. In dilute aqueous solution, however, hydrogen fluoride is a much weaker acid than the other hydrogen halides. This fact, when considered in conjunction with the well-known increase in dissociation constant along the series $CH_3{\cdot}CO_2H$, $CH_2I{\cdot}CO_2H$, $CH_2Br{\cdot}CO_2H$, $CH_2Cl{\cdot}CO_2H$, and $CH_2F{\cdot}CO_2H$, at first seems surprising ; in the carboxylic acids, however, ionisation always involves the breaking of the same bond, whereas in the hydrogen halides the bonds to be broken are all different. The general process of ionisation may be represented as taking place in the following stages : [23, 24]

$$HX_{(aq)} \rightarrow HX_{(g)} \rightarrow H{\cdot}_{(g)} + X{\cdot}_{(g)} \rightarrow H^+_{(g)} + X^-_{(g)} \rightarrow H^+_{(aq)} + X^-_{(aq)}$$

The stages involving the conversion of a hydrogen atom into a solvated proton are the same for all acids, and only four variables have to be considered : the energy of solution of the undissociated molecule, the dissociation energy of the H–X bond, the electron affinity of X, and the solvation energy of X^-. The first factor is approximately the same for all of the halides, the electron affinity of fluorine lies between those of chlorine and bromine, and the hydration energy of the F^- ion is much larger than those of other halide ions. The decisive factor must therefore be the strength of the bond in hydrogen fluoride (Bond energies : HF, 135 ; HCl, 103 ; HBr, 87 ; HI, 71 kcal.). In more concentrated solutions (5—15M), ionisation into H_3O^+ and HF_2^-, $H_2F_3^-$, and $H_3F_4^-$ takes place, and hydrogen fluoride becomes a strong acid.[25] The formation of these stable acid anions in liquid hydrogen fluoride accounts for the great proton-donating (*i.e.*, acidic) properties of this solvent.

Hydrogen Bonding in Fluorine Compounds.—As the most electronegative element, fluorine would be expected to take part in hydrogen bond formation, and some of the best known instances of this phenomenon do, in fact,

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[21] Oriani and Smyth, *J. Amer. Chem. Soc.*, 1948, **70**, 125.

[22] Atoji and Lipscomb, *Acta Cryst.*, 1954, **7**, 173.

[23] Bell, " Acids and Bases ", Methuen and Co., Ltd., London, 1952.

[24] McCoubrey, *Trans. Faraday Soc.*, 1955, **51**, 743.

[25] Bell, Bascombe, and McCoubrey, *J.*, 1956, 1286.

involve covalently bonded fluorine or the fluoride ion. The structural difference between hydrogen fluoride and other hydrogen halides has already been mentioned ; the strength of the bonding in the HF_2^- ion is also remarkable. The fluorine–fluorine distance in this ion is only 2·26 Å, and a neutron-diffraction study [26] of potassium hydrogen difluoride shows that the hydrogen is (to within 0·1 Å) in the middle of the linear ion. The structure of ammonium fluoride differs completely from those of the other ammonium halides (which crystallise with the sodium chloride or cæsium chloride structure) ; in this salt (which has the wurtzite structure) each nitrogen atom forms four N–H–F bonds of length 2·69 Å to the four fluoride ions arranged tetrahedrally around it.[27] The N–H vibration frequency is lowered from its normal value of about 3300 $cm.^{-1}$ to 2820 $cm.^{-1}$; rather surprisingly, nuclear magnetic resonance studies [28] indicate that this reduction in the N–H vibration frequency is not accompanied by any considerable stretching of the N–H bond (length in NH_4F, 1·04 ; in NH_4Cl, 1·038 Å). In hydrazinium fluoride, however (the structure of which is also determined by hydrogen bonding), a slightly greater N–H distance of 1·075 Å is reported.[29]

It should not be thought that all ammonium salts of fluoro-acids exhibit strong hydrogen bonding. In salts of complex acids this is certainly not so ; a wide variety of evidence (*X*-ray studies,[30–32] infrared spectra,[32, 33] and nuclear-resonance spectra [34]) suggests that in salts such as NH_4BF_4 and $(NH_4)_2TiF_6$ there can be no more than very weak hydrogen bonding. This somewhat unexpected conclusion shows that the participation of fluorine in hydrogen-bond formation is not nearly so general as that of nitrogen or oxygen. No satisfactory explantion of this fact has yet been put forward, and the recent discovery [35] of the HCl_2^- ion indicates that it may soon be necessary to modify present ideas about hydrogen bonding and its relation to the electronegativities of the halogens.

Fluorides of Non-metals : Bond Energies and Bond Lengths.—Fluorine often invokes highest covalencies (*e.g.*, in SF_6, IF_7), and although steric factors must be of some importance in this connection, a satisfactory discussion of this topic must involve consideration of the energy changes involved. The formation of sulphur hexafluoride may be represented as taking place in the following stages :

$$\begin{tikzcd}
S_8\text{ (solid)} \arrow[r] & S\text{ (gas ; ground state }3s^23p^4) \arrow[dr] & \\
 & & S\text{ (gas ; valency state }3s^13p^33d^2) \arrow[d] \\
3F_2\text{ (gas)} \arrow[r] & 6F\text{ (gas)} \arrow[r] & SF_6\text{ (gas)}
\end{tikzcd}$$

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[26] Peterson and Levy, *J. Chem. Phys.*, 1952, **20**, 704.

[27] Plumb and Hornig, *ibid.*, 1955, **23**, 947.

[28] Drain, *Discuss. Faraday Soc.*, 1955, **19**, 200.

[29] Deeley and Richards, *Trans. Faraday Soc.*, 1954, **50**, 560.

[30] Hoard and Blair, *J. Amer. Chem. Soc.*, 1935, **57**, 1985.

[31] Cox and Sharpe, *J.*, 1953, 1783.

[32] *Idem*, *J.*, 1954, 1798.

[33] Coté and Thompson, *Proc. Roy. Soc.*, 1951, *A*, **210**, 217.

[34] Pendred and Richards, *Trans. Faraday Soc.*, 1955, **51**, 468.

[35] Herbrandson, Dickerson, and Weinstein, *J. Amer. Chem. Soc.*, 1954, **76**, 4046.

In considering why sulphur forms a hexafluoride but not a hexahydride or a hexachloride the fundamental question to be answered is : will the energy liberated by bond formation in the compound compensate for the energy required to raise the sulphur atom from its ground state to its valency state and to effect dissociation of the halogen (or hydrogen) molecules ? In general (molecular fluorine constitutes an exception, and is discussed again below), smaller atoms form stronger bonds, a fact which is simply accounted for on modern valency theory by the greater overlapping of orbitals of low principal quantum number. Equally important, however, is the dissociation energy of the halogen (or hydrogen), and the low value for fluorine (F_2, 38 ; Cl_2, 58 ; H_2, 104 kcal.) is probably the most important factor in this case. Because of the weakness of the bond in molecular fluorine, most fluorine compounds are strongly exothermic (this term, it will be remembered, refers to heats of formation from elements *in their standard states*) ; conversely, because of the strength of the bond in molecular nitrogen (225 kcal.[36]) most nitrogen compounds containing a high proportion of the element are endothermic. The widely quoted fact that nitrogen trifluoride is an exothermic compound ($Q_f = +26$ kcal.) whilst the trichloride is endothermic ($Q_f = -55$ kcal.) thus represents a case essentially similar to the existence of SF_6 but not of SCl_6 or SH_6.

In discussing electronegativity, it was mentioned that bonds involving fluorine are usually much stronger than would be expected on the basis of an " arithmetic mean " rule. They are also much shorter than values calculated by adding standard covalent radii : the universally accepted carbon–carbon single bond length, for example, is 1·54 Å, and F–F in F_2 is 1·42 Å ; C–F in CF_4, however, is only 1·32 Å.[37] Similarly, unexpectedly short bonds have also been found in fluorides of silicon, nitrogen, phosphorus, arsenic, oxygen, and sulphur. For first-row elements such as carbon, multiple bond formation appears to be impossible in these compounds, and a suggestion which has met with much favour is that the observed bond length should be less than the sum of the covalent radii by an amount proportional to the difference between the Pauling electronegativity coefficients of the elements concerned, the actual length being given by the *empirical* Schomaker–Stevenson equation : [38]

$$r_{AB} = r_A + r_B - 0{\cdot}09(x_A \sim x_B)$$

The general applicability of this relation has been severely criticised by Wells,[39] but the qualitative conclusion that bonds between fluorine (and, to a smaller extent, oxygen, nitrogen, and chlorine) and less electronegative elements are shorter than expected on the basis of a simple additivity rule is unchallenged.

These generalisations about the energies and lengths of bonds involving fluorine suggest that perhaps it is once again a property of the reference

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[36] McDowell, *Proc. Roy. Soc.*, 1956, *A*, **236,** 278.

[37] Hoffman and Livingston, *J. Chem. Phys.*, 1953, **21,** 565.

[38] Schomaker and Stevenson, *J. Amer. Chem. Soc.*, 1941, **63,** 37.

[39] Wells, *J.*, 1949, 55 ; ref. 17, p. 56.

standard (the F_2 molecule) which lies at the root of the matter. If the weak bond in the fluorine molecule is due to repulsion of non-bonding electrons, it seems not unreasonable that as the molecule is split into atoms, which then combine with elements to form compounds in which there are few or no unshared electrons on the central atom (*e.g.*, CF_4, SF_6), such repulsion should disappear. This, it is suggested, may be the reason for the " abnormal " strength and shortness of bonds in other compounds formed between elements of widely differing electronegativities (*e.g.*, C and O, P and O, Si and F).

The stability of non-metal fluorides (especially of CF_4 and SF_6) is often cited as a remarkable feature of fluorine chemistry, and it is not always realised that these compounds are not *thermodynamically* particularly stable. The free energies of the following hydrolytic reactions (neither of which proceeds at a detectable rate under ordinary experimental conditions) have been calculated from standard thermochemical data :[11, 39a]

$$CF_{4(g)} + 2H_2O_{(g)} = CO_{2(g)} + 4HF_{(g)} \qquad \Delta G^o = -36 \text{ kcal.}$$

$$SF_{6(g)} + 3H_2O_{(g)} = SO_{3(g)} + 6HF_{(g)} \qquad \Delta G^o = -72 \text{ kcal.}$$

They show that the inertness of the fluorides must be due to activation-energy considerations ; these may well involve the failure of a water molecule to co-ordinate on to a combined fluorine atom (because of the octet restriction), but it cannot be said that a convincing explanation has yet been given.

Fluorides of Metals.—Two general features stand out in the chemistry of metal fluorides : first, many metals show their highest oxidation states attained in salts in their fluorides (*e.g.*, Co in CoF_3, Ag in AgF_2, Bi in BiF_5, Tb in TbF_4, Rh in RhF_4) ; secondly, many fluorides of high oxidation states are salt-like in properties where the corresponding chlorides are not (*e.g.*, AuF_3, PbF_4, TlF_3). (The highest fluorides of many transition metals, *e.g.*, MoF_6, UF_6, OsF_8, are volatile and generally resemble the fluorides of non-metallic elements.) Both of these generalisations are illuminated by consideration of a modified Born cycle. Suppose, for example, the possibility of a metal's forming a saline tetrahalide is examined by analysing the stages involved :

$$\begin{tikzcd}
M_{(s)} \arrow[r] & M_{(g)} \arrow[r] & M^{4+}_{(g)} \arrow[dr] & \\
 & & & MX_{4(s)} \\
2X_{2(g)} \arrow[r] & 4X_{(g)} \arrow[r] & 4X^{-}_{(g)} \arrow[ur] &
\end{tikzcd}$$

In this context the latent heat of sublimation of the metal will be relatively small ; for all of the halogens the sum of $E - D/2$, which represents the net energy change in forming a gram-ion of halide ions from half a gram-molecule of molecules, is about 60 kcal. The essential question is then : will $4(E - D/2)$ plus the lattice energy of MX_4 compensate for the energy required to remove four electrons from the metal atoms ? In the absence of a knowledge of the structure (and thence the lattice energy, if the calculation

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[39a] Kirkbride and Davidson, *Nature*, 1954, **174**, 79.

is simple enough) of the halide, no precise answer to this question can be given ; but since the lattice energy will depend inversely on the interionic separation it will clearly be a maximum when, for a given cation, the radius of the anion is a minimum. This condition is fulfilled by the anion's being fluoride.

The other common anion of similar size (O^{2-}) involves the absorption of a large amount of energy when it is formed from molecular oxygen ; this is, however, largely compensated for by the double charge and the consequent increase in the electrostatic lattice energy. It is not, therefore, surprising that ionic oxidation states in oxides are often as high as, or even higher than, those in fluorides (*e.g.*, MnO_2, AgO, PrO_2), or that many salt-like fluorides (*e.g.*, AuF_3, PbF_4, CoF_3) are hydrolysed by water with the formation of very insoluble oxides and fluoride ions ; the high hydration energy of the fluoride ion is also an important factor in bringing about hydrolysis.

One further argument which may be developed from the simple electrostatic treatment concerns the use of alkali-metal fluorides as halogen-exchange reagents in organic chemistry. If we consider the replacement

$$\mathrm{{>}C{-}Cl} + \mathrm{MF} \longrightarrow \mathrm{{>}C{-}F} + \mathrm{MCl}$$

where M = Na or K, the driving force of the reaction will depend on the free-energy difference (or, fairly accurately, the difference in lattice energy) between sodium fluoride and sodium chloride on the one hand and potassium fluoride and potassium chloride on the other. Lattice energy being inversely proportional to interionic distance, the increase in free energy when sodium chloride is formed from the fluoride will be proportional to

$$[1/(r_{\mathrm{Na}^+} + r_{\mathrm{F}^-}) - 1/(r_{\mathrm{Na}^+} + r_{\mathrm{Cl}^-})]$$

and it is easily seen that for a larger cation the amount of free energy which has to be supplied by the C–Cl ⟶ C–F change is less.

Fluorine-exchanging ability therefore increases steadily with increasing ionic size among fluorides of metals which form isomorphous compounds.[40] In the special case of the use of silver fluoride, it is easily shown from independent thermochemical data that the difference in lattice energy between silver fluoride and silver chloride is very small (owing to the contribution of non-ionic bonding in solid silver chloride) ; hence arises the especial power of silver fluoride as a halogen-exchange reagent.

Complex Fluorides and Fluoro-acids.—The factors which govern the stability of complex fluoro-ions will be similar to those concerned with the stabilities of simple fluorides. Among complex fluorides, the relatively small size of the anions (thus leading to increased lattice energy) will play an important part ; and within recent years, especially by the use of elemental fluorine at medium temperatures,[41] and of bromine trifluoride as a

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[40] Woyski, *J. Amer. Chem. Soc.*, 1950, **72**, 919.

[41] Klemm and Huss, *Z. anorg. Chem.*, 1949, **258**, 221, and later papers by Klemm and his co-workers.

non-aqueous solvent and fluorinating agent,[42, 43] many new complexes of unusual oxidation states have been obtained (*e.g.*, Cs_2CoF_6, K_2NiF_6, K_3CuF_6, K_2RhF_6, $KIrF_6$, $AgAuF_4$). Most of these compounds are hydrolysed to oxides by water.

Although, for base metals, fluorides are the most stable complex halide ions in solution, the reverse is true for noble metals such as platinum and gold.[44] This is often interpreted as being due to π-bond formation between the noble metal and chlorine, bromine, or iodine, *d*-electrons of the metal being used for this purpose.[45] Fluorine would not be able to accept more electrons and the bonds in complex fluorides would therefore necessarily be devoid of multiple character with its consequent strengthening effect. It must, however, be pointed out that this is not the only factor involved in an equilibrium such as

$$PtF_6^{2-} + 6Cl^- \rightleftharpoons PtCl_6^{2-} + 6F^-$$

and that the larger solvation energy of the fluoride ion must also play an important part in influencing the stability of the complex.

All complex fluoro-acids (and, indeed, complex halogeno-acids in general) are extremely strong. The univalency of fluorine provides a simple and convincing explanation of this fact in a case such as fluoroboric acid, where the formulation of the undissociated molecule HBF_4 is impossible without invoking quinquevalent boron or bivalent fluorine. A study of the HF–BF_3 system has shown the non-existence of a 1 : 1 compound ; only if a molecule such as NH_3, H_2O, or a second molecule of HF is available to combine with the proton (giving $NH_4^+BF_4^-$, $H_3O^+BF_4^-$, or $H_2F^+BF_4^-$) will the compounds combine. Reasonable formulæ for other undissociated molecules such as HPF_6, H_2SiF_6, and H_2PtCl_6 (none of which is known in the free state) are also impossible.

Because of the impossibility of a fluoroborate's having a covalent structure, this ion is very useful in studies in which it is desirable to be sure of the ionic nature of bonding, *e.g.*, in the interaction of silver salts and aromatic hydrocarbons[46] ($AgBF_4$ is soluble in, and forms stable complexes with, these substances), and in the investigation of the spectra of organic cations[47] (*e.g.*, Ph_3C^+ in $Ph_3C^+BF_4^-$). A mixture of hydrogen fluoride and boron trifluoride is, indeed, the most acidic solvent known, and in it even so weak a base as hexamethylbenzene is largely converted into the salt $[C_6(CH_3)_6H]^+BF_4^-$.[48, 49]

Conclusion.—The principal properties which confer on fluorine its remarkable chemical behaviour are the smallness of the fluorine atom and the fluorine ion, the restriction to an octet of electrons, and the weakness of

[42] Sharpe, *J.*, 1949, 2901, and later papers.

[43] Hepworth, Robinson, and Westland, *J.*, 1954, 4268.

[44] Sharpe, *J.*, 1950, 3444 ; Carleson and Irving, *J.*, 1954, 4390.

[45] See, *e.g.*, Chatt and Leden, *J.*, 1955, 2936.

[46] Sharp and Sharpe, *J.*, 1956, 1855.

[47] Sharp and Sheppard, *J.*, in press.

[48] McCaulay and Lien, *J. Amer. Chem. Soc.*, 1951, **73**, 2013.

[49] Kilpatrick and Luborsky, *ibid.*, 1953, **75**, 577.

the bond in the F_2 molecule. It would be entirely misleading to suggest that our understanding of the chemistry of the element is yet complete, but with the aid of physical methods of investigation a deeper insight into its properties is rapidly becoming possible.