

HALOGEN FLUORIDES AND OTHER COVALENT FLUORIDES

PHYSICAL AND CHEMICAL PROPERTIES

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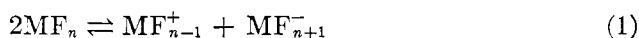
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I. INTRODUCTION

Since 1946 reliable fluorine generators and supplies of compressed fluorine have become readily available for research purposes. These developments have contributed materially to the advances in the chemistry of fluorine compounds.

Among the inorganic fluorides, great interest has centered on the halogen fluorides, with respect to both their physical characteristics and their chemical properties. The latter aspect has been largely influenced by the work of Emelús and Woolf (37), who proposed that bromine trifluoride and iodine pentafluoride act as ionizing solvents according to the equilibrium:



These fluorides have therefore been considered the parent substances of new acid-base solvent systems. The occurrence of such self-ionization should be reflected in the physical properties of these fluorides, but it is only in recent years that it has been possible to determine these properties accurately.

Very recently, other covalent fluorides such as some of the volatile fluorides of transition metals have been examined, not only to determine previously unknown properties but also to investigate the possible occurrence of this self-ionization. The matter has also been approached by the use of nuclear magnetic resonance spectroscopy and by the study of isotopic exchange reactions using the isotope ^{18}F . The aim of this review is to establish the importance of this ionization from a consideration of the physical and chemical properties of the halogen and other covalent fluorides. This latter group arbitrarily includes the pentafluorides of the elements (excepting phosphorus and bismuth) of Subgroups VA and VB of the Periodic Table, the hexafluorides of the Group VI elements, and the tetrafluorides of sulfur, selenium, and tellurium. Bismuth pentafluoride is not included, since little is known of its properties. The hexafluorides are considered, since they form a group for which association or ionization seems unlikely, and they may therefore be compared with those fluorides where such phenomena may occur. The literature has been surveyed up to December, 1957.

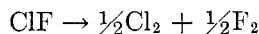
II. PHYSICAL PROPERTIES

Experimental difficulties in the handling of reactive fluorides have long prevented the accurate determination of their simple physical properties. The extent to which these difficulties have recently been overcome is revealed by the numerous precise results listed in the tables below. The known physical properties of the halogen fluorides are listed in table 1.

A. CHLORINE MONOFLUORIDE

Chlorine monofluoride is formed almost quantitatively by mixing chlorine trifluoride with chlorine (120); the earlier method of preparation by direct combination of the elements probably gives a product contaminated with the trifluoride. The physical properties measured by Ruff and Krug (112) must therefore be considered only approximate. However, taken at its face value, the Trouton's constant of $28.0 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ does appear to indicate some degree of association in the liquid state.

The monofluoride has been extensively studied spectroscopically. The heat of dissociation for the reaction



has been calculated (119) as $60.3 \pm 0.5 \text{ kcal. mole}^{-1}$ or $58.9 \text{ kcal. mole}^{-1}$, depending on whether the optical transition leads to excited fluorine and normal chlorine atoms, or to normal fluorine and excited chlorine atoms, respectively. From these spectroscopic data Potter (86) has derived values for the standard free energy, absolute entropy, and specific heat. Following preliminary investigations (60), Nielson and Jones (80) have obtained good resolution of the rotation-vibration fine structure. The interatomic distance in chlorine monofluoride has been determined both by electron diffraction (101) and by microwave spectroscopy (47) with good agreement between the respective values of $1.63 \pm 0.01 \text{ \AA.}$ and 1.628 \AA. The difference between these observed values and that of

TABLE 1
Physical properties of the halogen fluorides*

	ClF	ClF ₂	BrF	BrF ₂	BrF ₃	IF ₅	IF ₇
Density (g. cc. ⁻¹ at 25°C.)	—	1.8094 (8)	—	2.8050 (136)	2.460 (7, 136)	3.19 (98)	2.75 (111)
Freezing point (°K.)	119 (113)	196.84 (50)	240 (107)	281.03 (81)	212.7 (95)	282.61 (99)	278 (111)
Boiling point (°K.)	172 (113)	284.79 (50)	293 (107)	398.83 (81)	313.94 (95)	373.04 (99)	277 subl. (111)
Heat of fusion (kcal. mole ⁻¹)	—	1819.3 (50)	—	2874.6 (81)	1760 (105)	3600 (99)	—
Heat of vaporization (kcal. mole ⁻¹)	4800 (112)	6580 (50)	6000 (107)	10,200 (81)	7310 (95)	9880 (99)	7330 subl. (111)
Trouton's constant	28.0 (112)	23.1 (50)	20.5 (107)	25.7 (81)	23.2 (95)	26.3 (99)	?
Heat of formation (cal. mole ⁻¹)	13.3 ± 2.1 (38)	42 (120)	18.4 ± 0.5 (138)	75 (138)	—	204.7 (146)	—
Specific conductivity (ohm ⁻¹ cm. ⁻¹ at 25°C.)	—	3.9 × 10 ⁻⁹ (6)	—	8.0 × 10 ⁻⁸ (6)	9.1 × 10 ⁻⁸ (96)	5.4 × 10 ⁻⁶ (98)	—
Dielectric constant of liquid (at 25°C.)	—	4.304 (100)	—	—	7.76 (94)	36.14 (100)	—
Surface tension (dynes cm. ⁻¹ at 25°C.)	—	26.3 (5)	—	—	—	—	—
Viscosity (millipoises at 20°C.)	—	4.35 (5)	—	—	—	23.40 (56)	—
Parachor	—	111.5 (5)	—	—	—	—	—
Dipole moment of vapor (D)	0.88 (47)	0.65 (93)	1.29 (139)	1.19 (93)	1.51 (94)	2.13 (93)	—
Molar refractivities for vapor (cc. mole ⁻¹ at 25°C.)	7.62 (91)	10.34 (91)	—	12.92 (91)	15.48 (91)	19.17 (91)	—
Magnetic susceptibilities (xM × 10 ⁶)	—	-26.5 (92)	—	-39.4 (92)	-48.1 (92)	-58.4 (92)	—

* References are given in parentheses.

TABLE 2
Physical properties of pentafluorides of Group V elements*

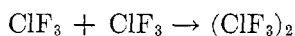
	VF ₅	NbF ₅	TaF ₅	AsF ₅	SbF ₅
Density (g. cc. ⁻¹ at 25°C.)	—	3.29 (116)	4.8 (116)	—	2.99 (115)
Freezing point (°K.)	292.6 ± 0.5 (27, 141)	353.1 (39, 65)	368.2 (39, 63)	193.4 (108)	281.5 ± 0.3 (57)
Boiling point (°K.)	324.4 ± 1.0 (27, 141)	508.0 (39)	502.5 (39)	220.0 (108)	415.9 (124)
Heat of vaporization (cal. mole ⁻¹)	10,640 (27, 141)	12,900 (39)	13,000 (39)	5200 (108)	10,730 (124)
Trouton's constant (cal. deg. ⁻¹ mole ⁻¹)	33.1 (27, 141)	25.4 (39)	25.9 (39)	23.6 (108)	25.9 (124)
Specific conductivity (ohm ⁻¹ cm. ⁻¹)	2.4 × 10 ⁻⁴ at 25°C. (27)	1.63 × 10 ⁻⁶ at 80°C. (40)	1.56 × 10 ⁻⁸ at 65.1°C. (40)	—	1.2 × 10 ⁻⁸ (148)

* References are given in parentheses.

1.712 Å. calculated from the mean values of the parent halogen radii has been interpreted (47) in terms of the bond being 80 per cent covalent and 20 per cent ionic.

B. CHLORINE TRIFLUORIDE

Chlorine trifluoride, first prepared (112) by direct combination of the elements, is now readily available commercially. As table 1 reveals, its physical constants are well documented, despite the experimental difficulties created by its high reactivity. The rather high value of the Trouton's constant may be attributed to dimerization in the liquid state. Dimerization also explains the observed departure (121) of chlorine trifluoride from the perfect gas laws; indeed it has thus been possible to calculate the heat of the reaction



to be 3.3 kcal. Further evidence of association in the liquid state may be deduced from a comparison of the dielectric constants and hence the dipole moments of the vapor and liquid phases. From the observed dielectric constant of 4.304 at 25°C., the dipole moment of the liquid was calculated (100) by Onsager's equation (82) to be 1.03 D. This is almost twice the dipole moment of 0.65 D observed for the gas, and this difference may be taken as evidence of association in the liquid phase (143). The observed physical properties offer little support for any self-ionization of chlorine trifluoride analogous to that postulated for bromine trifluoride. Although the specific conductivity of 3.9×10^{-9} ohm⁻¹ cm.⁻¹ is of the same order as that of liquid ammonia, which is known to behave as an ionizing solvent, there is a considerable difference in their dielectric constants, that of ammonia being 22 at -34°C. compared with a value of 4.304 at 25°C. for chlorine trifluoride. Hence, although the possibility of self-ionization occurring to a very small extent



cannot be excluded, any observed behavior of chlorine trifluoride as an ionizing solvent would be unexpected.

Chlorine trifluoride, like the monofluoride, has been widely studied spectroscopically. Its absorption spectrum in the visible and ultraviolet regions is known to be continuous (121), but despite several investigations (61, 118) no satisfactory assignment of the observed Raman and infrared spectral lines has yet been made. These studies have, however, thrown considerable light on the possible structure of chlorine trifluoride and may also provide further evidence of association in the liquid state. Unexpectedly, five active Raman frequencies are observed rather than the four or three which would be predicted for a symmetric pyramidal or planar symmetric structure, respectively. Jones, Parkinson, and Murray (61) have therefore suggested either that the molecule is unsymmetrical or that the fifth frequency is produced by an associated complex in the liquid state. The structure has been finally resolved by microwave spectroscopy (134) and x-ray diffraction (19) studies. The latter method shows the molecule to be planar with

two chlorine-fluorine bonds of 1.716 Å. and the other of 1.621 Å. The bond angles between the short chlorine-fluorine bond and the long chlorine-fluorine bonds are $86^{\circ} 59'$. The microwave data also reveal a planar-T structure with corresponding values of 1.698 Å., 1.598 Å., and $87^{\circ} 29'$, the differences between the bond lengths obtained by the two methods being considered real but unexplained. Confirmation of this structure has very recently been obtained by a study of the nuclear magnetic resonance spectrum of chlorine trifluoride (78).

This distorted planar-T structure, although perhaps unexpected, can be regarded as derived from a trigonal bipyramidal model. The fluorine atoms occupy

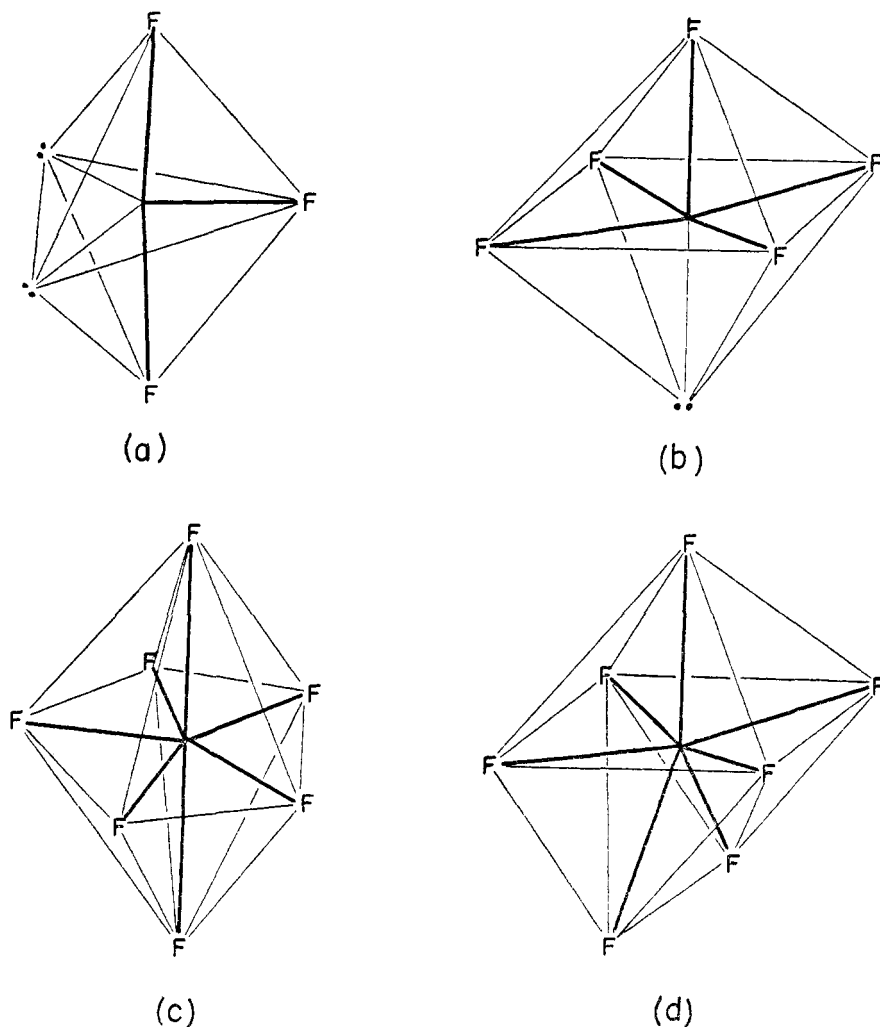
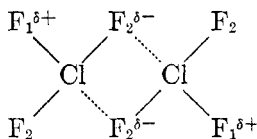


FIG. 1. The structures of the halogen fluorides: (a) chlorine and bromine trifluorides; (b) bromine and iodine pentafluorides; (c and d) alternative structures for iodine heptafluoride.

the two axial (F_2) and one of the equatorial (F_1) positions, the two remaining equatorial sites being occupied by the lone-pair electrons of the chlorine atom (figure 1). The occurrence of the planar-T structure in preference to the planar symmetrical model has been explained (48) in terms of lone-pair-lone-pair and lone-pair-bond-pair electron repulsions. The same authors also point out that the observed F_1 -Cl- F_2 bond angles of slightly less than 90° would be expected if lone-pair-bond-pair repulsions are greater than bond-pair-bond-pair electron repulsions. However, electron repulsions do not explain the large differences between the Cl- F_1 and Cl- F_2 bond distances. Burbank and Bensey (19) consider that the Cl- F_1 bond is shortened owing to a transfer of negative charge from the F_1 atom through the $3d$ chlorine orbitals to the F_2 atoms. This would mean that the simple Cl- F_1 bond has twice as much π -bond character as the Cl- F_2 bonds. The Cl- F_1 bond will therefore be shorter than the Cl- F_2 bonds. Moreover, the electrostatic interaction between the formal positive charge on the F_1 atom and the formal negative charge on the F_2 atoms may also be partly responsible for bond angles of less than 90° .

If this charge-transfer hypothesis is correct it may explain the dimerization of chlorine trifluoride. Muetterties and Phillips (78) consider that the dimer results from the formation of fluorine bridges between the two molecules, with lone-pair electrons from the fluorine atoms occupying the chlorine $3d$ orbitals. Since fluorine is not normally considered capable of acting as an electron pair donor, fluorine-bridge formation may involve the transfer of only this formal negative charge from the F_2 atoms to the $3d$ orbitals of the other chlorine atom and there will be no overall electron gain or loss for each ClF_3 monomer.

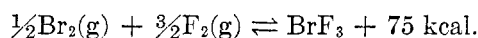


The configuration about each chlorine atom could then be considered as derived from the octahedral sp^3d^2 system with two lone electron pairs occupying the two axial positions, and the dimer will therefore be planar. In fact, the greater stability of this configuration over the original distorted trigonal bipyramidal model may also favor dimer formation.

C. BROMINE MONOFLUORIDE

The disproportionation of bromine monofluoride to bromine and the trifluoride occurs so readily that the monofluoride has not yet been prepared in a pure state. The physical properties of the monofluoride as listed in table 1 must therefore be regarded as approximate. Recently, phase equilibria in the system bromine-bromine trifluoride have been investigated. The liquid-vapor equilibrium (41) provides ample evidence for the existence in the vapor state of another molecular species, presumably bromine monofluoride. This does not necessarily imply that the monofluoride exists in the liquid state and, in fact, examination of the liquid-solid phase equilibrium in the same system (43) has

definitely shown the monofluoride to be absent in the solid state. A further manometric and spectrophotometric study of the gaseous bromine–bromine trifluoride system (138) has led to the calculation of the following heats of formation:



These results, together with a heat of dissociation of 49.8 ± 0.4 kcal. calculated from the visible emission spectrum (34), show that the bromine–fluorine bond in bromine monofluoride is not weak. The apparent instability of the monofluoride must therefore be attributed to the even greater stabilities of the higher fluorides. The interatomic distance, calculated from the microwave spectrum (135), is 1.759 Å.

D. BROMINE TRIFLUORIDE

Compared with its chlorine analog, bromine trifluoride has abnormally high freezing and boiling points. These, together with the high value of the Trouton's constant, are clear indications of association, probably dimerization, in the liquid state. It is unfortunate that the high reactivity of bromine trifluoride has so far prevented the determination of the dielectric constant, surface tension, or viscosity. However, its behavior as a polar solvent suggests that its dielectric constant is at least moderately high. Of even greater interest is the high specific conductivity of 8.0×10^{-3} ohm⁻¹ cm.⁻¹ at 25°C., decreasing with increasing temperature to a value of 6.75×10^{-3} ohm⁻¹ cm.⁻¹ at 60°C. (6). This conduction has been attributed to the existence in liquid bromine trifluoride of the ions BrF_2^+ and BrF_4^- . The formation of these ions may first require dimerization, although not necessarily so.



The negative temperature effect may then be due to a decrease in the stability of one or both of these ionic species with increasing temperature. Bromine trifluoride also conducts in the solid state, but this is difficult to explain in view of its structure discussed below. Other conductivity measurements of bromine trifluoride include the investigation of the bromine–bromine trifluoride and bromine trifluoride–bromine pentafluoride systems (88). The behavior of the former system may be interpreted in terms of the above self-ionization of the trifluoride, the formation of the Br^+ ion, the ion-pair $\text{Br}^+ \text{BrF}_4^-$, and the formation of bromine monofluoride.

Although differing from chlorine trifluoride in many physical properties, bromine trifluoride is closely related to it structurally. From the microwave spectrum (71) it has been shown that bromine trifluoride has the same distorted planar-T structure (figure 1). Again, there is a distinction between the fluorine atoms, one lying at a distance of 1.721 Å. (F_1) from the bromine atom, while the

two lateral fluorine (F_2) atoms lie at a distance of 1.810 Å. The F_1 —Br— F_2 bond angles are $86^\circ 12.6'$. Burbank and Bensey (21) have confirmed this structure by x-ray diffraction studies. Their calculated bond distances of Br— F_1 (1.72 Å.) and Br— F_2 (1.84 and 1.85 Å.) and the bond angles of 82° and 88.4° are rather different from the microwave results. However, little refinement of their data was attempted and there is at present no reason to conclude that these differences are significant. The interpretation of this planar-T structure in terms of bonding orbitals will clearly be the same as that for chlorine trifluoride. Some multiple-bond character may again be assigned, particularly to the Br— F_1 bond, for which the bond distance of 1.721 Å. is considerably less than the sum of the covalent radii, 1.78 Å. The formation and stability of a planar dimer involving fluorine bridges may therefore be described, as for chlorine trifluoride.

A structural determination of either the difluorobromonium ion, BrF_2^+ , or the bromofluoride ion, BrF_4^- , would support the self-ionization of bromine trifluoride. Their great reactivity and hence the inevitable presence of traces of impurities render such an investigation difficult. Siegel (130) has managed to interpret the x-ray diffraction pattern of a single crystal of potassium bromofluoride, $KBrF_4$, in terms of a tetrahedral configuration of the BrF_4^- ion. Unfortunately, the intensities and resolution are so low that the observed patterns can also be interpreted (131, 133) in terms of a planar BrF_4^- ion. This latter interpretation would be the expected one, since it would result from the use of either sp^3d^2 hybrid orbitals by the bromine atom, with the two lone pairs of electrons occupying the trans positions, or just the simpler sp^2d hybrid orbitals. Only a new determination of structure with greatly improved resolution can distinguish between the tetrahedral and planar models.

E. BROMINE PENTAFLUORIDE

Bromine pentafluoride is obtained (114) by the combination of the elements at $200^\circ C.$ or higher. Its physical properties have only recently been determined, and as yet it is difficult to determine whether association or self-ionization occurs to any extent. The freezing and boiling points and the heat of vaporization are much lower than the values for the trifluoride; however, Trouton's constant has approximately the same value as that of chlorine trifluoride, which is known to be associated. Moreover, the specific conductivity of $9.1 \times 10^{-8} \text{ ohm}^{-1} \text{ cm.}^{-1}$ is considerably higher than that of chlorine trifluoride, as is also the dielectric constant, so that the possibility of association and ionization of bromine pentafluoride cannot be entirely ignored.



From the observed dielectric constant and refractive index, the dipole moment of the liquid may be calculated as 1.68 D. This is larger than the moment of 1.51 D of the vapor, and this difference, although small, may indicate association in the liquid state. This interpretation is contrary to that originally given by Rogers, Pruett, Thompson, and Spiers (94), but is more consistent with the same workers' interpretation of similar measurements on chlorine trifluoride.

However, it is pertinent that the bromine trifluoride-bromine pentafluoride

system, studied by both refractive index (136) and conductivity (88) methods, shows no interaction between the two components. Also, measurements of the vapor pressure and conductance of the hydrogen fluoride–bromine pentafluoride system (96) provide no evidence of association or ionization of the pentafluoride and show that hydrogen fluoride does not possess electrolytic properties in bromine pentafluoride solutions.

The exact structure of bromine pentafluoride is still not conclusively known. From the observed Raman and infrared frequencies the molecule has been shown (23, 137) to belong to the C_{4v} symmetry group and hence to have the shape of a tetragonal pyramid. This is consistent with the use of sp^3d^2 hybrid orbitals, with the lone pair of electrons occupying the sixth octahedral position. This structure also seems to be confirmed by nuclear magnetic resonance studies (51). Stephenson and Jones (137) make the reasonable assumption, which they do not attempt to justify, that the bromine atom lies at the center of mass of the molecule; hence they calculate the force constants and thermodynamic properties. However, by analogy with the structures of chlorine and bromine trifluorides, Mellish and Linnett (76) suggest that the F—Br—F angles may be slightly less than 90° , so that all five fluorine atoms will lie on the same side of the bromine atom. The SbF_5^{2-} ion, which is isoelectronic with bromine pentafluoride, is known to have this configuration; moreover the observed dipole moment of bromine pentafluoride is of the expected magnitude. Recently, a fairly thorough determination of structure by x-ray diffraction (21) confirmed that bromine pentafluoride has four short bromine–fluorine bonds and one longer bromine–fluorine bond and bond angles of less than 90° . The bromine atom must therefore lie below the plane of the pyramidal base. This position of the bromine atom may be attributed in part to the partial double-bond character of certain of the bromine–fluorine bonds as in the trifluoride, or in part to the greater magnitude of lone-pair–bond-pair electron repulsions as compared with bond-pair–bond-pair repulsions (48). Considering that not all bromine–fluorine distances are equal, the first effect is probably more important.

F. IODINE MONOFLUORIDE

Isolation of the mono- and trifluorides of iodine has not yet been reported, although the monofluoride has been observed spectroscopically (34).

G. IODINE PENTAFLUORIDE

The physical properties of iodine pentafluoride, which is the normal product of the interaction of the two elements, are now accurately known. Clear evidence of association in the liquid state is provided by the high freezing and boiling points and the abnormally high value for Trouton's constant. The specific conductivity and dielectric constant also indicate that it should be a good ionizing solvent. There is therefore much support for the occurrence of the equilibrium



originally proposed on the basis of chemical studies.

Considering the lower reactivities of the iodine fluorides as compared with the chlorine and bromine fluorides, it is surprising that the structures of the iodine compounds are not yet conclusively known. Electron diffraction studies (17) have indicated a trigonal bipyramidal configuration for iodine pentafluoride, but later studies (101) have discredited this. A study of the infrared and Raman spectra (68) has led to the conclusion that the IF_5 molecule has C_{4v} symmetry and therefore, like bromine pentafluoride, has the shape of a tetragonal pyramid. A preliminary x-ray diffraction examination (21) has revealed a complicated crystal structure which has yet to be resolved. The exact position of the iodine atom is therefore unknown, and it may lie on the fourfold axis of symmetry either above or below the plane of the four fluorine atoms. The bond orbitals used by the iodine atom are also uncertain, as many geometrically suitable combinations of s , p , d , and f orbitals are possible (123).

H. IODINE HEPTAFLUORIDE

Accurate determinations of the physical properties of iodine heptafluoride have yet to be made. The value of $26.4 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ for Trouton's constant (111) is based incorrectly on the heat of sublimation rather than the heat of vaporization. The true value will therefore be somewhat lower, so that no reliable conclusions can be drawn from the quoted value.

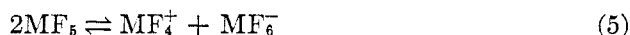
Several structural investigations of iodine heptafluoride have been reported, but the degree of agreement is far from satisfactory. Both electron diffraction (13) and Raman and infrared spectral (68) studies suggest a pentagonal bipyramidal structure. The iodine atom is placed at the center of a regular pentagon with the five iodine-fluorine distances being 1.83 Å. The two remaining fluorine atoms lie on the fivefold axis of symmetry, one above and one below the pentagonal plane at a distance of 1.94 Å. from the iodine atom. In direct contrast to this structure is that tentatively proposed (20) as the result of an x-ray diffraction examination. This suggests a structure in which five fluorine atoms form a tetragonal pyramid with the iodine atom below the base of the pyramid and the remaining two fluorine atoms lying below the iodine. For the pentagonal bipyramidal arrangement, it has been suggested (33) that the iodine atom uses sp^3d^3 hybrid orbitals, but until the structure of iodine heptafluoride is more definitely known, few valuable deductions can be made.

I. PENTAFLUORIDES OF GROUP V ELEMENTS

The physical properties of these pentafluorides are given in table 2.

Each of these pentafluorides may be prepared by the direct fluorination of the corresponding element at approximately $300\text{--}350^\circ\text{C}$. At room temperature, vanadium pentafluoride is a viscous, straw-colored liquid, niobium and tantalum pentafluorides are hygroscopic white solids, antimony pentafluoride is a colorless liquid, and arsenic pentafluoride is a colorless gas. Table 2 shows clearly that the pentafluorides of vanadium, niobium, tantalum, and antimony are associated in the liquid state. All have rather high boiling points and abnormally high values for Trouton's constant. For antimony pentafluoride, the observed

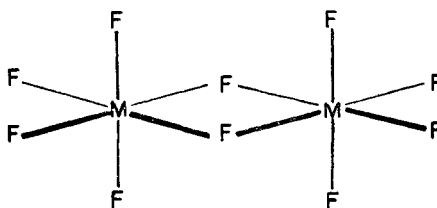
parachor of 169.5, as compared with the theoretical value of 194.5 (59), and the abnormally high viscosity (148) provide further evidence of association. Arsenic pentafluoride has a slightly high value of Trouton's constant, but the boiling point is low and there is little other positive evidence of association. The specific conductivities of vanadium, niobium, and tantalum pentafluorides in the liquid state suggest that partial self-ionization of the associated molecules may occur, possibly by the following equilibrium:



Unfortunately, the dielectric constants of the liquid pentafluorides are not yet available, but it appears that they may behave as new ionizing solvents. For antimony pentafluoride, the specific conductivity is of the same order as that of chlorine trifluoride and other more familiar solvents such as water and liquid ammonia. Since the dielectric constant is unknown and the conductivity is low, it seems likely that the associated molecules play the more important part in determining the physical and chemical properties of antimony pentafluoride, but the possibility of self-ionization occurring according to the above equilibrium cannot be excluded on the present evidence.

Although the structures of most of these pentafluorides are unknown, the two most probable configurations are a trigonal bipyramid as found in phosphorus pentafluoride, or a tetragonal pyramid by analogy with bromine and iodine pentafluorides. For these halogen pentafluorides, however, the structure is derived from a regular octahedron, one of the six positions being occupied by a lone pair of electrons. Since for the pentafluorides of these Group V elements there is no such lone pair, the trigonal bipyramidal structure would be expected. This can be readily attained from the $-(n-1)s^2(n-1)p^6(n-1)d^3ns^2$ electronic configurations of vanadium, niobium, and tantalum by the formation of $(n-1)d^3nsnp$ hybrid orbitals, while arsenic and antimony could produce the same geometrical configuration by the use of $nsnp^3nd$ hybridization. From very recent infrared and Raman studies (46) antimony pentafluoride does appear to have this trigonal bipyramidal configuration.¹ Quite independently of their normal shape, which can only be revealed by precise determinations of structure, these pentafluorides could very readily form dimers containing fluorine bridges between the two central atoms. These central atoms will then have an octahedral configuration, with two octahedra sharing an edge (see page 880). The change in coordination number from 5 to 6 may favor this dimerization. Similarly, the products of the self-ionization of this dimer, an octahedral MF_6^- ion and presumably a planar MF_4^+ ion, would also possess favorable coordination numbers and strong hybrid orbitals. The tendency to aggregate and

¹Very recent nuclear magnetic resonance measurements (W. D. Phillips and E. L. Muetterties: *J. Am. Chem. Soc.*, in press. C. J. Hoffman, B. E. Holder, and W. L. Jolly: *J. Phys. Chem.* **62**, 364 (1958)) conclusively show that the major species in liquid antimony pentafluoride is not trigonal bipyramidal, but rather consists of dimeric or polymeric groups. Some reinterpretation of the infrared and Raman spectral data is therefore necessary.



possibly form a stable dimer of the above type also appears to occur with the pentachlorides and pentabromides of niobium and tantalum and with tantalum pentaiodide, all of which have high values of Trouton's constant (39).

J. HEXAFLUORIDES OF GROUP VI ELEMENTS

Certain covalent fluorides of this group are included for completeness and for comparison with the fluorides of the Group V elements. Apart from forming the expected hexafluorides, the elements of Group VI also form lower fluorides, including tetrafluorides. Sulfur, selenium, and tellurium tetrafluorides are therefore described, since certain of them exhibit unusual solvent properties. Uranium, which, strictly speaking, does not belong to Group VI, forms an apparently ionic tetrafluoride, and molybdenum tetrafluoride has recently been prepared (84).

The hexafluorides of the Group VI elements are volatile and condense to white solids. From the low boiling or sublimation temperatures and the normal values of Trouton's constant (table 3), the hexafluorides seem to be nonassociated. Indeed, the volatility of molybdenum, tungsten, and uranium hexafluorides is remarkable, considering their high molecular weights. Numerous other properties of uranium hexafluoride are known, including the viscosity (65), the dielectric constant of the vapor (69), the surface tension, and the thermal conductivity (67). Studies of the phase equilibria in the condensed systems uranium hexafluoride-bromine trifluoride, uranium hexafluoride-bromine pentafluoride (44), uranium hexafluoride-chlorine trifluoride (10), and uranium hexafluoride-hydrogen fluoride (117) show that the solid phases consist only of the pure components and that the systems are of the simple eutectic type. Their physical properties thus show these hexafluorides to be nonassociated.

TABLE 3
*Physical properties of hexafluorides of Group VI elements**

	SF ₆	SeF ₆	TeF ₆	MoF ₆	WF ₆	UF ₆
Density (g. cc. ⁻¹ at freezing point).....	2.51 (149)	3.27 (149)	3.76 (149)	2.55 (106)	3.515 (106)	3.630 (58)
Freezing point (°K.).....	222.7 (149)	238.4 (149)	235.4 (149)	290.6 (106)	275.1±0.3 (9)	337.21 (58, 73)
Boiling point (°K.).....	209.4 subl. (149)	227.2 subl. (149)	234.7 subl. (149)	308.1 (106)	290.26±0.05 (9)	329.6 subl. (1, 142)
Trouton's constant (cal. deg. ⁻¹ mole ⁻¹).....	—	—	—	21.0 (106)	21.5 (9)	—
Heat of vaporization (cal. mole ⁻¹).....	—	—	—	6503 (106)	6245 (9)	6920 (67)

* References are given in parentheses.

Structural investigations of the hexafluorides have amply confirmed that they have the expected regular octahedral configurations. Early electron diffraction studies (12) seemed to indicate that the octahedra were irregular, with three short and three long bonds, but a later improvement in the theory of electron diffraction (49) has shown the regular octahedral structure to be correct. This is in agreement with infrared, Raman, and ultraviolet spectral measurements on all of these hexafluorides (22, 24, 26, 45). The bonding orbitals used in these octahedral structures may be simply described as involving the use of sp^3d^2 hybrid orbitals. However, this is certainly an oversimplification since, as for other fluorides, no allowance is made for any polar character of the M—F bonds caused by the high electronegativity of fluorine. Regardless of this difficulty, the occurrence of these molecules as regular octahedra probably accounts for their nonassociation. For, say, tungsten hexafluoride to form a dimer by the formation of fluorine bridges, each tungsten atom would be required to assume the unlikely coordination number of 7.

K. TETRAFLUORIDES OF GROUP VI ELEMENTS

Among the tetrafluorides of the Group VIB elements (table 4) the selenium compound in particular shows some unusual properties. There is also an unusually marked change in properties from sulfur tetrafluoride through selenium tetrafluoride to tellurium tetrafluoride.

Only in the past two or three years has the existence of sulfur tetrafluoride been conclusively established. This compound, like its selenium and tellurium analogs, is characterized by its high chemical reactivity; in all cases this has prevented other studies of their physical properties. According to the rather meagre data so far available, both sulfur and selenium tetrafluorides appear to be associated in the liquid state. This is further supported for the selenium compound by the observed low value of the parachor, 137.2, as compared with the theoretical value of 165.3 (4). Unfortunately the specific conductivities have yet to be determined, while the small amount of available information on tellurium tetrafluoride also provides no definite evidence of association.

Only for selenium tetrafluoride have any structural determinations been made. An electron diffraction study (16) indicates that the symmetry group is C_{2v} ; hence the selenium atom is said to be surrounded by a distorted tetrahedron of fluorine atoms. The selenium—fluorine distance is 1.765 ± 0.025 A.; two of the F—Se—F bond angles are 120° and the remaining four are 104.5° with an

TABLE 4
*Physical properties of tetrafluorides of Group VIB elements**

	SF ₄	SeF ₄	TeF ₄
Density (g. cc. ⁻¹).....	1.9191 at 200°K. (18)	2.72 at 25°C. (4)	—
Freezing point (°K.).....	152 (18)	263.7 (4)	402.8 (62)
Boiling point (°K.).....	232.7 (18)	379.1 (4)	—
Latent heat of vaporization (cal. mole ⁻¹).....	6320 (18)	11,240 (83)	8174 (62)
Trouton's constant.....	27.1 (18)	30.0 (83)	—

* References are given in parentheses.

uncertainty of $\pm 10^\circ$ for all angles. The calculation of these bond angles has been criticized (66), but the general shape of the molecule remains unquestioned. The Raman spectrum of liquid selenium tetrafluoride (102) also indicates C_{2v} symmetry. The chemical evidence to be discussed in the following section suggests that selenium tetrafluoride behaves as an ionizing solvent according to the equilibrium:



The formation of penta- and tricoordinated ions from the comparatively stable tetrafluoride is most unexpected and is markedly different from the behavior of the hexafluorides. At present it is difficult to give any reason for this self-ionization of selenium tetrafluoride and the stability of the resulting ions.

III. CHEMICAL PROPERTIES

In discussing the chemical properties of these fluorides, it seems scarcely necessary to mention that they all behave as fluorinating agents, although with varying degrees of reactivity. The mere tabulation of such fluorination reactions does not seem desirable; indeed it is of much greater interest to see if their chemical properties reflect the varying degrees of association and self-ionization. References will, however, be made to normal fluorination reactions which have been recently reported. Reviews of the chemical properties of the halogen fluorides with this special emphasis on self-ionization have been given by Emeléus (132) and Sharpe (125); this will now be extended to include more recent work as well as other covalent fluorides.

To establish from chemical evidence the self-ionization of a compound according to the equilibrium of equation 1, all of the following requirements should be met: (a) The isolation of compounds containing the MF_{n-1}^+ and MF_{n+1}^- ions and the establishment of at least partial ionic character for such compounds. (b) Since these ions can be regarded as the acidic and basic ions, respectively, of new solvent systems, it must be shown that salts can be obtained. (c) Titrations should be performed which give end points when equivalent proportions of acid and base have been mixed.

Full evidence of this type is available only for bromine trifluoride, while for others of these fluorides only one or two of these requirements have been met.

A. HALOGEN FLUORIDES

The chemical properties of the halogen fluorides have been reviewed by Booth and Pinkston (15). All the halogen fluorides behave as fluorinating agents, although in many cases the available information is only qualitative. The approximate order of reactivity is: chlorine trifluoride > bromine pentafluoride > iodine heptafluoride > chlorine monofluoride > bromine trifluoride > iodine pentafluoride > bromine monofluoride. In several cases, particularly the monofluorides, little progress has been made since 1947.

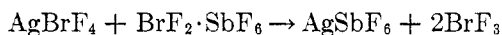
Of the trifluorides, that of bromine has been widely studied and will be con-

sidered first. The results may then be compared with the available data for other fluorides. From the physical evidence of association and ionization, the following equilibrium is said to occur in liquid bromine trifluoride:



The trifluoride is thus an ionizing solvent in which soluble compounds yielding the BrF_2^+ ion may be defined as acids, and those yielding the BrF_4^- ion as bases. The isolation of the bases KBrF_4 , AgBrF_4 , and $\text{Ba}(\text{BrF}_4)_2$ (127) and of the acids $\text{SbF}_5 \cdot \text{BrF}_3$ and $\text{AuF}_3 \cdot \text{BrF}_3$, which may be formulated as $\text{BrF}_2^+ \text{SbF}_6^-$ and $\text{BrF}_2^+ \text{AuF}_4^-$ (37), has been achieved. That these compounds contain the BrF_4^- and BrF_2^+ ions appears to be shown by (1) the increase in the conductivity of bromine trifluoride on the addition of one of these compounds, (2) the x-ray diffraction study of potassium bromofluoride (KBrF_4) discussed previously, and (3) the relative stability of these compounds to heat, organic solvents, and water as compared with the great reactivity of bromine trifluoride. Numerous other acids, of which the compounds $(\text{BrF}_2)_2 \text{SnF}_6$, $\text{BrF}_2 \text{NbF}_6$, and $\text{BrF}_2 \text{TaF}_6$ are typical, have since been isolated, and many others are thought to occur in bromine trifluoride solutions. It is, however, of great interest that the compound $\text{BrF}_3 \cdot \text{SbF}_5$, which has been used as a high-temperature fluorinating agent (129), has been found to melt at the low temperature of 129.8°C . and does not appear to dissociate in the liquid state (42). Hence, although this compound shows electrolytic dissociation in the ionizing solvent bromine trifluoride, its low melting point suggests that in the solid state it may be largely covalent in character. A covalent structure would presumably involve fluorine bridges, as discussed previously. A structural investigation of this solid compound would clearly be of great interest.

Salt formation in bromine trifluoride solutions has now been observed in numerous cases. The evaporation of a bromine trifluoride solution of silver chloride and antimony pentafluoride produced white silver hexafluoroantimonate, AgSbF_6 .



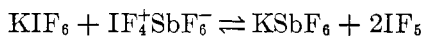
The formation of other salts containing such ions as BF_4^- , SiF_6^{2-} , GeF_6^{2-} , VF_6^- , NbF_6^- , TaF_6^- , and BiF_6^- has been previously discussed (132). Similarly, by postulating the existence in bromine trifluoride solution of the unstable bases $\text{NO}_2^+ \text{BrF}_4^-$ and $\text{NO}^+ \text{BrF}_4^-$, the formation of numerous nitronium and nitrosonium complex fluorides can be logically explained (144, 147). Solvolysis may also occur to an appreciable extent in bromine trifluoride. Thus, the reaction of potassium bromofluoride, KBrF_4 , with the acid $(\text{BrF}_2)_2 \text{TiF}_6$ produced potassium hexafluorotitanate solvated with bromine trifluoride, showing the neutralization reaction to be reversible (126).

The third requirement, that titrations giving good end points should be performed between acids and bases, also appears to have been met. A conductometric titration (37) of bromine trifluoride solutions of silver bromofluoride and the acid $\text{BrF}_2^+ \text{SbF}_6^-$ showed a well-defined minimum of conductivity for a

1:1 ratio of the reactants. Similarly, in a titration of potassium bromofluoride with the acid $(\text{BrF}_2)_2\text{SnF}_6$ the minimum conductivity appeared at a ratio of 2:1. Thus there seems ample chemical evidence in support of the self-ionization of bromine trifluoride.

The chemical evidence so far available shows that chlorine trifluoride has little or no tendency to form acids and bases. Thus chlorine trifluoride and potassium fluoride do not readily form the base KClF_4 , since both compounds can be recovered unchanged from a mixture of the two. Chlorine trifluoride is widely used as a fluorinating agent and its reactions with metals and hydrocarbons have been studied (35, 89).

Of the remaining halogen fluorides, only for iodine pentafluoride is there chemical evidence in support of self-ionization. The isolation from solutions in iodine pentafluoride of the base potassium hexafluoroiodate, KIF_6 , and the acid $\text{IF}_4^+\text{SbF}_6^-$ has been reported (145). The mixing of iodine pentafluoride solutions of these compounds in equimolar quantities and the removal of excess solvent gave the product $\text{KSbF}_6 \cdot 0.23\text{IF}_5$, according to the neutralization reaction:



The apparent solvolysis of the product seems characteristic of reactions in iodine pentafluoride. A further interesting observation is the formation of potassium fluoborate, KBF_4 , by the passage of boron trifluoride through an iodine pentafluoride solution of potassium fluoride. Although the chemical evidence is less complete than for bromine trifluoride, there seems to be considerable support for the self-ionization of iodine pentafluoride.

Very little is known of the chemical properties of bromine pentafluoride and iodine heptafluoride, and only slight progress has been made since 1947. Both compounds show the expected powerful fluorinating properties. It is, however, known that iodine heptafluoride does not yield compounds of the type MIF_8 with potassium, sodium, or rubidium fluoride (122).

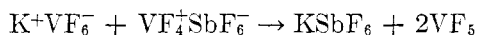
B. OTHER COVALENT FLUORIDES

The chemical properties of the covalent fluorides discussed in previous sections are still only slightly known. Very few have been considered in the role of ionizing solvents, but in most cases there is indirect evidence which may be related to the occurrence or nonoccurrence of association and self-ionization.

1. Pentafluorides of Group V elements

The pentafluorides of vanadium, niobium, tantalum, arsenic, and antimony are all believed to form the corresponding MF_6^- ion in bromine trifluoride solution, since salts containing these ions have been isolated from such solutions. Although the existence of these ions in the pure liquid pentafluorides may reasonably be suggested, it is only for vanadium pentafluoride that there is any direct chemical evidence. An attempt to isolate the acid $\text{VF}_4^+\text{SbF}_6^-$ from a solution of antimony pentafluoride in vanadium pentafluoride was unsuccessful.

However, when potassium fluoride was added to this mixture and the excess solvent removed, potassium hexafluoroantimonate was obtained (29). This can best be explained as a simple neutralization.



The possible existence of the unstable intermediate $\text{VF}_5 \cdot \text{SbF}_5$ as a partially ionized, covalent, fluorine-bridged molecule is still not excluded. Again, the product $\text{VF}_4^+\text{BF}_4^-$ could not be isolated from the reaction of vanadium pentafluoride with boron trifluoride. This is not altogether surprising, since the corresponding derivative of bromine trifluoride, $\text{BrF}_2^+\text{BF}_4^-$, has not yet been isolated. Nitronium and nitrosonium hexafluorovanadates have also been obtained by the reaction of nitryl and nitrosyl fluorides, respectively, with excess vanadium pentafluoride (29). These are analogous to the intermediates $\text{NO}_2^+\text{BrF}_4^-$ and $\text{NO}^+\text{BrF}_4^-$, thought to occur in bromine trifluoride solutions.

No studies have yet been made of antimony pentafluoride as a solvent, although several reactions resulting in the formation of products containing the SbF_6^- ion have already been discussed. It has recently been shown that this ion (140) and the corresponding AsF_6^- ion (103) are both octahedral. The formation of the fluoroarsenate ion by the action of hydrogen fluoride on arsenates has been examined (32). Antimony pentafluoride forms several interesting addition compounds such as $(\text{SbF}_5)\text{Br}$, $(\text{SbF}_5)\text{I}$, and $(\text{SbF}_5)_2\text{M}$, where M = sulfur, selenium, or tellurium (3). Since dimerization of antimony pentafluoride may result from the formation of a fluorine bridge, it seems reasonable to suggest that in these addition compounds, unshared electron pairs on the bromine, iodine, sulfur, selenium, or tellurium atoms are donated to the antimony atoms, giving a coordinatively saturated, octahedral arrangement. For the $(\text{SbF}_5)_2\text{M}$ type of compound, by the donation of two such electron pairs M may act as a bridge between two octahedral antimony atoms.

All these pentafluorides are powerful fluorinating agents, owing to the stability of the lower fluorides, which are generally ionic.

2. Hexa- and tetrafluorides of Group VI elements

In many respects there is a sharp contrast in chemical behavior between the pentafluorides of the Group V elements and the hexafluorides of the Group VI elements. Owing to the stability of the lower valence states of the metals, the hexafluorides of molybdenum, tungsten, and uranium are active fluorinating agents. Unfortunately, most of their reactions have only been studied qualitatively and the reaction products have not been identified (109, 110). From the few quantitative results available, the conclusion that these hexafluorides do not undergo association or show self-ionization seems to be supported. Two possible but not probable schemes of self-ionization could be proposed:



or



For either process to occur, the resulting ions must have a certain degree of stability, and the isolation of compounds containing at least one or other of these ions could reasonably be expected. Only for tellurium and uranium hexafluorides is there any evidence to suggest the existence of such ions. The compounds $3\text{AgF}\cdot\text{UF}_6$, $3\text{NaF}\cdot\text{UF}_6$, $3\text{KF}\cdot 2\text{UF}_6$, and $2\text{RbF}\cdot\text{UF}_6$ have been obtained (72) by reaction of the hexafluoride with the corresponding alkali metal fluoride, but the exact nature of the resultant products has not been definitely established. Ruff and Eisner (109) reported that molybdenum and tungsten hexafluorides gave complex fluorides by reaction with the alkali metal fluorides, but the products were not identified. The isolation of complexes of the general formulae M_2MoF_8 and M_2WF_8 has recently been claimed (31). However, under conditions whereby all traces of moisture and hydrogen fluoride are rigidly excluded, it has now been conclusively shown (28) that tungsten hexafluoride does not react with the alkali metal fluorides at room temperature. This does not exclude the possibility of complex formation under more severe conditions of temperature and pressure. The formation of complex fluorides of pentavalent molybdenum and tungsten has been reported (54) by the reaction of the hexafluorides with the alkali metal iodides in liquid sulfur dioxide, producing complexes of the type MMoF_8 and MWF_8 . The constitution of the addition compounds of tungsten hexafluoride with ammonia, pyridine, and methylamine (28) and with organic solvents (87) poses some interesting but as yet unsolved problems.

Since the hexafluorides of molybdenum and tungsten do not show the formation of complex fluorides, the production at 250°C . of a fluorotellurate such as $2\text{CsF}\cdot\text{TeF}_6$ from tellurium hexafluoride (77) is most unexpected. It is not yet certain whether the fluorotellurates contain the TeF_8^{2-} or the TeF_7^- ion. Under similar conditions, selenium hexafluoride does not form fluoroselenates, this being attributed to the excessively high energy level of the required selenium orbitals. This argument may possibly be extended to explain the formation of the fluorouranates (VI) and the nonformation of any corresponding octacoordinated molybdenum and tungsten complex fluorides. Muettertius (77) also reports that tellurium hexafluoride shows no interaction or fluorine exchange with the covalent trifluorides of boron and arsenic. This may mean, as expected from the physical properties, that association of the hexafluoride through fluorine-bridge formation and self-ionization plays little part in the formation of fluorotellurates. Structural investigations of the fluorouranates and fluorotellurates obtained from the hexafluorides should provide interesting results, mainly in determining which complex fluoride ions are formed.

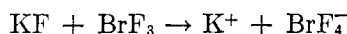
Little accurate information on the chemical properties of sulfur tetrafluoride seems to be available. The addition compounds $\text{SF}_4\cdot\text{BF}_3$ (11) and $\text{SF}_4\cdot 2\text{SbF}_5$ are known, while with sulfur trioxide, sulfur tetrafluoride forms pyrosulfuryl fluoride. Considerably more is known of selenium tetrafluoride. As a result of the formation of the compound KSeF_5 from selenium tetrafluoride and potassium fluoride, the ionization equilibrium



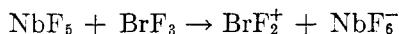
has been postulated (4). In this solvent system, compounds containing or producing the SeF_3^+ ion may be defined as acids, and those containing the SeF_5^- ion as bases. Three neutralization reactions have been performed (55), involving the acids $\text{SeF}_3^+\text{RuF}_6^-$, $\text{SeF}_3^+\text{OsF}_6^-$, and $\text{SeF}_3^+\text{IrF}_6^-$. That these are not merely addition compounds is deduced from the observation that the addition of water to the osmium and iridium compounds produced selenious and hydrofluoric acids, together with either hexafluoroosmic or hexafluoroiridic acid. If they are addition compounds, such treatment would completely precipitate the hydrated dioxide of osmium or iridium. The chemical properties of tellurium tetrafluoride have scarcely been investigated. Its preparation by the action of selenium tetrafluoride on tellurium dioxide (25) and the preparation of pyridinium pentafluorotellurite and dipyrindinium hexafluorotellurite (2) have been described.

C. RELATIVE ACIDITIES OF COVALENT FLUORIDES

Some interesting observations have been made on the relative acidities of covalent fluorides, acidity being defined as the ability to coordinate a fluoride ion to form ions of the type MF_n^- . The solubility of metal fluorides in bromine trifluoride has been examined (128). The moderate solubilities of the alkali metal fluorides are interpreted as being due to base formation:



and the high solubility of niobium pentafluoride as due to acid formation:

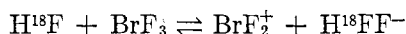


This is the only covalent fluoride examined, and the results are those expected from the evidence given previously. A more extensive study has been made (30) of the relative acidities of solutions of covalent fluorides in anhydrous hydrogen fluoride. The relative acidity was determined by the ability of these solutions to dissolve basic metallic fluorides such as CoF_3 , AgF_2 , AgF , and NaF . Although other covalent fluorides gave indirect evidence (such as salt formation) of acidity, only four fluorides— SbF_5 , AsF_5 , BF_3 , and SnF_4 —could be classified as strong acids. Owing to the nature of the reactants, many of the reactions were studied only qualitatively, so it is difficult to make an accurate and reliable comparison of acidities. From these results in hydrogen fluoride solutions, and taking into account the other chemical evidence discussed above, a reasonable order of decreasing acidity is $\text{SbF}_5 > \text{AsF}_5 > \text{PF}_5 > \text{VF}_5 > \text{NbF}_5 = \text{TaF}_5 > \text{UF}_6 > \text{MoF}_6 > \text{WF}_6$. Other fluorides are not included, owing to the lack of information. The inclusion of molybdenum and tungsten hexafluorides among the acidic fluorides by Clifford, Beachell, and Jack (30) is particularly interesting and is based primarily on the dissolution of these hexafluorides in hydrogen fluoride solutions of sodium fluoride, and also on the preparation of unidentified white silver salts. However, another, perhaps more accurate, method of evaluating various fluorides as acids in hydrogen fluoride has shown tungsten hexafluoride to have no acidic properties (74). When a metal fluoride capable of coordinating a fluoride ion is dissolved in hydrogen fluoride and the solution is treated with a

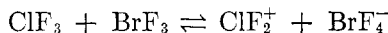
mixture of *m*- and *p*-xylenes, the released proton adds preferentially to the *m*-xylene. The resulting composition of the hydrocarbon mixture thus gives a measure of the acidity of the original fluoride. By this means, titanium tetrafluoride, niobium pentafluoride, and tantalum pentafluoride were found to be strong acids, while tungsten hexafluoride showed no acidic effect. This is the expected result, in view of the chemical evidence discussed previously.

IV. ISOTOPIC EXCHANGE REACTIONS

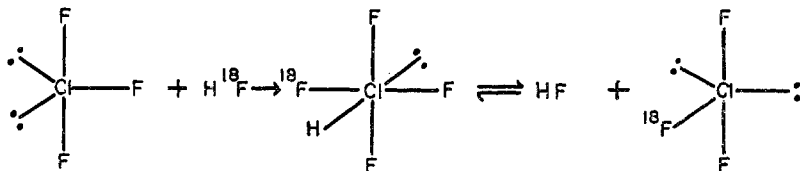
The proposed self-ionization of the halogen fluorides has been studied by an examination of the mechanisms of fluorine exchange between hydrogen fluoride and the halogen fluorides (90) and also between fluorine itself and the halogen fluorides (14, 64). Rapid exchange of ^{18}F was observed between H^{18}F and BrF_3 , ClF_3 , IF_5 , BrF_5 , or SbF_5 , and between Cl^{18}F_3 and BrF_3 , in both the liquid and the vapor phase. In the liquid state, the fast reaction rates may be readily explained by assuming the existence of ionic equilibria:



The exchange of fluorine between the trifluorides of bromine and chlorine is said to proceed as follows:



The fact that rapid fluorine exchange was observed with ClF_3 , BrF_5 , and SbF_5 seems of great importance to the theory of self-ionization, but it must be emphasized that a mechanism involving a nonionic intermediate complex is not precluded. Such a mechanism must be invoked to explain the observed rapid exchange of fluorine in the vapor state. The homogeneous exchange between HF and ClF_3 vapors is thus said to proceed by the mechanism shown involving the intermediate HClF_4 . Similarly, the nonionic activated intermediate HBrF_6 will



be responsible for the vapor-phase exchange of fluorine between H^{18}F and BrF_5 . This type of mechanism would clearly also explain the observed liquid-phase reactions; indeed, for reactions involving chlorine trifluoride and bromine and antimony pentafluorides, it provides a more satisfactory explanation than the ionic mechanism. Other evidence is also available to show the existence of the complexes $\text{ClF}_3 \cdot \text{HF}$, $\text{BrF}_3 \cdot \text{HF}$, and $\text{SbF}_5 \cdot \text{HF}$. From spectral studies of mixtures of hydrogen fluoride and chlorine trifluoride (85) the weak band observed at 2.57μ has been attributed to the presence in low concentration of the complex $\text{ClF}_3 \cdot \text{HF}$. Similar studies of bromine trifluoride in contact with hydrogen fluoride

vapor indicate the existence of the analogous compound $\text{BrF}_3 \cdot \text{HF}$ (53). From the liquid-vapor equilibrium of the system chlorine trifluoride-hydrogen fluoride (75) changes in the apparent heat of mixing with variations in composition have been attributed to the formation of the $\text{ClF}_3 \cdot \text{HF}$ complex, particularly in solutions rich in chlorine trifluoride. However, the solid-liquid equilibrium shows no evidence of compound formation. A slightly earlier study of the same system using measurements of vapor pressure and conductance (97) likewise shows that the $\text{ClF}_3 \cdot \text{HF}$ complex is unstable and probably present only in low concentration. Complex formation of the type $\text{SbF}_5 \cdot x\text{HF}$ is claimed to be partly responsible for the observed departures from ideality for the vapor-liquid equilibrium in the antimony pentafluoride-hydrogen fluoride system (124).

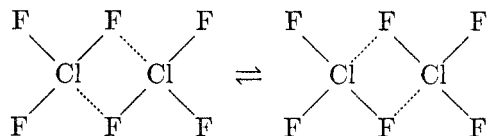
Negligible exchange of fluorine atoms between the halogen fluorides and fluorine molecules was observed below 100°C . Above 200°C . the exchange became rapid and was attributed partly to heterogeneous catalysis by the metal fluoride coating on the walls of the reaction vessel, and partly to homogeneous gas-phase exchange. Hence, while these exchange experiments do not discredit the concept of self-ionization, the results certainly emphasize the importance of the covalent combination of fluorides.

V. NUCLEAR MAGNETIC RESONANCE SPECTRA

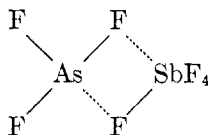
Reference has already been made to several structural determinations using nuclear magnetic resonance methods. The extension of these methods to the study of the temperature dependence of the nuclear magnetic resonance spectra of the halogen fluorides has already provided valuable information on acid-base equilibria. At -40°C . the F^{19} nuclear magnetic resonance spectrum of chlorine trifluoride consists of two peaks with multiplet structure (78). As the temperature is increased, these peaks merge until at 60°C . only one broad peak is observed. This change of a two-line spectrum into a single resonance is known to be due to exchange phenomena of high frequency (52). The spectrum change may thus be attributed to exchange of fluorine between the chlorine trifluoride molecules. Similar although less satisfactory changes were observed in the spectra of bromine trifluoride and iodine pentafluoride, although, owing to the high melting point of bromine trifluoride, the temperature could not be lowered to the point where the expected fine structure of the spectrum would appear. For bromine pentafluoride there was no significant broadening of the spectral lines up to 180°C . These differences between the spectral variations for the various halogen fluorides have been attributed to differences in the activation energy of fluorine exchange, the order of activation energies being $\text{BrF}_5 > \text{ClF}_3 > \text{IF}_5 > \text{BrF}_3$.

Of the three exchange mechanisms considered, that involving self-ionization is discounted, since the order of the halogen fluorides according to their varying degrees of ionization as reflected by their specific conductivities is quite different from the observed order of the rates of fluorine exchange. A simple dissociative mechanism is not possible at ordinary temperatures, in view of the thermal stability of the halogen fluorides. The conclusion is therefore reached that ex-

change probably occurs through dimer formation.



In a later paper, the interaction of inorganic fluorides with arsenic trifluoride is considered (79), and it is concluded from nuclear magnetic resonance measurements that the compound $\text{AsF}_3\text{-SbF}_5$ does not consist entirely of AsF_2^+ and SbF_6^- ions (146), but has a bridge-type structure.



Antimony pentafluoride itself is also said to exist as a dimer with the same fluorine-bridge configuration. These nuclear magnetic resonance measurements, therefore, again emphasize the importance of fluorine-bridged covalent structures. The extensive application of such studies to other covalent fluorides will clearly provide much valuable information.

VI. CONCLUSIONS

As the above evidence shows, perhaps too much emphasis has previously been placed on ionic reaction mechanisms and the self-ionization of these halogen and other covalent fluorides. The more recent evidence shows the importance of fluorine-bridged dimers and association complexes in the chemistry of the halogen fluorides, and it may reasonably be concluded that, with the exception of the hexafluorides of Group VI elements, the other covalent fluorides considered here are similarly associated in the liquid state. Differences in properties may then be largely due to the degree of ionic dissociation of the covalent dimer. The degree of such self-ionization will depend on several factors. (a) The electronegativity difference between the central atom and fluorine, a small difference apparently producing only slight self-ionization. (b) The possible saturation of coordination sites about the central atom. (c) Related to the electronegativity difference is the polar character of the molecule which directly determines its ability to solvate any solute. It should be emphasized, however, that the determination of relative degrees of self-ionization by a comparison of the solvent abilities of the pure fluorides is not strictly valid. The only reliable measure is the degree of ionization which each of these fluorides exhibits in dilute solution in some common solvent. Experimentally, this would be rather difficult to determine.

The halogen fluorides illustrate the interplay of these factors. Chlorine and fluorine have a small electronegativity difference, so that chlorine trifluoride will not undergo self-ionization to any extent but will exist as the associated covalent dimer. Bromine trifluoride, on the other hand, with a larger electro-

negativity difference and with the bromine atom still coordinatively unsaturated, will be expected to show a much higher degree of ionization and considerable solvating power. Of the two pentafluorides, where coordination saturation of the central atoms is being approached, only iodine pentafluoride with the larger electronegativity difference will show self-ionization. Owing to the already high coordination number of iodine in iodine heptafluoride, no self-ionization would be expected. Similar arguments can be extended to the other covalent fluorides. The achievement of coordination saturation may explain why the pentafluorides of the Group V elements are first able to associate, this being followed by self-ionization owing to the large electronegativity difference. The hexafluorides of Group VI elements are already in a coordinatively saturated state and will not therefore associate. There are still, however, difficulties which cannot be explained in these terms. For instance, it is difficult to see why antimony pentafluoride is not ionized to any extent, nor is there on this basis any reasonable explanation of the ionic behavior of selenium tetrafluoride. Hence much remains to be done in both the determination and the explanation of the physical and chemical properties of these covalent fluorides.

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