Structure and Exchange Processes in Some Inorganic Fluorides by Nuclear Magnetic Resonance[1]

BY E. L. MUETTERTIES AND W. D. PHILLIPS

Examination of the chemical shifts and nuclear spin coupling constants of a series of fluorides of the type MF_n, where n = 3, 4, 5, 6, has been made, and the results have yielded details concerning structure of these molecules and their fluorine exchange processes. The spectra of SF_4 and SeF_4 are consistent with C_{2v} rather than tetrahedral symmetries. Intermolecular fluorine exchange was established by temperature or pH dependences of the F^{19} spectra of SF_4, SeF_4 and SiF_6^-. Values of 4.5 ± 0.8 kcal. for ΔE_a and 10^7 to 10^9 sec.$^{-1}$ for ν_0 were obtained for fluorine exchange in SF_4. Fluorine-bridged structures are suggested as exchange intermediates in the tetrafluorides.

Introduction

Fluorine compounds are particularly suited for nuclear magnetic resonance studies. The F^{19} nucleus has a high resonance sensitivity, and chemical shifts between fluorine atoms of non-equivalent environments generally are quite large. Furthermore, fluorine forms a class of covalent inorganic compounds that is second only to organometallic compounds in size and diversity. Previous surveys of the F^{19} resonances of binary fluorides by Gutowsky and Hoffman[2] and by Gutowsky, McCall and Slichter[3] have significantly contributed not only to the understanding of structure and bonding in inorganic fluorides but also to the elucidation of the nuclear magnetic resonance phenomenon itself. Molecular processes, such as fluorine exchange, have also been detected and studied by nuclear magnetic resonance techniques.[4]

Experimental

Source and Purity of Materials.—All fluoride samples used in this study either were obtained from commercial sources or were prepared by standard literature procedures. Some of these fluorides were found to exhibit spectra sensitive to impurities and these specific cases are described below.

The spectra of all fluorides that are of tetrahedral or octahedral symmetry were found to be relatively insensitive to fluoride impurities such as hydrogen fluoride or arsenic trifluoride. On the other hand, fluorides of lower symmetry tended to undergo a catalyzed exchange in the presence of fluoride impurities. This condition was manifested by a broadening of spectra or collapse or multi-line spectra into single resonances. Those fluorides, e.g., AsF_5, SbF_5, SF_4 and SeF_4, whose spectra proved sensitive to the presence of fluoride impurities, were satisfactorily purified by treatment with or storage over dry sodium fluoride to remove traces of hydrogen fluoride and distillation prior to sampling. Because of the similarity of the boiling points of SF_4 and SOF_2, distillation of SF_4 (invariably contaminated with SOF_2) always yielded samples containing traces to 5% SOF_2. However, it was established that SOF_2 does not detectibly catalyze fluorine exchange in SF_4. Fluorine exchange in SeF_4 was so rapid that an inert solvent, propane, was required to lower the freezing point of the sample to temperatures below $-197°$ in order that fine n.m.r. structure characteristic of the slowly exchanging species could be observed at -200 to $-190°$. Although gross amounts of IF_5 or BrF_3 did not alter the fine structure of the BrF_5 spectrum, trace amounts of SbF_5 or AsF_5 were sufficient to

collapse the quintuplet and doublet of BrF_5 into a single peak. Iodine pentafluoride behaved similarly and was also found to undergo fast exchange in the presence of hydrogen fluoride (>3% HF) and in the presence of potassium, rubidium or cesium fluorides (>1% MF).

BrF_3 and ClF_3 proved exceptionally sensitive to impurities and required purification by distillation in quartz equipment which was predried under high vacuum at 250°. The distillation cuts were collected and sealed in 2 mm. i.d. quartz capillaries. The melting points found for purified samples of ClF_3 and BrF_3 were -76 and $+8.9°$, respectively. Samples of these fluorides purified by conventional techniques and even some samples purified by the above procedure produced single, broad, temperature-insensitive F^{19} resonances.

Arsenic pentafluoride was the only fluoride not purified to a degree deemed satisfactory for the n.m.r. measurements. This pentafluoride was distilled twice at atmospheric pressure, further vacuum distilled and then sampled in the same quartz equipment described above for the halogen trifluorides. Despite the precautions taken, the samples of the pentafluoride invariably contained very fine colloidal particles and these particles are believed to be at least partly responsible for the breadth of the AsF_5 resonance. The presence of colloidal solids is also believed to be responsible for the slight broadening of the main and satellite peaks in the MoF_6 spectrum. Colloidal solids also tended to be present in samples of BF_3 and IF_5, but distillation and sampling in quartz equipment was sufficient to rigorously exclude colloidal solids from the BF_3 and IF_5 samples.

Method.—The fluorine magnetic resonance spectra were obtained using a Varian high resolution n.m.r. spectrometer and electromagnet[5] at frequencies of 30 and 40 Mc. and fields of 7,500 and 10,000 gauss, respectively. The spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the fluorine resonance of trifluoroacetic acid. Because of the large chemical shifts found for some of the fluorides, it was necessary to use, as secondary standards, sulfur hexafluoride and molybdenum hexafluoride. Calibration was accomplished by superimposing an audio-frequency on the sweep field to produce side band peaks to the trifluoroacetic acid resonance.[6]

I. Chemical Shifts.—F^{19} chemical shifts obtained for 27 fluorides of the type MF_n, where n = 3, 4, 5, 6, are given in Table I. The results of Table I are usually in good agreement with the results of Gutowsky and Hoffman[2] and Gutowsky, McCall and Slichter[3] insofar as they overlap. As Gutowsky and Hoffman pointed out,[2] the F^{19} resonances of binary fluorides exhibit a general paramagnetic shift with increasing electronegativity of the atom to which fluorine is bonded. This general trend led Saika and Slichter[7] to their treatment of F^{19} shifts in terms of the occupancy of the bonding $2p_z$ orbital of fluorine. They showed that to a first approximation F^{19} chemical shifts (leav-

(1) Presented before the Division of Inorganic Chemistry, National Meeting of the American Chemical Society, San Francisco, California, April, 1958.

(2) H. S. Gutowsky and C. J. Hoffman, J. Chem. Phys., **19**, 1259 (1951); erratum, **20**, 200 (1952).

(3) H. S. Gutowsky, D. W. McCall and C. P. Slichter, ibid., **21**, 279 (1953).

(4) E. L. Muetterties and W. D. Phillips, THIS JOURNAL, **79**, 322 (1957).

(5) Varian Associates, Palo Alto, California.

(6) J. T. Arnold and M. E. Packard, J. Chem. Phys., **19**, 6108 (1951).

(7) A. Saika and C. P. Slichter, ibid., **22**, 26 (1954).

ing aside considerations of electronic excitation energies) should be a linear function of the ionic character of the M–F bond. It is to be expected that such a treatment should have greatest validity in application to diatomic molecules. Some of the difficulties inherent in the extensions of Saika and Slichter's treatment to polyatomic fluorides is exemplified by the large intramolecular shifts found in ClF_3, SF_4, BrF_5, IF_5 and SbF_5. In these compounds it would appear that other mechanisms, such as magnetic anisotropies discussed by Pople,[8] are important.

TABLE I

F^{19} CHEMICAL SHIFTS AND SPIN–SPIN SPLITTINGS IN SOME BINARY FLUORIDES

Compound	Chemical shift $= \dfrac{H_C - H_R}{H_R} \times 10^4$ (ref.: CF_3COOH)	M–F Coupling constant	J_{M-F} (c.p.s.)
NF_3	−2.19	N^{14}	160
ClF_3	−1.93, −0.810	...	..
BrF_3	−0.543	...	..
PF_3	− .423	P^{31}	1441
AsF_3	− .350	...	..
SbF_3	− .239	...	..
BF_3	+ .542	B^{11}	10
SF_4	−1.95, −1.48	...	..
SeF_4	−1.41	...	..
TeF_4	−0.514	...	..
CF_4	− .119	...	..
BF_4^-	+ .710	...	..
SiF_4	+ .833	Si^{29}	178
GeF_4	+ .990	...	..
BrF_5	−3.49, −2.19	...	..
IF_5	−1.38, −0.958	...	..
PF_5	−0.0520	P^{31}	916
AsF_5	− .113	...	..
SbF_5	+0.0683, +0.262, +0.520	...	..
MoF_6	−3.55	Mo^{95}, Mo^{97}	44
WF_6	−2.42	W^{183}	48
SeF_6	−1.28	Se^{77}	1400
SF_6	−1.27	...	..
TeF_6	−0.206	Te^{125}	3688
		Te^{123}	3052
PF_6^-	− .116	P^{31}	710
SiF_6^-	+ .498	Si^{29}	110
AsF_6^-	− .181	As^{75}	930
SbF_6^-	+ .323	Sb^{121}	1843

II. Coupling Constants.—M–F nuclear spin coupling constants were measured for 13 binary fluorides (Table I). A typical spectrum is that of TeF_6 shown in Fig. 1. The intense resonance at 617 c.p.s. is assigned to fluorine atoms bonded to the most abundant tellurium isotope, Te^{128} ($\mu = 0$). The satellites occurring at 2461 c.p.s. and −1227 c.p.s. are assigned to fluorine atoms bonded to the Te^{125} isotope ($\mu = -0.8824$ nuclear magnetons, $I = 1/2$, abundance = 7.03%), and those at 2143 c.p.s. and −909 c.p.s., to fluorine atoms bonded to the Te^{123} isotope ($\mu = -0.7319$ nuclear magnetons, $I = 1/2$, abundance = 0.89%). The ratio of Te^{125}–F^{19} and Te^{123}–F^{19} coupling constants (3688/3032 = 1.208) is in good agreement with the ratio of Te^{125} and Te^{123} nuclear moments (1.206). Similarly, resonance intensities are in semi-quanti-

(8) J. A. Pople, Proc. Roy. Soc. (London), **A239**, 541 (1957).

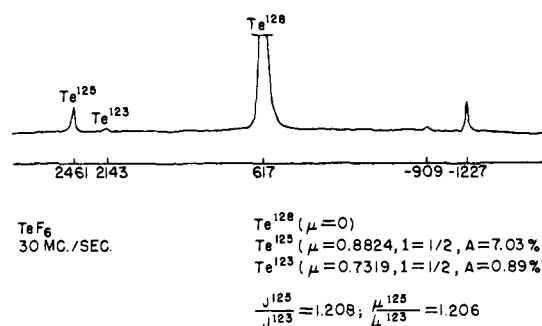Fig. 1.—F^{19} spectrum of TeF_6 at 30 Mc.

tative agreement with the Te^{125}/Te^{123} isotope abundance ratio (7.9:1).

The F^{19} magnetic resonance spectrum of MoF_6 (Fig. 2.) consists of a central, strong resonance ac-
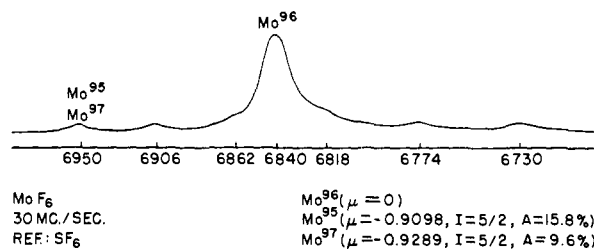

Fig. 2.—F^{19} spectrum of MoF_6 at 30 Mc.

companied by six satellites. The 6840 c.p.s. resonance arises from fluorine atoms bonded to the most abundant molybdenum isotope, Mo^{96} ($\mu = 0$). The six satellites arise from fluorine atoms bonded to the Mo^{95} isotope ($\mu = 0.9098$, $I = 5/2$, abundance = 15.78%) and the Mo^{97} isotope ($\mu = -0.9289$, $I = 5/2$, abundance = 9.60%). Because of the similarity of the magnetogyric ratios of the Mo^{95} and Mo^{97} isotopes and the breadths of the F^{19} resonances of MoF_6, multiplet components arising from fluorine atoms bonded separately to the Mo^{95} and Mo^{97} isotopes appear coincident.

Gutowsky, McCall and Slichter[3] concluded that for a series of compounds involving a given central atom, M, and various numbers of fluorine atoms, the magnitudes of the M–F coupling constants should depend largely on the fractional p-character of the bonding hybrid of M, since the p-component of the hybrid can couple significantly with the 2 p-
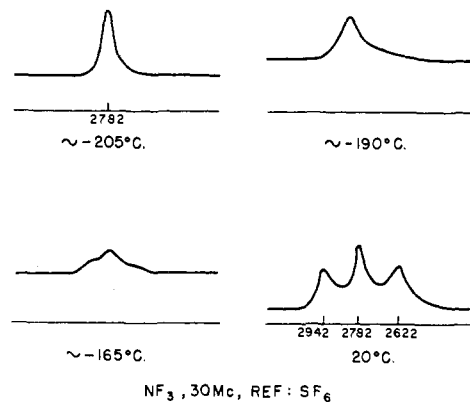

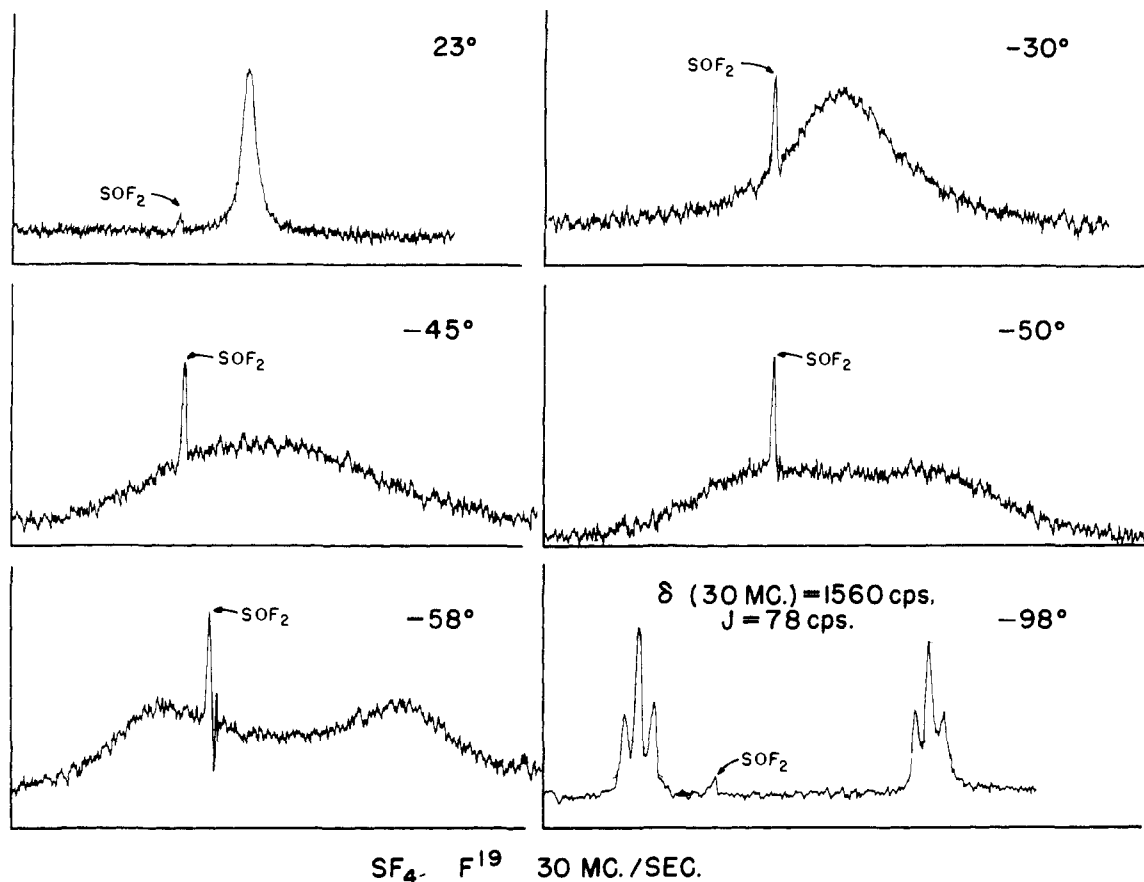Fig. 3.—Temperature dependence of F^{19} spectrum of NF_3.

Fig. 4.—Temperature dependence of F^{19} spectrum of SF_4.

orbital of fluorine to yield splitting. They have pointed out that such a trend is observed for the phosphorus fluorides. Si–F coupling constants of 178 and 110 c.p.s. were observed in SiF_4 and $SiF_6^=$, respectively. The bonding hybrids of silicon in SiF_4 and $SiF_6^=$ are probably sp^3 and sp^3d^2, respectively. Thus, the ratio of Si–F splittings in SiF_4 and $SiF_6^=$ might be expected to be $3/4:3/6 = 1.5$, in fair agreement with the observed ratio of splittings which is 1.6.

III. Temperature Dependence of the F^{19} Spectrum of NF_3.—The temperature dependence of the F^{19} spectrum of NF_3 is presented in Fig. 3. The triplet structure to the F^{19} resonance observed at room temperature is seen to collapse to a singlet at temperatures below about $-180°$. This behavior is similar to that observed by Roberts[9] for protons bonded to nitrogen in amines and seems to be due to effects of quadrupole relaxation on the N^{14} nucleus.

Pople[10] recently has discussed effects of quadrupole relaxation on nuclear resonances and has shown that fluorine (or proton) multiplet structure due to splittings by the N^{14} nucleus ($I = 1$) will disappear when τ, the lifetime of a given N^{14} nuclear spin state, is given by

$$\tau \approx 5/(2\pi J)$$

where J is the N^{14}–F^{19} coupling constant in c.p.s. Since $J = 160$ c.p.s. for NF_3, the lifetime of a given

(9) J. D. Roberts, THIS JOURNAL, **78**, 4495 (1956).
(10) J. A. Pople, *Molecular Physics*, **1**, 168 (1958).

N^{14} nuclear spin state must be less than about 10^{-3} sec. below $-180°$.

IV. Fluorine Exchange in SF_4 and SeF_4.—Recently, Cotton, George and Waugh[11] have concluded from the low temperature F^{19} spectrum of SF_4 that the molecule possesses C_{2v} rather than tetrahedral symmetry. A similar conclusion regarding the structure of SF_4 was reached earlier by Dodd, Woodward and Roberts[12] from analysis of the vibrational spectrum of the molecule. Cotton, George and Waugh[11] further analyzed the temperature dependence of the F^{19} spectrum of SF_4 in terms of fluorine exchange. An independent study of the kinetics of fluorine exchange in SF_4 is presented below.

The temperature dependence of the F^{19} spectrum of SF_4 is shown in Fig. 4. The width at half maximum of the $23°$ F^{19} resonance of SF_4 is about 90 c.p.s. This width increases as the temperature of the sample is reduced, reaching a value of about 1300 c.p.s. at $-45°$. At $-47°$, the single, broad F^{19} resonance of SF_4 is replaced by two resonances of equal intensity that sharpen at temperatures below $-47°$ and become resolved triplets at $-85°$. The sharp, extraneous peak in the spectra of Fig. 4 is due to $\sim 5\%$ SOF_2 occurring as impurity in our SF_4 samples.

The temperature dependence of the F^{19} spectrum

(11) F. A. Cotton, J. W. George and J. S. Waugh, *J. Chem. Phys.*, **28**, 994 (1958).
(12) R. E. Dodd, L. A. Woodward and H. L. Roberts, *Trans. Faraday Soc.*, **52**, 1052 (1955).

of SF_4 is ascribed to exchange of fluorine atoms between the two non-equivalent fluorine environments of the pseudo trigonal bipyramid. The data were treated by the method of Gutowsky and Holm[13] in which the observed separation between the chemically shifted resonances, $\delta\omega_e$, below $-47°$ is given by

$$\delta\omega_e = \left(1 - \frac{2}{\tau^2\delta\omega^2}\right)^{1/2}\delta\omega$$

where τ is the average lifetime of fluorine nuclei in the two environments and $\delta\omega$ is the chemical shift in the absence of exchange effects, e.g., $\tau\delta\omega \gg \sqrt{2}$. If fluorine exchange in SF_4 is assumed to be first order (intramolecular), the treatment of rate processes of Gutowsky and Holm[13] yields for SF_4 (Fig. 5) an activation energy of 4.5 ± 0.8 kcal. and a frequency factor of 10^7 to 10^9 sec.$^{-1}$ for fluorine exchange. If the exchange is not first order as assumed in the foregoing treatment, the frequency factor given above will, of course, be altered but the activation energy will remain unchanged. The value of 4.5 ± 0.8 kcal. is in good agreement with that of 4 ± 1 kcal. obtained by Cotton, George and Waugh.[11]
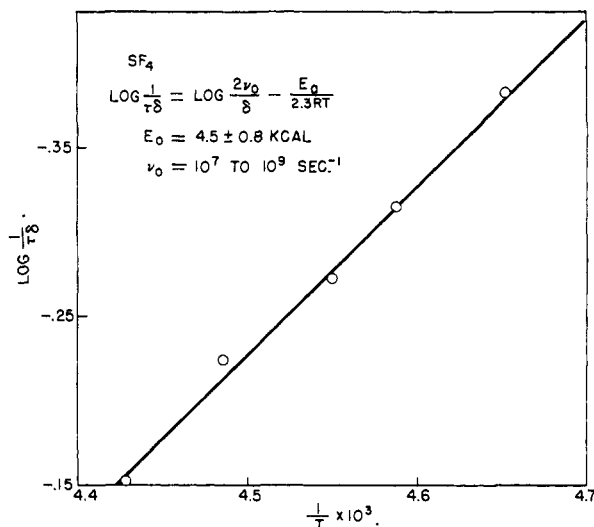

Fig. 5.—Determination of E_a and ν_0 for fluorine exchange in SF_4.

Some attempts were made to determine the order and mechanism of exchange in SF_4. A sample of SF_4 was sealed off in a 5 mm. o.d. "Pyrex" n.m.r. tube containing finely divided glass fragments. The increase of wall area by at least a factor of 100 did not affect the $-47°$ temperature of transition between "slow" and "fast" fluorine exchange in SF_4. Thus, a wall reaction can be ruled out as the exchange mechanism.

If fluorine exchange in SF_4 proceeds by a second-order process, i.e., through dimer or ionic intermediates, the average time between fluorine exchanges should be inversely proportional to SF_4 concentration. It was found that the temperature required to collapse the two resonances of SF_4 to a single peak for various concentrations of

(13) H. S. Gutowsky and C. H. Holm, J. Chem. Phys., 25, 1128 (1956).

SF_4 in carbon tetrachloride, toluene or diethyl ether ranged from 25 to 60° above the $-47°$ transition temperature observed for pure SF_4. Although concentrations of SF_4 in the solution studies were not sufficiently well known to establish the precise order of the SF_4 fluorine exchange reaction, it nevertheless is clear that exchange is not first order but is second or higher order.

Results of this study do not permit discrimination between ionic and associative mechanisms but dissociation of the type $SF_4 \rightleftarrows SF_3 + F$ can be rigorously ruled out because the solvents were not fluorinated by SF_4. The temperature required to collapse the triplet fine structure of solutions (mole fraction ~ 0.5) of SF_4 in carbon tetrachloride, toluene, perfluorodimethylcyclohexane, acetonitrile, diethyl ether, ethyl acetate or tetramethylene sulfide ranged from -15 to $+15°$ as compared with the temperature of $-85°$ for pure SF_4. A correlation did not appear to exist between dielectric constant of the medium and the observed exchange rate. This, however, does not rule out an ionization mechanism since nothing is known about solvation effects for possible ionic species. However, recent studies by Hoffman, Holder and Jolly[14] have indicated that liquid SbF_5 is associated to at least dimers and probably to cyclic or linear polymers through fluorine bridges and that such bridging could be acting as the mechanism for fluorine exchange observed also in SbF_5.[15] An intermediate formed by association of SF_4 to dimers (Fig. 6) or polymers through fluorine bridges could also be effective in producing fluorine exchange in SF_4.
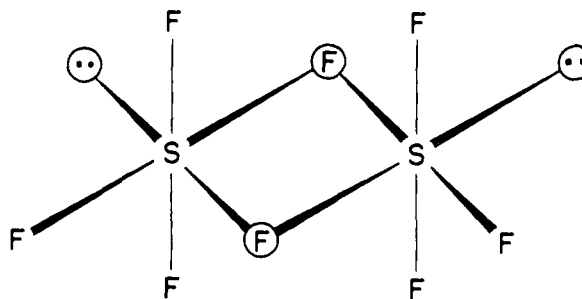

Fig. 6.—Possible SF_4 dimer intermediate in fluorine exchange.

The F^{19} magnetic resonance spectrum of SeF_4 consists of a single peak above its melting point of $-9°$. A solution of SeF_4 in propane displayed at $\sim -200°$ two fluorine resonances that broadened and merged when the temperature was raised

(14) C. A. Hoffman, B. E. Holder and W. L. Jolly, J. Phys. Chem., 62, 364 (1958).

(15) Of the pentafluorides investigated, only SbF_5,[14] BrF_5[8] and IF_5[8] exhibited fine structure due to expected non-equivalence of fluorine environments in these molecules. The pentafluorides of niobium and tantalum in the molten state (>75 and 97°, respectively) exhibited single resonances. Absence of fine structure may be due to fluorine exchange, and it is suggested that fluorine bridge-bonding similar to that found in SbF_5 contributes to the lattice energies and to the short-range order in the melts of NbF_5 and TaF_5. The spectrum of PF_5 was found temperature insensitive[8] thus ruling out fluorine exchange as the explanation for the apparent equivalence of fluorine environments. It has been suggested by G. A. Williams (University of Illinois Thesis, 1956) that apparent equivalence in PF_5 is a result of $J \gg \delta$ where J and δ are, respectively, the expected coupling constant and the chemical shift between non-equivalent fluorine atoms.

above $\sim -190°$. It was not possible to cool the sample sufficiently to resolve the expected triplet fine structure of the two resonances. In any case, this behavior is similar to that of SF_4 and indicates that SeF_4 also possesses C_{2v} symmetry and undergoes fluorine exchange at a much more rapid rate than does SF_4. Tellurium tetrafluoride, a relatively high-melting solid,[16] gave a single, fairly sharp fluorine resonance in toluene solution down to the freezing point ($\sim -100°$) of the solution. A lower melting solvent for TeF_4 was not found. The data suggest that the rates of fluorine exchange in the Group VI tetrafluorides follow the order: $SF_4 < SeF_4 < TeF_4$. This order is the same as the order of increasing molecular association (as evidenced by melting and boiling points) for these fluorides and is consistent with the suggested association mechanism for fluorine exchange.

V. Fluorine Exchange in Fluoroanions.—The F^{19} magnetic resonance spectrum of an aqueous solution of $(NH_4)_2SiF_6$ consists of an intense resonance arising from fluorine atoms bonded to the Si^{28} isotope ($\mu = 0$) and two weak satellites arising from fluorine atoms bonded to the Si^{29} isotope ($\mu = -0.5549$ nuclear magnetons, $I = 1/2$, abundance $= 4.70\%$). The appearance of the satellites to the F^{19} resonance of $SiF_6^=$ indicates that exchange of fluorine atoms between anions must be proceeding at an average rate of less than about 10^3 sec.$^{-1}$ in this solution. Separate F^{19} resonances are observed for F^- and $SiF_6^=$ in aqueous solutions containing NH_4F and $(NH_4)_2$-SiF_6 as well as Si^{29} satellite resonances to the $SiF_6^=$ resonance. This observation indicates that fluorine exchange between $SiF_6^=$ and F^-, if existent, is a slow process.

The F^{19} resonance of an aqueous solution of $MgSiF_6$ is broad and the Si^{29}–F^{19} fine structure is not observable. Slight acidification of the $(NH_4)_2$-SiF_6/H_2O solution by HCl produces a similar broadening of the F^{19} resonance of $SiF_6^=$. These results are consistent with a mechanism involving acid catalysis of fluorine exchange between $SiF_6^=$ species, inasmuch as Mg^{++} produces an acid solu-

(16) The large lattice energy of solid TeF_4 (m.p. $>200°$) relative to solid SF_4 (m.p. $-121°$) and SeF_4 (m.p. $9.5°$) may in fact be a reflection of *strong* fluorine bridge bonds that create a "polymeric" type of structure, *e.g.*, a cyclic tetramer with *cis* fluorine bridge bonds.

tion by hydrolysis equivalent to direct acidification. A possible mechanism for fluorine exchange between $SiF_6^=$ ions in aqueous solutions suggested by these qualitative observations is through an intermediate such as $F_5Si^=\cdots F\cdots H^+$ involving strong H–F bonding
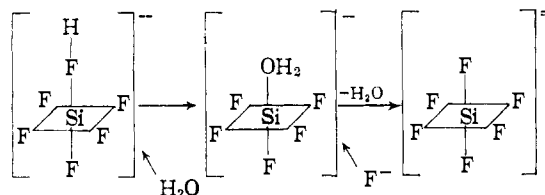
The F^{19} resonance of an aqueous solution of ammonium hexafluorophosphate consists of a strong fluorine resonance that is split into a doublet by spin-spin coupling between F^{19} and P^{31} ($I = 1/2$). Similarly, the spectrum of an aqueous solution of silver hexafluoroarsenate consists of a strong fluorine resonance that is split into a quadruplet by coupling between F^{19} and As^{75} ($I = 3/2$). These spectra are insensitive to pH (2 to 10) and to temperature (20 to 80°) indicating that, in agreement with literature reports,[17,18] these anions are resistant to hydrolysis and to fluorine exchange. The observed fine structure indicates that hydrolysis or exchange of fluorine atoms between anions must be proceeding at a rate less than $\sim 10^2$ sec.$^{-1}$ for PF_6^- and AsF_6^-.

The Sb^{121} spectrum of aqueous $KSbF_6$ consists of a strong resonance split into a septuplet[19] due to spin-spin coupling between F^{19} and Sb^{121}. The F^{19} resonance of SbF_6^- consists of a single, broad resonance in which absence of detail probably is ascribable to overlap of multiplet components arising from Sb^{121} and Sb^{123} splittings. The SbF_6^- anion like the AsF_6^- and PF_6^- anions is not susceptible to fast exchange ($\tau > 10^{-4}$ sec.) of fluorine atoms between anions.

WILMINGTON, DELAWARE

(17) H. M. Dess and R. W. Parry, THIS JOURNAL, 79, 1589 (1957).

(18) J. H. Simons, "Fluorine Chemistry," Vol. I, Academic Press Inc., New York, N. Y., 1950, p. 166.

(19) S. S. Dharmatti and H. E. Weaver, Jr., Phys. Rev., 87, 675 (1952).