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THE FLUORIDE COMPLEXING OF SCANDIUM(III) IN AQUEOUS SOLUTION: 
FREE ENERGIES, HEATS, AND ENTROPIES
John W. Kury, Armine D. Paul, Loren G. Hepler, and Robert E. Connick
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ABSTRACT

The complexing of Sc(III) in perchlorate solutions at an ionic strength of 0.5 M was determined by studying the potential of the ferrous-ferric electrode as a function of the HF, H+, and Sc(III) concentrations. The data can be interpreted by assuming the presence of the species ScF++, ScF4+, ScF3(aq) and ScF2-. Equilibrium constants for the formation of these complexes at 15°C, 25°C, and 35°C were evaluated and from them the heat and entropy changes of the reactions calculated. The scandium fluoride complexes are more stable than those of other trivalent ions of comparable radius. The extra stability of the complex scandium fluorides arises from an irregularity in the heat term, rather than in the entropy term.

INTRODUCTION

This investigation was undertaken because of the work of Dodgen(1) who

(1) H. W. Dodgen, private communication

found the scandium fluoride complexes to be more stable than those of other trivalent ions of similar radius. According to Pauling,(2) In(III) has

the same ionic radius (0.81 Å) as Sc(III). However, the first fluoride complex of Sc(III) is about 280 times more stable than the first fluoride complex of In(III).\(^3\) We wished to determine whether the greater stability


of the scandium fluoride complexes arises from the heat term or the entropy term.

The "ferri" method of Brosset and Orring\(^4\) was used. The complexing


of Sc(III) was determined indirectly by studying its effect on the ferric fluoride complexing equilibria, as measured potentiometrically through the ferrous-ferric couple.

**Experimental**

**Apparatus.** Descriptions of the cells, electrodes, measuring apparatus, and general procedure are given elsewhere.\(^3, 5, 6\)


**Solutions.** A scandium perchlorate-perchloric acid stock solution was prepared by dissolving spectrophotically pure Sc₂O₃ in perchloric acid. The solution was analyzed for scandium by precipitating it as the hydroxide and weighing as Sc₂O₃. The acidity was determined by precipitating the scandium as ScF₃ and titrating with standard base to the phenolphthalein end point.
Double vacuum-distilled perchloric acid was diluted with water and
the solution standardized against mercuric oxide. Sodium fluoride
solutions were prepared by dissolving weighed amounts of the CP salt which
had been dried at 150\(^\circ\).

A stock solution of sodium perchlorate was prepared by treating CP
sodium carbonate with an excess of perchloric acid. After boiling to
expel the carbon dioxide, the pH was adjusted to 5-6 with carbonate free
sodium hydroxide and the solution then filtered. Aliquots were evaporated
to dryness, dried for several hours at 160\(^\circ\), and weighed as NaClO\(_4\).

A ferrous perchlorate-ferric perchlorate-perchloric acid stock
solution was prepared by dissolving a weighed amount of electrolytic iron
in a known amount of perchloric acid. A portion of the resulting ferrous
perchlorate was oxidized to ferric perchlorate with hydrogen peroxide. The
ferrous ion concentration was determined by titration with standard ceric
sulfate. The ferric ion concentration and the acidity were determined by
difference.

Distilled water was re-distilled from alkaline permanganate for use
in all solutions.

Procedure. - Three half-cells were used which will be designated
A, B, and C. Half-cells A and C, and half-cells B and C, were connected
by sodium perchlorate-agar agar salt bridges. Each half-cell initially
contained the same concentrations of ferrous perchlorate, ferric perchlorate,
and perchloric acid. Half-cell A contained in addition a known concentration
of scandium perchlorate. The ionic strength in each half-cell was adjusted
to 0.50 M with sodium perchlorate. The volumes were equal.
After the initial zero potentials in each cell became constant, known quantities of sodium fluoride were added to half-cells A and B from a calibrated micropipet, and the potential measured after each addition. The fluoride addition was continued until a potential of about 150 millivolts was developed in each cell or until scandium fluoride precipitated. The potential reading became constant to a few hundredths of a millivolt within about one minute after each fluoride addition.

**Experimental Data**

The initial conditions for each experiment are summarized in Table 1.
### Table 1
Initial Experimental Conditions

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$\text{Sc(ClO}_4)_3$ (mole/liter) x $10^3$</th>
<th>$\text{HClO}_4$ (mole/liter)</th>
<th>$\text{Fe(ClO}_4)_2$ (mole/liter) x $10^4$</th>
<th>$\text{Fe(ClO}_4)_3$ (mole/liter) x $10^4$</th>
<th>$\text{NaClO}_4$ (mole/liter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1.273</td>
<td>0.1122</td>
<td>3.593</td>
<td>3.402</td>
<td>0.3087</td>
</tr>
<tr>
<td>25</td>
<td>1.587</td>
<td>0.05287</td>
<td>3.869</td>
<td>3.705</td>
<td>0.4355</td>
</tr>
<tr>
<td>25</td>
<td>2.733</td>
<td>0.05457</td>
<td>3.831</td>
<td>3.669</td>
<td>0.4257</td>
</tr>
<tr>
<td>35</td>
<td>1.587</td>
<td>0.05277</td>
<td>3.868</td>
<td>3.704</td>
<td>0.4350</td>
</tr>
<tr>
<td>35</td>
<td>2.741</td>
<td>0.05493</td>
<td>3.831</td>
<td>3.668</td>
<td>0.4252</td>
</tr>
<tr>
<td>35</td>
<td>6.665</td>
<td>0.1065</td>
<td>3.721</td>
<td>3.563</td>
<td>0.3502</td>
</tr>
<tr>
<td>15</td>
<td>1.587</td>
<td>0.05287</td>
<td>3.868</td>
<td>3.704</td>
<td>0.4350</td>
</tr>
<tr>
<td>15</td>
<td>6.665</td>
<td>0.1065</td>
<td>3.721</td>
<td>3.563</td>
<td>0.3502</td>
</tr>
<tr>
<td>15</td>
<td>2.741</td>
<td>0.05493</td>
<td>3.831</td>
<td>3.668</td>
<td>0.4252</td>
</tr>
</tbody>
</table>
At each temperature the acidity was varied two-fold and the scandium concentration was varied at least five-fold. The maximum stoichiometric fluoride concentration varied from 0.015 to 0.03 $\text{M}$, depending on the

(7) The symbol $\text{M}$ indicates concentrations in moles per liter of solution.

particular experiment.

Sample data for the second experiment of Table 1 are given in Table 2.
Table 2

Data for Second Experiment of Table 1

Initial Volume = 100.95 ml

<table>
<thead>
<tr>
<th>ml NaF added</th>
<th>E (mv)</th>
<th>ml NaF added</th>
<th>E (mv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0747</td>
<td>13.25</td>
<td>0.0747</td>
<td>0.72</td>
</tr>
<tr>
<td>0.1494</td>
<td>24.98</td>
<td>0.1494</td>
<td>1.74</td>
</tr>
<tr>
<td>0.2241</td>
<td>34.71</td>
<td>0.2241</td>
<td>5.16</td>
</tr>
<tr>
<td>0.2988</td>
<td>42.84</td>
<td>0.2988</td>
<td>5.12</td>
</tr>
<tr>
<td>0.3735</td>
<td>49.75</td>
<td>0.4482</td>
<td>11.15</td>
</tr>
<tr>
<td>0.4482</td>
<td>55.64</td>
<td>0.5976</td>
<td>20.18</td>
</tr>
<tr>
<td>0.5229</td>
<td>61.24</td>
<td>0.8964</td>
<td>41.90</td>
</tr>
<tr>
<td>0.5976</td>
<td>66.11</td>
<td>1.0458</td>
<td>51.60</td>
</tr>
<tr>
<td>0.6723</td>
<td>70.53</td>
<td>1.1952</td>
<td>60.60</td>
</tr>
<tr>
<td>1.1707</td>
<td>93.67</td>
<td>1.5687</td>
<td>78.68</td>
</tr>
<tr>
<td>1.6691</td>
<td>110.77</td>
<td>2.1418</td>
<td>99.97</td>
</tr>
<tr>
<td>2.1675</td>
<td>124.57</td>
<td>2.6402</td>
<td>114.69</td>
</tr>
<tr>
<td>2.6659</td>
<td>136.10</td>
<td>3.1386</td>
<td>127.61</td>
</tr>
<tr>
<td>3.1643</td>
<td>146.80</td>
<td>3.6370</td>
<td>159.00</td>
</tr>
</tbody>
</table>
Data for all but the last experiment are given by Paul.  

(8) A. D. Paul, Thesis, University of California, 1955; University of California Radiation Laboratory unclassified report UCRL-2966, April, 1955. The values listed for $\bar{n}$ are slightly in error at high fluoride concentrations because of the use of a poorer approximation than used here in calculating $\bar{n}$.

Analysis of Data

The equilibria in question are:

1. $\text{Sc}^{3+} + \text{HF} = \text{ScF}^{2+} + H^+$ \hspace{1cm} Q_1$
2. $\text{ScF}^{2+} + \text{HF} = \text{ScF}_2^+ + H^+$ \hspace{1cm} Q_2$
3. $\text{ScF}_2^+ + \text{HF} = \text{ScF}_3^{(aq)} + H^+$ \hspace{1cm} Q_3$
4. $\text{ScF}_3^{(aq)} + \text{HF} = \text{ScF}_4^- + H^+$ \hspace{1cm} Q_4$
5. $\text{Fe}^{3+} + \text{HF} = \text{FeF}^{2+} + H^+$ \hspace{1cm} Q_5$
6. $\text{FeF}^{2+} + \text{HF} = \text{FeF}_2^+ + H^+$ \hspace{1cm} Q_6$
7. $\text{FeF}_2^+ + \text{HF} = \text{FeF}_3^{(aq)} + H^+$ \hspace{1cm} Q_7$
8. $\text{Fe}^{3+} + \text{H}_2\text{O} = \text{FeOH}^{2+} + H^+$ \hspace{1cm} Q_n$
9. $\text{HF} = H^+ + F^-$ \hspace{1cm} Q_{HF}$

The hydrolysis of scandium ion and the hydrolytic dimerization of ferric ion


were both negligible under the conditions employed here. The $Q$'s are
equilibrium quotients expressed in concentrations, for example

\[ q_1 = \frac{(ScF^{+2})(H^+)}{(Sc^{+3})(HF)} \]

where the quantities in parenthesis represent the concentrations of the enclosed species in moles per liter. The values at \( \mu = 0.5 \) of \( q_5 \), \( q_6 \), \( q_7 \), \( q_9 \), and \( q_{HF} \) used in these calculations are given in Reference 11.


The difference between the moles of fluoride added to half-cell A and the moles of fluoride added to half-cell B when the potentials are equal is, to a very good approximation, the moles of fluoride in half-cell A present in the form of scandium fluoride complexes. Division by the volume of solution of half-cell A yields the concentration of fluoride as scandium complexes, symbolized by \( \Delta(2F^-) \). The moles of fluoride in half-cell B corresponding to each potential reading of A were read from a plot of the former versus potential.

From stoichiometry it can be seen that

\[ \Delta(2F^-) = (ScF^{+2}) + 2(ScF_2^{+}) + 3(ScF_3^{+}) + 4(ScF_4^{-}) \]  

(11)

\[ (2Sc^{+3}) = (Sc^{+3}) + (ScF^{+2}) + (ScF_2^{+}) + (ScF_3^{+}) + (ScF_4^{-}) \]  

(12)

where \((2Sc^{+3})\) signifies the total stoichiometric concentration of scandium.
Let \( \bar{n} \) represent the average number of fluoride ions held by each scandium ion:

\[
\bar{n} = \frac{\Delta(\text{HF}^-)}{(\text{HSc}^{+3})}
\]

Combining equations (12) and (13) with (1), (2), (3), and (4) yields the following expression for \( \bar{n} \):

\[
\bar{n} = \frac{Q_1 (\text{HF}) + 2Q_1Q_2 (\text{HF})^2 + 3Q_1Q_2Q_3 (\text{HF})^3 + 4Q_1Q_2Q_3Q_4 (\text{HF})^4}{1 + Q_1 (\text{HF}) + Q_1Q_2 (\text{HF})^2 + Q_1Q_2Q_3 (\text{HF})^3 + Q_1Q_2Q_3Q_4 (\text{HF})^4}
\]

In order to obtain values for \( Q_1, Q_2, Q_3 \) and \( Q_4 \) it is necessary to know the value of \( (\text{HF})/(\text{H}^+) \) for each value of \( \bar{n} \), that is as a function of \( E_{A-G} \). At the same potential, the ratio \( (\text{HF})/(\text{H}^+) \) in half-cells A and B is the same to a very good approximation. This ratio can be calculated from the data of cell B-G and the known ferric fluoride complexing constants by solving equation (15) by means of successive approximations.

\[
(1 + \frac{Q_2}{(\text{H}^+)}) \left( e^{\frac{E}{RT}} - 1 \right) = Q_2 (\text{HF}) + Q_2Q_3 (\text{HF})^2 + Q_2Q_3Q_4 (\text{HF})^3
\]

The observed potential is \( E \) and \( F \) is Faraday's constant. The derivation of this equation and the assumptions are given in Reference 3.

Knowing \( \bar{n} \) and \( (\text{HF})/(\text{H}^+) \) it is possible to calculate \( Q_1, Q_2, Q_3 \), and \( Q_4 \) from Equation (14). This was done by plotting \( \bar{n} \) versus log \( (\text{HF})/(\text{H}^+) \),
reading from the smoothed curve four points chosen at appropriate intervals, and solving the four simultaneous equations (14) for \( Q_1 \), \( Q_2 \), \( Q_3 \) and \( Q_4 \). It was then verified that the remaining data were consistent with this set of constants. A plot of \( \bar{n} \) versus log \( \frac{[HF]}{[H^+]} \) for the experiments at 25° is shown in Figure 1. The solid curve represents the curve calculated using the \( Q \)'s listed in Table 3. It can be seen that all the experimental points fall very close to the theoretical curve.

RESULTS

The values obtained in this investigation for \( Q_1 \), \( Q_2 \), \( Q_3 \), and \( Q_4 \) at 15°, 25°, and 35° at \( \mu = 0.50 \) M are summarized in Table 3.

Table 3
Summary of Equilibrium Quotients at \( \mu = 0.5 \)

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>( Q_1 )</th>
<th>( Q_2 )</th>
<th>( Q_3 )</th>
<th>( Q_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>15°</td>
<td>((2.12 \pm 0.17) \times 10^3)</td>
<td>288 + 22</td>
<td>16.3 + 1.6</td>
<td>0.7 + 0.2</td>
</tr>
<tr>
<td>25°</td>
<td>((1.91 \pm 0.15) \times 10^3)</td>
<td>233 + 16</td>
<td>14.6 + 1.4</td>
<td>0.65 + 0.2</td>
</tr>
<tr>
<td>35°</td>
<td>((1.63 \pm 0.15) \times 10^3)</td>
<td>182 + 14</td>
<td>11.4 + 1.1</td>
<td>0.5 + 0.2</td>
</tr>
</tbody>
</table>

The uncertainties were calculated by refitting the \( \bar{n} \) versus log \( \frac{[HF]}{[H^+]} \) curve assuming an error of 0.02 in \( \bar{n} \) at the point most important in determining the particular \( Q \). The values which Dodgen\(^1\) gives for \( Q_1 \), \( Q_2 \), \( Q_3 \), and \( Q_4 \) at 25° and the same ionic strength are 1750, 242, 12.7, and 0.88 respectively.
In Table 4 are presented the equilibrium quotients at 25°C for \( \mu = 0.5 \) and \( \mu = 0 \) for Reactions 1, 2, 3, and 4 written in terms of fluoride ion rather than HF.

**Table 4**

Equilibrium Quotients at 25°C for Reactions
Written in Terms of Fluoride Ion Reaction

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( Q' ) ( (\mu = 0.5) )</th>
<th>( K ) ( (\mu = 0) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Sc}^{3+} + F^- = \text{ScF}^2^- )</td>
<td>( 1.55 \times 10^6 )</td>
<td>( 1.2 \times 10^7 )</td>
</tr>
<tr>
<td>( \text{ScF}^2+ + F^- = \text{ScF}_2^+ )</td>
<td>( 1.89 \times 10^5 )</td>
<td>( 6.4 \times 10^5 )</td>
</tr>
<tr>
<td>( \text{ScF}_2^+ + F^- = \text{ScF}_3^{(aq)} )</td>
<td>( 1.19 \times 10^4 )</td>
<td>( 3.0 \times 10^4 )</td>
</tr>
<tr>
<td>( \text{ScF}_3^{(aq)} + F^- = \text{ScF}_4^- )</td>
<td>( 7 \times 10^2 )</td>
<td>( 7 \times 10^2 )</td>
</tr>
</tbody>
</table>

The values of \( Q' \) were obtained by dividing the \( Q \) values of Table 3 by the ionization constant of HF at \( \mu = 0.5 \).\(^{11}\) The true equilibrium constants at \( \mu = 0 \) were estimated using empirical relations of Rabinowitch and Stockmayer\(^{12}\) and Hasenan\(^{13}\) for activity coefficient corrections.


Table 5 summarizes the free energy, heat and entropy changes for reactions 1, 2, and 3 at an ionic strength of 0.5 M.
Table 5
Summary of Thermodynamic Functions of Scandium Fluoride Complexes (μ = 0.5)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔF^298 kcal/mole</th>
<th>ΔH^298 kcal/mole</th>
<th>ΔS^298 e.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc^{3+} + HF = ScF^{42-} + H^{+}</td>
<td>-4.48 ± 0.05</td>
<td>-2.5 ± 1.0</td>
<td>7 ± 5</td>
</tr>
<tr>
<td>ScF^{42-} + HF = ScF_{2}^{2-} + H^{+}</td>
<td>-5.25 ± 0.05</td>
<td>-4.1 ± 1.0</td>
<td>-3 ± 3</td>
</tr>
<tr>
<td>ScF_{2}^{2-} + HF = ScF_{3}^{(aq)} + H^{+}</td>
<td>-1.59 ± 0.05</td>
<td>-3.4 ± 2.2</td>
<td>-6 ± 4</td>
</tr>
</tbody>
</table>

The heats and entropies may be converted to those for the reactions written in terms of fluoride ion by subtracting the heat and entropy of ionization of HF from the values in Table 5. Beppler, Jolly and Latimer report the


heat and entropy of ionization of HF at infinite dilution. Estimation of the correction to μ = 0.5 gives -26 kcal/mole and -22 e.u. respectively.

DISCUSSION

In Table 6 are presented the thermodynamic data for the corresponding reactions of Fe(III), Al(III), and In(III) at an ionic strength of 0.5.  


(16) The ΔF values for aluminum were measured at an ionic strength of 0.55 while the ΔH values were measured at an ionic strength varying between 0.06 and 0.2 M. The entropy values were calculated from the ΔF and ΔH values without correction for the differences in ionic strength.
Table 6
Thermodynamic Functions of Fe(III), Al(III) and In\(^ {+3} \) Fluorides for an Ionic Strength of 0.5

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta F_{298}^\circ$, kcal</th>
<th>$\Delta H_{298}^\circ$, kcal</th>
<th>$\Delta S_{298}^\circ$, e.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(^ {+3} ) + HF = Fe(^ {+2} ) + H(^ + )</td>
<td>-3.09</td>
<td>-0.65</td>
<td>8.2</td>
</tr>
<tr>
<td>Fe(^ {+2} ) + HF = FeF(^ 2+ ) + H(^ + )</td>
<td>-1.36</td>
<td>-1.2</td>
<td>0.6</td>
</tr>
<tr>
<td>FeF(^ 2+ ) + HF = FeF(^ 3)(aq) + H(^ + )</td>
<td>~ 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al(^ {+3} ) + HF = AlF(^ {+2} ) + H(^ + )</td>
<td>-4.40</td>
<td>-1.45</td>
<td>9.9</td>
</tr>
<tr>
<td>AlF(^ {+2} ) + HF = AlF(^ 2+ ) + H(^ + )</td>
<td>-2.88</td>
<td>-1.8</td>
<td>3.6</td>
</tr>
<tr>
<td>AlF(^ 2+ ) + HF = AlF(^ 3)(aq) + H(^ + )</td>
<td>-1.28</td>
<td>-2.4</td>
<td>-3.8</td>
</tr>
<tr>
<td>In(^ {+3} ) + HF = InF(^ {+2} ) + H(^ + )</td>
<td>-1.14</td>
<td>-0.51</td>
<td>2.1</td>
</tr>
<tr>
<td>InF(^ {+2} ) + HF = InF(^ 2+ ) + H(^ + )</td>
<td>0.41</td>
<td>1.0</td>
<td>2</td>
</tr>
</tbody>
</table>

\(^a\)See Footnote 16

A comparison of Tables 5 and 6 shows that the entropies of complexing agree well and show the expected trend toward less positive values with increasing radius of the metal ion. The heat term for the Sc(III) complexes, however, is considerably more negative than for the Al(III), Fe(III), and In(III) complexes. Thus the greater stability of the scandium complexes arises from the more negative heat term, rather than from an entropy effect.

It has been shown previously\(^6\) that the complexing of a number of positive ions by fluoride ion agrees qualitatively with an ionic picture in which the fluoride ion is held to the positive ion by an electrostatic attraction. For example, for positive ions of a given charge
the equilibrium constants run roughly in the order of their ionic radii. Scandium appears to be an exception to this correlation. If the ionic radii of Sc(III), Fe(III), Al(III) and In(III) are taken to be 0.83 Å, 0.67 Å, 0.55 Å and 0.95 Å, respectively, \(^{17}\) it is obvious from a comparison


of Tables 5 and 6 that although Sc(III) is larger than either Al(III) or Fe(III), the fluoride complexes of Sc(III) are more stable than those of Al(III) and Fe(III). If one assumes the fluoride complexes to be purely ionic, which seems to be a reasonable assumption since the fluoride ion has a low polarizability, one would expect the scandium complexes to be stronger than those of indium but weaker than those of iron and aluminum.

The correlation of stability with interionic distance \(^{6}\) by means of ionic radii is subject to uncertainty because of the variability of ionic radii. Instead of radii we may use interatomic distances measured by X-ray diffraction for fluoride containing compounds of the elements of interest. In Table 7 are given such values. In all compounds the cation was 6-fold coordinated. Aluminum compounds were chosen for which the interatomic distances were believed to be most accurately determined.
Table 7
Interatomic Distances in Fluoride Salts

<table>
<thead>
<tr>
<th>Cation</th>
<th>M-F, Å</th>
<th>Compound</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al⁺³</td>
<td>1.80</td>
<td>Ave. for AlF₃, KAlF₄, RbAlF₄</td>
<td>a</td>
</tr>
<tr>
<td>Sc⁺³</td>
<td>2.02</td>
<td>ScF₃</td>
<td>b</td>
</tr>
<tr>
<td>Fe⁺³</td>
<td>2.07</td>
<td>FeF₃</td>
<td>a</td>
</tr>
<tr>
<td>In⁺³</td>
<td>2.07</td>
<td>InF₃ • 3H₂O</td>
<td>c</td>
</tr>
</tbody>
</table>

c. G. B. Bokii and T. S. Khodasheva, Kristallografiya, 1, 197 (1956).

For the other elements, data on only the fluoride compounds tabulated are available, except for iron. In the latter case, in addition to FeF₃, one can approximate Fe-F distances from the lattice parameters of alkali double fluorides of the formula M₂FeF₆ using Pauling's¹⁹ structure.


determination and subtracting off the appropriate M-F distance as determined
from ionic radii. 'The resulting estimates give Fe-F distances appreciably
greater than the value of 2.07 for FeF$_3$.'

The interatomic distances of Table 7 are not consistent with Pauling's
ionic radii$^2$ or those given by Wyckoff$^{17}$ in that ferric ion appears to be
larger than Sc$^{3+}$ and the same size as In$^{3+}$. Presumably such discrepancies
arise because ionic radii are not truly constant. In any case it may be
concluded that the greater stability of scandium fluoride complexes
relative to ferric complexes may be consistent with an ionic picture
which would require a smaller metal-fluoride distance in the case of
scandium.

The greater stability of the scandium complexes compared to aluminum
cannot be similarly explained in that the radius of aluminum is surely
smaller than that of scandium. Although the correlation between radius
and stability of fluoride complexes of cations of the same charge is
clearly not perfect in other cases, this discrepancy between scandium
and aluminum seems to be particularly marked. It may be noted also that
the greater stability of scandium complexes compared to aluminum complexes
is also found for hydrolysis,$^{20,21,6}$ i.e., formation of the hydroxide


complex, and apparently for the thiocyanate complexes.$^{22}$

The relatively greater stability of the scandium fluoride complex is almost certainly not due to covalent bond formation since such ions as Fe$^{3+}$ and In$^{3+}$ would be expected to deviate even further, and they do not. It is unlikely that the polarizability of scandium ion is responsible, because all of these positive ions have very small polarizabilities. Unfortunately, the polarizabilities are not known with sufficient accuracy to permit a definite conclusion to be drawn.

One obvious explanation is that there may be a change in the coordination number of scandium which enhances the stability of the fluoride complexes. Thus if Sc$^{3+}$ has a highly strained, coordinated layer of eight water molecules around it, replacement of a water by the slightly smaller fluoride ion would relieve this strain and lead to an unusually stable complex. It would be necessary that additional strain be relieved as each of the next three replacements of water by fluoride ion occur because the first four complexes are known to be exceptionally stable. This explanation however, is contrary to the fact that scandium shows only a coordination number of six in its solids$^2$ and that the radius ratio$^2$ fits a coordination number of six with oxygen.

It is possible that it is the aluminum complex which has unusually low stability relative to the stability expected from an ionic model. Such a decrease in stability could arise from steric repulsion. Aluminum ion is on the border line between four-fold and six-fold coordination by fluoride ion$^2$ consequently there should be strong steric repulsion for six-fold coordinated aluminum ion. Since the water molecules on the hydrated ion are held considerably less tightly than the fluoride ions, the net effect of steric repulsion would be to decrease the
binding of the fluorides and lower the values of the complexing constants. It is not apparent, however, how such an effect would lead to equilibrium constants for the aluminum complexes which are actually smaller than for scandium.

Although some of the above suggestions offer possible, partial explanations of the apparent unusual stability of the scandium fluoride complexes, none of them is really satisfying. The reason for this degree of failure of the simple ionic model is not clear.

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Fig. 1 - Data for $\bar{n}$ as a function of $(HF)/(H^+)$ at $25^\circ$. 