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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^{++} , ScF_2^+ , $ScF_3(aq)$ and ScF_4^- . Equilibrium constants for the formation of these complexes at 15°, 25°, and 35° 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 Dodgen¹ 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

(2) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1945.

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

(3) L. G. Hepler, J. W. Kury, and Z. Z. Hugus, J. Phys. Chem., 58, 26 (1954).

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

The "ferri" method of Brosset and Orring⁴ was used. The complexing

(4) C. Brosset and J. Orring, Svensk. Kem. Tid 55, 101 (1943).

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}

(5) H. W. Dodgen and G. K. Rollefson, J. Am. Chem. Soc., 71, 2600 (1949).

(6) R. E. Connick and M. Tsao, J. Am. Chem. Soc., 76, 5311 (1954).

Solutions. - A scandium perchlorate-perchloric acid stock solution was prepared by dissolving spectroscopically pure Sc_2O_3 in perchloric acid. The solution was analyzed for scandium by precipitating it as the hydroxide and weighing as Sc_2O_3 . The acidity was determined by precipitating the scandium as ScF_3 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° .

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° , 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

Temp.	$\text{Sc}(\text{ClO}_4)_3$	HClO_4	$\text{Fe}(\text{ClO}_4)_2$	$\text{Fe}(\text{ClO}_4)_3$	NaClO_4
	moles/liter $\times 10^3$	moles/liter	moles/liter $\times 10^4$	moles/liter $\times 10^4$	moles/liter
25°	1.273	0.1122	3.553	3.402	0.3087
25°	1.387	0.05287	3.869	3.705	0.4355
25°	2.735	0.05457	3.831	3.669	0.4257
35°	1.387	0.05277	3.868	3.704	0.4350
35°	2.741	0.05493	3.831	3.668	0.4252
35°	6.665	0.1065	3.721	3.563	0.3502
15°	1.387	0.05277	3.868	3.704	0.4350
15°	6.665	0.1065	3.721	3.563	0.3502
15°	2.741	0.05493	3.831	3.668	0.4252

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 M,⁷ depending on the

(7) The symbol 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		0.4702 M NaF added	
Cell B-C (no Sc^{+++} present)		Cell A-C (Sc^{+++} present in A)	
ml NaF added	E (mv)	ml NaF added	E (mv)
0.0747	13.25	0.0747	0.72
0.1494	24.98	0.1494	1.74
0.2241	34.71	0.2241	3.16
0.2988	42.84	0.2988	5.12
0.3735	49.75	0.4482	11.15
0.4482	55.64	0.5976	20.18
0.5229	61.24	0.8964	41.90
0.5976	66.11	1.0458	51.60
0.6723	70.53	1.1952	60.60
1.1707	93.67	1.5687	78.68
1.6691	110.77	2.1418	99.97
2.1675	124.57	2.6402	114.89
2.6659	136.10	3.1386	127.61
3.1643	146.80	3.6370	139.00

Data for all but the last experiment are given by Paul.⁸

(8) A. D. Paul, Thesis, University of California, 1955; University of California Radiation Laboratory unclassified report UCRL-2926, 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:

The hydrolysis of scandium ion⁹ and the hydrolytic dimerization of ferric ion¹⁰

(9) M. Kilpatrick and L. Pocras, J. Electrochem. Soc. 100, 85 (1953).

(10) R. M. Milburn and W. C. Vosburgh, J. Am. Chem. Soc. 77, 1352 (1955).

were both negligible under the conditions employed here. The Q 's are

equilibrium quotients expressed in concentrations, for example

$$Q_1 = \frac{(\text{ScF}^{+2})(\text{H}^+)}{(\text{Sc}^{+3})(\text{HF})} \quad (10)$$

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_8 , and Q_{HF} used in these calculations are given in Reference 11.

(11) R. E. Connick, L. G. Hepler, Z. Z. Huges, Jr., J. W. Kury, W. M. Latimer and Maak-Sang Tsao, J. Am. Chem. Soc. 78, 1827 (1956).

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 $\Delta(\text{F}^-)$. 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

$$\Delta(\text{F}^-) = (\text{ScF}^{+2}) + 2(\text{ScF}_2^+) + 3(\text{ScF}_3) + 4(\text{ScF}_4^-) \quad (11)$$

$$(\Sigma \text{Sc}^{+3}) = (\text{Sc}^{+3}) + (\text{ScF}^{+2}) + (\text{ScF}_2^+) + (\text{ScF}_3) + (\text{ScF}_4^-) \quad (12)$$

where (ΣSc^{+3}) signifies the total stoichiometric concentration of scandium.

Let $\bar{n}$ represent the average number of fluoride ions held by each scandium ion:

$$\bar{n} = \frac{\Delta(EF^-)}{(E_{Sc}^{+3})} \quad (13)$$

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

$$\bar{n} = \frac{q_1 \frac{(HF)}{(H^+)} + 2q_1 q_2 \frac{(HF)^2}{(H^+)^2} + 3q_1 q_2 q_3 \frac{(HF)^3}{(H^+)^3} + 4q_1 q_2 q_3 q_4 \frac{(HF)^4}{(H^+)^4}}{1 + q_1 \frac{(HF)}{(H^+)} + q_1 q_2 \frac{(HF)^2}{(H^+)^2} + q_1 q_2 q_3 \frac{(HF)^3}{(H^+)^3} + q_1 q_2 q_3 q_4 \frac{(HF)^4}{(H^+)^4}} \quad (14)$$

In order to obtain values for q_1 , q_2 , q_3 and q_4 it is necessary to know the value of $(HF)/(H^+)_A$ for each value of $\bar{n}$, that is as a function of E_{A-C} . At the same potential, the ratio $(HF)/(H^+)$ 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-C and the known ferric fluoride complexing constants by solving equation (15) by means of successive approximations.

$$\left(1 + \frac{Q_B}{(H^+)}\right) \left(e^{E/RT} - 1\right) = q_5 \frac{(HF)}{(H^+)} + q_5 q_6 \frac{(HF)^2}{(H^+)^2} + q_5 q_6 q_7 \frac{(HF)^3}{(H^+)^3} \quad (15)$$

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 $(HF)/(H^+)$ 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 $\log (HF)/(H^+)$,

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 $\log (HF)/(H^+)$ 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 $\mu = 0.5$

Temp $^\circ\text{C}$	Q_1	Q_2	Q_3	Q_4
15°	$(2.12 \pm 0.17) \times 10^3$	288 ± 22	16.3 ± 1.6	0.7 ± 0.2
25°	$(1.91 \pm 0.15) \times 10^3$	233 ± 16	14.6 ± 1.4	0.85 ± 0.2
35°	$(1.63 \pm 0.13) \times 10^3$	182 ± 14	11.4 ± 1.1	0.5 ± 0.2

The uncertainties were calculated by refitting the $\bar{n}$ versus $\log (HF)/(H^+)$ curve assuming an error of 0.02 in $\bar{n}$ at the point most important in determining the particular Q . The values which Dodgen¹ 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

Reaction	$Q' (\mu = 0.5)$	$K (\mu = 0)$
$\text{Sc}^{+3} + \text{F}^- = \text{ScF}^{+2}$	1.55×10^6	1.2×10^7
$\text{ScF}^{+2} + \text{F}^- = \text{ScF}_2^+$	1.89×10^5	6.4×10^5
$\text{ScF}_2^+ + \text{F}^- = \text{ScF}_3(\text{Aq})$	1.19×10^4	3.0×10^4
$\text{ScF}_3(\text{aq}) + \text{F}^- = \text{ScF}_4^-$	7×10^2	7×10^2

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 Stockmayer¹² and Nasanen¹³ for activity coefficient corrections.

(12) E. Rabinowitch and W. H. Stockmayer, J. Am. Chem. Soc. 64, 335 (1942).

(13) R. Nasanen, Acta Chem. Scand. 4, 140, 816 (1950).

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 ($\mu = 0.5$)

Reaction	ΔF_{298} kcal/mole	ΔH_{298} kcal/mole	ΔS_{298} e.u.
$\text{Sc}^{+3} + \text{HF} = \text{ScF}^{+2} + \text{H}^+$	-4.48 ± 0.05	-2.3 ± 1.0	7 ± 3
$\text{ScF}^{+2} + \text{HF} = \text{ScF}_2^+ + \text{H}^+$	-3.23 ± 0.05	-4.1 ± 1.0	-3 ± 3
$\text{ScF}_2^+ + \text{HF} = \text{ScF}_3(\text{aq}) + \text{H}^+$	-1.59 ± 0.05	-3.4 ± 1.2	-6 ± 4

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. Hepler, Jolly and Latimer¹⁴ report the

(14) L. G. Hepler, W. L. Jolly and W. M. Latimer, J. Am. Chem. Soc. 75, 2809 (1953).

heat and entropy of ionization of HF at infinite dilution. Estimation of the correction to $\mu = 0.5$ gives -2.6 kcal/mole and -22 e.u. respectively.

DISCUSSION

In Table 6 are presented the thermodynamic data for the corresponding reactions of Fe(III),¹¹ Al(III),^{4,15} and In(III)³ at an ionic strength of 0.5.¹⁶

(15) W. M. Latimer and W. L. Jolly, J. Am. Chem. Soc. 75, 1548 (1953).

(16) The ΔF values for aluminum were measured at an ionic strength of 0.53 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^a

Reaction	ΔF_{298} , kcal	ΔH_{298} , kcal	ΔS_{298} , e.u.
$\text{Fe}^{+3} + \text{HF} = \text{FeF}^{+2} + \text{H}^+$	-3.09	-0.65	8.2
$\text{FeF}^{+2} + \text{HF} = \text{FeF}_2^+ + \text{H}^+$	-1.38	-1.2	0.6
$\text{FeF}_2^+ + \text{HF} = \text{FeF}_3(\text{aq}) + \text{H}^+$	~ 0		
$\text{Al}^{+3} + \text{HF} = \text{AlF}^{+2} + \text{H}^+$	-4.40	-1.45	9.9
$\text{AlF}^{+2} + \text{HF} = \text{AlF}_2^+ + \text{H}^+$	-2.88	-1.8	3.6
$\text{AlF}_2^+ + \text{HF} = \text{AlF}_3(\text{aq}) + \text{H}^+$	-1.28	-2.4	-3.8
$\text{In}^{+3} + \text{HF} = \text{InF}^{+2} + \text{H}^+$	-1.14	-0.51	2.1
$\text{InF}^{+2} + \text{HF} = \text{InF}_2^+ + \text{H}^+$	0.41	1.0	2

^aSee 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 previously⁶ 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

(17) R. W. G. Wyckoff, "Crystal Structure," Interscience Publishers, Inc., New York, 1951, Chapter III, Table page 15.

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 distance⁶ 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

Cation	M-F, Å	Compound	Reference
Al^{+3}	1.80	Ave. for AlF_3 , $KAlF_4$, $RbAlF_4$, $TlAlF_4$, Na_3AlF_6	a
Sc^{+3}	2.02	ScF_3	b
Fe^{+3}	2.07	FeF_3	a
In^{+3}	2.07	$InF_3 \cdot 5H_2O$	c

a. R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York, 1951.

b. W. Nowacki, Z. Krist., 101A, 273 (1939).

c. G. B. Bokii and T. S. Khodashova, 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 FeF_3 , one can approximate Fe-F distances from the lattice parameters¹⁸ of alkali

(18) W. Minder, Z. Krist., A96, 15 (1937).

double fluorides of the formula M_2FeF_6 using Pauling's¹⁹ structure

(19) L. Pauling, J. Am. Chem. Soc., 46, 2738 (1924).

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 radii² or those given by Wyckoff¹⁷ 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,^{20,21,8} i.e., formation of the hydroxide

(20) M. Kilpatrick and L. Pokras, *J. Electrochem. Soc.* 100, 85 (1953).

(21) J. Faucherre, *Compt. rend.* 227, 1367 (1948).

complex, and apparently for the thiocyanate complexes.²²

(22) R. Bock, *Z. Anal. Chem.* 153, 110 (1951).

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 solids² and that the radius ratio² 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 $(\text{HF})/(\text{H}^+)$ at 25° .

1. 1349/