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The Affinities of Chromic Ion and Gallium Ion for Fluoride Ion

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The equilibria existing in solutions containing Cr^{+++}, H^+, F^- and ClO_4^- have been studied. The quotient $(CrF^{++})(H^+)/(Cr^{+++})(HF)$ at 25° and $\mu = 0.5$ has been measured as 26.0. The approximate values 2.5 and 0.3 were obtained for the analogous quotients governing the second and third stages of association. The equilibria are established slowly. The hydrolysis quotient for Fe^{+++} at 25° and $\mu = 0.5$ has been measured as 1.6×10^{-3}, and for the hydrolysis of Ga^{+++} under the same conditions the value of 1.2×10^{-3} was observed. The quotient $(GaF^{++})(H^+)/(Ga^{+++})(HF)$ has the value $1.2 \pm 0.2 \times 10^2$.

In addition to the specific interest they may provoke, data on complex ion stabilities for simple lignands such as the halide ions are of more general interest in forming a basis for the development of ideas on factors affecting complex ion stabilities. Data for chromic ion have a further aspect of interest. Chromic ion is unusual among the aquo cations of the first row transition elements in that the rate of formation of complex ions is very slow. Comparisons of the stabilities of complex ions are useful in reaching conclusions about bond type, and are therefore also pertinent to the problem of understanding the rate behavior of complex ions.[1]

Measurements of the stability of chromic chloride complexes have been reported.[2] A recent paper[3] reports observations on the Cr(III)–F^- system, but no data on the stabilities of the complex ions. The present paper presents results for CrF^{++}, CrF^+, CrF_3. The analytical method developed for a study of the chromic fluoride system can be readily extended to other systems, and some measurements using it in the study of Ga(III)–F^- complex ions are reported.

Experimental

As seems to be general with other substitution reactions of chromic ion in acid solution, the system $Cr(H_2O_6)^{+++}$–HF reaches equilibrium slowly. Experiments were performed testing various substances as catalysts for the reaction: $Cr_2O_7^=$ (this substance has a slight catalytic effect on the exchange[4] of water between $Cr(H_2O)_6^{+++}$ and solvent), I^- (this was tested on the view that since iodide complex ions are generally more labile than those of other halides, iodide ion might provide a path for the fluoride reaction), H_2O_2 (this substance could conceivably operate by producing an alternation between Cr(III) and some higher oxidation state of chromium), activated charcoal (this is known to be a useful catalyst for certain transformations with Co(III) complexes).[5] No striking effects on the rate were observed. Zinc induces a fairly rapid formation of the fluoride complexes, but is objectionable because acid is consumed. The effort to find a useful catalyst was abandoned and the equilibrium study undertaken accepting the fact of slow reaction.

For solutions of the composition used and handled as described, equilibrium appears to be established within 11 weeks, which was the minimum time before analyses for equilibrium concentrations were made. A demonstration that equilibrium had been attained was made for a solution in the more acid range of composition. No change had been observed in the solution for 20 days. Perchloric acid was then added, bringing the over-all composition to that of another solution, which also had persisted without change for 20 days. After 50 days, the free fluoride concentration in the treated solution had increased threefold, and was within 25% of that in the comparison solution. Analogy with the Cr(III)–Cl^- system suggests the view, which is supported also by visual observations on the Cr(III)–F^- system, that the less acidic solutions are more labile. The internal consistency of the data, and the fact that analyses after 77 days agree with those after 110 days are a further check on the attainment of equilibrium.

To shorten the time required to reach equilibrium the reactants were first mixed under conditions favoring rapid reaction. Initially, only the chromic nitrate and sodium fluoride in small volume, were added to the reaction vessel. After a week, during which the color had changed from the blue-violet characteristic of $Cr(H_2O)_6^{+++}$ to green,[6] the perchloric acid was added. After a second week, sodium perchlorate was added to bring the ionic strength to 0.5, and the solutions were diluted to final volume. The bottles were sealed, and kept in a constant temperature bath (24.95 ± 0.05°) until the time of analysis. Analyses were made after a period of 11 weeks or longer.

Chemicals were of analytical reagent grade. The solution of sodium perchlorate was prepared by neutralizing perchloric acid with sodium carbonate, the solution being boiled to remove carbon dioxide. Redistilled water was used in making up all solutions. The reaction vessels were polyethylene bottles.

The problem of determining the concentrations of the reacting substances in the equilibrium mixture is somewhat simplified because of the inertia of the system. The method used exploits the change in optical density of a solution of ferric ion when F^- is added.[7] At 325 mμ, the wave length chosen for the extinction measurements, $FeOH^{++}$ has a much higher extinction coefficient than Fe^{+++}, Cr^{+++} or Cr(III)–F^- complexes, and apparently than Fe(III)–F^- complexes. The optical density in a certain acidity range is markedly decreased as fluoride ion is added. Measurements were made yielding curves showing the variation of optical density with fluoride ion concentration at constant total Fe(III), ionic strength and (H^+) at various values of (H^+). The family of curves thus obtained is shown in Fig. 1. In making an analysis, a portion of the equilibrium solution was measured out and diluted, $HClO_4$, Fe^{+++} and $NaClO_4$ having been added to make the amount of these equal to the concentrations in the standard solutions. The amount of the solution for analysis, and the amount of $HClO_4$ added were selected to bring the solutions into a composition range in which the optical density is relatively sensitive to the concentration of free fluoride ion. Comparison of the optical density of the unknown solution (after correction for the small absorption by chromic species) with the data in Fig. 1, and interpolation when necessary, yielded the value of the concentration of free fluoride ion. The measurements were made using a Beckman Quartz spectrophotometer, Model DU, fitted with a thermostated cell compartment, on the solution after it had been brought to temperature equilibrium by immersion in a bath for *ca.* 15 min. There is no noticeable readjustment of the Cr(III)–F^- equilibrium within this time period. The method of analysis makes the assumption that absorption of light by $FeOH^{++}$ is not affected by the presence of Cr^{+++} or Cr(III)–F^- species. The equilibrium solutions were

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[1] J. P. Hunt and H. Taube, *J. Chem. Phys.*, **19**, 602 (1951).

[2] N. Bjerrum, *Z. physik. Chem.*, **59**, 336 (1907).

[3] E. R. Scheffer and E. M. Hammaker, THIS JOURNAL, **72**, 2575 (1950).

[4] R. A. Plane and H. Taube, *J. Phys. Chem.*, **56**, 33 (1952).

[5] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, p. 241.

[6] Although the visual color change is quite marked, the change in the absorption coefficients at least in the range of λ greater than 3000 Å. is not very marked, 50% at most.

[7] This method of analysis was suggested by D. W. Weiser.

always diluted at least tenfold in making them up for analysis, thus the chromic species were present at low concentration, and interference by them is expected to be very slight. Owing to the slowness with which water is replaced from the first sphere of coördination, any effects will be limited to outer sphere effects.

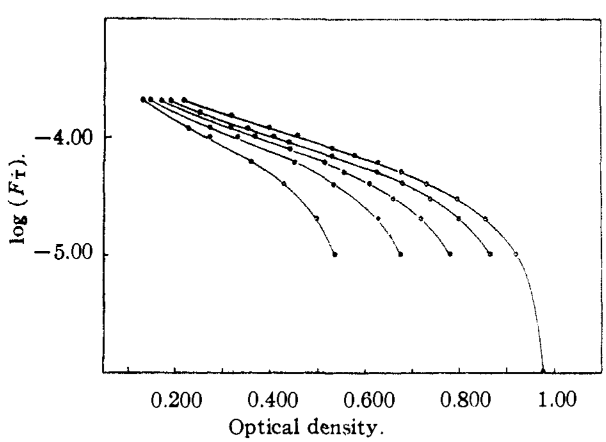

Fig. 1.—The optical densities of solutions containing $Fe(NO_3)_3$, NaF, $HClO_4$ and $NaClO_4$; λ 325 mμ; cell length, 10 cm.; temp., 25.0°; μ 0.5 (largely $NaClO_4$); ($Fe(NO_3)_3$) 1.000×10^{-4} *M;* ($HClO_4$) $\times 10^3$ 3.036, 2.024, 1.518, 1.215 and 1.012 for curves in order from left to right.

In determining the affinity of fluoride for gallium ion, gallium ion was added to a solution made up to be in the field of composition of the solutions represented in Fig. 1. When gallium ion associates with fluoride ion, the optical density of the solution changes. From the measurements of optical density, and the known over-all compositions of the solution, the affinity constant of Ga(III) for F^- can be calculated.

Some definitions useful in the succeeding sections follow:

Parentheses denote concentrations in moles/l.

Subscript T refers to the concentration in all forms of the species referred to

F_f^-, the "free fluoride," refers to the fluoride ion not associated with the cation under study, whether Cr(III) or Ga(III)

$\bar{n}$, represents the average number of fluoride ions per Cr_T^{+++}

$$K_1 = \frac{(CrF^{++})(H^+)}{(Cr^{+++})(HF)};\quad K_2 = \frac{(CrF_2^{+})(H^+)}{(CrF^{++})(HF)};\quad K_3 = \frac{(CrF_3)(H^+)}{(CrF_2^{+})(HF)}$$

$$K_{1G} = \frac{(GaF^{++})(H^+)}{(Ga^{+++})(HF)}$$

$$K_{HF} = \frac{(H^+)(F^-)}{(HF)}$$

OD = optical density = log I_0/I, cell length, 10 cm.

Analysis of the Data on the Extinction of Ferric Solutions.—The data obtained on the extinction of the solutions containing Fe^{+++}, H^+ and F^- serve to establish a value for the hydrolysis quotient of Fe^{+++} under the experimental conditions, and to check on reported values of the affinity of H^+ and Fe^{+++} for F^-.

For solutions identical with those used in Fig. 1 except that F^- was omitted the optical densities were measured as 0.995, 0.735 and 0.594 when the concentrations of perchloric acid were 1.100×10^{-3}, 2.024×10^{-3} and 3.036×10^{-3} *M*, respectively. Assuming that $FeOH^{++}$ is the principal absorbing species, the variation of optical density requires for $((FeOH^{++})(H^+))/(Fe^{+++})$ the value 1.6×10^{-3}. The hydrolysis quotient can also be calculated directly from the measured optical densities of the solutions. The decadic extinction coefficient of $FeOH^{++}$ at λ 340 mμ has been determined[8] as 890. Using the known variation[9] of ε with λ, ε at 325 mμ is estimated as 1680. Since the absorption of Fe^{+++} in comparison to $FeOH^{++}$ is negligible at λ 325 mμ, the measured optical density leads at once to the concentration of $FeOH^{++}$ in the solutions, and thus to values for the hydrolysis quotient. These are found to be $1.6_8 \times 10^{-3}$, $1.6_0 \times 10^{-3}$ and $1.6_8 \times 10^{-3}$ for the solutions at 1.100×10^{-3}, 2.024×10^{-3} and 3.036×10^{-3} *M* $HClO_4$. At μ 0, the hydrolysis quotient[8] for Fe^{+++} is 6.5×10^{-3}. Using the known extinction coefficient, and the optical densities measured by Rabinowitch and Stockmayer,[9] the quotient at μ = 2 ($NaClO_4$) is found to be 2.5×10^{-3}. The mean value $1.6_5 \times 10^{-3}$ at intermediate ionic strengths is reasonable in comparison with these.

In analyzing the extinction data for solutions containing also F^-, the assumption is made that $FeOH^{++}$ continues to be the principal absorbing species. The equilibrium quotients $(FeF^{++})(H^+)/(Fe^{+++})(HF)$ and $(FeF_2^{+})(H^+)/(FeF^{++})(HF)$ have been determined[10] for an ionic environment similar to ours as 189 and 10.4. Using these values and the value for the hydrolysis quotient of Fe^{+++}, the equilibrium quotient K_{HF} can be calculated for our conditions. The results of these calculations for some of the experimental data are recorded in Table I.

TABLE I

ANALYSIS OF THE DATA ON OD OF SOLUTIONS CONTAINING Fe^{+++}, H^+ AND F^- (0.5 *M* $NaClO_4$, 25°)

Series at ($HClO_4$) = 3.036×10^{-3}

(F_T^-) $\times 10^5$	2.00	4.00	6.00	10.00	12.00
OD	0.502	0.435	0.363	0.268	0.230
$K_{HF} \times 10^3$	0.8	1.0	0.9	1.5	1.5

Series at ($HClO_4$) = 1.012×10^{-3} *M*

(F_T^-) $\times 10^5$	4.00	6.00	10.00	12.0
OD	0.735	0.632	0.460	0.402
$K_{HF} \times 10^3$	0.8	1.2	1.5	1.5

At low (F_T^-), K_{HF} as calculated is very sensitive to experimental error and to error in the values of the other equilibrium quotients. Only the data at higher (F_T^-) contribute to a dependable value for K_{HF}. The data are satisfactorily accounted for by the values which have been adopted for the other equilibrium quotients using $K_{HF} = 1.3 \pm 0.2 \times 10^{-3}$. This result for K_{HF} cannot be regarded as a good independent determination, but does serve to decide between conflicting values for K_{HF} reported in the literature, for conditions similar to ours. Using our result, we have rejected the value of 0.4×10^{-3} reported by Roth[11] in favor of the value 1.16×10^{-3} determined by Brosset and Gustaver,[12] and have also used the value 0.27 reported by the latter authors for the quotient $(HF)(F^-)/(HF_2^-)$.

The Association of Cr(III) and F^-—Results and Calculations.—The concentration of free fluoride in the equilibrium solutions was measured by means of the method described. The difference between the total fluoride, and free fluoride is the concentration of fluoride associated with chromic ion. The distribution of free fluoride among the various forms can be calculated making use of the relations

$$(H_T^+) = (H^+) + (HF) + (HF_2^-)$$

$$(F_f^- = (F^-) + (HF) + 2(HF_2^-)$$

$$K_{HF} = \frac{(H^+)(F^-)}{(HF)}$$

$$K_{HF_2} = \frac{(HF)(F^-)}{(HF_2^-)}$$

In most cases (HF_2^-) could be neglected in comparison with other forms of free fluoride. The calculation of the concentration of HF_2^- was done by

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[8] T. H. Siddall and W. C. Vosburgh, THIS JOURNAL, **73**, 4270 (1951).

[9] E. Rabinowitch and W. H. Stockmayer, *ibid.*, **64**, 335 (1942).

[10] H. W. Dodgen and G. K. Rollefson, *ibid.*, **71**, 2600 (1949). It should be pointed out that the equilibrium quotients for the Fe(III)–F^- reaction as measured by Dodgen and Rollefson are not very sensitive to the value of K^{HF}.

[11] W. A. Roth, *Ann.*, **542**, 35 (1939).

[12] C. Brosset and B. Gustaver, *Sv. Kem. Tidsk.*, **54**, 155 (1942).

an iteration method, starting as a first approximation with the compositions calculated assuming no HF_2^- formed. In the least acid solutions, the contribution to the acidity by hydrolysis of the chromic ion was included, using as hydrolysis quotient[13] the value 1.5×10^{-4}.

The experimental results and the results of the calculations of equilibrium composition of the solutions are presented in Table II. For series a, b, c, d each result is the mean of two, analysis for the first one having been made after 77 days, and for the second after 110 days. In every case, the values in the duplicate experiments agreed within the precision expected from the method, and showed no systematic trend with time. In series e, the duplicates were analyzed after the same elapsed time, 110 days.

TABLE II

RESULTS FOR Cr(III)–F^- EQUILIBRIA AT 24.95 ± 0.05°; μ = 0.50 ± 0.02 (Cr(III) AS $Cr(NO_3)_3$; F^- AS NaF; H^+ AS $HClO_4$; $NaClO_4$)

Series a, $(F_T^-) = 0.00500$; $(Cr_T^{+++}) = 0.0104$; (H_T^+), 4.93×10^{-3} to 29.39×10^{-3}

Series b, $(F_T^-) = 0.01000$; $(Cr_T^{+++}) = 0.0104$; (H_T^+), 4.93×10^{-3} to 29.39×10^{-3}

Series c, $(F_T^-) = 0.02000$; $(Cr_T^{+++}) = 0.0104$; (H_T^+), 4.93×10^{-3} to 29.39×10^{-3}

Series d, $(F_T^-) = 0.03000$; $(Cr_T^{+++}) = 0.0104$; (H_T^+), 4.93×10^{-3} to 29.39×10^{-3}

Solution 1e, $(F_T^-) = 0.01000$; $(Cr_T^{+++}) = 0.03042$; (H_T^+), 9.87×10^{-3}

Solution 2e, $(F_T^-) = 0.01000$; $(Cr_T^{+++}) = 0.00507$; (H_T^+), 9.87×10^{-3}

Solution 3e, $(F_T^-) = 0.01000$; $(Cr_T^{+++}) = 0.00203$; (H_T^+), 9.87×10^{-3}

Solution	(HF) $\times 10^4$	(F^-) $\times 10^4$	(HF_2^-) $\times 10^4$	$\bar n$	log (HF)/(H^+)
1a	6.86	0.28	...	0.423	−1.62
2a	4.85	.17	...	.444	−1.59
3a	2.64	.32	...	.464	−1.56
4a	1.45	.35	...	.475	−1.53
1b	18.8	.8	...	.792	−1.17
2b	14.4	.9	...	.835	−1.10
3b	8.5	1.1	...	.891	−1.02
4b	4.4	1.2	...	.936	−1.00
1c	59.0	2.9	...	1.362	−0.60
2c	47.8	3.8	...	1.463	− .49
3c	33.1	5.9	...	1.588	− .30
4c	19.3	7.5	...	1.708	− .19
1d	7.3	7.3	0.3	1.76	− .20
2d	10.9	10.9	.4	1.91	− .03
3d	19.4	19.4	.4	2.15	+ .22
4d	32.2	32.2	.4	2.22	+ .44
1e	22.2	3.4	...	1.56	− .54
2e	47.2	10.6	...	2.08	− .04
3e	1.4	.14	...	0.32	−1.81

Analysis of the data at constant Cr(III) shows that they are adequately accounted for by assuming that in the concentration range studied, only the first three stages in the stepwise association of Cr(III) and F^- are important. The equation[14]

$$\bar n + \frac{(\bar n - 1)(HF)K_1}{(H^+)} + \frac{(\bar n - 2)(HF)^2K_1K_2}{(H^+)^2} + \frac{(\bar n - 3)(HF)^3K_1K_2K_3}{(H^+)^3} = 0$$

applies to the data, and was used in calculating the values of K_1, K_2 and K_3. The calculations were made selecting pairs of experiments for which the fourth term of the equation was small compared to the others, and using these results to obtain provisional values for K_1 and K_2. The provisional values of K_1 and K_2 were used in obtaining a provisional value of K_3, which in turn was used to obtain corrected values of K_1 and K_2. This iteration method yielded values of the quotients to a sufficient degree of approximation in the second cycle. The results are shown in Tables III and IV.

TABLE III

CALCULATED VALUES OF K_1 AND K_2 (PROVISIONAL VALUES 25.6 AND 2.75)

Solutions	K_1	K_2
1a, 1b	25.7	2.85
2a, 2b	26.9	2.32
3a, 3b	26.8	2.13
4a, 4b	24.6	2.88
Mean	26.0	2.54

TABLE IV

CALCULATED VALUES OF K_3 WHEN K_1 = 26.0 AND K_2 = 2.54

1c	0.63	1d	0.41
2c	.48	2d	.32
3c	.20	3d	.30
4c	.25	4d	.23

Mean = 0.35

Figure 2 shows $\bar n$ as a function of log (HF)/(H^+), the experimental points being represented by circles, and the solid line being drawn in to conform to the requirements imposed by the mean values of K_1, K_2 and K_3. For the data at constant total chromium, the agreement is satisfactory. The experimental result at 0.03 *M* Cr(III) falls at the extreme range of (HF)/(H^+) concentrations and agrees well with the other data. In this concentration range, CrF^{++} is the principal Cr(III)–F^- species, and it seems safe to conclude that the present work fixes the value of K_1. The deviation of the points corresponding to low Cr(III) [these fall in the range of low (H^+)/(HF)] has not been explained. It is unlikely that the deviation is produced by the presence in the solutions of polynuclear complexes. Condensation of Cr(III) ions would be expected to enhance the affinity of F^- for Cr(III); the affinity,

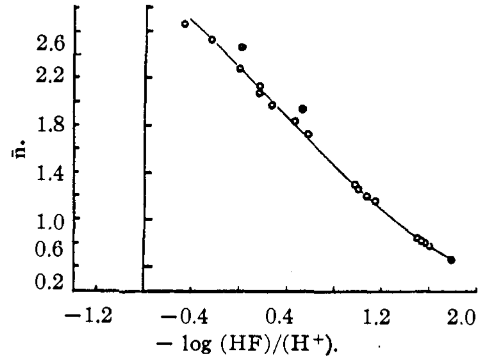

Fig. 2.—The formation curve for $Cr(III)^nF^-$. ○, (Cr_T^3) = 0.01014 *M*; ●, (Cr_T^3) = 0.03042 *M*; ◑, (Cr_T^3) = 0.00407 *M*; ◒, (Cr_T^3) = 0.002028 *M*.

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[13] W. M. Latimer, "Oxidation Potentials," Prentice-Hall Co., Inc., New York, N. Y., 1938, p. 229.

[14] Ref. 5, p. 20 *et seq.*

however, apparently increases as [Cr(III)] is reduced. Nor can the effect be explained as due to changes in the acidity of the solutions produced by condensation of Cr(III) species, since within a series at constant [Cr(III)] and (F^-), there is no unusual trend as (H^+) is changed. The calculated values of K_2 and K_3 show a reasonable trend when compared with K_1 [as judged by comparing successive quotients in the Al(III)–F^- and Fe(III)–F^- systems] and it seems likely that the tabulated values are substantially correct. Any revision of K_{HF} will affect K_1 only slightly, but K_2 and K_3 somewhat more.

The Affinity of Ga^{+++} and F^-–Results and Calculation.—The data for the Experiments on Ga(III)–F^- are shown in Table V.

TABLE V

DETERMINATION OF THE AFFINITY OF Ga(III) AND F^-
(Temp., 25°; 0.5 *M* $NaClO_4$; concn. *M* × 10^5)

	Solution 1	Solution 2	Solution 3
$(Ga(ClO_4)_3)$	140	140	140
(NaF)	. . . . .	11.0	21.9
$(HClO_4)$	110	110	110
$(Fe(NO_3)_3)$	10.0	10.0	10.0
OD	0.821	0.754	0.660
OD without $Ga(ClO_4)_3$	.995	.325^a	170^a

^{a} From Fig. 1.

It is evident from the observations recorded for solutions 2 and 3 that Ga^{+++} has a marked effect in increasing the optical density of a solution containing Fe^{+++} and F^-. This effect is interpreted as resulting from the association of Ga(III) with F^-.

The treatment of the data for Ga(III) differs from that for the Cr(III) since in the present system, Fe^{+++} and Ga^{+++} are in labile equilibrium with the fluoride complexes. In calculating K_{1G} the equilibrium constant for the hydrolysis of the ferric ion, for the hydrolysis of the gallium ion, and for the formation of Fe^{+++}–F^- complex ions must be known. The data of Table V make possible an estimate of the quotient $(GaOH^{++})(H^+)/(Ga^{+++})$. The decrease in optical density which is observed when gallium perchlorate is added to the ferric perchlorate solution can be attributed to an increase in acidity. Part of this increase is caused by the perchloric acid added with the gallium perchlorate $(Ga(ClO_4)_3.0.03HClO_4)$ and the balance by the acid resulting from the hydrolysis of Ga^{+++}. This interpretation yields for the hydrolysis quotient of Ga^{+++} under our conditions 1.2 × 10^{-3}. For low ionic strengths, values of 2.3 × 10^{-3} [15] and 1.9 to 3.4 × 10^{-3} [16] have been reported for K_{hyd} of Ga^{+++}. The values reported by the former authors at higher salt concentration are almost certainly wrong. The measurements were made on solutions prepared by adding acid to freshly prepared gallium hydroxide, and the assumption (incorrect[16,17]) was made that the ratio of OH^- to Ga(III) in the hydroxide is 3.00. The ionic compositions of the solutions studied by Moeller and King were distinctly different from ours. Assuming the same variation with concentration of sodium perchlorate of the hydrolysis quotients of Ga^{+++} and Fe^{+++}, our value for Ga^{+++} is consistent with 4 to 5 × 10^{-3} at zero ionic strength.

The optical densities of solutions 2 and 3 yield $(FeOH^{++})$ directly. The acidity is only slightly affected by the addition of F^-, hence Fe^{+++} can be calculated, and by difference (FeF^{++}). (F_f^-) is obtained using the data of Fig. 1, and the difference between (F_T^-) and (F_f^-) yields (GaF^{++}). The distribution of the remaining Ga(III) between Ga^{+++} and $GaOH^{++}$ can be calculated from the hydrolysis quotient and the acidity. All the quantities appearing in the quotient $(FeF^{++})/(Fe^{+++}) \times (GaF^{++})/(Ga^{+++})$ are then known and the ratios of the affinity constants for iron and gallium fluorides are thus found to be 1.5_0 and 1.6_5 for the data observed for solutions 2 and 3. The corresponding values for K_{1G} are $1.2_6 \times 10^2$ and $1.1_4 \times 10^2$. Of the two, the lower value is more dependable, since in this experiment a greater fraction of the gallium ion was converted to the complex ion. No other value[18] for K_{1G} appears in the literature.

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(15) R. Fricke and K. Meyring, *Z. anorg. allgem. Chem.*, **176**, 329 (1928).

(16) T. Moeller and G. L. King, *J. Phys. Chem.*, **54**, 999 (1950).

(17) S. La Croix, *Ann. chim.*, [12] **4**, 5 (1949).

(18) The value 230 based on the present work was quoted in Reference 1. It was calculated using 2.5 × 10^{-3} (*cf.* ref. 15) as the hydrolysis quotient for Ga^{+++}.