J. Inorg. Nucl. Chem., 1960, Vol. 15, pp. 115 to 124. Pergamon Press Ltd. Printed in Northern Ireland

COMPLEXITY OF TITANIUM(IV) FLUORIDE SOLUTIONS

V. CAGLIOTI, L. CIAVATTA and A. LIBERTI
Istituto di Chimica Generale-Universita di Roma ed Istituto di Chimica Analitica
Universita di Messina, Italy

(*Received* 10 *November* 1959)

Abstract—The complexity of solutions of titanium(IV) and fluoride ions has been investigated in a constant ionic medium (3 M ClO_4^-) at 25° by means of potentiometric titrations with a quinhydrone electrode. The complex formation is entirely mononuclear and the highest complex is found to be $TiOF_4^{2-}$. All equilibrium constants have been calculated with the exception of $TiOF^+$, the the formation constant of which cannot be found by hydrogen ion measurements. The following equilibrium constants were found:

$$TiOF^+ + F^- \rightleftarrows TiOF_2 \qquad \log \beta_1 = 4,35\ M^{-1}$$
$$TiOF^+ + 2F^- \rightleftarrows TiOF_3^- \qquad \log \beta_2 = 8,31\ M^{-2}$$
$$TiOF^+ + 3F^- \rightleftarrows TiOF_4^{=} \qquad \log \beta_3 = 12,03\ M^{-3}$$

THOUGH it is well known that titanium(IV) is strongly complexed by fluoride no quantitative evaluation has been made of the complexes which are formed in aqueous solutions. Various investigators report⁽¹⁾ that a dihydrate $TiF_4 \cdot 2H_2O$ may be crystallized from a solution of titanium oxide in hydrofluoric acid and that this compound in solution slowly hydrolyses, yielding an oxyfluoride $TiOF_2$. Fluotitanates are also described as salts derived from the hypothetical H_2TiF_6, which is said to be a strong acid. The existence of TiF_6^{2-} was suggested as long ago as 1908.

Recently WOODS and COCKERELL⁽²⁾, from studies of the absorption on strongly basic ion-exchange resins, claim that titanium(IV) is adsorbed as TiF_5^- or a higher complex. The only quantitative result available is given by KLEINER⁽³⁾, who by means of spectrophotometric measurements calculated the formation constant for $TiOF^+$ as $\log \beta_1 = 6{\cdot}44$.

In the studies of titanium(IV) solutions there is considerable uncertainty regarding the ionic species which may be present, and whether titanium(IV) exists as Ti^{4+} or TiO^{2+}. In a potentiometric investigation of titanium(IV) hydrolysis⁽⁴⁾ it has been shown that the Ti^{4+} ion does not exist at all in aqueous solutions. Up to a very high acid concentration ($[H^+] = 0{\cdot}4$ M) the ion TiO^{2+} is the only species of titanium present. The effect of higher acidities upon the nature of this species was investigated in the present work by comparing the optical absorbancy of a titanium(IV) solution over a range of hydrogen ion concentrations up to 5 M $HClO_4$ (Fig. 1). It was found that the plot of optical density (D/M) against the wavelength was independent of titanium concentration in the range $10 \leq M \leq 73$ mM and of $[H^+]$ in the range $5 \leq [H^+] \leq 0{\cdot}2$ M. Therefore we may conclude that the titanyl ion may be regarded as a stable entity which behaves similarly to a metal ion having a constant charge within wide limits of acidity.

⁽¹⁾ J. H. SIMONS, *Fluorine Chemistry*. Academic Press, New York (1950).

⁽²⁾ P. H. WOODS and L. COCKERELL, *J. Amer. Chem. Soc.* **80**, 1534 (1958).

⁽³⁾ K. E. KLEINER, *Zh. Obshch. Khim.* **22**, 17 (1952).

⁽⁴⁾ L. CIAVATTA. Unpublished results (1959).

When the pH of an acid solution of titanyl perchlorate is increased, hydrolysis occurs, and even at high values of $[H^+]$ (200 mM), this reaction is noticeable. Studies on complexes formed by TiO^{2+} are quite difficult because these equilibria are always complicated by hydrolysis unless the complex is a very strong one.

The complex-formation between TiO^{2+} and fluoride has been studied by potentiometric titration, the complexity of hydrogen fluoride solutions being determined in a previous investigation.⁽⁵⁾ The reaction of a metal ion with a ligand when hydrolysis occurs can be represented, omitting charges for clarity, by the following expression:

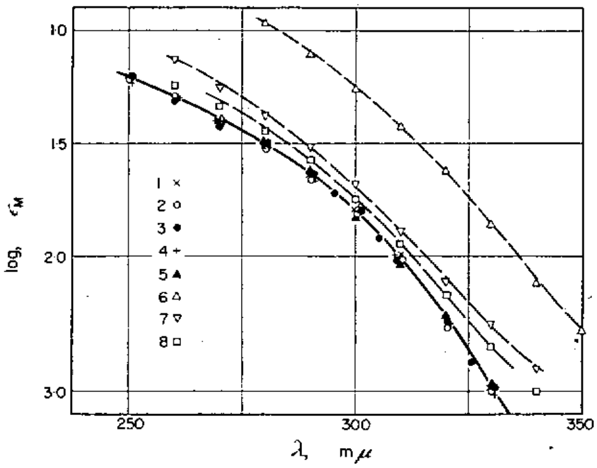

FIG. 1.—Absorption spectra of titanyl ion in acid solution ($ClO_4^- = 3$ M). Full line: non-hydrolysed solutions. Broken lines: hydrolysed solutions.

(1) $C_M = 10{\cdot}0$ mM $H = 207{\cdot}6$ mM
(2) $C_M = 20{\cdot}0$ mM $H = 455{\cdot}1$ mM
(3) $C_M = 72{\cdot}9$ mM $H = 1514$ mM
(4) $C_M = 35{\cdot}0$ mM $H = 811{\cdot}6$ mM
(5) $C_M = 36{\cdot}5$ mM $H = 5$ M
(6) $C_M = 170{\cdot}5$ mM $H = 105{\cdot}8$ mM
(7) $C_M = 19{\cdot}1$ mM $H = 170{\cdot}0$ mM
(8) $C_M = 20{\cdot}0$ mM $H = 206{\cdot}6$ mM

$$pM + qH_2O + nA \rightleftarrows M_p(OH)_qA_n + qH^+ \tag{1}$$

where p, q and n are integral. If the ionic strength of the solution is large and constant, activity factors can be considered constant and the stoicheiometric formation constant can be written:

$$K_{p,q,n} = \frac{[M_p(OH)_qA_n][H^+]^q}{[M]^p[A]^n} \tag{2}$$

The formation function $\bar{n}$ is dependent therefore on [A], [M] and $[H^+]$:

$$\bar{n} = \frac{C_A - [A]}{C_M} = \frac{\Sigma_p\Sigma_q\Sigma_n nK_{p,q,n}[M]^p[H^+]^{-q}[A]^n}{[M] + \Sigma_p\Sigma_q\Sigma_n p[M]^p[H^+]^{-q}[A]^n} \tag{3}$$

p, q and n can take values from 1 to P, 0 to Q and 1 to N, respectively.

If the formation function is found to be independent of $[H^+]$ no hydrolytic equilibria occur in solution. If $\bar{n}$ is independent of [M], polynuclear reactions can be ignored and only mononuclear complexes should exist in solution.

⁽⁵⁾ L. CIAVATTA and A. LIBERTI. Unpublished results (1959).

In the absence of hydrolytic and polynuclear reactions equation (3) is therefore simplified to:

$$\bar{n} = \frac{\sum_1^N n\beta_n[\mathrm{A}]^n}{1 + \sum_1^N \beta_n[\mathrm{A}]^n} \tag{3a}$$

where $\beta_n = K_{1,0,n}$

The existence of polynuclear complexes may be checked by working at different values of C_M, and the contribution of non-hydrolytic complexes may be found by making measurements in more acid solutions and extrapolating to $[\mathrm{H}^+]^{-q} \rightarrow 0$.

Calculation of $\bar{n}$ and [A] *by e.m.f. measurements*

Since no reversible electrodes are available to measure the free concentrations of fluoride and of titanyl ions, only $[\mathrm{H}^+]$ can be determined by experiment.

In the absence of fluoride ions and of hydrolysis $[\mathrm{H}^+] = H$, where H is the analytical concentration of hydrogen ion. When sodium fluoride is added to an acid solution of titanyl perchlorate, in addition to reaction (1) F^- is also bound to H to form HF and $\mathrm{HF_2}^-$.

For the material balance we can write, neglecting hydrolytic equilibria and assuming that only F^- behaves as a ligand:

$$H = [\mathrm{H}^+] + K_{11}[\mathrm{H}^+][\mathrm{A}] + K_{12}[\mathrm{H}^+][\mathrm{A}]^2 \tag{4}$$

The formation constants of the proton–fluoride system in 3 M $\mathrm{NaClO_4}$ are: $\log K_{11} = 3{\cdot}27\ \mathrm{M}^{-1}$ and $\log K_{12} = 4{\cdot}36\ \mathrm{M}^{-2}$

By rearranging equation (4):

$$H/[\mathrm{H}^+] = 1 + k_{11}[\mathrm{A}] + K_{12}[\mathrm{A}]^2 \tag{5}$$

Since $[\mathrm{H}^+]$ is measured and H is known from the composition of the solutions equation (5) can be solved for [A].

The formation function is calculated from the expression

$$\bar{n} = \frac{C_A - [\mathrm{A}] - Z \cdot H}{C_M} \tag{6}$$

where C_A and C_M are respectively the total analytical concentrations of fluoride and titanium, and Z is the average number of complex-bound fluoride ions per hydrogen atom. When $[\mathrm{H}^+]$ and [A] are known, it can be calculated by means of the expression

$$ZH = K_{11}[\mathrm{H}^+][\mathrm{A}] + 2K_{12}[\mathrm{H}^+][\mathrm{A}]^2 \tag{7}$$

The relationship (7) holds when hydrolytic equilibria can be neglected; should this occur, equation (7) can be obtained by extrapolation to $C_M \rightarrow 0$.

EXPERIMENTAL

Apparatus

The titration cell was of the type described by FORSLING *et al.*(6) The reference electrode was:

$$\mathrm{Ag}/[\mathrm{Ag}^+] = 10\ \mathrm{mM},\ [\mathrm{Na}^+] = 2990\ \mathrm{mM},\ [\mathrm{ClO_4}^-] = 3000\ \mathrm{mM}/\mathrm{NaClO_4} = 3000\ \mathrm{mM}// = \mathrm{RE}$$

The silver electrode was prepared as recommended by BROWN(7). Measurements of the free hydrogen ion concentration were made with a quinhydrone electrode:

$$\mathrm{RE}\ //\ [\mathrm{H}^+], [\mathrm{ClO_4}^-] = 3000\ \mathrm{mM}/\mathrm{QH_2}\text{—}\mathrm{Q}\text{—}/\mathrm{Pt}$$

---

(6) W. FORSLING, S. HIETANEN and L. G. SILLÉN, *Acta Chem. Scand.* **6**, 901 (1952).

(7) A. S. BROWN, *J. Amer. Chem. Soc.* **56**, 646 (1934).

Quinhydrone electrodes were bright platinum foils which were cleaned before use with 50% HNO_3 washed with water and ignited in an alcohol flame.

An extinctiometric investigation was carried out in order to check whether a reaction occurs between titanyl ion and quinhydrone. It was found that slight complex formation takes place; it seems however that this interaction may be neglected, since no variation of the quinhydrone spectrum was observed when the ratio fluoride/titanyl ion was about one. According to the conclusions of this research this behaviour does not affect the experimental results.

Attempts were made to measure the free hydrogen ion concentration of titanyl solutions by means of a hydrogen electrode, but reproducible potential values were not obtained. Since detectable amounts of chloride ions were found in the solution it seems very likely that titanium(IV) is reduced to titanium(III) which is responsible for the reduction of perchlorate.

e.m.f. measurements were performed to 0·01 mV with an SEB potentiometer (Milano). In all cases the potentials were stable within 0·1 mV.

All parts of the apparatus which were in contact with the solutions were constructed in polystyrene.

Chemicals

Titanyl perchlorate solutions were prepared as follows: titanyl sulphate $TiOSO_4, 2H_2O$, prepared as recommended by Pamfilov *et al.*[8], was treated in a beaker with Montecatini C-300 cation exchange resin in hydrogen form until exchange was complete. The resin was washed free from SO_4^{2-} with water; then a glass column (32 cm length, 3·5 cm diameter) was filled with the resin and exchange carried out with 1·5 M perchloric acid. The eluate was tested for SO_4^{2-} and Fe^{3+}; these ions were absent. The titanium content of the solution was determined by igniting a known volume of the solution at 800°C in a platinum crucible. The perchlorate concentration was determined by flowing a sample of solution through a cation resin in hydrogen form and titrating the eluate with NaOH. Thus the free hydrogen ion concentration was known:

$$[H^+] = [ClO_4^-] - 2[TiO^{2+}]$$

Sodium fluoride solutions were prepared from analytical grade Merck's product without further purification. The concentration of the stock solutions was checked by ion exchange and subsequent acidimetric titration. The results agreed within 0·2 per cent.

Perchloric acid was of analytical grade; the concentration of stock solutions was determined by titration with Na_2CO_3 using methyl-red and bromo-cresol green as visual indicators.

Sodium perchlorate was prepared by neutralizing $HClO_4$ with sodium hydrogen carbonate to the extent of 98 per cent and boiling off CO_2. Neutralization was complete with NaOH. The solution was filtered to remove the iron and silicon which were precipitated. The salt concentration was determined by evaporating a known amount of solution in an electric oven at 125°C; the sample was dried and weighed as $NaClO_4$.

Sodium hydroxide solutions were prepared from 50% NaOH and stored in plastic bottles. Stock solutions were standardized with $HClO_4$ and by evaporation of a known amount after addition of hydrochloric acid in slight excess. The sample was dried at 360°C and weighed as NaCl. The results agreed within 0·1 per cent.

Silver perchlorate solutions were prepared by boiling diluted $HClO_4$ with excess of Ag_2O. The solutions were standardized by Volhard's method.

Quinhydrone (Merck) was free of iron and alkali, and was used without purification.

Procedure

This study has been carried out by means of potentiometric titrations at 25°C in a thermostat. In order to use concentrations instead of activities in the formulae for e.m.f. and for equilibrium constants, all solutions were made 3 M in ClO_4^- by the addition of sodium perchlorate. Solutions were mixed by a stream of nitrogen, purified by passing over copper at 400°C, and then through 10% H_2SO_4, 10% NaOH, and 3 M $NaClO_4$ solutions, the last in order to equilibrate the gas at the correct aqueous vapour pressure.

An acid–base determination was first made to calculate the value of E_0. The measured e.m.f. E is related to H by:

$$E = E_0 + E_j + 59{\cdot}16 \log [H^+] \tag{8}$$

---

[8] A. V. Pamfilov and T. A. Kudiatova, *Chem. Abstr.* **44**, 1354 (1950).

where, in the absence of the complexing agents, $[H^+] = H$, the total analytical concentration, E_0 is a constant and E_j is the liquid junction potential, which is approximately given by $E_j = -j[H^+]$. By plotting the experimental values $E - 59{\cdot}16 \log [H^+](= E_0 + j[H^+])$ against $[H^+]$ a straight line is obtained; by extrapolating to $[H^+] \rightarrow 0$, E_0 is found. The slope of the straight line gives j, which is a constant around 0·017 ± 0·001 mV mM.

Known amounts of sodium fluoride were added to the cell from a calibrated burette together with a solution of titanyl perchlorate. The total analytical concentration of TiO^{2+} was kept constant during the titration; this is not essential but greatly simplifies the calculations.

TABLE 1.—DETERMINATION OF CORRESPONDING VALUES OF $\bar{n}$ AND [A] FROM POTENTIOMETRIC MEASUREMENTS OF $[H]^+$ WITH QUINHYDRONE ELECTRODE

$C_M = 15{\cdot}07$ mM $H = 189{\cdot}2$ mM

A (mM)	H (mM)	C_M (mM)	$[H^+]$ (mM)	$H/[H^+]$	ZH (mM)	$\bar{n}$	log [A] (mM)
19·93	189·2	15·07	188·0	1·0065	1·42	1·23	−2·398
26·02	185·1	14·74	180·4	1·0261	4·73	1·44	−1·854
31·85	181·2	14·43	171·9	1·0539	9·61	1·54	−1·523
37·33	177·5	14·13	164·7	1·0772	12·62	1·74	−1·387
42·64	173·9	13·84	157·1	1·1071	16·98	1·86	−1·237
47·84	170·4	13·56	150·1	1·1348	19·50	2·10	−1·150
52·74	167·1	13·30	143·0	1·1677	22·60	2·26	−1·070
57·45	163·9	13·05	137·3	1·1933	24·60	2·50	−1·001
62·03	160·8	12·80	130·6	1·2306	29·02	2·67	−0·920
66·36	158·2	12·57	125·5	1·2603	31·60	2·75	−0·854
70·61	155·0	12·34	120·0	1·2912	34·96	2·88	−0·807
74·63	152·3	12·12	114·9	1·3255	37·52	3·05	−0·760
78·55	149·6	12·02	109·4	1·3676	40·28	3·20	−0·708
82·38	147·0	11·71	102·9	1·4291	44·45	3·23	−0·639
86·04	144·6	11·50	97·2	1·4872	47·52	3·32	−0·585
89·64	142·1	11·20	91·2	1·5580	51·11	3·39	−0·528
96·38	137·6	10·95	79·5	1·7309	58·56	3·43	−0·409

When E_0 and j are known and E is measured, H can be obtained from equation (8). From the composition of the solution the total concentrations of metal and of ligand (C_M and C_A respectively) are known and by means of (5), (6) and (7) the values for [A], n and ZH are calculated.

RESULTS

The first addition of sodium fluoride to a titanyl perchlorate solution which is not hydrolysed causes no detectable change in hydrogen ion concentration; this indicates that the fluoride ion is very strongly bound and therefore the first step formation constant cannot be evaluated by direct potentiometric measurements of hydrogen ion concentration.

A measurable decrease in hydrogen ion concentration is observed in hydrolysed solutions. Since for these solutions the ratio $H/[H^+] \leq 1$ these variations should obviously be attributed to repression of the hydrolysis of the metal ion by fluoride complex formation. When the ratio C_A/C_M becomes higher than one, A is bound also to H^+ and from the variations in the ratio $H/[H^+]$ the equilibria due to the other complexes may be calculated.

Table 1 gives an example of the potentiometric titration carried out at $C_M = 15{\cdot}07$

TABLE 2.—THE FORMATION FUNCTION $\bar{n}$ AT CORRESPONDING VALUES OF [A] FOR DIFFERENT TOTAL CONCENTRATIONS OF C_M, BY POTENTIOMETRIC MEASUREMENTS

$C_M = 10{\cdot}0$ mM $H = 100{\cdot}0$ mM		$C_M = 15{\cdot}0$ mM $H = 150{\cdot}0$ mM		$C_M = 10{\cdot}29$ mM $H = 165{\cdot}4$ mM		$C_M = 5{\cdot}00$ mM $H = 50{\cdot}0$ mM	
$\bar{n}$	log [A]	$\bar{n}$	log [A]	$\bar{n}$	log [A]	$\bar{n}$	log [A]
1·39	−2·125	1·42	−1·960	1·21	−2·194	1·45	1·820
1·54	−1·660	1·93	−1·290	1·38	−1·793	1·69	−1·390
1·68	−1·456	2·18	−1·170	1·56	−1·585	2·00	−1·315
1·85	−1·334	2·36	−1·080	1·78	−1·398	2·34	−1·080
2·04	−1·250	2·47	−1·020	1·90	−1·284	2·57	−0·980
2·33	−1·122	2·62	0·955	2·09	1·194	2·95	−0·715
2·59	−1·040	2·69	−0·900	2·25	−1·135		
2·76	−0·885	2·80	−0·860	2·46	−1·071		
2·83	−0·824	2·88	−0·820	2·50	−0·996		
2·93	−0·780	2·84	−0·745	2·63	0·929		
3·03	−0·660	2·87	−0·730	2·78	−0·876		
3·18	−0·630	2·89	−0·700	2·82	−0·810		
				3·05	−0·693		
				3·14	−0·635		
				3·28	−0·579		

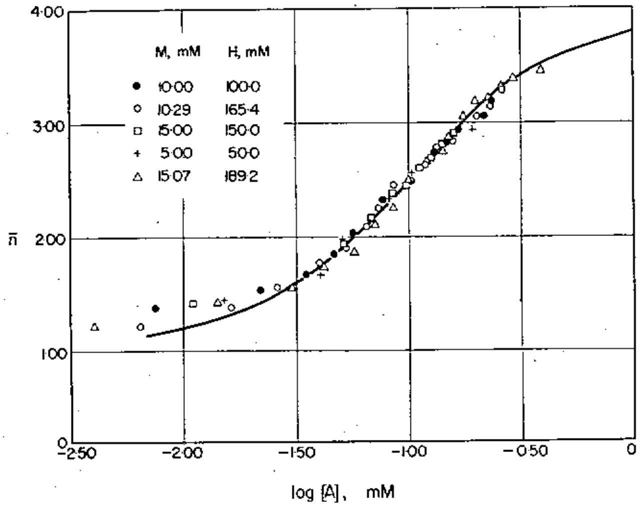

FIG. 2.—The complex formation curve at different values of C_M and H. Full curve calculated from the complexity constants obtained from the potentiometric measurements.

mM and $H = 189{\cdot}2$ mM. The results of the main titration are collected in Table 2 and plotted in Fig. 2.

The formation curve starts at $\bar{n} = 1{\cdot}00$ and reaches a maximum at $\bar{n} = 4{\cdot}00$; therefore the highest complex present in solution is $TiOF_4^{2-}$. Since the experimental points for different metal and hydrogen ion concentrations fall on the same curve polynuclear and hydrolytic equilibria can be ignored.

From a plot of $\bar{n}$ as a function of log [A] the formation constants for the following equilibria may be calculated:

$$TiOF^+ + F^- \rightleftharpoons TiOF_2$$

$$TiOF^+ + 2F^- \rightleftharpoons TiOF_3^-$$

$$TiOF^+ + 3F^- \rightleftharpoons TiOF_4^=$$

This calculation has been carried out by two methods.

(*a*) *Bjerrum's spreading factor method*(9)

The slope of the formation function $\bar{n}$ vs. log [A] at its midpoint is obtained from Fig. 2 where $N = 3$

$$\Delta = \left(\frac{d\bar{n}}{d\log[\mathrm{A}]}\right)_{n=N/2} \cdot 0{\cdot}434 = 0{\cdot}952 \tag{8}$$

From this value of Δ, the spreading factor was calculated by means of the expression

$$x^2 = \frac{9 - 4\Delta}{12\Delta - 3} \tag{9}$$

which on solution gives $x = 0{\cdot}785$.
By means of the relationship:

$$\log k_n = \log K + \log \frac{N + 1 - n}{n} x^{N+1-2n} \tag{10}$$

where $\log K = -\log[\mathrm{A}]_{\bar{n}=N/2} = 4{\cdot}00$

the following provisional formation constants were calculated:

$$\log k_{11} = 4{\cdot}26\ \mathrm{M}^{-1} \qquad \log \beta_1 = 4{\cdot}26\ \mathrm{M}^{-1}$$
$$\log k_2 = 4{\cdot}00\ \mathrm{M}^{-1} \qquad \log \beta_2 = 8{\cdot}26\ \mathrm{M}^{-2}$$
$$\log k_3 = 3{\cdot}73\ \mathrm{M}^{-1} \qquad \log \beta_3 = 11{\cdot}99\ \mathrm{M}^{-3}$$

(*b*) *Fronaeus' method*(10)

The formation function $\bar{n}$ as a function of log [A] may be written in the form:—

$$\frac{\bar{n} - 1}{[\mathrm{A}]} = \frac{d \ln X([\mathrm{A}])}{d[\mathrm{A}]} \tag{11}$$

where

$$X([\mathrm{A}]) = 1 + \sum_{1}^{N} \beta_n [\mathrm{A}]^n$$

From the experimental data shown in Fig. 3, by graphical integration, FRONAEUS' function $X([\mathrm{A}])$ was calculated:

$$X([\mathrm{A}]) = \exp \int_0^{[\mathrm{A}]} \frac{\bar{n} - 1}{[\mathrm{A}]} d[\mathrm{A}] = \sum_{0}^{N} \beta_n [\mathrm{A}]^n$$

The complexity constants can be calculated by introducing a new function X_1 ([A]):

$$X_1([\mathrm{A}]) = \frac{X([\mathrm{A}]) - 1}{[\mathrm{A}]} = \beta_1 + \beta_2[\mathrm{A}] + \beta_3[\mathrm{A}]^2 \tag{13}$$

---

(9) J. BJERRUM, *Metal Ammine Formation in Aqueous Solutions.* P. Haase, Copenhagen (1957).
(10) see S. AHRLAND, *Acta Chem. Scand.* 3, 783 (1949).

The plot of X_1 ([A]) against [A] gives a curve which is easily extrapolated to $[A] = 0$; the intercept on the axis gives β_1 and the slope at the intercept is equal to β_2. The latter constant is more accurately determined by calculating a new function X_2 ([A]):

$$X_2([A]) = \frac{X_1([A]) - \beta_1}{[A]} = \beta_2 + \beta_3[A]$$

which by extrapolation allows β_2 to be calculated as the intercept on the axis and β_3 as the slope at the intersection. The function X_3 ([A]) is practically constant over the whole [A]-range so that $X_3([A]) = \beta_3$. In Table 3 the values of $X_1([A])$, $X_2([A])$ and $X_3([A])$ obtained from the data of Fig. 3 have been calculated. In Fig. 4 the functions X_1 ([A]) and X_2 ([A]) are plotted and from the graph the following values of the formation constants have been obtained:

TABLE 3.—$X_1([A])$, $X_2([A])$ AND X_3 ([A]) AS FUNCTIONS OF [A]

[A]	ln $X([A])/X([A_0])$	$X([A])/X([A_0])$	$X([A])$	$X_1([A])$	$X_2([A])$	$X_3([A])$
0·01	—					
0·02	0·2337	1·26	1·58	29·0		
0·03	0·4517	1·57	1·96	32·0		
0·04	0·6550	1·92	2·40	35·0		
0·05	0·8463	2·32	2·90	38·0	310	
0·06	1·0263	2·78	3·47	41·2	312	
0·07	1·1963	3·30	4·13	44·6	315	
0·08	1·3587	3·86	4·84	48·0	318	
0·09	1·5015	4·45	5·55	50·5	312	
0·10	1·6637	5·25	6·58	55·8	333	
0·12	1·9437	6·92	8·65	64·0	346	
0·14	2·2037	9·08	11·40	74·2	370	
0·16	2·4463	11·35	14·20	82·5	375	1065
0·18	2·6737	14·4	18·00	94·0	396	1065
0·20	2·8887	17·8	22·20	105·0	412	1040
0·22	3·0913	21·8	27·40	120	445	1090
0·24	3·2813	26·3	32·80	132	456	1050
0.26	3·4613	31·6	39·40	147·5	481	1065
0·28	3·6315	37·3	46·40	163	503	1070
0·30	3·7937	43·9	54·90	179	522	1060
0·34	4·0987	59·2	74·00	215	566	1065
0·38	4·3737	79·3	99·00	258	618	1060

$$\beta_1 = 2{\cdot}25 \times 10^4\ \mathrm{M}^{-1} \qquad \log \beta_1 = 4{\cdot}35\ \mathrm{M}^{-1}$$
$$\beta_2 = 2{\cdot}04 \times 10^8\ \mathrm{M}^{-2} \qquad \log \beta_2 = 8{\cdot}31\ \mathrm{M}^{-2}$$
$$\beta_3 = 1{\cdot}06 \times 10^{12}\ \mathrm{M}^{-3} \qquad \log \beta_3 = 12{\cdot}03\ \mathrm{M}^{-3}$$

The agreement between the methods is fairly good and the latter values of the constants can be considered definitive. In Fig. 5 is shown the distribution of the four complexes $TiOF^+$, $TiOF_2$, $TiOF_3^-$ and $TiOF_4^{2-}$ as a function of [A].

DISCUSSION

The potentiometric investigation of the fluoride–titanyl system shows that in the metal concentration range $5{\cdot}0 < C_M < 15{\cdot}0$ mM and the hydrogen ion range 200

$< [\mathrm{H^+}] <$ 50 mM a series of mononuclear complexes is formed, viz. $\mathrm{TiOF^+}$, $\mathrm{TiOF_2}$, $\mathrm{TiOF_3^-}$ and $\mathrm{TiOF_4^{2-}}$. Though the hydrogen ion concentration has been kept high in order to repress hydrolysis of titanyl ion and to permit detectable variations of $[\mathrm{H^+}]$ even at low values of fluoride concentration, the formation constant of $\mathrm{TiOF^+}$ cannot be calculated from experimental data obtained by potentiometric titrations. An estimate of its value may be obtained by taking into consideration the sensitivity of the experimental techniques which have been employed.

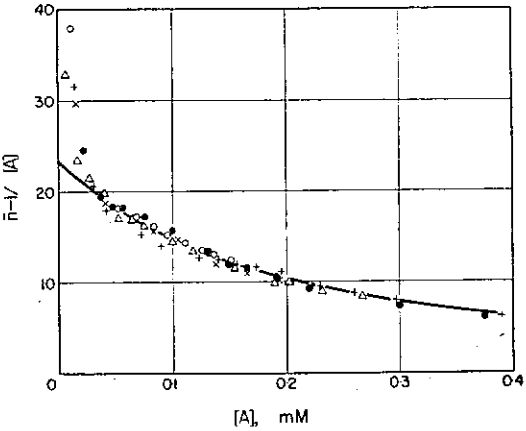

FIG. 3.—$\bar{n} - 1/[\mathrm{A}]$ as a function of [A], the integration of which gives the $X([\mathrm{A}])$ function.

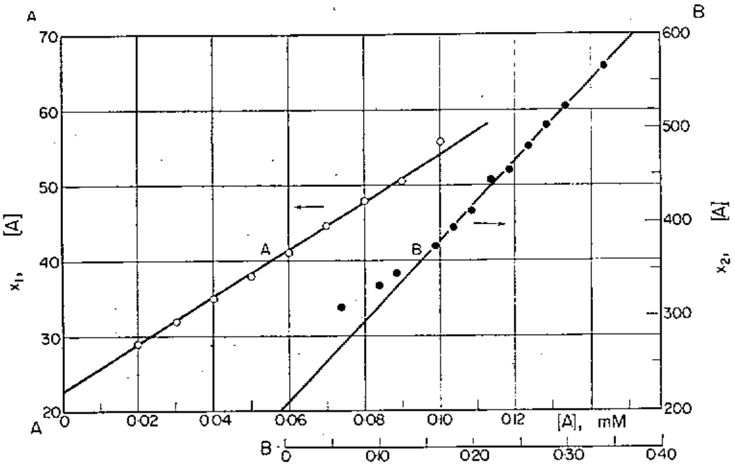

FIG. 4.—The functions $X_1([\mathrm{A}])$(line A) and $X_2([\mathrm{A}])$(line B) which give the complexity constants.

If the minimum detectable variation of E, ΔE, is 0·2 mV, the corresponding variation of $\Delta[\mathrm{H^+}]$ will be, according to (8):

$$\Delta E = j\,\Delta[\mathrm{H^+}] + 59{\cdot}16\,\frac{\Delta[\mathrm{H^+}]}{[\mathrm{H^+}]}\,0{\cdot}434 \cong 59{\cdot}16\,\frac{\Delta[\mathrm{H^+}]}{[\mathrm{H^+}]}\,0{\cdot}434 \qquad (15)$$

But from equation (5) it follows that

$$\frac{H - [\mathrm{H}^+]}{[\mathrm{H}^+]} = \frac{\Delta[\mathrm{H}^+]}{[\mathrm{H}^+]} = k_{11}[\mathrm{A}] + k_{12}[\mathrm{A}]^2 \qquad (16)$$

By taking $\Delta E = 0{\cdot}2$ mV and H = 200 mM, then from (15) and (16), $[\mathrm{A}] = 4{\cdot}2 \times 10^{-6}$ Thus the formation constant of the first complex should be higher than $1/[\mathrm{A}] = 2{\cdot}4 \times 10^5$.

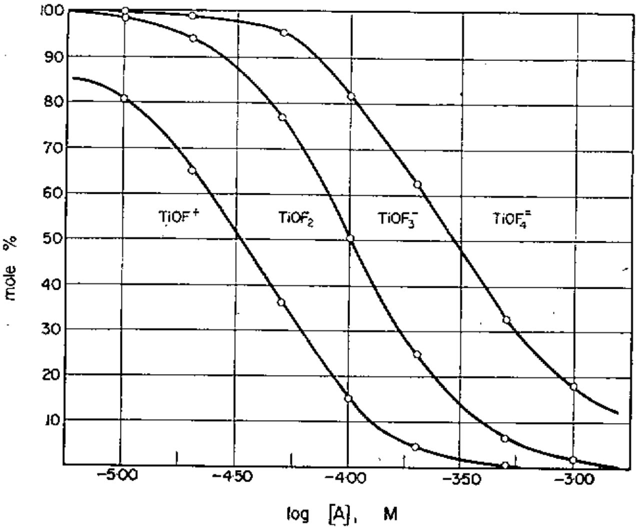

FIG. 5.—Distribution of complexes of titanyl and fluoride as a function of the logarithm of fluoride concentration, using the constants calculated in this work.

As far as the hexafluotitanate ion is concerned its existence in the range of hydrogen ion concentration which has been investigated must be ruled out, since $\bar{n}$ tends to four and the highest complex formed is therefore $\mathrm{TiOF_4}^{2-}$. The non-existence of $\mathrm{TiF_6}^{2-}$ in acid solution is in agreement with the results obtained in work on the hydrolysis of fluotitanates,[11] where it was found that the hydrolysis takes place in two steps: a very fast reaction consuming two equivalents of alkali and a fairly slow reaction. In the light of these results it seems that $\mathrm{TiF_6}^{2-}$ hydrolyses almost instantaneously to $\mathrm{TiOF_4}^{2-}$, which slowly undergoes further hydrolysis.

[11] A. LIBERTI and L. CIAVATTA, *J. Inorg. Nucl. Chem.* **8**, 365 (1958).