of the mixture, it is doubtful that the uncertainties in the C's offer a satisfactory explanation of the discrepancies at lower pressures. But the fact that variations in the C's improve the agreement lends some support to the tentative hypothesis that horizontal interactions in the first layer account for the wrong distribution between the adsorbates, since such interactions would make the C's variable.

However naive it may be to consider that closer fitting of Fig. 11 by equation (42 or 44) establishes the validity of the refinement of the B.E.T. model to allow for capillary effects, it seems considerably more significant that the parameters obtained by fitting the oxygen isotherm can so much improve the predicted adsorption from the mixtures. On the other hand, the validity of using 1.5 for g seems questionable, in view of the fact that the value calculated from Hill's equation (54), with $k = 1$ and S calculated from the cross-section of the oxygen molecule,[16] is 18. In other words, the observed value of kS was only one seventh of the value to be expected for smooth, liquid packing of the top layer. That such a discrepancy can really be due to irregularities of packing seems unlikely.

Arnold[17] has recently measured adsorption

(16) P. H. Emmett, in E. O. Kraemer's "Advances in Colloid Science," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1942, p. 8.

(17) J. R. Arnold, THIS JOURNAL, 71, 104 (1949). For comparing Arnold's results with ours, it must be emphasized that V_m and P_0 have different meanings in his paper than in ours.

from mixtures of oxygen and nitrogen on anatase. His results and ours agree in that the total adsorption conforms as well to Hill's theory as do the pure isotherms. But on anatase, nitrogen is adsorbed more strongly than theory predicts and oxygen, less strongly; this is just the reverse of the situation on chromic oxide gel. In fact, Arnold's results differ from Hill's theory much further than ours do in the pressure range we investigated. The differences between his results and ours at the lower pressure can hardly be attributed to capillary condensation and must rather be due to differing degrees of horizontal interactions on the two adsorbents.

Further experiments with other temperatures, adsorbents, and mixtures of adsorbates are being undertaken in the hope of obtaining more definite evidence as to the ultimate cause of such discrepancies between theory and experiment as those in the low-pressure region with oxygen–nitrogen mixtures.

Summary

1. Adsorption isotherms of binary mixtures of oxygen and nitrogen on chromic oxide gel at $-185.6°$ have been measured and compared with Hill's[4] extension of the B.E.T. theory.

2. With allowance for capillary condensation, the theoretical and experimental isotherms agree semi-quantitatively for both mixtures over the pressure range investigated.

SOUTHERN RESEARCH INSTITUTE
BIRMINGHAM, ALABAMA   RECEIVED JANUARY 24, 1949

The Complex Ions Formed by Iron and Thorium with Fluoride in Acid Solution[1a]

BY H. W. DODGEN[1b] AND G. K. ROLLEFSON

It has long been known that ferric fluoride is a weak electrolyte. Measurements[1c] of the freezing point lowering, electrical conductivity, and the absence or very great inhibition of reactions characteristic of ferric ions and fluoride ions in solutions of ferric fluoride demonstrate this fact quite clearly. Peters[2] found that the electrical conductivity of a solution containing sodium fluoride and ferric fluoride was less than that of the separate solutions and that in a solution of Na_3FeF_6 the iron moved with fluoride toward the anode. This and other evidence[1c] shows that a ferric fluoride anion does exist in solution; however, none of the above work yields the formulas of the complex ions or their degree of stability.

(1a) This work was performed under the auspices of the Manhattan District at the University of California during 1945 and 1946.

(1b) Present address: Department of Chemistry and Chemical Engineering, The State College of Washington, Pullman, Washington.

(1c) Abegg "Handbuch der anorganischen Chemie," 4 Band, 3 Abt. 2 Teil, p. B158, Verlag von S. Hirzel, Leipzig, 1935.

(2) Peters, Z. physik. Chem., 26, 195, 219 (1898).

It has become customary to write $FeF_6^=$ as the formula of the ferric fluoride complex ion, but Low and Pryde[3] showed that this could not be the formula in acid solutions by studying the potential of the ferrous–ferric half cell as a function of hydrogen fluoride concentration. Their data can be interpreted quantitatively by assuming the equilibrium $Fe^{+3} + HF \rightleftharpoons FeF^{++} + H^+$. More recently Brosset and Gustaver[4] interpreted potentiometric measurements on the ferrous–ferric half cell by assuming the existence of the ions FeF^{++} and FeF_2^+, and Babko and Kleiner[5] obtained equilibrium constants for the formation of the ions FeF^{++}, FeF_2^+, FeF_3, FeF_4^-, and $FeF_5^=$ from measurements on the decolorization of the ferric thiocyanate complexes with fluoride.

The first part of this paper presents the results of measuring the potential of the ferrous–ferric

(3) Low and Pryde, THIS JOURNAL, 61, 2237 (1939).

(4) Brosset and Gustaver, Sv. Kem. Tidskr., 54, 185 (1942).

(5) Babko and Kleiner, J. Gen. Chem. (U. S. S. R.), 17, 1259 (1947).

electrode as a function of the hydrofluoric and perchloric acid concentrations and a quantitative interpretation of the data by assuming the existence of the complex ions FeF^{++} and FeF_2^+ and FeF_3 molecules in solution. The second part of the paper deals with the measurement of the potential of the ferrous–ferric half cell as a function of the hydrofluoric acid and thorium nitrate concentrations and the quantitative interpretation of the data by assuming the existence of the complex ions ThF^{+++}, ThF_2^{++} and ThF_3^+. The solubility product of $ThF_4 \cdot 4H_2O$ was also determined. This technique has been used by Brosset and Orring[6] in a study of the aluminum–fluoride complex ions.

The existence of complex ions of thorium with fluoride in solution was discovered while developing a method of analysis for thorium based upon the precipitation of thorium fluoride. The procedure being used was the titration with sodium fluoride of a solution containing Th^{+4}, Fe^{+3} and Fe^{+2} and measuring the potential of a gold electrode inserted in the solution. When the precipitation was complete the potential would change suddenly by a large amount due to the complexing of ferric ion by the excess fluoride. During the titration there was no precipitate formed and only a very small change in potential up to the point where $\sim$2 moles of fluoride per mole of thorium had been added. At this point a precipitate formed and there was a discontinuity in the potential; the potential then changed continuously until the large change at the end-point. Upon completion of the titration thorium nitrate was added to the solution until there was slightly less than 2 moles of fluoride per mole of thorium; the precipitated thorium fluoride dissolved after stirring and heating and a light beam passed through the solution gave no Tyndall effect. This was very good evidence for the existence of thorium–fluoride complex ions.

Experimental

The Cell.—The cell used for the electrometric titrations is shown in Fig. 1. The containers, A and B, and the caps with entrances for the stirrers, etc., were made from large ground glass joints of about 5 cm. diameter. The containers held about 100 cc. of solution when filled to the level shown in the diagram. The electrodes were made of gold sheet and wire; they had a surface area of about 8 sq. cm. Initially they were cleaned with warm aqua regia and were stored in distilled water when not in use.

The two halves of the cell were connected by an agar–agar–sodium perchlorate salt bridge. In an effort to minimize junction potentials 1.6 M sodium perchlorate was used in making the salt bridge. At the beginning of an experiment the solutions in A and B had identical compositions; however, during a titration the composition of B changed. In a typical experiment the initial composition was 0.398 M NaClO$_4$, 0.111 M HClO$_4$, and the final composition was 0.395 M NaClO$_4$, 0.090 M HClO$_4$, 0.016 M HF. A net junction potential of 0.7 millivolt was calculated from the Henderson equation.[7] This result indicates that junction potentials were probably negligible.
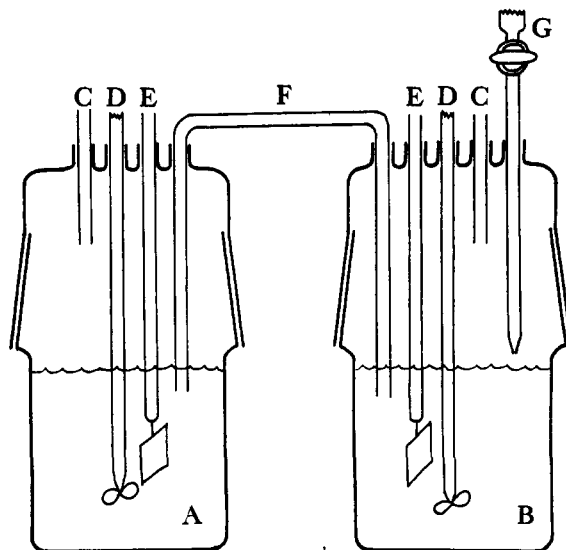

Fig. 1.—The cell: A and B, containers; C, carbon dioxide jets; D, stirrers; E, gold electrodes; F, agar–agar salt bridge; G, 5-cc. buret.

The other ports on the cell were used for introducing a carbon dioxide atmosphere to prevent oxidation of the ferrous ion by atmospheric oxygen and for introducing sodium fluoride solution with a calibrated 5-cc. buret. Potential measurements were made with a Leeds and Northrup type K potentiometer.

The Solutions.—A standard sodium perchlorate solution was prepared by weighing the anhydrous C. P. salt. Sodium perchlorate was used for maintaining constant ionic strength rather than the lithium or potassium salts because lithium fluoride is sparingly soluble and potassium fluoride forms double salts with thorium fluoride.[8] Sodium fluoride does not form double salts with thorium fluoride.[8]

The perchloric acid solution was prepared by diluting 70% C. P. perchloric acid and standardizing with mercuric oxide and potassium iodide using methyl red as the end-point indicator. A stock solution containing perchloric acid, ferrous and ferric perchlorate was prepared by partially oxidizing a solution of C. P. ferrous perchlorate with hydrogen peroxide; the solution was standardized in the manner described by Schumb, Sherrill and Sweetser.[9] Sodium fluoride was prepared by distilling concentrated C. P. hydrogen fluoride from a platinum still into C. P. sodium bicarbonate in a platinum crucible. The material in the crucible was evaporated to dryness on a steam-bath, ground in a mortar, heated to 300° for two hours, and then stored in a desiccator. The standard sodium fluoride solution was prepared by weighing. A standard thorium nitrate solution was prepared by weighing the C. P. salt; the thorium content of the salt was determined by igniting samples to thorium oxide.

The Procedure for Carrying Out a Titration.—The containers, A and B, of the cell were filled by transferring the desired volumes of the stock solutions with calibrated pipets. The perchloric acid concentration varied from 0.03 to 0.3 M in different runs; enough sodium perchlorate was used to make the ionic strength 0.5. The ferrous and ferric perchlorate concentrations were approximately 0.0002 and 0.0006 M. The thorium concentrations used ranged from 0.005 to 0.0002 M. In each case enough distilled water was added to make the volume 100 cc. After filling the other parts of the cell were assembled and then it was placed in a thermostat regulated

(6) Brosset and Orring, *Sv. Kem. Tidskr.*, **55**, 101 (1943).

(7) P. Henderson, *Z. physik. Chem.*, **59**, 118 (1907); **63**, 325 (1908).

(8) A. Rosenheim, V. Samter and J. Davidsohn, *Z. anorg. allgem. Chem.*, **35**, 424 (1903).

(9) W. C. Schumb, M. S. Sherrill and S. B. Sweetser, This Journal, **59**, 2360 (1937).

TABLE I
THE POTENTIAL vs. TOTAL FLUORIDE CONCENTRATION FOR CELLS CONTAINING IRON ONLY

| $(Fe_t^{+3}) = 0.000654\ M,\ (Fe_t^{+2}) = 0.001136\ M$ | | | | | | $(Fe_t^{+3}) = 0.000622\ M,\ (Fe_t^{+2}) = 0.000257\ M$ | | | | | |
| $(H_0^+) = 0.03245\ M$ | | $(H_0^+) = 0.05328\ M$ | | $(H_0^+) = 0.1110\ M$ | | $(H_0^+) = 0.05360\ M$ | | $(H_0^+) = 0.1119\ M$ | | $(H_0^+) = 0.2781\ M$ | |
$(F_t^-) \times 10^3$	ΔE, mv.	$(F_t^-) \times 10^3$	ΔE, mv.	$(F_t^-) \times 10^3$	ΔE, mv.	$(F_t^-) \times 10^3$	ΔE, mv.	$(F_t^-) \times 10^3$	ΔE, mv.	$(F_t^-) \times 10^3$	ΔE, mv.
0.364	12.40	0.363	10.50	0.148	3.08	0.222	6.91	0.368	7.55	0.739	8.19
0.730	25.67	0.584	16.86	.292	6.09	.444	13.30	0.738	14.72	1.478	15.11
1.093	37.96	0.803	22.93	.440	8.95	.665	19.81	1.104	21.23	2.57	23.80
1.460	48.80	1.022	28.86	.730	14.59	.884	25.81	1.840	32.20	4.38	34.88
1.810	57.61	1.242	34.08	1.461	26.77	1.106	31.46	2.570	41.31	7.38	47.90
2.180	65.55	1.461	39.00	2.182	36.46	1.478	39.88	3.66	51.77	10.98	60.21
		1.823	46.24	2.90	44.55	1.840	47.12	5.49	65.41	14.60	69.90
		2.182	52.65	3.98	54.33	2.57	59.35	7.69	78.32	18.22	77.75
		2.900	63.51	5.06	62.48	3.29	69.17	10.60	91.92		
		3.615	72.47	6.50	71.54	4.38	81.24	13.88	104.24		
		4.70	83.73	8.30	81.19	5.84	94.57	18.23	118.18		
		6.14	96.35	10.50	91.12	7.67	108.77				
		7.95	110.06	13.02	101.10	9.86	123.00				
		10.12	123.67	15.55	109.69	12.40	137.18				
		13.74	142.93	18.04	117.28	15.00	149.64				
		18.03	162.33			18.23	164.08				

TABLE II
THE POTENTIAL vs. TOTAL FLUORIDE CONCENTRATION FOR CELLS CONTAINING IRON AND THORIUM

| $(Fe_t^{+3}) = 0.000622\ M,\ (Fe_t^{+2}) = 0.000257\ M,\ (H_0^+) = 0.0536\ M$ | | | | | | $(Fe_t^{+3}) = 0.0006160,\ (Fe_t^{+2}) = 0.000255,\ (H_0^+) = 0.0559$ | |
| $(Th_t^{+4}) = 0.004773\ M$ | | $(Th_t^{+4}) = 0.001196\ M$ | | $(Th_t^{-4}) = 0.0002390$ | | $(Th_t^{+4}) = 0.0002369$ | |
$(F_t^-) \times 10^3$	ΔE, mv.	$(F_t^-) \times 10^3$	ΔE, mv	$(F_t^-) \times 10^3$	ΔE, mv.	$(F_t^-) \times 10^3$	ΔE, mv.
1.477	0.19	0.739	0.08	0.074	0.04	0.148	0.25
2.933	.32	1.106	0.47	.148	.15	.364	2.41
4.385	.70	1.477	1.91	.221	.45	.731	9.74
5.480	1.67	1.841	4.41	.265	.73	1.095	18.67
6.57	3.82	2.205	8.11	.295	1.20	1.463	27.53
7.67	7.01	2.569	13.06	.368	2.23	1.823	35.39
8.77	11.91	2.933	18.79	.441	3.44	2.183	42.33
9.87	15.28	3.293	25.13	.518	4.91	2.544	48.02
10.97	15.63	3.654	26.73	.587	6.34	2.904	52.39
12.43	17.01	4.021	28.21	.659	7.98	3.261	56.89
13.88	18.46	4.385	30.05	.731	9.62	3.617	61.02
15.34	20.05	5.116	34.83	.877	13.13	5.066	75.63
16.79	23.23	6.57	50.54	1.023	16.80		
18.25	28.18	9.50	84.63	1.314	24.09		
		18.25	140.69	2.193	43.15		
				3.649	62.94		

at 25.00 ± 0.01°. The stirrers were started and the potential of the cell was followed for one-half to one hour. In principle the initial potential of the cell should have been zero, but in almost every case a potential of from 0.1 to 0.5 millivolt was observed. The titration was started after this small potential had remained constant for twenty to thirty minutes. Aliquots of sodium fluoride solution were added from the buret every eight to ten minutes; after each addition the solutions in the cell were stirred for ~5 minutes and then the potential of the cell was measured with the stirrers turned off. The potential readings were very steady and showed no signs of drifting. One cell was run with nitrogen sweeping out one side and carbon dioxide being bubbled in the other side. The carbon dioxide had no effect on the potential.
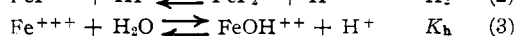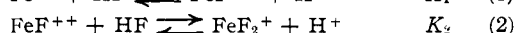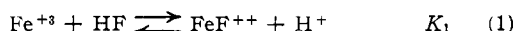
The Results.—The experimental results on cells which contained no thorium are shown in Fig. 2 and Table I. They demonstrate the effect of acid concentration on the variation of the e. m. f. with hydrofluoric acid concentration.

The results with cells containing various concentrations of thorium nitrate are shown in Fig. 3 and Table II. All of the curves are for a perchloric acid concentration of ~0.05 M. Curve 1 shows the potentials observed on a cell containing no thorium. The breaks in the curves are the points at which thorium fluoride was observed to start precipitating.

Interpretation and Discussion

Analysis of the Data for Cells Containing Iron Only.—In analyzing the data it is necessary to consider the equilibria.
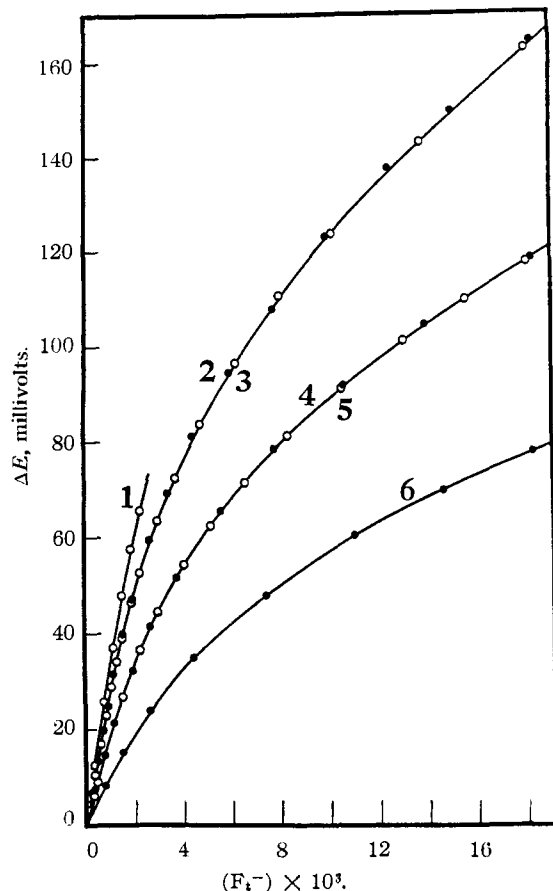
$$Fe^{+3} + HF \rightleftarrows FeF^{++} + H^+ \qquad K_1 \quad (1)$$
$$FeF^{++} + HF \rightleftarrows FeF_2^+ + H^+ \qquad K_2 \quad (2)$$
$$Fe^{+++} + H_2O \rightleftarrows FeOH^{++} + H^+ \qquad K_h \quad (3)$$
$$HF \rightleftarrows H^+ + F^- \qquad K_4 \quad (4)$$
$$HF + F^- \rightleftarrows HF_2^- \qquad K_5$$

Fig. 2.—The change in potential $vs.$ the total concentration of fluoride as a function of acidity (for cells containing iron only): Curve 1, $(H_0^+) = 0.03245\ M$; 2, $(H_0^+) = 0.05360\ M$; 3, $(H_0^+) = 0.05328\ M$; 4, $(H_0^+) = 0.1119\ M$; 5, $(H_0^+) = 0.1110\ M$; 6, $(H_0^+) = 0.2781\ M$. Solid lines were not drawn through points for curves 2 and 4.

Fig. 3.—The change in potential $vs.$ the total concentration of fluoride for cells containing iron and thorium: Curve 1, O, $(Th_t^{+4}) = 0$ (same as curve 2, Fig. 2); Curve 2, ▲, $(Th_t^{+4}) = 0.0002390\ M$; Curve 3, Δ, $(Th_t^{+4}) = 0.0002369\ M$; Curve 4, ●, $(Th_t^{+4}) = 0.001196\ M$; Curve 5, O, $(Th_t^{+4}) = 0.004773\ M$.

The K's are equilibrium constants; $K_1 = (FeF^{++})(H^+)/(Fe^{+3})(HF) = K_1^0\gamma_{HF}\cdot\gamma_{Fe^{+++}}/\gamma_{FeF^{++}}\cdot\gamma_{H^+}$, where parentheses are used to designate concentrations in moles per liter, K_1^0 is the equilibrium constant at zero ionic strength, and the γ's are activity coefficients. All experiments were performed at an ionic strength of 0.5, this value being chosen because the activity coefficient of many electrolytes has a small rate of change with ionic strength in this region and because equilibria of the type (1) and (3) show almost no change with ionic strength at $\mu = 0.5$.[10]

At the acid concentrations used in the experiments equilibria (3), (4) and (5) are shifted predominantly to the left and hence enter into the analysis of the data more or less as "corrections"; because of this fact it is not necessary to know the values of these constants with high accuracy. The values chosen for use at $\mu = 0.5$ and 25° are $K_h = 0.0019$, from the calculations of Bray and
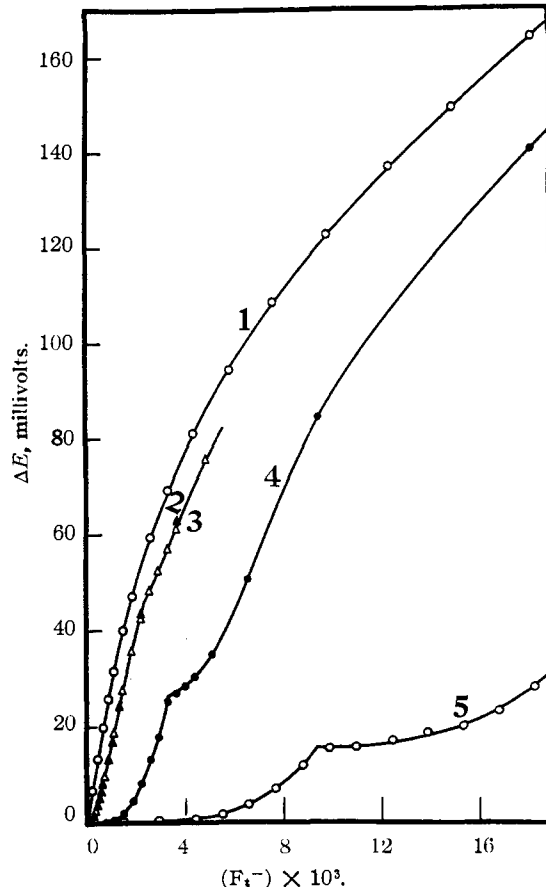
Hershey[10] and $K_4 = 0.00042$, $K_5 = 33$ from the work of Roth.[11]

Equilibria (1) and (2) are assumed and it will be shown that the data can be interpreted quantitatively on the basis of these equilibria. It is also assumed that Fe^{++} is not complexed by fluoride ion; this assumption and the possibility of interpreting the data by assuming equilibria other than (1) and (2) will be discussed at the end of this section.

It will be noted that equilibria (1) and (2) are not volume dependent, whereas equilibria (3), (4) and (5) are volume dependent. During the titration the volume increased by 5%; this change is well within the accuracy of K_h, K_4 and K_5, and it is therefore neglected. All concentrations were calculated with respect to the initial volume.

The quantities observed in a titration are (F_t^-), the total concentration of fluoride; and ΔE, the change in potential of the ferrous–ferric half cell.

(10) Bray and Hershey, $ibid.$, 56, 1889 (1934).

(11) Roth, $Ann.$, 542, 35 (1939).

We also know (H_0^+) the initial hydrogen ion concentration and (Fe_t^{+3}), the total ferric ion concentration. We can calculate (Fe^{+3}), the concentration of ferric ions from the equation

$$\ln (Fe^{+3})/(Fe_0^{+3}) = -F\Delta E/RT \quad (6)$$

by assuming that the activity coefficients of the ferrous and ferric ions are constant; this is very likely since the ionic strength and composition of the solution changes but slightly during a titration. (Fe_0^{+3}) is the concentration of ferric ions when no fluoride is present and is given by

$$(Fe_0^{+3}) = (Fe^{+3})/[1 + K_h/(H_0^+)] \quad (7)$$

which may be derived by considering equilibrium (3).

(Fe_c^{+3}), the concentration of ferric ion present as fluoride complexes, was calculated from the equation

$$(Fe_c^{+3}) = (Fe^{+3})[1 - (Fe^{+3})/(Fe_t^{+3})] \quad (8)$$

which was derived from the stoichiometric relationship for ferric iron and equilibrium (3). In deriving equation (8) the quantity $[1 + K_h/(H^+)]$ was replaced by $[1 + K_h/(H_0^+)]$; since this quantity ranged from 1.000 to 1.057 and in a given experiment changed by a maximum of 0.3% the substitution was justified.

Having calculated (Fe^{+3}) and (Fe_c^{+3}), K_1 and K_2 were determined by successive approximations from the equations

$$2(Fe_c^{+3}) - (F_t^-) = (HF)[K_1(Fe^{+3})/(H^+) - \alpha] \quad (9)$$

$$(HF)\alpha = (F_t^-) - (Fe_0^{+3})[1 + 2K_3(HF)/(H^+)]/[1 + K_2(HF)/(H^+)] \quad (10)$$

$$(H^+) = (H_0^+) - (HF) - (HF_2^-) \quad (11)$$

$$K_2 = [(Fe_c^{+3})(H^+)^2/K_1(Fe^{+3})(HF)^2] - (H^+)/(HF) \quad (12)$$

Equation (9) was derived from the stoichiometric relationship for fluoride and equilibria (1), (4) and (5); equation (10) from the stoichiometric relationship for fluoride and equilibria (2), (4) and (5); equation (11) from the stoichiometric relationship for hydrogen ion; and equation (12) from equilibria (1) and (2). In the above equations the symbol α represents the quantity $[1 + K_4/(H^+) + 2K_4K_3(HF)/(H^+)]$; under the experimental conditions used this quantity ranged from 1.002 to 1.024 and for any given experiment was very nearly a constant. In equation (11) (HF_2^-) was small enough to be neglected in the calculations.

The first step in the approximation was to determine a value of K_1 by plotting $2(Fe_c^{+3}) - (F_t^-)$ against ΔE. From equation (9) we see that $K_1 = (H^+)/(Fe^{+3})$ when $2(Fe_c^{+3}) - (F_t^-)$ is zero. This procedure gave a value of K_1 within 2% of the final adjusted value. Next approximate values of (HF) were determined from the equation $(HF)\alpha \simeq (F_t^-) - (Fe_c^{+3})$; these values are good to 10% or better. Having a good value of K_1

and approximate values of (HF) equations (11) and (12) were used to calculate an approximate value of K_2 for each point. Next equation (10) was used to get better values of (HF) and then the procedure for obtaining K_2 was repeated. Finally K_1 was adjusted slightly to make K_2 as constant as possible. In practice it was found that the third approximation to (HF) was practically identical with the second; this rapid convergence is due to the fact that (HF) is comparatively insensitive to a change in K_2. The physical reason for the rapid convergence is the fact that most of the fluoride added simply reacts with hydrogen ion to form HF; a small percentage forms ferric–fluoride complexes and a very small percentage is present as F^- and HF_2^- ions.

Table III summarizes the values of K_1 and K_2 determined at different acidities. There seems to be a trend with (H^+). It may be due to the behavior of activity coefficients in mixed electrolytes, however, most of the trend could be removed by using the smaller value of K_h given by Lamb and Jacques.[12]

TABLE III

(H_0^+)	K_1	K_2
0.0325	193	10.6
.0533	190	10.6
.0536	192	10.6
.1110	187	10.2
.1119	187	10.5
.2781	182	9.6
Average	189	10.4

Table IV gives a comparison of our results with those of other investigators.[4,5] Neither of the authors mention the temperature; however, it may be presumed that Brosset and Gustaver's work was done at 25° since they used values for the dissociation constant of hydrofluoric acid, the complexing constant of ferric ion by chloride ion, and the hydrolysis constant of ferric ion which apply at 25°. The agreement is good; the small differences are within a range that could be explained by differences in activity coefficients.

TABLE IV

A COMPARISON OF THE RESULTS OF THIS RESEARCH ON IRON WITH THOSE OF OTHER INVESTIGATORS

	This research	Babko and Kleiner[5]	Brosset and Gustaver[4]
t, °C.	25	.....	....
Ionic strength	0.50	0.1	0.54
Medium	NaClO$_4$ HClO$_4$	HNO$_3$	0.53 M KNO$_3$ 0.01 M HCl
K_1	189	200	165
K_2	10.4	25	11.4
K_3	0.58	2	....
K_4	.....	0.1	....
K_5	.....	0.002	....

Figure 4 illustrates how well all the data have

(12) Lamb and Jacques, THIS JOURNAL, **60**, 977, 1215 (1938).

been interpreted using two arbitrary constants, K_1 and K_2. The equation

$$(Fe_t^{+3})/(Fe^{+3}) - K_h/(H^+) = 1 + K_1(HF)/(H^+) + K_1K_2(HF)^2/(H^+)^2 \quad (13)$$

can be derived from the stoichiometric relationship for iron and equilibria (1), (2) and (3). The solid curve in Fig. 4 is a plot of log $[(Fe_t^{+3})/(Fe^{+3}) - K_h/(H^+)]$ against log $(HF)/(H^+)$ using the average values of K_1 and K_2, 189 and 10.4, respectively. The experimental points fall on the calculated curve with the exception of the few points at the highest values of $(HF)/(H^+)$. These points gave calculated values of K_2 which were 10 to 20% higher than the average of 10.4; since it was believed that this was due to the formation of FeF_3 these points were not used in obtaining the values of K_2 given in Table III. If one considers the equilibrium

$$FeF_2^+ + HF \rightleftharpoons FeF_3 + H^+ \quad K_3 \quad (14)$$
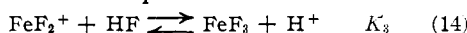
it is found that equation (13) should have a term $K_1K_2K_3(HF)^3/(H^+)^3$ added to the right side. By fitting this term to the deviations of the points on the upper part of the curve a value for K_3 of 0.58 was obtained. The dashed curve in Fig. 4 is a plot of equation (13) with the added term.

In analyzing the data we have assumed that the complexes FeF^{++}, FeF_2^+ and FeF_3 exist. Freezing point lowering and electrical conductivity data[1c] prove the existence of FeF_3. By inspection of some of the initial points it is observed that the iron complexed, (Fe_c^{+3}), is greater than 1/2 the total fluoride added; from this we concluded that FeF^{++} must be present. This leaves the possibility of interpreting the data by assuming only the complexes FeF^{++} and FeF_3, which could not be done.

By studying the electrical conductivity and freezing points of mixed and separate solutions of NaF and $FeCl_2$, Peters[2] concluded that FeF_2 was essentially as dissociated as $FeCl_2$. The activity coefficients of $FeCl_2$ indicate that it is completely dissociated.[13] By allowing for a reasonable experimental error in Peters' freezing point data and by considering an equilibrium of the type
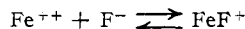
$$Fe^{++} + F^- \rightleftharpoons FeF^+$$

we get $K < 30$. At the highest fluoride ion concentration reached in these experiments this gives $(FeF^+)/(Fe^{++}) < 0.006$. This result indicates that complexing of ferrous ion by fluoride ion was not important in these experiments.

Analysis of the Data for Cells Containing Thorium.—Since the equilibrium constants for equilibria (1) and (2) are known we can calculate the following quantities for cells containing thorium; $(HF)/(H^+)$; $(HF) + (F^-) + (HF_2^-) = (HF)\alpha$; and $(F_{Fe}^-) = (FeF^{++}) + 2(FeF_2^+)$,

(13) See Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, p. 444.
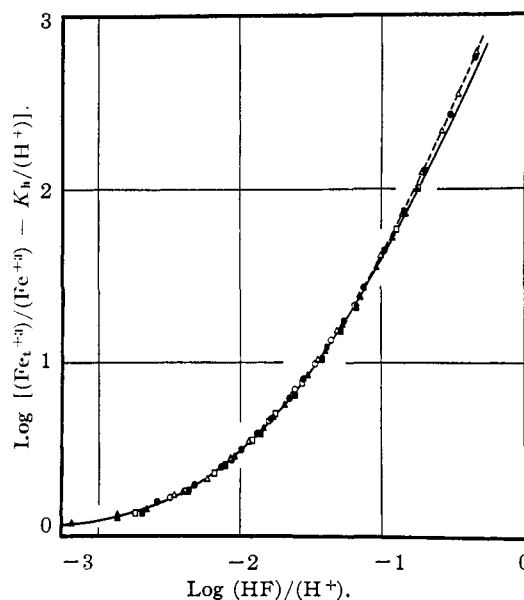

Fig. 4.—O corresponds to data of curve 1, Fig. 2; △ to curve 2; ● to curve 3; □ to curve 4; ▲ to curve 5; ■ to curve 6.

the total fluoride complexed by ferric iron. The necessary equations are

$$(Fe_c^{+3})/(Fe^{-3}) = K_1(HF)/(H^+) + K_1K_2(HF)^2/(H^+)^2 \quad (15)$$

$$(HF)\alpha = (H^+)\alpha/[1 + (H^+)/(HF)] \quad (16)$$

$$(F_{Fe}^-) = (Fe_c^{+3}) + K_1K_2(Fe^{+3})(HF)^2/(H^+)^2 \quad (17)$$

Equations (15) and (17) are derived by considering equilibria (1) and (2); in both equations FeF_3 was neglected because the fluoride ion concentration for cells with thorium was never high enough to form important concentrations of this species. Equation (16) comes directly from equation (11) after omitting (HF_2^-) which is negligible. Since all of the experiments on cells with thorium were carried out at $(HClO_4) \cong 0.05$ M, $K_1 = 191$ and $K_2 = 10.6$ were used in equations (15) and (17). After (Fe_c^{+3}) and (Fe^{+3}) had been calculated from the observed change in potential and equations (6), (7) and (8) equation (15) was solved for $(HF)/(H^+)$. $(HF)\alpha$ and (F_{Fe}^-) were obtained from (16) and (17). The important quantity $\bar{n}$, the total fluoride, complexed by thorium divided by the total concentration of thorium was then calculated from the equations

$$(F_{Th}^-) = (F_t^-) - (HF)\alpha - (F_{Fe}^-) \quad (18)$$

$$\bar{n} = (F_{Th}^-)/(Th_t^{+4}) \quad (19)$$

where (Th_t^{+4}) is the total concentration of thorium.

In Fig. 5 $\bar{n}$ is plotted against log $(HF)/(H^+)$. Several qualitative features of the curves should be noted. The abrupt breaks in the curves represent the points at which the solution has become saturated with respect to $ThF_4 \cdot 4H_2O$. These points shift with the total thorium con-
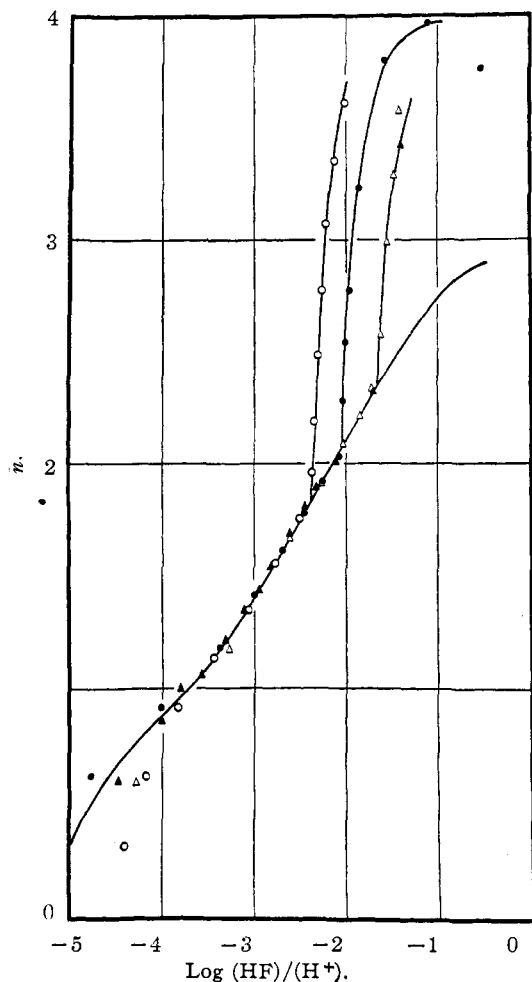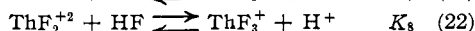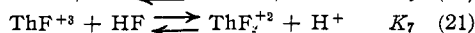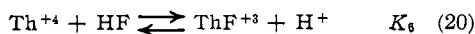
Fig. 5.—The symbols used in this figure represent the same data as the corresponding symbols used in Fig. 3.

centration as they should, since the solubility product of thorium fluoride is volume dependent. $\bar{n}$ rises above 2 indicating that a complex ion ThF_3^+ is present. Finally the points for different total thorium concentrations where no solid is present fall on the same curve indicating that the equilibria which determine the shape of this curve are not volume dependent with respect to the thorium species. The scattering of points below $\bar{n} = 1$ is due to the fact that ThF^{+++} is so much more stable than FeF^{++} that almost no potential change is observed until one mole of fluoride per mole of thorium has been added to the cell.

If we assume the equilibria

$$Th^{+4} + HF \rightleftarrows ThF^{+3} + H^+ \qquad K_6 \quad (20)$$
$$ThF^{+3} + HF \rightleftarrows ThF_2^{+2} + H^+ \qquad K_7 \quad (21)$$
$$ThF_2^{+2} + HF \rightleftarrows ThF_3^+ + H^+ \qquad K_8 \quad (22)$$

the equation for $\bar{n}$ in the region where no solid thorium fluoride is present is

$$\bar{n} = \frac{[K_6(HF)/(H^+) + 2K_6K_7(HF)^2/(H^+)^2 + 3K_6K_7K_8(HF)^3/(H^+)^3]}{[1 + K_6(HF)/(H^+) + K_6K_7(HF)^2/(H^+)^2 + K_6K_7K_8(HF)^3/(H^+)^3]} \quad (23)$$

In deriving equation (23) it was assumed that the degree of hydrolysis of thorium is negligible in 0.05 M perchloric acid. This is indicated by the fact that a 0.23 M thorium nitrate solution shows a pH of 2.4 on a Beckman pH meter. Equation (23) was fitted to the data plotted in Fig. 5 by taking three points and solving the equations for K_6, K_7 and K_8. The curve drawn through the experimental points in Fig. 5 is a plot of equation (23) using $K_6 = 4.5 \times 10^4$, $K_7 = 649$, and $K_8 = 31.6$. Another curve drawn with the values 3.8×10^4, 659 and 30.6 did not fit the data, hence the final values were taken as $K_6 = 4.5 \pm 0.5 \times 10^4$, $K_7 = 650 \pm 15$, and $K_8 = 32 \pm 2$.

An attempt was made to fit the experimental data using combinations of equilibria (20), (21) and (22) two at a time, but it could not be done.

After the break has occurred in the curve it is necessary to consider the equilibrium between the solid and the complex ions in solution. It has been shown that the thorium fluoride precipitate obtained under the conditions of this experiment is $ThF_4 \cdot 4H_2O$,[8] hence we define the solubility product by the equilibrium

$$ThF_4 \cdot 4H_2O + 2H^+ \rightleftarrows ThF^{++} + 2HF + 4H_2O;$$
$$K_s = (ThF^{++})(HF)^2/(H^+)^2 \quad (24)$$
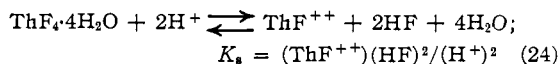
The ion ThF_2^{++} was used in defining the solubility product because it was the predominant species at the point of precipitation. (ThF_2^{++}) was calculated for each experimental point where solid was present from the equation

$$(ThF_2^{++}) = [4(Th_t^{+4}) - (F_{Th}^-)]/[4(H^+)^2/K_6K_7(HF)^2 + 3(H^+)/K_7(HF) + 2 + K_8(HF)/(H^+)] \quad (25)$$

which can be derived from the stoichiometric relationships for fluoride and thorium and equilibria (20), (21) and (22). The calculated values of K_s and (ThF_2^{++}) are given in Table V.

TABLE V

O, Fig. 5		●, Fig. 5		Δ, Fig. 5	
(ThF_2^{++}) $\times 10^4$	$K_s \times 10^8$	(ThF_2^{++}) $\times 10^4$	$K_s \times 10^8$	(ThF_2^{++}) $\times 10^4$	$K_s \times 10^8$
30.1	5.4	7.35	6.1	1.15	6.5
27.0	5.1	6.27	6.1	0.78	6.2
23.3	5.5	5.24	6.2	0.53	5.7
19.3	5.6	3.31	6.2	0.30	(4.4)
15.0	5.5	0.81	5.5	Av.	6.1
10.8	5.9	0.095	5.9		
6.5	6.3	Av.	6.0		
Av.	5.6				

There seems to be a trend in K_s with (ThF_2^{++}); this may be due to some systematic experimental error or the omission of higher complexes of thorium in analyzing the data. The final value for K_s is taken as 5.9 $\pm$ 0.5 $\times 10^{-8}$.

In Figure 5 the solid curves drawn through the precipitation points were calculated using the individual aver-

ages for K_8. The equation for the curve can be obtained immediately from equation (25) and is

$$\bar{n} = 4 - [4(H^+)^2/K_6K_7(HF)^2 + 3(H^+)/K_7(HF) + 2 + K_8(HF)/(H^+)]K_8(H^+)^2/(Th_t^{+4})(HF)^2 \quad (26)$$

Summary

1. The potential of the ferrous–ferric half cell was studied as a function of the hydrofluoric and perchloric acid concentrations, and the data were interpreted by assuming the existence of the ions FeF^{++}, FeF_2^+ and FeF_3. The equilibrium con-stants for the formation of the above ions has been determined at 25° and an ionic strength of 0.5.

2. The potential of the ferrous–ferric half cell was studied as a function of the hydrofluoric acid and thorium nitrate concentrations, and the data were interpreted by assuming the existence of the ions ThF^{+++}, ThF_2^{++} and ThF_3^+. The equilibrium constants for the formation of these ions and the solubility product of $ThF_4 \cdot 4H_2O$ were determined.

The Basic and the Acid Strength of Cacodylic Acid in Water

BY MARY L. KILPATRICK

Zawidzki,[1a] Johnston[1b] and Holmberg[1c] estab-lished the fact that cacodylic acid in water is am-photeric, as may be expected from the position it occupies in the series:

H_3AsO_4	arsenic acid
$CH_3AsO(OH)_2$	methylarsenic acid
$(CH_3)_2AsOOH$	cacodylic acid
$(CH_3)_3AsO$	trimethylarsine oxide
$(CH_3)_4AsOH$	tetramethylarsonium hydroxide

where the acid strength decreases from top to bot-tom.

For the acid strength of cacodylic acid in water

$$K_A = [H_3O^+][(CH_3)_2AsOO^-]/[(CH_3)_2AsOOH]$$

and for the basic strength (then called the hydrol-ysis constant)

$$K_B = [(CH_3)_2AsOOH \cdot H^+]/[H_3O^+][(CH_3)_2AsOOH]$$

they obtained at 25° the following values: for K_A, 4.2×10^{-7}, Zawidzki, by measurement of conductance and application of Ostwald's dilution law; 6.4×10^{-7}, Johnston, by measurement of conductance and application of Walker's method for the determination of K_A and K_B for an ampho-teric electrolyte; 7.5×10^{-7}, Holmberg, by measurement of the rate of decomposition of di-azoacetic ester. For K_B, 34, Zawidzki, by meas-urement of the conductance of solutions containing equivalent amounts of cacodylic and hydrochloric or nitric acid; 32, Johnston, estimated from the conductance data for cacodylic acid, in the manner of Walker; 51, Holmberg, by measurement of the rate of decomposition of diazoacetic ester in solu-tions containing cacodylic acid and picric or nitric acid. A number of additional values of K_A, but none of K_B, have subsequently been reported; of these, the most reliable appears to be that of Morton,[2] viz., $K_A = 5.66 \times 10^{-7}$ at 30°. Mor-ton's determination was made electrometrically

with a cell consisting of a hydrogen electrode, a saturated calomel half-cell, and a saturated potas-sium chloride bridge. The figure 5.66×10^{-7} rep-resents the average obtained upon extrapolating to infinite dilution values found with 1:1 cacodylic acid–sodium cacodylate buffer solutions with and without added salt; for acetic acid, by the same procedure, Morton obtained 1.84×10^{-5}, which may be compared with 1.749×10^{-5} as deter-mined by Harned and Ehlers.[3]

A number of objections may be raised to the methods employed for the determination of K_B. Zawidzki was not able, by addition of excess caco-dylic acid, to repress the reaction .

$$(CH_3)_2AsOOH \cdot H^+ + H_2O \longrightarrow (CH_3)_2AsOOH + H_3O^+$$
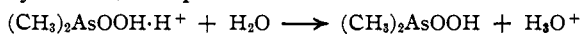
so as to obtain the mobility of the cation, and in his computation of the degree of hydrolysis he took $\Lambda_{HCac \cdot H^+} = \Lambda_{Cac^-}$. Johnston's value is an estimated one based on Zawidzki's Λ_{Cac^-}. Turn-ing to Holmberg's kinetic determination, the four values of K_B show considerable variation (54, 42, 48, 60); this Holmberg believed due to the speed of the reaction, which made it necessary to work at low concentrations (ca. 0.001 M) of strong acid. It may also be mentioned that the decomposition of diazoacetic ester is known to have a very high positive primary kinetic salt effect, and that in the presence of many anions, among them nitrate, a side reaction occurs.

In this paper there are presented the results of another kinetic determination of K_B, the reaction employed being the hydrolysis of ethylene acetal, which Brönsted and Grove[4] showed to be cata-lyzed specifically by the hydrogen ion.

There are also presented some colorimetrically and some electrometrically determined values of K_A; the latter are due to Chase.[5]

(1) (a) Zawidzki, Ber., **36**, 3325 (1903); **37**, 2289 (1904); (b) Johnston, ibid., **37**, 3625 (1904); (c) Holmberg, Z. physik. Chem., **70**, 153 (1910).

(2) Morton, J. Chem. Soc., 1401 (1928).

(3) Harned and Ehlers, THIS JOURNAL, **55**, 652 (1933); the con-stant has been converted from the molality to the molarity scale.

(4) Brönsted and Grove, ibid., **52**, 1394 (1930).

(5) Present address of Dr. E. F. Chase, Drexel Institute of Tech-nology, Philadelphia.