

propyl sulfoxide, but not in ethyl sulfate, ethyl sulfone or ethylisopropyl sulfone, where there is greater symmetry about the sulfur atom. The non-equivalence is not confined to ethyl-sulfur derivatives but is shown also in the salt Et_2MeNHI . In this case, the difference in chemical shift of the two methylene protons is particularly pronounced, being 0.54 p.p.m. for the compound measured in saturated solution in dichloromethane. In this case, two distinct quartets are observed, overlapped by the strong absorption of the N-methyl groups.

It is particularly noteworthy that the spectrum of the adduct $\text{Et}_2\text{S}\cdot\text{BF}_3$ is quite simple, showing no evidence of non-equivalence of the methylene protons. Since non-equivalence would be expected, even in the case of rapid rotation about the C-S bond, and since it is observed in the analogous BH_3 adduct, this result suggests strongly that some sort of averaging process, perhaps an exchange of

the BF_3 group between the two lone-pair positions, is occurring. A study of the temperature dependence of this spectrum would be welcome.

NOTE ADDED IN PROOF.—Since the submission of this article, Waugh and Cotton²⁴ have reported their observation that the protons of the single methylene group in $\text{C}_6\text{H}_5\text{S}(\text{O})\text{OC}_2\text{H}_5$ are non-equivalent. Their conclusion that the low molecular symmetry is the source of this non-equivalence is in accord with our interpretation of the spectrum of the somewhat analogous $\text{Et}_2\text{S}\cdot\text{BH}_3$.

A further indication that exchange of the Lewis acid groups is responsible for the absence of similar effects in the spectrum of $\text{Et}_2\text{S}\cdot\text{BF}_3$ is the observation that the resonance due to the B-H hydrogen atoms in the borane adduct is split into a quartet of broad lines by spin coupling to the ^{11}B nucleus. In the ^{19}F spectra of a number of weak BF_3 adducts (and of several addition compounds of other metal fluorides²⁵), B-F spin coupling is not observed, presumably because of the effects of rapid breaking and reforming of the donor-acceptor links. Any similar exchange processes in the BH_3 adducts are therefore, in all probability, slower.

(24) J. S. Waugh and F. A. Cotton, *J. Phys. Chem.*, **65**, 562 (1961).

(25) E. L. Muetterties, *J. Am. Chem. Soc.*, **82**, 1082 (1960).

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Stability of the Mixed Complex FeSCNF^+

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Evidence was obtained from potentiometric and spectrophotometric experiments for the formation of FeSCNF^+ in solutions containing iron(III), thiocyanate and hydrofluoric acid.

Rabinowitch and Stockmayer¹ were the first to suggest the existence of the mixed complex, FeSCNCl^+ , in the iron(III)-thiocyanate-chloride system. Spectrophotometric evidence for this complex² as well as for FeSCNBr^+ , FeSCNOH^+ , FeSCNSO_4 and related complexes has been obtained by Lister and Rivington.² The purpose of this paper was to investigate the iron(III)-thiocyanate-fluoride system spectrophotometrically for evidence for the formation of FeSCNF^+ . In addition the system was investigated potentiometrically using the ferrous-ferri cell.³⁻⁵

As a check on the experimental procedures the formation constants of FeF^{++} , FeF_2^+ , FeSCN^{++} and $\text{Fe}(\text{SCN})_2^+$ were determined potentiometrically while the formation constant of FeSCN^{++} was determined spectrophotometrically. All measurements were made on solutions containing 0.5 M perchloric acid and the ionic strength of these solutions varied from 0.51 to 0.53. Under these conditions the variation in ionic strength can be ignored; the dimerization of iron(III),⁶ the hydrolysis of iron(II)⁷ and the formation of HF_2^{-3} are negligible; and the hydrolysis of iron(III)⁶

and the ionization of hydrofluoric acid⁸ is less than 0.5%. Although iron(III) perchlorate ion pairs⁹ may be present, their formation is not dependent upon the hydrogen ion concentration, and they will not affect the results obtained significantly. Finally the concentrations of iron(III), fluoride and thiocyanate were chosen so as to prevent complications due to the formation of FeF_3^4 and $\text{Fe}(\text{SCN})_3$.¹⁰

Experimental

Reagents.—Ferric perchlorate monohydrate was prepared by dissolving freshly precipitated ferric hydroxide in dilute perchloric acid and crystallizing the salt from hot concentrated perchloric acid. The salt was white when hot and lilac when cold. Ferric hydroxide was prepared by precipitation with ammonia vapors from hot solutions of ferric nitrate. The precipitate was washed by decantation with hot water until the washings were nitrate free. Stock solutions of ferric perchlorate were prepared by dissolving the salt in 1M perchloric acid. When they contained less than 0.01 M iron, the perchloric acid solutions had no absorbancy in the visible region.

Ferrous perchlorate was prepared by reducing perchloric acid solutions of ferric perchlorate with analytical grade iron wire. These solutions were found to be stable in air for periods up to two weeks. Ammonium thiocyanate solutions were prepared from freshly opened bottles of C.P. A.C.S. grade ammonium thiocyanate and stored in the dark. All other reagents were also of C.P. A.C.S. grade. Solutions containing fluoride were stored in polyethylene bottles and hydrofluoric acid solutions were measured with calibrated polyethylene burets. All solutions were carefully filtered before diluting to final volume and then analyzed by standard volumetric procedures.

Potentiometric Measurements.—All measurements were made at $26.7^\circ \pm 0.1$ with Leeds and Northrup type K poten-

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

(2) M. W. Lister and D. E. Rivington, *Can. J. Chem.*, **33**, 1572, 1591, 1603 (1955).

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

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

(5) R. E. Connick, L. G. Hepler, Z. Z. Hugus, Jr., K. W. Kury, W. M. Latimer and Maak-Sang Tsao, *ibid.*, **78**, 1827 (1956).

(6) R. M. Milburn, *ibid.*, **79**, 537 (1957).

(7) D. M. Leussing and I. M. Kolthoff, *ibid.*, **75**, 2476 (1952).

(8) H. H. Broene and T. Devries, *ibid.*, **69**, 1644 (1947).

(9) J. Sutton, *Nature*, **169**, 71 (1952).

(10) D. D. Perrin, *J. Am. Chem. Soc.*, **80**, 3852 (1958).

tiometer. Two cells, A and B, were arranged in the manner described by Dodgen and Rollefson,³ except that the electrodes consisted of cylindrical platinum gauze 2.5 cm. long and 1.3 cm. diameter, stirring was done by introducing oxygen-free nitrogen through small glass tubes centered in the electrode and the agar-agar salt bridge was made from 2 *M* sodium perchlorate. Differences in potential between the electrodes were less than 0.2 mv.

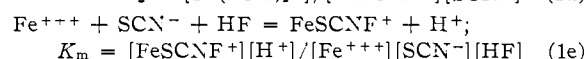
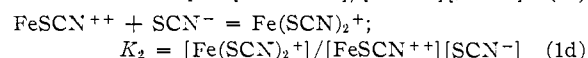
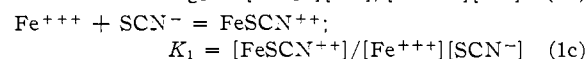
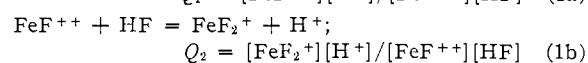
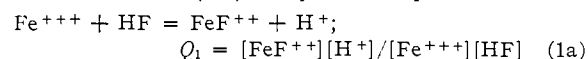
Initially each cell contained 100 ml. of a stock solution whose composition was 0.5000 *M* perchloric acid, 0.002000 *M* ferrous perchlorate and 0.001000 *M* ferric perchlorate. During the course of the experiment measured amounts of the desired reagent were added to one of the cells (A) by means of a calibrated polyethylene buret. The reagent solution was identical to the cell solutions; in addition it contained ammonium thiocyanate and/or hydrofluoric acid. In the runs on the formation of the mixed complex the reagent solution was 0.1729 *M* in ammonium thiocyanate and 0.06755 *M* in hydrofluoric acid. The ratio of $[\text{SCN}^-]:[\text{HF}]$ in this solution is equal to 2.54 which is the value of $Q_1/K_1 \cdot [\text{H}^+]$ under our experimental conditions (see equations 1a to 1e for notation).

Spectrophotometric Measurements.—Optical density measurements were made with a Beckman Model DU Spectrophotometer using silica cells. The cell compartment was thermostated and controlled to $\pm 0.1^\circ$. The samples were prepared by mixing desired volumes of two stock solutions. In the iron(III)-thiocyanate experiments the stock solutions contained identical concentrations of ferric perchlorate and perchloric acid; in addition one of the stock solutions also contained ammonium thiocyanate. In the iron(III)-thiocyanate-fluoride experiments each stock solution contained perchloric acid, ferric perchlorate and ammonium thiocyanate; in addition one of the solutions contained hydrofluoric acid.

After mixing, the solutions were placed in the silica cells and allowed to come to the temperature of the cell compartment. This required up to ten minutes for measurements made at the highest and lowest temperatures. There was no change in the optical density of solutions which were in the silica cells for as long as 2 hr. In general, however, measurements were made within thirty minutes. Preliminary experiments showed that the absorbancy of ferric fluoride solutions was negligible in the visible region and could be ignored.

Calculations

Potentiometric.—The notation and the interpretation of the potentiometric measurements follows that of references 5 and 10. Thus Q_1 and Q_2 refer to the first and second formation constants of the iron(III) fluoride complexes and K_1 and K_2 to the iron(III) thiocyanate complexes.



Since the maximum concentration of thiocyanate ion or hydrofluoric acid solutions was less than 0.03 *M*, the formation of higher complexes can be ignored.^{4,10}

In the iron(III)-thiocyanate system the total concentration of iron(III) in cell A containing thiocyanate is $[\text{Fe}^{+++}]_0 = [\text{Fe}^{+++}] + [\text{FeSCN}^{++}] + [\text{Fe}(\text{SCN})_2^+]$ (2)

where $[\text{Fe}^{+++}]_0$ is also the concentration of iron(III) in cell B. Upon substituting for $[\text{FeSCN}^{++}]$ and $[\text{Fe}(\text{SCN})_2^+]$ from the mass action expressions and rearranging

$$([\text{Fe}^{+++}]_0/[\text{Fe}^{+++}] - 1)/[\text{SCN}^-] = \frac{K_1 + K_1K_2[\text{SCN}^-]}{K_1 + K_1K_2[\text{SCN}^-]} \quad (3)$$

which is equation 7 of reference 10. K_1 and K_2 then were obtained by plotting the left hand side of equation 3 against $[\text{SCN}^-]$. The quotient $[\text{Fe}^{+++}]_0/[\text{Fe}^{+++}]$ was calculated

in the usual way from the potential measurements using the Nernst equation while $[\text{SCN}^-]$ was calculated by a series of approximations beginning with

$$[\text{SCN}^-] = [\text{SCN}^-]_0 - ([\text{Fe}^{+++}]_0 - [\text{Fe}^{+++}])$$

where $[\text{SCN}^-]_0$ is the total thiocyanate concentration in cell A. More exact values of $[\text{SCN}^-]$ were then obtained from the stoichiometric relation

$$[\text{SCN}^-]_0 = [\text{SCN}^-] + [\text{FeSCN}^{++}] + 2[\text{Fe}(\text{SCN})_2^+]$$

and the preliminary values of K_1 and K_2 .

The values of Q_1 and Q_2 for the iron(III) fluoride complexes were determined in the same way from the expression $([\text{Fe}^{+++}]_0/[\text{Fe}^{+++}] - 1)[\text{H}^+]/[\text{HF}] =$

$$\frac{Q_1 + Q_1Q_2[\text{HF}]/[\text{H}^+]}{Q_1 + Q_1Q_2[\text{HF}]/[\text{H}^+]} \quad (4)$$

If the mixed complex, FeSCNF^+ , is formed in solutions containing both thiocyanate ion and hydrofluoric acid, then

$$[\text{SCN}^-] = [\text{SCN}^-]_0 - [\text{FeSCN}^{++}] - 2[\text{Fe}(\text{SCN})_2^+] - [\text{FeSCNF}^+]$$

By assigning K_m the value of 2000,¹¹ it can be shown that the approximation $[\text{SCN}^-] = [\text{SCN}^-]_0 - [\text{FeSCN}^{++}]$ is valid for mixtures containing less than two-three hundredth molar thiocyanate and hydrofluoric acid. By using the mass action relationship this becomes

$$[\text{SCN}^-] = [\text{SCN}^-]_0/(1 + K_1[\text{Fe}^{+++}]) \quad (5a)$$

Similarly

$$[\text{HF}] = [\text{HF}]_0/(1 + Q_1[\text{Fe}^{+++}]/[\text{H}^+]) \quad (5b)$$

By combining equations 5a and 5b with the conditions of these experiments, namely, $[\text{SCN}^-]_0 = [\text{HF}]_0Q_1/K_1[\text{H}^+]$, and ignoring second and higher order terms in $[\text{Fe}^{+++}]$, $[\text{SCN}^-]$ is found to be related to $[\text{HF}]$ by

$$[\text{SCN}^-] = [\text{HF}]Q_1\{1 + [\text{Fe}^{+++}](Q_1/[\text{H}^+] - K_1)\}/K_1[\text{H}^+] \quad (6)$$

In the cell containing thiocyanate and hydrofluoric acid

$$[\text{Fe}^{+++}]_0 = [\text{Fe}^{+++}] + [\text{FeSCN}^{++}] + [\text{FeF}^{++}] + [\text{Fe}(\text{SCN})_2^+] + [\text{FeF}_2^+] + [\text{FeSCNF}^+]$$

From equations 1a - 1e

$$[\text{Fe}^{+++}]_0 = [\text{Fe}^{+++}] + K_1[\text{Fe}^{+++}][\text{SCN}^-] + Q_1[\text{Fe}^{+++}][\text{HF}]/[\text{H}^+] + K_1K_2[\text{Fe}^{+++}][\text{SCN}^-]^2 + Q_1Q_2[\text{Fe}^{+++}][\text{HF}]^2/[\text{H}^+]^2 + K_m[\text{Fe}^{+++}][\text{SCN}^-][\text{HF}]/[\text{H}^+] \quad (7)$$

Upon dividing through by $[\text{Fe}^{+++}]$, substituting for $[\text{SCN}^-]$ from equation 6 and rearranging, equation 7 becomes

$$([\text{Fe}^{+++}]_0/[\text{Fe}^{+++}] - 1)[\text{H}^+]/[\text{HF}] - [\text{Fe}^{+++}]Q_1(Q_1/[\text{H}^+] - K_1)\{1 + (2K_2Q_1 + K_m)[\text{HF}]/[\text{H}^+]K_1\} = 2Q_1 + (Q_1Q_2 + K_2Q_1^2/K_1 + K_mQ_1/K_1)[\text{HF}]/[\text{H}^+] \quad (8)$$

This equation has the same form as equations 3 and 4. However, there are two correction terms on the left hand side of equation 8. The first depends on $[\text{Fe}^{+++}]$ only and decreases rapidly with increasing concentrations of thiocyanate and hydrofluoric acid (see Table I); the second is a function of the product $[\text{Fe}^{+++}][\text{HF}]/[\text{H}^+]$ and is nearly constant.

At low $[\text{HF}]$ the first correction term is quite large and a plot of $([\text{Fe}^{+++}]_0/[\text{Fe}^{+++}] - 1)[\text{HF}]$ vs. $[\text{HF}]/[\text{H}^+]$ will be concave upwards (Fig. 1). However, at higher hydrofluoric acid concentrations the plot will be nearly linear and an approximate value of K_m can be calculated. Again the value of $[\text{Fe}^{+++}]_0/[\text{Fe}^{+++}]$ can be obtained from the potentiometric measurements while $[\text{HF}]$ is computed with the aid of the previously determined values of Q_1 and Q_2 .

From the stoichiometric relation

$$[\text{HF}]_0 = [\text{HF}] + [\text{FeF}^{++}] + 2[\text{FeF}_2^+] + [\text{FeSCNF}^+]$$

and the approximate value of K_m the correction terms on the left hand side of equation 8 can be calculated. A straight line will now be obtained by plotting the left hand side of equation 8 against $[\text{HF}]/[\text{H}^+]$. It will have an in-

(11) This choice was made on the assumption that the value of K_m would be nearly equal to $(K_1K_2 \times Q_1Q_2)^{1/2}$.

TABLE I

Reagent, ml.	CORRECTION TERMS FOR EQUATION 8: $[\text{Fe}^{+++}]_0 = 0.001000; 26.7 \pm 0.1^\circ$						Correction terms ^c	
	$[\text{HF}]_0 \times 10^3$ ^a	$[\text{SCN}^-]_0 \times 10^3$	E.m.f., mv.	$[\text{Fe}^{+++}]^a \times 10^3$	$[\text{HF}]^{\text{b,c}} \times 10^3$	1st	2nd	
0.00	0.00	0.00	-0.12	1.0000	0.00	40.55	0.0	
1.00	0.6590	1.687	8.12	0.708	0.520	28.8	1.2	
2.00	1.321	3.382	16.05	.5343	1.091	21.6	2.0	
3.00	1.975	5.056	22.06	.4257	1.677	17.2	2.4	
4.00	2.621	6.659	27.07	.3495	2.262	13.9	2.6	
5.05	3.249	8.317	31.33	.2950	2.876	12.0	2.8	
6.00	3.882	9.928	35.51	.2580	3.470	10.4	2.8	
7.00	4.430	11.315	38.98	.2115	4.032	8.6	2.9	
8.10	5.062	12.96	41.87	.1974	4.614	8.0	2.9	
9.05	5.558	14.23	44.17	.1803	5.105	7.2	3.1	
10.10	6.200	15.87	46.89	.1628	5.727	6.6	3.1	
11.00	6.698	17.15	49.20	.1486	6.228	6.1	3.2	
12.00	7.241	18.54	51.41	.1359	6.756	5.5	3.1	
12.95	7.768	19.89	53.13	.1273	7.208	5.1	3.0	
14.05	8.322	20.82	55.06	.1180	7.802	4.8	3.1	

^a Calculated from the Nernst equation. ^b Calculated by a series of approximations beginning with $[\text{HF}] = [\text{HF}]_0 - ([\text{Fe}^{+++}]_0 - [\text{Fe}^{+++}])$. ^c Using the values for the equilibrium constants obtained in this study (see Table II).

cept $2Q_1$ and a slope $(Q_1Q_2 + K_2Q_1^2/K_1 + K_mQ_1/K_1)$. From the latter a more exact value of K_m can be obtained.

Spectrophotometric Measurements.—Frank and Oswalt¹² and Perrin¹⁰ have shown that the optical density of dilute solutions of iron(III) and thiocyanate is determined only by the concentration of FeSCN^{++} present, *i.e.*, $D = \beta_1[\text{FeSCN}^{++}]$ where D is the optical density of light passing

optical region, the optical density of perchloric acid solutions containing iron(III) thiocyanate and hydrofluoric acid will be given by

$$D = \beta_1[\text{FeSCN}^{++}] + \beta_2[\text{Fe}(\text{SCN})_2^+] + \beta_m[\text{FeSCNF}^+] \quad (10)$$

where β_2 and β_m are the molar extinction coefficients of $\text{Fe}(\text{SCN})_2^+$ and FeSCNF^+ , respectively. Values of β_1 at various wave lengths can be determined in dilute thiocyanate solutions,^{10,12} while β_2 can be determined in more concentrated solutions.¹⁰ Using these values and the concentrations of the various iron(III) species calculated from the observed equilibrium constants, the value of β_m can be determined at any desired wave length.

Results

In agreement with equations 3 and 4 straight line curves were obtained from the potentiometric data on the iron(III)–thiocyanate and iron(III)–fluoride systems. Although Perrin¹⁰ found that the curve for the thiocyanate system was concave upwards at low $[\text{SCN}^-]$, no deviation from linearity was observed in any of the present experiments.

The formation constants were calculated by the method of least squares and corrected for the hydrolysis of Fe^{+++} in 0.50 *M* perchloric acid at 26.7° using the data of Milburn.⁶ As the summary in Table II shows, the results obtained here are in good agreement with the results of similar experiments performed elsewhere.

The results of a typical set of potentiometric measurements on the mixed iron(III)–thiocyanate–fluoride system are shown in Fig. 1. Curve I was obtained by plotting $([\text{Fe}^{+++}]_0/[\text{Fe}^{+++}] - 1) [\text{H}^+]/[\text{HF}]$ against $[\text{HF}]/[\text{H}^+]$ using the experimental data given in columns two, three and four of Table I. $[\text{HF}]$ was determined by successive approximations using the formation constants obtained above. In agreement with equation 8 this curve is linear at high values of $[\text{HF}]/[\text{H}^+]$ and concave upwards near the ordinate. From the upper part of the curve an approximate value of K_m was obtained. This value then was used to recalculate $[\text{HF}]$ which is given in column five of Table I. Table I also includes the calculated values of the correction terms (columns seven and eight) for the left hand side of equation 8.

Curve II in Fig. 1 is a plot of the left hand side of equation 8 against the corrected values of $[\text{HF}]/$

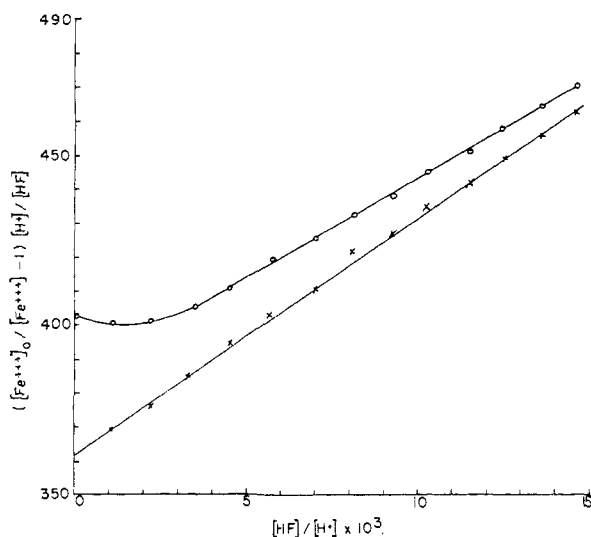


Fig. 1.—Plot of potentiometric data for iron(III) solutions containing thiocyanate and hydrofluoric acid: o—o—o, original data, x—x—x, corrected for the two terms on the left hand side of equation 8.

through a 1 cm. path and β_1 is the molar extinction coefficient of $[\text{FeSCN}^{++}]$. Upon substituting into the mass action expression (equation 1c), Frank and Oswalt were able to derive the relationship

$$[\text{Fe}^{+++}]_0[\text{SCN}^-]_0/D = ([\text{Fe}^{+++}]_0 + [\text{SCN}^-]_0/\beta_1 + 1/\beta_1K_1) \quad (9)$$

A straight line with intercept $1/\beta_1K_1$ and slope $1/\beta_1$ will be obtained by plotting $[\text{Fe}^{+++}]_0[\text{SCN}^-]_0$ against $([\text{Fe}^{+++}]_0 + [\text{SCN}^-]_0)$.

Preliminary experiments showed that the maximum in the absorption spectrum of iron(III) thiocyanate solutions is shifted to shorter wave lengths upon the addition of hydrofluoric acid. Since neither FeF^{++} nor FeF_2^+ absorb in the

(12) H. S. Frank and R. L. Oswalt, *J. Am. Chem. Soc.*, **69**, 1321 (1947).

TABLE II

RESULTS OF POTENTIOMETRIC MEASUREMENTS				
Complex	T, °C.	μ	K	Ref.
FeSCN^{++}	18	0.65	133	10
	26.7	.50	141	This work
$\text{Fe}(\text{SCN})_2^+$	18	.65	10	10
	26.7	.50	13.2	This work
FeF^{++}	25	.50	186	3
	25	.50	183	4
	26.7	.50	182	This work
FeF_2^+	25	.50	14	3
	25	.50	10.6	4
	26.7	.50	11	This work
FeFSCNF^+	26.7	.50	1370 ± 150^a	This work

^a Average of three experiments.

$[\text{H}^+]$. It is linear over the concentration range examined here. A final value of $1350 \text{ moles}^{-2} \text{ liters}^{-2}$ was calculated for K_m from the slope of this curve by the method of least squares. A third approximation gave no significant changes in the value of K_m . The results of several experiments reported in Table II have been corrected for the hydrolysis of Fe^{+++} .

The over-all formation constants K_1K_2 and Q_1Q_2 for $\text{Fe}(\text{SCN})_2^+$ and FeF_2^+ are 1860 and 2000, respectively. From this it may be estimated that the value for the formation constant of FeSCNF^+ will also be on the order of 2000. However, the somewhat lower value of 1370 observed here is in agreement with the corresponding quantities for the formation of FeSCNCl^+ and FeSCNBr^+ calculated from data obtained by Lister and Rivington² and Rabinowitch and Stockmayer.¹ In each case the constant K_m for the mixed complex, FeXY^+ , is related empirically to the over-all constants K_X and K_Y for the formation of FeX_2^+ and FeY_2^+ by

$$K_m = \frac{(K_X K_Y)^{1/2}}{2} \quad (11)$$

This can be seen from the data in Table III where the observed formation constants of the various complexes are given in column two and the calculated value of K_m in column three. On the other hand, when one of the ligands occupies two bonding positions, as in the case of $\text{Fe}(\text{SO}_4)\text{SCN}$, K_m is nearly equal to $2(K_X K_Y)^{1/2}$.

Although further work is necessary to determine the general applicability of these relationships, they do suggest the formation of FeClO_4F^+ and $\text{FeClO}_4\text{SCN}^+$ in the systems examined here. The formation constant for FeClO_4^{++} is 4.3×10^{-2} moles/liter in $0.5 M \text{ HClO}_4$.⁹ If the ratio of the formation constants for FeClO_4^{++} and $\text{Fe}(\text{ClO}_4)_2^+$ is 15:1 (see Table II), then the formation constant for the latter complex in $0.5 M \text{ HClO}_4$ can be estimated to be 3×10^{-3} and that for the formation of mixed iron(III) perchlorate complexes containing either fluoride or thiocyanate will be on the order of 1.0. The formation of FeClO_4^{++} and $\text{Fe}(\text{ClO}_4)_2^+$ will introduce a constant error of 2.3% in the calculation of $[\text{Fe}^{+++}]$ in $0.5 M \text{ HClO}_4$ solutions. The error due to the formation of FeClO_4F^+ and $\text{FeClO}_4\text{SCN}^+$ will increase with increasing concentrations of HF and SCN^- , respectively, but it will only amount to about 1% in the most concentrated solutions examined here (Table I).

TABLE III

FORMATION CONSTANTS FOR MIXED IRON(III) COMPLEXES

Complex	Over-all constant (K_1K_2 or K_m)	K_m calcd. (eq. 11)
a. $\mu = 0.5$		
FeF_2^+	2000	
$\text{Fe}(\text{SCN})_2^+$	1860	
FeSCNF^+	1350	965
b. $\mu = 1.2$		
$\text{Fe}(\text{SCN})_2^+$	2015	
FeCl_2^+	183	
FeSCNCl^+	260	304
c. $\mu = 1.2$		
$\text{Fe}(\text{SCN})_2^+$	2015	
FeBr_2^+	1.8	
FeSCNBr^+	21	30
d. $\mu = 1.2$		
$\text{Fe}(\text{SO}_4)_2^-$	17000	
$\text{Fe}(\text{SCN})_2^+$	2015	
$\text{Fe}(\text{SO}_4)\text{SCN}$	11500	11,700 ^a

^a Calculated from $2(K_X K_Y)^{1/2}$.

The estimated value for the formation constant of FeClO_4F^+ is of the same order of magnitude as Q_3 ,^{4,5} the formation constant for FeF_3 , and it can be shown readily that in $0.5 M$ perchloric acid solutions the ratio of $[\text{FeF}_3]:[\text{FeClO}_4\text{F}^+]$ will be approximately $Q_1Q_2[\text{HF}]^2$. Consequently at high HF concentrations the error due to the formation of FeClO_4F^+ will not contribute greatly to the determination of Q_3 . The same situation applies to the determination of K_3 , the formation constant for $\text{Fe}(\text{SCN})_3$.

Spectrophotometric Experiments.—The average results of three separate sets of spectrophotometric experiments taken over a period of three months are given in Table IV, Part A. Over the temperature range investigated here a maximum in the absorption spectrum of FeSCN^{++} was observed at $460 \pm 2 \text{ m}\mu$. At each temperature K_1 was calculated using the observed value of the molar extinction coefficient β_1 . The results at 26.7° are in good agreement with the values obtained from the potentiometric experiments.

The interpolated values of K_1 at 18 and 25° are given in Table IV, part B, together with the results of other authors at $\mu = 0.5$. The value of 138 reported by Frank and Oswalt¹¹ at room temperature is not included due to the fact that their cell compartment was not thermostated. The excellent agreement at 18° between the results obtained here and that reported by Perrin¹⁰ is fortuitous because his value of $\beta_1 K_1$ (see equation 9) is approximately 3.5% greater than that observed here and in calculating K_1 he used a value of $\beta = 4946 \text{ cm}^{-1} M^{-1}$ selected from the data of MacDonald, *et al.*¹²

At 25° the calculated value of K_1 is slightly lower than that obtained by Lister and Rivington.² The differences of 1% and 3.5% in the experimentally determined values of β_1 and $\beta_1 K_1$, respectively, are of the order of magnitude of the limits of accuracy of the spectrophotometric technique.

(12) J. Y. MacDonald, K. M. Mitchell and A. T. S. Mitchell, *J. Chem. Soc.*, 1574 (1951).

TABLE IV
 RESULTS OF SPECTROPHOTOMETRIC STUDIES IN THE IRON(III)-THIOCYANATE SYSTEM

T, °C.	μ	β_1	K_1^a	ΔF^b	ΔH^b	ΔS^c	Ref.
A. Observed							
16.0	0.52	4781	146.5				
26.7	.52	4621	142.5				
35.0	.52	4535	138.5				
44.8	.52	4456	135.0				
B. Comparison							
18.0	0.52	4756	145.5				This work
18.0	0.56	4946 ^d	145				10
25.0	0.52	4640	142.6	-4.2 ^e	-0.52	12	This work
25	0.50	4680	146	1070g	-4.1 ^e	-0.8	11

^a Corrected for the hydrolysis of iron(III); uncorrected for the formation of iron(III) perchlorate complexes. ^b In kcal./mole. ^c In e.u. ^d This value was selected from ref. 12. ^e Computed at $\mu = 0$ using the method of Rabinowitch and Stockmayer.¹

In the temperature range 16–45° the plot of $\log K_1$ vs. $1/T$ is a straight line and the values of the thermodynamic functions at 25° and $\mu = 0$ compare favorably with those of Lister and Rivington.² Betts and Dainton¹³ obtained a value of $H = -1.6$ kcal./mole. However these authors assumed β_1 to be constant and, in effect plotted $\log \beta_1 K_1$ vs. $1/T$.

Both Perrin¹⁰ and this author obtained lower values of K_1 from the potentiometric experiments than from the spectrophotometric experiments. Both techniques measure the sum of K_1 values for the formation of outer sphere complexes as well as that for FeSCN^{++} . However the value of K_1 from the spectrophotometric experiments is calculated from the observed value of β_1 which is the weighted average of the molar absorption coefficients of all of the 1-1 complexes.¹⁴ From a comparison of the Fe^{3+} - SCN^- system¹⁵ the error in

(13) R. H. Betts and F. S. Dainton, *THIS JOURNAL*, **75**, 572 (1953).

(14) L. E. Orgel and R. S. Mulliken, *ibid.*, **79**, 4839 (1957).

(15) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955).

calculating K_1 from potentiometric data would be less than 1% while a somewhat larger error would be anticipated from the spectrophotometric experiments.

The absorption spectra of FeSCN^{++} and $\text{Fe}(\text{SCN})_2^+$ were found to be substantially the same as that reported by Frank and Oswalt¹¹ and Perrin,¹⁰ respectively. The absorption spectrum of FeSCNF^+ was obtained from optical density measurements of 0.5 M perchloric acid solutions containing iron(III), thiocyanate and hydrofluoric acid. The molar extinction coefficient β_m of FeSCNF^+ was calculated over the range of 300–600 m μ using equation 10. This mixed complex has a single narrow band in the optical region with a maximum at 380 m μ ($\beta_m = 6240$ moles⁻¹ cm.⁻¹).

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Polarographic Studies of Aqueous Solutions of Metal and Azide Ions. I. The Cadmium Azide Reaction

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Polarographic studies of solutions of cadmium and azide ions were carried out in perchlorate medium in the range of 0.05 to 2.00 M azide concentration at an ionic strength of 2.0 at $25 \pm 0.1^\circ$. The application of the method of De Ford and Hume³ revealed the existence of five reaction products: CdN_3^+ , $\text{Cd}(\text{N}_3)_2$, $\text{Cd}(\text{N}_3)_3^-$, $\text{Cd}(\text{N}_3)_4^{2-}$, $\text{Cd}(\text{N}_3)_5^{3-}$ with formation constants 25, 400, 800, 1000 and 1800, respectively. These values were confirmed by applying Leden's⁴ method of calculation. The formation constants of the four species known to be formed in solution of cadmium and thiocyanate ions also were determined in the same range of concentration in perchlorate medium and were compared with those determined in nitrate solution.

The reactions between a number of metal ions and azide ions in aqueous solutions are being studied systematically in this Laboratory by the polarographic method.

This first paper reports results obtained in the study of solutions containing cadmium and azide ions.

Experimental

Measurements were made with a Sargent Model III Polarograph, the voltage being checked with a Leeds and

Northrup student potentiometer. A small H cell similar to that described by Pecsok and Juvet¹ was employed. Both compartments of the cell were separated by a medium porosity sintered glass disc from the cross arm which had two small openings allowing the use of small rubber stoppers. In all experiments carried out in perchlorate medium the cross arm was filled with 2.0 M sodium perchlorate solution (about 2.5 ml.). The reference electrode was a saturated calomel electrode prepared with saturated sodium chloride solution instead of potassium chloride in order to avoid

(1) R. L. Pecsok and R. S. Juvet, *Anal. Chem.*, **27**, 165 (1955).