reports. The several values of $-\Delta U_{R}^{0}$ at 25° for phenanthrene compare as follows: Milone and Rossignoli,[13] 1673.1 kcal. mole^{-1}, specified precision ±0.5%; Fries, et al.,[14] 1681.6 ± 0.01%; Richardson and Parks,[15] 1674.1 ± 0.01%; present work, 1683.8 ± 0.02%.

Again the discrepancies are assigned to differences in sample purity since phenanthrene is notoriously difficult to purify. The material used in the present work was probably of as high quality as any ever prepared in quantity; this purity is considered responsible for the higher result here reported, which again confirms, relatively at least, that of Fries, et al. The considerable attention given in the latter work to sample purification is noteworthy.

It is obvious that for neither anthracene nor phenanthrene has a definitive value for the standard heat of combustion been established as yet. Further measurements should be carried out on samples of established high purity.

Studies on the System Iron–Ethylenediamine Tetraacetate[1]

BY I. M. KOLTHOFF AND CLEMENS AUERBACH

The system iron–ethylenediamine tetraacetate has been studied polarographically over the pH range 1–11. Waves corresponding to reversible reduction of the ferric complex to the ferrous state are obtained up to pH 9; in more alkaline solution the reaction proceeds irreversibly. The ferrous complex yields reversible anodic waves under proper conditions. The diffusion currents are proportional to concentration of the complex. The half-wave potential of the system is constant and equal to −0.13 v. vs. S.C.E. in the pH region 3.5–6.5; outside this range the half-wave potential is pH dependent. The stability constant of the ferric complex has been obtained from a spectrophotometric analysis of its dissociation equilibrium in 0.6–1 M perchloric acid. The value is close to 5×10^{23}.

Ethylenediamine tetraacetic acid is denoted by Schwarzenbach[2] as complexone III and abbreviated as H_4Y. Its tetrasodium and disodium salts are commercially available in this country under the respective trade names Versene and Disodium Dihydrogen Versenate; for the sake of simplicity we shall refer to both the acid and all of its salts as Versene. The ferric iron complexes were first prepared by Brintzinger, et al.,[3] and inferences as to their structure were drawn both from their qualitative chemical behavior[3] and from magnetic measurements.[4]

The solution chemistry of Versene and of its complexes with a large number of metal ions was studied most extensively by Schwarzenbach and co-workers. Analysis of the protolytic equilibria established the following successive pK values for the tetraacid (concentration constants at 20° and ionic strength 0.1): pK_1 2.00, pK_2 2.67, pK_3 6.16, pK_4 10.26.[2a] Similar studies led to the elucidation of the acidic and/or basic properties of a large number of complexes including those of ferrous and ferric iron, and also to the evaluation of some of the stability constants.[2b,c,d] The following stability constant was reported for ferrous iron[2c]

$$K_{red} = \frac{[FeY^=]}{[Fe^{++}][Y^\equiv]} = 10^{14.25}$$

Schwarzenbach also made a potentiometric study of the system iron–Versene over a wide pH range.[2d] The polarography of the system has been considered briefly by Furness and co-workers[5] who were interested in analyzing commercial Versene preparations.

The present paper is devoted mainly to the polarographic properties of the system iron–Versene over the pH range 1.0–10.9. In addition, a spectrophotometric method for determining the stability constant of the ferric complex is given.

Experimental

A stock solution of ferric iron was obtained from A. R. ferric chloride and standardized by the stannous chloride–dichromate method. A chloride free solution was prepared by dissolving a weighed amount of high purity iron powder in perchloric acid and oxidizing with hydrogen peroxide. Ferrous ammonium sulfate hexahydrate, found to assay 99.7%, served as source of ferrous iron.

Approximately 0.1 M stock solutions were prepared from A.R. Disodium Dihydrogen Versenate, $Na_2H_2Y \cdot 2H_2O$ (Hach Chemical Co., Ames, Iowa). They were standardized by adding excess calcium chloride solution to an aliquot portion and titrating with standard base to the same mixed methyl red–brom cresol green end-point obtained with a blank containing calcium in the absence of Versene.

High purity Airco or Linde nitrogen, further purified by passage through alkaline pyrogallol or vanadous sulfate[6] solution, was employed.

Unless otherwise specified, the pH of the solution was adjusted without the use of a special buffer system, by appropriate additions of perchloric acid or sodium hydroxide. pH values of 2 and above were measured with a glass electrode (Leeds and Northrup pH Meter, Model No. 7661); those below were calculated, using the activity coefficients given by Latimer.[7] The ionic strength was kept at either ca. 0.15 or 1.0 by addition of sodium perchlorate or nitrate. All polarographic experiments were performed at 25 ± 0.2° in a thermostatically controlled water-bath.

The ferrous complex was found to be extremely rapidly air oxidized. In order to prevent this the procedure finally developed for solutions containing this complex makes use of a 3-neck modification of the 2-compartment rapid mixing

(1) This work was carried out under the sponsorship of the Reconstruction Finance Corporation, Synthetic Rubber Division, in connection with the Synthetic Rubber Program of the United States Government.

(2) (a) G. Schwarzenbach, et al., Helv. Chim. Acta, 30, 1798 (1947); (b) ibid., 31, 459 (1948); (c) ibid., 32, 1543 (1949); (d) ibid., 34, 576 (1951).

(3) H. Brintzinger, H. Thiele and U. Müller, Z. anorg. allgem. Chem., 251, 285 (1943).

(4) W. Klemm, ibid., 252, 225 (1944).

(5) W. Furness, P. Crawshaw and W. Cole Davis, Analyst, 74, 629 (1949).

(6) L. Meites and T. Meites, Anal. Chem., 20, 984 (1948).

(7) W. M. Latimer, "Oxidation Potentials," Prentice–Hall, Inc., New York, N. Y., 1938, p. 323.

vessels described by Kolthoff and Medalia.[8] A stopcock was sealed to the end of the capillary tube to prevent entrance of atmospheric oxygen. Furthermore, 2 of the necks were equipped with standard taper joints sealed to 3-way stopcocks, permitting samples to be pushed into the polarographic cell under nitrogen pressure, in the absence of air; the third neck, communicating with the inner compartment, was closed as described.[8] All joints and stopcocks were carefully greased. The constituents were placed into the appropriate compartment and flushed with purified nitrogen for about 30 minutes. At the end of this period the vessel was closed and the gas flow terminated by proper manipulation of the stopcocks, and the contents were mixed by vigorous shaking. Samples were subsequently transferred to the polarographic cell.

Most of the polarograms were recorded with a Sargent XXI polarograph. Half-wave potentials and diffusion current constants were determined manually, using a technique which permits independent potentiometric measurement of both the potential of the dropping electrode and the IR-drop across a standard 10,000 ohm resistance in series with the cell.[9] An outside saturated calomel electrode was employed. Nitrogen was bubbled through the cell for 20 minutes prior to each experiment (except for the special technique used in the presence of the ferrous complex) and allowed to pass over the solution during the actual measurements.

Spectrophotometric measurements were carried out on a Beckman model DU quartz spectrophotometer at $25 \pm 2°$, using 1.01-cm. quartz cells.

Potentials refer to the saturated calomel electrode unless stated otherwise. All equilibrium constants mentioned represent concentration constants at the ionic strength indicated.

Polarography of the System Iron–Versene

Ferric iron in Versene medium yields a single wave, corresponding to reduction to the $+2$ state; the reduction proceeds reversibly at the dropping electrode, except at pH higher than 9. The waves analyze for a one-electron reaction.[10] Composite polarograms obtained in mixtures of ferric and ferrous iron in Versene medium are shown in Fig. 1; they serve as further evidence for the reversibility of the system.
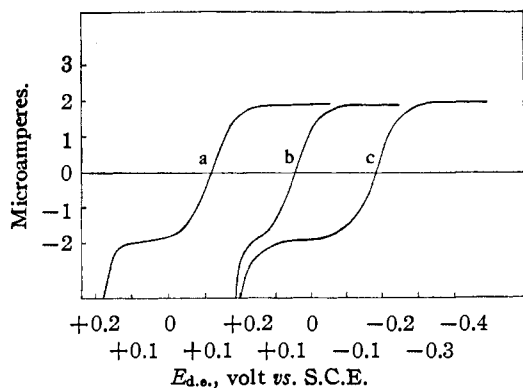

Fig. 1.—Composite polarograms of the system iron–Versene, 1.00×10^{-3} M Fe(ClO$_4$)$_3$, 1.00×10^{-3} M Fe-(NH$_4$)$_2$(SO$_4$)$_2$: (a) 0.04 M Versene, pH 4.00; (b) 0.04 M Versene, pH 6.05; (c) 0.00205 M Versene, pH 7.40.

In the absence of maximum suppressors maxima occurred in the polarograms of the ferric complex, especially at relatively low Versene concentrations, at pH 7.5 and below. The maxima shifted from

(8) I. M. Kolthoff and A. I. Medalia, THIS JOURNAL, **71**, 3777 (1949).

(9) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 220.

(10) Reference 9, Chapter X.

$+0.1$ to -0.3 v. and decreased in height as the pH was raised from 1 to 7.5. Gelatin was used as a suppressor where necessary; at concentrations of 0.005–0.01% it was found to have no undesirable effect in the presence of excess Versene.

TABLE I

HALF-WAVE POTENTIALS AND DIFFUSION CURRENT CONSTANTS

0.94×10^{-3} M FeCl$_3$ at $pH \leq 3.5$, 1.89×10^{-3} M at $pH \geq 3.5$ unless otherwise specified; $25 \pm 0.2°$; ionic strength 0.12–0.15.

pH	Versene concentration (M)	$(E_{1/2})_c$ (v. vs. S.C.E.)	I_c[e]	I_a
1.10	0.0041	$+0.115$	1.52	
1.10	.0021	$+$ .115	1.52	
1.10	.0041	$+$ .110[b]	1.51	
1.10	.0021	$+$ .111[b]	1.47	
1.60	.0041	$+$ .025	1.52	
1.60	.0021	$+$ .038	1.52	
2.00	.0041	$-$ .049	1.53	
1.95	.0021	$-$ .030	1.53	
2.40	.0041	$-$ .093	1.49	
2.40	.0021	$-$ .085	1.53	
3.45	.0041	$-$ .127	1.53	
3.50	.04	$-$ .130	1.49	
4.00	.04	$-$ .122[c]	1.48	1.43[f]
3.80	.0041	$-$ .124[c]	1.52	1.46[f]
4.50	.04	$-$ .138	1.48	
5.00	.008	$-$ .132	1.52	
5.60	.04	$-$ .137	1.48	
6.60	.04	$-$ .137	1.43	
7.00[a]	.01	$-$ .150	1.47	
7.00[a]	.0041	$-$ .151		
7.05[a]	.04	$-$ .153	1.37	
7.80	.04	$-$ .170	1.44	
9.00	.04	$-$ .213	1.41	
10.90	.04	$-$ .330[d]	1.40	

[a] Phosphate buffer. [b] 1.00×10^{-3} M Fe(ClO$_4$)$_3$, chloride absent. [c] Equal concentrations of Fe(ClO$_4$)$_3$ and Fe(NH$_4$)$_2$(SO$_4$)$_2$; total iron concentration = $2.00 \times 10^{-3} M$. Chloride absent. [d] Irreversible. [e] Diffusion current measured at -0.60 v. [f] Diffusion current measured at $+0.05$ v.

Table I lists the half-wave potentials obtained in excess Versene (denoted as $(E_a)_c$) and also the pertinent diffusion current constants, defined as
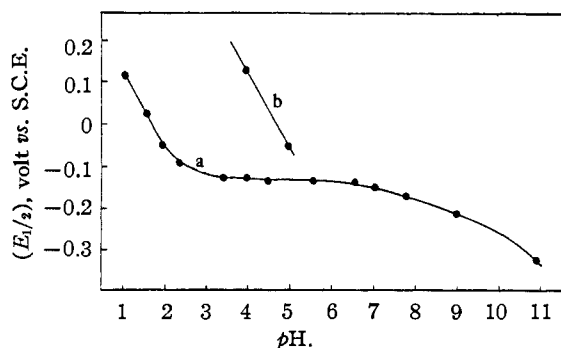

Fig. 2.—Half-wave potentials of ferric iron in excess Versene as a function of pH. Up to pH 3.5: 0.94×10^{-3} M FeCl$_3$, 0.0041 M versene; above pH 3.5; 1.89×10^{-3} M FeCl$_3$, 0.04 M versene. Ionic strength 0.12–0.15, 25°: (a) experimental curve; (b) theoretical plot for half-reaction FeY$^-$ + 3H$^+$ + e^- ⇌ Fe^{++} + H$_3$Y$^-$.

$I = i_d/Cm^{2/3}t^{1/6}.$[11] I_c corresponds to cathodic, I_a to anodic processes. The half-wave potentials are plotted as a function of pH in Fig. 2. The total iron concentration was decreased from 0.002 to 0.001 M in the low pH region; this made possible the use of correspondingly lower Versene concentrations, minimizing the danger of precipitation of the slightly soluble acid. Table I shows that the half-wave potential is independent of Versene concentration at pH above 3.5 so that it is permissible to include the whole pH range in one graph, although the Versene concentration is changed at pH 3.5.

The accessible potential range is limited on the positive side by the anodic dissolution potential of mercury in Versene medium. This was determined by extrapolation to zero current of current–voltage curves obtained from iron-free, deaerated Versene solutions. The results are given in Table II; they must be regarded as approximate.

TABLE II

ANODIC DISSOLUTION POTENTIAL OF MERCURY IN VERSENE MEDIUM AS A FUNCTION OF pH

Chloride absent unless otherwise specified; 25°

pH	Versene concentration. M	$E_{diss.}$ (v. vs. S.C.E.)
0.1	0	+0.39
.1	0.001	+ .38
1.1	0	+ .39
1.1	.004	+ .21
2.0[a]	.004	+ .22
3.0[a]	.04	+ .16
3.1[a]	.004	+ .19
4.0[b]	0	+ .30
4.3[b]	0.04	+ .12
4.0	.004	+ .18
5.5[c]	.04	+ .04
5.6	.004	+ .14
6.3[c]	.04	− .04
7.2[c,a]	.008	.00
7.5[c]	.04	− .05
8.0[d]	0	+ .06
9.0[c]	0.04	− .11
10.9[c]	.04	− .13

Note: In 0.005 M KCl, $E_{diss.}$ = +0.16 v. [a] Acetic-perchloric acid mixture. [b] Acetate buffer. [c] Chloride present. [d] Phosphate buffer.

Apparently the dropping electrode is anodically depolarized even at appreciable acidities, according to an electrode process such as

$$Hg + H_4Y \rightleftharpoons HgY^= + 4H^+ + 2e^-   (1)$$
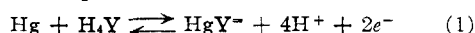
Chloride, if present in the small amounts used (0.004 or 0.008 M, depending on the concentration of ferric chloride taken), evidently does not restrict the accessible potential range in neutral and weakly acid medium. At pH lower than about 4, however, formation of the mercury complex proceeds at a more positive potential than does that of mercurous chloride; the presence of chloride, rather than that of Versene, thus becomes the limiting factor at the stated Versene concentrations.

A comparison of the data in Tables I and II shows that the separation between the half-wave and dissolution potentials attains a maximum in weakly acid medium. Consequently, the anodic

(11) J. J. Lingane, *Ind. Eng. Chem.. Anal. Ed.*, **15**, 583 (1943).

diffusion current would be expected to be less well developed at higher pH values than at pH near 4. In more acid medium (pH <3) the ferrous complex dissociates appreciably (*v.i.*). From Fig. 1 it is clear that a perfect composite wave is obtained at a pH of 4, even at a Versene concentration as high as 0.04 M. At a pH of 6 to 7.5 the excess Versene concentration must be small in order to get a well-defined anodic wave.

Proportionality of the cathodic diffusion current to concentration of the ferric complex was checked in 2, 1 and 0.4 millimolar solutions of pH 4.5, using Versene concentrations of 0.04 and 0.008 M; a value of 1.50 ± 0.03 was obtained for the diffusion current constant. In a pH 9 borate buffer 5 and 2 millimolar solutions yielded a value of 1.43 ± 0.01. The diffusion current thus lends itself very satisfactorily for analytical purposes. The anodic diffusion current was found to be 1.44 ± 0.02 at pH 4 for 2 and 1 millimolar solutions of the ferrous complex.

Figure 3 shows polarograms of solutions of pH 1 and 2 containing ferric iron in excess over Versene. Polarograms of this type have been described by Furness and co-workers[5] who use them in connection with determining Versene in the presence of excess metal. Two limiting currents are obtained, the wave of the ferric complex being preceded by the limiting current of aquo ferric ion. The extent to which the latter develops depends on the half-wave potential of the complex at the pH under consideration. It is seen that the aquo ferric ion current is fairly well-developed at pH 2 but considerably less so at pH 1. While gelatin, added to suppress a maximum at +0.1 v., was found to have no undesirable effect at pH 2, it suppressed the first limiting current by *ca.* 85% at pH 1. The analytical results are given in Table III; it appears safe to conclude, especially in view of the errors attending measurement of the small currents involved, that the first limiting current is fully diffusion controlled, *i.e.*, that the complex does not dissociate sufficiently rapidly at the electrode surface to give rise to a kinetic current. The occurrence of the first plateau suggests the possibility of the amperometric titration of small amounts of ferric iron with Versene at the rotated platinum microelectrode.

TABLE III

POLAROGRAPHY OF MIXTURES OF FERRIC VERSENATE AND AQUO FERRIC ION

0.41 × 10⁻³ M Versene, 1.00 × 10⁻³ M Fe(ClO₄)₃, 25°, ionic strength *ca.* 0.12.

pH	$(i_d)_1$, μa.	$(i_d)_2$, μa.	[Fe⁺⁺⁺] (mM) Taken	[Fe⁺⁺⁺] (mM) Found[b]	[FeY⁻] (mM) Taken	[FeY⁻] (mM) Found
1.10	1.10	0.77	0.59	0.63	0.41	0.39
1.80[a]	0.90	.95	.59	.53	.41	.47

[a] 0.005% gelatin present. [b] Using diffusion current constant of ferric iron determined independently in the appropriate perchloric acid supporting electrolyte.

Discussion

Not much can be added to the excellent analysis of the system iron–Versene given by Schwarzenbach[2d] for the pH range 2.2–8.4. The half-wave potential is seen to be essentially independent both
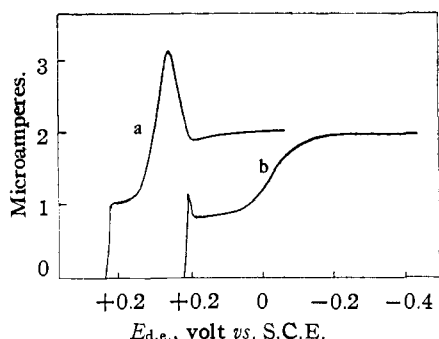
Fig. 3.—Polarograms of ferric iron at low pH in the presence of a limited amount of Versene; 1.00×10^{-3} M Fe-$(ClO_4)_3$, 0.41×10^{-3} M Versene: (a) pH 1.10; (b) pH 1.80, 0.005% gelatin.

of pH and Versene concentration between pH 3.5 and 6.5; the electrode reaction in this region is therefore
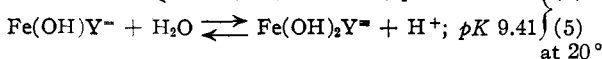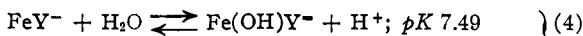
$$FeY^- + e^- \rightleftharpoons FeY^= \qquad (2)$$

$i.e.$, analogous to the ferri–ferrocyanide system. The half-wave potential is -0.13 ± 0.01 v., leading to a value of $+0.12$ v. $vs.$ N.H.E. for the formal oxidation potential of (2) at $25°$ and ionic strength $ca.$ 0.1. Schwarzenbach[2d] obtained potentiometrically $+0.117$ v. $vs.$ N.H.E. at $20°$ and a similar ionic strength; the ferrous complex is therefore a reducing agent comparable in strength to $+3$ titanium. The equation

$$(E_{1/2})_c - (E_{1/2})_s = -0.059 \log K_{ox}/K_{red} \qquad (3)$$

can be used to calculate the ratio K_{ox}/K_{red}, where $K_{ox} = [FeY^-]/([Fe^{+++}] [Y^{\equiv}])$ and $K_{red} = [FeY^=]/([Fe^{++}] [Y^{\equiv}])$; $(E_{1/2})_s$ may be identified[10] with the formal potential of the aquo ferric-ferrous couple at $25°$ and ionic strength 0.1, which has been reported to be $+0.75$ v. $vs.$ N.H.E. by Schumb, et $al.$[12] The value thus calculated is $10^{10.8}$, in agreement with Schwarzenbach's figure of $10^{10.74}$,[2d] showing the very high degree of stability of the ferric as compared to the ferrous complex.

As is shown in Table I, the half-wave potentials become rapidly more negative at pH values above $ca.$ 6.5, but remain independent of Versene concentration. In this range the acidic properties of the complex FeY^- come into play, with $Fe(OH)Y^=$ (and in still more basic medium $Fe(OH)_2Y^=$) becoming the predominant species. Schwarzenbach obtained the following data from an analysis of the protolytic equilibria[2d]

$$FeY^- + H_2O \rightleftharpoons Fe(OH)Y^= + H^+; \quad pK\ 7.49 \qquad \rbrace (4)$$
$$Fe(OH)Y^= + H_2O \rightleftharpoons Fe(OH)_2Y^= + H^+; \quad pK\ 9.41 \rbrace (5)$$
$$\text{at } 20°$$

Neglecting the second ionization stage and assuming occurrence of the electrode process

$$Fe(OH)Y^= + e^- \rightleftharpoons FeY^= + OH^-$$
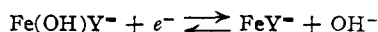
the half-wave potential at pH 8 should be $-0.13 + 0.054 \times 7.49 - 0.059 \times 8 = -0.16$ v., compared to the experimental value of -0.17 v. (Table I). The weakly acidic properties of the ferrous

(12) W. C. Schumb, M. S. Sherrill and S. B. Sweetser, THIS JOURNAL, **59**, 2360 (1937).

complex have not been taken into account here; the analogous pK values are 9.07 and 9.84.[2d]

A change in the nature of the predominating species is also indicated by the color of the solutions. A pale yellow color was observed up to pH 7.8, at the concentrations used, while a distinct orange tinge developed in the more alkaline region. Figure 4 shows the absorption spectra of the ferric complex at pH 3 and 9 (no appreciable absorption was observed at higher wave lengths than those indicated). It is seen that the 2 spectra differ considerably; at the higher pH, moreover, strong deviations from Beer's law were observed. These and other observations are indicative of a mixture of various species in the more alkaline medium. The slight but marked decrease in the cathodic diffusion current constant at high pH (Table I) can probably be explained similarly.
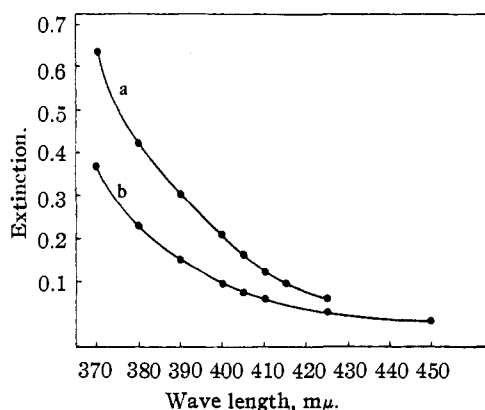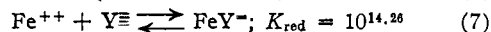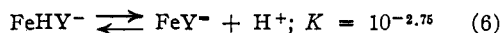

Fig. 4.—Absorption spectra of ferric iron in excess Versene, $25 \pm 2°$: (a) 0.94×10^{-3} M $FeCl_3$, 0.01 M Versene, pH 3.15; (b) 0.94×10^{-3} M $FeCl_3$, 0.02 M Versene, 0.05 M borate buffer, pH 8.80.

The dependence of the half-wave potentials on both pH and Versene concentration at pH less than 3.5 has already been explained by Schwarzenbach.[2d] In this region the ferrous complex dissociates extensively, through the intermediate formation of the moderately weak acid $FeHY^-$

$$FeHY^- \rightleftharpoons FeY^= + H^+; \quad K = 10^{-2.75} \qquad (6)$$
$$Fe^{++} + Y^{\equiv} \rightleftharpoons FeY^=; \quad K_{red} = 10^{14.26} \qquad (7)$$

The ferric complex, however, is affected only at considerably higher acidities ($v.i.$). It follows that hydrogen ion and uncombined Versene become involved in the electrode reaction. Approximate calculations, based on equations (6) and (7) and on the known ionization constants of ethylenediamine tetraacetic acid, show that $ca.$ 90% of the ferrous iron formed at the electrode surface exists in the form of Fe^{++} when the pH has dropped to 2.0. The electrode reaction can, in all probability, be represented mainly by

$$FeY^- + 3H^+ + e^- \rightleftharpoons Fe^{++} + H_3Y^- \qquad (8)$$

Figure 2 actually demonstrates that the pH dependence of the half-wave potential corresponds closely to equation (8) at pH less than 2. It is to be noted that the half-wave potential appears to be independent of Versene concentration at pH 1, contrary to the interpretation just given; a possible

explanation is that the solubility of ethylenediamine tetraacetic acid has been exceeded, the remaining uncombined acid being present in a colloidal state.

The stability constant of the ferric complex, given by

$$K_{ox} = \frac{[FeY^-]}{[Fe^{+++}][Y^{\equiv}]} \qquad (9)$$

may be evaluated indirectly from a knowledge of K_{red} (equation 7) and the ratio K_{ox}/K_{red} (equation 3). Using Schwarzenbach's values for these quantities, measured at 20°, one obtains $10^{14.26} \times 10^{10.74} = 10^{25.00}$ for the concentration constant at ionic strength 0.1. Schwarzenbach's technique[2c] does not lend itself to the direct determination of such large stability constants. The direct method presented below leads to fairly satisfactory results. Another independent approach employing radioactive indicators, has recently been reported[13]; a value close to 10^{24} was found.

Calculations based on the above value and on the ionization constants of ethylenediamine tetraacetic acid show that the ferric complex dissociates very appreciably in 0.1–1 M acid solution. Knowing the acidity and the total concentrations of ferric iron and Versene, a measurement of the concentration of the complex should therefore enable one to evaluate the stability constant. If we represent the total stoichiometric concentrations by C_{Fe} and C_Y, we can write

$$K_{ox} = \frac{[FeY^-]}{(C_{Fe} - [FeY^-])[Y^{\equiv}]} =$$
$$\frac{[FeY^-][H^+]^4 (1 + ([H^+]/K_1))}{(C_{Fe} - [FeY^-])\Sigma[Y]K_2K_3K_4} \qquad (9')$$

here $K_1 \ldots K_4$ denote the ionization constants of ethylenediamine tetraacetic acid and $\Sigma[Y]$ signifies the total concentration of uncombined Versene. Equation (9') is based on the fact that at the acidities considered

$$\Sigma[Y] = C_Y - [FeY^-] = [H_4Y] + [H_3Y^-]$$

Since $K_1 = 1 \times 10^{-2}$,[2a] the ratio $[Fe^{+++}]/[FeY^-]$ varies approximately as the *fourth* power of the acidity.

The concentration of the complex was determined spectrophotometrically. Attempts to analyze equilibrium mixtures polarographically proved unsuccessful; under the experimental conditions the oxidation potential of the iron–Versene system is too positive to permit the development of two separate limiting currents.

Equilibrium mixtures were prepared from known amounts of ferric chloride, Versene and standard perchloric acid; the ionic strength was kept at 1 by appropriate addition of sodium nitrate. A solution of similar ionic strength, pH 3 and 0.01 M Versene served as blank. Measurements were made at room temperature, *i.e.*, 25 ± 2°; all mixtures were analyzed at 4 different wave lengths in the 370–400 mμ range. The absorption spectrum

(13) (a) S. S. Jones and F. A. Long, Abstracts, A.C.S. Symposium on Complex Ions and Polyelectrolytes, Cornell University, June 18–21, 1951; (b) *J. Phys. Chem.*, **56**, 25 (1952).

of the complex at pH 3 in 0.01 M Versene is shown in Fig. 4; Beer's law was found to be obeyed to ±2% or better over the 0.5–2 millimolar range. A standard solution of the complex (ionic strength 1) was analyzed along with each equilibrium mixture, since small irreproducibilities in the wave length settings may cause appreciable errors in the spectral region studied. A separate investigation of the spectrum of ferric iron in 1 M perchloric acid revealed that aquo ferric ion does not interfere at concentrations up to *ca.* 1 millimolar; even in 0.1 M acid the contribution of the aquo ion to the total extinction was found not to exceed 4%. At concentrations higher than 1 millimolar, however, the aquo ferric iron absorption, which was found not to obey Beer's law, ceases to be negligible. The results are given in Table IV.

TABLE IV

SPECTROPHOTOMETRIC DETERMINATION OF THE STABILITY CONSTANT OF THE FERRIC COMPLEX

Ionic strength 1; $K_{ox} = [FeY^-]/[Fe^{+++}][Y^{\equiv}])$

	$[H^+]$ $(M)^a$	C_{Fe} (mM)	C_Y (mM)	$[FeY^-]$ (mM)^b	$[Fe^{+++}]$ (mM)	$[Y]$ (mM)	K_{ox} $\times 10^{22}$
(1)	1.00	0.944	1.55	0.271	0.673	1.28	3.9
(2)	1.00	.708	1.56	.202	.506	1.36	3.7
(3)	1.00	.472	1.56	.136	.336	1.42	3.6
(4)	1.00	.944	1.03	.198	.746	0.83	4.0
(5)	1.00	.944	0.825	.182	.762	.643	4.6
(6)	1.00	.944	0.516	.114	.830	.402	4.2
(7)	0.80	.944	1.56	.445	.499	1.11	4.1
(8)	.80	.944	1.03	.334	.610	0.70	4.0
(9)	.80	.944	0.825	.289	.655	.536	4.2
(10)	.80	.944	0.516	.201	.743	.315	4.4
(11)	.60	.944	1.55	.714	.230	.84	6.0
(12)	.60	.944	1.03	.598	.346	.43	6.5
(13)	.60	.944	0.825	.520	.424	.305	6.5
(14)	.60	.944	.516	.368	.576	.148	7.0
(15)	.60	.708	.516	.310	.398	.206	6.1
(16)	.60	.472	.516	.245	.227	.271	6.5
						Av.	5.5 ± 1.2

a Perchloric acid. *b* Average of values at 4 different wave lengths, measured at 25°.

At a given acidity a precision of *ca.* ±6% is attained upon varying the concentrations of iron and Versene over, respectively, a twofold and a threefold range. The relatively high divergence of the values obtained in 0.6 M acid from the rest may be at least in part attributable to the near *fourth* power dependence of the ratio $[FeY^-]/[Fe^{+++}]$ on acidity.

Agreement with the value of Jones and Long,[13b] who worked at 25° and an ionic strength of one, is satisfactory. The figure obtained indirectly from Schwarzenbach's measurements is one order of magnitude higher. His experiments were carried out at an ionic strength 0.1, and a decrease in the concentration constant with increasing ionic strength is to be expected from the Debye–Hückel equation. Furthermore, in the present investigation quantities measured at 25° were used in conjunction with the ionization constants of ethylenediamine tetraacetic acid reported by Schwarzenbach at 20° and an ionic strength of 0.1.