The manometer is desirable both to indicate the pressure and to act as a vent if the pressure becomes too great while the oxygen is being distilled. The measuring tube is made of sufficiently large capacity to hold enough liquid oxygen to give the desired pressure in the reactor.

In the procedure for preparing UO_3, pure U_3O_8 is placed in the quartz liner of the reactor which is then bolted shut. The tubing connected to the oxygen tank is flushed with oxygen by opening stopcock 1 and bubbling oxygen through the manometer. Stopcock 1 is then shut and the system evacuated by opening stopcocks 2 and 3. Valve 4 is open and valve 5 is kept shut. The U_3O_8 is thoroughly dried during the evacuation by heating at 850° for about one hour. When the apparatus is evacuated, as determined by a McLeod gage on the vacuum system, the vacuum line is shut off at stopcock 2. Stopcock 3 and valve 4 are also shut.

To collect liquid oxygen in the trap, the trap is immersed in liquid nitrogen and stopcock 1 is opened. About 10% more oxygen than is needed to fill the reactor to 400 p. s. i. is condensed in the trap. The amount required for the reactor is dependent on its volume and is determined from the gas laws. After the apparatus has once been used, the necessary volume of liquid oxygen can be determined more accurately.

After sufficient liquid oxygen has been condensed in the trap, stopcock 1 is shut. A dewar containing liquid nitrogen is placed around the measuring tube and stopcock 3 opened. The dewar of liquid nitrogen around the trap is replaced by a dewar containing liquid oxygen. The proper amount of oxygen, calculated to produce the proper pressure, is measured into the graduated tube and stopcock 3 closed. The reactor is cooled with a bath of liquid nitrogen. Valve 4 is then opened and the measuring tube placed in a dewar of liquid oxygen to maintain the liquid oxygen in the measuring tube at approximately 1 atmosphere while it distills into the reactor. Valve 4 is then shut and the reactor warmed to room temperature slowly[4] to prevent scattering of the U_3O_8 by the evaporating oxygen. A furnace placed around the reactor is maintained at 600–700° for forty hours. Should too much oxygen have been collected in the reactor, the excess can be vented through valve 5. The residual liquid oxygen in the trap can be removed through the pumps or can be slowly evaporated through the manometer by keeping the trap in a dewar containing liquid nitrogen and permitting the latter to evaporate by itself. Examination of X-ray diffraction patterns of the yellow product by Dr. W. H. Zachariasen of the Physics Division of this Laboratory and ignition to U_3O_8 have shown the product to be pure UO_3 of the type obtained by ignition of uranyl nitrate.

(4) Replacing the dewar containing the liquid nitrogen by an empty one is adequate.

Summary

The method for the preparation of UO_3 described here is considered to be superior to those commonly used because the purity of the product is dependent only on the purity of the original U_3O_8, which should be high for good results, and the product is obtained in 100% yield. The oxygen is dried and purified during the liquefaction so that this presents no problem, while U_3O_8 is generally obtained sufficiently pure.

Within wide limits the temperature at which the reaction is run is not critical. The upper temperature limit, however, is important. Experiments run at 750° yielded oxides intermediate between U_3O_8 and UO_3. Even at 750°, however, UO_3 can be prepared by going to pressures over 400 p. s. i. Preparations made at temperatures as low as 550° also yielded UO_3, but required somewhat longer time for complete reaction.

CHICAGO, ILLINOIS RECEIVED AUGUST 29, 1949

[CONTRIBUTION FROM SCHOOL OF CHEMISTRY, INSTITUTE OF TECHNOLOGY, UNIVERSITY OF MINNESOTA]

Reaction of Ferrous and Ferric Iron with 1,10-Phenanthroline. III. The Ferrous Monophenanthroline Complex and the Colorimetric Determination of Phenanthroline

BY I. M. KOLTHOFF, D. L. LEUSSING AND T. S. LEE

One of the most important methods for the determination of iron is the colorimetric method based on the formation of the red ferrous triphenanthroline complex ion. In addition to this well-known complex there appear to be two other complex ions of ferrous iron and phenanthroline, the pale yellow ferrous monophenanthroline and ferrous diphenanthroline.[1] The latter is relatively unstable with respect to the other ferrous phenanthroline complex ions and for most purposes its existence may be neglected. In the investigation described below the dissociation constant of ferrous monophenanthroline was determined and the visible spectrum recorded.

The knowledge of this constant is of importance in the determination of complex constants of other metals with *o*-phenanthroline when the excess of phenanthroline is being determined colorimetrically. In the present work an excess of iron was added to the phenanthroline solution and the intensity of the red ferrous triphenanthroline color was measured with a spectrophotometer. The formation of ferrous monophenanthroline causes low results unless a correction is made. A systematic study of the effect of ferrous ion concentration, acidity, and phenanthroline concentration on the equilibria and the accuracy of the determination has been made.

(1) T. S. Lee, I. M. Kolthoff and D. L. Leussing, THIS JOURNAL, 70, 2348, 3596 (1948).

Experimental

Materials Used.—The preparation of most of the reagents used was described in previous papers. The purity of the *o*-phenanthroline monohydrate was determined by conductometric titration with acid. Experience has shown that the product obtained from the G. Frederick Smith Chemical Company can probably be depended upon to be more than 99% pure. This cannot be said for "phenanthroline dihydrochloride" from the same source.

The *p*H of the acetic acid–acetate buffer used in the determination of *o*-phenanthroline was measured with a *p*H meter equipped with glass electrode.

Formation of Ferrous Monophenanthroline

Spectrum of the Yellow Complex.—The spectrum of the yellow complex of ferrous iron and phenanthroline (Curve I, Fig. 1) was determined in a solution of high acidity and high iron concentration. The separate iron and *o*-phenanthroline solutions in dilute sulfuric acid were brought to 25° and were maintained at this temperature after mixing. The extinction of the mixture was measured after five minutes at various wave lengths with a Beckman Model DU Spectrophotometer (1 cm. absorption cell). The extinction did not change when the solution was allowed to stand several hours.

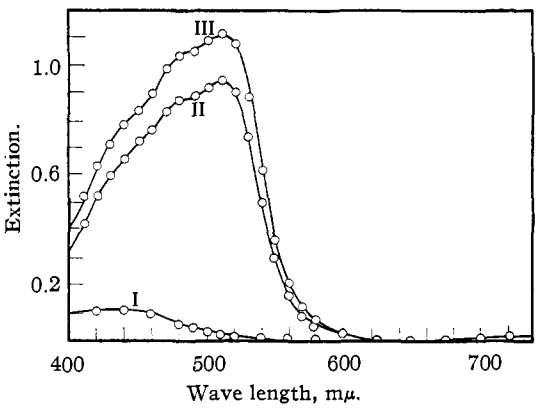

Fig. 1.—Spectra of solutions containing ferrous iron and phenanthroline (1 cm. cells): I, ferrous iron 0.25 *M*, phenanthroline 4.4×10^{-4} *M*, sulfuric acid 0.625 *M* (approx. 3×10^{-4} *M* in ferrous monophenanthroline); II, ferrous iron 2.01×10^{-3} *M*, phenanthroline 3.00×10^{-4} *M*, *p*H 5.5; III, ferrous iron 1.01×10^{-4} *M*, phenanthroline 1.0×10^{-3} *M*, *p*H 5.5.

Under the conditions of the experiment no detectable amount of ferrous triphenanthroline was formed. This can be seen in Fig. 1 by comparing Curve I with Curve II, that of ferrous triphenanthroline. It is seen that Curve I shows no maximum in the region of 520 mμ, the region of maximum absorption of ferrous triphenanthroline. From Curve I it is concluded that the yellow complex has a broad absorption maximum in the region of 400–450 mμ. The concentration of the yellow complex was approximately 3×10^{-4} *M* (calculated by means of equation 3 and the value of K_1—see below). Consequently, the molar absorption coefficient of the complex is seen to be very small even in the region of maximum absorption.

Identification of the Yellow Complex.—The effect of phenanthroline and iron concentrations on the extinction at 420 mμ of the yellow complex was investigated in solutions of high acidity and high iron concentration. The results are given in Table I and Fig. 2.

Under the conditions of the experiments of Table I the concentration of red ferrous triphenanthroline is, as shown by calculation[1] or by examination of the spectra of the solutions, negligible. Inasmuch as phenanthroline is a monacidic base it would be expected that under the conditions of the experiments of Table I the hydrogen ion and ferrous ion compete for the phenanthroline. Assuming that the yellow complex is ferrous monophenanthroline, the equilibrium expressions are

$$(H^+)(Ph)/(PhH^+) = K_A \quad (1)$$

$$(Fe^{++})(Ph)/(FePh^{++}) = K_1 \quad (2)$$

where Ph represents phenanthroline, K_A is the acid dissociation constant of the phenanthroline ion, and K_1 is the dissociation constant of ferrous monophenanthroline. If the concentrations of iron and of acid are high relative to the concentration of ferrous monophenanthroline, as is true in the experiments of Table I, equation (3) can be derived readily from equations (1) and (2)

$$(FePh^{++}) = (Fe^{++})(Ph)_t/[(Fe^{++}) + (K_1/K_A)(H^+)] \quad (3)$$

where $(Ph)_t$ represents the total, analytical concentration of phenanthroline. From equation (3) it would be expected that the extinction due to the ferrous monophenanthroline concentration would be directly proportional to the total concentration of phenanthroline, provided that the iron and hydrogen ion concentrations are held constant. In Fig. 2 this is seen to be true. On the other hand the concentration of ferrous monophenanthroline would not be expected to be directly proportional to the iron concentration. Taking the reciprocals of both sides of the equation

$$\frac{1}{(FePh^{++})} = \frac{1}{(Ph)_t}\left[1 + \frac{K_1(H^+)}{K_A}\frac{1}{(Fe^{++})}\right] \quad (4)$$

TABLE I

EFFECT OF PHENANTHROLINE AND FERROUS IRON CONCENTRATIONS ON CONCENTRATIONS OF YELLOW COMPLEX (CONCENTRATION OF SULFURIC ACID 0.625 *M*)

Total concn. of phenanthroline, $M \times 10^4$	Concn. of iron, *M*	Log I_0/I (at 420 mμ)
2.2	0.25	0.051
4.4	.25	.103
8.8	.25	.202
4.4	.125	.066
4.4	.375	.120

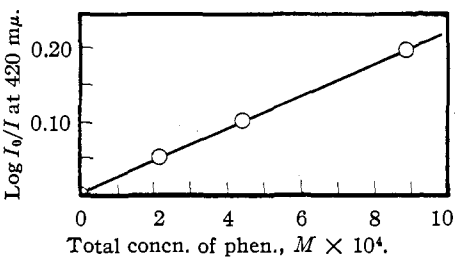

Fig. 2.—Effect of phenanthroline concentration on concentration of yellow complex (concn. of sulfuric acid 0.625 *M*, concn. of iron 0.25 *M*).

From equation (4) it appears that if the total phenanthroline and hydrogen ion concentrations are held constant, a plot of the reciprocal of the extinction due to the ferrous monophenanthroline concentration *vs.* the reciprocal of the iron concentration should yield a straight line. In Fig. 3 this is seen to be true. From Fig. 2 and 3 it can be concluded that the yellow complex is indeed ferrous monophenanthroline, $FePh^{++}$. It should be mentioned that ferrous monophenanthroline complex has apparently been observed by Thiel and Logemann, but its composition has not definitely been proved previously.[2]

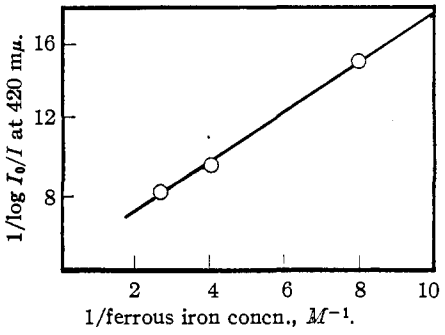

Fig. 3.—Effect of ferrous iron concentration on concentration of yellow complex (concn. of sulfuric acid 0.625 *M*, total concn. of phenanthroline 4.4×10^{-4} *M*).

Dissociation Constant of Ferrous Monophenanthroline.—The formation of ferrous monophenanthroline was also investigated in solutions of relatively low acidity (*p*H 5.5 to 4.5). In solutions of low acidity and in the presence of excess iron, the amounts of phenanthrolium ion and of free phenanthroline are very small as compared with the amounts of phenanthroline present as iron complexes. In Fig. 1 are shown the spectrum of a solution containing phenanthroline and an excess of iron (curve II) and the spectrum of a solution of iron and an excess of phenanthroline (curve III). The concentration of phenanthroline in the former solution was exactly three times as great as the concentration of iron in the latter solution. Therefore, curves II and III would be identical if the formation of ferrous triphenanthroline were quantitative in both solution. It is known that the formation of ferrous triphenanthroline is quantitative under the conditions of curve III.[1] From the fact that curve II is lower than curve III, it can be concluded that the formation of ferrous triphenanthroline is not complete in the presence of excess iron. A careful comparison of the two curves indicates that only the color of ferrous triphenanthroline is detectable in the solutions. (The color of ferrous monophenanthroline is so weak that the absorption at 500 mμ is not detectable if the concentration is below about 5×10^{-5} *M*.)

(2) Thiel and Logemann, *Sitzber. Ges. Beförder. ges. Naturw. Marburg*, **69**, 60 (1934).

Assuming that the low results of curve II are due to the formation of ferrous monophenanthroline the dissociation constant K_1 of that complex can be calculated. The dissociation constant of ferrous triphenanthroline is given by the expression

$$(Fe^{++})(Ph)^3/(FePh_3^{++}) = K_3 \qquad (5)$$

Combination of equation (5) with equation (2) gives

$$\frac{(FePh^{++})}{(FePh_3^{++})} = \frac{K_3^{1/3}}{K_1}\left[\frac{(Fe^{++})}{(FePh_3^{++})}\right]^{2/3} \qquad (6)$$

From curve II of Fig. 1 the following values can be computed: $(FePh_3^{++}) = 8.60 \times 10^{-5}$, $(Fe^{++}) = 1.87 \times 10^{-3}$, $(FePh^{++}) = 4.20 \times 10^{-5}$. The value[1] of K_3 is 5×10^{-22}. Substitution of the above values in equation (6) yields a value of 1.3×10^{-6} for K_1, the dissociation constant of ferrous monophenanthroline. The validity of this value and of equation (6) will be demonstrated below.

The values of K_1 and K_3 were used in calculating the curves of Fig. 4. In Fig. 4 are shown the relative amounts of ferrous iron, ferrous monophenanthroline, and ferrous triphenanthroline under various conditions. In interpreting this figure it should be kept in mind that the relative amounts of these species are directly dependent only on the concentration of free phenanthroline. The relative amounts are independent of total iron, total phenanthroline, and hydrogen ion concentrations, except as they influence the concentration of free phenanthroline.[3] It can be

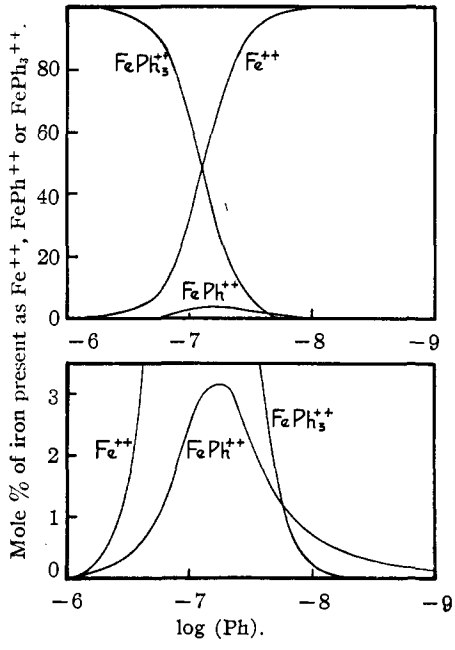

Fig. 4.—Composition of solutions containing iron and phenanthroline (temp. 25°).

(3) In this connection see J. Bjerrum, "Metal Amine Formation in Aqueous Solution," Haase and Son, Copenhagen, 1941, p. 287.

seen from Fig. 4 that the fraction of iron present as ferrous monophenanthroline can never exceed about 3 mole per cent. However, if the concentration of free phenanthroline is very small (less than $10^{-8.2}$ M) as is true in a solution containing a large excess of iron over phenanthroline, the ratio of ferrous monophenanthroline to ferrous triphenanthroline is large.

It should also be pointed out that the metal amine and metal ethylenediamine complex ions investigated by J. Bjerrum[4] show a regular stepwise formation if the free ammonia or ethylenediamine concentration is steadily increased and if time is allowed for equilibrium to be established. Each of the complexes (like ferrous mono-ethylenediamine, ferrous di-ethylenediamine, and ferrous tri-ethylenedianine) successively constitutes the predominant species. The three zinc phenanthroline complexes, to be described in a subsequent paper, also fall into this category, showing regular stepwise formation. As can be seen from Fig. 4, the ferrous phenanthroline complexes behave otherwise. The mono and especially the diphenanthroline complexes are relatively unstable under all conditions.

Calculation of Equilibrium in Mixtures Containing an Excess of Ferrous Iron Over Phenanthroline.—When ferrous iron is added to a solution of phenanthroline, the phenanthroline is present as Ph (free phenanthroline), PhH^+, $FePh^{++}$ and $FePh_3^{++}$. In the colorimetric determination of phenanthroline it would be desirable to convert essentially all of the phenanthroline into $FePh_3^{++}$. By using an excess of iron and by buffering the solution at a pH of about 5, the amounts of Ph and PhH^+ can be made negligible. Unfortunately, the amount of $FePh^{++}$ is not negligible if an excess of iron is present. Indeed, if the excess is large, the relative amount of $FePh^{++}$ is also large. It is apparent that the percentage error in the determination can be calculated by means of equation (6) and the values of the total concentration of iron and the total concentration of phenanthroline. If the error is small (less than about 10%), the error is given with sufficient accuracy by the following equation that is readily derived from equation (6)

$$\% \text{ error} = \frac{K_1^{1/3}}{3K_1}\left[\frac{a-b}{b}\right]^{1/3} \times 100 = 2.0 \times \left[\frac{a-b}{b}\right]^{1/3} \quad (7)$$

where a is the total concentration of iron and b is one-third of the total concentration of phenanthroline. If the error is greater than about 10%, it must be calculated from equation (6) by successive approximations. In any case the computation of the error is not difficult. Unless the error is extremely large (greater than about 50%), the absorption of ferrous monophenanthroline can be neglected.

(4) J. Bjerrum, ref. 3, p. 295.

The results of a number of determinations of phenanthroline under different conditions are given in Table II. It is seen that low results varying between 0.5 to 44% were obtained. The theoretical values of the errors, calculated by means of equations (7) or (6) are also given in Table II. It is seen that the calculated errors agree with the observed errors within 1-2% (absolute), the limit of accuracy of the spectrophotometric determination. The agreement constitutes experimental proof of the validity of equation (6).

TABLE II

DETERMINATION OF PHENANTHROLINE UNDER VARIOUS CONDITIONS

Expt.	Total concn. of phenanthroline, $M \times 10^4$	Total concn. of iron, $M \times 10^4$	Log I_0/I at 500 mμ	Concn. of ferrous triphenanthroline found, $M \times 10^4$	Observed error, %	Calcd. error, % Eq. (6)	Eq. (8)
1[a]	3.00	1.5	1.065	0.995	0.5	1.3	8.4
2	3.00	2.0	1.05	.982	1.8	2.0	10.6
3	3.00	5.0	1.02	.953	4.7	5.0	15
4	3.00	10	0.998	.933	6.7	8.6	19
5	3.00	15	.965	.902	9.7	11.4	21
6	3.00	20	.920	.860	14.0	13.5	24
7	0.60	2.0	.191	.178	10.8	8.6	19
8	1.20	2.0	.402	.376	6.0	5.0	15
9	1.80	2.0	.620	.580	3.5	3.5	13.3
10	2.40	2.0	.830	.775	3.1	2.6	12
11	1.00	50	.199	.186	44	47	40
12	2.00	50	.492	.460	31	31	34
13	2.50	50	.650	.608	27	27	32

[a] The pH of the solution of Expts. 1–10 was 5.5 and that of the solutions of Expts. 11–13 was 4.5. In all experiments acetic acid–acetate buffers were used.

Theoretical errors were also calculated with the assumption that the low results were due entirely to formation of the ferrous diphenanthroline complex. If this were true, the equation from which the error could be calculated would be

$$\frac{(FePh_2^{++})}{(FePh_3^{++})} = \frac{K_2^{1/3}}{K_2}\left[\frac{(Fe^{++})}{(FePh_3^{++})}\right]^{1/3} \quad (8)$$

where K_2 is the dissociation constant of ferrous diphenanthroline. The hypothetical value of $K_2(4 \times 10^{-14})$ was calculated from experiments 11–13 of Table II. It is seen from Table II that the error calculated on the basis of the diphenanthroline complex does not agree with the observed error.

In the determination of phenanthroline the practical upper limit of the phenanthroline concentration in the final solution is about 3×10^{-4} M with an absorption cell 1 cm. in thickness. From Table II it is seen that the total concentration of iron should be 1.5×10^{-4} M iron to insure that there is an excess of iron over phenanthroline. In Table III are given results of the determination of phenanthroline solutions in which a total iron concentration of 1.5×10^{-4} M was used. It is seen that the error is not unduly large. It should be emphasized that in

routine analyses it is more convenient to use a calibration curve obtained by treating known amounts of phenanthroline by the procedure recommended below than to determine the amount of ferrous triphenanthroline and correct for ferrous monophenanthroline (see Table III). Of course the data given in Table III can be used for finding the correction without making a calibration curve.

TABLE III

DETERMINATION OF PHENANTHROLINE (TOTAL CONCN. OF FERROUS IRON 1.5×10^{-4}, *p*H 5.5)

Expt.	Concn. of phenanthroline present, $M \times 10^4$	Log I_0/I at 500 mμ	Apparent concn. of phenanthroline found,[a] $M \times 10^4$	Corrected concn. of phenanthroline found,[b] $M \times 10^4$
1	0.60	0.2075	0.581	0.62
2	1.20	.413	1.16	1.21
3	1.80	.628	1.76	1.81
4	2.40	.855	2.40	2.44
5	3.00	1.06	2.97	3.01

[a] Apparent concn. of phen. found = 3 × concn. of ferrous triphenanthroline = (log I_0/I) $[3/1.07 \times 10^4]$. [b] Equation (7) used to compute the correction.

The effect of acidity on the determination was also investigated. It would be concluded from equation (6) that acidity would not affect the error due to formation of ferrous monophenanthroline. This conclusion was confirmed experimentally. It was found that the error of experiments, similar to Expt. 2, Table II, were not affected by change of acidity between *p*H 5.5 and *p*H 4.0. At high acidities an error in the determination of phenanthroline results from the formation of phenanthrolium ion. The magnitude of the error can be calculated from the equation

$$\frac{(PhH^+)}{(FePh_3^{++})} = \frac{K_3^{1/3}(H^+)}{K_A} \times \frac{1}{(Fe^{++})^{1/3}(FePh_3^{++})^{2/3}} \quad (9)$$

Equation (9) is derived from equations (1) and (5). From equation (9) it can be shown that if K_a' is 1.1×10^{-5}, the total concentration of iron is 1.5×10^{-4}, and if the total concentration of phenanthroline is between 2×10^{-5} and 3×10^{-4} *M*, the *p*H should be 4 (or greater) in order that the error be less than 1%. On the other hand it is not desirable to carry out the determination at *p*H greater than about 5.5, because the rate of air oxidation of ferrous iron is then rapid. Hydroxylamine hydrochloride is added to the reaction mixture to keep the iron reduced to the divalent state (see below) but at a *p*H greater than 5.5 the hydroxylamine is rapidly exhausted. It is concluded that the determination of phenanthroline should be carried out at *p*H 4.5 to 5.5 with a total concentration of iron of 1.5×10^{-4} *M*.

Recommended Procedure for Determination of *o*-Phenanthroline

Reagents.—Ferrous ammonium sulfate reagent, 0.0074 *M*, is prepared by dissolving exactly 0.29 g. of reagent grade ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, in 0.01 *M* sulfuric acid and diluting to 100 ml. One tenth gram of hydroxylamine hydrochloride is added to inhibit oxidation. The reagent solution should not be used if more than a week old.

Procedure.—A 5- to 25-ml. portion of aqueous solution containing 0.2 to 3 mg. (0.001 to 0.015 millimole) of phenanthroline is added to a 50-ml. volumetric flask. If the phenanthroline solution contains free acid or base, the solution should be neutralized so that the *p*H of the final solution is between 4.5 and 5.5. Exactly 1 ml. of ferrous sulfate reagent is added. The solution is diluted to the mark with a buffer solution that is 0.05 *M* in acetic acid and 0.1 *M* in sodium acetate. The extinction at 500 mμ is read after thirty minutes. The amount of phenanthroline present is found by comparing the observed extinction with a calibration curve. The calibration curve, which is nearly a straight line, is established by treating known amounts of phenanthroline by the same procedure, using the empirical procedure. No correction need be applied for formation of ferrous monophenthroline. Without a calibration curve the correction for the amount of ferrous monophenanthroline formed can be calculated from equation (7) (see Table III).

If phenanthroline of the requisite purity is not available for establishment of the calibration curve, an alternative procedure may be employed. The extinction of the unknown, found as described above, is used to compute the molar amount of ferrous triphenanthroline. This value multiplied by three, yields the apparent molar amount of phenanthroline, uncorrected for ferrous monophenanthroline formation. A correction is applied according to equation (7). This is illustrated in Table III. (The extinction coefficient of ferrous triphenanthroline is found by adding an excess of phenanthroline to a solution containing a known amount of ferrous iron.[5])

Acknowledgment.—Acknowledgment is made to the Graduate School of the University of Minnesota for a grant which enabled us to carry out this investigation.

Summary

The pale yellow complex of ferrous ion and phenanthroline has been demonstrated to be ferrous monophenanthroline. The dissociation constant of this complex is about 1.3×10^{-6} at 25°.

Conditions for the colorimetric determination of phenanthroline (as ferrous triphenanthroline) have been established. Error resulting from variations in acidity and iron concentration have been investigated experimentally and theoretically.

MINNEAPOLIS, MINNESOTA RECEIVED NOVEMBER 28, 1949

(5) Fortune and Mellon, *Ind. Eng Chem., Anal. Ed.*, **10**, 60 (1938); E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, N. Y., 1944, p. 271; Smith and Richter, "Phenanthroline and Substituted Phenanthroline Indicators," G. Frederick Smith Chemical Co., Columbus, Ohio, 1944, p. 59.