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STABILITY CONSTANTS OF SOME M(I)- AND M(II)- 1,10-PHENANTHROLINE COMPLEXES

by

Richard Fullerton

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TABLE OF CONTENTS

Page

INTRODUCTION AND LITERATURE SURVEY

The determination of stability constants of complexes is of great interest to both the theoretical analytical chemist and the analytical chemist who is searching for means of separating ions prior to their determination, or, more ideally, their determination without the necessity of preliminary separations. Stability constant study provides the theoretical chemist with a way of studying bond type and strength in complexes, the effect of variations in the ligand, and the different complexing abilities of various metal ions. A knowledge of the stability constants of complexes can eliminate much tedious, trial-and-error experimenting on the part of the methods development chemist.

An effort is usually made in the determination of stability constants to maintain a constant ionic strength. The easiest way to do this is to have present a high concentration of an "inert" cation, i.e., one which is not expected to take part in the reaction under investigation. Because of their poor complexing ability, alkali metal ions are usually selected, and it is assumed in making calculations that no ligand is tied up in any way with the ion used.

Grimes (10) has shown spectrophotometric evidence for the existence in solution of 1,10-phenanthroline-alkali metal complexes under the conditions usually used in determining the stability constants of other 1,10-phenanthroline complexes. Grimes (11) measured the stability constants of these complexes as well as those of poly-1,10-phenanthroline-hydrogen species; evidence for the existence of such complexes was also presented.

The presence of previously unknown alkali metal- and hydrogen-1,10-phenanthroline species is of vital importance in the measurement of the stability constants of other metal constants. Those determined in the past will be in error to some degree because of the presence of these complexes, and, because the buffer metal concentration is not known very accurately in most experiments of this type, better values for the constants are not possible in most cases by recalculation of the data. Therefore, it becomes necessary to re-determine most of the published constants.

The purpose of this work is to evaluate the method of Grimes (11) further by (1) testing the reproducibility of the method by determining the same stability constants previously measured by this method and comparing the results with those previously reported, (2) testing the reliability of the method by determining constants for which values had previously been published, and (3) determining the range of magnitude of stability constants which could be measured by the proposed method.

The reaction of hydrogen ions with 1,10-phenanthroline has been studied by many investigators, primarily to determine the acid dissociation constant. Knowledge of this constant is necessary in the study of the stability of complexes and in kinetic measurements.

A potentiometric titration by Dwyer and Nyholm (6) indicated that only one hydrogen ion reacted with one 1,10-phenanthroline molecule. Three solutions, 2.5×10^{-2} M in 1,10-phenanthroline and 1×10^{-2} M in hydrochloric acid, were made up and the pH measured. The pH of each solution was 5.35. From the pH and the concentrations, a pKa value of 5.2 was calculated. According to these authors, Albert and Goldacre found the pKa to be 4.8. This value was obtained from measurements made in 50% ethanol.

Lee *et al.* (19), from the results of potentiometric titrations, drew the same conclusion as did Dwyer and Nyholm (6), i.e., that only one hydrogen ion reacts with one 1,10-phenanthroline molecule at moderate acidity. They concluded that the two nitrogen atoms are too close together (approximately 2.5 Å) to permit the presence of two hydrogen ions. Their extrapolation to infinite dilution of a plot of pH vs. the square root of the ionic strength gave a value for pKa of 4.77 at 25° C. Calculation from conductometric data of the degree of hydrolysis of monoprotonated-1,10-phenanthroline give a value for pKa of 4.96. The conductometric titration of 1×10^{-2} M 1,10-phenanthroline with 2×10^{-1} M hydrochloric acid showed a break in the titration curve at an acid:base ratio of 1:1.

Schilt and Smith (29) have measured the acid dissociation constants of forty substituted 1,10-phenanthrolines. Their technique was the dissolution of the 1,10-phenanthrolines in acid and dilution to volume with water-dioxane mixtures. The use of water-dioxane mixtures was dictated by the low aqueous solubility of many of the substituted 1,10-phenanthrolines. The pH was measured with a glass-saturated calomel electrode pair and a Beckman Model G pH meter. Extrapolation of a plot of relative pKa vs. % dioxane concentration to 0% dioxane concentration gave a pKa of 4.86 at 25° C for 1,10-phenanthroline. Base concentration was 5×10^{-3} $\underline{M}$ and that of the acid was 2.5×10^{-3} $\underline{M}$.

The acid dissociation constant of 1,10-phenanthroline was measured at several ionic strengths and at 0° C, 25° C, and 50° C by Nasanen and Uusitalo (25) using a technique similar to that of Lee *et al*. (19). The pH measurements were made using a glass-silver/silver chloride electrode system. They reported pKa values of 5.070 (0° C), 4.857 (25° C), and 4.641 (40° C) at infinite dilution. Acid and base concentrations used were approximately 5×10^{-3} $\underline{M}$ and 2.5×10^{-3} $\underline{M}$ respectively. Adsorption of 1,10-phenanthroline on the glass electrode and reaction of 1,10-phenanthroline with the silver-silver chloride electrode may have caused errors in their work.

Margerum et al. (21) and Nasanen and Uusitalo (25) have shown spectrophotometric evidence of diprotonated-1,10-phenanthroline in very acidic solutions. The former have calculated a stability constant of 5 for this species from spectrophotometric data.

The acid dissociation constant has been measured by several other workers*,** (1, 11, 28) whose results are summarized in Table 26. Brandt and Gullstrom (3), using a method similar to that of Schilt and Smith (29), obtained a value of 4.96. The values of Lee et al. (19) were reproduced by Yamasaki and Yasuda (37).

Generally, the total concentration of 1,10-phenanthroline in the above experiments was 2 x 10^{-2} M or less, and the acid concentration was half or less than half of the base concentration.

Margerum et al. (22) and Nasanen and Uusitalo (25) have been the only investigators thus far to suggest the possibility of any hydrogen-1,10-phenanthroline species other than the

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*Albert, A. and Goldacre, R., Sidney, Australia. Stability of phenanthrolium ion. Private communication to H. Irving. 1945.

**Irving, H. and Mellor, D. H., Oxford, England. Stability of 1,10-phenanthroline complexes. Private communication to R. I. Bystroff. 1955.

mono-(10,10-phenanthroline)hydrogen ion. However, certain experiments carried out by Grimes (11) gave strong indications of other species. A discussion of his findings is desirable since they are novel in the study of 1,10-phenanthroline.

A solution 4.83×10^{-1} $\underline{M}$ in hydrochloric acid was made 6.396×10^{-1} $\underline{M}$ in 1,10-phenanthroline and the resulting solution was titrated with the hydrochloric acid titrant. A quinhydrone-saturated calomel electrode pair was used to follow the course of the titration. Using the starting concentrations of acid and ligand and an average stability constant from the values in the literature for the monoprotonated-1,10-phenanthroline ion, the solubility of 1,10-phenanthroline can be calculated as 1.56×10^{-1} $\underline{M}$. Smith and Richter (33, p. 54) report the solubility of 1,10-phenanthroline as 1.6×10^{-2} $\underline{M}$. The difference in ionic strength is not sufficient to account for a ten-fold increase in solubility. It will also be noted that the ratio of total 1,10-phenanthroline concentration to total hydrogen ion concentration, which is essentially the $\bar{n}$ value of Bjerrum (2), is 1.856 at the beginning of the titration. This is evidence of at least a bis- as well as a mono-(1,10-phenanthroline)hydrogen ion complex.

In order to study the solubility of 1,10-phenanthroline as a function of acid concentration, solutions containing hydrochloric acid in various concentrations were saturated with 1,10-phenanthroline by constant shaking for 24 hours at 25 ± .01° C and at 40 ± .01° C. Aliquots were analyzed for total 1,10-phenanthroline by conductometric titration with hydrochloric acid. A plot of molar solubility vs. acid concentration was linear and had a slope of 2.48 at 25° C and 2.64 at 40° C. The slope of the curve, i.e., the ratio of the molar solubility of 1,10-phenanthroline to the molar concentration of hydrochloric acid, is essentially equal to Bjerrum's $\bar{n}$ value (2). Values of $\bar{n}$ equal to 2.48 or 2.64 imply the presence of at least three complexes, a tris-, a bis-, and a mono-(1,10-phenanthroline)hydrogen ion.

In another series of experiment Grimes titrated saturated solutions of 1,10-phenanthroline with hydrochloric acid. Plots of the data from these titrations show a break in the curve at a mole ratio of one 1,10-phenanthroline to one hydrochloric acid, and another break at the ratio of two moles of ligand to one of acid. The sharpness of the second break increased with increasing total 1,10-phenanthroline concentration. Presumably a break in the curve at a ratio of three moles of 1,10-phenanthroline to one of hydrochloric acid would have been observed had the range of the conductivity bridge in use permitted.

It seems evident from these experiments that at least three 1,10-phenanthroline-hydrogen ion species exist in which the ratios of 1,10-phenanthroline to hydrogen ion are 1:1, 2:1, and 3:1, respectively. A knowledge of their stability constants is necessary in the study of the complexes of metal ions.

Coordination or complex compounds of the alkali metals are relatively rare, as one would expect from their large ionic radii, small electronegativies and high degree of hydration. The effect of these factors on the properties of complexes has been reviewed by Martell and Calvin (23, chapter 5). In studies on the correlations between stability constants and ionization potential, charge and radius of the metal ion, and degree of hydration, it has been found that the stability of complexes decreases with increasing ionic radius, decreasing ionization potential, and increasing degree of hydration. Most of these correlations were made with transition or rare earth elements.

Practically the only work reported thus far on the alkali metal complexes of 1,10-phenanthroline has been the isolation of salts of the complexes. Pfeiffer and Christeleit (26) prepared the perchlorates of mono(1,10-phenanthroline)lithium(I) and bis(1,10-phenanthroline)-sodium(I) from 50% methanol. These white crystalline solids were reported to be soluble in hot water, nitrogenzens, and dioxane. Mono(1,10-phenanthroline)potassium(I) iodide and bis(1,10-phenanthroline)ammonium(I) perchlorate were prepared by Herzog(12). In the study of the stability of the complexes of the alkali metals, Grimes

(11) prepared the perchlorates of the bis(1,10-phenanthroline)-lithium(I) and bis(1,10-phenanthroline)sodium(I) ions. Grimes (10) has also shown spectrophotometric evidence for alkali metal complexes. Schilt and Taylor (30) have prepared bis(1,10-phenanthroline)sodium(I) perchlorate and the perchlorate salt of what the authors believe to be a mixture of the mono- and the bis(1,10-phenanthroline)lithium(I) complexes. Grimes (11) has measured the stability of the 1:1, and 2:1 1,10-phenanthroline complexes of lithium, sodium, and potassium in the first application of the method described in the present work. The attempted determination of the stability of these complexes by Grimes (11) by means of pH measurement, competition with iron (II), and spectrophotometry was unsuccessful because of the very low stability of the complexes.

The literature is replete with the results of studies of the complexes of zinc with 1,10-phenanthroline. Kolthoff *et al*. (16) reported 6.6, 12.15, and 17.0 for log K_1, log K_2, and log K_3, respectively, from partition measurements. These authors also report a value of 6.43 for log K_1, obtained from competition measurements. The symbols K_1, K_2, and K_3 signify the over-all formation constants. McClure (24), using spectrophotometric measurements, gave 6.47, 12.0, and 13.1 for log K_1, log K_2, and log K_3, respectively. By means of experimental conditions in which only the mono complex could form, he obtained K_1. A method of successive approximations was applied to obtain K_2 and K_3. While K_1 and K_2 compare favorably with other values of these constants in the literature, the value of K_3, in the light of other work, bears out the inadequacy of approximation procedures in many cases. Kruse and Brandt (18) obtained a value for log K_2 of 11.62 from ultraviolet spectrophotometry. By a competition method, Irving and Mellor (13) found 6.5, 11.95, and 17.05 for log K_1, log K_2, and log K_3, respectively. The same authors obtained the values 6.4, 12.03, and 17.00 by partition methods.* Yasuda et al. (38) published values for the second and third step-wise formation constants for the zinc complexes. They reported 5.9 and 4.8 for log k_2 and log k_3, respectively. Their results are from pH measurements. Bystroff (4), who also used pH measurements, obtained 6.36, 12.00 and 17.00 for the three over-all log K values. Grimes (11) found 6.58, 12.38, and 17.18.

In their polarographic study of various amine complexes of cadmium, Douglas et al. (5) reported 15.19 for log K_3 and 13.15 for log K_2. The latter value was calculated from data obtained in an alcohol-water solution. Yasuda et al. (38), again reporting only values for the second and third step-wise formation constants, gave 5.2 and 4.2 as the values of log k_2 and

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*Irving, H. and Mellor, D. H., Oxford, England. Stability of 1,10-phenanthroline complexes. Private communication to R. I. Bystroff. 1955.

log k_3. Values obtained by Irving and Mellor* for log K_1, log K_2, and log K_3 are 5.17, 10.0, and 14.3, respectively. These values were determined by partition methods.

The stability constants of the copper-1,10-phenanthroline complexes have been measured by fewer investigators than have those of the zinc complexes, and with considerably poorer agreement between the results reported. Pflaum and Brandt (27), by means of pH measurements, found 6.3, 12.45, and 17.95 for log K_1, log K_2 and log K_3, respectively. It is interesting to note that their application of the method of continuous variations of Vosburg and Cooper (35) gave very clear evidence of only a 2:1 1,10-phenanthroline-copper(II) complex at pH 4, while their titrations for the determination of stability constants showed evidence of the presence of three complexes, a mono-, a bis-, and a tris(1,10-phenanthroline)copper(II) species. The authors state that this situation requires very unusual relationships of stability and color intensity of the species involved. Irving and Mellor** have calculated the values 8.82, 15.39, and 20.41 for log K_1, log K_2, and log K_3 from partition experiments. By a combination of partition and pH measurement methods, Bystroff (4) has obtained two sets

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*Ibid.

**Irving, H. and Mellor, D. H., Oxford, England. Stability of 1,10-phenanthroline complexes. Private communication to R. I. Bystroff. 1955.

of constants. These are 9.15, 15.80 and 21.05; and 9.00, 15.70, and 20.80 for log K_1, log K_2, and log K_3, respectively.

Little work on the 1,10-phenanthroline complexes of cobalt(II) has been reported. Irving and Mellor* have found 7.02, 13.72, and 20.10 for log K_1 and log K_2, and K_3, respectively, by means of a partition method. Margerum** reports log K_3 to be 20.1.

In nearly all determinations of stability constants, alkali metals are present either incidentally or to control ionic strength. Thus the stability constants of the transition metals discussed above should be somewhat in error, depending upon the amount of alkali metal-1,10-phenanthroline complexes present which were not taken into account during the calculations. The presence of the poly(1,10-phenanthroline)-hydrogen species would introduce a similar error. A knowledge of the stability of the alkali metal- and hydrogen-1,10-phenanthroline complexes is necessary for the accurate determination of the stability constants of other metal complexes in solutions in which these species occur.

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*Ibid.

**Margerum, D. W., Lafayette, Indiana. Result of work by J. M. Duncan. Private communication to C. V. Banks. 1958.

THE DETERMINATION OF STABILITY CONSTANTS OF COMPLEXES BY CONVENTIONAL MEANS

Introduction

A great change in emphasis in research on complex compounds has occurred in the last few years. Formerly, new complexing agents were investigated on a qualitative basis for use in analytical determinations. Recently, studies on the nature of the complexes themselves and the equilibria involved in their formation have been made, with stress on the stability constants of the complexes and the use of these stability constants in designing new separations and determinations of ions. Martell and Calvin (23, p. 76) and Sullivan and Hindman (34) have reviewed and summarized the approaches to measuring stability constants. The success of a particular method in the study of a metal complex system is greatly a function of that particular system.

Regardless of the means of measurement used, the mathematics involved, or the metal complex system itself, some generalizations may be made which pertain to any metal complex system.

In a solution containing a metal salt, MX, a ligand, L, and an acid, HA, the following reactions may take place:

a) $MX \rightleftharpoons M^+ + X^-$ Eq. (1)

b) $HA \rightleftharpoons H^+ + A^-$ Eq. (2)

c) $H^+ + L \rightleftharpoons HL^+$ Eq. (3)

d) $H^+ + HL^+ \rightleftharpoons H_2L^{++}$ Eq. (4)

e) $HL^+ + L \rightleftharpoons HL_2^+$ Eq. (5)

f) $HL^+_{(i-1)} + L \rightleftharpoons HL_i^+$ Eq. (6)

g) $M^+ + L \rightleftharpoons ML^+$ Eq. (7)

h) $ML^+ + L \rightleftharpoons ML_2^+$ Eq. (8)

i) $ML^+_{(i-1)} + L \rightleftharpoons ML_i^+$ Eq. (9)

The stability constants for these reactions may be determined as follows:

$$K_i = k_1k_2k_3----k_i = (ML_i^+)/(M^+)(L)^i \qquad \text{Eq. (10)}$$

$$k_i = (ML_i^+)/(ML_{(i-1)}{}^+)(L) \qquad \text{Eq. (11)}$$

$$K_{ai} = k_{a1}k_{a2}k_{a3}----k_{ai} = (HL_i^+)/(H^+)(L)^i \qquad \text{Eq. (12)}$$

The various constants may be named as follows: K_i is the over-all formation constant of the i-th complex and k_i is the step-wise formation constant of the i-th complex. The subscript a refers to the special case of the hydrogen-ligand formation constants.

Expressions for the known analytical concentrations of the metal ion, ligand, and hydrogen ion may be given as follows:

$$(M)_t = (M^+) + \sum_{i=1}^{I} (ML_i^+) \qquad \text{Eq. (13)}$$

$$(L)_t = (L) + \sum_{i=1}^{I} i(ML_i^+) + \sum_{i=1}^{I} i(HL_i^+) \qquad \text{Eq. (14)}$$

$$(H)_t = (H^+) + \sum_{i=1}^{I} (HL_i^+) \qquad \text{Eq. (15)}$$

where t refers to total. Upon substitution of the proper values from the stability equations for ML_i^+ and HL_i^+, the following equations can be derived:

$$(M^+)_t = (M^+) \left[1 + \sum_{i=1}^{I} K_i (L)^i \right] \qquad \text{Eq. (16)}$$

$$(L)_t = (L) + (M^+) \left[\sum_{i=1}^{I} i\, K_i (L)^i \right] + (H^+) \left[\sum_{i=1}^{I} i\, K_{ai} (L)^i \right] \qquad \text{Eq. (17)}$$

$$(H^+)_t = (H^+) \left[1 + \sum_{i=1}^{I} K_{ai} (L)^i \right] \qquad \text{Eq. (18)}$$

In a system containing only ligand and hydrogen ions, the concentration of hydrogen ions, (H^+), can be eliminated from Eq. (17) and Eq. (18) as follows:

$$\bar{n} = \frac{(L)_t - (L)}{(H)_t} = \frac{\sum_{i=1}^{I} i\, K_{ai} (L)^i}{1 + \sum_{i=1}^{I} K_{ai} (L)^i} \qquad \text{Eq. (19)}$$

When metal ions are also present the concentration of free metal ion, (M^+), can be eliminated from Eq. (16) and Eq. (17) as follows:

$$\bar{n} = \frac{(L)_t - (L) - (H^+)\left(1 + \sum_{i=1}^{I} i\, K_{ai}\, (L)^i\right)}{(M^+)_t}$$

$$= \frac{\sum_{i=1}^{I} i\, K_i\, (L)^i}{1 + \sum_{i=1}^{I} K_i (L)^i} \qquad \text{Eq. (20)}$$

The term $\bar{n}$ represents the average number of ligands bound to each central entity.

Therefore, from a knowledge of the total analytical concentrations of ligand and metal ion, and a measurement related unambiguously to the concentration of one of the other species involved, $\bar{n}$ may be calculated. From a sufficient number of these values of $\bar{n}$, which have been determined under appropriate conditions, and the corresponding values of the free ligand concentration, (L), the stability constants of the species involved may be calculated.

Methods of Measurement

pH Measurement

According to Martell and Calvin (23, p. 78), the potentiometric method of measuring hydrogen ion concentration is probably the most accurate and reliable method for determining the stability constants of complexes. The general method was first described by Bjerrum (2), and since then, titrimetric methods, and the concept of the formation function, $\bar{n}$, have been extensively employed in the determination of stability constants of complexes of all types. The method consists essentially of measuring the number of protons released by the ligand when it complexes the metal. If the proton-ligand complex stability constants are known this becomes a measure of the amount of ligand complexed, and $\bar{n}$ can therefore be calculated. The free ligand concentration is derivable from the known concentration of uncomplexed ligand and the pH of the solution. Experimentally this is accomplished by titration with base of an acidic solution of the ligand of known concentration, followed by a similar titration of the ligand with a known quantity of metal present in the solution. Providing the ligand is present in sufficient excess, the degree of association of protons with the ligand will not be altered, and the difference in the amount of base required to reach the same pH in the two titrations corresponds to the amount of ligand complexed with the metal. The accuracy of pH measurement is the principal limitation of the method. For very strong complexes the pH must be quite low to insure only partial complex formation, while for weak complexes, the pH, the total ligand concentration, and the total metal concentration must be relatively high to insure a sufficient degree of complex formation. In both cases it is possible that changes in pH are of the same order of magnitude as the error in the determination of pH. Bystroff (4) has been able to measure the stability constants of some strong transition metal-1,10-phenanthroline complexes with the aid of the Beckman Model GS pH meter, which is capable of measuring pH changes as small as 0.003 unit. Grimes (11) found that even with the use of this meter he was unable to measure the stability constants of alkali metal-1,10-phenanthroline complexes accurately.

Spectrophotometric equilibrium

The quantitative relationship between absorbancy and concentration makes spectrophotometric measurements very useful means for stability measurements. This is especially true for metal complexes for which a wave length can be found where the complex species absorbs appreciably but the ligand absorption is negligible. The iron(II)-1,10-phenanthroline complexes are good examples. The iron complexes absorb greatly in the visible region of the spectrum, while the ligand absorbs only in the ultraviolet region. Most metal complexes of the 1,10-phenanthroline show spectra which are only slightly different from that of the free ligand. In cases like this stability constants can be determined fairly readily if one can be assured that only two species, the free ligand and one complex, exist in a given solution. The formation of only a mono(1,10-phenanthroline) metal complex can generally be assured if a large excess of metal ion over the ligand is present. Under these conditions, the formation constant of the mono complex can be calculated, and, if the successive constants differ by a factor of one hundred or more, they may be determined in a similar manner. Since this ideal condition is seldom true in 1,10-phenanthroline complexes, a tedious technique of successive approximations with very accurate data is necessary. Such a technique was used by McClure (24) in his study of zinc-1,10-phenanthroline complexes.

Partition

The use of partition methods in the measurement of stability constants has been discussed by Irving and Williams (14) and applied to 1,10-phenanthroline complexes by Irving and Mellor*, Kolthoff *et al*. (16), and Bystroff (4). While this method becomes very complex if more than one species distributes itself between the solvents used, it is especially useful if only the ligand tends to distribute. In the case of transition metal-1,10-phenanthroline complex systems, only the free 1,10-phenanthroline can be extracted into the non-aqueous solvent, because it is the only uncharged species.

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*Irving, H. and Mellor, D. H., Oxford, England. Stability of 1,10-phenanthroline complexes. Private communication to R. I. Bystroff. 1955.

An independent experiment determines the partition coefficient of the free ligand, and its value establishes the free ligand concentration in the solution of metal complexes by measurement of the free ligand in the extractive solvent. The amount of complexed ligand is found from the total moles of ligand, the amount of ligand in the extractive solvent, the partition coefficient, and the pH of the metal solution. By varying the total moles of ligand in the system the whole formation curve may be calculated, and the stability constants determined.

In practice the method suffers from several limitations. Ion pair formation, which has been observed in 1,10-phenanthroline systems by Grimes (10) can seriously impair the interpretation of the data. The partition coefficient is a function of both ionic strength and the solubility of the free ligand in each phase. The ionic strength may be controlled, but the very high concentrations of free ligand required to insure measurable complex formation with metals forming very weak complexes are, if attainable at all, subject to considerable error in their measurement. In the case of alkali metal complexes the upper portion of the $\bar{n}$ curve cannot be obtained by this method, and the lower part of the curve is subject to large errors. In 1,10-phenanthroline systems, both the free ligand and the complexes of most metals absorb only in the ultraviolet region, so solvents must be chosen which show little or no absorption in this region, and tedious procedures to prepare and store spectrally pure solvents are necessary. Other factors, such as photochemical decomposition of the solvent, formation of emulsions, absence of side reactions and availability must, of course, be considered.

Competition

Kolthoff *et al.* (16), Irving and Mellor (13), and Bystroff (4) have used the competition of various metals with iron for the available 1,10-phenanthroline for the measurement of stability constants of complexes of these metals. In this method the absorbancy at 510 mμ due to the iron complex is reduced by the presence of the other metal. In principle, the method consists of the following steps:

1. A solution of known iron(II) concentration and known 1,10-phenanthroline concentration is prepared, and the absorbancy is read.
2. A known amount of a second metal is added to this solution. The absorbancy will be lowered, indicating dissociation of the iron complex due to competition.
3. 1,10-phenanthroline is added to the solution until the original absorbancy is again attained. It is assumed that no volume change occurs in these steps, and that the pH does not change.

Because the absorbancy of the initial and final solutions is the same, it is known that the concentrations of iron complexes must be the same, and therefore, the free 1,10-phenanthroline concentration is also the same in these solutions. From the known stability constants of the iron complexes, the free ligand concentration can be calculated. The amount of 1,10-phenanthroline added in step 3 is equal to the amount complexed with the second metal added in step 2. The ratios of these two amounts is $\bar{n}$, and one point on the formation curve has been calculated. Other points may be obtained by starting with different initial absorbancies, the iron concentration being held constant.

The most important limitation of the method is that only a small section of the formation curve can be obtained, specifically, that portion lying between free 1,10-phenanthroline concentrations of 2×10^{-8} $\underline{M}$ and 2×10^{-7} $\underline{M}$. This portion has little usefulness for calculating stability constants except under very specific conditions. Because the study of the weak alkali metal-1,10-phenanthroline complexes requires a high concentration of free ligand to insure measurable complex formation as well as the availability of a metal complex the stability of which is known and within a few orders of magnitude of the stability of the complex under study, the competition method is not applicable to the study of weak metal-1,10-phenanthroline complexes.

Other methods

Kinetic measurements have been used by Lee et al. (20) to determine the over-all stability constant of the tris(1,10-phenanthroline)iron(II) complex, by Margerum et al. (22) to study the nickel(II) system of 1,10-phenanthroline, and by Margerum and Banks(21) to study the 1,10-phenanthroline complexes of vanadium, chromium, manganese, and nickel. Polarographic methods have enabled Douglas et al. (5) to study the cadmium complexes of 1,10-phenanthroline.

Use of Silver/Bis(1,10-phenanthroline)Silver(I) Nitrate Electrode

Grimes (11) has attempted to apply conventional means to the determination of the stability constants of alkali metal-1,10-phenanthroline complexes. The inability of these methods to measure stability constants of these very weak complexes led to the development of a method using a silver/bis(1,10-phenanthroline)silver(I) nitrate electrode.

APPARATUS AND REAGENTS

Potentiometric and pH measurements were made with a Beckman Model GS pH meter. Conductometric measurements were made with a Leeds and Northrup Model No. 4866 conductivity bridge.

Anhydrous 1,10-phenanthroline obtained from the Aldrich Chemical Company, Milwaukee, Wisconsin, was recrystallized twice from a benzene-petroleum ether mixture with decolorization by means of activated charcoal, and twice from water. The purity was then determined by conductometric titration with nitric acid.

All inorganic chemicals were of reagent-grade quality. Lithium wire from the Lithium Corporation of America, Minneapolis, Minnesota, was used in making up the lithium solution.

Class A glassware was used for all measurements.

A Beckman double junction sleeve-type saturated calomel electrode whose outer sleeve was filled with saturated potassium nitrate was used as a reference electrode.

Calculations of stability constants were made with the aid of an IBM 650 electronic digital computor. The programming system used was a floating decimal interpretive system designed by Wolontis (36).

DETERMINATION OF STABILITY CONSTANTS OF METAL-1,10-PHENANTHROLINE COMPLEXES WITH THE SILVER/BIS(1,10-PHENANTHROLINE)SILVER(I) NITRATE ELECTRODE

Introduction

The methods previously discussed are adequate for the determination of the stability constants of metal-1,10-phenanthroline complexes of relatively great stability, but, for the reasons given above, cannot be used for the study of the stability of weak complexes. A method which would measure the free 1,10-phenanthroline directly over a wide concentration range would find wide application in the measurement of stability constants of both weak and strong complexes. An electrode responding to the concentration of 1,10-phenanthroline would furnish a rapid, easy, and accurate technique.

Schmid and Reilley (31) and Schwarzenbach and Anderegg (32) have used a mercury electrode to determine the stability constants of metal complexes of ethylenedinitrilotetraacetic acid (EDTA). The method is one involving competition between mercury ions and the metal ions forming the complex with EDTA the stability of which is being studied. The method is rapid and simple mathematically, at least in the study of metal complexes where the ligand-metal ratio is 1:1, as is the case with EDTA complexes.

Because of a lack of knowledge of mercury-1,10-phenanthroline complexes, and the insolubility of bis(1,10-phenanthroline)silver(I) nitrate which promised a simplification of the mathematics involved, Grimes (11) chose silver as a suitable electrode metal.

Reaction of silver(I) with 1,10-phenanthroline

Pfeiffer and Christeleit (26) have prepared bis(1,10-phenanthroline)silver(I) nitrate, Schilt and Taylor(30) the perchlorate salt. Fortune and Mellon (7) have observed the interference by silver ion in the iron(II) determination with 1,10-phenanthroline.

In this work the reaction of silver(I) with 1,10-phenanthroline was studied by means of potentiometric titrations.

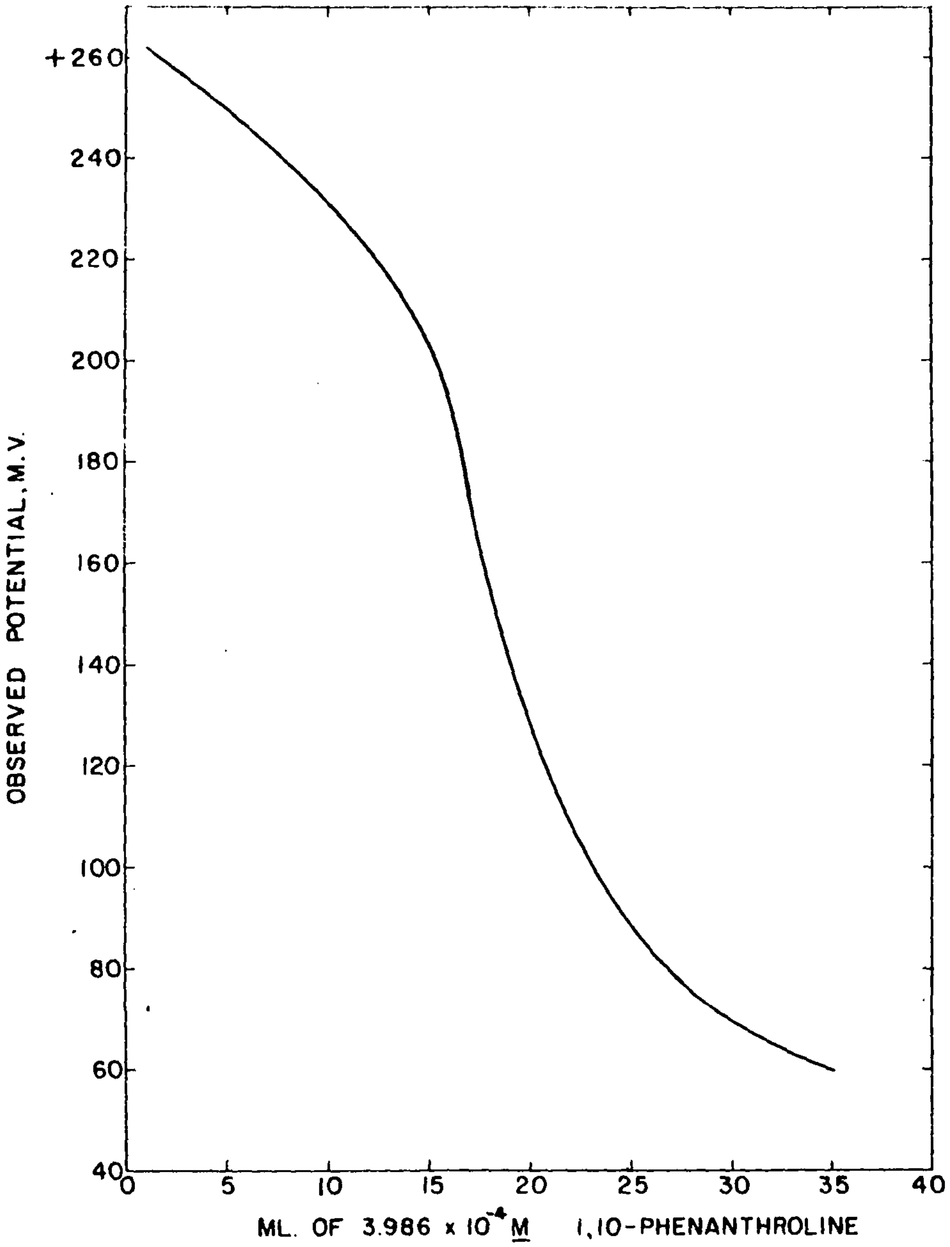
Twenty five ml. of a 1.142×10^{-4} M. silver nitrate solution was titrated with a 3.956×10^{-4} M 1,10-phenanthroline solution. A silver-saturated calomel electrode pair was used to follow the titration. The saturated calomel electrode was of the double junction sleeve type, with saturated potassium nitrate in the outer sleeve. A yellow precipitate formed shortly after the titration was begun. The data is shown in Table 1 and Fig. 1.

A 1.033×10^{-3} M. silver sulfate solution was titrated with 1.943×10^{-3} M. 1,10-phenanthroline using the same electrode system. In this case no precipitate formed. Data

Table 1. Titration of 25 ml. of 1.142 x 10^{-4} M. silver nitrate with 3.986 x 10^{-4} M. 1,10-phenanthroline. E^{o}ref. = +0.300v. pH at end of titration = 5.58

Vol. titrant, ml.	Observed E, v.	Vol. titrant, ml.	Observed E, v.
0	+0.265	16.5	+0.186
1.0	+0.262	17.0	+0.170
2.0	+0.260	17.7	+0.160
3.0	+0.256	18.0	+0.153
4.0	+0.253	18.5	+0.145
5.0	+0.250	19.0	+0.140
6.0	+0.245	20.0	+0.128
7.0	+0.243	21.0	+0.119
8.0	+0.240	22.0	+0.110
9.0	+0.235	23.0	+0.101
10.0	+0.230	24.0	+0.095
11.0	+0.227	25.0	+0.087
12.0	+0.222	27.0	+0.078
13.0	+0.215	29.0	+0.075
14.0	+0.209	32.0	+0.065
15.0	+0.202	35.0	+0.060
16.0	+0.193		

Fig. 1. Titration of 25 ml. of 1.142 x 10^{-4} M. silver nitrate with 3.986 x 10^{-4} M. 1,10-phenanthroline


OBSERVED POTENTIAL, M.V.
+260
240
220
200
180
160
140
120
100
80
60
40
0
5
10
15
20
25
30
35
40
ML. OF 3.986 x 10^{-4} M 1,10-PHENANTHROLINE

is shown in Table 2 and Fig. 2.

No indication of the formation of a tris(1,10-phenanthroline)silver(I) species was seen in the titration curves, and there was no break in the curves to indicate the formation of the mono(1,10-phenanthroline)silver(I) species, indicating the mono(1,10-phenanthroline)silver(I) complex is much less stable than the bis(1,10-phenanthroline)silver(I) complex, and the tris species is weak or nonexistent.

Grimes (11) analyzed the precipitate obtained in a silver nitrate titration by dissolving a weighed, purified sample in sulfuric acid and measuring the absorbancy at 272 mu due to the mono-protonated-1,10-phenanthroline)silver(I) nitrate. Richard* investigated the possibility of using the precipitation of the compound as a gravimetric method for silver and nitrate. Difficulty in filtering the precipitate and interference by many anions and cations are severe handicaps, though the method is quantitative.

The over-all stability constant for the bis(1,10-phenanthroline)silver(I) complex and the solubility product of the bis(1,10-phenanthroline)silver(I) nitrate were calculated from the preceding titrations as follows.

Because the bis(1,10-phenanthroline)silver(I) complex is of much greater stability than the mono(1,10-phenanthro-

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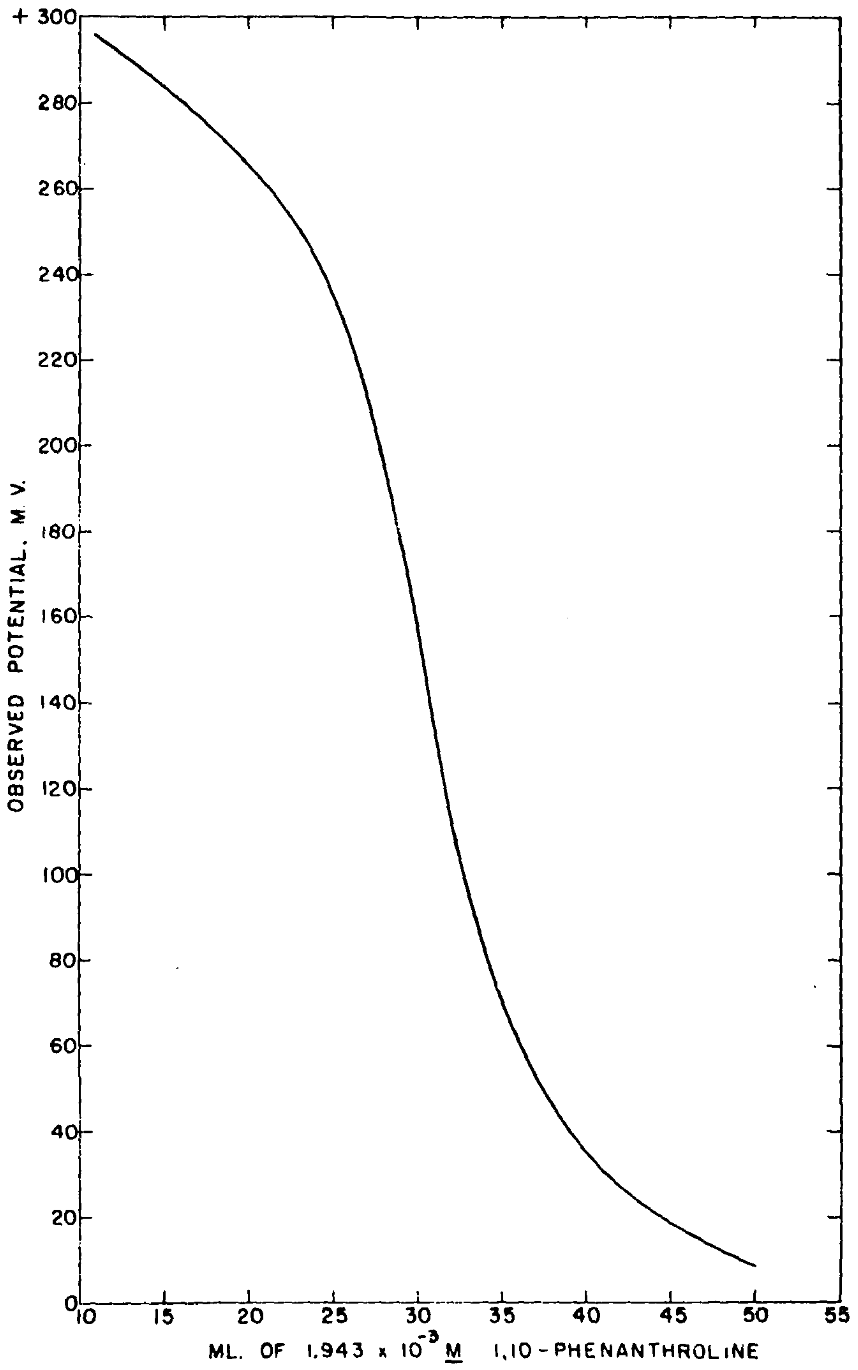
*Richard, J., Ames, Iowa. Determination of silver and nitrate. Private communication. 1958.

Table 2. Titration of 25 ml. of 1.033×10^{-3} M. silver sulfate with 1.943×10^{-3} M. 1,10-phenanthroline. E^o ref. = +0.300v. pH at end of titration = 5.77

Vol. titrant, ml.	Observed E, v.	Vol. titrant, ml.	Observed E, v.
0	+0.323	29.0	+0.174
1.0	+0.318	29.5	+0.165
2.0	+0.315	30.0	+0.153
5.0	+0.310	30.5	+0.147
8.0	+0.302	31.0	+0.135
11.0	+0.296	31.5	+0.120
13.0	+0.290	32.0	+0.110
15.0	+0.283	33.0	+0.092
17.0	+0.276	34.0	+0.081
19.0	+0.270	35.0	+0.069
21.0	+0.262	36.0	+0.060
23.0	+0.250	37.0	+0.053
24.0	+0.243	38.0	+0.045
25.0	+0.236	39.0	+0.040
26.0	+0.225	40.0	+0.034
26.5	+0.220	41.0	+0.030
27.0	+0.211	43.0	+0.025
27.5	+0.203	45.0	+0.020
28.0	+0.194	47.0	+0.013
28.5	+0.184	50.0	+0.009

Fig. 2. Titration of 25 ml. of 1.033 x 10^{-3} M. silver sulfate with 1.943 x 10^{-3} M. 1,10-phenanthroline


+ 300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
OBSERVED POTENTIAL, M V.
10
15
20
25
30
35
40
45
50
55
ML. OF 1.943 x 10^{-3} M 1,10-PHENANTHROLINE

line)silver(I) species, it may be assumed that all the 1,10-phenanthroline after the equivalence point in the silver sulfate titration is in the form of uncomplexed ligand, the mono(1,10-phenanthroline)hydrogen(I) species, and the bis(1,10-phenanthroline)silver(I) complex. Such a system can be described by the following equations:

$$K_{2S} = \frac{(AgP_2^+)}{(Ag^+)(P)^2} \qquad \text{Eq. (21)}$$

$$(P)_t = (P) + (PH^+) + 2(AgP_2^+) \qquad \text{Eq. (22)}$$

$$(Ag)_t = (Ag^+) + (AgP_2^+) \qquad \text{Eq. (23)}$$

If equations 21, 22, and 23 are combined one may write

$$K_{2S} = \frac{(Ag)_t - (Ag^+)}{(Ag^+)\left\{\dfrac{(P)_t - 2\left[(Ag)_t - (Ag^+)\right]}{1 + k_{a1}\ (H^+)}\right\}^2} \qquad \text{Eq. (24)}$$

The uncomplexed silver ion concentration is measured with the silver electrode, the total 1,10-phenanthroline and silver concentrations are known, and the pH is known, so K_2 can readily be calculated. The value obtained by this method is $10^{11.42}$.

The conditions which obtain after the equivalence point in the silver nitrate titration can be described by the following equations:

$$(P)_t = (P) + (PH^+) + 2(AgP_2^+) + (AgP_2NO_3) \qquad \text{Eq. (25)}$$

$$(NO_3^-) = (AgP_2^+) + (Ag^+) \cong (AgP_2^+) \qquad \text{Eq. (26)}$$

$$K_{sp} = (AgP_2^+)\ (NO_3^-) \qquad \text{Eq. (27)}$$

Upon rearrangement of equation 25, and combination of the three equations one obtains

$$K_{sp} = \left\{ K_{2S}(Ag^+) \left[\frac{(P)_t - 2\ K_2(Ag^+)\ (P)^2}{1 + k_{a1}(H^+)} \right]^{\cancel{2}} \right\}^2 \qquad \text{Eq. (28)}$$

The uncomplexed silver ion concentration was again measured with a silver electrode and K_{sp} was calculated to be $10^{-8.49}$.

Silver/bis(1,10-phenanthroline)silver(I) nitrate electrode

The competition of silver ions and ions of another metal can be used to determine the strength of the metal-1,10-phenanthroline complexes. The insolubility of the bis(1,10-phenanthroline)silver(I) nitrate simplifies the mathematics required. Such a system may be defined by the following equations:

$$(M)_t = (M^+) + \sum_{i=1}^{I} (MP_i^+) \qquad \text{Eq. (29)}$$

$$(Ag^+)_t = (Ag^+) + \sum_{i=1}^{I} (AgP_i^+) \qquad \text{Eq. (30)}$$

$$(H^+)_t = (H^+) + \sum_{i=1}^{I} (HP_i^+) \qquad \text{Eq. (31)}$$

$$(P)_t = (P) + \sum_{i=1}^{I} i(MP_i^+) + \sum_{i=1}^{I} i(AgP_i^+) + \sum_{i=1}^{I} i(HP_i^+) \qquad \text{Eq. (32)}$$

$$K_{sp} = (AgP_2^+)\ (NO_3^-) \qquad \text{Eq. (33)}$$

$$k_{1M} = \frac{(MP^+)}{(M^+)(P)} \qquad \text{Eq. (34)}$$

$$k_{iM} = \frac{(MP_i)}{(MP^+_{i-1})\ (P)} \qquad \text{Eq. (35)}$$

$$k_{1S} = \frac{(AgP^+)}{(Ag^+)\ (P)} \qquad \text{Eq. (36)}$$

$$k_{2S} = \frac{(AgP_2^+)}{(AgP^+)\ (P)} \qquad \text{Eq. (37)}$$

$$k_{1a} = \frac{(HP^+)}{(H^+)\ (P)} \qquad \text{Eq. (38)}$$

$$k_{2a} = \frac{(HP_2^+)}{(HP^+)\ (P)} \qquad \text{Eq. (39)}$$

$$k_{3a} = \frac{(HP_3^+)}{(HP_2^+)\ (P)} \qquad \text{Eq. (40)}$$

The subscript t refers to total.

Combining Eq. 33, Eq. 36, and Eq. 37, the following is obtained:

$$(Ag^+) = \frac{K_{sp}}{k_{1S}k_{2S}\ (P)^2\ (NO_3^-)} \qquad \text{Eq. (41)}$$

If activities are considered this equation becomes

$$a_{Ag^+} = \frac{K_{sp}}{K_{2S}\ (P)^2\ a_{NO_3^-}} \qquad \text{Eq. (42)}$$

At low concentrations the activity coefficient of a neutral molecule may be considered to be unity.

A combination of the Nernst equation for a silver electrode

$$E = E^o{}_{Ag^+/Ag} + .059 \log a_{Ag^+} \qquad \text{Eq. (43)}$$

with Eq. (42) gives

$$E = E^o{}_{Ag^+/Ag} + .059 \log \frac{K_{sp}}{K_{2S}\ (P)^2\ a_{NO_3^-}} \qquad \text{Eq. (44)}$$

Thus by the use of a silver-reference electrode pair the concentration of the free ligand can be calculated from the potential observed if the activity of the nitrate ion and the solubility product and stability constants are known for the silver species. Stability constants of the metal-1, 10-phenanthroline complexes may be calculated from the concentration of free 1,10-phenanthroline, the total 1,10-phenanthroline concentration, the total metal concentration, the pH, and the total buffer metal concentration. The insolubility of the bis(1,10-phenanthroline)silver(I) nitrate would make the concentrations of the bis(1,10-phenanthroline)-silver(I) and the mono(1,10-phenanthroline)silver(I) complexes negligible so that these species could be ignored.

Equation 44 indicates that when solid bis(1,10-phenanthroline)silver(I) nitrate is present in the solution being studied, the potential of the silver-reference electrode pair is a function of the free 1,10-phenanthroline in solution. In this work the solid was present in the form of a coating on the silver electrode. The addition of solid bis(1,10-phenanthroline)silver(I) nitrate directly to the solution being investigated would accomplish the same end.

The coating is deposited on the silver electrode in a manner similar to that used in making silver-silver halide electrodes. If the reaction

$$AgP_2NO_3 + e \rightleftharpoons Ag + 2P + NO_3^- \qquad \text{Eq. (45)}$$

is considered for this electrode, an electrode equation

$$E = E^o_{AgP_2NO_3/Ag} + .059 \log \frac{1}{(P)^2 a_{NO_3^-}} \qquad \text{Eq. (46)}$$

is obtained. When such an electrode is combined with a reference electrode, the potential observed is a function of the free 1,10-phenanthroline concentration.

Calculation of the working potential

By combination of the constant terms in Eq. 44, a working potential for the silver/bis(1,10-phenanthroline)-silver(I) nitrate (Ag/AgP_2NO_3) electrode was obtained. The value calculated was -0.378 volt vs. saturated calomel electrode.

Preparation and response of the electrode

The bis(1,10-phenanthroline)silver(I) nitrate electrode was prepared according to the following procedure. A Beckman billet type silver electrode was cleaned with wet scouring powder, rinsed and dried, polished with dry scouring powder, rinsed and dried, and polished further with a clean dry cloth. A platinum flag electrode was cleaned in dilute nitric acid. The silver electrode was connected to the positive terminal of a 1.5 volt battery, and the platinum electrode to the negative terminal. The electrodes were then dipped into a 1×10^{-3} $\underline{M}$. potassium nitrate solution which had been saturated with 1,10-phenanthroline. An electrolysis time of about 45 minutes produced an adherent layer of the yellow bis(1,10-phenanthroline)silver(I) nitrate.

The concentrations of the 1,10-phenanthroline and potassium nitrate, and the electrolysis voltage are important.

If either reagent concentrations or the voltage are too low, the electrolysis becomes extremely slow. If the potassium nitrate concentration is made much greater than 1 x 10^{-3} M., a white, gelatinous material forms on the silver electrode.

To test the response of the electrode to free 1,10-phenanthroline concentration the following experiment was carried out. A portion of a solution approximately 1 x 10^{-4} M. in potassium nitrate and buffered at pH 9.2 with potassium hydroxide-boric acid buffer was made about 2 x 10^{-2} M. in 1,10-phenanthroline and this solution was titrated with more of the potassium nitrate. Purified nitrogen gas was bubbled through the solution throughout the titration. The course of the titration was followed with a silver/bis (1,10-phenanthroline)silver(I) nitrate-saturated calomel electrode pair. Since the total 1,10-phenanthroline concentration was about one hundred times as great as the total potassium ion concentration, the free ligand concentration was essentially equal to the total ligand concentration, and Eq. 46 could be written

$$E = E^{o}_{AgP_2NO_3/Ag} + .0591 \log \frac{1}{(P)_t^{2} a_{NO_3^-}} \qquad \text{Eq. (47)}$$

Because the activity of the nitrate ion was kept constant, the constant terms could be combined and a plot of the observed potential vs. the total 1,10-phenanthroline concentration yielded a straight line the slope of which averaged, for nine determinations, 0.119 volt. The theoretical slope is 0.1183 volt.

Reversibility of the electrode

The reversibility of the electrode was studied by two methods. The first method used was that described by Glasstone (9, p. 184). The cell containing a metal-1,10-phenanthroline solution and the Ag/AgP_2NO_3 saturated calomel electrode pair was connected to a potentiometer so the potential of the cell opposed the potential of the slidewire. In place of the usual null-detecting galvanameter a vacuum tube electrometer capable of measuring currents as small as 10^{-10} amperes was placed in the circuit. The potential developed by the cell was balanced by the battery-slidewire circuit ("working circuit") of potentiometer. A current flow resulted when the potential developed by the working circuit was changed in either direction by as much as 5% of the balance potential. The current which flowed was (1 to 2) x 10^{-10} amperes.

Another method used to check the reversibility of the electrode was suggested by Duke*.

In a reversible cell at equilibrium the current flowing

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*Duke, F. R., Ames, Iowa. Reversibility of electrodes. Private communication. 1959.

in one direction is balanced by the current flowing in another direction, or, in other words, there is no net current flow. Such an equilibrium could be described by the following equation:

$$kS_a = k'S_a' \qquad \text{Eq. (48)}$$

where k and k' are constants and S_a and S_a' are functions of the surface area of the electrodes. In an actual system, there may be some net current flow, necessitating the modification of equation 48 as follows

$$kS_a = k'S_a + k''I \qquad \text{Eq. (49)}$$

where the k"I term represents a flow of current in some direction. If the cell is connected to a potentiometer in the usual manner a balance can be attained. If, however, a variable external resistance is placed in series with the cell, the balance potential will change according to the amount of resistance. Beyond some value of the resistance, however, the balance potential will be unaffected by further increases in the value of the resistance. At this point the cell can be said to be reversible. It follows that the lower the value of this external resistance when reversibility is attained the more reversible the cell.

To carry out the experiment the same circuit was used as in the previous experiment except that a large variable resistance was connected in series with the cell under investigation. After the circuit was balanced with no external resistance the resistance was varied in steps from 0 to 45 megohms, with balancing of the potentiometer after each increase. No change in balance potential was observed when the external resistance was changed from zero to 45 megohms.

Both the above experiments indicate the cell, and therefore the silver bis(1,10-phenanthroline)silver(I) nitrate electrode, is reversible.

Application of the Silver/Bis(1,10-Phenanthroline)-Silver(I) Nitrate Electrode to the Determination of Stability Constants

The method proposed would be of maximum usefulness if it could be used in studying complexes over a wide range of stability. One would expect the complexes of the alkali metals of 1,10-phenanthroline to be weak; the complexes of the transition metals are relatively strong, and can be measured by conventional means. Some of these metals were studied to serve as a check on the reliability of the method, as well as to demonstrate the range of stability constants which can be determined by the method.

Stability constants of the 1,10-phenanthroline-hydrogen(I) complexes

A portion of 1,10-phenanthrdine was dissolved in 25 ml. of the nitric acid titrant solution, and the resulting solution was titrated with the nitric acid titrant. This means of titration was used in order to maintain a constant ionic strength, constant nitrate ion activity, and in the case of later titrations with metal solutions, constant pH, total metal concentration, and total buffer concentration. This method of titration was employed in all titrations involving the determination of stability constants. The titration was followed with the Ag/AgP_2NO_3-saturated calomel electrode system. Data from all titrations are presented in Tables 3 through 5. Results are in Table 26.

Stability constants of the 1,10-phenanthroline-alkali metal complexes

In the determinations of the stability constants of lithium(I)-, sodium(I)-, and potassium(I)-1,10-phenanthroline complexes the alkali metal nitrate solution was buffered at about pH 9.2 with an alkali metal borate-boric acid buffer, and purified nitrogen gas was bubbled through the solutions during the titrations. The presence of hydrogen ion complexes was taken into consideration in making calculations. All titration data are shown in Tables 6 through 14. Results are in Table 26.

Table 3. Titration of 1,10-phenanthroline in nitric acid with nitric acid[a]

Vol. titrant, ml.	Observed E (v.)	Vol. titrant, ml.	Observed E (v.)
0	-0.136	56.0	+0.008
3.0	-0.130	59.0	+0.020
5.0	-0.127	62.0	+0.030
7.0	-0.124	65.0	+0.038
10.0	-0.118	68.0	+0.046
13.0	-0.114	72.0	+0.054
16.0	-0.108	76.0	+0.061
19.0	-0.102	80.0	+0.067
22.0	-0.097	85.0	+0.075
25.0	-0.090	90.0	+0.081
28.0	-0.084	95.0	+0.085
31.0	-0.077	100.0	+0.092
35.0	-0.069	110.0	+0.101
39.0	-0.058	125.0	+0.110
43.0	-0.048	150.0	+0.122
46.0	-0.037	175.0	+0.132
50.0	-0.018	200.0	+0.140
53.0	-0.003		

[a] A portion of the titrant solution (1.014×10^{-2} M. in HNO_3) was made 2.991×10^{-2} M. in 1,10-phenanthroline and the resulting solution was titrated with the titrant. Activity coefficient of the nitrate ion taken as 0.90.

Table 4. Titration of 1,10-phenanthroline in nitric acid with nitric acid[a]

Vol. titrant, ml.	Observed E (v.)	Vol. titrant, ml.	Observed E (v.)
0	-0.144	59.0	+0.018
3.0	-0.140	62.0	+0.028
5.0	-0.138	65.0	+0.038
8.0	-0.132	68.0	+0.047
11.0	-0.128	71.0	+0.053
14.0	-0.122	75.0	+0.060
17.0	-0.117	80.0	+0.068
20.0	-0.110	85.0	+0.074
23.0	-0.102	90.0	+0.080
25.0	-0.098	95.0	+0.085
30.0	-0.086	100.0	+0.090
35.0	-0.075	110.0	+0.099
40.0	-0.062	120.0	+0.106
45.0	-0.047	135.0	+0.116
50.0	-0.022	150.0	+0.123
53.0	-0.008	175.0	+0.133
56.0	+0.008	200.0	+0.140

[a] A portion of the titrant solution (1.014×10^{-2} M. in HNO_3) was made 2.991×10^{-2}M. in 1,10-phenanthroline and the resulting solution was titrated with the titrant. Activity coefficient of the nitrate ion taken as 0.90.

Table 5. Titration of 1,10-phenanthroline in nitric acid with nitric acid[a]

Vol. titrant, ml.	Observed E (v.)	Vol. titrant, ml.	Observed E (v.)
0	-0.161	67.0	+0.042
3.0	-0.155	70.0	+0.051
5.0	-0.152	73.0	+0.056
7.0	-0.148	77.0	+0.062
10.0	-0.141	80.0	+0.068
15.0	-0.132	85.0	+0.075
20.0	-0.119	90.0	+0.081
25.0	-0.106	95.0	+0.086
30.0	-0.094	100.0	+0.092
35.0	-0.081	110.0	+0.100
40.0	-0.068	120.0	+0.107
45.0	-0.052	135.0	+0.117
50.0	-0.023	150.0	+0.124
55.0	0.000	170.0	+0.132
58.0	+0.011	185.0	+0.138
61.0	+0.024	200.0	+0.142
64.0	+0.033		

[a] A portion of the titrant solution (1.014×10^{-2} M. in HNO_3) was made 2.991×10^{-2} M. in 1,10-phenanthroline and the resulting solution was titrated with the titrant. Activity coefficient of the nitrate ion taken as 0.90.

Table 6. Titration of 1,10-phenanthroline in lithium nitrate with lithium nitrate[a]

Vol. titrant, ml.	Observed E (v.)	Vol. titrant, ml.	Observed E (v.)
0	-0.192	60.0	-0.137
5.0	-0.185	70.0	-0.131
10.0	-0.179	80.0	-0.127
15.0	-0.173	100.0	-0.117
20.0	-0.168	125.0	-0.109
25.0	-0.162	150.0	-0.102
30.0	-0.158	175.0	-0.098
40.0	-0.149	200.0	-0.092
50.0	-0.141	225.0	-0.086

[a] A portion of the titrant solution (4.992×10^{-3} M. in $LiNO_3$, 7.167×10^{-3} M. in LiH_2BO_3, and 2.857×10^{-3} M. in H_3BO_3) was made $1.15\overline{0} \times 10^{-2}$ M. in 1,10-phenanthroline and the resulting solution was titrated with the titrant. Activity coefficient of the nitrate ion taken as 0.90.

Table 7. Titration of 1,10-phenanthroline in lithium nitrate with lithium nitrate[a]

Vol. titrant, ml.	Observed E (v.)	Vol. titrant, ml.	Observed E (v.)
0	-0.171	60.0	-0.124
5.0	-0.165	70.0	-0.121
10.0	-0.161	80.0	-0.115
15.0	-0.155	100.0	-0.108
20.0	-0.151	125.0	-0.101
25.0	-0.148	150.0	-0.095
30.0	-0.143	175.0	-0.090
40.0	-0.136	200.0	-0.084
50.0	-0.129	225.0	-0.080

[a] A portion of the titrant solution (4.992×10^{-3} M. in $LiNO_3$, 7.167×10^{-3} M. in LiH_2BO_3, and 2.857×10^{-3} M. in H_3BO_3) was made 1.150×10^{-2} M. in 1,10-phenanthroline and the resulting solution was titrated with the titrant. Activity coefficient of the nitrate ion taken as 0.90.

Table 8. Titration of 1,10-phenanthroline in lithium nitrate with lithium nitrate[a]

Vol. titrant, ml.	Observed E (v.)	Vol. titrant, ml.	Observed E (v.)
0	-0.174	60.0	-0.125
5.0	-0.168	70.0	-0.121
10.0	-0.162	80.0	-0.117
15.0	-0.158	100.0	-0.110
20.0	-0.153	125.0	-0.102
25.0	-0.150	150.0	-0.097
30.0	-0.145	175.0	-0.091
40.0	-0.138	200.0	-0.087
50.0	-0.132	225.0	-0.082

[a] A portion of the titrant solution (4.992×10^{-3} M. in $LiNO_3$, 7.167×10^{-3} M. in LiH_2BO_3, and 2.857×10^{-3} M. in H_3BO_3) was made 1.510×10^{-2} M. in 1,10-phenanthroline and the resulting solution was titrated with the titrant. Activity coefficient of the nitrate ion taken as 0.90.

Table 9. Titration of 1,10-phenanthroline in sodium nitrate with sodium nitrate[a]

Vol. titrant, ml.	Observed E (v.)	Vol. titrant, ml.	Observed E (v.)
0	-0.192	60.0	-0.138
5.0	-0.184	70.3	-0.132
10.0	-0.178	80.0	-0.128
15.0	-0.172	100.0	-0.120
20.0	-0.167	125.0	-0.112
25.0	-0.162	150.0	-0.106
30.0	-0.158	175.0	-0.101
40.0	-0.150	200.0	-0.096
50.0	-0.142	225.0	-0.092

[a] A portion of the titrant solution (4.984×10^{-3} M. in $NaNO_3$, 7.534×10^{-3} M. in NaH_2BO_3, and 2.486×10^{-3} in H_3BO_3) was made 1.509×10^{-2} M. in 1,10-phenanthroline and the resulting solution was titrated with the titrant. Activity coefficient of the nitrate ion taken as 0.90.

Table 10. Titration of 1,10-phenanthroline in sodium nitrate with sodium nitrate[a]

Vol. titrant, ml.	Observed E (v.)	Vol. titrant, ml.	Observed E (v.)
0	-0.171	60.0	-0.126
5.0	-0.166	70.0	-0.122
10.0	-0.161	80.0	-0.118
15.5	-0.157	100.0	-0.112
20.0	-0.153	125.0	-0.105
25.0	-0.150	150.0	-0.099
30.0	-0.145	175.0	-0.094
40.0	-0.138	200.0	-0.090
50.0	-0.132	225.0	-0.085

[a] A portion of the titrant solution (4.984×10^{-3} M. in $NaNO_3$, 7.534×10^{-3} M. in NaH_2BO_3, and 2.486×10^{-3} in H_3BO_3) was made 1.509×10^{-2}M. in 1,10-phenanthroline and the resulting solution was titrated with the titrant. Activity coefficient of the nitrate ion taken as 0.90.

Table 11. Titration of 1,10-phenanthroline in sodium nitrate with sodium nitrate[a]

Vol. titrant, ml.	Observed E (v.)	Vol. titrant, ml.	Observed E (v.)
0	-0.166	60.0	-0.124
5.0	-0.160	70.0	-0.120
10.0	-0.158	80.0	-0.115
15.0	-0.152	100.0	-0.108
20.0	-0.148	125.0	-0.102
25.0	-0.144	150.0	-0.096
30.0	-0.141	175.0	-0.092
40.0	-0.134	200.0	-0.088
50.0	-0.129	225.0	-0.084

[a] A portion of the titrant solution (4.984×10^{-3} M. in $NaNO_3$, 7.534×10^{-3} M. in NaH_2BO_3, and 2.486×10^{-3} in H_3BO_3) was made 1.509×10^{-2} M. in 1,10-phenanthroline and the resulting solution was titrated with the titrant. Activity coefficient of the nitrate ion taken as 0.90.

Table 12. Titration of 1,10-phenanthroline in potassium nitrate with potassium nitrate[a]

Vol. titrant, ml.	Observed E (v.)	Vol. titrant, ml.	Observed E (v.)
0	-0.194	60.0	-0.148
5.0	-0.190	70.0	-0.142
10.0	-0.185	80.0	-0.139
15.0	-0.180	100.0	-0.130
20.0	-0.177	125.0	-0.122
25.0	-0.172	150.0	-0.115
30.0	-0.168	175.0	-0.109
35.0	-0.164	200.0	-0.104
40.0	-0.160	225.0	-0.099
50.0	-0.154		

[a] A portion of the titrant solution (4.994×10^{-3} M. in KNO_3, 6.9×10^{-3} M. in KH_2BO_3 and 3.039×10^{-3} M. in H_3BO_3) was made 1.509×10^{-2} M. in 1,10-phenanthroline and the resulting solution was titrated with the titrant. Activity coefficient of the nitrate ion taken as 0.90.

Table 13. Titration of 1,10-phenanthroline in potassium nitrate with potassium nitrate[a]

Vol. titrant, ml.	Observed E (v.)	Vol. titrant, ml.	Observed E (v.)
0	-0.208	60.0	-0.161
5.0	-0.203	70.0	-0.155
10.0	-0.199	80.0	-0.151
15.0	-0.193	100.0	-0.142
20.0	-0.188	125.0	-0.135
25.0	-0.184	150.0	-0.128
30.0	-0.180	175.0	-0.123
40.0	-0.173	200.0	-0.117
50.0	-0.166	225.0	-0.111

[a] A portion of the titrant solution (4.994×10^{-3} M. in KNO_3, 6.9×10^{-3} M. in KH_2BO_3 and 3.039×10^{-3} M. in H_3BO_3) was made 1.509×10^{-2} M. in 1,10-phenanthroline and the resulting solution was titrated with the titrant. Activity coefficient of the nitrate ion taken as 0.90.

Table 14. Titration of 1,10-phenanthroline in potassium nitrate with potassium nitrate[a]

Vol. titrant, ml.	Observed E (v.)	Vol. titrant, ml.	Observed E (v.)
0	-0.196	60.0	-0.149
5.0	-0.191	70.0	-0.144
10.0	-0.186	80.0	-0.140
15.0	-0.182	100.0	-0.132
20.0	-0.177	125.0	-0.124
25.0	-0.173	150.0	-0.117
30.0	-0.169	175.0	-0.111
35.0	-0.165	201.0	-0.105
40.0	-0.161	225.0	-0.101
50.0	-0.154		

[a] A portion of the titrant solution (4.994 x 10^{-3} $\underline{M}$. in KNO_3, 6.9 x 10^{-3} $\underline{M}$. in KH_2BO_3, and 3.039 x 10^{-3} $\underline{M}$. in H_3BO_3) was made 1.509 x 10^{-2} $\underline{M}$. in 1,10-phenanthroline and the resulting solution was titrated with the titrant. Activity coefficient of the nitrate ion taken as 0.90.

Stability constants of some M(II)-1,10-phenanthroline complexes

The determination of the stability constants of the zinc(II), cadmium(II), copper(II), and cobalt(II) complexes was carried out using solutions buffered at about pH 4.6 with a potassium acetate-acetic acid buffer mixture. In calculations the presence of the potassium and hydrogen complexes was taken into account. Data are shown in Tables 15 through 25. Results are in Table 26.

Calculations

In the selection of data for computation of stability constants, all data from each titration with a particular metal titrant were used. An attempt was made to select sets of data in such a manner that in each calculation of stability constants all of the stability constants were of significance. For example, in a system of three complexes, a point near the beginning of the titration was used to obtain one of the three necessary simultaneous equations, a point close to the end of the titration was chosen for the second, and an intermediate point for the third. Thus $\bar{n}$ values over a large range were used in each calculation.

Values for the activity coefficient of the nitrate ion were taken from the table by Kielland (15).

Table 15. Titration of 1,10-phenanthroline in zinc nitrate with zinc nitrate[a]

Vol. titrant, ml.	Observed E (v.)	Vol. titrant, ml.	Observed E (v.)
0	-0.117	18.0	+0.114
1.0	-0.112	20.0	+0.122
2.0	-0.101	22.0	+0.130
3.0	-0.086	25.0	+0.140
4.0	-0.070	30.0	+0.152
5.0	-0.045	35.0	+0.163
6.0	-0.016	40.0	+0.173
6.5	0.000	45.0	+0.181
7.0	+0.012	50.0	+0.187
7.5	+0.026	60.0	+0.199
8.0	+0.033	70.0	+0.208
9.0	+0.048	80.0	+0.215
10.0	+0.059	90.0	+0.222
11.0	+0.069	100.0	+0.228
12.0	+0.077	125.0	+0.239
13.0	+0.084	150.0	+0.246
14.0	+0.092	175.0	+0.252
15.0	+0.100	200.0	+0.256
16.0	+0.104	225.0	+0.260

[a] A portion of the titrant solution (1.018×10^{-2} M. in $Zn(NO_3)_2$, 4.574×10^{-1} M. in KOAc, and 6.0×10^{-1} in HOAc was made 3.760×10^{-2} M. in 1,10-phenanthroline and the resulting solution was titrated with the titrant. Activity coefficient of the nitrate ion taken as 0.60.

Table 16. Titration of 1,10-phenanthroline in zinc nitrate with zinc nitrate[a]

Vol. titrant, ml.	Observed E (v.)	Vol. titrant, ml.	Observed E (v.)
0	-0.117	22.0	+0.129
1.0	-0.111	25.0	+0.139
3.0	-0.090	30.0	+0.152
5.0	-0.056	35.0	+0.162
6.0	-0.023	40.0	+0.172
6.5	-0.006	45.0	+0.180
7.0	+0.007	50.0	+0.187
7.5	+0.018	60.0	+0.199
8.0	+0.027	70.0	+0.208
9.0	+0.045	80.0	+0.217
10.0	+0.058	90.0	+0.223
11.0	+0.067	100.0	+0.229
12.0	+0.077	125.0	+0.239
13.0	+0.086	150.0	+0.246
14.0	+0.092	175.0	+0.251
16.0	+0.103	200.0	+0.255
18.0	+0.113	225.0	+0.260
20.0	+0.122		

[a] A portion of the titrant solution (1.018×10^{-2} M. in $Zn(NO_3)_2$, 4.574×10^{-1} M. in KOAc, and 6.0×10^{-1} M. in HOAc) was made 3.786×10^{-2} M. in 1,10-phenanthroline and the resulting solution was titrated with the titrant. Activity coefficient of the nitrate ion taken as 0.60.

Table 17. Titration of 1,10-phenanthroline in zinc nitrate with zinc nitrate[a]

Vol. titrant, ml.	Observed E (v.)	Vol. titrant, ml.	Observed E (v.)
0	-0.116	16.0	+0.109
1.0	-0.109	18.0	+0.118
2.0	-0.097	20.0	+0.127
3.2	-0.078	22.0	+0.133
4.0	-0.058	25.0	+0.142
5.0	-0.031	30.0	+0.154
5.5	-0.015	35.0	+0.166
6.0	0.000	40.0	+0.174
6.5	+0.012	45.0	+0.182
7.0	+0.025	50.0	+0.188
7.5	+0.033	60.0	+0.200
8.0	+0.042	70.0	+0.209
8.5	+0.047	80.0	+0.217
9.0	+0.054	90.0	+0.222
10.0	+0.066	100.0	+0.228
11.0	+0.076	125.0	+0.237
12.0	+0.083	150.0	+0.244
13.0	+0.091	175.0	+0.249
14.0	+0.098	200.0	+0.252
15.0	+0.102	227.0	+0.258

[a] A portion of the titrant solution (1.018×10^{-2} M. in $Zn(NO_3)_2$, 4.574×10^{-1} M. in KOAc, and 6.0×10^{-1} M. in HOAc) was made 3.705×10^{-2} M. in 1,10-phenanthroline and the resulting solution was titrated with the titrant. Activity coefficient of the nitrate ion taken as 0.60.

Table 18. Titration of 1,10-phenanthroline in cadmium nitrate with cadmium nitrate[a]

Vol. titrant,ml.	Observed E (v.)	Vol. titrant,ml.	Observed E (v.)	Vol. titrant,ml.	Observed E (v.)
0	-0.098	16.0	+0.002	50.0	+0.104
1.0	-0.096	17.0	+0.010	55.0	+0.112
3.0	-0.083	18.0	+0.014	60.0	+0.119
4.0	-0.078	20.0	+0.023	65.0	+0.125
5.0	-0.070	22.0	+0.031	70.0	+0.130
6.0	-0.062	24.0	+0.039	80.0	+0.140
7.0	-0.055	26.0	+0.046	90.0	+0.148
8.0	-0.048	28.0	+0.053	100.0	+0.154
9.0	-0.042	30.0	+0.059	125.0	+0.170
10.0	-0.034	32.0	+0.064	150.0	+0.181
11.0	-0.029	34.0	+0.071	175.0	+0.189
12.0	-0.020	36.0	+0.076	200.0	+0.196
13.0	-0.012	38.0	+0.081	225.0	+0.203
14.0	-0.006	40.0	+0.085		
15.0	0.000	45.0	+0.095		

[a] A portion of the titrant solution (9.949×10^{-3} M. in $Cd(NO_3)_2$, 4.534×10^{-1} M. in KOAc, and 6.1×10^{-1} M. in HOAc) was made 3.382×10^{-2} M. in 1,10-phenanthroline and the resulting solution was titrated with the titrant. Activity coefficient of the nitrate ion taken as 0.60.

Table 19. Titration of 1,10-phenanthroline in cadmium nitrate with cadmium nitrate[a]

Vol. titrant,ml.	Observed E (v.)	Vol. titrant,ml.	Observed E (v.)	Vol. titrant,ml.	Observed E (v.)
0	-0.098	15.0	0.000	45.0	+0.098
1.0	-0.092	16.0	+0.003	50.0	+0.107
2.0	-0.087	17.0	+0.010	56.0	+0.115
3.0	-0.080	18.1	+0.016	60.0	+0.120
4.0	-0.075	20.0	+0.025	70.0	+0.132
5.0	-0.069	22.0	+0.032	80.0	+0.142
6.0	-0.061	24.0	+0.041	90.0	+0.150
7.0	-0.055	26.0	+0.048	100.0	+0.157
8.0	-0.048	28.0	+0.055	110.0	+0.163
9.0	-0.040	30.0	+0.061	125.0	+0.171
10.0	-0.033	32.0	+0.068	150.0	+0.182
11.0	-0.028	34.0	+0.073	175.0	+0.190
12.0	-0.021	36.0	+0.078	200.0	+0.197
13.0	-0.013	38.0	+0.082		
14.0	-0.006	40.0	+0.087		

[a] A portion of the titrant solution (9.949 x 10^{-3} M. in $Cd(NO_3)_2$, 4.534 x 10^{-1} M. in KOAc, and 6.1 x 10^{-1} M. in HOAc) was made 3.372 x 10^{-2} M. in 10-phenanthroline and the resulting solution was titrated with the titrant. Activity coefficient of the nitrate ion taken as 0.60.

Table 20. Titration of 1,10-phenanthroline in cadmium nitrate with cadmium nitrate[a]

Vol. titrant,ml.	Observed E (v.)	Vol. titrant,ml.	Observed E (v.)	Vol. titrant,ml.	Observed E (v.)
0	-0.088	15.0	+0.002	45.0	+0.101
1.0	-0.086	16.0	+0.008	50.0	+0.110
2.0	-0.081	17.0	+0.017	55.0	+0.118
3.0	-0.074	18.0	+0.023	60.0	+0.123
4.0	-0.068	20.0	+0.032	65.0	+0.130
5.0	-0.060	22.0	+0.041	70.0	+0.135
6.0	-0.053	24.0	+0.048	80.0	+0.143
7.0	-0.046	26.0	+0.055	90.0	+0.151
8.0	-0.039	28.0	+0.061	100.0	+0.158
9.0	-0.033	30.0	+0.068	125.0	+0.172
10.0	-0.027	32.0	+0.073	150.0	+0.182
11.0	-0.019	34.0	+0.079	175.0	+0.190
12.0	-0.012	36.0	+0.083	200.0	+0.198
13.0	-0.007	38.0	+0.088		
14.0	0.000	40.0	+0.092		

[a] A portion of the titrant solution (9.949×10^{-3} M. in $Cd(NO_3)_2$, 4.534×10^{-1} M. in KOAc, and 6.1×10^{-1} M. in HOAc) was made 3.279×10^{-2} M. in 10-phenanthroline and the resulting solution was titrated with the titrant. Activity coefficient of the nitrate ion taken as 0.60.

Table 21. Titration of 1,10-phenanthroline in copper nitrate with copper nitrate[a]

Vol. titrant,ml.	Observed E (v.)	Vol. titrant,ml.	Observed E (v.)	Vol. titrant,ml.	Observed E (v.)
0	-0.053	15.0	+0.072	30.0	+0.192
1.0	-0.048	16.0	+0.078	32.0	+0.202
2.0	-0.040	17.0	+0.084	34.0	+0.212
3.0	-0.032	18.0	+0.091	36.0	+0.221
4.0	-0.023	19.0	+0.099	38.0	+0.229
5.0	-0.012	20.0	+0.108	40.0	+0.236
6.0	-0.001	21.0	+0.119	45.0	+0.250
7.0	+0.010	22.0	+0.129	50.0	+0.261
8.0	+0.020	23.0	+0.140	55.0	+0.270
9.0	+0.029	24.0	+0.150	60.0	+0.279
10.0	+0.038	25.0	+0.158	65.0	+0.286
11.0	+0.046	26.0	+0.167	70.0	+0.291
12.0	+0.053	27.0	+0.174	80.0	+0.302
13.0	+0.059	28.0	+0.180	90.0	+0.309
14.0	+0.065	29.0	+0.188	100.0	+0.313

[a] A portion of the titrant solution (9.766×10^{-3} M. in $Cu(NO_3)_2$, 4.661×10^{-1} M. in KOAc, and 6.0×10^{-1} M. in HOAc) was made 3.68×10^{-2} M. in 1,10-phenanthroline and the resulting solution was titrated with the titrant. Activity coefficient of the nitrate ion taken as 0.60.

Table 22. Titration of 1,10-phenanthroline in copper nitrate with copper nitrate[a]

Vol. titrant,ml.	Observed E (v.)	Vol. titrant,ml.	Observed E (v.)	Vol. titrant,ml.	Observed E (v.)
0	-0.050	16.0	+0.088	34.0	+0.209
1.0	-0.045	17.0	+0.095	36.0	+0.214
2.0	-0.039	18.0	+0.103	38.0	+0.220
3.0	-0.030	19.0	+0.112	40.0	+0.225
4.0	-0.021	20.0	+0.121	42.0	+0.230
5.0	-0.010	21.0	+0.130	44.0	+0.235
6.0	+0.001	22.0	+0.140	46.0	+0.240
7.0	+0.011	23.0	+0.150	48.0	+0.244
8.0	+0.022	24.0	+0.158	50.0	+0.250
9.0	+0.032	25.0	+0.164	55.0	+0.260
10.0	+0.042	26.0	+0.172	60.0	+0.267
11.0	+0.051	27.0	+0.179	70.0	+0.278
12.0	+0.056	28.0	+0.183	80.0	+0.283
13.0	+0.063	29.0	+0.188	90.0	+0.283
14.0	+0.075	30.0	+0.191	100.0	+0.288
15.0	+0.081	32.0	+0.201		

[a] A portion of the titrant solution (9.766×10^{-3} *M*. in $Cu(NO_3)_2$, 4.661×10^{-1} *M*. in KOAc, and 6.0×10^{-1} *M*. in HOAc) was made 3.639×10^{-2} *M*. in 1,10-phenanthroline and the resulting solution was titrated with the titrant. Activity coefficient of the nitrate ion taken as 0.60.

Table 23. Titration of 1,10-phenanthroline in cobalt nitrate with cobalt nitrate[a]

Vol. titrant,ml.	Observed E (v.)	Vol. titrant,ml.	Observed E (v.)	Vol. titrant,ml.	Observed E (v.)
0	-0.030	12.0	+0.102	40.0	+0.206
1.0	-0.023	13.0	+0.106	42.0	+0.215
2.0	-0.012	14.0	+0.110	44.0	+0.221
3.0	-0.003	16.0	+0.115	46.0	+0.228
4.0	+0.010	18.0	+0.118	48.0	+0.233
5.0	+0.040	20.0	+0.123	50.0	+0.239
5.5	+0.050	22.0	+0.130	52.0	+0.242
6.0	+0.059	24.0	+0.138	55.0	+0.245
6.5	+0.065	26.0	+0.144	60.0	+0.250
7.0	+0.071	28.0	+0.151	70.0	+0.257
7.5	+0.075	30.0	+0.159	80.0	+0.263
8.0	+0.080	32.0	+0.168	90.0	+0.266
9.0	+0.085	34.0	+0.177	100.0	+0.270
10.0	+0.090	36.0	+0.187		
11.0	+0.097	38.0	+0.198		

[a] A portion of the titrant solution (3.345×10^{-3} $\underline{M}$. in $Co(NO_3)_2$, 5.115×10^{-1} $\underline{M}$. in KOAc, and 6.7×10^{-1} $\underline{M}$. in HOAc) was made 1.005×10^{-2} $\underline{M}$. in 1,10-phenanthroline and the resulting solution was titrated with the titrant. Activity coefficient of the nitrate ion taken as 0.60.

Table 24. Titration of 1,10-phenanthroline in cobalt nitrate with cobalt nitrate[a]

Vol. titrant,ml.	Observed E (v.)	Vol. titrant,ml.	Observed E (v.)	Vol. titrant,ml.	Observed E(v.)
0	-0.060	11.5	+0.069	40.0	+0.161
1.0	-0.057	12.0	+0.073	45.0	+0.175
2.0	-0.052	13.0	+0.081	50.0	+0.192
3.0	-0.046	14.0	+0.087	55.0	+0.210
4.0	-0.038	15.0	+0.092	60.0	+0.228
5.0	-0.030	16.0	+0.096	65.0	+0.242
6.0	-0.022	18.0	+0.103	70.0	+0.252
7.0	-0.013	20.0	+0.110	75.0	+0.261
8.0	0.000	22.0	+0.119	80.0	+0.267
9.0	+0.025	24.0	+0.126	90.0	+0.271
9.5	+0.038	26.0	+0.131	100.0	+0.276
10.0	+0.048	28.0	+0.135	125.0	+0.283
10.5	+0.056	30.0	+0.140	150.0	+0.287
11.0	+0.062	35.0	+0.150	175.0	+0.290

[a] A portion of the titrant solution (3.345×10^{-3} M. in $Co(NO_3)_2$, 5.115×10^{-1} M. in KOAc, and 6.7×10^{-1} M. in HOAc) was made 1.154×10^{-2} M. in 1,10-phenanthroline and the resulting solution was titrated with the titrant. Activity coefficient of the nitrate ion taken as 0.60.

Table 25. Titration of 1,10-phenanthroline in cobalt nitrate with cobalt nitrate[a]

Vol. titrant, ml.	Observed E (v.)	Vol. titrant, ml.	Observed E (v.)
0	-0.080	15.0	+0.080
1.0	-0.075	17.0	+0.092
2.0	-0.068	19.0	+0.100
3.0	-0.062	22.0	+0.111
4.0	-0.056	25.0	+0.119
5.0	-0.048	30.0	+0.131
6.0	-0.040	35.0	+0.142
7.0	-0.031	40.0	+0.154
8.0	-0.026	45.0	+0.170
9.0	-0.014	50.0	+0.185
10.0	0.000	55.0	+0.207
10.5	+0.010	60.0	+0.230
11.0	+0.025	65.0	+0.247
11.5	+0.037	70.0	+0.258
12.0	+0.048	80.0	+0.269
12.5	+0.056	90.0	+0.275
13.0	+0.061	100.0	+0.280
14.0	+0.072		

[a] A portion of the titrant solution (3.345×10^{-3} M. in $Co(NO_3)_2$, 5.115×10^{-1} M. in KOAc, and 6.7×10^{-1} M. in HOAc) was made 1.195×10^{-2} M. in 1,10-phenanthroline and the resulting solution was titrated with the titrant. Activity coefficient of the nitrate ion taken as 0.60.

Table 26. Experimental conditions and results[a]

Metal	MNO_3 $M \times 10^2$	KOAc $M \times 10^2$	HOAc $M \times 10^2$	MOH $M \times 10^2$	H_3BO_3 $M \times 10^2$	pH	μ	$\gamma_{NO_3^-}$	log k_1	log k_2	log k_3	log K (over-all)	Ref.
H	1.014						.01	.90	5.27	2.83	3.97	12.07±.38	--[b]
									5.05	3.35	1.9	10.3	11
									4.857				25
									5.2				6
									4.77				19
									4.86				29
									4.96				3
									4.92				17, 37
									5.02				28
									4.8				--[c]
									4.27				1
									5.0				--[d]
Li	0.4992			0.7167	0.2863	9.52	.01	.90	2.32	3.05		5.37±.09	--[b]
									1.78	4.4		6.18	11

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[a] Each log stability constant listed is the average of many values obtained. The metal studied, the number of titrations using that metal solution, and the number of calculations of each stability constant from each titration are as follows: H,3,12; Li,3,6; Na,3,6; K,3,7; Zn,3,14; Cd,3,15; Cu,2,16; Co,3,13.

[b] This work.

[c] Albert, A. and Goldacre, R., Sidney, Australia. Stability of phenanthrolium ion. Private communication to H. Irving. 1945.

[d] Irving, H. and Mellor, D. H., Oxford, England. Stability of 1,10-phenanthroline complexes. Private communication to R. I. Bystroff. 1955.

Table 26. (Continued)

Metal	MNO_3 $Mx10^2$	KOAc $Mx10^2$	HOAc $Mx10^2$	MOH $Mx10^2$	H_3BO_3 $Mx10^2$	pH	μ	$\gamma_{NO_3^-}$	log k_1	log k_2	log k_3	log K (over-all)	Ref.
Na	0.4984			0.7534	0.2486	9.63	.01	.90	2.15	3.25		5.40±.09	--[b]
									1.58	4.25		5.83	11
K	0.4994			0.6905	0.3039	9.60	.01	.90	2.09	2.84		4.93±.01	--[b]
									1.0	4.04		5.04	11
Zn	1.018	45.74	58.93			4.64	.5	.60	6.31	6.09	4.77	17.17±.21	--[b]
									6.58	5.8	4.8	17.18	11
									6.36	5.64	5.2	17.00	4
									6.5	5.45	5.10	17.05	13
									6.4	5.63	5.00	17.00	--[d]
									6.6	5.72	4.85	17.00	16
										5.9	4.8		38
									6.47	5.5	1.1	13.07	24
												11.62	18
Cd	0.995	45.34	61.16			4.62	.5	.60	5.75	5.09	3.07	13.91±.03	--[b]
											2.0	15.2	5
									5.17	4.83	4.26	14.26	--[d]
										5.2	4.2		38
Cu	0.9766	46.61	60.05			4.64	.5	.60	7.53	6.07	4.99	18.60±.18	--[b]
									9.15	6.65	5.25		4
									9.0	6.7	5.1	20.8	4
									8.82	6.57	5.02	20.41	--[d]
									6.3	6.15	5.5	17.95	27

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[e] Margerum, D. W., Lafayette, Indiana. Result of work by J. M. Duncan. Private communication to C. V. Banks. 1958.

Table 26. (Continued)

Metal	MNO_3 $M \times 10^2$	KOAc $M \times 10^2$	HOAc $M \times 10^2$	MOH $M \times 10^2$	H_3BO_3 $M \times 10^2$	pH	μ	$\gamma_{NO_3^-}$	log k_1	log k_2	log k_3	log K (over-all)	Ref.
Co	0.3345	5.115	6.743			4.63	.06	.79	7.01	5.43	4.50	16.95±.03	--^{b}
									7.02	6.70	6.38	20.10	--^{d}
												20.1	--^{e}

DISCUSSION AND SUMMARY

Grimes (11) has proposed a method for the determination of the stability constants of 1,10-phenanthroline complexes using a silver/bis(1,10-phenanthroline)silver(I) nitrate electrode. It was felt desirable to evaluate this method further by the study of several metal complexes whose stability constants had been previously reported, as well as to re-determine the stability constants of several species proposed by Grimes but which had not been observed or studied quantitatively in solution heretofore.

In order to obtain a value for the working potential of the Ag/AgP_2NO_3 electrode, it was necessary to determine the over-all stability constant for the bis(1,10-phenanthroline)-silver(I) ion and the solubility product constant for the nitrate salt of this ion.

From a silver sulfate-1,10-phenanthroline titration, log K_2 for the bis(1,10-phenanthroline)silver(I) complex was calculated to be 11.42. Grimes reported a value of 11.6. The solubility product constant for bis(1,10-phenanthroline)-silver(I) nitrate was obtained from a silver nitrate-1,10-phenanthroline titration. A value of $10^{-8.49}$ was found, whereas Grimes reported $11^{-8.8}$. In the calculation of both log K_2 and K_{sp}, the presence of mono(1,10-phenanthroline)-hydrogen(I) ion was taken into account. Grimes ignored this species in his calculations. From these values and the reduction potential of the silver electrode a working potential for the Ag/AgP$_2$NO$_3$ electrode was calculated to be -0.378 volt vs. the saturated calomel electrode. Grimes found -0.311 volt. These figures are in good agreement when one considers that the reference electrodes in the two determinations were different, and therefore different junction potentials exist. Grimes used a fiber-type saturated calomel electrode connected to the solution under study with a 0.1 M. potassium nitrate in agar-agar salt bridge, while the reference electrode in this work was a double junction sleeve-type saturated calomel electrode the sleeve of which was filled with a saturated potassium nitrate solution. The potential of this electrode was measured by comparison with a fiber-type saturated calomel electrode in a buffer solution. In the measurements made by Grimes, the unknown junction potentials should not adversely affect the accuracy of stability constant determinations, because the working potential of the electrode was measured under quite similar conditions to those used for stability constant determinations.

The stability constants of the mono-, bis-, and tris-1,10-phenanthroline-hydrogen complexes have been measured. The stability constant of the mono(1,10-phenanthroline)-hydrogen(I) ion is seen to be somewhat higher than most of the other values of this constant that have been reported.

Dwyer and Nyholm (6), however, have published a value of 5.2. It is interesting to note that among the values discussed above, only the work done by these authors was done with solutions in which an appreciable amount of the poly-1,10-phenanthroline-hydrogen species could form. One would expect that their value would be higher than those of other investigators. The differences between the values of log k_2 and log k_3, and thus log K_3, found in this work and the corresponding values found by Grimes (11) were unexpected, and more difficult to explain. Several possible reasons present themselves. The first explanation to come to mind is that the proposed method is not capable of greater precision. If this were so, much greater variations would be expected between individual determinations than has been observed. The results reported here are averages calculated from three different titrations, and from each titration about 12 separate calculations of each stability constant were made. Another possibility is that the response of the Ag/AgP_2NO_3 electrode changes in use, and that in some cases an old electrode was used which did not function properly. It has been noted that this is so if an electrode is reused many times. To avoid this, a new electrode was used in the study of each metal ion complex system, including the hydrogen system. Thus no electrode was used more than three times, providing ample insurance against incorrect response. The method of treating the data obtained could also introduce some variation in the calculated constants. Time spent studying the best method of treating the data obtained would be well worth the effort.

The structure of the complex formed by reaction of three 1,10-phenanthroline molecules with one hydrogen ion is of interest. It is rather improbable that an octahedral complex could be formed with the hydrogen ion. The very high energies involved in the hybridization of the hydrogen ion orbitals would seem to preclude this possibility. Another explanation would be the reaction of the 1,10-phenanthroline with the hydronium ion, H_3O^+. Both nitrogen atoms of each 1,10-phenanthroline molecule could bond with a single hydrogen atom, but this is a rather remote possibility. Such a structure would involve the formation of a three center hydrogen bond, which has been observed thus far only in boron-hydrogen compounds. It is more likely that one nitrogen atom of each 1,10-phenanthroline molecule bonds with a hydrogen atom, forming an N-H-O bond. Molecular models show this structure to be feasible. Fritz *et al*. (8) have measured the heat of hydration of 1,10-phenanthroline and have calculated the strength of the N-H bond as 7.25 calories per mole. The strength of this bond may account for the great stability of the ions formed when 1,10-phenanthroline reacts with a hydrogen ion. Ions with ratios of 1,10-phenanthroline to hydrogen greater than three are thus possible if the reaction of 1,10-phenanthroline with $H(H_2O)_x^+$ ions is considered.

The stability constants of the alkali metal constants proposed by Grimes (11) were measured. The order of stabilities of the mono complexes is that expected from consideration of ionic radii, low electronegativities, and high degree of hydration. Comparison of values for the constants measured in this work show that they are appreciably larger than those found by Grimes. On the other hand, the over-all formation constants for the bis complexes are somewhat lower than Grimes obtained for the lithium and sodium complexes, and approximately the same for the potassium complex. As in the case of the constants for the hydrogen complexes, it is not possible at this time to state categorically which are the better values.

Agreement between the over-all formation constant of the tris(1,10-phenanthroline-zinc(II) species determined in this work and in the work of Grimes is excellent. Both of these values agree very well with previously-published values when one considers that both determinations carried out with the Ag/AgP_2NO_3 electrode took into consideration alkali metal and hydrogen ion complexes which were previously unknown. These very good results obtained with zinc are good indication of the reliability of the results. With the exception of the

1,10-phenanthroline complexes of iron(II), which are probably too stable to be studied with the Ag/AgP$_2$NO$_3$ electrode, zinc is the only metal the complex stability of which has been studied by a number of workers. Thus comparison of the previously-published values with those obtained with the Ag/AgP$_2$NO$_3$ electrode is probably the best means of estimating the accuracy of the results. It must be emphasized, however, that rigorous comparison of values is not possible, for the reasons given above.

The stability constant values for cadmium, copper, and cobalt are, in general, comparable to those previously published. Only the work of Irving and Mellor* is available for comparison of all three step-wise formation constants of the cadmium complexes. These differ appreciably from the values obtained in this work, but the over-all formation constant for the tris complex is comparable to the value reported by Irving*. There is some disparity between the formation constants of the copper complexes as determined by Pflaum and Brandt (27) and the values of Bystroff (4) and Irving and Mellor*. The values obtained with the Ag/AgP$_2$NO$_3$ electrode are intermediate, the over-all constant for the tris complex being closer to the value of Pflaum and Brandt (27).

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*Irving, H. and Mellor, D. H., Oxford, England. Stability of 1,10-phenanthroline complexes. Private communication to R. I. Bystroff. 1955.

The constant for the mono complex of cobalt with 1,10-phenanthroline obtained by the proposed method is in excellent agreement with the corresponding value found by Irving and Mellor*. The other constants differ too widely to permit comparison. Attempted determinations of the nickel complex stability constants failed because of their great stability and the slowness of their formation. The kinetics of the reactions of nickel with 1,10-phenanthroline have been measured by Margerum _et_ _al_. (22).

The results of the above determinations cannot be evaluated fully as yet. To permit more strict comparisons of the various stability constants with published values, it would be very useful to recalculate these constants from the same data while ignoring the presence of alkali metal complexes and the two poly-1,10-phenanthroline-hydrogen complexes. In this way the measurements made by the electrode can be more easily weighed. Another fact that should be considered is that the stability of some of the complexes studied are appreciably greater than the stability of the silver species in solution. It is possible that the stability of complexes of metals such as copper and cobalt are too high to be measured accurately with Ag/AgP_2NO_3 electrode. Again, recalculation of the data while ignoring the alkali metal and higher hydrogen complexes should be of great aid.

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*_Ibid_.

SUGGESTIONS FOR FUTURE WORK

1) Since the published stability constants of several metal complexes studied in this work vary somewhat, it would be helpful to recalculate the constants determined with the Ag/AgP_2NO_3 electrode but ignoring the presence of the two higher 1,10-phenanthroline-hydrogen complexes, and the buffer metal complexes. In this way more direct comparisons of the results with values in the literature could be made.

2) A study should be made to determine the best method of treating the data obtained in the titrations, since it appears that the method can be used to measure stability constants over a fairly wide range. It might be found that one method is more suitable for calculation of stability constants of complexes of low stability, while another is better for those of great stability. The number of complexes present in a given solution should also be considered, as well as their relative stability. Because of the shortness of the computor programs used, it is felt that the floating decimal interpretive system (36) used in making calculations is entirely adequate.

3) A potentiometer circuit capable of measuring potentials more precisely than the Model GS pH meter could be substituted for the pH meter in an attempt to improve accuracy and precision.

4) The Ag/AgP_2NO_3 electrode could be used in the determination of the stability constants of a great many 1,10-phenanthroline complexes. The electrode should be particularly useful in studying weak complexes, where conventional methods are inapplicable.

5) Various substituted 1,10-phenanthroline electrodes could be prepared. In this way studied of ligand substituent effects could be studied with several metals. With the aid of the electronic computor a great number of systems could be studied in this manner.

6) Electrodes could be made from metals other than silver. For instance a nickel/tris(1,10-phenanthroline)-nickel(II) perchlorate electrode might possibly be used to measure stability constants of very stable complexes. Several metal-1,10-phenanthroline complexes perchlorates are insoluble and could be considered.

7) The techniques applied in this work could possibly be extended to other ligands. For instance, a mercury/mercury(I) oxalate electrode could be used to study the stability of oxalate complexes. A mercury/mercury(I) tartrate electrode could likewise be applied to the study of tartrate complexes.

8) Because the tris(1,10-phenanthroline)hydrogen(I) species is unique, a study to determine its structure should be carried out.

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