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# Study of metal-1, 10-phenanthroline complex equilibria by potentiometric measurement

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PLEX EQUILIBRIA BY POTENTIOMETRIC  
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STUDY OF METAL-1,10-PHENANTHROLINE COMPLEX  
EQUILIBRIA BY POTENTIOMETRIC MEASUREMENT

by

John Mart Dale

A Dissertation Submitted to the  
Graduate Faculty in Partial Fulfillment of  
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1963

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## INTRODUCTION

Coordination compounds are used extensively throughout almost all phases of analytical chemistry. When a metal ion undergoes complexation, the resulting species, or solution in which the reaction occurs, takes on different characteristics which in many cases may be used to the advantage of the analyst.

The subject of volumetric analysis is replete with examples of coordination phenomena. Besides the use of solutions of complexing agents as direct titrants for metal ions, many cases are reported wherein interfering metals are preferentially complexed permitting the determination of a metal without prior separation. The use of the metallochromic indicator depends upon the difference in stability of a metal-indicator complex as compared to the complex formed with the titrant.

Another important example of coordination in volumetric analysis is the oxidation-reduction indicator which is exemplified by the work with the 1,10-phenanthroline complexes of the two oxidation states of iron. The change in color upon oxidation of the tris(1,10-phenanthroline)iron(II) complex ion to the tris(1,10-phenanthroline)iron(III) complex ion was first described by Walden, Hammett, and Chapman (59) followed by the adaptation to titrations using strong oxidizing agents. Brandt and Smith (7) showed that the addition of substituents

on the phenanthroline ring changed the reduction potential of the iron system. The substituent effect with respect to complex stability of the transition metal complexes was later studied by Banks and Bystroff (4).

Probably one of the most striking examples of tailoring an organic molecule for the purpose of colorimetric analysis is exemplified by the determination of iron with bathophenanthroline (56). The molar extinction coefficient for the tris(4,7-diphenyl-1,10-phenanthroline)iron(II) complex ion is over 22,000 permitting the colorimetric determination of iron in the parts per billion range. Reports of the subsequent use of the reagent by several other authors has been compiled by Diehl and Smith (16).

In addition, coordination compounds have played a large role in the subject of gravimetric and polarographic analysis as well as solvent extraction and ion exchange separations.

A starting point for the development of new methods of approach to chemical separation and analysis is provided by the knowledge of the degree of formation of a complexing agent with the various metals in question. The methods for the determination of stability constants are, therefore, of considerable interest to the analytical chemist.

#### General Considerations

Martell and Calvin (37) have reviewed and summarized the approaches to measuring stability constants. Rossotti and

Rossotti (47) have presented a book as a comprehensive guide to the study of complex formation in solution.

Regardless of the experimental methods used for the determination of stability constants, some generalizations may be made concerning the equilibria which must be considered when studying mononuclear complexes. The equilibria involved for a solution containing a metal, M, and a ligand, L, may be described by the following reactions where ion charges are omitted for convenience



If it is possible to carry out the experimental work in solutions of constant ionic strength, the activity coefficients of each species may be considered constant and the stoichiometric stability or stoichiometric formation constants may be expressed in terms of concentrations by

$$k_{a1} = \frac{(HL)}{(H)(L)}$$

$$k_{ai} = \frac{(H_iL)}{(H)(H_{i-1}L)}$$

$$K_i = k_{a1} k_{a2} \dots k_{ai} = \frac{(H_iL)}{(H)^i(L)} \quad (3)$$

$$k_1 = \frac{(ML)}{(M)(L)}$$

$$k_n = \frac{(ML_n)}{(ML_{n-1})(L)}$$



$$\beta_n = k_1 k_2 \dots k_n = \frac{(ML_n)}{(M)(L)^n} \quad (4)$$

where the brackets indicate equilibrium concentrations. The constants may be named as follows:  $k_{ai}$  is the step-wise acid association constant for the  $i$ -th proton complex,  $K_i$  is the over-all acid association constant for the  $i$ -th complex,  $k_n$  is the step-wise stability constant for the  $n$ -th metal complex, and  $\beta_n$  is the over-all stability constant for the  $n$ -th metal complex.

If the experimental conditions are such that materials other than L are present which can complex M, then the equilibria may be described by conditional stability constants (46) which are only valid for a particular set of conditions. This may be expressed as follows:

$$\beta_n' = \frac{(ML_n)}{(M')(L')^n} \quad (5)$$

where  $\beta_n'$  is the over-all conditional stability constant for the  $n$ -th metal complex, the term  $M'$  represents the total concentration of metal that is not bound to L, and  $L'$  represents the total concentration of ligand not bound to M. Due to the fact that the ligand normally reacts to some extent with hydrogen ion, the conditional stability constant is a function of the pH of the solution. If a pH buffer is added to the experimental solution to control the hydrogen ion concentration, the metal may react to a certain extent with the buffer. The conditional stability constant is then also

a function of the concentration of the buffer present.

The total metal ion concentration may be represented by

$$M_T = (M) + \sum_1^N (ML_n) \quad (6)$$

and the total ligand concentration by

$$L_T = (L) + \sum_1^N n(ML_n) \quad (7)$$

where  $N$  is the maximum number of ligands bound to a metal atom. Using Equation 4, the total metal and total ligand concentrations may be expressed as

$$M_T = (M) \sum_0^N \beta_n (L)^n \quad (8)$$

$$L_T = (L) + (M) \sum_1^N n\beta_n (L)^n \quad (9)$$

where  $\beta_0$  is equal to 1.

### Methods for Calculating Stability Constants

#### General treatment

In order to arrive at reliable stability constants for metal complex systems it is necessary to obtain precise experimental data from valid experimental techniques. It is equally important that the data be treated in a mathematically rigorous and physically significant manner.

Three general mathematical methods for the calculation of successive complexity constants have been proposed by Bjerrum (6), Leden (33) and Fronaeus (20). Sullivan and Hindman (57)

have reviewed these methods by restating the general mathematical formulation for the calculation of successive complexity constants, by examining the foundations in each case, by analyzing the physical significance of the treatment, by applying the various methods to a particular set of data and by critically comparing the results obtained. They also point out the aspects of each treatment that might be expected to introduce uncertainties.

Bjerrum (6) has defined a term designated by  $\bar{n}$  which represents the average number of ligands combined with each central atom.

$$\bar{n} = \frac{L_T - (L)}{M_T} = \frac{\sum_0^N n\beta_n(L)^n}{\sum_0^N \beta_n(L)^n} \quad (10)$$

This equation may be rearranged to give

$$\begin{aligned} \bar{n} &= (\bar{n} - 1) \beta_1(L) + (\bar{n} - 2) \beta_2(L)^2 + \dots \\ (\bar{n} - n) \beta_n(L)^n &= 0 \end{aligned} \quad (11)$$

Bjerrum (6) gives several approximation methods for the solution of Equation 11. If the successive step-wise stability constants are sufficiently spaced so that the formation curve ( $\bar{n}$  versus  $\log(L)$ ) is wave-like, the simultaneous equations of the form of Equation 11 may be solved by taking  $(L)$  values at half-integral values of  $\bar{n}$ . Half-integral values of  $\bar{n}$  correspond to the condition that approximately equal amounts

of the  $ML_n$  and  $ML_{n-1}$  complexes are present in the solution. Approximate step-wise stability constants are determined from

$$k_n = \frac{1}{(L)} \quad (12)$$

This technique has been used where the formation curve was not wave-like to obtain first approximations for the various step-wise stability constants (10). Better estimates were then obtained by the convergence equations of Carlson, et al. (12).

If  $L_T \cong (L)$ , it is difficult to obtain  $\bar{n}$  from Equation 10. For this case the degree of formation,  $\alpha_c$ , of a given complex,  $ML_c$ , has been defined.

$$\alpha_c = \frac{(ML_c)}{M_T} = \frac{\beta_c(L)^c}{\sum_0^N \beta_n(L)^n} \quad (13)$$

Subsequent mathematical operations upon this equation (57) yield

$$c - \bar{n} = \frac{\delta \ln \alpha_c}{\delta \ln(L)} \quad (14)$$

If the concentration of the free metal ion or any one of the complexes is known as a function of the free ligand concentration, it is possible to obtain  $\bar{n}$  by the graphical differentiation of a curve of  $\log(L)$  versus  $\log \alpha_c$ . A plot of  $\bar{n}$  versus  $\log(L)$  then gives the formation curve of the system. If the concentration of free metal is the measured quantity then  $c$  is zero and

$$\alpha_0 = \frac{(M)}{M_T} \quad (15)$$

and

$$-\bar{n} = \frac{\delta \ln \alpha_0}{\delta \ln(L)} \quad (16)$$

Leden (33) defined the function  $F((L))$  as

$$F((L)) = \frac{M_T - (M)}{(M)(L)} = \beta_1 + \beta_2(L) + \dots + \beta_n(L)^{n-1} \quad (17)$$

which is obtained by rearranging Equation 8. By plotting the second term of this equation versus  $(L)$  and extrapolating to zero concentration of free ligand,  $\beta_1$  is obtained.

$$\lim_{(L) \rightarrow 0} F((L)) = \beta_1 \quad (18)$$

In a similar fashion new functions are defined to find the successive constants in order.

$$G((L)) = \frac{F((L)) - \beta_1}{(L)} = \beta_2 + \beta_3(L) + \dots + \beta_n(L)^{n-2} \quad (19)$$

$$\lim_{(L) \rightarrow 0} G((L)) = \beta_2 \quad (20)$$

It is possible to form a system of equations of the form of Equation 17 and treat the equations as linear in the unknown  $\beta$ 's. In order to evaluate  $F((L))$  it is necessary to know both the concentration of uncomplexed metal and uncomplexed ligand.

The method proposed by Fronaeus (20) uses the average number of ligands bound to the central atom and a limiting

procedure similar to Leden's method for evaluating the constants. The function  $X((L))$  is defined as being equal to the denominator of the second term defining  $\bar{n}$  in Equation 10.

$$X((L)) = \sum_0^N \frac{\beta_n(L)^n}{\beta_n(L)^n} = 1 + \beta_1(L) + \beta_2(L)^2 \dots + \beta_n(L)^n \quad (21)$$

The expression for the derivative of this function with respect to  $(L)$  is equal to the numerator of Equation 10 divided by  $(L)$ , or

$$\frac{\bar{n}}{(L)} = \frac{\delta X((L))}{\delta (L)} / X((L)) \quad (22)$$

and 
$$\bar{n} = \frac{\delta \ln X((L))}{\delta \ln(L)} \quad (23)$$

The value of the function,  $X((L))$ , is evaluated by graphical integration. Equation 21 is then transformed to give

$$\frac{X((L))}{(L)} - \frac{1}{(L)} = \beta_1 + \beta_2(L) \dots + \beta_n(L)^{n-1} \quad (24)$$

and the values of the stability constants are obtained by graphical extrapolation to zero concentration of  $(L)$  as in the case of Leden's method. It is also possible to solve a system of simultaneous equations of the form of Equation 24.

The advantages and disadvantages of these methods have been thoroughly discussed (57). Two advantages to Bjerrum's method are that it is applicable whether the measured quantities are  $(M)$ ,  $(L)$  or one of the  $(ML_n)$  complexes, and the plot of the formation function directly indicates the

maximum number of ligands bound to a central metal ion under the conditions of the experiment.

Irving and Rossotti (24) have discussed several methods for obtaining  $k_1$  and  $k_2$  from the formation curve as applied to cases where the maximum ratio of ligand to central ion is two. The methods covered were successive approximations, solution of simultaneous equations, interpolation at half  $\bar{n}$  values, and interpolation at various  $\bar{n}$  values. It was also shown that a graphical method proposed by Schwarzenbach (54) could be adapted to the computation of stability constants from experimental values of  $\bar{n}$  and the free ligand concentration. Some of the assumptions and limitations of these methods are given here.

The first two methods are limited in that only a few experimental points of the formation curve are used for one set of values of the stability constants. The set of equations used for the successive approximations where the maximum value of  $\bar{n}$  is three are

$$k_1 = \frac{1}{(L)} \frac{\bar{n}}{(1-\bar{n}) + (2-\bar{n})k_2(L) + (3-\bar{n})k_2k_3(L)^2} \quad (25)$$

$$k_2 = \frac{1}{(L)} \frac{(\bar{n}-1) + \bar{n}/(k_1(L))}{(2-\bar{n}) + (3-\bar{n})k_3(L)} \quad (26)$$

$$k_3 = \frac{1}{(L)} \frac{(\bar{n}-2) + (\bar{n}-1)/k_2(L) + \bar{n}/k_1k_2(L)^2}{(3-\bar{n})} \quad (27)$$

which are derived from Bjerrum's  $\bar{n}$  equation

$$\bar{n} + (\bar{n}-1)k_1(L) + (\bar{n}-2)k_1k_2(L)^2 + (\bar{n}-3)k_1k_2k_3(L)^3 = 0 \quad (28)$$

Sets of simultaneous equations may also be formed directly from this equation. If  $m$  experimental points are available then there are  $m!/(N!(m-N)!)$  sets of equations which could be treated in this manner where  $N$  represents the highest attainable ratio of ligand to metal in the complex. Because of small experimental errors the equations will probably be inconsistent and sets of equations formed from neighboring points will be ill-conditioned.

Interpolation at half  $\bar{n}$  values, which was considered briefly above, employs Equations 25, 26, and 27 where  $\bar{n}$  is  $1/2$ ,  $3/2$ , and  $5/2$  respectively. This method also suffers from the small number of points used. In addition, unless the ratios of the successive step-wise formation constants are sufficiently large, considerable error may be introduced by this method. Although interpolation at various  $\bar{n}$  values employs more experimental points its use is still limited by the ratios of the successive constants.

The graphical method of Schwarzenbach (54) may be adapted to the computation of stability constants from experimental values of  $\bar{n}$  and  $(L)$  by plotting values of  $(\bar{n}-1)(L)/\bar{n}$  versus  $(\bar{n}-1)/((2-\bar{n})(L))$ . These terms are the independent and dependent variables, respectively, of an equation of a straight line which may be obtained by rearranging the  $\bar{n}$  equation for the case where  $\bar{n}_{\max}$  equals two. An extrapolation is involved here



which proves to be unreliable if a long extrapolation is necessary and in any case should only be used with data of high precision.

Rossotti and Rossotti (47) have discussed the above method in more detail. They have also discussed the various methods available for the computation of stability constants. Most of the methods are the same as or variations of the ones presented here.

#### Least squares treatment

In contrast to the discussions above, the ideal method for computing stability constants should minimize the smoothing effect which is implicit in most graphical procedures and should use all of the experimental data which are not obviously questionable.

The least squares treatment for experimental data where  $\bar{n}_{\max}$  equals two was first proposed by Irving and Rossotti (24) and offers an improvement over the methods previously discussed. The  $\bar{n}$  equation where  $\bar{n}_{\max}$  equals two may be rearranged to give

$$\frac{\bar{n}}{(\bar{n}-1)(L)} = \frac{(2-\bar{n})(L)}{(\bar{n}-1)} k_1 k_2 - k_1 \quad (29)$$

which is the equation of a straight line. To apply this equation the constants were evaluated by the method of least squares which made use of all the experimental data. Therefore, subjective smoothing of the data by drawing the best

straight line through the coefficients obtained from the experimental points was avoided. The method was tested on three systems with widely different values of  $k_1/k_2$  using as many experimental points as possible.

With the exception of the least squares treatment proposed by Irving and Rossotti (24), earlier calculations, as presented above generally involved approximation or graphical techniques. The least squares treatment becomes difficult for systems involving more than two complex species if the calculations are attempted using a desk type calculator. This is not only due to the large amount of data which is normally processed but also to the fact that the normal equations obtained are often ill-conditioned.

Recently Sullivan, Rydberg and Miller (58) proposed a weighted least squares technique for the calculation of stability constants for mononuclear complexes. In order to make this objective treatment feasible, programs for high speed digital computers were developed. Because one of the programs was used in the present work, a discussion of the work of these authors is desirable.

A digital computer developed at Argonne National Laboratory has available a program for the least squares calculation of  $a_n$  in the polynomial

$$y = \sum_{n=0}^N a_n x^n \quad (30)$$

The input data are  $y$ ,  $x$  and the weight of  $y$ . This type program may be used for the computation of the  $\beta_n$  in the polynomial used by Leden (Equation 17) for graphical estimations of the parameters. Sullivan et al. (58) applied this program to the treatment of solvent extraction data for the Np(IV)- $\text{HSO}_4^-$  system using thenoyltrifluoroacetone. The partition ratio,  $Q$ , of the concentration of Np(IV) in the organic phase to the total concentration of Np(IV) in the aqueous phase was expressed as,

$$Q = Q_0 \sum_0^N \beta_n (\text{HSO}_4^-)^n \quad (31)$$

where  $\beta_0 = 1$ , and  $N = 2$ . Transformation of this equation puts it into the form of Equation 30.

$$y = a_0 + a_1 (\text{HSO}_4^-) + a_2 (\text{HSO}_4^-)^2 \quad (32)$$

where  $y = 1/Q$ ,  $a_0 = 1/Q_0$ ,  $a_1 = \beta_1/Q_0$  and  $a_2 = \beta_2/Q_0$ .  $Q_0$  was defined as the normalized distribution coefficient of N(IV) in the absence of  $\text{HSO}_4^-$ .

A program was also developed for solvent extraction investigations for use with the IBM 704. The procedure calculates the values of  $a_n$  in the least squares sense in the polynomial

$$yx^N = \sum_0^N a_n x^n \quad (33)$$

This treatment was applied to data previously obtained for the

Pu(IV)-acetylacetonone system (50). In terms of this system Equation 33 becomes

$$(A)^4/Q = a_0 + a_1(A) + a_2(A)^2 + a_3(A)^3 + a_4(A)^4 \quad (34)$$

where  $Q$  is the measured partition ratio of the concentration of  $PuA_4$  in the organic phase with respect to the concentration of all species of Pu in the aqueous phase,  $(A)$  is the free acetylacetonone ligand concentration in the aqueous phase,  $a_4 = 1/D_4$  where  $D_4$  is the distribution coefficient of  $PuA_4$ ,  $a_3 = \beta_3/D_4\beta_4$ ,  $a_2 = \beta_2/D_4\beta_4$ ,  $a_1 = \beta_1/D_4\beta_4$ , and  $a_0 = 1/D_4\beta_4$ . An interesting result of the least squares treatment of the original data was that the system could be completely described in terms of only three parameters,  $a_1$ ,  $a_3$ , and  $a_4$ . Attempts to force a fit to the data in terms of the assumption that the formation of the complex ions  $PuA^{+3}$ ,  $PuA_2^{+2}$ ,  $PuA_3^+$ , and  $PuA_4$  took place in a regular manner, always resulted in values for the parameters  $a_0$  and  $a_2$  which were inconsistent with the specified model. This example shows one of the most useful features of the least squares treatment in that it provides a description of the results in a manner which is consistent only with the precision of the observations. Sullivan (58) felt that the values obtained in the original paper for  $a_0$  and  $a_2$  by the limiting value and ligand number methods were due to bias coupled with a highly ill-conditioned system. The results of the least squares treatment implied that at equilibrium the

aqueous phase concentration of  $\text{PuA}_2^{+2}$  was not large enough to have any observable influence on the measured distribution coefficient. The data were adequate to provide reliable values only for the distribution coefficient, the product  $k_2k_3$  and  $k_4$ .

Equilibrium constants for the systems, Th(IV)-acetyl-acetone-benzene-0.01 M  $\text{NaClO}_4$ , and Zr(IV)- $\text{F}^-$  (and  $-\text{HSO}_4^-$ ) - thenoyltrifluoroacetone-benzene-2.0 M  $\text{HClO}_4$ , were also calculated (51). The results are discussed and compared with constants originally computed from graphical methods by the original authors (13, 48). In the thorium systems the least squares method showed that the experimental data in the original paper were not accurate enough to provide for the first two equilibrium constants which were dominant in the region where the partition ratio had its lowest values. In the second case the equilibrium constants agreed well with those in the original paper.

In a later paper, Rydberg (49) applied the least squares technique to complexes formed between a number of different organic ligands and rare earth and actinide metals. The data were from selected papers already in the literature in which either the ligand number method, the limiting value method, or the two-parameter method (18) had been used for calculations. A general conclusion in this case was that with good data, the ligand number and limiting value methods should give the same

equilibrium constants as the least squares method. This was true with the two-parameter method as long as only two complexes were present in the system studied. It was also concluded from the investigation, however, that more refined techniques in solvent extraction work were needed.

In addition to the programs discussed above, Sullivan et al. (58) have developed a program for the IBM 704 to calculate the best values in the least squares sense for the  $\beta_n$  from the equation

$$0 = \sum_0^N (y-x-nz)\beta_n x^n \quad (35)$$

This equation is of the form of the  $\bar{n}$  relation of Bjerrum.

$$0 = \sum_0^N (\bar{n}-n)\beta_n (L)^n \quad (36)$$

Substituting  $(L_T-(L))/M_T$  for  $\bar{n}$  gives

$$0 = \sum_0^N (L_T-(L)-nM_T)\beta_n (L)^n \quad (37)$$

The input data are  $y = L_T$ ,  $x = (L)$ , and  $z = M_T$  as well as the estimated standard deviation that occurs in the measurement of  $x$ . This treatment is applicable to the processing of data from any system where the total metal, total ligand, and free ligand concentrations are the measured quantities. Because this particular program was used by the present author for processing potentiometric titration data, some details of the program will be given with respect to this treatment.

When a potentiometric titration is used to determine stability constants, one equation of the form of Equation 37 is obtained for each experimental point. The result is that due to experimental error a large number of nearly correct solutions to the equations exist. Also during the titration the concentration of free ligand changes by several orders of magnitude while  $\bar{n}$  changes from zero to some small integral number. These conditions result in an inconsistent or ill-conditioned system. Recognizing the inconsistency, Equation 37 is written as

$$U = \sum_0^N (L_T - (L) - nM_T) \beta_n (L)^n \quad (38)$$

The least squares treatment determines that set of  $\beta_n$  which makes  $U$  nearest to zero by minimizing

$$S = \sum_1^I w_1 U^2(x_1, y_1, z_1) \quad (39)$$

with respect to variation of the parameters,  $\beta_n$ , where  $I$  is the total number of experimental points. The weighting factors,  $w_1$ , were taken as

$$w_1 = \frac{1}{\Delta U_1^2} \quad (40)$$

where  $\Delta U$  is the variation in  $U$  for the variations in the variables ( $x, y, z$ ). External consistency was assumed, that is that most of the variation in  $U$  was due to the errors in the measurement of the free ligand concentration. Therefore,

$\Delta U$  is given by

$$\Delta U_i = \frac{\delta U_i}{\delta x_i} \sigma_{x_i} \quad (41)$$

where  $\sigma_{x_i}$  is the estimated standard deviation in  $x_i$ .

In order to determine the value of  $\Delta U$  it is necessary to know the values of  $\beta_n$ . The program provides for the calculation of the  $\beta_n$  first with  $w_i$  equal to one. Using these approximate  $\beta_n$ , values of new weighting factors are determined followed by the calculation of new values for the  $\beta_n$ . This process is repeated until one minus the ratio of  $\beta_n$  obtained from successive iterations is less than 0.05, all coefficients become negative or ten iterations are completed.

The output includes the values of the stability constants with their standard deviations and calculated values of the function,  $\bar{n}$ , for the original experimental values of  $x$  using the derived constants.

Before computer calculations are carried out, the data must be examined graphically to determine the largest value of  $N$  (Equation 38) to be considered, and that a smooth curve can be drawn through the experimental points. The input data are also examined with regard to the expression  $(y-x-nz)$  in order to omit any experimental points for which this term vanishes or cancels out to only one or two significant digits.



## Potentiometry

Applications of the silver electrode

Several authors have used the silver electrode to study various complexes of silver. Complex formation between silver and thiosulfate ions has been investigated by Nilsson (40). Berne and Leden (5) have combined potentiometric measurements with solubility determinations to show the presence of and to calculate the stability constants for various complexes of silver and bromide ions.

Studies of the soluble silver-iodide complex in lithium perchlorate-ether solutions have been made by Alin, Evers and Sillen (1). Koch (28) has determined the solubilities of silver chloride, silver bromide and silver iodide in methanol and ethanol. Brukenstein and Kolthoff (8) have determined the over-all dissociation constants of the chloride salts of some organic amines in glacial acetic acid. Peard and Pflaum (42) have prepared and characterized a series of solid silver(I)-heterocyclic amine compounds and have determined the relative stability values in acetonitrile and ethanol. The free silver ion concentration in the solution of the silver-amine complex was ascertained by comparison of the observed potential to values on a calibration curve for the particular solvent system used.

Formation constants for the two complexes formed by silver and pyridine have been reported by Curthoys and

Swinkels (14) in which case the free silver ion concentration was determined with a silver-silver bromide electrode. Grimes (22) and Fullerton (21) used the silver/bis (1,10-phenanthroline) silver(I) nitrate electrode to study the complex equilibria between 1,10-phenanthroline and several metal ions. The metals for which a study was made were lithium, sodium, potassium, zinc, cadmium, copper, and cobalt.

### Competitive methods

If it is not convenient to directly measure the free concentrations of metal ion or of a complexing ligand in solution, it is often possible to study complex formation between a metal and the ligand by adding a second cation which also reacts with the ligand. If the free concentration of the competing ion can be measured and the formation constants of its complexes are known then this in effect gives a measure of the concentration of the free ligand.

The use of the competitive method for the study of complex formation was first introduced by Bjerrum (6) in his work on metal ammine formation in aqueous solutions. In this study advantage was taken of the competitive complex formation between hydrogen ions and metal ions with ammonia. The concentration of ligand was varied by titrating an acid solution of the metal ions with ammonia. The glass electrode was employed to measure the free hydrogen ion concentration which, combined with the acid dissociation constant,  $k_{\text{NH}_4^+}$ , was used

used to calculate the concentration of free  $\text{NH}_3$ . Formation curves for the tetrammine copper(II), diammine silver(I), tetrammine zinc(II), tetrammine cadmium(II), hexammine cobalt(II), and the hexammine nickel(II) were determined. A study using high concentrations of ammonia was also made for magnesium, calcium, and lithium.

Calvin and Wilson (11) studied the influence of structural factors upon the stability of chelate compounds of copper(II) in which the four atoms bound to the metal were all oxygen. The method consisted of determining the hydrogen ion concentration of a solution containing known quantities of copper, chelating agent, acid, and base. From the known acid dissociation constant of the chelating substance and the concentrations of each of the other reactants, it was possible to calculate all the quantities necessary to determine the formation constants of the metal chelates. In contrast to Bjerrum's (6) work where metal solutions were titrated with the ligand, Calvin and Wilson (11) performed titrations with alkali, starting with fixed amounts of metal, chelating agent and excess acid. This permitted a wider variation of free ligand concentration to be attained.

The use of hydrogen as a competing ion is limited in some respects. If the metal-ligand complex is considerably more stable than the conjugate acid of the ligand, the hydrogen ion is not very effective as a competing ion. It would be

necessary to work in quite acid solutions where relatively large changes of hydrogen ion concentration produce small differences in the glass electrode response.

Several metal complexes have been studied by using two metal ions in solution which compete for the available complexing agent present in the solution. If the formation constants for the reaction of one of the metals with the ligand are known, and the concentration of uncomplexed metal may be determined, then it is generally possible to determine the formation constants for the reaction of the ligand with the second metal.

Schmid and Reilley (52) have described a method for determining metal chelate stabilities using mercury(II) as the competing ion. The method was developed for the determination of stability constants of 1:1 metal chelates and was applied to the reaction of ethylenediaminetetraacetic acid with several alkaline earth and transition metals. The principle is based upon the determination of the position of exchange equilibria of the type  $\text{HgZ}^- + \text{M}^{++} \rightleftharpoons \text{MeZ}^- + \text{Hg}^{++}$  by means of potentiometric measurements with a mercury electrode. The Nernst equation for the mercury electrode was combined with the equations for the stability constants of a 1:1 mercury chelate and the 1:1 metal chelate to give at 25°C (ion charges omitted)

$$E_{\text{Hg}} = E_{\text{Hg}}^0 + 0.0296 \log \frac{(\text{M})(\text{HgZ})}{(\text{MZ})\beta_{\text{HgZ}}} + 0.0296 \log \beta_{\text{MZ}} \quad (42)$$

The potential of the mercury electrode depends linearly on  $\log \beta$  of the particular metal chelate involved, if the concentrations of the mercury chelate, the metal ion, and the metal chelate are kept constant. The  $\log \beta$  of the metal chelate complexes were calculated from experimental data after determining the stability constant for the mercury complex.

Limitations listed for the method are (1) stability constants of metal chelate complexes whose cations hydrolyze easily cannot be determined and (2) metal complexes with relatively low reduction potentials are oxidized by the mercury(II)-EDTA complex with the formation of free mercury. This same method was also used to determine the stability of several metal-tetraethylenepentamine complexes (14).

Schwarzenbach and Anderegg (53) have discussed the use of the mercury(II)-mercury system for the determination of stability constants and have applied it to metal-EDTA complexes. The method was also applied to complexes with diethylenetriamine-pentaacetic acid by Anderegg et al. (3).

Leden (32) has studied the complexity of silver and cadmium sulfates using the silver electrode. Initially the silver-sulfate system was investigated which was subsequently used to determine the concentration of free sulfate in solutions containing both silver and cadmium. Cabani and Scrocco (9) studied the silver-2,2'-dipyridyl system and evaluated the two formation constants,  $\log \beta_1$  and  $\log \beta_2$ , in

fifty per cent ethanol. This system was then used to study the complexes of cadmium and 2,2'-dipyridyl. Anderegg (2) made a similar study to that of Fullerton (21) using the mercury electrode. In this case, however, mercury(I) nitrate and the nitrate of the second metal were both in the experimental solution. Upon addition of 1,10-phenanthroline, the amount which reacted with mercury(I) formed the precipitate  $\text{Hg}_2\text{P}_2(\text{NO}_3)_2$ . The relatively large stability of the mercury-1,10-phenanthroline complex permitted the evaluation of only the  $\log \beta_1$  for cobalt, zinc, and cadmium. Values were reported for the  $\log \beta_2$  for copper and for all of the constants for nickel.

#### Complexes of Some Transition Metals with 1,10-Phenanthroline

Miller and Brandt (39) have studied the manganese(II) complexes of 1,10-phenanthroline and have reported a maximum of three 1,10-phenanthroline molecules per manganese(II) ion in solution. They report 7.35 for  $\log \beta_3$ . Irving and Mellor<sup>1</sup> have measured the stability constants of the 1,10-phenanthroline complexes by partition methods and obtained 4.8, 8.9, and 14.3 for  $\log \beta_1$ ,  $\log \beta_2$ , and  $\log \beta_3$ , respectively.

Douglas *et al.* (17) made a polarographic study of various amine complexes of cadmium. They report 15.19 for  $\log \beta_3$  and

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

13.15 for  $\log \beta_2$ . The latter value was calculated using data which had been obtained from experimental work in alcohol-water solutions. The second and third step-wise stability constants,  $\log k_2$  and  $\log k_3$ , have been reported as 5.2 and 4.2, respectively, by Yasuda *et al.* (61). Partition methods have been used by Irving and Mellor<sup>1</sup> to obtain 5.17, 10.00, and 14.26 for  $\log \beta_1$ ,  $\log \beta_2$ , and  $\log \beta_3$ , respectively. These same constants were reported as 5.75, 10.84, and 13.91 by Fullerton (21) using a potentiometric method. Anderegg (2) has reported 6.01 for  $\log \beta_1$  which was obtained from potentiometric measurements employing the mercury electrode.

Partition measurements have been used by Kolthoff *et al.* (30) to study the complexes of zinc with 1,10-phenanthroline. They report 6.6, 12.32, and 17.17 for  $\log \beta_1$ ,  $\log \beta_2$ , and  $\log \beta_3$ , respectively. These authors also report a value of 6.43 for  $\log \beta_1$  which was obtained from competition measurements. Using spectrophotometric measurements, McClure (38) found  $\log \beta_1$ ,  $\log \beta_2$ , and  $\log \beta_3$  to be 6.47, 12.0, and 13.1, respectively.  $\log \beta_1$  was determined using conditions in which only the 1:1 complex could form.  $\log \beta_2$  and  $\log \beta_3$  were calculated by a method of successive approximations. A value for  $\log \beta_2$  of 11.62 was obtained from ultraviolet spectrophotometric measurements by Kruse and Brandt (31). Irving and Mellor (23), using a competition method, found

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<sup>1</sup>Ibid.

values of 6.5, 11.95, and 17.05 for  $\log \beta_1$ ,  $\log \beta_2$ , and  $\log \beta_3$ , respectively. Values of 6.4, 12.03, and 17.00 were also obtained by these authors from partition methods.<sup>1</sup> Values for the log of the step-wise stability constants,  $k_2$  and  $k_3$ , have been reported by Yasuda *et al.* (61) as 5.9 and 4.8, respectively. These values were obtained from pH measurements. Values for  $\log \beta_1$ ,  $\log \beta_2$ , and  $\log \beta_3$ , obtained from pH measurements, have been reported by Banks and Bystroff (4) to be 6.36, 12.00, and 17.00. Grimes (22) has reported 6.58, 12.38, and 17.18 and Fullerton (21) has reported 6.31, 12.40, and 17.17 for the over-all  $\log \beta$  values. Both of these authors used a potentiometric method involving the silver/bis (1,10-phenanthroline) silver(I) nitrate electrode. Anderegg (2) has reported 6.40 for  $\log \beta_1$ .

Pflaum and Brandt (43) have used pH measurements to study the copper-1,10-phenanthroline complexes. They report 6.3, 12.45, and 17.95 for  $\log \beta_1$ ,  $\log \beta_2$ , and  $\log \beta_3$ , respectively. Irving and Meller,<sup>2</sup> by means of partition experiments, report values of 8.82, 15.39, and 20.41 for these same constants. By a combination of partition and pH methods, Banks and Bystroff (4) obtained two sets of values; 9.15, 15.80, 21.05 and 9.00, 15.70, 20.80. Fullerton (21) has reported 7.53, 13.60 and 18.60 for  $\log \beta_1$ ,  $\log \beta_2$ , and  $\log \beta_3$ , respectively, obtained

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<sup>1</sup>Ibid.

<sup>2</sup>Ibid.



from potentiometric data. Anderegg (2) has reported 9.30 and 16.14 for  $\log \beta_1$  and  $\log \beta_2$ , respectively.

Irving and Meller<sup>1</sup> have studied the nickel-1,10-phenanthroline system by partition methods and obtained 8.0, 16.0, and 23.9 for  $\log \beta_1$ ,  $\log \beta_2$ , and  $\log \beta_3$ , respectively. Using spectrophotometric measurements, Margerum, Bystroff, and Banks (36) report 8.6, 16.7, and 24.25 for these same constants. From potentiometric measurements, Anderegg (2) obtained values of 8.80, 17.10, and 24.80.

#### Purpose of This Work

The ultimate purpose of this work was to investigate the complexes of silver with 1,10-phenanthroline using the silver electrode and to apply this known system to the study of complexes of 1,10-phenanthroline with other metals.

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<sup>1</sup>Ibid.

## APPARATUS AND REAGENTS

All potentiometric measurements were made with a Leeds and Northrup No. 7552 Type K-2 potentiometer coupled with a No. 2430-C Type E galvanometer having a sensitivity of 0.005  $\mu$ a/mm. Titrations were performed in a constant temperature bath at  $25 \pm 0.05^\circ\text{C}$ .

The reagents used were of reagent-grade quality. Stock silver sulfate solutions were prepared by weight and checked by potentiometric titrations with chloride. A stock solution of potassium sulfate which was used to control ionic strength was standardized by passing aliquots through Dowex 50w cation exchange resin in the hydrogen form and titrating the resulting sulfuric acid with base. The buffer solution which was prepared by dissolving potassium acetate in a solution of acetic acid was also standardized by means of ion exchange. Stock solutions of the divalent salts were standardized with ethylenediaminetetraacetic acid. The purity of the 1,10-phenanthroline used was checked by titrations with perchloric acid in acetonitrile. Stock solutions were prepared and standardized by potentiometric titrations with a standard silver solution.

The pipettes used for measuring standard amounts of the 1,10-phenanthroline stock solution were coated with desicote. This was necessary to insure satisfactory drainage of the solution, otherwise "beading" of the solution would occur

on the walls of the pipette. The pipettes were calibrated after applying the desicote.

## PRELIMINARY INVESTIGATIONS

## Silver/bis(1,10-phenanthroline)silver(I) Nitrate Electrode

The silver/bis(1,10-phenanthroline)silver(I) nitrate electrode was first used by Grimes (22) in a study of the reactions of 1,10-phenanthroline with hydrogen, lithium, sodium and potassium ions. Later, Fullerton (21) used this electrode in a study of the reactions of 1,10-phenanthroline with a few of the transition metals. Both of the above authors calculated stability constants for poly(1,10-phenanthroline)-hydrogen species from data obtained with this electrode.

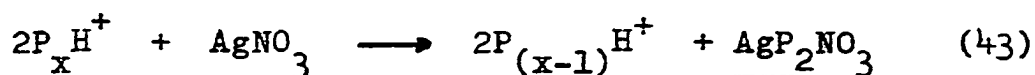
Due to the work of Grimes and Fullerton with regard to the poly(1,10-phenanthroline)-hydrogen species, the initial aspect of this work was concerned with an attempt to find a method which would more positively prove or disprove the existence of these species.

Assuming that the silver/bis-(1,10-phenanthroline)silver-(I) nitrate ( $\text{Ag}/\text{AgP}_2\text{NO}_3$ ) electrode was reversible to 1,10-phenanthroline as reported by Grimes and Fullerton, titrations were carried out wherein perchloric acid solutions were titrated with an aqueous solution of 1,10-phenanthroline. The observed emf of the  $\text{Ag}/\text{AgP}_2\text{NO}_3$  electrode versus the saturated calomel electrode was followed. A plot of the observed emf versus milliliters of titrant showed a small break at the ratio of  $H_T/P_T$  equal to two and a larger break at a ratio of  $H_T/P_T$  equal to one, however, neither break was

very sharp. No attempt was made to control the nitrate concentration as it was assumed that this quantity should remain relatively constant from the dissolution of the  $\text{AgP}_2\text{NO}_3$ . No other variations in the titration were noted after the break at the 1:1 ratio. Margerum, Bystroff, and Banks (36) have reported spectrophotometric evidence for the diprotonated 1,10-phenanthroline ion which, however, was in 1 M perchloric acid.

A second approach involved the titration of acid solutions of phenanthroline with tetrabutylammonium hydroxide. The potential of the  $\text{Ag}/\text{AgP}_2\text{NO}_3$  electrode and a glass electrode, both versus a saturated calomel electrode, were followed during the titration. No breaks were observed as the potential of the  $\text{Ag}/\text{AgP}_2\text{NO}_3$  electrode showed only a gradual change with increasing pH.

Another approach was decided upon in which phenanthroline solutions were titrated with standard silver nitrate. Assuming that the poly(1,10-phenanthroline)-hydrogen species exist, then Equation 43 would describe the reaction.



Several of these titrations were completed and free phenanthroline concentrations and apparent  $\bar{n}$  values were calculated from the observed potential assuming reversibility of the  $\text{Ag}/\text{AgP}_2\text{NO}_3$  electrode. Although the calculated values of  $\bar{n}$

appeared to approach 3, it was shown later that when the ratio of total 1,10-phenanthroline to total hydrogen ion was increased to 5, the potential of the  $\text{Ag}/\text{AgP}_2\text{NO}_3$  electrode indicated a  $\bar{n}$  value even greater than 3.

A titration described by the reaction above was also performed in which the pH and the potential of the  $\text{Ag}/\text{AgP}_2\text{NO}_3$  electrode were followed. A solution which was 0.01 M in nitric acid and 0.03 M in phenanthroline was titrated with 0.01 M  $\text{AgNO}_3$ . Only one break in both the pH curve and the potentiometric curve was apparent corresponding to the complete reaction of the phenanthroline with the silver in a ratio of 2:1.

Because the solution titrated, as described by the above reaction, is always saturated with  $\text{AgP}_2\text{NO}_3$ , a silver electrode should give the same response as the  $\text{Ag}/\text{AgP}_2\text{NO}_3$  electrode. Titrations were carried out in which the responses of a silver billet electrode and the  $\text{Ag}/\text{AgP}_2\text{NO}_3$  electrode were followed. The observed potentials of the two electrodes became identical only after the starting solution had been stirred for about one hour. The potentials remained the same throughout the first one-third of the titration whereupon the  $\text{Ag}/\text{AgP}_2\text{NO}_3$  electrode gradually became negative to the silver electrode by about 50 millivolts. The response of the silver electrode presented a smooth curve compared to that for the  $\text{Ag}/\text{AgP}_2\text{NO}_3$  electrode. It was subsequently shown that it was possible to

observe comparatively large potential differences between two Ag/AgP<sub>2</sub>NO<sub>3</sub> electrodes when both were in the same solution of 1,10-phenanthroline. This problem was also indicated by Fullerton (21) which he tried to eliminate by using one electrode for no more than three titrations of metal ion with 1,10-phenanthroline.

Because of the difficulties encountered by the present author with the Ag/AgP<sub>2</sub>NO<sub>3</sub> electrode, it was decided to investigate the possibility of using the silver electrode as an indicating electrode for free 1,10-phenanthroline in aqueous solution. If this were successful then it might be possible to study the complexes of other metals using the silver electrode.

#### Silver Electrode Prepared from Silver Oxalate

Silver electrodes were prepared by decomposition of silver oxalate on platinum spirals (19). Pure silver oxalate was prepared by the successive precipitation and dissolution of silver oxalate which was then made into a paste with water. This was applied to platinum spirals and heated slowly to about 180°C (silver oxalate decomposes at 140°C and also explodes if the heating rate is too fast). The electrodes were then placed in a furnace at 500°C for about six hours. A white silver coating was produced. The electrodes were checked by measuring the potential difference of two electrodes in dilute silver solutions. By selection of electrodes,

potentials differences in the hundredths of a millivolt were observed.

A three-compartment cell was designed for use in the measurement of the response of the silver electrodes to varying concentrations of silver ion. The center compartment which was separated from the outer two compartments by ultra-fine porosity pyrex disks was made to contain inert salt solutions which served as a salt bridge between the two silver solutions in the end compartments. The concentration of silver ion in one compartment was held constant while varying the silver concentration in the other compartment. The potential difference between two silver electrodes, one in each solution, was followed.

Because Grimes (22) reported the existence of the 1,10-phenanthroline complexes of the alkali metals, it was felt that it may be desirable to work with solutions in which the concentration of alkali metals was kept to a minimum. This prompted the study to determine the observed potential of a silver electrode in a series of silver solutions in which the concentration of alkali metal would be decreased. If reasonable potentiometric measurements could be made in solutions of low ionic strength, it was felt that this would eliminate the use of an inert electrolyte. That is, it would only be necessary for the silver ion and the metal ion under study to be present in the solution. Table 1 lists some of the results



Table 1. Potential measurements of dilute silver solutions containing varying amounts of potassium sulfate

Solution concentrations	E, millivolts					
	(Ag <sup>+</sup> ) = $\underline{1 \times 10^{-3} M}$	$\underline{5 \times 10^{-4} M}$	$\underline{1 \times 10^{-4} M}$	$\underline{5 \times 10^{-5} M}$	$\underline{1 \times 10^{-5} M}$	$\underline{5 \times 10^{-6} M}$
E theoretical	-41.35	-59.15	-100.50	-118.30	-159.65	-177.45
(K <sub>2</sub> SO <sub>4</sub> ) = 0.05M <sup>a</sup> Bridge = 0.05M K <sub>2</sub> SO <sub>4</sub>	-41.05	-58.84 -58.44 -58.58	-99.20	-115.70 -116.91	-153.70	-168.80 -167.17
(K <sub>2</sub> SO <sub>4</sub> ) = 0.005M <sup>a</sup> Bridge = 0.005M K <sub>2</sub> SO <sub>4</sub>	-38.67	-55.48	-96.56	-114.09	-153.16	-166.43
(Ag <sub>2</sub> SO <sub>4</sub> )+(K <sub>2</sub> SO <sub>4</sub> ) = 0.0075M <sup>a</sup> Bridge = 0.005M	-41.09	-59.45	-100.70	-118.10	-157.13	-170.87
(Ag <sub>2</sub> SO <sub>4</sub> )+(K <sub>2</sub> SO <sub>4</sub> ) = 0.0025M <sup>a</sup> No K <sub>2</sub> SO <sub>4</sub> in reference Bridge = 0.0025M	-43.40	-61.46	-102.82	-120.28	-155.73	-166.20
(Ag <sub>2</sub> SO <sub>4</sub> )+(K <sub>2</sub> SO <sub>4</sub> ) = 0.005M <sup>a</sup> Bridge = 0.005M	-42.18 -42.12	-60.05 -60.10	-101.70 -101.34	-119.12 -119.04	-157.33 -157.39	-171.25 -171.99
	(Ag <sup>+</sup> ) = $\underline{5 \times 10^{-4} M}$	$\underline{2.5 \times 10^{-4} M}$	$\underline{5 \times 10^{-5} M}$	$\underline{2.5 \times 10^{-5} M}$	$\underline{5 \times 10^{-6} M}$	$\underline{2.5 \times 10^{-6} M}$
(Ag <sub>2</sub> SO <sub>4</sub> )+(K <sub>2</sub> SO <sub>4</sub> ) = 0.0025M <sup>b</sup> Bridge = 0.0025M K <sub>2</sub> SO <sub>4</sub>	-42.23	-60.14	-101.28	-118.79	-151.63	-161.80

<sup>a</sup>(Ag<sup>+</sup>) in reference =  $5 \times 10^{-3} M$ .

<sup>b</sup>(Ag<sup>+</sup>) in reference =  $2.5 \times 10^{-3} M$ .

obtained. All measurements were made on separate solutions which had been prepared prior to placing them in the cell. Sulfate salts were used in anticipation of the experimental work with 1,10-phenanthroline as perchlorate and nitrate form insoluble salts with the bis(1,10-phenanthroline)silver(I) complex ion.

#### Junction Potential

Using the conditions of the last set of data in Table 1, a series of measurements was made of a solution  $2.5 \times 10^{-4} \text{M}$  in silver using a reference solution which was  $2.5 \times 10^{-3} \text{M}$ . In both solutions the total concentration of silver plus potassium was  $5 \times 10^{-3} \text{M}$ . The concentration of the salt bridge was varied and the following results were obtained.

$\text{K}_2\text{SO}_4$ in bridge	$1.25 \times 10^{-3} \text{M}$	$2.5 \times 10^{-3} \text{M}$	$5.0 \times 10^{-3} \text{M}$	$5.0 \times 10^{-1} \text{M}$
E (observed) mv.	-60.2	-60.0	-59.8	-59.4

These results indicate that the difference in the junction potentials at the two frits in the three-compartment cell is small and depends very little upon the salt bridge concentration when only silver and potassium are present in the experimental solutions.

Quite different results were obtained when these same measurements were made for silver solutions containing 1,10-phenanthroline. The results shown below are for a  $2.5 \times 10^{-3} \text{M}$  silver solution in which the concentration of 1,10-

phenanthroline was  $0.001M$ .

$K_2SO_4$ in bridge	$1.25 \times 10^{-3}M$	$5.0 \times 10^{-1}M$
E (observed) mv.	-4.70	-17.2

The absence of any appreciable junction potential in the silver solutions containing no 1,10-phenanthroline is apparently due to the small difference in the mobilities of the silver and potassium ion. When 1,10-phenanthroline is introduced, a silver complex is formed which is present at one junction and not at the other. The resultant potential of the two junctions is due then to the difference in mobility of the silver ion and the silver complex.

In order to decrease the junction potentials to a minimum it was decided that a saturated salt bridge would have to be used. It was hoped that this could be avoided because with no inert electrolyte in the experimental solutions the amount of diffusion from the salt bridge would contribute appreciably to the total concentration of ions. This diffusion, however, could still be controlled by using a five-compartment cell. The center compartment would contain the salt bridge, the right two compartments would contain the reference solution, and the left two compartments would contain the experimental solution. Under these conditions it would be necessary for the ions from the bridge to diffuse completely through one compartment of still solution before reaching the compartment

where measurement was taking place.

Experiments were conducted to measure the response of the silver electrodes in dilute silver solutions using the above mentioned cell. In each solution including the reference solution, the concentration of silver plus that of potassium equalled  $0.005M$ . The concentration of silver in the reference solution was  $2.5 \times 10^{-3}M$ . Table 2 shows the results obtained.

Table 2. Potential measurements of dilute silver solutions in a five compartment cell

$(Ag^+)$	E observed, millivolts	E theoretical, millivolts
$1.67 \times 10^{-3}$	10.5	10.42
$1.00 \times 10^{-3}$	23.8	23.54
$5.00 \times 10^{-3}$	41.2	41.35
$2.50 \times 10^{-4}$	59.4, 59.3	59.15
$1.67 \times 10^{-4}$	69.6	69.57
$1.00 \times 10^{-4}$	82.9, 82.7	82.69
$2.50 \times 10^{-5}$	118.5	118.30
$1.00 \times 10^{-5}$	140.0, 140.4	141.84

#### Silver-1,10-phenanthroline Equilibria

In order to determine the first formation constant for the reaction of silver with 1,10-phenanthroline, experimental solutions were adjusted so that the concentration of 1,10-phenanthroline was low compared to that of silver. If it is assumed that only the  $AgP^+$  species is formed, then the total concentration of 1,10-phenanthroline is represented by

$$P_T = (P) + (AgP^+) \quad (42)$$

The concentration of  $HP^+$  should be negligible in neutral solution. Total concentration of silver is represented by

$$Ag_T = (Ag^+) + (AgP^+) \quad (43)$$

The concentration of free silver was measured potentiometrically and it was intended to find (P) by difference. However, for very low concentrations of  $P_T$ , experimental results indicated that the concentration of  $AgP^+$  and  $P_T$  were almost identical precluding any calculation of reliable results for (P).

In order to partially inhibit the reaction of 1,10-phenanthroline with silver, a known quantity of acid was added to the experimental solutions. In this case the hydrogen ions act as antagonist ions which compete with the silver for 1,10-phenanthroline. The total concentration of 1,10-phenanthroline was then represented by

$$P_T = (HP^+) + (AgP^+) \quad (44)$$

After determining the concentration of  $AgP^+$  from Equation 43, the amount of  $HP^+$  could be found by difference. The concentration of free (P) could then be determined through the formation constant for  $HP^+$ . For concentrations of  $P_T$  ranging from  $3 \times 10^{-4} M$  to  $17 \times 10^{-4} M$  where the silver concentration was  $25 \times 10^{-4} M$ , calculated values of the first formation constant

ranged from  $2.64 \times 10^5$  to  $3.31 \times 10^5$ . Some discrepancy was noted, however, in that the pH of the solutions did not increase to account for the formation of  $HP^+$ . This led to the premise that most of the 1,10-phenanthroline over that needed for the formation of  $AgP^+$  was reacting to form  $AgP_2^+$  instead of reacting with the hydrogen ions, even though all of the silver had not yet been converted to  $AgP^+$ .

In light of the foregoing observation, a new approach was taken to calculate the concentration of  $AgP_2^+$  from potentiometric data as shown by the following equations.

$$P_T = (AgP^+) + 2(AgP_2^+) \text{ (neglect (P) and (HP}^+)) \quad (45)$$

$$\text{subtract: } Ag_T = (Ag^+) + (AgP^+) + (AgP_2^+) \quad (46)$$

$$P_T - Ag_T + (Ag^+) = (AgP_2^+) \quad (47)$$

It was desirable to compare the concentrations of  $AgP_2^+$  calculated from Equation 47 to values obtained by an independent method. It was found by means of a Job's plot at 360 m $\mu$  shown in Figure 1 that the yellow color of silver-1,10-phenanthroline solutions was due to the  $AgP_2^+$  species. This made it possible to compare the results from Equation 47 with respect to potentiometric measurements to those from spectrophotometric measurements on the same solutions. This comparison for a few solutions is shown in Table 3.

After the concentration of  $AgP_2^+$  is found, the

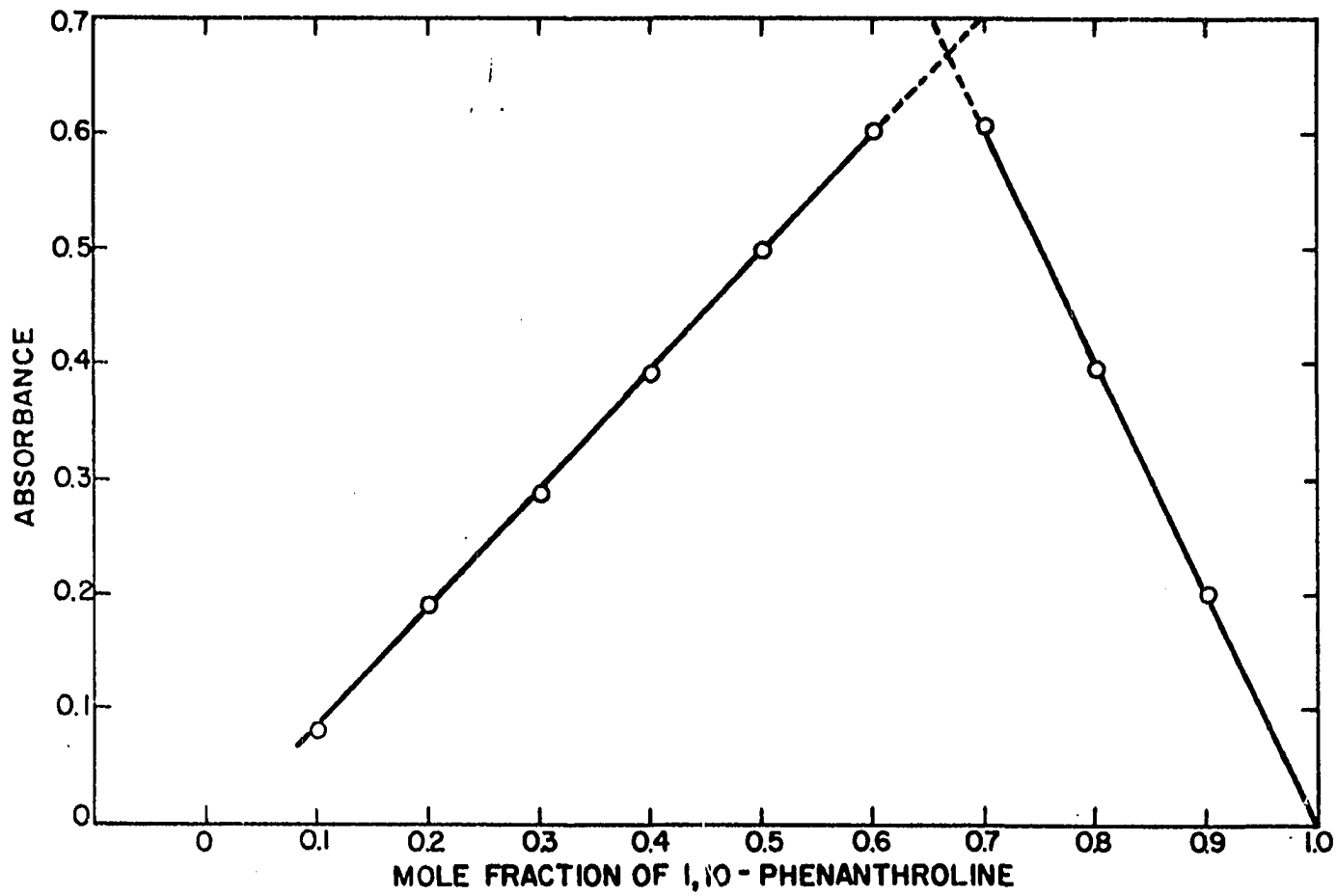


Figure 1. Job's plot at 360 m $\mu$  for silver-1,10-phenanthroline solution

Table 3. Concentrations of  $\text{AgP}_2^+$  from potentiometric and spectrophotometric measurements<sup>a</sup>

$P_T \times 10^3 \underline{M}$	$(\text{AgP}_2^+) \times 10^3 \underline{M}$ emf	$(\text{AgP}_2^+) \times 10^3 \underline{M}$ spectrophotometric (370 m $\mu$ )
2.112	0.927	0.946
2.416	1.093	1.097
2.718	1.224	1.243
3.014	1.378	1.406
3.318	1.564	1.542

$${}^a\text{Ag}_T = 2.5 \times 10^{-3} \underline{M}.$$

concentration of  $\text{AgP}^+$  may be calculated from Equation 46. If (P) and  $(\text{HP}^+)$  are considered, Equation 47 becomes

$$(\text{AgP}_2^+) + (\text{P}) + (\text{HP}^+) - (P_T - (\text{Ag}_c)) = 0 \quad (48)$$

where  $(\text{Ag}_c)$  is the concentration of complexed silver or  $\text{Ag}_T - (\text{Ag}^+)$ . Equation 48 may be written as

$$(\text{Ag}^+)(\text{P})^2 \beta_2 + (\text{P})(1 + k_a(\text{H}^+)) - (P_T - (\text{Ag}_c)) = 0 \quad (49)$$

If  $\beta_2$  and  $k_a$  are known, then (P) may be calculated by solving Equation 49.

Several determinations of  $\beta_2$  for the reaction  $(\text{Ag}^+) + 2(\text{P}) \rightleftharpoons (\text{AgP}_2^+)$  were made using the silver electrodes prepared by the silver oxalate decomposition. For seven determinations using varying concentrations of total 1,10-phenanthroline, the constants varied from  $0.08 \times 10^{12}$  to  $1.36 \times 10^{12}$ .



It was then discovered that it was possible for the potential difference for two of the prepared electrodes in the same dilute silver solution to be less than 0.1 mv. and then to change quite appreciably when both electrodes were placed in a solution containing excess 1,10-phenanthroline over that required to react with the silver present in the solution. The potential also varied with stirring. This was not observed when the silver was in excess.

Because the above was not observed when silver billet electrodes were used, determinations of  $\beta_2$  were made using the silver billet electrodes. The values for seven determinations varied from  $2.47 \times 10^{12}$  to  $5.13 \times 10^{12}$ . Although agreement of the individual determinations was much better in this case than when the prepared electrodes were used, better reproducibility was still desirable.

It had been observed when using both types of electrodes that a quite rapid change of potential occurred immediately after introducing the salt bridge between the two half cells. After about twenty minutes a fairly stable reading was obtained. Because the ionic concentration is relatively low in both half cells ( $0.005M$ ), it was decided to check the potentials versus time using experimental solutions containing excess potassium sulfate. The standard solution in this case was  $1.25 \times 10^{-3}M$  in silver sulfate and  $5.0 \times 10^{-2}M$  in potassium sulfate. The experimental solution was the same except that it was also  $5.8 \times 10^{-3}M$  in

1,10-phenanthroline. The potential of the concentration cell observed twenty seconds after introducing the salt bridge differed from the potential observed twenty minutes later by only about 0.5 mv. In view of this improvement it was considered to be desirable to use experimental solutions of higher ionic strength.

Because of the possibility of the potassium ions being complexed by 1,10-phenanthroline, as reported by Grimes (22), potential measurements were made using the same concentrations as above except that the concentration of potassium sulfate was varied. Measurements were also made where the potassium sulfate was omitted and lithium sulfate, sulfuric acid or copper(II) sulfate was added. The results obtained using the silver billet electrodes are shown in Table 4.

When a second ion is added to a solution containing silver and 1,10-phenanthroline, an increase in the concentration of free silver ion should occur if the second ion is also complexed by the 1,10-phenanthroline. This is shown to be the case with  $\text{H}_2\text{SO}_4$  and  $\text{CuSO}_4$  by the increase in the observed value of E. No increase in silver ion was observed, however, in the case of  $\text{K}_2\text{SO}_4$  and  $\text{Li}_2\text{SO}_4$ .

The absorbance of several of the above solutions was measured. All solutions were  $2.5 \times 10^{-3} \text{M}$  in silver and  $5.8 \times 10^{-3} \text{M}$  in 1,10-phenanthroline. The concentration of the added ion is shown in Table 5 with the results. It is to be

Table 4. Effect of other ions upon silver-1,10-phenanthroline equilibria

Potassium	E observed millivolts	Lithium	E observed millivolts	Hydrogen	E observed millivolts	Copper	E observed millivolts
0.02M	-392.4	0.02M	-393.2	0.02M	-56.2	0.001M	-37.7
0.04M	-394.8	0.02M <sup>a</sup>	-391.7	0.05M	-35.3		
0.06M	-395.5	0.10M	-393.5				
0.08M	-395.9	0.10M <sup>a</sup>	-395.4				
0.10M	-397.2						
1.00M	-400.6						

<sup>a</sup>Li<sub>2</sub>SO<sub>4</sub> bridge was used having the same concentration as a solution of saturated K<sub>2</sub>SO<sub>4</sub>.

Table 5. Absorbance of silver-1,10-phenanthroline solutions with added ions

Wave-length	No ion added	0.08M potassium	1M potassium	0.002M lithium	0.1M lithium	0.2M lithium	0.02M hydrogen	0.05M hydrogen
400 m $\mu$	0.368	0.370	0.379	0.370	0.370	0.374	0.332	0.287
390 m $\mu$	0.546	0.547	0.555	0.550	0.547	0.547	0.490	0.423
380 m $\mu$	0.750	0.743	0.750	0.742	0.740	0.740	0.679	0.590

noted that the added hydrogen ion decreased the absorbance of the solution indicating that the concentration of  $\text{AgP}_2^+$  was decreased due to the reaction of hydrogen ion with 1,10-phenanthroline. No decrease in absorbance was observed for the lithium or potassium salt even though, as in the case of potassium, a concentration as high as  $1.0\text{M}$  was used.

The implication of the results shown in Tables 4 and 5 is the following. If complexes of 1,10-phenanthroline and potassium exist in solution then the formation constants for these complexes appear to be much lower than the values which were determined with the  $\text{Ag}/\text{AgP}_2\text{NO}_3$  electrode by previous workers.

In view of the results with regard to the effect of potassium on the silver-1,10-phenanthroline equilibria it was judged to be permissible to use potassium salts to control ionic strength and pH. Also, the three-compartment concentration cell could replace the one with five compartments if diffusion from the saturated salt bridge were not appreciable. This would be a decided advantage as the concentration of 1,10-phenanthroline in the experimental solutions could be varied by titration, eliminating the necessity of preparing individual solutions for each measurement.

In order to check the diffusion of potassium sulfate from the saturated salt bridge through the ultra-fine porosity pyrex disk, a conductometric time study was carried out. Distilled water was placed in the experimental compartment

and saturated potassium sulfate in the center compartment. In approximately two hours the conductance had risen to a value corresponding to a potassium sulfate concentration of  $5 \times 10^{-5} \text{M}$ . Because this amount would be negligible compared to the concentration of salt needed to control the ionic strength and pH, all further measurements were made with the three-compartment cell.

## PRINCIPAL INVESTIGATIONS

## Evaluation of the System

After it had been determined that the saturated potassium sulfate salt bridge should be used and that potassium sulfate could be used to control ionic strength, the response of the silver billet electrodes to dilute silver solutions was evaluated. The billet electrodes were cleaned by buffing lightly with fine steel wool followed by thorough rinsing with distilled water. Although this did not produce electrodes whose potential differences were as low in the same silver solution as the electrodes prepared from silver oxalate, the over-all response including that to 1,10-phenanthroline solutions was much better. With the titration scheme it was also possible to evaluate the inherent potential difference in the electrodes by starting each experiment with identical solutions in both sides of the concentration cell. The conditions for calibration of the cell are shown below.

Ag	Experimental	K <sub>2</sub> SO <sub>4</sub> saturated solution	Reference	Ag
	Ag <sub>2</sub> SO <sub>4</sub> < 1.25x10 <sup>-3</sup> M		Ag <sub>2</sub> SO <sub>4</sub> = 1.25x10 <sup>-3</sup> M	
	KAc = 3.0x10 <sup>-2</sup> M		KAc = 3.0x10 <sup>-2</sup> M	
	HAc = 3.013x10 <sup>-2</sup> M		HAc = 3.013x10 <sup>-2</sup> M	
	K <sub>2</sub> SO <sub>4</sub> (to make μ=0.1)		K <sub>2</sub> SO <sub>4</sub> (to make μ=0.1)	

In all solutions measured the concentrations of sulfate, acetate, and acetic acid were equal to those in the reference solution. The ionic strength in both the reference and

experimental solutions was 0.1 and the pH was 4.80. The concentrations of silver were calculated from the emf's of the concentration cell and compared to the concentrations known to be present.

The potential of the working electrode as compared to the reference electrode may be expressed as

$$E = - \frac{RT}{F} \ln \frac{f_R(\text{Ag}^+)_R}{f_X(\text{Ag}^+)_X} \quad (50)$$

where  $f$  represents the activity coefficient and  $r$  and  $x$  stand for the reference solution and experimental solution, respectively. Because the ionic strength of both the reference solution and the experimental solution was 0.1, the activity coefficients cancel out. If  $\text{Ag}'$  is defined as

$$(\text{Ag}') = (\text{Ag}^+) + (\text{AgSO}_4^-) + (\text{AgAc}) \quad (51)$$

then 
$$(\text{Ag}') = (\text{Ag}^+) (1 + k_s(\text{SO}_4^{=}) + k_c(\text{Ac}^-)) \quad (52)$$

and 
$$(\text{Ag}^+) = (\text{Ag}') / (1 + k_s(\text{SO}_4^{=}) + k_c(\text{Ac}^-)) \quad (53)$$

When this expression is substituted into Equation 50, the potential of the working electrode with respect to the reference electrode is

$$E = - \frac{RT}{F} \ln \frac{(\text{Ag}')_R}{(\text{Ag}')_X} \quad (54)$$

as the concentration of sulfate and acetate remain constant. Therefore, if the value of the total silver, i.e.  $(\text{Ag}^+) +$



(AgSO<sub>4</sub><sup>-</sup>) + (AgAc), in the reference solution is substituted for (Ag<sup>+</sup>)<sub>r</sub> in Equation 54, then the value of (Ag<sup>+</sup>)<sub>x</sub> calculated from the observed emf also includes these complexes. If on the other hand, the free silver ion concentration in the reference solution is calculated from the total silver present employing the formation constants, k<sub>s</sub> and k<sub>c</sub>, and substituted for (Ag<sup>+</sup>)<sub>r</sub>, then the value of (Ag<sup>+</sup>)<sub>x</sub> calculated from Equation 54 should represent the free silver ion present in the experimental solution. Table 6 shows the comparison of the silver concentration known to be present and that calculated from Equation 54.

The first approach which was used for the determination of the conditional formation constants for silver from potentiometric titration data is described below. The expressions for the conditional formation constants are

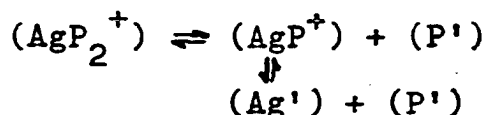
$$\beta_1^i = \frac{(AgP^+)}{(Ag^+)(P^+)} \quad \text{and} \quad \beta_2^i = \frac{(AgP_2^+)}{(Ag^+)(P^+)^2} \quad (55)$$

Table 6. Potential measurements of dilute silver solutions

E millivolts	pAg <sub>x</sub> <sup>i</sup>		E millivolts	pAg <sub>x</sub> <sup>i</sup>	
	taken	emf		taken	emf
-17.8	2.90	2.90	-94.8	4.20	4.20
-28.2	3.08	3.08	-118.0	4.60	4.60
-35.8	3.20	3.21	-135.5	4.90	4.89
-59.1	3.60	3.60	-145.6	5.08	5.06
-76.8	3.90	3.90	-152.6	5.20	5.18
-87.2	4.08	4.08			

The term,  $(Ag')$ , is defined above and the term,  $(P')$ , is defined as the concentration of free 1,10-phenanthroline plus the concentration of the phenanthrolium ion.

Assuming that a soluble compound of  $AgP_2^+$  is dissolved in a solution containing sulfate, acetate, and acetic acid, the complex would dissociate in the following manner.



The total concentration of 1,10-phenanthroline uncomplexed by silver is then represented by

$$(P') = 2(Ag') + (AgP^+) \quad (56)$$

$$(P') = 2(Ag') + \beta_1^i (Ag')(P') \quad (57)$$

$$(P') = \frac{2(Ag')}{1 - \beta_1^i (Ag')} \quad (58)$$

This is a special case of an equation which describes the concentration of  $(P')$  where either silver or 1,10-phenanthroline may be in excess as is shown below.

$$2 Ag_T = 2(Ag') + 2(AgP^+) + 2(AgP_2^+) \quad (59)$$

$$P_T = (P') + (AgP^+) + 2(AgP_2^+) \quad (60)$$

Subtract Equation 60 from 59

$$\begin{aligned} 2 Ag_T - P_T &= 2(Ag') - (P') + (AgP^+) \\ &= 2(Ag') - (P') + \beta_1^i (Ag')(P') \end{aligned} \quad (61)$$

and rearrange

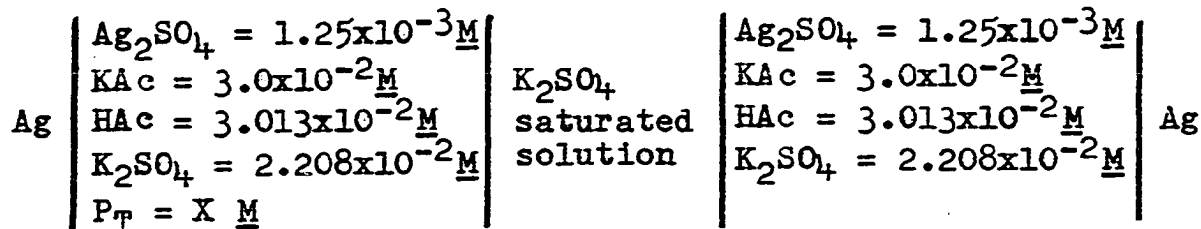
$$(P') = \frac{P_T - 2 Ag_T + 2 (Ag')}{1 - \beta_1' (Ag')} \quad (62)$$

When Equation 62 is substituted into either Equation 59 or 60, the following equation is obtained.

$$\begin{aligned} \beta_2' (P_T - 2Ag_T + 2(Ag'))^2 + \beta_1'^2 (Ag')(Ag_T - P_T - (Ag')) \\ + \beta_1' P_T + \frac{Ag_T - (Ag')}{(Ag')} = 0 \end{aligned} \quad (63)$$

This equation is a function of the known quantities,  $P_T$  and  $Ag_T$ ; the uncomplexed silver,  $(Ag')$ , which is measured; and the unknown conditional stability constants,  $\beta_1'$  and  $\beta_2'$ .

Titration were carried out holding  $Ag_T$  constant while varying  $P_T$ . The cell conditions during the titration are represented below.



By making the titrant identical to the solution being titrated except for the concentration of 1,10-phenanthroline, the ionic strength and pH were held constant at 0.1 and 4.80, respectively. Table 7 shows the results of five titrations giving an indication of the reproducibility that can be expected in this range.

Table 7. Titration of silver with 1,10-phenanthroline

$P_T \times 10^3 \underline{M}$	E observed, millivolts					Ave.
	1	2	3	4	5	
0.3973	- 2.49	- 2.55	- 2.45	- 2.44	- 2.55	- 2.50
0.8039	- 4.94	- 4.98	- 4.95	- 4.86	- 4.99	- 4.94
1.197	- 7.54	- 7.56	- 7.54	- 7.44	- 7.54	- 7.52
1.601	-10.4	-10.5	-10.5	-10.4	-10.5	-10.5
2.001	-13.7	-13.9	-13.8	-13.7	-13.8	-13.8
2.400	-17.4	-17.6	-17.6	-17.4	-17.5	-17.5
2.802	-21.8	-22.0	-22.0	-21.8	-21.9	-21.9
3.199	-26.9	-27.2	-27.2	-27.0	-27.1	-27.1
3.598	-33.4	-33.8	-33.7	-33.5	-33.7	-33.6
4.001	-42.2	-42.6	-42.6	-42.4	-42.5	-42.5
4.401	-55.8	-56.3	-56.2	-56.1	-56.2	-56.1
4.800	-86.5	-86.6	-86.5	-86.4	-86.7	-86.5

Conditional formation constants,  $\beta_1'$  and  $\beta_2'$  for the reaction of 1,10-phenanthroline with silver, were calculated by the method of least squares using Equation 63. The values of  $\beta_1'$  and  $\beta_2'$  were  $2.04 \times 10^3$  and  $3.68 \times 10^8$ , respectively. These constants were used to calculate the concentration of total 1,10-phenanthroline for each experimental point which was compared to the known concentration. This was accomplished by solving Equation 64 which is derived from Equation 59 and substituting into Equation 65 which is derived from Equation 60.

$$(Ag')(P')^2\beta_2' + (Ag')(P')\beta_1' + (Ag') - Ag_T = 0 \quad (64)$$

$$P_T = (P') + (Ag')(P')\beta_1' + 2(Ag')(P')^2\beta_2' \quad (65)$$

The results are shown in Table 8 where  $P_{Tx}$  and  $P_{Tc}$  are, respectively, the experimental and calculated values of total 1,10-phenanthroline.  $Ag'$  is the concentration of silver uncomplexed by 1,10-phenanthroline which was calculated from the emf data.

Table 8. Comparison of experimental and calculated values of 1,10-phenanthroline

$(Ag') \times 10^5 \underline{M}$	$P_{Tx} \times 10^3 \underline{M}$	$P_{Tc} \times 10^3 \underline{M}$	$(Ag') \times 10^5 \underline{M}$	$P_{Tx} \times 10^3 \underline{M}$	$P_{Tc} \times 10^3 \underline{M}$
226.8	0.397	0.412	106.7	2.802	2.799
206.2	0.804	0.806	87.09	3.199	3.205
186.6	1.197	1.191	67.56	3.598	3.618
166.2	1.601	1.593	47.86	4.001	4.046
146.1	2.001	1.996	28.13	4.401	4.499
126.4	2.400	2.394	8.608	4.800	5.053

Preliminary titrations were performed wherein a second metal was introduced into the experimental silver solutions. The total concentrations of silver and the second metal were held constant while varying the concentration of 1,10-phenanthroline. When the data were compared to those of Table 7 where only silver was present, it was evident that  $\bar{n}$  for copper and cadmium did not approach three until the concentration of silver was of the order of  $10^{-7}$  or  $10^{-8}$  M. Table 8 shows that the deviation of  $P_{Tc}$  from  $P_{Tx}$  is becoming appreciable when the silver concentration is of the order of  $10^{-4}$  M when

the constants given above are used to calculate  $P_{Tc}$ .

A tentative new  $\beta_2^1$  for silver was calculated from a single titration with 1,10-phenanthroline using data obtained after the stoichiometric point and was found to be approximately  $2 \times 10^{11}$ . This is in the same range as values previously obtained when measurements were made on singly prepared solutions. The constants used to calculate the results in Table 8, therefore, only described the system because of the limited ratio of total 1,10-phenanthroline to total silver which was used.

In order to describe the silver-1,10-phenanthroline system in the presence of excess 1,10-phenanthroline, it was predetermined that silver concentrations of the order of  $10^{-8}$  or  $10^{-9}$  M would have to be measured. This made it desirable to calibrate the concentration cell for silver concentrations in this range.

The calibration in this range was made by means of a titration with chloride. At the beginning of the titration the reference and experimental solutions were both  $1.0 \times 10^{-3}$  molar in total silver. The sodium chloride titrant was made to contain the same amounts of sulfate, acetate, and acetic acid as the reference solution and the experimental solution to be titrated. Due to the increasing amount of sodium chloride, the ionic strength of the solution being titrated varied from 0.1 to approximately 0.14 during the titration.

The concentration of silver calculated from emf measurements was compared to that calculated from the known concentration of chloride and the solubility product of silver chloride (26). Even though the ionic strength was not exactly 0.1 throughout the titration, the solubility product constant was adjusted for  $\mu = 0.1$  using the ion activity coefficients described by Kielland (27). Because only the free silver ion is involved in the solubility product, it was necessary in this case to account for the sulfate (45) and acetate (35) complexes of silver. The values of the formation constants for these complexes were also adjusted for  $\mu = 0.1$ . All potentiometric measurements were taken beyond the equivalence point. It was shown that a negligible amount of the excess chloride ion was present as  $\text{AgCl}_2^-$  (26). Table 9 shows the results from the titration with chloride.

Table 9. Potential measurements of silver solutions<sup>a</sup> containing chloride

$(\text{Cl}^-)$ $\times 10^3$	E millivolts (s.p.)	$\text{pAg}_x$	$\text{pAg}_x$ (emf)	$(\text{Cl}^-)$ $\times 10^3$	E millivolts (s.p.)	$\text{pAg}_x$	$\text{pAg}_x$ (emf)
2.885	-230.0	6.97	6.99	18.56	-277.4	7.78	7.79
4.720	-242.3	7.18	7.20	22.32	-282.1	7.86	7.88
8.186	-256.2	7.42	7.44	27.87	-287.8	7.95	7.97
11.41	-264.8	7.57	7.58	36.89	-295.0	8.08	8.09
15.84	-273.3	7.71	7.73	43.91	-299.6	8.15	8.17

<sup>a</sup>Reference solution:  $\text{Ag}_2\text{SO}_4 = 5.00 \times 10^{-4} \text{M}$ ;  $\text{K}_2\text{SO}_4 = 2.28 \times 10^{-2} \text{M}$ ;  $\text{KOAc} = 3.00 \times 10^{-2} \text{M}$ ;  $\text{HOAc} = 3.01 \times 10^{-2} \text{M}$ .

In view of the assumptions and adjustments made in order to make the comparisons of Table 9, it was felt that the results were satisfactory. Equation 54 was therefore also used for the calculation of silver concentrations from emf data obtained from silver solutions in which 1,10-phenanthroline was in excess.

### Stability Constants of Silver-1,10-phenanthroline Complexes

Titration of silver with 1,10-phenanthroline were performed as described previously using the three-compartment cell. In this case the conditions of the reference solution which was also the solution being titrated was as follows:  $\text{Ag}_2\text{SO}_4 = 5.00 \times 10^{-4} \text{M}$ ;  $\text{K}_2\text{SO}_4 = 2.28 \times 10^{-2} \text{M}$ ;  $\text{KAc} = 3.00 \times 10^{-2} \text{M}$ ;  $\text{HAc} = 3.01 \times 10^{-2} \text{M}$ ;  $\mu = 0.1$ , and  $\text{pH} = 4.80$ . The titrant was identical in composition except that it was also  $1.056 \times 10^{-2} \text{M}$  in 1,10-phenanthroline. The titration curve is shown in Figure 2 which represents the data in Table 10. Each potential measurement represents an average for the particular concentration of total 1,10-phenanthroline.

Values for the over-all conditional formation constant,  $\beta_2'$ , were calculated from the measured concentration of silver, ( $\text{Ag}'$ ), and the known excess of 1,10-phenanthroline, ( $\text{P}'$ ), present after the end point. Due to the small concentration of uncomplexed silver present after the stoichiometric point, the concentration of  $\text{AgP}_2^+$  was  $1.0 \times 10^{-3} \text{M}$ . Table 11 lists the



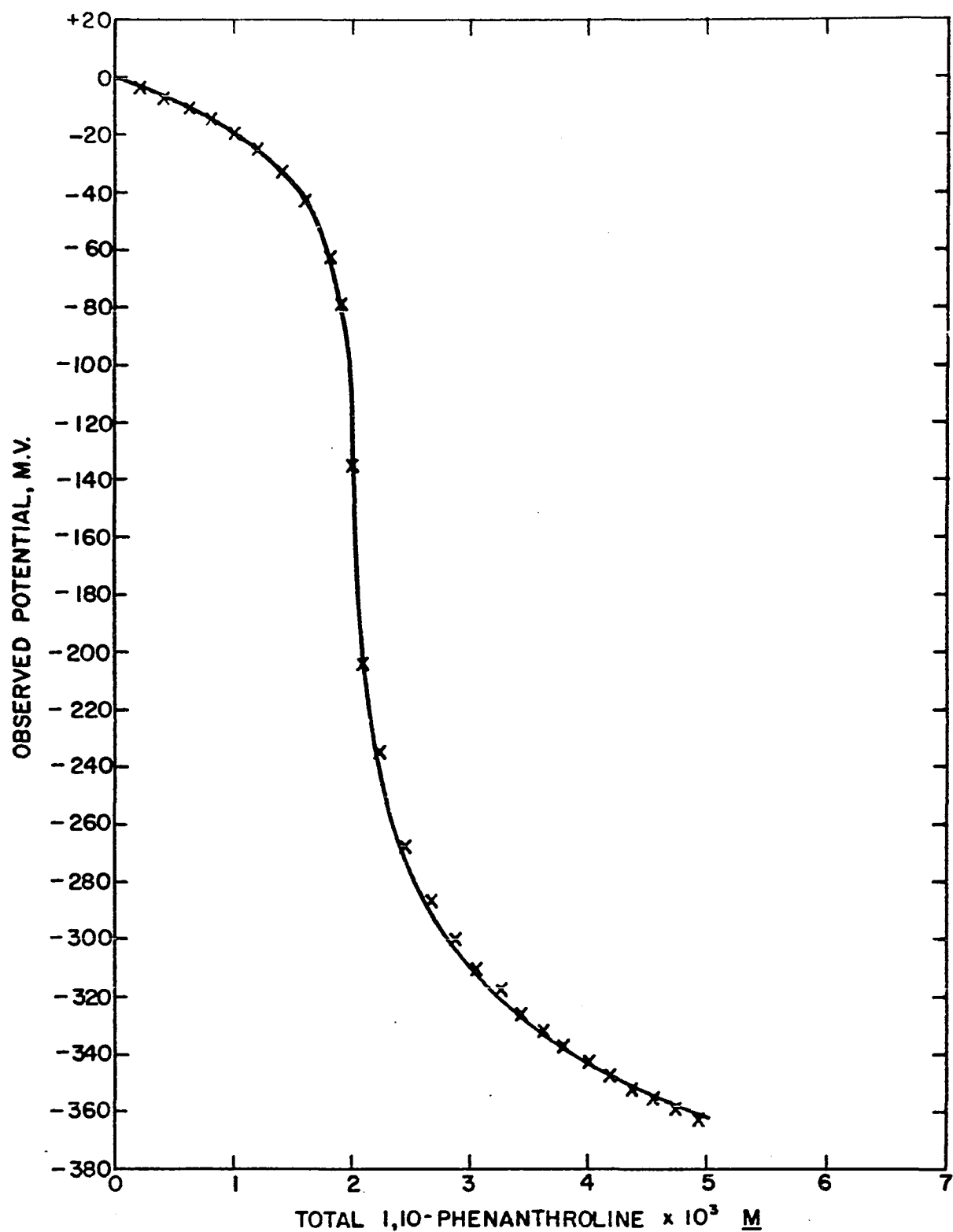


Figure 2. Titration of silver with 1,10-phenanthroline

Table 10. Titration of silver with 1,10-phenanthroline

$P_T \times 10^3 \underline{M}$	E, millivolts	$P_T \times 10^3 \underline{M}$	E, millivolts
0.1969	3.3	2.602	286.8
0.3963	6.4	2.800	299.9
0.5976	10.0	3.000	310.3
0.8001	14.0	3.200	318.0
1.003	19.0	3.400	325.6
1.198	24.6	3.598	331.5
1.401	32.5	3.799	336.8
1.603	43.2	4.000	342.2
1.803	62.0	4.202	346.9
1.897	79.2	4.402	351.0
2.002	135.3	4.600	354.9
2.098	203.5	4.801	358.5
2.198	235.4	5.001	362.3
2.399	267.6		

Table 11. Values of  $\log \beta_2^i$  for silver

E millivolts	$P^{P^i}$	$\log \beta_2^i$	E millivolts	$P^{P^i}$	$\log \beta_2^i$
-318.0	2.921	11.217	-346.9	2.657	11.179
-325.6	2.854	11.212	-351.0	2.619	11.173
-331.5	2.796	11.197	-354.9	2.585	11.170
-336.8	2.745	11.184	-358.5	2.553	11.166
-342.2	2.699	11.183	-362.3	2.523	11.170

$\log \beta_2^i = 11.186 \pm 0.018$   
 $\log \beta_2 = 12.07$

values calculated from the last ten points of the titration. The value of  $\beta_2$  is also given wherein the concentrations of the sulfate and acetate complexes of silver and the 1,10-phenanthroline ion (34) are taken into account.

Once  $\beta_2^!$  is known it is possible to calculate  $\beta_1^!$  using experimental points prior to the stoichiometric point. Equation 68 results from subtracting the expression for total silver from that representing total 1,10-phenanthroline.

$$P_T = (P') + (AgP^+) + 2(AgP_2^+) \quad (66)$$

$$Ag_T = (Ag') + (AgP^+) + (AgP_2^+) \quad (67)$$

$$P_T - Ag_T = (P') - (Ag') + (AgP_2^+) \quad (68)$$

Upon substitution for  $(AgP_2^+)$  and rearranging, Equation 69 is obtained from which  $(P')$  may be determined using

$$(Ag') \beta_2^! (P')^2 + (P') + Ag_T - (Ag') - P_T = 0 \quad (69)$$

the values of  $(Ag')$  calculated from the experimental emf's. The concentration of  $AgP_2^+$  is calculated from

$$(AgP_2^+) = (Ag') \beta_2^! (P')^2 \quad (70)$$

and the concentration of  $AgP^+$  from

$$(AgP^+) = Ag_T - (Ag') - (AgP_2^+) \quad (71)$$

All quantities necessary for the calculation of  $\beta_1^!$  are now known and the values calculated are listed in Table 12.

Table 12. Values of  $\log \beta_1^I$  for silver

E millivolts	$P^{P^I}$	$\log \beta_1^I$	E millivolts	$P^{P^I}$	$\log \beta_1^I$
-14.0	5.686	4.544	-32.5	5.402	4.536
-19.0	5.591	4.536	-43.2	5.280	4.488
-24.6	5.504	4.492	-62.0	5.095	4.550
$\log \beta_1^I = 4.525 \pm 0.027$					
$\log \beta_1 = 5.02$					

Using the values for  $\beta_1^I$  and  $\beta_2^I$ , the concentration of total 1,10-phenanthroline,  $P_T$ , was calculated for each experimental point using Equations 64 and 65 as described previously. The calculated values are plotted in Figure 2 as a comparison to the experimental curve.

#### Metal(II)-1,10-phenanthroline System

##### The competitive system of silver(I)-M(II)-1,10-phenanthroline

When silver and a second metal are both present in a solution of 1,10-phenanthroline, a new equilibria is established due to the competition for 1,10-phenanthroline caused by the presence of the second metal. This will be true only if the stabilities of the complexes of the second metal are somewhat similar to those of silver.

A system containing silver, a second metal, (M), and 1,10-phenanthroline may be described as follows where ion

charges are left out for convenience and  $\beta_0$  is defined as having a value of one.

$$\beta_i^{\text{Ag}} = \frac{(\text{AgP}_i)}{(\text{Ag}')(\text{P}')^i}, \quad \beta_j^{\text{M}} = \frac{(\text{MP}_j)}{(\text{M}')(\text{P}')^j} \quad (72)$$

$$\text{Ag}_T = (\text{Ag}') + \sum_1^{I=2} (\text{AgP}_i) = (\text{Ag}') \sum_0^{I=2} \beta_i^{\text{Ag}} (\text{P}')^i \quad (73)$$

$$\text{M}_T = (\text{M}') + \sum_1^J (\text{MP}_j) = (\text{M}') \sum_0^J \beta_j^{\text{M}} (\text{P}')^j \quad (74)$$

$$\text{P}_T = (\text{P}') + (\text{Ag}') \sum_1^{I=2} i \beta_i^{\text{Ag}} (\text{P}')^i + (\text{M}') \sum_1^J j \beta_j^{\text{M}} (\text{P}')^j \quad (75)$$

Bjerrum's (6) formation function for each metal is given by

$$\bar{n}_{\text{Ag}} = \frac{(\text{Ag}') \sum_1^{I=2} i \beta_i^{\text{Ag}} (\text{P}')^i}{\text{Ag}_T} \quad (76)$$

and

$$\bar{n}_{\text{M}} = \frac{(\text{M}') \sum_1^J j \beta_j^{\text{M}} (\text{P}')^j}{\text{M}_T} = \frac{\text{P}_T - \bar{n}_{\text{Ag}} \text{Ag}_T - (\text{P}')}{\text{M}_T} \quad (77)$$

The formation function  $\bar{n}_{\text{M}}$  may also be expressed as

$$\bar{n}_{\text{M}} = \frac{\sum_1^J j \beta_j^{\text{M}} (\text{P}')^j}{\sum_0^J \beta_j^{\text{M}} (\text{P}')^j} \quad (78)$$

Combination of Equations 77 and 78 gives

$$\sum_0^J (\text{P}_T - \bar{n}_{\text{Ag}} \text{Ag}_T - (\text{P}') - j \text{M}_T) \beta_j^{\text{M}} (\text{P}')^j = 0 \quad (79)$$

which is of the same form as Equation 37 (equation for which

the least squares program was designed).

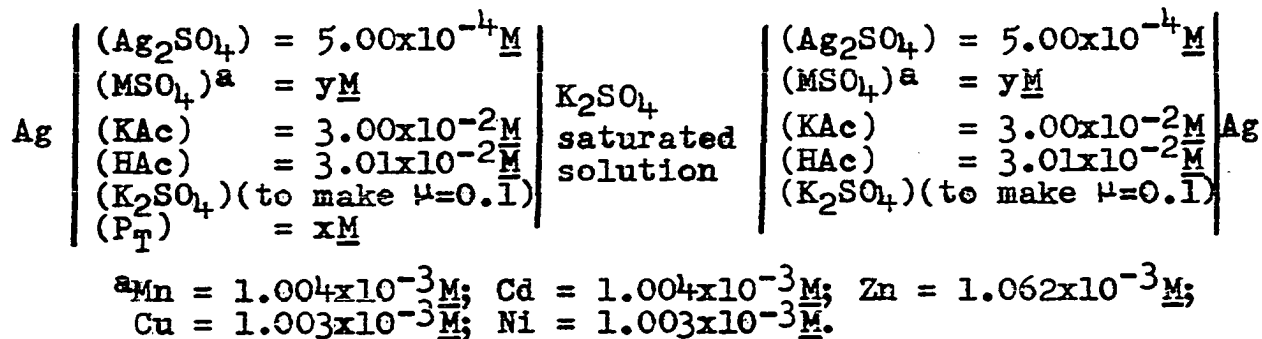
Titration were performed which were identical to those with silver alone except that a known amount of a second metal was present. As before the reference solution, the solution to be titrated, and the titrant were of identical composition except for the 1,10-phenanthroline in the titrant.

The metals studied were cadmium(II), zinc(II), copper(II) nickel(II), and manganese(II). No attempt was made for iron because iron(II) reduced silver(I) in the initial solutions. An attempt was made to study cobalt(II) with no success.

In the case of cobalt, it was evident that the system was not functioning properly after the first increment of titrant had been added. The potential drop of the working electrode was too large to be accounted for only by complexation reactions. After the solution had sat overnight the presence of metallic silver was noted. Apparently cobalt(III) forms a complex which is sufficiently more stable than cobalt(II) with the result that the reduction potential for  $\text{Co(III)} + e^- \rightleftharpoons \text{Co(II)}$  is reduced to a value less than that for  $\text{Ag(I)} + e^- \rightleftharpoons \text{Ag}$ . This appears reasonable when it is considered that the logarithm of the over-all formation constants for the reaction of ethylenediamine with cobalt(III) and cobalt(II) have been reported as 48.69 and 13.82, respectively (6). Also, Paglia and Sironi (41) have reported  $E^\circ$  to be -0.42 volts for the reaction,

$\text{CoP}_3(\text{ClO}_4)_3 + e^- \rightleftharpoons \text{CoP}_3(\text{ClO}_4)_2 + \text{ClO}_4^-$ . This is considerably lower than the reduction potential for silver(I) to silver which is 0.80 volts.

The cell conditions during the titrations in which a second metal was present are represented below.



After each addition of titrant the system came to equilibrium in approximately three to five minutes in most cases. Equilibrium was assumed to have been attained when two consecutive potential measurements, one minute apart, did not differ by more than 0.01 to 0.02 of a millivolt. Equilibrium was very slowly established in the titration of nickel, an hour being required for certain experimental points.

The titration curves are shown in Figures 3, manganese; 4, cadmium; 5, zinc; 6, copper; 7, nickel; and are superimposed in Figure 8. In each case the curve for silver is shown for means of comparison.

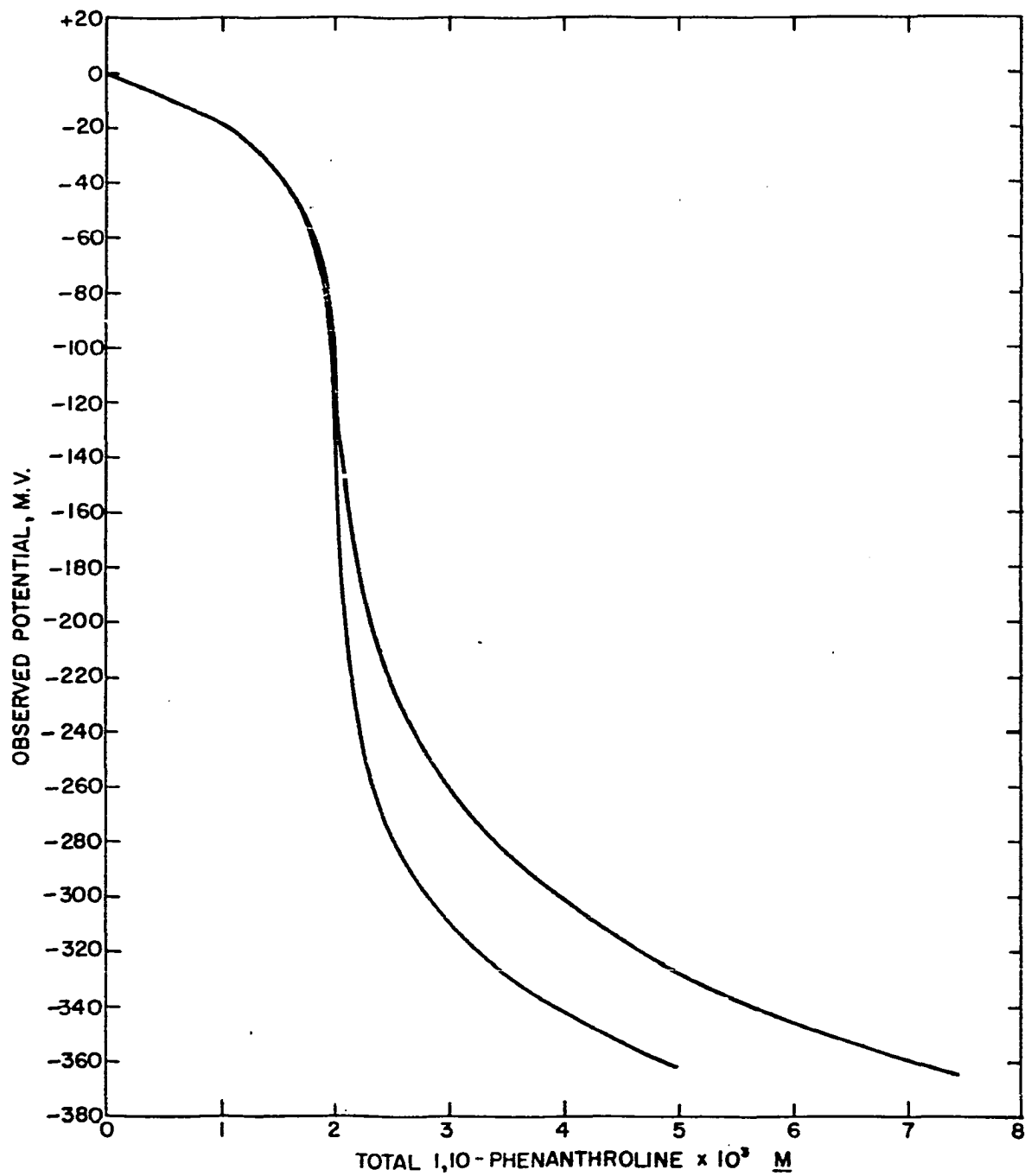


Figure 3. Titration of manganese with 1,10-phenanthroline



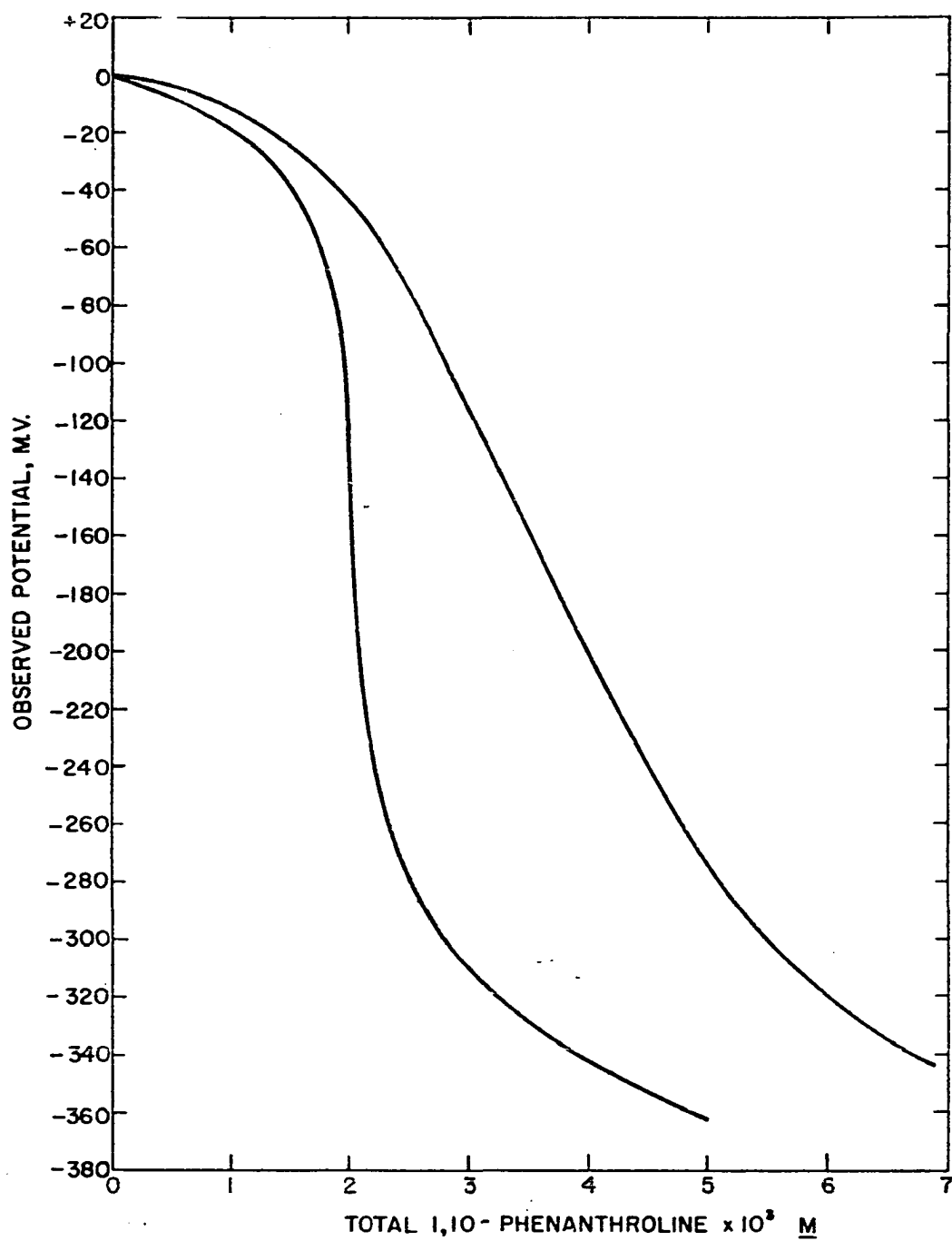


Figure 4. Titration of cadmium with 1,10-phenanthroline

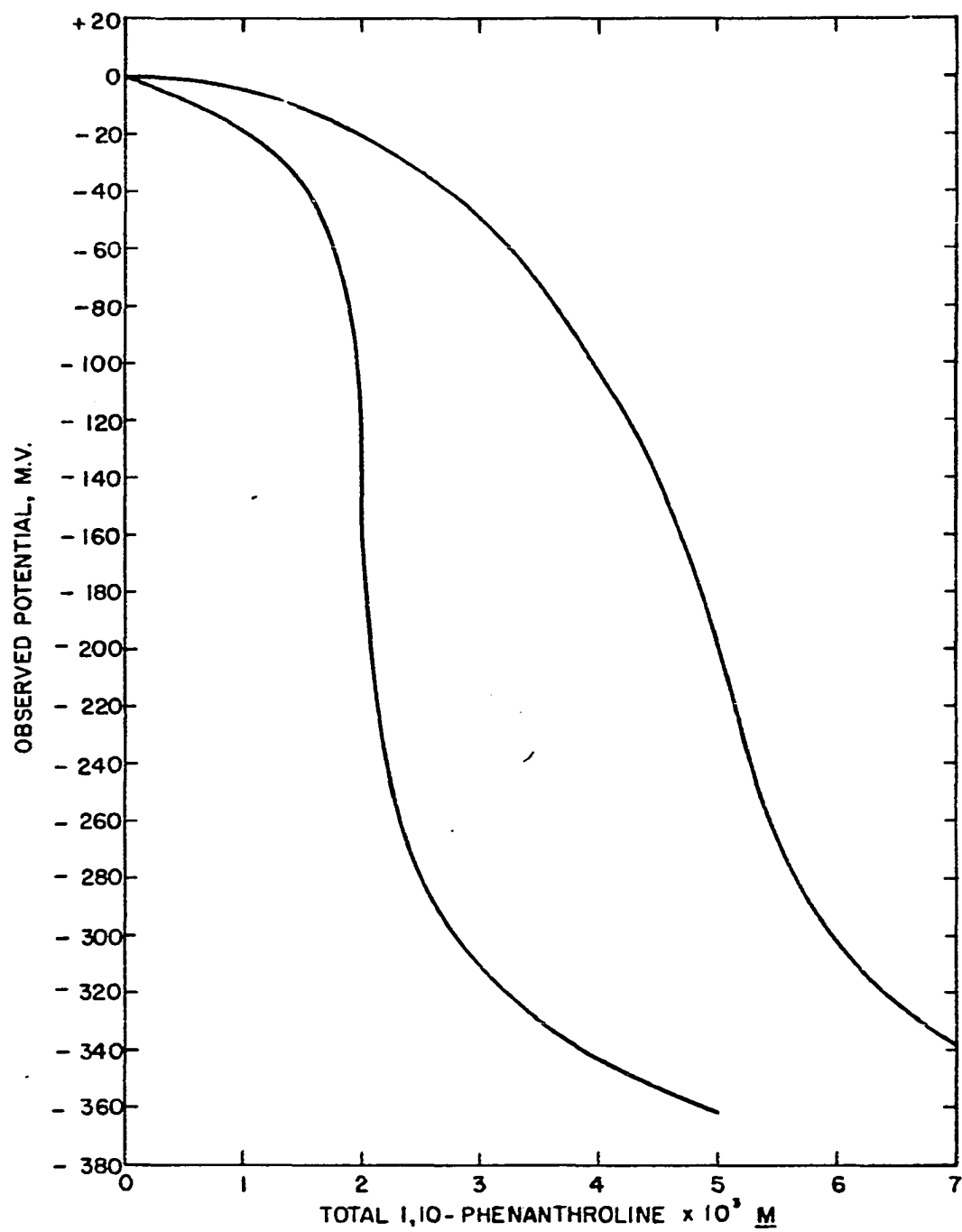


Figure 5. Titration of zinc with 1,10-phenanthroline

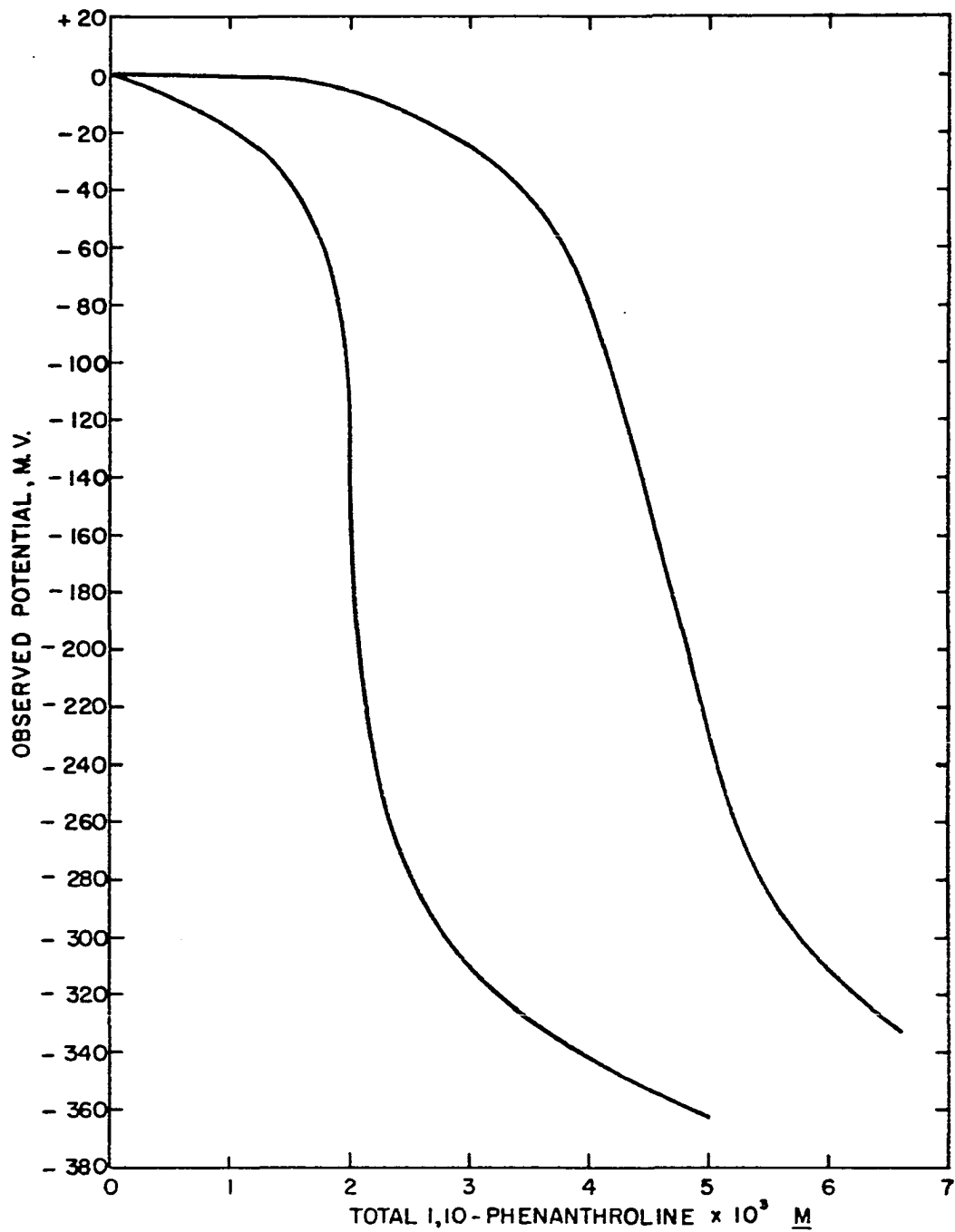


Figure 6. Titration of copper with 1,10-phenanthroline

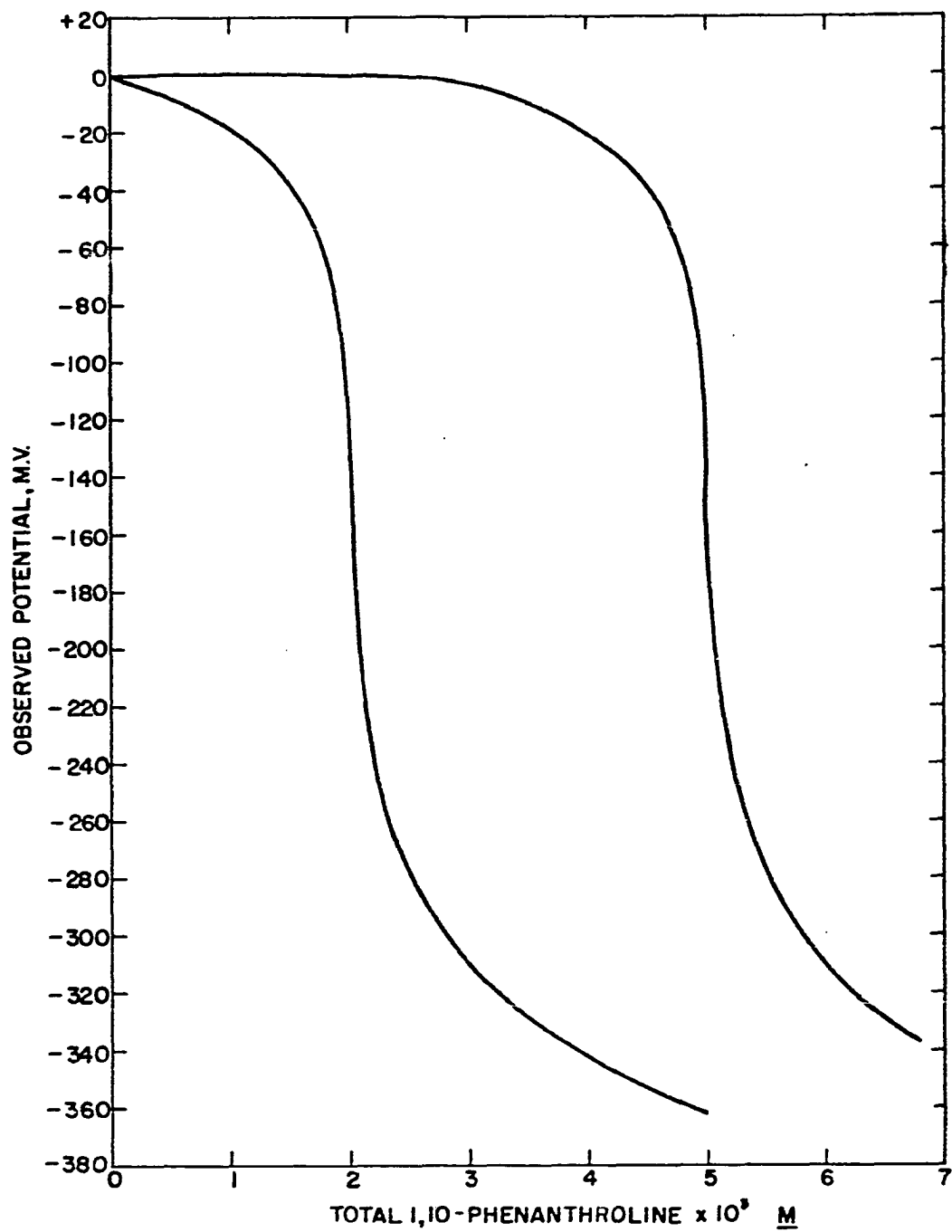


Figure 7. Titration of nickel with 1,10-phenanthroline

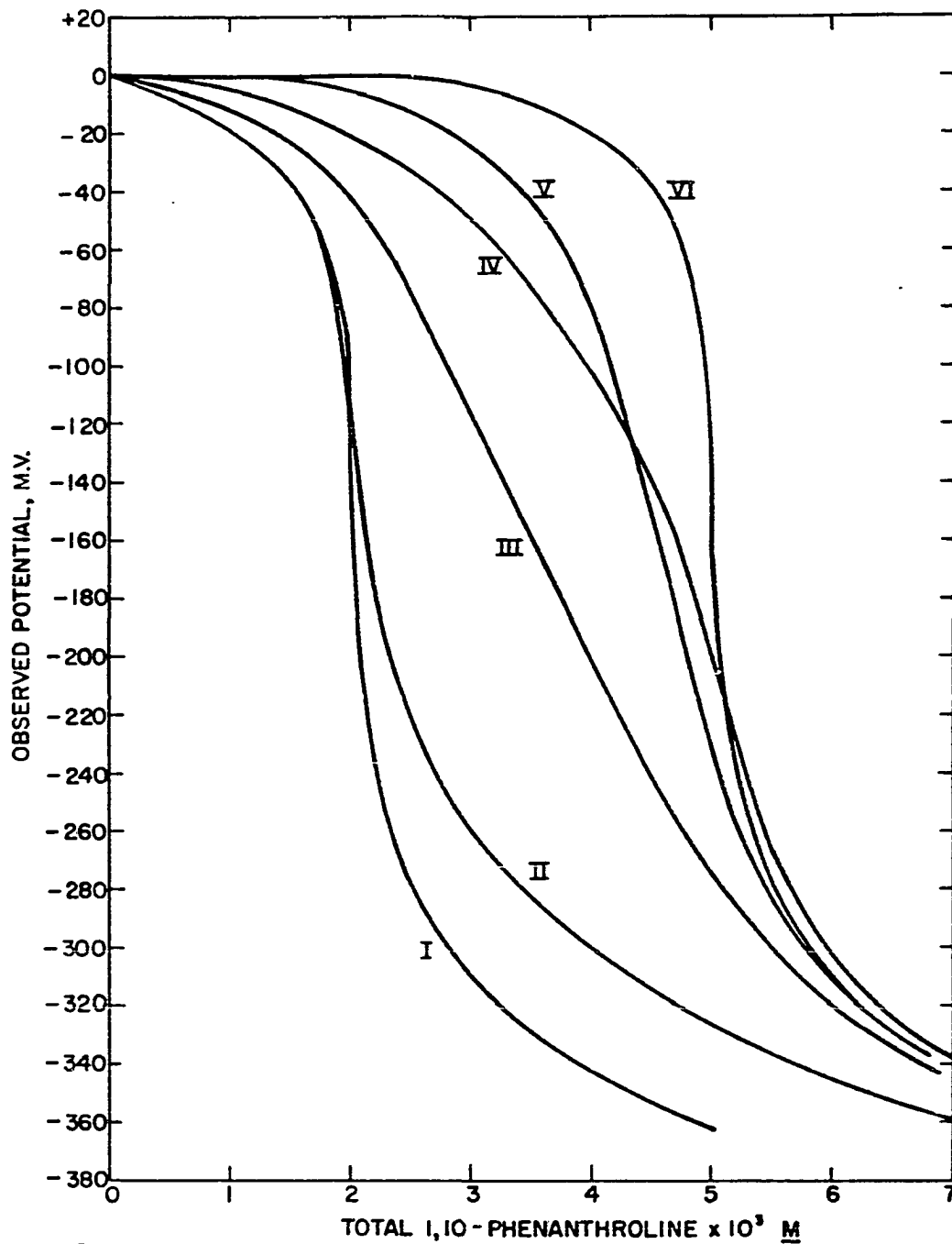


Figure 8. Titration of metal solutions with 1,10-phenanthroline: I, silver; II, manganese + silver; III, cadmium + silver; IV, zinc + silver; V, copper + silver; VI, nickel + silver

### Sequence of calculations and results

Examination of each titration curve showed that  $\bar{n}_M$  increased to a value which was larger than two in all cases and approached three for cadmium, zinc, copper, and nickel. This was determined by noting from the graph the approximate amount of 1,10-phenanthroline which was required to reach a particular potential value as compared to that required when only silver was titrated. The additional amount represents that which reacted with the second metal. The largest value of  $J$ , therefore, to be considered in Equation 79 was three in all cases except for copper which will be explained below.

For each significant experimental point on the titration curves, values of the terms of Equation 79 and an estimated standard deviation in  $(P')$  were calculated. The total concentration of 1,10-phenanthroline,  $P_T$ , was known from the amount of titrant added,  $Ag_T$  and  $M_T$  remained constant throughout the titration;  $(P')$  was calculated from Equation 73 using the known stability constants for silver and the experimentally determined value of  $(Ag')$ ;  $\bar{n}_{Ag}Ag_T$  was calculated from Equation 76. The value of  $\Delta P$  from Equation 80 was taken as the estimated standard deviation in  $(P')$ .

$$\begin{aligned}
 (\Delta P)^2 = & \left( \frac{\delta(P')}{\delta\beta_1^{Ag}} \Delta\beta_1^{Ag} + \frac{\delta(P')}{\delta\beta_2^{Ag}} \Delta\beta_2^{Ag} + \frac{\delta(P')}{\delta(Ag')} \Delta(Ag') \right. \\
 & \left. + \frac{\delta(P')}{\delta Ag_T} \Delta Ag_T \right)^2
 \end{aligned}
 \tag{80}$$

Expressions for the partial derivatives were derived from Equation 73 and the  $\Delta$ 's represent estimated standard deviations of the respective terms shown.

A slightly different approach was taken in the case of copper. The potential measurements below a  $\bar{n}_{Cu}$  value of about 1.5 were not significant due to the strength of the 1:1 complex. This system was described as follows where  $k_2$  and  $k_3$  are the step-wise formation constants for the 2:1 and 3:1 complexes, respectively.

$$P_T - \bar{n}_{Ag} Ag_T - (P') = (CuP)(1 + 2k_2(P') + 3k_2k_3(P')^2) \quad (81)$$

$$Cu_T - (Cu') = (CuP)(1 + k_2(P') + k_2k_3(P')^2) \quad (82)$$

$$\frac{P_T - \bar{n}_{Ag} Ag_T - (P')}{Cu_T - (Cu')} = \frac{1 + 2k_2(P') + 3k_2k_3(P')^2}{1 + k_2(P') + k_2k_3(P')^2} \quad (83)$$

When  $\bar{n}_{Cu}$  is larger than about 1.5,  $(Cu')$  is negligible compared to  $Cu_T$  and the first term of Equation 83 equals  $\bar{n}_{Cu}$ . Eliminating  $(Cu')$  and rearranging Equation 83 gives

$$\sum_0^{J=2} (P_T - \bar{n}_{Ag} Ag_T - (P') - (j+1)Cu_T) \frac{\beta_j^{Cu}}{\beta_1^{Cu}} (P')^j = 0 \quad (84)$$

By making  $P_T'$  equal to  $P_T$  minus  $Cu_T$ , this equation becomes

$$\sum_0^{J=2} (P_T' - \bar{n}_{Ag} Ag_T - (P') - jCu_T) B_j (P')^j = 0 \quad (85)$$

where  $B_j = \beta_{(j+1)}^{\text{Cu}} / \beta_1^{\text{Cu}}$ . This equation which is now of the same form as Equation 79 may be solved by the least squares program.

The input data for each of the metals are listed in Tables 13, 14, 15 and 16. The input data are  $y = P_T - \bar{n}_{\text{Ag}} \text{Ag}_T$  or in the case of copper,  $y = P_T - \text{Cu}_T - \bar{n}_{\text{Ag}} \text{Ag}_T$ ;  $x = (P')$ ;  $z = M_T$  and the estimated standard deviation in  $x$ ,  $\Delta P'$ . In Table 17, the log of the conditional stability constants obtained from the least squares treatment of the data are shown. The adjusted constants wherein the concentrations of the sulfate (15, 25, 60) and acetate (29, 55) complexes of the metals and the 1,10-phenanthroline ion have been taken into account are listed in Table 18. These values are compared to those obtained by other workers. The stabilities of the nickel complexes were too strong for silver to be an effective competitor. Therefore, no constants could be calculated for this system. This was also true for the 1:1 complex of copper, which was indicated previously.

Figures 9, 10, 11 and 12 compare the experimentally determined formation function with values of  $\bar{n}_M$  calculated from experimental values of  $(P')$  and the conditional formation constants.

#### Hydrogen-1,10-phenanthroline System

It was of interest to determine if any evidence for the poly(1,10-phenanthroline)-hydrogen species proposed by Grimes



Table 13. Manganese data

E millivolts	$P_T \times$ $10^3 M$	$\bar{n}_{Ag} Ag_T \times$ $10^3 M$	(P')	$\Delta P'$
-176.0	2.198	1.995	$7.831 \times 10^{-5}$	$1.916 \times 10^{-6}$
-210.8	2.399	1.998	$1.543 \times 10^{-4}$	4.373
-232.2	2.602	1.999	2.341	6.633
-247.7	2.800	1.999	3.166	8.352
-260.0	3.000	1.999	4.023	8.574
-270.4	3.200	1.999	4.926	$1.098 \times 10^{-5}$
-279.2	3.400	2.000	5.847	1.542
-286.9 <sup>a</sup>	3.598	2.000	6.792	2.056
-293.9 <sup>a</sup>	3.799	2.000	7.784	2.810
-300.4	4.002	2.000	8.834	3.533
-306.4	4.202	2.000	9.928	4.164
-311.8	4.402	2.000	$1.103 \times 10^{-3}$	4.411
-317.1	4.600	2.000	1.223	5.604
-322.1	4.801	2.000	1.348	5.914
-326.4	5.001	2.000	1.465	6.431
-330.6	5.199	2.000	1.590	7.288
-334.7	5.400	2.000	1.722	6.888
-341.6	5.800	2.000	1.970	8.261
-348.0 <sup>a</sup>	6.199	2.000	2.231	9.357
-353.7	6.599	2.000	2.493	9.970
-358.9	7.000	2.000	2.758	$1.050 \times 10^{-4}$
-361.6	7.200	2.000	2.907	$9.929 \times 10^{-5}$
-364.0	7.400	2.000	3.046	9.218

<sup>a</sup>These data were not used because the expression (y-x-nz) was not significant for these points.

(22) could be obtained using the silver-1,10-phenanthroline system.

A  $1.00 \times 10^{-3} M$  silver solution which was not buffered with acetate-acetic acid was titrated with 1,10-phenanthroline in the same manner as previously described. The ionic strength was controlled at 0.1 with potassium sulfate. An

Table 14. Cadmium data

$E$ millivolts	$P_T \times$ $10^3 M$	$\bar{n}_{Ag}^{Ag_T} \times$ $10^3 M$	$(P')$	$\Delta P'$
- 27.2	1.603	1.267	$3.395 \times 10^{-6}$	$8.185 \times 10^{-8}$
- 42.8	2.002	1.589	5.180	$1.161 \times 10^{-7}$
- 53.4	2.199	1.722	6.642	1.432
- 66.6	2.399	1.828	8.866	1.958
- 82.1	2.602	1.901	$1.225 \times 10^{-5}$	2.790
- 98.8	2.800	1.945	1.717	4.065
-116.1 <sup>a</sup>	3.000	1.969	2.421	5.380
-133.0	3.200	1.982	3.377	7.822
-149.8	3.400	1.990	4.694	$1.095 \times 10^{-6}$
-166.2	3.598	1.994	6.468	1.482
-182.8	3.799	1.996	8.942	2.013
-199.6	4.000	1.997	$1.241 \times 10^{-4}$	2.936
-216.3 <sup>a</sup>	4.202	1.998	1.718	4.366
-232.0	4.402	1.999	2.332	6.198
-246.8	4.600	1.999	3.111	8.207
-261.0	4.801	1.999	4.102	$1.162 \times 10^{-5}$
-273.8	5.001	2.000	5.263	1.490
-285.2	5.199	2.000	6.571	1.733
-295.5	5.400	2.000	8.030	2.430
-304.4	5.599	2.000	9.549	2.890

<sup>a</sup>These data were not used because the expression  $(y-x-nz)$  was not significant for these points.

identical titration was then performed where the titrant and solution to be titrated was also  $1.00 \times 10^{-3} M$  in hydrogen ion.

These two titration curves are compared in Figure 13. The displacement of the silver-hydrogen curve to the right illustrates the competition between the hydrogen ions and silver ions for 1,10-phenanthroline. Because the  $\Delta P_T$  between the two titration curves never became larger than the concentration of added hydrogen ion, no conclusions

Table 15. Zinc data

E millivolts	$P_T \times$ $10^3 M$	$\bar{n}_{Ag}^{Ag_T} \times$ $10^3 M$	(P')	$\Delta P'$
- 6.84	1.198	0.4340	$1.305 \times 10^{-6}$	$3.881 \times 10^{-8}$
- 9.83	1.401	0.5984	1.637	4.931
- 13.1	1.603	0.7591	1.975	4.675
- 16.8	1.803	0.9191	2.346	5.948
- 20.7	2.002	1.066	2.733	6.769
- 25.0 <sup>a</sup>	2.198	1.204	3.168	7.088
- 30.0 <sup>a</sup>	2.399	1.339	3.691	7.875
- 35.8 <sup>a</sup>	2.602	1.468	4.335	9.332
- 42.3	2.800	1.582	5.116	$1.135 \times 10^{-7}$
- 49.6	3.000	1.680	6.089	1.343
- 58.1	3.200	1.766	7.376	1.603
- 67.4	3.400	1.833	9.019	1.933
- 77.9	3.598	1.885	$1.123 \times 10^{-5}$	2.494
- 89.4	3.799	1.924	1.421	3.201
-102.2 <sup>a</sup>	4.000	1.951	1.837	4.201
-109.2 <sup>a</sup>	4.096	1.961	2.112	5.200
-116.5 <sup>a</sup>	4.202	1.970	2.440	6.001
-124.3	4.303	1.977	2.846	7.551
-132.2	4.402	1.982	3.325	7.505
-140.4	4.501	1.986	3.905	8.808
-149.6	4.600	1.989	4.676	$1.008 \times 10^{-6}$
-160.1	4.702	1.992	5.741	1.237
-171.2	4.801	1.994	7.131	1.536
-197.5	5.001	1.997	$1.191 \times 10^{-4}$	2.912
-212.6	5.102	1.998	1.598	3.751
-227.2	5.199	1.999	2.124	4.777
-241.6	5.300	1.999	2.812	6.103
-254.6	5.400	1.999	3.608	7.759

<sup>a</sup>These data were not used because the expression (y-x-nz) was not significant for these points.

concerning the presence of any 1,10-phenanthroline-hydrogen species other than the 1:1 specie could be drawn.

Table 16. Copper data

E millivolts	$P_T \times$ $10^3 M$	$\bar{n}_{Ag}^{Ag_T} \times$ $10^3 M$	(P')	$\Delta P'$
- 5.76	2.002	0.3702	$1.175 \times 10^{-6}$	$3.654 \times 10^{-8}$
- 8.62	2.198	0.5340	1.506	4.473
- 11.9	2.399	0.7024	1.853	4.934
- 15.6	2.602	0.8696	2.226	5.698
- 19.9	2.800	1.037	2.654	6.599
- 24.9	3.000	1.201	3.157	7.680
- 31.0	3.200	1.364	3.799	9.076
- 38.6	3.400	1.520	4.663	$1.217 \times 10^{-7}$
- 48.3 <sup>a</sup>	3.598	1.665	5.908	1.512
- 61.6 <sup>a</sup>	3.799	1.794	7.963	1.831
- 70.4 <sup>a</sup>	3.901	1.850	9.609	2.402
- 80.7 <sup>a</sup>	4.000	1.896	$1.190 \times 10^{-5}$	3.201
- 92.7	4.096	1.932	1.519	4.062
-106.2	4.202	1.957	1.988	4.897
-121.0	4.303	1.974	2.664	6.547
-135.4	4.402	1.984	3.544	8.692
-150.4	4.501	1.990	4.750	$1.164 \times 10^{-6}$
-165.6	4.600	1.993	6.392	1.565
-181.8	4.702	1.996	8.769	2.145
-197.8	4.801	1.997	$1.198 \times 10^{-4}$	2.929
-214.4	4.903	1.998	1.655	4.046
-229.6	5.001	1.999	2.226	5.439
-243.7	5.102	1.999	2.929	7.156

<sup>a</sup>These data were not used because the expression (y-x-nz) was not significant for these points.

Table 17. Over-all conditional formation constants<sup>a</sup>

Metal	Log $\beta_1^i$	Log $\beta_2^i$	Log $\beta_3^i$
Ag	4.525 $\pm$ 0.027	11.186 $\pm$ 0.018	
Mn	3.230 $\pm$ 0.011	6.004 $\pm$ 0.031	8.685 $\pm$ 0.031
Cd	5.028 $\pm$ 0.016	9.225 $\pm$ 0.024	12.624 $\pm$ 0.033
Zn	6.081 $\pm$ 0.036	10.906 $\pm$ 0.036	15.388 $\pm$ 0.036
Cu		6.030 $\pm$ 0.024 <sup>b</sup>	10.274 $\pm$ 0.030 <sup>c</sup>

<sup>a</sup>Values not corrected for acetate and sulfate complexes or for the presence of phenanthroline ion,  $\mu = 0.1$  and  $t = 25^\circ \pm 0.05^\circ\text{C}$ .

<sup>b</sup>, <sup>c</sup>Values reported for  $\log k_2^i$  and  $\log k_2^i k_3^i$ , respectively, where  $k_n^i$  indicates the step-wise conditional formation constant.

Table 18. Over-all stoichiometric formation constants

Metal	Log $\beta_1$	Log $\beta_2$	Log $\beta_3$
Mn	3.88 4.8 <sup>a</sup>	7.04 8.9 <sup>a</sup>	10.11 14.3 <sup>a</sup> 7.35(39)
Cd	5.93 5.17 <sup>a</sup> 5.75 6.01(2)	10.52 10.00 <sup>a</sup> 10.84(21) 13.15(17)	14.30 14.26 <sup>a</sup> 13.91(21) 15.19(17)
Zn	6.83 6.5(23) 6.4 <sup>a</sup> 6.36(4)	12.05 11.95(23) 12.03 <sup>a</sup> 12.00(4)	16.92 17.05(23) 17.00 <sup>a</sup> 17.00(4)

<sup>a</sup>Irving, H. and D. H. Mellor, Oxford, England. Stability of 1,10-phenanthroline complexes. Private communication to R. I. Bystroff. 1955.

Table 18. (Continued)

Metal	Log $\beta_1$	Log $\beta_2$	Log $\beta_3$
Zn	6.6(30)	12.32(30)	17.17(30)
	6.31(21)	12.40(21)	17.17(21)
	6.47(38)	12.0(38)	13.1(38)
	6.40(2)		
		Log $k_2$	Log $k_2k_3$
Cu	8.82a	6.42	11.05
	9.15(4)	6.57 <sup>a</sup>	11.59 <sup>a</sup>
	6.3(43)	6.65(4)	11.90(4)
	7.53(21)	6.15(43)	11.65(43)
	9.30(2)	6.07(21)	11.07(21)
		6.84(2)	

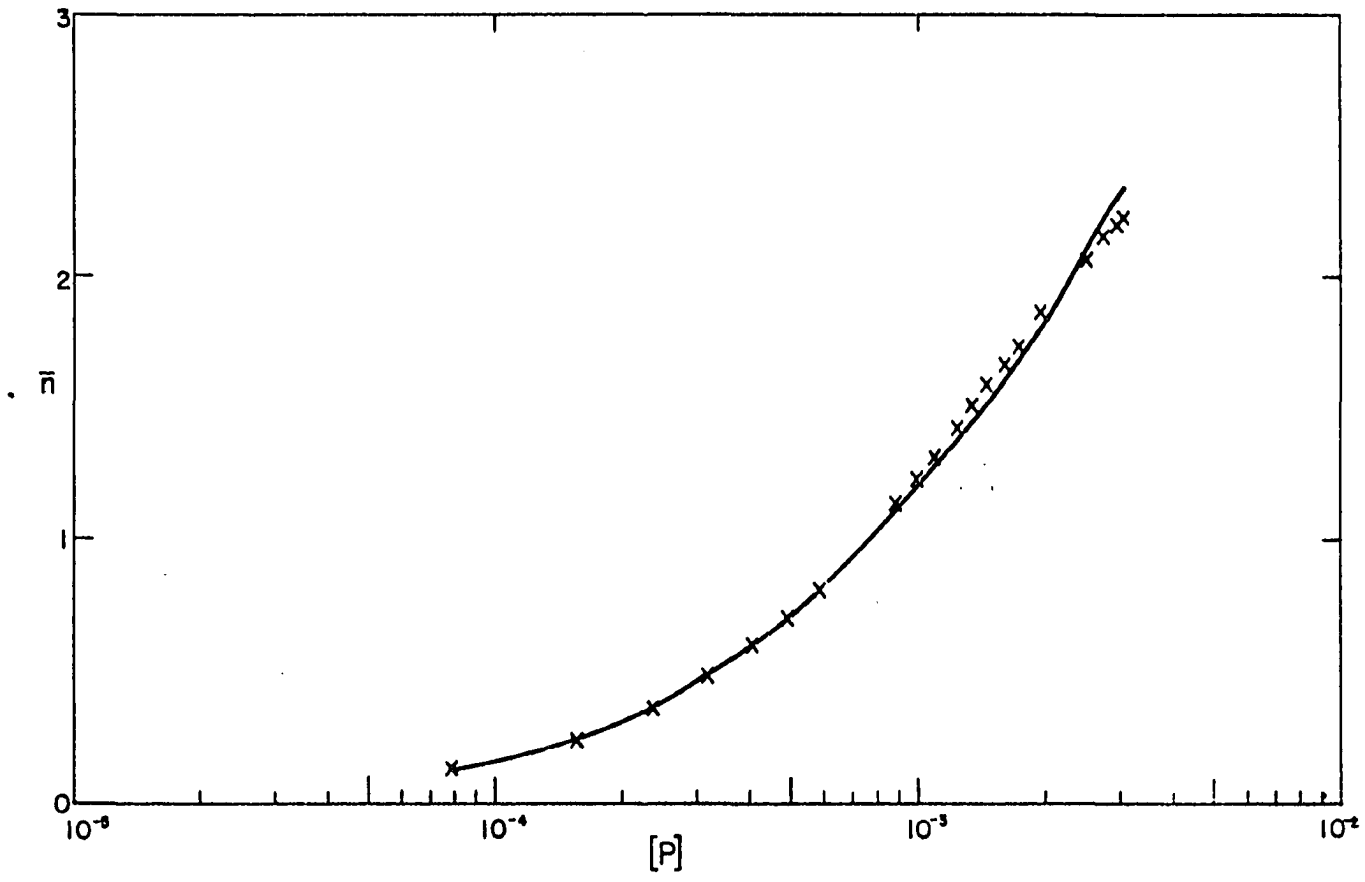


Figure 9. Formation function for manganese

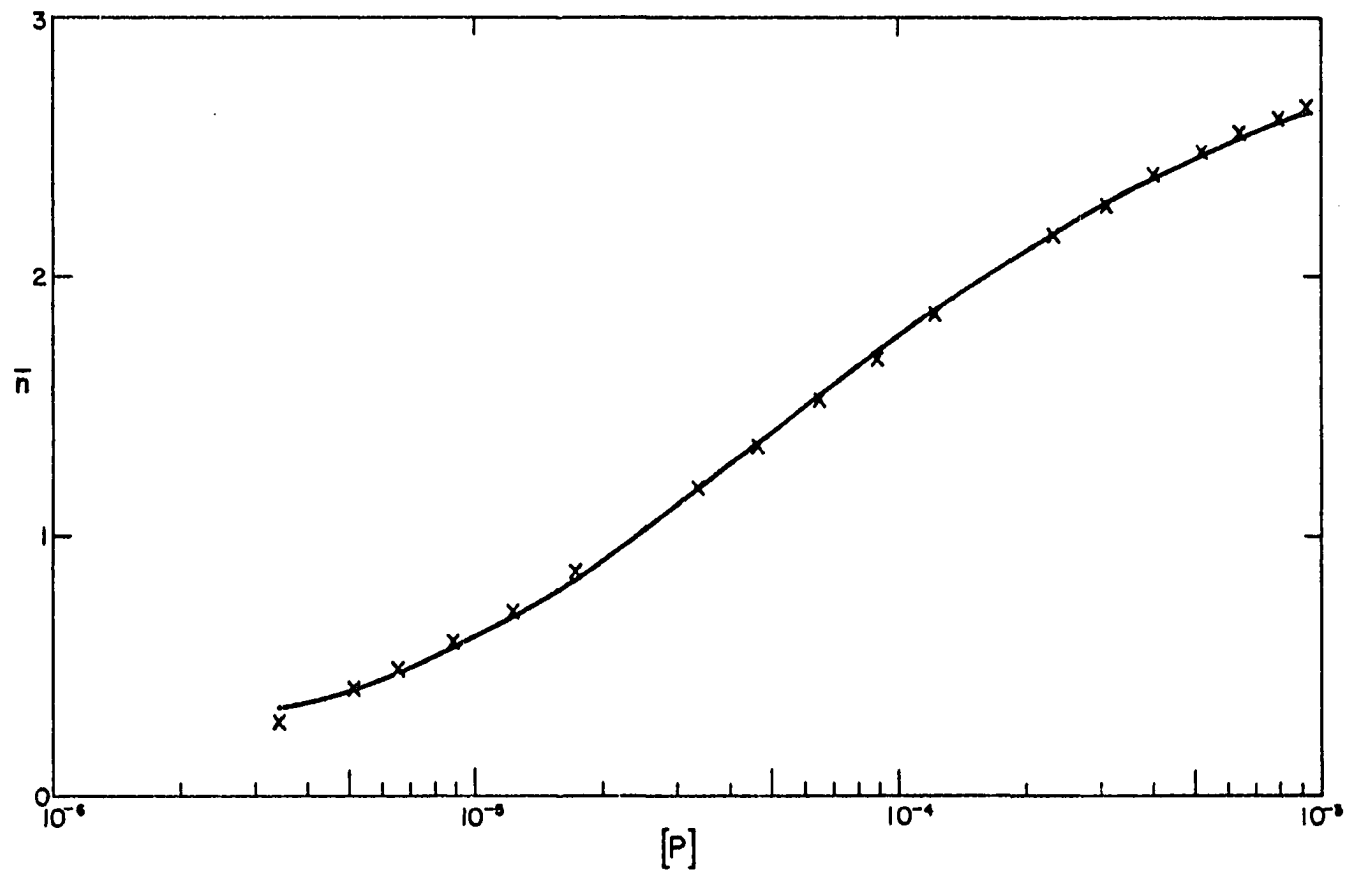


Figure 10. Formation function for cadmium



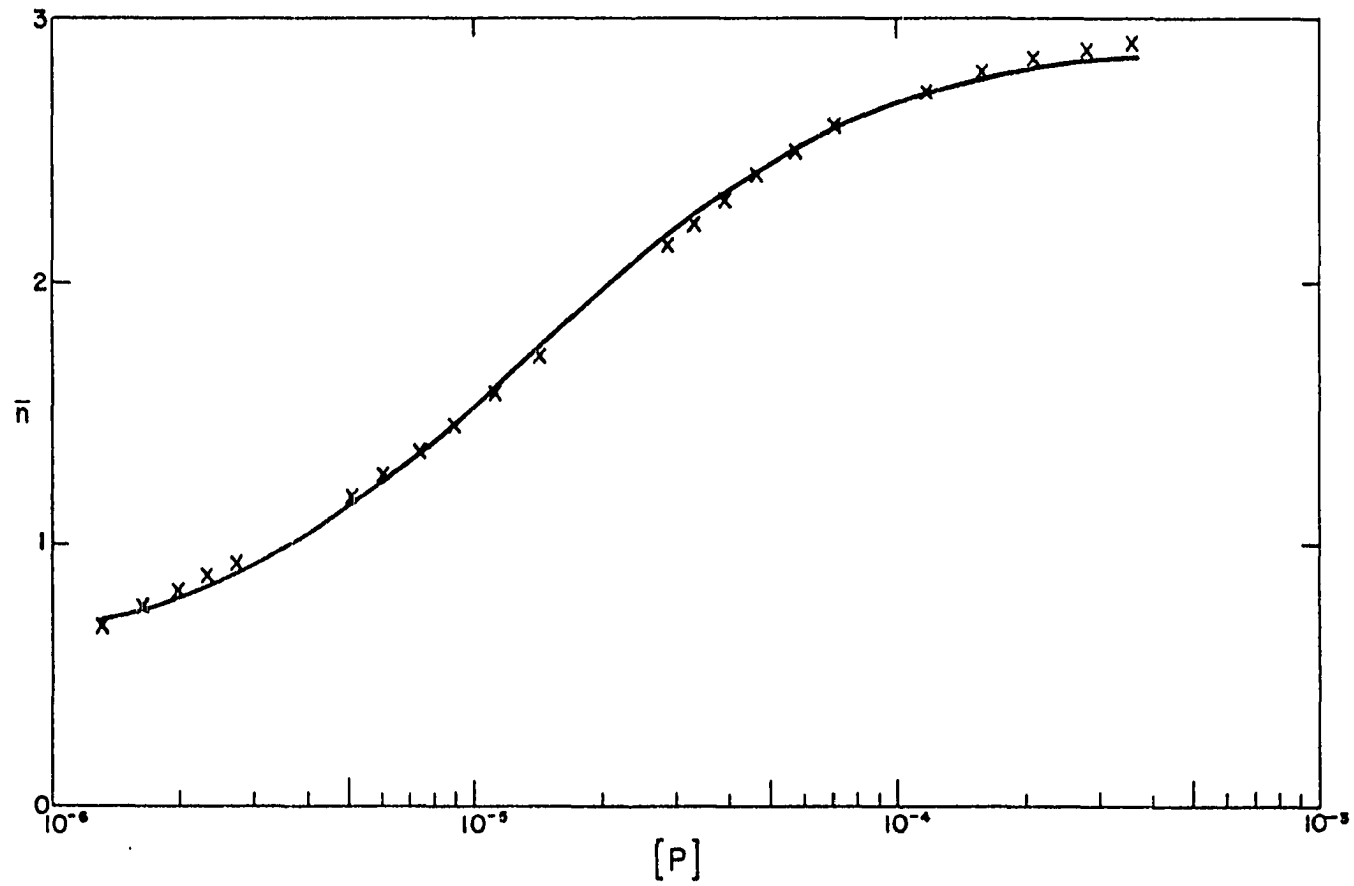


Figure 11. Formation function for zinc

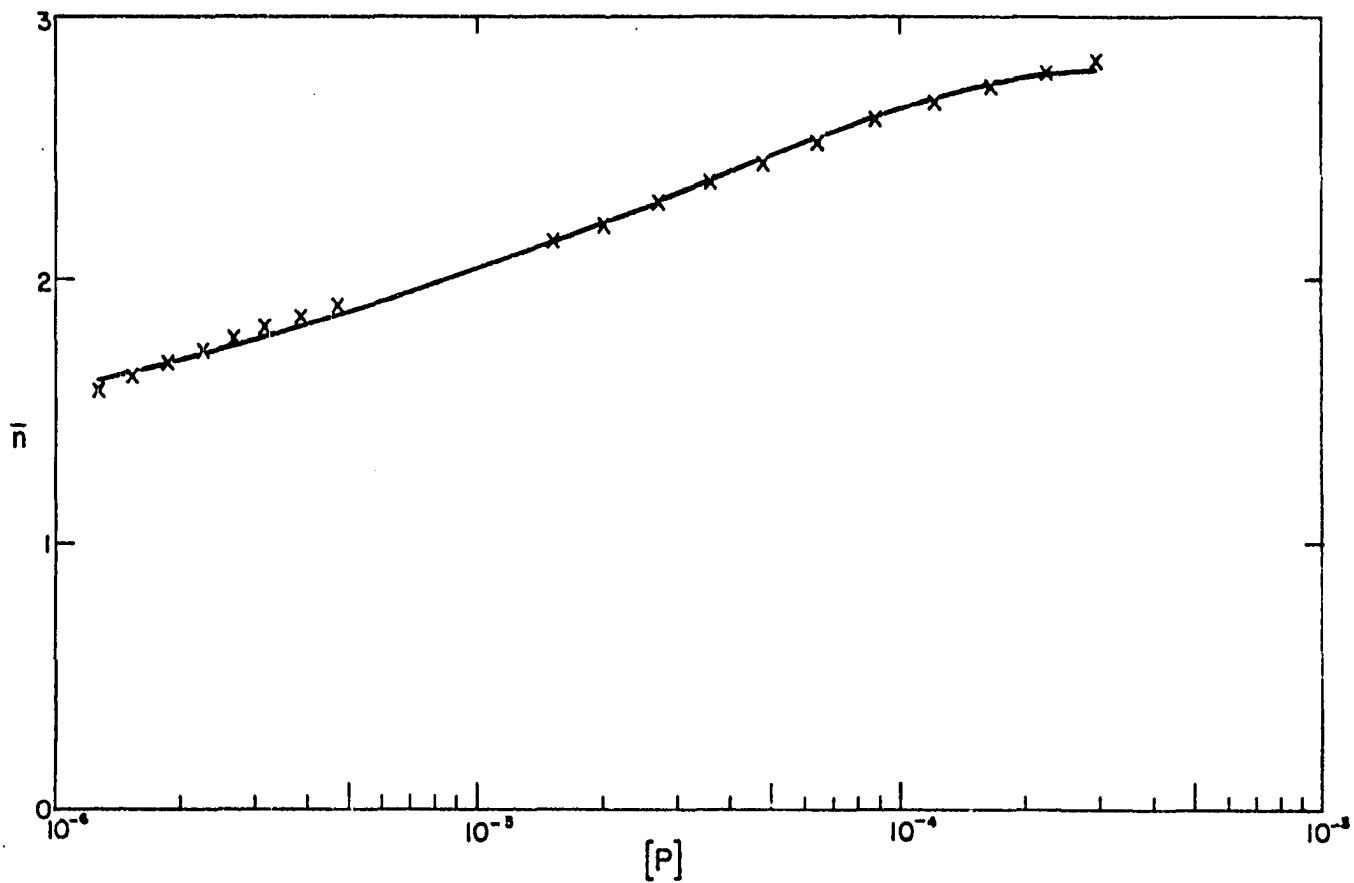


Figure 12. Formation function for copper

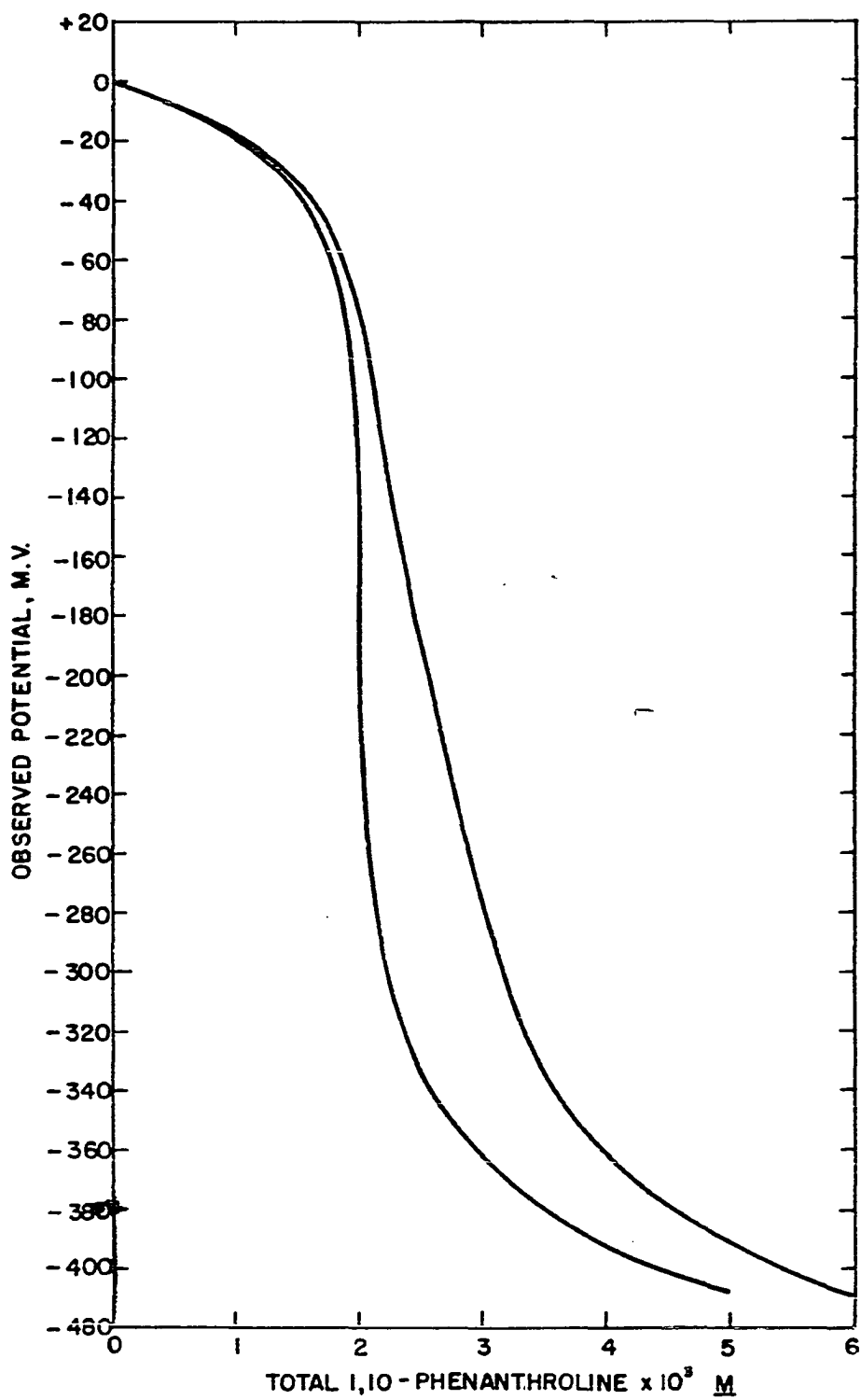


Figure 13. Titration of hydrogen ion with 1,10-phenanthroline

## DISCUSSION AND SUMMARY

Grimes (22) proposed a method for determining the stability constants of 1,10-phenanthroline complexes of metal ions using the silver/bis(1,10-phenanthroline)silver(I) nitrate electrode. Fullerton (21) evaluated the method further by studying several metal complexes whose stability constants had been previously reported as well as re-determining the stability constants of several species proposed by Grimes. As a result of the work of these authors an interest developed concerning the possible use of the silver electrode for studying metal-1,10-phenanthroline complexes.

The first aspect of this work was concerned with the experimental equipment and techniques to be used. Two types of silver electrodes were compared with respect to reproducibility of response to silver solutions and to the effect of 1,10-phenanthroline upon this response. With regard to the over-all requirements, it was shown that the silver billet electrodes were better suited for the purpose of this work than the electrodes prepared from silver oxalate.

The need for a calomel reference electrode was eliminated by performing the experimental work with a concentration cell. The use of the concentration cell also presented a means of checking any potential differences between the silver reference electrode and the silver working electrode at the beginning of each titration in which case the solutions in

the two half-cells were identical. The fact that the titrant, except for the 1,10-phenanthroline concentration, was the same as the solution being titrated was also conducive to minimal changes in the junction potential at the salt bridge-experimental solution interface.

Grimes (22) and Fullerton (21) have calculated formation constants for 1,10-phenanthroline complexes of some alkali metals using data obtained from the  $\text{Ag}/\text{AgP}_2\text{NO}_3$  electrode. Potentiometric and spectrophotometric measurements from the present work showed no appreciable effect of increasing concentrations of potassium and lithium sulfates on the silver-1,10-phenanthroline equilibria. It was concluded that if these complexes exist, their stabilities should be somewhat lower than previously reported.

In order to use the silver-1,10-phenanthroline system to study the 1,10-phenanthroline complexes of other metals, it was necessary to determine the formation constants for the 1:1 and 2:1 complexes. From the titrations of silver sulfate with 1,10-phenanthroline, the logarithm of the over-all conditional formation constants,  $\log \beta_1'$  and  $\log \beta_2'$ , were found to be 4.525 and 11.186, respectively. After adjusting for the sulfate and acetate complexes of silver and for the concentration of the phenanthrolium ion, the logarithm of the stoichiometric stability constants were found to be 5.02 and 12.07. Grimes reported 11.6 and Fullerton reported 11.42 for

the over-all stability constant of the 2:1 complex. These authors, however, did not control the ionic strength or pH during the titration and no attempt was made to determine the constant for the 1:1 complex.

Only the work of Irving and Mellor (23) was available for comparison of all three formation constants for the manganese complexes. Although these authors found the 1:1 and 2:1 complexes for manganese to be slightly less stable than the corresponding complexes for cadmium, their  $\log \beta_3$  values for these two metals were essentially the same. Comparison of the titration curves of manganese and cadmium from the present work shows that the manganese complexes must be much less stable than those of cadmium since no appreciable amount of the manganese reacts until practically all of the silver has been complexed. For this reason it is felt that the constants reported in the present work more nearly represent the true values.

The stability constant values for cadmium, zinc, and copper are, in general, in agreement with the values found by previous workers.

The value of  $\log \beta_1$  for cadmium is in very good agreement with the value determined by Anderegg (2) with the mercury electrode. The value for  $\log \beta_3$  is essentially the same as that determined by Irving and Mellor (23) by partition measurements. The values of  $\log \beta_2$  and  $\log \beta_3$  determined from

polarographic measurements by Douglas et al. (17) appear to be out of line.

The over-all stability constants for zinc from the present work agree well with the majority of the values reported by previous workers except that the value for  $\log \beta_1$  is slightly larger.

The step-wise formation constant for the 2:1 complex of copper from this work is approximately in the middle of the range of values reported previously.  $\log k_2k_3$  is lower than the values of Irving and Mellor (23), Banks and Bystroff (4), and Pflaum and Brandt (43) and is essentially the same as that reported by Fullerton (21). The 1:1 complex of copper was too stable to be able to determine its formation constant by the method of the present work. Because the present method is capable of determining constants of the order of magnitude of those reported by Fullerton, and Pflaum and Brandt for the 1:1 complex, it is the opinion of the author that these values are in error.

From the standpoint of electrode reproducibility and reproducibility of potential measurements it is felt that the present method using the silver electrode is a better method for determining stability constants than that employing the  $\text{Ag}/\text{AgP}_2\text{NO}_3$  electrode. One disadvantage, however, is the use of sulfate as the anion. In general, it appears that the limitations of the two methods concerning the range of

constants which can be determined are about the same. The present method was not capable of determining the stability constant for the 1:1 complex of copper whereas the value obtained from the use of the  $\text{Ag}/\text{AgP}_2\text{NO}_3$  electrode appears to be too low. Neither method appears to be capable of determining the constants for the nickel-1,10-phenanthroline system due to the relatively large stability of the complexes. Difficulty was experienced in the present work when an attempt was made to study the complexes of cobalt(II). The values for  $\log \beta_2$  and  $\log \beta_3$  reported by Fullerton and by Irving and Meller are in disagreement. Grimes and Fullerton, however, present data from which stability constants for the alkali metals were calculated. It would be of interest to reproduce their work in this area using the concentration cell of the present method.

The computer programs developed by Sullivan et al. (58) for the least squares treatment of potentiometric, ion exchange, spectrophotometric and solvent extraction data, appear to be the most objective method in the literature for calculating formation constants. Application of this treatment to future work is recommended.



## SUGGESTIONS FOR FUTURE WORK

1. Investigate the possibility of determining the formation constants of complexes of other metals with 1,10-phenanthroline by this method. It should be possible to calculate the stability constants for some or all of the 1,10-phenanthroline complexes of a metal if its titration curve lies between that of silver and that of nickel.
2. Investigate the possibility of determining the formation constants of complexes of substituted 1,10-phenanthrolines with different metals by this method. Due to the solubility of the substituted 1,10-phenanthrolines an alcohol-water medium would probably be necessary.
3. Investigate the possibility of using a metal electrode such as nickel for determining the formation constants of complexes of 1,10-phenanthroline which are of relatively high stability.
4. If a metal electrode which is reversible to its own ions and which forms weaker 1,10-phenanthroline complexes than silver could be found, then some information concerning the poly(1,10-phenanthroline)-hydrogen species proposed by Grimes (22) might be obtained. This information would be obtained from titrations similar to those in this work where comparison was made between the titration of an unbuffered silver solution and a silver solution containing a known amount of acid.

5. If a method for preparing reproducible  $\text{Ag}/\text{AgP}_2\text{NO}_3$  electrodes can be found, then further studies of this electrode could be made using the experimental techniques of this work, specifically, the concentration cell. The activity of the nitrate ion cancels out in the Nernst relationship for the concentration cell if the concentration of this ion is maintained at a constant value.

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