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# A study of the rare-earth chelate stability constants of some aminopolyacetic acids

John Linn Mackey  
Iowa State University

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RARE-EARTH CHELATE STABILITY  
CONSTANTS OF SOME AMINOPOLYACETIC  
ACIDS.**

**Iowa State University of Science and Technology  
Ph. D., 1960  
Chemistry, physical**

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A STUDY OF THE RARE-EARTH CHELATE STABILITY CONSTANTS  
OF SOME AMINOPOLYACETIC ACIDS

by

John Linn Mackey

A Dissertation Submitted to the  
Graduate Faculty in Partial Fulfillment of  
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In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University  
Of Science and Technology  
Ames, Iowa

1960

## TABLE OF CONTENTS

	Page
INTRODUCTION	1
REVIEW	3
Aminopolyacetic Acids	3
Methods Which Have Been Used to Determine the Stability Constants of The Rare Earths with Aminopolycarboxylic Acids	5
Variation of Stability Constants with Metal and Chelating Agent	14
EXPERIMENTAL	20
Derivation of the Experimental Methods Used to Measure Stability Constants	20
Materials and Equipment	29
HEDTA	36
Rare-Earth DE and ME Constants	55
DISCUSSION AND CONCLUSIONS	68
SUMMARY	80
LITERATURE CITED	81
ACKNOWLEDGMENTS	85
APPENDIX A - DETERMINATION OF HYDROGEN-ION CONCENTRATION WITH A GLASS ELECTRODE pH METER	86
APPENDIX B - A METHOD TO DETERMINE $R_{HgY}$ FOR HEDTA	92

## INTRODUCTION

This dissertation is concerned with the measurement of rare earth-aminopolyacetic acid stability constants which provide information pertaining to the ion-exchange separation of rare earths. The measurement of stability constants of metal chelates also provides quantitative information about the interaction between metal ions and chelating agents.

In recent years many applications of chelating agents have been developed (1, 2). The ion-exchange method of separating macro-amounts of pure rare earths is an excellent example of a practical application of chelation (3, 4, 5). This method is based on the exchange of the metal ions between an ion-exchange resin and a chelating agent. The degree of separation depends to a large extent on the relative affinity of the chelating agent for the metal ions. The stability constants are a measure of this affinity, and they provide valuable information about the separation of the rare earths.

One of the aims of a theoretical study of chelation is to evaluate the factors which effect the properties of chelated metal ions. Theoretical studies have been made in an attempt to elucidate the way in which stability constants depend on the nature of the metal ion and the structure of the chelating agent<sup>1</sup>. The rare earths provide a

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<sup>1</sup>Chaberek, S. and Martell, A. E. "Organic Sequestering Agents", John Wiley and Sons, New York (1959) pp. 124-170.

unique opportunity for such studies. This series offers a set of fourteen trivalent metal ions that differ one from the other only in the number of electrons in the inner 4f shell.

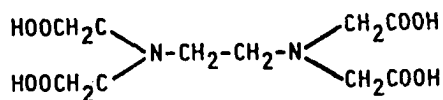
The research described in this thesis involves an application of the mercury electrode to the study of the interaction of rare earths with aminopolyacetate chelating agents.

## REVIEW

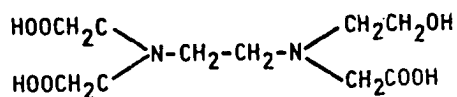
## Aminopolyacetic Acids

Smith (2) has given a historical account of the development of the aminopolycarboxylic acids, and Debbrecht (6) has reviewed the use of amino acids as chelating agents for metal ions as well as the preparation of ethylenediamine-N, N, N', N', -tetraacetic acid (EDTA) and related compounds. The tables of stability constants published by Bjerrum et al. (7) represent an extensive compilation of stability constants of metal chelates of aminopolycarboxylic acids.

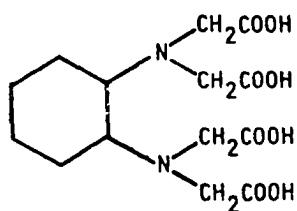
Aminopolyacetic acids are important as chelating agents for metal ions because they form stable, soluble metal chelates. The chelating agents that have been studied in this work are structurally similar to EDTA. The structural formulas for these chelating agents are given in Figure 1.



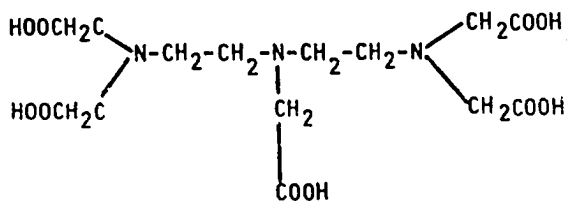
EDTA



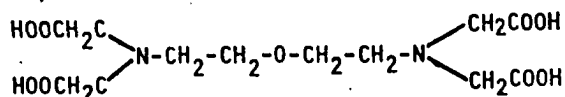
HEDTA



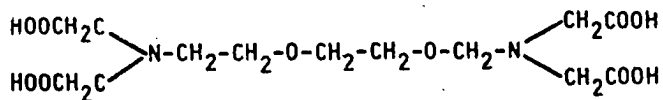
DCTA



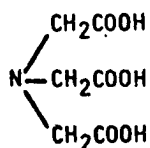
DTPA



ME



DE



NTA

Figure 1. Structural formulas of some aminopolyacetic acid chelating agents



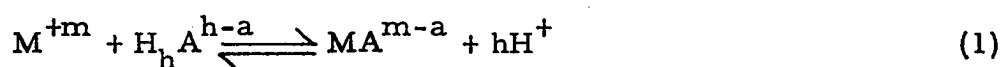
Methods Which Have Been Used to Determine the Stability  
Constants of the Rare Earths with Aminopolycarboxylic Acids

A consideration of the literature on chelation shows that a variety of methods have been used for the determination of metal chelate stability constants. Several adequate summaries of these methods (6, 8, 9) have appeared, and no attempt will be made to review all of the methods here. This section will be restricted to those methods which have been used to determine rare earth-aminopolycarboxylic acid stability constants, and those which appear to be potentially useful.

The rare earths form very stable chelates with the aminopolycarboxylic acids and this eliminates from consideration a number of methods which are applicable only to weak and moderately stable chelates.

General considerations

Most measurements of stability constants make use of a competition between two cations for the chelating agent. The cations in question may be two different metal ions or one of them may be hydrogen ion. For the case in which one of the competing cations is hydrogen ion, the equilibrium can be written:



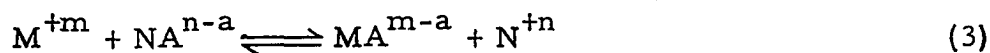
where A is the chelate anion and M the metal ion. The equilibrium

constant for 1 is:

$$K_1 = \frac{[MA^{m-a}][H^+]^h}{[M^{+m}][H_hA^{h-a}]} = K_{MA} \cdot K_a \quad (2)$$

where  $K_a$  is the dissociation constant for  $H_hA$  to  $h[H^+]$  and  $[A^{-a}]$ .

For the case of two metal ions the equilibrium is:

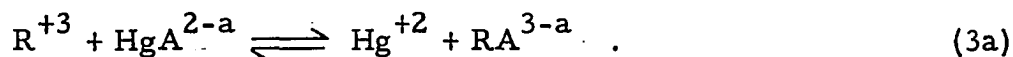
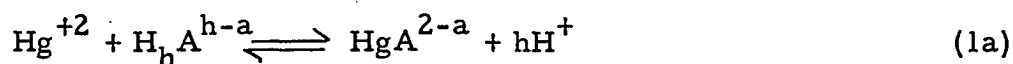


$$\text{and } K_3 = \frac{[MA^{m-a}][N^{+n}]}{[NA^{n-a}][M^{+m}]} = \frac{K_{MA}}{K_{NA}} \quad (4)$$

From the initial concentrations and the experimentally determined equilibrium concentration of any one of the reactants or products in 1 or 3, it is possible to calculate  $K_1$  or  $K_3$ . If the acid dissociation in 2 or one of the stability constants in 4 is known, then the stability constant of the metal chelate can be found. The methods which will be reviewed provide different ways of determining the equilibrium concentrations of the quantities in either 1 or 3.

### The mercury electrode

In this method the equilibrium concentration of mercuric ion in equations 1 and 3 is measured potentiometrically with the mercury electrode. These equations may now be written:



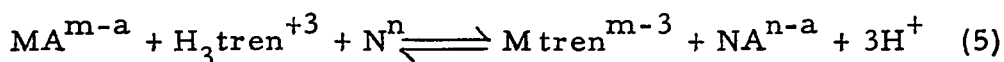
The mercury chelate stability constant is found from the measured mercuric-ion concentration in 1a, provided the acid dissociation

constants of  $H_n A$  are known. Measurements with the mercury electrode of equilibrium 3a give  $K_3$ . From this and mercury chelate stability constant,  $K_{RA}$  can be found. Reilley and Schmid applied this method to the determination of EDTA stability constants, and found their results to be in agreement with values determined by other methods (10). They have applied their method to several other chelating agents (11). Schwarzenbach has developed the theory for this method in general terms for any complexant and has shown that, from a simultaneous measurement of the hydrogen-ion concentration and the mercuric-ion concentration, the formation constants of protonated and hydroxy substituted complexes may be determined in addition to the primary stability constant (12). Schwarzenbach and his co-workers have applied the method to a number of aminopolycarboxylic acids (13,14). This method appears to be useful for determining many moderately stable and very stable chelate constants. In the experimental part of this thesis the mercury electrode has been applied to the measurement of rare-earth chelate stability constants, and a complete discussion of the method will be given there.

#### The modified pH method

Since most chelating agents are weak acids, the formation of a metal chelate by displacement of a proton as shown in 1 provides one of the most general and useful methods for determination of stability constants. For very stable chelates equilibrium 1 is displaced almost completely to the right, and a measurement of the

hydrogen-ion concentration can no longer be used to find  $K_1$ . The simple pH method was modified by Schwarzenbach and co-workers so that it could be applied to stable chelates (15). The modified pH method uses two chelating agents which compete for a metal ion M. A second metal ion N is introduced which forms a very stable complex with one of the complexants but does not form a complex with the second agent. When a solution of this kind is titrated with base, it is possible to determine the equilibrium constant for the reaction.



from the pH. In 5,  $A^{-a}$  is an aminopolycarboxylic acid and  $H_3tren$  is  $\beta, \beta', \beta''$ -triaminotriethylamine, which is the second agent often used in the measurement of rare-earth stability constants. The equilibrium constant for 5 is

$$K_5 = \frac{[NA^{n-a}][Mtren^{m-3}][H^+]^3}{[MA^{m-a}][H_3tren^{+3}][N^n]} = \frac{K_{Mtren} K_{NA}}{K_{H_3tren} K_{MA}} \quad (6)$$

$K_5$  can be calculated from the measured pH value and material balance equations which describe the concentrations of all important quantities in 5. It is seen from 6 that the constants  $K_{MA}$ ,  $K_{Mtren}$ , and the acid dissociation constants of tren must be determined independently. Any error in these constants will be reflected in  $K_{NA}$ . This method has been applied to the determination of the rare-earth stability constants of EDTA by Wheelwright et al. (16) and to the

rare earth-HEDTA<sup>1</sup> constants by Spedding et al. (17). Recently Chaberek and Harder reported the rare earth-carboxymethyl-bis-[2-di(carboxymethyl)-aminoethyl] amine (DTPA) stability constants which were determined by this method (18).

### Polarographic methods

Two general methods of using the polarograph to measure chelate stability constants have appeared in the literature. Each method will be discussed separately.

Method A In this method the polarograph is used simply as an analytical tool to measure the concentration of one of the reactants or products in 3. If the rate of formation and dissociation of the metal chelates is slow, then each species present will be reduced at the dropping mercury electrode, and a distinct wave will be found for each. The height of the wave, which is a measure of the diffusion current, is proportional to the concentration of the species being reduced at the mercury electrode. If the half-wave potentials for each reduction differ by 0.2 volts then the polarographic waves do not overlap, and the individual diffusion currents may be measured. From the polarographically measured concentration of one of the species in 3 and the material balance equations, it is possible to calculate  $K_3$ . It is seen from 3 that  $K_3$  is equal to the ratio of the stability constants of the two metals used. One of these constants

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<sup>1</sup>N'-(hydroxyethyl) ethylenediamine-N, N, N'-triacetic acid

must be measured independently to find the absolute value of the other. This method has been used by a number of people for the determination of stable-chelate formation constants (19, 20).

Wheelwright et al. used this method to determine the rare earth-EDTA and HEDTA stability constants (16, 17). Schwarzenbach and co-workers reported the chelate stability constants of 29 metal ions (including the rare earths) with EDTA and 1, 2-diaminocyclohexane-N, N, N', N'-tetraacetic acid (DCTA) (21). Recently Hiller determined the stability constants of the rare earth and scandium complexes of 1, 2-bis-[2-di(carboxymethyl)-aminoethoxy] ethane (DE) and 2, 2'-bis-[di(carboxymethyl)-amino] diethyl ether (ME) (22). The results obtained in the experimental part of this thesis provide a direct comparison with Hiller's values, and a further comment on this method will be presented later.

Method B This method can only be applied if the electrode reaction is thermodynamically reversible. If this condition is met, it is possible to determine both the formula and stability constant from the half-wave potential. It can be shown that the half-wave potential of the dropping mercury electrode depends on the logarithm of the stability constant of the chelated metal ion. The stability constant can be estimated directly from the observed value of the half-wave potential, but a more accurate procedure is to determine the stability constant from the difference between the  $E_{\frac{1}{2}}$  of the chelate and the  $E_{\frac{1}{2}}$  of the corresponding metal ion. Lingane has given a complete review of this method (23). Koryta and Kössler<sup>11</sup> studied the nitrilotriacetate complex of some alkaline earths (24),

and Matyska and Kössler reported the formation constants of three mercury-EDTA complexes,  $\text{HgY}$ ,  $\text{HHgY}$ , and  $\text{HgOHY}$ , obtained by this method (25). Onstott has studied the polarographic reduction of the europium chelates of EDTA. The measurements were of solutions with a large excess of EDTA. Various complex ions were identified from half-wave potential and diffusion current data including one species that apparently involved two chelating anions per  $\text{Eu(III)}$  ion (26).

#### Radiochemical methods

Two methods for determining stability constants using radioactive isotopes have been reported. The first method depends on equilibrium 1. In very acid solutions the metal ion is partially displaced by hydrogen ion. The amount of uncomplexed metal is determined by use of a radioactive indicator. For this method it is necessary that the exchange of complexed metal take place slowly enough to be measurable. Metal ions are added to an equilibrated solution of  $\text{M}^*\text{A}$  where  $\text{M}^*$  is the radioactive isotope. A portion of the free metal ions is removed from solution at measured time intervals after mixing, and the radioactivity of this portion is measured. The increase in radioactivity with time is due to the exchange of  $\text{M}$  with  $\text{M}^*\text{A}$ . The fractional exchange plotted as a function of time gives a straight line which can be extrapolated to zero time to yield the amount of dissociated ion originally present at equilibrium. The stability constant of the metal can be calculated from  $K_1$  with the acid dissociation constants. Long and co-workers

have developed this method and have used it to measure the iron (III) and nickel constants of EDTA (27, 28, 29). Betts et al. have developed a radiochemical method based on equilibrium 3 (30). They measured  $K_3$  for the different rare earths with EDTA at several temperatures using this method (31). Solutions were prepared containing known amounts of two lanthanides, one of which was radioactive, and an amount of the chelating agent EDTA which was about half the sum of the concentrations of the two lanthanides. The position of 3 was calculated from the distribution of the radioactive tracer between the complexed species and free metal ion. This was done by passing the solution through a cation-exchange column. The  $RY^-$  passed through the column and the  $R^{+3}$  was retained. The relative amounts of radioactive isotopes, both free and chelated, were calculated from the radioactivity in the effluent and in the original solution. The radiotracers used were  $La^{140}$ ,  $Nd^{147}$ ,  $Dy^{165}$ , and  $Yb^{175}$ .

#### Spectrophotometric method

Both equilibria 1 and 3 have been used to measure stability constants by the spectrophotometric method. If at least one of the ions present in 1 or 3 absorbs light in the visible or ultraviolet regions of the spectrum, then the spectrophotometer may be used to determine stability constants. The equilibrium concentration of the absorbing species can be used to solve for  $K_1$  or  $K_3$ . Kolthoff and Auerback measured the stability of the ferric-EDTA chelate using 1 (32). They measured the amount of ferric chelate in a very acidic solution so that the chelate was partially dissociated.



Martell and Hughes determined the nickel-EDTA stability constant by this method (33). Martell and co-workers used equilibrium 3 to determine the stability constants of stable chelates with the spectrophotometer (34, 35). They found the relative values of the stability constants of a number of metals from the measured optical densities of solutions containing two metal ions and the chelate.

## Variation of Stability Constants with Metal and Chelating Agent

Martell and Calvin (8) and more recently Chaberek and Martell (1) have summarized and discussed the stability of metal chelates in terms of the structure of the chelating agent and the nature of the metal ion. The characteristics of chelating agents which have been considered to influence the stability constant are:

1. The basicity of the ligand;
2. The nature of the coordinating atom;
3. The number of metal chelate rings formed;
4. The size of the chelate ring;
5. Steric effects; and
6. Resonance effects.

Some of the general trends that are pertinent to aminopolyacetic acids will be briefly discussed. Both hydrogen and metal ions are Lewis acids so that a strongly basic ligand might be expected to show a strong tendency to interact with metal ions. Martell and Calvin have shown that plots of  $pK_N$  versus  $\log K_{MA}$  are linear in a number of cases (8). Schwarzenbach and co-workers (13, 36) have investigated the effect of the number and size of metal chelate rings formed by aminopolyacetic acids similar to EDTA. Stability constants of chelating agents of the types I, II, and III were studied:

- I.  $(\text{HOOC-CH}_2)_2\text{=N-(CH}_2)_n\text{-N=(CH}_2\text{-COOH)}_2$  where  $n=2-8$ ,
- II.  $(\text{HOOC-CH}_2)_2\text{=N-(CH}_2)_n\text{-X-(CH}_2)_n\text{-N=(CH}_2\text{-COOH)}_2$   
where  $n=2-4$  and  $X = \text{-O-}, \text{-S-}, \text{-NCH}_3\text{-}$ ,
- III.  $(\text{HOOC-CH}_2)_2\text{=N-(CH}_2)_2\text{-X-(CH}_2)_2\text{-X-(CH}_2)_2\text{-N=(CH}_2\text{-COOH)}_2$

where X = -O-, -S-, -NCH<sub>3</sub>- .

The metals used were Ca<sup>+2</sup>, Cd<sup>+2</sup>, and Hg<sup>+2</sup>. The stability of chelates for agents of type I is greatest for n=2 or a five-membered chelate ring. The stability falls with increasing n until n=4, after which it remains almost constant with increasing n. The addition of -O-, -S-, and -NCH<sub>3</sub>- in II and III increases the stability of the chelate by a considerable amount due apparently to the formation of new five-membered chelate rings with these heteroatoms.

The dependence of chelate stability on the nature of the metal ion has been correlated with ionization potentials, the reciprocal of the ionic radius, the (charge)<sup>2</sup>/radius, and electronegativity. Data for the alkaline earths and transition metal complexes are plentiful, and some interesting correlations have been discovered. One example is the so-called "natural order" of stability for bivalent transition metal complexes. The complex stability order of Mn < Fe < Co < Ni < Cu > Zn has been found to hold in nearly all cases regardless of the nature of the ligand (37). Extensive data are not available for the rare-earth complexes because only a few complex stability constants have been measured. However, some correlations have been suggested for the constants which have been measured, and this will be reviewed. Martell and Plumb (34) suggested that the stability constants of the rare earths with EDTA increased with decreasing ionic radius or increasing charge-radius ratio. They used as the basis of their suggestion ratios of the stability constants for about half the rare earths.

Jones (38) noted that a plot of the rare-earth-EDTA stability constants versus  $(\text{charge})^2/\text{radius}$  gave a straight line. By comparing the rare earths with the alkalis and heavy alkaline earth-EDTA chelates, he proposed that the lanthanon chelates were ionic in nature. Jones used the constants measured by Vickery (39) which have been criticized as inaccurate (16). Wheelwright *et al.* (16) called attention to the increase of stability constants in going from lanthanum to lutetium which paralleled the decrease in radius across the series. An irregularity in the curve of stability constant versus atomic number occurred around gadolinium. It was suggested that the break in the curve at gadolinium was due to a change in coordination. With the earlier members of the series EDTA acts as a hexadentate ligand, but due to steric factors it acts as pentadentate with the heavier rare earths. When data on other rare-earth chelates became available, Schwarzenbach and Gut suggested that the break at gadolinium was not due to a change in coordination (40). They called attention to the fact that both DCTA and nitrilotriacetate (NTA) chelates show a break similar to EDTA. Since NTA had only four ligand groups, it seemed unlikely that the break was due to a change in the number of groups coordinated to the metal ion. The authors called attention to other properties of the rare earths where a break is also noticed at gadolinium and suggest that this is characteristic of the rare-earth ion.

Schwarzenbach also suggested that complex formation in the case of the rare earths may involve forces besides those of a pure

electrostatic nature. If the rare earths were considered as rigid ionic spheres that were attached to the ligand only by electrostatic attraction, the stability would be a specific function of the ionic radius. In this case one might expect yttrium to always occur at the same place in the stability sequence. This is not the case since yttrium falls between terbium and dysprosium for EDTA, gadolinium and terbium for DCTA, and europium and gadolinium for NTA. Further information regarding the type of coordination for EDTA in rare-earth chelates was provided by Moeller et al. (41). From infrared data and for other reasons they concluded that EDTA occupies only five coordination positions.

The stability constant is related to both the entropy and enthalpy;

$$-RT \ln K = \Delta F = \Delta H - T \Delta S. \quad (7)$$

It has been shown in a number of cases that for chelates of high stability the entropy term in 7 may make up the largest part of  $\Delta F$  (30, 42, 43). This fact has led several people to consider the correlation of stability with the entropy. Foreman and Smith (44) considered the partial molal entropy of metal ions to be a guide to the relative order of stability constants for similar elements with a particular ligand. A plot of partial molal entropy of rare earths above gadolinium versus  $\log K$  of EDTA was linear. The authors apparently accepted the fact that a change in coordination took place at gadolinium and did not try to plot the lower rare earths. Betts and Dahlinger (30) measured the heat and entropy of association of the lanthanides with EDTA from the temperature dependence of the equilibrium constant. They found

that the partial molal entropies of the complex ions were divided into two groups (La to Gd and Tb to Lu). Within the two groups the entropy was constant within experimental error. They account for the two groups by a change in coordination like that proposed by Wheelwright. The  $\Delta H$  values found by Betts and Dahlinger differ considerably from the few calorimetrically determined values of Staveley and Randall (43). The  $\Delta H$  values obtained from the temperature dependence of  $K$  are often inaccurate, and it is questionable if Betts and Dahlinger's conclusions are valid. Staveley and Randall (43) have criticized the view that EDTA affords five or six co-ordination centers around the rare-earth ion. To explain the stability order they suggest that the effect of the ligand field on the 4f electrons must be considered. George et al. also have suggested the need to consider crystal field stabilization for these chelates (45). Harder and Chaberek (18) noted for plots of  $\log K$  for the rare-earth chelates of EDTA, HEDTA, and DTPA versus reciprocal radius that only EDTA exhibited a linear relationship. If the reciprocal of the radius were a valid correlation, a maximum in the stability series should occur with Yb. For DTPA it occurs at Dy. The authors noted that this corresponds to the maximum in the magnetic susceptibility of the rare earth ions. An explanation of the stability series similar to Wheelwright's was offered.

The discussion so far has dealt only with chelates and mainly with EDTA chelates. Very little data on simple complexes have appeared. Sonesson has recently determined the rare-earth acetate

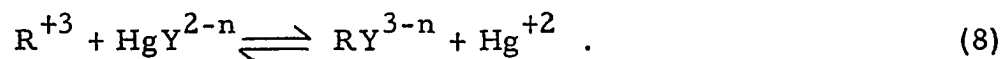
formation constants (46, 47). It is interesting to note that the first formation constant increases to a maximum at samarium, or possibly europium, then falls and remains almost constant. It appears that the formation of the first acetate complex becomes more difficult after the 4f-orbitals have been half-filled. Sonesson (48) has also measured the rare-earth glycolate constants which show similar behavior.

## EXPERIMENTAL

Derivation of the Experimental Methods Used  
to Measure Stability Constants

The stability constants of the rare-earth chelates of HEDTA, ME, and DE have been measured by the mercury electrode method. The equations for this method for a general aminopolycarboxylic acid  $H_nY$  and rare-earth ions  $R^{+3}$  are given below.

In this method rare-earth and mercury(II) ions were mixed with an amount of chelating agent equal to about half the sum of the concentrations of the two metal ions. The exchange reaction shown in equation 8 is the basic reaction involved in the mercury electrode method:



The equilibrium constant for 8 can be written,

$$K_8 = \frac{[RY^{3-n}][Hg^{+2}]}{[R^{+3}][HgY^{2-n}]} = \frac{K_{RY}}{K_{HgY}} \quad (9)$$

Material balance equations which relate all the important species found in a solution of the two metals and the chelating agent can be written. The following equations will not include species with two or more chelating agents per metal ion. The aminopolycarboxylic acids studied were pentadentate or higher and would not be expected to require more than one chelating agent per metal ion under the conditions used. Mercurous ions must be considered in the material balance equations because the measurements took place in the



presence of metallic mercury and reaction 10 will occur,



The material balance equations are:

$$[\text{R}]_{\text{T}} = [\text{R}^{+3}] + [\text{RY}^{3-n}] + 2[\text{R}_2\text{Y}^{6-n}] + [\text{RHgY}^{5-n}] + \sum_{h=0}^h [\text{H}_h\text{RY}^{3+h-n}] \quad (11)$$

$$[\text{Hg}]_{\text{T}} = [\text{Hg}^{+2}] + 2[\text{Hg}_2^{+2}] + [\text{RHgY}^{5-n}] + [\text{HgY}^{2-n}] + \sum_{p=0}^p [\text{H}_p\text{HgY}^{2+p-n}] \quad (12)$$

$$[\text{Y}]_{\text{T}} = [\text{RY}^{3-n}] + [\text{HgY}^{2-n}] + [\text{R}_2\text{Y}^{6-n}] + [\text{RHgY}^{5-n}] + \sum_{h=0}^h [\text{H}_h\text{RY}^{3+h-n}] + \sum_{p=0}^p [\text{H}_p\text{HgY}^{2+p-n}] + \sum_{n=0}^n [\text{H}_n\text{Y}] \quad (13)$$

$$[\text{H}]_{\text{T}} = [\text{H}^+] - [\text{OH}^-] + \sum_{h=0}^h h[\text{H}_h\text{RY}^{3+h-n}] + \sum_{n=0}^n n[\text{H}_n\text{Y}] + \sum_{p=0}^p p[\text{H}_p\text{HgY}^{2+p-n}] \quad (14)$$

In their general form these equations are rather complicated, however, for the chelating agents which have been studied in this thesis many terms are insignificant and can be neglected. In all cases where the mercury electrode was used, the concentration of free mercury ions was neglected. This is because equilibrium 8 was displaced to the extreme left. Due to the high stability constant of both metal chelates in 8 and the presence of excess metal ion, the term  $\sum_{n=0}^n \text{H}_n\text{Y}$  is negligible in both 13 and 14. It was necessary

to consider only singly protonated metal chelates for the agents studied. The quantities in the material balance equations can be expressed in terms of the following formation constants which can be measured independently;

$$K_{RHgY}^R = \frac{[RHgY^{5-n}]}{[R^{+3}][HgY^{2-n}]},$$

$$K_{R_2Y}^R = \frac{[R_2Y^{6-n}]}{[R^{+3}][RY^{3-n}]},$$

$$K_{HHgY}^H = \frac{[HHgY^{3-n}]}{[H^+][HgY^{2-n}]},$$

$$K_{HRY}^H = \frac{[HRY^{4-n}]}{[H^+][RY^{3-n}]}.$$

These four equations can be solved for the quantities  $[RHgY^{5-n}]$ ,  $[R_2Y]$ ,  $[HHgY]$ , and  $[HRY]$ ,

$$[RHgY^{5-n}] = [R^{+3}][HgY^{2-n}] K_{RHgY}^R \quad (a)$$

$$[R_2Y^{6-n}] = [R^{+3}][RY^{3-n}] K_{R_2Y}^R \quad (b)$$

$$[HHgY^{4-n}] = [H^+][HgY^{2-n}] K_{HHgY}^H \quad (c)$$

$$[HRY]^{4-n} = [H^+][RY^{3-n}] K_{HRY}^H \quad (d)$$

(15)

With these quantities substituted in the material balance equations and the omission of insignificant terms, equations 11, 12, 13 and 14 become:

$$[R]_T = [R^{+3}] (1 + [HgY^{2-n}] K_{RHgY}^R + 2 [RY^{3-n}] K_{R_2Y}^R) + [RY^{3-n}] (1 + [H^+] K_{HRY}^H) \quad (16)$$

$$[Hg]_T = [HgY^{2-n}] (1 + [H^+] K_{HHgY}^H + [R^{+3}] K_{RHgY}^R) \quad (17)$$

$$[Y]_T = [RY^{3-n}] (1 + [R^{+3}] K_{R_2Y}^R + [H^+] K_{HRY}^H) + [HgY^{2-n}] (1 + [H^+] K_{HHgY}^H + [R^{+3}] K_{RHgY}^R) \quad (18)$$

$$[H]_T = [H^+] - [OH^-] + [H^+] [RY^{3-n}] K_{HRY}^H + [H^+] [HgY^{2-n}] K_{HHgY}^H \quad (19)$$

If the constants  $K_{R_2Y}^R$ ,  $K_{HRY}^H$ ,  $K_{HHgY}^H$ , and  $K_{RHgY}^R$  are known, then equations 16, 17, and 18 can be solved for  $[R^{+3}]$ ,  $[RY^{3-n}]$ , and  $[HgY^{2-n}]$ . The potential of the mercury electrode is a measure of the mercuric-ion concentration. Thus the mercuric-ion concentration, the pH, and equations 16, 17, and 18 yield the quantities in 9 so that  $K_1$  can be calculated. If the mercury chelate stability constant is known, then  $K_{RY}$  can be found.

#### Determination of the mercury chelate stability constants

To determine the mercury chelate stability constant, mercuric ions and an excess of the chelating agent were mixed. The equilibrium constant for the formation of mercury chelate is:

$$K_{HgY} = \frac{[HgY^{2-n}]}{[Hg^{+2}][Y^{-n}]} \quad (20)$$

The material balance equations for a solution of mercury(II) and an excess of chelating agent are:

$$[\text{Hg}]_T = [\text{HHgY}^{3-n}] + [\text{HgY}^{2-n}] + [\text{HgYOH}^{2-(n+1)}] \quad (21)$$

$$[\text{Y}]_T = [\text{HHgY}^{3-n}] + [\text{HgY}^{2-n}] + [\text{HgYOH}^{2-(n+1)}] + \sum_{n=0}^n [\text{H}_n\text{Y}] \quad (22)$$

In these equations only 1:1 complexes have been considered. If 21 is subtracted from 22 we obtain:

$$[\text{Y}]_T - [\text{Hg}]_T = \sum_{n=0}^n [\text{H}_n\text{Y}] \quad (23)$$

The formation constants for  $[\text{HHgY}^{3-n}]$  and  $[\text{HgYOH}^{2-(n+1)}]$  are written:

$$K_{\text{HHgY}}^{\text{H}} = \frac{[\text{HHgY}^{3-n}]}{[\text{H}^+][\text{HgY}^{2-n}]},$$

$$K_{\text{HgYOH}}^{\text{OH}} = \frac{[\text{HgYOH}^{2-(n+1)}]}{[\text{OH}^-][\text{HgY}^{2-n}]}$$

and can be solved to give;

$$[\text{HHgY}^{3-n}] = [\text{H}^+][\text{HgY}^{2-n}] K_{\text{HHgY}}^{\text{H}} \quad (24)$$

and

$$[\text{HgYOH}] = [\text{OH}^-][\text{HgY}^{2-n}] K_{\text{HgYOH}}^{\text{OH}} \quad (25)$$

We can substitute 24 and 25 in 21 to give,

$$[\text{Hg}]_T = [\text{HgY}^{2-n}] (1 + [\text{H}^+] K_{\text{HHgY}}^{\text{H}} + [\text{OH}^-] K_{\text{HgYOH}}^{\text{OH}}) \quad (21a)$$

It is convenient to define

$$a = (1 + [H^+] K_{HHgY}^H + [OH^-] K_{HgYOH}^{OH})$$

Equation 21a now becomes

$$[Hg]_T = [HgY^{2-n}] a \quad (21b)$$

Equation 23 can be expressed in terms of the acid association constants,

$$K_n = \frac{[H_n Y]}{[H^+][H_{n-1} Y]} \quad \text{and} \quad [Y^{-n}]$$

Thus

$$\sum_{n=0}^n [H_n Y] = [Y^{-n}] \left( 1 + \frac{[H^+]}{K_n} + \frac{[H^+]^2}{K_n \cdot K_{n-1}} + \dots + \frac{[H^+]^n}{\prod_{i=1}^n K_i} \right) \quad (26)$$

It is convenient to define the term

$$\phi = \left( 1 + \frac{[H^+]}{K_n} + \frac{[H^+]^2}{K_n \cdot K_{n-1}} + \dots + \frac{[H^+]^n}{\prod_{i=1}^n K_i} \right) \quad (27)$$

We can now write 23 in the form,

$$[Y]_T - [Hg]_T = [Y^{-n}] \phi \quad (23a)$$

Equations 23a and 21b can be solved for  $[Y^{-n}]$  and  $[HgY^{2-n}]$  and substituted into 20 to give,

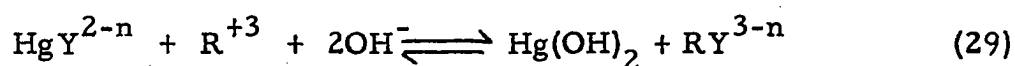
$$K_{HgY} = \frac{[Hg]_T \phi}{a [Hg^{+2}] ([Y]_T - [Hg]_T)} \quad (28)$$

If the acid association constants are known, then  $\phi$  can be calculated from the measured pH. Also if  $K_{\text{HHgY}}^{\text{H}}$  and  $K_{\text{HgYOH}}^{\text{OH}}$  are known, then  $\alpha$  can be calculated. The concentration of mercury(II) can be measured with the mercury electrode so that  $K_{\text{HgY}}$  can be calculated.

#### Limitations of the mercury electrode method

The derivation of the equations for the mercury electrode method was made with the assumption that the metal ion combined with the chelating agent to form stable 1:1 chelates. Other factors will be considered which may limit the use of the mercury electrode for determining stability constants.

It is necessary that the mercury chelate stability constant be higher than the metal chelate constant being determined. If  $\frac{K_{\text{HgY}}}{K_{\text{RY}}}$  becomes smaller than  $10^3$ , then the non-chelated mercurous ions can no longer be neglected in the material balance equations. The pH range in which the mercury electrode may be used to determine stability constants is also limited. In very acid solutions HRY or HHgY may precipitate. At higher pH's the hydrolysis and formation of metal hydroxide may occur. For the rare earths this limits the pH range to below approximately 5. Schwarzenbach and Anderegg (12) called attention to another factor which may limit the pH range. They showed that the reaction,



can occur, and the pH at which it becomes significant depends on the ratio  $K_{RY}/K_{HgY}$ . The equilibrium constant for 29 is:

$$K = \frac{[Hg(OH)_2][RY^{3-n}]}{[R^{+3}][HgY^{2-n}][OH^-]^2} = K_{Hg(OH)_2} \frac{K_{RY}}{K_{HgY}} \quad (30)$$

Schwarzenbach et al. (49) have shown that  $Hg^{+2}$  takes up two moles of hydroxide in one step and,

$$K_{Hg(OH)_2} = \frac{[Hg(OH)_2]}{[Hg^{+2}][OH^-]^2} = \frac{[Hg(OH)_2][H^+]^2}{[Hg^{+2}]K_W^2} = 10^{21.40} \quad (31)$$

Thirty may now be written:

$$\frac{[Hg(OH)_2][RY^{3-n}][H^+]^2}{[R^{+3}][HgY^{2-n}]K_W^2} = 10^{21.40} \frac{K_{RY}}{K_{HgY}} \quad (30a)$$

Reaction 29 will introduce a significant error in the stability constant measurements when  $[Hg(OH)_2]$  is greater than  $10^{-2} \cdot [Hg]_T$ . Equation 30a can be solved using experimental concentrations to determine the upper pH limit. For the cases studied in this dissertation reaction 29 becomes significant in the same region where rare-earth hydrolysis occurs i. e. 4.5 to 5. Formation of insoluble chelate precipitates may also limit the application of the mercury electrode method. Schwarzenbach and Anderegg (12) found that  $\{Hg_2Y\}$  and  $\{Hg_3Y\}$  for EDTA were very insoluble. They reported the solubility products to be:

$$[Hg^{+2}][HgY^{-2}] = 10^{-10.5} \text{ and } [Hg_2^{+2}][HgY^{-2}] = 10^{-10} .$$

The authors found it necessary to adjust the concentrations so that the solubility products of these species were not exceeded when the mercury electrode method was used to measure EDTA stability constants.



## Materials and Equipment

Conductance water All solutions were prepared from conductivity water which was redistilled from an alkaline permanganate solution in a Barnstead Conductivity Still. The water was freed of carbon dioxide by passing nitrogen through the boiling water, and it was then stored under nitrogen.

Carbonate-free potassium hydroxide Standard solutions of carbonate-free potassium hydroxide were prepared by the method of Powell and Hiller (50).

Carbonate-free sodium hydroxide A standard solution of sodium hydroxide was prepared by the method suggested by Diehl and Smith (51). All solutions of base were standardized against potassium acid phthalate and were stored in a Pyrex bottle which had a gas train consisting of an Ascarite tube and a small bubbler containing dilute potassium hydroxide.

Acetate buffer A 0.4 M acetate buffer solution was prepared by mixing equal molar amounts of reagent grade acetic acid and sodium acetate.

Mercuric nitrate A standard solution of mercuric nitrate was prepared by dissolving reagent grade mercuric nitrate in dilute nitric acid. The solution was standardized potentiometrically against standard EDTA using the mercury indicator electrode (52, 53).

Chelating agents The chelating agents HEDTA, ME, and DE were obtained from Geigy Industrial Chemicals. The chelating

agents were further purified by recrystallization. In the case of HEDTA and ME the acids were prepared and standardized by potentiometric titration with standard potassium hydroxide and by a complexometric titration against standard mercuric nitrate solution using the mercury indicator electrode. The results of the two methods were in good agreement. The acid form of DE was insoluble so the disodium salt was prepared. An aliquot of the acid was titrated potentiometrically to find the pH of the equivalence point. The chelating agent was brought up to this pH to give a solution of disodium salt. The DE was then standardized by a complexometric titration against standard mercuric nitrate.

Rare-earth nitrate solutions      The rare-earth oxides, 99.9% pure or greater, were supplied by the rare-earth separation group under the direction of Dr. J. E. Powell at the Ames Laboratory of the Atomic Energy Commission. Stock solutions were prepared by dissolving the oxides in excess nitric acid. The excess acid was removed by boiling to almost dryness. An aliquot of each solution was titrated potentiometrically to find the pH of the neutral equivalence point. All solutions were then adjusted to the neutral equivalence pH. Most of the solutions were analyzed gravimetrically by precipitation with oxalic acid followed by ignition to the oxide. Several of the stock solutions were standardized by complexometric titration with EDTA using the mercury indicator electrode.

### Description of equipment

pH meter      pH measurements were made with a Beckman G. S. meter using the regular pH scale. A "General Purpose" glass electrode was used. The problem of converting pH recorded on the pH meter to hydrogen-ion concentration is discussed in Appendix A. The equation  $\text{pH} = \text{pH}_r - 0.10$  will be used to find hydrogen-ion concentration where  $\text{pH}_r$  is the reading from the pH meter.

Potentiometer      The potential of the mercury electrode was measured with a Rubicon Potentiometer.

Apparatus for determination of stability constants      The experimental set-up used to measure stability constants was similar to that used by Sillen *et al.* (54) to measure hydrolysis constants and is pictured in Figure 2. The calomel electrode is joined to the salt bridge at  $J_1$ , and the titration cell is joined at  $J_2$ . The reservoir on the left was filled with 0.1 M KCl and the one on the right with 0.1 M  $\text{KNO}_3$ . The stopcock at  $C_1$  is three way so that the liquid junction at  $C_1$  may be renewed by flushing alternately with KCl and  $\text{KNO}_3$ . A fritted glass disc is used at the point where the bridge enters the cell. The calomel cell and liquid junction were immersed in a constant temperature bath which was maintained at  $20.00 \pm 0.02^\circ\text{C}$ . The cell was jacketed so that water from the bath could be circulated around the solution. The mercury electrode was a J-shaped tube with a platinum wire sealed into the end which connected the drop of mercury in the cup-shaped end to the poten-

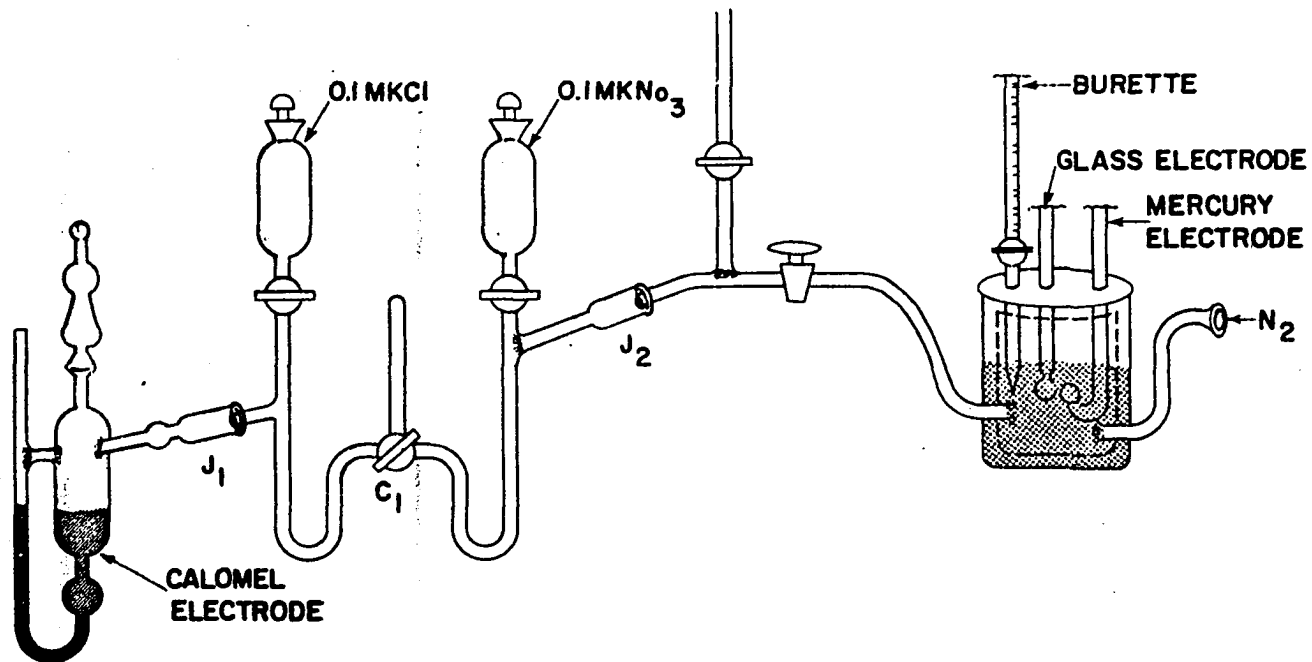
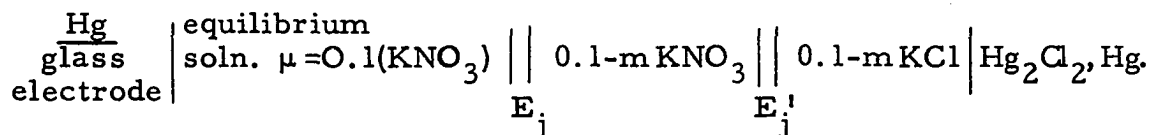


Figure 2. Cell with calomel electrode, salt bridge and titration vessel

tiometer. The cell was fitted with a stopper through which the glass electrode, mercury electrode, and a microburette could extend into the solution. A stream of nitrogen was bubbled into the solution at all times. The cell may be expressed:



The potential is given by the Nernst equation,

$$E = E^\circ_{\text{Hg}} + E_j + E_j' + s/2 \log a_{\text{Hg}^{+2}}, \quad (32)$$

where  $E^\circ_{\text{Hg}}$  is the standard reduction potential of  $\text{Hg}^{+2}$  to  $\text{Hg}^\circ$  measured against the 0.1-m calomel cell and  $s = 2.3026 \text{ RT/F}$ .

$E_j$  is the liquid-liquid junction potential between the experimental solution and the 0.1-m  $\text{KNO}_3$ , and  $E_j'$  is the junction potential between 0.1-m  $\text{KNO}_3$  and 0.1-m  $\text{KCl}$ .  $E_j'$  will remain constant while  $E_j$  would be expected to vary at both low and high pH's due to the large mobility of  $\text{H}^+$  and  $\text{OH}^-$ . However, between a pH of 3 to 11,  $E_j$  will be constant. Equation 32 can be written in the form:

$$E = E^\circ_{\text{Hg}} + E_j + E_j' + s/2 \log \gamma_{\text{Hg}^{+2}} + s/2 \log [\text{Hg}^{+2}]$$

or  $E = E_o' + s/2 \log [\text{Hg}^{+2}] \quad (33)$

where  $E_o' = E^\circ_{\text{Hg}} + E_j + E_j' + s/2 \log \gamma_{\text{Hg}^{+2}}$ .

$E_o'$  will be a constant at constant ionic strength in the pH range 3 to 11.  $E_o'$  is a sort of formal reduction potential for  $\mu = 0.1 (\text{KNO}_3)$  and was evaluated by the following method.

Method for determining  $E_o'$  A solution of known mercuric-ion concentration with ionic strength of 0.1-m ( $\text{KNO}_3$ ) was placed

in the titration cell, and the pH and potential of the mercury electrode were recorded. To avoid hydrolysis of mercury the measurements had to be made below a pH of three. Unfortunately  $E_o'$  is no longer constant in this pH range and  $E_o'$  for the constant range 3 to 11 was found by extrapolation. A plot of  $E_o'$ , calculated from 33, versus  $[H^+]$  was made, and the constant junction potential was found from the limiting slope at pH = 3. The measurements were made in the presence of metallic mercury so that most of the  $Hg^{+2}$  was reduced. The concentration of  $Hg^{+2}$  was calculated from the equilibrium constant

$$\frac{[Hg_2^{+2}]}{[Hg^{+2}]} = 88 \quad (\mu = 0.1, \text{ temp.} = 20^\circ\text{C}) .$$

The results for the determination of  $E_o'$  are shown in Figure 3.

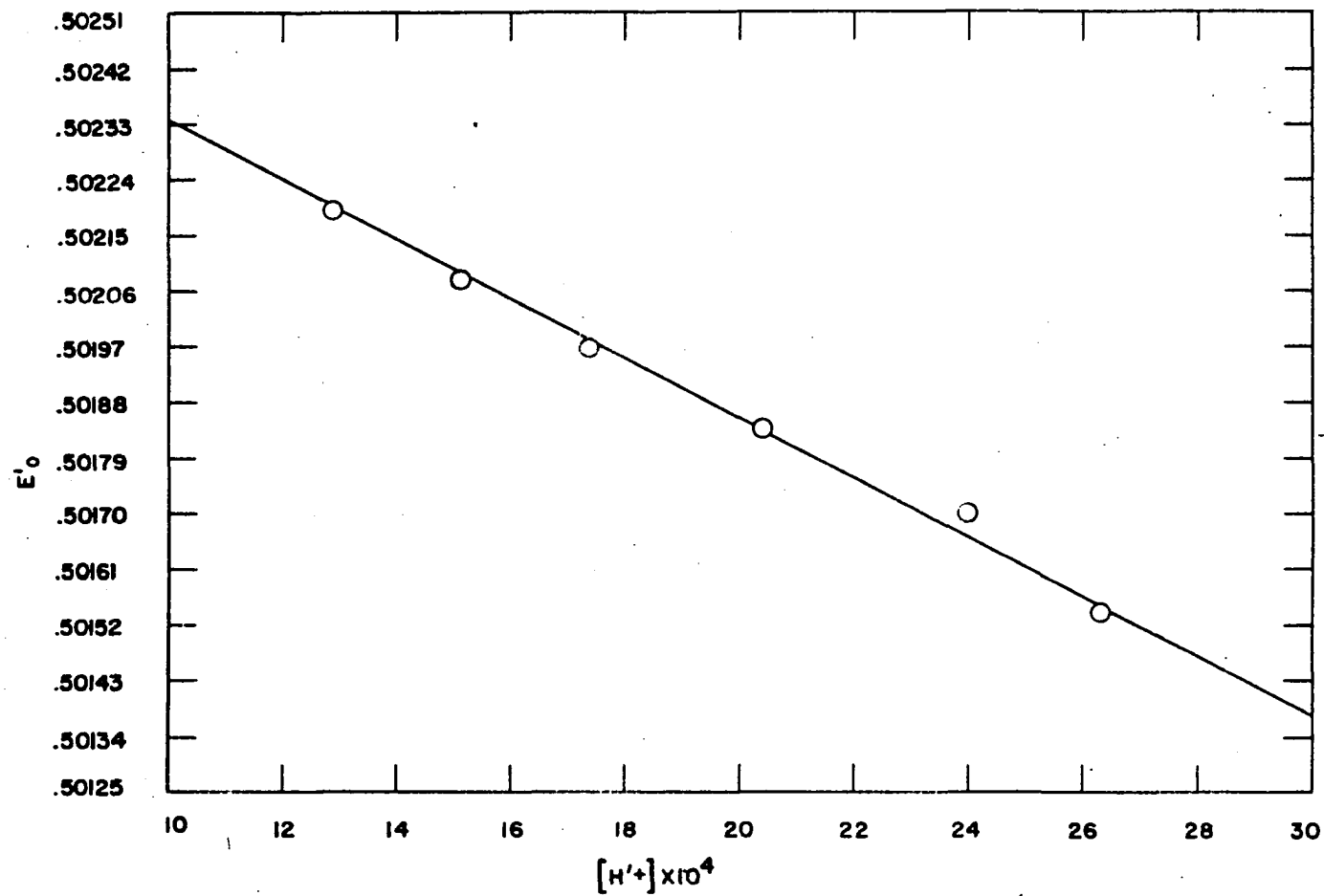


Figure 3. Junction potential from a plot of  $E_o$  versus  $[H^+]$

## HEDTA

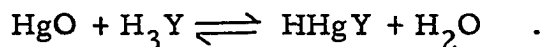
Chelates of HEDTA were studied by the mercury electrode method. This triply charged anion with five or possibly six coordinating groups was a simpler system to study than chelating agents with higher charge and more coordinating groups. Also the results could be checked with values determined by polarographic and modified pH methods.

The value of the mercury-HEDTA stability constant was not found in a search through the chemical literature. Consequently, this constant was measured with the mercury electrode. The protonated mercury chelate was studied first.

James (55) prepared and studied some protonated divalent metal chelates of HEDTA. These compounds were all strong acids and James reported a pK of 2.57 for HCdY. He did not study the protonated mercury chelate.

Preparation and Measurements of HHgY

HHgY was prepared by combining equal molar amounts of HEDTA and mercuric oxide,



The compound formed was a white insoluble substance. HHgY behaves as an insoluble strong acid in the sense that calcium hydroxide is a relatively insoluble strong base. Whereas HCdY is only a moderately strong acid, HHgY appears to be completely dissociated in water and exhibits a well-defined solubility product.



The solubility product was determined by pH measurements according to equations 34-36.



$$K_{\text{s.p.}} = [\text{H}^+][\text{HgY}^-] , \quad \text{and} \quad (35)$$

$$[\text{HgY}^-] = [\text{H}^+] + b \quad (36)$$

where  $b$  is the moles of KOH added per liter of solution.

Equation 36 is the charge balance equation. By substituting 36 into 35, the solubility product is given in terms of measurable quantities,

$$K_{\text{s.p.}} = [\text{H}^+] ([\text{H}^+] + b) . \quad (35a)$$

A suspension of {HHgY} was prepared and potassium nitrate added to keep the ionic strength at 0.1 m. This mixture was titrated with base which was also at ionic strength 0.1 m. After each addition of base the pH was recorded and the solubility product was calculated. The value of  $K_{\text{s.p.}}$  for HHgY was  $1.08 \times 10^{-6}$ . The results are shown in Table 1.

#### The mercury stability constant of HEDTA

Two solutions were prepared having different relative concentrations of mercury and chelate. A drop of metallic mercury was added to the solutions, and they were left in a constant temperature bath for 24 hours. Aliquots of each solution were then placed in the titration cell, and both the potential and pH were measured as the solutions were titrated with base. For the solutions used the solubility product of {HHgY} was not exceeded and  $\alpha$  was equal to one. The equation for the mercury-chelate constant was, therefore,

Table 1. Measurement of the solubility product of {HHgY} at 20.00  $\pm$  0.02°C and ionic strength = 0.10 (KNO<sub>3</sub>)

ml 0.0900 mKOH	pH	[H <sup>+</sup> ]	[NaOH]	K <sub>sp</sub>
0	2.94	1.148x10 <sup>-4</sup>	0	1.321x10 <sup>-6</sup>
2.00	3.32	4.786x10 <sup>-4</sup>	2.224x10 <sup>-3</sup>	1.064x10 <sup>-6</sup>
3.00	3.47	3.388x10 <sup>-4</sup>	2.621x10 <sup>-3</sup>	1.003x10 <sup>-6</sup>
4.00	3.57	2.692x10 <sup>-4</sup>	3.461x10 <sup>-3</sup>	1.005x10 <sup>-6</sup>
5.00	3.64	2.291x10 <sup>-4</sup>	4.288x10 <sup>-3</sup>	1.035x10 <sup>-6</sup>
6.00	3.71	1.950x10 <sup>-4</sup>	5.098x10 <sup>-3</sup>	1.032x10 <sup>-6</sup>
7.00	3.78	1.660x10 <sup>-4</sup>	5.886x10 <sup>-3</sup>	1.005x10 <sup>-6</sup>
8.00	3.81	1.549x10 <sup>-4</sup>	6.664x10 <sup>-3</sup>	1.056x10 <sup>-6</sup>
9.00	3.87	1.349x10 <sup>-4</sup>	7.436x10 <sup>-3</sup>	1.021x10 <sup>-6</sup>
10.00	3.89	1.288x10 <sup>-4</sup>	8.181x10 <sup>-3</sup>	1.070x10 <sup>-6</sup>
11.00	3.91	1.230x10 <sup>-4</sup>	9.006x10 <sup>-3</sup>	1.122x10 <sup>-6</sup>
12.00	3.93	1.175x10 <sup>-4</sup>	9.640x10 <sup>-3</sup>	1.147x10 <sup>-6</sup>
13.00	3.98	1.047x10 <sup>-4</sup>	10.35 x10 <sup>-3</sup>	1.095x10 <sup>-6</sup>
14.00		1.023x10 <sup>-4</sup>	11.15 x10 <sup>-3</sup>	1.139x10 <sup>-6</sup>
			Average	1.08 x10 <sup>-6</sup>

$$K_{\text{HgY}} = \frac{[\text{Hg}]_{\text{T}} \phi}{([\text{Y}]_{\text{T}} - [\text{Hg}]_{\text{T}})[\text{Hg}^{+2}]} \quad (28a)$$

where

$$\phi = 1 + \frac{[\text{H}^+]}{K_3} + \frac{[\text{H}^+]^2}{K_3 K_2} + \frac{[\text{H}^+]^3}{K_3 K_2 K_1}$$

The acid association constants of HEDTA were determined at 296° by Chaberek and Martell (56) and at 25° by Wheelwright (9). The values at 20° were found from a plot of log K versus 1/T from the above values and are shown in Table 2.

Table 2. HEDTA acid association constants

$K_1$	$K_2$	$K_3$	Temp. °C	Ionic Strength
2.60	5.33	9.73	29.6	0.10
2.90	5.41	9.89	25	0.10
3.23	5.50	10.09	20	0.10

Table 3 and Table 4 show the results for the determination of the mercury(II)-HEDTA stability constants.

#### The rare-earth HEDTA stability constants

Two sets of solutions with different concentrations were prepared.

The concentrations were:

$$A. [\text{R}]_{\text{T}} = 2.200 \times 10^{-3}$$

Table 3. Determination of the mercuric-HEDTA stability constant from a solution with  $[\text{Hg}]_{\text{T}} = 9.935 \times 10^{-4}$ ,  $[\text{Y}]_{\text{T}} = 2.1925 \times 10^{-3}$ , temperature =  $20.00 \pm 0.02^{\circ}\text{C}$  and ionic strength =  $0.10(\text{KNO}_3)$

$\text{pH}_{\text{r}}$	E	$\log \phi$	$\log K_{\text{HgY}}$
3.78	0.14885	8.34	20.42
4.02	0.13502	7.82	20.37
4.21	0.12564	7.42	20.30
4.40	0.11496	7.03	20.27
4.62	0.10355	6.59	20.23
4.86	0.09268	6.11	20.12
5.03	0.08360	5.82	20.14

Table 4. Determination of mercuric-HEDTA stability constant from a solution with  $[\text{Hg}]_{\text{T}} = 4.9685 \times 10^{-4}$ ,  $[\text{Y}]_{\text{T}} = 4.380 \times 10^{-3}$ , temperature =  $20.00 \pm 0.02^{\circ}\text{C}$ ; ionic strength =  $0.10(\text{KNO}_3)$

$\text{pH}_{\text{r}}$	E	$\log \phi$	$\log K_{\text{HgY}}$
3.81	0.12141	8.28	20.49
3.99	0.11074	7.88	20.46
4.20	0.09957	7.44	20.40
4.42	0.08764	6.99	20.46
4.63	0.07708	6.61	20.34
4.82	0.06684	6.21	20.30

Table 4. (Continued)

$\text{pH}_r$	$E$	$\log \phi$	$\log K_{\text{HgY}}$
5.02	0.05721	5.84	20.26
5.37	0.04304	5.23	20.14

The average value of the constant was  $K_{\text{HgY}} = 20.30 \pm 0.20$  where 0.20 is the maximum variation from the mean.

$$\begin{aligned}
 [\text{Hg}]_T &= 9.935 \times 10^{-3} \\
 [\text{Y}]_T &= 2.190 \times 10^{-3} \\
 \text{B. } [\text{R}]_T &= 4.400 \times 10^{-3} \\
 [\text{Hg}]_T &= 4.9675 \times 10^{-4} \\
 [\text{Y}]_T &= 4.381 \times 10^{-3}
 \end{aligned}$$

A drop of mercury was added to each of the individual rare-earth solutions and they were left in a constant temperature bath for 24 hours. Then each solution was placed in the titration cell, and the pH and potential of the mercury electrode were found as the pH was raised from about 3.5 to 4.5. Several terms in the general material balance equations 16, 17 and 18 were not necessary for the HEDTA system. The solutions were prepared in such a manner that the solubility product of  $\{\text{HHgY}\}$  was not exceeded. All terms containing  $K_{\text{HHgY}}^{\text{H}}$  were dropped. The tendency of the primary 1:1 chelate species R(HEDTA) to associate with hydrogen ions is probably not great. This primary 1:1 chelate is neutral in charge

and seems even less likely to associate with hydrogen ion than  $\text{HgY}^-$  which was completely dissociated. All terms with  $K_{\text{HRY}}^{\text{H}}$  in the material balance equations were of the form  $(1 + [\text{H}^+] K_{\text{HRY}}^{\text{H}})$ . The measurements were made at about a pH of four so that  $K_{\text{HRY}}^{\text{H}}$  would have to exceed  $10^3$  to be of any significance in the material balance equations. This is unlikely, and all terms with  $K_{\text{HRY}}^{\text{H}}$  were neglected. The values of  $K_{\text{R}_2\text{Y}}^{\text{R}}$  and  $K_{\text{RHgY}}^{\text{R}}$  are not known. However, they might be expected to be small. That such bimetallic chelates do form has been shown by several investigators (14,18). The constants found were small and the magnitude increased with the number of coordinating groups present in the chelating agent. Again, the terms in the material balance equations with  $K_{\text{R}_2\text{Y}}^{\text{R}}$  and  $K_{\text{RHgY}}^{\text{R}}$ , are of the form,  $(1 + [\text{R}^{+3}] K_{\text{RHgY}}^{\text{R}})$ ,  $(1 + [\text{HgY}^-] K_{\text{RHgY}}^{\text{R}})$ , and  $(1 + [\text{R}^{+3}] K_{\text{R}_2\text{Y}}^{\text{R}})$ . An estimate of  $K_{\text{RHgY}}^{\text{R}}$  was made from the change in solubility of  $\{\text{HHgY}\}$  when rare-earth ions were added to solutions containing this insoluble compound. Details of this method are given in Appendix B. A value of  $K_{\text{RHgY}}^{\text{R}} \approx 10^2$  was found. Since  $[\text{R}^{+3}]$  is  $10^{-3}$  or less, the term  $[\text{R}^{+3}] K_{\text{RHgY}}^{\text{R}}$  will be small compared to 1 and may be omitted. It was reasonable to assume that  $K_{\text{R}_2\text{Y}}^{\text{R}}$  would be even less than  $K_{\text{RHgY}}^{\text{R}}$  and the terms  $[\text{R}^{+3}] K_{\text{R}_2\text{Y}}^{\text{R}}$  were assumed to be negligible compared to 1. The material balance equations reduce to a very simple form when the above assumptions were

made:

$$[\text{R}]_{\text{T}} = [\text{R}^{+3}] + [\text{RY}]$$

$$[\text{Hg}]_{\text{T}} = [\text{HgY}]$$

$$[\text{Y}]_{\text{T}} = [\text{HgY}^-] + [\text{RY}]$$

The rare-earth stability constants were determined from these equations and the mercuric-ion concentrations. The results are shown in Table 5. It should be noted that, if the assumptions which were made are valid, the values in Table 5 should be independent of pH and changes in the composition of the stock solution. The agreement in values for A and B in the pH range 3.5 to 4.5 is excellent (see Table 5).

#### The mercury electrode as a pM electrode

Both Reilley and Schmid (10) and Schwarzenbach and Anderegg (12) have pointed out that the mercury electrode will act as a pM electrode under certain conditions, where  $pM = -\log[M]$ . Schwarzenbach and Anderegg used the mercury electrode as a pMg electrode to determine the oxalate complexes of magnesium, and they suggested that this method could be applied to other carboxylic and polycarboxylic acids. Anderegg (57) has recently commented further on this method. A workable rare-earth electrode has not been developed, so an investigation into the possibility of using the mercury electrode as a pR electrode was undertaken. An attempt was made to determine the formation constants of the rare-earth-acetate complexes. This work was unsuccessful. Nevertheless, a description of the method and the reason for its failure may serve a useful purpose for any further work.

In a mixture of rare earth, mercury(II), and chelating agent, the displacement reaction 8 is the basic one of the mercury electrode method. The equilibrium constant for this reaction,

Table 5. Determination of rare-earth HEDTA stability constants at  $20.00 \pm 0.02^\circ\text{C}$ ; ionic strength = 0.10 ( $\text{KNO}_3$ )

Rare Earth	$\text{pH}_r$	E in volts	$\log K_{RY}$	Av.
La-A	3.54	0.22455	13.83	13.82
	3.78	0.22465	13.83	
	4.00	0.22446	13.82	
	4.24	0.22414	13.81	
	4.51	0.22375	13.80	
	4.76	0.22370	13.80	
La-B	3.35	0.19315	13.85	13.82
	3.61	0.19177	13.80	
	3.84	0.19151	13.79	
	4.06	0.19165	13.80	
	4.28	0.19199	13.81	
	4.52	0.19247	13.83	
	4.77	0.19265	13.83	
Ce-A	3.49	0.24355	14.48	14.48
	3.74	0.24384	14.49	
	3.97	0.24375	14.49	
	4.21	0.24355	14.48	
	4.54	0.24335	14.47	
	4.80	0.24335	14.47	
Ce-B	3.52	0.21001	14.43	14.42
	3.80	0.21000	14.43	
	4.08	0.20980	14.42	
	4.31	0.20962	14.41	
	4.58	0.20963	14.41	
	4.81	0.20972	14.42	
Pr-A	3.49	0.25855	15.00	14.99
	4.09	0.25840	14.99	
	4.32	0.25834	14.99	
	4.52	0.25845	14.99	
	4.76	0.25865	15.00	
Pr-B	3.38	0.22455	14.92	14.92
	3.81	0.22480	14.94	
	4.00	0.22472	14.93	
	4.44	0.22425	14.92	
	4.51	0.22416	14.91	



Table 5. (Continued)

Rare Earth	$pH_r$	E in volts	$\log K_{RY}$	Av.
	4.55	0.22405	14.91	
	4.58	0.22400	14.91	
Nd-A	3.38	0.26371	15.17	
	3.60	0.26394	15.18	
	3.82	0.26393	15.18	
	4.08	0.26369	15.17	15.17
	4.38	0.26348	15.17	
	4.62	0.26357	15.17	
	4.87	0.26354	15.17	
Nd-B	3.10	0.26198	15.11	
	3.40	0.26263	15.14	
	3.70	0.26281	15.14	
	3.91	0.26305	15.15	15.14
	4.15	0.26333	15.16	
	4.43	0.26311	15.15	
	4.75	0.26291	15.15	
Sm-A	3.69	0.27522	15.56	
	4.22	0.27576	15.58	
	4.48	0.27671	15.62	15.62
	4.54	0.27694	15.62	
	4.59	0.27698	15.62	
Sm-B	3.58	0.26952	15.66	
	4.03	0.26965	15.67	15.67
	4.41	0.26975	15.67	
	4.50	0.26978	15.67	
	4.58	0.26971	15.67	
Eu-A	3.42	0.27789	15.66	
	3.68	0.27785	15.66	
	3.88	0.27764	15.65	15.65
	4.11	0.27740	15.64	
	4.49	0.27760	15.65	
	4.71	0.27760	15.65	
Eu-B	3.40	0.24415	15.60	
	3.69	0.24434	15.61	
	3.98	0.24408	15.60	15.60
	4.24	0.24368	15.59	

Table 5. (Continued)

Rare Earth	$pH_r$	E in volts	$\log K_{RY}$	Av.
	4.69	0.24387	15.59	
	4.88	0.24415	15.60	
Gd-A	3.48	0.27168	15.45	
	3.70	0.27155	15.44	
	3.98	0.27117	15.43	15.43
	4.23	0.27085	15.42	
	4.48	0.27093	15.42	
	4.78	0.27086	15.42	
Gd-B	3.38	0.23964	15.45	
	3.62	0.23969	15.45	
	3.84	0.23950	15.44	15.44
	4.09	0.23916	15.43	
	4.61	0.23881	15.42	
	4.81	0.23915	15.43	
Tb-A	3.51	0.27419	15.53	
	3.77	0.27394	15.53	
	4.02	0.27361	15.51	15.52
	4.29	0.27365	15.52	
	4.54	0.27394	15.53	
	4.79	0.27360	15.51	
Tb-B	3.41	0.24376	15.59	
	3.68	0.24384	15.59	
	3.93	0.24355	15.58	15.58
	4.19	0.24325	15.57	
	4.48	0.24306	15.56	
	4.71	0.24336	15.57	
Dy-A	3.34	0.27454	15.55	
	3.61	0.24434	15.54	
	3.81	0.27400	15.53	
	4.02	0.27336	15.52	15.54
	4.28	0.27385	15.52	
	4.52	0.27454	15.55	
	4.74	0.27476	15.55	
Dy-B	3.36	0.24110	15.50	
	3.61	0.24114	15.50	
	3.88	0.24089	15.49	

Table 5. (Continued)

Rare Earth	$pH_r$	E in volts	$\log K_{RY}$	Av.
	4.10	0.24044	15.47	15.48
	4.32	0.24001	15.46	
	4.57	0.24001	15.46	
	4.79	0.24039	15.47	
Ho-A	3.38	0.27474	15.55	15.55
	3.64	0.27499	15.56	
	3.88	0.27489	15.56	
	4.19	0.27466	15.55	
	4.40	0.27468	15.55	
	4.66	0.27464	15.55	
Ho-B	3.38	0.27474	15.55	15.55
	3.64	0.27499	15.56	
	3.88	0.27489	15.56	
	4.19	0.27466	15.55	
	4.40	0.27468	15.55	
	4.66	0.27464	15.55	
Er-A	3.52	0.27653	15.62	15.61
	3.75	0.27635	15.61	
	3.98	0.27606	15.60	
	4.29	0.27606	15.60	
	4.53	0.27650	15.62	
	4.76	0.27630	15.61	
Er-B	3.32	0.24470	15.62	15.62
	3.57	0.24500	15.63	
	3.81	0.24498	15.63	
	4.05	0.24464	15.62	
	4.27	0.24434	15.61	
	4.51	0.24415	15.60	
	4.73	0.24433	15.61	
Tm-A	3.50	0.28914	16.05	16.03
	3.79	0.28924	16.05	
	4.02	0.28906	16.05	
	4.27	0.28872	16.03	
	4.50	0.28828	16.02	
	4.74	0.28715	15.98	

Table 5. (Continued)

Rare Earth	$pH_r$	E in volts	$\log K_{RY}$	Av.
Tm-B	3.49	0.25477	15.97	15.97
	3.78	0.25504	15.98	
	4.01	0.25496	15.97	
	4.28	0.25476	15.97	
	4.51	0.25961	15.96	
	4.76	0.25465	15.96	
Yb-A	3.50	0.29003	16.08	16.12
	3.68	0.29100	16.11	
	3.90	0.29115	16.12	
	4.15	0.29130	16.12	
	4.40	0.29173	16.14	
	4.65	0.29190	16.14	
Yb-B	3.31	0.26207	16.22	16.22
	3.59	0.26245	16.23	
	3.82	0.26297	16.23	
	4.09	0.26230	16.23	
	4.39	0.26220	16.22	
	4.61	0.26225	16.22	
	4.83	0.26204	16.22	
Lu-A	3.76	0.29023	16.09	16.17
	3.98	0.29113	16.12	
	4.22	0.29345	16.20	
	4.48	0.29493	16.25	
	4.68	0.29446	16.23	
	4.91	0.29186	16.14	
Lu-B	3.20	0.26508	16.32	16.33
	3.48	0.26551	16.34	
	3.75	0.26535	16.33	
	3.98	0.26498	16.32	
	4.24	0.26473	16.31	
	4.53	0.26525	16.33	
	4.75	0.26561	16.34	

$$K_8 = \frac{[\text{Hg}^{+2}][\text{RY}^{3-n}]}{[\text{R}^{+3}][\text{Hg}^{2-n}]}, \text{ can be solved for } [\text{Hg}^{+2}]$$

$$\text{to give } [\text{Hg}^{+2}] = [\text{R}^{+3}] K_8 \frac{[\text{Hg}^{2-n}]}{[\text{RY}^{3-n}]} \quad (36)$$

This equation shows a proportionality between  $[\text{Hg}^{+2}]$  and  $[\text{R}^{+3}]$  provided the ratio  $[\text{HgY}^{2-n}]/[\text{RY}^{3-n}]$  remains constant. If a second complexant,  $\text{A}^-$  is added, which is much less stable than Y, some of the free  $\text{R}^{+3}$  is complexed.  $[\text{Hg}^{+2}]$  is then lowered proportionally as long as the ratio of  $[\text{HgY}^{2-n}]/[\text{RY}^{3-n}]$  does not change. The conditions which must hold if the ratio is to remain constant can be stated. First Y must be completely complexed as HgY and RY, i.e.  $[\text{Y}]_{\text{T}} = [\text{HgY}^{2-n}] + [\text{RY}^{3-n}]$ . Second the variation of  $[\text{R}^{+3}]$  and  $[\text{Hg}^{+2}]$  must not lead to any relative change in the concentrations of HgY and RY. For these reasons the stability constants of the chelates involved must be of the order of  $10^5$  times those of  $\text{RA}_n$  and  $\text{HgA}_n$ . The chelating agent HEDTA satisfies these conditions and was used in this work. The material balance equations for this chelate are:

$$[\text{R}]_{\text{T}} = [\text{R}^{+3}] + [\text{RY}]$$

$$[\text{Hg}]_{\text{T}} = [\text{HgY}^-]$$

$$[\text{Y}]_{\text{T}} = [\text{HgY}^-] + [\text{RY}]$$

Now if acetate is added to a solution containing rare earth, mercury(II), and chelating agent, the  $[\text{RY}]$  will not be changed appreciably since the acetate is a weak complexant. The effect noted is simply a reduction in the  $\text{R}^{+3}$  concentration. If  $[\text{RY}]$  is

not changed by addition of acetate then  $[\text{HgY}^-]$  will not be changed either. Equation 36 can be written,  $[\text{Hg}^{+2}] = [\text{R}^{+3}] K'$  where

$$K' = K_8 \frac{[\text{HgY}^-]}{[\text{RY}]} . \quad \text{If the mercuric ion is substituted in the}$$

Nernst equation one gets:  $E = E_o' + s/2 \log [\text{R}^{+3}] K'$  or

$$E = \bar{E} + s/2 \log [\text{R}^{+3}] \quad (37)$$

$$\text{where} \quad \bar{E} = E_o' + s/2 \log K'.$$

Equation 37 shows that the mercury electrode is now a pR electrode.

To determine the acetate formation constants of the rare earths, solutions of the following concentration were used:

$$\text{A. } [\text{RY}] = 10^{-3}$$

$$[\text{HgY}] = 10^{-3}$$

$$[\text{R}^{+3}] = 10^{-3}$$

$$\text{B. } [\text{RY}] = 4 \times 10^{-3}$$

$$[\text{HgY}] = 5 \times 10^{-4}$$

$$[\text{R}^{+3}] = 5 \times 10^{-4} .$$

These solutions were placed in the electrode cell and titrated with acetate buffer. Each solution was first brought to the pH of the buffer and the potential of the mercury electrode was recorded.

The concentration of the rare earth not bound to HEDTA is given by:

$$[\text{R}^{+3}]_A = [\text{R}^{+3}] + [\text{Rac}^{+2}] + [\text{Rac}_2^{+1}] + [\text{Rac}_3^{+1}] . \quad (38)$$

Equation 38 can be expressed in terms of the complexity constants

$$\beta_n \text{ which are defined by: } \beta_n = \frac{[\text{Rac}_n^{3-n}]}{[\text{R}^{+3}] [\text{ac}^-]^n} . \quad (39)$$

When values from 39 are substituted in 38 the equation becomes:

$$[R^{+3}]_A = [R^{+3}] (1 + \beta_1 [ac^-] + \beta_2 [ac^-]^2 + \beta_3 [ac^-]^3). \quad (38a)$$

Dividing through by  $[R^{+3}]$  gives:

$$\frac{[R^{+3}]_A}{[R^{+3}]} = F(ac) = 1 + \beta_1 [ac^-] + \beta_2 [ac^-]^2 + \beta_3 [ac^-]^3 \quad (39)$$

The potential of the mercury electrode before addition of acetate

$$\text{is given by } E_A = \bar{E} + s/2 \log [R^{+3}]_A \quad (40)$$

After addition of acetate the potential is given by  $E =$

$$\bar{E} + s/2 \log [R^{+3}] \quad (41)$$

Subtracting 41 from 40 gives,

$$E_A - E = s/2 \log \frac{[R^{+3}]_A}{[R^{+3}]} = s/2 \log F(ac) \quad (42)$$

The acetate added to solution is expressed by equation 43;

$$[ac]_T = [ac^-] + [Hac] + [Rac^{+2}] + 2[Rac_2^+] + 3[Rac_3] \quad (43)$$

$$\text{or } [ac]_T = [ac^-] \left( 1 + \frac{[H^+]}{K_{Hac}} + [R^{+3}] \beta_1 + 2[R^{+3}] \beta_2 [ac^-] + 3[R^{+3}] \beta_3 [ac^-]^2 \right) \quad (43a)$$

where  $K_{Hac}$  is the ionization constant of acetic acid. This equation was solved for  $[ac^-]$  by approximation. At low acetate concentration only a 1:1 complex would be expected to form. For low concentrations of acetate equations 39 and 43a become  $F(ac) = 1 + \beta_1 [ac^-]$  and  $[ac]_T = [ac^-] (1 + [H^+]/K_{Hac} + [R^{+3}])$ . In the region where these equations are valid a plot of  $F(ac)$  versus  $[ac^-]$  will give a straight line which can be solved for  $\beta_1$ . With  $\beta_1$  known higher terms can be considered and other  $\beta$ 's can be calculated. Figure 4 shows the

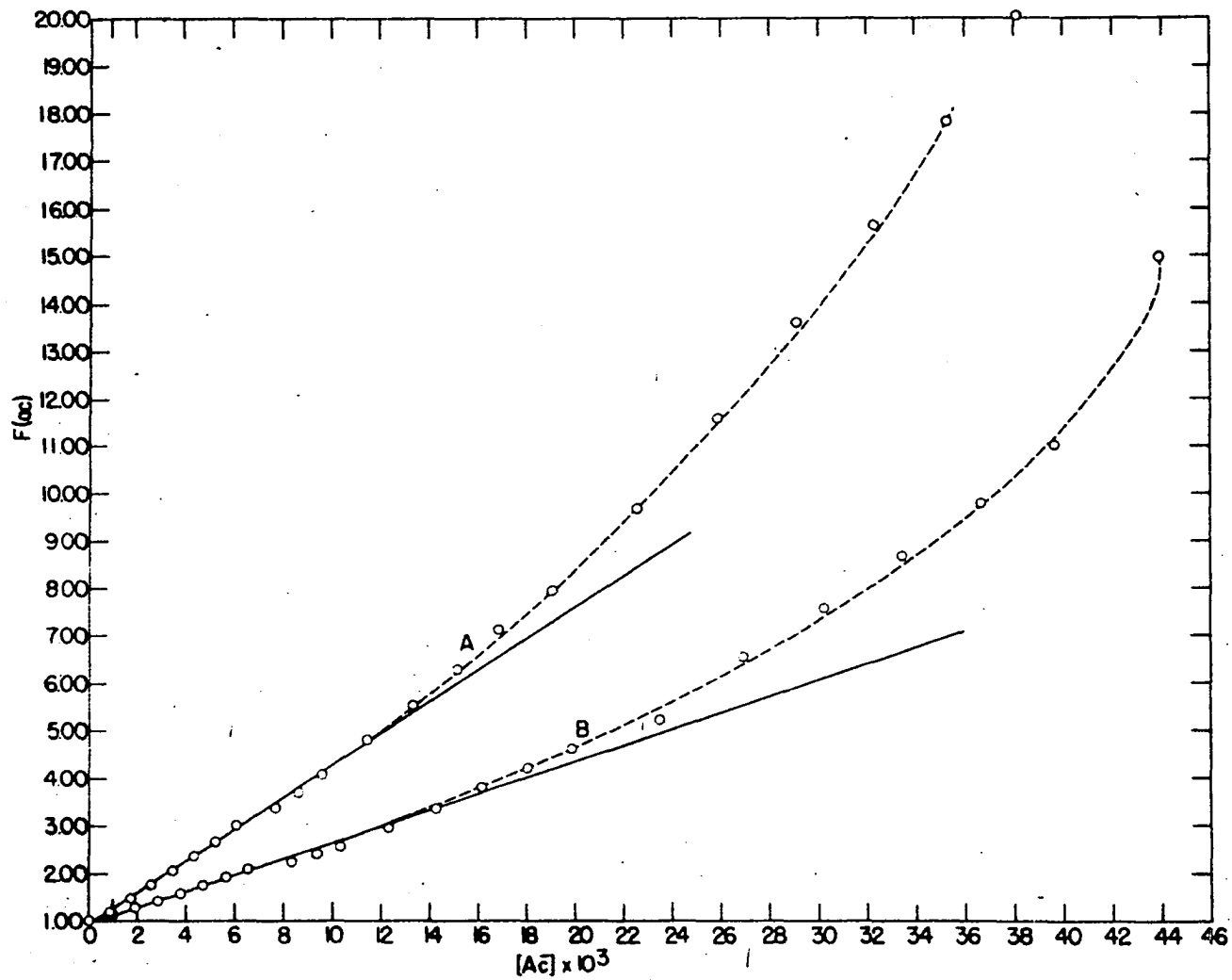
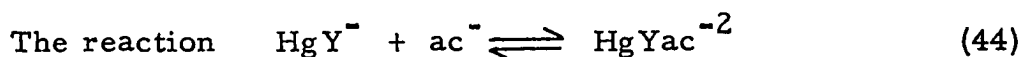


Figure 4. Titration curves for praseodymium with acetate



results of a titration of praseodymium solutions. The curves obtained with different concentrations of rare earth, mercury(II), and HEDTA do not coincide. The difference in the two curves is probably due to the formation of bimetallic chelates. The pM method assumes that all the rare earth not tied up as RY is free rare-earth ions. The formation constants of bimetallic chelates appear to be about the same magnitude as the rare earth-acetate constants. Formation of these species, therefore, competes with the formation of acetate complexes. This is a rather serious fault in the use of the mercury electrode as a pR electrode.

Addition of acetate to mercury(II) chelate



was studied with the mercury electrode. Schwarzenbach et al.

(13) have measured the formation constants of the reaction



where  $\text{A}^-$  was  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{NH}_3$ . Acetate adds to the mercury chelate of HEDTA like these other anions, and the formation constant of 44 was measured,

$$K_{\text{HgYac}}^{\text{ac}} = \frac{[\text{HgYac}^{-2}]}{[\text{HgY}^-][\text{ac}^-]} \quad (46)$$

The equations for this method will be developed below. Equation 28 for the value of  $K_{\text{HgY}}$  can be solved for  $[\text{Hg}^{+2}]$  and substituted into the Nernst equation to give 
$$E = E_0' + s/2 \log \frac{[\text{HgY}^-] \phi}{K_{\text{HgY}} [\text{Y}]_T},$$

and this can be rearranged to give

$$E = E_o' + s/2 \log \frac{\phi}{K_{\text{HgY}}[\text{Y}]_T} + s/2 \log [\text{HgY}^-] \quad (47)$$

As long as the pH is constant this equation shows that the mercury electrode is a  $\text{HgY}^-$  electrode. Solutions of mercury(II) and excess HEDTA were titrated with acetate buffer, and the titration was followed with the mercury electrode. The material balance equations for this system are:

$$[\text{Hg}]_T = [\text{HgY}^-] + [\text{HgYac}^{-2}] \quad \text{and} \quad (48)$$

$$[\text{ac}]_T = [\text{ac}^-] + [\text{Hac}] + [\text{HgYac}^{-2}] \quad (49)$$

Equation 48 can be subtracted from 49 to give

$$[\text{ac}]_T - [\text{Hg}]_T + [\text{HgY}^-] = [\text{ac}^-] \left(1 + \frac{[\text{H}^+]}{K_{\text{Hac}}}\right) \quad (50)$$

where  $K_{\text{Hac}}$  is the ionization constant of acetic acid. This equation can be solved for  $[\text{ac}^-]$ ,

$$[\text{ac}^-] = \frac{[\text{ac}]_T - [\text{Hg}]_T + [\text{HgY}^-]}{\left(1 + \frac{[\text{H}^+]}{K_{\text{Hac}}}\right)} \quad (51)$$

Equation 46 can be solved for  $[\text{HgYac}^{-2}]$  and this value can be substituted in 48 to give

$$[\text{Hg}]_T = [\text{HgY}^-] \left(1 + K_{\text{HgYac}}^{\text{ac}} [\text{ac}^-]\right) \quad (52)$$

Dividing through by  $[\text{HgY}^-]$  gives

$$\frac{[\text{Hg}]_T}{[\text{HgY}^-]} = 1 + K_{\text{HgYac}}^{\text{ac}} [\text{ac}^-] \quad (53)$$

The potential of the solution before any acetate is added is given

$$\text{by } E_i = E_o' + s/2 \log \frac{\phi}{K_{\text{HgY}}[\text{Y}]_T} + s/2 \log [\text{HgY}^-] . \quad (54)$$

After the addition of acetate the potential is:

$$E = E_o' + s/2 \log \frac{\phi}{K_{\text{HgY}}[\text{Y}]_T} + s/2 \log [\text{HgY}^-] . \quad (55)$$

$$\text{Subtracting 55 from 54 gives } \frac{E_i - E}{s/2} = \log \frac{[\text{HgY}^-]_o}{[\text{HgY}^-]} . \quad (56)$$

Before acetate is added  $[\text{HgY}]_o = [\text{Hg}]_T$  so

$$\frac{E_i - E}{s/2} = \log \frac{[\text{Hg}]_T}{[\text{HgY}^-]} = 1 + K_{\text{HgYac}}^{\text{ac}} [\text{ac}^-] . \quad (57)$$

The value of  $K_{\text{HgYac}}^{\text{ac}}$  was found from a plot of  $\log \frac{[\text{HgY}]_o}{[\text{HgY}]}$ ,

determined from 57, versus  $[\text{ac}^-]$  found from 51. This plot should give a straight line whose slope is  $K_{\text{HgYac}}^{\text{ac}}$ . Figure 5 shows the results for two different determinations. The value of  $K_{\text{HgYac}}^{\text{ac}}$  calculated from the slopes in Figure 5 is  $16.6 \pm 1.6$ . This equilibrium would effect the mercury electrode when used as a pM electrode. The result shows that the coordination number of mercury(II) is not completely satisfied by HEDTA.

#### Rare-Earth DE and ME Stability Constants

Schwarzenbach and Anderegg (13) have determined the mercury chelate stability constants and acid dissociation constants,  $K_{\text{HHgY}}^{\text{H}}$ , for DE and ME. Their values will be used for the determination

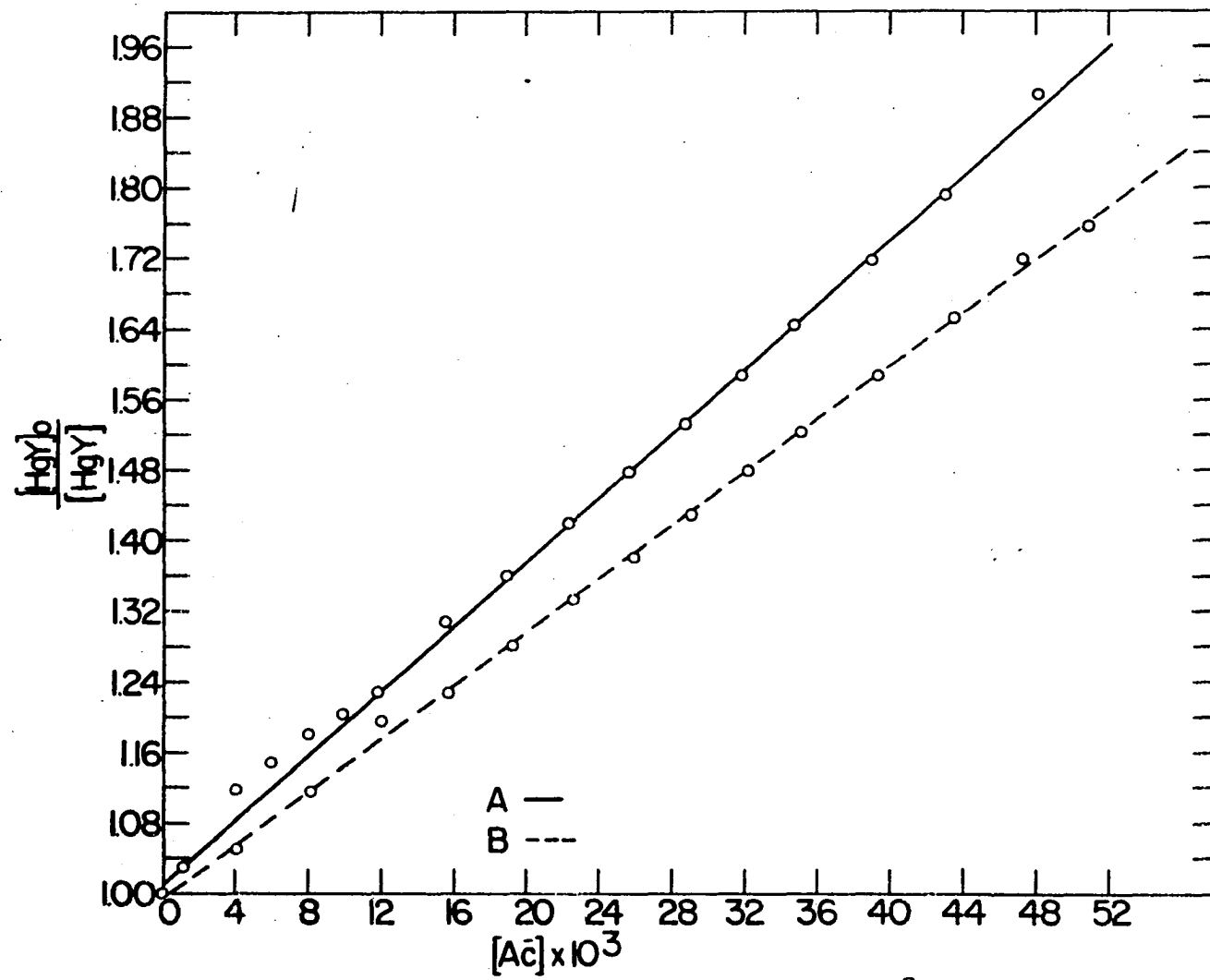


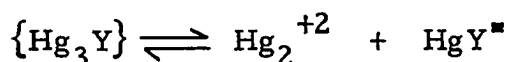
Figure 5. Titration curves for the formation of  $[\text{HgYac}^{-2}]$

of the rare-earth chelate stability constants. The values of these constants are listed in Table 6.

Table 6. Formation constants determined by Schwarzenbach and Anderegg at 20°C and ionic strength = 0.10 (NaNO<sub>3</sub>)

	DE	ME
$\log K_{\text{HgY}}$	23.20	23.09
$\log K_{\text{HHgY}}^{\text{H}}$	3.0	2.5

It was mentioned in the section on the derivation of equations that the insoluble compounds  $\{\text{Hg}_2\text{Y}\}$  and  $\{\text{Hg}_3\text{Y}\}$  were formed for EDTA. The concentrations of  $[\text{HgY}^{\text{m}}]$  and mercury(I) and (II) had to be maintained low enough so that the solubility products of these compounds were not exceeded. Since ME and DE are similar to EDTA, a check was made to see if insoluble mercury compounds would form for these chelating agents. The solubility product of  $\{\text{Hg}_3\text{Y}\}$  can be estimated from measurements with the mercury electrode. The solubility product of  $\{\text{Hg}_3\text{Y}\}$  can be written:



$$\text{and } K_{\text{s.p.}} = [\text{HgY}^{\text{m}}] [\text{Hg}_2^{+2}] \quad (58)$$

$[\text{Hg}_2^{+2}]$  can be found in terms of  $[\text{Hg}^{+2}]$  from the equilibrium

$$\text{constant } \frac{[\text{Hg}_2^{+2}]}{[\text{Hg}^{+2}]} = 88 .$$

Thus  $[\text{Hg}_2^{+2}] = 88[\text{Hg}^{+2}]$ , and this quantity can be substituted back into the solubility product expression to give

$$K_{s.p.} = [\text{HgY}^-] 88[\text{Hg}^{+2}] \quad (58a)$$

Equation 58a can be solved for  $[\text{Hg}^{+2}]$  and this value substituted into the Nernst equation to give

$$E = E_o' + s/2 \log \frac{K_{s.p.}}{88[\text{HgY}^-]} \quad (59)$$

A solution  $2 \times 10^{-3}$  molar in  $[\text{HgY}^-]$  was prepared and half the equivalent amount of  $\text{Hg}_2^{+2}$  was added. Since  $\{\text{Hg}_3\text{Y}\}$  is very insoluble it will precipitate almost quantitatively leaving  $[\text{HgY}^-] = 1 \times 10^{-3}$ . Equation 59 becomes  $E = E_o' + s/2 \log \frac{K_{s.p.}}{88 \times 10^{-3}}$ ,

and the solubility product of  $\{\text{Hg}_3\text{Y}\}$  can be calculated from the potential of the mercury electrode. ME was found to have a  $K_{s.p.} \approx 10^{-7}$ . It is, therefore, more soluble than the corresponding EDTA compound. DE appears to be still more soluble. It should be noted that equation 59 shows that in the presence of  $\{\text{Hg}_3\text{Y}\}$  the mercury electrode is a  $[\text{HgY}^-]$  electrode. This suggests a good way of determining formation constants of bimetallic chelates.

The same procedure as used for HEDTA was used to measure the rare-earth ME and DE stability constants. The solutions were prepared so that the solubility product of  $\{\text{Hg}_3\text{Y}\}$  was not exceeded. The values of  $K_{\text{HR}_2\text{Y}}$ ,  $K_{\text{RHgY}}^{\text{R}}$ , and  $K_{\text{R}_2\text{Y}}^{\text{R}}$  are, again, not known and as in the case of HEDTA their effect was assumed to be negligible in material balance equations.  $K_{\text{HgY}}^{\text{H}}$  was known and

was used to determine the quantities in the material balance equations. The results for the determination of the rare-earth stability constants are shown in Tables 8 and 9. These results show more variation than the HEDTA constants did, and it appears that the assumptions are not quite as good in these cases. This might be expected since the higher charge and increased coordinating potential would enhance the formation of protonated and bimetallic chelates. The concentration of the solutions used are given in Table 7.

Table 7. Concentrations of solutions used to determine stability constants

	$[R]_T$	$[Hg]_T$	$[Y]_T$
A-DE	$2.200 \times 10^{-3}$	$9.917 \times 10^{-4}$	$2.326 \times 10^{-3}$
B-DE	$4.400 \times 10^{-3}$	$4.959 \times 10^{-4}$	$4.611 \times 10^{-3}$
A-ME	$2.200 \times 10^{-3}$	$9.935 \times 10^{-4}$	$2.302 \times 10^{-3}$
B-ME	$4.495 \times 10^{-3}$	$4.968 \times 10^{-4}$	$4.603 \times 10^{-3}$

Table 8. Determination of the rare-earth DE stability constants at  $20.00 \pm 0.02^\circ\text{C}$  and ionic strength = 0.10 ( $\text{KNO}_3$ )

Rare Earth	$\text{pH}_r$	E in volts	$\log K_{RY}$	Av.
La-A	3.99	0.18164	15.42	15.41
	4.32	0.18204	15.41	
	4.56	0.18217	15.40	

Table 8. (Continued)

Rare Earth	$pH_r$	E in volts	$\log K_{RY}$	Av.
	4.79	0.18206	15.39	
La-B	3.99	0.15545	15.86	
	4.22	0.15625	15.87	15.84
	4.22	0.15620	15.85	
	4.64	0.15555	15.83	
	4.89	0.15518	15.80	
Ce-A	3.82	0.19020	15.74	
	4.02	0.19065	15.72	15.71
	4.28	0.19076	15.70	
	4.50	0.19076	15.69	
	4.73	0.19081	15.71	
Ce-B	3.87	0.15585	15.88	
	4.03	0.15530	15.85	15.84
	4.22	0.15394	15.79	
Pr-A	3.87	0.20018	16.07	
	4.20	0.20061	16.04	16.07
	4.42	0.20148	16.06	
	4.67	0.20206	16.08	
	4.80	0.20213	16.08	
Pr-B	3.81	0.16637	16.26	
	4.02	0.16573	16.20	16.18
	4.24	0.16518	16.18	
	4.49	0.16485	16.14	
	4.72	0.16450	16.13	
Nd-A	3.81	0.20697	16.31	
	4.07	0.20727	16.29	16.29
	4.31	0.20752	16.28	
	4.58	0.20767	16.28	
	4.82	0.20808	16.28	
Nd-B	3.91	0.17261	16.46	
	4.14	0.17197	16.41	16.42
	4.48	0.17154	16.37	
	4.77	0.17314	16.42	



Table 8. (Continued)

Rare Earth	pH <sub>r</sub>	E in volts	log K <sub>RY</sub>	Av.
Sm-A	3.78	0.22148	16.81	16.82
	4.01	0.22211	16.80	
	4.23	0.22260	16.81	
	4.51	0.22345	16.82	
	4.72	0.22452	16.85	
Sm-B	3.88	0.19177	17.12	17.09
	4.09	0.19198	17.11	
	4.32	0.19206	17.09	
	4.57	0.19210	17.08	
	4.81	0.19205	17.07	
Eu-A	3.81	0.22931	17.08	17.08
	4.01	0.22977	17.07	
	4.28	0.23024	17.06	
	4.49	0.23088	17.07	
	4.77	0.23198	17.10	
Eu-B	3.88	0.19715	17.29	17.27
	4.09	0.19720	17.29	
	4.31	0.19720	17.27	
	4.56	0.19723	17.26	
	4.78	0.19730	17.25	
Gd-A	3.80	0.22404	16.90	16.95
	4.32	0.22571	16.91	
	4.61	0.22774	16.97	
	4.84	0.22991	17.03	
Gd-B	3.87	0.19134	17.12	17.09
	4.08	0.19160	17.09	
	4.35	0.19179	17.08	
	4.57	0.19200	17.08	
	4.79	0.19190	17.06	
Tb-A	3.29	0.23435	17.39	17.32
	3.51	0.23504	17.35	
	3.77	0.23560	17.31	
	4.01	0.23624	17.29	
	4.23	0.23681	17.30	
	4.47	0.23779	17.31	

Table 8. (Continued)

Rare Earth	$pH_r$	E in volts	$\log K_{RY}$	Av.
Tb-B	3.85	0.19896	17.49	17.38
	3.65	0.19888	17.38	
	3.88	0.19908	17.37	
	4.12	0.19935	17.35	
	4.38	0.19947	17.34	
	4.62	0.19958	17.34	
Dy-A	3.79	0.24265	17.54	17.53
	4.07	0.24314	17.53	
	4.32	0.24355	17.52	
	4.60	0.24410	17.53	
	4.88	0.24460	17.55	
Dy-B	3.91	0.20314	17.52	17.48
	4.18	0.20320	17.46	
	4.41	0.20328	17.48	
	4.67	0.20328	17.47	
Ho-A	3.80	0.24138	17.50	17.49
	4.02	0.24185	17.48	
	4.31	0.24241	17.48	
	4.58	0.24326	17.50	
	4.82	0.24376	17.51	
Ho-B	3.87	0.20234	17.48	17.44
	4.07	0.20229	17.46	
	4.30	0.20216	17.44	
	4.59	0.20171	17.41	
	4.78	0.20170	17.40	
Er-A	3.83	0.24069	17.47	17.50
	4.10	0.24140	17.46	
	4.38	0.24239	17.48	
	4.64	0.24390	17.52	
	4.89	0.24518	17.56	
Er-B	3.88	0.20260	17.49	17.47
	4.08	0.20276	17.48	
	4.33	0.20296	17.46	
	4.58	0.20295	17.45	
	4.79	0.20314	17.46	

Table 8. (Continued)

Rare Earth	pH <sub>r</sub>	E in volts	log K <sub>RY</sub>	Av.
Tm-A	3.88	0.23700	17.34	17.38
	4.14	0.23760	17.33	
	4.40	0.23946	17.37	
	4.69	0.24215	17.46	
Tm-B	3.89	0.21054	17.76	17.74
	4.12	0.21065	17.74	
	4.35	0.21080	17.85	
	4.68	0.21045	17.71	
Yb-A	3.81	0.25169	17.85	17.87
	4.08	0.25245	17.85	
	4.38	0.25336	17.86	
	4.68	0.25528	17.91	
Yb-B	3.69	0.21349	17.90	17.84
	3.96	0.21377	17.87	
	4.19	0.21385	17.85	
	4.49	0.21327	17.81	
Lu-A	3.88	0.25402	17.92	17.97
	4.10	0.25539	17.94	
	4.38	0.25739	18.00	
	4.68	0.25860	18.03	
Lu-B	3.88	0.21276	17.84	17.81
	4.09	0.21311	17.83	
	4.37	0.21311	17.77	
	4.66	0.21328	17.81	
Y-A	3.82	0.22339	16.88	16.86
	4.09	0.22382	16.86	
	4.39	0.22420	16.85	
	4.63	0.22434	16.85	
Y-B	3.90	0.18861	17.01	16.94
	4.18	0.18854	16.96	
	4.40	0.18839	16.89	
	4.89	0.18769	16.92	

Table 9. Determination of the rare-earth ME stability constants at  $20.00 \pm 0.02^\circ\text{C}$  and ionic strength = 0.10 ( $\text{KNO}_3$ )

Rare Earth	$\text{pH}_r$	E in volts	$\log K_{RY}$	Av.
La-A	4.02	0.20606	16.07	16.05
	4.28	0.20500	16.04	
	4.48	0.20410	16.00	
	4.93	0.20670	16.09	
La-B	3.92	0.18190	16.42	16.37
	4.14	0.18194	16.40	
	4.58	0.18215	16.41	
	4.98	0.17782	16.26	
Ce-A	4.00	0.23146	16.94	16.98
	4.28	0.23155	16.95	
	4.60	0.23288	16.99	
	4.95	0.23462	17.05	
Ce-B	4.09	0.19436	16.83	16.82
	4.28	0.19320	16.79	
	4.59	0.19365	16.80	
	4.88	0.19581	16.88	
Pr-A	4.01	0.24766	17.50	17.55
	4.31	0.24815	17.52	
	4.58	0.24950	17.56	
	4.88	0.25105	17.62	
Pr-B	3.98	0.21530	17.55	17.56
	4.27	0.21445	17.52	
	4.69	0.21685	17.60	
Nd-A	3.98	0.25462	17.74	17.81
	4.22	0.25546	17.75	
	4.51	0.25746	17.84	
	4.87	0.25920	17.90	
Nd-B	4.01	0.22650	17.93	17.94
	4.31	0.22625	17.93	
	4.63	0.22650	17.93	
	4.91	0.22685	17.95	
Sm-A	4.00	0.27300	18.37	18.43
	4.25	0.27344	18.39	

Table 9. (Continued)

Rare Earth	$pH_r$	E in volts	$\log K_{RY}$	Av.
	4.42	0.27494	18.44	
	4.70	0.27600	18.48	
	4.89	0.27538	18.45	
Sm-B	3.98	0.2390	18.36	
	4.28	0.23865	18.35	18.37
	4.52	0.23925	18.37	
	4.83	0.24044	18.41	
Eu-A	4.32	0.27438	18.42	
	4.55	0.27650	18.49	18.48
	4.69	0.27670	18.50	
	4.82	0.27706	18.51	
Eu-B	3.96	0.24468	18.56	
	4.25	0.24420	18.54	18.56
	4.40	0.24428	18.55	
	4.70	0.24510	18.58	
Gd-A	4.10	0.27090	18.30	
	4.42	0.27350	18.39	18.38
	4.63	0.27465	18.43	
	4.81	0.27450	18.42	
Gd-B	4.00	0.23730	18.31	
	4.32	0.23675	18.29	18.31
	4.61	0.23778	18.32	
Tb-A	3.98	0.23755	18.39	
	4.22	0.27570	18.47	18.49
	4.52	0.27800	18.54	
	4.82	0.27810	18.55	
Tb-B	3.99	0.24450	18.55	
	4.28	0.24428	18.55	18.56
	4.54	0.24494	18.57	
	4.82	0.24536	18.58	
Dy-A	3.99	0.26855	18.22	
	4.28	0.27100	18.30	18.34
	4.49	0.27345	18.39	
	4.67	0.27496	18.44	

Table 9. (Continued)

Rare Earth	$pH_r$	E in volts	$\log K_{RY}$	Av.
Dy-B	4.01	0.24370	18.53	18.51
	4.29	0.24262	18.49	
	4.52	0.24264	18.49	
	4.83	0.24325	18.51	
Ho-A	3.98	0.26750	18.18	18.33
	4.26	0.27045	18.29	
	4.52	0.27313	18.38	
	4.73	0.27411	18.41	
	4.88	0.27376	18.40	
Ho-B	3.98	0.23925	18.37	18.36
	4.28	0.23854	18.35	
	4.52	0.23853	18.35	
	4.83	0.23915	18.37	
Er-A	3.97	0.26360	18.05	18.18
	4.12	0.26500	18.10	
	4.34	0.26758	18.19	
	4.60	0.27004	18.27	
	4.82	0.27050	18.29	
Er-B	3.98	0.23450	18.21	18.21
	4.22	0.23372	18.18	
	4.49	0.23410	18.20	
	4.80	0.23530	18.24	
Tm-A	4.00	0.26000	17.93	18.01
	4.22	0.26157	17.98	
	4.48	0.26400	18.00	
	4.69	0.26565	18.12	
Tm-B	3.99	0.23115	18.09	18.07
	4.20	0.23005	18.07	
	4.49	0.23005	18.06	
Yb-A	4.02	0.25955	17.91	17.98
	4.22	0.26046	17.94	
	4.50	0.26232	18.01	
	4.77	0.26361	18.05	

Table 9. (Continued)

Rare Earth	$pH_r$	E in volts	$\log K_{RY}$	Av.
Yb-B	3.88	0.23240	18.14	18.13
	4.14	0.23195	18.12	
	4.41	0.23196	18.12	
	4.78	0.23278	18.15	
Lu-A	3.93	0.25415	17.72	17.79
	4.22	0.25505	17.76	
	4.58	0.25706	17.82	
	4.82	0.25810	17.86	
Lu-B	3.88	0.23240	18.14	18.13
	4.14	0.23195	18.12	
	4.41	0.23196	18.12	
	4.78	0.23278	18.15	
Y-A	3.98	0.25185	17.65	17.71
	4.24	0.25250	17.67	
	4.58	0.25455	17.74	
	4.82	0.25585	17.78	
Y-B	4.08	0.21615	17.58	17.58
	4.28	0.21570	17.56	
	4.52	0.21675	17.60	

## DISCUSSION AND CONCLUSIONS

Rare-earth chelate stability constants

Table 10 shows the stability constants of HEDTA determined by the mercury electrode method and Wheelwright's values determined by the modified pH and polarographic methods (9). Wheelwright's values were determined at 25°C while the others were measured at 20°C. This probably accounts for some of the difference in the two sets of constants. The modified pH method requires the values of  $\bar{K}_{H_3tren}$ ,  $K_{CuY}$ , and  $K_{Cutren}$  in the calculation of the rare-earth constants. Because of the accumulative error in these constants, Wheelwright considered the HEDTA stability constants to be uncertain to the extent of about  $\pm 0.2$  units in absolute value. However, he considered the relative values of the constants to be good to  $\pm 0.06$ . The errors shown in Table 10 for the constants determined with the mercury electrode are the maximum deviations from the mean. The absolute values of the rare-earth constants depend on the mercury chelate constant. This constant showed a maximum deviation from the mean of  $\pm 0.20$  so the rare-earth constants would have a possible error in absolute magnitude of this amount. The difference between the two sets of values in Table 10 is a nearly constant amount (0.45). If this value is added to Wheelwright's constants the two sets coincide well within the limits of experimental error of both methods. The two methods, therefore, appear to be in excellent agreement except for the constant difference. The accuracy of the two methods is comparable,



Table 10. Stability constants of the rare-earth HEDTA chelates

Rare Earth	$\log K_{RY}$ pHg	$\log K_{RY}$ pH(9)	$\log K_{RY}$ polarograph(9)
La	13.82 $\pm$ 0.02	13.22	
Ce	14.45 $\pm$ 0.04	14.08	
Pr	14.96 $\pm$ 0.05	14.39	
Nd	15.16 $\pm$ 0.04	14.71	
Sm	15.64 $\pm$ 0.06	15.15	15.3
Eu	15.62 $\pm$ 0.03	15.21	
Gd	15.44 $\pm$ 0.02	15.10	15.4
Tb	15.55 $\pm$ 0.03	15.10	
Dy	15.51 $\pm$ 0.04	15.08	15.3
Ho	15.55 $\pm$ 0.03	15.06	15.4
Er	15.61 $\pm$ 0.03	15.17	15.4
Tm	16.00 $\pm$ 0.04	15.38	15.5
Yb	16.17 $\pm$ 0.05	15.64	15.8
Lu	16.25 $\pm$ 0.10	15.79	16.0
Y	15.03 $\pm$ 0.01	14.49	14.8

however, the mercury electrode has the advantage of eliminating the need for a second chelating agent. The polarographically determined constants in Table 10 are not as accurate as the other two methods. Wheelwright reports a relative error of from  $\pm 0.2$  to  $\pm 0.4$  units in these constants.

The results for ME and DE are shown in Table 11. The polarographic values determined by Hiller (22) are listed for comparison. The errors shown for the constants in the first and third columns in Table 11 are the maximum variations from the means. The absolute error of each constant depends on the values of  $K_{HgY}$  determined by Schwarzenbach. No estimation of the error was reported for these constants, however, it would probably be similar

Table 11. Stability constants of the rare-earth DE and ME chelates at 20°C and ionic strength = 0.1

Rare Earth	pHg $K_{RY}$	DE polar. $K_{RY}$	pHg $K_{RY}$	ME polar. $K_{RY}$
La	15.63+0.2	15.87	16.21+0.20	15.92
Ce	15.78+0.1	16.09	16.90+0.10	16.76
Pr	16.13+0.08	16.20	17.57+0.06	17.24
Nd	16.36+0.10	16.62	17.88+0.10	17.44
Sm	16.96+0.16	17.28	18.40+0.08	17.88
Eu	17.18+0.10	17.80	18.52+0.10	18.04
Gd	17.02+0.10	17.53	18.34+0.08	17.84
Tb	17.35+0.10	17.83	18.52+0.10	17.94
Dy	17.50+0.04	17.87	18.42+0.20	17.92
Ho	17.46+0.05	17.93	18.34+0.10	17.80
Er	17.48+0.05	18.03	18.20+0.15	17.81
Tm	17.56+0.20	17.99	18.04+0.11	17.64
Yb	17.86+0.05	18.25	18.06+0.20	17.69
Lu	17.89+0.10	19.51	17.96+0.23	17.55
Y	16.90+0.05	17.19	17.65+0.10	17.42

to that reported for the mercury(II)-HEDTA constant. The greater variation in the constants is probably due to the influence of bi-metallic and protonated chelates. Hiller measured the rare-earth ME and DE constants using both cadmium and europium as standards in the polarographic method. The europium constant was not known so he did not find the absolute values of the rare-earth constants against this standard. The value he used for cadmium was taken from Schwarzenbach *et al.* (13) and was determined with the mercury electrode. The polarographic values should, therefore, provide a direct comparison with the values determined by the mercury electrode method. The results of the two methods are plotted in

Figures 6 and 7. In the case of DE the polarographic values are higher while for ME the mercury-electrode values are higher. The relative error in the polarographic constants was from 0.08 to 0.17.

There are several possible reasons for the difference in the absolute values of these constants. Although both sets of constants were based on the same mercury stability constants, the polarographic values include the additional step of measuring the cadmium constants of ME and DE. Any error in this constant would affect the absolute value of the rare-earth constants. Hiller assumed that the effect of protonated and bimetallic chelates would be negligible. Using Schwarzenbach's value of  $K_{\text{HCdY}}$  for ME shows, however, that this would increase the rare-earth constants by 0.02 units. The two curves in Figures 6 and 7 could be nearly superimposed by a shift in the absolute magnitude of one set of values. The deviation is greatest at the middle of the series. Some of the deviation is probably due to the formation of metal-acetate complexes since the solutions for polarographic measurements were buffered with acetate. Sonesson (46, 47) has shown recently that acetate forms weak complexes with the rare earths, and Hiller has shown how the equations for the polarographic method could be modified for acetate complexing.

Sonesson's values for the rare-earth acetate formation constants, however, were determined at an ionic strength of 2 m, and consequently could not be used to give accurate corrections at an ionic

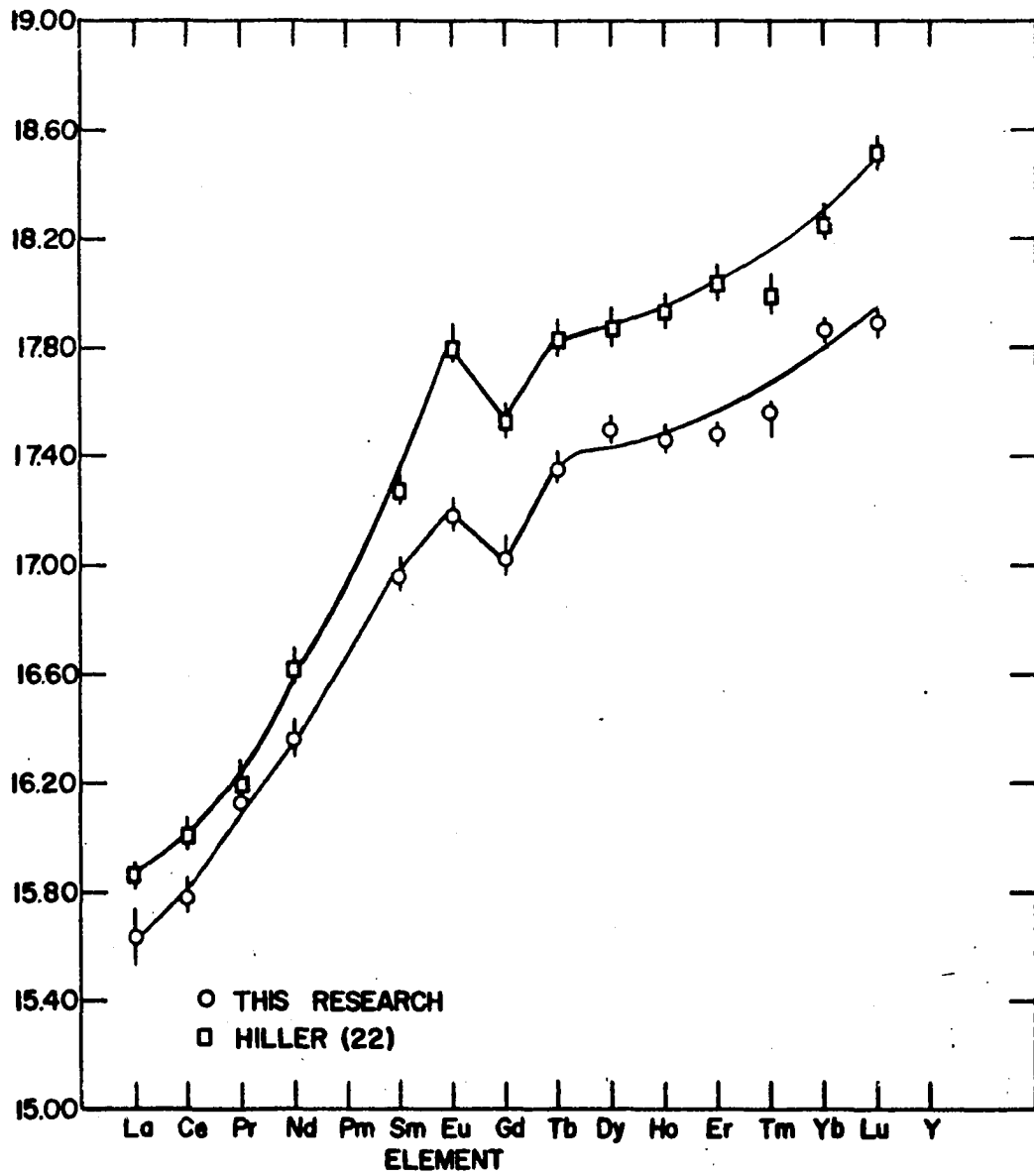


Figure 6. A comparison of the polarographic and mercury electrode methods for DE

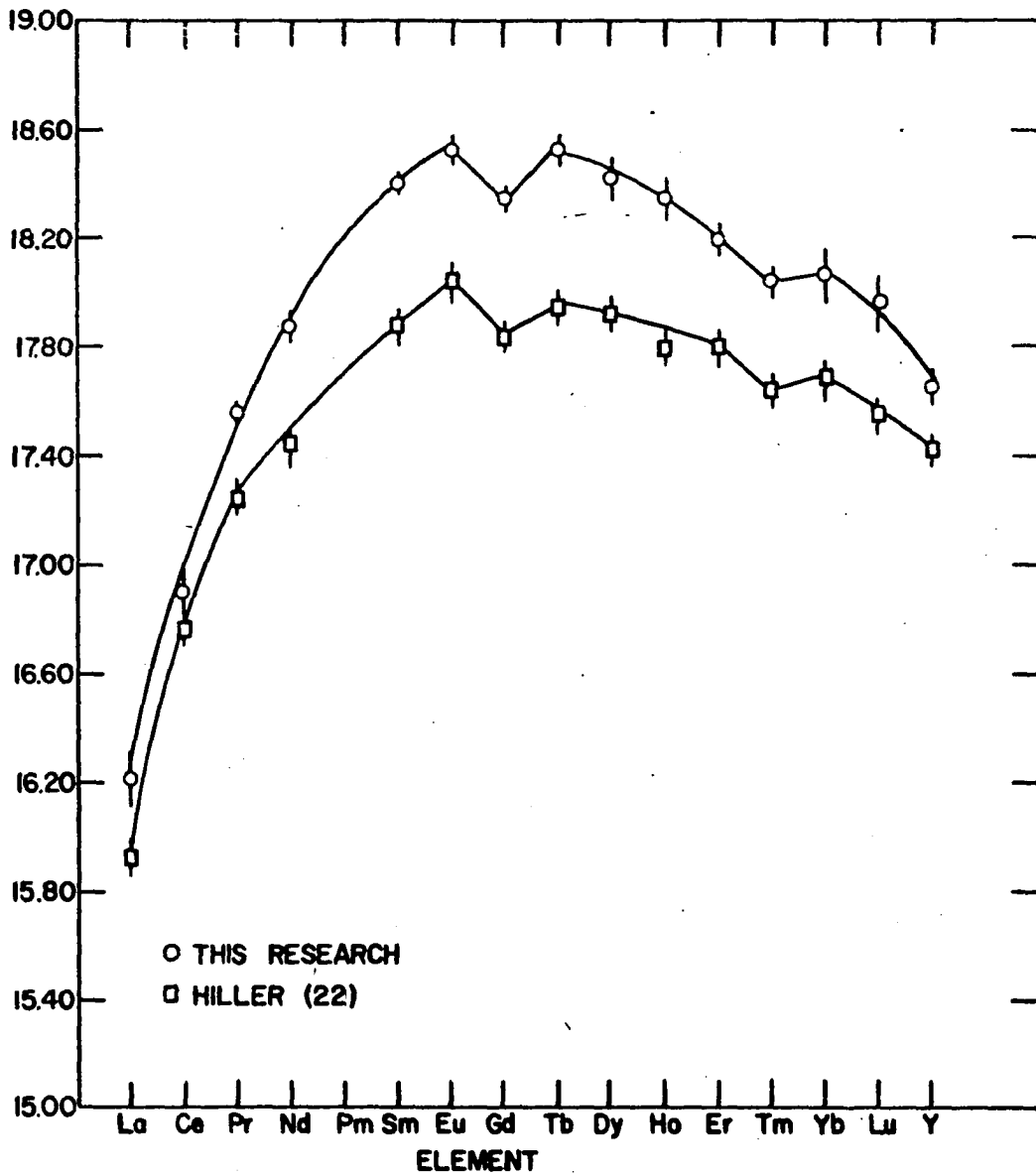


Figure 7. A comparison of the polarographic and mercury electrode methods for ME

strength of 0.1 m. Nevertheless, approximations using Sonesson's data show that acetate complexing of the metal-ions could change the constants as much as 0.2 units. The polarographic method seems to be comparable to the mercury electrode method in accuracy provided an acetate correction is applied.

The ion-exchange separation factor for a pair of rare earths was shown by Spedding and Powell (58) to be equal to the ratio of the stability constants of the individual rare-earth chelates. Powell (59) has evaluated ME and DE as eluants on the basis of Hiller's values. ME was interesting since there is a reversal in the stability-constant curve near the middle of the series. This caused a corresponding reversal in the order of elution. Powell reported that the elution order was: (Dy, Tb), (Ho, Gd), (Sm, Er), Tm, Yb, Lu, Y, Nd, Pr, Ce, and La. This was very close to the order predicted from the stability constants.

#### Trends in stability of the rare-earth aminopolyacetate chelates

Figures 8, 9, and 10 show plots of the stability constants of various aminopolyacetate chelates versus the reciprocal radius of the metal ion. The groupings have been made in pairs to show the similarity in behavior of these chelates. The stability sequences for DCTA and EDTA are very much alike. This is in accord with the structural similarities of these chelating agents.

Both DE and HEDTA constants increase regularly until the middle of the series where they remain fairly constant. The values rise again at the end of the series. The DE constants are higher

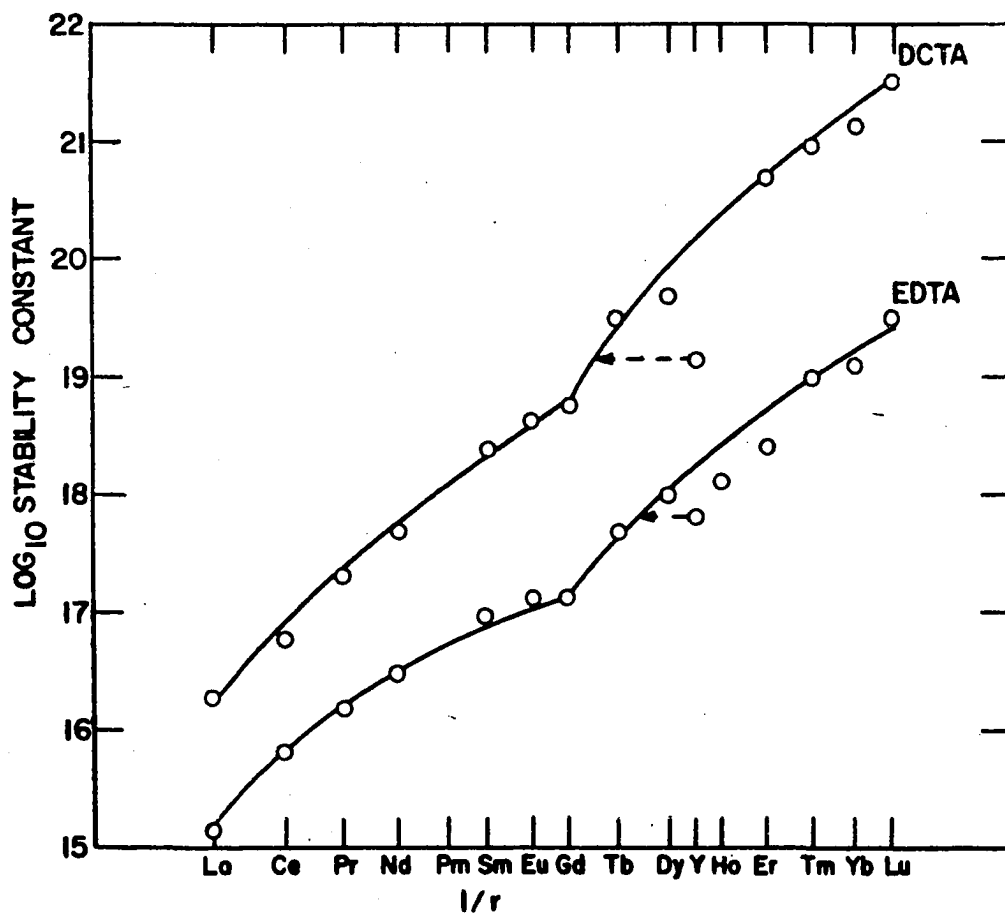


Figure 8. A plot of the stability constants of the rare earths with EDTA and DCTA versus the reciprocal radius; radius values from Templeton, D. H. and Douben, C. H., J. Am. Chem. Soc., 76, 5237 (1954)

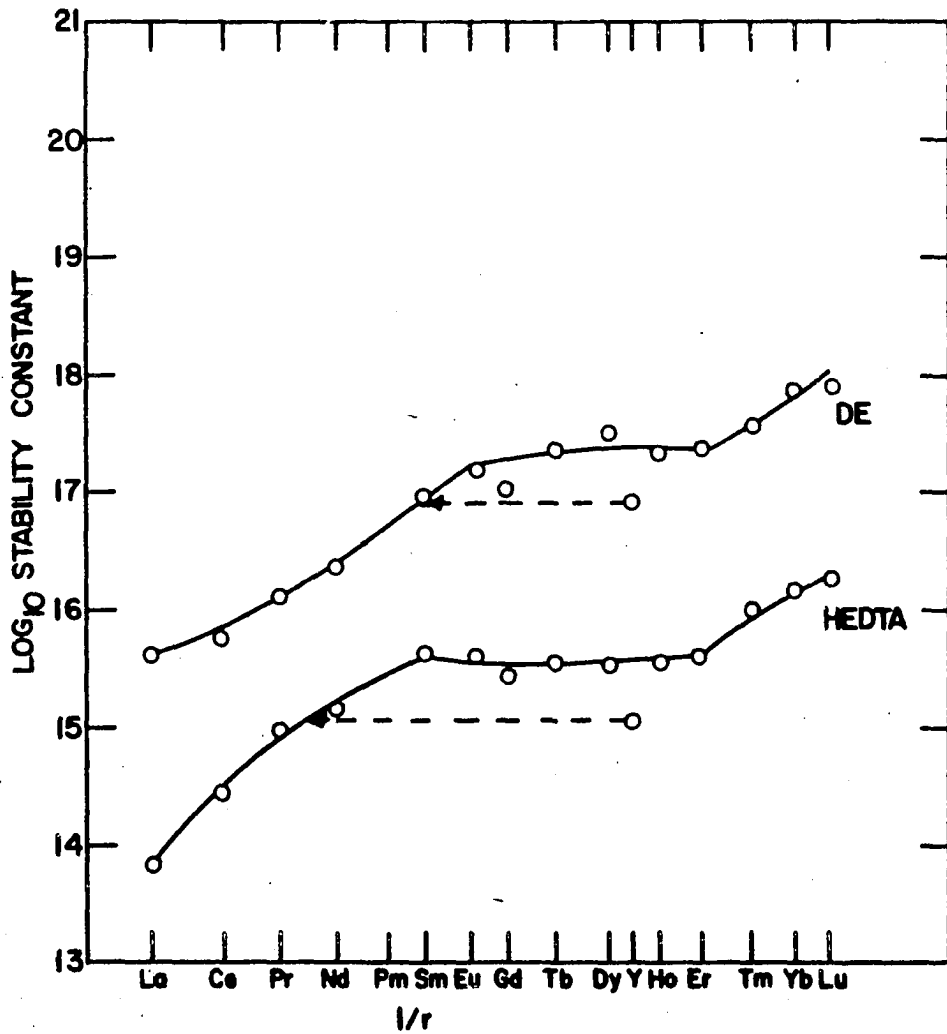


Figure 9. A plot of the stability constants of the rare earths with DE and HEDTA versus the reciprocal radius



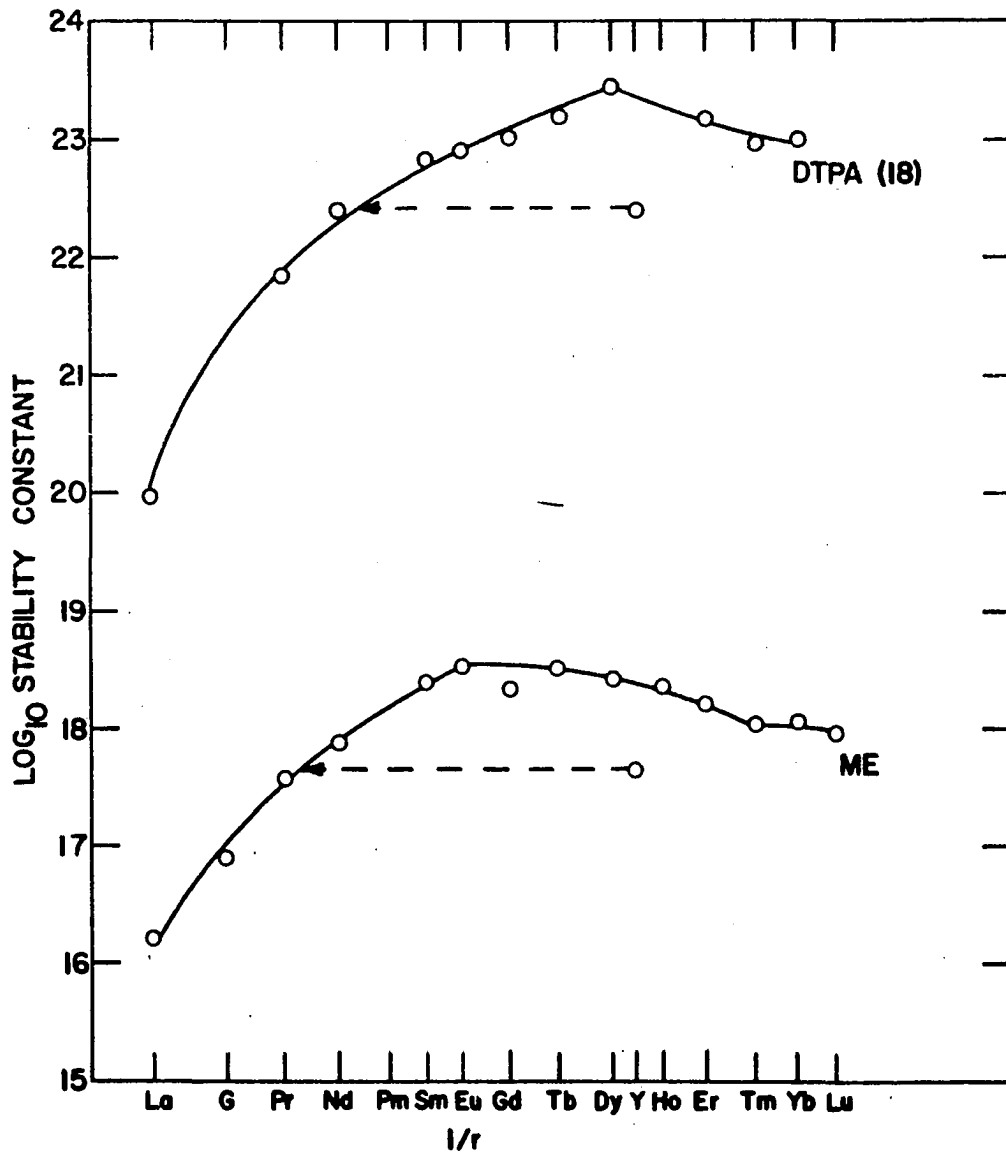


Figure 10. A plot of the stability constants of the rare earths with DTPA and ME versus the reciprocal radius

than the HEDTA constants due probably to the presence of more coordinating groups in the DE molecule.

Both DTPA and ME show a reversal in chelate stability. For DTPA this occurs at dysprosium, while for ME it occurs in the vicinity of europium. The high stability of the DTPA chelates is again no doubt due to the presence of a large number of coordinating groups in this molecule. For almost all the chelates there is a noticeable irregularity at gadolinium.

A recent paper by Duncan (60) provides information which can be applied to the correlation of rare-earth stability constants. Duncan discussed the formation of complexes in terms of simple electrostatic forces. By evaluating the energy terms from a thermodynamic cycle, he showed that the enthalpy change in complex formation is dependent on a number of functions of the ionic radius, which plotted as a function of the reciprocal radius of the metal-ion radius, are linear for the restricted range of ionic radii found in nature. If the entropy change is negligible compared to  $\Delta H$  or is linear with  $\Delta H$ , then the free energy will be a linear function of the reciprocal radius of the metal ion. The Figures 8, 9 and 10 show that only DCTA and EDTA approach any sort of linear variation with  $1/r$ . Results were cited earlier which showed that the entropy terms are large for chelation of metals with EDTA. The large entropy terms in  $\Delta F$  probably cause the variation and non-linear behavior for the chelates in Figures 9 and 10.

It is interesting to note that yttrium falls below the position in the stability constant curves where it might be expected from a consideration of its radius. Several people (43, 45) have suggested that correlations of stability constants of the rare earths should consider the ligand field stabilization on the 4f electrons. Such a consideration can explain the gadolinium break and the low values for yttrium. Yttrium has no 4f electrons and gadolinium with a half-filled shell would not be stabilized by the ligand field. More data is needed on the rare-earth complexes and chelates before a precise correlation can be made. Calorimetric data for the rare-earth chelates would provide some very interesting information regarding the nature of chelation and the trends in the stability constant curves.

## SUMMARY

The stability constants of the complexes formed between the rare earths and N'-(hydroxyethyl) ethylenediamine-N, N, N'-triacetic acid, 1, 2-bis-[2-di(carboxymethyl)-aminoethoxy] ethane, and 2, 2'-bis-[di(carboxymethyl)-amino] diethyl ether were measured with the mercury electrode. This method was shown to yield results which were as accurate as other methods used to determine very stable chelates.

The stability constant of the mercury(II) chelate with N'-(hydroxyethyl) ethylenediamine-N, N, N'-triacetic acid was measured with the mercury electrode, and several protonated and bimetallic chelates were studied.

An attempt was made to employ the mercury electrode as a pR electrode, where  $pR = -\log [\text{rare-earth ion}]$ . This method did not give good results because of the formation of bimetallic chelates. The formation constant for the addition of acetate to mercury(II)-N'-(hydroxyethyl) ethylenediamine-N, N, N'-triacetate was determined.

Trends in the stability of rare-earth aminopolyacetate chelates were discussed. Similarity in the stability constant curves of some of the chelating agents was noted. The "gadolinium break" appears to be quite general for the chelates studied. The position of yttrium in the stability constant curve and the "gadolinium break" may indicate ligand field stabilization of the 4f electrons.

## LITERATURE CITED

1. Chaberek, S. and Martell, A. E. "Organic Sequestering Agents", John Wiley and Sons, New York (1959)
2. Smith, R. L. "The Sequestration of Metals", The Macmillan Co., New York (1959)
3. Spedding, F. H. and Powell, J. E. Chem. Engr. Prog. Symposium Ser., 50, no. 14 (1954)
4. \_\_\_\_\_ and \_\_\_\_\_ "Basic Principles Involved in the Macro-Separation of Adjacent Rare Earths from Each Other by Means of Ion Exchange", U. S. Atomic Energy Commission Report, ISC-857 [Iowa State College] (1959)
5. \_\_\_\_\_, \_\_\_\_\_, and Wheelwright, E. J. J. Am. Chem. Soc., 76, 2557 (1954)
6. Debbrecht, F. J. "Synthesis and Studies of Some Polyamino Acid Chelating Agents", Unpublished Ph.D. Thesis, Library, Iowa State University of Science and Technology, Ames, Iowa (1956)
7. Bjerrum, J., Schwarzenbach, G., and Sillén, L. G. "Stability Constants, Part I: Organic Ligands", The Chemical Society, London (1957)
8. Martell, A. E. and Calvin, M. "Chemistry of the Metal Chelate Compounds", Prentice-Hall, New York (1952)
9. Wheelwright, E. J. "The Use of Chelating Agents in the Separation of the Rare Earth Elements by Ion-Exchange Methods", Unpublished Ph.D. Thesis, Library, Iowa State University of Science and Technology, Ames, Iowa (1955)
10. Reilly, C. N. and Schmid, R. W. J. Am. Chem. Soc., 78, 5513 (1956)
11. \_\_\_\_\_ and \_\_\_\_\_ J. Elisha Mitchell Sci. Soc., 20, 2588 (1957)
12. Schwarzenbach, G. and Anderegg, G. Helv. Chim. Acta, 40, 1773 (1957)
13. \_\_\_\_\_, \_\_\_\_\_, and Senn, H. ibid., 40, 1886 (1957)
14. \_\_\_\_\_, \_\_\_\_\_, Nagli, P., and Müller, F. ibid., 42, 827 (1959)

15. \_\_\_\_\_ and Freitag, E. ibid., 34, 1492, 1503 (1951)
16. Wheelwright, E. H., Spedding, F. H., and Schwarzenbach, G. J. Am. Chem. Soc., 75, 4196 (1953)
17. Spedding, F. H., Powell, J. E., and Wheelwright, E. J. ibid., 78, 34 (1956)
18. Harder, R. and Chaberek, S. J. Inorg. Nucl. Chem., 11, 1972 (1959)
19. Schwarzenbach, G. and Ackermann, H. Helv. Chim. Acta, 35, 485 (1952)
20. Brill, K. and Krunholz, P. J. Phys. Chem., 57, 874 (1953)
21. Schwarzenbach, G., Gut, R., and Anderegg, G. Helv. Chim. Acta, 37, 937 (1954)
22. Hiller, M. A. "Some Physical and Chemical Properties of Scandium and the Rare Earths", Unpublished Ph.D. Thesis, Library, Iowa State University of Science and Technology, Ames, Iowa (1959)
23. Lingane, J. J. Chem. Revs., 29, 1 (1949)
24. Koryta, J. and Kössler, J. Coll. Czech. Chem. Comm., 15, 241 (1950)
25. Matyska, B. and Kössler, I. ibid., 16, 221 (1951)
26. Onstott, E. I. J. Am. Chem. Soc., 74, 3773 (1952)
27. Cook, C. N. and Long, F. A. J. Am. Chem. Soc., 73, 4119 (1951)
28. Jones, S. S. and Long, F. A. J. Phys. Chem., 56, 25 (1952)
29. Cook, C. M. Jr. and Long, F. A. Determination of dissociation constants of complex ions by a radioactive indicator method. U. S. Atomic Energy Commission Report 1210 [Brookhaven National Laboratory and Cornell University] . [No date given]
30. Betts, R. H., Dahlinger, O. F., and Munro, D. M. "Radioisotopes in Scientific Research", United Nations Educational Scientific and Cultural Organization Conference on Radioisotopes, Paris, Sept., 1957, Pergamon Press, New York (1958)

31. Betts, R. H. and Dahlinger, O. F. Can. J. Chem., 37, 91 (1959)
32. Kolthoff, I. M. and Auerback, C. J. Am. Chem. Soc., 74, 1452 (1952)
33. Hughes, V. L. and Martell, A. E. J. Phys. Chem., 57, 694 (1953)
34. Martell, A. E. and Plumb, R. C. ibid., 56, 993 (1952)
35. \_\_\_\_\_, \_\_\_\_\_, and Bersworth, F. C. ibid., 54, 1208 (1950)
36. Schwarzenbach, G. and Ackermann, H. Helv. Chim. Acta, 31, 1029 (1948)
37. Irving, H. and Williams, R. Nature, 162, 746 (1948)
38. Jones, M. M. Science, 121, 371 (1955)
39. Vickery, R. C. J. Chem. Soc., 1952, 1895
40. Schwarzenbach, G. and Gut, R. Helv. Chim. Acta, 39, 1589 (1956)
41. Moeller, T., Moss, F. A. J., and Marshall, R. H. J. Am. Chem. Soc., 77, 3182 (1955)
42. Charles, R. C. ibid., 76, 5854 (1954)
43. Staveley, L. A. K. and Randall, T. Discussions Faraday Soc., No. 26, 157 (1958)
44. Foreman, J. K. and Smith, T. D. J. Chem. Soc., 1957, 1752
45. George, P., Mc Clure, D. S., Griffith, J. S. and Orgel, L. E. J. Chem. Phys., 24, 1269 (1956)
46. Sonesson, A. Acta Chem. Scand., 12, 165 (1958)
47. \_\_\_\_\_ ibid., 12, 1937 (1958)
48. \_\_\_\_\_ ibid., 13, 998 (1959)
49. Schwarzenbach, G., Anderegg, G., Padmoyo, M., and Borg, O. R. Helv. Chim. Acta, 41, 988 (1958)

50. Powell, J. E. and Hiller, M. A. J. Chem. Ed., 34, 330 (1957)
51. Diehl, H. and Smith, G. F. "Quantitative Analysis", John Wiley and Sons, New York (1952)
52. Reilley, C. N. and Schmid, R. W. Anal. Chem., 25, 1640 (1953)
53. Fritz, J. S., Richard, M. J., and Karraker, S. K. Anal. Chem., 30, 1347 (1958)
54. Sillen, L. G., Hietamen, S., and Forsling, W. Acta Chem. Scand., 6, 901 (1952)
55. James, D. B. "Ion-Exchange Elution Sequences with Chelating Eluants", Unpublished Ph.D. Thesis, Library, Iowa State University of Science and Technology, Ames, Iowa (1960)
56. Chaberek, S. and Martell, A. E. J. Am. Chem. Soc., 77, 1477 (1955)
57. Anderegg, G. J. Inorg. Nucl. Chem., 8, 360 (1958)
58. Powell, J. E. and Spedding, F. H. Chem. Engr. Prog., No. 24, 101 (1959)
59. Powell, J. E. "The Separation of Rare Earths by Ion Exchange" in Spedding, F. H., and Daane, A. H. "Rare Earths and Related Metals", chap. 5, Am. Soc. of Metals, Novelty, Ohio [To be published ca. 1960.]
60. Duncan, J. F. Australian J. Chem., 12, 356 (1959)
61. Feldman, I. Anal. Chem., 28, 1859 (1956)
62. Sørensen, S. P. L. Biochem. Z., 21, 134 (1909)
63. Bates, R. G., Analyst, 77, 653 (1952)
64. \_\_\_\_\_ Chem. Revs., 42, 1 (1948)
65. \_\_\_\_\_ "Electrometric pH Determinations", John Wiley and Sons, New York (1954)
66. \_\_\_\_\_, Pinching, G. D., and Smith, E. R. J. Research Natl. Bur. Standards, 45, 418 (1950)



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## APPENDIX A - DETERMINATION OF HYDROGEN-ION CONCENTRATION WITH A GLASS ELECTRODE pH METER

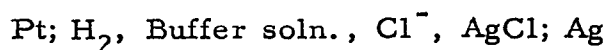
An article by Feldman (61) reviewed the possible sources of error and the range of accuracy of the pH meter in determining hydrogen-ion concentration.

The problems involved in measuring hydrogen-ion concentration with a glass electrode pH meter are two related ones. The first is the fact that it is impossible to measure the activity of a single ionic species without resorting to non-thermodynamic assumptions, and the second is the problem of liquid junction potentials.

To understand the nature of the first problem one must explore the concept of pH more thoroughly. Sørensen (62) originally defined pH by the equation  $\text{pH} = -\log C_{\text{H}^+}$ . He determined pH values from cells containing HCl - NaCl mixtures by measuring the electromotive force. At that time it was not known that the e.m.f. of cells depends on activities rather than concentrations. Therefore, there is no direct relationship between Sørensen's pH and the hydrogen-ion concentration. Later Sørensen modified the pH concept by defining a new pH term  $\text{p}a_{\text{H}^+} = -\log a_{\text{H}^+}$  where  $a_{\text{H}^+}$  is the hydrogen-ion activity. The difficulty with this definition is that it is impossible to measure experimentally the activity of a single ionic species. There have been many attempts to define a useful pH scale. Several of these methods are practical as long as no attempt is made to interpret them in terms of hydrogen-ion concentration, however, the hydrogen-ion concentration is very often what is sought from

pH measurements. Several scales have been devised so that pH measurements can be interpreted as hydrogen-ion concentration. The scale which is most widely used for this purpose is the National Bureau of Standards scale indicated by  $\text{pH}_S$  (63, 64, 65).

The  $\text{pH}_S$  scale is based on cells without liquid junction. It is defined in three steps (63). First for the cell



the e.m.f. is given by

$$E = E^\circ - \frac{2.3 RT}{F} \log a_{\text{H}^+} a_{\text{Cl}^-},$$

substituting activity coefficients in this equation gives

$$E = E^\circ - \frac{2.3 RT}{F} \log f_{\text{H}^+} \cdot C_{\text{H}^+} \cdot f_{\text{Cl}^-} \cdot C_{\text{Cl}^-} \text{ and on rearranging}$$

$$\log f_{\text{H}^+} f_{\text{Cl}^-} C_{\text{H}^+} = \frac{-(E - E^\circ)F}{2.3 RT} - \log C_{\text{Cl}^-} \quad \text{or}$$

$$-\log f_{\text{H}^+} f_{\text{Cl}^-} C_{\text{H}^+} = \frac{(E - E^\circ)F}{2.3 RT} + \log C_{\text{Cl}^-}.$$

If we define  $\text{pWH} = -\log (f_{\text{H}^+} \cdot f_{\text{Cl}^-} \cdot C_{\text{H}^+})$ , then

$$\text{pWH} = \frac{-(E - E^\circ)F}{2.3 RT} + \log C_{\text{Cl}^-}.$$

For each of three or more portions of the buffer solution with different small concentrations of added soluble chloride,  $\text{pWH}$  is determined by measuring the e.m.f. of the cell above. Secondly, these  $\text{pWH}$  values are plotted against the molality of added chloride to give a straight line, the intercept of which corresponds to  $\text{pWH}$  when the buffer is infinitely dilute with respect to chloride. This intercept is designated as  $\text{pWH}^\circ$ . Thirdly  $\text{pH}_S$  is defined as  $-\log f_{\text{H}^+} C_{\text{H}^+}$  and is calculated by  $\text{pH}_S = \text{pWH}^\circ + \log f^\circ \text{Cl}^-$ , where  $f^\circ \text{Cl}^-$

is the chloride activity coefficient in a solution of ionic strength equal to that of the buffer but infinitely dilute with respect to chloride. Obviously at this point some nonthermodynamic assumption must be made in order to evaluate  $f_{\text{Cl}^-}^\circ$ , the individual ion activity coefficient. Bates (63) has computed pHs values for the equimolal phosphate buffer,  $\text{KH}_2\text{PO}_4 : \text{NaH}_2\text{PO}_4 = 1:1$ , at  $25^\circ$  from three sets of  $\text{pH}^\circ$  values (Cl, Br, I) and with five different assumptions for the individual activity coefficients. Three important conclusions can be drawn from his data. First, equally reasonable assumptions regarding the magnitude of the individual ionic activity coefficients yield pHs values that differ appreciably at ionic strengths above 0.1; second, a change in the type of cell has no great effect upon the value of pHs other than a change in the assumption; and third, the results furnished by all three cells and all five assumptions are in agreement within  $\pm 0.01$  pH unit below an ionic strength of 0.1. By this procedure the National Bureau of Standards has set up a number of standard buffers which have known pHs values accurate to  $\pm 0.01$  pH unit. The Beckman buffers used in this dissertation were based on the N. B. S. standards. Thus under the restricted conditions that the measured solution matches the standard of reference, namely aqueous solution of buffers and simple salts with ionic strengths between 0.01 and 0.1, the measured pH may be expected to approach  $-\log f_{\text{H}^+} C_{\text{H}^+}$ . In order to calculate  $C_{\text{H}^+}$  we are again confronted with the problem of making some assumption for calculating the individual ionic activity coefficient  $f_{\text{H}^+}$ . Feldman (61) has calculated  $f_{\text{H}^+}$  employing assumptions

similar to those made by Bates in determining  $f_{\text{Cl}^-}^\circ$ . His results show that at ionic strength 0.1 all the different assumptions for obtaining  $f_{\text{H}^+}$  agree to within  $\pm 0.01$  pH unit. He found a value for  $f_{\text{H}^+}$  close to the mean for all the assumptions by assuming that the activity coefficient of hydrogen ion in the solution measured was equal to the mean activity coefficient squared of hydrochloric acid in a HCl-NaCl mixture having the same ionic strength as the mixture under study, divided by the mean activity coefficient of KCl in pure KCl solution having the same ionic strength as the mixture under study,

$$f_{\text{H}^+} = \frac{f_{\text{HCl}}^2 (\text{HCl-NaCl})}{f_{\text{KCl}} (\text{KCl})}$$

In summary, if one is using a glass electrode pH meter and standardizing it against a N. B. S. standard buffer, the maximum possible error due to non-thermodynamic assumptions for estimating single ionic activities would be  $\pm 0.02$  pH units at ionic strength 0.1 m.

The second problem in pH meter measurements is the liquid junction potential that exists at the boundary of two solutions which differ in composition. This potential is due to a difference in the rates of diffusion of ions of opposite charge. The junction potential at a boundary would be expected to be a function of pH, ionic strength, the nature of the diffusing ions, solvents, temperature and, in fact, of anything which affects the mobility of ions in solution. Since the  $\text{pH}_\text{S}$  of the N. B. S. standard buffer is based on cells without liquid junction, the standardization of a glass electrode pH meter by means

of this standard buffer is subject to an error due to the junction potential term. This error is partially compensated when the electrodes are placed in the test solution. The error due to junction potentials cannot be calculated accurately, however, indications of its magnitude have been obtained. Bates, Pinching and Smith (66) determined the apparent  $\text{pH}_j$  for a number of test solutions in a cell with liquid junction. For each of the same test solutions they determined  $\text{pH}_S$  using cells without liquid junction by the method described for assigning standard buffers. The difference,  $\text{pH}_j - \text{pH}_S$ , for each solution is equivalent to the  $\Delta\text{pH}$  which would prevail if the pH meter were employed for the pH measurements using the phosphate buffer as standard. They studied some 38 solutions ranging in pH from 1 to 13.5. Their results may be summarized as follows:  $\Delta\text{pH}$  did not exceed  $\pm 0.02$  unit for any of the buffers having  $\text{pH}_S$  between 2.15 and 10 and this included a reasonable uncertainty in  $f_{\text{Cl}^-}$ . A somewhat higher  $\Delta\text{pH}$  value was found at very high and very low pH. The effect of changing ionic strength seems to be included in the  $\Delta\text{pH}$  values reported by Bates, since the test solutions varied in ionic strength from 0.15 to 0.003. Feldman, citing data from various sources states, "If KCl or NaCl is the predominant constituent in an aqueous solution having a pH between 2 and 12, the variation in  $\Delta\text{pH}$  due to ionic strength is less than 0.04 pH unit when the ionic strength is increased from 0.05 to 3."

From the above considerations one might conclude that; using the glass electrode pH meter for determining hydrogen-ion concentrations

in aqueous solutions having pH's between 2 and 12, ionic strengths between 0.05 and 3, and standardizing with a N. B. S. buffer; one could calculate  $C_{H^+}$  to an accuracy of  $\pm 0.04$  pH unit. Feldman's method was used to convert pH to hydrogen ion concentrations in this dissertation.

## APPENDIX B - A METHOD TO DETERMINE RHgY FOR HEDTA

The formation of LaHgY was estimated from the change in solubility of HHgY when lanthanum nitrate was added to a solution containing {HHgY}.

The solubility product of {HHgY} is given by

$$K_{s.p.} = [H^+][HgY^-] \quad (60)$$

The material balance equation for the lanthanum added to the solution is,

$$[La]_T = [La^{+3}] + [LaHgY] \quad (61)$$

Equation 62 expresses the fact that for each  $HgY^-$  and  $LaHgY^{+2}$  in solution an equivalent amount of  $H^+$  is produced,

$$[HgY^-] + [LaHgY^{+2}] = [H^+] + b, \quad (62)$$

where b is the equivalent amount of KOH added per liter of solution.

The formation constant for  $LaHgY^{+2}$  is written

$$K_{LaHgY}^{La} = \frac{[LaHgY^{+2}]}{[La^{+3}][HgY^-]} \quad (63)$$

Equations 60, 61 and 62 can be solved for  $[LaHgY^{+2}]$ ,  $[La^{+3}]$  and  $[HgY^-]$  knowing the hydrogen-ion concentration.  $K_{s.p.}$ , of course, is measured from HHgY solutions without addition of lanthanum nitrate.