[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA]

A Rapid Electrochemical Method for the Determination of Metal Chelate Stability Constants

BY R. W. SCHMID AND CHARLES N. REILLEY

RECEIVED MAY 17, 1956

A method for the determination of metal chelate stability constants is described. The principle is based upon the determination of the position of exchange equilibria of the type $HgZ^{=} + Me^{++} \rightleftarrows MeZ^{=} + Hg^{++}$ by means of potentiometric measurements with a mercury electrode. The method is applied to the Ba^{++}, Sr^{++}, Mg^{++}, Ca^{++}, Mn^{++}, Cd^{++}, Zn^{++}, Pb^{++}, Cu^{++} and Hg^{++} complexes of ethylenediaminetetraacetic acid. Log K values of 7.9, 8.7, 8.9, 10.7, 13.8, 16.4, 16.4, 17.9, 18.7 and 22.1, respectively, were found at ionic strength of 0.1 and at 25° in good agreement with published values. The formation of various bimetal compounds derived from mercuric ethylenediaminetetraacetate is discussed. The applicability of the mercury electrode as a pM indicator electrode is described as well as a general method for obtaining metal-ion buffer solutions at definite pM levels, independent of pH.

Among the various methods[1] employed for the determination of equilibrium constants for chelate formation, the original[2] and modified[3] Bjerrum method and the polarographic[4] method have been most frequently used. The original Bjerrum method is applicable only to chelates of low or intermediate stability. It requires considerable time for the experiments and tedious calculations are involved. The Bjerrum method was modified by Schwarzenbach and Freitag[3] for the determination of stability constants for chelates of high stability but the work required in determining the stability constants became even greater. The polarographic method[4] is rapid and straightforward but imposes the severe requirement of a reversible equilibrium in the over-all electrode reaction. The effect of insufficiently rapid attainment of equilibria is that high values for the stability constants are obtained. This situation is frequently encountered in the case of chelates of high stability. The polarographic method also requires the presence of an electrolyte, frequently a buffered solution, which often interacts with the free metal ion and precludes determination of an accurate half-wave potential for the free metal ion under identical solution conditions. Schwarzenbach, Gut and Anderegg[5] have described a method for determining relative stability constants by polarographic determination of the positions of exchange equilibria. The equilibrium concentration of one or more of the reacting species can be determined polarographically only with systems in which the equilibrium for the displacement of a metal from its chelate by another metal ion is attained slowly relative to the rate of diffusion of the metal ions to the dropping mercury electrode.

In this article a potentiometric method is outlined which affords a *rapid* and *simple* determination of stability constants of 1:1 metal chelates (where 1 mole of chelating agent reacts with 1 mole of metal ion) under equilibrium conditions.[6] It is to be expected that this *kind* of measurement could also be applied in the study of higher complexes, *e.g.*, 2:1 chelates. The algebra, however, would be more involved and difficulties may be encountered in the stepwise complex formation.

For purposes of illustration the stability constants of various metal ions with the chelating agent, ethylenediaminetetraacetic acid, were determined. The chelating agent, ethylenediaminetetraacetic acid. (EDTA or Y) was chosen because the metal chelates of this compound have been extensively studied and their stability constants have been evaluated by several different methods, thus permitting a comparison of the proposed method with procedures already established.

Principle

A combination of the Nernst equation for a mercury electrode

$$E = E^0_{Hg} + 0.0296 \log [Hg^{++}]$$

with the equations for the stability constants of a 1:1 mercury chelate

$$K_{HgZ} = \frac{[HgZ^{2-n}]}{[Hg^{++}][Z^{-n}]}$$

and a 1:1 metal ($Me^{+\nu}$) chelate complex

$$K_{MeZ} = \frac{[MeZ^{\nu-n}]}{[Me^{+\nu}][Z^{-n}]}$$

gives at 25°

$$E_{Hg} = E^0_{Hg} + 0.0296 \log \frac{[Me^{+\nu}][HgZ^{2-n}]}{[MeZ^{\nu-n}]K_{HgZ}} + 0.0296 \log K_{MeZ} \quad (1)$$

From eq. 1, the potential of the mercury electrode is seen to depend *linearly* on log K of the particular metal chelate involved, provided the concentrations of the mercury chelate, the metal ion, and the metal chelate are kept constant. The log K of the metal chelate complex can be calculated readily from experimental data provided the value of the stability constant for the mercury complex, K_{HgZ}, is known.

The latter can also be determined experimentally from potential measurements with the mercury electrode. The potential of a mercury electrode in a solution containing free chelating agent and mercuric chelate is given at 25° by

$$E = E^0_{Hg} + 0.0296 \log \frac{[HgZ^{2-n}]\,\phi}{[Z^{-n}]K_{HgZ}} \quad (2)$$

---

[1] For a review, see Martell and Calvin, "Chemistry of the Metal Chelate Compounds," Chap. III, Prentice-Hall, New York, N. Y., 1952.

[2] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[3] G. Schwarzenbach and E. Freitag, *Helv. Chim. Acta*, **34**, 1492 (1951).

[4] J. J. Lingane, *Chem. Revs.*, **29**, 1 (1941).

[5] G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954).

[6] Schwarzenbach and co-workers (ref. 5; G. Schwarzenbach and G. Anderegg, *Helv. Chim. Acta*, **37**, 1289 (1954)) have mentioned briefly the use of a mercury electrode for the determination of metal chelate stability constants although neither the principle of the method nor details of operation were described.

where

$$\phi = 1 + \frac{[H^+]}{K_n} + \frac{[H^+]^2}{K_n \cdot K_{n-1}} + \ldots + \frac{[H^+]^n}{\Pi_1 K_1}$$

and K_1 are the acidity constants of the complexing agent. With a knowledge of ϕ, K_{HgZ} can then be calculated from the measured potential–pH function and the concentrations involved. Curve I in Fig. 1 shows this experimentally determined potential as a function of pH for a solution which contains equal amounts of free chelating agent (ethylenediaminetetraacetic acid) and the corresponding mercuric–chelate complex.

With the help of this constant, K_{HgZ}, a log K scale was calculated from eq. 1 and plotted at the right hand side of Fig. 1. Next, a potential–pH diagram was constructed from experimental data for each of several metal ions in such a way that, for definite concentrations of the chemicals involved in eq. 1, the log K value for the metal chelate could then be read directly from the measured potential of the mercury electrode, in its pH-independent region (Fig. 1). A difference in log K of one unit corresponds to a difference of 29.6 mv. in potential.

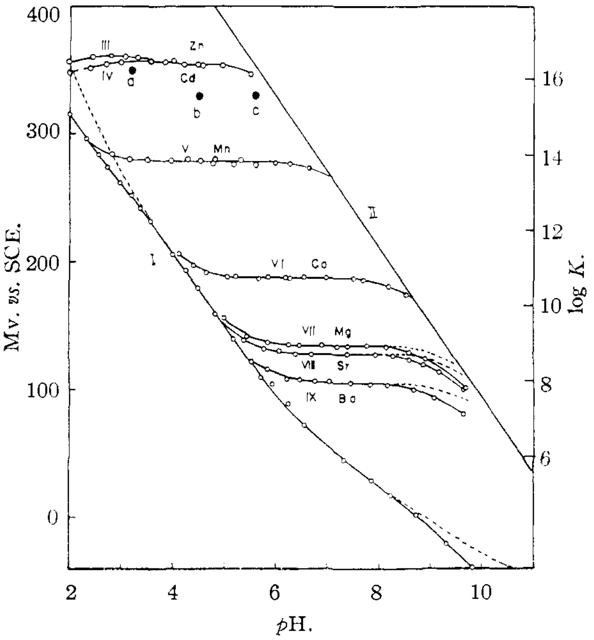


Fig. 1.—Potential–pH diagram for determination of chelate stability constants (moderate stability); 25° and ionic strength of 0.1 ($NaClO_4$): I, 0.001 M HgY^{--} + 0.001 Y; II, calculated (W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1952, p. 179) potential for $Hg + 2OH^- \longrightarrow HgO + H_2O + 2e^-$; III–IX. 0.001 M HgY^{--} + 0.001 M MeY^{--} + 0.001 M Me^{++}; a, b, c, Hg[HgY] (solid) shaken with mercury in a solution containing 0.001 M HgY^{--}

The process also can be considered as an exchange reaction

$$HgZ^{2-n} + Me^{+\nu} \rightleftarrows MeZ^{\nu-n} + Hg^{++} \qquad (3)$$

the extent to which this reaction takes place being measured by the mercury electrode. This procedure is somewhat analogous to the method employed by Schwarzenbach, Gut and Anderegg[5] in which the position of equilibrium is found by polarographic determination of the concentrations of one or more of the species involved. In order to obtain accurate results with this polarographic method, the log K difference of the metal ions involved could not exceed 2 whereas with potential measurements the difference may be much higher. However, stability constants higher than K_{HgZ} cannot be determined in any simple manner by the potentiometric method with the mercury electrode. In fact, when K_{MeZ}/K_{HgZ} becomes larger than about 10^{-4} the mercury electrode itself is oxidized by the mercuric ions to form mercurous ions in such considerable amounts that a correction would have to applied by taking into account the formal equilibrium constant[7]

$$\frac{[Hg_2^{++}]}{[Hg^{++}]} = 85 \pm 2 \; (\mu = 0.1,\ T = 25°) \qquad (4)$$

Discussion of Results

Stability constants of various metal–EDTA chelate complexes have been measured by means of the method outlined above and are listed in Table I, together with values reported in the literature.

TABLE I

STABILITY CONSTANTS OF VARIOUS METAL–EDTA COMPLEXES

Metal ion	Stability constant Proposed method[a]	Literature[b]
Ba^{++}	7.9	7.76[c]
Sr^{++}	8.7	8.63[c]
Mg^{++}	8.9	8.69[c]
Ca^{++}	10.7	10.59,[c] 10.70,[d] 10.96[d]
Mn^{++}	13.8	13.58,[d] 14.04,[d] 13.79[d]
Cd^{++}	16.4[g]	16.59,[d] 16.46[d]
Zn^{++}	16.4[g]	16.26,[d] 16.50[d]
Pb^{++}	17.9	18.3,[d] 18.04[d]
Cu^{++}	18.7	18.80,[d] 18.8[e]
Hg^{++}	22.1	21.80,[d] 22.15[f]

[a] 25.0°, in 0.1 N $NaClO_4$. [b] 20.0°, in 0.1 N KCl or KNO_3. [c] G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1798 (1947). [d] Ref. 5. [e] R. L. Pecsok, *Anal. Chem.*, **25**, 561 (1953). [f] J. Goffart, G. Michel and D. Duyckaerts, *Anal. Chim. Acta*, **9**, 184 (1953). [g] Under the experimental conditions described in Fig. 2, a value of 16.5 was found.

Stability Constants of Metal–EDTA Complexes.—For a solution containing ethylenediaminetetraacetic acid (EDTA) and mercuric–EDTA complex, each 0.001 M as well as 0.1 M sodium perchlorate to keep the ionic strength constant, potential–pH measurements were obtained and are plotted in Fig. 1, curve I. By means of equation 2 a stability constant of $10^{+22.1}$ for the mercuric–EDTA chelate complex was calculated from the experimental data within the pH range between 4 and 8, using the value of ϕ as determined by Schwarzenbach.[8] At pH values lower than 4 and higher than 8 the experimental curve (solid line) deviates from the one predicted by the function ϕ (dotted line) because of the formation of $HgHY^-$ in the acid and $Hg(OH)Y^{---}$ in the alkaline region.

---

(7) G. Schwarzenbach and G. Anderegg, *Helv. chim. Acta*, **37**, 129 (1954).

(8) G. Schwarzenbach and H. Ackermann, *ibid.*, **31**, 1029 (1948).

From the amount of deviation the following acidity constants were calculated

$$K_{\mathrm{HgHY}} = \frac{[\mathrm{H}^+][\mathrm{HgY}^{=}]}{[\mathrm{HgHY}^-]} = 10^{-3.3} \qquad (5)$$

$$K_{\mathrm{HgOHY}} = \frac{[\mathrm{H}^+][\mathrm{Hg(OH)Y}^{\equiv}]}{[\mathrm{HgY}^{=}]} = 10^{-9.3}$$

These values agree with the ones reported by Schwarzenbach[5,9] to be $pK_{\mathrm{HgHY}} = 3.1$ and $pK_{\mathrm{HgOHY}} = 9.1$.

In order to determine the stability constants involving other metal ions, potential–*p*H measurements were obtained for solutions containing mercuric–EDTA, metal–EDTA and the free metal ion, each in a concentration of 10^{-3} *M* as well as 0.1 *M* in sodium perchlorate. A plot of the results yielded curves (III-IX) as shown in Fig. 1 for the different metal ions indicated. The log *K* of the metal complex was then read directly from the *p*H-independent potential of the graph, the log *K* scale having been plotted with help of eq. 1. The *p*H-independent range of the potential is limited by the decomposition of the metal–EDTA complex into free metal ions and free EDTA in the acid region and by the formation of mercuric oxide on the alkaline side. In Fig. 1 these limits are represented by the curves I and II.

Furthermore, the potential–*p*H curves for the alkaline earths bend toward more negative potentials at *p*H values higher than 8, a fact caused by the formation of $\mathrm{HgY(OH)}^{---}$. A correction (dotted line) for this effect is made simply by adding the potential deviation of curve I (experimental) from the theoretical curve I (dotted line) to the experimental potentials obtained for the complexes in question. A similar phenomenon occurs at *p*H values less than 4, where the mercury–EDTA complex begins to add a proton forming HgHY^-. The curves for cadmium, zinc and manganese show only a weak deviation below *p*H 4. This rather small deviation is attributed to the fact that these metal complexes undergo an analogous protonization, forming MeHY^-. Because the *pK*'s (as an acid) of HMeY^- and HHgY^- are all around 3,[5] these two effects tend to cancel. As a result of this tendency of metal chelates to act as bases, only the region above *p*H 4 is useful for the simple determination of the stability constants.

Formation of Precipitates Containing the HgY^{--} Anion.—In the case of metal ions which form rather strong EDTA complexes such as lead, nickel and copper the potential of the mercury electrode was found to be very unstable, and precipitates at the surface of the mercury electrode were noticed. It is likely that these interferences are caused by the formation of the very insoluble $\mathrm{Hg_2[HgY]}$.

In a separate experiment mercuric–EDTA complex was found to react with excess mercuric ions or with mercurous ions to form white precipitates even in very dilute solutions. The assumption that these precipitates correspond to the mercuric or mercurous salt of the HgY^{--} anion was then confirmed by analysis. The results are satisfactory considering the accuracy (0.3%) of the titration procedure and the fact that the precipitates cannot be recrystallized. Analogous insoluble salts such as $\mathrm{Co^{II}[Co^{III}Y]_2}$[10] and $\mathrm{Pb[PbY]}$[11] have been described.

	Hg, % Found	Hg, % Calcd.
$\mathrm{Hg[HgY]}$	58.6	58.3
$\mathrm{Hg_2[HgY]}$	66.5	67.6

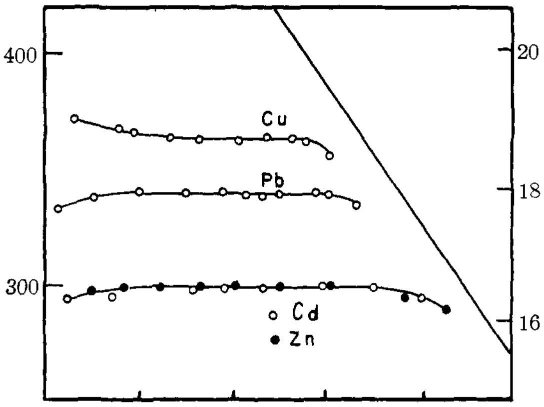


Fig. 2.—Potential–*p*H diagram for determination of chelate stability constants (high stability); 25° and ionic strength of 0.1 ($\mathrm{NaClO_4}$); 0.0001 *M* HgY^{--} + 0.01 *M* MeY^{--} + 0.001 *M* Me^{++}.

The mode of formation of $\mathrm{Hg_2[HgY]}$ from a solution used for a stability constant determination is illustrated by example. A typical solution containing Cu^{++}, CuY^{--} and HgY^{--}, each in a concentration of 0.001 *m*, at a *p*H of 4, and with a ionic strength of 0.1, frees $10^{-6.4}$ *M* of mercuric ions (*cf.* eq. 3, $K_{\mathrm{CuZ}}/K_{\mathrm{HgZ}} = 10^{-3.4}$). Because the solubility product of $\mathrm{Hg[HgY]}$ is not yet reached, no precipitate is formed.[12] However, when this solution was shaken with mercury metal, a white precipitate formed. Mercuric ions in contact with mercury metal are converted partially into mercurous ions according to equilibrium (4). Therefore this precipitate was attributed to $\mathrm{Hg_2[HgY]}$, especially since this compound is more insoluble than $\mathrm{Hg[HgY]}$. An analogous experiment with nickel or lead involved gave the same effects. An analysis of the precipitates formed in such a way was not carried out, because they contained appreciable quantities of metallic mercury as a result of the shaking and purification is difficult. In the case of cadmium ($K_{\mathrm{CdY}}/K_{\mathrm{HgY}} = 10^{-5.7}$) no precipitate was formed.

Because of high insolubility of $\mathrm{Hg_2[HgY]}$ only a certain concentration of mercurous ions (or also mercuric ions in view of eq. 4) can be tolerated in solution for the potential measurement. In order to determine this limit, mixtures containing 0.001 *M* mercuric perchlorate and 0.002 *M* mercuric–

---

(9) G. Schwarzenbach, "Die Komplexometrische Titration," Stuttgart. 1955, p. 8.

(10) G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 839 (1949).

(11) H. Brinzinger, H. Thiele and U. Müller, *Z. Anal. Chem.*, **251**, 285 (1943).

(12) However, at higher concentrations of the ions involved, a very gelatinous white precipitate forms. With a sample containing Ni^{++}, NiY^{--} and HgY^{--} a rough analysis of the precipitate, which is hard to purify, gave 57% Hg (calculated for $\mathrm{Hg[HgY]}$, 58.3% Hg). No nickel was found in the precipitate.

EDTA complex and 0.1 *M* sodium perchlorate (Hg[HgY], of course, precipitated) at different *p*H's were shaken 12 hours with mercury and then the potential and the *p*H were measured. The following values were obtained

*p*H	3.2	4.5	5.6	
E	0.350	0.330	0.330	mv. *vs.* S.C.E.

These points are plotted in Fig. 1 (a, b, c) and show that, at a concentration of mercuric–EDTA equal to 0.001, all log *K* higher than about 15.6 should be leveled to this value. However, as the formation of the precipitate at the mercury electrode takes time, zinc and cadmium, having a log *K* of 16.4 could be measured without this interference, but the log *K* of lead, copper and nickel could no longer be determined under these conditions.

In order to extend this upper limit, the log *K* scale was shifted 59 mv. more negative by changing the concentrations to 0.0001 *M* HgY^{--}, 0.001 *M* Me^{++} and 0.01 *M* MeY^{--}. Because the concentration of the mercuric–EDTA was lowered 10 times, a 10 times higher concentration of free mercuric ions can be tolerated before the solubility product of $Hg_2[HgY]$ is reached. Therefore, under these latter conditions, the formation of $Hg_2[HgY]$ does not interfere up to a log *K* of 18.5. Furthermore, the region where the potential is *p*H-independent is wider. In this way, the stability constants of copper, lead, zinc and cadmium have been determined (Fig. 2).

Formation of Unusual Bimetal Chelates.—Under certain solution conditions *one* ethylenediaminetetraacetate ion can react with *two* different metal ions to form unusual bimetal chelates. In a brief study it was found that such a behavior could occur if at least one of the metal ions was mercury(II). For instance, it has been noticed that the normally insoluble Hg[HgY] dissolves in alkaline solution. The formula $Hg\text{–}Y\text{–}Hg(OH)_2^{--}$ has been given to the resulting compound on the basis of the following observations. A suspension of Hg[HgY], formed by mixing equivalent amounts of a mercuric and a mercuric–EDTA solution, was titrated with sodium hydroxide. The titration curve is shown as a dotted line in Fig. 3. Up to point A the free acid in solution is titrated. Between A and B the Hg[HgY] consumes hydroxyl ions and slowly dissolves while at point B the solution becomes entirely clear. At this point, two moles of alkali have been consumed per mole of Hg[HgY] corresponding to the formula $Hg\text{–}Y\text{–}Hg(OH)_2^{--}$ for the soluble species.

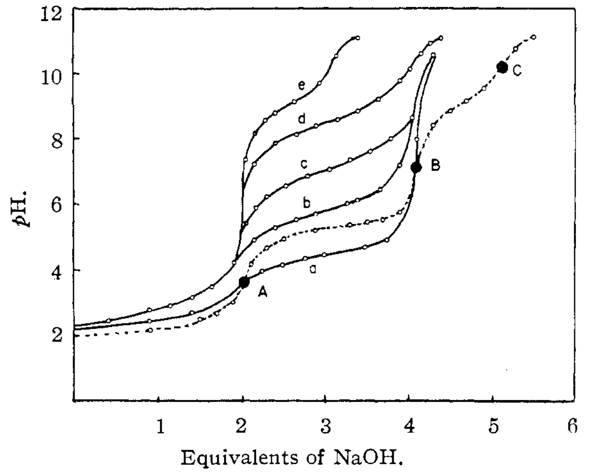


Fig. 3.—Titration of mixtures of $HgY^{--} + 2H^+ + Me^{++}$ with 0.1 *M* NaOH; 0.1 *M* $NaClO_4$ at 25°: a, 0.01 *M* Cu^{++} + 0.01 *M* HgY^{--} + 0.02 *M* H^+; b, 0.01 *M* Cd^{++} + 0.01 *M* HgY^{--} + 0.02 *M* H^+; c, 0.01 *M* Mn^{++} + 0.01 *M* HgY^{--} + 0.02 *M* H^+; d, 0.01 *M* Ca^{++} + 0.01 *M* HgY^{--} + 0.02 *M* H^+; e, 0.01 *M* HgY^{--} + 0.02 *M* H^+; dotted line, 0.01 *M* Hg^{++} + 0.01 *M* HgY^{--} + 0.02 H^+.

Upon further addition of alkali, this complex decomposes into mercuric oxide and $HgY(OH)^{---}$ The third break occurring at point C corresponds to the completion of this reaction with one mole of alkali consumed

$$HgYHg(OH)_2^{--} + OH^- \longrightarrow HgO + HgY(OH)^{-3} + H_2O \quad (6)$$

The formation of analogous complexes of the type $Me\text{–}Y\text{–}Hg(OH)_2^{--}$ has been observed with many other metal ions and appears to be a general type of behavior for metal ions which are able to form EDTA chelates. This behavior was demonstrated by the following experiments. If an acid solution of mercury(II)–EDTA complex is titrated with base, a sharp *p*H change occurs after the free acid is consumed as illustrated in curve e of Fig. 2. Upon further addition of base a buffer region corresponding to a *pK* of 9.1[13] occurs and is attributed to the reaction

$$HgY^{--} + OH^- \longrightarrow HgYOH^{---} \quad (7)$$

If, however, calcium ion (equimolar with respect to HgY^{--}) is added prior to the titration of the acid solution of mercuric–EDTA complex, the titration with base yields a titration curve as illustrated in curve d, Fig. 3. The second break corresponds to the consumption of two equivalents of base according to the reaction

$$HgY^{--} + Ca^{++} + 2OH^- \longrightarrow CaYHg(OH)_2^{--} \quad (8)$$

Similar results were obtained with other metal ions and Fig. 3 shows as examples the cases with manganese(II) (curve c), cadmium (curve b) and copper (curve a). In general the bimetal complex is formed more easily (thus at lower *p*H values) as the complexing tendency of the metal toward EDTA increases. Thus Cu>Cd>Mn>Ca whose log K_{MeY} are 18.7, 16.4, 13.8 and 10.7, respectively. This behavior is reasonable in view of the structure proposed below for the bimetal complexes (*cf.* Fig. 6). The logarithms of the formation constants

$$K = \frac{[MeYHg(OH)_2]}{[OH]^2[Me][HgY]}$$

of these bimetal complexes are calculated for comparison. The formation of a precipitate of Hg[HgY] in the case of mercury(II) ions (dotted curve) and of copper(II) ions (curve a) affects the

Metal ion	log $K_{MeY^{--}}$	log $K_{MeYHg(OH)_2^{--}}$	Δ log *K*
Ca^{++}	10.7 ± 0.1	13.3 ± 0.2	2.6
Mn^{++}	13.8	16.1	2.3
Cd^{++}	16.4	18.7	2.3
Zn^{++}	16.4	19.1	2.7

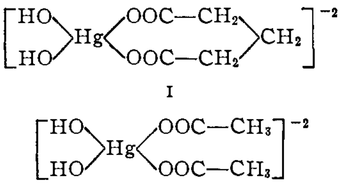
---

[13] *Cf.* footnote 9.

shape of their titration curves and also precludes calculation of their formation constants in the absence of an accurate solubility product constant for Hg[HgY].

In proposing a structure for the bimetal complex two factors should be considered. The first is that calcium actually forms this complex, and in view of the weak complexing ability of calcium ion, the proposed structure should show effective chelation of calcium. Secondly, the bimetal complex required consumption of *two* equivalents of base *regardless of whether one or both of the metal ions were mercury(II)*. This indicates that the *two* equivalents of base were attached directly to *one* mercury and also that the two metal ions in the complex are not in equivalent positions. A configuration which agrees with this behavior is given in Fig. 6.

A possible objection to this configuration is the presence of the *eight*-membered ring in which mercury is bound through carboxyl oxygens. That such a configuration may actually occur is demonstrated by the following experiment. A solution containing 0.005 *M* mercury(II) perchlorate and 0.005 *M* glutaric acid was titrated with sodium hydroxide. A precipitate is present in the original solution. A small break is obtained after the addition of two equivalents of base and a large *p*H break after the addition of four equivalents of base. The solution is then clear with the complex I (Fig. 4) probably present. Further addition of base causes precipitation of HgO. Similar results (with no precipitates occurring however) are obtained in the titration of a mixture of 0.01 *M* mercury(II) perchlorate and 0.02 *M* acetic acid with standard base, illustrating the formation of the complex II (Fig. 4). The *p*H of this solution after the addition of three equivalents of base was 5.2 (ionic strength 0.1, 25.0°), thus pointing to the stability of such complexes even in the absence of a "chelate effect." These complexes are analogous to the lower half of the bimetal complex given in Fig. 6.



$$\left[\begin{matrix}HO\\HO\end{matrix}>Hg<\begin{matrix}OOC—CH_2\\OOC—CH_2\end{matrix}>CH_2\right]^{-2}$$

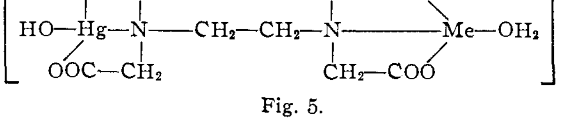
I

$$\left[\begin{matrix}HO\\HO\end{matrix}>Hg<\begin{matrix}OOC—CH_3\\OOC—CH_3\end{matrix}\right]^{-2}$$

II

Fig. 4

A second possible configuration, which may seem preferable in view of the strong tendency of mercury(II) to coördinate nitrogen, is illustrated in Fig. 5.



$$\left[\begin{array}{l}\quad \text{OH}\quad \text{CH}_2\text{—COO}(-)\qquad \text{CH}_2\text{—COO}\\ \text{HO—Hg—N——CH}_2\text{—CH}_2\text{—N————Me—OH}_2\\ \quad \text{OOC—CH}_2\qquad\qquad\quad \text{CH}_2\text{—COO}\end{array}\right]^{-2}$$

Fig. 5.

This configuration was ruled out because only *two*, not *four*, equivalents of base are consumed in reaction 8 when Me is Hg(II). Further evidence that the configuration in Fig. 5 is incorrect may be seen from the fact that the bimetal complex, $MeYHg(OH)_2^{-2}$, is formed with greater ease than would be expected from a knowledge of the stability of analogous methyliminodiacetatometal complexes. This conclusion comes from the following consideration. The *p*H (*p*H$_{1/2}$, MeYHg-$(OH)_2^{-2}$) corresponding to the conversion of one half of the metal ion into the $MeYHg(OH)_2^{-2}$ complex (reaction 8) and the *p*H (*p*H$_{1/2}$, MeZ) at which the methyliminodiacetato-metal complex is 50% dissociated are very nearly equal, yet the species whose empirical formula corresponds to the acid-stabilized open form of Fig. 5 (where Me is absent and H^+ is bound to the nitrogen)—that is, $HgYOH^{---}$—is found only around *p*H9.

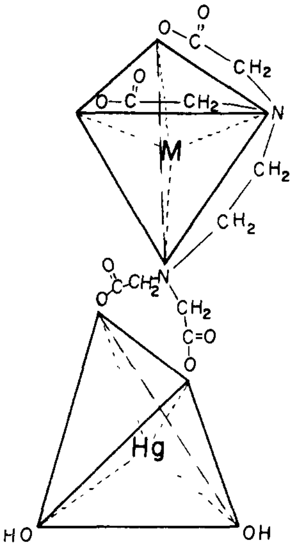


Fig. 6.—Proposed structure for bimetal complex, MeY $Hg(OH)_2^{-2}$.

Metal ion →	Ca^{++}	Cd^{++}	Mn^{++}	Zn^{++}
*p*H$_{1/2}$,[a] $MeYHg(OH)_2^{-2}$	8.5	5.8	7.1	5.6
*p*H$_{1/2}$,[b] MeZ	8.2	5.2	6.6	4.3

[a] Determined experimentally. [b] Calculated from equilibrium constants reported by G. Schwarzenbach, G. Anderegg, W. Schneider and H. Senn, *Helv. chim. Acta*, **38**, 1147 (1955).

Limitations of the Method.—The stability constants of metal chelate complexes whose cations hydrolyze easily, *e.g.*, even at a *p*H of 4 or less (as aluminum), cannot be determined. Furthermore, the method fails with a few metal chelates which have a rather negative oxidation potential as cobalt(II)–EDTA and iron(II)–EDTA. (E_{redox} for $Co^{III}Y/Co^{II}Y = +0.14$[14]; $Fe^{III}Y/Fe^{II}Y = -0.12$[15] volt *vs.* SCE). Complexes of this type are oxidized by the mercuric–EDTA according to reactions such as

$$2Co^{II}Y^{--} + HgY^{--} + nH^{+} \longrightarrow Co^{III}Y^{-} + H_nY^{n-4} + Hg$$

This reaction, incidentally, was found to be accelerated by the presence of mercury metal.

Extensions and Further Applications of the Method

Mercury as a *p*M Indicator Electrode.—From eq. 1, it may be seen that the potential of the electrode may also bear a *linear* relationship with log [Me] and consequently the electrode may serve as a *p*M indicator electrode (analogous to a *p*H indicator electrode) in the presence of fixed concentrations of the metal chelate and mercuric chelate. This feature is particularly significant in situations where suitable electrodes of the first

---

(14) C. N. Reilley, W. G. Scribner and C. Temple, *Anal. Chem.*, **28**, 450 (1956).

(15) G. Schwarzenbach and G. Heller, *Helv. Chim. Acta*, **34**, 576 (1951).

class, *i.e.*, a metal electrode in contact with a solution containing the metal ion, are not applicable—such as with the alkaline earth metals. Thus, for example, the electrode system

$$\text{Hg/Hg–EDTA}^{-2},\ \text{Ca–EDTA}^{-2},\ \text{Ca}^{++}$$

would be, within certain *p*H limits, a *p*Ca electrode in the presence of fixed added concentrations of mercuric–EDTA and calcium–EDTA complexes.

Such a *p*M indicator electrode could be used to study the interaction of a metal ion (*e.g.*, Ca^{++}) with many types of complexing agents provided the complexing agent does not react with the metal ion more strongly than the reference chelate (*e.g.*, EDTA).

This principle of the *p*M indicator electrode has been applied to the potentiometric detection of end-points in chelation titrations involving a variety of metals, chelating agents and conditions.[16] For example, in the coulometric titration of lead, copper, calcium or zinc with electrically liberated ethylenediaminetetraacetic acid[17] the mercury electrode was found to be a suitable *p*M indicator electrode for detecting the end-points.

Metal–Ion Buffer Solutions.—Consideration of Fig. 1 points out another possible application. The potential is, of course, a measure of the Hg^{++} activity and Figs. 1 and 2 illustrate that the activity of mercuric ions can be adjusted to almost any desired level by addition of a certain metal ion and its corresponding EDTA complex to a solution of mercuric–EDTA complex. The particular metal ion selected allows the *p*Hg level to be adjusted close to the desired value, *e.g.*, Ba^{++} for high *p*Hg levels, Ca^{++} and Mn^{++} for intermediate values, Cd^{++} and Cu^{++} for low levels. The relative concentrations of these ingredients may be varied to allow fine adjustments in the *p*Hg level. Addition or removal of mercuric ions in small amounts will result in only small changes in the *p*Hg level, hence a *buffered* solution in respect to the mercuric ion. *An important feature of this technique is that the pHg level remains virtually constant over a reasonable pH range.*

Obviously the method is not restricted to *p*Hg levels but can also be employed to obtain *pM levels of almost any metal ion that forms 1:1 complexes.* The selection of the chelating agent offers another variable which can be employed for obtaining a desired *p*M value. For example nitrilotriacetic acid would yield lower *p*M levels than EDTA for the same pair of metal ions.

Experimental

Chemicals.—All chemicals used were AR grade. The metal ion solutions were standardized against a standard EDTA solution.

Determination of Potential *p*H Diagrams.—The cell consisted of a 50-ml. beaker surrounded by a condenser-type jacket connected in turn to a constant temperature bath maintained at 25.0 ± 0.1°. A glass electrode (Beckman #1199-30), a J-tube mercury electrode[17] and a saturated calomel electrode with an agar bridge were used. About 30 ml. of solution was taken for a measurement and stirred continuously by means of a magnetic stirrer. The *p*H was varied by dropwise addition of sodium hydroxide or perchloric acid. The *p*H was measured with a L and N *p*H meter (type 7664) and the potential by means of a L and N student potentiometer. Equilibrium within ±1 mv. generally was reached in about a minute. In the samples containing manganese(II) deaeration of the solution was necessary in order to prevent the oxidation of manganese(II) by air. The cell therefore was closed with a cork stopper provided with the necessary holes and nitrogen was bubbled through the solution.

***p*H Titrations.**—The titration curves in Fig. 3 were carried out in the same cell as described above.

Preparation and Analysis of Hg[HgY] and Hg_2[HgY].—Ten ml. of 0.1 *M* mercuric nitrate and 10 ml. of 0.1 *M* disodium ethylenediaminetetraacetate were mixed, diluted to 50 ml. and the acid liberated neutralized by addition of 4 ml. of 0.5 *M* sodium hydroxide. Into this solution of mercuric–EDTA complex 0.1 *M* mercuric nitrate in 20% excess was added dropwise with stirring. The voluminous precipitate of Hg[HgY] was allowed to stand overnight, then centrifuged and washed four times with water. The compound then was dried three days at 80° in a vacuum (1 mm.). In the analysis of this precipitate for mercury 200 mg. of the compound were decomposed by refluxing 0.5 hour with 5 ml. of concentrated nitric acid. The solution then was diluted, and any nitrous acid present was destroyed by addition of urea and boiling. The solution next was buffered by addition of sodium acetate and the mercuric ions were titrated with standard EDTA solution. The end-point was detected by means of a mercury electrode.[17] For the preparation and analysis of Hg_2(HgY) an analogous procedure was followed with a few alterations. Mercurous nitrate was added to mercuric EDTA with the latter present in 10% excess at the completion. The decomposition of the Hg_2[HgY] could not be achieved by refluxing with nitric acid, but treatment of 60 mg. of substance with 1 ml. of concentrated nitric acid in a sealed tube at 200° for 12 hours gave complete decomposition.

Acknowledgment.—This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under contract No. AF18(600)-1160.

CHAPEL HILL, N. C.

---

[16] C. N. Reilley, unpublished results.

[17] C. N. Reilley and W. W. Porterfield, *Anal. Chem.*, **28**, 443 (1956).