0.20 *M* oxalate, and excess, were substituted into equation 13 to solve β_{20}. The concentration, (B), was calculated in the usual way while (A) was calculated by subtracting bound oxalate from the total oxalate concentration.

$$\beta_{20} = \frac{(\mathrm{Cu(C_2O_4)_2}^{2-})}{(\mathrm{Cu}^{2+})(\mathrm{C_2O_4}^{2-})^2} = 10^{9.36 \pm 0.14} \qquad (24)$$

This may be compared to the value $10^{9.70}$ obtained on the basis of polarographic half-wave potentials.[3] Substituting the same data into equations 14 or 15 yielded the value of β_{11}.

$$\beta_{11} = \frac{(\mathrm{Cu(C_2O_4)en}^0)}{(\mathrm{Cu}^{2+})(\mathrm{C_2O_4}^{2-})(\mathrm{en})} = 10^{15.39} \qquad (25)$$

This value compares favorably with the mean value $10^{15.44} + ^{0.14}$ reported previously[3] on the basis of spectrophotometric data.

To calculate β_{10} the data for solutions containing $(\mathrm{Cu}^{2+}):(\mathrm{C_2O_4}^{2-})$ in a 1:1 ratio shown in curve 4, Fig. 1 and summarized in Table IB were used. The concentration of $(\mathrm{A})_{1\ 1/2}$ in the solution for which $\bar{n}_a = 1$ and $\bar{n}_b = {}^1/_2$ was first calculated by equation 18. A small extrapolation from $\bar{n}_b = 0.576$ was used since precipitation occurred beyond this point. Substituting into equation 19 yielded a value for β_{10}.

$$\beta_{10} = \frac{(\mathrm{CuC_2O_4}^0)}{(\mathrm{Cu}^{2+})(\mathrm{C_2O_4}^{2-})} = 10^{5.43 \pm 0.14} \qquad (26)$$

Combining with the value $10^{9.36}$ for β_{20} yields the value for k_{20}.

$$k_{20} = \frac{(\mathrm{Cu(C_2O_4)_2}^{2-})}{(\mathrm{CuC_2O_4}^0)\ (\mathrm{C_2O_4}^{2-})} = 10^{3.93 \pm 0.14} \qquad (27)$$

The stepwise constants of this complex and many other oxalato complexes, as well, have not been reported previously due to the experimental difficulties associated with the low solubility of oxalates in oxalate deficient solutions.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE STEELE CHEMISTRY LABORATORY, DARTMOUTH COLLEGE]

The Polarography of Hg(II)EDTA in the Presence of Other Metallic Ions

BY DAVID M. H. KERN

RECEIVED JULY 24, 1958

The equilibrium Hg(EDTA) + M^{++} = M(EDTA) + Hg^{++} has been studied polarographically for various metal ions in 0.6 *M* acetate solution. It is shown that by such measurements the *p*Hg method for determining metal concentrations in complexing media can be extended to those media which compete successfully for mercury with EDTA. A polarographic method for determining metal chelate association rates is described, which requires the existence of a stable chelate that is reversibly reduced to the metal at the dropping mercury electrode.

The mercury(II) complex of ethylenediaminetetraacetate ion (EDTA) rapidly establishes a reversible potential at a mercury electrode. The dissociation constant for this chelate is therefore easily measured potentiometrically, and has been used by several authors[1,2] as the reference standard for evaluating the stability of other EDTA complexes. The complex is also reduced reversibly at the dropping mercury electrode,[3,4] a property which among the bivalent metal complexes is shared only by the cupric complex[5] and that to an inferior degree. The mercury complex is by far the stablest of the common bivalent metal complexes (pK = 21.8). This combination of reversibility and stability satisfies, in principle, the requirements of a novel polarographic method for the determination of rates of metal–chelate formation. Preliminary experiments showed, however, that the $\mathrm{HgY}^=$, Hg couple did not possess the degree of reversibility required for this purpose. Nevertheless, the observations made on mixtures of $\mathrm{HgY}^=$ and other metallic ions in the course of these experiments were of sufficient interest to warrant further investigation and form the main subject of this paper. Since the proposed method for determining metal–chelate association rates may find application in systems with the requisite reversibility, an account of the theory is given in the last section of the article.

Results

Polarograms of millimolar $\mathrm{HgY}^=$ solutions were obtained in the presence of varying amounts of zinc, manganese, lead and cadmium ions.

In the *p*H range 4–9 the half-wave potential of $\mathrm{HgY}^=$ is related to the acidity by the expression

$$E_{1/2} = \text{constant} + \frac{RT}{nF} \ln\left(1 + (\mathrm{H}^+)/K_4 + (\mathrm{H}^+)^2/K_3K_4\right)$$

where K_3 and K_4 are dissociation constants of $\mathrm{H_2Y}^=$. It is seen that the wave shifts to more positive potentials as the hydrogen ion concentration increases, until in weakly acid solutions the half-wave potential lies inconveniently near the mercury dissolution potential. In an investigation of the effect of metal ions on the wave, it is desirable to buffer the solution at as high a *p*H as feasible, in order to allow space for positive shifts. A 1:50 HOAc–OAc buffer (*p*H 6.35) was used in most of the experiments.

The effects of adding increasing amounts of zinc ion (pK of EDTA complex = 16.5) to a 1 m*M* $\mathrm{HgY}^=$ solution in this medium is shown in Fig. 1. As the zinc concentration increases, a preliminary wave extending to the dissolution

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(1) R. W. Schmid and C. N. Reilley, THIS JOURNAL, **78**, 5513 (1956).

(2) (a) G. Schwarzenbach and G. Anderegg, *Helv. Chim. Acta*, **40**, 1773 (1957); (b) G. Schwarzenbach, R. Gut and G. Anderegg, *ibid.*, **37**, 937 (1954).

(3) J. Goffert, G. Michel and G. Duyckaerts, *Anal. Chim. Acta*, **9**, 184 (1953).

(4) J. Watters, J. Mason and D. Schupp, THIS JOURNAL, **78**, 5782 (1956).

(5) R. L. Pecsok, *Anal. Chem.*, **25**, 561 (1953).

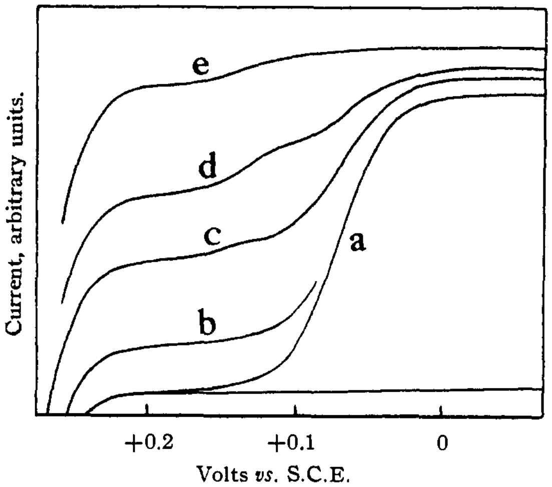

Fig. 1.—Polarograms of *ca.* 1 m*M* $HgY^=$ in presence of varying amounts of zinc ion. Concentration of $ZnSO_4$: (a) none; (b) 0.16 m*M;* (c) 0.47 m*M;* (d) 0.78 m*M;* (e) 2.5 m*M.* Medium: 0.62 *M* NaOAc + 0.012 *M* HOAc.

potential is followed by a second wave which soon replaces the original $HgY^=$ wave altogether. The second wave then stops growing, while the first gradually approaches it in height. When the zinc concentration is over three times that of the complex, essentially one wave remains, which extends to the dissolution potential. These changes are accompanied by a progressive increase in the total height of the three waves.

The complexity of this behavior points to the existence of more than one mercury species in the solution. An explanation for the first wave that early suggested itself depended on the assumed presence of a small amount of bimetallic complex. The reduction: $ZnHgY + 2e = Hg + ZnY^=$ should occur at potentials more positive than that of $HgY^=$ alone, because of the greater affinity of Zn^{++} for Y^{-4} than for $HgY^=$. This complex cannot be present in large amount, as it would have introduced large errors into the mercury electrode determinations of Schmid and Reilley,[1] whereas their K_{ZnY} value agrees well with that of Schwarzenbach[2b] obtained by other methods; and there is other evidence[6] that such bimetallic complexes are unstable. But only a very small equilibrium concentration of ZnHgY need be postulated if the first wave be kinetic in character.[7] Unfortunately, the familiar reservoir-height test does not give the desired information here, because the first wave almost exhausts the available zinc ion and will accordingly show diffusion controlled behavior whether it is kinetic or not. In fact, experiments showed all three waves to be diffusion controlled.

A decisive answer to the problem of wave assignment is provided by the observation that the shape of the polarogram is unaffected by ten-fold dilution at constant buffer concentration. This excludes any equilibrium or kinetic explanation involving the formation of ZnHgY from Zn^{++} and $HgY^=$. It points unequivocally to a process with an equal number of reactants and products, *e.g.*, $Zn^{++} + HgY^= = Hg^{++} + ZnY^=$. The virtually complete displacement of the mercury by zinc must be attributed to complex formation between the mercury and the 0.62 *M* acetate ion of the buffer solution.

The main features of the polarogram are accounted for as follows.

1. The first wave is a measure of the equilibrium concentration of mercury displaced by zinc.

2. The second wave is a measure of the equilibrium zinc concentration, the electrode reaction being $HgY^= + 2e + Zn^{++} \rightarrow Hg + ZnY^=$. To the extent that Zn^{++} is available at the drop surface, $HgY^=$ is more easily reduced because of the removal of liberated complexing agent by the diffusing zinc ion. A similar effect has been described by Bril[8] in the reduction of $CuY^=$. The sum of the first two waves is therefore proportional to the total original zinc concentration, if allowance is made for the difference in diffusion constant of zinc and mercury. This relationship is confirmed in Fig. 2.

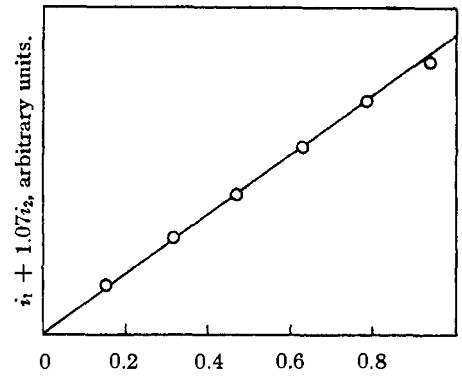

Fig. 2.—Sum of first two wave heights of Zn^{++}–$HgY^=$ polarograms as function of the zinc ion concentration. The linearity has been improved by correcting for the small difference in diffusion constant between Zn^{++} and Hg^{++} in 0.62 *M* acetate.

3. The sum of the second and third waves is a measure of the equilibrium $HgY^=$ concentration.

4. The increase in total wave height as zinc ion is added occurs because the diffusion coefficient of the mercury acetate complex is greater than that of $HgY^=$.

This interpretation is borne out by a quantitative analysis of the wave heights. If i_1, i_2 and i_3 are the successive current increments, we have

$$K_{eq} = (Hg^{++})(ZnY^=)/(HgY^=)(Zn^{++}) = D^{1/2}_{HgY} \times D^{1/2}_{Zn}/D_{Hg} \times i^2_1/i_2(i_2 + i_3) \quad (1)$$

where the constant term corrects for the difference in the diffusion coefficients of the various species.

In Table I are listed the currents observed at different zinc ion concentrations in an approximately 1.7m*M* $HgY^=$ solution. The constancy of the current quotient of equation 1 confirms the

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[6] M. C. Bennett and W. S. Wise, *Trans. Faraday Soc.*, **52**, 696 (1956).

[7] A similar mechanism based on the irreversible reduction of a transitory MCdY ion pair was recently proposed to explain the Cd-(EDTA) prewave, R. Schmid and C. Reilley, THIS JOURNAL, **80**, 2101 (1958).

[8] K. Bril and P. Krumholz, *J. Phys. Chem.*, **58**, 339 (1954).

TABLE I

POLAROGRAPHIC DIFFUSION CURRENTS IN Zn^{++}–$HgY^{=}$ MIXTURES

Arbitrary units, 25°, 0.62 *M* acetate buffer

i_1	$i_2 + i_3$	i_2	$i^2_1/i_2(i_2 + i_3)$
3.25	7.83	(0.15)	9.0
6.10	5.41	0.73	9.6
8.20	3.63	1.82	10.3
9.51	2.48	(3.8)	9.9
10.37	1.73	(6.7)	9.6

equilibrium hypothesis. The method of obtaining the bracketed i_2 values is described in the Experimental section.

Lead and cadmium were found to give triple waves similar to those of zinc. While zinc came to equilibrium in a few seconds, the first two metal ions required five or ten minutes for the attainment of constant current readings. The current ratios are given in Table II. Copper was found to displace mercury completely in the acetate medium, so no equilibrium data could be derived.

TABLE II

POLAROGRAPHIC DIFFUSION CURRENTS IN Cd^{++}– AND Pb^{++}–$HgY^{=}$ MIXTURES

Arbitrary units, 25°, 0.62 *M* acetate buffer

i_1	$i_2 + i_3$	i_2	$i^2_1/i_2(i_2 + i_3)$
Cd: 2.70	8.03	(0.34)	2.6
4.75	6.36	1.33	2.6
6.22	5.11	2.58	2.9
8.10	3.44	(6.3)	3.0
Pb: 5.70	5.53	0.55	10.5
7.95	3.61	1.55	11.2

To evaluate the constant term in equation 1, the ratios of the diffusion constant (proportional to $D^{1/2}$) of mercury to that of zinc, cadmium and lead were measured in the acetate medium and found to equal 1.07, 1.08 and 1.01, respectively. The ratio for mercury and mercury EDTA was found to be 1.20, by noting the change in diffusion current on addition of excess complexing agent to a solution of mercuric ion in acetate buffer. According to the fourth item in the interpretation given above, this last ratio should correspond to the maximum increase in total wave height when excess zinc (or other efficient displacing agent) is added to $HgY^{=}$ solution. This is confirmed in Fig. 3, in which it is also shown that the increase occurs proportionately with the growth of the first wave, *i.e.*, the conversion of $HgY^{=}$ to $Hg(OAc)_2$.

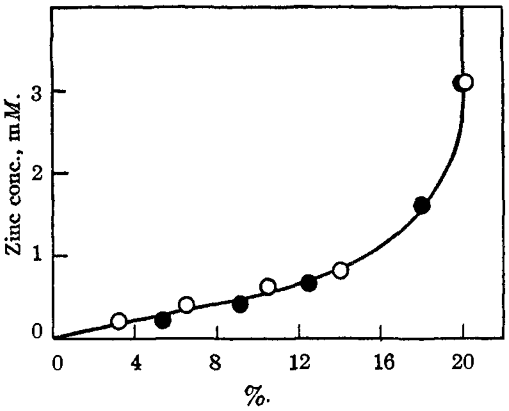

Fig. 3.—First wave height (solid circles, arbitrary units), and % increase in total wave height as function of added zinc ion concentration. Currents corrected for dilution.

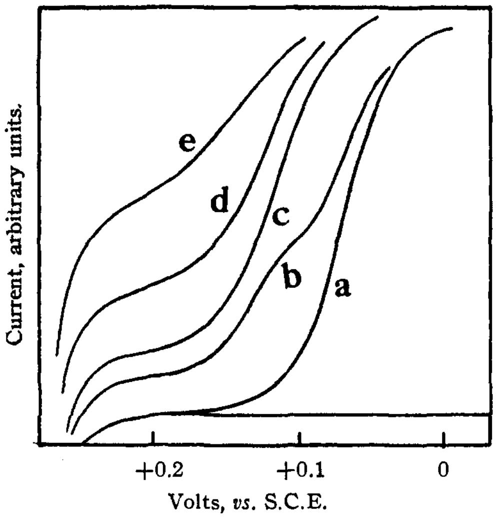

Fig. 4.—Polarograms of *ca.* 1.2 m*M* $HgY^{=}$ in presence of varying amounts of manganese ion. Concentration of $MnSO_4$: (a) none; (b) 0.45 m*M*; (c) 1.3 m*M*; (d) 5.7 m*M*; (e) 26.4 m*M*. Medium: 0.62 *M* NaOAc + 0.012 *M* HOAc.

Manganese likewise gives a triple wave. But its complexing power is so small that the first wave due to displaced mercury was still embryonic when the second wave had reached maximum height (Fig. 4). Even with a fifty-fold excess, the displacement was far from complete. As expected from the second item of the above interpretation, the second wave was less well separated from the $HgY^{=}$ regular wave than in the case of the more stable complexing zinc. The poor development of the first wave and the lack of a dependable i_2 made necessary a less accurate method for determining K_{eq}. The ratio $(Hg^{++})/(HgY^{=})$ was determined from $i_1/1.20(i_2+i_3)$. Total manganese was calculated stoichiometrically in millimoles, $(MnY^{=}) = (Hg^{++})$ was obtained in the same units by comparing i_1 with a known mercury standard, and the equilibrium free manganese concentration was set equal to the difference. The calculated *K*'s are listed in Table III. They show a downward drift, but in view of the wide range in total manganese, the results are satisfactory.

TABLE III

DATA USED IN CALCULATION OF K_{eq} IN Mn^{++}–$HgY^{=}$ MIXTURES

25°, 0.62 *M* acetate buffer

i_1	1.20 × $(L_2 + L_3)$	Mn^{++} (total), m*M*	Hg_{eq}^{++}, m*M*	Mn_1^{++}–Hg_{eq}^{++}	K_{eq}
1.05	10.37	0.450	0.135	0.31	(0.044)
1.45	9.95	0.896	.186	0.71	.038
1.75	9.58	1.335	.224	1.11	.037
2.70	8.60	3.54	.346	3.19	.034
3.32	7.95	5.74	.425	5.31	.0335
4.52	6.61	12.8	.579	12.2	.032
5.61	5.28	26.4	.720	25.7	.030
6.47	3.90	51.9	.829	51.1	.027

pHg Determination of Complex Formation Constants.—Schwarzenbach[2a] has applied the potentiometric pHg method to the determination of metal ion activities in complexing media (*e.g.*, of Mg^{++} in oxalate solution). Simple proportionality is maintained between the Mg^{++} and Hg^{++} concentrations in the equilibrium

$$Mg^{++} + HgY^{=} \rightleftarrows Hg^{++} + MgY^{=}$$

because the displacement is slight, and the concentrations of the metal complexes are fixed at a known ratio. The method is restricted to media in which the equilibrium lies far to the left.

The results described above show that the method can be extended to media in which displacement has proceeded to a considerable extent because of complexation of mercury by the medium. Gross displacement of mercury from Hg(EDTA) can under proper conditions be detected and quantitatively measured polarographically. The corrected concentrations of the EDTA complexes are then combined with the potentiometrically measured pHg to give the free metal concentration. (The formation of an HgYX type complex with the medium has not been considered in this treatment. Provided it were reduced at potentials similar to that of $HgY^{=}$ itself, its presence would certainly not be excluded by the equilibrium observations described above. If such a complex occurs, the pHg method in whatever form must be corrected for the resulting change in the free HgY concentration; its presence would exert no further influence on the refinement described in this paper. The symbol $HgY^{=}$ should simply be read as the equilibrium mixture of all $HgY^{=}$ species.)

The data presented above for 0.62 *M* acetate are not suitable for accurate calculations of the degree of complexation by acetate, because the formation constants required in the calculation have been measured[2b] only at $\mu = 0.1$. It is instructive, however, to compare the relative displacing power of the metals in the concentrated medium with that measured by Schwarzenbach in 0.01 *M* acetate. It is clear from Table IV, col. 5 that the degree of complexation by acetate increases in the order Mn, Zn, Cd, Pb.

TABLE IV

COMPARATIVE DISPLACING POWERS OF METALLIC IONS IN 0.01 *M* AND 0.6 *M* ACETATE MEDIA

	pK_{MY}[a]	K_{MY}/K_{ZnY}	K_{eq}[b]	K_{eqM}/K_{eqZn}	Col. 2/ col. 4
Zn	16.5	1	7.5	1	1
Mn	13.9	0.0025	0.034	0.0045	0.6
Cd	16.46	1	2.1	0.3	3
Pb	18.04	35	9	1.2	30

[a] Schwarzenbach, ref. 2b. Medium: 0.1 *M* KNO_3 + 0.01 *M* HOAc + 0.01 *M* NaOAc; $\mu = 0.1$. [b] Calcd. from equation 1 and Tables I–III. Medium: 0.62 *M* OAc^-; $\mu = 0.6$.

Preliminary experiments in potassium hydrogen phthalate solution (0.03 *M* adjusted to pH 4.7 with NaOH) have shown that copper and zinc produce triple waves in the presence of $HgY^{=}$ that indicate a displacing power fifty times as great for copper as for zinc, compared with a ratio of 200 calculated from the K_{MY}'s in phthalate free solution. A triple wave also has been observed with calcium ion in borate medium.

This extension of Schwarzenbach's polarographic method continues to be subject to the limitation imposed by the small solubility of Hg_2Y and $Hg(OH)_2$, but in strongly complexing media these precipitates are not likely to form. Schwarzenbach[9] reports the formation of molecularly dispersed $Hg(OH)_2$ by displacement of mercury in unbuffered solution. This species was not responsible for the first wave in 0.6 *M* acetate, for the relative wave heights were not significantly altered when the acetic acid content was varied over a fifty-fold range. (In the more acid solutions, the triple nature of the waves becomes indistinct because of coalescence of the half-wave potentials.) When the acetate ion was decreased, the displacement was much diminished.

Displacement in 0.01 *M* Acetate.—Schwarzenbach[2b] used a weak acetate buffer in his displacement experiments for the determination of EDTA formation constants, but his value for $HgY^{=}$ was fortunately obtained from cell measurements in acetate free solution, as was also his value for $CdY^{=}$. All the others were deduced directly or indirectly from displacement of the cadmium in 0.01 *M* acetate. The question arises whether a significant correction for acetate complexation need be applied to his results.

As a rough estimate of the degree of complexation in 0.01 *M* acetate, polarograms of millimolar zinc, cadmium, copper and lead were run in solutions of 0.1 *M* KNO_3 + 0.002 *M* HNO_3, with and without 0.01 *M* OAc^- + 0.01 *M* HOAc. The final acetate concentration was thus 0.008 *M*, in agreement with Schwarzenbach. The shifts in $E^1/_2$ are listed in Table V. Since the reversibility of the waves in this medium was not established, we may accept the observed shifts only as minimum values for the thermodynamic shifts. They suggest that for the ions studied the correction is small although somewhat outside the limits of error assigned to the original measurement, especially in the case of lead.

The dissociation constants of acetate complexes of the metals in Table V have recently been measured by Aditya,[10] using cell and solubility methods. His figures (measured at 30 and 35°) lead to substantially larger pK corrections: Zn, −0.08; Cu, +0.32; Pb, +0.40.

TABLE V

$E_{1/2}$ SHIFT ON ADDING 0.01 *M* OAc^- +0.01 *M* HOAc TO 1 m*M* M^{++}

Supporting electrolyte, 0.1 *M* KNO_3 + 2 m*M* HNO_3

	$\Delta E_{1/2}$, mv.	ΔpK
Zn^{++}	0	−0.07
Cd^{++}	2	0
Cu^{++}	4.5	+0.08
Pb^{++}	6.5	+0.15

Schwarzenbach[2b] made brief mention of trial displacements with $HgY^{=}$ in 0.01 *M* acetate solution, which were

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(9) G. Anderegg, G. Schwarzenbach, M. Padmoyo and Ö. Borg, *Helv. Chim. Acta*, **41**, 988 (1958).

(10) S. Aditya, *et al.*, *J. Ind. Chem. Soc.*, **30**, 213, 255, 509, 633 (1953); **32**, 102, 109 (1955). *C. A.*, **47**, 10320f (1953); **48**, 488i, 5611di (1954); **49**, 15390e (1955).

abandoned because the space between the HgY wave and the mercury dissolution potential was too small for the development of satisfactory waves (at *p*H 4.3). The author has repeated the attempt and found that the mercury wave is not indeed well developed but that the chief experimental difficulty (as also in acetate free solution) arises from the formation of white precipitates of Hg_2Y, which have been observed previously[1,2a] when working with $HgY^=$ but do not occur in 0.6 *M* acetate. Cadmium and zinc gave the familiar triple wave. The polarograms were not suitable for accurate quantitative deductions, but the relative displacing powers of Co, Cd, Zn, Pb, Ni and Cu were in essential agreement with the published *K*'s. However, the apparent numerical values were too great by a factor[11] of about 10^4, the greater part of which doubtless was due to mercury complexation.

Experimental

Reagents.—Reagent grade disodium ethylenediaminetetraacetate dihydrate (Baker) was standardized against $CaCO_3$. Solutions of $ZnSO_4$, $CdSO_4$, $MnSO_4$, $CuSO_4$, $Pb(NO_3)_2$, $CoSO_4$, $Ni(OAc)_2$, $MgSO_4$, $Hg(NO_3)_2$, $Ca(NO_3)_2$ and $Ba(NO_3)_2$ were standardized with the EDTA solution. Na_2HgY solutions were produced by mixing overnight an excess of HgO with a known concentration of EDTA solution.

Apparatus.—The cell was a double H-cell of three compartments, each of 50-ml. capacity, separated by sintered glass disks and agar plugs. The calomel electrode solution was separated from the polarographic supporting electrolyte by saturated KNO_3 solution, which was changed after every run. In this way the supporting electrolyte was protected from chloride contamination, while the cell resistance was kept at so low a figure that no *IR* corrections needed to be made. In the presence of chloride, mercury is totally displaced from its EDTA complex by most metals. The agar plug was not in direct contact with the d.m.e. cell solution.

Polarograms were recorded photographically with a Sargent Heyrovsky Model XII polarograph. When $E_{1/2}$ measurements were made, the span e.m.f. was accurately measured with a Rubicon potentiometer. All measurements were at 25°. The solutions were freed from air by nitrogen bubbling.

Procedure.—The supporting electrolyte for the 0.62 *M* acetate displacements consisted of 25 ml. of 1 *M* NaOAc + 5 ml. of 1 *M* HOAc + 10 ml. of H_2O, with 0.0075% gelatin. Smaller volumes of the same composition were also used. The solution was made 1–2 m*M* in $HgY^=$ and the metal ion added in increments by micropipet. The mercury complex is subject to a mild maximum, which greatly enlarges when more than an equivalent quantity of metal ion has been added. Neither methyl orange, Triton X-100 nor Aerosol-T were as effective as gelatin, which suppressed the maximum completely at concentrations between 0.0075 and 0.01%. The maxima disappeared in dilute (0.1 m*M*) $HgY^=$ solutions.

The mercury from the electrode was allowed to accumulate at the bottom of the cell in contact with the solution. The solution was stirred only briefly after each volume increment. In view of the undesirability of interaction between displaced mercuric ion and mercury metal to give Hg_2^{++}, the influence of 15-minute bubbling in contact with mercury was observed in several equilibrium solutions. The polarograms either remained unchanged, or suffered an insignificant decrease in the height of the first wave, which did not materially influence the numerical results.

In the estimation of wave heights, residual current corrections were made, and also volume corrections where necessary. The greatest error was associated with the small second wave. These commonly overlapped the foot of the $HgY^=$ wave; the latter contribution was calculated from the wave of $HgY^=$ prior to addition of the metal ion, corrected for the proportion which had been used up in the equilibrium reaction. When this contribution was subtracted out, the i_1+i_2 readings remained constant over a satisfactory voltage interval.

The second wave could be accurately measured over only a small range of metal concentration. This range was extended (in experiments with zinc and cadmium) by exploiting the proportionality between added metal concentration and $i_1 + i_2 \sqrt{_{\mathrm{DHG}})/D_{\mathrm{M}}}$ demonstrated in Fig. 3. By extrapolating this relationship to concentrations of metal greater than that of $HgY^=$, and subtracting out the observed i, one could calculate fictitious i_2's which were an accurate measure of the equilibrium free metal concentrations. It is clear that after the disappearance of the third wave, the observed i_2 is no longer a measure of the free metal. The device was also used in estimating very small values of i_2.

The capillary characteristics were m = 2.72 mg./sec., t = 3.0 sec.

Kinetic Shifts in $E_{1/2}$ of the $HgY^=$ Wave

The rates of association of several metal-EDTA complexes[12,13] have been incidentally estimated from the kinetics of displacement reactions of the type: $M_aY^= + M_b^{++} \rightleftarrows M_bY^= + M_a^{++}$. An alternative technique is suggested here, which is applicable only when the chelate forms at least one metal complex which combines high stability with the property of being reversibly reduced to the metallic state at the dropping mercury electrode. The EDTA complex of Hg(II) exhibits these properties to a considerable degree, but unfortunately not sufficiently for a strict application of the method. It is hoped that complexes with the necessary attributes may be discovered in the future. Rapid measurement of the association rates of the less stable metal complexes of the chelate would then be possible.

Polarographic kinetics has already been applied[7,14,15] to the determination of *dis*sociation rates of certain complexes whose polarograms exhibit a kinetic wave preceding the reduction wave of the complex proper. The prewave is fed by the rapid dissociation of the unreduced complex at the drop surface to produce the free, reducible metal ion, and its height is therefore directly related to the dissociation rate.

Another type of kinetic effect is that observed in the oxidation of ascorbic acid[16]

$$H_2Q \rightleftarrows Q^* + 2H^+ + 2e \qquad (2)$$

$$Q^* \xrightarrow{k} Q \qquad (3)$$

The initial product at the electrode surface is an activated (unhydrated) dehydroascorbic acid which is in thermodynamic equilibrium with the reduced form. The concentrations in equation 2 are strictly related to the potential by the Nernst equation. The steady-state concentration of Q^* at the surface is much diminished by the drain of reaction 3. The disappearance of Q^* by a first-order reaction has precisely the same effect on the wave as would an exceptionally large diffusion coefficient for Q^*: the wave, retaining its reversible shape, is shifted to more negative potentials, the oxidation being facilitated. The shift of half-wave potential from the value when reaction 3 does not occur can be used to determine k.

A similar shift may occur when a metal complex is reduced in the presence of a metal ion of smaller complexing power. The mechanism then takes the form

$$M_aY^= + 2e \rightleftarrows M_a + Y^{-4} \qquad (4)$$

$$Y^{-4} + M_b^{++} \xrightarrow{k} M_bY^= \qquad (5)$$

The analog with the oxidation of ascorbic acid is exact, provided the following requirements are satisfied: (1) exclu-

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[11] This is consistent with the factor 1.7 × 10^4 one calculates from the equilibrium: $Hg(OAc)_2 = Hg^{++} + 2OAc^-$, $K = 3.75 \times 10^{-9}$ reported by Aditya, ref. 10.

[12] H. Ackermann and G. Schwarzenbach, *Helv. Chim. Acta*, **35**, 485 (1952).

[13] K. Bril, S. Bril and P. Krumholz, *J. Phys. Chem.*, **59**, 597 (1955).

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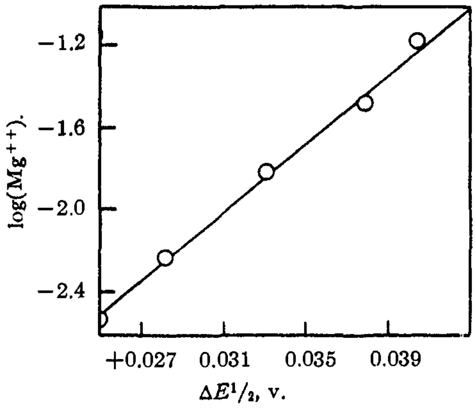

Fig. 5.—Shift in half-wave potential of $HgY^{=}$ produced by various concentrations of magnesium ion in acetate buffer. Slope = 0.0117 volt.

sively 1:1 complexes must form. (2) Electrode reaction 4 must remain strictly reversible even under the drain on Y^{-4} exerted by the subsequent reaction. This requirement is very severe and provides the greatest limitation to the application of the method. (3) The reverse rate of reaction 5 must be negligible. Otherwise the shift in $E_{1/2}$ simply corresponds to the new reversible electrode reaction

$$2e + M_aY^{=} + M_b^{++} \rightleftarrows M_a + M_bY^{=} \qquad (6)$$

(4) M)$_b^{++}$ must be present in sufficient excess to make reaction 5 pseudo first order, without at the same time displacing a significant quantity of M_a^{++}.

If k is large enough so that reaction 5 has effectively replaced diffusion as the mode of Y^{-4} removal, which is true of $\Delta E_{1/2}$ = *ca.* 30 mv.,[16] it can be shown by analogy with the ascorbic acid case that[17]

$$\Delta E_{1/2} = \frac{0.059}{2n}\log kt(M_b^{++}) + \frac{0.059}{n}\log 0.87 - \frac{0.059}{2n}\log D_Y/D_{HgY} \qquad (7)$$

at 25°, where n = no. of electrons in electrode reaction 4, t = drop time and D represents the diffusion coefficient.

As also in the conventional kinetic methods, it must be assumed that a rapid equilibration of Y^{-4} with the anionic species stable at the prevailing *p*H (*e.g.*, HY^{-3} and H_2Y^{-4}) intervenes between reactions 4 and 5, so that the apparent rate constant is the resultant of the interaction of the metal ions with various species, each with its own constant. Thus k can be set equal to $k_1a + k_2b + \ldots.$, where $a, b, \ldots$ are the fractions of the total free complex present as Y^{-4}, HY^{-3}, etc., at the prevailing *p*H.

The shifting of a metal chelate half-wave potential in the presence of other metal ions was first recognized by Bril and Krumholz,[8] in the case of $CuY^{=}$ By comparing the polarographic shift with that obtaining at the mercury jet electrode, they proved qualitatively its kinetic nature. The mercury complex was chosen in this paper to illustrate the above quantitative derivation on account of its more reversible reduction. Previous authors,[3,4] however, have reported that in the absence of excess complexing agent the wave is not completely reversible in very weakly basic and acidic solutions, and this was confirmed. The shifted waves exhibit a more reversible shape than that of $HgY^{=}$ alone.

Nitrate, borate and acetate media were investigated, of which the latter offered the most advantages. The influence of strongly complexing metal ions cannot be studied, because when present in the required excess they shift the $HgY^{=}$ wave beyond the dissolution potential. The alkaline earth ions were found to shift the wave by a convenient amount. The effect of different concentrations of magnesium sulfate on the half-wave potential of 0.5 mM $HgY^{=}$ in 0.62 M acetate (*p*H 6.4) is shown in Fig. 5. Using Schwarzenbach's data for K_{MgY} and the dissociation constants of H_4Y (measured, however, at μ = 0.1), we readily calculate that at the median magnesium concentration investigated (0.016 M) the equilibrium shift corresponding to reaction 6 would be 83 mv. instead of the observed 33 mv. The third requirement listed above is therefore amply satisfied. On the other hand, the slope of $\Delta E_{1/2}$ *vs.* log-(Mg^{++}), while constant, is not in good agreement with the theoretical 0.015. Nevertheless, to complete the calculation of k for purposes of illustration, we substitute into equation 7 the coordinates of the median point in Fig. 5, letting t = 3.0 sec. and neglecting the insignificant final term, and obtain $k = 5 \times 10^8$ sec.$^{-1}$ mol./l.

NOTE ADDED IN PROOF.—In a recent paper C. Auerbach[18] has shown that in polarograms of M^{++}, $My^{=}$ mixtures in which both species are reducible, the waves are not additive because Y^{-4} released by the reduction of $My^{=}$ diffuses out and complexes free M^{++}, thus decreasing its diffusion coefficient. In the calculation of K_{eq} in equation (1) above, ($HgY^{=}$) was set proportional to $i_2 + i_3$, on the assumption that the Hg^{++} and $HgY^{=}$ waves were additive. Although the difference in the diffusion constants of the species is only 20% an estimate of the error introduced by this effect was sought from polarograms of Hg^{++}, $HgY^{=}$ mixtures of total concentration 1.5 mM in acetate medium. The % error in the estimation of ($HgY^{=}$) from the difference $i_{total} - i_{Hg^{++}}$ was found to be:

($HgY^{=}$), mM	0.26	0.52	0.78	1.04	1.29
% error	0	−6.7	−4.6	−3.0	−1.0

The error at the smaller $HgY^{=}$ concentrations represents an overestimate of the actual error in the equilibrium experiments; for then $i_2 > i_3$, and the major part of the released Y^{-4} is scavenged by the added metal ion rather than by inflowing Hg^{++}. The error disappears completely when $i_3 = 0$, *i.e.*, when the metal ion is present in excess at the drop surface. It follows that this effect does not introduce significant errors into the equilibrium calculations. Its influence is possibly observable in Fig. 3, in which the lag in the % increase in total wave height (open circles) at a given $(Zn)^{++}$ may be caused by partial conversion of Hg^{++} to $HgY^{=}$ in the combined wave.

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(17) D. M. Kern, THIS JOURNAL, **76**, 4234 (1954), last paragraph. (The third term should read $(RT/2nF)$ ln kt.) The derivation refers to the ascorbic acid case, an oxidation; hence the negative signs. The last term in equation 7 above is introduced when $E_{1/2} - E_0$ is replaced by $\Delta E_{1/2}$.

(18) Clemens Auerbach, *Anal. Chem.*, **30**, 1723 (1958).