INTERPRETATION OF THE POLAROGRAPHIC WAVES OF COMPLEX METAL IONS

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I. INTRODUCTION

The general principles and practical applications of polarographic analysis with the dropping mercury electrode have been reviewed by Heyrovsky (4), Hohn (7), Semerano (16), Stackelberg (18), and Kolthoff and Lingane (9), among others, and Heyrovsky and Klumpar (6) have compiled a complete bibliography of this field up to 1939. Although the utility of the polarographic method as a practical analytical technique is becoming well known, the fact that the method can also be applied advantageously to more abstract problems in inorganic chemistry and electrochemistry has been less generally recognized. The purpose of this paper is to discuss the application of the polarographic technique to the study of complex metal ions in aqueous solution, with emphasis on the fundamental principles that are involved in the interpretation of the "polarographic waves."

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The study of complex metal ions by the polarographic method rests on the fact that the reduction potentials of metal ions at the dropping electrode are shifted (usually to a more negative value) by complex formation, and by measuring this shift as a function of the concentration of the complex-forming substance both the formula and the dissociation constant of the complex can be determined. *It should be emphasized that this information can only be obtained when the reduction or oxidation of the metal ion complex is reversible at the dropping electrode.* Therefore it is essential to establish the reversibility of the electrode reaction in any given case, before attempting to draw quantitative conclusions from the experimental data. For this reason, the following discussion is devoted chiefly to the derivation, and illustration by typical experimental examples, of relations that can be used for testing the reversibility at the dropping electrode of the various types of electrode reactions of complex metal ions. The fundamental principles on which these relations are based were first recognized by Heyrovsky and Ilkovič (5) in 1935.

The polarographic literature contains numerous papers dealing with the behavior of complex metal ions, chiefly from a practical analytical viewpoint (4, 6, 7, 9), but most of these studies were published prior to 1935 before the thermodynamic significance of the half-wave potential was appreciated. The older data have generally been reported in terms of the arbitrary "45° tangent reduction potential," and, since in most instances complete polarograms and other essential information are lacking, a satisfactory interpretation of this material from the modern viewpoint is virtually impossible and will not be attempted here. A complete review of the papers in this field has been given by Kolthoff and Lingane (9).

The various possible types of electrode reactions that involve complex metal ions may be divided into the following categories: (*1*) reduction to the metallic state with the formation of an amalgam on the surface of the dropping electrode; (*2*) reduction or oxidation from one ionic oxidation state to another; (*3*) stepwise reduction, resulting in the appearance of two or more separate waves; and (*4*) reduction of incompletely dissociated metal salts. The characteristics of the waves of each of these cases, with experimental examples, are discussed in the following pages.

II. REDUCTION TO THE METALLIC STATE

The reduction to the metallic state (amalgam) of a complex ion of a metal that is soluble in mercury may be represented by

$$\mathrm{MX}_p^{(n-pb)+} + ne + \mathrm{Hg} \rightleftarrows \mathrm{M(Hg)} + p\mathrm{X}^{-b} \tag{1}$$

where M(Hg) represents the amalgam formed on the surface of the dropping electrode, and X^{-b} is the complex-forming substance. It is convenient, although not strictly necessary, to regard this net reaction as the sum of the two partial reactions

$$MX_p^{(n-pb)+} \rightleftarrows M^{n+} + pX^{-b} \tag{2}$$

and

$$M^{n+} + ne + Hg \rightleftarrows M(Hg) \tag{3}$$

where M^{n+} symbolizes the "simple" or hydrated ions of the metal. The assumption of these two partial reactions is merely an artifice which assists in clarifying the thermodynamic relations that are involved, and it is not intended to indicate an actual kinetic mechanism. The following derivations are independent of the kinetics of the electrode reaction, provided that all the intermediate steps are very rapid compared to diffusion rates.

The fundamental assumption used to derive the equation of a polarographic wave is that the rates of all of the possible intermediate steps in the electrode reaction are so much more rapid than diffusion rates that the dropping electrode is subject only to concentration polarization (5). When this condition is fulfilled the electrode reaction will proceed reversibly, and the current at any point on the wave will be diffusion controlled and can be expressed in terms of the diffusion processes around the dropping electrode.

If the foregoing reactions are rapid and reversible at the dropping electrode, then the potential of the latter at any point on the wave should be given by

$$E_{d.e.} = E_{\mathrm{a}}^0 - \frac{RT}{nF_y} \ln \frac{C_{\mathrm{a}}^0 f_{\mathrm{a}}}{a_{\mathrm{Hg}} C_{\mathrm{M}}^0 f_{\mathrm{M}}} \tag{4}$$

In this equation, C_{a}^0 is the concentration of the amalgam formed on the surface of the mercury drops, C_{M}^0 is the concentration of the simple metal ions *at the electrode surface*, f_{a} and f_{M} are the corresponding activity coefficients, and a_{Hg} is the activity of the mercury on the surface of the dropping electrode. E_{a}^0 is the standard potential of the metal amalgam, which may be defined as the E.M.F. of the cell

Reference electrode | M^{n+} | M(Hg)

when the quantity $C_{\mathrm{a}}^0 f_{\mathrm{a}}/a_{\mathrm{Hg}} C_{\mathrm{M}}^0 f_{\mathrm{M}}$ is equal to 1. Since the amalgams formed on the surface of the dropping electrode are very dilute, a_{Hg} is virtually the same as the activity of pure mercury and may be regarded as a constant. Hence equation 4 may be written

$$E_{d.e.} = \epsilon - \frac{RT}{nF_y} \ln \frac{C_{\mathrm{a}}^0 f_{\mathrm{a}}}{C_{\mathrm{M}}^0 f_{\mathrm{M}}} \tag{5}$$

where the constant ϵ is equal to

$$E_{\mathrm{a}}^{0} + \frac{RT}{nF_y} \ln a_{\mathrm{Hg}} \tag{6}$$

If the dissociation of the complex ion is sufficiently rapid so that equilibrium with respect to reaction 2 is practically maintained at the electrode surface, then C_{M}^{0} can be replaced by

$$C_{\mathrm{M}}^{0} = K_{\mathrm{c}} \frac{C_{\mathrm{MX}}^{0} f_{\mathrm{MX}}}{(C_{\mathrm{X}}^{0})^{p} f_{\mathrm{X}}^{p} f_{\mathrm{M}}}$$

where K_{c} is the dissociation constant of the metal ion complex, C_{MX}^{0} and C_{X}^{0} are, respectively, the concentrations *at the electrode surface* of the complex metal ion and the complex-forming substance, X^{-b}, and the f's are activity coefficients. Therefore equation 5 becomes

$$E_{d.e.} = \epsilon + \frac{RT}{nF_y} \ln \frac{K_{\mathrm{c}} f_{\mathrm{MX}}}{f_{\mathrm{a}} f_{\mathrm{X}}^{p}} - \frac{RT}{nF_y} \ln \frac{C_{\mathrm{a}}^{0}(C_{\mathrm{X}}^{0})^{p}}{C_{\mathrm{MX}}^{0}} \tag{7}$$

The values of $E_{d.e.}$, and the various concentrations at the electrode surface, vary periodically during the life of each mercury drop, owing to the periodic change in the electrode area as each drop grows and falls (8, 9). Unless stated to the contrary, the *average* values of these quantities during the life of each drop will be understood in the following discussion.

We shall also assume that sufficient supporting electrolyte is present to eliminate the "migration current" (9, 13), so that diffusion is the sole process by which the reaction components are transferred between the electrode surface and the body of the solution.

A. Equation of the wave

In order to express the various concentrations at the electrode surface as a function of the current, we employ the fact that the diffusion layer around the mercury drops is so thin (*ca.* 0.05 mm.) that the concentration gradients are practically linear. If this assumption is valid, the concentration of the complex metal ions at the electrode surface will decrease in direct proportion to the increase in current along the wave, and we have

$$i = k_{\mathrm{c}}(C_{\mathrm{MX}} - C_{\mathrm{MX}}^{0}) \tag{8}$$

or

$$C_{\mathrm{MX}}^{0} = C_{\mathrm{MX}} - \frac{i}{k_{\mathrm{c}}} \tag{9}$$

where C_{MX} and C_{MX}^{0} are, respectively, concentrations in the body of the solution and at the electrode surface, and i is the *average* current (microamperes) during the life of each mercury drop at any given value of $E_{d.e.}$. The constant k_c is defined by the Ilkovič equation (8) and at 25°C., and when C_{MX} is expressed in millimoles per liter, it is given by (8, 9, 13)

$$k_c = 605nD_{MX}^{1/2}m^{2/3}t^{1/6} \tag{10}$$

where D_{MX} is the diffusion coefficient of the metal ion complex (cm.^{2} sec.$^{-1}$), t is the drop time (sec.), and m is the rate of flow of mercury from the dropping electrode (mg. sec.$^{-1}$). When the diffusion current, i_d, is reached, C_{MX}^0 has decreased to a constant minimal value which is negligibly small compared to C_{MX}; hence from equation 8 we have

$$i_d = k_cC_{MX} \tag{11}$$

which is the well-known linear relation between the diffusion current and concentration on which quantitative polarographic analysis is based (4, 7, 9, 13). In view of equation 11, equation 9 may be written

$$C_{MX}^0 = \frac{i_d - i}{k_c} \tag{12}$$

It will be evident that the concentration of the amalgam formed at any point on the wave must be directly proportional to the current,—

$$C_a^0 = k'i = \frac{i}{k_a} \tag{13}$$

where k_a is defined by an equation identical with equation 10, except that the square root of the diffusion coefficient of the metal in the amalgam, $D_a^{1/2}$, is employed.

Since the complex-forming substance X^{-b} is a product of the electrode reaction, its concentration at the electrode surface increases with increasing current. We have

$$C_X^0 = C_X + p\frac{i}{k_X} \tag{14}$$

where k_X is proportional to the square root of the diffusion coefficient of X^{-b} (equation 10), and C_X is the concentration of X^{-b} in the body of the solution. However, for the sake of simplicity, and since this is usually the case, we shall assume that the solution originally contains an excess of X^{-b} at a concentration that is relatively large compared to the concentration of the complex metal ion. When this condition is fulfilled, the quantity pi/k_X in equation 14 will be negligibly small, and C_X^0 can be regarded as virtually a constant and equal to C_X.

When the foregoing relations are substituted into equation 7, we obtain for the equation of the wave at 25°C., with an excess of the complex-forming substance present in the solution,

$$E_{d.e.} = E_{1/2} - \frac{0.0591}{n} \log \frac{i}{i_d - i} \tag{15}$$

The half-wave potential, $E_{1/2}$, is given by

$$E_{1/2} = \epsilon + \frac{0.0591}{n} \log \frac{K_c f_{MX} k_a}{f_a k_c} - p \frac{0.0591}{n} \log C_X f_X \tag{16}$$

Equation 15 is valuable for testing the reversibility of the reduction, as will be shown later by several experimental examples.

It will be noted that the concentration of the metal ion complex does not enter into the foregoing expression for its half-wave potential; hence $E_{1/2}$ should be constant and independent of the concentration of the complex metal ion. The fundamental reason for this is that the ratio $i/(i_d - i)$ is always equal to 1 at the midpoint of the wave, where $i = i_d/2$, and hence the log term in equation 15 becomes zero at this point regardless of the concentration of the complex metal ion. As a matter of fact, the half-wave potential exhibits this important property in any type of reversible reaction for which the equation of the wave has the symmetrical form shown by equation 15, and it has received ample experimental verification (5, 7, 9, 12, 21).

B. Determination of the coördination number

From equation 16 the half-wave potential of a complex metal ion should shift with changing activity of the complex-forming substance according to

$$\frac{\Delta E_{1/2}}{\Delta \log C_X f_X} = -p \frac{0.0591}{n} \tag{17}$$

This relation is important because it enables us to determine the coördination number p of the complex metal ion, and thus its formula. For this purpose it is usually sufficiently accurate to employ the concentration of X^{-b} in place of its activity.

C. Relation between the half-wave potential and the dissociation constant

From equation 16 we see that the half-wave potential depends on the logarithm of the dissociation constant of the complex metal ion, and it is more negative the smaller the value of K_c, i.e., the more stable the complex ion. Although K_c can be evaluated from the observed value of the half-wave potential itself, it is usually more accurate to determine it from the *difference* between the $E_{1/2}$ value of the complex metal ion and that of the corresponding simple metal ion. Lingane (12) and Stackelberg (18) have shown that the half-wave potential of a simple metal ion is expressable by

$$(E_{1/2})_s = \epsilon - \frac{0.0591}{n} \log \frac{f_a k_s}{f_s k_a} \tag{18}$$

where k_s is proportional to the square root of the diffusion coefficient of the simple metal ions, and is defined by equation 10 when $D_{\mathrm{MX}}^{1/2}$ is replaced by $D_{\mathrm{S}}^{1/2}$. Hence from equations 16 and 18 it follows that the shift of the half-wave potential by complex formation should obey the relation

$$(E_{1/2})_c - (E_{1/2})_s = \frac{0.0591}{n} \log \frac{K_c f_c k_s}{f_s k_c} - p \frac{0.0591}{n} \log C_{\mathrm{X}} f_{\mathrm{X}} \tag{19}$$

in which the subscripts "c" and "s" refer to the complex and simple metal ions, respectively. In this equation $(E_{1/2})_c$ and $(E_{1/2})_s$ are to be given their proper signs with respect to the particular reference electrode against which they are measured.

Since the best precision with which $E_{1/2}$ values can be measured is about ±3 millivolts, the retention of activity coefficient terms in the foregoing equations is usually of minor importance. Furthermore, the ratio k_s/k_c, which is equal to $(D_s/D_c)^{1/2}$, is usually so close to 1 that it also may be neglected. Hence for *approximate* purposes equation 19 can be simplified to

$$(E_{1/2})_c - (E_{1/2})_s \cong \frac{0.0591}{n} \log K_c - p \frac{0.0591}{n} \log C_{\mathrm{X}} \tag{20}$$

When a more exact result is desired, the ratio k_s/k_c can be determined experimentally from the ratio of the observed diffusion currents of the simple and complex metal ions at the same concentration and with all other conditions constant.

Instead of employing K_c explicitly, the quantity $\frac{0.0591}{n} \log K_c$ may be replaced by $E_c^0 - E_s^0$, where E_c^0 and E_s^0 are, respectively, the ordinary standard potentials of the reactions

$$\mathrm{MX}_p^{(n-pb)+} + ne \rightleftarrows \mathrm{M(s)} + p\mathrm{X}^{-b} \tag{21}$$

and

$$\mathrm{M}^{n+} + ne \rightleftarrows \mathrm{M(s)} \tag{22}$$

Equation 20 then becomes

$$(E_{1/2})_c - (E_{1/2})_s = E_c^0 - E_s^0 - p \frac{0.0591}{n} \log C_{\mathrm{X}} \tag{23}$$

D. Reduction of the biplumbite ion

The reduction of the biplumbite ion in strongly alkaline medium furnishes a good example of the practical application of the foregoing relations. A typical polarogram of 5×10^{-4} *M* lead nitrate in 1.09 *N* sodium hydroxide and 0.8 *N* potassium nitrate is shown in figure 1. To test the reversibility of the reduction, values of $i/(i_d - i)$ were carefully measured from this polarogram and the logarithms of these values are shown plotted against $E_{d.e.}$ in figure 2. As predicted by equation 15, the points of the log plot form a good straight line, whose slope of 0.029 volt is an excellent agreement with the theoretical value, 0.0296 volt, for $n = 2$. It is evident that the reduction of lead from strongly alkaline medium proceeds reversibly at the dropping electrode.

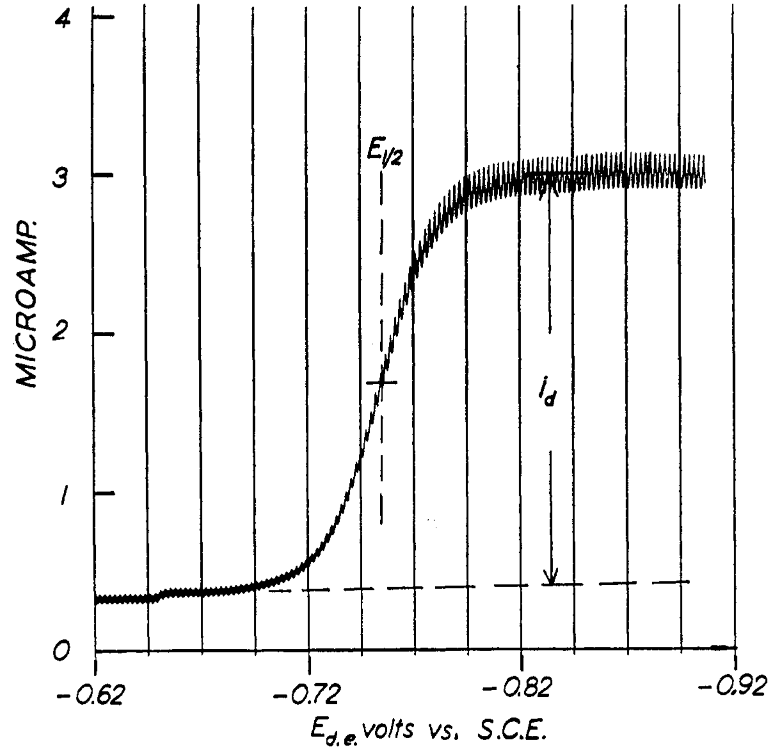

FIG. 1. Polarogram of 5×10^{-4} *M* lead nitrate in 1.09 *N* sodium hydroxide at 25°C.

The fact that the lead exists as the $HPbO_2^-$ ion in strongly alkaline solutions is demonstrated by the data in table 1 for the half-wave potential as a function of the hydroxyl-ion concentration. Polarograms were recorded in the usual way with a polarograph of the Heyrovsky–Shikata type (4, 9).

A relatively small concentration of lead was employed (*ca.* 5 × 10^{-4} *M*), so that the currents at the midpoints of the waves would be small (about 2 microamperes) and thus keep the *iR* drop in the cell negligibly small.

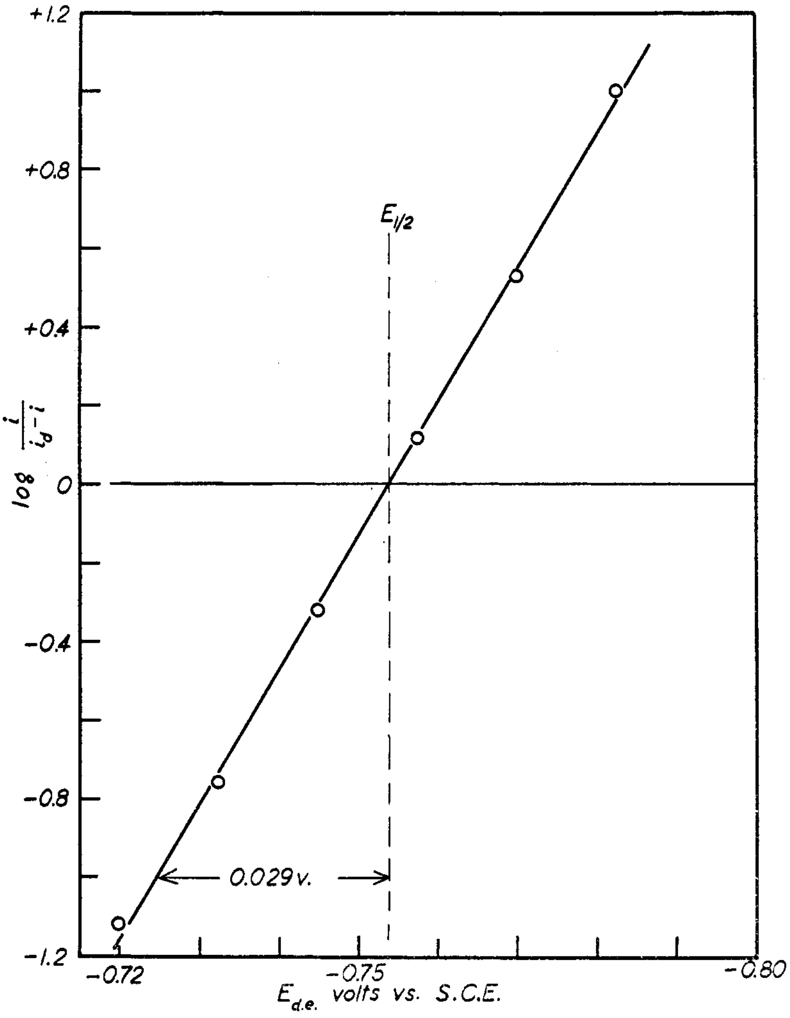

FIG. 2. Test of the equation of the wave of the biplumbite ion. Experimental points from figure 1.

In order to attain maximum precision, the total potential drop across the bridge of the polarograph was adjusted so that each revolution of the drum corresponded to only 0.025 volt of applied E.M.F. A quiet pool of mercury in the cell served as anode, and the cell was provided with a salt bridge in order that the anode potential could be measured against an external saturated calomel electrode at any time during the experiments (9, 13). The $E_{1/2}$ values were obtained by algebraic subtraction of the anode potential from the half-wave values of the total applied E.M.F. (9). With this technique the $E_{1/2}$ values were reproducible to about ±3 millivolts. No correction was made for the liquid-junction potential between the cell solution and the saturated potassium chloride solution in the calomel electrode, because experience has shown that this correction is of minor importance for the purpose of determining the value of p. Experiments 1 to 8 in table 1 were run with 0.6 to 1 N potassium nitrate as additional supporting electrolyte, but in experiments 9 to 12 no additional supporting electrolyte was present. Identical results were obtained in both series.

TABLE 1

Half-wave potential of the biplumbite ion as a function of the hydroxyl-ion concentration

Half-wave potentials with respect to the saturated calomel electrode at 25°C.

NO.	EXCESS NaOH	LOG C_{OH^-}	$E_{1/2}$
	In 0.6 to 1 N KNO_3		
	N		*volts*
1	0.011	−1.95	−0.603
2	0.038	−1.42	−0.649
3	0.060	−1.21	−0.666
4	0.099	−1.00	−0.681
5	0.201	−0.70	−0.708
6	0.448	−0.35	−0.734
7	0.702	−0.15	−0.747
8	1.09	+0.04	−0.755
	Without additional supporting electrolyte		
9	0.050	−1.30	−0.658
10	0.124	−0.91	−0.690
11	0.263	−0.58	−0.714
12	0.576	−0.24	−0.736

The data in table 1 are represented graphically in figure 3, and it is seen that the observed $E_{1/2}$ values are a linear function of log C_{OH^-}, as predicted by equations 16 and 17. The observed slope of the $E_{1/2}$ vs. log C_{OH^-} line is −0.083 volt, in satisfactory agreement with the theoretical value, which is $-\frac{3}{2} \times 0.0591$, or −0.089 volt, for $p = 3$ and $n = 2$. The small deviation of the experimental points from the theoretical slope for $p = 3$ can be attributed to the simplifying assumption that the concentration of the hydroxyl ion was equal to its activity. These data demonstrate that correction for activity coefficients is not necessary for the particular purpose of determining p. It is evident that the ionic state of the lead at hydroxyl-

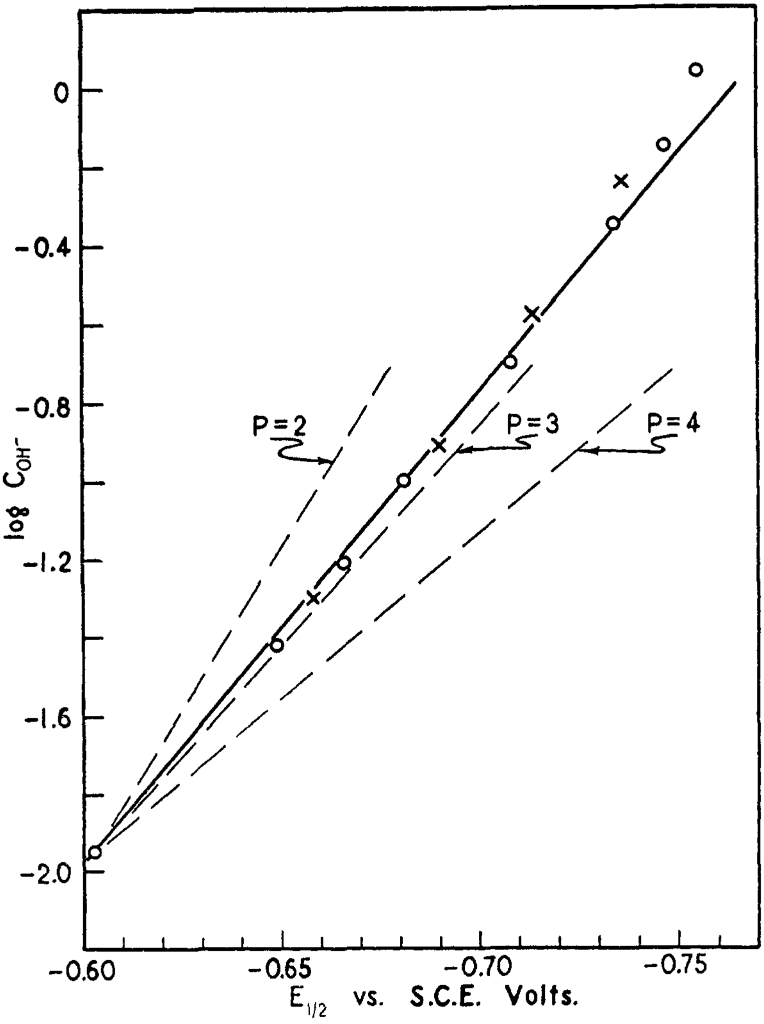

FIG. 3. Half-wave potential of lead in alkaline medium as a function of the hydroxyl-ion concentration. Data from table 1.

ion concentrations from 0.01 to 1 *N* corresponds to the biplumbite ion $HPbO_2^-$, which is reduced reversibly at the dropping electrode according to[2]

$$HPbO_2^- + 2e + H_2O + Hg \rightleftarrows Pb(Hg) + 3OH^- \tag{24}$$

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[2] According to M. Randall and H. M. Spencer (J. Am. Chem. Soc. **50**, 1572 (1928)), the ionic state of lead in sodium hydroxide solutions is $HPbO_2^-$, rather than $Pb(OH)_3^-$.

The half-wave potential of Pb^{++} in 0.1 N potassium nitrate is -0.388 volt against the saturated calomel electrode (12), and from table 1 the half-wave potential of $HPbO_2^-$ in 0.1 N sodium hydroxide (either with or without potassium nitrate present) is -0.681 volt against the saturated calomel electrode. Thus the observed difference in the half-wave potentials under these conditions is -0.29 volt. In order to calculate the theoretical difference between the half-wave potentials of $HPbO_2^-$ and Pb^{++} we shall employ the following data given by Latimer (11):

$$Pb^{++} + 2e \rightleftarrows Pb \qquad E_s^0 = -0.126 \text{ volt (N.H.E.)}$$

$$HPbO_2^- + 2e + H_2O \rightleftarrows Pb + 3OH^- \qquad E_c^0 = -0.54 \text{ volt (N.H.E.)}$$

From these data and equation 23 we have

$$(E_{1/2})_{HPbO_2^-} - (E_{1/2})_{Pb^{++}} = -0.41 - \frac{3}{2} \times 0.0591 \log C_{OH^-} \qquad (25)$$

This equation predicts that the difference between the half-wave potentials should be -0.32 volt when $C_{OH^-} = 0.1\,M$. The agreement of the observed value (-0.29 volt) with this theoretical value is quite satisfactory. The fact that the observed difference of the half-wave potentials is slightly smaller than the theoretical difference appears to be due chiefly to the fact that the measured half-wave potential of $HPbO_2^-$ includes an appreciable liquid-junction potential between the strongly alkaline cell solution and the saturated potassium chloride solution in the calomel reference electrode. Although the exact value of this liquid-junction potential is unknown, its *direction* is such that it decreases the measured half-wave potential of $HPbO_2^-$.

The ratio k_s/k_c, determined experimentally from the diffusion currents of equal concentrations of Pb^{++} and $HPbO_2^-$, respectively, was found to be 1.05, and hence so close to 1 that it was neglected in the foregoing calculations.

III. REDUCTION OR OXIDATION FROM ONE IONIC OXIDATION STATE TO ANOTHER

Various cases are known in which metal ion complexes are reduced to a lower oxidation state, or oxidized to a higher oxidation state, at the dropping electrode. We shall consider a general case in which the net electrode reaction may be represented by

$$MX_p^{(n-pb)+} + ae \rightleftarrows MX_q^{(n-a-qb)+} + (p-q)X^{-b} \qquad (26)$$

The various kinds of waves that result from this type of reaction are represented schematically in figure 4. In this figure we employ the usual convention of giving a positive sign to a cathodic current (electroreduction) and a negative sign to an anodic current (electroöxidation).

Curve 1 represents the type of wave obtained with a solution that originally contains only the oxidized form, and it is entirely cathodic. Curve 3 represents the other extreme case, in which only the reduced form is originally present in the solution, and it is entirely anodic. The type of composite cathodic–anodic curve obtained for a reversible reaction, when the solution contains both the oxidized and reduced forms at about equal concentrations, is shown by curve 2. The cathodic part of the wave above the zero line corresponds to the reduction of the oxidized form (equation 26 from left to right), while the lower anodic part of the wave is due to the oxidation of the reduced form. It should be emphasized that curves 1, 2, and 3 correspond to a reversible reaction. *When this condition is fulfilled,*

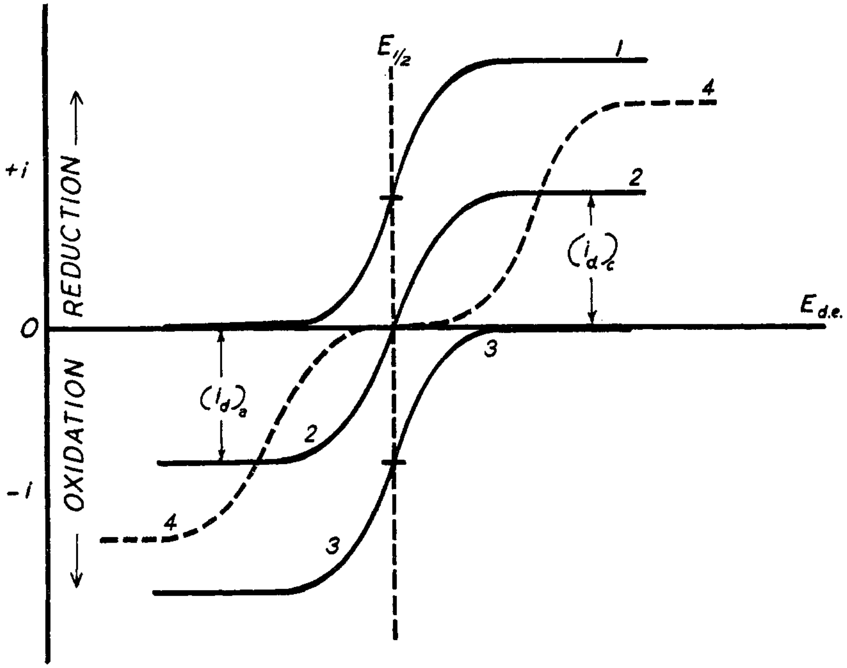

FIG. 4. Schematic representation of polarographic waves due to the reduction or oxidation of metal ions, or other substances, from one oxidation state to another. Curve 1, cathodic wave of oxidized form. Curve 2, composite cathodic–anodic wave of a mixture of the oxidized and reduced forms. Curve 3, anodic wave of the reduced form. Curve 4, composite cathodic-anodic wave of a mixture of the reduced and oxidized forms when the electrode reaction is irreversible.

the cathodic, anodic, and composite cathodic–anodic waves will have identical half-wave potentials. In such cases the dropping electrode functions simply as an "indifferent" electrode, and its potential at the point where $i = 0$ coincides with the potential that one would observe with a platinum or other noble-metal indicator electrode by the classical potentiometric technique.

When reaction 26 is irreversible at the dropping electrode, the composite cathodic–anodic wave will have the form shown by curve 4. In this case more or less overvoltage is involved in either the cathodic or anodic reactions, or both, and consequently the two half-wave potentials will not be equal.

A. Equation of the waves

A general equation of these waves will be derived on the basis of the following assumptions: (1) that the electrode reaction is reversible; (2) that sufficient supporting electrolyte is present so that the current is entirely diffusion controlled; and (3) that a sufficient excess of the complex-forming substance is present in the solution to insure that its concentration at the electrode surface will remain virtually constant and independent of the current. The potential of the dropping electrode at any point on either a cathodic, an anodic, or a composite wave will then be expressable (assuming concentrations equal to activities) by

$$E_{d.e.} = E^0 - \frac{0.0591}{a} \log \frac{C^0_{\mathrm{Red.}}}{C^0_{\mathrm{Ox.}}} - \left(\frac{p - q}{a}\right) 0.0591 \log C_{\mathrm{X}} \qquad (27)$$

In this equation, E^0 is the ordinary standard potential of reaction 26, $C^0_{\mathrm{Red.}}$ and $C^0_{\mathrm{Ox.}}$ are, respectively, the concentrations *at the electrode surface* of the complex ions in the lower and higher oxidation states, and C_{X} is the concentration of X^{-b}.

The cathodic diffusion current is directly proportional to the concentration of the oxidized form in the body of the solution,—

$$(i_d)_c = k_{\mathrm{Ox.}} C_{\mathrm{Ox.}} \qquad (28)$$

where $k_{\mathrm{Ox.}}$ is defined by equation 10. Similarly, the anodic diffusion current is directly proportional to the concentration of the reduced form in the body of the solution,—

$$-(i_d)_a = k_{\mathrm{Red.}} C_{\mathrm{Red.}} \qquad (29)$$

If we assume that the changes in the concentrations of the reduced and oxidized forms at the electrode surface are directly proportional to the current, then at each value of i we have

$$C^0_{\mathrm{Red.}} = C_{\mathrm{Red.}} + \frac{i}{k_{\mathrm{Red.}}} = \frac{-(i_d)_a + i}{k_{\mathrm{Red.}}} \tag{30}$$

and

$$C_{\mathrm{Ox.}} = C_{\mathrm{Ox.}} - \frac{i}{k_{\mathrm{Ox.}}} = \frac{(i_d)_c - i}{k_{\mathrm{Ox.}}} \tag{31}$$

In these equations i is to be given its proper sign of $(+)$ for the cathodic part of a wave and $(-)$ for the anodic part.

When the foregoing relations are substituted into equation 27 we obtain the following general equation, which is applicable to either a cathodic, an anodic, or a composite wave,

$$E_{d.e.} = E_{1/2} - \frac{0.0591}{a} \log \frac{i - (i_d)_a}{(i_d)_c - i} \tag{32}$$

and the half-wave potential is given by

$$E_{1/2} = E^0 - \frac{0.0591}{a} \log \frac{k_{\mathrm{Ox.}}}{k_{\mathrm{Red.}}} - \left(\frac{p - q}{a}\right) 0.0591 \log C_{\mathrm{X}} \tag{33}$$

Since the curve of equation 32 is symmetrical about its midpoint, the half-wave potential should be constant and independent of both the absolute and relative concentrations of the oxidized and reduced forms. The relative values of p and q can be obtained from the shift of $E_{1/2}$ as the concentration of the complex-forming substance is varied. If p happens to be equal to q, then it is evident from equation 33 that the half-wave potential should be constant and independent of the concentration of the complex-forming substance.

It should also be noted that the ratio $k_{\mathrm{Ox.}}/k_{\mathrm{Red.}}$, which is equal to $(D_{\mathrm{Ox.}}/D_{\mathrm{Red.}})^{1/2}$, can be evaluated experimentally from the ratio of the cathodic and anodic diffusion currents obtained with a solution containing equal concentrations of the oxidized and reduced forms. In most cases this ratio is sufficiently close to 1 so that it can be neglected. When this is true, the half-wave potential observed when $C_{\mathrm{X}} = 1\ M$ should practically coincide with the ordinary standard oxidation–reduction potential of the system.

B. Ferric and ferrous oxalate complexes

As a practical example of the application of the foregoing relations, we shall consider the reduction and oxidation of the complex ions formed between ferric and ferrous iron and oxalate ion;

$$\mathrm{Fe(C_2O_4)_3}^{---} + e \rightleftarrows \mathrm{Fe(C_2O_4)}_q^{(2-2q)+} + (3 - q)\mathrm{C_2O_4}^{--} \tag{34}$$

The polarographic behavior of this system has been studied by Stackelberg and Freyhold (19). The formula of the ferrous complex is written in the general form because it depends on the concentration of excess oxalate, as will be shown below.

The reversibility of this reaction at the dropping electrode is demonstrated by the polarogram in figure 5 and the log plot in figure 6. This polarogram was obtained with a mixture of about 0.001 *M* ferric iron and 0.001 *M* ferrous iron in 1 *M* potassium oxalate, and it has the expected shape of a composite cathodic–anodic wave of a reversible reaction. The part of the curve above the galvanometer zero line is due to the reduction of the trioxalato ferric ion, and the lower part to the oxidation of the oxalato ferrous ion. In order to test the reversibility of the reaction, various corresponding values of $E_{d.e.}$ and the quantity $\frac{i - (i_d)_a}{(i_d)_c - i}$ were care-

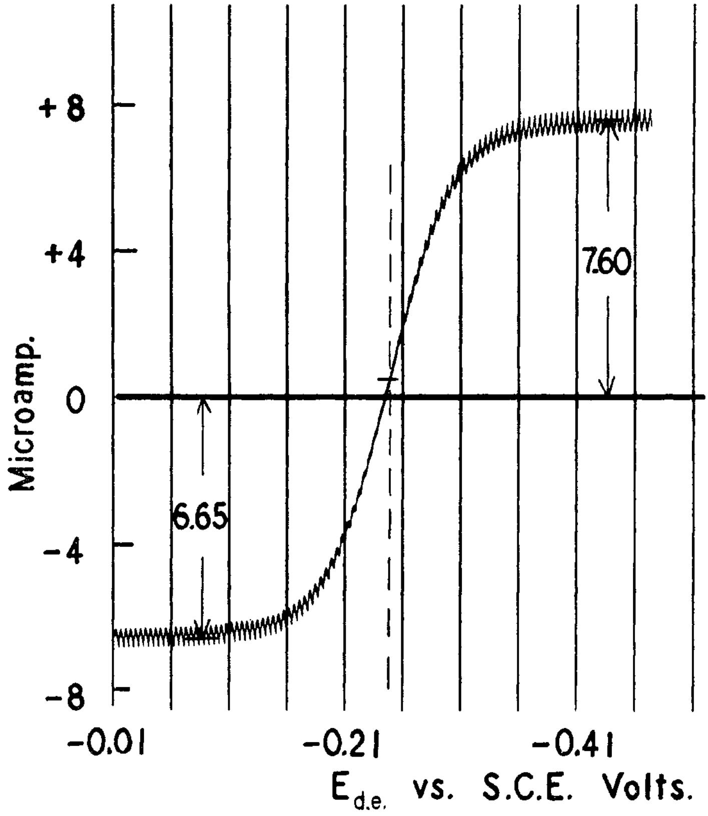

FIG. 5. Composite cathodic–anodic wave of a mixture of approximately 0.001 *M* each of ferric and ferrous iron in 1 *M* potassium oxalate at 25°C.

fully measured from the polarogram in figure 5 and are shown plotted in figure 6. In agreement with equation 32 the experimental points fall on a straight line, whose slope of 0.063 volt is in good agreement with the theoretical value, 0.059 volt, for $a = 1$.

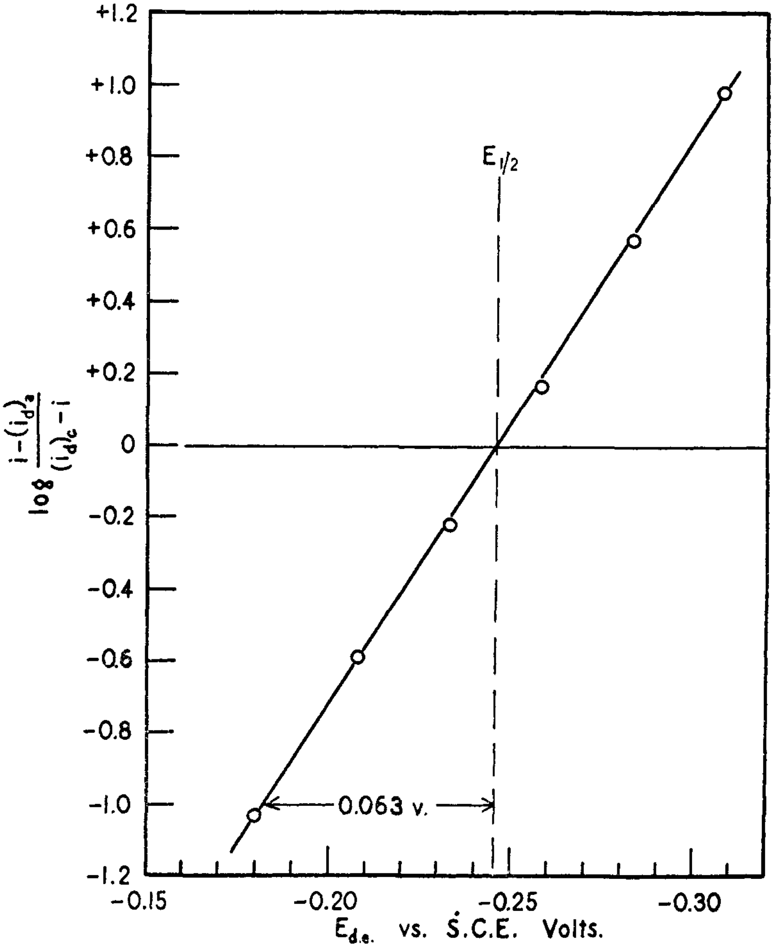

FIG. 6. Test of the reversibility of the ferric–ferrous system in oxalate medium. Experimental points from figure 5.

It will be evident from equation 33, since $k_{Ox.}$ is approximately equal to $k_{Red.}$, that the $E_{1/2}$ of reaction 34 should be practically equal to its ordinary standard potential when $C_{C_2O_4^{--}} = 1\ M$. From figures 5 and 6 the observed half-wave potential in 1 M oxalate is -0.245 volt against the saturated calomel electrode. This agrees reasonably well with the value -0.23 volt (S.C.E.) for the standard potential of this system that Shaper (17) observed by the classical potentiometric method. The polarographic value actually appears to be more reliable than Shaper's value, since he erroneously assumed that the formula of the ferrous complex was $Fe(C_2O_4)_2^{--}$, independent of the oxalate-ion concentration, and this is correct only when the concentration of excess oxalate is relatively small.

Stackelberg and Freyhold (19) stated that the half-wave potential in the reduction of the trioxalato ferric ion was constant and independent of the concentration of oxalate between 0.01 and 1 *M*. However, Mr. John Scott and the author were unable to confirm this statement. We obtained the data in table 2, which demonstrate that, although $E_{1/2}$ is constant at −0.242 ± 3 volt (S.C.E.) when the concentration of excess oxalate is greater than about 0.15 *M*, with smaller concentrations of oxalate it is shifted to a more positive value as $C_{C_2O_4^{--}}$ decreases.

TABLE 2

Half-wave potential of trioxalato ferric ion as a function of the oxalate concentration

Each solution contained 0.3 to 0.5 *N* KCl as additional supporting electrolyte. Concentration of ferric iron was 0.001 to 0.002 *M*. Temperature = 25°C.

$K_2C_2O_4$ IN EXCESS	LOG $C_{C_2O_4^{--}}$	$E_{1/2}$ AGAINST SATURATED CALOMEL ELECTRODE
M		*volts*
0.0061	−2.21	−0.179
0.0122	−1.91	−0.204
0.0193	−1.71	−0.209
0.0298	−1.53	−0.212
0.053	−1.28	−0.232
0.0747	−1.13	−0.230
0.118	−0.93	−0.236
0.158	−0.80	−0.241
0.171	−0.77	−0.242
0.357	−0.45	−0.240
0.617	−0.21	−0.245
0.817	−0.09	−0.242
1.76	+0.25	−0.242

This effect is shown more clearly by the plot of these data in figure 7. The dotted lines are the theoretical slopes predicted by equation 33 for $p - q = 1$ and $p = q$. In view of the large scale of this plot the agreement of the experimental points with the theoretical lines is reasonably satisfactory.

It is evident that $p - q = 1$ when the concentration of excess oxalate is smaller than about 0.15 *M* (with 0.001 to 0.002 *M* ferric iron), and at higher oxalate-ion concentrations q becomes equal to p. Since there is no doubt that the formula of the ferric complex is $Fe(C_2O_4)_3^{---}$, it follows that the formula of the ferrous complex is $Fe(C_2O_4)_2^{--}$ when $C_{C_2O_4^{--}}$ is less than 0.15 *M*, and that the trioxalato ferrous ion, $Fe(C_2O_4)_3^{----}$, is formed only with a larger excess of oxalate ion.

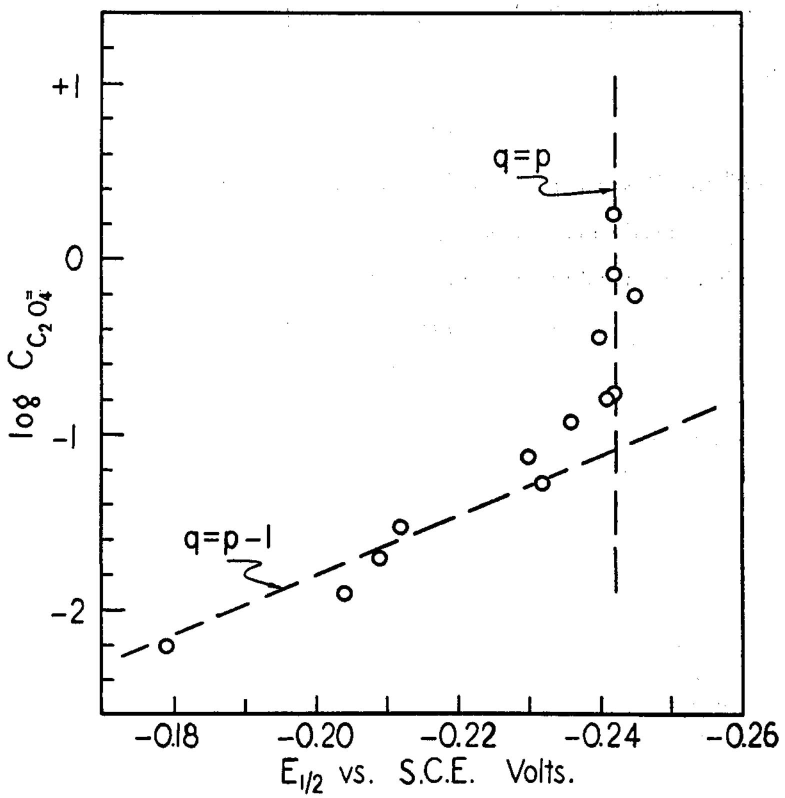

FIG. 7. Half-wave potential of trioxalato ferric ion as a function of the excess oxalate concentration. Data from table 2.

C. Relation between the half-wave potential and the dissociation constants of the oxidized and reduced complex ions

The difference between the half-wave potentials in the partial reduction of a simple metal ion and in the reduction of a complex ion of the same metal can be derived by considering the two corresponding reactions

$$M^{n+} + ae \rightleftarrows M^{(n-a)+} \tag{35}$$

and

$$MX_p^{(n-pb)+} + ae \rightleftarrows MX_q^{(n-a-qb)+} + (p-q)X^{-b} \tag{36}$$

Since the number of electrons involved is the same for both reactions, the difference between their standard potentials is equal to the standard E.M.F. of the reaction

$$\mathrm{MX}_p^{(n-pb)+} + \mathrm{M}^{(n-a)+} \rightleftarrows \mathrm{MX}_q^{(n-a-qb)+} + \mathrm{M}^{n+} + (p - q)\mathrm{X}^{-b} \tag{37}$$

We have

$$E^0_{37} = E^0_{\mathrm{c}} - E^0_{\mathrm{s}} \tag{38}$$

where E^0_{c} and E^0_{s} are the standard potentials in the reduction of the complex and simple metal ions. In turn, E^0_{37} is equal to $\dfrac{RT}{aF_y} \ln K_{37}$, where K_{37} is the equilibrium constant of reaction 37. However, it is evident that

$$K_{37} = \frac{(\mathrm{MX}_q^{(n-a-qb)+})(\mathrm{M}^{n+})(\mathrm{X}^{-b})^{p-q}}{(\mathrm{MX}_p^{(n-pb)+})(\mathrm{M}^{(n-a)+})} = \frac{K_{\mathrm{O.C.}}}{K_{\mathrm{R.C.}}} \tag{39}$$

where $K_{\mathrm{O.C.}}$ and $K_{\mathrm{R.C.}}$ are, respectively, the dissociation constants of the complex ions in the higher and lower oxidation states. It follows, therefore, that

$$E^0_{\mathrm{c}} - E^0_{\mathrm{s}} = \frac{RT}{aF_y} \ln K_{37} = \frac{RT}{aF_y} \ln \frac{K_{\mathrm{O.C.}}}{K_{\mathrm{R.C.}}} \tag{40}$$

From reasoning analogous to that in the preceding section, it can be shown that the half-wave potential in the reduction of a *simple* metal ion to a lower oxidation state (equation 35) is related to the ordinary standard potential of the reaction, E^0_{s}, by

$$(E_{1/2})_{\mathrm{s}} = E^0_{\mathrm{s}} - \frac{0.0591}{2a} \log \frac{D_{\mathrm{O.S.}}}{D_{\mathrm{R.S.}}} \tag{41}$$

where $D_{\mathrm{O.S.}}$ and $D_{\mathrm{R.S.}}$ are the diffusion coefficients of the oxidized and reduced forms of the simple metal ion, respectively, and concentrations have been assumed equal to activities. Since $D_{\mathrm{O.S.}}$ and $D_{\mathrm{R.S.}}$ will usually not differ by more than a factor of 1.5, the last term in this equation has only minor significance, and $(E_{1/2})_{\mathrm{s}}$ is practically equal to E^0_{s}. For the same reason we may neglect the second term in equation 33, and write, as a good approximation,

$$(E_{1/2})_{\mathrm{c}} = E^0_{\mathrm{c}} - \left(\frac{p - q}{a}\right) 0.0591 \log C_{\mathrm{X}} \tag{42}$$

From these relations, and equation 40, it follows that

$$(E_{1/2})_c - (E_{1/2})_s \cong E_c^0 - E_s^0 - \left(\frac{p-q}{a}\right) 0.0591 \log C_X \tag{43}$$

or

$$(E_{1/2})_c - (E_{1/2})_s \cong \frac{0.0591}{a} \log \frac{K_{\mathrm{O.C.}}}{K_{\mathrm{R.C.}}} - \left(\frac{p-q}{a}\right) 0.0591 \log C_X \tag{44}$$

The shift of the half-wave potential thus depends on the *ratio* of the dissociation constants of the oxidized and reduced complex ions, and also, of course, on the concentration of the complex-forming substance. If, as is usually the case, the oxidized complex ion is considerably more stable than the corresponding reduced form, then $K_{\mathrm{O.C.}}$ is smaller than $K_{\mathrm{R.C.}}$, and $(E_{1/2})_c$ is more negative than $(E_{1/2})_s$, when $C_X = 1\ M$. If in a particular case $K_{\mathrm{O.C.}}$ and $K_{\mathrm{R.C.}}$ should happen to be equal, then $(E_{1/2})_c$ would be more *positive* than $(E_{1/2})_s$ when C_X was less than 1 molar; the two half-wave potentials would be equal when $C_X = 1\ M$; and $(E_{1/2})_c$ would become more *negative* than $(E_{1/2})_s$ only when C_X was greater than 1 M. In general, when

$$(C_X)^{p-q} \gtreqless \frac{K_{\mathrm{O.C.}}}{K_{\mathrm{R.C.}}}$$

then $(E_{1/2})_c - (E_{1/2})_s \lesseqgtr 0$.

These relations, combined with the data in table 2, may be used to evaluate the dissociation constants of the trioxalato ferric ion and the dioxalato ferrous ion. For the reduction of the simple ferric ion we have (11)

$$\mathrm{Fe}^{+++} + e \rightleftarrows \mathrm{Fe}^{++} \qquad E_s^0 \cong (E_{1/2})_s = +0.525 \text{ volt (S.C.E.)}$$

This value is so much more positive than the potential at which anodic dissolution of mercury takes place from the dropping electrode that it is impossible to measure the half-wave potential of ferric ion directly (10). For the reduction of the trioxalato ferric ion $(E_{1/2})_c = -0.242$ volt (S.C.E.), and $p = q$ when the oxalate concentration is greater than about 0.15 M. Hence from equation 44 we have

$$0.0591 \log \frac{K_{\mathrm{Fe(C_2O_4)_3^{-3}}}}{K_{\mathrm{Fe(C_2O_4)_3^{-4}}}} = -0.242 - 0.525 = -0.767 \text{ volt}$$

and therefore

$$\frac{K_{\mathrm{Fe(C_2O_4)_3^{-3}}}}{K_{\mathrm{Fe(C_2O_4)_3^{-4}}}} = 1 \times 10^{-13} \tag{45}$$

From data obtained by Shaper (17) on the solubility of ferrous oxalate in 0.25 to 1.4 *M* potassium oxalate solutions, the dissociation constant of the trioxalato ferrous ion is found to be 6.1×10^{-7}. Combining this value with equation 45, the dissociation constant of the trioxalato ferric ion is calculated to be 6×10^{-20}.

An approximate value for the dissociation constant of the dioxalato ferrous ion can be obtained from the $E_{1/2}$ data in table 2 at oxalate-ion concentrations less than 0.15 *M*. For example, in 0.0193 *M* oxalate $(E_{1/2})_c$ is equal to -0.209 volt, and $p - q = 1$. Hence from equation 44 we obtain

$$\frac{K_{\mathrm{Fe(C_2O_4)_3^{-3}}}}{K_{\mathrm{Fe(C_2O_4)_2^{-2}}}} = 8 \times 10^{-15}$$

and employing the above value of 6×10^{-20} for $K_{\mathrm{Fe(C_2O_4)_3^{-3}}}$, the dissociation constant of the dioxalato ferrous ion comes out to be about 8×10^{-6}.

The $\mathrm{Cu(NH_3)_4^{++}} \rightarrow \mathrm{Cu(NH_3)_2^{+}}$ system furnishes another test of equation 44. The half-wave potential of the reaction

$$\mathrm{Cu(NH_3)_4^{++}} + e \rightleftarrows \mathrm{Cu(NH_3)_2^{+}} + 2\mathrm{NH_3} \tag{46}$$

is -0.214 volt (S.C.E.) in a supporting electrolyte composed of 0.2 *N* ammonium perchlorate and 1 *N* ammonia (see figure 9). It is impossible to measure experimentally the half-wave potential of the reaction $\mathrm{Cu^{++}} \rightarrow \mathrm{Cu^{+}}$, because its value is more negative than that of the reaction $\mathrm{Cu^{++}} \rightarrow \mathrm{Cu(Hg)}$ (compare equations 62 and 63), and hence in non-complex-forming supporting electrolytes simple cupric ions produce only a single wave corresponding to the latter reaction. However, if the reduction of the simple $\mathrm{Cu^{++}}$ ion is reversible, the hypothetical $E_{1/2}$ value of the reaction $\mathrm{Cu^{++}} \rightarrow \mathrm{Cu^{+}}$ will be practically equal to its standard potential. From data compiled by Latimer (11) we have

$$\mathrm{Cu^{++}} + e \rightleftarrows \mathrm{Cu^{+}} \qquad E_s^0 \cong (E_{1/2})_s = -0.079 \text{ volt (S.C.E.)}$$

$$\mathrm{Cu(NH_3)_4^{++}} \rightleftarrows \mathrm{Cu^{++}} + 4\mathrm{NH_3} \qquad K_{\mathrm{O.C.}} = 4.6 \times 10^{-14}$$

$$\mathrm{Cu(NH_3)_2^{+}} \rightleftarrows \mathrm{Cu^{+}} + 2\mathrm{NH_3} \qquad K_{\mathrm{R.C.}} = 1.4 \times 10^{-11}$$

When these data are substituted into equation 44 we obtain

$$(E_{1/2})_c = -0.079 + 0.0591 \log \frac{4.6 \times 10^{-14}}{1.4 \times 10^{-11}} = -0.226 \text{ volt (S.C.E.)}$$

as the theoretical half-wave potential of reaction 46 when $C_{\mathrm{NH_3}} = 1$ molar. This value agrees sufficiently well with the observed value, -0.214 volt, to demonstrate the general validity of equation 44. It should also be noted that in 1 *M* ammonia only about three-fourths of the cupric copper is present as the tetrammino cupric ion, and the remainder is present as the pentammino cupric ion $Cu(NH_3)_5^{++}$ (see table 3), which was neglected in the foregoing calculations.

TABLE 3

Dissociation constants of the various ammonia complexes of cuprous and cupric ions, and their relative proportions as a function of the excess ammonia concentration (according to J. Bjerrum)

The figures given are the relative proportions of the various ionic species calculated from the indicated dissociation constants. A dash signifies that the proportion of the ion is less than 0.01

NH_3 MOLARITY	CUPROUS COMPLEXES	
	$Cu(NH_3)^+$	$Cu(NH_3)_2^+$
	$K_c = 1.2 \times 10^{-6}$	$K_c = 1.35 \times 10^{-11}$
1	—	1.00
0.01	—	1.00
0.001	0.01	0.99
10^{-4}	0.11	0.89

NH_3 MOLARITY	CUPRIC COMPLEXES					
	Cu^{++}	$Cu(NH_3)^{++}$	$Cu(NH_3)_2^{++}$	$Cu(NH_3)_3^{++}$	$Cu(NH_3)_4^{++}$	$Cu(NH_3)_5^{++}$
		$K_c = 4.9 \times 10^{-5}$	$K_c = 1.05 \times 10^{-8}$	$K_c = 9.5 \times 10^{-12}$	$K_c = 4.7 \times 10^{-14}$	$K_c = 1.36 \times 10^{-13}$
1	—	—	—	—	0.74	0.26
0.01	—	—	0.03	0.32	0.65	—
0.001	—	0.08	0.40	0.44	0.08	—
10^{-4}	0.24	0.50	0.23	0.03	—	—
10^{-5}	0.82	0.17	0.01	—	—	—

IV. STEPWISE REDUCTION OF COMPLEX METAL IONS

When the free energies of the various possible oxidation states of a complex metal ion are sufficiently different, reduction from a higher to a lower oxidation state can proceed in stages at the dropping electrode to produce a polarogram consisting of two or more separate waves. We shall consider a general case in which the polarogram consists of two waves, as shown in figure 8, which correspond to the two consecutive reactions

$$MX_p^{(n-pb)+} + ae \rightleftarrows MX_q^{(n-a-qb)+} + (p - q)X^{-b} \qquad (47)$$

and

$$MX_q^{(n-a-qb)+} + (n - a)e + Hg \rightleftarrows M(Hg) + qX^{-b} \qquad (48)$$

If these reactions are reversible at the dropping electrode, the potential of the latter at points on the first wave will be governed by reaction 47, and it will obey the relation

$$E_{d.e.} = E_1^0 - \frac{RT}{aF_y} \ln \frac{C^0_{\mathrm{Red.}} C_{\mathrm{X}}^{(p-q)}}{C^0_{\mathrm{Ox.}}} \tag{49}$$

where E_1^0 is the standard potential of reaction 47. It will be evident that the first wave corresponds in every respect to the case discussed in the preceding section. Hence the equation of the first wave will be equation 32 (with $(i_d)_a$ equal to zero), and the half-wave potential of the first wave ($E'_{1/2}$ in figure 8) will be given by equation 33.

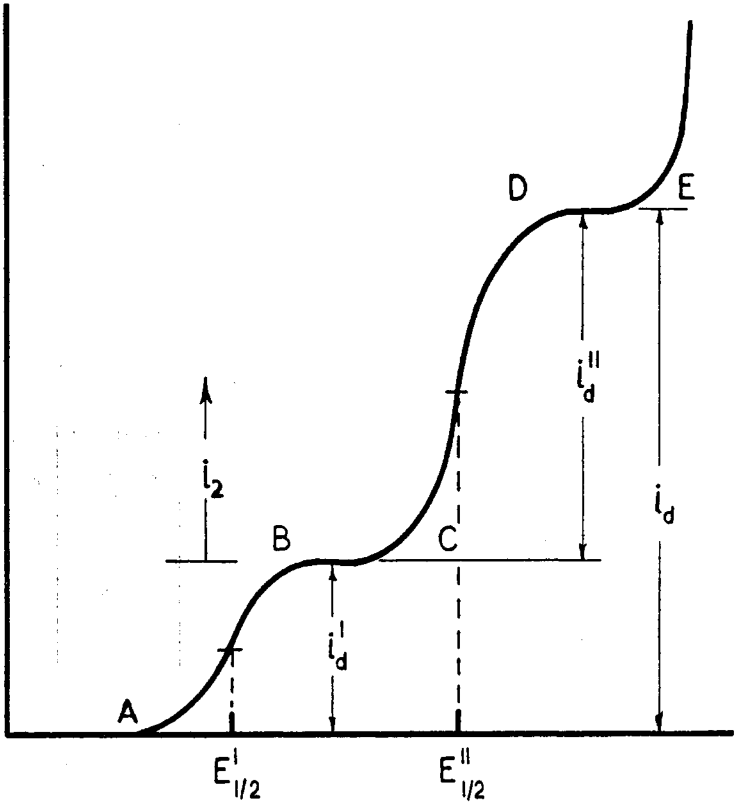

FIG. 8. Schematic polarogram of a stepwise reduction

At points on the second wave the potential of the dropping electrode is governed by reaction 48, and is given by

$$E_{d.e.} = E_2^0 - \frac{RT}{(n-a)F_y} \ln \frac{C_a^0 C_{\mathrm{X}}^q}{C^0_{\mathrm{Red.}}} \tag{50}$$

where E_2^0 is the standard potential of reaction 48.

Although the potential of the dropping electrode is governed by different reactions on the first and second waves, the *current* at any point on *either* wave is controlled by the rate of diffusion of the oxidized complex ions. If we neglect the slight effect on the diffusion current of the decrease in drop time with increasing negative potential (8, 9, 13), then it follows from the Ilkovič equation (equation 19) that the following relations will hold for the first and second diffusion currents *taken separately,*

$$i_d' = k'aD_{\mathrm{Ox.}}^{1/2}C_{\mathrm{Ox.}} = k_1C_{\mathrm{Ox.}} \tag{51}$$

and

$$i_d'' = k'(n - a)D_{\mathrm{Ox.}}^{1/2}C_{\mathrm{Ox.}} = k_2C_{\mathrm{Ox.}} \tag{52}$$

where in both cases $D_{\mathrm{Ox.}}$ is the diffusion coefficient of the oxidized form, and $C_{\mathrm{Ox.}}$ is its concentration in the body of the solution. The ratio of the two separate diffusion currents is equal to $a(n - a)$. The *total* diffusion current at *DE* in figure 8 is given by

$$i_d = i_d' + i_d'' = k'nD_{\mathrm{Ox.}}^{1/2}C_{\mathrm{Ox.}} = kC_{\mathrm{Ox.}} \tag{53}$$

At points on the first wave (*A* to *B*, figure 8) the concentration of the reduced complex ions at the surface of the dropping electrode is given by

$$(C^0_{\mathrm{Red.}})_{A\rightarrow B} = \frac{i}{k_{\mathrm{Red.}}} \tag{54}$$

When the first diffusion current is reached (*B* to *C* in figure 8) $C^0_{\mathrm{Red.}}$ attains a maximal value, and from equations 51 and 54 this maximal value is expressable by

$$(C^0_{\mathrm{Red.}})_{B\rightarrow C} = \frac{i_d'}{k_{\mathrm{Red.}}} = \frac{k_1C_{\mathrm{Ox.}}}{k_{\mathrm{Red.}}} = \left(\frac{D_{\mathrm{Ox.}}}{D_{\mathrm{Red.}}}\right)^{1/2}C_{\mathrm{Ox.}} \tag{55}$$

If the diffusion coefficients of the oxidized and reduced forms happen to be equal, then the maximal concentration of the reduced form present at the electrode surface when the first diffusion current is reached will be equal to the concentration of the oxidized form in the body of the solution.

As the potential is increased beyond point *C* the value of $C^0_{\mathrm{Red.}}$ decreases again, and it finally becomes practically equal to zero when the second diffusion current is reached at *D*. On the other hand, the concentration of the oxidized form at the electrode surface will have decreased to practically zero when point *B* is reached, and it will remain negligibly small at all values of the potential beyond *B*. If we assume that $C^0_{\mathrm{Red.}}$ decreases in direct proportion to the increase in current (in excess of i_d') at points on the second wave, we have

$$(C^0_{\mathrm{Red.}})_{C\rightarrow D} = \frac{i_d'}{k_{\mathrm{Red.}}} - bi_2 \tag{56}$$

where i_2 is the total current minus i'_d (see figure 8). Since $C^0_{\text{Red.}}$ becomes practically zero at point D, it is evident that the constant b is given by

$$b = \frac{i'_d}{k_{\text{Red.}}\, i''_d} = \frac{a}{k_{\text{Red.}}(n - a)} \tag{57}$$

and hence equation 56 becomes

$$(C^0_{\text{Red.}})_{C \to D} = \frac{i'_d}{k_{\text{Red.}}\, i''_d}(i''_d - i_2) = \frac{a}{k_{\text{Red.}}(n - a)}(i''_d - i_2) \tag{58}$$

When these relations are substituted into equation 50, we obtain for the equation of the second wave, when an excess of X^{-b} is present,

$$E_{d.e.} = E''_{1/2} - \frac{0.0591}{(n - a)} \log \frac{i_2}{i''_d - i_2} \tag{59}$$

where $E''_{1/2}$ is given by

$$E''_{1/2} = E^0_2 - \frac{0.0591}{(n - a)} \log \frac{k_{\text{Red.}}(n - a)}{k_a a} - q\, \frac{0.0591}{(n - a)} \log C_{\text{X}} \tag{60}$$

A. Copper-ammonia complexes

The double waves obtained in the reduction of various cupric complexes serve as good examples to test the foregoing relations, particularly the double wave in ammoniacal medium, which has been studied in detail by Stackelberg and Freyhold (19).

In the absence of complex-forming substances, simple cupric ions (actually tetraquo cupric ions, $Cu(H_2O)_4^{++}$) are reduced directly to the metallic state at the dropping electrode and the polarogram shows only a single wave. The reason for this is evident from the standard potentials of the following reactions,

$$Cu^+ + e + Hg \rightleftarrows Cu(Hg) \qquad E^0 = +0.108 \text{ volt (N.C.E.)} \tag{61}$$

$$Cu^{++} + 2e + Hg \rightleftarrows Cu(Hg) \qquad E^0 = -0.003 \text{ volt (N.C.E.)} \tag{62}$$

$$Cu^{++} + e \rightleftarrows Cu^+ \qquad E^0 = -0.115 \text{ volt (N.C.E.)} \tag{63}$$

The potentials of reactions 61 and 62 were calculated from the standard potentials of the corresponding reactions involving the solid metal (11) and the known solubility of copper in mercury, by means of relations that have been discussed elsewhere (12, 18). Since the potential of the $Cu^+ \rightarrow Cu(Hg)$ system is more positive than that of the $Cu^{++} \rightarrow Cu(Hg)$ system, cuprous ions are incapable of stable existence at the potential at which cupric ions are reduced, and hence the polarogram of a solution of simple cupric ions shows only the single wave corresponding to $Cu^{++} \rightarrow Cu(Hg)$.

However, if some substance which forms stable complex ions with cupric and cuprous ions, or with cuprous ions alone, is added to a cupric salt solution, then the standard potential and the half-wave potential of the $Cu^+ \rightarrow Cu(Hg)$ system will usually be shifted in the negative direction to a greater extent than that of the $Cu^{++} \rightarrow Cu^+$ system, and the polarogram shows a double wave. This is due to the fact that the shift of the $Cu^{++} \rightarrow Cu^+$ half-wave potential is proportional to $\log \frac{K_{\text{O.C.}}}{K_{\text{R.C.}}}$ (see equation 44), whereas the shift of the half-wave potential of the $Cu^+ \rightarrow Cu(Hg)$ system is proportional to $\log K_{\text{R.C.}}$ alone (see equation 20), which ordinarily is a much larger negative quantity than $\log \frac{K_{\text{O.C.}}}{K_{\text{R.C.}}}$. The effect of this unequal shift is evident by comparing the foregoing standard potentials of the simple cupric and cuprous ions with the values for the corresponding ammonia complexes, which are as follows (11, 19):

$$Cu(NH_3)_2^+ + e + Hg \rightleftarrows Cu(Hg) + 2NH_3 \qquad E^0 = -0.522 \text{ volt (N.C.E.)} \tag{64}$$

$$Cu(NH_3)_4^{++} + 2e + Hg \rightleftarrows Cu(Hg) + 4NH_3 \qquad E^0 = -0.397 \text{ volt (N.C.E.)} \tag{65}$$

$$Cu(NH_3)_4^{++} + e \rightleftarrows Cu(NH_3)_2^+ + 2NH_3 \qquad E^0 = -0.262 \text{ volt (N.C.E.)} \tag{66}$$

The order of these potentials is just the reverse of those for the corresponding simple ions.

In 1 molar ammonia solution the potential required to reduce the $Cu(NH_3)_2^+$ ion is so much more negative than that at which the $Cu(NH_3)_4^{++}$ ion is reduced to $Cu(NH_3)_2^+$ that the polarogram consists of two separate waves of equal height, as shown in figure 9. The first wave corresponds to $Cu(NH_3)_4^{++} \rightarrow Cu(NH_3)_2^+$, and the second to $Cu(NH_3)_2^+ \rightarrow Cu(Hg)$. Similar double waves are obtained with the thiocyanate (14), pyridine (14), and chloride complexes (19) of copper.

The reversibility of both stages of the reduction of the $Cu(NH_3)_4^{++}$ ion is easily demonstrable by comparing the difference in potential between two given points on each of the two waves in figure 9 with the theoretical values predicted by the equations of the waves. The values of $E_{d.e.}$ at $i = (1/4)i_d$ and $i = (3/4)i_d$ are convenient reference points. Whenever the equation of the wave of any type of reaction has the familiar symmetrical form

$$E_{d.e.} = E_{1/2} - \frac{0.0591}{n} \log \frac{i}{i_d - i} \tag{67}$$

then

$$E_{3/4} - E_{1/4} = -\frac{0.0591}{n} \log \frac{3}{1/3} = \frac{0.058}{n} \tag{68}$$

This relation was originally suggested by Tomeš (21) as a criterion of reversibility.

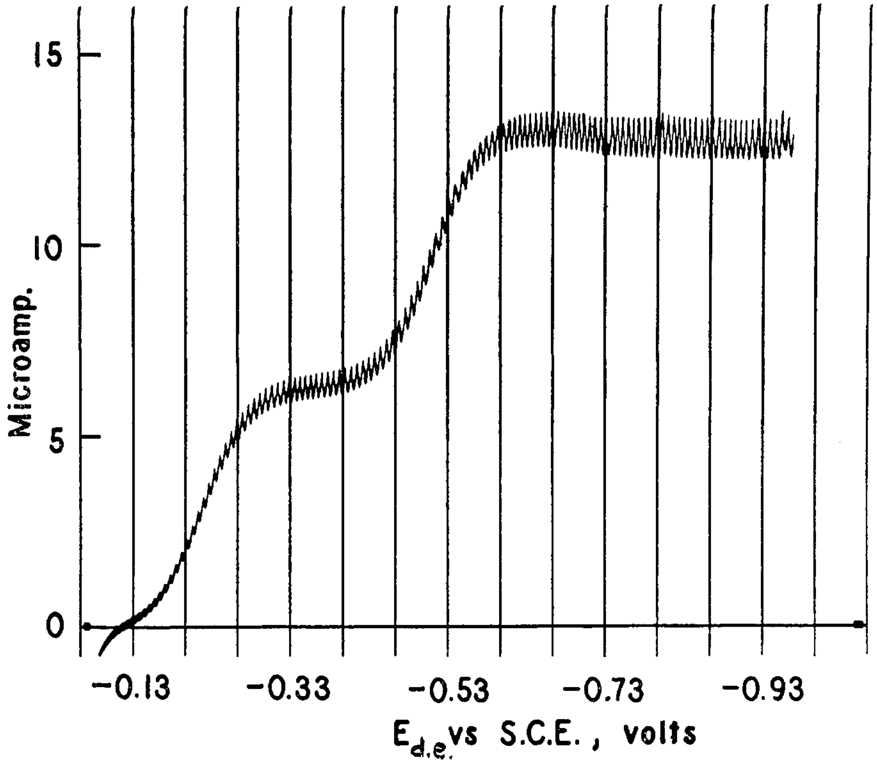

FIG. 9. Polarogram of a solution of 0.002 M $Cu(NH_3)_4^{++}$ in 0.2 N ammonium perchlorate and 1 N ammonia, plus 0.01 per cent gelatin as a maximum suppressor.

In the reduction of the $Cu(NH_3)_4^{++}$ ion each wave is due to a one electron change, and hence for each wave $E_{3/4} - E_{1/4}$ should be equal to -0.058 volt. From the polarogram in figure 9 the observed values of $E_{3/4} - E_{1/4}$ are -0.064 volt for the first wave and -0.058 volt for the second, in good agreement with the theoretical value.

Stackelberg and Freyhold (19) investigated the influence of the ammonia concentration on the half-wave potentials of the ammonia–cupric complex. Their experimental results are shown in figure 10, in which the circles are experimental points. The curves in this graph are the theoretical curves calculated by Stackelberg and Freyhold. The agreement of the experimental points with the theoretical curves is quite satisfactory.

In the calculation of the theoretical curves in figure 10, Stackelberg and Freyhold took account of the fact that cupric ion forms a series of different ammonia complexes from Cu(NH$_3$)$^{++}$ to Cu(NH$_3$)$_5^{++}$, and that cuprous ion forms the two complexes Cu(NH$_3$)$^+$ and Cu(NH$_3$)$_2^+$, depending on the concentration of excess ammonia. From the dissociation constants of these various complexes, as determined by J. Bjerrum (1), their relative proportions in different concentrations of excess ammonia can be calculated. This is shown in table 3, which is an expansion of a similar tabulation given by Stackelberg and Freyhold.

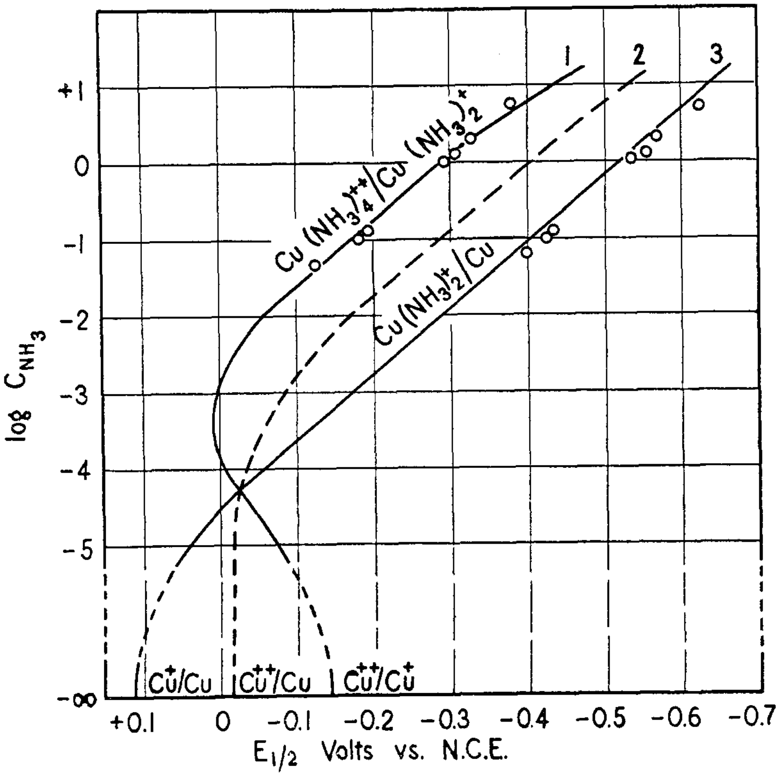

FIG. 10. Half-wave potentials of tetrammino cupric ion and diammino cuprous ion as a function of the ammonia concentration. The lines are theoretical curves, and the circles are experimental points (according to Stackelberg and Freyhold).

It is seen that the predominant cuprous complex is the diammino cuprous ion, and the proportion of the monammino cuprous ion is negligible for the present purpose. In the case of the cupric complexes, the tetrammino ion $Cu(NH_3)_4^{++}$ predominates at concentrations of ammonia between about 0.05 and 1 *M*. When the concentration of excess ammonia is decreased below 0.05 *M* the lower order complexes are formed in increasing amount, and at 10^{-4} *M* ammonia the monammino cupric ion, $Cu(NH_3)^{++}$, predominates. These facts are responsible for the *positive* shift of the half-wave potential of the $Cu^{++} \rightarrow Cu^+$ system at very small concentrations of ammonia, shown by curve 1 in figure 10.

From equation 44 the shift of the half-wave potential of the $Cu^{++} \rightarrow Cu^+$ system by formation of the ammonia complexes should follow the equation

$$(E_{1/2})_c - (E_{1/2})_s = 0.0591 \log \frac{K_{ic}}{K_{ous}} - (p - q)0.0591 \log C_{NH_3} \qquad (69)$$

where K_{ic} and K_{ous} are the dissociation constants of the particular cupric and cuprous complexes that predominate at a given concentration of ammonia. The positive shift of the $E_{1/2}$ of the $Cu^{++} \rightarrow Cu^+$ system at very small concentrations of excess ammonia is due to two factors. In the first place, when C_{NH_3} is less than about 5×10^{-4} molar the predominant cupric complexes are the $Cu(NH_3)_2^{++}$ and $Cu(NH_3)^{++}$ ions, and since both of these complexes have larger dissociation constants than the diammino cuprous ion, the quantity $\log \frac{K_{ic}}{K_{ous}}$ in equation 69 has a positive value when they predominate. Furthermore, at small concentrations of ammonia where the $Cu(NH_3)_2^{++}$ and $Cu(NH_3)^{++}$ ions predominate, $p - q$ in equation 69 becomes equal to 0 and -1, respectively. Both of these factors shift $E_{1/2}$ in the positive direction. The inflection point in curve 1 at C_{NH_3} equal to about 5×10^{-4} *M* is due to the fact that the $Cu(NH_3)_2^{++}$ ion predominates, and hence $p = q$ at this concentration of ammonia.

The dotted curve 2 is the hypothetical curve corresponding to direct reduction of the ammonia–cupric complexes to the metallic state (amalgam). This curve is unattainable experimentally, because no $Cu(NH_3)_4^{++}$ ions exist at the surface of the dropping electrode, and the copper is present entirely as the diammino cuprous ion, at potentials more negative than that at which the first diffusion current is reached.

V. ANALYSIS OF THE WAVE OF AN INCOMPLETELY DISSOCIATED METAL SALT: MERCURIC CYANIDE

Tomeš (21) has made a careful polarographic study of the reduction of the weak electrolyte mercuric cyanide, a case which has much in common with the reduction of complex metal ions. The net electrode reaction which controls the current is

$$Hg(CN)_2 + 2e \rightleftarrows Hg + 2CN^- \qquad (70)$$

Since the activity of the deposited mercury is constant, the potential of the dropping electrode will be given by

$$E_{d.e.} = E^0 - \frac{0.0591}{2} \log \frac{(C^0_{\mathrm{CN^-}})^2}{C^0_{\mathrm{Hg(CN)_2}}} \tag{71}$$

where E^0 is the standard potential of reaction 70.

Tomeš (21) studied the reduction of mercuric cyanide in buffered solutions *that did not contain excess cyanide,* and under this condition the concentration of CN^- at the electrode surface is a function of the current. Since hydrocyanic acid is very weak ($K_a = 7.2 \times 10^{-10}$), the CN^- ions liberated at the electrode surface are more or less completely hydrolyzed to HCN, depending on the pH of the solution. At any given pH value we have

$$C^0_{\mathrm{CN^-}} = K_a \frac{C^0_{\mathrm{HCN}}}{C^0_{\mathrm{H^+}}} = 7.2 \times 10^{-10} \frac{C^0_{\mathrm{HCN}}}{C^0_{\mathrm{H^+}}} \tag{72}$$

If we represent the sum of the concentrations of CN^- and HCN at the electrode surface by C^*, then

$$C^* = C^0_{\mathrm{HCN}} + C^0_{\mathrm{CN^-}} = \frac{i}{k_1} \tag{73}$$

and, combining this relation with equation 72, we obtain

$$C^0_{\mathrm{CN^-}} = \frac{K_a i}{(K_a + C^0_{\mathrm{H^+}})k_1} \tag{74}$$

It will also be evident that

$$C^0_{\mathrm{Hg(CN)_2}} = \frac{i_d - i}{k_2} \tag{75}$$

When these relations are substituted into equation 71 we obtain, for the equation of the wave when the solution does not contain excess cyanide,

$$E_{d.e.} = \epsilon' - 0.0591 \log \frac{K_a}{K_a + C^0_{\mathrm{H^+}}} - 0.0296 \log \frac{i^2}{i_d - i} \tag{76}$$

where the constant ϵ' is equal to $E^0 - 0.0296 \log \frac{k_1}{k_2}$.

Equation 76 predicts that the wave of mercuric cyanide should have the following characteristics: (*1*) In a well-buffered solution a plot of $E_{d.e.}$ *versus* log $\frac{i^2}{i_d - i}$ should produce a straight line with a slope of 0.0296 volt at 25°C. (*2*) Because of the i^2 term, the wave is unsymmetrical about its midpoint and the half-wave potential should shift by 0.0296 volt to a more negative value for a tenfold increase in the concentration of mercuric cyanide. (*3*) Since K_a is about 10^{-9}, it becomes negligibly small compared to $C^0_{H^+}$ when the pH is smaller than about 8. Hence, at pH values less than about 8, the half-wave potential should shift by 0.059 volt to a more positive value for each unit decrease in the pH of the buffer, provided that the concentration of mercuric cyanide is kept constant. On the other hand, when the pH is greater than about 10, $C^0_{H^+}$ becomes negligibly small compared to K_a, and hence, at a constant concentration of mercuric cyanide, the half-wave potential should become constant and independent of the pH when the latter is greater than 10.

The experimental data obtained by Tomeš are in good agreement with these predictions at pH values less than 10. In more alkaline solutions Tomeš observed deviations from the theoretical relations, which he logically ascribed to the formation of complex $Hg(CN)_4^{--}$ ions at the electrode surface, due to the relatively large proportion of free CN^- ions present at a pH greater than 10. The formation of this complex was neglected in the foregoing derivations, but it will be evident that it could be taken into account from a consideration of the equilibrium $Hg(CH)_2 + 2CN^- = Hg(CN)_4^{--}$.

VI. POLAROGRAPHIC WAVES DUE TO IRREVERSIBLE REDUCTION OF COMPLEX METAL IONS

The foregoing derivations were based on the assumption that the dissociation and reduction of complex metal ions are rapid reversible processes. Although, as already shown, this assumption is valid in many cases, it is not always true; the rate of formation and dissociation of certain complex metal ions is often quite slow. In the reduction or oxidation of such complexes at the dropping electrode, other polarization effects in addition to concentration polarization come into play, and an exact interpretation of the wave becomes very difficult. In such cases the equation of the wave will involve, among other factors, the rate constant of the slow step in the electrode reaction. Since a satisfactory quantitative analysis of such irreversible waves has not yet been obtained, the following remarks will be limited to a brief description of some of the experimental observations that have been reported.

The slow dissociation of certain complex metal ions is strikingly illustrated by the results obtained by Pines (15) in his polarographic study of the cyanide complexes of zinc. Pines found that the polarograms of saturated solutions of zinc cyanide in 0.001 to 0.01 *N* potassium cyanide consist of three distinct waves, with $E_{1/2}$ values of -1.0 volt, -1.2 volts, and -1.4 volts against the saturated calomel electrode. These waves obviously cannot be due to stepwise reduction to intermediate oxidation states since none exist, and Pines concluded that they were due to the reduction of three different species of zinc–cyanide complexes whose rate of dissociation and interconversion is so slow that each one produces its own characteristic wave. This conclusion is strengthened by further experiments performed by Pines, in which he added increasing amounts of potassium cyanide to a 5×10^{-4} *M* zinc chloride solution (no other supporting electrolyte). When the concentration of cyanide was smaller than 4×10^{-4} *N*, the polarogram showed only the first wave at −1.0 volt. When the cyanide-ion concentration was increased above 4×10^{-4} *N*, the height of the first wave steadily decreased, and the two other waves at −1.2 and −1.4 volts appeared and gradually increased in height until the cyanide-ion concentration was about 2×10^{-3} *N*, at which point the first wave had disappeared. With further increase in the concentration of cyanide, the remaining waves at −1.2 volts and −1.4 volts decreased in height, and the wave at −1.2 volts disappeared when the cyanide concentration was greater than about 0.003 *N*. With further increase in the cyanide concentration the last remaining wave at −1.4 volts also disappeared, and no wave at all was observed when the concentration of cyanide was greater than ten times that of the zinc salt. Pines concluded that the first wave at −1.0 volt is due to the reduction of simple Zn^{++} ions, the second at −1.2 volts to the $Zn(CN)_4^{--}$ ion, the third at −1.4 volts to $Zn(CN)_5^{---}$, and with a large excess of cyanide $ZN(CN)_6^{----}$ is apparently formed, the reduction potential of which is more negative than that of potassium ions. The fact that separate waves were observed shows that the rate of conversion of one complex into the other is relatively slow, as otherwise the higher complexes would simply have dissociated into the lower more easily reducible one when its reduction potential was reached, and only a single wave would have been obtained.

It should also be mentioned that Herman (3) has obtained polarographic evidence that the rates of dissociation of gold–cyanide and gold–hydroxide complexes, and the rate of conversion of one complex into the other, are relatively slow. When excess cyanide was added to an alkaline gold solution the characteristic wave of the auric–hydroxide complex persisted, and when excess sodium hydroxide was added to a solution containing the auric–cyanide complex the characteristic wave of the cyanide complex remained unchanged. The latter result is not surprising, since the cyanide complex is the more stable of the two, but the first experiment shows that the rate of conversion of the hydroxide complex into the cyanide complex is very slow.

Some observations of Brdička (2) are also of interest in this connection. In neutral solutions of cobaltous chloride he observed a small "pre-wave" which preceded the main cobaltous wave by about 0.2 volt. The pre-wave disappeared when the solution was acidified, which led Brdička to conclude that it was due to the reduction of the pentaquo-hydroxy cobaltous ion,

$[Co(H_2O)_5OH]^+$, formed by hydrolysis of the hexaquo cobaltous ion. The fact that the pre-wave was obtained indicates that the equilibrium

$$Co(H_2O)_6^{++} = Co(H_2O)_5OH^+ + H^+$$

is established quite slowly.

The reduction of the aquo complex ions of certain heavy metals is often more irreversible than that of the other complexes of these metals. For example, in non-complex-forming supporting electrolytes the half-wave potential of the hexaquo nickel ion is -1.05 volt against the saturated calomel electrode, a value more than 0.5 volt more negative than one would predict from the standard potential of nickel. This fact and the small slope of the wave shows that the reduction of the $Ni(H_2O)_6^{++}$ ion is very irreversible. When thiocyanate is added to the solution to form the thiocyanate complex (probably $Ni(CNS)_4^{--}$), the half-wave potential is *decreased* to -0.68 volt, and the slope of the wave becomes much steeper, indicating a fairly reversible reduction (14). Similar results were obtained by Lingane and Kerlinger (14) when pyridine was added to a nickel solution to form the pyridine complex.

A similar behavior was noted by Brdička (2) in the case of cobalt. He found that pink solutions of cobaltous chloride, in which the cobalt is present chiefly as $Co(H_2O)_6^{++}$, are reduced very irreversibly. When a large excess of chloride (5 *M* calcium chloride) was added to form the blue chloro complex ions, the reduction potential was shifted by about 0.3 volt to a more *positive* value, and the increased slope of the wave indicated a more reversible reduction.

The author has observed this same effect in the reduction of indium ions. From perchlorate solutions the reduction of the hexaquo indic ion, $In(H_2O)_6^{+++}$, is irreversible and requires a large overvoltage, but the reduction of the chloro indic complex ions, formed by adding excess chloride to the solution, is reversible (12).

Strubl (20) has shown that the shape of the composite cathodic–anodic wave of a mixture of simple titanic and titanous ions is like curve 4 in figure 4; the cathodic and anodic reactions are both irreversible. However, the complex ions formed by adding citrate or tartrate to the titanic–titanous solution are reversibly reduced and oxidized, and the shape of the composite wave of the complexes is like curve 2 in figure 4.

The magnitude and direction of the shift of the half-wave potential with temperature is often a very useful criterion of the reversibility of a given electrode reaction, and it can be used to supplement the tests for reversibility that have been described above. When an electrode reaction is irreversible, $E_{1/2}$ is usually (although not invariably) shifted to a more positive value with increasing temperature (easier reduction), and the magnitude of the temperature coefficient is several times larger than that of a reversible reaction. This effect has been observed by Brdička (2) and by Mr. H. Kerlinger and the author, in the irreversible reduction of the $Co(H_2O)_6^{++}$ and $Ni(H_2O)_6^{++}$ ions. The excessively large temperature coefficient is related to the activation energy of the irreversible step in the electrode reaction.

These examples illustrate the caution that must be observed in the interpretation of the waves of certain complex metal ions. The tests described in the preceding sections must always be applied to establish the reversibility of the electrode reaction in any given case before quantitative conclusions can be drawn regarding the formula and dissociation constant of the complex.

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