I. THE ELECTROCHEMISTRY OF CERTAIN METAL CATIONS IN PYROPHOSPHATE MEDIA

II. A THEORETICAL STUDY OF CHRONOPOTENTIOMETRY AND CHRONOAMPEROMETRY AT UNSHIELDED ELECTRODES

III. DETERMINATION OF COBALT BY CONSTANT CURRENT COULOMETRY

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ABSTRACT

In Part I results are reported for the electrolytical reduction of iron(III), copper(II), lead(II), zinc(II), and cadmium(II) in sodium pyrophosphate media. In the cases of iron(III) and copper(II), reduction in neutral and basic pyrophosphate media is irreversible. However, if a pyrophosphate ligand is dissociated from the metal complex, a species is obtained that is reversibly reduced. In the case of iron(III) in the region $4 < pH < 6$, loss of a hydrogen pyrophosphate ligand results in a species that is reversibly reduced. The dissociation constant is 2.8×10^{-3}, the rate constant for dissociation of the ligand is 24 $sec.^{-1}$, and the rate constant for association is 8.5×10^{3} $M^{-1}sec.^{-1}$. In the case of copper(II) the loss of a sodium pyrophosphate ligand yields a species that is reversibly reduced. The dissociation constant is 3.2×10^{-3}, the rate constant for dissociation of the ligand is 19 $sec.^{-1}$, and the rate constant for association is 5.9×10^{3} $M^{-1}sec.^{-1}$. These constants were determined by chronopotentiometry.

The reduction of zinc(II) is irreversible in neutral pyrophosphate media; however, this irreversibility is not due to a slow chemical reaction. The reduction of lead(II)

is not reversible in neutral pyrophosphate media, but this reduction is not sufficiently irreversible to allow the mechanism of the reduction to be studied by polarography or chronopotentiometry.

Reduction of cadmium(II) was studied by polarography, but no quantitative results were obtained.

In Part II equations for the product $i\tau^{\frac{1}{2}}$ and the product $it^{\frac{1}{2}}$ are derived for the cases of chronopotentiometry and chronoamperometry, respectively, at an unshielded electrode. The equations for an annular electrode or radius r are

$$i\tau^{\frac{1}{2}} = \tfrac{1}{2}\pi^{\frac{1}{2}}nFAC^{O}D^{\frac{1}{2}}\left[1 + 0.796(D\tau)^{\frac{1}{2}}/r + 1.2D\tau/r^{2}\right]$$

$$it^{\frac{1}{2}} = \frac{nFAC^{O}D^{\frac{1}{2}}}{2\pi^{\frac{1}{2}}}\left[1 + 1.736(Dt)^{\frac{1}{2}}/r\right]$$

For a rectangular electrode with dimensions b and c the above equations are valid if the quantity $bc/(b+c)$ is substituted for the variable r.

In Part III a method is described by which cobalt may be determined with a relative error of less than 0.1%. In this method triscarbonatocobaltate(III) oxidizes iodide to iodine. Arsenic(III) is added to reduce the iodine and coulometrically generated iodine is employed to titrate excess arsenic(III).

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GENERAL INTRODUCTION

It has been known for many years that metal pyrophosphates, with the exception of the alkali metal pyrophosphates, are very insoluble (1) and that strong complexes are formed upon the addition of excess pyrophosphate to solutions containing metal pyrophosphate precipitates. For this reason pyrophosphate has long been used as a water softening agent. However, little work has been done to determine the nature of the complexes formed by metal ions in pyrophosphate solutions. Further, in much of this work it is erroneously assumed that only the pyrophosphate ion serves as a complexing agent in pyrophosphate solutions. However, the hydrogen ion concentration of such solutions is sufficiently large in general that mono- and dihydrogen pyrophosphate ions exist in appreciable concentrations and may form complexes with metal ions present in the solution. Moreover, alkali metal ion salts are generally employed to maintain ionic strength of the pyrophosphate solutions. Lambert and Watters (2) have demonstrated that alkali metal ions associate with pyrophosphate ions and the resulting complexes can associate further with metal ions. Thus complexing agents other than pyrophosphate ions exist in pyrophosphate solutions and the literature concerning the nature of the pyrophosphate complexes formed may be incorrect. Quarternary ammonium ions appear to associate to a much lesser degree with pyrophosphate ions than do alkali metal ions. Thus Schupp, Sturrock, and Watters (3) have employed solutions of tetramethyl ammonium pyrophosphate and tetramethyl ammonium nitrate, the latter salt being present to maintain ionic strength. In such solutions the problem of determining the types of complexes present is more easily solved than in solutions containing alkali metal ions.

It is not possible, however, to employ quarternary ammonium ions in every circumstance. A serious difficulty arises in the preparation of the desired quarternary ammonium salt. Ion exchange is probably the best method of preparation; however, ion exchange columns elute nonionic species that can adsorb on the electrode and change the kinetics of the electrode reaction. Moreover, the quarternary ammonium ions adsorb on mercury electrodes and shift the effective potential of the electrode.

Only one study has been performed to determine all of the possible association constants for reactions of the type

$$M^{m+} + iP_2O_7^{4-} + jH^+ = \left[M(P_2O_7)_iH_j\right]^{(m-4i+j)}$$

where $i = 1, 2, \ldots, I$, $j = 0, 1, \ldots, 2i$, and I is the maximum number of pyrophosphate ligands with which the metal ion M^{m+} associates. This study was devoted to the copper pyrophosphate system.

Part I of this work is devoted primarily to the kinetics of electrolysis of certain metal ions and secondarily to the elucidation of the complexes of these metal ions in pyrophosphate media. This study was initiated to determine the reason for the irreversibility of the reduction of iron(III) in neutral or basic pyrophosphate media. It was found that this reduction is irreversible due to slow dissociation of a pyrophosphate ligand from the iron(III) complex. From the literature the polarographic behavior of copper in pyrophosphate media appears to be identical to the behavior of iron. This writer's results in the case of copper have demonstrated that the reduction is irreversible due to slow dissociation of a pyrophosphate ligand from the copper complex.

It might be inferred that in alkaline metal-pyrophosphate solutions the rate of dissociation of pyrophosphate ligands from the predominant pyrophosphate complex is not rapid. Additional ions were studied in order to verify this hypothesis. It was found that while reduction of zinc(II) in pyrophosphate media is irreversible, dissociation of pyrophosphate ligands is probably rapid compared to the rate of electron transfer. However, reduction of cadmium(II) in pyrophosphate media is probably irreversible due to slow dissociation of a pyrophosphate ligand. Also, reduction of lead(II) was found to be irreversible due most probably to slow dissociation of a pyrophosphate ligand.

Lambert and Watters (2) have determined the association constants for the reactions given below, at unit ionic strength; these values are employed in this thesis.

$$H^+ + H_3P_2O_7^{1-} = H_4P_2O_7 \qquad K_4 = 10^{0.82}$$

$$H^+ + H_2P_2O_7^{2-} = H_3P_2O_7^{1-} \qquad K_3 = 10^{1.81}$$

$$H^+ + HP_2O_7^{3-} = H_2P_2O_7^{2-} \qquad K_2 = 10^{6.13}$$

$$H^+ + P_2O_7^{4-} = HP_2O_7^{1-} \qquad K_1 = 10^{8.93}$$

$$Na^+ + P_2O_7^{4-} = NaP_2O_7^{3-} \qquad K_{Na} = 10^{1.00}$$

In Part II of this thesis an approximate equation expressing the product $i\tau^{\frac{1}{2}}$ as a function of τ for a finite electrode is formulated for the case of chronopotentiometry. A similar relation expressing the product $it^{\frac{1}{2}}$ as a function of t is formulated for the case of chronoamperometry. These relations are derived in order to approximate the error resulting from the assumption that an unshielded electrode is equivalent to a shielded or semi-infinite electrode.

In Part III of this thesis, a method is given for the analysis of cobalt by constant current coulometry. In this method a solution of cobalt(II) is treated with potassium hydrogen carbonate and hydrogen peroxide to form triscarbonatocobaltate(III). This complex oxidizes iodide to iodine in a neutral pyrophosphate media. An excess amount of arsenic(III) is added to the solution and this excess is titrated with electrogenerated iodine.

1. THE ELECTROCHEMISTRY OF IRON IN PYROPHOSPHATE MEDIA

Rogers and Reynolds (4) investigated the polarographic reduction of iron(III) in 100mF sodium pyrophosphate solutions. From an analysis of the polarographic wave they reported that the reduction of iron(III) to iron(II) is reversible and that the half-wave potential is -820 millivolts vs. SCE (saturated calomel electrode). From a conductometric titration of sodium pyrophosphate with iron(III) they concluded that iron(III) associates with one or two pyrophosphate ligands.

Banerjee and Mitra (5) report that the dissociation constant for bis(pyrophosphato)ferrate(III) is 2.8×10^{-6}. If the pH is less than ten, iron(III) hydroxide does not precipitate from solutions of 1mF iron(III) and 100mF sodium pyrophosphate. However, the dissociation constant reported by Banerjee and Mitra (5) is so large that if the pH is greater than eight, iron(III) hydroxide should precipitate from a solution of 1mF iron(III) and 100mF sodium pyrophosphate. Since the dissociation constant is too large to be consistent with experimental observations, it will not be considered in this thesis.

Subrananya (6) reports that if the pH of the solution is greater than four, the polarographic reduction of iron(III) in pyrophosphate media consists of two waves, in the absence of nitrate ions and gelatin. The first wave is a reversible reduction while the second wave is irreversible. Further, the height of the first wave is decreased upon addition of nitrate ions or gelatin.

A polarographic study which confirms many of the results of this thesis was reported by Ram, Kunar, and Sinha (7). From a polarographic study of the variation of the half wave potential as a function of dihydrogen pyrophosphate concentration (calculated from the dissociation constants and total pyrophosphate concentration) they conclude that the complexing ligand is dihydrogen pyrophosphate in the region $1.3 < pH < 3.2$, that the difference between the number of ligands associated with iron(III) and iron(II) is unity, and that the ratio between the dissociation constants of the iron(III) and iron(II) complexes is 2.9×10^{-13}.

<u>Experimental</u>. All solutions were prepared by dissolving reagent grade chemicals in distilled water. A 12.5mF solution of $Fe_2(SO_4)_3$ was prepared by dissolving ferric sulfate in a warm solution of 3F sulfuric acid and diluting with water and sulfuric acid to make the final solution 1F in sulfuric acid. Solutions for the chronopotentiometric study were prepared by diluting an aliquot of the ferric

sulfate solution, adding solid sodium pyrophosphate, adjusting the pH with sulfuric acid, and diluting to volume. The resulting concentration was 5mF $Fe_2(SO_4)_3$. The solutions for polarography were prepared by adding sodium pyrophosphate to a solution of ferric nitrate and adjusting the pH with nitric acid. The resulting concentration was 1mF ferric nitrate. It was found that nitric and perchloric acids could not be used to adjust the pH of the electrolysis solutions, since, if these acids are employed, the wave for the reduction of iron(III) becomes increasingly irreversible with increasing pH, only one wave being observed. On the other hand, if sulfuric acid is used to adjust the pH, then two waves are observed for the reduction of iron(III) in the region $4 < pH < 6$, the first wave representing a reversible reduction and the second wave an irreversible reduction.

The cell was a glass beaker with a fitted Teflon stopper. The reference electrode was a Beckman fiber junction saturated calomel electrode. The auxiliary electrode was a platinum wire helix with a diameter of 1 cm., centered about the indicator electrode. The solutions were deaerated by bubbling nitrogen through them, and were maintained oxygen free by passing nitrogen over their surfaces during the experiments. The current source was a Heathkit P-4 power supply with an adjustable resistance in series with the auxiliary and indicator electrodes. The output of the power supply was 300 to 400 volts. The current was determined by measuring the potential drop across a precision resistor with an L&N student potentiometer.

The indicator electrode was a cylindrical mercury electrode prepared by sealing a 0.050 inch platinum wire in glass, leaving 2 mm. of wire exposed. The exposed wire was amalgamated by dipping it in sodium amalgam (9). One minute prior to electrolysis the indicator electrode was dipped in mercury that had been freshly caught in a spoon beneath a dropping mercury electrode. The chronopotentiograms were recorded by photographing the trace of a Tektronix oscilloscope, model 536 with a type D plug-in unit, with a Polaroid camera. The transition times were determined by the method of Delahay and Berzins (10). At least three chronopotentiograms were recorded for each value of the current and the transition time was takn to be the average of the three or more individual values.

Results and discussion. The electrode reaction for the iron(III)-iron(II) couple in sodium pyrophosphate media may be written as

$$e^- + Fe(III)Pyp_a \rightleftharpoons Fe(II)Pyp_b + (a-b)Pyp$$

where Pyp represents some pyrophosphate species. The potential of the mercury electrode, E, at 25°C is (22) given by

$$E = E_{\frac{1}{2}} + 0.0591 \log\left[\frac{i_{dc}-i}{i-i_{da}}\right] \qquad (1.1)$$

where

$$E_{\frac{1}{2}} = E^o - 0.0591 \log \frac{K_o}{K_f} - 0.0591(a-b)\log[Pyp] \qquad (1.2)$$

Here i_{da} and i_{dc} are the maximum values for the anodic and cathodic diffusion currents respectively, i is the maximum value for the current at the potential E, E^o is the formal potential for the iron(III)-iron(II) couple in a noncomplexing media, and K_o and K_r are the dissociation constants for $Fe(III)Pyp_a$ and $Fe(II)Pyp_b$. Equations 1.1 and 1.2 are exact only if the diffusion coefficients of the iron(III) and iron(II) species are equal. However, equations 1.1 and 1.2 are approximately true in most cases. The current is considered to be positive for cathodic currents and negative for anodic currents. In the case of irreversible electrode reactions, the potential-log plot is either not a straight line or a line of slope greater than 59 mv.

In the experiments in which the oxidation of iron(II) was studied, i_{dc} was zero due to the fact that the concentration of iron(III) is zero. Graphs of potential vs. $\log (i/(i_{da}-i))$ were constructed from polarograms for the oxidation of iron(II) in solutions of sodium pyrophosphate for $1 \leq pH \leq 10$. Each graph was a straight line having a slope of approximately 59 mv. Thus the oxidation of iron(II) appears to be reversible for $1 \leq pH \leq 10$.

In the experiments in which the reduction of iron(III) was studied, i_{da} was zero due to the fact that the concentration of iron (II) was zero. Graphs of potential vs. $\log((i_{dc}-i)/i)$ were constructed for the reduction of iron(III) in solution of sodium pyrophosphate for the region $1 \leq pH \leq 10$. Each graph was a straight line; however, the slopes of these lines depended upon the pH of the solution. If the pH was less than three, the slope was approximately 59 mv. Thus if the pH is less than three the reduction of iron(III) in sodium pyrophosphate media appears to be reversible. If the pH is greater than three, the slope of the resulting graph is greater than 59 mv. Thus if the pH is greater than three, the reduction of iron(III) appears to be irreversible in sodium pyrophosphate solutions.

In view of the fact that in solutions of sodium pyrophosphate of pH greater than three the oxidation of iron(II) appears to be reversible, while the reduction of iron(III) appears to be irreversible, two iron(III) species appear to exist in this pH region. These two iron(III) species are denoted by O and Y . The reduction of O is reversible and the reduction of Y is irreversible. Iron(II) is oxidized to O and subsequently O is rapidly transformed into Y. The oxidation of iron(II) appears to be reversible due to the fact that a small amount of O is present at the surface of the electrode. The reduction of iron(III) appears to be irreversible due to the fact that the equilibrium favors Y in solution and the rate of conversion of Y to O is slow.

For a reversible electrode reaction it is possible to determine the difference between the number of pyrophosphate ligands associated with the iron(III) and iron(II) complexes from a study of the variation of the half-wave potential as a function of the pyrophosphate concentration. The relation between the half-wave potential and the pyrophosphate concentration is given by equation 1.2. At constant pH the concentration of each pyrophosphate species is proportional to the formal concentration of sodium pyrophosphate and equation 1.2 becomes

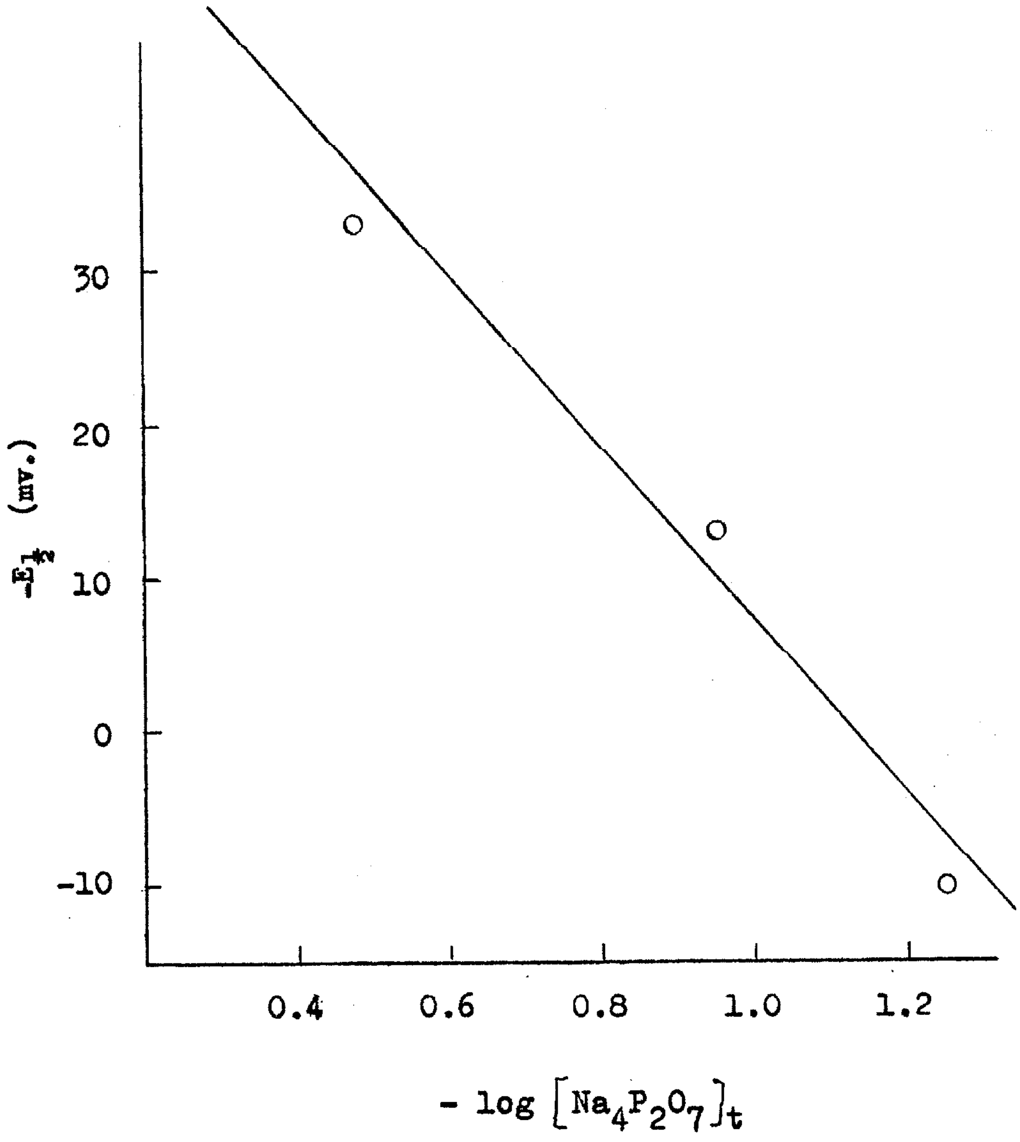
$$E_{\frac{1}{2}} = E^{o} - 0.0591 \log \frac{K_o}{K_r} - 0.0591(a-b)\log K_p$$

$$- 0.0591(a-b)\log \left[Na_4P_2O_7\right]_t$$

where $\left[Na_4P_2O_7\right]_t$ is the formal concentration of sodium pyrophosphate and K_p is the ratio of $[Pyp]$ to $\left[Na_4P_2O_7\right]_t$. If the half-wave potential is plotted vs. the logarithm of the formal concentration of sodium pyrophosphate at constant pH, the resulting graph should be a line with a slope of 59(a-b) mv.

At pH two the reduction of iron(III) is reversible in pyrophosphate solutions and the preceding equation is applicable. Figure 1 shows a graph of $E_{\frac{1}{2}}$ vs. $\log\left[Na_4P_2O_7\right]_t$. The slope of the line is 56 mv., which is very close to the value expected for $a-b = 1$. Ram, Kunar, and Sinha (7) studied the variation of the half-wave potential for the reduction of iron for various values of the concentration of sodium pyrophosphate in the region $1.3 \leq pH \leq 3.2$. They calculated the concentration of each pyrophosphate species and plotted the half-wave potential vs. the logarithm of the concentration of each pyrophosphate species. They obtained a straight line if

Figure 1. Variation of half-wave potential for reduction of iron(III) with log$[Na_4P_2O_7]_t$



they assumed that Pyp is in fact dihydrogen pyrophosphate. From the slope of the line they also concluded that a-b is equal to one. They assumed a value of 0.525 v. vs. SCE for the formal potential for the iron(III)-iron(II) couple in a noncomplexing media and concluded that the ratio of K_o to K_r is 2.9×10^{-13}. Accurate extrapolation of the line in Figure 1 is not possible due to the scatter of the experimental points. However, the value of the half-wave potential for 1M dihydrogen pyrophosphate at pH two is approximately -78 mv. from which a value of 6×10^{-11} may be calculated for the ratio of K_o to K_r. This value agrees fairly well with the value obtained by Ram, Kunar, and Sinha (7); the latter value will be used in this thesis as it was determined with a greater number of experimental points than was the former.

The polarographic study of the variation of the half-wave potential for the reduction of iron(III) as a function of the formal concentration of sodium pyrophosphate at pH two yields the difference between the number of pyrophosphate ligands associated with the iron(III) and iron(II) complexes but yields no information concerning the number of pyrophosphate ligands associated with each complex ion. By analogy with the pyrophosphate complexes of lead and cadmium one may conclude that iron(II) does not associate with any pyrophosphate ligands if the pH is less than six. In the case of lead, a pyrophosphate precipitate is present in the region $1.5 < pH < 5$. If the pH is less than 1.4, lead(II) does not associate with any pyrophosphate ligands. No complex is formed at pH 1.4, as is demonstrated by the fact that the half-wave potential for the reduction of lead(II) is independent of the pyrophosphate concentration at this pH. In the case of cadmium(II) a precipitate forms in the region $4 < pH < 6$. Cadmium(II) does not form a pyrophosphate complex if pH is less than three. No complex is formed as is demonstrated by the fact that the half-wave potentials are equal for pH 1, 2 and 3, at constant formal sodium pyrophosphate concentration.

In the cases of lead and cadmium it appears that no dihydrogen or hydrogen pyrophosphate complexes form in solutions in which the pH is less than the pH at which a pyrophosphate precipitate forms. It may also be true that in the case of iron(II) no pyrophosphate complexes are formed if the pH is less than the pH at which the pyrophosphate precipitate forms. Since iron(II) pyrophosphate precipitates at pH six, it is possible that iron(II) does not form a pyrophosphate complex if the pH is less than six. If this is the case, then iron(III) does not associate with any pyrophosphate ligands at pH two and thus iron(III) associates with one dihydrogen pyrophosphate ion, the dissociation constant for (dihydrogen pyrophosphato)iron(III) being 2.9 x 10^{-13}.

Ram, Kunar, and Sinha (7) conclude that iron(III) associates with three dihydrogen pyrophosphate ligands. They employed Riecke's relation(11) between the masses of two species diffusing in separate solutions to determine the mass of the iron(III) species. Riecke's relation is

$$M_1 = \left(\frac{Z_2 D_2}{Z_1 D_1}\right)^2 M_2$$

where Z_i is the viscosity of solution i, D_i is the diffusion coefficient of species i, and M_i is the molecular weight of diffusing species i, i = 1, 2. However, Baker and Pope (13) have demonstrated that Riecke's relation is not valid.

Further, having concluded that iron(III) associates with three dihydrogen pyrophosphate ligands in acid solution, Ram, Kunar, and Sinha (7) conclude from the conductometric experiments of Rogers and Reynolds (4) that iron(III) associates with either two hydrogen pyrophosphate ions or one pyrophosphate ion in nuetral or basic solutions.

For the case of copper, Schupp, Sturrock and Watters (3) found that the pyrophosphate ion always forms a stronger complex than does the hydrogen pyrophosphate ion and that the hydrogen pyrophosphate ion always forms a stronger complex than does the dihydrogen pyrophosphate ion. It is not unreasonable therefore to expect that in general protonation of a metal pyrophosphate complex weakens the complex.

Ram, Kunar and Sinha (7) state that the iron(III) pyrophosphate complex in solutions of $pH < 10.5$ or $pH > 4$ is either pyrophosphatoferrate(III) or bis(hydrogen pyrophosphato)ferrate(III). They do not indicate the presence of any hydroxide ligands. If the pH of a solution of tris(dihydrogen pyrophosphato)ferrate(III) at pH three is increased, the only effect expected would be the removal of protons from the iron(III) complex, and hence the number of pyrophosphate ligands associated with iron(III) would not decrease. Hence, if iron(III) associates with three dihydrogen pyrophosphate ions in acid solution, then in neutral or basic solution iron(III) should associate with three pyrophosphate ions. Further, if iron(III) associates with two pyrophosphate ligands in basic solution, then iron(III) should associate with two or less pyrophosphate ligands in acid solution. These remarks indicate that Ram, Kunar, and Sinha's (7) conclusions concerning the iron(III) pyrophosphate complexes present in the case of acid solutions and in the case of basic solutions are in contradiction to each other.

The polarographic studies of this thesis indicate that two iron(III) species exist in pyrophosphate solution and that the rate of interconversion between the two species is not rapid. Chronopotentiometry offers an experimental method by which one may determine the rate of interconversion between two such species.

If two species are in sluggish equilibrium and are reduced at different potentials, that is, if

$$Y \underset{k'_b}{\overset{k'_f}{\rightleftharpoons}} O \qquad (1.3)$$

$$O + ne^- \rightleftharpoons R \qquad (1.4)$$

where the species Y does not undergo reduction at the potentials at which the species O is reduced, then τ, the transition time (i.e., the time at which the concentration of species O is zero at the surface of the electrode), is given implicitly (8) by

$$i\tau^{\frac{1}{2}} = \tfrac{1}{2}nFAC^{o}\pi^{\frac{1}{2}}D^{\frac{1}{2}} - \frac{\pi^{\frac{1}{2}}i}{2K'(k_f'+k_b')^{\frac{1}{2}}}\,\mathrm{Erf}((k_f'+k_b')\tau)^{\frac{1}{2}} \qquad (1.5)$$

Here i is the current, n is the number of electrons involved in the reduction of species O, C^{o} is the sum of the bulk concentrations of species O and Y, A is the area of the electrode, D is the common diffusion coefficient of species O and Y, F is Faraday's number, and K', the ratio of k_f' and k_b', is the equilibrium constant for reaction 1.3. The error function, denoted by Erf, is defined by the relation

$$\mathrm{Erf}(x) = 2\pi^{-\frac{1}{2}}\int_{0}^{x}\exp(-\beta^{2})d\beta$$

If $x > 2$, then $\mathrm{Erf}(x)$ is approximately unity. In the limit as x approaches zero, $\mathrm{Erf}(x)$ approached $2x\pi^{-\frac{1}{2}}$.

If $(k_f' + k_b')\tau^{\frac{1}{2}} > 2$, then equation 1.5 becomes

$$i\tau^{\frac{1}{2}} = \tfrac{1}{2}nFAC^{o}\pi^{\frac{1}{2}}D^{\frac{1}{2}} - \frac{\pi^{\frac{1}{2}}i}{2K'(k_f' + k_b')^{\frac{1}{2}}} \qquad (1.6)$$

Thus, if the product $i\tau^{\frac{1}{2}}$ is plotted as a function of the current, a straight line having a slope of

$$-\tfrac{1}{2}\pi^{\frac{1}{2}}(k_f' + k_b')^{-\frac{1}{2}}/K'$$

and an intercept of

$$\tfrac{1}{2}nFAC^{o}\pi^{\frac{1}{2}}D^{\frac{1}{2}}$$

on the $i\tau^{\frac{1}{2}}$ axis is obtained. As the quantity $((k_f' + k_b')\tau)^{\frac{1}{2}}$ approaches zero, equation 1.5 becomes

$$i\tau^{\frac{1}{2}} = \tfrac{1}{2}nFAC^{o}\pi^{\frac{1}{2}}D^{\frac{1}{2}} - \frac{i\tau^{\frac{1}{2}}}{K'} \qquad (1.7)$$

Thus, in this limiting case the product $i\tau^{\frac{1}{2}}$ is independent of the current. Since the numerical value of the product $\tfrac{1}{2}nFAC^{o}\pi^{\frac{1}{2}}D^{\frac{1}{2}}$ can be obtained by graphical methods, as above, K' may be determined from equation 1.7. By substituting this value into the expression for the slope of the line determined by equation 1.6, the values of k_f' and k_b' may be determined. The rate constants k_f' and k_b' are first-order rate constants for the interconversion of the species O and Y.

Let us now consider the reactions

$$Y \underset{k_b}{\overset{k_f}{\rightleftharpoons}} O' + Pyp \qquad (1.8)$$

$$O' + ne^- \rightleftharpoons R \qquad (1.9)$$

where Pyp represents one of the pyrophosphate species. In this case we have

$$k_b = k_b' / [Pyp], \quad K = K'[Pyp], \quad k_f = k_f'$$

If K' is plotted as a function of the reciprocal of the concentration of Pyp, a straight line with slope K should be obtained. In a similar manner k_b may be obtained by graphing k_b' as a function of [Pyp].

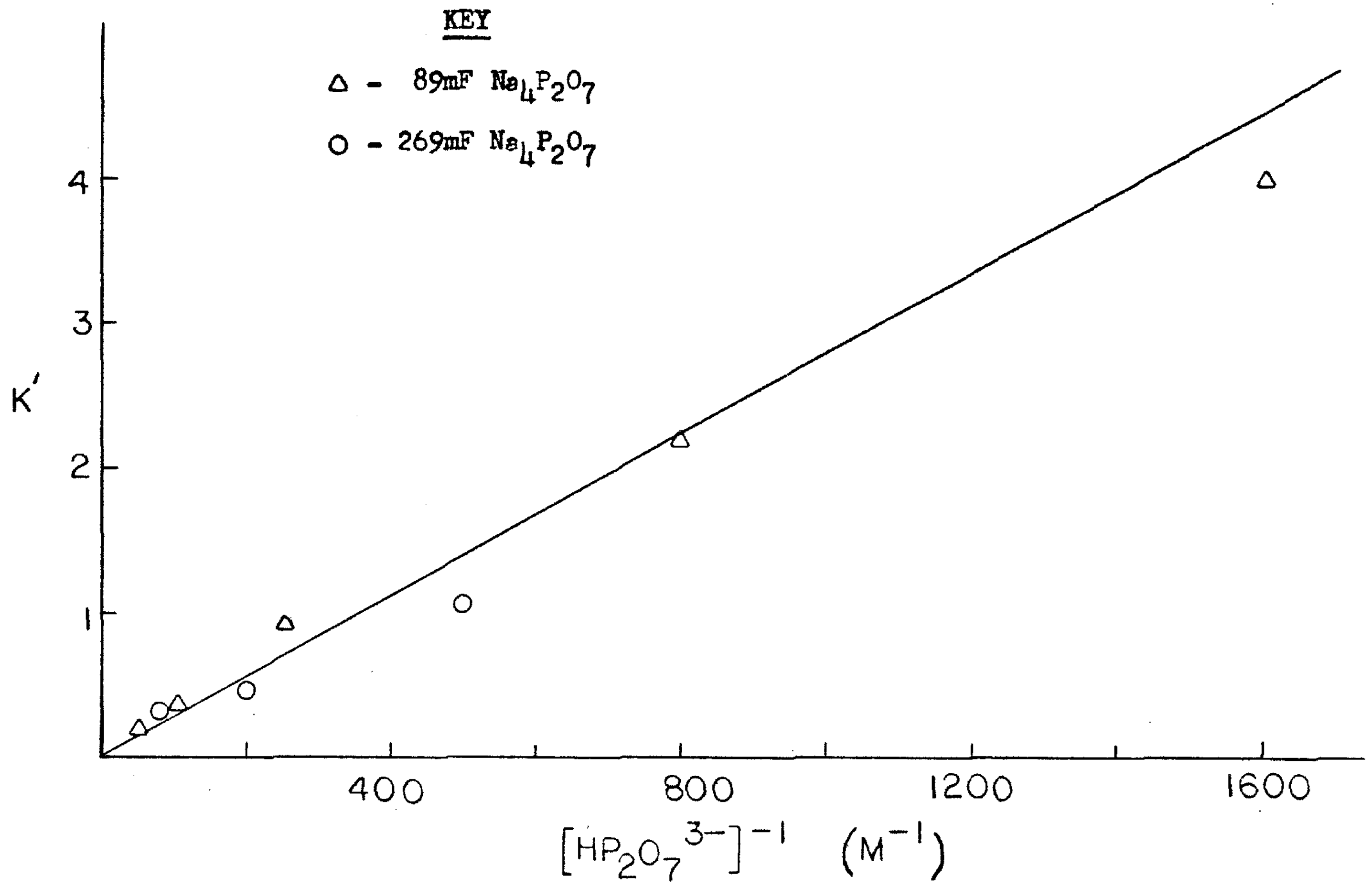
The reduction of iron(III) in sodium pyrophosphate media was studied by chronopotentiometry in the region $3 < pH < 6$. If the pH of the sodium pyrophosphate solution is greater than four, two waves are observed for the reduction of iron(III). (Due to the fact that nitric acid, rather than sulfuric acid, was employed to adjust the pH of the solutions, two waves were not observed in the case of the polarographic experiments at pH greater than four. However, if sulfuric acid is employed to adjust the pH, two polarographic waves are to be expected.) The first wave appears to be a wave for the reversible reduction of iron(III). The second wave appears to be an irreversible reduction of iron(III). The reversibility of a reduction may be determined qualitatively from the dependence of the potential at which reduction occurs on the current density; if there is no dependence, the reduction is reversible, and if there is dependence, the reduction is irreversible. The product $i\tau^{\frac{1}{2}}$, where i is the current and τ is the transition time for the first wave, initially decreases linearly with an increase in the current and approaches a limiting value with increasing current. This behavior agrees with that predicted by equation 1.5 for the case in which there are two iron(III) species that are reduced at difference potentials present in solution. From the linear decrease of the product $i\tau^{\frac{1}{2}}$ it is possible to calculate the quantity $K'(k_f' + k_b')^{\frac{1}{2}}$. From the limiting value for the product $i\tau^{\frac{1}{2}}$ it is possible to calculate K'. The method employed to determine these quantities has been discussed previously.

The values for the quantities K' and $K'(k_f' + k_b')^{\frac{1}{2}}$ determined by chronopotentiometry are given in Table I. A graph of K' vs. $[HP_2O_7^{3-}]^{-1}$ is given in Figure 2, and a graph of k_b' vs. $[HP_2O_7^{3-}]$ is plotted in Figure 3. The values obtained from Figures 2 and 3 for the constants K, k_f, and k_b for the reaction

Table I. Results of the chronopotentiometric experiments for the case of iron(III) in pyrophosphate media.

pH	$[Na_4P_2O_7]$, mF	$[HP_2O_7^{3-}]$, mM	$K'(k_f'+k_b')^{\frac{1}{2}}$, sec.$^{-\frac{1}{2}}$	K'	k_f', sec.$^{-1}$	k_b', sec.$^{-1}$
4.05	267	2.19	7.23	1.07	27.2	25.5
4.41		4.99	4.19	0.48	24.8	51.5
4.80		11.91	2.09	0.31	10.7	34.7
3.98	89	0.62	18.66	4.0	17.4	4.36
4.29		1.26	12.67	2.2	22.8	10.4
4.80		3.97	6.61	0.93	24.4	26.2
5.19		9.17	3.40	0.36	24.0	66.7
5.60		20.3	1.98	0.21	15.4	70.5

Figure 2. Variation of K' with $[HP_2O_7^{3-}]^{-1}$ for the case of iron(III)



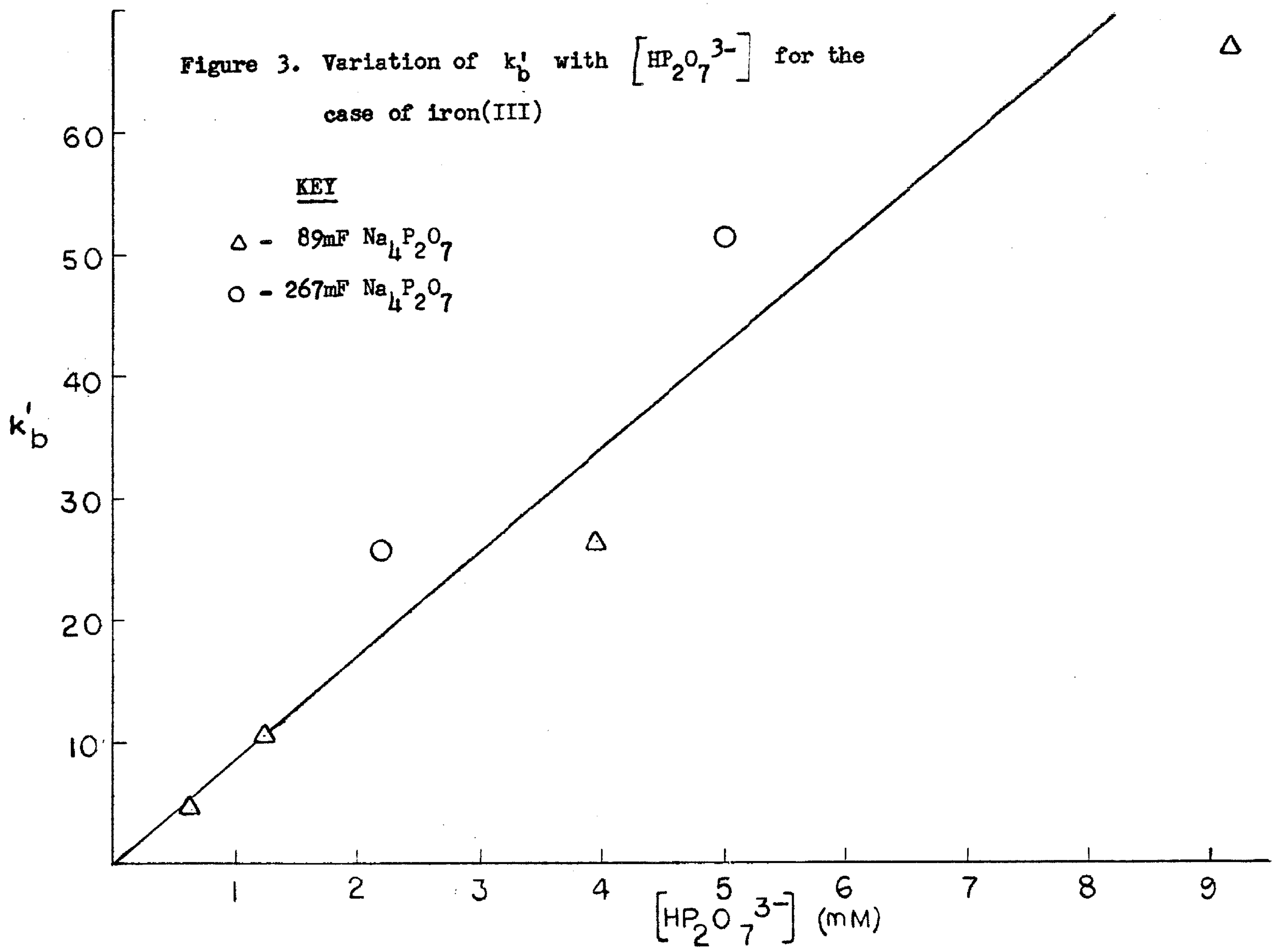


Figure 3. Variation of k'_b with $[HP_2O_7^{3-}]$ for the case of iron(III)

$$Y \underset{k_b}{\overset{k_f}{\rightleftharpoons}} O' + HP_2O_7^{3-} \qquad (1.10)$$

are

$K = 2.8 \times 10^{-3}$

$k_f = 24$

$k_b = 8.5 \times 10^{3}$

Here O' is some reversibly reduced iron pyrophosphate complex. While the hydrogen pyrophosphate ligand may be lost directly as in the above reaction, such a direct loss is not the only alternative implied by the data in Table I. It is possible to write down a number of reactions which may occur but which are less likely. Such reactions are governed by the restriction that the loss of some pyrophosphate species must be the slow step in the overall reaction. The most probable alternative scheme is

$$Y \underset{\text{fast}}{\overset{+H^+}{\rightleftharpoons}} HY \underset{\text{slow}}{\overset{-H_2P_2O_7^{2-}}{\rightleftharpoons}} O' \qquad (1.11)$$

which assumes that the loss of a hydrogen pyrophosphate ligand is very slow compared to the loss of a dihydrogen pyrophosphate ligand and that protonation of the hydrogen pyrophosphate ligand is rapid compared to the loss of a dihydrogen pyrophosphate ligand. Here Y and O' are the same species as in reaction 1.10.

If K' and k_b' are plotted as functions of dihydrogen pyrophosphate or pyrophosphate ion concentration, straight lines are not obtained. This is to be expected in view of the fact that in the region $4 < pH < 6$ the concentration of dihydrogen pyrophosphate decreases with increasing pH and the concentration of pyrophosphate is very small.

Summary. From the preceding discussions the iron-pyrophosphate system may be described as follows. From an argument based upon the behavior of cadmium and lead in pyrophosphate media we conclude that iron(II) does not associate with any pyrophosphate species if the pH is less than six. If this conclusion is correct, then from the polarographic study of the half-wave potential for the reduction of iron(III) as a function of the concentration of sodium pyrophosphate it is possible to conclude that the predominant iron(III) species is (dihydrogen pyrophosphato)iron(III) in the region $1.3 < pH < 3.2$ and that the dissociation constant of this species is 2.9×10^{-13}. As the pH of the solution is increased, a second pyrophosphate ligand associates with the iron(III) species. This ligand is probably hydrogen pyrophosphate. If this is the case, the dissociation constant for the reaction

$$\mathrm{Fe(III)(Pyp)(HP_2O_7)} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{Fe(III)Pyp} + \mathrm{HP_2O_7}^{3-}$$

where Pyp represents either a dihydrogen or a hydrogen pyrophosphate species, is 2.8×10^{-3}. The rate constants k_f and k_b are 24 and 8.5×10^{3}, respectively.

2. THE ELECTROCHEMISTRY OF COPPER IN PYROPHOSPHATE MEDIA

The purpose of this study was to determine the cause of the irreversibility of the reduction of copper(II) in pyrophosphate solutions of pH greater than 6. It was hopefully anticipated that loss of a pyrophosphate ligand would be the cause of the irreversibility and that it would be possible to compare the equilibrium constant obtained in a chronopotentiometric study with value of this constant taken from the literature.

Many studies have been made on the copper-pyrophosphate system. Schupp, Sturrock, and Watters (3) performed a potentiometric study and were able to determine the association constants for complexes of the type

$$CuH_i(P_2O_7)_j^{(2+i-4j)}$$

where $j = 1, 2$ and $i = 0, 1, \ldots, 2j$. As their study was performed employing tetramethyl ammonium ions as cations, it is not necessary to take into consideration the association of alkali metal ions with pyrophosphate ions.

Watters and Aaron (14) investigated the copper-pyrophosphate system by spectrophotometry. Their results are complicated due to the fact that they used sodium pyrophosphate as their source of pyrophosphate ion and maintained the ionic strength with potassium nitrate. Laitinen and Onstott (15) performed a polarographic investigation of the copper-pyrophosphate system. In their investigation they observed two waves for the reduction of copper(II). They concluded that the two waves are due to reduction of two copper(II) species that are in a sluggish equilibrium. Rogers and Reynolds (4) also observed the appearance of two steps for the reduction of copper(II) but they concluded that these two waves are due to a two step electron transfer. In the first electron transfer, copper(II) is reduced to copper(I) and in the second, copper(II) is reduced to the metal.

While equation 1.5 and the subsequent discussion of the determination of the rate constants k_f' and k_b' from the chronopotentiometric data are valid for the case of the reduction of copper(II), it was not possible to determine the equilibrium constant, K', for the copper system, due to the fact that no limiting value for the product $i\tau^{\frac{1}{2}}$ was observed for large currents. In order to extract values for K, k_f, and k_b from the experimental values for the quantity $K'(k_f' + k_b')^{\frac{1}{2}}$, it is necessary to apply a different treatment of the data.

Let us assume that the loss of species A from a metal-pyrophosphate complex is the rate-determining step, that is to say, that the following reaction occurs prior to electrolysis

$$Y \underset{k_b}{\overset{k_f}{\rightleftharpoons}} O + A \qquad (2.1)$$

where $k_f = k_f'$, $k_b = k_b'/[A]$, and $K = k'[A]$, and, as before, species Y is not reduced at the potential at which species O is reduced. Thus,

$$K'(k_f' + k_b')^{\frac{1}{2}} = \frac{k_f}{k_b[A]}(k_f + k_b[A])^{\frac{1}{2}} \qquad (2.2)$$

or, upon multiplying by $[A]$ and squaring,

$$[A]^2\left[K'(k_f' + k_b')^{\frac{1}{2}}\right]^2 = \left[\frac{k_f}{k_b}\right]^2 \cdot (k_f + k_b[A]) \qquad (2.3)$$

The value of $K'(k_f' + k_b')^{\frac{1}{2}}$ is experimentally known and $[A]$ may be determined from dissociation constants. Therefore, if y is defined to be the quantity

$$[A]^2\left[K'(k_f' + k_b')^{\frac{1}{2}}\right]^2$$

and is plotted as a function of the concentration of species A, a straight line having a slope of ${k_f}^2/k_b$ with a y-intercept of ${k_f}^3/k_b^2$ should be obtained. From the slope and y-intercept the constants k_f, k_b, and K may be calculated.

If the rate-determining step is instead the association of species A with the metal-pyrophosphate complex rather than the loss of species A from this complex, then a relation between k_f and k_b can be derived in a fashion analagous to the derivation of equation 2.3. The resulting equation is

$$\left\{\frac{K'(k_f' + k_b')^{\frac{1}{2}}}{[A]}\right\}^2 = \left(\frac{k_f}{k_b}\right)^2 (k_f[A] + k_b) \qquad (2.4)$$

If z is defined to be

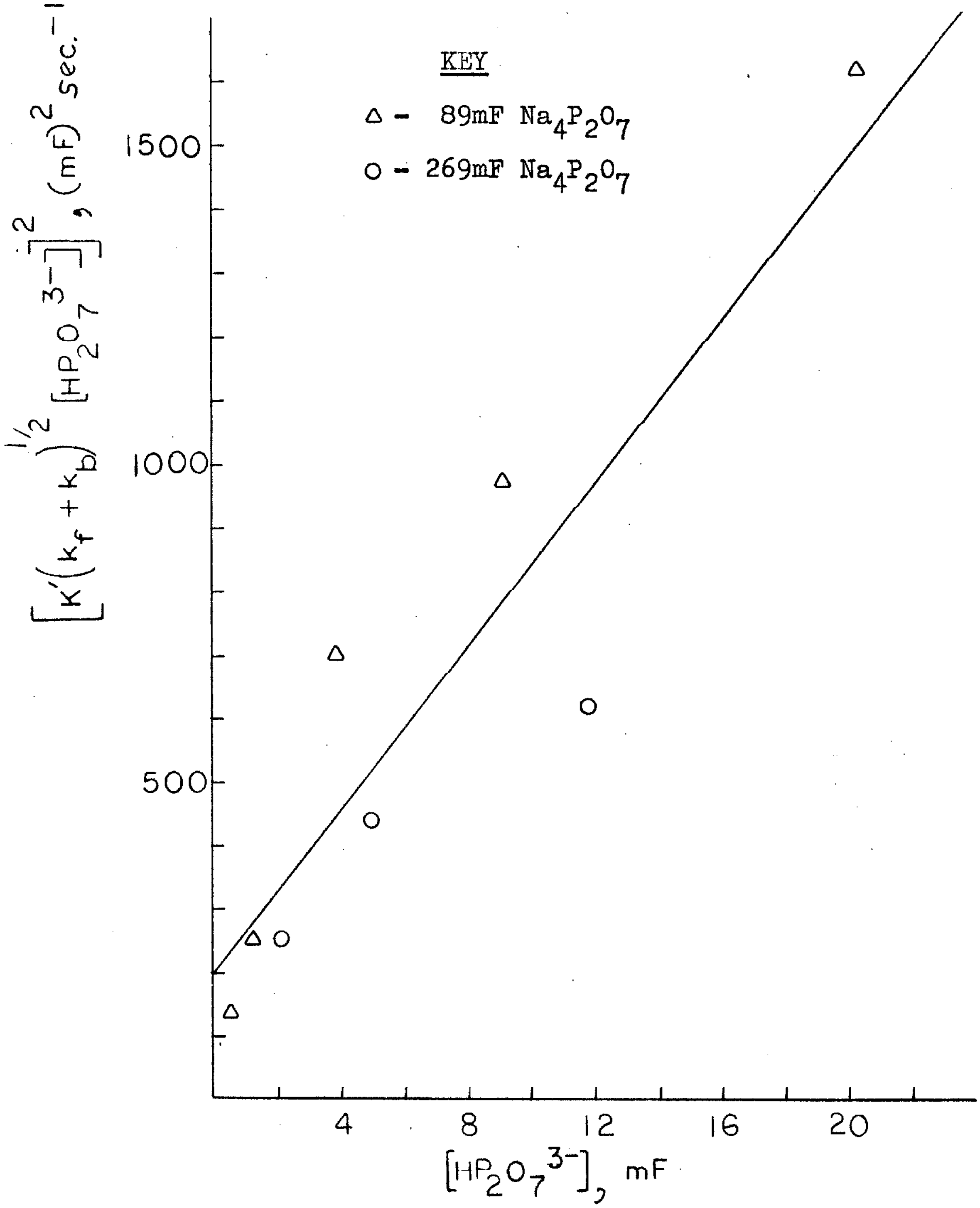
$$\left[K'(k_f' + k_b')^{\frac{1}{2}}\right]^2/[A]^2$$

and is plotted as a function of the concentration of species A, a straight line having a slope of $k_f{}^3/k_b{}^2$ with a z-intercept of $k_f{}^2/k_b$ should be obtained.

If the equilibrium between the species Y and O is strictly first order, then the quantity $K'(k_f' + k_b')^{\frac{1}{2}}$ is a constant and thus it is not possible to determine k_f' and k_b'.

In order to test the reliability of the values of k_f, k_b, and K obtained from equation 2.3, values of $K'(k_f' + k_b')^{\frac{1}{2}}$ from the data obtained in the case of iron were plotted in Figure 4. Values for K, k_f, and k_b were determined from this graph. (In this case species A is the hydrogen pyrophosphate species.) Since K' was determined in each experiment for iron, and since values for K, k_f,

Figure 4. Variation of $\left\{K'(k_f' + k_b')^{\frac{1}{2}}[HP_2O_7^{3-}]\right\}^2$ with $[HP_2O_7^{3-}]$ for the case of iron(III)



and k_b for iron may be determined independently of equation 2.3, this test provides a useful method of verifying the constants K, k_f, and k_b obtained from the graph of equation 2.3. The values for K, k_f, and k_b obtained employing equation 2.3 are

3.1×10^{-3}, 21, 6.6×10^{3}

respectively and the values from Section I are

2.8×10^{-3}, 24, 8.5×10^{3}

respectively. The agreement between the two sets of values is good in view of the relative uncertainty in the determination of the y-intercept.

Experimental. The experimental procedure for copper is essentially the same as the procedure described for iron. However, there is a difference between the indicator electrodes employed in the two cases. For the case of copper the indicator electrode is a hanging drop electrode. This electrode was prepared by sealing a 0.010 in. platinum wire in glass tubing, and amalgamating the exposed platinum surface by dipping the electrode in sodium amalgam (9).

Sulfuric acid was employed to adjust the pH of the pyrophosphate solutions in the case of copper as in the case of iron, although nitric acid could have been employed in the case of copper due to the fact that nitrate ion does not appear to effect the characteristics of the chronopotentiogram. A 50mF stock solution of copper(II) sulfate was prepared and aliquots of this solution were employed in the preparation of electrolysis solutions. The electrolysis solutions were 5mF in copper(II) sulfate.

Results. As previously mentioned, conflicting conclusions have been published concerning the reduction of copper(II) in pyrophosphate solutions. It is possible to employ chronopotentiometry to determine whether the two-step reduction wave of copper(II) is due to the stepwise reduction of copper(II) or to the existence of a sluggish equilibrium between two species of copper(II). Employing the reverse-current technique, two waves are observed in the forward, cathodic portion of the current. After the reversal of the current, however, only one wave is observed. This wave occurs at the same potential as does the first wave obtained during the forward current. Further, the ratio of the forward generation time to the reversed-current transition time is equal to three. If copper(I) were involved in the reduction, two waves, rather than one, would be expected upon current reversal. If the solution is stirred during the experiment, then copper(II) is continually being replaced at the surface of the electrode and the potential of the indicator electrode is the same as the potential on the plateau of the first wave during the forward, cathodic portion of the current in an unstirred solution. If in fact copper(I) is formed as an intermediate during electrolysis, then this species is swept away from the surface of the electrode and the transition time upon current reversal should be zero. However, the ratio of the forward generation time to the reverse-current transition time is found to be equal to three. This is to be expected in the case in which the product of reduction is soluble in the mercury electrode, i. e., the product of reduction is copper metal. Thus, the two-step reduction of copper(II) in the presence of pyrophosphate must be due to two copper(II) species existing in a sluggish equilibrium.

Since it was determined that two copper(II) species exist in a sluggish equilibrium, chronopotentiometry was employed to determine the rate constants for this equilibrium. From the chronopotentiometric data of several experiments the product $i\tau^{\frac{1}{2}}$ was plotted as a function of the current. From these graphs values for the quantity $K'(k_f' + k_b')^{\frac{1}{2}}$ were obtained (as discussed for the case of iron); these values are given in Table II. However, no limiting values for the product $i\tau^{\frac{1}{2}}$ were found for large values of the current and thus no values for K' could be obtained directly from these graphs.

If the loss of a sodium pyrophosphate ligand is assumed to be the rate-determining step, then a graph of

Table II. Results of the chronopotentiometric experiments for the case of copper(II) in pyrophosphate media

pH	$[Na_4P_2O_7]$, mF	$[NaP_2O_7^{3-}]$, mM	$K'(k'_f + k'_b)^{\frac{1}{2}}$, sec.$^{-\frac{1}{2}}$
5.89	269	0.9	20.5
6.96		24.0	1.76
5.61		0.328	41.3
6.20		2.83	10.53
5.21		0.0583	158.
6.61		9.86	2.10
6.18	89.7	0.304	50.9
6.51		0.853	26.2
6.87		2.29	10.82
7.23		5.40	5.50
7.53		10.22	2.82
7.82		17.4	2.00
8.11		27.2	1.46
6.88	269	20.2	1.29
6.09		1.99	6.51
5.63	538	1.39	8.08
5.38		0.581	18.9

equation 2.3, where A represents the sodium pyrophosphate ion, is as is shown in Figure 5. A large uncertainty is associated with the values calculated for the rate constants due to the fact that the y-intercept is small. Even though this uncertainty exists, the data support the assertion that a sodium pyrophosphate ligand is lost prior to electrolysis. Thus, values of the constants k_f, k_b, and K for the reaction

$$Y \rightleftharpoons O' + NaP_2O_7^{3-} \qquad (2.5)$$

are

$$K = 3.2 \times 10^{-3} \qquad (2.6)$$

$$k_f = 19 \qquad (2.7)$$

$$k_b = 5.9 \times 10^3 \qquad (2.8)$$

In the region of pH in which the chronopotentiometric measurements of this author were performed, Schupp, Sturrock, and Watters (3) report that the predominate copper(II) species is bis(pyrophosphato)cuprate(II) in solutions of tetramethyl ammonium pyrophosphate. Further, the constants reported by Watters and Aaron (14) also indicate that copper(II) is associated with two pyrophosphate ligands. Thus the species O' in equation

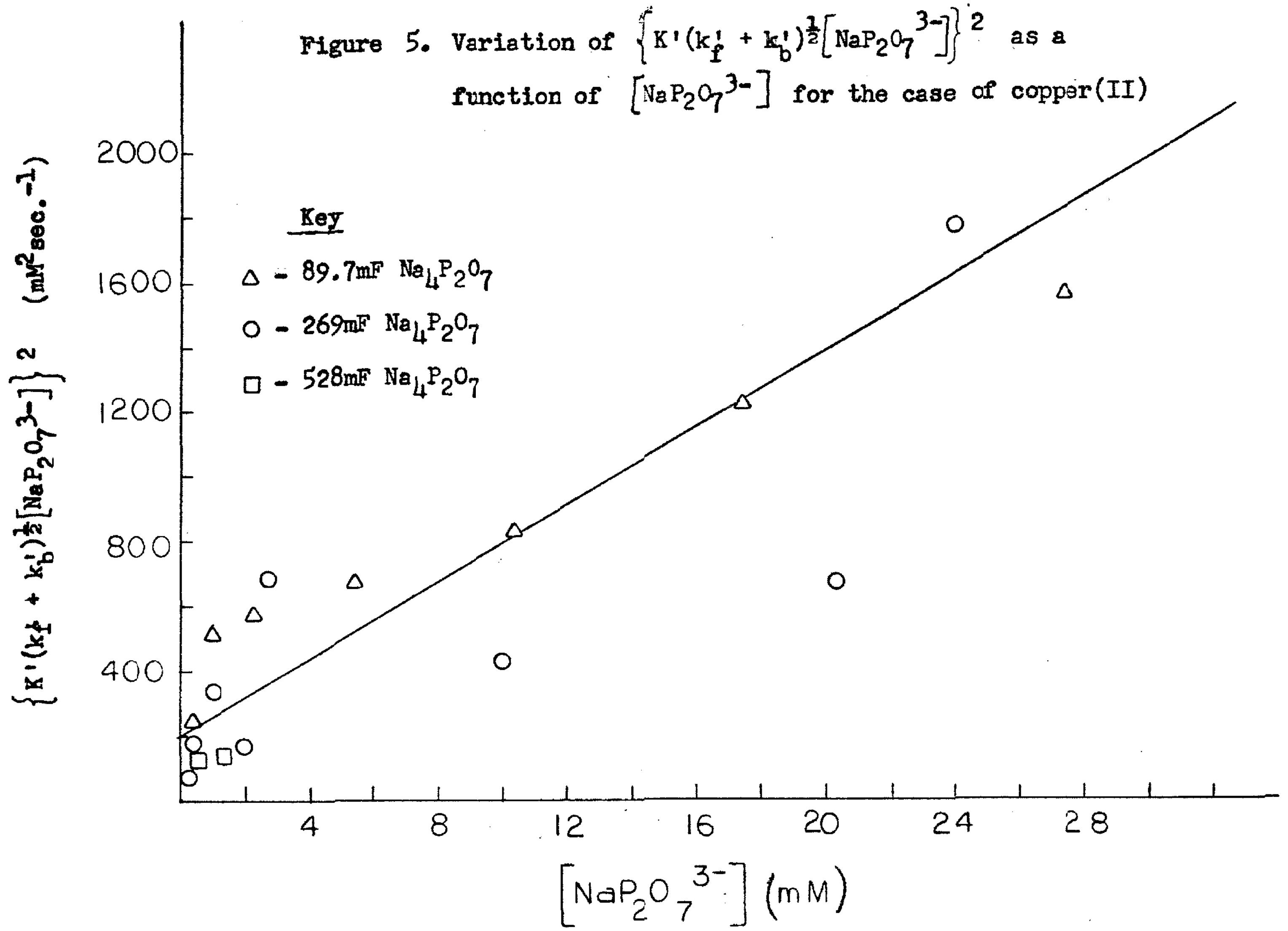


Figure 5. Variation of $\left\{K'(k_f' + k_b')^{\frac{1}{2}}[NaP_2O_7^{3-}]\right\}^2$ as a function of $[NaP_2O_7^{3-}]$ for the case of copper(II)

2.5 consists of a copper(II) ion associated with one pyrophosphate ligand.

If the loss of a hydrogen pyrophosphate ion is assumed to be the rate-determining step, then a graph of equation 2.3, where A is a hydrogen pyrophosphate ion, is not a straight line. This is to be expected in view of the fact that for $5 < pH < 8$ the concentration of hydrogen pyrophosphate decreases as the pH increases. However, if the loss of a pyrophosphate ion, rather than a hydrogen pyrophosphate ion, is assumed to be the rate-determining step, then a graph of equation 2.3, where A represents a pyrophosphate ion, takes the form of three straight lines, each line representing a different formal concentration of sodium pyrophosphate. Since the graph of equation 2.3 should consist of precisely one straight line, one can conclude that neither the simple loss of a hydrogen pyrophosphate ion nor the loss of a pyrophosphate ion is the rate-determining step.

The data in Table II do not require that the loss of a sodium pyrophosphate ligand from the copper(II) complex must occur prior to electrolysis. (A similar statement was true in the case of iron.) The data may in fact support the occurrence of reactions such as

$$Y \underset{\text{fast}}{\overset{-Na^+}{\rightleftharpoons}} Y' \overset{\text{slow}}{\rightleftharpoons} O' + P_2O_7^{4-}$$

where Y is as in reaction 2.5.

There are two significant results from this study. The first is that the loss of a pyrophosphate ligand from the copper(II) complex is slow. The second is the fact that at least one sodium ion is associated with the copper(II) complex. In fact, regardless of the actual reactions which occur prior to electrolysis, the irreversibly reduced copper(II) species is associated with a sodium pyrophosphate ion. In view of the fact that one ligand associated with the copper(II) complex is a sodium pyrophosphate ion, it is not unreasonable to conclude that the other ligand associated with copper(II) is also a sodium pyrophosphate ion, and that, in general, in solutions containing sodium or potassium ions, pyrophosphate complexes are not formed from pyrophosphate ions but are in fact formed from sodium or potassium pyrophosphate ions.

From a spectrometric investigation Watters and Aaron (14) report the following dissociation constants

$$CuP_2O_7^{2-} \rightleftharpoons Cu^{2+} + P_2O_7^{4-} \qquad K_{12} = 1.6 \times 10^{-9}$$

$$Cu(P_2O_7)_2^{6-} \rightleftharpoons CuP_2O_7^{2-} + P_2O_7^{4-} \qquad K_{11} = 1.7 \times 10^{-4}$$

As these constants were determined from solutions in which sodium pyrophosphate was employed as the source of pyrophosphate ion and potassium nitrate was employed to maintain unit ionic strength, they cannot , in view of the preceding discussion, be the correct constants for the reactions given above. The equilibrium constant (2) for the association of potassium ions with pyrophosphate is 6.3, so that both sodium and potassium complexes of pyrophosphate are present in the above solutions of Watters and Aaron (14) and the concentration of the pyrophosphate ion is very small compared to the total concentration of pyrophosphate. Since the study of Watters and Aaron (14) was spectrometric, their value for the concentration of the copper(II) ion is presumably correct. Further, the equilibrium constants are also correct provided that the formal concentration of sodium pyrophosphate is employed in place of the concentration of the pyrophosphate ion in the expression for the equilibrium constants.

Schupp, Sturrock, and Watters (3) give the following association constants

$Cu^{2+} + P_2O_7^{4-} \rightleftharpoons CuP_2O_7^{2-}$ $\beta_{010} = 1.2 \times 10^9$

$CuP_2O_7^{2-} + P_2O_7 \rightleftharpoons Cu(P_2O_7)_2^{6-}$ $K_{020} = 3.8 \times 10^4$

These values were obtained from a potentiometric study of solutions of copper(II) nitrate, tetramethyl ammonium pyrophosphate and tetramethyl ammonium nitrate.

In this writer's research the dissociation constant for reaction 2.3 was determined to be 3.2×10^{-3}. This value very closely approximates the value reported by Watters and Aaron (14). Although this value agrees less well with the value reported by Schupp, Sturrock and Watters (3), this is not unexpected in view of the effect of the presence of alkali metal ions.

Thus in view of the above discussion, it is this writer's opinion that the reduction of copper(II) in sodium pyrophosphate media is irreversible if a significant concentration of bis(sodium pyrophosphato)cuprate(II) is present, and the reduction of other copper-pyrophosphate complexes is reversible.

It is also reasonable to extend these results to solutions which do not contain alkali metal ions. Hence we might conclude that reduction of copper(II) is irreversible in solutions containing a significant amount of bis(pyrophosphato)cuprate(II).

3. THE ELECTROCHEMISTRY OF ZINC IN PYROPHOSPHATE MEDIA

Experimental. The zinc(II) solutions were prepared by adding an aliquot of a zinc sulfate solution to an aliquot of a sodium pyrophosphate solution. Sodium sulfate was added to maintain unit ionic strength and sulfuric acid was added to adjust the pH. The concentration of zinc sulfate in the solutions employed for polarography was 0.24mF. The current-potential curves were determined by measuring the current with a Sargent model XV polarograph and measuring the constant potential impressed on the cell with a Beckman model G pH meter. The current was measured with the damping switch off. The maximum current was employed in all calculations. The diffusion constants were determined from the Ilkovic equation (16).

Results. Experimentally the polarography of zinc(II) in pyrophosphate solutions is difficult. Zinc(II) pyrophosphate does not completely redissolve until the pH is increased to greater than about five. At pH six the diffusion plateau for the reduction of zinc(II) is not reached before the reduction of hydrogen ions begins. No precipitate was present in any of the polarographic solutions.

A study of the polarographic wave for reduction of zinc(II) was made with concentrations of sodium pyrophosphate of 100, 50, and 10mF at pH five. The polarographic steps were analysed by the procedure of Sathyanarayana (18). The steps were assumed to be totally irreversible so that the equations given by Sathyanarayana take the form

$$\frac{i_t}{i_d} = \varphi(\chi) \qquad (3.1)$$

$$\chi = \left(\frac{12t}{7D}\right)^{\frac{1}{2}} k_f \qquad (3.2)$$

where φ is a function defined by Koutecky (19), t is the length of the drop life, i_t is the current at the end of the drop life, i_d is the current under the conditions of diffusion control, D is the diffusion coefficient, and k_f is the heterogeneous rate constant for reduction. Values of χ were read from a graph constructed from a table of values of χ and $\varphi(\chi)$ given by Delahay (17). It may easily be shown from a paper by Randles (20) that if C^o is redefined to be the total concentration of species Z, the species undergoing reduction, (rather than the molar concentration of species Z), then k_f becomes

$$k_f = k_s K' \exp(-\alpha nF(E - E_f^o)/RT) \qquad (3.3)$$

where k_s is the standard rate constant for reduction of species Z, K' is the ratio of the molar concentration of species Z to the total concentration of species Z, E_f^o

is the standard potential for the reduction of species Z, and the remaining symbols are standard notation. If the common logarithm of k_f is plotted as a function of the potential, the graph is a straight line having a slope of $-2.303\alpha nF/RT$. The product $k_s K'$ may be calculated if the standard potential for reduction of species Z is known.

If the species undergoing reduction, ZnB_q, where B is an arbitrary ligand, is irreversibly reduced and is in equilibrium with another species, ZnB_{q+m}, which does not undergo reduction at the potentials at which ZnB_q is reduced, i. e.,

$$ZnB_{q+m} \overset{fast}{\rightleftharpoons} ZnB_q + mB \tag{3.4}$$

$$ZnB_q + 2e^- \overset{slow}{\rightleftharpoons} Zn(Hg) + qB \tag{3.5}$$

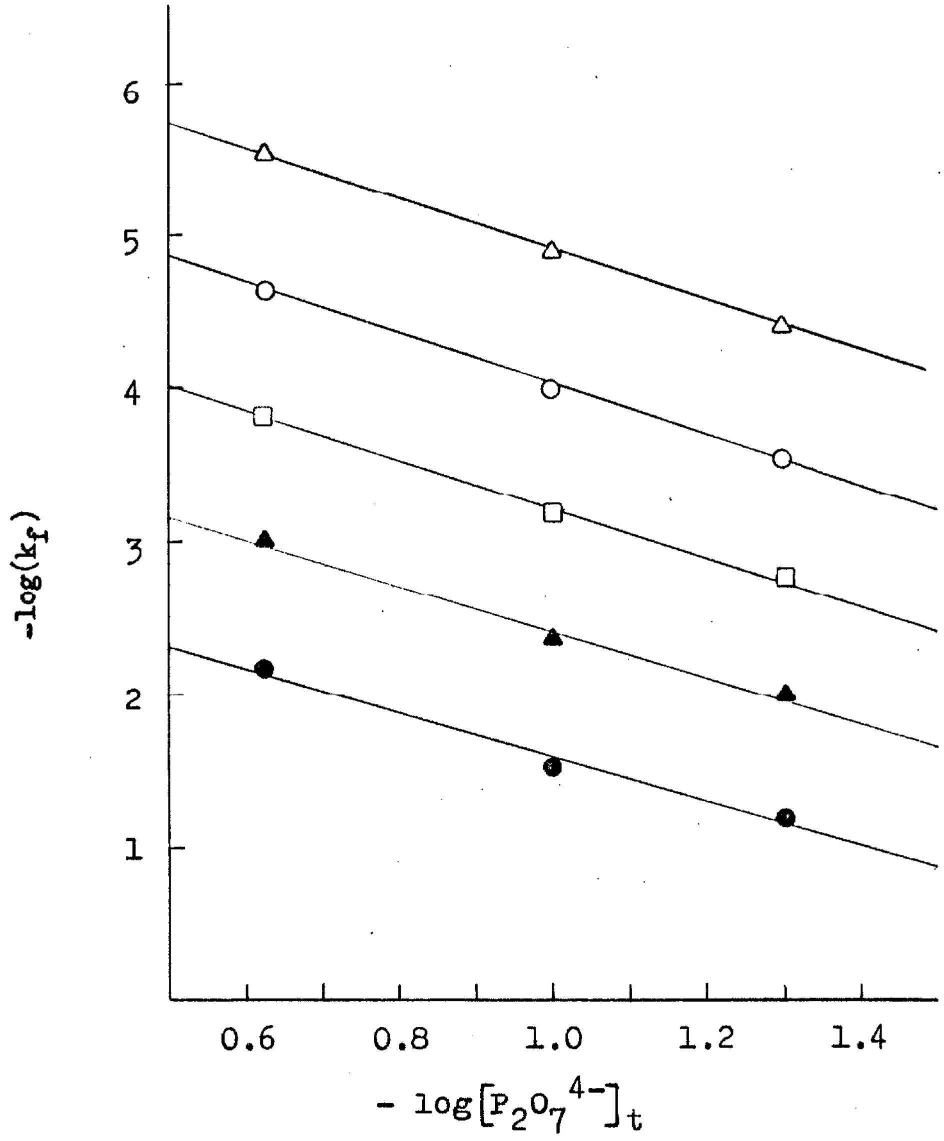
then

$$K' = [ZnB_q]/[ZnB_{q+m}] \quad or \quad K/[B]^m$$

where K is the equilibrium constant for reaction 3.4. Here it has been assumed that the dissociation constant is small so that $[ZnB_{q+m}]$ is approximately equal to the total metal ion concentration. In this case the product $k_s K'$ depends inversely upon $[B]^m$. Thus, if $\log(k_f)$ is plotted as a function of the formal concentration of sodium pyrophosphate, a line having a slope of -m should be obtained in the case in which B is some pyrophosphate species. Graphs of the logarithm of k_f as a function of the logarithm of the formal concentration of sodium pyrophosphate for E = -0.99, -1.10, -1.20, -1.30, and -1.40 volts vs. SCE are given in Figure 6. The average value for m from these graphs is 1.61. Thus, the average number of ligands lost prior to electrolysis is 1.6.

It is not possible to determine q from these experiments. However, some of the implications associated with the possible values of q may be discussed. If q is equal to zero, then a mixture of zinc(II) complexes, some containing one pyrophosphate ligand and some containing two pyrophosphate ligands, exists in solution. The standard rate constant for the reduction of zinc(II) in a solution of 1M potassium nitrate is 3.5×10^{-3} (21). Knowing this rate constant, K' may be determined if a value is assumed for E_f^o. From polarograms for the reduction of zinc(II) sulfate in 1M sodium nitrate solutions, E_f^o is -0.99 volts vs. SCE. At unit formal concentration of sodium pyrophosphate the product $k_s K'$ is equal to 2.8×10^{-7} for E = -0.99 volts. Thus K' is 8.0×10^{-5}. From the value of K' a relationship between the formal concentration of sodium pyrophosphate and the molar concentration of zinc(II) may be calculated. Thus,

Figure 6. Variation of $\log(k_f)$ with the logarithm of the formal concentration of sodium pyrophosphate at various potentials: △, 0.99 v.; ○, 1.1 v.; □, 1.2 v.; ▲, 1.3 v.; ●, 1.4 v.



$$\frac{[Zn^{+2}]C_B^{1.6}}{C_{Zn}} = 8.0 \times 10^{-5}$$

where C_B is the formal concentration of sodium pyrophosphate and C_{Zn} is the total concentration of zinc(II).

If q is equal to one, then a mixture of complexes formed by the association of zinc(II) with two and three pyrophosphate ligands exists in solution. The value for k_s is not known for the reduction of ZnB and there is no method to determine the value of K'.

It is also possible that two parallel mechanisms are in effect and that part of the zinc undergoes reduction by one path involving on zinc(II) complex and the rest of the zinc(II) undergoes reduction by another path involving a different zinc(II) complex. An example would be

$$ZnB_s \overset{\text{fast}}{\rightleftharpoons} ZnB_{s-1} + B \qquad (3.6)$$

$$ZnB_{s-1} + 2e^- \longrightarrow Zn(Hg) + (s-1)B \qquad (3.7)$$

and

$$ZnB_s \overset{\text{fast}}{\rightleftharpoons} ZnB_{s-2} + 2B \qquad (3.8)$$

$$ZnB_{s-2} + 2e^- \longrightarrow Zn(Hg) + (s-2)B \qquad (3.9)$$

If in fact these reactions occur, the ratio of the rates of electron-transfer for reactions 3.7 and 3.9 respectively is equal to the ratio of the equilibrium constant for reaction 3.8 to the concentration of B. In this case s may be either two of three and ZnB_s is the predominant species in solution.

It would appear that the assumption that $q = 0$ is more reasonable than the assumption that $q = 1$. The conductometric experiments of Rogers and Reynolds (4) show that zinc(II) pyrophosphate, like other metal pyrophosphates studied, redissolves as the 1:1 complex after having formed the pyrophosphate precipitate.

Thus in this author's opinion zinc(II) is associated with one or two pyrophosphate ligands at pH 5 and the concentration of free zinc(II) ion is given by

$$\frac{[\mathrm{Zn(II)}]\,C_B^{1.6}}{C_{Zn}} = 8 \times 10^{-5}$$

where C_B and C_{Zn} are as defined above.

4. THE ELECTROCHEMISTRY OF LEAD IN PYROPHOSPHATE MEDIA

Rogers and Reynolds (4) report that the reduction of lead(II) in a 100mF sodium pyrophosphate solution is reversible and that the half-wave potential is -690 millivolts vs. SCE. They assert that one pyrophosphate ligand is associated with lead(II). However, they offer no proof of this assertion.

Experimental. With one exception, all solutions were prepared by adding an aliquot of a lead nitrate solution to an aliquot of a solution of sodium pyrophosphate, adding a weighed amount of sodium nitrate to maintain unit ionic strength, adjusting the pH with nitric acid, and diluting to volume. The 243mF solution of sodium pyrophosphate was prepared by adding an aliquot of lead(II) solution to the sodium pyrophosphate solution and adjusting the pH of the resulting solution with nitric acid. Nitrate ion was employed as the anion after it was determined that the presence of nitrate ions does not effect the reduction step in the case of lead(II) as it effects the reduction step in the case of iron(III). The current-voltage curves were obtained employing a manual method in which the constant potential impressed across the cell was measured with a Beckman model G pH meter and the peak current was measured with a Sargent model XV polarograph with no RC damping.

Results. The results of the analysis of the polarographic steps are given in Table III. The quantities $E'_{\frac{1}{2}}$ and $E''_{\frac{1}{2}}$ are the half-wave potentials at pH 11 and 12, respectively, assuming that the following electrode reaction occurs

$$Pb(OH)_3^{1-} + 2e^- \rightleftharpoons Pb(Hg) + 3OH^- \qquad (4.1)$$

Qualitatively the results of the polarography are as follows. If the pH is less than 1.4, there is no precipitate present and the half-wave potential for reduction of lead(II) is independent of the formal concentration of sodium pyrophosphate and is equal to -394 millivolts vs. SCE. From the value of the half-wave potential and the independence of the potential from the formal concentration of sodium pyrophosphate it may be concluded that lead(II) does not associate with pyrophosphate ligands at a pH less than 1.4. As the pH is increased a precipitate appears that redissolves if the pH exceeds approximately five. From an analysis of the polarographic step, the reduction of lead(II) is reversible at pH five. As the pH of the solution is increased, the reduction of lead(II) becomes irreversible. If the pH is greater than about ten, the reduction is again reversible.

The effects of variation of the formal concentration of sodium pyrophosphate on the polarographic step were studied. At pH five it appears that the 1:1 complex is

Table III. Results of the polarographic experiments for case of lead(II) in pyrophosphate media

pH	$[Na_4P_2O_7]$, mF	$-E_{\frac{1}{2}}$, mv.	Slope,[a] mv.	$-E_{\frac{1}{2}}'$, mv.
1.07	100	395		
1.35	30	395		
1.37	10	394		
5.00	243	511	32.7	
5.02	100	491	31.8	
4.98	35	470	30.2	
5.03	10	452	32.5	
6.03	100	534	33.	
7.01	100	583	41.	
7.98	10	569	58.	
8.07	100	633	45.	
9.80	10	559	36.	
9.78	33	633	50.	
9.63	100	647	45.	
10.96	100	625	> 40.	629[b]
10.95	35	594	32.	599[b]
11.01	10	572	30.5	571[b]
10.95	0	555	20.5	560[b]

Table III. (continued)

pH	$[Na_4P_2O_7]$, mF	$-E_{\frac{1}{2}}$ mv.	Slope,[a] mv.	$-E_{\frac{1}{2}}''$ mv.
11.85	100	643	32.	657[c]
12.02	35	651	29.	649[c]
12.04	10	655	31.	651[c]
12.11	0	668	30	658[c]

a. Slope of line from the graph of the potential of the DME as a function of $\log((i_d - i)/i)$.

b. Half-wave potential at pH 11 assuming that $Pb(OH)_3^{1-}$ is the predominant lead(II) complex.

c. Half-wave potential at pH 12 assuming that $Pb(OH)_3^{1-}$ is the predominant lead(II) complex.

predominant at sodium pyrophosphate concentrations of less than 30mF and that the 1:2 complex is predominant at greater concentrations. With increasing pH in the range $6 < pH < 11$ and increasing formal concentration of sodium pyrophosphate the polarographic wave for the reduction of lead(II) becomes less reversible as indicated by the slope of the graph of the potential as a function of $\log((i_d - i)/i)$. The decrease in reversibility coincides with the increase of the concentration of monosodium pyrophosphate. In this respect the lead(II)-pyrophosphate system is very similar to the copper(II) system. A further increase in the pH converts the lead into the trihydroxo- complex as is demonstrated by the independence of the half-wave potential with respect to the formal concentration of sodium pyrophosphate at pH 12 and the dependence of the half-wave potential on the pH. Lingane (22) reports that the predominant lead(II) species in the region $12 < pH < 14$ is $Pb(OH)_3^{-1}$ which confirms this writer's results. The discrepancies between the potentials given in Table III and those given by Lingane (22) may be due to junction potentials or to the differences between the methods by which the concentration of the hydroxide ion was determined.

Neither chronopotentiometry nor polarography offers a simple method with which to elucidate the mechanism for reduction of lead(II) in pyrophosphate media. The polarographic step is not sufficiently irreversible to allow one to employ the method used in the case of zinc. Further, there is no evidence of two steps in the polarography of lead(II) so that the method employed in the cases of copper and iron cannot be used. In order to determine the number of ligands lost prior to the slow electron-transfer step, a more rapid technique such as galvanostatics or potentiostatics might be employed.

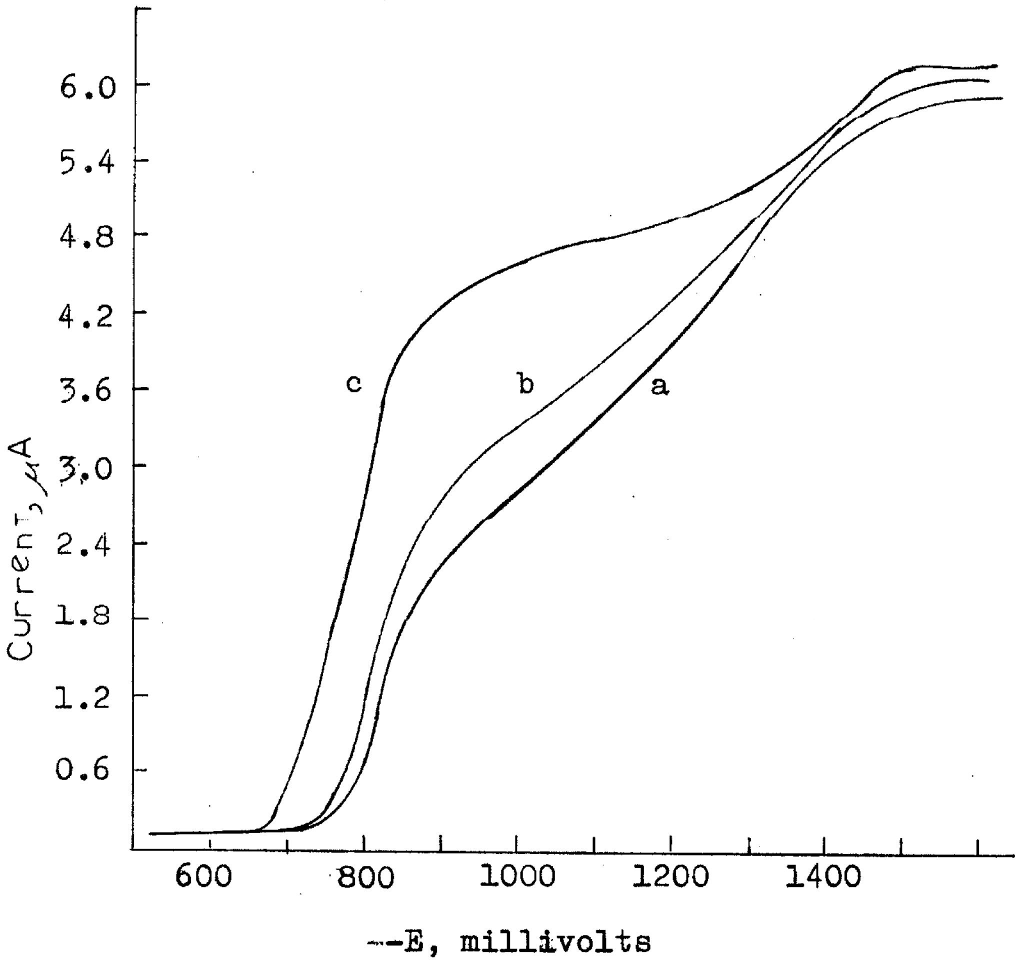
Although the reduction of lead(II) is not reversible in pyrophosphate media in the region $6 < pH < 11$, the number of ligands lost prior to the slow electron-transfer step is not known. However, the data support the conclusion that the lead(II)-pyrophosphate system may be similar to the copper(II)-pyrophosphate system. In such a case, bis(sodium pyrophosphato)plumbate(II) would be irreversibly reduced due to the fact that dissociation of a sodium pyrophosphate ligand is slow. As the pH of the solution is increased, trihydroxoplumbate(II) becomes the predominant lead(II) species and the reduction of this species is reversible.

5. THE ELECTROCHEMISTRY OF CADMIUM IN PYROPHOSPHATE MEDIA

Experimental. The cadmium-pyrophosphate solutions were prepared by adding an aliquot of a sodium pyrophosphate solution to an aliquot of a cadmium sulfate solution, adding sodium sulfate to maintain an ionic strength of unity, and adjusting the pH with sulfuric acid. The concentration of cadmium sulfate in these solutions was 1mF.

Results. Polarograms obtained in 100mF sodium pyrophosphate solutions at various values of the pH are shown in Figure 7. The polarograms obtained at pH 9.10 and pH 10.00 are identical. However, the wave obtained at pH 8.00 differs from the waves obtained at pH 9.10 and 10.00. The wave for pH 8.00 is initially much steeper than the wave for pH 9.10. Further, the former wave reaches a much higher current before breaking than does the latter wave. Also, the half-wave potential of the first part of the wave for pH 8.00 is 10 millivolts more anodic than the corresponding potential for the wave at pH 9.10. The characteristics of the wave obtained at pH 7.05 are similar to those of the wave obtained at pH 8.00. However, in the former case the first break occurs at a higher current than in the latter case and the half-wave potential is shifted 30

Figure 7. Polarograms for reduction of cadmium(II) in 100mF sodium pyrophosphate at various values of pH: a, 9.1; b, 8.0; c, 7.05



millivolts towards a more anodic potential. A precipitate is formed if the pH is greater than four and less than six. The polarographic steps for reduction of cadmium(II) are reversible and have the same half-wave potential of -610 millivolts for values of the pH of three, two, and one in 100mF sodium pyrophosphate solution. No polarograms could be obtained for any solution with pH greater than four in 10mF sodium pyrophosphate due to the fact that cadmium pyrophosphate precipitates.

In view of the fact that the half-wave potential for reduction of cadmium(II) is independent of the pH in solutions of pH less than three, it would appear that no cadmium(II)-pyrophosphate complex exists in this region. There is no quantitative explanation for the shape of the polarographic waves in solutions in which the pH is greater than seven.

II

6. CHRONOPOTENTIOMETRY AT UNSHIELDED ELECTRODES

It is common practice in electrochemistry to consider that the concentration at any plane electrode, regardless of its dimensions, is given by an equation which is derived for an infinite-plane electrode. While it is entirely possible that a finite electrode may be approximated by an infinite-plane electrode, it is important to know the limits for which this approximation is applicable. Thus, it is the desire here to make an approximation to the real electrode and to determine the constancy of the $i\tau^{\frac{1}{2}}$ product as a function of the transition time for the case of chronopotentiometry.

We consider a rectangular electrode in the plane $x = 0$ with corners at $(y,z) = (a,b)$, $(-a,b)$, $(a,-b)$, and $(-a,-b)$. The diffusion equation, the initial condition, and the boundary conditions are

$$\frac{1}{D}\cdot\frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \tag{6.1}$$

$$C\Big|_{t=0} = C^{o} \tag{6.2}$$

$$\left.\frac{\partial C}{\partial y}\right|_{y=0} = \left.\frac{\partial C}{\partial z}\right|_{z=0} = 0 \qquad (6.3)$$

$$\left.\frac{\partial C}{\partial x}\right|_{x\to\infty} = \left.\frac{\partial C}{\partial y}\right|_{y\to\infty} = \left.\frac{\partial C}{\partial z}\right|_{z\to\infty} = 0 \qquad (6.4)$$

$$\left.\frac{\partial C}{\partial x}\right|_{x=0} = f(y,z,t)\cdot h_1(y)\cdot h_2(z) \qquad (6.5)$$

where $C = C(x,y,z,t,a,b)$ is the concentration and

$$h_1(y) = \begin{cases} 1, & \text{if } -a \leq y \leq a \\ 0, & \text{otherwise} \end{cases} \qquad (6.6)$$

$$h_2(z) = \begin{cases} 1, & \text{if } -b \leq z \leq b \\ 0, & \text{otherwise} \end{cases} \qquad (6.7)$$

For a real electrode we have the additional boundary condition that the concentration is constant across the surface of the electrode.

The diffusion equation cannot be solved subject to the boundary conditions that exist for a real electrode due to the fact that the flux at the surface of the electrode is not known. However, if we assume the flux to be constant across the surface of the electrode, it is possible to solve the diffusion equation and from this solution it is possible to approximate the actual boundary conditions stated in equations (3), (4), and (5) and the boundary condition that the concentration is constant across the surface of the electrode.

The diffusion equation is solved by applying the method of integral transforms. Knowledge of the Laplace transform is assumed and a short explanation is given for the Fourier cosine transform. If $\bar{f}(p)$ is the Fourier cosine transform of $f(x)$, that is, if

$$\bar{f}(p) = \int_0^\infty f(x)\mathrm{cox}(px)dx \qquad (6.8)$$

then $f(x)$ is given by

$$f(x) = 2\pi^{-1}\int_0^\infty \bar{f}(p)\cos(px)dp \qquad (6.9)$$

The transformation, $\bar{g}(p)$, of the second derivative, $d^2f(x)/dx^2$ is given by

$$\bar{g}(p) = \int_0^\infty \frac{d^2f(x)}{dx^2}\cos(px)dx$$

$$= \frac{df(x)}{dx}\cos(px)\Big|_{x=0}^{\infty} + pf(x)\sin(px)\Big|_{x=0}^{\infty}$$

$$- p^2\bar{f}(p) \tag{6.10}$$

where $\bar{f}(p)$ is the Fourier cosine transform of $f(x)$.

Rather than solving the diffusion equation 6.1 as written, the following substitution is made

$$U(x,y,z,\alpha,a,b) = C^o - C(x,y,z,t,a,b) \tag{6.11}$$

where $\alpha = Dt$. Equation 6.1 becomes

$$\frac{\partial U}{\partial \alpha} = \frac{\partial^2 U}{\partial x^2} + \frac{\partial^2 U}{\partial y^2} + \frac{\partial^2 U}{\partial z^2} \tag{6.12}$$

where $U = U(x,y,z,\alpha,a,b)$. The boundary condition 6.5 under the assumption that the current density is constant across the surface of the electrode is

$$\frac{\partial U}{\partial x}\Big|_{x=0} = -\beta h_1(y)h_2(z) \tag{6.13}$$

where $\beta = i/(nFD)$ and i is the current density. We shall refer to those electrodes that satisfy the above condition as uniform-flux electrodes. (Planar uniform-flux electrodes are constructs and may only be approximated in the real world.)

Using the Laplace transform with respect to α with transform variable s, equation 6.12 becomes

$$s\bar{U} = \frac{\partial^2 \bar{U}}{\partial x^2} + \frac{\partial^2 \bar{U}}{\partial y^2} + \frac{\partial^2 \bar{U}}{\partial z^2} \qquad (6.14)$$

where $\bar{U} = \bar{U}(x,y,z,s,a,b)$. Using the Fourier cosine transform with respest to x with transform variable p, equation 6.14 becomes

$$s\bar{\bar{U}} = \frac{\beta}{s} h_1(y)h_2(z) - p^2\bar{\bar{U}} + \frac{\partial^2 \bar{\bar{U}}}{\partial y^2} + \frac{\partial^2 \bar{\bar{U}}}{\partial z^2} \qquad (6.15)$$

where $\bar{\bar{U}} = \bar{\bar{U}}(p,y,z,s,a,b)$. Using the Fourier cosine transform with respect to y with transform variable q, equation 6.15 becomes

$$(s + p^2 + q^2)\bar{\bar{\bar{U}}} = \frac{\beta}{s} h_2(z) \int_0^a \cos(qy)dq + \frac{\partial^2 \bar{\bar{\bar{U}}}}{\partial z^2}$$

$$= \frac{\beta h_2(z)}{sq} \sin(qa) + \frac{\partial^2 \bar{\bar{\bar{U}}}}{\partial z^2} \qquad (6.16)$$

where $\bar{\bar{\bar{U}}} = \bar{\bar{\bar{U}}}(p,q,z,s,a,b)$. Finally, using the Fourier cosine transform with respect to the variable z with transform variable r, equation 6.16 becomes

$$(s + p^2 + q^2 + r^2)\overline{\overline{\overline{U}}} = \frac{\beta \sin(qa)}{sq}\int_0^b \cos(rz)dz$$

$$= \frac{\beta}{sqr}\sin(qa)\sin(rb) \qquad (6.17)$$

where $\overline{\overline{\overline{U}}} = \overline{\overline{\overline{U}}}(p,q,r,s,a,b)$. Rearranging equation 6.17 we have

$$\overline{\overline{\overline{U}}} = \frac{\beta \sin(qa)\sin(rb)}{sqr(s + q^2 + r^2 + p^2)} \qquad (6.18)$$

Having solved for U in terms of the transform variables, we employ inverse transforms to obtain U as a function of the original variables x, y, z, and t. Using the Faltung theorem for the Laplace transform, equation 6.18 becomes

$$\overline{\overline{\overline{U}}}' = \beta\int_0^{\alpha}\left[\frac{\sin(qa)}{q}\, e^{-q^2\varepsilon}\right]\left[\frac{\sin(rb)}{r}\, e^{-p^2\varepsilon}\right]d\varepsilon \qquad (6.19)$$

where $\overline{\overline{\overline{U}}}' = \overline{\overline{\overline{U}}}'(p,q,r,\alpha,a,b)$ is the inverse Laplace transform of $\overline{\overline{\overline{U}}}$. Using the trigonometric identity

$$\sin(c)\cos(d) = \tfrac{1}{2}\sin(c + d) + \tfrac{1}{2}\sin(c - d) \qquad (6.20)$$

we may perform the remaining inverse transforms to obtain

$$U = \frac{2\beta}{\pi^3}\int_0^{\alpha}\left\{\int_0^{\infty}\frac{e^{-q^2\varepsilon}}{q}\Big[\sin(q(a+y)) + \sin(q(a-y))\Big]dq\right\}$$

$$\cdot\left\{\int_0^{\infty}\frac{e^{-r^2\varepsilon}}{r}\Big[\sin(r(b+z)) + \sin(r(b-z))\Big]dr\right\}$$

$$\cdot\left\{\int_0^{\infty} e^{-p^2\varepsilon}\cos(px)dp\right\}d\varepsilon$$

$$= \frac{2\beta}{\pi^3}\iint_0^{\alpha}\left\{\left[\frac{\pi}{2}\,\mathrm{Erf}\left(\frac{a+y}{2\sqrt{\varepsilon}}\right) + \frac{\pi}{2}\,\mathrm{Erf}\left(\frac{a-y}{2\sqrt{\varepsilon}}\right)\right]\right.$$

$$\cdot\left[\frac{\pi}{2}\,\mathrm{Erf}\left(\frac{b+z}{2\sqrt{\varepsilon}}\right) + \frac{\pi}{2}\,\mathrm{Erf}\left(\frac{b-z}{2\sqrt{\varepsilon}}\right)\right]$$

$$\left.\cdot\left[\frac{\pi^{\frac{1}{2}}}{2\sqrt{\varepsilon}}\,e^{-x^2/4\varepsilon}\right]\right\}d\varepsilon \qquad (6.21)$$

In order to simplify the discussion to follow, we shall solve for the concentration at the surface of the electrode, that is, we set the variable x to zero so that equation 6.21 becomes

$$V = \frac{\beta}{4\sqrt{\pi}}\int_0^{\alpha}\left[\mathrm{Erf}\left(\frac{a+y}{2\sqrt{\varepsilon}}\right) + \mathrm{Erf}\left(\frac{a-y}{2\sqrt{\varepsilon}}\right)\right]\left[\mathrm{Erf}\left(\frac{b+z}{2\sqrt{\varepsilon}}\right) + \mathrm{Erf}\left(\frac{b-z}{2\sqrt{\varepsilon}}\right)\right]\frac{d\varepsilon}{\varepsilon^{\frac{1}{2}}} \quad (6.22)$$

where $V = V(y,z,\alpha,a,b) = U(0,y,z,\alpha,a,b)$. If the substitution $w = \varepsilon^{\frac{1}{2}}$ is made, equation 6.22 becomes

$$V = \frac{\beta}{2\sqrt{\pi}}\int_0^{\alpha^{\frac{1}{2}}}\left[\mathrm{Erf}\left(\frac{a+y}{2w}\right) + \mathrm{Erf}\left(\frac{a-y}{2w}\right)\right]\left[\mathrm{Erf}\left(\frac{b+z}{2w}\right) + \mathrm{Erf}\left(\frac{b-z}{2w}\right)\right] dw$$

(6.23)

Equation 6.23 may be further simplified for the purpose of discussion by setting

$$V = \frac{\beta}{2\sqrt{\pi}}\left\{I_1 + I_2 + I_3 + I_4\right\} \quad (6.24)$$

where

$$I_1 = \int_0^{\alpha^{\frac{1}{2}}} \mathrm{Erf}\left(\frac{a+y}{2w}\right)\mathrm{Erf}\left(\frac{b+z}{2w}\right)dw \quad (6.25)$$

$$I_2 = \int_0^{\alpha^{\frac{1}{2}}} \mathrm{Erf}\left(\frac{a+y}{2w}\right)\mathrm{Erf}\left(\frac{b-z}{2w}\right)dw \qquad (6.26)$$

$$I_3 = \int_0^{\alpha^{\frac{1}{2}}} \mathrm{Erf}\left(\frac{a-y}{2w}\right)\mathrm{Erf}\left(\frac{b+z}{2w}\right)dw \qquad (6.27)$$

$$I_4 = \int_0^{\alpha^{\frac{1}{2}}} \mathrm{Erf}\left(\frac{a-y}{2w}\right)\mathrm{Erf}\left(\frac{b-z}{2w}\right)dw \qquad (6.28)$$

Special Case I: The infinite-plane electrode. In the limit as $a, b \rightarrow \infty$ the arguments of the error function are large and the error function approaches a limiting value of unity. Under these conditions the integrals I_1, I_2, I_3, and I_4 are readily evaluated and the concentration at the surface of the electrode is

$$C(0,y,z,t) = C^o - 2\beta \cdot \left[\frac{Dt}{\pi}\right]^{\frac{1}{2}} \qquad (6.29)$$

Thus, the transition time, τ, as a function of the current density is given implicitly by

$$C^o = \frac{2i}{nF} \cdot \left(\frac{\tau}{\pi D}\right)^{\frac{1}{2}} \qquad (6.30)$$

Equation 6.35 is the familiar Sand equation (23).

Special Case II: The infinite-strip electrode. In the limit as $b \longrightarrow \infty$ we have $I_i = I_{i1}$, $i = 1, 2, 3, 4$, where

$$I_{11} = I_{21} = \int_0^{\alpha^{\frac{1}{2}}} \mathrm{Erf}\left(\frac{a+y}{2w}\right) dw \qquad (6.31)$$

$$I_{31} = I_{41} = \int_0^{\alpha^{\frac{1}{2}}} \mathrm{Erf}\left(\frac{a-y}{2w}\right) dw \qquad (6.32)$$

These integrals may be solved by integration by parts and a change of variables. Integration by parts yields

$$I_{11} = w\mathrm{Erf}\left(\frac{a+y}{2w}\right)\Bigg|_{w=0}^{\alpha^{\frac{1}{2}}} + \int_0^{\alpha^{\frac{1}{2}}} \frac{a+y}{w\sqrt{\pi}} \exp\left[-\frac{(a+y)^2}{4w^2}\right] dw \qquad (6.33)$$

The latter integral may be put in a more standard form by the substitution $v = (a+y)^2/4w^2$; we have

$$I_{11} = \alpha^{\frac{1}{2}}\mathrm{Erf}\left(\frac{a+y}{2\sqrt{\alpha}}\right) + \frac{a+y}{2\sqrt{\pi}} \int_{\frac{(a+y)^2}{4\alpha}}^{\infty} \frac{\exp(-v)}{v}\, dv$$

$$= \alpha^{\frac{1}{2}}\mathrm{Erf}\left(\frac{a+y}{2\sqrt{\alpha}}\right) - \frac{a+y}{2\sqrt{\pi}}\, \mathrm{Ei}\left[- \frac{(a+y)^2}{4\alpha}\right] \qquad (6.34)$$

By a similar transformation equation 6.31 becomes

$$I_{31} = I_{41} = \alpha^{\frac{1}{2}}\mathrm{Erf}\left(\frac{a-y}{2\sqrt{\alpha}}\right) - \frac{a-y}{2\sqrt{\pi}}\, \mathrm{Ei}\left[- \frac{(a-y)^2}{4\alpha}\right] \qquad (6.35)$$

Let us define the function $H = H(y,\alpha,a)$ by

$$H = \frac{\pi}{\beta}\, V$$

$$= (\pi\alpha)^{\frac{1}{2}} \left[\mathrm{Erf}\left(\frac{a+y}{2\sqrt{\alpha}}\right) + \mathrm{Erf}\left(\frac{a-y}{2\sqrt{\alpha}}\right)\right]$$

$$- \frac{a+y}{2}\, \mathrm{Ei}\left[- \frac{(a+y)^2}{4\alpha}\right] - \frac{a-y}{2}\, \mathrm{Ei}\left[- \frac{(a-y)^2}{4\alpha}\right] \qquad (6.36)$$

Values of H for $a = 0.25$ cm. and $a = 0.0005$ cm. have been calculated for α ranging from 0.00001 cm^2. to

0.00100cm.^2 in steps of 0.00001cm.^2, and for values of $y-a$ from 0 cm. to approximately 0.05 cm. in steps of 0.0005 cm. These values are punched on IBM cards and are labeled CØN and CN respectively.

Because the differential equation that describes diffusion is linear in the concentration, we may calculate the concentration due to several uniform-flux electrodes as the sum of the concentrations due to each electrode in the absence of any other electrode. (If we were considering an equipotential surface, the above principal would be inapplicable because the presence of an equipotential surface must change the concentration profile, and hence the flux, of any other electrode.)

It would be reasonable to superimpose several uniform-flux, infinite-strip electrodes in such a manner that the system of electrodes has the approximate properties of a real electrode. To this end we superimpose several uniform-flux, infinite-strip electrodes on a uniform-flux, infinite-strip electrode E_o. Electrode E_o has a half width of a and the flux at this electrode is β. The real electrode that we are trying to approximate, E, has a half width of a and the average flux at this electrode is β.

We superimpose three electrodes, E_k, E'_k, and E''_k

at time $t = t_k$. Electrode E_k' is centered at $y = Y_k$, has a half width of a', and has a flux of βB_k. Electrode E_k'', a replica of E_k', is centered at $y = -Y_k$, has a half width of a', and has a flux of βB_k. Electrode E_k has a half width of a and coincides with E_o. The flux at E_k is $-\beta B_k(2a'/a)$. This method of adding electrodes retains the symmetry and preserves a constant current flowing into the system of electrodes. We denote the system of electrodes consisting of electrodes E_o, E_1, E_1', E_1'', $\ldots$, E_k, E_k', E_k'' by $E(k)$. If $\alpha_k = Dt_k$, then the concentration, $\frac{\beta}{\pi} V_o(y,\alpha,a) = \frac{\beta}{\pi} V_o$, in the plane of the electrode $E(k)$ is given by

$$\frac{\beta}{\pi} V_o = \frac{\beta}{\pi} H(y,\alpha,a) + \frac{\beta}{\pi} \sum_k \left[B_k(H(y',\alpha-\alpha_k,a') - \frac{2a'}{a} H(y,\alpha-\alpha_k,a)) \right] \tag{6.37}$$

where we define $H(y,\alpha,a) = 0$ for $\alpha \leq 0$, and $y' = y-Y_k$.

In order to approximate a real electrode, we need to determine electrodes E_k' (and thus determine E_k and E_k'') such that V_o is approximately constant for $-a \leq y \leq a$. The algorithm by which the values for

B_k, Y_k, and α_k are calculated is as follows. Using an initial value for α of 0.00001 cm.^{2}, values of V_o are calculated on the (one-dimensional) grid $y-a = 0.0005, 0.0010, 0.0015, \ldots$ cm., in this order. If the concentration at a point on the grid is less than 99% of the concentration at the center of the electrode E_o, then we let Y_1 be the point on the grid at which the concentration attains its first minimum (in the order of calculation) and place electrode E_1' at Y_1, electrode E_1'' at $-Y_1$ and electrode E_1 coincident with electrode E_o. The value of α_1 is $\alpha - 0.00001$ cm.^{2} The value for B_1 is calculated to be the difference between 101% of the concentration at the center of the electrode E_o at time α/D sec. and the concentration at Y_1, divided by the concentration at the center of an electrode of half width 0.0005 cm. for $\alpha = 0.00001$ cm.^{2}, i.e., $H(0,0.00001,0.0005)$. The calculation of V_o begins again with $y-a = 0.0005$ cm. In general, at time $t = t_k + 0.00001/D$, if the concentration at a point on the electrode is less than 99% of the concentration at the center of the electrode $E(k-1)$, we let Y_k be the point on the grid at which the minimum occurs and place electrodes E_k' and E_k'' at Y_k and $-Y_k$ respectively. The value for B_k is the difference between the concentration at Y_k and 101% of the concentration at the center of electrode E(k-1), divided by H(0,0.00001, 0.0005). The calculation of V_o begins again with y-a = 0.0005 cm. If the concentration at electrode E(k) does not fall below 99% of the concentration at the center of the electrode E(k) on the grid from y-a = 0.0005 cm. to y-a = 0.0490 cm., then the concentration at the point y = a is calculated and $V_o(0,\alpha,a)$ and the value of V_o for a-y = 0., 0.0005, 0.0010, 0.0015, ..., 0.0490 cm. are printed. The value of α is increased to $\alpha + 0.00001$ cm.^{2} We then proceed to determine E(k+1), E(k+2), ... Graphs of the current density at time α/D as a function of a-y obtained from the above calculations for a = 0.25 cm. are shown in Figure 8 for certain values of α.

The concentration, C(y,t,a), at the surface of the electrode is

$$C(y,t,a) = C^o - \frac{\beta}{\pi} V_o(y,\alpha,a) \tag{6.38}$$

The transition time is given implicitly by

$$\begin{aligned} V_o(y,D\tau,a) &= \frac{\pi}{\beta} C^o \\ &= \frac{\pi nFDC}{i} \end{aligned} \tag{6.39}$$

Figure 8. Graphs of $X = (d(\delta,\alpha) - d(0,\alpha))/\beta$ vs. δ, for various values of α, where $d(\delta,\alpha)$ is the current density at a distance δ from the edge of an electrode of half-width 0.25 cm. at time α/D.

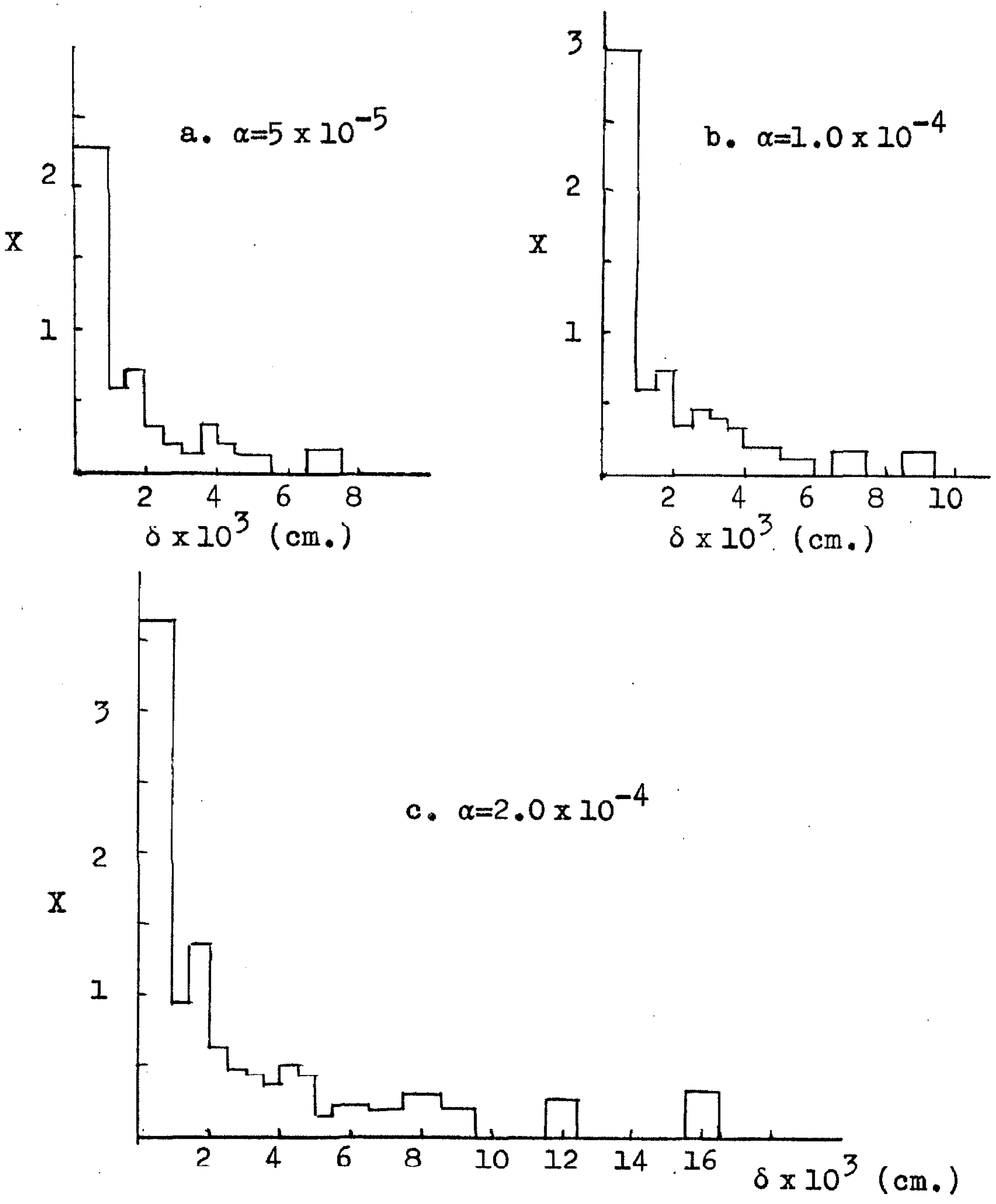


Figure 8.(Continued)

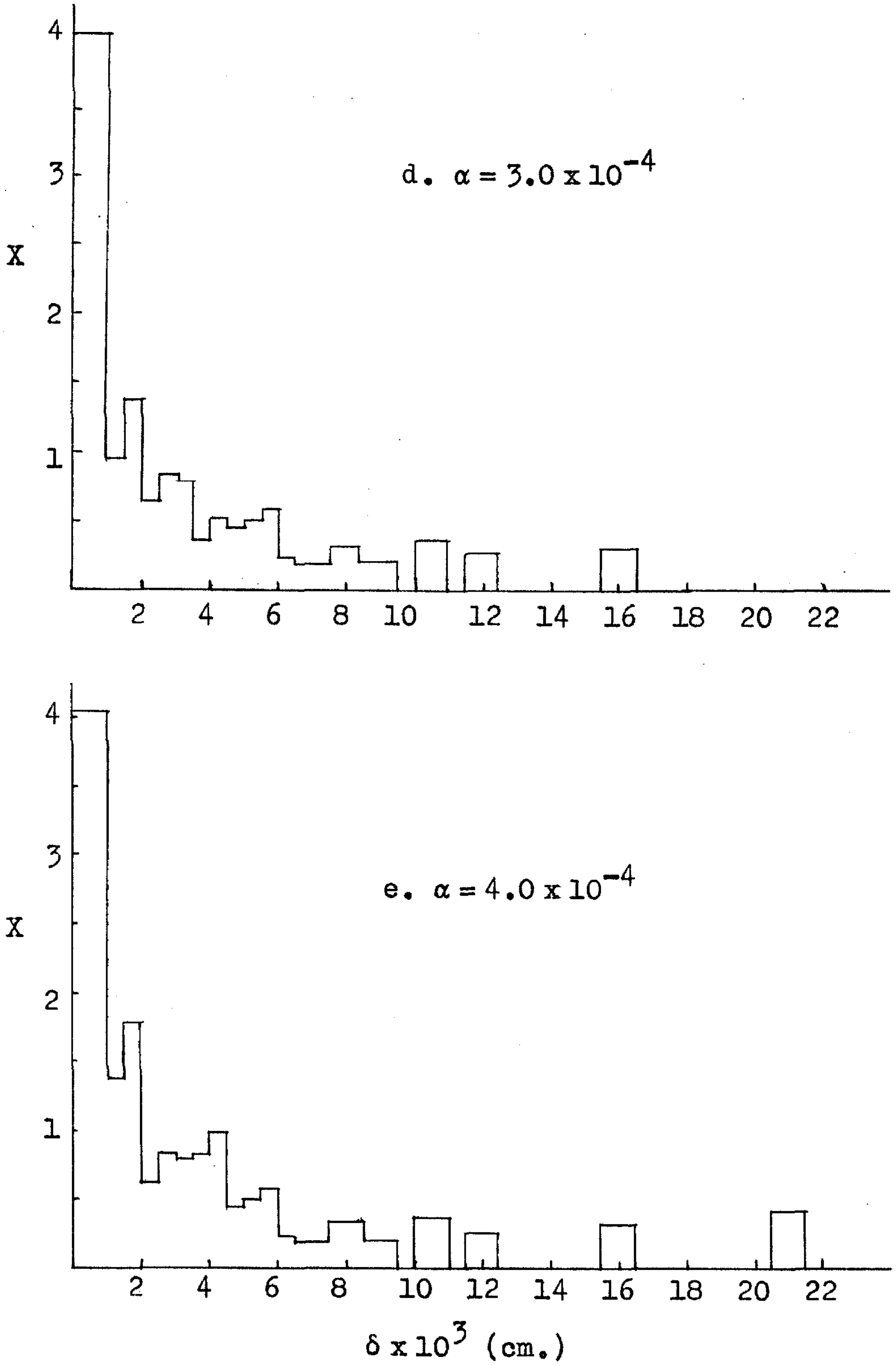
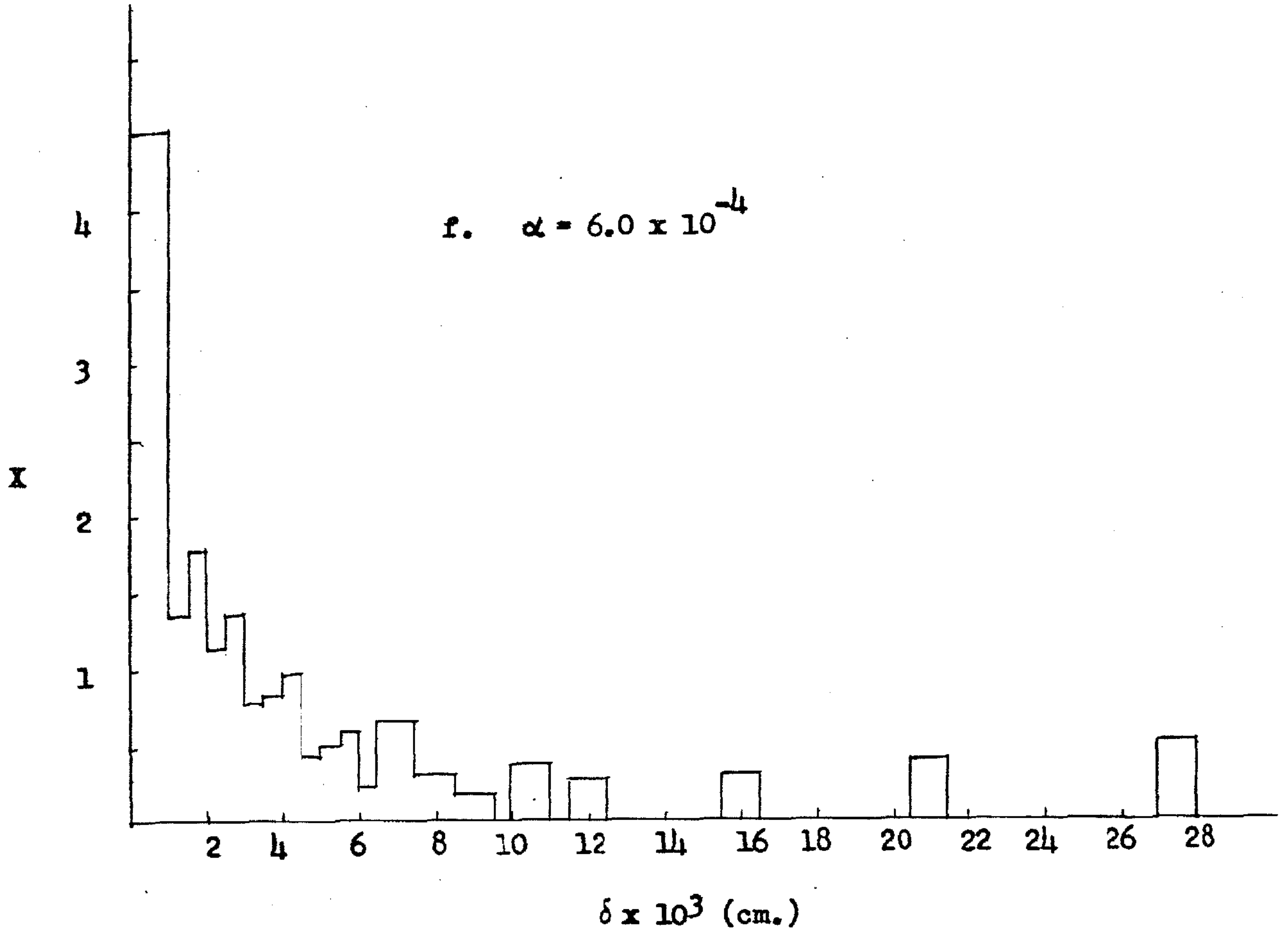


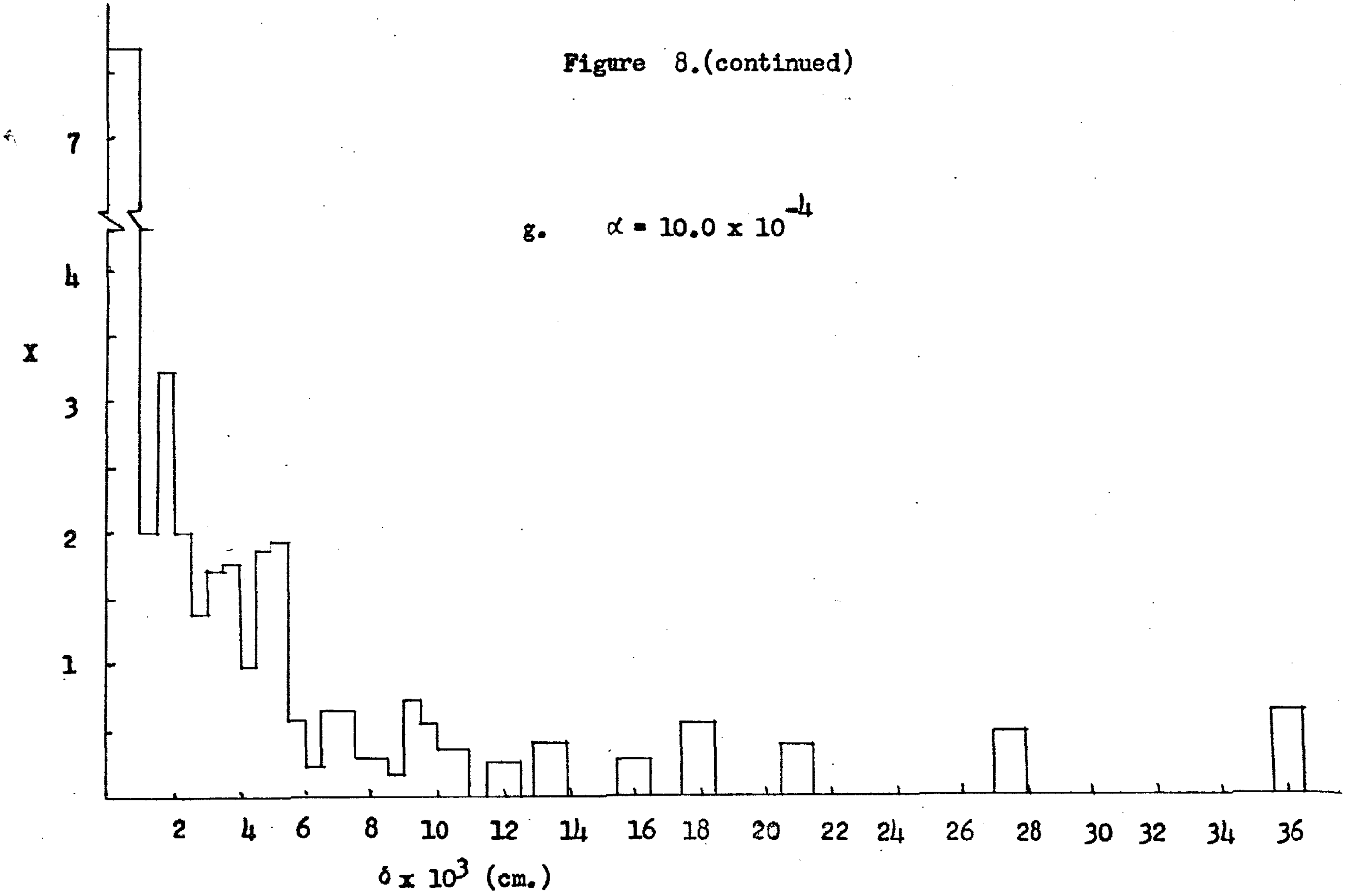
Figure 8. (continued)



f. $\alpha = 6.0 \times 10^{-4}$

Figure 8.(continued)

g. $\alpha = 10.0 \times 10^{-4}$



In the limit of very short transition times the concentration is very nearly constant across the surface of a uniform-flux electrode. Thus for very short transition times the Sand equation should be valid. Further, it has been suggested by Lingane (24) that the correction to the Sand equation should be a polynomial in $\tau^{\frac{1}{2}}$, of that the transition time should be given by

$$\frac{2i\tau^{\frac{1}{2}}}{nFC^{o}(\pi D)^{\frac{1}{2}}} = 1 + A_1\tau^{\frac{1}{2}} + A_2\tau + \ldots \qquad (6.40)$$

Thus it would appear reasonable that if the quantity $Q = 2(\pi D\tau)^{\frac{1}{2}}/V_o(y,D\tau,a)$ is plotted as a function of $\alpha^{\frac{1}{2}}$, it would be expected that the y-intercept should be unity. Graphs of these quantities are shown in Figure 9 for half widths of 0.125, 0.25, and 0.5 cm. Three polynomials of the form $Q = A_o + A_1\alpha^{\frac{1}{2}} + A_2\alpha$ have been determined from the above graphs by the least-squares method. The coefficients are given in Table IVA. Four sets of values for the coefficients are given for an electrode of half width 0.25 cm., corresponding to maximum values of α of 0.00025, 0.00050, 0.00075, and 0.00100 cm.^{2} We define the quantity X as the product of $\alpha^{\frac{1}{2}}$ and the half width of the electrode; our data then determines a

Figure 9. Graphs of $Q = 2(\pi D\tau)^{\frac{1}{2}}/V_o(y,D\tau,a)$ as a function of $\alpha^{\frac{1}{2}}$ for electrodes of various half-widths: a, 0.125 cm.; b, 0.25 cm.; c, 0.50 cm.

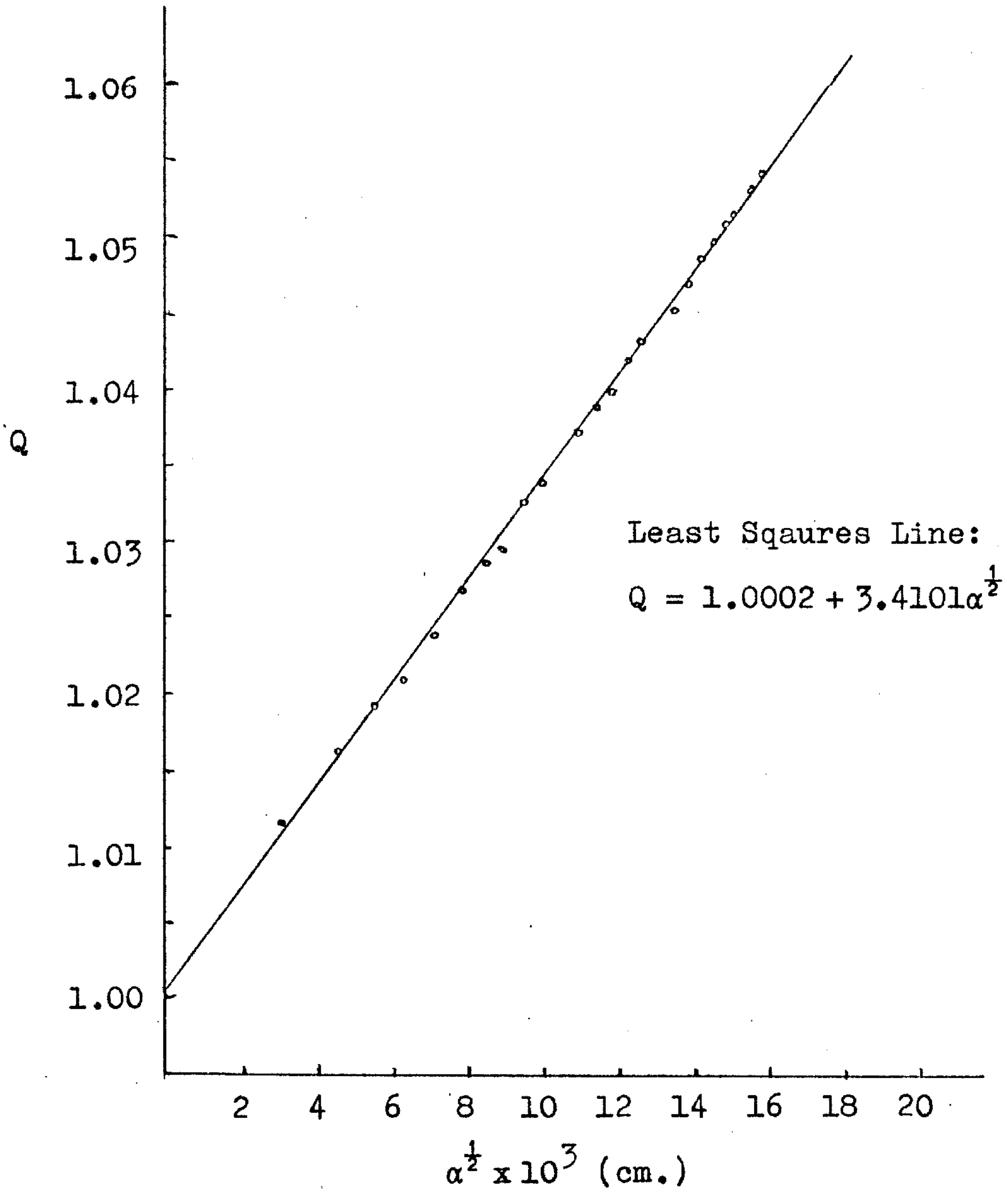
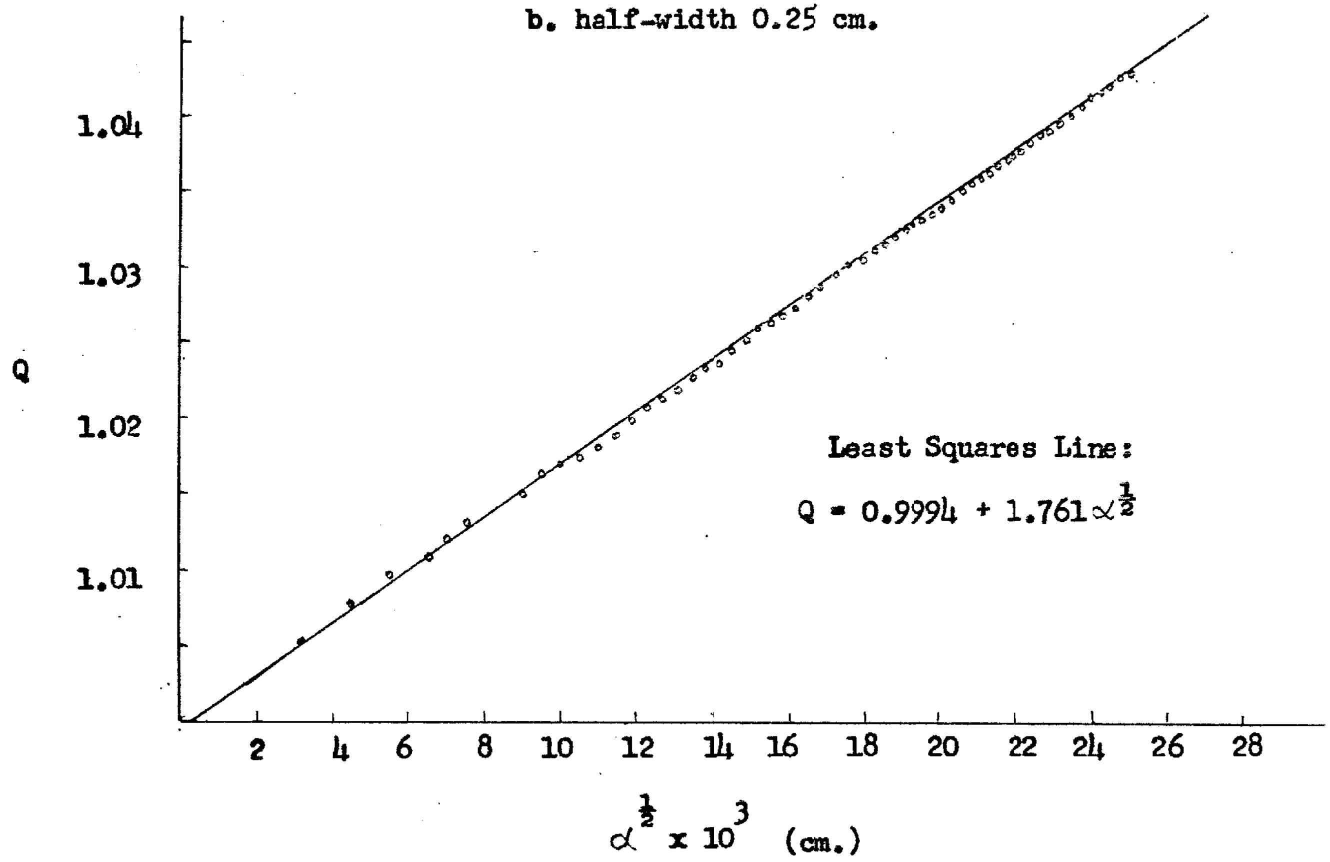

a. half-width 0.125 cm.

Figure 9. (continued)

b. half-width 0.25 cm.



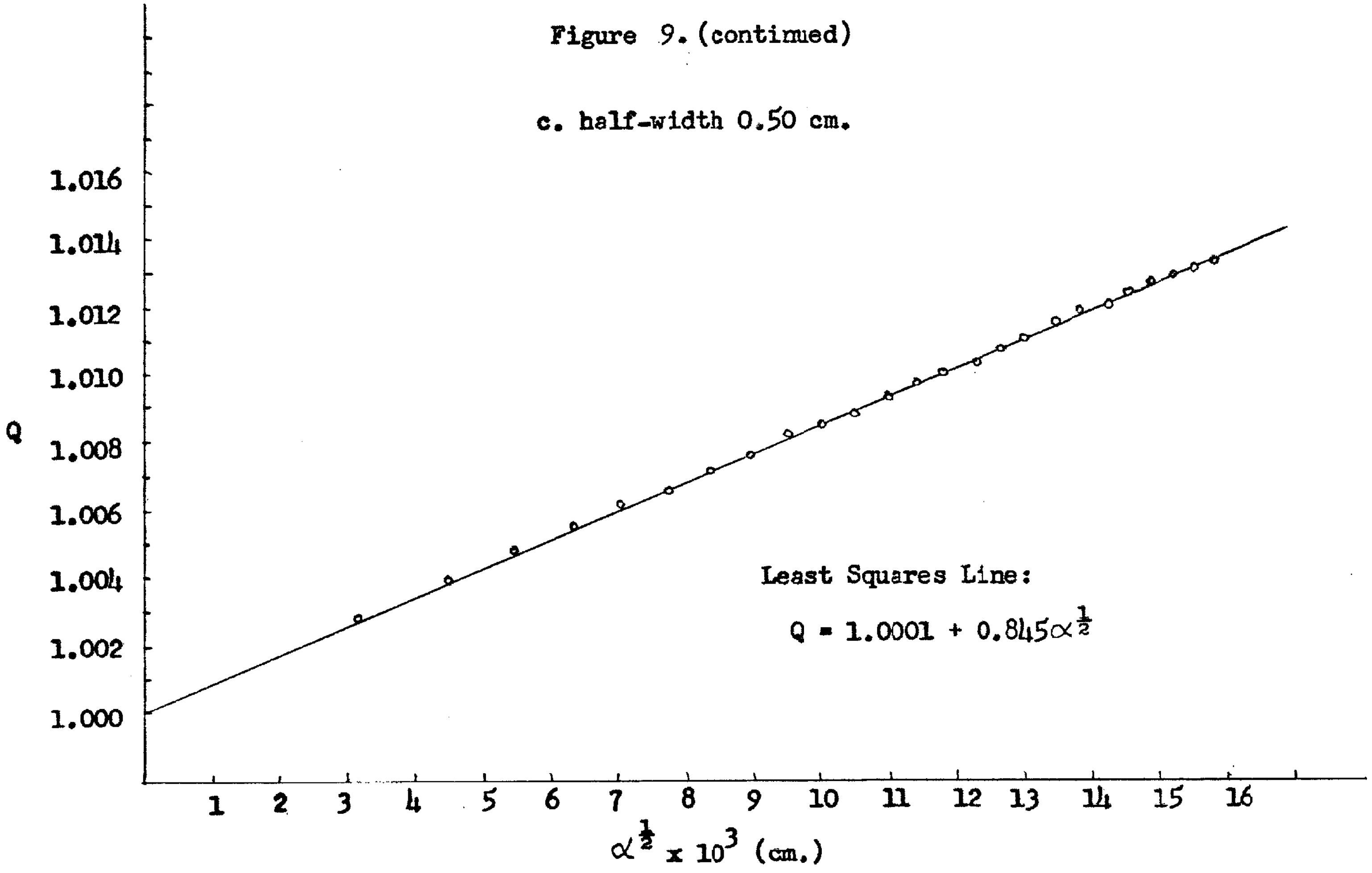


Figure 9. (contimed)

c. half-width 0.50 cm.

Least Squares Line:

$Q = 1.0001 + 0.845\alpha^{\frac{1}{2}}$

curve of the form $Q = A_0 + A_1'X + A_2'X^2$, the coefficients of which are given in Table IVB. The values of A_1' do not vary substantially with the half width of the electrode and we may thus use the average value of 0.398 for A_1' for an electrode of arbitrary half width. The variations of A_2' are not very significant in view of the magnitude of X under consideration. Thus we may suppose that $A_2' \sim 0.3$ for an arbitrary electrode.

Hence, for an infinite-strip electrode of half width a, the transition time is given approximately by

$$\tau^{\frac{1}{2}} = \frac{\pi^{\frac{1}{2}} nFC^0 D^{\frac{1}{2}}}{2i} \left[1 + 0.398 \cdot \frac{(D\tau)^{\frac{1}{2}}}{a} + 0.3 \frac{D\tau}{a^2} \right] \qquad (6.41)$$

It might be appropriate at this point to discuss a circular disk electrode of radius r. This electrode is not unlike the infinite-strip electrode just discussed. It has no corners and, if the radius of the electrode is sufficiently large, the curvature at the edge of the electrode is small. In order to approximate a real disk electrode in terms of the infinite-strip electrode, we must make two assumptions. The first assumption is that we may neglect the cylindrical diffusion that occurs at the edge of the electrode. The second assumption is that the current necessary to produce a given current density

Table IV. Values of the coefficients of quadratic polynomials calculated from the data by the method of least squares.

A. Coefficients of the equation $Q = A_o + A_1\alpha^{\frac{1}{2}} + A_2\alpha$

Maximum value of $\alpha \times 10^5$, cm.^{2}		Half width of electrode, cm.		
		0.125	0.25	0.50
	A_o =	1.00139	1.00067	1.00031
25	A_1 =	3.1408	1.6910	0.79461
	A_2 =	13.50	5.469	2.522
	A_o =		1.00059	
50	A_1 =		1.6025	
	A_2		4.496	
	A_o =		1.00065	
75	A_1 =		1.5912	
	A_2		4.769	
	A_o =		1.00051	
100	A_1 =		1.6204	
	A_2 =		3.655	

Table IV. (continued)

B. Coefficients of the equation $Q = A_o + A_1'X + A_2'X^2$

25	$A_1' =$	0.393	0.395	0.397
	$A_2' =$	0.211	0.342	0.630
50	$A_1' =$		0.401	
	$A_2' =$		0.281	
75	$A_1' =$		0.398	
	$A_2' =$		0.298	
100	$A_1' =$		0.405	
	$A_2' =$		0.228	

is not a function of the radius of the annular ring on which the current is impressed. (For very large radii these assumptions are very nearly true.)

To construct an approximation to a real electrode, we superimpose several annular, uniform-flux electrodes, E_k', and several uniform-flux disk electrodes, E_k. The annular electrodes have a thickness of 0.001 cm. and the disks have a radius of r. We superimpose two electrodes, E_k and E_k' at time $t = t_k$. Electrode E_k' has a flux of βB_k and electrode E_k has a flux of $-2\beta(0.001)/r$. As in the case of the infinite-strip electrode this method of adding flux preserves a constant current flowing into the system of electrodes. It would appear reasonable for large radii to use the same value of B_k for the disk electrode as we use for the infinite-strip electrode and the electrodes E_k' are placed the same distance from the edge of the electrode E_o for the case of a disk electrode as for the case of an infinite-strip electrode. There is one important difference, however, because the flux at electrode E_k is twice the flux at the corresponding infinite-strip electrode. Doubling the flux corresponds to giving an "effective half width" of one-half the radius of the disk electrode. Substituting the effective radius of the electrode, r/2, into equation (6.41), the transition time for a disk electrode of radius r is given implicitly by

$$\tau^{\frac{1}{2}} = \frac{\pi^{\frac{1}{2}} nFC^{o} D^{\frac{1}{2}}}{2i} \left[1 + 0.796 \frac{(D\tau)^{\frac{1}{2}}}{r} + 1.2 \frac{D\tau}{r^{2}} \right] \qquad (6.42)$$

In his experimental study of chronopotentiometry at unshielded electrodes, Lingane (24) reports that the value of the coefficient of $\alpha^{\frac{1}{2}}/r$ is 0.98 ± 0.10. This value is in good agreement with the value of 0.796 determined in this thesis.

General Case. The finite electrode. Assuming only that a and b are greater than $4\alpha^{\frac{1}{2}}$, the integrals I_i become I_{i3}, $i = 1, 2, 3, 4$, where

$$I_{13} = \alpha^{\frac{1}{2}} \qquad (6.43)$$

$$I_{23} = \int_{0}^{\alpha^{\frac{1}{2}}} \mathrm{Erf}\left(\frac{b-z}{2w}\right) dw$$

$$= \alpha^{\frac{1}{2}} \mathrm{Erf}\left(\frac{b-z}{2\sqrt{\alpha}}\right) - \frac{b-z}{2\sqrt{\pi}} \mathrm{Ei}\left[- \frac{(b-z)^{2}}{4\alpha} \right] \qquad (6.44)$$

$$I_{33} = \int_0^{\alpha^{\frac{1}{2}}} \mathrm{Erf}(\frac{a-y}{2w})dw$$

$$= \alpha^{\frac{1}{2}} \mathrm{Erf}(\frac{a-y}{2\sqrt{\alpha}}) - \frac{a-y}{2\sqrt{\pi}} \mathrm{Ei}\left[-\frac{(a-y)^2}{4\alpha}\right] \qquad (6.45)$$

$$I_{43} = \int_0^{\alpha^{\frac{1}{2}}} \mathrm{Erf}(\frac{a-y}{2w})\mathrm{Erf}(\frac{b-z}{2w})dw \qquad (6.46)$$

Thus, at the surface of a uniform-flux electrode of half width a and b in the y and z directions, the concentration is

$$U(0,y,z,\alpha,a,b) = \frac{\beta}{2\pi}\left[G(a-y) + G(b-z) - (\pi\alpha)^{\frac{1}{2}} + \pi^{\frac{1}{2}}I_{43}\right] \qquad (6.47)$$

where $G(u) = (\pi\alpha)^{\frac{1}{2}}\left[1 + \mathrm{Erf}(\frac{u}{2\sqrt{\alpha}})\right] - \frac{1}{2}u\mathrm{Ei}(-u^2/(4\alpha))$ (6.48)

If $\frac{a+y}{2\sqrt{\alpha}} > 2$, then H approximates G(a-y). Because $I_{43} \leq \alpha^{\frac{1}{2}}$, the concentration at any point on the electrode is less than the average concentration from two infinite-strip electrodes that are centered on the z-axis and the y-axis.

As an approximation we construct an electrode with the property that the current density along the edges of the electrode is the same as the current density along the edge of an infinite-strip electrode. Thus, on the surface of the electrode at $z = 0$, the concentration is uniform for all y because the ends are sufficiently distant that in the y direction the electrode appears to be an infinite-strip electrode.

The electrode that we are constructing as an approximation to the real electrode is formed from an initial uniform-flux, rectangular electrode E_o having flux β. At time $t = t_k$ we superimpose five electrodes on the system of electrodes $E(k-1)$. Rectangular, uniform-flux electrodes E_k^z and E_k^{-z} are centered at $y = Y_k$ and $-Y_k$ respectively. These electrodes are of length 2b (in the z direction) and have a half width, a', of 0.0005 cm. Rectangular, uniform-flux electrodes E_k^y and E_k^{-y} are centered at $z = Y_k$ and $-Y_k$ respectively. These electrodes are of length 2a (in the y direction) and have a half width, a', of 0.0005 cm. The flux at each of these four electrodes is βB_k, where B_k is as defined in the case of the infinite-strip electrode. Electrode E_k has the same dimensions as electrode E_o. The flux at electrode E_k is $-\beta B_k(2a')(a+b)/(ab)$. From the flux on electrode E_k we would conclude that the system of electrodes $E(k)$ is equivalent to an infinite-strip electrode of half width $ab/(a+b)$ and that the transition time is given implicitly by

$$\tau^{\frac{1}{2}} = \frac{\pi^{\frac{1}{2}} nFC^{o}D^{\frac{1}{2}}}{2i}\left[1 + 0.398(D\tau)^{\frac{1}{2}}\frac{(a+b)}{ab} + 0.3D\tau\frac{(a+b)^2}{a^2b^2}\right] \tag{6.49}$$

However, it is not possible to ascertain whether the concentration at the corners of the electrode is much greater or much less than the concentration at the center of the electrode.

In order to determine the concentration at the corners of the electrode, we shall calculate the difference between the concentration at the corners of the electrode $E(k)$ and the concentration we would have if we had superimposed two approximate, infinite-strip electrodes (as given by Special Case II) at right angles.

For the electrodes E_k^z the integrals $I_i = I_{i4}$, $i = 1, 2, 3, 4$, are

$$I_{14} = \int_0^{\alpha^{\frac{1}{2}}} \mathrm{Erf}\left[\frac{a'+y_k'}{2w}\right]dw$$

$$= \alpha^{\frac{1}{2}}\ \mathrm{Erf}\left[\frac{a'+y_k'}{2\sqrt{\alpha}}\right] - \frac{a'+y_k'}{2\sqrt{\pi}}\ \mathrm{Ei}\left[-\ \frac{(a'+y_k')^2}{4\alpha}\right] \tag{6.50}$$

$$I_{24} = \int_0^{\alpha^{\frac{1}{2}}} \mathrm{Erf}\left[\frac{a'+y_k'}{2w}\right]\mathrm{Erf}(\frac{b-z}{2w})dw \tag{6.51}$$

$$I_{34} = \int_0^{\alpha^{\frac{1}{2}}} \mathrm{Erf}\left[\frac{a'-y_k'}{2w}\right]dw$$

$$= \alpha^{\frac{1}{2}}\ \mathrm{Erf}\left[\frac{a'-y_k'}{2\sqrt{\alpha}}\right] - \frac{a'-y_k'}{2\sqrt{\pi}}\ \mathrm{Ei}\left[-\ \frac{(a'-y_k')^2}{4\alpha}\right] \tag{6.52}$$

$$I_{44} = \int_0^{\alpha^{\frac{1}{2}}} \mathrm{Erf}\left[\frac{a'-y_k'}{2w}\right]\mathrm{Erf}(\frac{b-z}{2w})dw \tag{6.53}$$

where $y_k' = |y - Y_k|$. For the electrodes E_k^y the integrals $I_i = I_{i5}$, $i = 1, 2, 3, 4$, are

$$I_{15} = \int_0^{\alpha^{\frac{1}{2}}} \mathrm{Erf}\left[\frac{a'+z_k'}{2w}\right]dw$$

$$= \alpha^{\frac{1}{2}}\,\mathrm{Erf}\left[\frac{a'+z_k'}{2\sqrt{\alpha}}\right] - \frac{a'+z_k'}{2\sqrt{\pi}}\,\mathrm{Ei}\ -\left[\frac{(a'+z_k')^2}{4\alpha}\right] \qquad (6.54)$$

$$I_{25} = \int_0^{\alpha^{\frac{1}{2}}} \mathrm{Erf}\left[\frac{a'-z_k'}{2w}\right]dw$$

$$= \alpha^{\frac{1}{2}}\,\mathrm{Erf}\left[\frac{a'-z_k'}{2\sqrt{\alpha}}\right] - \frac{a'-z_k'}{2\sqrt{\pi}}\,\mathrm{Ei}\left[-\frac{(a'-z_k')^2}{4\alpha}\right]$$

$$(6.55)$$

$$I_{35} = \int_0^{\alpha^{\frac{1}{2}}} \mathrm{Erf}\left(\frac{a-y}{2w}\right)\mathrm{Erf}\left[\frac{a'+z_k'}{2w}\right]dw \qquad (6.56)$$

$$I_{45} = \int_0^{\alpha^{\frac{1}{2}}} \mathrm{Erf}\left(\frac{a-y}{2w}\right)\mathrm{Erf}\left[\frac{a'-z_k'}{2w}\right]dw \qquad (6.57)$$

where $z_k' = |z-Y_k|$.

In order to determine the concentration at the surface of the electrode, $\frac{\beta}{\pi} V_1 = \frac{\beta}{\pi} V_1(y,z,\alpha,a,b)$, we form a sum similar to the sum in equation 6.37. Thus,

$$
\begin{aligned}
\frac{\beta}{\pi}V_1 = \frac{\beta}{2\sqrt{\pi}} \Big\{ & I_{13}(\alpha) + I_{23}(b-z,\alpha) + I_{33}(a-y,\alpha) \\
& + I_{43}(a-y,b-z,\alpha) + \sum_k B_k \Big[I_{14}(a'+y'_k,\alpha-\alpha_k) \\
& + I_{24}(a'+y'_k,b-z,\alpha-\alpha_k) + I_{34}(a'-y'_k,\alpha-\alpha_k) \\
& + I_{44}(a'-y'_k,b-z,\alpha-\alpha_k) + I_{15}(a'+z'_k,\alpha-\alpha_k) \\
& + I_{25}(a'-z'_k,\alpha-\alpha_k) + I_{35}(a-y,a'+z'_k,\alpha-\alpha_k) \\
& + I_{45}(a-y,a'-z'_k,\alpha-\alpha_k) + \frac{2a'(a+b)}{ab} \Big(I_{13}(\alpha-\alpha_k) \\
& + I_{23}(b-z,\alpha-\alpha_k) + I_{33}(a-y,\alpha-\alpha_k) \\
& + I_{43}(a-y,b-z,\alpha-\alpha_k) \Big) \Big] \Big\}
\end{aligned}
\tag{6.58}
$$

where the integrals are zero if $\alpha-\alpha_k \leq 0$.

We now consider an electrode, S, consisting of two infinite-strip electrodes (as in Special Case II). One of these electrodes is centered on the y-axis and has a half-width of $ab/(a+b)$ and an average flux of $\beta/2$. The other is centered on the z-axis and has the same half width and average flux. The concentration due to the electrode S is approximately a constant, K, in the region

$$-\frac{ab}{a+b} \leq y \leq \frac{ab}{a+b}, \qquad -\frac{ab}{a+b} \leq z \leq \frac{ab}{a+b}$$

Hence by manipulation of equations 6.37 and 6.58 we see that $\frac{\beta}{\pi} V_1(y,z,\alpha,a,b) = K + \Delta$, where $\Delta = \Delta(y,z,\alpha,a,b) =$ $K + \Delta$, where $\Delta = \Delta(y,z,\alpha,a,b)$ and

$$\Delta = \frac{\beta}{2\sqrt{\pi}}\Bigg\{ I_{43}(a-y,b-z,\alpha) - \alpha^{\frac{1}{2}} + \sum_k B_k \Bigg[I_{24}(a'+y'_k,b-z,\alpha-\alpha_k)$$

$$+ \; I_{44}(a'-y'_k,b-z,\alpha-\alpha_k) \; + \; I_{35}(a-y,a'+z'_k,\alpha-\alpha_k)$$

$$+ \; I_{45}(a-y,a'-z'_k,\alpha-\alpha_k)$$

$$+ \; \frac{2a'(a+b)}{ab}\Big((\alpha-\alpha_k)^{\frac{1}{2}} - I_{43}(a-y,b-z,\alpha-\alpha_k)\Big)\Bigg]\Bigg\} \qquad (6.59)$$

All of the integrals that appear in equation 6.59 may be written in the form

$$I_6(u,v,\alpha) = \int_0^{\alpha^{\frac{1}{2}}} \mathrm{Erf}(u/(2w))\mathrm{Erf}(v/(2w))dw \qquad (6.60)$$

Consider a grid on the surface of the electrode $E(k)$ consisting of lines parallel to the edge of the electrode. The lines are $b-z = 0$, 0.0005, 0.0010, 0.0015, ..., 0.0170 cm. and $a-y = 0$, 0.0005, 0.0010, 0.0015, ..., 0.0170 cm. We calculate Δ at the intersections of the grid lines. Thus in the case of each integral in equation 6.59, u and v are integral multiples of 0.0005 cm. The integral $I_6(u,v,0.00001)$ is evaluated by the Gauss-legendre method, subdividing the interval $0 \leq w \leq (0.00001)^{\frac{1}{2}}$ into three parts. Inductively, to obtain $I_6(u,v,\alpha)$ we add $I_6(u,v,\alpha-0.00001)$ to

$$\int_{(\alpha-0.00001)^{\frac{1}{2}}}^{\alpha^{\frac{1}{2}}} \mathrm{Erf}(u/(2w))\mathrm{Erf}(v/(2w))dw \qquad (6.61)$$

In this manner we obtain values of $I_6(u,v,\alpha)$ for $0.00001 \leq \alpha \leq 0.00025$ cm.^{2}, $0 \leq u \leq 0.0170$ cm., and $0 \leq v \leq 0.0170$ cm.^{2} Values for $\frac{\pi^{\frac{1}{2}}}{2} I_6(u,v,\alpha)$ have been punched on IBM cards under the deck name DI.

The absolute value of Δ is less than approximately 2% of the concentration at the center of the electrode if a-y and b-z ≥ 0.0005 cm. However this is not the case if both a-y and b-z are small, i.e., ≤ 0.0015 cm. At the corner of the electrode Δ is negative and $|\Delta|$ is approximately equal to 20% of the concentration at the center of the electrode.

Since Δ is generally very small, we conclude that the electrode E(k) behaves approximately as a real electrode for times $t \leq t_k$. Thus we have shown that the transition time is given approximately by equation 6.60 for a real electrode of half widths a and b.

While the derivation of the transition time has been long and involved, two very important conclusions may be derived from this work. The first is that for very careful analytical work one whould either use a shielded electrode or adjust the experimental conditions such that the transition time and the dimensions of the electrode are the same as the experiment in which the $i\tau^{\frac{1}{2}}/C^{0}$ "constant" was determined. The second is that if a shielded electrode is to be employed, the shield must be carefully constructed. If the shield is further than 0.2 mm.

from the edge of the electrode, the electrode behaves completely as if it were not shielded for $\alpha < 0.00025$ cm.[2] If the shield is an intermediate distance from the edge of the electrode, the transition is longer than the time predicted by the Sand equation.

7. CHRONOAMPEROMETRY AT AN UNSHIELDED ELECTRODE

Having considered the case of chronopotentiometry at an unshielded electrode, it is reasonable to proceed to the case of chronoamperometry at an unshielded electrode. We shall use a method very similar to the method used in the case of chronopotentiometry. We shall derive an equation for the concentration at an infinite-strip electrode assuming that the current density, i_a, at the surface of the electrode is given by the Cottrell equation (26),

$$i_a = nFC^{o}(D/(\pi t))^{\frac{1}{2}} \qquad (7.1)$$

In order to adjust the concentration to be constant across the surface of the electrode, we shall superimpose infinite-strip electrodes with a half width of 0.0005 cm. upon the infinite-strip electrode described above. These small electrodes have a uniform current density and have been discussed in Section 6.

Rather than deriving the general equations for a finite planar electrode, we shall derive the equation for the concentration at the surface of an infinite-strip electrode and then apply the results in this case to the case of a finite planar electrode. This approach was empirically justified in Section 6.

Thus we consider an infinite strip electrode in the plane $x = 0$, with boundaries at $y = \pm a$, that obeys the following boundary conditions

$$t \leq 0, \quad C = C^{o} \tag{7.2}$$

$$t > 0, \quad C \rightarrow C^{o}, \ \frac{\partial C}{\partial x} \rightarrow 0, \quad \frac{\partial C}{\partial y} \rightarrow 0, \qquad \text{as} \quad x \rightarrow \infty \quad \text{or} \quad y \longrightarrow \infty \tag{7.3}$$

$$i_a = nFC^{o}\left(\frac{D}{\pi t}\right)^{\frac{1}{2}} \cdot h(y) \quad = nFD \left.\frac{\partial C}{\partial x}\right|_{x=0} \tag{7.4}$$

where $C = C(x,y,t,a)$ and

$$h(y) = \begin{cases} 1, \text{ if } & |y| \leq a \\ 0, \text{ if } & |y| > a \end{cases} \tag{7.5}$$

We make two changes of variables

$$\alpha = Dt \tag{7.6}$$

and

$$U = C^{o} - C \tag{7.7}$$

where $U = U(x,y,\alpha,a)$.

The diffusion equation becomes

$$\frac{\partial U}{\partial t} = \frac{\partial^2 U}{\partial x^2} + \frac{\partial^2 U}{\partial y^2} \tag{7.8}$$

To solve the diffusion equation, we employ Laplace and Fourier cosine transforms, assuming that the orders of the integrations and differentiations may be freely exchanged. Employing the Laplace transformation with respect to α using the variable s, we have

$$s\overline{U} = \frac{\partial^2\overline{U}}{\partial x^2} + \frac{\partial^2\overline{U}}{\partial y^2} \tag{7.9}$$

where $\overline{U} = \overline{U}(x,y,s,a)$. Employing the Fourier cosine transformation with respect to x using the transform variable p, we have

$$(s + p^2)\overline{\overline{U}} = \frac{C^o}{\sqrt{s}}\,h(y) + \frac{\partial^2\overline{\overline{U}}}{\partial x^2} \tag{7.10}$$

where $\overline{\overline{U}} = \overline{\overline{U}}(p,y,s,a)$. Employing the Fourier cosine transformation with respect to y using the transform variable q, we have

$$\overline{\overline{\overline{U}}} = \frac{C^o}{\sqrt{s}\,(s + p^2 + q^2)}\int_0^a \cos(qy)dy \tag{7.11}$$

$$= \frac{C^o\sin(qa)}{\sqrt{s}\,(s + p^2 + q^2)q} \tag{7.12}$$

where $\overline{\overline{\overline{U}}} = \overline{\overline{\overline{U}}}(p,q,s,a)$.

Employing the Faltung theorem for Laplace transforms, we have

$$\overline{\overline{U}}'(p,q,\alpha,a) = \frac{C^{o}\sin(qa)}{q}\int_{0}^{\alpha} \frac{e^{-p^{2}\varepsilon}\, e^{-q^{2}\varepsilon}}{\sqrt{\pi(\alpha-\varepsilon)}}\, d\varepsilon \qquad (7.13)$$

where $\overline{\overline{U}}'(p,q,\alpha,a)$ denotes the inverse Laplace transform of $\overline{\overline{\overline{U}}}$. Using the trigonometric relation

$$\sin(c)\cos(d) = \tfrac{1}{2}\sin(c+d) + \tfrac{1}{2}\sin(c-d) \qquad (7.14)$$

we have

$$U = \frac{2C^{o}}{\sqrt{\pi^{5}}}\int_{0}^{\alpha}\left\{(\alpha - \varepsilon)^{-\frac{1}{2}}\left[\int_{0}^{\infty} e^{-p^{2}\varepsilon}\cos(px)dp\right]\right.$$

$$\left.\cdot\left[\int_{0}^{\infty}\frac{e^{-q^{2}\varepsilon}}{q}\Big(\sin(q(a+y)) + \sin(q(a-y))\Big)\, dq\right]\right\}d\varepsilon$$

$$(7.15)$$

In order to simplify the equations to follow, we shall solve for the concentration at the surface of the electrode. Thus we set $x = 0$ so that equation 7.15 becomes

$$U\Big|_{x=0} = \frac{C^{o}}{2\pi}\int_{0}^{\alpha}\frac{(\alpha-\varepsilon)^{-\frac{1}{2}}}{\sqrt{\varepsilon}}\left[\operatorname{Erf}\frac{y+a}{2\sqrt{\varepsilon}} + \operatorname{Erf}\frac{a-y}{2\sqrt{\varepsilon}}\right]d\varepsilon \qquad (7.16)$$

In the limit as a approaches infinity, the error function approaches unity and equation 7.16 becomes

$$U\Big|_{x=0} = C^{o}$$

Thus, the concentration at the surface of the electrode, $C\Big|_{x=0}$, is zero. This limiting value is to be expected in view of the fact that the Cottrell equation is based on one-dimensional diffusion.

Rather than considering the case of an arbitrary α, we shall consider only the case for which $a > 4\sqrt{\alpha}$. Under this assumption equation 7.16 becomes

$$U\Big|_{x=0} = \frac{C^{o}}{2}\left[1 + \pi^{-1}\int_{0}^{\alpha} (\alpha - \varepsilon)^{-\frac{1}{2}}\varepsilon^{-\frac{1}{2}}\mathrm{Erf}(k\varepsilon^{-\frac{1}{2}})\,d\varepsilon \right] \quad (7.17)$$

where $k = \frac{1}{2}(a - y)$. Integrating by parts we obtain

$$U\Big|_{x=0} = \frac{C^{o}}{2}\left[1 + 2\pi^{-1}\tan^{-1}\left(\frac{\varepsilon}{\alpha - \varepsilon}\right)^{\frac{1}{2}} \mathrm{Erf}(k\varepsilon^{-\frac{1}{2}}) \Bigg|_{\varepsilon=0}^{\alpha} \right.$$

$$\left. + 2\pi^{-3/2}\int_{0}^{\alpha} \tan^{-1}\left(\frac{\varepsilon}{\alpha - \varepsilon}\right)^{\frac{1}{2}} e^{-k^{2}/\varepsilon}\varepsilon^{-3/2}\,d\varepsilon \right] \quad (7.18)$$

$$= \tfrac{1}{2}C^{o}\left[1 + \mathrm{Erf}(k\alpha^{-\frac{1}{2}}) + \frac{2k}{\pi^{3/2}} \int_{0}^{\alpha} e^{-k^2/\varepsilon} \frac{\tan^{-1}\left(\frac{\varepsilon}{\alpha-\varepsilon}\right)^{\frac{1}{2}}}{\varepsilon^{3/2}} d\varepsilon \right] \tag{7.19}$$

If we define $\beta = k(\varepsilon^{-\frac{1}{2}} - \alpha^{-\frac{1}{2}})$, then

$$U\Big|_{x=0} = \tfrac{1}{2}C^{o}\Bigg[1 + \mathrm{Erf}(k\alpha^{-\frac{1}{2}}) + 4\pi^{-3/2} \int_{0}^{\infty} e^{-(\beta+k\alpha^{-\frac{1}{2}})^2} \tan^{-1}\left(\frac{\beta^2\alpha}{k^2} + \frac{2\beta\sqrt{\alpha}}{k}\right)^{-\frac{1}{2}} d\beta \Bigg] \tag{7.20}$$

$$= C^{o}P(k,\alpha) \tag{7.21}$$

where P is a function defined by this equation. Values of the function P have been calculated for a - y = 0, 0.0005, 0.0010, 0.0015, ..., 0.0395 cm. and α = 0.00001, 0.00002, ..., 0.00025 cm.^{2}, employing a fifteen point Gauss-Laguerre quadrature scheme to solve the integral.

Having solved for the concentration at the surface of the primary electrode, E_o, we superimpose several uniform-flux electrodes of half-width 0.0005 cm. on the primary electrode, in order to produce a concentration that is essentially constant at the points on the grid

$a - y = 0.0005, 0.0010, \ldots, 0.0395$ cm. on the surface of the electrode. The procedure of placing electrodes is identical to the procedure employed in the case of chronopotentiometry. There are three minor exceptions. (1) Two electrodes, E'_m and E''_m, are superimposed on the primary electrode, E_o, at time $t = t_m$, and centered at $y = Y_m$ and $-Y_m$, respectively. A third electrode, such as was employed in the case of chronopotentiometry, is not necessary because the total current flowing into the system of electrodes is not constrained to be constant with respect to t. (2) Electrode E_m may have a negative current density if the concentration at Y_m is less than $-0.01 \cdot C^o$. (3) The current density is adjusted so that the concentration at Y_m is equal to zero.

From the work on chronopotentiometry it is known that the concentration, C, at the surface of a uniform flux, infinite-strip electrode is

$$C = iH(y,\alpha,0.0005)/(nFD\pi) \tag{7.22}$$

The concentration, V, at the surface of the system of electrodes is

$$V = C^oP(k,\alpha) + (nFD)^{-1}\sum_m i_m(\alpha)H(y_m,\alpha_m,0.0005)/\pi \tag{7.23}$$

where $i_m(\alpha)$ is the current density on the m-th electrode, $y_m = |y - Y_m|$, $\alpha_m = \alpha - Dt_m$, and $i_m = 0$ if $\alpha_m < 0$. If V is approximately equal to C^o, then equation 7.23 becomes approximately

$$1 = P(k,\alpha) + (nFD)^{-1}\sum_m \beta_m(\alpha)H(y_m,\alpha_m,0.0005)/\pi \qquad (7.24)$$

where $\beta_m(\alpha) = i_m(\alpha)/(nFDC^o)$.

It is very easy to determine, in the manner previously described, the values for β_m, y_m, and α_m so that equation 7.24 is satisfied.

The total current, i, per unit length, flowing in the system of electrodes is

$$i = 2ai_a + 0.002(nFDC^o)\sum_m \beta_m(\alpha) \qquad (7.25)$$

Further, if we define

$$\psi(\alpha) = i(\pi\alpha)^{\frac{1}{2}}/(nFDC^oA),$$

where A is the area of the primary electrode, then

$$\psi(\alpha) = \frac{i_a(\pi\alpha)^{\frac{1}{2}}}{nFC^oDA} + \frac{0.001(\pi\alpha)^{\frac{1}{2}}}{a}\sum_m \beta_m(\alpha) \qquad (7.26)$$

$$= 1 + (0.001/a)(\alpha\pi)^{\frac{1}{2}}\sum_m \beta_m(\alpha) \qquad (7.27)$$

The least-squares line for $\psi(\alpha)$ as a function of $\alpha^{\frac{1}{2}}$ for $\alpha \leq 25 \times 10^{-5}$ is

$$\psi(\alpha) = 1.000 + 0.868\alpha^{\frac{1}{2}}/a \tag{7.28}$$

An attempt was made to fit the data given by equation 7.27 to a curve of the form $\psi(\alpha) = a_0 + a_1\alpha^{\frac{1}{2}} + a_2\alpha$, as was done in the case of chronopotentiometry. However, the value of a_2 is strongly dependent upon the method of determining values for the product $i\alpha^{\frac{1}{2}}$. Three methods were tried. In the first method, values for i were taken to be the left-hand limits as α approaches $N \times 10^{-5}$, $N = 0, 1, 2, \ldots$. The second method was essentially the same, right-hand rather than left-hand limits being employed. In the third method, values for i at $\alpha = M/2 \times 10^{-5}$ were chosen, where $M = 1, 3, 5, \ldots$. The third method is probably the best due to the fact that values of i are chosen from neighborhoods in which i is continuous.

The current flowing to the chronopotentiometric electrodes is independent of a if $a > 4\alpha^{\frac{1}{2}}$. The current flowing in the primary electrode is $2ai_a$ per unit length. Thus the ratio of the current flowing in the chronopotentiometric electrodes is proportional to a. Hence for an infinite-strip electrode

$$\psi(\alpha) = 1 + 0.868\alpha^{\frac{1}{2}}/a \tag{7.29}$$

Based upon reasoning directly analogous to the reasoning employed in Section 6, we have, for a circular electrode of radius r the relation

$$\frac{i(\alpha\pi)^{\frac{1}{2}}}{nFDC^{o}A} = 1 + 1.736\alpha^{\frac{1}{2}}/r \qquad (7.30)$$

For a rectangular electrode with dimensions b and c we have

$$\frac{2(\alpha\pi)^{\frac{1}{2}}}{nFDC^{o}A} = 1 + 1.736\left(\frac{b+c}{bc}\right)\alpha^{\frac{1}{2}} \qquad (7.31)$$

The value of the coefficient of $\alpha^{\frac{1}{2}}$ in equation 7.28 is very nearly $\frac{1}{2}\pi^{\frac{1}{2}}$. If in fact, this value is taken to be $\frac{1}{2}\pi^{\frac{1}{2}}$ then equation 7.30 becomes identical to the equation for chronoamperometry at a sphere of radius r. This apparent coincidence was unanticipated. The analogous constants, 0.796 and $\sqrt{\pi}/2$, for the case of chronopotentiometry, compare less well.

In an experimental study of chronoamperometry at unshielded electrodes, Lingane (24) reports that the value of the coefficient of $\alpha^{\frac{1}{2}}/r$ is 2.12. In his opinion, this value agrees well with the value of 1.736 determined in this thesis. In a theoretical study Soos and Lingane (29) derive a value of 2.26 for this coefficient. However, in my opinion this value is excessively high.

III

DETERMINATION OF COBALT BY CONSTANT CURRENT COULOMETRY

Of the volumetric methods for the quantitative determination of cobalt, only the reduction of triscarbonatocobaltate(III) (26,27) appears to be practical as the basis of a coulometric method for the analysis of cobalt. It would be advantageous to reduce triscarbonatocobaltate(III) in basic or neutral solution due to the effervesence which occurs during the acidification of the carbonate solution. Investigation showed that iodide is oxidized by triscarbonatocobaltate(III) in a neutral sodium pyrophosphate solution. Thus it seemed of interest to investigate the possibility that triscarbonatocobaltate(III) may be determined by adding a known amount of arsenic(III) to a solution of iodide and triscarbonatocobaltate(III) complex and determining the excess arsenic(III) by titration with electrogenerated iodine. **A brief review of various analytical procedures involving the use of the triscarbonatocobaltate(III) complex is given by Laitinen and Burdett (27).**

Experimental. The cell used for the electrogeneration of iodine consisted of a 200 ml. Berzeluis beaker and a rubber stopper with holes to accommodate the following: a platinum generating electrode with an area of 2 $cm.^2$, an auxiliary (platinum) electrode isolated from the generating solution by a glass tube closed with a fine fritted disk, and two platinum indicating electrodes.

The constant current source employed is described by Lingane (28) and is capable of maintaining a current with a deviation of less than 0.05%. The current was determined by measuring the voltage drop across a $20\Omega \pm 0.05\%$ standard resistor (General Radio) with an L&N student potentiometer.

All chemicals were reagent grade and were used without further purification. The cobalt nitrate stock solution was standardized by an ammonium phosphate gravimetric method (26). Due to the fact that the nitrate ion interferes in this method, the aliquots of stock solution to be analysed were twice evaporated to dryness in the presence of sulfuric acid in order that the conversion of nitrate ions to sulfate ions be complete. An analysis of four 25 ml. aliquots of the stock solution yielded 209.46 ± 0.06 mg. of cobalt per 25 ml. of stock solution.

The arsenic(III) solution was prepared by dissolving arsenic(III) oxide in a sodium hydroxide solution and adjusting the pH to 6 with dilute hydrochloric acid. The solution was standardized with electrogenerated iodine in a pyrophosphate-hydrogen carbonate buffer solution.

The pyrophosphate buffer solution was prepared by dissolving 0.3 moles (135 grams) of tetrasodium pyrophosphate decahydrate in 900 ml. of water, adjusting the pH of the solution to 6.8 with 15F nitric acid, and diluting to a total volume of one liter. The generating solution was prepared by dissolving 5g. potassium iodide in 25 ml. of buffer solution.

Procedure. Preparation of the triscarbonatocobaltate(III) complex is as follows: Pipet 10-25 ml. of the cobalt solution to be analysed into a 100 ml. volumetric flask. Add a sufficient amount of potassium hydrogen carbonate to neutralize any excess acid and then add an additional 10g. Add 5 ml. 30% hydrogen peroxide. After the effervescence subsides, wash the side of the flask and heat gently to decompose the remaining hydrogen peroxide. Cool and dilute to the mark on the flask.

An aliquot of the triscarbonatocobaltate(III) solution is added to the generating solution. After approximately 300 seconds the reduction of the cobalt is complete. An excess amount of arsenic(III) is added to the generating solution and the excess is titrated with electrogenerated iodine. The end point of the titration is determined by dual electrode amperometry. The potential across the indicator electrodes is 160 mv.

The results of several determinations of the amount of cobalt in cobalt nitrate solutions are shown in Table V.

Discussion. The method described yields good results. One difficulty associated with the procedure is the decomposition of the hydrogen peroxide subsequent to the oxidation of cobalt to the triscarbonatocobaltate(III) complex. If the solution is not heated sufficiently, some hydrogen peroxide remains which may oxidize iodide to iodine, resulting in a positive titration error. If, on the other hand, the solution is heated excessively, the triscarbonatocobaltate(III) complex may decompose, resulting in a negative titration error.

Addition of arsenic(III) to the generating solution prior to reduction of triscarbonatocobaltate(III) may cause large negative errors. However, if oxygen is removed from the mixture of buffer solution and triscarbonatocobaltate(III) solution before arsenic(III) is added, the titration error is less than 1%. Since triscarbonatocobaltate(III) is a one-electron oxidizing agent, it is possible that arsenic(IV), obtained by a one-electron oxidation of arsenic(III), may react with oxygen. Thus, either the cobalt(III) complex should be completely reduced prior

Table V. Results of analysis of cobalt nitrate stock solution by coulometric method

Sample	Cobalt, mg.		Error,%
	Taken	Found	
1	20.925	20.95	0.11
2		20.95	0.11
3		20.94	0.07
4		20.93	0.03
5		20.94	0.07
6		20.93	0.03
7		20.96	0.16
8		20.96	0.16
9		20.95	0.11
	Average	20.94	**0.09**
	Std. dev.	0.01	

to the addition of arsenic(III), or the solution should be free from oxygen, if good results are to be obtained.

A pyrophosphate media is employed as a buffer to decrease the pH of the carbonate solution and as a complexing agent. Increasing the hydrogen ion concentration increases the rate of oxidation of iodide by triscarbonatocobaltate(III). A complexing agent is necessary in order to prevent precipitation of cobalt(II) hydroxide. Due to the difficulty in decomposing the excess hydrogen peroxide, the minimum amount of cobalt necessary for an accurate analysis is approximately 10 mg.

The intent of this study was to find a method of determining cobalt in the presence of nickel and iron by constant current coulometry. It was thought that the pyrophosphato- complexes of iron and nickel would prevent these ions from interfering with the titration, either as precipitates or as species which could oxidize iodide or reduce iodine. The method described above was found to yield good results. Hence 5 g.of sodium pyrophosphate were added to the cobalt(II)-carbonate mixture prior to the addition of hydrogen peroxide and then the amount of cobalt present was determined by the method described above. The presence of sodium pyrophosphate caused a negative titration error of 1 to 2%. This titration error may be due to the formation of a cobalt(II) pyrophsophate complex which interferes with the complete oxidation of cobalt(II), or, it may be due to the formation of a pyrophosphate complex of cobalt(III). A compound has been prepared from triscarbonatocobaltate(III) and sodium dihydrogen pyrophosphate which is assumed to be a pyrophosphato-complex of cobalt(III). This complex does not oxidize iodide under the conditions employed in the determination of cobalt, but does oxidize iodide when the pH of the solution is lowered to approximately 4. Thus the above procedure is not applicable to the determination of cobalt when iron or nickel is present, due to the fact that there appears to be no method of prevention of the formation of a precipitate.

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Proposition 1

It is proposed that the pyrophosphate complexes of some of the metal ions studied in this thesis be investigated in order to supplement the kinetic data obtained in this work.

In order to augment the work of this thesis, studies need to be performed in order to determine the complexes present in pyrophosphate solutions, and the association constants for these complexes. For, it is not known, except in the case of copper, precisely which complexes, if any, are irreversibly reduced in pyrophosphate media.

As discussed in this thesis, the number of ligands associated with iron in pyrophosphate media is not definitely known. The average number of pyrophosphate ligands may be determined by employing a pH titration of pyrophosphate in the presence and absence of iron, according to the method of Bjerrum (1). If the pH of a sodium pyrophosphate solution is less than approximately three, then it may be assumed that the complexing ion is dihydrogen pyrophosphate. If the pH of a sodium pyrophosphate solution is greater than approximately seven, it may be assumed that the complexing ion is sodium pyrophosphate.

In the intermediate region of pH, the number of hydrogen ions bound to the pyrophosphate ligand is not known and as a consequence the number of pyrophosphate ligands associated with the metal ion cannot be determined. Hence, for pH less than three and greater than seven, one can employ the procedure of Bjerrum (1) to determine the number of pyrophosphate ligands associated with both iron(II) and iron(III).

A potentiometric study of the pyrophosphate complexes of copper(II), similar to the study of Schupp, Sturrock, and Watters (2) could be made in the presence of potassium, sodium, and lithium ions. There should be no experimental difficulty in the proposed study since the experimental conditions would not be changed significantly by replacing some of the tetramethyl ammonium ions with alkali metal ions. The results should be interesting as relative metal-ligand bond strength for potassium pyrophosphate, sodium pyrophosphate, lithium pyrophosphate, and hydrogen pyrophosphate ligands should be the same for other metal ions as for copper(II).

The equilibrium constants for the various cadmium-(II)-pyrophosphate complexes might be determined from a pH titration. It is especially important to determine the equilibrium constants for the cadmium-pyrophosphate complexes from an equilibrium method, since it appears that the kinetics of the reduction of cadmium(II) in pyrophosphate media are very involved and that it may not be possible to interpret the kinetics of reduction without prior knowledge of the equilibrium constants.

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Proposition 2

Methods are proposed to study the pyrophosphate complexes of manganese(II) and manganese(III).

Kolthoff and Watters (1) employed manganese(III) in pyrophosphate media in a polarographic method for determining manganese. In order to characterize the manganese(III)-pyrophosphate complex, Kolthoff and Watters compared the diffusion coefficients of the manganese(III)-pyrophosphate and tris(oxalto)cobaltate(III) complexes and employed Riecke's expression to determine the molecular weight of the manganese(III) complex ion. Thus the manganese(III) complex was determined to be tris(dihydrogen pyrophosphate)manganate(III). As mentioned in this thesis, it has been determined that Riecke's expression is not valid and therefore the characterization of the manganese(III) complex by Kolthoff and Watters is in doubt.

Watters and Kolthoff (2) performed a potentiometric study of the manganese(II)-manganese(III) couple in sodium pyrophosphate media. From a study of the variation of the potential as a function of the sodium pyrophosphate concentration at a constant ratio of manganese(II) to manganese(III) concentrations, they concluded that manganese-(II) is associated with one less pyrophosphate ligand than is manganese(III) at pH two. They do not repeat their study for other values of pH. It is reasonable that for different values of the pH the difference between the number of pyrophosphate ligands associated with manganese(III) and manganese(II) might vary.

Lingane and Karplus (3) have developed an analytical method for the determination of manganese(II) or permanganate based upon the results of Kolthoff and Watters (2). In this method a solution of manganese(II) and sodium pyrophosphate is titrated with a solution of permanganate to form the manganese(III)-pyrophosphate complex. However, Lingane and Karplus did not investigate the number of pyrophosphate ligands associated with the manganese ions. Manganese(III)-pyrophosphate has been employed by Levesley, Waters, and Wright (4) as an oxidizing agent for organic compounds; however, in these studies the manganese(III)-pyrophosphate complex was not investigated.

Several methods for the determination of the number of pyrophosphate ligands associated with manganese are given below. It appears that no one method is capable of determining the number of pyrophosphate ligands in the entire range of pH for both manganese(II) and manganese(III). However, a combination of the methods should suffice for such a determination of the types of manganese complexes present in pyrophosphate solutions. We would expect to employ pH titrations for solutions of pH greater than seven and the potentiometric method given below for solutions of pH less than six.

<u>pH titration</u>. If the pH of a solution of sodium pyrophosphate and manganese(II) is greater than approximately seven, it may be assumed that the ligands associated with the manganese ions are sodium pyrophosphate ions. In this case $\bar{n}$, the average number of ligands associated with the manganese ions, may be determined by the method of Bjerrum (5). In a similar fashion, if the pH of a solution of sodium pyrophosphate and manganese(II) or manganese(III) is less than approximately three, it may be assumed that the complexing ligand is dihydrogen pyrophosphate, and $\bar{n}$ may be determined by the method of Bjerrum (5).

<u>Potentiometry</u>. It is proposed to study the manganese(III)-permanganate couple as a function of the pH and pyrophosphate concentration employing potentiometry. In potentiometric studies involving the manganese(II)-manganese(III) couple only the difference between the number of ligands gained or lost during electrolysis may be determined. Since permanganate does not associate

with hydrogen or pyrophosphate ions, the equilibrium constants for the manganese(III) species and the types of complexes formed by manganese(III) may be determined from a study of the permanganate-manganese(III) couple as a function of sodium pyrophosphate concentration and pH. Thus the reduction of permanganate may be written

$$4e^- + MnO_4^- + nP_2O_7^{4-} + (8+m)H^+ \rightleftharpoons MnH_m(P_2O_7)_n^{3+m-4n} + 4H_2O$$

It may be difficult to determine the number of protons involved in this reaction due to the fact that eight protons are required for the reaction in the case in which no protons are associated with the manganese(III)-pyrophosphate complex. However, if the potential of the electrode is studied as a function of the concentration of sodium pyrophosphate at constant pH, the number of pyrophosphate ligands associated with manganese(III) may be determined. From the study of Lingane and Karplus (3), this method is valid for pH less than six. If the pH is greater than six, manganese dioxide precipitates.

<u>Polarography</u>. In solutions of pH less than seven, no wave is observed for the reduction of manganese(II). In a neutral solution of 1F potassium chloride the

half-wave potential for the reduction of manganese(II) is -1.51 volts vs. SCE (6). Due to this very negative reduction potential it may not be possible to study the variation of the half-wave potential as a function of the sodium pyrophosphate concentration if manganese(II) forms a strong complex with pyrophosphate.

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Proposition 3

A complex of cobalt(III) with an organic radical appears to be an intermediate in the oxidation of two cobalt(III) complexes. Chronopotentiometry is proposed as a method to determine the rate of decomposition of the complexes of cobalt(III) with the organic radicals.

Fraser and Taube (1) have found that the oxidation of p-aldehydobenzoatopentamminecobalt(III), (I), may proceed by one of two reaction paths, depending on whether the oxidizing agent is a one-electron or two-electron oxidant; one electron oxidants, such as hexaquocobalt(III) or basic permanganate yield cobalt(II) and terephthalic acid, while two-electron oxidants such as chlorine or hydrogen peroxide yield terephthalatopentamminecobalt(III). Oxidation (2) of oxalatopentamminecobalt(III) procceds in a similar fashion to the oxidation of complex I; a one-electron oxidant yields cobalt(II) and carbon dioxide while a two-electron oxidant yields cobalt(III) (presumably aquopentamminecobalt(III)).

It would appear that some unstable intermediate is formed by the abstraction of one electron from the cobalt complex. If an oxidizing agent is near the radical complex, abstraction of a second electron may occur, yielding a cobalt(III) complex. On the other hand, if no oxidizing agent is near, the organic ligand transfers an electron to the metal ion to yield cobalt(II).

If in fact an unstable intermediate is formed by the abstraction of one electron from the cobalt complex, then it may be possible to determine the rate at which this complex decomposes by some chronopotentiometric technique. There are three chronopotentiometric techniques that may be employed. All three are based upon the assumption that complex I is oxidized to the unstable intermediate. If the chronopotentiogram for the oxidation of complex I consists of two distinguishable waves, then any one of the three techniques given below may be employed to determine the rate constant for the decomposition of the unstable intermediate. If a single wave is observed for the oxidation of complex I, analysis of the product of oxidation should disclose whether the single wave is a one-electron or two-electron oxidation. If the wave represents a two-electron oxidation, no information is given concerning the rate of decomposition of the intermediate. If the wave represents a one-electron oxidation, the first two methods outlined below are applicable.

The general reactions occurring at the electrode are

$$R \rightarrow O_1 + e^- \tag{III-1}$$

$$O_1 \rightarrow O_2 + e- \tag{III-2}$$

$$O_1 \xrightarrow{k} Co(II) + Z \tag{III-3}$$

where species R is the cobalt(III) complex with the reduced form of the organic ligand, species O_1 is the cobalt(III)-radical complex, species O_2 is the cobalt-(III) complex with the oxidized form of organic ligand, and species Z is the free oxidized form of organic ligand.

Method 1. In this method the potential-time curves for reaction III-1 are recorded. The value of $E_{1/4}$, the potential at time $t = \tau/4$, is given by (3)

$$E_{1/4} = E_{\frac{1}{2}} - \frac{RT}{F}\ln(Q_{1/4}) \tag{III-4}$$

where

$$Q_{1/4} = \tfrac{1}{2}\pi^{\frac{1}{2}}(k\tau/4)^{-\frac{1}{2}}\mathrm{Erf}(k\tau/4)^{\frac{1}{2}} \tag{III-5}$$

The value of $E_{1/4}$ is approximately equal to $E_{\frac{1}{2}}$ for short transition times for which $\tau < 0.25k^{-1}$ and $E_{1/4}$ is greater than $E_{\frac{1}{2}}$ for transition times greater than k^{-1}. This method is applicable only if the oxidation of species R is reversible. In view of the fact that most organic compounds are oxidized irreversibly, this method may not be applicable.

Method 2. The second method is reverse-current chronopotentiometry. In this method, species R is oxidized to species O_1 and then the direction of the current is reversed. If k is zero, then the ratio of the forward electrolysis time to the transition time after the current is reversed is equal to three. If, however, k is not zero, the ratio is greater than three due to the transformation of species O_1 to Z. In this case the relation between t, the forward electrolysis time, τ, the transition time after current reversal, and k is (4)

$$2\mathrm{Erf}(k\tau)^{\frac{1}{2}} = \mathrm{Erf}(k(t + \tau))^{\frac{1}{2}} \qquad \text{(III-6)}$$

The oxidation need not be reversible for equation III-6 to be applicable. It is possible, however, that reduction of species R might interfere with the reduction of species O_1 and this method may thus not be applicable.

Method 3. In this method species R is oxidized to species O_1 during the first wave and species R and O_1 are oxidized concurrently during the second wave. If k is equal to zero, the ratio of τ_1, the transition time measured for the first wave, to τ_2, the transition time measured for the second wave, is equal to 1/3. If k is not zero, the transformation of species O_1 into Z results in a decrease in τ_2 and an increase in the ratio of τ_1 to τ_2. This author has derived the relation between τ_1, τ_2, and k. This relation is

$$3\mathrm{Erf}(k\tau_2)^{\frac{1}{2}} + 4\pi^{-1}(\tau_1\tau_2)^{\frac{1}{2}}I = \mathrm{Erf}(k(\tau_1 + \tau_2))^{\frac{1}{2}}$$

where

$$I = \int_0^1 (\tau_2 v^2 + \tau_1)^{-1}\mathrm{Erf}(k\tau_2(1 - v^2))^{\frac{1}{2}}dv$$

This technique has the disadvantage that the second wave, the wave for the oxidation of species O_1, must occur prior to the wave for background, in order that τ_2 may be determined.

Oxidation of the cobalt complex is expected in view of the fact that electrolytic oxidation of terephthalaldehydic acid to terephthalic acid occurs (5).

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Proposition 4

Rumpel, Davidson, and Kleinberg (1) have hypothesized that Sn(I) is an intermediate in the electrolytic oxidation of tin metal. These authors' arguments are critically examined and two experiments are proposed to determine if in fact Sn(I) is present.

Rumpel, Davidson, and Kleinberg (1) have recently proposed that the electrolytic oxidation of tin metal proceeds through the intermediate Sn(I). They hypothesize that tin metal is electrolytically oxidized to Sn(I). If no chemical oxidant is present in solution, Sn(I) is electrolytically oxidized to Sn(II). If, however, a chemical oxidant such as nitrate or chlorate is present, Sn(I) is oxidized chemically to Sn(II). The initial mean valance number, V_i, is calculated from the ratio of the number of faradays passed to the number of gram atoms of metal dissolved. The number of faradays are measured with a silver coulometer in series with the electrolysis cell. The number of gram atoms of tin dissolved are determined by weighing the anode before and after electrolysis. Rumpel, Davidson, and Kleinberg report values of V_i of 2.0 in solutions of sodium acetate and sodium chloride and values of V_i of 1.02

to 1.81 in solutions of sodium nitrate and potassium chlorate. From the low values of V_i the authors conclude that some of the tin is dissolving as Sn(I).

Uncommon valence states have been reported for the electrolytic oxidation of some metals other than tin. In most cases effects other than uncommon valence states account for the apparent deviation from Faraday's law. Such effects are the "chunk" effect and the "difference" effect.

In the chunk effect pieces of metal are lost from the anode. These pieces of metal either fall to the bottom of the cell or, due to their very small size and large surface, dissolve by chemical oxidation. Electrolytic oxidation of beryllium (2), aluminum (3), and magnesium (4) offer examples of the chunk effect. In the case of beryllium small particles of metal may be found on the bottom of the cell after electrolytic oxidation of beryllium in neutral sodium chloride media. These particles resemble very strongly the particles which may be found on the bottom of the cell if the metal is chemically dissolved in hydrochloric acid. Thus if the value of V_i for the oxidation of the metal is calculated from the weight lost by the metal during electrolysis, a number less than 2 is obtained, due to the undissolved metal on the bottom of the cell. If this undissolved metal on the bottom of the cell is taken into account in calculating the amount of metal dissolved, then Faraday's law is obeyed, the normal valence state being assumed.

In the difference effect electrolytic dissolution of the metal causes some change in the rate of chemical oxidation of the metal. An example is the case in which the metal is passive due to the fact that a film forms on the metal, isolating the metal from the solution. In this case no chemical oxidation of the metal may occur. If an anodic current is passed through the metal, the film may be broken and chemical oxidation may occur where the film is broken. The oxidation of aluminum in hydrochloric acid offers an example of the difference effect. Marsh and Schaschl (3) have observed that when aluminum is placed in hydrochloric acid, hydrogen is evolved on the surface of the metal, but the rate of evolution decreases to zero. If an anodic current is passed through the metal, hydrogen evolution occurs. If the anodic current is discontinued, the evolution of hydrogen continues but the rate of evolution decreases to zero. Thus it would appear that in this case there is no chemical oxidation of aluminum unless there is also electrolytic oxidation of the metal.

Rumpel, Davidson, and Kleinberg (1) obtained the same values for V_i for anodes of a tin amalgam as for anodes of tin metal. If the tin amalgam was handled properly to avoid oxidation of the amalgam by air, then it is reasonable to conclude that the chunk effect could not have occurred, as bits of metal could not have split off of the amalgam.

Further, Rumpel, Davidson, and Kleinberg employ a specious argument in an attempt to prove that the difference effect does not produce their low values of V_i. They argue that in some cases the potential of the anode is greater than 2.5 volts vs. NHE (normal hydrogen electrode) and that at this potential oxidation of the electrode by nitrate ion is impossible. Since the same values of V_i were obtained in the case in which the potential of the electrode was as high as 2.5 volts vs. NHE as in the case in which the potential of the electrode was significantly lower, they conclude that no chemical oxidation of the metal occurs. However, one can criticize the authors' conclusion concerning the potential of +2.5 volts. Latimer (5) gives the overvoltage for the evolution of oxygen at several metal electrodes other than tin. For a current density of 10 ma./cm.^{2} the overvoltage ranges from 350 to 720 mv. The standard potential for the reaction (5)

$$2H_2O = O_2 + 4H^+ + 4e^-$$

is -1.229 volts vs. NHE. If the overvoltage of tin is less than 720 mv., then oxygen should be evolved at +2 volts vs. NHE if the pH is zero, and at less than two volts if the pH is greater than zero. Thus it would appear unreasonable not to expect a relatively large amount of oxygen to be evolved if the potential of the electrode is +2.5 volts vs. NHE. Since the authors report no gas evolution, their argument concerning the difference effect is incorrect.

If the potential of the anode of +2.5 volts was measured incorrectly, then the potential must have been less than +2 volts (since oxygen was not evolved) and hence nitrate ion could have oxidized the anode directly. If the potential was in fact measured correctly, then a large iR drop must have existed in the cell. The effect of an iR drop would be to increase the measured potential so that the potential of the electrode appears greater in the presence of a current than the potential in the absence of a current. If there was in fact an iR drop, then it might have been possible for nitrate ions to oxidize the electrode. Hence the argument of Rumpel, Davidson, and

Kleinberg concerning the difference effect is incorrect.

In order to demonstrate that the tin electrode was not being dissolved directly by chemical action, Rumpel, Davidson, and Kleinberg placed a tin metal control sample in the anode compartment. They report that the weight loss from the control was never significant. However they have overlooked the difference between the hydrogen ion concentration at the control and the hydrogen ion concentration at the anode. The concentration of Sn(II) is much larger at the surface of the anode than in the bulk of the unstirred solution. Since appreciable hydrolysis of Sn(II) occurs, the concentration of hydrogen ion is greatest at the surface of the anode. Because the reactivity of the nitrate ion increases with increasing hydrogen ion concentration, nitrate ion may be able to oxidize the anode and may not be able to oxidize the control.

In order to determine if the Sn(I) species is involved in the anodic oxidation as proposed by Rumpel, Davidson, and Kleinberg (1), two studies are proposed. The first is a chronopotentiometric study of the reduction of Sn(I). The second is a chemical study to determine the rate of oxidation of tin metal by nitrate ions in solutions of various pH.

If the Sn(I) species exists and is capable of being reduced, then it may be possible to demonstrate the existance of the Sn(I) species by reverse-current chronopotentiometry. The procedure is as follows: an anodic current is passed through the tin electrode and then the direction of the current is reversed. If Sn(I) does in fact exist, two waves should appear upon reversal of the direction of the current. The first wave represents the reduction of Sn(I) and the second wave represents the reduction of Sn(II). (Sn(I) may be present and not detected by this procedure as this species may be very short lived.)

The tin anodes employed by Rumpel, Davidson, and Kleinberg (1) are cylindrical and have a diameter of one cm. The concentration, C, of a species at a cylindrical electrode of radius r is given by (6)

$$C = \frac{ir}{nFD}\left[2\pi^{-\frac{1}{2}}\left(\frac{Dt}{r^2}\right)^{\frac{1}{2}} - \frac{1}{2}\,\frac{Dt}{r^2} + \frac{1}{2}\pi^{-\frac{1}{2}}\left(\frac{Dt}{r^2}\right)^{3/2} - \;\cdots\right] \tag{IV-1}$$

where i is the current density, t is the time, n is the number of electrons involved in the redox couple, F is Faraday's number, and D is the diffusion coefficient. Equation IV-1 is applicable if the current density is constant and if there is no convection or precipitation. Assuming that the diffusion coefficient of Sn(II) is 7×10^{-6}, the concentration of Sn(II), C', at the surface of the electrode is given approximately by

$$C' = 0.021(t^{\frac{1}{2}} - 0.0027t) \qquad \text{(IV-2)}$$

where the units of C' are moles/liter and t is the time in seconds. The equilibrium constant for the reaction

$$H_2O + Sn^{2+} = SnOH^+ + H^+ \qquad \text{(IV-3)}$$

is 2×10^{-2}. It is apparent from equation IV-2 that the concentration of tin at the surface of the electrode is large and that due to the hydrolysis of Sn(II) the hydrogen ion concentration is also large. Thus the control employed by Rumpel, Davidson, and Kleinberg is meaningless due to the fact that its environment is not the same as the environment of the anode. It is necessary to determine the conditions under which tin metal dissolves at a significant rate in sodium nitrate as a function of pH. If it is found that tin metal dissolves under conditions that are similar to the conditions that exist at the surface of the anode during electrolysis, then Sn(I) is not an intermediate in the oxidation of tin metal as hypothesized by Rumpel, Davidson, and Kleinberg (1), but rather the direct oxidation of tin metal is responsible for the low values of V_i.

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Proposition 5

Iron(II) is proposed as a reductant in neutral sodium pyrophosphate solutions that may be coulometrically generated by reduction of iron(III).

There is no suitable reductant that may be generated by constant coulometry in a neutral or basic medium. Iron(II) in neutral pyrophosphate solution is proposed as such a titrant, which may be generated from iron(III). Experiments were performed by this author on this reductant; however, the iron(II) species could not be generated with 100% current efficiency in these experiments. The subsequent chronopotentiometric studies of this author have resulted in a better understanding of the reduction of iron(III) in pyrophosphate media. Hence it may be possible to describe the conditions under which the current efficiency for the generation of iron(II) may be increased.

Thus, the pH of the generating solution must be adjusted with sulfuric acid. Nitric or perchloric ions must be avoided. In the original work of this author, iron(III) nitrate was employed as the source of iron(III) and nitric acid was employed to adjust the pH of the generating solution. As stated in Section 1 of this thesis, nitrate ion makes the reduction of iron(III) less reversible in pyrophosphate media.

Further, the solution should contain only the minimum amount of sodium pyrophosphate necessary to prevent the precipitation of iron(III) hydroxide and the pH of the solution should be as low as possible. These conditions minimize the concentration of irreversibly reduced iron(III)-pyrophosphate complexes.

Moreover, the current density should be as small as is practical. Small current densities should be employed due to the fact that the reduction of iron(III) may still not be completely reversible, and the smaller current density decreases the overvoltage for the reduction of iron(III).

Even with these precautions, the reduction of iron(III) may not proceed with 100% current efficiency. In this case it may be possible to generate iron(II) externally as described by DeFord, Johns, and Pitts (1). In this method the iron(II) is generated prior to being added to the titration cell.

A possible use for the iron(II) titrant is in a variation of the determination for cobalt described in this thesis. This variation would simplify the experimental procedure, allow smaller samples of cobalt to be determined, and might allow the cobalt to be determined in the presence of iron. In the method of determination of cobalt described in this thesis, a small aliquot of the triscarbonatocobaltate(III) solution is diluted with generating solution. This dilution is necessary in order to decrease the stability of the cobalt complex. Without this decrease in the stability of the cobalt(III) complex, iodide is not oxidized. The iron(II)-pyrophosphate complex, however, reduces the cobalt complex in hydrogen carbonate solutions, so that if iron(II) were employed as the titrant, no dilution of the cobalt solution would be necessary.

Further, in the procedure of this thesis, introduction of pyrophosphate into the cobalt(II)-carbonate mixture results in a negative titration error. As was discussed, this error may be due to the formation of a pyrophosphate complex of cobalt(III) which does not oxidize iodide under the conditions of the titration. If in fact the titration error is due to the formation of a cobalt(III) complex, then the use of iron(II) as the reductant should decrease the magnitude of this error, since the iron(II)-pyrophosphate complex is capable of reducing the cobalt(III)-pyrophosphate complex. Thus if the titration error is zero in the presence of sodium pyrophosphate, then sodium pyrophosphate may be employed as a complexing agent to prevent the precipitation of iron, which might be present in the cobalt sample, as the hydroxide. Hence cobalt could be determined in the presence of iron.

A second titration in which the iron(II)-pyrophosphate complex may be employed as a reductant is the determination of ammonia by coulometrically generated bromine. Arcand and Swift (2) generated bromine until an excess was present. The excess bromine was then determined by acidifying the solution and measuring the excess bromine amperometrically or by generating copper(I). The back titration was necessary due to the fact that the two electrode amperometric system did not function reprodicibly with bromine in alkaline media. Rather than acidifying the solution in order to determine the amount of excess bromine present, it would be possible to generate iron(II) to titrate the excess bromine. In this case the end point could be determined potentiometrically. However, two papers (3,4) have recently been published in which two electrode amperometry is employed in order to detect the end point for the bromine titration. If the end point can be detected in the alkaline solution, there is no necessity for the generation of iron(II) to titrate excess bromine.

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