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WATER RESEARCH PROGRAM

BIENNIAL PROGRESS REPORT
FOR THE PERIOD
MARCH 15, 1968, TO NOVEMBER 1, 1970
REACTIONS AND TRANSPORT PHENOMENA
AT SURFACES

for the
OFFICE OF SALINE WATER
U.S. Department of the Interior

MASTER

OAK RIDGE NATIONAL LABORATORY

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WATER RESEARCH PROGRAM BIENNIAL PROGRESS REPORT

For the Period March 15, 1968, to November 1, 1970

REACTIONS AND TRANSPORT PHENOMENA AT SURFACES

Compiled by Franz A. Posey and George E. Moore

K. A. Kraus, Program Director

For the
OFFICE OF SALINE WATER
U.S. DEPARTMENT OF THE INTERIOR
OSW-AEC INTERAGENCY AGREEMENT 14-01-0001-937

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*Paper published in open literature.

PREFACE

The Water Research Program at the Oak Ridge National Laboratory, sponsored by the Office of Saline Water, U.S. Department of the Interior, was authorized in March 1962 under an interagency agreement (14-01-0001-937) between the Department of the Interior and the U.S. Atomic Energy Commission. Results of the work carried out under this program have been reported on a regular basis to the Office of Saline Water, and completed portions of the work were published in the open literature. A biennial report covering the activities under the program for the period March 15, 1962 to March 15, 1964, was issued in a single volume as U.S. Office of Saline Water Research and Development Progress Report 302 (ORNL-CF-67-8-55). For the second biennium, March 15, 1964 to March 15, 1966, work was divided into three categories, "Properties of Solutions," "Reactions and Transport Phenomena at Surfaces. Corrosion Studies," and "Separations Processes." The report for "Separations Processes" was issued as U.S. Office of Saline Water Research and Development Progress Report 508 (February 1970) and also issued as ORNL-CF-69-5-41 (September 1969). The report for "Properties of Solutions" for this period was issued as U.S. Office of Saline Water Research and Development Progress Report 685 (July 1971) and was previously issued as ORNL-CF-70-6-30 (October 1970). The 1964-1966 biennial reports for "Reactions and Transport Phenomena at Surfaces" and for "Corrosion Studies" were combined into a single document because the work in these fields was so closely related; a joint report (ORNL-TM-4097) is planned. The progress report for "Reactions and Transport Phenomena at Surfaces" for the third biennium, March 15, 1966 to March 15, 1968, was issued as ORNL-TM-4099 (March 1973). The present report covers work during the period March 15, 1968 to November 1, 1970, which was the termination date of work in this category under support of the Office of Saline Water.

In the interest of economy and completeness of presentation, work that was reported in the open literature is given as a direct reproduction of the corresponding journal articles. We are grateful to the Elsevier Publishing Company for permission to reprint the complete texts of these articles. A notation of the source appears at the head of each reprinted article. Part of the work reported here was cosponsored by the U.S. Atomic Energy Commission; such support is acknowledged in the individual articles.

The desalination program at the Oak Ridge National Laboratory has two branches: the Water Research Program directed by K. A. Kraus during the period of this report, and the Nuclear Desalination Program directed by R. P. Hammond. This report is concerned with the Water Research Program, Reactions and Transport Phenomena at Surfaces, coordinated by Franz A. Posey.

SUMMARY

Numerous technologies, including water desalination, depend on favorable kinetic properties of various reactions and transport phenomena at phase boundaries. For example, corrosion processes, involving destruction of the crystalline lattice of metals by dissolution reactions or by formation of additional surface phases such as oxide layers, are frequently important factors to be considered in the selection of materials of construction for desalting plants. A continuing need exists for extension of our knowledge of the corrosion behavior of metals, particularly with respect to factors which influence the susceptibility of metals and alloys to localized forms of corrosion, such as pitting. During this biennium we have developed a theoretical model for pitting corrosion of metals which takes into account the interaction between interfacial and mass-transport processes during passage of anodic current through confined regions. Other studies of reactions and transport phenomena at phase boundaries have been concerned with electroanalytical applications of several different electrode systems, such as channel electrodes for voltammetry and chronopotentiometry and porous electrodes for quantitative electroanalysis of trace amounts of oxidizable or reducible solutes. In addition, we have investigated the properties of the suspension electrode, a configuration allowing optimum interaction between hydrodynamic and electrochemical factors, for electrolytic treatment of aqueous streams and have developed a device, based on the suspension-electrode principle, for pH control and bicarbonate removal from seawater.

In continuing studies of pitting corrosion, especially of titanium and its alloys in chloride solutions, an approximate mass-transport model for pitting of metals was developed (Section 1). The model, which is a special case of the more general problem of corrosion in restricted geometries, considers some of the consequences of passage of anodic current through a pit-like region. Certain concepts of macroscopic mass-transport theory were used in the analysis together with some of the classical relations of electrode kinetics. It was shown that the existence of a pitting potential, above which self-sustained pit growth may take place but below which pit growth cannot be maintained, is a natural consequence of the

coupling of mass-transport processes and interfacial reactions.

Investigations on chronopotentiometry and voltammetry in flowing streams were carried out with emphasis on analysis of constituents of saline waters (Section 2). In particular, the properties of the Ag-AgCl electrode as a monitor of chloride-ion concentration in flowing streams were studied. The electrode was mounted flush with one of the walls of a rectangular channel, which had dimensions such that fully developed laminar flow was established at the electrode surface. Two modes of operation were investigated. In the voltammetric mode, limiting currents were observed for the transport of chloride ion to the surface when silver chloride was formed anodically. This current is a function of the flow rate and is directly proportional to chloride-ion concentration. In the chronopotentiometric mode of operation, the effect of the flow is to increase the transition time in a reproducible and predictable manner. These two modes of operation may therefore be used for the analysis of solutions containing chloride ions. Voltammetric measurements could be used for chloride analysis in the concentration range 1×10^{-4} to 5×10^{-3} M (approximately 4 to 200 ppm). In the chronopotentiometric mode of operation, the analysis was best carried out in the concentration range 3×10^{-4} to 10^{-1} M (approximately 10 to 3500 ppm).

In related work (Section 3), solutions to the equation of convective diffusion were derived for chronopotentiometry and voltammetry of an electrode located in a channel where the electrode process involved formation of a solid phase. The relations derived for voltammetry permitted computation of reactant concentration from experimental polarization curves, polarization resistances, or limiting currents with a knowledge of solution flow rate, applied current, electrode and channel dimensions, and other parameters. An approximate method was used to obtain the effect of flow rate and other pertinent variables on transition times for chronopotentiometry in flowing streams.

In Section 4, the design, construction, and testing of a new cell for use in rapid chronopotentiometric analysis are described. In addition, a new electrochemical instrument was designed and built for use with the cell. Accurate analysis requires precise control of the applied current density and of the geometry of a chronopotentiometric cell. In addition,

electrodes should be easily replaceable, and the entire cell should be easy to disassemble and clean. These requirements were met by the new cell design. The electronic instrument designed for use with the cell incorporated three basic functions in one instrument by using three integrated-circuit, miniature, operational amplifiers. One of the amplifiers was used to control the current to a preset value and thus to maintain a constant current regardless of changes in cell impedance. The magnitude of the current was determined by settings on a digital potentiometer and a range switch. The other amplifiers were used for measurement of the electrode potential and of the time-derivative of the electrode potential. The time-derivative was used for precise determination of the transition time. A switch converted the control circuit to a potentiostat for operation of the test electrode at constant potential. This instrument may be used as a general-purpose electrochemical instrument designed for easy portability and low cost (less than \$500). An instruction manual was written for both the instrument and the cell. This apparatus was used and tested for several months, resulting in a considerable increase in precision of measurement and convenience of operation.

In continuing studies of electroanalytical methods for use in saline waters, it was shown (Section 5) that anodic chronopotentiometry in alkaline solutions with the silver-silver sulfide electrode may be used for determination of sulfide-ion concentration over the range 10^{-3} to 10^{-2} M, with a precision of 1 to 2%. The technique is unaffected by pH or the presence of chloride ions. Analysis of chronopotentiometric waves shows that the interfacial reaction is irreversible.

An electrochemical device for monitoring the dissolved oxygen content of aqueous streams, such as distillation plant process streams, at the part-per-billion level was developed (Section 6). This device makes use of an exchanger in which the dissolved oxygen in the test stream penetrates an oxygen-permeable membrane and equilibrates with the dissolved oxygen in an internal sensor stream. The oxygen content of the internal sensor stream is then monitored by quantitative reduction in a porous silver electrode maintained at an appropriate potential. Accuracy of the device is one or two parts per billion in the 0-100 ppb range.

Experiments were carried out on the properties of the suspension (or slurry) electrode system (Section 7), which consists of a charging electrode in contact with a rapidly stirred suspension of finely divided, catalytically active, conducting material in a solution of strong electrolyte. The particles of the catalyst, which are normally from 10 to 100 μ in diameter, are charged by intermittent contact with the stationary electrode. Contact may be effected either by stirring the suspended particles or by flowing the suspension past a charging electrode fixed in a channel. This electrode shows promise for use in electrochemical processing and perhaps also in electroanalytical applications. Normally, electrode materials must be selected for a combination of favorable properties including catalytic activity, mechanical strength, and corrosion resistance. With the suspension electrode, the suspended material may be selected primarily for its catalytic activity, and the charging electrode may be selected principally for its mechanical and corrosion properties. Removal of gaseous products from a suspension electrode appears to be far less difficult than from a conventional porous electrode of comparable surface area. On deterioration of the suspended catalyst material, it may be replaced easily without dismantling the cell. In addition, many types of suspended materials have very large active surface areas (e.g., 10 to 50 m^2/g), and therefore increased current output for certain types of reactions is possible.

Measurements were carried out with a variety of catalyst particles, charging electrodes, and solutions. Considerable enhancement in the current output of cathodes for the hydrogen evolution reaction was obtained with suspensions of platinum or palladium blacks or Raney nickel in KOH solutions. Current output was found to depend on the identity of the catalyst particles, on the conductivity of the solution, on the exchange current density of the interfacial reaction, on the stirring rate, and on the configuration of the cell. Unlike conventional electrodes, the current output of the suspension electrode was observed to vary linearly with the potential of the charging electrode over very wide limits, up to several volts in some cases. The system is potentially capable of very high current output at modest voltages. Extensive measurements by an oscilloscopic technique of individual pulses due to contact of catalyst particles with the charging electrode were carried out. Most of the

pulse shapes were characterized by a sharp increase to a peak current followed by a somewhat slower decay. Pulse durations for the prevailing experimental conditions were generally of the order of one millisecond. A great number of pulses was examined, and average pulse heights were determined as a function of overpotential and solution conductivity. These experiments confirmed the linear relationship between current and overpotential, and the increase in current with solution conductivity.

In related work we investigated the operation of a flow cell designed for relatively high current output. The cell, containing an array of nickel charging electrodes through which the suspension could be pumped at various velocities, was operated with finely divided Raney nickel catalyst in 1 N KOH. At moderately high catalyst contents (~0.25 g Raney Ni per ml 1 N KOH) the current output of the cell was observed to be greater than 1 A/cm² (~10³ A/ft²), calculated with respect to the area of the charging electrodes, at only 300 mV overvoltage for the cathode. Thus the flow-cell configuration of the suspension electrode is a very efficient device for the generation of electrolytic hydrogen. Still greater current output could be obtained by use of a more concentrated electrolyte (6 N KOH, for example), with high catalyst contents (larger apparatus and special pumps would be required), and by operation at elevated temperatures. In addition, overall performance of the cell could be increased even further by appropriate arrangement and spacing of additional charging electrodes.

A theoretical model for the suspension-electrode system is developed in Section 8 based on the following assumptions: (1) individual catalyst particles are highly porous and behave like miniature porous electrodes on contact with the charging electrode; (2) the resistance of the electrolyte is the predominant factor in determining the overpotential during the course of a charging transient; (3) since most of the total overpotential lies within the solution phase, the potential at the metal-solution interface on the catalyst particles departs only a few millivolts from the equilibrium potential (this fact is ultimately responsible for the linear relation observed between current and overpotential); and (4) the effective rate constant at the surface of catalytically active particles is large during the important first few milliseconds of the charging transient. Solution

of the pertinent mass-transport relations with appropriate boundary conditions leads to predicted current transients which are in good agreement with those observed experimentally, both as to magnitude and time constant. Reaction inside the pores of the catalyst particles is propagated in a "wave," in a manner very similar to charging of the double layer in a porous or capillary electrode.

A prototype device for simultaneous removal of bicarbonate and acidification of seawater was designed and constructed (Section 9). The cell, based on the suspension-electrode principle and having concentric cylindrical geometry, had a central anode compartment separated from the surrounding cathode compartment by a porous barrier. The anode assembly used a high-efficiency suspension electrode in which a suspension or slurry of palladium black catalyst particles was forced to impinge upon a large array of charging electrodes. Incoming seawater entered the surrounding cathode compartment and was circulated through a loop consisting of the cathode compartment and a settling tank. The reaction at the stainless steel cathodes was production of hydrogen gas and hydroxide ions. The latter first react with Mg^{2+} ions in the seawater and would ordinarily tend to form a tight coating of $Mg(OH)_2$ on the cathode surfaces which would soon prevent further reaction and lead to greatly increased voltage requirements. However, keeping the cathode surfaces clean, allowed continuous, efficient operation of the cathode reaction.

Continued production of hydroxide ions raised the pH of the solution in the cathode loop until conversion of bicarbonate ions to carbonate caused precipitation of $CaCO_3$, with subsequent removal in the settling tank. Essentially carbonate-free seawater from the cathode loop was forced into the anode compartment through the porous separator, where acidification took place due to the anodic reaction, oxidation of hydrogen to hydrogen ions. The hydrogen for the anode reaction was the product of the cathodic process and was extracted from the cathode loop and fed into the solution in the anode loop. The output of the cell--decarbonated, acidified seawater--was taken from the suspension-anode loop and could then be used for acidification pretreatment of larger volumes of seawater. This mode of operation, based upon a hydrogen feedback cycle, circumvented the old problem of anode attrition in

electrolysis of seawater and chloride solutions and allowed operation at greatly reduced cell voltages and therefore modest power requirements. In addition, the use of expensive membrane materials and catalyzed electrode structures was avoided.

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1. AN APPROXIMATE MASS-TRANSPORT MODEL FOR PITTING OF METALS

F. A. Posey

In continuation of studies on theoretical and experimental aspects of localized attack of metals,¹ especially titanium, an approximate mass-transport model for pitting of metals was developed. The model, which is a special case of the more general problem of corrosion in restricted geometries, considers some of the consequences of passage of anodic current through a pit-like region. Certain concepts of macroscopic mass-transport theory are used in the analysis together with some of the classical relations of electrode kinetics.

Pitting corrosion is one of several manifestations of localized attack of metals. Other include crevice corrosion, stress-corrosion cracking, attack at points of contact of metals with dielectrics, and attack in three-phase regions, such as at menisci (i.e., water-line attack). Many of the common metallic materials of construction which depend for corrosion protection upon the existence of a passive oxide layer on their surfaces are subject to pitting attack under certain conditions. Anodic polarization curves of these metals shows that, in general, there exists a more or less well-defined value of the electrode potential above which self-sustained pit growth may take place, but below which pit growth cannot be maintained. This potential, the pitting potential, is essentially independent of the current applied to the electrode. The pitting potential also appears to be independent of the size of pits and thus independent of time. In many cases the pitting potential has been found to decrease logarithmically with increasing concentration of so-called activator ions (such as Cl^- , Br^- , etc.) and to increase logarithmically with increasing concentration of so-called passivator ions (SO_4^{2-} , CrO_4^{2-} , NO_3^- , etc.). Depending upon conditions, pits have been observed to repassivate after a certain stage of growth. In addition, the value of the pitting potential depends considerably in some cases upon alloy composition and temperature.

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1. F. A. Posey, et. al., Water Research Program Biennial Progress Report for the Period March 15, 1966 to March 15, 1968, Reactions and Transport Phenomena at Surfaces, ORNL-TM-4099 (March 1973).

Although a large literature exists on the subject of pitting corrosion, the phenomenology of sustained pit growth is much better characterized than the process of pit initiation, i.e., the sequence of events which first leads to penetration of the passive oxide layer and formation of an incipient pit. Furthermore, few attempts have been made to analyze the growth of pits on a quantitative basis. In this report we examine the properties of a rudimentary model which bears an obvious relation to the pitting situation.

Most investigators agree that, because of the high current densities involved in pitting, a considerable potential difference exists in the solution phase inside a pit so that the base of the pit can corrode at a low potential in the active potential region while the unattacked passive surface of the metal is at a much more noble potential in the passive region. In fact, direct measurements of the potential drop inside pits have been carried out by use of micro-Luggin capillaries. Such a potential difference is supported by the resistance of the electrolyte phase inside the pit, so that so-called "resistance stabilization" plays an important role in allowing the coexistence of both active and passive areas on the same electrode surface. There also exists simultaneously a large difference in electrolyte concentration between the interior of a pit and the external solution. In many cases extensive hydrolysis of anodic reaction products leads to the development of a concentrated acid solution within pits as a consequence of diffusion and migration of ionic species. This qualitative picture is reasonably consistent with the observed facts but does not by itself account for such observations as the independence of the pitting potential with respect to applied current and pit size, or the dependence on concentrations of activator and passivator ions.

A simple model of a cylindrical pit-like region is shown in Fig. 1.1. The mouth of the pit is located at $z = 0$ in a cylindrical coordinate system (because of symmetry the angular coordinate is ignored). The radius of the circular pit mouth is denoted by a and the base of the pit is located at $z = -\delta$. The solution phase occupies the half-space $z > 0$. A constant anodic current density (j , amp/cm²) is forced through the base of the pit. If I (amp) is the total current applied to the pit, then $j = I/\pi a^2$.

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FIG. 1.1 SCHEMATIC DIAGRAM OF SIMPLE MODEL FOR PITTING OF METALS.

It is necessary to consider transport processes and the associated potential and concentration distributions in the solution phase in the region $z > 0$ because of the current densities encountered in pitting. Simple calculations suffice to show that in general ion concentrations at and near the pit mouth ($z = 0$) may be different from ion concentrations at points far removed from the vicinity of the pit. Consequently we shall not specify that ion concentrations at $z = 0$ are the same as those in the bulk of the solution, but shall use, as one of the boundary conditions to the problem, the fact that ion concentrations only attain the bulk values for large values of r and/or z .

Next, in order to obtain a tractable set of transport relations, it will be necessary to assume a very simple stoichiometry for the interfacial reaction which takes place at $z = -\delta$. (Note that for the purposes of this model and in order to avoid mathematical complexity it has been assumed that no reaction takes place at the cylindrical surface of the pit region at $r = a$.) The overall stoichiometry of the anodic interfacial reaction is assumed to be given by

in which the metal M reacts with the aqueous solvent to produce "instantly" the uncharged hydrolyzed species, MOH , and hydrogen ions. The species MOH is assumed not to affect in any way the transport processes in the system. In addition it is assumed that chloride ions, Cl^- , are the sole anions present so that one is dealing with the case of a binary electrolyte, HCl . One might just as well have used a stoichiometry of the form, $M \rightarrow M^+ + e^-$, with no hydrolysis, so that again the transport of a binary electrolyte (MCl) could be considered. Even though the reaction of Eq. (1) is not very realistic, use of this form allows the influence of mass transport to be examined in some detail, and the principal results of more elaborate models can be shown not to differ qualitatively from those developed below.

The flux equations for the motion of H^+ and Cl^- ions in the region $-\delta \leq z \leq 0$ are given by

$$J_H(z,t) = -D_H \left[\frac{\partial C_H(z,t)}{\partial z} + C_H(z,t) \frac{F}{RT} \frac{\partial \phi(z,t)}{\partial z} \right] \quad (2)$$

$$J_{Cl}(z,t) = -D_{Cl} \left[\frac{\partial C_{Cl}(z,t)}{\partial z} - C_{Cl}(z,t) \frac{F}{RT} \frac{\partial \phi(z,t)}{\partial z} \right] \quad (3)$$

In these equations $J_H(z,t)$ and $J_{Cl}(z,t)$ are fluxes of hydrogen and chloride ions (moles/cm²·sec), D_H and D_{Cl} are ionic diffusion coefficients (cm²/sec), $C_H(z,t)$ and $C_{Cl}(z,t)$ are concentrations of hydrogen and chloride ions (moles/cm³), $\phi(z,t)$ is the inner or Galvani potential of the solution phase (volts), RT/F is the thermal volt equivalent (volts), dilute solution transport theory has been assumed to be applicable, and the Nernst-Einstein relation between ionic mobilities and diffusion coefficients has been used. Components of flux due to natural and forced convection are ignored compared to diffusion and migration. It will be noticed that in the region $z < 0$ a one-dimensional approximation is used, and radial components of the flux have been set equal to zero. Use of this approximation greatly simplifies the mathematics, but leads to a minor inconsistency (to be discussed later) in matching boundary conditions in the $z = 0$ plane. A cylindrical coordinate system could have been used in the confined region, but the resulting equations are cumbersome to handle, and the results of the approximate method are quite similar to those of the exact treatment.

The continuity equations for the present case are given by:

$$\frac{\partial C_H(z,t)}{\partial t} = D_H \left[\frac{\partial^2 C_H(z,t)}{\partial z^2} + \frac{\partial}{\partial z} \left(C_H(z,t) \frac{F}{RT} \frac{\partial \phi(z,t)}{\partial z} \right) \right] \quad (4)$$

$$\frac{\partial C_{Cl}(z,t)}{\partial t} = D_{Cl} \left[\frac{\partial^2 C_{Cl}(z,t)}{\partial z^2} - \frac{\partial}{\partial z} \left(C_{Cl}(z,t) \frac{F}{RT} \frac{\partial \phi(z,t)}{\partial z} \right) \right] \quad (5)$$

In general these relations must be solved together with appropriate initial and boundary conditions subject to the electroneutrality condition

$$C_H(z,t) = C_{Cl}(z,t) = C_{HCl}(z,t) = C(z,t), \quad (6)$$

in which identifying subscripts may be dropped since a binary electrolyte is to be considered. Boundary conditions at $z = -\delta$ are given by:

$$J_H(-\delta, t) = -D_H \left[\frac{\partial C_H(z, t)}{\partial z} \right]_{z = -\delta} + C_H(-\delta, t) \frac{F}{RT} \frac{\partial \phi(z, t)}{\partial z} \bigg|_{z = -\delta} = \frac{j}{F} \quad (7)$$

$$J_{Cl}(-\delta, t) = -D_{Cl} \left[\frac{\partial C_{Cl}(z, t)}{\partial z} \right]_{z = -\delta} - C_{Cl}(-\delta, t) \frac{F}{RT} \frac{\partial \phi(z, t)}{\partial z} \bigg|_{z = -\delta} = 0, \quad (8)$$

where the net flux of hydrogen ions is due to the anodic reaction of Eq. (1) and the net flux of chloride ions is zero at the interface.

Equations (4) and (5) may be equated as a consequence of the electro-neutrality condition of Eq. (6) to give

$$(D_H - D_{Cl}) \frac{\partial^2 C(z, t)}{\partial z^2} + (D_H + D_{Cl}) \frac{\partial}{\partial z} \left\{ C(z, t) \frac{F}{RT} \frac{\partial \phi(z, t)}{\partial z} \right\} = 0, \quad (9)$$

which relates concentration and potential gradients. This expression will be useful later in calculating the potential distribution. Furthermore, if Eq. (4) is divided by D_H and Eq. (5) by D_{Cl} and the two are added, one obtains

$$\frac{\partial C(z, t)}{\partial t} = D_o \frac{\partial^2 C(z, t)}{\partial z^2}, \quad (10)$$

in which the contribution of migration terms has been subtracted by use of Eq. (6). Equation (10) is simply Fick's second law in which $D_o = 2 D_H D_{Cl} / (D_H + D_{Cl})$ is the "salt" diffusion coefficient for the binary electrolyte, HCl. Solution of Eq. (10) may be effected by standard methods with use of the boundary condition

$$\frac{\partial C(z, t)}{\partial z} \bigg|_{z = -\delta} = - \frac{j}{2FD_H}, \quad (11)$$

which is a consequence of Eqs. (6), (7), and (8).

Principal interest is attached to the solution for the steady state, in which case Eq. (10) becomes

$$\frac{d^2 C(z)}{dz^2} = 0 \quad (12)$$

where the time variable has been dropped. Integration of Eq. (12) with the boundary condition of Eq. (11) leads to

$$C(z) = C(0) - \frac{j}{2FD_H} z \quad (13)$$

for the concentration distribution in the region $z < 0$, where the constant $C(0)$ is to be determined later following solution of the mass-transport problem in $z > 0$.

A first integration of Eq. (9) leads to:

$$\frac{d\phi(z)}{dz} = - \frac{j}{\left[\frac{F}{RT} F(D_H + D_{Cl}) C(z) \right]} - \frac{RT}{F} \frac{(D_H - D_{Cl})}{(D_H + D_{Cl})} \frac{1}{C(z)} \frac{dC(z)}{dz} \quad (14)$$

for the electric field in the solution phase. The first term on the right-hand-side of Eq. (14) is an ohmic contribution to the field and the second term is essentially the gradient of a junction potential due to differences in ion mobilities. The term in brackets is the conductivity of the binary electrolyte which varies with position inside the pit; for the case of constant concentration, Eq. (14) thus reduces simply to Ohm's law. A second integration with use of Eq. (13) leads immediately to the simple form

$$\phi(z) = \phi(0) + \frac{RT}{F} \ln \left[\frac{C(z)}{C(0)} \right], \quad (15)$$

where the constant $\phi(0)$ is to be determined from the solution in $z > 0$. The form of Eq. (15) might also have been inferred from Eq. (8); this relation arises repeatedly in steady-state mass-transport problems in binary electrolytes.

In the region $z > 0$, a procedure similar to that used above (but carried out in the cylindrical coordinate system) leads to

$$\frac{\partial^2 C(r,z)}{\partial r^2} + \frac{1}{r} \frac{\partial C(r,z)}{\partial r} + \frac{\partial^2 C(r,z)}{\partial z^2} = 0 \quad (16)$$

for the concentration distribution in the steady state. This relation will be recognized as Laplace's equation in cylindrical coordinates. A convenient form of the solution to this equation is given by:

$$C(r,z) = C_0 + \int_0^\infty e^{-\lambda z} J_0(\lambda r) f(\lambda) d\lambda, \quad (17)$$

where $J_0(\lambda r)$ is Bessel's function of the first kind of zero order, λ is a separation factor, and the function $f(\lambda)$ is to be chosen so as to satisfy the boundary condition in the $z = 0$ plane. One notes that, for large values of r and/or z , the HCl concentration approaches C_0 , the bulk concentration, as required.

Use of a one-dimensional approximation in $z < 0$ has the consequence that both the concentration, $C(z)$, and the current density, j , are independent of the radial coordinate. Either one or the other of these quantities may be constant at $z = 0$, but not both if Laplace's equation is to be satisfied simultaneously in $z > 0$. We therefore adopt the following device in order to obtain an approximate solution: (a) let $C(0)$ be constant and independent of r at $z = 0$ when $r < a$; (b) determine the value of $C(0)$ such that the total current (I) applied to the pit at $z = -\delta$ is equal to the total current flowing out the pit mouth at $z = 0$. As a result of this procedure there will be a functional discontinuity of the current density and therefore of the concentration gradient in the $z = 0$ plane for $r < a$, but the correct qualitative behavior of the system will be obtained. The boundary condition for the concentration at $z = 0$ will be satisfied if $f(\lambda)$ is given by:

$$f(\lambda) = \frac{2}{\pi} [C(0) - C_0] \frac{\sin(\lambda a)}{\lambda} . \quad (18)$$

Substitution of Eq. (18) into Eq. (17) and evaluation of the resulting integral then leads to

$$C(r, z) = C_0 + \frac{2}{\pi} [C(0) - C_0] \sin^{-1} \left[\frac{2a}{\sqrt{z^2 + (a+r)^2} + \sqrt{z^2 + (a-r)^2}} \right] \quad (19)$$

for the concentration distribution in $z > 0$. The constant $C(0)$ in Eq. (19) is to be determined by equating the total current at $z = 0$ to the total current applied at $z = -\delta$.

At $z = 0$ the total current is given by

$$I = 2\pi F \int_0^a J(r, 0) r dr, \quad (20)$$

where $J(r, 0)$ is the net flux of HCl in $r < a$. The net flux can be shown to be given by

$$J(r, 0) = -2D_H \left. \frac{\partial C(r, z)}{\partial z} \right|_{z=0} . \quad (21)$$

Evaluation of the concentration derivative at $z = 0$ from Eq. (19) and substitution of $J(r, 0)$ from Eq. (21) into Eq. (20) then leads to a relation which can be integrated to give

$$I = 8FD_H [C(0) - C_0] a . \quad (22)$$

Since $I = j \cdot \pi a^2$ at $z = -\delta$, the HCl concentration at $z = 0$ is given by Eq. (23) as a function of the applied current density:

$$C(0) = C_o + \frac{\pi a}{8FD_H} j. \quad (23)$$

With this value of $C(0)$, the HCl concentration in $z > 0$ is given by

$$C(r, z) = C_o + \frac{ja}{4FD_H} \sin^{-1} \left[\frac{2a}{\sqrt{z^2 + (a+r)^2} + \sqrt{z^2 + (a-r)^2}} \right]. \quad (24)$$

The potential in the solution phase in $z > 0$ is given by a relation of the form of Eq. (15). If the position of the reference electrode in $z > 0$ is assumed to be given by the coordinates r_o, z_o , the potential difference between the mouth of the pit at $z = 0$ and the position of the reference electrode is given by

$$[\phi(0) - \phi(r_o, z_o)] = \frac{RT}{F} \ln \left[\frac{1 + \frac{\pi a}{8FD_H C_o} j}{1 + \frac{a}{4FD_H C_o} \sin^{-1} \left[\frac{2a}{\sqrt{z_o^2 + (a+r_o)^2} + \sqrt{z_o^2 + (a-r_o)^2}} \right] j} \right]. \quad (25)$$

This equation relates the measurable potential difference in the solution phase outside the pit mouth to the pit radius (a), the diffusion coefficient of hydrogen ions (D_H), the bulk electrolyte concentration (C_o), the position of the reference electrode (r_o, z_o), and the applied current density (j). Since $C(0)$ is known, the potential difference in the electrolyte phase inside the pit ($z < 0$) is:

$$[\phi(-\delta) - \phi(0)] = \frac{RT}{F} \ln \left[\frac{1 + \frac{(\frac{\pi a}{4} + \delta)}{2FD_H C_o} j}{1 + \frac{\pi a}{8FD_H C_o} j} \right], \quad (26)$$

which follows from Eqs. (13), (15), and (23).

The form of Eq. (26) shows immediately that it is possible to obtain a potential difference in the solution phase inside the pit which is independent of the applied current density, if the current density is high enough. This means that the conductivity of the solution inside the pit increases in direct proportion to the applied current. Such a conclusion

is reasonable since the mass transport of the material being produced by the interfacial reaction is hindered from mixing with the bulk electrolyte by the restricted geometry of the pit. Distributions of potential in the solution phase along the z-axis of the model pit are shown plotted in Fig. 1.2 for various values of the dimensionless parameter $\beta = j_a / (2FD_H C_o)$, for the special case where $\delta = 2a$. On increase of current density the value of the potential at any point along the z-axis increases as expected. But for large values of β (large j), the potential difference between the base and the mouth of the pit, $\phi(-2) - \phi(0)$, approaches a constant value. This approach to a constant potential difference inside the pit with increasing β is shown clearly in curve A of Fig. 1.3. For large values of j , Eq. (26) reduces to

$$\lim_{(\text{large } j)} [\phi(-\delta) - \phi(0)] = \frac{RT}{F} \ln \left(1 + \frac{4\delta}{\pi a} \right), \quad (27)$$

which can be interpreted to mean that the limiting potential difference will depend on relative pit dimensions, as expressed by the ratio δ/a . In the case of a hemispherical pit, a geometrical form which occurs frequently in pitting of metals, one might then infer that the corresponding potential difference would be independent of pit radius, as found experimentally in many cases.

One sees from the form of Eq. (25) and from the curves in Fig. 1.2 that the potential difference between the pit mouth ($z = 0$) and the position of the reference electrode (r_o, z_o) will depend in some manner upon the location of the reference electrode. Curves B, C, D, and E of Fig. 1.3 show how this potential difference varies with increase in β for several locations of the reference electrode along the z-axis ($z_o/a = 1, 2, 5$, and 10). Again a constant potential difference may be obtained if the current density is large enough. Under these conditions Eq. (26) reduces to Eq. (28) for the potential difference along the z-axis in the region $z > 0$:

$$\lim_{\substack{(\text{large } j) \\ r = 0}} [\phi(0) - \phi(z_o)] = \frac{RT}{F} \ln \left[\frac{\pi/2}{\sin^{-1} \left[\frac{1}{\sqrt{1 + (z_o/a)^2}} \right]} \right], \quad (28)$$

FIG. 1.2 DISTRIBUTION OF POTENTIAL IN MODEL PIT SYSTEM AS A FUNCTION OF CURRENT DENSITY.

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FIG. 1.3 POTENTIAL DIFFERENCE ALONG z-AXIS INSIDE MODEL PIT AND IN EXTERNAL SOLUTION PHASE AS A FUNCTION OF CURRENT DENSITY.

Although the potential difference in $z > 0$ becomes independent of applied current density for large β , it does depend upon the size of the pit through a dependence on pit radius, a [cf. Eq. (28)]. Normally pit radius increases with time as a consequence of the anodic dissolution reaction. Provided the current density is large enough so that β remains large, this increase of pit radius with time will have little effect upon the potential difference in the solution phase inside the pit. Such a conclusion depends upon the condition that the relative dimensions of the pit remain essentially unchanged ($\delta/a \approx \text{constant}$). In the common situation of a hemispherical pit where the applied current density is uniform over the pit wall, the relative dimensions of the pit will remain unchanged during pit growth, so that the potential difference inside the pit will also be essentially constant. However, the measurable potential difference in $z > 0$ will decrease with time as the pit radius increases [cf. Eq. (28)].

If relative pit dimensions (δ/a) are constrained to be constant during pit growth, it can be shown that the pit radius will follow a law of the form

$$a(t) = a_0 \left[1 + \frac{t}{\tau} \right]^{1/3} \quad (29)$$

for constant total applied current (I). In Eq. (29) $a(t)$ is pit radius at time t (sec), a_0 is initial pit radius, and τ is a time constant (sec) which depends upon such factors as total applied current, initial pit radius, and the molecular weight and density of the metal. The effect of pit growth according to Eq. (29) on the potential differences in the model pit system, is shown in Fig. 1.4 for various positions of the reference electrode. Curve E shows that the potential difference inside the pit remains essentially constant with time. Curves A, B, C, and D give the time behavior of the potential difference between the mouth of the pit and the position of the reference electrode. This potential contribution decreases with time. The total potential drop in the electrolyte phase (measurable in principle) is shown in curves F, G, H, and I. Such potential transients are typical for galvanostatic pitting of metals, and it is common practice to wait until the electrode potential attains a reasonably constant value; this value is then taken to

FIG. 1.4 POTENTIAL DIFFERENCES ALONG z-AXIS OF MODEL PIT SYSTEM AS A FUNCTION OF TIME.

be the pitting potential of the metal in question. The present model suggests that the decrease of electrode potential with time during galvanostatic pitting of metals is due to the decrease in the potential difference in the electrolyte phase outside the pit mouth during pit growth. Consequently so-called pitting potentials consist additively of the metal-solution potential difference at the base of a pit under current flow (to be discussed below) and the essentially constant potential difference in the electrolyte phase inside the pit plus a generally small contribution from the potential drop between the pit mouth and the position of the reference electrode; the latter contribution diminishes slowly with time.

The previous considerations have shown that for passage of a sufficiently large anodic current density through a confined area it is possible to attain an essentially constant potential drop in the solution phase under certain conditions. But in order for the overall potential difference to be constant it is also necessary for the metal-solution potential difference at the base of a pit to be constant and independent of both applied current and pit dimensions. It will be shown below that such potentials arise quite naturally from mass-transport effects in restricted geometries.

Again with reference to the model of Fig. 1.1, let the rate of the anodic dissolution reaction which takes place at the base of the model pit ($z = -\delta$) be described by

$$j = n_a F k_a C(-\delta) e^{+\frac{\beta_a F}{RT} \Delta\phi}, \quad (30)$$

where j is applied current density, n_a is the number of electrons involved in the anodic process, F is Faraday's constant (coulombs/equivalent), k_a is a heterogeneous specific rate constant (cm/sec), $C(-\delta)$ is the HCl concentration at the base of the pit (moles/cm³), β_a is the transfer coefficient of the anodic process (dimensionless), and $\Delta\phi$ is the metal-solution potential difference (volts). The rate of the anodic process thus obeys the conventional Tafel equation of electrode kinetics and is first order with respect to HCl concentration. Combination of Eqs. (13) and (23) leads to

$$C(-\delta) = C_o + \frac{(\frac{\pi a}{4} + \delta)}{2FD_H} j \quad (31)$$

for the HCl concentration at $z = -\delta$. Substitution of Eq. (31) into Eq. (30) and solution for $\Delta\phi$ then leads immediately to the polarization behavior at the base of the pit:

$$\Delta\phi = \frac{RT}{\beta_a F} \ln \frac{j/(n_a F k_a C_o)}{\left[1 + \frac{(\frac{\pi a}{4} + \delta)}{2FD_H C_o} j \right]} \quad (32)$$

The behavior of this function for certain values of the parameters is shown in Fig. 1.5. For small current densities $\Delta\phi$ is given approximately by $\frac{RT}{\beta_a F} \ln [j/(n_a F k_a C_o)]$, the conventional Tafel behavior of a simple anodic reaction in the absence of mass-transport effects. But, in the restricted geometry of the model pit, the HCl concentration at the pit base depends linearly on the applied current density, so that for large j , $\Delta\phi$ approaches a limiting value ($\Delta\phi_L$) given by

$$\Delta\phi_L = \lim_{(large\ j)} \Delta\phi = \frac{RT}{\beta_a F} \ln \left[\frac{2D_H}{n_a k_a (\frac{\pi a}{4} + \delta)} \right]. \quad (33)$$

The limiting value of the interfacial potential difference, $\Delta\phi_L$, although independent of applied current density, will nevertheless vary during pit growth because of the dependence of this quantity on pit dimensions as seen in Eq. (33). However, this case seems to correspond closely to certain experiments on artificial pits which have been reported in the literature.

In the case of metals like titanium which are subject to pitting attack, it is known that the rates of both the anodic and the cathodic processes during corrosion in the active state depend on acid concentration. It is therefore possible in such cases, as shown below, to attain a steady-state mixed potential which is independent of the applied anodic current density and the dimensions of the confined region. A simple kinetic description of such a system is given by

$$j = n_a F k_a C(-\delta) e^{+\frac{\beta_a F}{RT} \Delta\phi} - n_c F k_c C(-\delta) e^{-\frac{\beta_c F}{RT} \Delta\phi}, \quad (34)$$

where the concentration and the potential dependence of the anodic reaction

FIG. 1.5 POLARIZATION OF ANODIC REACTION AT BASE OF MODEL PIT SYSTEM.

is similar to that in Eq. (30). The net applied current density (j) is the difference between the rates of the anodic and cathodic reactions. In the case of titanium the anodic process is the dissolution of titanium to form trivalent titanium ions while the cathodic process is the hydrogen evolution reaction. Substitution of Eq. (31) into Eq. (34) and solving for $\Delta\phi$ for the special case where $\beta_a = \beta_c = 1/2$, leads to

$$\Delta\phi = \frac{2RT}{F} \ln \left[\frac{j/2n_a F k_a C_o}{1 + \frac{(\frac{\pi a}{4} + \delta)}{2FD_H C_o} j} \right] + \sqrt{\left[\frac{j/2n_a F k_a C_o}{1 + \frac{(\frac{\pi a}{4} + \delta)}{2FD_H C_o} j} \right]^2 + \left[\frac{n_c k_c}{n_a k_a} \right]} \quad (35)$$

for the interfacial potential difference as a function of applied current density. As the applied current density increases, a limiting potential is approached which is given by:

$$\Delta\phi_L = \frac{2RT}{F} \ln \left[\frac{2D_H}{n_a k_a (\frac{\pi a}{4} + \delta)} \right] + \sqrt{\left[\frac{2D_H}{n_a k_a (\frac{\pi a}{4} + \delta)} \right]^2 + \left[\frac{n_c k_c}{n_a k_a} \right]} \quad (36)$$

There are two special cases of Eq. (36): (a) for small k_c the applied current density is large compared to the rate of the cathodic process, and the limiting potential is given by a relation of the form of Eq. (33); (b) however, for $n_a k_a n_c k_c \gg [2 D_H / (\frac{\pi a}{4} + \delta)]^2$, the limiting potential is given approximately by

$$\Delta\phi_L \approx \frac{RT}{F} \ln \left[\frac{n_c k_c}{n_a k_a} \right]; \quad (37)$$

this result could also have been obtained from Eq. (34) by setting j equal to zero. The condition necessary for validity of Eq. (37) is easily attained for metals having substantial spontaneous corrosion rates in the active potential region. The limiting potential given by Eq. (37) is seen to be an essentially unpolarizable steady-state mixed potential which is independent of both applied current density and pit dimensions. It will of course depend on alloy composition and temperature because the rate constants of interfacial processes are in general dependent upon these factors.

Similar considerations may be applied to metals which exhibit typical active-passive behavior during anodic polarization. This situation is shown schematically in Fig. 1.6 where anodic and cathodic polarization curves for a metal such as titanium are plotted as a function of current density and acid concentration. An unpolarizable mixed potential ($\Delta\phi_L$), as given by Eq. (37), exists in the active region. In addition, another unpolarizable potential ($\Delta\phi'_L$) can exist at more noble potentials; this potential is quite analogous to that described by Eq. (33). One sees further that for large applied current density a potential region exists which is inaccessible to the metal at the base of the pit. The width of the inaccessible potential region is influenced both by the parameters of the interfacial reactions and by the pit geometry. The existence of such an inaccessible potential region for corrosion in restricted geometries is a consequence of the influence of mass transport on the polarization behavior of metals which exhibit typical active-passive behavior.

During pit growth at constant total applied current, the current density at the pit wall will continually decrease. A point will eventually be reached where an unpolarizable mixed potential can no longer be maintained. Simultaneously the current density in the electrolyte phase may also eventually become too small to sustain a constant potential difference inside the pit. If this happens, then the locus of quasi-steady states available to the system will finally shift fully into the passive region; i.e., repassivation will eventually take place after a sufficient length of time.

The present model does not consider the process of pit initiation on a metal surface. For some metals, such as iron and aluminum, the number of pits has been observed to increase nearly linearly with time. Of these, some or all eventually repassivate as others are initiated and grow. The preceding analysis suggests that repassivation takes place when it is no longer possible, under the existing mass-transport conditions, to maintain an unpolarizable mixed potential at the wall of a pit.

In the case of the binary electrolyte discussed above, the overall limiting potential difference between the metal phase and the position of the reference electrode ($\Delta\phi_p$) is given approximately by

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FIG. 1.6 SCHEMATIC POLARIZATION BEHAVIOR OF TYPICAL ACTIVE-PASSIVE METAL IN MODEL PIT SYSTEM.

$$\Delta\phi_p \approx \frac{RT}{F} \ln \left[\frac{k_c}{k_a} \left(1 + \frac{4\delta}{\pi a} \right) \right]. \quad (38)$$

This relation is obtained by combining Eqs. (27) and (37) and neglecting the potential difference between the mouth of the pit and the position of the reference electrode (cf. Fig. 1.4). Equation (38) contains no dependence upon the HCl concentration in the bulk of the electrolyte (C_o). Experimental data to be found in the literature are somewhat contradictory on the influence of the concentration of activator ions (Cl^-) on the pitting potential. Instances are known where clearly only a binary electrolyte is present, with only one kind of anion (Cl^- , for example), and in some of these cases the measured pitting potential seems to be independent of chloride-ion concentration, as suggested by Eq. (38). In other cases this is certainly not true; but for the most part a logarithmic dependence of $\Delta\phi_p$ on $[Cl^-]$ is observed when there is also an additional anion present in the system (such as SO_4^{2-} , OH^- , etc.) which can function as a passivator ion. In such a case it is possible, using the mass-transport model outlined above, to account for the observed behavior, as shown below.

Again with reference to the model of Fig. 1.1, let there be three kinds of ions in the electrolyte phase, H^+ , Cl^- , and X^- , where X^- is an inert anion which does not affect the rates of either of the interfacial reactions. In the bulk of the electrolyte the HCl concentration is denoted by C_{HCl}^o and the HX concentration is given by C_{HX}^o . On carrying out the mass-transport analysis for this case (ternary electrolyte), the unpolarizable mixed potential at the metal-solution interface at the base of the pit is given by Eq. (39), instead of Eq. (37):

$$\Delta\phi_L \approx \frac{RT}{(\beta_a + \beta_c)F} \ln \left[\frac{n_c k_c (C_{HCl}^o + C_{HX}^o)}{n_a k_a C_{HCl}^o} \right]. \quad (39)$$

In the derivation of Eq. (39) it was assumed that the rate of the anodic process depends directly upon the chloride-ion concentration at $z = -\delta$ while the rate of the cathodic process depends directly upon the hydrogen-ion concentration at $z = -\delta$. When the concentration of inert electrolyte is in excess ($C_{HX}^o \gg C_{HCl}^o$), which is true in many instances cited in the

literature (Fe in SO_4^{2-} solutions, for example), Eq. (39) reduces to the following:

$$\Delta\phi_L \approx \frac{RT}{(\beta_a + \beta_c)F} \ln \left(\frac{n_c k_c}{n_a k_a} \right) + \frac{RT}{(\beta_a + \beta_c)F} \ln \left(\frac{C_{\text{HX}}^\circ}{C_{\text{HCl}}^\circ} \right). \quad (40)$$

The unpolarizable mixed potential at the pit wall thus increases logarithmically with the concentration of the passivator ion (X^-) and decreases logarithmically with the concentration of the activator ion (Cl^-). Furthermore, as noted above, the value of the mixed potential will be independent of applied current (for large currents) and of pit dimensions but dependent upon the nature of the metal and upon temperature through the dependence of $\Delta\phi_L$ on the rate constants of the interfacial reactions. However, if the concentration of passivator ions becomes too large, it may become impossible to maintain a limiting potential of the type discussed above because the rate of the anodic process will be insufficient to maintain an unpolarizable mixed potential and repassivation will take place.

Certainly many other mechanistic choices could be made for the processes which take place in the interior of a pit. For example, various hydrolysis and complexing reactions, as well as processes involving absorption and surface intermediates, surely play an important role in many cases. Nevertheless, the qualitative behavior is likely to be similar to that noted above because of the operation of mass-transport effects.

One of the factors which was ignored in the preceding treatment was the influence of natural and forced convection. There is no doubt that natural convection can play a role within a confined area like a pit because of large density gradients which must accompany the large concentration gradients set up by passage of high current densities. In addition, when the hydrogen evolution reaction takes place at pit walls, one expects an influence of forced convection due to bubbles of hydrogen gas. Furthermore, forced convection in the external solution phase can be expected to affect concentration and potential distributions in the vicinity of a pit. In many cases, however, natural and forced convection can be expected to function principally as perturbations of the basic mass-transport situation, especially when ion fluxes are determined primarily by migration in the

presence of large current densities. Perhaps the erratic potential fluctuations that are frequently observed when metals undergo pitting at constant applied current are due in large part to the influence of convection upon potential, concentration, and current-density distributions.

An additional factor which may influence pitting potentials is the hydrolysis and precipitation of corrosion products within a pit. Pits on titanium in chloride solution are nearly completely filled with titanium dioxide corrosion product of very low porosity. True current densities within the pores of such corrosion products should be very much higher than for pits of a more open type (such as on Fe, Al, etc.). Consequently, one might expect that pitting potentials in such systems would be very much higher than for metals with soluble corrosion products. Related to this factor would be the possibility that the presence of alloying elements might affect not only the interfacial potential difference at the base of a pit, but also the morphology of precipitated corrosion products and thus the value of the limiting potential difference within the solution phase inside a pit that can be attained at high current densities. Such matters need a great deal more study before the mechanism of pitting attack of metals can be understood in more detail.

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2. CHRONOPOTENTIOMETRY AND VOLTAMMETRY OF THE Ag-AgCl ELECTRODE IN FLOWING STREAMS. I. EXPERIMENTAL

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INTRODUCTION

In previous work¹ we have described a chronopotentiometric technique for the analysis of solutions containing chloride ion. This work is extended here to include chronopotentiometric and voltammetric analyses of the chloride ion in flowing streams.

Passage of a liquid through a narrow channel can produce a reproducible flow pattern in the case of laminar flow. If an electrode is set into the wall of the channel, mass transport to the electrode due to forced convection can be controlled with considerable precision. This configuration thus appears to be a good choice for electroanalysis in flowing streams.

Previous studies of electrolytic reactions in a flowing stream have included studies with tubular electrodes² and the theoretical work of Matsuda³. An extensive discussion of convective mass transport is given by Levich⁴. A more complete listing of these and other references is given in our companion paper⁵.

A schematic diagram of a channel electrode is given in Fig. 1. Flow of solution is assumed to take place along the x-direction. The electrode length in the x-direction

Fig. 1. Typical exptl. configuration for electroanalysis in flowing soln.

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is denoted by l (cm), and the width of the working surface of the electrode is w (cm). The dimensions of the channel which define the flow pattern are the width (d), height (h), and the distance from the entrance of the channel to the leading edge of the electrode (L). These dimensions are determined by the requirement that fully developed Poiseuille flow be established at the electrode in the vertical (y) direction. In our experiments the width of the channel (d) was always made much larger than the height (h), and the electrode was placed at the center of the channel in order to avoid possible disturbances at the corners of the channel cross-section. By use of this configuration, a fairly uniform velocity front could be established across the width (w) of the electrode.

Two modes of operation of the channel electrode were investigated in this work. In the voltammetric mode, we were primarily interested in the relation between the limiting current and the parameters which determine flow rate, and in applying these results to the analysis of solutions containing low concentrations of chloride ion (10^{-4} – 10^{-3} M). For analysis of solutions containing higher concentrations of chloride ions, we investigated the chronopotentiometric mode of operation.

The equation for the limiting current of a single species to the surface of a channel electrode with fully-developed laminar flow is²⁻⁵

$$I_L = 1.282 z F A c_0 D^{1/2} (U_0/hl)^{1/2} \quad (1)$$

where z is ion charge, F is Faraday's constant (equiv.⁻¹), A is the area of the electrode (cm²), c_0 is bulk reactant concentration (mol cm⁻³), D is the diffusion coefficient (cm² s⁻¹), and U_0 is the mid-stream velocity (cm s⁻¹). For fully developed flow in the configuration used here, the volume flow rate is given approximately by $U_v = 2 U_0 h d / 3$. In terms of volume flow rate and the parameters of Fig. 1, the limiting current is therefore given by

$$I_L = 1.467 z w F c_0 (Dl/h)^{1/2} (U_v/d)^{1/2} \quad (2)$$

The limiting current thus increases directly with the concentration, with the two-thirds power of the electrode length, and with the one-third power of the fluid velocity.

From a practical analytical viewpoint, we are principally concerned with the validity of eqn. (2) when applied to the Ag-AgCl electrode and with the precision with which these measurements can be carried out. In this respect, the relative lack of sensitivity of the limiting current to the flow velocity is particularly advantageous, since flow velocity need not be so carefully controlled and determined. Our measurements therefore consist primarily in the determination of limiting currents obtained on oxidation of the silver electrode in the presence of chloride ion. In addition, these measurements have been checked by reduction of potassium ferricyanide on a platinum electrode of exactly the same dimensions and configuration as the silver electrode.

We have previously shown that chronopotentiometry of the Ag-AgCl electrode may be used for accurate analysis of solutions containing chloride ion¹. However, chronopotentiometry in a flow cell is considerably more complex. In this case, a constant current is supplied which is of sufficient magnitude so that the solution adjacent to the electrode surface is depleted of the chloride ion. At the same time, this solution layer is replenished with chloride ion from the direction of the flow. Moreover, the resulting distribution of chloride ion along the x -direction will be non-uniform. Although on first consideration it might seem hopeless to attempt chronopotentiometry under these circumstances, our preliminary experiments showed

that reproducible chronopotentiograms could be obtained at surprisingly large flow rates. Closer analysis shows, of course, that solution velocities in the region of the diffusion layer (ca. 10^{-2} cm thickness for transition times of 10 s) are small relative to the mid-stream velocity because of the velocity gradient developed by the flow. In fact, forced convection will tend to suppress temperature and density gradients which might develop under stagnant conditions.

At very low fluid velocities there will be little measurable change in the transition time. As the flow rate is increased, sufficient ions are introduced into the diffusion layer by the flow to increase measurably the transition time and distort the chronopotentiogram by delaying the rate at which the potential changes to the potential region of the next accessible electrode reaction. Ultimately, at high flow rates, chloride ions will be supplied at a rate sufficient to prevent completely depletion of reactant ions in the diffusion layer, and no transition time will be observed.

It is shown in the companion paper⁵ that an approximate solution of the equation of convective diffusion yields the following expression for the increase in transition time caused by the flow:

$$\frac{\tau}{\tau_0} = -\frac{2}{3\xi^2} \left\{ \ln \left[\frac{1-\xi}{(1+\xi+\xi^2)^{\frac{1}{2}}} \right] + 3^{\frac{1}{2}} \tan^{-1} \left[\frac{3^{\frac{1}{2}} \xi}{2+\xi} \right] \right\} \quad (3)$$

where the parameter ξ is defined by:

$$\xi = 1.155 (zFc_0/j) D^{\frac{1}{2}} (U_0/hl)^{\frac{1}{2}} \quad (4)$$

In eqns. (3) and (4), j is the average current density ($A\text{ cm}^{-2}$), τ is the measured chronopotentiometric transition time with flow (s), and τ_0 is the chronopotentiometric transition time at zero flow rate which is given by the customary relation (Sand equation),

$$\tau_0^{\frac{1}{2}} = zFc_0(\pi D)^{\frac{1}{2}}/2j$$

We may therefore rewrite eqn (4) in terms of τ_0 :

$$\xi = 1.492 \tau_0^{\frac{1}{2}} D^{\frac{1}{2}} h^{-\frac{1}{2}} (U_v/dl)^{\frac{1}{2}} \quad (5)$$

The increase in transition time due to the flow should therefore depend only on the zero-velocity transition time and the flow parameters. A graph of eqn. (3) in the region of practical interest is shown in Fig. 2, which shows that ξ must reach about 0.5 before the transition time is increased by 5%. We note also that as the value of the parameter ξ approaches unity, the transition time tends to infinity. The value of the flow rate at $\xi = 1$ is therefore the critical velocity at which a transition time can no longer be observed.

For chronopotentiometry in a channel, distortion of the chronopotentiogram presents a problem with respect to determination of the transition time, since the potential change on depletion of the diffusion layer is less abrupt than in unstirred solution. We have shown previously¹ that a derivative technique may be used to determine transition times for the Ag-AgCl electrode system with considerable precision in unstirred solution. This technique relies on the fact that, after depletion of the diffusion layer, the rate of change of the potential will be a maximum as the

Fig. 2. Relative transition time as a function of the parameter ξ .

electrode progresses from the silver chloride reaction to the next available electrode reaction. A peak in the (potential derivative)-(time) curve will be observed and the time interval between application of the current and the derivative peak may for *practical* purposes be equated to the transition time. The product, $I\tau^{\frac{1}{2}}$, found in this manner is found to be constant over a wide range of transition times. In the present work only the ratios, τ/τ_0 , are significant and systematic errors resulting from use of this technique will tend to cancel.

Our experiments on chronopotentiometry in a channel consist in the determination of the increase in transition time as a function of the flow rate for various values of the zero-velocity transition time and the geometric parameters of the channel-electrode system. In this case also, we have checked our results by chronopotentiometry of potassium ferricyanide on a platinum electrode of similar configuration.

II. EXPERIMENTAL

Two different cells were constructed for these experiments. One of the cells was a large, multi-electrode cell designed to test several sizes and shapes of electrodes under identical flow conditions. The other cell, shown in Fig. 3, was used for most of the experiments and contained a single silver electrode having dimensions, 0.5 cm $\times$ 1.5 cm. Other dimensions of the cell are shown in the caption to Fig. 3. The cells were similar in construction and were machined from blocks of Lucite. The electrode was set with epoxy cement into a depression milled in a $\frac{1}{4}$ -in.* Lucite plate.

Initially, the surface of the silver electrode was slightly raised over the working surface of the Lucite so that the entire face of this piece (cf. A in Fig. 3) could be polished

* 1 in. = 2.54 cm.

Fig. 3. Exptl. cell: channel cross section, 1.27 cm $\times$ 0.476 cm; silver electrode, 0.5 cm $\times$ 1.5 cm; length of entrance region, 7 cm, (A) Bottom half, (B) top half, (C) silver electrode, (D) platinum counter electrode, (E) reference port, (F) "O"-ring.

smoothly, ensuring a continuous transition from the Lucite to the silver. This piece was secured to the other half of the cell by eight bolts which, when tightened, compressed a neoprene "O"-ring set in slots surrounding the channel. When the bolts were tightened completely, the "O"-ring was compressed enough so that the two halves of the cell fit tightly against each other. A platinum counter electrode was situated in the channel wall opposite the silver electrode. A saturated calomel reference electrode was bridged into the cell through a small hole immediately downstream from the platinum counter electrode. The solution inlet and exit were set into the half of the cell which held the counter electrode. In this way the working electrode could easily be changed without opening the fluid connections to the cell. An absolute reference electrode was not needed in the chronopotentiometric experiments; instead, a short piece of 20 mil* silver wire was set in the reference hole, and silver chloride was formed on the tip of the wire by anodization. This arrangement simplified filling the cell and avoided possible difficulties with gas bubbles in a reference bridge.

The overall size and relative dimensions of the cell were determined by hydrodynamic factors, minimum solution hold-up, and ease of machining. The height of the channel (h) was $\frac{3}{16}$ in. = 0.476 cm for the small cell. Use of too narrow a cell could lead to irreproducible behavior due to surface irregularities near the electrode. Because these irregularities (due to machining faults and to formation of the AgCl layer) are likely to be of the order of 1 mil or less, a total height of 100–200 mils was used to ensure that such irregularities were a small percentage of the overall height.

* 1 mil = 2.54×10^{-3} cm.

This height fixed the length of the entrance region, which should be of the order of $0.05 \times h \times Re$ (cf. ref. 4, p. 113) for fully developed flow, where Re is the Reynolds number. Since the Reynolds number did not exceed 200 in this work, the length of the entrance region (L) could be as short as about 5 cm. We allowed 7 cm for the entrance region and 10 cm for the overall length of the cell. The resulting solution hold-up (ca. 6 cm³) was satisfactorily small for our purposes. Total electrode areas of the order of 1 cm² were considered desirable in order to help eliminate any effects due to edge diffusion. Since diffusion lengths of about 10^{-2} cm ($(Dt)^{1/2}$) are developed in chronopotentiometry, dimensions of the order of 1 cm were considered necessary to minimize this factor. Electrodes obviously could not be shielded at the edges to minimize this effect as in chronopotentiometry in unstirred solution.

The large cell contained three rectangular electrodes which were 0.4, 2.0, and 4.0 cm in length. This cell also contained a shielded and recessed circular electrode and a flush $\frac{1}{4}$ in. circular electrode. The recessed electrode was included to test whether chronopotentiometric analysis in a flow system could be carried out by shutting off the flow. However the time required for the solution to become stagnant was much too long for practical use. The $\frac{1}{4}$ in. circular electrode did not give reproducible results and was abandoned.

Flow was maintained by a gravity feed system controlled by a Teflon-bore stopcock. Flow rates were determined by use of calibrated rotameters. Liberal use of Swagelok fittings and $\frac{1}{4}$ in. o.d. plastic tubing simplified assembly and disassembly of the system. Electrode preparation, electrical apparatus, and other experimental details have been described previously¹.

One of the real nuisance problems encountered with flow cells is the entrapment of bubbles in the cell at critical points in the flow stream. Once they are formed, it is almost impossible to dislodge them. The best method of dealing with these is to prevent them from forming by slowly filling the entire system and eliminating all gas pockets. If a bubble should be formed in the cell, it should be emptied to the point where the bubble is eliminated, and then slowly refilled. Mounting of the cell at a slight angle facilitates this procedure.

III. RESULTS AND DISCUSSION

Voltammetry

Equation (2) predicts that the limiting current of a channel electrode in fully-developed laminar flow should have a one-third power dependence on flow rate (U_v) and a two-thirds power dependence on electrode length (l). These relations are confirmed by the results shown in Figs. 4 and 5. Slopes having values from 0.32 to 0.34 were obtained also from the dependence of the current on the flow rate for the case of reduction of potassium ferricyanide on a platinum electrode having exactly the same configuration. These relations have been confirmed by other investigators² and are presented here to demonstrate conformity of our experimental system to theory.

Calculation of the magnitude of the limiting current by use of eqn. (2) from the results of Fig. 4 yields a value of 5.16×10^{-5} A at $U_v = 1$ cm³ s⁻¹. We used $D = 2.0 \times 10^{-5}$ cm² s⁻¹, a value for the self-diffusion coefficient of the chloride ion at zero ionic strength⁶. This value is not strictly comparable to our case but should not be in error by more than a few percent. The measured value (cf. Fig. 4) is 5.62×10^{-5} A,

Fig. 4. Limiting current as a function of volume flow rate; $0.5 \text{ cm} \times 1.5 \text{ cm}$ electrode, $5 \times 10^{-4} \text{ M NaCl}$, 0.25 M KNO_3 , $+0.300 \text{ V vs. SCE}$.

Fig. 5. Limiting current as a function of electrode length at various flow rates; $2.5 \times 10^{-3} \text{ M NaCl}$, 0.25 M KNO_3 , $+0.300 \text{ V vs. SCE}$. Flow rates: (upper line) 0.737 , (middle line) 0.485 , (lower line) $0.189 \text{ cm}^3 \text{ s}^{-1}$. Slope of lines = 0.66 .

but this includes a blank current (to be discussed below) of $0.30 \times 10^{-5} \text{ A}$ which is not due to chloride ion. The difference between $5.16 \times 10^{-5} \text{ A}$ and the corrected value, $5.32 \times 10^{-5} \text{ A}$, is satisfactorily small.

Similarly for the limiting current from the reduction of potassium ferricyanide, we measured $5.0 \times 10^{-4} \text{ A}$ in $5 \times 10^{-3} \text{ M K}_3\text{Fe(CN)}_6$ at a flow rate of $5.95 \text{ cm}^3 \text{ s}^{-1}$. The calculated value is $4.9 \times 10^{-4} \text{ A}$ using $D = 7.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for the diffusion coefficient of the ferricyanide ion⁷.

In Fig. 6, limiting currents are shown for four different concentrations of the chloride ion at a flow rate of $0.189 \text{ cm}^3 \text{ s}^{-1}$, along with a determination of the blank current. This blank current was determined with 0.25 M KNO_3 in chloride-free distilled water. However, this blank current also showed a one-third power dependence on the flow rate. In addition, the slope of the linear (Tafel) portion of the complete polarization curve for the blank is $60 \text{ mV decade}^{-1}$. The open-circuit potential of the Ag-AgCl electrode was about $+0.270 \text{ V vs. SCE}$, a value which corresponds to the saturation solubility of AgCl (ca. $1.3 \times 10^{-5} \text{ M Cl}^-$). When this electrode is polarized in the anodic direction, the only accessible reaction is the oxidation of silver

Fig. 6. Limiting current as a function of NaCl concn.; 0.25 M KNO₃, 0.5 cm × 1.5 cm electrode, volume flow rate = 0.189 cm³ s⁻¹. NaCl concn.: (A) 10⁻³, (B) 5 × 10⁻⁴, (C) 2 × 10⁻⁴, (D) 10⁻⁴ M, (E) blank.

metal, which passes into solution through the film of AgCl. Assuming that equilibrium is maintained at all times at the electrode surface, the concentrations of silver and chloride ions will be determined by the potential and the solubility product. Thus at +0.300 V vs. SCE, the concentration of the chloride ion will be about 3.5×10^{-6} M and the concentration of silver ion about 5×10^{-5} M. The current will therefore be determined primarily by the rate of mass transport of silver ion from the electrode surface. This rate may be calculated from eqn. (2) assuming that the bulk concentration of silver ion is zero and the interfacial concentration is related to the electrode potential by the Nernst equation*. Using a diffusion coefficient of 1.64×10^{-5} cm² s⁻¹ for the silver ion⁸, we calculate a current of 2.6×10^{-6} A, in approximate agreement with our measured value of 3.3×10^{-6} A at +0.300 V vs. SCE. This blank current should be roughly independent of the bulk concentration of chloride ion, since the concentration of the silver ion is determined only by the equilibrium conditions at the surface. When this blank current is subtracted from the overall current, the dotted lines of Fig. 6 are obtained. These lines are horizontal and almost exactly proportional to the concentration of the chloride ion. This proportionality is therefore the basis for a simple and accurate analysis of the chloride ion in this concentration range. Analyses by this method at concentrations above about 5×10^{-3} M are limited by excessive film growth on the electrode surface. Within limits, the voltammetric method could be extended to analysis of more concentrated solutions by use of a controlled dilution technique with added concentrated electrolyte.

* Application of the method described in Part II⁵ to the boundary value problem implied for the blank current leads to an expression identical to eqn. (2).

Fig. 7. Effect of flow rate on chronopotentiograms; $5.63 \times 10^{-3} M$ NaCl, $0.25 M$ KNO₃, $0.5 \text{ cm} \times 1.5 \text{ cm}$ electrode, $I = 0.518 \text{ mA}$. Flow rate: (A) 0.0, (B) 0.162, (C) 0.273, (D) 0.392, (E) $0.565 \text{ cm}^3 \text{ s}^{-1}$.

Fig. 8. Effect of flow rate on derivatives of chronopotentiograms; $5.63 \times 10^{-3} M$ NaCl, $0.25 M$ KNO₃, $0.5 \text{ cm} \times 1.5 \text{ cm}$ electrode, $I = 0.518 \text{ mA}$. Flow rate: (A) 0.0, (B) 0.162, (C) 0.273, (D) 0.392, (E) $0.565 \text{ cm}^3 \text{ s}^{-1}$.

Chronopotentiometry

As noted above, the effect of increasing the solution flow rate is to increase the transition time and to broaden or retard the transition of the potential from the Ag-AgCl electrode reaction to the next available reaction (which in the absence of other precipitating ions will normally be the dissolution of silver metal to silver ions).

This broadening effect is shown in Fig. 7, where chronopotentiograms for various flow rates are shown for a solution of $5.63 \times 10^{-3} M$ NaCl. Little change in the initial sections of the curves is noted, but in the final section the slope of the rising portion decreases considerably. It is quite difficult to determine the transition time by conventional graphical techniques, but with the derivative technique described above¹ transition times may be determined with considerable precision. The (potential derivative)-(time) curves for the chronopotentiograms shown in Fig. 7 are shown in Fig. 8. As expected, the derivative peaks broaden, but the maximum may be determined with reasonable precision.

These measurements were repeated for transition times of about 4 s and about 10 s for five different chloride ion concentrations. For transition times greater than about 12 s the range of flow velocities was too limited for successful measurements.

The results of these experiments are shown in Tables 1 and 2. For analytical purposes the chronopotentiometric constant is of significance, and these are shown

TABLE 1

VALUES OF TRANSITION TIME (τ) AND CHRONOPOTENTIOMETRIC CONSTANT ($\kappa = \tau^2 I / c_0 \times 10^{-2}$) AS A FUNCTION OF FLOW RATE (U_v) AND CONCENTRATION (c_0)

$U_v / \text{cm}^3 \text{ s}^{-1}$	c_0 / M	1.02×10^{-2}	7.37×10^{-3}	5.63×10^{-3}	3.67×10^{-3}	1.00×10^{-3}
	I / mA	1.48	1.00	0.802	0.535	0.156
0.000	τ :	4.09	4.76	4.05	3.94	4.14
	κ :	2.93	2.96	2.87	2.90	3.18
0.162	τ :	4.44	4.78	4.08	3.98	3.97
	κ :	3.05	2.98	2.88	2.91	3.23
0.439	τ :	4.36	4.94	4.20	4.05	4.46
	κ :	3.01	3.01	2.92	2.94	3.29
0.685	τ :	4.51	5.14	4.28	4.08	4.66
	κ :	3.08	3.09	2.95	2.94	3.37
0.905	τ :	4.72	5.36	4.37	4.15	4.84
	κ :	3.15	3.15	2.98	2.97	3.43
1.155	τ :	5.02	5.80	4.51	4.21	4.94
	κ :	3.24	3.27	3.02	2.99	3.47
1.349	τ :	5.54	6.46	4.65	4.30	5.09
	κ :	3.40	3.45	3.08	3.02	3.52
	I / mA	0.91	0.685	0.518	0.340	0.101
0.000	τ :	10.7	9.97	9.98	9.01	8.67
	κ :	2.92	2.94	2.91	2.78	2.98
0.162	τ :	11.64	10.53	10.50	9.62	9.67
	κ :	3.04	3.02	2.98	2.88	3.14
0.211	τ :	12.30	10.65	10.72	9.87	9.87
	κ :	3.13	3.03	3.02	2.91	3.17
0.273	τ :	13.30	11.10	11.00	10.07	10.10
	κ :	3.25	3.09	3.05	2.94	3.21
0.334	τ :	14.70	11.30	11.50	10.42	10.47
	κ :	3.41	3.12	3.12	2.99	3.27
0.392	τ :	16.27	11.65	11.98	10.62	10.77
	κ :	3.62	3.18	3.18	3.02	3.31

TABLE 2

DUPLICATE EXPERIMENTS: VALUES OF TRANSITION TIME (τ) AND CHRONOPOTENTIOMETRIC CONSTANT ($\kappa = \tau^{\frac{1}{2}} I / c_0 \times 10^{-2}$) AS A FUNCTION OF FLOW RATE (U_v)^a

$U_v / \text{cm}^3 \text{ s}^{-1}$	c_0 / M	5.63×10^{-3}		3.67×10^{-2}	
		I / mA		0.802	
		# 1	# 2	# 1	# 2
0.000	τ :	4.05	4.28	3.94	3.97
	κ :	2.87	2.95	2.90	2.91
0.162	τ :	4.08	4.18	3.98	3.97
	κ :	2.88	2.91	2.91	2.91
0.439	τ :	4.20	4.24	4.05	4.06
	κ :	2.92	2.93	2.94	2.94
0.685	τ :	4.28	4.37	4.08	4.11
	κ :	2.95	2.98	2.94	2.96
0.905	τ :	4.37	4.47	4.15	4.13
	κ :	2.98	3.01	2.97	2.96
1.155	τ :	4.51	4.61	4.21	4.21
	κ :	3.02	3.06	2.99	2.99
1.349	τ :	4.65	4.90	4.30	4.30
	κ :	3.08	3.16	3.02	3.02

^a In each case run #2 was carried out a few hours after run #1.

adjacent to the transition times. These data were obtained with the $0.5 \text{ cm} \times 1.5 \text{ cm}$ electrode in the single-electrode cell. This electrode was used for two months without resurfacing. The silver chloride layer was partially removed after each chronopotentiogram by reversing the current and reducing the layer. The electrode had to be resurfaced before the experiments with $10^{-3} M$ chloride, because the silver chloride layer became loose and poorly adherent. The chronopotentiometric constant is somewhat high for the $10^{-3} M$ solution, but this effect was noted also for chronopotentiometry in unstirred solution¹. This increase in transition time at low concentrations is caused by a drop in current efficiency due to capacity current and by direct oxidation to silver ions because of the limits of insolubility of AgCl. Calibration of the system is necessary for accurate analyses at this concentration and below.

The effect of electrode length is shown in Fig. 9. The "safe" operating range of the 4 cm electrode is seen to be considerably larger than that of the smaller electrode. The dashed curves in Fig. 9 are lines calculated from eqns. (3) and (5). The constant of eqn. (5) was adjusted to fit the curve of the 2 cm electrode at $\tau/\tau_0 = 1.15$. However the constant so obtained, 1.60, was not far different from the value, 1.492, derived theoretically⁵. Agreement among the shapes of the curves is quite good and the approximate agreement of the magnitude of values of τ/τ_0 seems satisfactory considering the approximations involved in the derivation of eqn. (3) and the difficulties of measurement. For the 0.4 cm electrode, the values of the flow rate are such that the function, ξ , is in a steeply rising and thus highly sensitive portion of the curve. For the 4 cm electrode, transition times are increased only slightly and the percentage error in the determination of the transition time is therefore large. We feel on the basis of our

Fig. 9. Effect of electrode length on relative transition time; $5 \times 10^{-3} M$ NaCl, $0.25 M$ KNO₃, $\tau_0 \cong 4$ s; (—) exptl., (-----) calcd. (cf. text), l : (A) 0.4, (B) 2.0, (C) 4.0 cm.

Fig. 10. Flow rate vs. zero-velocity transition time (τ_0) for various values of relative transition time, calcd. for cell of Fig. 3. τ/τ_0 : (A) 1.05, (B) 1.10, (C) 1.15, (D) 1.20. Exptl. points: (O) $\tau/\tau_0 = 1.05$, (x) $\tau/\tau_0 = 1.15$.

observations that eqns. (3), (4), and (5) are accurate enough to be of considerable use in the design and use of chronopotentiometric flow cells.

Finally in Fig. 10 we show plots of τ_0 as a function of flow rate for various values of τ/τ_0 , which were calculated from the dimensions of the single-electrode cell. These "contours" are of use in selecting safe operating limits for the cell. Some actual experimental points for various conditions are also shown in Fig. 10.

Chronopotentiometric measurements were also carried out on the reduction of potassium ferricyanide on platinum. There were no significant differences between these results and the results of the measurements on the Ag-AgCl electrode.

IV. APPLICATION TO ANALYSIS

The results of these experiments are directly applicable to the analysis of solutions containing chloride ion. A complete system will include, besides the cell, a flowmeter, reservoirs for blank and standard solutions, and a combination potentiostat-galvanostat. If the unknown solution does not contain sufficient inert electrolyte, a controlled leak into the line ahead of the cell is required from a reservoir containing a highly concentrated electrolyte (*e.g.* 1:1 H_2SO_4).

Analysis by chronopotentiometry in a flowing stream is similar to normal chronopotentiometry except that the observed transition time is a function of both initial transition time and flow rate. Because all comparisons between unknown and standard should be made at approximately the same transition time, the current may have to be adjusted once or twice before a final determination. The correct current can be calculated in advance if the approximate concentration is known. Care must also be taken not to enter regions of excessive increase in transition time, so that for each cell a graph such as shown in Fig. 10 should be prepared. (In determining the safe region, the actual rather than the zero-rate transition time may be used, since $\tau > \tau_0$ under all conditions.)

One notes from Tables 1 and 2 that the chronopotentiometric constant is reproducible enough at given flow rates so that analyses accurate to a few percent may be made without recalibration. The excellent reproducibility of the duplicate runs shows that very precise analyses can be carried out when the cell is calibrated immediately before the determination. As mentioned above, electrode life is long and the surface is renewed by cathodic reduction of the surface, a procedure which helps prevent accumulation of contaminants on the surface. Finally, we note that approximate concentrations may be calculated from the equilibrium potential of the Ag-AgCl electrode when a saturated calomel or other reference electrode is bridged into the cell. However, we have not found these potentials to be reproducible enough for analyses which are as accurate as those based on the kinetic methods described above.

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SUMMARY

Cells are described which may be used for voltammetry and chronopotentiometry of the Ag-AgCl electrode in flowing streams. In the voltammetric mode of operation, limiting currents are observed for the transport of chloride ion to the surface when silver chloride is formed anodically. This current is a function of the flow rate and is directly proportional to chloride ion concentration. In the chrono-

potentiometric mode of operation, the effect of the flow is to increase the transition time in a reproducible and predictable manner. These two modes of operation may therefore be used for the analysis of solutions containing chloride ions.

REFERENCES

- 1 R. E. MEYER, F. A. POSEY AND P. M. LANTZ, *J. Electroanal. Chem.*, 19 (1968) 99.
- 2 W. J. BLAEDEL, C. L. OLSEN AND L. R. SHARMA, *Anal. Chem.*, 35 (1963) 2100; W. J. BLAEDEL AND L. N. KLATT, *Anal. Chem.*, 38 (1966) 879; L. N. KLATT AND W. J. BLAEDEL, *Anal. Chem.*, 39 (1967) 1065.
- 3 H. MATSUDA, *J. Electroanal. Chem.*, 15 (1967) 109; 15 (1967) 325; 16 (1968) 153; 21 (1969) 433; 22 (1969) 413.
- 4 V. G. LEVICH, *Physicochemical Hydrodynamics*, Prentice-Hall, Englewood Cliffs, N. J., 1962.
- 5 F. A. POSEY AND R. E. MEYER, *J. Electroanal. Chem.*, 30 (1971) 359.
- 6 J. H. WANG, *J. Amer. Chem. Soc.*, 74 (1952) 1612.
- 7 M. VON STACKELBURG, M. PURITAN AND V. TOOME, *Z. Elektrochem.*, 57 (1953) 57.
- 8 S. G. WHITEWAY, D. F. MACLENNAN AND C. C. COFFIN, *J. Chem. Phys.*, 18 (1950) 229.

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3. CHRONOPOTENTIOMETRY AND VOLTAMMETRY OF THE Ag-AgCl ELECTRODE IN FLOWING STREAMS. II. THEORETICAL

F. A. Posey and R. E. Meyer

I. INTRODUCTION

Use of the Ag-AgCl electrode system for chronopotentiometric analysis of the chloride content of unstirred solutions was investigated earlier¹. We have subsequently carried out a number of measurements on electrodes located in the walls of channels through which the electrolyte to be analyzed could flow at various velocities, and the experimental results are presented in Part I². It was found that at very low flow rates in fully-developed laminar flow transition times are nearly equal to those observed in unstirred solution. Increase of solution flow rate ultimately causes a significant increase in transition time. At sufficiently high flow rates transition times cannot be observed because for the current densities employed it may not be possible to reduce the reactant concentration to zero anywhere on the electrode surface. One may therefore consider two alternative modes of operation of electrodes in channels through which a constant total current is passed: (a) operation in a transient mode wherein a transition time can be observed (chronopotentiometry); (b) operation in the steady state (voltammetry).

For analytical purposes it is not only desirable but nearly essential to develop theoretical guidelines which relate observables to system parameters such as channel and electrode dimensions and solution flow rate. A number of authors have investigated theoretical and experimental aspects of voltammetry in rectangular channels and cylindrical tubes³⁻²². Other electrode configurations in flowing streams, such as stagnation-point electrodes, cones, and wedges, have also been studied²³⁻²⁸. Much related work has been carried out on voltammetry with the rotating disk^{3,29-31}, ring-disk³², and double channel electrode configurations³³⁻³⁵. Relatively little study seems to have been given to transient processes and the kinetics of attainment of the steady state in channels and tubes³⁶. We present below some exact and approximate solutions of the equation of convective diffusion for chronopotentiometry and voltammetry of the Ag-AgCl electrode and similar electrodes in a channel for fully-developed laminar flow.

II. MODEL AND THEORETICAL DESCRIPTION

The electrode process to be considered is the formation of an insoluble phase on an electrode surface in a channel by passage of current through the interface. In the case of the Ag-AgCl electrode, passage of anodic current leads to formation of

Fig. 1. Typical exptl. configuration for electroanalysis in flowing soln.

a layer of AgCl, where the concentration of the reactant ion, Cl^- , is determined by diffusion and convection processes in the electrolyte phase and by reaction at the surface of the electrode. A large excess of inert electrolyte is assumed to be present so that migration effects may be neglected to a fair approximation³⁷. A rectangular electrode of length l (cm) and width w (cm) is located flush with one of the surfaces of a rectangular channel ($y=0$), as shown schematically in Fig. 1. The channel width (d) is considered to be much larger than the channel height (h) or the electrode width (w) to avoid undesirable edge effects and to ensure favorable hydrodynamic conditions. The mid-stream solution velocity is denoted by U_0 (cm s^{-1}). The polarizing electrode, not shown in Fig. 1, could be located above the test electrode in the opposing channel wall (at $y=h$). The length L is considered to be sufficiently large so that a Poiseuille velocity profile is established with respect to the y direction at the position of the test electrode.

For fully developed laminar flow the velocity distribution is given by the well-known formula:

$$U_x(y) = U_0 \frac{4y}{h} \left(1 - \frac{y}{h} \right) \quad (1)$$

where $U_x(y)$ is the x -component of the solution velocity (cm s^{-1}). In channels where the width (d , cf. Fig. 1) is much larger than the height (h), the mid-stream solution velocity (U_0) may be related to the mean solution velocity (U_m , cm s^{-1}) or to the volume flow rate (U_v , $\text{cm}^3 \text{s}^{-1}$) by the expression $U_0 \cong \frac{3}{2} U_m = \frac{3}{2} U_v / hd$. Since the thickness of the diffusion layer is small compared to h in most configurations of interest, one may justifiably neglect the quadratic term in y in eqn. (1). The equation of convective diffusion^{3,38,39}, expressing the rate of change of chloride ion concentration in the electrolyte due to diffusion and convection, is then given in this case by

$$\frac{\partial c(x, y, t)}{\partial t} = D \frac{\partial^2 c(x, y, t)}{\partial y^2} - \frac{4U_0}{h} y \frac{\partial c(x, y, t)}{\partial x} \quad (2)$$

where $c(x, y, t)$ is chloride ion concentration (mol cm^{-3}) and D is the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$). Equation (2) is to be solved with use of initial and boundary conditions appropriate to the two cases considered below.

III. OPERATION IN THE STEADY STATE (VOLTAMMETRY)

For steady-state operation eqn. (2) reduces to

$$\frac{\partial^2 c(x, y)}{\partial y^2} - \frac{4U_0}{Dh} y \frac{\partial c(x, y)}{\partial x} = 0 \quad (3)$$

in which the time variable has been dropped. Since the thickness of the diffusion layer is small, it is customary in problems of this type^{3,8,11,37} to employ the boundary conditions:

$$c(0, y) = \lim_{y \rightarrow \infty} c(x, y) = c_0 \quad (4)$$

where c_0 is the chloride ion concentration (mol cm^{-3}) in the bulk of the electrolyte outside the diffusion layer. In the case of the Ag-AgCl electrode and similar electrode systems, the boundary condition at $y=0$ may be expressed by

$$j(x) = j_a \frac{c(x, 0)}{c_0} - j_c = zFD \left. \frac{\partial c(x, y)}{\partial y} \right|_{y=0} \quad (5)$$

where $j(x)$ is the current density at a point on the electrode surface (A cm^{-2}), j_a and j_c are defined by

$$\left. \begin{aligned} j_a &= j_0 \exp[\beta nF\eta/RT] \\ j_c &= j_0 \exp - [(1-\beta)nF\eta/RT] \end{aligned} \right\} \quad (6)$$

and z is the absolute value of the charge on the reactant ion ($z=1$ for the Cl^- ion). In eqns. (6), j_0 is the exchange current density of the reaction (A cm^{-2}), β is the transfer coefficient of the anodic process, n is the number of electrons involved in the charge transfer step of the reaction ($n=1$ for Ag-AgCl), η is the overpotential (V), and RT/F is the thermal volt equivalent (V). Equation (5) thus expresses the equivalence of the current density of the electrode process to the flux of the reactant ion at the interface.

A solution of eqn. (3) has been reported by Matsuda¹¹ and by Klatt and Blaedel¹² for the case of an oxidation-reduction couple where both oxidized and reduced species are soluble in the electrolyte. We give below a similar solution which pertains specifically to the present problem of formation of a solid phase on the electrode surface. Application of the Laplace transform method to eqns. (3)–(5) leads to

$$\bar{c}(p, 0) = \frac{c_0}{p} - c_0 \frac{j_a - j_c}{j_a} \frac{Q^\dagger}{p(p^\dagger + Q^\dagger)} \quad (7)$$

for the transform of the reactant concentration at $y=0$, where p is the Laplace parameter corresponding to the x coordinate and Q is defined by

$$Q^\dagger = \frac{j_a}{zFDc_0} \cdot \frac{\Gamma(\frac{1}{3})}{\Gamma(\frac{2}{3})} \left(\frac{Dh}{12 U_0} \right)^\dagger \quad (8)$$

Inversion of eqn. (7) may be accomplished in terms of an incomplete gamma function⁴⁰, $\gamma^*(a, z)$, defined by

$$\gamma^*(a, z) = (z^{-a}/\Gamma(a)) \int_0^z \exp(-t) t^{a-1} dt \quad (9)$$

The resulting concentration distribution is given by

$$c(x, 0)/c_0 = 1 - [(j_a - j_c)/j_a] [1 - \exp(-Qx) \{1 + (Qx)^{\frac{2}{3}} \gamma^*(\frac{2}{3}, -Qx) - (Qx)^{\frac{1}{3}} \gamma^*(\frac{1}{3}, -Qx)\}] \quad (10)$$

Numerical evaluation of the concentration distribution could be accomplished by use of the following series⁴⁰:

$$\gamma^*(a, -z) = \frac{1}{\Gamma(a)} \sum_{n=0}^{\infty} \frac{z^n}{(a+n)n!} \quad (11)$$

In series form, eqn. (10), with some rearrangement, becomes

$$\left[j_a \frac{c(x, 0)}{c_0} - j_c \right] / (j_a - j_c) = \exp(-Qx) + (Qx)^{\frac{2}{3}} \sum_{n=0}^{\infty} \frac{(-1)^n (Qx)^n}{\Gamma(\frac{5}{3} + n)} - (Qx)^{\frac{1}{3}} \sum_{n=0}^{\infty} \frac{(-1)^n (Qx)^n}{\Gamma(\frac{4}{3} + n)} \quad (12)$$

For values of Qx very much greater than unity, convergence of the series in eqn. (12) is very slow (cf. Matsuda¹¹). One may therefore use the asymptotic expansion

$$\left[j_a \frac{c(x, 0)}{c_0} - j_c \right] / (j_a - j_c) = \exp(-Qx) + \frac{1}{\Gamma(\frac{2}{3})(Qx)^{\frac{2}{3}}} \sum_{n=0}^{\infty} \frac{(\frac{1}{3})_n}{(Qx)^n} - \frac{1}{\Gamma(\frac{1}{3})(Qx)^{\frac{1}{3}}} \sum_{n=0}^{\infty} \frac{(\frac{2}{3})_n}{(Qx)^n} \quad (13)$$

which converges fairly rapidly for values of Qx greater than unity. In eqn. (13), $(a)_n = \Gamma(a+n)/\Gamma(a)$ is Pochhammer's symbol⁴⁰. The behavior of the function in eqn. (12) is shown in Fig. 2 as a function of the parameter $(Qx)^{\frac{2}{3}}$. For large values of Qx (large j_a , small U_0 , etc.), the right-hand side of eqn. (13) becomes approximately equal to $1/\Gamma(\frac{2}{3})(Qx)^{\frac{2}{3}} = 0.7385/(Qx)^{\frac{2}{3}}$, as shown in Fig. 2. On the other hand, for very small values of Qx (small j_a , large U_0 , etc.), the right-hand side of eqn. (12) is given approximately by $1 - (Qx)^{\frac{1}{3}}/\Gamma(\frac{4}{3}) = 1 - 1.1199(Qx)^{\frac{1}{3}}$; this approximation is also shown in Fig. 2.

Substitution of eqn. (10) into eqn. (5) leads immediately to

$$j(x)/(j_a - j_c) = \exp(-Qx) \{1 + (Qx)^{\frac{2}{3}} \gamma^*(\frac{2}{3}, -Qx) - (Qx)^{\frac{1}{3}} \gamma^*(\frac{1}{3}, -Qx)\} \quad (14)$$

for the distribution of the net current density along the electrode surface. This is the same function shown plotted in Fig. 2 with the special cases for small and large values

Fig. 2. Concn. and current density distributions at electrode surface for voltammetry in channel.

of Qx .

The total applied current, I (A), may be obtained by integration of the net current density, $j(x)$, over the length of the electrode (l), using the relation

$$I = w \int_0^l j(x) dx \quad (15)$$

where w is the width of the electrode as in Fig. 1. The result of the integration is given by

$$\frac{I}{I_\infty} \equiv G(\zeta) = [1 - \exp(-\zeta)] / \zeta + \exp(-\zeta) \zeta^{\frac{1}{3}} \gamma^*(\frac{5}{3}, -\zeta) - \exp(-\zeta) \zeta^{\frac{1}{3}} \gamma^*(\frac{4}{3}, -\zeta) \quad (16)$$

where $I_\infty = A(j_a - j_c)$ is the total current for no concentration polarization ($U_0 \rightarrow \infty$) ($A = wl$ is electrode area, cm^2), and $\zeta^{\frac{1}{3}} = (Ql)^{\frac{1}{3}}$ is given explicitly by

$$\zeta^{\frac{1}{3}} = \frac{j_a}{zFDc_0} \frac{\Gamma(\frac{1}{3})}{\Gamma(\frac{2}{3})} \left(\frac{Dhl}{12 U_0} \right)^{\frac{1}{3}} \quad (17)$$

In series form eqn. (16) becomes

$$\frac{I}{I_\infty} = [1 - \exp(-\zeta)] / \zeta + \zeta^{\frac{1}{3}} \sum_{n=0}^{\infty} \frac{(-1)^n \zeta^n}{\Gamma(\frac{8}{3} + n)} - \zeta^{\frac{1}{3}} \sum_{n=0}^{\infty} \frac{(-1)^n \zeta^n}{\Gamma(\frac{7}{3} + n)} \quad (18)$$

which converges satisfactorily for values of ζ less than about unity. For $\zeta > 1$, the asymptotic expansion:

$$\frac{I}{I_\infty} \cong [1 - \exp(-\zeta)] / \zeta + \frac{1}{\Gamma(\frac{5}{3}) \zeta^{\frac{1}{3}}} \sum_{n=0}^{\infty} \frac{(-\frac{2}{3})_n}{\zeta^n} - \frac{1}{\Gamma(\frac{4}{3}) \zeta^{\frac{1}{3}}} \sum_{n=0}^{\infty} \frac{(-\frac{1}{3})_n}{\zeta^n} \quad (19)$$

is more convenient. Some numerical values of the function $G(\zeta)$ are given in Table 1. The behavior of the function $G(\zeta)$ is shown plotted in Fig. 3. Concentration polarization begins to become significant when $\zeta^{\frac{1}{3}}$ is greater than about 10^{-1} .

TABLE I
VALUES OF THE FUNCTION $G(\zeta)$

ζ	$\zeta^{\frac{1}{3}}$	$G(\zeta)$
10^{-6}	1.000×10^{-2}	0.99167
10^{-5}	2.154×10^{-2}	0.98583
10^{-4}	4.643×10^{-2}	0.96239
10^{-3}	1.000×10^{-1}	0.92220
10^{-2}	2.154×10^{-1}	0.84560
10^{-1}	4.643×10^{-1}	0.71589
10^0	1.000×10^0	0.53614
10^1	2.154×10^0	0.34599
10^2	4.643×10^0	0.19525
10^3	1.000×10^1	0.10050
10^4	2.154×10^1	0.04911
10^5	4.643×10^1	0.02335
10^6	1.000×10^2	0.01097

Fig. 3. Total current as a function of the ζ parameter for voltammetry in channel.

For very small values of ζ (small j_a , large U_0 , small l , etc.), $I/I_\infty \cong 1 - \zeta^{\frac{1}{3}}/\Gamma(\frac{7}{3}) = 1 - 0.8399 \zeta^{\frac{1}{3}}$, as shown in Fig. 3. Conversely, for large ζ (small U_0 , etc.), the limiting behavior of the function is given by $I/I_\infty \cong 1/\Gamma(\frac{5}{3})\zeta^{\frac{1}{3}} = 1.1077/\zeta^{\frac{1}{3}}$; this is also shown in Fig. 3. In this region the total current is thus given explicitly by

$$I \cong zFADc_0[1 - \exp(-nF\eta/RT)] \frac{3}{2\Gamma(\frac{4}{3})} \left(\frac{12 U_0}{Dhl} \right)^{\frac{1}{3}} \quad (20)$$

One sees from eqn. (20) that, for large anodic polarization, a limiting current (I_L) is obtained which is given by

$$I_L = \frac{3(12)^{\frac{1}{3}}}{2\Gamma(\frac{4}{3})} zFAc_0 D^{\frac{1}{3}} \left(\frac{U_0}{hl} \right)^{\frac{1}{3}} \quad (21)$$

This relation is identical to Levich's equation^{3,5,11} for the limiting current. On the

Fig. 4. Polarization curves as a function of the ζ_0 parameter for voltammetry in channel.

other hand, no limiting current exists for large cathodic polarization in the case of the Ag-AgCl electrode and similar systems.

A set of polarization curves, calculated on the basis of eqn. (16) for the special case where $\beta = \frac{1}{2}$, is shown in Fig. 4 as a function of the convenient parameter, ζ_0 . In Fig. 4, $I_0 = Aj_0$ is the exchange current of the electrode (A) and ζ_0 is defined by

$$\zeta_0^\dagger = \frac{j_0}{zFDc_0} \frac{\Gamma(\frac{1}{3})}{\Gamma(\frac{2}{3})} \left(\frac{Dhl}{12 U_0} \right)^\dagger \quad (22)$$

It follows from eqns. (6), (17), and (22) that

$$\zeta^\dagger = \zeta_0^\dagger \exp(\beta nF\eta/RT)$$

One sees from Fig. 4 that increasing values of ζ_0 cause a shift of the limiting current to smaller values. Simultaneously an increase in the polarization resistance of the electrode is to be expected as concentration polarization becomes more important. Differentiation of eqn. (16) with respect to η and evaluation at $\eta=0$ leads to the following equation for the polarization resistance:

$$\left. \frac{d\eta}{dI} \right|_{\eta=0} = \frac{RT}{nFI_0} \cdot \frac{1}{G(\zeta_0)} \quad (23)$$

The function $G(\zeta_0)$ is defined by eqn. (16) and its behavior as a function of ζ_0 is shown in Fig. 3, as noted above. For small values of ζ_0 , $G(\zeta_0) \cong 1$, and the polarization resistance is approximately RT/nFI_0 , as in the case of no concentration polarization. But for large values of ζ_0 , $G(\zeta_0) \cong 1/\Gamma(\frac{2}{3})\zeta_0^\dagger$, and the polarization resistance is given approximately by

$$\left. \frac{d\eta}{dI} \right|_{\eta=0} \cong \frac{RT}{nF} \cdot \frac{2\Gamma(\frac{1}{3})}{3zFADc_0} \left(\frac{Dhl}{12 U_0} \right)^\dagger \quad (24)$$

A decrease in solution flow rate therefore decreases the limiting current (*cf.* eqn. (21)) and increases the polarization resistance (*cf.* eqn. (24)).

In the region of positive polarization, one may plot the function $\ln(I/I_L - I)$ against η , according to standard polarographic practice, and obtain a straight line (*cf.* Matsuda¹¹). The equation of the straight line is given explicitly for the case of small ζ by

$$\ln \frac{I}{I_L - I} = \ln \left\{ \frac{2\Gamma(\frac{1}{3})}{3} \cdot \frac{j_0}{zFDc_0} \left(\frac{Dhl}{12U_0} \right)^{\frac{1}{3}} \right\} + \frac{\beta nF}{RT} \eta \quad (25)$$

If all other quantities are known, this relation could be used to estimate j_0 and β from the values of the slope and intercept of such a plot. Furthermore, when $I = I_L/2$, $E_{\frac{1}{2}} = E_0 + \eta_{\frac{1}{2}}$ is the half-wave potential, where E_0 is the reversible potential (V), and substitution of these quantities into eqn. (25) leads to

$$E_{\frac{1}{2}} = E_0 + \frac{RT}{\beta nF} \ln \left[\frac{3(12)^{\frac{1}{3}}}{2\Gamma(\frac{1}{3})} \cdot \frac{zFc_0}{j_0} D^{\frac{1}{3}} \left(\frac{U_0}{hl} \right)^{\frac{1}{3}} \right] \quad (26)$$

for the (irreversible) half-wave potential when ζ is small. At constant solution flow rate, measurement of the anodic limiting current (*cf.* eqn. (21)) is probably the most useful voltammetric method for monitoring reactant ion concentration

IV. TRANSIENT OPERATION (CHRONOPOTENTIOMETRY)

Exact solution of the equation of convective diffusion (*cf.* eqn. (2)) for chronopotentiometry in flowing streams presents a number of difficulties. We have therefore applied an approximate method to the problem, and have arrived at a formulation which describes reasonably well the experimental results for the Ag-AgCl electrode, as reported in Pat I² Oldham⁴¹ has developed an approximate method for the solution of boundary value problems involving electrolyses controlled by diffusion and electrode kinetics. The method used below for chronopotentiometry in a channel is very similar to Oldham's method.

With reference to eqn. (2), consideration is restricted to small values of x and consequently to small electrode length (l), so that the x -derivative in eqn. (2) may be approximated by a difference:

$$\left. \frac{\partial c(x, y, t)}{\partial x} \right|_{y=0} \cong \frac{c(x, 0, t) - c_0}{x} \quad (27)$$

Additionally, it will be assumed that the interfacial reaction is completely irreversible, and that the boundary condition at $y=0$ is given by

$$\left. \frac{\partial c(x, y, t)}{\partial y} \right|_{y=0} \cong \frac{j}{zFD} \quad (28)$$

where j ($A\ cm^{-2}$) is the current density due to reaction at the surface. The current density is thus assumed to be independent of both distance on the electrode surface (x) and time (t). This is clearly not true for times very close to or exceeding the chronopotentiometric transition time (τ), but it should be a sufficiently good approximation for the purpose of deriving the functional dependence of the transition time on system

parameters when U_0 is not too large. Further, it is assumed that the thickness of the developing diffusion layer is described by

$$\delta(x, t) = (\delta_0/c_0)[c_m - c(x, 0, t)] \quad (29)$$

where $\delta(x, t)$ is the thickness of the diffusion layer (cm) at the point x and time t , and δ_0 is the "ultimate" thickness of the diffusion layer (cm) when $c(x, 0, t) = 0$. The appropriate value of δ_0 will be assigned later by comparison to another approximate solution of eqn. (2). As in the case of similar computations using a Nernstian diffusion layer, one may set the y -derivative of the concentration equal to zero at $y = \delta(x, t)$, so that in the limit of small $\delta(x, t)$, as $y \rightarrow 0$, one obtains

$$\left. \frac{\partial^2 c(x, y, t)}{\partial y^2} \right|_{y=0} \cong \frac{1}{\delta(x, t)} \left[\left. \frac{\partial c(x, y, t)}{\partial y} \right|_{y=\delta(x, t)} - \left. \frac{\partial c(x, y, t)}{\partial y} \right|_{y=0} \right] = - \frac{j}{zFD\delta(x, t)} \quad (30)$$

Substitution of eqns. (27)–(30) into eqn. (2) then leads to

$$\frac{dc(x, 0, t)}{dt} \cong - \frac{jc_0}{\delta_0 zF} \frac{1}{[c_0 - c(x, 0, t)]} + \frac{4U_0\delta_0}{hxc_0} [c_0 - c(x, 0, t)]^2 \quad (31)$$

on the assumption that $y \cong \delta(x, t) \rightarrow 0$. Equation (31), an ordinary differential equation, is to be solved with use of the conditions, $c(x, 0, 0) = c(0, 0, t) = c_0$.

One notes that when $U_0 = 0$ the solution of eqn. (31) is given by

$$c(0, t) = c_0 [1 - (2jt/zF\delta_0 c_0)^{\frac{1}{2}}] \quad (32)$$

where the x -variable has been dropped. If $\delta_0 = \pi zFDc_0/2j$ is used as the thickness of the diffusion layer in this case, then on setting $c(0, \tau_0) = 0$ at $t = \tau_0$ (the transition time

for $I/I_0 \equiv 0$), one gets

$$\tau_0^{\frac{1}{2}} = zFc_0(\pi D)^{\frac{1}{2}}/2j \quad (33)$$

which is the exact solution (Sand equation) obtained by standard methods for the transition time in unstirred solution in the presence of excess inert electrolyte.

Equation (31) may be simplified to yield

$$(z^3 - 1)^{-1} z dz = -\alpha P^2 dt \quad (34)$$

by making use of the following substitutions:

$$z = P [1 - c(x, 0, t)/c_0] \quad (35)$$

$$P = (4U_0\delta_0^2 zFc_0/hxj)^{\frac{1}{2}} \quad (36)$$

$$\alpha = j/\delta_0 zFc_0 \quad (37)$$

Integration of eqn. (34) with use of the condition, $z = 0$ at $t = 0$, then leads to

$$\ln \frac{1-z}{(1+z+z^2)^{\frac{1}{2}}} + 3^{\frac{1}{2}} \cdot \tan^{-1} \left[\frac{3^{\frac{1}{2}} \cdot z}{2+z} \right] = -(3 \alpha P^2) t \quad (38)$$

for the desired relation between reactant concentration and time. Combination of eqns. (32) and (37) gives the transition time for $U_0=0$ as $\tau_0 = \frac{1}{2} \alpha$. We now assume that when $t = \tau$ (transition time for non-zero U_0) the reactant concentration at $x=l$ attains the value zero. When $c(l, 0, \tau) = 0$ eqn. (38) becomes

$$\frac{\tau}{\tau_0} = -\frac{2}{3\xi^2} \left\{ \ln \left[\frac{1-\xi}{(1+\xi+\xi^2)^{\frac{1}{2}}} \right] + 3^{\frac{1}{2}} \cdot \tan^{-1} \left[\frac{3^{\frac{1}{2}} \cdot \xi}{2+\xi} \right] \right\} \quad (39)$$

which gives the relative transition time as a function of the parameter ξ , defined as

$$\xi = (4 U_0 z F c_0 / h l j)^{\frac{1}{2}} \delta_0^{\frac{1}{2}} \quad (40)$$

Equation (39) thus gives the transition time as a function of solution flow rate and other parameters of the cell system. As noted above, the constant δ_0 is to be determined later by comparison to another approximate solution of eqn. (2).

The relative transition time, τ/τ_0 (cf. eqn. (39)), depends upon the value of the parameter ξ . In order for transition times to be attained, ξ must be less than unity; otherwise a steady state will be attained for which $c(x, 0, \infty) > 0$ for all x . The parameter ξ of eqn. (40) may also be expressed by the relation $\xi = (U_0/U_\infty)^{\frac{1}{2}}$, where U_∞ (cm s^{-1}) is the maximum value of the mid-stream solution velocity for which a transition time may be observed. The limiting behavior of eqn. (39) when ξ approaches unity is given by

$$\lim_{\xi \rightarrow 1} \frac{\tau}{\tau_0} = -\frac{2}{3} \ln \left[(1-\xi)/3^{\frac{1}{2}} - \frac{1}{2} \pi / 3^{\frac{1}{2}} \right] \quad (41)$$

On the other hand, when ξ is very small, series expansion of the functions in eqn. (39) leads to

Fig. 5. Variation of transition time with soln. flow rate.

$$\lim_{\xi \rightarrow 0} \frac{\tau}{\tau_0} = 1 + \frac{2}{5} \xi^3 \quad (42)$$

The curves in Fig. 5 show the behavior of the functions of eqns. (39), (41), and (42). For small values of U_0 the transition time increases directly with U_0 , as implied by eqn. (42) since $\xi^3 = U_0/U_\infty$. As U_0 approaches U_∞ , the transition time increases to large values. For $U_0 > U_\infty$, corresponding to $\xi > 1$, no transition time would be observed, as noted above. A logarithmic plot of the relative change in transition time, $(\tau/\tau_0 - 1)$, against solution flow rate is shown in Fig. 6. One notes that the approxima-

Fig. 6. Relative transition time as a function of soln. flow rate.

tion of eqn. (42) is valid up to $\xi^3 \cong 10^{-1}$, or $\xi \cong 0.464$. Some numerical values of the function τ/τ_0 in eqn. (39) and the function $(\tau/\tau_0 - 1)$ are given in Table 2.

An estimate of δ_0 (cf. eqn. (29)) may be obtained by an approximate solution of eqn. (2) for chronopotentiometry in a channel. As in the derivation of eqns. (38) and (39), consideration is restricted to small values of x so that the x -derivative in eqn. (2) may be approximated by the difference form:

$$\frac{\partial c(x, y, t)}{\partial x} \cong \frac{c(x, y, t) - c_0}{x} \quad (43)$$

Substitution of eqn. (43) into eqn. (2) leads to

$$\frac{\partial c(x, y, t)}{\partial t} = D \frac{\partial^2 c(x, y, t)}{\partial y^2} - \frac{4U_0}{hx} y [c(x, y, t) - c_0], \quad (44)$$

an approximation of the equation of convective diffusion. At $x=0$ and $t=0$, con-

TABLE 2
VALUES OF THE FUNCTIONS τ/τ_0 AND $(\tau/\tau_0 - 1)$

ξ	$\xi^3 = U_0/U_\infty$	τ/τ_0	$(\tau/\tau_0 - 1)$
0.1	0.001	1.00040	4.0019×10^{-4}
0.2	0.008	1.00322	3.2160×10^{-3}
0.3	0.027	1.01098	1.0986×10^{-2}
0.4	0.064	1.02667	2.6674×10^{-2}
0.5	0.125	1.05430	5.4300×10^{-2}
0.6	0.216	1.10028	1.0028×10^{-1}
0.7	0.343	1.17672	1.7672×10^{-1}
0.8	0.512	1.31198	3.1198×10^{-1}
0.9	0.729	1.60228	6.0228×10^{-1}
0.95	0.857	1.94908	9.4908×10^{-1}
0.99	0.970	2.88922	1.8892×10^0
0.999	0.997	4.37552	3.3755×10^0

ditions for the solution of eqn. (44) are given by $c(0, y, t) = c(x, y, 0) = c_0$. At $y=0$ the boundary condition is given by

$$j(x, t) = j_a \left[\frac{c(x, 0, t)}{c_0} \right] - j_c = zFD \frac{\partial c(x, y, t)}{\partial y} \Big|_{y=0} \quad (45)$$

which is comparable to eqn. (5). Application of the Laplace transform method leads to

$$c(x, 0, s) = (c_0/s) - [(j_a - j_c)/zFD^{\frac{1}{2}}] \times \frac{K_{\frac{1}{2}}(hxs^{\frac{1}{2}}/6U_0D^{\frac{1}{2}})}{s^{\frac{1}{2}}[s^{\frac{1}{2}}K_{\frac{1}{2}}(hxs^{\frac{1}{2}}/6U_0D^{\frac{1}{2}}) + (j_aK_{\frac{1}{2}}/zFc_0D^{\frac{1}{2}})(hxs^{\frac{1}{2}}/6U_0D^{\frac{1}{2}})]} \quad (46)$$

for the transform of the reactant concentration at $y=0$, where s is the Laplace parameter corresponding to the t variable and $K_{\frac{1}{2}}(z)$ and $K_{\frac{3}{2}}(z)$ are modified Bessel functions of the second kind of fractional order. We now assume that U_0 is small enough so that the argument of the Bessel functions is large. Since primary interest is attached to the behavior at times far from a steady state, we assume further that the Laplace parameter (s) is large and that $(j_a - j_c) \cong j$, as for a completely irreversible reaction. Asymptotic expansion of the Bessel functions then leads, after some rearrangement, to the approximate transform:

$$\bar{c}(x, 0, s) \cong \frac{c_0}{s} - \frac{j}{zFD^{\frac{1}{2}}} \cdot \frac{1}{s^{\frac{1}{2}}} \left[1 - \frac{U_0D^{\frac{1}{2}}}{hx} \frac{1}{s^{\frac{1}{2}}} \right] \quad (47)$$

One notes that when $U_0=0$, inversion of eqn. (47) leads eventually to eqn. (33) for the transition time in unstirred solution.

Inversion of eqn. (47) gives

$$c(x, 0, t) = c_0 \left[1 - \left(\frac{2j}{zFc_0(\pi D)^{\frac{1}{2}}} \right) t^{\frac{1}{2}} + \left(\frac{U_0 j}{2zFhxc_0} \right) t^2 \right] \quad (48)$$

for the concentration distribution as a function of time. This relation is not valid for values of x very near to zero because of the approximations made above in the derivation of eqn. (47). As in the derivation of eqn. (39), it is assumed that $c(l, 0, \tau) = 0$ when $t = \tau$. This assumption, together with eqn. (33) for τ_0 , then leads to

$$\left(\frac{\tau}{\tau_0} \right)^{\frac{1}{2}} - \left[\frac{\pi^2}{32} \left(\frac{U_0}{hl} \right) D^2 \left(\frac{zFc_0}{j} \right)^3 \right] \left(\frac{\tau}{\tau_0} \right)^2 = 1 \quad (49)$$

for the relative transition time as a function of the parameters of the system. Since U_0 has been assumed to be very small, further expansion of eqn. (49) leads finally to the limiting form:

$$\frac{\tau}{\tau_0} \cong 1 + \frac{\pi^2}{16} \left(\frac{U_0}{hl} \right) D^2 \left(\frac{zFc_0}{j} \right)^3 \quad (50)$$

Comparison of eqn. (50) with eqn. (42), which is of the same form, then allows δ_0 to be calculated:

$$\delta_0 = \frac{\pi\sqrt{5}}{8\sqrt{2}} \frac{zFDc_0}{j} = 0.6209 \frac{zFDc_0}{j} \quad (51)$$

Use of this value of δ_0 should result in reasonably good agreement between the predictions of eqn. (39) of the approximate method and experimental measurements of relative transition times when U_0 and l are not too large (cf. Part I²). With the value of δ_0 given by eqn. (51), the parameter ξ defined in eqn. (40) is given explicitly by

$$\xi = \frac{5^{\frac{1}{2}} \pi^{\frac{1}{2}}}{2^{\frac{1}{2}}} \left(\frac{zFc_0}{j} \right) D^{\frac{1}{2}} \left(\frac{U_0}{hl} \right)^{\frac{1}{2}} = 1.1553 \left(\frac{zFc_0}{j} \right) D^{\frac{1}{2}} \left(\frac{U_0}{hl} \right)^{\frac{1}{2}} \quad (52)$$

In addition, since $\xi = (U_0/U_\infty)^{\frac{1}{2}}$, the maximum value of the mid-stream solution velocity for which transition times may be observed is given by

$$U_\infty^{\frac{1}{2}} = \frac{2^{\frac{1}{2}}}{5^{\frac{1}{2}} \pi^{\frac{1}{2}}} \left(\frac{j}{zFc_0} \right) \frac{(hl)^{\frac{1}{2}}}{D^{\frac{1}{2}}} = 0.8656 \left(\frac{j}{zFc_0} \right) \frac{(hl)^{\frac{1}{2}}}{D^{\frac{1}{2}}} \quad (53)$$

It is of interest to compare the steady-state distribution of reactant concentration, as given by the approximate method in eqn. (38), with the appropriate special case of eqn. (10). For small values of Qx , expansion of eqn. (10) leads to the following approximate relation:

$$\begin{aligned} \frac{c(x, 0)}{c_0} &\cong 1 - \frac{3^{\frac{1}{2}}}{4^{\frac{1}{2}} \Gamma(\frac{2}{3})} \cdot \frac{j}{zFc_0} \cdot \frac{1}{D^{\frac{1}{2}}} \left(\frac{hx}{U_0} \right)^{\frac{1}{2}} \\ &= 1 - 0.9677 \frac{j}{zFc_0} \cdot \frac{1}{D^{\frac{1}{2}}} \left(\frac{hx}{U_0} \right)^{\frac{1}{2}} \end{aligned} \quad (54)$$

On the other hand, eqn. (38) shows that the electrode has attained a steady state when $z = 1$, corresponding to $t = \infty$. Then from eqns. (35) and (36) the concentration distribution in the steady state is given by

$$\frac{c(x, 0, \infty)}{c_0} = 1 - \frac{1}{P} = 1 - \left(\frac{hxj}{4zFc_0U_0} \right)^{\frac{1}{2}} \frac{1}{\delta_0^{\frac{1}{2}}} \quad (55)$$

Substitution of δ_0 from eqn. (51) therefore leads to the following concentration distribution:

$$\begin{aligned} \frac{c(x, 0, \infty)}{c_0} &= 1 - \frac{4}{10^{\frac{1}{2}}\pi^{\frac{1}{2}}} \cdot \frac{j}{zFc_0} \cdot \frac{1}{D^{\frac{1}{2}}} \left(\frac{hx}{U_0} \right)^{\frac{1}{2}} \\ &= 1 - 0.8656 \frac{j}{zFc_0} \cdot \frac{1}{D^{\frac{1}{2}}} \left(\frac{hx}{U_0} \right)^{\frac{1}{2}} \end{aligned} \quad (56)$$

Comparison of eqns. (54) and (56) shows that these relations are identical except for the values of the numerical constants, which differ only by 10.5%. Such agreement suggests that in spite of the rather restrictive nature of the assumptions used in the derivation of eqns. (38) and (39), the approximate theory of chronopotentiometry in channels should prove to be useful in correlating results of measurements in practical situations when proper precautions are taken with respect to cell design and operating conditions.

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SUMMARY

Solutions to the equation of convective diffusion are presented for chronopotentiometry and voltammetry of an electrode located in a channel where the electrode process involves formation of a solid phase. The relations derived for voltammetry permit computation of reactant concentration from experimental polarization curves, polarization resistances, or limiting currents with a knowledge of solutions flow rate, applied current, electrode and channel dimensions, and other parameters. An approximate method is used to obtain the effect of flow rate and other pertinent variables on transition times for chronopotentiometry in flowing streams.

REFERENCES

- 1 R. E. MEYER, F. A. POSEY AND P. M. LANTZ, *J. Electroanal. Chem.*, 19 (1968) 99.
- 2 R. E. MEYER, M. C. BANTA, P. M. LANTZ AND F. A. POSEY, *J. Electroanal. Chem.*, 30 (1971) 345.
- 3 V. G. LEVICH, *Physicochemical Hydrodynamics*, Prentice-Hall, Englewood Cliffs, N.J., 1962.
- 4 G. WRANGLÉN AND O. NILSSON, *Electrochim. Acta*, 7 (1962) 121.
- 5 W. J. BLAEDÉL, C. L. OLSEN AND L. R. SHARMA, *Anal. Chem.*, 35 (1963) 2100.
- 6 YU. S. GURINOV AND S. V. GORBACHEV, *Zh. Fiz. Khim.*, 38 (1964) 2245.

- 7 S. V. GORBACHEV AND YU. S. GURINOV, *Zh. Fiz. Khim.*, 39 (1965) 1712.
- 8 W. J. BLAEDEL AND L. N. KLATT, *Anal. Chem.*, 38 (1966) 879.
- 9 K. JODKAZIS AND R. VISOMIRSKIS, *Mater. Respub. Konf. Elektrokhim. Litov. SSR*, 8th, 1966, p. 161.
- 10 S. V. GORBACHEV, T. D. PRISHLETSOVA AND N. P. BALUSOVA, *Zh. Fiz. Khim.*, 40 (1966) 2317.
- 11 H. MATSUDA, *J. Electroanal. Chem.*, 15 (1967) 325.
- 12 L. N. KLATT AND W. J. BLAEDEL, *Anal. Chem.*, 39 (1967) 1065.
- 13 S. V. GORBACHEV, *Zh. Fiz. Khim.*, 42 (1968) 147.
- 14 L. N. KLATT AND W. J. BLAEDEL, *Anal. Chem.*, 40 (1968) 512.
- 15 J. SUZUKI, *Rev. Polarog. (Kyoto)*, 19 (1968) 23.
- 16 K. JODKAZIS, V. JASINSKAITE AND R. VISOMIRSKIS, *Liet. TSR Mokslu Akad. Darbai, Ser. B*, 3 (1968) 3.
- 17 K. JODKAZIS AND R. VISOMIRSKIS, *Liet. TSR Mokslu Akad. Darbai, Ser. B*, 4 (1968) 37.
- 18 L. R. SHARMA AND J. DUTT, *Indian J. Chem.*, 6 (1968) 593.
- 19 L. R. SHARMA AND J. DUTT, *Indian J. Chem.*, 6 (1968) 597.
- 20 L. R. SHARMA AND J. DUTT, *Indian J. Chem.*, 7 (1969) 485.
- 21 W. R. PARRISH AND J. NEWMAN, *J. Electrochem. Soc.*, 116 (1969) 169.
- 22 W. R. PARRISH AND J. NEWMAN, *J. Electrochem. Soc.*, 117 (1970) 43.
- 23 H. MATSUDA, *J. Electroanal. Chem.*, 15 (1967) 109.
- 24 S. L. MARCHIANO AND A. J. ARVIA, *Electrochim. Acta*, 12 (1967) 801.
- 25 J. S. W. CARROZZA, S. L. MARCHIANO AND A. J. ARVIA, *Electrochim. Acta*, 12 (1967) 809.
- 26 J. C. BAZAN, S. L. MARCHIANO AND A. J. ARVIA, *Electrochim. Acta*, 12 (1967) 821.
- 27 H. MATSUDA, *J. Electroanal. Chem.*, 21 (1969) 433.
- 28 H. MATSUDA, *J. Electroanal. Chem.*, 22 (1969) 413.
- 29 A. C. RIDDIFORD in P. DELAHAY (Ed.), *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 4, Interscience, New York, 1966, p. 47.
- 30 J. NEWMAN, *J. Electrochem. Soc.*, 113 (1966) 1235.
- 31 J. NEWMAN, *J. Electrochem. Soc.*, 114 (1967) 239.
- 32 A. FRUMKIN, L. NEKRASSOV, V. G. LEVICH AND YU. IVANOV, *J. Electroanal. Chem.*, 1 (1959) 84.
- 33 H. GERISCHER, I. MATTES AND R. BRAUN, *J. Electroanal. Chem.*, 10 (1965) 553.
- 34 H. MATSUDA, *J. Electroanal. Chem.*, 16 (1968) 153.
- 35 R. BRAUN, *J. Electroanal. Chem.*, 19 (1968) 23.
- 36 E. YA. KLIMENKOV, B. M. GRAFOV, V. G. LEVICH AND I. N. STRIZHEVSKII, *Elektrokhimiya*, 5 (1969) 202.
- 37 J. NEWMAN, *Int. J. Heat Mass Transfer*, 10 (1967) 983.
- 38 J. NEWMAN, in C. W. TOBIAS (Ed.), *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 5, Interscience, New York, 1967, p. 87.
- 39 J. NEWMAN, *Ind. Eng. Chem., Fundam.*, 60 (1968) 12.
- 40 M. ABRAMOWITZ AND I. A. STEGUN (Eds.), *Handbook of Mathematical Functions*, National Bureau of Standards, Washington, D.C., 1964.
- 41 K. B. OLDHAM, *Electrochim. Acta*, 11 (1966) 1475.

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4. RAPID BATCH AND CONTINUOUS ELECTROANALYSIS FOR THE CHLORIDE ION*

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SUMMARY

Rapid electroanalytical methods for analysis of the chloride content of saline waters are discussed. Special cells and instrumentation are described which allow electroanalysis to be carried out conveniently and accurately with batch-type static cells and with flow cells for continuously monitoring the chloride content of process streams. The theory of operation and analytical procedures are described for chronopotentiometry in unstirred solutions and in a flowing stream, for voltammetry in a flowing stream, and for an improved form of potentiometry.

INTRODUCTION

The determination of chloride ion concentration is one of the desirable or necessary analytical procedures in the operation of certain types of desalination equipment. In desalination research, frequent analyses of samples for chloride ion content can become a burdensome portion of the overall research program. No really rapid methods seem to be available at present for chloride analyses in flowing streams with high precision ($< 2\%$ error). For this reason, we have investigated electrochemical methods for analysis of the chloride ion and, in particular, their application to flowing streams. We have also developed special instrumentation and cells with which these analyses may be performed conveniently and accurately. Our description of these methods is intended to be general in scope; specific details of the theory have already been published (1-3) and detailed plans and instructions are available from us.

Most methods of chloride analysis which are in use at the present time fall into either of two general types. Potentiometric methods use either the Ag/AgCl electrode or any of a number of types of specific ion electrodes. The response of these electrodes is logarithmic; *i.e.*, the observed signal (a voltage) is proportional

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to the logarithm of the activity (not the concentration) of the chloride ion. Calibration with solutions of known composition and similar ionic strength is necessary to compensate for any errors due to liquid junction potentials and to change of activity coefficients with composition. A precision of measurement of about 0.5 mV is necessary for 2% absolute accuracy. The main advantage of the method is the ease with which in-line analyses may be carried out. Disadvantages are the high precision required and the fact that drifting of either the reference or sensor electrodes could produce significant errors in the observed signal, thus leading to large errors in the estimation of chloride concentration.

If greater precision is desired, it is still possible to use potentiometric methods if sufficient care is used. However, it usually is better to use any of a number of titration methods based upon the precipitation of chloride ion as AgCl with silver ion which is generated electrolytically or obtained from standard AgNO_3 solutions. These methods, although rapid and accurate, require skilled analysts for manipulation of the required volumetric apparatus. In addition, these methods are not readily adaptable to in-line flow analyses.

The methods of analysis described below actually represent a system of analyses, all using the same basic instrument and cell. Also, with the use of a separate cell, the same instrument may be used for precise (0.5%) batch analyses. The various methods to be described include (I) chronopotentiometry in unstirred solution, (II) chronopotentiometry in a flowing stream, (III) voltammetry in a flowing stream, and (IV) an improved form of potentiometry. Such methods appear to be especially suited for use with modern digital methods of data acquisition, analysis, and display, and could prove to be useful in automation of desalination processes.

I. CHRONOPOTENTIOMETRY IN UNSTIRRED SOLUTION

Theory

Studies on the feasibility and theory of using the Ag/AgCl electrode in chronopotentiometric analysis of the chloride ion in unstirred solution have been reported by us (1) and by Peters and Kinjo (4). Detailed general reviews of the theory of chronopotentiometry and its application to analysis are available (5, 6). Here we summarize the theory and describe new apparatus and procedures for carrying out chloride analyses.

If a constant anodic (oxidizing) current is applied to a silver electrode in the presence of dissolved chloride ions, a film of AgCl will be formed on the surface. In this process, the silver ions formed at the interface from oxidation of the silver combine with chloride ions diffusing from the bulk of the solution to form a film of AgCl. If certain conditions are met, the chloride ion concentration at the surface of the electrode will be reduced to a very small value (essentially zero) in a time interval that is precisely reproducible for a given current and bulk concentration

of chloride ions. These conditions are: (1) the current density is large enough to deplete chloride ions at the electrode surface; (2) the current density is uniformly constant over the surface; (3) the solution is stagnant and initially uniform in concentration (this condition implies that there must be no other means of transport to the surface besides diffusion); (4) the conductivity of the solution must be high enough (sufficient inert electrolyte present) to suppress migration of chloride ions in the electric field in the electrolyte.*

The time interval required to deplete chloride ions in the solution layer immediately adjacent to the electrode surface by anodic formation of AgCl is called the transition time (τ) and is determined from the behavior of the potential with time as the interfacial chloride ion concentration decreases. The potential (vs standard hydrogen electrode) of the Ag/AgCl electrode (a reversible electrode for present purposes) is given by the Nernst-type equation

$$E(\text{volts}) = 0.222 - 0.059 \log [\text{Cl}^-] \quad (1)$$

where $[\text{Cl}^-]$ represents the concentration at the surface of the electrode. As the chloride ion is depleted, the potential will shift in the positive direction. At the "endpoint", the concentration of Cl^- will rapidly approach "zero", and the potential calculated by use of Eq. (1) will theoretically approach infinity. In practice, however, the potential will shift to the next possible oxidation process. The exact "endpoint" (equivalent to the point in time at which the interfacial chloride ion concentration falls essentially to zero) is difficult to determine for various reasons, but for analytical purposes a reproducible "endpoint" may be determined precisely by electronically differentiating the potential-time curve and measuring the time at which the peak on the dE/dt vs time curve occurs (1).

A typical chronopotentiogram (E vs t curve) and its derivative (dE/dt vs t curve), recorded at the same time, are shown in Fig. 1.** The current is switched on at point A. The electrode potential immediately swings positively by an amount which depends on the resistance of the solution and the polarization of the electrode. As the AgCl film is formed and the chloride ion concentration is reduced at the interface, the potential slowly moves in a more positive direction. In the region between 18 and 22 sec, the potential rises most rapidly as the chloride ion concentration tends toward zero. The exact "endpoint" of the chronopotentiogram (E vs t curve) is indicated by the peak of the derivative (dE/dt vs t) curve at point B. The (practical) transition time is measured from the leading edge of the first pulse (point A) to the tip of the peak on the derivative curve (point B).

* Transition times are also observed in the case of low solution conductivity but the relations are complicated and less adaptable to convenient analysis.

** The output polarity of the derivative unit is inverted in sign from the polarity of the time derivative of the electrode potential.

Fig. 1. Typical chronopotentiogram and time-derivative, as observed in chloride determinations. (ORNL-DWG. 71-4837).

The initial or bulk concentration may be calculated from the equation (5, 6)

$$C(\text{moles/liter}) = \kappa I \tau^{\frac{1}{2}} \quad (2)$$

where I is the applied anodic current (amp) and τ is the transition time (sec). In the presence of a large excess of inert or supporting electrolyte, the constant κ is given by

$$\kappa = 2 \times 10^3 / (z F A (\pi D)^{\frac{1}{2}}) \quad (3)$$

where z is the number of electrons involved in the interfacial reaction ($z = 1$ for Cl^-), F is Faraday's constant (coul/equiv), A is the electrode area (cm^2), and D is the diffusion coefficient of the diffusing species (cm^2/sec). In practice the constant κ is determined by a calibration experiment rather than by calculation from Eq. (3).

Apparatus

A schematic diagram of the apparatus used for chronopotentiometry is shown in Fig. 2A. The cell, described in detail below, contains the silver electrode, a reference electrode, and a platinum polarizing electrode through which the current is applied. The instrument which we have developed and constructed is enclosed by dashed lines in Fig. 2A and contains a constant current generator plus circuits for monitoring the potential and the derivative of the potential with respect to time. This instrument is described in more detail in the Appendix. An accurate, high speed recorder completes the apparatus.

Details of the cell are shown in Fig. 3. The principal aims in the design of this cell were to provide for rapid change of samples, for reproducible electrode geometry, and for easy replacement of the electrode. The electrode is a flat silver

Fig. 2. Schematic diagrams of apparatus for chronopotentiometry and voltammetry of the chloride ion with a silver electrode. *A.* Set-up for chronopotentiometry; *B.* Set-up for voltammetry. (ORNL-DWG. 71-4838).

Fig. 3. Static cell for chronopotentiometric chloride analysis. *A.* Electrode and stirrer assembly. *B.* Lucite cell body. *C.* Stainless steel bolt. *D.* Stirring motor. *E.* Ag/AgCl reference electrode. *F.* Pt polarizing electrode. *G.* Ag disk. *H.* Stainless steel disk. *I.* Reference electrode connection. *J.* Polarizing electrode connection. *K.* Banana jack for connection to silver working electrode. (ORNL-DWG. 70-5515).

disk (*G*) with a working area precisely defined by a 1/2 in. diameter hole cut into the body of the Lucite cell (*B*). The electrode is held firmly in position by a stainless steel disk (*H*) secured with a stainless steel bolt (*C*). Electrical contact to the electrode is made by use of a banana jack (*K*) inserted into a hole in the head of the bolt (*C*). Cleaning and rinsing of the cell and changing of the sample solution may be carried out simply by loosening the clamp which holds the body of the cell and disconnecting the jack. The reference electrode (*E*) is a length of silver wire insulated with epoxy cement except for the tip which is covered with electrolytically-formed AgCl. The reference electrode, the platinum polarizing electrode (*F*), and the stirrer are secured to the top of the cell which is normally clamped permanently to a ring stand. The body of the cell (*B*) is 2 in. in diameter, the bore is 1 in. in diameter, and the overall height is 2 3/4 in. The cell is normally filled half way with about 9 cm³ of solution. If it is desired to use smaller samples, as little as 4-5 cm³ will cover the electrodes.

Procedure

Prior to a series of analyses, the silver disk electrode is carefully cleaned of any tarnish or any contaminant that might prevent coherent formation of the AgCl layer. Normally we use silver polish to remove tarnish and then alcohol followed by distilled water to remove any residues. Just before assembly of the cell, the electrode is lightly polished with a fine grade of polishing paper and rinsed with distilled water.

The cell is then assembled and the sample is introduced. If the cell is wet, it first must be rinsed with a little of the sample. If the solution does not contain a sufficient excess of inert electrolyte (at least 20:1), any of a number of methods of increasing the conductivity may be used. Generally, the cell is always filled to the same mark with sample, and then a few drops of a highly concentrated electrolyte are added. Reagents useful for this purpose are 1:1 H₂SO₄ (ca. 18 *N*), saturated NaNO₃ (8 *M*), or saturated KNO₃ (3.3 *M*). If care is taken always to fill the cell to the same mark ($\pm 10\%$) and to add the same number of drops of concentrated electrolyte, the resulting slight change in concentration will be only a few percent. If the standard solution is treated the same way, this error will largely cancel. This technique avoids time-consuming operations with volumetric apparatus.

The proper current setting must then be selected and set on the instrument. If the approximate concentration range is known, the current setting may be computed from a graph of concentration vs the quantity $I \tau^{1/2}$, such as that shown in Fig. 4. Best results are obtained if transition times are kept between 10 and 30 sec. If the actual concentration is much greater than the estimate, no transition time will be observed and the current must be increased for the next trial. Conversely, if the true concentration is smaller than the estimate, the transition will be observed at times too short for the desired accuracy and the current must be reduced. How-

Fig. 4. Typical plots of chloride concentration vs $I\tau^{1/2}$ for chronopotentiometric analysis of the chloride ion. Static cell: electrode area = 1.27 cm², ca. 10 cm³ of solution + 10 drops 1:1 H₂SO₄. Flow cell: electrode area = 0.75 cm², 0.2 M KNO₃, solution flow rate = 5 cm³/min. (ORNL-DWG. 71-4839).

ever, the solution does not have to be changed because use of this method does not change the chloride ion concentration significantly.

After the appropriate current is selected, the recorder is turned on at a chart speed which is fast enough to record the transition. The current is then applied to the cell and the derivative recorded (*cf.* Fig. 1). In order to prevent excessive buildup of the AgCl film on the silver disk, the current is next reversed and the AgCl film is reduced almost to the point where it has disappeared. The curves on the right side of Fig. 1 show the course of both the potential and the derivative in a typical determination as the film is being reduced. The potential slowly decreases and as the last amount of AgCl is removed, the potential begins to move more rapidly and the derivative begins to form another peak. At that point (*ca.* 46 sec in Fig. 1) the current is switched off. The operator can easily determine this point by watching either the recorder or a panel meter on the instrument which can be set to monitor either the potential or its time derivative. Reduction of the film beyond this point is undesirable because the potential may fall to the hydrogen evolution region, in which case the resulting gas bubbles must be removed before further determinations are carried out.

If a duplicate determination is desired, the process may be repeated without changing the solution. However, care must be taken to ensure that the solution is uniform and stagnant before the duplicate determination. In order to ensure the proper conditions, we follow a procedure of stirring 15 sec and waiting 20

sec before each determination. This is particularly important after removing the film by reduction, for the removal of the film will temporarily increase the chloride ion concentration at the surface by the reaction $\text{AgCl} + e^- \rightarrow \text{Ag}(\text{metal}) + \text{Cl}^- (\text{sol'n})$.

Table I shows data which we have obtained using the procedure described above. In each case, the transition time was determined in duplicate and the constant of Eq. (2) calculated from the average of the transition times. A small but reproducible decrease of the constant with decreasing concentration is always observed. The reasons for this decrease are complex and will not be discussed here. Perhaps the best method of practical analysis is to select several standard solutions in the region of interest and construct a calibration curve of concentration vs $I \tau^{\frac{1}{2}}$, as shown in Fig. 4 (data for static cell). By use of these techniques we have been able to carry out rapid chloride analyses with an absolute accuracy of 1% or better.

Calibration should be checked daily for highest precision. However, we have found that the calibration constant rarely changes by more than 1% after the electrode has been used for a short time. If the electrode is replaced or cleaned, it should of course be recalibrated.

The total length of time for determination of a given sample, including filling and rinsing of the cell, is 2-3 minutes. It should also be noted that a single instrument could be operated with several cells.

Any solution species which will form a precipitate with silver ions, such as sulfide or iodide, will interfere with the analysis. However, these ions are usually not present in large enough quantity in desalination applications to cause interference.

The ideal concentration range for this method is from about 5×10^{-4} to $5 \times 10^{-2} M \text{Cl}^-$ (approx. 20 to 2000 ppm Cl^-). Analyses can be carried out at higher concentrations but large currents are required and therefore the silver disk electrode deteriorates rapidly. At concentrations below $10^{-3} M \text{Cl}^-$ the peaks observed on the derivative curve begin to broaden and the analysis begins to lose accuracy as the concentration is decreased further. Well-defined peaks are not observed below about $5 \times 10^{-4} M \text{Cl}^-$.

II. CHRONOPOTENTIOMETRY IN FLOWING STREAMS

The chloride ion concentration in process streams may of course be determined by collecting samples from various points and analyzing by the batch method. In practice, it would be better if inexpensive sensors could be used to monitor the streams. The chronopotentiometric method can easily be adapted for use in flowing streams. A determination may be made in a few seconds, and no absolute reference electrode is needed.

The cell which we have developed for use with this technique is shown in

Fig. 5. Flow cell: Channel cross section, 1.27 cm $\times$ 0.476 cm; Silver electrode, 0.5 cm $\times$ 1.5 cm; Length of entrance region, 7 cm; (A) Bottom half, (B) Top half, (C) Silver electrode, (D) Platinum counter electrode, (E) Reference port, (F) "O"-ring. (ORNLDWG. 70-1316).

Fig. 5. The Ag/AgCl electrode (0.5 cm $\times$ 1.5 cm) is set with epoxy cement into a depression milled in a 0.635 cm Lucite plate (*cf.* A in Fig. 5). Initially, the surface of the silver electrode is slightly raised over the surface of the Lucite so that the entire face of this piece may be polished smoothly, thus ensuring a continuous transition from the Lucite to the silver. This piece is secured to the other half of the cell (B) by eight bolts which, when tightened, compress a neoprene "O"-ring set in a slot surrounding the channel. When the bolts are tightened completely, the "O"-ring is compressed enough so that the two halves of the cell fit tightly against each other. A platinum counter electrode (D) is set in the channel wall immediately opposite the silver electrode. A small hole (E) is set in the channel immediately downstream from the platinum counter electrode. For chronopotentiometry, an absolute reference electrode (such as a saturated calomel electrode) is not needed; instead a short piece of silver wire is set into a fitting which screws into the hole. Silver chloride is formed on the tip of the wire by anodization. The potential of both the reference wire and the working electrode depend solely on the concentration of the chloride ions and therefore, except when current is forced through the silver working electrode, no potential difference between these two electrodes is normally observed. As explained below, this cell may be used for potentiometry and voltammetry, but for these applications, a saturated calomel reference electrode is bridged into the cell through the small reference hole (E).

The overall size and relative dimensions of the cell are determined by hydro-

dynamic factors, minimum solution hold-up, and ease of machining. These factors are explained elsewhere (2) and are not discussed here. The overall size of the cell is 3.18 cm $\times$ 4.45 cm $\times$ 14.0 cm, and the dimensions of the channel cross section are 1.27 cm $\times$ 0.476 cm. The distance between the electrode and the entrance must exceed a certain critical length because of the requirement that fully-developed laminar flow exist at the electrode (2). We therefore allow 10 cm for the overall length of the channel and place the electrode 7 cm from the solution entrance. The holdup (*ca.* 6 cm³) is satisfactorily small for most purposes.

A complete analytical system will include, besides the cell, a flowmeter, a reservoir for standard solutions, and the electronic instrument. If the unknown solution does not contain sufficient inert electrolyte, a means must be provided to introduce small quantities of highly concentrated electrolyte (*e.g.*, 1:1 H₂SO₄). We have found that a micrometering pump is ideal for this purpose. We have also tried a controlled leak into the stream and found this technique to be almost as good. The concentrated electrolyte must be introduced far enough ahead of the cell to ensure complete mixing. If this is inconvenient, a small (*ca.* 3 cm³) stirred mixing chamber may be introduced just upstream of the cell.

Chronopotentiometry carried out in a flow cell is more complex than the static case discussed above. As in the static method, a constant current is supplied which is of sufficient magnitude so that the solution adjacent to the electrode surface is depleted of chloride ions. At the same time, this solution layer is replenished with chloride ions from the direction of the flow. Moreover, the resulting distribution of chloride ions along the direction of flow will be nonuniform. Although on first consideration it might seem hopeless to attempt chronopotentiometry under these circumstances, we have shown (2) that reproducible chronopotentiograms may be obtained at surprisingly large flow rates. Closer analysis shows, of course, that solution velocities in the region near the electrode surface are small relative to the mid-stream velocity because of the velocity gradient developed by the laminar flow. In fact, the flow will tend to suppress temperature and density gradients which might tend to develop under stagnant conditions.

Little measurable change in the transition time is observed at very low fluid velocities. As the flow rate is increased, sufficient ions are introduced into the diffusion layer by the flow to increase measurably the transition time. Ultimately, at high flow rates, chloride ions will be supplied at a rate sufficient to prevent completely depletion of chloride ions by formation of the AgCl layer, and no transition time will be observed.

It has been shown elsewhere (3) that the effect of flow on transition time is described by

$$\frac{\tau}{\tau_0} = -\frac{2}{3\xi^2} \left\{ \ln \left[\frac{1-\xi}{\sqrt{(1+\xi+\xi^2)}} \right] + 3^{\frac{1}{2}} \cdot \tan^{-1} \left[\frac{(3^{\frac{1}{2}} \cdot \xi)}{2+\xi} \right] \right\} \quad (4)$$

where the dimensionless parameter ξ is defined by

$$\xi = 1.49 \tau_0^{1/2} D^{1/6} h^{-2/3} \left(\frac{U_v}{dl} \right)^{1/3} \quad (5)$$

In Eqs. (4) and (5) τ is the transition time (sec) at volume flow rate U_v (cm³/sec), τ_0 is the transition time (sec) at zero flow rate, D is the diffusion coefficient of the chloride ion (cm²/sec), h is channel height (cm), d is channel width (cm), and l is electrode length (cm).

A graph of Eq. (4) is shown in Fig. 6, from which it may be seen that ξ must reach about 0.5 before the transition time is increased by about 5%. As the value of the parameter ξ approaches unity, the transition time tends to infinity. The flow rate corresponding to $\xi = 1$ is therefore the critical velocity at which a transition time can no longer be observed. Plots of τ_0 as a function of flow rate for various values of the ratio τ/τ_0 are shown in Fig. 7; these contours were calculated from Eq. (4) with the dimensions of the cell in Fig. 5. Some actual experimental points for various conditions are also shown in Fig. 7. Such contours are useful in selecting safe operating limits for flow cells. In order to carry out rapid, precise analyses with this system it is only necessary to avoid regions of excessive increase in transition time. In fact, operation of the cell is simpler than in the batch method because filling of the cell and adding of the inert electrolyte are accomplished by the flow.

Two precautions must be considered in operation of the flow cell. Firstly, the measurements temporarily disturb the chloride ion concentration at the electrode surface. In particular, formation of the film depletes the chloride ion at the surface, but the subsequent reduction of the film temporarily increases the concentration. Sufficient time must be allowed for the solution to reach the correct

Fig. 6. Relative transition time as a function of the parameter ξ . (ORNL-DWG. 70-1315).

Fig. 7. Contours for various values of relative transition time, calculated for cell of Fig. 5 and plotted as a function of flow rate and zero-flow-rate transition time. τ/τ_0 : A. 1.05, B. 1.10, C. 1.15, D. 1.20. Experimental points (τ/τ_0): $\circ$ (1.05); $\times$ (1.15). (ORNL-DWG. 70-1323).

(initial) concentration between determinations. This time is best found by experiments with standard solutions at the flow rate to be used. This time is generally less than 1 min for the range of flow rates shown in Fig. 7. The second precaution to be considered is avoidance of sudden changes in density or temperature. Such changes produce turbulence which in turn affects the transition time.

Finally, for very precise work (0.5%) comparisons between standard and unknown should be carried out at roughly the same transition time, for the observed transition time with flow is a function of both the flow and the initial (zero-flow) transition time (*cf.* Eq. (4)). However, this effect is small and, for routine 2% accuracy, need not be considered as long as the analysis is carried out in a "safe" region (*cf.* Fig. 7).

Transition times and constants obtained by using the flow cell are shown in Table II. Independent determinations (typically 4 to 25) were carried out at intervals of 2-10 min at each concentration. Only the last 4 or 5 determinations in each series are given in Table II. The transition times are quite reproducible and the constants do not vary by more than a few percent. Routine analytical accuracy of 1-2% may therefore be expected. The calibration curve for the cell is shown in Fig. 4.

TABLE I

TRANSITION TIMES AND CALIBRATION CONSTANTS FOR CHRONOPOTENTIOMETRIC ANALYSIS OF CHLORIDE ION (STATIC CELL)

Chloride Conc. (M)	Current (mA)	Transition time (sec) (duplicates)	κ	$I \tau^{1/2}$ (A-sec ^{1/2}) ($\times 10^2$)
0.05	6.0	18.5, 18.5	1.93 ₈	2.58
0.025	3.0	18.9, 19.0	1.91 ₄	1.30 ₇
0.01	1.2	19.1, 19.1	1.90 ₇	0.524 ₄
0.005	0.60	19.7, 19.7	1.87 ₇	0.266 ₄
0.0025	0.30	20.3, 20.6	1.84 ₀	0.135 ₈

TABLE II

TRANSITION TIMES AND CALIBRATION CONSTANTS FOR CHRONOPOTENTIOMETRIC ANALYSIS OF CHLORIDE ION (FLOW CELL; FLOW RATE = 5 CM³/MIN)

Experiment no.	Chloride conc. (M)	Current (mA)	Transition times (sec) (duplicates)	κ (average)	$I \tau^{1/2}$ (A-sec ^{1/2}) ($\times 10^3$)
1	0.01	1.20	6.50, 6.45, 6.45, 6.55, 6.50	3.26 ₈	3.06
2	0.005	0.60	6.65, 6.60, 6.55, 6.70	3.23 ₈	1.54 ₅
3	0.002	0.24	6.60, 6.70, 6.60, 6.60, 6.70	3.23 ₀	0.619 ₈
4	0.007	0.84	6.40, 6.45, 6.50, 6.50, 6.40	3.28 ₀	2.13 ₄
5	0.01	1.20	6.45, 6.35, 6.30, 6.35, 6.40	3.30	3.03

These determinations were made by use of a timer which switches the applied current and the recorder on and off at preset intervals. By making use of this type of timer, the flow cell may be used to monitor chloride ion concentrations unattended over long periods of time, provided the concentration does not change excessively. As an example, consider the analysis of samples which may range from 0.005 to 0.01 M Cl⁻. If the current is set at 1 mA with the cell of Fig. 5, transition times would range from 9.6 sec at 0.01 M Cl⁻ to 3.1 sec at 0.005 M Cl⁻. Care should be exercised, for maximum precision in such applications, that concentration variations do not result in excessively large (> 30 sec) or small (< 2 sec) transition times.

III. VOLTAMMETRY IN FLOWING STREAMS

Theory

The cell shown in Fig. 5 may also be used in a second mode of operation which is useful for continuous monitoring of chloride ion in the concentration range 10^{-4} to 2×10^{-3} M Cl⁻ (approx. 3 to 75 ppm Cl⁻). In this case, however, the instrument is converted to a potentiostat (with a panel switch). The apparatus

Fig. 8. Voltammetric current as a function of electrode potential and NaCl concentration: 0.25 M KNO_3 , 0.5 cm $\times$ 1.5 cm electrode, volume flow rate = 0.189 cm^3/sec , NaCl Concentration: A. 10^{-3} M, B. 5×10^{-4} M, C. 2×10^{-4} M, D. 10^{-4} M, E. Blank. (ORNL-DWG. 70-1319).

is shown schematically in Fig. 2B. The potentiostat operates by forcing just enough current through the silver electrode to maintain it at a preset potential with respect to a reference electrode, usually a saturated calomel electrode.

The analytical method is illustrated by the experimental results shown in Fig. 8. The cell of Fig. 5 is used and solutions of varying concentration flow through the cell at a rate of 5 cm^3/min . The curves represent the current required to maintain the potential of the electrode at the indicated value. The bottom line (E) represents the current observed for a blank solution containing no chloride ions and, as explained elsewhere (2), corresponds to the small amount of silver ion that goes directly into solution. If this "blank" curve is subtracted from the other curves, the horizontal dashed lines are obtained. These horizontal lines in Fig. 8 represent the limiting rate of convective diffusion of chloride ions to the surface of the electrode. Under these conditions, the rate of reaction (formation of the AgCl layer) at the electrode surface is exactly equal to the amount of chloride ions brought into the diffusion layer by the flow.

The equation for the limiting current of a single species to the surface of a channel electrode with fully-developed laminar flow is (3, 7)

$$I_L = 1.47 z w F C_0 \left(\frac{Dl}{h} \right)^{2/3} \left(\frac{U_v}{d} \right)^{1/3} \quad (6)$$

where I_L is the limiting current (amp), z is the number of electrons involved in

the charge-transfer reaction at the surface ($z = 1$ for Cl^-), w is electrode width (cm), F is Faraday's constant (coul/equiv), C_0 is bulk concentration (moles/cm³), D is diffusion coefficient (cm²/sec), l is electrode length (cm), h is channel height (cm), d is channel width (cm), and U_v is volume flow rate (cm³/sec). The limiting current thus increases directly with the concentration, with the two-thirds power of the electrode length, and with the one-third power of the fluid velocity. These relations have been confirmed by us (2) for the case of the Ag/AgCl channel electrode. The proportionality between current and chloride ion concentration is therefore the basis for a simple and accurate method of chloride analysis.

Apparatus and procedure

The apparatus used for flow chronopotentiometry may also be used for this method. However, the electronic instrument is used as a potentiostat and the reference electrode must be an "absolute" reference such as a saturated calomel electrode.

The flow rate should be maintained at a constant rate. Since the current depends on the one-third power of the flow rate, the rate must be maintained with an accuracy of only 3% for an analytical accuracy of 1%. A chemical metering pump is ideal for this application.

Electrode preparation is similar to that described above for chronopotentiometry. However, the AgCl layer must be removed periodically because the film builds up continuously in this method. In general, we find it necessary to remove the film every 20 to 30 hrs depending upon the concentration level. The film may be removed by polishing the entire face of the Lucite plate (*cf.* *A* in Fig. 5) with a fine grade of polishing paper.

Our observations show that a potential of +300 mV vs S.C.E. is the best potential for this type of analysis. At this potential the blank current is low and the electrode reaction has reached the limiting current region (*cf.* Fig. 8).

The analytical procedure is simple. After the system is assembled as indicated in Fig. 2B, the electrode is set at a potential of +300 mV vs S.C.E. and the flow is set at a convenient value. (Introduction of inert electrolyte may be required in this method also in order to provide for sufficient conductivity.) A blank solution containing no chloride is then run through the cell and the blank current recorded. Subsequently, a standard solution is introduced into the cell for exact calibration. Finally the sample is run through the cell and the current recorded continuously. In each case the chloride ion concentration is directly proportional to the difference between the observed and blank currents at the set potential of +300 mV vs S.C.E.

Two precautions should be observed. First, the current will tend to decrease slightly as the film of AgCl thickens on the surface of the silver electrode. The calibration should therefore be checked periodically. Second, a freshly prepared, film-free electrode will read slightly high for the first few minutes. The electrode calibration should be checked after about 15 min. of operation.

With sufficient care, analyses may be made to 1 %. One of the great advantages of this method is that the signal is directly proportional to chloride concentration. The method would therefore be ideal for high-precision monitoring of transients in the appropriate concentration range. Finally, this method may be extended to higher concentrations by any method of controlled dilution, such as by the use of two chemical metering pumps set at appropriate flow rates.

IV. POTENTIOMETRY

The apparatus may also be used directly for potentiometric analysis. Our instrument (*cf.* Fig. 2A) also includes a potential-monitoring circuit with a recorder output. Of course, the measured potential may be related to the chloride ion concentration only when a layer of AgCl has been formed on the surface.

One of the disadvantages of potentiometry is that Ag/AgCl electrodes which are not periodically renewed will slowly dissolve in the flowing stream. By making use of the polarizing circuits in the instrument the AgCl layer may be periodically removed and renewed.

According to the Nernst equation the measured potential is proportional to the (logarithm of the) activity rather than the concentration of chloride ions. If the total ionic strength of the solution changes, the activity coefficient will also change and a significant error may result. Our system includes reservoirs for adding small amounts of highly concentrated inert electrolyte. By addition of constant amounts of inert electrolyte to the flowing stream, large changes in ionic strength may be avoided and the activity coefficient correction may be minimized.

APPENDIX

Instrument for rapid electroanalysis of the chloride ion

For the most part, the equipment used in development of the methods described above was adapted from our available research instrumentation. However, such equipment is far too complex for convenience in routine analytical use. We have therefore designed and constructed an electronic instrument which is especially suited for use in chloride analyses.* In order to obtain optimum accuracy and precision from chronopotentiometric analyses it is necessary to have a very steady source of constant current and to employ a sensitive means of detecting the transition time. These requirements are met by the instrument shown in block diagram in Fig. 9; its operation is described below.

* The design and construction of the electroanalytical instrument was carried out in collaboration with J. L. Lovvorn of the ORNL Instrumentation and Controls Division.

Fig. 9. Diagram of instrument for voltammetric and chronopotentiometric analysis of the chloride ion. (ORNL-DWG. 70-9746).

This instrument makes use of three miniature operational amplifiers* (cf. A_1 , A_2 , and A_3 in Fig. 9) with output capability of ± 10 mA at ± 10 V. The circuit associated with amplifier A_1 is a constant current generator (galvanostat). The output of A_1 is fed back to the summing point and thence through resistor R_1 and the cell to ground. A voltage $E = I \cdot R_1$ appears across the resistor and is compared to a reference voltage at the summing point of A_1 . The high gain of A_1 ensures that the voltage drop across R_1 and the reference voltage are virtually equal. Thus the current pumped through R_1 and the cell is equal to the reference voltage divided by the value of R_1 . In general, cell impedance varies during electrolysis, but A_1 exactly compensates for this by adjustment of the output voltage, thus automatically maintaining a constant current through the cell. The reference supply consists of a mercury cell-resistor assembly; output over the range ± 1 V is selected by use of a 10-turn precision potentiometer. The current range is determined by the value of R_1 . Three switch-selected resistors (100 Ω , 1 k Ω , and 10 k Ω) are incorporated into the circuit, thus allowing maximum current outputs of 10^{-1} mA, 1 mA, or 10 mA.

Amplifier A_2 is used as a non-inverting, unity-gain voltage follower which measures the potential of the silver working electrode with respect to the Ag/AgCl (or other) reference electrode. The output of the follower may be read on a panel meter or on an external recorder. The circuit consisting of amplifier A_3 , resistor R_2 , and capacitor C_1 is used to differentiate the chronopotentiometric potential-time transient. The transition time is determined by measuring the time interval between application of polarizing current and the appearance of the maximum in the time derivative of the potential transient. This may be done most conveniently by monitoring the output of A_3 on a strip-chart recorder** and subsequent measure-

* Type 741C, manufactured by Fairchild Semiconductor Co., Div. of Fairchild Camera and Instrument Co., Mountain View, Calif. (U.S.A.).

** For example, Hewlett-Packard Model 7100B.

ment of the proper time interval. The output of A_3 may also be monitored on a panel meter.

The electroanalytical instrument may also be used for continuous voltammetric analysis of the chloride ion in a flowing stream. In this method a silver working electrode is located flush with one of the walls of a rectangular channel in which fully-developed laminar flow is established. The electrode potential is held constant at a value such that convective diffusion of chloride ions to the surface of the electrode determines the rate of the reaction. As noted above, the observed limiting current is directly proportional to chloride ion concentration. Thus use of a potentiostat is required for this method, and our instrument may be converted into a potentiostat simply by selection of the proper mode of operation with a panel switch. The reference supply for the constant current mode of operation then becomes the reference supply for the potentiostat. In yet another mode of operation, the follower circuit of the instrument (cf. A_2 in Fig. 9) may be used for conventional potentiometric analyses with many types of indicator electrodes. This instrument, although specially designed for chloride analyses, may thus be used for many types of analyses and electrochemical experiments. The entire instrument fits into a 10" x 8" x 8" cabinet and can be built for less than \$500. To our knowledge no commercial instrument is available with comparable sensitivity and stability for the price. An instruction manual has been prepared which describes in detail the use of the various cell assemblies and the instrument for rapid electroanalysis of the chloride ion content of saline waters; this is available from us.

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REFERENCES

1. R. E. MEYER, F. A. POSEY AND P. M. LANTZ, *J. Electroanal. Chem.*, 19 (1968) 99.
2. R. E. MEYER, M. C. BANTA, P. M. LANTZ AND F. A. POSEY, *J. Electroanal. Chem.*, 30 (1971) 345.
3. F. A. POSEY AND R. E. MEYER, *J. Electroanal. Chem.*, 30 (1971) 359.
4. D. G. PETERS AND A. KINJO, *Anal. Chem.*, 41 (1969) 1806.
5. P. DELAHAY IN I. M. KOLTHOFF AND P. J. ELVING, Eds., *Treatise on Analytical Chemistry*, Part I, Vol. 4, Interscience, New York, N.Y., 1963, p. 2233.
6. M. PAUNOVIC, *J. Electroanal. Chem.*, 14 (1967) 447.
7. V. G. LEVICH, *Physicochemical Hydrodynamics*, Prentice-Hall, Englewood Cliffs, N.J., 1962, p. 112.

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5. CHRONOPOTENTIOMETRY OF THE SILVER-SILVER SULFIDE SYSTEM*

M. C. Banta,[†] R. E. Meyer, and F. A. Posey

It has been shown on theoretical grounds¹ that the reversible anodic oxidation of a metal accompanied by formation of an adherent, insoluble film should give a mathematically describable chronopotentiogram if certain conditions are met. In addition, the necessary theory has been developed² for the same kind of system in the case of both irreversible and quasi-reversible oxidation. A simple form of the rate equation for the interfacial reaction was assumed in the latter derivations. The results were then applied to determination of the chloride ion using the silver-silver chloride electrode and to determination of chloride, bromide, and iodide by Peters and Kinjo³. Because silver sulfide is quite insoluble ($K_{sp} = 1.6 \times 10^{-49}$), it appeared that sulfide might also be determined by this technique.

THEORY

Because the theory is given in detail in the references cited above, only the basic equations will be given here.

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The following equations apply for standard chronopotentiometric conditions⁴⁻⁶:

$$C_i/C_o = 1 - (t/\tau)^{\frac{1}{2}} \quad (1)$$

with

$$\tau^{\frac{1}{2}} = \pi^{\frac{1}{2}} z F D^{\frac{1}{2}} C_o / 2i \quad (2)$$

where C_i is the concentration of the diffusing species at the interface (moles/cm³), C_o is the bulk concentration of the diffusing species (moles/cm³), t is the time (sec), D is the diffusion coefficient (cm²/sec), and τ , the transition time, is the time (sec) at which the concentration C_i theoretically goes to zero. In eq. (2), i is the current density (A/cm²) and the rest of the terms have their usual significance.

In the reversible case, the potential is determined by the equilibrium of the reaction, $2Ag + S^{-2} = Ag_2S + 2e^-$, and combination of eq. (1) with the Nernst equation yields the following expression:

$$E - E_o = - \frac{2.3RT}{2F} \log[1 - (t/\tau)^{\frac{1}{2}}] \quad (3)$$

Here, E_o is the equilibrium potential (volts) corresponding to the bulk concentration C_o . If the reaction proceeds reversibly, then according to this equation a plot of $(E - E_o)$ vs. $\log[1 - (t/\tau)^{\frac{1}{2}}]$ should extrapolate through the origin and have a slope of about 30 mV per log unit.

If the reaction is irreversible or quasi-reversible, a form of the rate equation must be assumed before the shape of the chronopotentiogram can be calculated. A large number of possibilities exist for a reaction as complex as the formation of Ag_2S . However, if we assume that the rate equation takes the following simple form,

$$i = i_o (C_i/C_o) \exp[\alpha z (E - E_o) F/RT] - i_o \exp[-(1-\alpha) z (E - E_o) F/RT] \quad (4)$$

with i_o (exchange current density, A/cm^2) given by

$$i_o = z F k_a C_o \exp(\alpha z E_o F/RT) = z F k_c \exp[-(1-\alpha) z E_o F/RT] \quad (5)$$

where k_a and k_c are heterogeneous rate constants (cm/sec) for the anodic and cathodic reactions, then we may calculate the shape of the irreversible and quasi-reversible waves. We do not wish to imply by this calculation that eq. (4) is the most likely form of the rate equation; depending on the mechanism, other forms are possible.

For the irreversible case, combination of eqs. (1) and (4) leads to the following expression:

$$E = E_o + (2.3RT/\alpha z F) \log(i/i_o) - (2.3RT/\alpha z F) \log[1 - (t/\tau)^{\frac{1}{2}}] \quad (6)$$

In the quasi-reversible case, both anodic and cathodic reactions must be considered in deriving the shape of the wave^{2,4}. The following equation may be derived under these

conditions

$$E = E_0 + (2.3RT/\alpha zF) \log(i/i_0) - (2.3RT/\alpha zF) \log[1 - (t/\tau)^{\frac{1}{2}} - \exp(-z(E-E_0)F/RT)] \quad (7)$$

In both cases, the kinetic constants may be determined by plotting the potential vs. the log term which contains the time t .

EXPERIMENTAL

The cell and apparatus used for these measurements are similar to those used by Meyer, Posey, and Lantz². Thus, the test electrode was a silver disk, the reference electrode was a silver wire, and the polarizing electrode was a spectroscopic-grade carbon rod. The Ag-Ag₂S reference electrode was prepared by anodically polarizing the wire at a small current density for about one minute. Generally, the silver was cleaned with a commercial silver polish and then rinsed with water and acetone. After placement in the cell the electrode was cycled anodically and cathodically several times.

Sodium sulfide was prepared for use by grinding, washing the small crystals thus obtained with distilled water, and drying in a desiccator. It was found by titration with silver nitrate that the sodium sulfide solutions did not require standardization unless potassium hydroxide, which was used to adjust pH, was present. Possibly, heavy metal impurities in the potassium hydroxide reduce the sulfide ion concentration. Inert electrolyte, either sodium nitrate (1 M), potassium

chloride (1 M), or sodium sulfate (0.5 M), was added to the test solution to reduce potential drops in the electrolyte phase due to passage of current and to suppress migration effects. Chloride ion did not interfere with the analysis, although it of course forms an insoluble compound with silver ion.

RESULTS AND DISCUSSION

A typical chronopotentiogram and its derivative are shown in Fig. 1. The derivative was obtained by electronic differentiation as was done earlier². A slight overshoot is generally observed in the initial section of the potential-time curve. This overshoot did not interfere with the analysis. Transition times were determined by measurement of the time corresponding to the peak of the derivative curve^{2,5}. The transition times so determined do not necessarily correspond exactly to the true theoretical transition times, but for practical analytical purposes they may be considered to be correct.

It is shown in Fig. 2 that for this system the inverse of the current is proportional to the square root of the transition time (at constant concentration). Further, it is shown in Table 1 that the quantity $K = i\tau^{\frac{1}{2}}/C_0$ is a constant for these data as it should be according to eq. (2). It is interesting that the same chronopotentiometric constant is obtained for both pH = 10.8 and pH = 14, since at pH = 10.8 the bulk of the sulfur is in the form of the HS^- ion, while

ORNL-DWG. 72-6333

FIGURE 1

TYPICAL CHRONOPOTENTIOTRAPH (LOWER TRACE) AND ITS DERIVATIVE
(UPPER TRACE). $i = 1.54 \text{ mA/cm}^2$, $C_0 = 0.00846 \text{ M}$, $\text{pH} = 10.8$,
 $\tau = 9.45 \text{ sec}$.

ORNL-DWG. 72-6334

FIGURE 2

PLOT OF RECIPROCAL CURRENT DENSITY vs. SQUARE ROOT OF TRANSITION TIME. (a) $C_O = 0.00846 \text{ M}$, $\text{pH} = 10.8$; (b) $C_O = 0.00663 \text{ M}$, $\text{pH} = 10.8$; (c) $C_O = 0.00560 \text{ M}$, $\text{pH} = 14$; (d) $C_O = 0.00328 \text{ M}$, $\text{pH} = 14$.

Table 1
Chronopotentiometric Constant as a Function of
Sulfide Concentration and pH

C_{actual}	i	τ	pH	$i\tau^{1/2}/C_0$	C_{measured}	% Error
0.00239	0.361	13.5	10.8	561	0.00235	-1.67
0.00445	0.615	16.6	10.8	564	0.00443	-0.34
0.00663	0.923	17.0	10.8	566	0.00673	1.59
0.00846	1.54	9.45	10.8	554	0.00839	-0.95
0.00328	0.863	4.49	14	558	0.00324	-1.32
0.00560	1.03	9.67	14	575	0.00566	1.23
0.00290	0.43	14.2	14	578	0.00287	-1.06

at pH = 14 most of the sulfur is in the form of the S^{-2} ion. The lack of dependence of K on pH would be expected if the diffusion coefficients of HS^{-} and S^{-2} are about the same and if the rates of conversion of one form to the other are high enough⁶.

In Table 1, data in the column marked C_{measured} were computed by averaging the chronopotentiometric constant K for all of the concentrations. This average constant was then used to recompute the concentrations. Thus this computation indicates the order of magnitude of error that might be expected in the determination of sulfide concentration by this technique. Generally, in a practical case, an analyst would determine the constant for several concentrations in the range to be determined, average the constants, and then proceed with actual analyses using this averaged chronopotentiometric constant. Another method of determining concentrations is illustrated by Fig. 3. All transition times in Fig. 3 were determined at the same current density. The concentration is therefore directly proportional to the square root of the transition time and may be read directly from a calibration curve like the one shown in Fig. 3. This would be an especially useful mode of operation for automatic determination of sulfide ion in a flow cell^{7,8}, since the current would not have to be reset between analyses.

A plot of $(E-E_0)F/2.3RT$ vs. $\log[1 - (t/\tau)^{\frac{1}{2}}]$ is shown in Fig. 4. Except for the initial section, which corresponds to

FIGURE 3

CALIBRATION PLOT AT CONSTANT CURRENT DENSITY. $i = 1.54 \text{ mA/cm}^2$.
(●) pH = 10.8, (○) pH = 14.

FIGURE 4

TEST FOR REVERSIBILITY. $C_o = 0.0063 \text{ M}$, $i = 1.12 \text{ mA/cm}^2$
 $\tau = 17.8 \text{ sec}$, $\text{pH} = 10.8$.

the initial overshoot in Fig. 1, the plot is linear and has a slope of 67 mV per log unit. The line does not extrapolate through the origin, and can therefore be interpreted as an irreversible wave. For the plot shown in Fig. 4, the exchange current can be computed to be about 0.2 mA/cm² and the slope corresponds to $\alpha = 0.44$ with $z = 2$. The average values of the constants for ten chronopotentiograms with the same current and concentration were $\alpha = 0.44$ and i_0 (exchange current) = 0.165 mA/cm². These constants would be reasonable, for example, for a mechanism in which the irreversibility is associated with transfer of sulfide ion through a thin layer of silver sulfide. Other mechanisms are possible, of course, and it should be noted that chronopotentiometry, in combination with other techniques, might be useful for determination of mechanisms of film growth. Use of eq. (7) gives essentially the same result as eq. (6) since the correction term, $\exp[-z(E-E_0)F/RT]$, is negligible at the potentials shown in Fig. 4.

We conclude that the silver-silver sulfide system is irreversible and may be described by eq. (6). The kinetic parameters are reasonable and support our conclusion. The system is also quite satisfactory for analytical use, especially in the concentration range, 10^{-3} to 10^{-2} M. Daily recalibrations of the electrode will yield precise results (ca. 1-2%), while good results (ca. 5%) may be obtained with less frequent calibration.

SUMMARY

It is shown that anodic chronopotentiometry in alkaline solutions with the silver-silver sulfide electrode may be used for determination of sulfide ion concentration over the range, 10^{-3} to 10^{-2} M, with a precision of 1-2%. The technique is unaffected by pH or the presence of chloride ions. Analysis of chronopotentiometric waves shows that the interfacial reaction is irreversible.

REFERENCES

1. P. Delahay, C. C. Mattax, and T. Berzins, J. Am. Chem. Soc., 76 (1954) 5319.
2. R. E. Meyer, F. A. Posey, and P. M. Lantz, J. Electroanal. Chem. 19 (1968) 99.
3. D. G. Peters and A. Kinjo, Anal. Chem., 41 (1969) 1806.
4. L. B. Anderson and D. J. Macero, Anal. Chem., 37 (1965) 321.
5. R. T. Iwamoto, Anal. Chem., 31 (1959) 1062.
6. P. Delahay and T. Berzins, J. Am. Chem. Soc., 75 (1953) 2486.
7. R. E. Meyer, M. C. Banta, P. M. Lantz, and F. A. Posey, J. Electroanal. Chem., 30 (1971) 345.
8. R. E. Meyer, M. C. Banta, P. M. Lantz, and F. A. Posey, Desalination, 9 (1971) 333.

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6. AN ELECTROCHEMICAL METHOD FOR MONITORING THE OXYGEN CONTENT OF AQUEOUS STREAMS AT THE PART-PER-BILLION LEVEL

R. E. Meyer, F. A. Posey, and P. M. Lantz

SUMMARY

A device for monitoring the dissolved oxygen content of aqueous streams at the part-per-billion level is described. This device makes use of an exchanger in which the dissolved oxygen in the test stream penetrates an oxygen-permeable membrane and equilibrates with the dissolved oxygen in an internal sensor stream. The oxygen content of the internal sensor stream is then monitored by quantitative reduction in a porous silver electrode maintained at an appropriate potential. Accuracy of the device is one or two parts per billion in the 0-100 ppb range.

INTRODUCTION

Determination of the dissolved oxygen content of aqueous streams in the 0 to 50 ppb range has always been a difficult problem. Because the corrosion properties of desalination equipment depend so strongly upon the dissolved oxygen content of the aqueous streams contained by the metallic materials of construction (1, 2), it is important to monitor the oxygen concentration with considerable precision. The principal requirements for a desirable method of determination are precision of one or two ppb and simplicity of operation so that highly skilled technicians are not required.

At present this analysis is usually carried out either by the classical Winkler method or by a modification of the polarographic sensor. The Winkler method is a difficult wet chemistry method requiring a skilled analyst. The polarographic sensor relies for its operation on electrochemical determination of the dissolved oxygen which diffuses through a plastic membrane (usually Teflon) permeable only to gases. The response of this device therefore depends on the properties of the membrane, the temperature, and the concentration of oxygen on either side of the membrane. In order for the device to operate properly, the diffusion rate through the membrane must not be too large relative to the diffusion rate in the solution; otherwise the response will be too strongly dependent upon the hydrodynamic conditions at the solution-membrane interface. Thus, highly permeable membranes like the silicone rubbers may not be used. This limitation places a

maximum limit on the current sensitivity of this device which is of the order of 10^{-7} to 10^{-8} amperes for dissolved oxygen contents in the low ppb range. These difficulties can be overcome to some extent, but only by increasing the complexity of the instrument and by periodic recalibration, usually by the Winkler method (3).

We describe here a device for determining the dissolved oxygen content of flowing streams in the ppb range which is self-calibrating and does not possess the disadvantages of the polarographic sensor. In order to achieve this, rapid response time is sacrificed. However, this is not a serious disadvantage, for in large-scale equipment the oxygen content of the various process streams is not likely to change rapidly.

As in the polarographic sensor, our device couples an electrochemical sensor with a permeable membrane. A schematic diagram of our device is shown in Fig. 1. The test stream flows through an exchanger (B) which contains the gas-permeable membrane. This exchanger is used to equilibrate the oxygen content of the test stream and a solution which ultimately passes through an electrochemical sensor. An exchanger is used in our device in order to separate dissolved oxygen from other reducible substances (such as iron and copper ions) which might be contained in the streams to be monitored and in order to avoid fouling of the electrochemical sensor by various substances. The sensor stream is allowed to remain in the exchanger long enough for it to attain essentially the same dissolved oxygen content as the test stream. In order to achieve this equilibration practically, the test stream is passed through at a high volume flow rate and the sensor stream either allowed to flow at a rate of a few milliliters per minute or at zero flow rate. The sensor

Fig. 1. Schematic diagram of laboratory model of ppb O₂-monitoring device: (A) Test solution inlet and exit, (B) Exchanger, (C) O₂ sensor, (D) Metering pump, (E) Solution reservoir, (F) Purging gas inlet, (G) Flow meter, (H) Electrolytic O₂ stripper. (ORNL-DWG. 72-4023).

stream is then passed through the electrolytic sensor (C) at a known flow rate, and the dissolved oxygen is completely reduced. This reduction is carried out in the sensor by a packed-bed cathode of finely divided silver. The current required to reduce the oxygen is a measure of the oxygen content, which may be calculated from the equation,

$$C = I/(n F U) \quad (1)$$

where C is the oxygen concentration (moles/cm³), I is the current (amp), n is the number (4) of electrons required for the complete reduction of an oxygen molecule, F is Faraday's constant (96,487 coulombs/equivalent), and U is the volume flow rate (cm³/sec). Thus, if a solution containing 10 ppb of O₂ is passed through the sensor at a flow rate of 2 cm³/min (0.033 cm³/sec), a current of 4 μA will be produced. This magnitude of current is easily measured and recorded. The sensor (cf. C in Fig. 1) is a simplification of a device described by Eckfeldt and Shaffer (4)

In comparison with the polarographic sensor, this device has far greater current sensitivity. Temperature excursions do not affect the ultimate precision, and if conditions are arranged for complete equilibration, the response is independent of hydrodynamic conditions and the condition of the membrane. Finally, by procedures described below, the device may be checked for proper operation with internal checks. The response time will depend on the design of the exchanger and the flow rate of the sensor stream. Very thin-walled membranes or tubes will give response times of the order of a few minutes but may be subject to frequent rupture. We describe below a very simple and rugged exchanger made of glass and silicone rubber tubing (1/8" I.D., 1/32" wall thickness) with which complete equilibration can be achieved in about thirty minutes.

As with the polarographic sensor, the response depends on the activity, not the concentration, of oxygen. Consequently, the concentration calculated by use of Eq. (1) may have to be adjusted for differences in oxygen partial pressure if the test solution and sensor solution differ substantially.

THEORY

The reduction of oxygen in alkaline solution occurs according to the following over-all equation:

The specific mechanism by which this occurs is irrelevant to our purpose here; it is only necessary to know that the reduction occurs completely and does not stop at a peroxide-containing species. A competing and unavoidable reaction is the reduction of water. Silver was selected as the cathode material because its overvoltage for water reduction is high and its overvoltage for oxygen reduction is small (5). We carried out a large number of preliminary experiments which showed

that oxygen is reduced by a four-electron reaction on silver in alkaline solution at potentials below (more negative than) about -500 mV vs. SCE. At about -900 mV vs. SCE, water reduction begins to become significant.

A cross section of our electrolytic sensor is shown in Fig. 2. The solution enters the bottom of the cell and immediately passes through a bed of finely divided silver. It is clear that the primary design consideration is that the electrode be large enough to remove essentially all of the oxygen at the maximum flow rate to be used. The size of the electrode may be estimated from the following considerations.

Fig. 2. Cross section of oxygen sensor: (A) Finely divided silver cathode, (B) Ag screen anode, (C) Ag-AgCl reference electrode, (D) Lead to anode, (E) Lead to cathode, (F) Glass wool, (G) 35/20 O-ring joint, (H) Plastic tubing, (I) Section of porous glass filter tube. (ORNL-DWG.72-4024).

We first assume that the solution is conductive enough so that potential drops in the pores of the electrode are negligible. The reduction of oxygen at our operating potential of about -700 mV vs. SCE is in the mass-transfer-controlled region; the rate of reduction is therefore independent of electrode potential in this region. Finally, we assume that the concentration of oxygen is radially uniform within the porous electrode and varies only along the length, l , of the porous bed. The decrease in concentration (c) at any point, l , along the direction of flow is given by the expression,

$$\frac{dc(l)}{dl} = - \frac{i(l)S}{U} \quad (2)$$

where $c(l)$ is the concentration (moles/cm³), $i(l)$ is the rate of reaction at a point

(moles-cm⁻²sec⁻¹), S is the surface area per unit length of the porous bed (cm²/cm), and U is the flow velocity (cm³/sec).

If the rate of reaction is mass-transfer limited, then we may approximate the rate of reaction by the expression $i(l) = \mathcal{D}c(l)/\delta$ where $\mathcal{D}$ is the diffusion coefficient (cm²/sec) and δ is the effective diffusion layer thickness (cm). Combining this expression with Eq. (3) and integrating, we obtain

$$C = C_{l=0} \exp\left(-\frac{\mathcal{D}Sl}{\delta U}\right) \quad (3)$$

where $C_{l=0}$ is the concentration of the oxygen in the solution entering the electrode. We wish to find the length of electrode (L) necessary to reduce the ratio $C/C_{l=0}$ by a given amount. For $C/C_{l=0} = 0.01$ we have

$$L = \frac{4.6 \delta U}{\mathcal{D} S}$$

The diffusion coefficient $\mathcal{D}$ of oxygen in solution has been reported to be 2.6×10^{-5} cm²/sec (6). We estimate S to be about 40 cm²/cm for our configuration (described below). The effective diffusion layer thickness within a porous electrode is difficult to estimate and will be a function of flow rate. We will assume that it is of the same order as that in well-stirred solutions, *i.e.*, $\sim 10^{-3}$ cm. Using these figures we have $L \approx 20 U$. For our flow velocities of 0.02 to 0.5 cm³/sec, we calculate that $L \approx 0.4$ to 10 cm. This is of course a rough estimate considering the assumptions and approximations involved. Experimentally, we have found that a packed bed of finely divided silver (particle size $\sim 500\mu$) about 5 cm long and 1 cm in diameter will remove all of the oxygen from our solutions at flow rates up to 0.5 cm³/sec.

In the design of the exchanger the obvious goal is to provide for complete equilibration between the sensor solution and the test solution in as little time as possible. This is a complex mass-transfer problem which depends on the permeability of the membrane to oxygen and upon the mass-transfer rate of oxygen in the sensor stream. Solutions for this mass-transfer problem are readily attainable for idealized geometries and conditions, and we have carried out numerous calculations. However, these calculations are only approximate, and for our purpose here it is only necessary to point out the obvious conclusion that the diffusion paths must be kept as small as possible and that the sensor solution must remain in the exchanger long enough (*i.e.*, one must use a slow enough flow rate) so that the solutions are completely equilibrated. We have determined the required equilibration times empirically for our various designs.

APPARATUS

The general configuration of the device is shown in Fig. 1, as noted above.

The test solution enters the exchanger (described in detail below) and exits from the top. The sensor stream is pulled through the exchanger by a variable-speed tubing pump (Sage Model 375 or Cole-Parmer Model 7013). In our laboratory device the solution runs into a reservoir through which pure He is passed. The primary purpose of this reservoir is to assist in the initial degassing of the system. This reservoir could be eliminated in any actual system because deoxygenated solution could be introduced into the sensor stream when it is first filled up. The sensors would then remove the remaining oxygen, for essentially all of the oxygen is removed by the electrolytic sensor. The circuit is completed by passage of the solution through a flow meter (Fisher-Porter Precision Bore Flowrator Tube No. 08F 1/16-20 5/36) and finally through an electrolytic stripper similar to the sensor. This stripper serves two purposes: (1) it removes any residual oxygen that leaks into the system; (2) it removes and reduces any silver compounds that may be formed on the anode of the sensor and carried into the stream. The stripper is arranged so that the solution passes through the cathode portion last. In this way any silver compounds formed by the anode will be trapped and reduced by the cathode. The entire circuit is made of glass capillary tubing and is constructed with an absolute minimum number of joints. The sensor stream is 0.1 *M* NaCl made slightly alkaline with 0.01 *M* NaHCO₃.

The final design of our sensor is illustrated in Fig. 2. The cathode of finely divided silver (particle size $\sim 500\mu$) is about 5 cm in length and 1 cm in diameter. It is separated from a silver screen anode by a 5 cm piece of fine-porosity sintered glass filter tube. Part of the flow is directed past the anode and out the bottom of the cell. This portion of the flow serves to renew the solution at the anode and keep it free of oxygen. In chloride solution the principal anode reaction is the formation of silver chloride. Depending on the oxygen concentrations of the streams to be monitored, the anode will eventually completely convert to AgCl and will have to be replaced. The relative flow rate out of the bottom and top of the sensor may be regulated by a pinch clamp on the short piece of plastic tubing. An O-ring joint at the top of the cell allows access to the silver electrodes for renewal. The reference electrode is a piece of silver wire covered with AgCl formed electrolytically. At low current densities the silver anode also may serve as the reference electrode. Connections are made to the various electrodes with silver wire passed through short sections of capillary tubing and held in place with epoxy cement. Flow through the sensor is always upward in order to remove any gas bubbles trapped in the stream.

Any standard commercial potentiostat may be used to hold the potential of the silver cathode at the required potential. We have found a potentiostat constructed of commercially available operational amplifiers (*e.g.*, Fairchild 741C) with an output of 10 mA at 10 V to be entirely satisfactory. A dual potentiostat would be especially convenient since one unit is required to operate the stripper. A recorder, panel meter, or other device used to monitor the current output of

the potentiostat used for the sensor may, of course, be calibrated so that oxygen concentration can be read directly in parts per billion or other convenient units.

Two designs of exchangers are shown in Fig. 3. The glass exchanger on the left is constructed from a 25-mm O.D. glass tube about 50 cm long with O-ring joints at both ends. This exchanger contains a circuit which consists of seven lengths of silicone rubber tubing (1/8" I.D., 1/32" wall thickness).

Fig. 3. Schematic diagram of exchangers: (A) Sensor stream, (B) Test stream. (ORNL-DWG. 72-4021).

A plastic (Lucite) exchanger was constructed which was used to test thin sheets of membrane material. This exchanger is shown schematically on the right side of Fig. 3. The sensor stream pursues a serpentine path up the exchanger, while the test stream flows up a channel on the opposite side. A thick sheet (0.2 mm) of silicone rubber separated the two halves of the exchanger. Double O-ring seals (not shown on the diagram) effectively prevented inleakage of atmospheric oxygen.

In order to test this system, an electrolytic oxygen generator was placed in the test stream ahead of the exchanger. The generator consisted of two small platinum electrodes fused into the capillary tubing. Immediately downstream from the exchanger in the test stream, a second oxygen sensor (not shown in Fig. 1) was used to monitor the oxygen leaving the exchanger. The reason for monitoring this test stream rather than relying on the current supplied to the oxygen generator

was that some of the oxygen left the platinum electrode as bubbles which tended to collect at bends in the tubing. Thus not quite all of the oxygen dissolved into the test stream.

OPERATION AND RESULTS

Our first experiments dealt with the operation of the sensor alone, without use of the exchanger. In order to test the efficiency of the sensor, the electrolytic oxygen generator was placed immediately upstream of the sensor so that any gas bubbles formed would be swept into the electrode. Table I shows some typical results of these experiments. In all cases, essentially all of the oxygen produced by the electrolyzer is reduced by the sensor. The hydrogen produced by the electrolysis does not affect the operation of the sensor.

TABLE I

EFFICIENCY OF OXYGEN SENSOR

<i>Flow rate (ml/min)</i>	<i>Current added (μA)</i>	<i>ppb added</i>	<i>Current found (μA)</i>	<i>ppb found</i>
20	9.3	2.3	8.5	2.1
20	20.2	5.1	19.2	4.8
20	29.8	7.4	28.5	7.1
20	40.0	10.0	39.0	9.7
20	50.0	12.4	49.0	12.2
20	60.0	14.9	59.0	14.7
20	70.0	17.4	70.0	17.4
20	81.5	20.3	82.0	20.3
20	100.0	24.9	100.0	24.9
10	10.0	5.0	10.0	5.0
10	20.0	10.0	18.5	9.3

The complete system (*cf.* Fig. 1) was then tested with a variety of exchangers. Figs. 4-6 show the results of these experiments for various operating conditions. In Fig. 4, results are presented for the exchangers shown in Fig. 3. In these experiments, the flow of the sensor stream was kept between one and two ml/min and the flow of the test stream was 20 ml/min. The average deviation of the points from the line is about one ppb of oxygen. The maximum error is 2.2 ppb at an applied concentration of 26 ppb, or about 8.5% error. In order to carry out this determination, four separate measurements are needed, each of which is subject to several per cent error. These are the two flow-rate measurements of the test and sensor streams and the two current measurements of the sensors on the two streams. The errors involved in these four measurements can add up to a significant error if

Fig. 4. Test of O₂-monitoring device. (ORNL-DWG. 72-4018).

Fig. 5. Test of O₂-monitoring device. (ORNL-DWG. 72-4022).

Fig. 6. Test of O_2 -monitoring device, zero flow rate in sensor stream. ● Static runs, 7 mil membrane. ○ Static runs, silicone rubber tubing. (ORNL-DWG. 72-4019)

they are in the same direction. Part of this difficulty can be overcome if the flow rates of the sensor and test streams are kept in a constant proportion. Examination of Eq. (3) shows that under these circumstances the currents indicated by the sensors on the test and sensor streams should be in the same ratio as the flow rates if equilibration is attained. Experiments were therefore carried out using the Sage 4-channel tubing pump (Model 375) which maintained a constant 10:1 flow ratio when using two appropriate sizes of tubing. Flow rates were set at 16 ml/min and 1.6 ml/min for test and sensor streams, respectively. Examination of Fig. 5 shows that the errors were much smaller in the experiments carried out under these conditions. At the flow rate of 1.6 ml/min in the sensor stream, 100% equilibration between the two channels was not achieved; the currents shown in Fig. 5 correspond to approximately 90% equilibration.

This device may also be operated by completely stopping the flow in the sensor stream long enough for complete equilibration to be achieved. The time necessary to achieve complete equilibration may be determined by progressively increasing the time interval of zero flow until a constant ppb reading is attained. This must be done at a time when the oxygen level of the test stream is not changing. Thus, operation in this manner serves as a check on the operation of the exchanger. However, care must be taken in the design that there is enough solution in the exchanger to operate the sensor properly; if insufficient volume is present all of the solution originally present in the sensor will not be flushed out. In this mode of operation, any flow rate (within the range of the sensor) may be used in the sensor stream after it is started. Flow rates higher than those used in the continuous mode

of operation may be used; this will provide higher current sensitivity for a given oxygen concentration (*cf.* Eq. 1). This method of operation is therefore especially suited for low concentrations of oxygen. Fig. 6 shows some data taken by use of this technique.

About 30 minutes had to be allowed before complete equilibration for the data shown in Fig. 6. If this instrument were set up for automatic analysis (which could easily be done with timer relays), a determination could be made each 30 minutes. More frequent analysis could be achieved by using thinner-walled rubber tubing with a smaller bore, raising the operating temperature of the exchanger, or both. However, the use of such tubing would mean that the length of tubing necessary to supply a given volume of equilibrated solution to the sensor would be considerably increased. Also the possibility of eventual rupture would be greatly increased. For use with large-scale equipment, determinations at 30-min intervals are probably satisfactory for many purposes. A particularly advantageous combination might be a conventional polarographic sensor in series with this device. In operation, the polarographic sensor would indicate quickly any rapid changes in the oxygen level and could be recalibrated periodically with our device.

As mentioned above, proper operation of the exchanger can be checked by completely stopping the flow of the sensor stream. At the same time, the current in the sensor, if it is working properly, should drop to a background level less than a microampere. If an excessive background current is observed at zero flow, the potential is probably not being maintained at the desired potential and another reaction is occurring (*e.g.*, reduction of water). Finally, current response may be checked when the solution is flowing by incorporating a small electrolytic oxygen generator in the capillary tubing leading to the sensor.

In the design and operation of this device, several precautions should be observed. Crevices and bends where air bubbles can be trapped should be avoided. Plastic materials should be kept to an absolute minimum since they tend to adsorb and dissolve oxygen. Thus, the Lucite exchanger described above would work properly only after a three- or four-day period of degassing. All tubing should be made of glass and no joints (other than fused glass) should be allowed in the circuit between the stripper and the exchanger and between the exchanger and the sensor (*cf.* Fig. 1).

The system must be conditioned before use in order to remove all adsorbed and dissolved oxygen, a process which generally takes a day or two. The silver in the electrolytic sensors is usually covered with silver oxide (or possibly other silver compounds) when it is first introduced into the cell. When the potential is first set at -700 mV vs. SCE, currents of the order of milliamperes may be required for several hours before the sensor operates properly. Generally, the blank current will decrease in a few days to levels considerably below one microampere and no blank correction is needed.

We conclude on the basis of these measurements that the device described

above should be especially useful for monitoring the dissolved oxygen content of desalination plant streams and other process streams where plant operation and/or corrosion behavior of metallic materials depends critically on the oxygen level. Because of ease of operation, insensitivity to temperature, and freedom from calibration problems, it should be possible to develop instrumentation modules having a wide variety of monitoring and readout capabilities. However, this device has been tested, so far, only in the laboratory. Operating experience in a plant is necessary in order to determine whether the various components will operate properly over extended periods of time. It is especially important to determine whether the silicone membrane material will maintain its integrity and permeability under plant conditions.

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REFERENCES

1. E. H. PHELPS, R. T. JONES AND H. D. LECKIE, *J. Electrochem. Soc.*, 116 (1969) 213C.
2. H. C. BEHRENS, *et al.*, *Office of Saline Water, Res. Develop. Progr. Rept. No. 417*, Sea Water Corrosion Test Program, March, 1969.
3. H. C. BEHRENS *et al.*, *Office of Saline Water, Res. Develop. Progr. Rept. No. 572*, Assembly and Evaluation of an Improved PPB Oxygen Analyzer for Sea Water, July, 1970.
4. E. L. ECKFELDT AND E. W. SHAFFER, JR., *Anal. Chem.*, 36 (1964) 2008.
5. J. P. HOARE, *The Electrochemistry of Oxygen*, Interscience, New York, N.Y., 1968, p. 236.
6. I. M. KOLTHOFF AND C. S. MILLER, *J. Am. Chem. Soc.*, 63 (1941) 1015.

7. PROPERTIES OF THE SUSPENSION ELECTRODE

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Studies were carried out during the biennium on the properties of the suspension (or slurry) electrode system, a configuration of potential usefulness in the treatment of saline and other waters. The suspension electrode is a relatively little-known type of electrode system in which the electrode is a finely divided catalytic material suspended in a solution of strong electrolyte. The particles of the catalyst, which are usually from 10 to 100 μ diameter, are charged by intermittent contact with a stationary electrode. Contact may be effected either by stirring the suspended particles or by flow of the suspension past a charging electrode fixed in a channel. In principle, the finely divided particles of the suspension are charged to the potential of the charging electrode by repeated contact with it and by charge-exchange between particles. A charged suspension can react with electroactive species in solution and undergo simultaneous discharge. The operation of a suspension electrode in the steady state thus consists of a charging process (between charging electrode and particles and between particles) and a discharge process involving oxidation or reduction of reactants.

The suspension electrode offers several advantages compared with conventional electrode systems. Normally, electrode materials must be selected for a combination of favorable properties, including catalytic activity, mechanical strength, and corrosion resistance. With the suspension electrode the suspended material may be selected primarily for its catalytic activity, and the charging electrode may be selected primarily for its mechanical and corrosion properties. If the suspended material should deteriorate in use, it can easily be replaced without dismantling the cell. In addition, many types of suspended materials have very large active surface areas (e.g., 10 to 50 m^2/g), and therefore increased current densities for certain types of reactions are possible. Finally, removal of gaseous products from a suspension electrode should be less difficult than from a conventional porous electrode of comparable surface area.

The factors influencing the magnitude of the current in the suspension electrode system have not been understood satisfactorily, and some of the reported results are contradictory. Our initial experiments were designed to verify certain published data and to determine important parameters which affect operation of this type of cell. We found that not all finely divided catalytic materials provided enhanced reaction rates when used in the suspension electrode configuration. For example, finely divided nickel powder did not enhance the rate of the hydrogen evolution reaction, but the same amount of Raney nickel had a considerable effect. Also, finely powdered gold greatly enhanced the rate of reduction of dissolved molecular oxygen, but had no measurable effect on the hydrogen evolution reaction. We concluded that specific materials would be required for the enhancement of specific reactions in the suspension-electrode system.

All systems tested in our exploratory experiments were affected by the presence of dissolved oxygen in the cell and meaningful results were obtained only after removal of the oxygen. Reaction rates were found to be very sensitive to hydrodynamic conditions within the cell, such as cell geometry, charging electrode area and placement, stirring mode and rate, etc. These factors may account for some of the contradictory results found in the literature.

In subsequent experiments we examined the kinetics of the hydrogen evolution reaction, using suspensions of Raney catalysts, platinum black, and palladium black. This electrochemical process is of considerable interest because it has been studied extensively on conventional electrodes and because a knowledge of the kinetics of the hydrogen evolution reaction is nearly essential in studies of any reactions which take place under cathodic polarization. Current-voltage curves for the hydrogen evolution reaction with the palladium-black suspension electrode are shown in Fig. 7.1, where it can be seen that the current from the suspension electrode is a linear function of the overvoltage. This relation, which had been reported previously by other workers, is surprising at first sight, because normally in electrochemical processes the current is an exponential function of the overpotential. Similar results for the Raney nickel suspension electrode are shown in Fig. 7.2. We have also shown that the slopes of the current-voltage curves are identical for both the anodic and the cathodic process

FIG. 7.1 EFFECT OF CATALYST CONCENTRATION ON POLARIZATION OF THE PALLADIUM BLACK SUSPENSION ELECTRODE.

FIG. 7.2 EFFECT OF CATALYST CONCENTRATION ON POLARIZATION OF THE RANEY NICKEL SUSPENSION ELECTRODE.

with the hydrogen electrode reaction, as may be seen in Fig. 7.3. The slope of this line has been found to be a function of the nature of the catalytic material, the solution conductivity, and the geometric and hydrodynamic factors which control the frequency and duration of contact between the particles and the charging electrode. The effect of solution conductivity is illustrated in Fig. 7.4. The sodium sulfate solution referred to in Fig. 7.4 had a conductivity only slightly greater than that of 0.1 N KOH but of course a considerably different pH; similar results in experiments in which the composition of the solution was changed showed that the pertinent variable is the solution conductivity. In general, a change of conductivity by a factor of 10 changes the current by a factor of from 2 to 4 at constant electrode potential, catalyst concentration, and stirring conditions.

We confirmed these results by observing individual pulses due to contact of catalyst particles with the charging electrode using an oscilloscopic technique. Lowering the concentration of the catalyst to a few milligrams per liter and reducing the size of the charging electrode reduced the frequency of contact events to only a few per second, and individual pulses could then be observed. Some typical pulses are shown in Fig. 7.5. Most of the pulse shapes were characterized by a sharp increase to a peak current followed by a slow decay. The duration of the pulses for our stirring conditions was generally of the order of 1 msec. Many pulses were examined, and average pulse heights were determined as a function of overpotential and solution conductivity. Some results of these measurements are shown in Figs. 7.6 and 7.7. These experiments confirmed the linear relation between current and overpotential and the increase in current with concentration of the electrolyte (i.e., conductivity).

A model for the suspension electrode system was developed based on the following assumptions: (1) individual catalyst particles are highly porous and behave like miniature porous electrodes; (2) the resistance of the electrolyte is the predominant factor in determining the overpotential during the course of a current transient; (3) since most of the overpotential lies within the solution phase, the potential at the metal-solution interface on the catalyst particles departs only a few millivolts from the equilibrium potential (this fact is ultimately responsible for the linear relation

FIG. 7.3 ANODIC AND CATHODIC CURRENT-VOLTAGE CHARACTERISTICS.
Conditions: 0.3 N KOH, cell capacity 150 ml, 25°C.

FIG. 7.4 OXIDATION OF HYDROGEN. Conditions: 1 gm palladium black in 150 ml solution.

FIG. 7.5 PULSE SHAPES FOR CHARGE TRANSFER TO INDIVIDUAL SUSPENSION PARTICLES. Conditions: palladium black catalyst, platinum charging electrode, 1 N KOH, -200 mV overvoltage.

FIG. 7.6 EFFECT OF OVERPOTENTIAL ON PULSE HEIGHT. Conditions:
Pd catalyst, 0.3 N KOH.

FIG. 7.7 EFFECT OF CONDUCTIVITY ON PULSE HEIGHT.

observed between current and overpotential); and (4) the effective rate constant at the surface is very large during the important first few milliseconds of the charging transient. Details of the theoretical model are described in Section 8 of this report.

As noted above, some of the important parameters which affect current output of the suspension electrode were found to be the amount of catalyst material suspended in the electrolyte and the rate and mode of stirring, which influences the rate of particle impact with the charging electrode. In subsequent experiments we investigated the operation of a flow cell designed for relatively high current output. This cell contains an array of charging electrodes through which the suspension can be pumped at various velocities. A description of the cell and its operation and some of the principal observations are presented below.

A schematic diagram of the flow system constructed for use with the suspension electrode is shown in Fig. 7.8. The slurry, consisting of particles of Raney nickel catalyst suspended in 1 N KOH, was pumped through the two compartments of the flow cell (cf. A in Fig. 7.8) by use of magnetic impeller plastic centrifugal pumps (B). After passage upward through the cell (details of which are described below) the suspension was discharged into vented glass reservoirs (H) located several feet above the cell. Continuous recycling of the suspension was accomplished by connecting the reservoirs to the intakes of the pumps. The flow rate of the suspension through the cell half which contained nickel charging electrodes was controlled by means of a bypass line and clamp (E) and by a resistance control on the pump motor. The flow rate of the suspension was monitored by use of calibrated glass standpipes containing a number of holes (I) and incorporated into the reservoirs. Constant temperature of the suspension entering the cathode side of the cell was controlled by use of a glass condenser (D). In order to expedite removal of dissolved atmospheric oxygen at the start of an experiment, hydrogen gas was bubbled (F) through the suspension in the reservoir and discharged through a water trap (G).

Current was supplied by a Kepco regulated-voltage power supply (160 V, 4 A). Saturated-calomel reference electrodes (C), bridged into the cathode and anode streams in the cell, were used to monitor the

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FIG. 7.8 SCHEMATIC DIAGRAM OF FLOW SYSTEM FOR SUSPENSION ELECTRODE. A, flow cell; B, pumps; C, reference electrodes and chambers; D, heat exchanger; E, bypass line clamp for flow control; F, inlet for H₂ gas; G, gas outlet; H, slurry reservoirs; I, flow monitors.

potential of the charging electrodes. Electrode potentials were measured by use of a Keithley Model 610R electrometer. Both applied current and electrode potential were recorded on a Hewlett-Packard Model 7100B strip-chart recorder.

Previously it was found that, of several finely divided, catalytically active metals, Raney nickel was most effective as a suspension material in the enhancement of the hydrogen evolution reaction in 1 N KOH. This property may be due in large part to the large internal surface area of the porous particles of Raney nickel. Activated Raney nickel catalyst was prepared from sized particles (>350 mesh) of nickel-aluminum alloy powder (W. R. Grace & Co.) by a method suggested by others.¹ The activated catalyst in absolute ethanol was stored in a refrigerator until needed.

Details of the flow cell are shown in Fig. 7.9. The two halves of the cell were machined from Lucite with a 4 1/2 x 1/2 x 1/8-in. depression milled into each half. The ends of the depressions were tapered to match inlet and outlet tubes (3/16-in. OD) which entered obliquely at each end of the cell. Seven electrodes [nickel for the cathode side (A) and platinum for the anode side (D)] passed through each half of the cell perpendicular to the direction of flow (cf. F and G in Fig. 7.9) and were sealed into the cell halves with epoxy cement. The electrodes, 0.041-in. OD, were spaced 3/8-in. apart in the channel. The compartments were separated with a 0.004-in. thick membrane (C) of Webril, a nonwoven Dacron (The Kendall Co., Walpole, Mass.). Thin rubber gaskets (B) sealed the membrane into the cell and a rubber O-ring gasket (H) was used to assemble the cell. Two reference-electrode capillaries (E) were provided in each cell half. These capillaries terminated within 1/16-in. of the surfaces of the first and fifth electrodes (counting from the inlet ends of each cell half). The capillaries were connected with tubing to separate compartments containing saturated-calomel reference electrodes (cf. C in Fig. 7.8). The principal electrode process occurring in the anode compartment was the oxygen evolution reaction on the platinum electrodes. Current-voltage characteristics of this process were not of primary interest in this part of our study.

1. H. Adkins and H. R. Billica, J. Amer. Chem. Soc. **70**, 695 (1948).

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FIG. 7.9 FLOW CELL FOR SUSPENSION ELECTRODE. A, half cell with nickel wire electrodes; B, rubber gaskets; C, Dacron membrane; D, half cell with platinum wire electrodes; E, ports to reference electrodes (S.C.E.); F, nickel electrodes; G, platinum electrodes; H, O-ring gasket.

Figure 7.10 shows a number of current-voltage curves for the hydrogen evolution reaction on the suspension electrode. The total geometrical surface area of the seven nickel wire electrodes used in the cathode compartment of the flow cell was $\sim 2.9 \text{ cm}^2$. At the highest catalyst content (70 g Raney Ni in 275 ml 1 N KOH) the current output of the cell at 25°C is greater than 1 A/cm^2 ($\sim 10^3 \text{ A/ft}^2$), calculated with respect to the area of the charging electrodes, at only 300 mV over-voltage. Thus the flow-cell configuration of the suspension electrode is a very efficient device for the generation of electrolytic hydrogen. Still greater current output could be obtained by use of a more concentrated electrolyte (6 N KOH, for example), with higher catalyst contents (larger apparatus and special pumps would be required), and by operation at elevated temperatures.

The data of Fig. 7.10 represent the enhancement of the output current due to addition of Raney Ni catalyst. A background current, due to the rate of hydrogen evolution on the nickel charging electrodes in the absence of the catalyst, was subtracted from all the data of Fig. 7.10. Precise determination of the background current presents certain difficulties, however. Impingement of catalyst particles upon the charging electrodes erodes the surfaces and increases the surface area and therefore the background current with time. More consistent results are obtained, particularly at low catalyst contents, by use of charging electrodes which have been exposed previously to the flow of suspended particles for a considerable length of time.

It may be seen from the data in Fig. 7.10 that current output appears not to be a linear function of catalyst content. There are a number of reasons for this. First of all, there exists for each amount of catalyst an optimum flow rate for which the current output is a maximum. The data in Fig. 7.10 represent the maximum current output obtainable from our cell configuration as a function of catalyst content. Maximum current output implies maximum frequency and efficiency of contact of suspended particles with the charging electrodes. Some of the factors which affect contact frequency are the hydrodynamic conditions within the cell, the presence of an appreciable void fraction of hydrogen gas bubbles in the liquid phase due to the great rate of hydrogen production, and the existence of a "clumping" phenomenon with respect to the catalyst

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FIG. 7.10 EFFECT OF OVERVOLTAGE AND CATALYST CONTENT ON OUTPUT OF SUSPENSION ELECTRODE AT OPTIMUM FLOW RATE.

particles. After operation of the suspension electrode for some time, the nickel particles tend to agglomerate in clusters, thus probably affecting the efficiency of contact with the charging electrodes. Because of this phenomenon, reproducible data were difficult to obtain with catalyst contents less than about 10 g per 275 ml solution.

Under conditions where gas evolution is not so vigorous and where clumping of catalyst particles is not too significant, the current output is roughly proportional to catalyst content. This may be seen from the data in Fig. 7.11, which were measured with relatively small catalyst contents on charging electrodes which had been used extensively so that a nearly constant background current was obtained.

Data on the effect of flow rate on current output of the suspension electrode are shown in Fig. 7.12. The current density is roughly proportional to the flow rate for the catalyst content used in these measurements. In this case also, deviations are probably due to lack of uniformity of catalyst distribution (clumping), change of flow pattern within the cell with change in flow rate, variation of void fraction with flow rate, and doubtless other factors which affect particle contact frequency and efficiency.

When the current output of the individual nickel charging electrodes was examined, it was found that the outputs of all electrodes downstream of the first were quite similar. Current output of the first electrode was at least 25% higher than the others, suggesting that the overall performance of the cell could be increased even further by appropriate arrangement and spacing of the nickel charging electrodes. Investigation of configurations capable of higher current output would require larger-scale apparatus than that shown in Figs. 7.8 and 7.9, as well as a power supply of increased capacity. Development of such a device, based on the suspension-electrode principle, for direct electrochemical generation of acid from seawater for acidification pretreatment (pH control and bicarbonate removal) of the seawater intake stream of desalting plants, or for similar applications, is described in Section 9.

FIG. 7.11 EFFECT OF CATALYST CONTENT ON CURRENT OUTPUT OF THE SUSPENSION ELECTRODE.

FIG. 7.12 EFFECT OF SOLUTION FLOW RATE ON CURRENT OUTPUT OF THE SUSPENSION ELECTRODE.

8. THEORY OF THE SUSPENSION ELECTRODE

F. A. Posey and R. E. Meyer

A theoretical model of the suspension electrode, which explained a number of the principal experimental observations, was developed. The current output of the suspension electrode has been found to vary linearly over wide limits with the potential of the charging electrode (Section 7). Observations on current transients due to contact of single catalyst particles with the charging electrode have shown the existence of a maximum in the current transient which cannot be explained simply by charging of the double layer. It was possible to account for these facts by considering current, potential, and concentration transients which would occur at the surface of a hemispherical catalyst particle on contact with the charging electrode. However, detailed predictions of the simple hemisphere model could not account for the variation of current with solution conductivity, for the magnitude of the current observed on individual particles, or for the variation in the shape and time constant of the current transient with change in electrode potential. These and other observations led to the conclusion that most of the current observed during a transient arises from reaction on the internal surfaces of the catalyst particles, which are known to be highly porous and to possess very large surface areas of high catalytic activity. Therefore, a model for the suspension electrode, which considers the nature of the current transient due to reaction in the pores of a catalyst particle in contact with the charging electrode, was developed. In any real system consisting of a catalyst particle in contact with a charging electrode, we expect that both modes of reaction must be considered, but we find that predictions of the pore model are in much better agreement with experiment, as shown below.

8.1 Formulation of the Pore Model

A schematic cross-sectional diagram of a cylindrical pore [radius a (cm) and length l (cm)] in a catalyst particle is shown in Fig. 8.1. The current density of the hydrogen evolution reaction which occurs on the walls of the pore is assumed to be given by the conventional form

FIG. 8.1 SCHEMATIC DIAGRAM OF PORE MODEL FOR THE HYDROGEN EVOLUTION REACTION IN THE SUSPENSION ELECTRODE SYSTEM.

$$j(x,t) = j_o \left[\frac{C(x,t)}{C_o} e^{+\frac{\beta_a F}{RT} \eta(x,t)} - e^{-\frac{\beta_c F}{RT} \eta(x,t)} \right], \quad (1)$$

where $j(x,t)$ is the current density (amp/cm²) at a distance x (cm) from the mouth of the pore ($0 < x < \ell$) at time t (sec), j_o is the exchange current density of the hydrogen reaction (amp/cm²), $C(x,t)$ is the hydroxide-ion concentration (moles/cm³), C_o is the initial hydroxide-ion concentration (moles/cm³), β_a and β_c are dimensionless transfer coefficients of the anodic and cathodic processes, respectively, $\eta(x,t)$ is the interfacial overpotential (volts), and RT/F is the thermal volt equivalent (volts). Since a one-dimensional model is used and $a \ll \ell$ for most cases of interest, any reaction at the base of the pore (at $x = \ell$) may be neglected. For the purposes of this model, we also neglect any current due to reaction on the external surface of the catalyst particle.

The total current flowing from the mouth of the pore, due to the distributed current density along the pore, is given by

$$i(t) = S \int_0^{\ell} j(x,t) dx, \quad (2)$$

where $i(t)$ is total current (amp) at time t , and S is the surface area of the pore per unit length (cm²/cm). In the case of a cylindrical pore of radius a , $S = 2\pi a$. The flow of current $i(t)$ in the bulk electrolyte surrounding the catalyst particle causes an "IR" drop, $\Delta\phi_s(t)$ (volts), which may be assumed to be given to a good approximation by

$$\Delta\phi_s(t) = \frac{i(t)}{\pi a \sigma}, \quad (3)$$

in which σ is the conductivity of the electrolyte (ohm⁻¹cm⁻¹). Equation (3) is the total potential drop due to passage of current $i(t)$ from the mouth of a cylindrical pore of radius a in a medium of conductivity σ , and we use it here as a sufficiently good approximation for our purposes.

During the time of contact of the catalyst particle with the charging electrode (which is held at the constant potential E by a potentiostat), the potential constraint is given by

$$E = \eta(0,t) + \Delta\phi_s(t), \quad (4)$$

where E is the potential of the charging electrode referred to the hydrogen electrode potential (volts), $\eta(0,t)$ is the interfacial overpotential at the pore mouth (volts), and $\Delta\phi_s(t)$ is given by Eq. (3). It is evident that large values of $i(t)$ will cause $\eta(0,t)$ to be small compared to E . This fact is ultimately responsible for the linearity of current-potential curves in the suspension-electrode system, since the reaction in the pores of a catalyst particle is constrained to take place at small values of overpotential, thus implying linearity between current density and overpotential [cf. Eq. (1) with expansion of exponential terms for small $\eta(x,t)$].

We now specify the form of the mass-transport equations for the case of a binary electrolyte (KOH, in this example). The fluxes of potassium and hydroxide ions are assumed to be given by

$$J_K(x,t) = D_K \left[\frac{\partial C_K(x,t)}{\partial x} + C_K(x,t) \frac{F}{RT} \frac{\partial \phi_s(x,t)}{\partial x} \right] \quad (5)$$

and

$$J_{OH}(x,t) = D_{OH} \left[\frac{\partial C_{OH}(x,t)}{\partial x} - C_{OH}(x,t) \frac{F}{RT} \frac{\partial \phi_s(x,t)}{\partial x} \right], \quad (6)$$

where $J_K(x,t)$ and $J_{OH}(x,t)$ are ion fluxes (moles/cm²·sec), D_K and D_{OH} are diffusion coefficients (cm²/sec), $C_K(x,t)$ and $C_{OH}(x,t)$ are ion concentrations (moles/cm³), and $\phi_s(x,t)$ is the inner or Galvani potential of the solution phase inside the pore (volts). The rates of change of ion concentrations are then given by

$$\frac{\partial C_K(x,t)}{\partial t} = D_K \left[\frac{\partial^2 C_K(x,t)}{\partial x^2} + \frac{\partial}{\partial x} \left\{ C_K(x,t) \frac{F}{RT} \frac{\partial \phi_s(x,t)}{\partial x} \right\} \right] \quad (7)$$

and

$$\frac{\partial C_{OH}(x,t)}{\partial t} = D_{OH} \left[\frac{\partial^2 C_{OH}(x,t)}{\partial x^2} - \frac{\partial}{\partial x} \left\{ C_{OH}(x,t) \frac{F}{RT} \frac{\partial \phi_s(x,t)}{\partial x} \right\} \right] - \frac{S}{VF} j(x,t), \quad (8)$$

in which diffusion, migration, and reaction have been considered. The last

term in Eq. (8) is the rate of change of hydroxide-ion concentration due to the hydrogen reaction at the wall of the pore. In Eq. (8), V is the volume of electrolyte inside the pore per unit length (cm^3/cm); for a cylindrical pore $V = \pi a^2$. The parameter V may also be regarded as the average cross-sectional area of electrolyte in the pore.

Combination of Eqs. (7) and (8) with recognition of the electro-neutrality condition for the binary electrolyte, $C_K(x,t) = C_{OH}(x,t) = C(x,t)$, leads immediately to

$$\frac{\partial [C(x,t)/C_o]}{\partial t} = D_o \frac{\partial^2 [C(x,t)/C_o]}{\partial x^2} - \frac{SD_K}{VF(D_K + D_{OH})C_o} j(x,t) \quad (9)$$

and

$$\frac{\partial}{\partial x} \left\{ \left[\frac{C(x,t)}{C_o} \right] \frac{\partial \phi_s(x,t)}{\partial x} \right\} = -\frac{S}{V\sigma} j(x,t) - \frac{RT}{F} \cdot \frac{(D_K - D_{OH})}{(D_K + D_{OH})} \cdot \frac{\partial^2 [C(x,t)/C_o]}{\partial x^2}, \quad (10)$$

in which D_o is the so-called "salt" diffusion coefficient given by $D_o = 2 D_K D_{OH} / (D_K + D_{OH})$ and $\sigma = F^2 (D_K + D_{OH}) C_o / RT$ is the initial conductivity of the electrolyte in the pore ($\text{ohm}^{-1} \text{cm}^{-1}$). As usual in problems of this type, the first term on the right hand side of Eq. (10) is an ohmic contribution to the field and the second term is essentially a junction potential. Since the current density, $j(x,t)$, is expressed in terms of the overpotential, $\eta(x,t)$, one may transform Eq. (10) into a more convenient form by noting that $\partial \phi_s(x,t) / \partial x = -\partial \eta(x,t) / \partial x$, so that Eq. (10) becomes

$$\frac{\partial}{\partial x} \left\{ \left[\frac{C(x,t)}{C_o} \right] \frac{\partial \eta(x,t)}{\partial x} \right\} = \frac{S}{V\sigma} j(x,t) + \frac{RT}{F} \cdot \frac{(D_K - D_{OH})}{(D_K + D_{OH})} \cdot \frac{\partial^2 [C(x,t)/C_o]}{\partial x^2}. \quad (11)$$

Equations (9) and (11) must be solved simultaneously, subject to the appropriate initial and boundary conditions, which are given by

$$C(x,0) = C_o \quad (12)$$

$$\eta(0,t) = E - \frac{S}{\pi a \sigma} \int_0^{\ell} j(x,t) dx \quad (13)$$

$$\left. \frac{\partial \eta(x,t)}{\partial x} \right|_{x=\ell} = 0. \quad (14)$$

The boundary condition of Eq. (13) is obtained by combination of Eqs. (2), (3), and (4). The solution of this set of equations leads ultimately to the current transient which would be observed in such a system and to the current density, concentration, and overpotential distributions in the pore as a function of time. A general analytical solution is not available, due to the nonlinearity of Eqs. (9) and (11) and to the complexity of the boundary condition of Eq. (13), but a number of important special cases, which allow insight into the behavior of the system, may be solved explicitly; these are reported below, together with results of a direct numerical integration obtained by use of a digital computer.

8.2 The Initial Current

At $t = 0$ the concentration in the pore is given by $C(x,0) = C_0$ [cf. Eq. (12)], so that Eq. (11) reduces to

$$\frac{\partial^2 \eta(x,0)}{\partial x^2} = \frac{Sj_0(\beta_a + \beta_c)F}{V\sigma RT} \eta(x,0), \quad (15)$$

where it has been assumed that the exchange current density (j_0) is large enough so that exponentials in Eq. (1) may be expanded to first-order terms [$\eta(x,0) \ll RT/F$]. In this case it can also be shown that the boundary condition of Eq. (13) becomes

$$\eta(0,0) = E + \frac{V}{\pi a} \cdot \frac{\partial \eta(x,0)}{\partial x} \Big|_{x=0}. \quad (16)$$

Solution of Eq. (15) with the conditions of Eqs. (14) and (16) then leads to

$$\eta(x,0) = E \frac{\cosh [\gamma(1 - \frac{x}{\ell})]}{\cosh(\gamma) + \frac{V}{\pi a \ell} \sinh(\gamma)} \quad (17)$$

for the potential distribution in the pore at $t = 0$, where the dimensionless parameter γ is given by

$$\gamma = \sqrt{\frac{Sj_0 \ell^2 (\beta_a + \beta_c) F}{V\sigma RT}}. \quad (18)$$

We find on further manipulation that the initial current is given by

$$i(0) = E \cdot \frac{V\sigma\gamma}{\ell} \cdot \frac{\sinh(\gamma)}{\cosh(\gamma) + \frac{V\gamma}{\pi a \ell} \sinh(\gamma)} \quad (19)$$

One notes immediately that the initial current is directly proportional to E , the potential of the charging electrode; this is true whenever the potential drop in the bulk of the solution, $\Delta\phi_s(t)$, constrains the reaction in the pores of a catalyst particle to proceed at small overpotentials [cf. Eq. (4)]. For moderately large values of the exchange current density (j_0), i.e., when γ is somewhat greater than unity, Eq. (19) becomes approximately

$$i(0) \approx E \frac{\sqrt{i_0} \sqrt{\frac{V\sigma}{\ell}} \sqrt{\frac{(\beta_a + \beta_c)F}{RT}}}{1 + \frac{\sqrt{i_0}}{\pi a \sigma} \sqrt{\frac{V\sigma}{\ell}} \sqrt{\frac{(\beta_a + \beta_c)F}{RT}}}, \quad (20)$$

where $i_0 = S j_0 \ell$ is the total exchange current (amp) in the pore. This relation shows that over a certain range of operation, especially for large values of solution conductivity, the initial current will be proportional to the square root of the solution conductivity. As mentioned before, such a relationship has been observed repeatedly in experimental studies on the current transients which occur during contact of individual catalyst particles with the charging electrode, and we have until now lacked a theoretical interpretation of this phenomenon.

8.3 The Complete Current Transient

Solutions of Eqs. (9) and (11), together with the initial and boundary conditions of Eqs. (12) to (14), have been obtained by numerical integration using parameters thought to be typical of those in our experimental measurements. Figure 8.2 shows the current transient for reaction in a cylindrical pore calculated for a particular set of parameters, which are given in the figure. One notes the existence of a maximum in the current transient; this type of transient occurs frequently, as mentioned before. The maximum in the current appears at approximately 10^{-4} sec, a value which is quite typical of those observed experimentally. The initial current is slightly larger than that predicted by Eq. (19) because $\eta(0,t)$ is somewhat greater than RT/F for the chosen

FIG. 8.2 CALCULATED CURRENT TRANSIENT FOR HYDROGEN REACTION IN CYLINDRICAL PORE OF CATALYST PARTICLE IN SUSPENSION-ELECTRODE SYSTEM.

parameters. The increase in current corresponds to the increase in solution conductivity with time inside the pore as a consequence of the production of hydroxide ions by the (cathodic) hydrogen evolution reaction. Increase of solution conductivity allows the current-density distribution to penetrate to greater depths along the pore, thus enhancing the total current output. With time, however, the increase in hydroxide-ion concentration increases the rate of the anodic process to such an extent that the net (cathodic) current density begins to decrease. This explanation of the origin of the maximum in the current transient is quite similar to that based on a simple hemisphere model derived earlier, differing only in the nature of the geometric constraint.

The change of overpotential with time during the course of the transient is shown in Fig. 8.3, where a dimensionless time variable, defined by $\tau = D_o t / \ell^2$, has been used. The maximum in the current transient occurs in this case when $\tau \approx 0.1$. The corresponding variation of the current density distribution with time is shown in Fig. 8.4. Reaction inside the pore is propagated in a "wave," in a manner very similar to charging of the double layer in a porous or capillary electrode.

8.4 Case of Excess Inert Electrolyte (Constant Conductivity)

The mass-transport relations may be solved explicitly for quantities of interest in the case of a large excess of inert electrolyte, so that solution conductivity may be assumed to be approximately constant during the course of a transient due to the hydrogen evolution reaction in the pores of a catalyst particle. In this case, in order to linearize the mass-transport relations, one must assume that j_o is large enough so that $\eta(x,t) \ll RT/F$ at all times during the transient and also that the rate of the anodic process does not depend on overpotential but only on the hydroxide-ion concentration, $C(x,t)$. Thus, the rate law of Eq. (1) becomes

$$j(x,t) \approx j_o \left(\left[\frac{C(x,t)}{C_o} \right] - 1 + \frac{\beta_c F}{RT} \eta(x,t) \right) \quad (21)$$

on setting $\beta_a = 0$ and expanding exponentials to first-order terms. We

FIG. 8.3 CALCULATED VARIATION OF OVERPOTENTIAL WITH TIME IN CYLINDRICAL PORE OF CATALYST PARTICLE..

FIG. 8.4 CALCULATED VARIATION OF CURRENT DENSITY WITH TIME IN CYLINDRICAL PORE OF CATALYST PARTICLE.

then assume for simplicity that diffusion and migration are negligible compared to reaction, and obtain

$$\frac{\partial [C(x,t)/C_o]}{\partial t} = - \frac{S}{VFC_o} j(x,t) \quad (22)$$

and

$$\frac{\partial^2 \eta(x,t)}{\partial x^2} = \frac{S}{V\sigma} j(x,t) \quad (23)$$

instead of Eqs. (9) and (11). Equation (22) gives the rate of change of hydroxide-ion concentration due to the interfacial reaction, and Eq. (23) may be recognized as a form which has been used extensively for calculating potential and current distributions in porous and capillary electrode systems.

Equations (22) and (23) must be solved simultaneously with the previously stated boundary conditions of Eqs. (12) to (14). For this case Eq. (13) may be simplified to

$$\eta(0,t) = E + \frac{V}{\pi a} \cdot \frac{\partial \eta(x,t)}{\partial x} \Big|_{x=0}, \quad (24)$$

which will be recognized to be a generalization of Eq. (16). Use of the method of Laplace transforms leads to

$$\overline{i(s)} = E \frac{\gamma \sigma V}{\ell} \frac{\sinh \left[\gamma \sqrt{\frac{s}{s+\epsilon}} \right]}{\sqrt{s(s+\epsilon)} \left[\cosh \left[\gamma \sqrt{\frac{s}{s+\epsilon}} \right] + \left(\frac{a}{\ell} \right) \gamma \sqrt{\frac{s}{s+\epsilon}} \sinh \left[\gamma \sqrt{\frac{s}{s+\epsilon}} \right] \right]} \quad (25)$$

for the current transform, where s is the Laplace parameter (sec^{-1}) and ϵ (sec^{-1}) is a parameter defined by

$$\epsilon = \frac{Sj_o}{VFC_o} = \frac{i_o}{VFC_o \ell} \quad (26)$$

which is equal to the ratio of the exchange current in the pore to the total coulombs available for reaction from the hydroxide-ion "reservoir." The parameter γ appearing in Eq. (25) is equal to that defined by Eq. (18) when $\beta_a = 0$.

Inversion of Eq. (25) leads to the current transient

$$i(t) = E \cdot \frac{\sigma \gamma^2 V}{\ell} \cdot 2 \sum_m \frac{e^{-\frac{m^2 \epsilon t}{m^2 + \gamma^2}}}{(m^2 + \gamma^2) [m^2 (\frac{a}{\ell})^2 + (\frac{a}{\ell}) + 1]}, \quad (27)$$

where the summation extends over all values of m , the positive roots of

$$(\frac{a}{\ell}) m \cdot \tan(m) = 1. \quad (28)$$

One notices immediately from Eq. (27) that the current transient for the case of constant solution conductivity does not exhibit a maximum, and this is also in agreement with experimental observation. Instead the current is a monotonic decreasing function of time.

In most cases of interest the ratio of pore radius to length is small, so that $(a/\ell) \ll 1$; hence solutions of Eq. (28) are given to a good approximation by $m = (n + 1/2)\pi$, where $n = 1, 2, \dots, \infty$. The current transient then becomes

$$i(t) = E \cdot \frac{\sigma \gamma^2 V}{\ell} \cdot 2 \sum_{n=0}^{\infty} \frac{e^{-\frac{(n + \frac{1}{2})^2 \pi^2 \epsilon t}{[(n + \frac{1}{2})^2 \pi^2 + \gamma^2]}}}{[(n + \frac{1}{2})^2 \pi^2 + \gamma^2]}. \quad (29)$$

At $t = 0$, the exponential term in Eq. (29) is equal to unity, and one can show by suitable transformations that the initial current is given by

$$i(0) = E \sqrt{\frac{\beta F}{RT}} \sqrt{\frac{\sigma V}{\ell}} \sqrt{i_0} \cdot \tanh(\gamma). \quad (30)$$

We may conclude that when the exchange current in a pore system of constant conductivity is large, the initial current will be proportional to the square root of the conductivity and, of course, directly proportional to the potential of the charging electrode (E). On the other hand, if the situation should arise that the exchange current is very small (small γ), then the initial current (for the case of small E only) would be given by

$$i(0) = E \cdot \frac{\beta F}{RT} \cdot i_0, \quad (31)$$

which is simply the equation for the polarization curve of the interfacial reaction alone when all potential gradients in the solution phase (both in the pore and in the bulk electrolyte) are negligible, so that the current is independent of conductivity. We have never observed this case with particles having sufficient catalytic activity to cause significant enhancement of the hydrogen evolution reaction in the suspension-electrode system.

One can see from Eqs. (27) or (29) that the "time constant" (θ , sec) for the reaction in the pore system will be given approximately by

$$\theta \approx \frac{\ell}{V\sigma} \left[\frac{\beta_c F}{RT} (V F C_o \ell) \right] = R_o C_R. \quad (32)$$

The quantity $R_o = \ell/(V\sigma)$ is simply the resistance of the electrolyte in the pore and $C_R = \beta_c F (V F C_o \ell)/(RT)$ is essentially a "reaction capacity." We find by comparison of values of the reaction capacity with values of the double-layer capacity which would reasonably be expected in systems of this type that current due to charging of the double layer can generally be neglected compared to current due to the interfacial (Faradaic) reaction.

For the parameters used in calculation of the results of Figs. 8.2 to 8.4, we find that $\theta \approx 10^{-4}$ sec, in good agreement with the results of the more exact computation of the transient in the case of the binary electrolyte.

The current from the suspension electrode consists of the total coulombs per unit time due to reaction of the sum of all the particles which contact the charging electrode. The current output thus depends on the contact time of particles with the charging electrode as well as on the other variables mentioned above. We find by integration of Eq. (29) that the charge due to reaction of a single pore in a catalyst particle (for $a/\ell \ll 1$) is given by

$$q(t) = E \cdot \frac{\sigma \gamma^2 V}{\ell} \cdot \frac{2}{\pi^2} \sum_{n=0}^{\infty} \frac{\left[1 - e^{-\frac{(n + \frac{1}{2})^2 \pi^2 \epsilon t}{[(n + \frac{1}{2})^2 \pi^2 \gamma^2]}} \right]}{(n + \frac{1}{2})^2}. \quad (33)$$

For very short contact times, Eq. (33) reduces, as expected, to

$$\lim_{t \rightarrow 0} q(t) = i(0) \cdot t, \quad (34)$$

where $i(0)$ is given by Eq. (30). But if the charging transient is essentially complete during the time of contact of particle and charging electrode, the total charge due to reaction is given by

$$q(\infty) = E \cdot \frac{\beta F}{RT} (V F C_o \ell), \quad (35)$$

in which the term $(V F C_o \ell)$ is the total coulombs available for reaction from the hydroxide-ion "reservoir" [cf. Eq. (26)]. In all cases the number of coulombs due to reaction in the pore system depends linearly on E , for constant contact time. Therefore one can surmise that the total current output of the electrode system, which would be the summation of the coulombs per unit time due to reaction of all pores in a particle and of all particles which collide with the charging electrode, will also be directly proportional to E , as found experimentally.

One should note that the conclusions drawn from the present theoretical treatment do not depend on the unique form of the rate law of Eq. (1). Alternative reaction mechanisms, such as those involving adsorbed hydrogen atoms on the catalyst surface, can also lead to transients having properties similar to those discussed above and to similar relations among output current, electrode potential, solution conductivity, etc.

We have not considered here the events which take place on the surface and in the pores of a catalyst particle after contact with the charging electrode is broken. Immediately following loss of contact, the over-potential on the surface and in the pores of the particle will tend to return to zero, corresponding to the state of equilibrium which normally exists on isolated catalyst particles in the solution phase. One of the interesting aspects of the suspension-electrode system is that reaction proceeds on the surface and in the pores of a particle both during and following contact with the charging electrode. Nevertheless the total charge passed during contact is equivalent (by Faraday's law) to the total amount of net reaction which takes place both during and after contact.

Optimum utilization of the potentialities of the suspension-electrode system will require a knowledge of the time required for a particle to return to the equilibrium state which exists prior to impact with the charging electrode.

9. DEVELOPMENT OF A DEVICE FOR PRETREATMENT OF SEAWATER FOR pH CONTROL AND BICARBONATE REMOVAL

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Acidification of the seawater feed stream in various types of desalination plants is commonly carried out in order to convert scale-forming bicarbonates to carbon dioxide, which is subsequently removed from the stream; thus, one of the principal sources of scale on heat-transfer surfaces is readily eliminated. Addition of mineral acids (H_2SO_4 or HCl) is conventionally employed for the purpose, somewhat more than 100 ppm H_2SO_4 being required to neutralize the bicarbonate content of normal seawater (approx $2.3 \times 10^{-3} \text{ M HCO}_3^-$). Convenient and economical use of mineral acid additions may not always be possible for future large desalting plants because of location and quantities of acid required. During the past biennium we have developed an (on-site) electrochemical method for seawater pretreatment which not only provides an alternative to use of mineral acids but produces bicarbonate-free, acidified seawater which can then be further used for treatment (acidification, followed by removal of CO_2) of additional incoming seawater. We describe in this Section the construction and operation of a prototype electrochemical cell and the other associated components of the pretreatment system, and we also present a brief summary of results of a number of experimental tests carried out with various modes of operation of the system.

A schematic diagram of the principal components of the prototype electrochemical pretreatment system is shown in Fig. 9.1. The electrochemical cell, to be described in more detail below, is based on concentric cylindrical geometry (not indicated in Fig. 9.1), with a central anode compartment (D in Fig. 9.1) separated from the surrounding cathode compartment (F) by a porous separator (E). There are several unique aspects of this electrochemical device which allow acidification and bicarbonate removal to be carried out more conveniently and efficiently than possible with a comparable acid-generation device described in the literature.¹ These will become evident during the following description of the mode of operation of the device.

1. L. H. Shaffer and R. A. Knight, J. Electrochem. Soc. **116**, 1595 (1969).

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FIG. 9.1 DIAGRAM OF ELECTROCHEMICAL DEVICE FOR SEAWATER PRE-TREATMENT. A, seawater intake; B, acid outlet; C, base outlet; D, anode compartment; E, porous separator; F, cathode compartment; G, settling tank; H, anolyte pump; I, catholyte pump; J, gas saturator; K, auxiliary H₂ source and pressure regulator; L, anolyte exit filter.

Incoming seawater enters the cathode loop, consisting of a pump (I), the cathode compartment (F), and a settling tank (G). The cathode assembly has a number of stainless steel rods for the working-electrode surfaces, as indicated in the cell cross section in Fig. 9.2 (cf. B). The seawater in the cathode loop is circulated at a relatively high rate compared to the rate of acid (and/or base) output of the system. The cathode reaction is production of hydrogen gas and hydroxide ions at the stainless steel electrode surfaces. Hydroxide ions react with magnesium ions in the seawater very near the cathode surfaces and would ordinarily tend to form a tight coating of $\text{Mg}(\text{OH})_2$ on the cathode surfaces, thus preventing further reaction and causing a large increase in the applied voltage necessary to drive the required current through the cell. However, the problem of solid hydroxide deposition on the cathode surfaces was solved by employing a fluidized bed of small Pyrex-glass spheres (5-mm diameter) in the cathode compartment. The quantity of glass spheres and the flow rate of the solution in the cathode loop ensure that complete fluidization up to the top of the cell assembly is maintained by the catholyte flow. The scouring action of the fluidized bed of glass spheres very efficiently removes the hydroxide deposit from the stainless steel cathode surfaces, thus allowing continuous operation of the cathodes without fouling and without the necessity for using ion-selective membranes.¹

Continued production of hydroxide ions raises the pH of the solution in the cathode loop until bicarbonate ions are converted into carbonate ions, which then precipitate with the excess calcium ions ($\sim 10^{-2} \text{ M Ca}^{2+}$) in the seawater as CaCO_3 [with some co-precipitated $\text{Mg}(\text{OH})_2$]. Precipitated CaCO_3 deposits at the bottom of the settling tank (G in Fig. 9.1) for withdrawal from the system as desired. More efficient precipitation may be obtained under some conditions by use of a column (not shown in Fig. 9.1) packed with short lengths of glass tubing (or other configuration) on which the precipitate can accumulate and thus provide easy nucleation for further precipitation. Essentially carbonate-free seawater is forced into the anode compartment through the porous separator, which consists (cf. Fig. 9.2) of a porous polypropylene tube (average pore size, 60μ) surrounded by a fire-hose jacket. The porous separator allows easy passage of electrolyte and current, but prevents significant penetration

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FIG. 9.2 CROSS SECTION OF CYLINDRICAL ELECTRODE SYSTEM. A, Pyrex pipe (3-in.); B, stainless steel rod cathodes (1/8-in.); C, catholyte space (with fluidized bed of 5-mm glass spheres); D, fire-hose jacket (1-in. ID); E, porous polypropylene (3/4-in. ID); F, anolyte space (with palladium catalyst suspension); G, splined Lucite cylinder for anode support; H, platinum spiral anode.

of precipitated CaCO_3 [and $\text{Mg}(\text{OH})_2$] into the anode compartment or, contrariwise, of anode catalyst into the cathode compartment (see below).

The anolyte loop contains a pump (H in Fig. 9.1), a device for saturation of the anolyte with hydrogen gas (J), a filter for acidified, carbonate-free product water (L), and the anode assembly itself (F, G, and H in Fig. 9.2). In the present mode of operation, the anode assembly uses a suspension electrode. In Section 7 we described the operation of a suspension electrode, especially for use as a cathode for the hydrogen evolution reaction in alkaline solutions. It was shown that, in some cases, reactions may be carried out more efficiently using a suspension electrode than with practically any other electrode configuration. The suspension electrode consists of a charging electrode in contact with a rapidly stirred (or pumped) suspension of finely divided, catalytically active conducting material (such as Pt or Pd black, or Raney Ni). In the present application we use a suspension of palladium black as an anode for the oxidation of dissolved molecular hydrogen. The molecular hydrogen for the anode reaction, which leads to acidification of the anolyte ($\text{H}_2 \rightarrow 2 \text{H}^+ + 2 \text{e}^-$), is the gaseous product of the cathode reaction, which is extracted from the cathode loop and fed into the anolyte by use of a gas saturator (J, Fig. 9.1). Dissolved molecular hydrogen is rapidly absorbed by the circulating palladium suspension and is subsequently oxidized in the anode compartment of the cell, producing acid. Construction of the anode assembly is indicated in Fig. 9.2; a spiral of 14-gauge platinum wire (H) is wound on a splined Lucite cylinder (G). The hydrogen-containing palladium suspension is circulated through the annular anode space (F) where it contacts the platinum anode and reacts to produce acid in the anolyte. Use of a filter arrangement (L, Fig. 9.1), incorporating a length of porous polypropylene tubing, has been found to be desirable in order to prevent loss of catalyst particles in the acidified product water. Use of this method of operation circumvents the old problem of anode attrition due to corrosion reactions at high anode potentials in electrolysis of seawater and chloride solutions, since the anode operates very near the reversible hydrogen potential of the anolyte. The great reduction in cell voltage (and thus in power consumption) is brought about by circulation of the hydrogen gas (product of the cathode reaction) to

the anode compartment where it serves as the anodic reactant. As a result, the stoichiometry of the overall cell reaction is changed from the ordinary electrolysis of water into its elements (i.e., $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$) to the ionization of water (i.e., $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$); the latter process requires a much smaller potential than the former. In addition, the configuration described operates on a hydrogen-feedback cycle, which avoids the use of the expensive, catalyzed electrode structures and membrane materials described in ref. (1).

The electrochemical pretreatment device, operating as described above on a hydrogen-feedback cycle, has been tested on artificial seawater feed (initial pH = 7.5) under a variety of operating conditions. Flow rates of product water (pH = 2.5 to 3.0, depending on applied current) varied over the range 1 to 4 liter/hr (~6 to 25 gal/day) with the small test cell. Analyses for inorganic-carbon content showed that the initial bicarbonate content of 28 ppm had been essentially completely removed (less than 1 ppm remaining), along with ~20% of the initial calcium (~400 ppm) and several percent of the initial magnesium. This performance was observed using only 5 to 10 g palladium black catalyst in the ~200 ml volume of the anolyte loop, and power consumption was observed to be on the order of 0.5 kWhr/1000 gal of acidified product water. The acidified product water could of course be used to treat more incoming seawater, releasing CO_2 and forming weakly acidified seawater, as is now done with mineral acid additions.

Catalyst life appears so far to be reasonably long, although after many days of operation with a single charge, regeneration may be required. It is possible that, in large-scale operation, continuous addition and withdrawal of catalyst from the anode system for regeneration could be carried out. Base (pH ~10) from the cathode loop (cf. C in Fig. 9.1) might be used to adjust acidified, decarbonated seawater to the proper pH for optimum service life of the structural materials of the desalting plant. Moreover, it should be possible to incorporate (uncatalyzed) porous carbon cathodes at appropriate points in the system to remove electrochemically all dissolved oxygen from the process stream, and thus allow a reduction in size of the deaeration units, which are now an important and expensive part of desalting plants. Future tests of the apparatus are

needed, of course, to provide information on optimum operating conditions so that the feasibility of scaling up the device to practical levels can be realistically assessed.