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REVERSIBLE DEPOSITION OF METALS ON SOLID ELECTRODES BY VOLTAMMETRY WITH LINEARLY VARYING POTENTIAL

It has been shown by extending the treatment of BERZINS AND DELAHAY that for the reversible deposition of metals on solid electrodes by voltammetry with linearly varying potential, the plot of $\log(i_p - i)$ vs. E approaches linearity over the approximate current range $0.5-0.9 i_p$, the slope being $2.2 nF/RT$. The experimental data for the reduction of Ag(I) in 1 M KNO₃ at silver and pyrolytic graphite electrodes, the reduction of Fe(II) in molten LiF-B₂F₆ (66-34 mole%) and LiF-NaF-KF (46.5-11.5-42 mole%) at 500°, and Ni(II) in LiF-NaF-KF (46.5-11.5-42 mole%) at pyrolytic graphite electrodes, agreed satisfactorily with the theory.

G. MAMANTOV, D. L. MANNING AND J. M. DALE,
J. Electroanal. Chem., 9 (1965) 253-259

THE ENTRY CORRECTION IN THE ELECTROSTATIC CHARGING OF FLUIDS FLOWING THROUGH PIPES

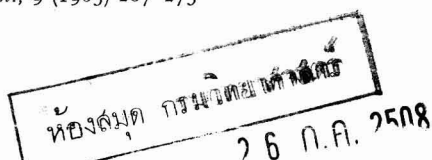
Entry effects are shown to exist when a liquid acquires electrostatic charge upon flowing through a pipe. The streaming current measured in a pipe of finite length is normally converted to that which would develop in a pipe of infinite length by using a formula which neglects entry effects. A correction to this formula for the case when entry effects cannot be assumed to be negligible is demonstrated. The numerical value of the correction is determined for a specific example of turbulent flow in the experimental apparatus used.

E. T. HIGNETT AND J. C. GIBBINGS.
J. Electroanal. Chem., 9 (1965) 260-266

A STUDY OF THE FORMATION OF THE FIRST ELECTROLYTIC PRODUCT IN STEP-WISE PROCESSES IN CHRONOPOTENTIOMETRY

The relation between the amount of the first electrolytic product formed and the time of electrolysis for the case of step-wise processes in chronopotentiometry is extracted from a previously derived equation. The relation predicts that the net formation of the first electrolytic product continues beyond the first transition time and ceases at a time equal to twice the first transition time when $n_1 = n_2$. Beyond this time there is net consumption of the first electrolytic product. The theory was tested with the oxygen system in which the quantity of hydrogen peroxide formed was determined as a function of electrolysis time. The significance of this refinement for alternate path reactions in chronopotentiometry is discussed.

D. H. EVANS,
J. Electroanal. Chem., 9 (1965) 267-275



MODIFICATION OF THE SURFACE AREA OF PLATINUM ELECTRODES BY THE APPLICATION OF SINGLE PULSES

The application of a pulse sequence to a platinum electrode at elevated temperatures leads to variation in the estimated surface roughness, as calculated from hydrogen-deposition or "oxygen-adsorption" measurements. These variations are brought about during the reduction of surface "oxygen". Relatively rapid reduction causes an increase in roughness, whereas relatively slow reduction leads to a decrease in roughness. By use of the proper signal, it is possible to adjust the roughness factor of the surface to any value somewhat above 1.0 and below the values corresponding to platinum "blacks".

S. GILMAN,
J. Electroanal. Chem., 9 (1965) 276-281

THE MECHANISM OF CATHODIC REDUCTION OF OXYGEN AT A SMOOTH, ACTIVE PLATINUM ELECTRODE IN ALKALINE SOLUTION

Using a rotating disk electrode with a ring, it can be shown that the surface oxide of platinum retards the reduction of oxygen to H_2O_2 in alkaline solution, and that this reaction can occur rapidly only where the surface is free from the surface oxide. The accelerating action of the surface oxide of platinum on the reduction of H_2O_2 is explained by the singularity of this process, in that the H_2O_2 diffusing to the platinum surface is partially decomposed catalytically there, and the reduction of H_2O_2 is represented by the reduction of the oxygen formed in the catalytic decomposition. The accelerating action of the surface oxide of platinum therefore arises because the speed of the catalytic decomposition of H_2O_2 at an oxidized platinum electrode is larger than that at a reduced platinum electrode.

L. MÜLLER AND L. N. NEKRASOV,
J. Electroanal. Chem., 9 (1965) 282-289

THE DETERMINATION OF IONIC ZINC IN SEA-WATER BY ANODIC STRIPPING VOLTAMMETRY USING ORDINARY CAPILLARY ELECTRODES

Direct determinations, with an extremely high sensitivity, of zinc in samples of sea-water, have been carried out using a cathode-ray polarograph operating for anodic polarography. The apparatus is designed to use special capillary electrodes with a very long dropping time in order to obtain a pre-electrolysis of about 60 sec.

The persistence of the cathode-ray tube is long enough to facilitate synchronized operation which eliminates any difficulty with the time measurements.

Reproducible stirring conditions must be used during the pre-electrolysis to obtain a good enrichment of the drop with zinc. The apparatus allows for compensation of the current due to the double-layer charge and of the slope due to the growth of the drop. A concentration of about 1 $\mu\text{g/l}$ (about $1.5 \times 10^{-8} M$) can be measured reproducibly.

The measurements have been carried out on sea-water samples from the Ligurian Sea (Mediterranean).

G. MACCHI,
J. Electroanal. Chem., 9 (1965) 290-298

DETERMINATION OF MIXTURES BY SINGLE-SWEEP OSCILLOPOLAROGRAPHY

Single-sweep oscillopolarography was used to analyze multi-component systems by initiating voltage sweeps from the diffusion plateau of the preceding reaction at a dropping mercury electrode. Both anodic and cathodic sweeps were employed. The procedure is applicable to the determination of a trace of a substance in the presence of a large excess of a more easily reduced substance.

R. A. OSTERYOUNG AND E. P. PARRY,
J. Electroanal. Chem., 9 (1965) 299-304

FILM FORMATION ON PYROLYTIC GRAPHITE ELECTRODES

It has been shown that electrochemical or chemical oxidation with a strong oxidant, such as Ce(IV), results in the formation of a film on the surface of pyrolytic graphite. The film produced anodically differs electrochemically from the film produced chemically, although in both cases reduction of the film is observed at $\sim +.5$ V vs. the saturated calomel electrode. The reduction of the film apparently proceeds irreversibly. Attempts to study the film by high voltage electron diffraction were unsuccessful. The nature of the film has not been determined.

G. MAMANTOV AND D. B. FREEMAN,
F. J. MILLER AND H. E. ZITTEL,
J. Electroanal. Chem., 9 (1965) 305-310

UNEVEN CURRENT DISTRIBUTION ON THE SURFACE OF A DROPPING MERCURY ELECTRODE AND ITS POSSIBLE RELATION TO MAXIMA OF THE FIRST KIND

The downward movement of a growing mercury drop electrode is taken into account in a treatment in which all other assumptions inherent in the Ilkovič treatment are retained. It is shown that the downward movement results in a non-uniform distribution of mass transport towards the electrode. On this basis, also taking into account specific adsorption, a tentative explanation is given for the origin of polarographic maxima of the first kind. Finally some difficulties with the polarographic determination of rates of electrode reactions are briefly discussed.

R. DE LEVIE,
J. Electroanal. Chem., 9 (1965) 311-320

POLAROGRAPHIC STUDIES OF THE PYRIDINE COMPLEXES OF ZINC AND CADMIUM IN AQUEOUS MEDIUM

(*Short Communication*)

V. K. SHARMA AND J. N. GAUR,
J. Electroanal. Chem., 9 (1965) 321-325

THE MECHANISM OF CHARGE TRANSFER AT ELECTRODES

(*Short Communication*)

J. O'M. BOCKRIS AND D. B. MATTHEWS,
J. Electroanal. Chem., 9 (1965) 325-327

REVERSIBLE DEPOSITION OF METALS ON SOLID ELECTRODES BY VOLTAMMETRY WITH LINEARLY VARYING POTENTIAL*

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(Received October 30th, 1964)

The equations that are often used for reversibility tests and for the determination of n -values in the case of current-voltage curves for the deposition of metals at solid micro-electrodes are:

$$E = E_M^o - \frac{2.3 RT}{nF} \log \frac{k_s}{f_s} + 2.3 \frac{RT}{nF} \log (i_l - i) \quad (1)$$

and

$$E = E_{\frac{1}{2}} + \frac{2.3 RT}{nF} \log \frac{i_l - i}{i} \quad (2)$$

where E = applied potential i_l = limiting current i = current at any applied potential k_s = a constant, the value of which depends on the conditions of mass transfer** f_s = activity coefficient of the metal ion

and the remaining symbols have their usual significance.

For the application of eqn. (1) which was proposed by KOLTHOFF AND LINGANE², it is assumed that the metal is deposited on the electrode at constant activity without alloy formation, and that the reaction proceeds reversibly. The failure of eqn. (1) to be generally applicable (*e.g.*, fused salts) has been pointed out by DELIMARSKII AND MARKOV³. Using the assumption that the deposited metal forms a surface alloy with the metal electrode, they arrive at eqn. (2) which is the same as the Heyrovský-Ilkovič equation. Several references for examples of the applicability of this equation are listed. The applicability of these equations is also discussed by LIU, JOHNSON AND LAITINEN⁴.

* Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

** For a reversible diffusion-controlled process, $k_s = nFAD^{1/2}/\pi^{1/2}t^{1/2}$ where D is the diffusion coefficient of the metal ion and t is the time elapsed from the beginning of electrolysis; for a reversible convection-controlled process with some value δ of the Nernst diffusion layer thickness, $k_s = D/\delta$. These results can be readily obtained from eqns. (3-34) and (9-15), ref. 1.

MUELLER AND ADAMS⁵ have concluded that for voltammetry with linearly varying potential for the case in which both the reactants and products are soluble, the plot of E vs. $\log [(i_p - i)/i]$ ($i_p =$ peak current) has a slope of about $0.056/n$ at 25° . This corresponds to $2.2 RT/nF$.

NICHOLSON AND SHAIN⁶ have recently published a comprehensive paper on the theory of stationary electrode polarography (voltammetry with linearly varying potential). Using the theoretical data from Table 1 of their paper, it is concluded that the plot of $(E - E_{1/2})n$ vs. $\log [(\sqrt{\pi}x(at))^{\max} - \sqrt{\pi}x(at)]/\sqrt{\pi}x(at)^*$ (which is equivalent to the plot nE vs. $\log [(i_p - i)/i]$) is linear in the approximate range 0.35 – $0.70 i_p$, the slope being 0.044 instead of 0.056 , which is the value obtained by MUELLER AND ADAMS⁵.

THEORETICAL

The above relationships are not applicable to current–voltage curves obtained by rapid scan voltammetry for the deposition of metals at solid micro-electrodes under diffusion-controlled conditions. Such peak-shaped polarograms are defined by the equation:

$$i = \frac{2}{\pi^{1/2}} \frac{n^{3/2} F^{3/2}}{R^{1/2} T^{1/2}} AC^0 D^{1/2} v^{1/2} \Phi \left[\left(\frac{nF}{RT} vt \right)^{1/2} \right] \quad (3)$$

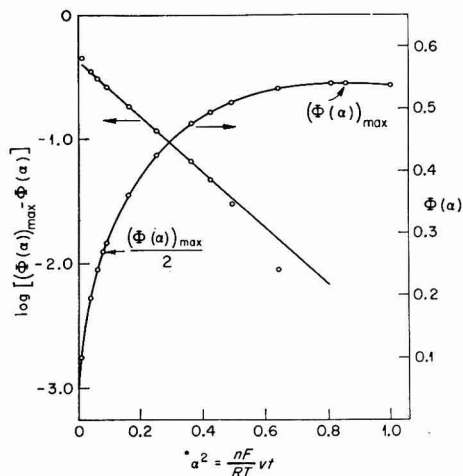


Fig. 1. Plots of $\log [(\Phi(\alpha))_{\max} - \Phi(\alpha)]$ and $\Phi(\alpha)$ vs. α^2 .

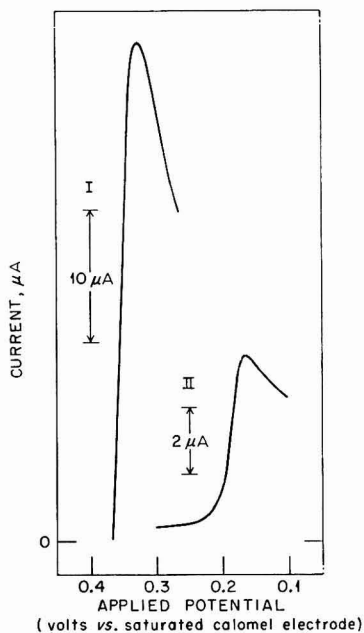


Fig. 2. Current–voltage curves for the reduction of Ag(I) in $1 M \text{KNO}_3$ at 25° . (I), Silver electrode, 0.08 cm^2 ; Ag(I) concn., 1.27 mM ; scan rate, 3 V/min . (II), Pyrolytic graphite electrode, 1.16 cm^2 ; Ag(I) concn., 0.0404 mM ; scan rate, 0.3 V/min .

* $x(at)$ represents a function of $nFvt/RT$.

which was derived by BERZINS AND DELAHAY⁷ where

- v = rate of voltage scan (V/sec);
 A = electrode area (cm²);
 C^o = concentration of electroactive species (moles cm⁻³);
 D = diffusion coefficient (cm²/sec);
 t = scan time, (sec).

The term $\Phi[(nF/RT)vt]^{\frac{1}{2}}$, noted as $\Phi(\alpha)$, represents the function $\Phi(\alpha) = e^{-\alpha^2} \int_0^\alpha e^{-z^2} dz$. Values of $\Phi(\alpha)$ for different values of α have been tabulated by MILLER AND GORDON⁸.

It is of interest to obtain a relationship from eqn. (3) between the applied electrode potential, E , and $\log(i_p - i)$ in similarity to the Kolthoff-Lingane equation. Because an explicit relationship appears to be difficult to obtain, the problem was approached in the following manner. In voltammetry with linearly varying potential, the electrode potential may be expressed as

$$E = E_i - vt \quad (4)$$

where E_i is the initial potential and $-vt$ is negative for a cathodic process. It may also be shown from eqn. (3) that

$$\log(i_p - i) = \text{constant} + \log([\Phi(\alpha)]_{\text{max}} - \Phi(\alpha)) \quad (5)$$

It follows that a plot of $\log([\Phi(\alpha)]_{\text{max}} - \Phi(\alpha))$ vs. α^2 (*i.e.* $(nF/RT)vt$) is equivalent to the theoretical curve for $\log(i_p - i)$ vs. E displaced only by constant terms. Plots of $\Phi(\alpha)$ vs. α^2 and $\log([\Phi(\alpha)]_{\text{max}} - \Phi(\alpha))$ vs. α^2 are shown in Fig. 1.

It is apparent that a plot of $\log([\Phi(\alpha)]_{\text{max}} - \Phi(\alpha))$ vs. α^2 approaches linearity in the approximate range 0.5 $[\Phi(\alpha)]_{\text{max}}$ to 0.9 $[\Phi(\alpha)]_{\text{max}}$. The slope of this line corresponds to a slope of 2.2 nF/RT for the plot of $\log(i_p - i)$ vs. E over the approximate current range 0.5 i_p –0.9 i_p , or 1/2.2 RT/nF for a plot of E vs. $\log(i_p - i)$.

It was noted by MATSUDA AND AYABE⁹ that for the reversible cathodic electrode process involving a soluble product, $\Delta E = E_p - E_{p/2} = -0.057/n$ V, at 25°; or at any temperature, $\Delta E = \pm 2.2 RT/nF$, the minus sign being applicable to a cathodic process and the plus sign to an anodic process*.

A relationship for $\Delta E = E_p - E_{p/2}$ for the reversible deposition of an insoluble substance can be obtained by noting that at E_p , $[(nF/RT)vt]^{\frac{1}{2}} = 0.9241$ and at $E_{p/2}$, $[(nF/RT)vt]^{\frac{1}{2}} = 0.2855$. Therefore, it follows that $\Delta E = E_p - E_{p/2} = -0.77 RT/nF$. For the reversible deposition of an insoluble substance at 25°, $\Delta E = 0.020/n$. Thus, the current-voltage curve rises more sharply than the curve for reactions involving soluble products.

EXPERIMENTAL AND RESULTS

The reduction of Ag(I), a known reversible system, was chosen to test the applicability of the $\log(i_p - i)$ vs. E relationship. Current-voltage curves for the reduction of Ag(I) in 1 M KNO₃ at a pyrolytic graphite and silver indicator electrode at 25° are shown in Fig. 2. The corresponding $\log(i_p - i)$ vs. E plots are shown in Fig. 3, where the experimental points are compared to a line having the theoretical slope of 2.2 nF/RT .

* NICHOLSON AND SHAIN⁶ obtained a value of $\Delta E = \pm 2.20RT/nF$.

A theoretical plot of $\log(i_p - i)$ vs. E represented by the solid points is also shown in Fig. 3, curve I. The values of $\log(i_p - i)$ were calculated from eqn. (5) after evaluating the constant term where $A = 0.08 \text{ cm}^2$, $C^0 = 1.27 \times 10^{-6} \text{ moles/cm}^3$, $v = 0.05 \text{ V/sec}$, and $D = 1.56 \times 10^{-5} \text{ cm}^2/\text{sec}^{10}$. The E -values for each point were obtained from the relationship $\alpha^2 = (nF/RT)vt$.

Further knowledge of the applicability of the $\log(i_p - i)$ vs. E plots was gained by analyzing representative current-voltage curves for the reduction of Fe(II) and Ni(II) in molten fluorides^{11,12} at 500°; a pyrolytic graphite indicator electrode sheathed in boron nitride was used. Current-voltage curves and $\log(i_p - i)$ vs. E plots are shown in Figs. 4, 5 and 6, respectively. A summary of n -values calculated from the slope of the $\log(i_p - i)$ vs. E plots is presented in Table 1. Also shown in Table 1 are experimental and theoretical values for the difference between the peak potential and the half-peak potential.

TABLE 1

EXPERIMENTAL VALUES OF n AND $E_p - E_{p/2}$ FOR THE REDUCTION OF Ag(I) IN 1 M KNO₃ AT 25° AND OF Ni(II) AND Fe(II) IN MOLTEN FLUORIDES AT 500°

Concn. of Ag(I) (mM)	Scan rate (V/min)	n^a	$E_p - E_{p/2}$ (V)
1.27 ^b	0.5	1.1	0.021
1.27 ^b	2	0.9	0.025
1.27 ^b	3	1.0	0.024
0.04 ^c	0.3	1.1	0.023
0.04 ^c	1.5	1.1	0.030
0.06 ^c	0.3	1.0	0.036
0.08 ^c	0.3	0.9	0.036
0.08 ^c	3	0.9	0.042
0.10 ^c	1.5	0.9	0.044
		Theor. 1.0	0.020
Concn. of Ni(II) (mM)			
2.7 ^d	0.5	1.7	0.045
	0.5	1.7	0.045
	1.0	1.9	0.035
		Theor. 2.0	0.026
Concn. of Fe(II) (mM)			
9.5 ^d	1.0	1.7	0.045
	10	1.9	0.045
8.0 ^e	5.0	1.8	0.032
		Theor. 2.0	0.026

^a n -values were obtained by equating the experimentally obtained slope of $\log(i_p - i)$ vs. E to $2.2 nF/RT$; ^b silver electrode; ^c pyrolytic graphite electrode; ^d LiF-KF-NaF (46.5-11.5-42 mole%) solvent; ^e LiF-BeF₂ (66-34 mole%) solvent.

DISCUSSION AND CONCLUSIONS

In general, the agreement of the experimental results with theory appears to

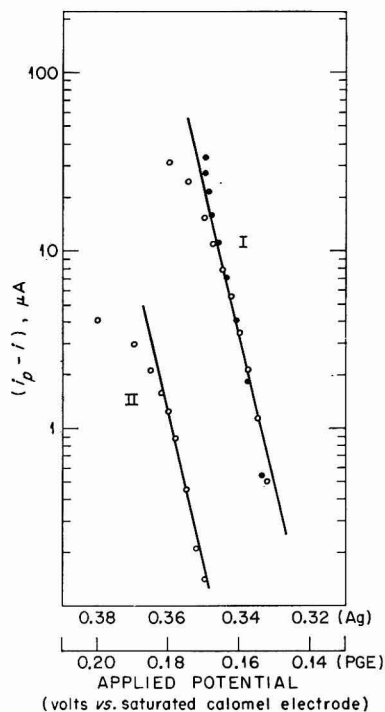


Fig. 3. Plots of $\log(i_p - i)$ vs. E for reduction of Ag(I) in 1 M KNO_3 at 25° . (I), Silver electrode; (II), pyrolytic graphite electrode. \circ , experimental; \bullet , theoretical.

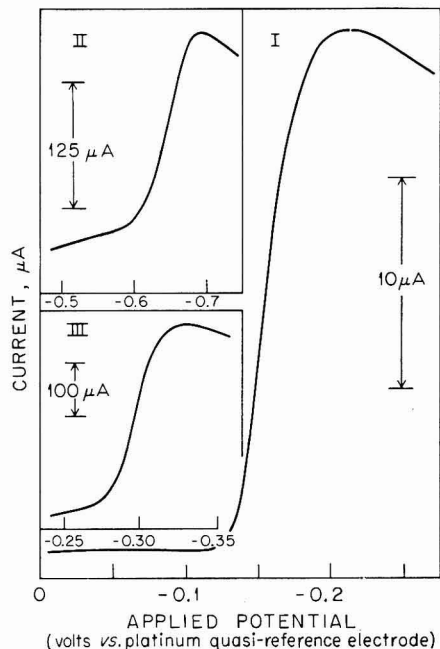


Fig. 4 Current-voltage curves for the reduction of Fe(II) and Ni(II) at pyrolytic graphite in molten fluorides at 500° . Electrode area $\sim 0.08\text{ cm}^2$. (I), 2.3 mM Ni(II) in LiF-NaF-KF ; scan rate, 0.5 V/min . (II), 9.5 mM Fe(II) in LiF-NaF-KF ; scan rate, 10 V/min . (III), 8.0 mM Fe(II) in LiF-BeF_2 ; scan rate, 5 V/min .

be quite satisfactory. It is of interest to note that for the $\log(i_p - i)$ vs. E plots, the portion of the curve which more nearly exhibits the expected $2.2 nF/RT$ slope extends from about $0.7 i_p$ to approximately $0.9 i_p$ as compared to $0.5 [\Phi(\alpha)]_{\max}$ to $0.9 [\Phi(\alpha)]_{\max}$ for the plot of $\log([\Phi(\alpha)]_{\max} - \Phi(\alpha))$ vs. α^2 . The linear portion of the $\log(i_p - i)$ vs. E plots for the reduction of Ag(I) at the silver electrode in general extended to lower fractions of the peak current than for any of the reductions at pyrolytic graphite. A comparison of the $E_p - E_{p/2}$ values for the different reductions indicates that the steepest current-voltage curves were obtained using the silver electrode.

These results can probably be best explained by following the reasoning of BERZINS AND DELAHAY⁷ that the activity of the deposited metal varies during the initial stages of electrolysis. Thus unit activity of the deposited metal is approached further along the wave, whereas in the theoretical treatment, unit activity is assumed from the start. Even for the reduction of Ag on a silver electrode, it appears that the activity of the freshly deposited Ag is different from that of the electrode material.

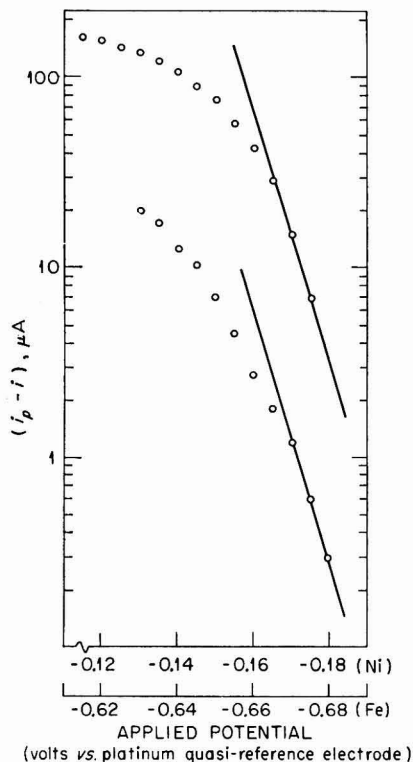


Fig. 5. Plots of $\log(i_p - i)$ vs. E for reduction of Fe(II) (upper line) and Ni(II) (lower line) in molten LiF-NaF-KF.

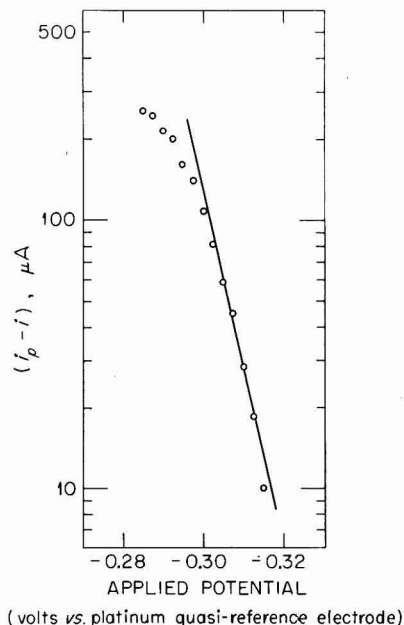


Fig. 6. Plots of $\log(i_p - i)$ vs. E for reduction of Fe(II) in molten LiF-BeF₂.

Attempts to record current-voltage curves for Ag without stripping off the deposited Ag from previous experiments did not significantly improve the results.

In conclusion, it is believed that the agreement of the experimentally determined $\log(i_p - i)$ vs. E plots with the theoretical $\log([\Phi(\alpha)]_{\max} - \Phi(\alpha))$ vs. α^2 relation is reasonable in view of the uncertainty in the activity of the deposited metal. It is also felt that such an analysis of current-voltage curves when viewed in conjunction with anodic stripping experiments can be of considerable value for the estimation of n -values, and for checking the reversibility of electrode reactions which involve metal depositions.

SUMMARY

It has been shown by extending the treatment of BERZINS AND DELAHAY that for the reversible deposition of metals on solid electrodes by voltammetry with linearly varying potential, the plot of $\log(i_p - i)$ vs. E approaches linearity over the approximate current range $0.5-0.9 i_p$, the slope being $2.2 nF/RT$. The experimental

data for the reduction of Ag(I) in 1 M KNO₃ at silver and pyrolytic graphite electrodes, the reduction of Fe(II) in molten LiF-BeF₂ (66-34 mole%) and LiF-NaF-KF (46.5-11.5-42 mole%) at 500°, and Ni(II) in LiF-NaF-KF (46.5-11.5-42 mole%) at pyrolytic graphite electrodes, agreed satisfactorily with the theory.

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THE ENTRY CORRECTION IN THE ELECTROSTATIC CHARGING OF FLUIDS FLOWING THROUGH PIPES

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INTRODUCTION

A liquid having a sufficiently low conductivity can become electrically charged when flowing past a solid surface. Convection of this charge by the motion of the liquid provides what has been called the streaming current. Recent reviews of this phenomenon include those of KLINKENBERG AND VAN DER MINNE¹ and WINTER²; it has been examined theoretically by KOSZMAN AND GAVIS³ and a dimensional analysis has been made by GIBBINGS AND HIGNETT⁴. Most of the experimental investigations have been concerned with the flow of liquids in circular pipes and the effect of the length of such a pipe upon the electrical charge generated is discussed in this paper.

Analyses by various workers^{1,3,5} of the dependence of the streaming current upon the pipe length vary in the degree of approximation that is incurred. The least restrictive treatment is given by KOSZMAN AND GAVIS³ but all three lead to a relation for the streaming current, i_s , generated in a pipe of finite length, of the form:

$$i_s = i_\infty(1 - e^{-J}) \quad (1)$$

where i_∞ is the streaming current generated in a pipe of infinite length and where the dimensionless group,

$$J \equiv \frac{L\lambda}{u\epsilon_r\epsilon_0}$$

is a particular example of the dimensionless group $l\lambda/u\epsilon_r\epsilon_0$. Here L is the pipe length, λ is the electrical conductivity and ϵ_r the dielectric constant of the liquid which is flowing at a mean velocity u . The physical significance of this dimensionless group (it is indicative of the ratio of the conduction current to the convection current) has been previously demonstrated⁴.

All three analyses assume a fully-developed uniform flow condition, no account being taken of the entrance-length region. Thus, as has been pointed out by KLINKENBERG AND VAN DER MINNE¹, these analyses are only valid for large length: diameter ratios. The entrance-region effect is important because the charge can lie close to the

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wall³ where the velocity is changing rapidly. In this region the boundary layer velocity profile is changing rapidly and the rate of charging may be correspondingly affected.

The number of independent variables controlling the streaming current must now include a second length so that both the shape and the size of the system is described. Dimensional analysis⁴ shows that a further dimensionless group is required. If the two representative lengths are chosen as the pipe length L , and the pipe diameter d , then the extra dimensionless group can be formed as the length: diameter ratio L/d . To investigate the effect of the length: diameter ratio all the remaining variables must be held constant. This entails fixing (i) the electrical and mechanical properties of the fluid⁴; (ii) other shape parameters such as the shape at the entrance of the pipe together with its immediate surroundings and also the pipe surface roughness⁵; and (iii) the flow conditions.

Experiments to investigate the effect of pipe length^{1,6} have shown that variation of the streaming current with pipe length does not result in a constant value for i_{∞} using eqn. (1)¹ and it was concluded that this equation does not completely express the dependence of the streaming current upon the pipe length. The experiments of KOSZMAN AND GAVIS⁶ were performed with pipes of an approximately constant length: diameter ratio of about 200. Thus the derivation of the length effect was dependent upon a separate assessment of the diameter effect and the pipe-entry conditions were of no significance.

An experimental investigation to determine the accuracy of eqn. (1) is described in this report.

EXPERIMENTAL

The apparatus used in these experiments was constructed at the University of Liverpool⁵ for use in general investigations of the static electrification of flowing hydrocarbon liquids. It consisted of a stainless steel reservoir from which the liquid was allowed to flow through a capillary tube, before discharging into an insulated stainless steel receiver. The reservoir and the stainless steel capillary tube were both electrically earthed. The streaming current was determined by measuring the current flowing from the receiver to earth.

A constant head of liquid was maintained by rotating the reservoir and capillary tube about a horizontal axis through the lower end of the tube (Fig. 1). The flow rate was determined by weighing the quantity of liquid discharged in a measured time. The experimental conditions were restricted to the turbulent flow regime, the Reynolds number being varied over a small range. A single capillary tube of initial length 2.00 m and internal diameter 5.975 mm was used in the experiments. The procedure was to obtain a set of streaming-current measurements for flow rates over a Reynolds number range 4000–5000 and then to shorten the tube and repeat the measurements. To maintain constant inlet flow conditions, the tube was shortened *in situ* by cutting a length from the discharge end. This end was then freed from any burrs or sharp edges. The apparatus was adjustable so that the axis of rotation was always through the lower tip of the capillary tube. Lengths of 2.00, 1.50, 1.00 and 0.75 m were used in the experiments. The liquid used was kerosene with a conductivity of approximately 8.4×10^{-12} mho m⁻¹. The conductivity of the liquid was measured

before and after the streaming current measurements, for each tube length. The extreme divergence of these measurements was 10% of the above value.

The measuring techniques are described in further detail by HIGNETT⁵ and in a manuscript at present in preparation.

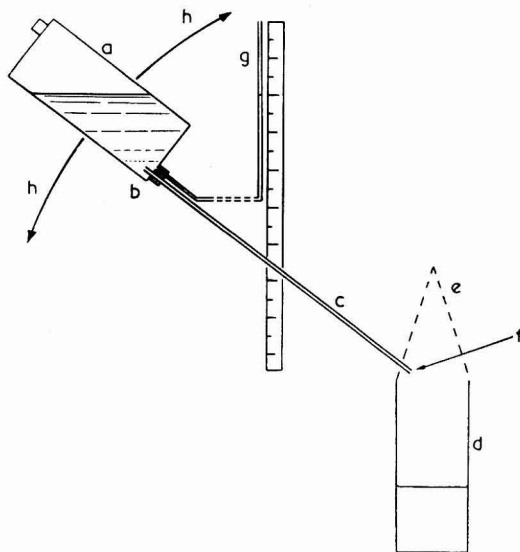


Fig. 1. Liquid flow charging apparatus: (a), reservoir (capacity 10^{-2} m³); (b), polythene plug; (c), stainless steel tube; (d), receiver (capacity 10^{-2} m³); (e), P.T.F.E. suspension; (f), axis of rotation through end of tube; (g), manometer; (h), direction of rotation.

RESULTS AND DISCUSSION

The streaming-current measurements are plotted in Fig. 2 for each of the four tube-lengths. Corresponding values of i_{∞} are plotted in Fig. 3. It is apparent that the relation of eqn. (1) does not satisfactorily represent the effect of pipe length because i_{∞} is not obtained as a single curve. The results indicate that as the length of a pipe is increased, i_{∞} at a chosen Reynolds number tends to an asymptotic value. The streaming current, i_s , has been plotted against e^{-J} in Fig. 4 for Reynolds numbers of 4000 and 5000, mean values being taken from Fig. 2. Each of the curves in Fig. 4 can be expressed in the form

$$i_s = A - Be^{-J}$$

where A and B are constants. This indicates that as the length tends to infinity the streaming current tends to a finite value equal to A . Calling the asymptotic value i_{∞}' , the above relation can be written in the form

$$i_s = i_{\infty}'[1 - e^{-(J-J_0)}] \quad (2)$$

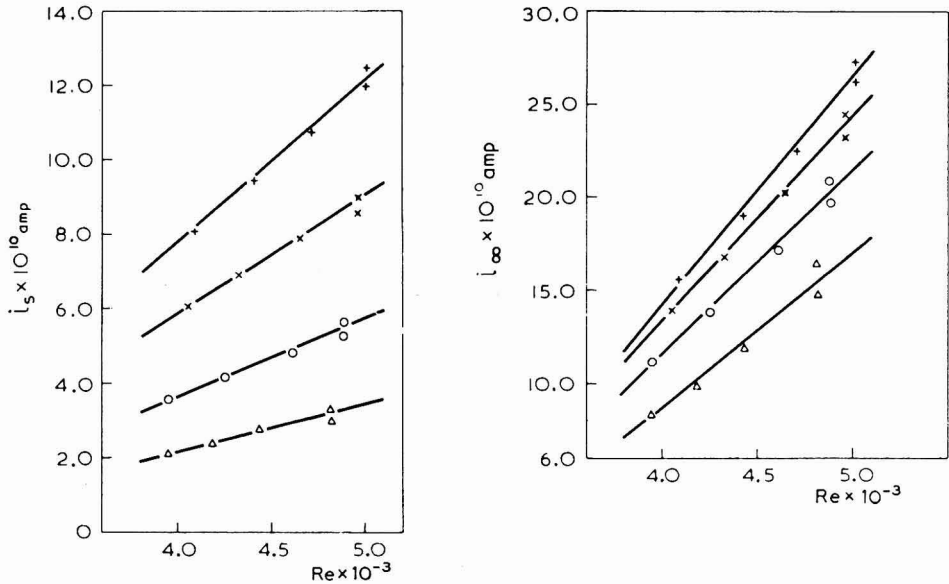


Fig. 2. The variation of i_s with Reynolds number for turbulent flow in tubes of different lengths but of the same diameter (+), $L = 2.00$ m, $L/d = 335$; (x), $L = 1.50$ m, $L/d = 251$; (o), $L = 1.00$ m, $L/d = 167$; (Δ), $L = 0.75$ m, $L/d = 126$.

Fig. 3. The variation of i_∞ with Reynolds number calculated from eqn. (1).

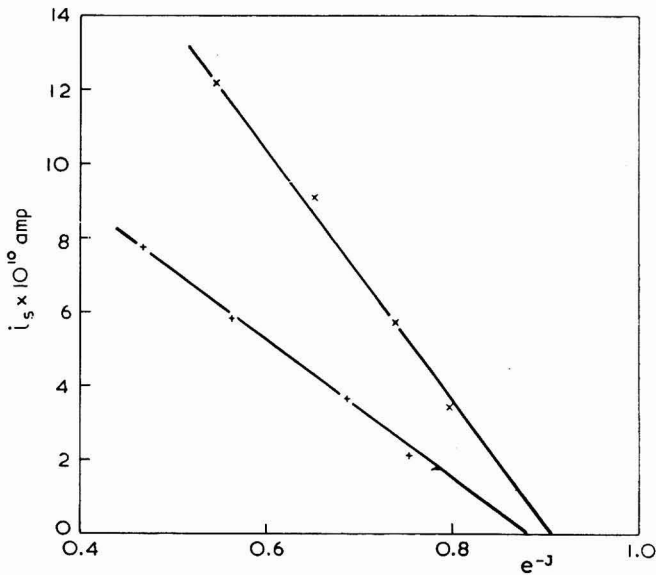


Fig. 4. Variation of i_s with e^{-J} for the following Reynolds numbers: (+), $Re = 4000$; (x), $Re = 5000$.

where

$$i_{\infty}' e^{J_0} = B.$$

Using the expression

$$J_0 \equiv \frac{L_0 \lambda}{u \varepsilon_r \varepsilon_0},$$

L_0 can be regarded as a correction to the true length of the pipe which will account for the effect of the entry region before the flow becomes fully developed.

The value of L_0 can be calculated, for each Reynolds number value, from the intercept on the axis at zero-streaming current in Fig. 4. The mean of the two calculated values of L_0 is 0.325 m giving a length: diameter ratio of

$$L_0/d = 54.4.$$

This value is not expected to be a universal constant because the connection between the charging rate and the velocity gradient at the wall would make the streaming current dependent upon the flow conditions at the entry to the pipe. Thus such parameters as the inlet turbulence level, the time average flow conditions at the inlet, the pipe entry shape, the Reynolds number, and the degree of smoothness of the pipe surface might well affect the value of L_0/d . In the present experiments these parameters were maintained constant with the exception of the Reynolds number, the effect of which is apparently negligible.

In Fig. 5, i_{∞}' is plotted as a function of the Reynolds number using eqn. (2) and the value of 54.4 for L_0/d . This shows a satisfactory collapse of the results over the full range of Reynolds number. The slight discrepancies in the results obtained using the tube of length 0.75 m can be explained as follows. One of the difficulties in conducting these experiments was to keep the conductivity of the liquid at a constant

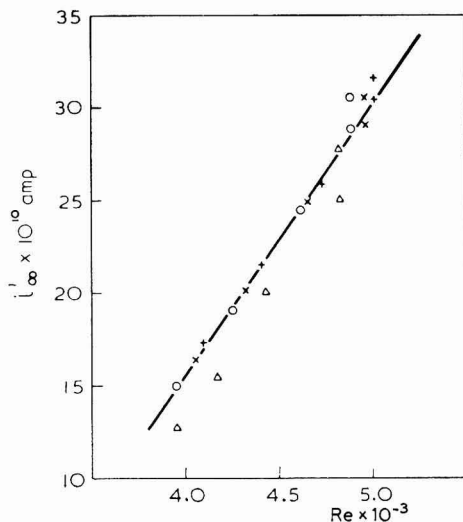


Fig. 5. Variation of i_{∞}' with Reynolds number calculated from eqn. (2). $L_0/d = 54.4$.

value. Liquids of conductivity in this range tend to be affected by minute quantities of impurity which may be dissolved during the experiments causing a change in the conductivity; the conductivity of the liquid also changes during storage. In the present case the conductivity varied up to 2% during the measurements at tube lengths of 2.00, 1.50 and 1.00 m but following a delay of some weeks between these measurements and those conducted with a tube length of 0.75 m, the conductivity had decreased by approximately 8%. For this reason, the conductivity used in calculating the results was taken as the average of the measured values when making streaming-current measurements at tube lengths of 2.00, 1.50 and 1.00 m. It was expected that the value of i_{∞} calculated for the tube of length 0.75 m would fall below the results obtained for the other tubes⁵.

CONCLUSIONS

An electrokinetic entry effect has been demonstrated in that the streaming current developing in a pipe may be expressed as that which would develop in a pipe of infinite length using the formula

$$i_s = i_{\infty}' [1 - e^{-(J-J_0)}]$$

where

$$J - J_0 \equiv (L - L_0)\lambda/4\pi\epsilon_r\epsilon_0.$$

The correction length, L_0 , has been found to be equal to 54.4 pipe diameters. This figure is not expected to be a universal constant nor to apply to laminar flow; the experiment has been designed to demonstrate the existence of entry effects in electrokinetic phenomena and their possible expression by the general formula given above.

NOTATION

- A constant;
- B constant;
- d internal diameter of pipe;
- i_s streaming current in a pipe;
- i_{∞} streaming current in an infinitely long pipe (eqn. 1);
- i_{∞}' streaming current in an infinitely long pipe (eqn. 2);
- J eqn. (1);
- J_0 eqn. (2);
- l length;
- L pipe length;
- L_0 correction length for entry effects;
- Re Reynolds number;
- u mean flow velocity;
- ϵ_r dielectric constant of the liquid;
- ϵ_0 permittivity of free space;
- λ electrical conductivity of the liquid.

ACKNOWLEDGEMENT

This work was carried out as part of a program of research into electrostatic effects arising from fluid dynamic causes suggested by Professor J. H. PRESTON to whom the authors express their gratitude.

SUMMARY

Entry effects are shown to exist when a liquid acquires electrostatic charge upon flowing through a pipe. The streaming current measured in a pipe of finite length is normally converted to that which would develop in a pipe of infinite length by using a formula which neglects entry effects. A correction to this formula for the case when entry effects cannot be assumed to be negligible is demonstrated. The numerical value of the correction is determined for a specific example of turbulent flow in the experimental apparatus used.

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A STUDY OF THE FORMATION OF THE FIRST ELECTROLYTIC PRODUCT IN STEP-WISE PROCESSES IN CHRONOPOTENTIOMETRY

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Considerable attention has been directed to the theory of step-wise processes in chronopotentiometry¹⁻⁶. In the general case the substance O can be reduced first to the substance R_1 , then to R_2 as in the following scheme:



E_1 and E_2 are the standard reduction potentials for half-reactions (1) and (2). The theory applies also to step-wise oxidations with appropriate modification of the reaction scheme.

The current up to the first transition time, τ_1 , is due only to electrode reaction (1). It has generally been stated^{1,3-6} that after the first transition time the current is due only to reactions (2) and (3). It will be shown in this communication that reaction (1) continues after the first transition time, its rate decreasing to zero at a definite point after the first transition time, after which net reduction of R_1 commences. The significance of this clarification on previously reported work of the author is discussed.

EXPERIMENTAL

The electrolysis cell was a modification of one reported earlier⁷. The working electrode was a 25-cm² mercury pool to which electrical contact was made by means of a platinum wire sealed into the base of the cell. The diameter of the pool was large enough to ensure that the surface was planar and the walls of the cell served to shield the edges of the electrode so that conditions for semi-infinite linear diffusion were obtained. The auxiliary electrode compartment was removed. A platinum disc electrode, the diameter of which was slightly less than that of the cell, was made from 0.004-in. platinum foil. A heavy platinum wire was heat-welded to the disc; it served both as an electrical contact and as a means of supporting the platinum disc electrode 4-6 mm above the mercury pool so that it was just touching the surface of the electrolysis solution. A notch was cut in the periphery of the disc to allow the reference electrode probe to be positioned close to the mercury pool and to permit direct bubbling of oxygen gas through the thin layer of solution. The experimental apparatus was set up in a ground-floor room in order to eliminate vibrational effects.

The electrolysis circuit used a bank of three 45-V "B" batteries in series as a power supply and a large resistor to control the magnitude of the constant current⁷.

The current used in this study was 7.5 mA; it was found to be constant to within 1% for the duration of the electrolysis. Chronopotentiograms were recorded using a Sargent Model MR recording potentiometer with a full-scale response time of 1 sec.

Since oxygen oxidizes the mercury electrode, it was found necessary to pre-polarize³ the mercury electrode at the potential (+0.2 V *vs.* S.C.E.) at which mercury is not appreciably oxidized and oxygen not appreciably reduced, *i.e.*, at the point of zero current as indicated by a polarogram of oxygen in the supporting electrolyte used, 0.1 *F* acetic acid–0.1 *F* sodium acetate. Without pre-polarization the rest potential of the electrode was +0.27 V *vs.* S.C.E., and the first transition time too long, due to concomitant reduction of oxidized mercury species. With pre-polarization at +0.2 V *vs.* S.C.E. the τ_2/τ_1 ratio was 3.02 ± 0.07 from four trials, compared to the theoretical value of three¹.

Hydrogen peroxide was determined by measuring the absorbance of the yellow titanium–peroxide species obtained when a hydrogen peroxide solution is added to a solution of titanyl sulfate in sulfuric acid. The molar absorptivity of the titanium–peroxide species was obtained by adding an acidic hydrogen peroxide solution to an excess of the titanium reagent, 0.03 *F* titanyl sulfate in 3.6 *F* sulfuric acid. The hydrogen peroxide had been standardized *vs.* ceric sulfate using ferrous-*o*-phenanthroline as indicator. After dilution of the titanium–peroxide species to the concentration range of interest, $1 \cdot 10^{-6}$ – $2 \cdot 10^{-5}$ *F* peroxide, the absorbance at 405 m μ was measured on the Beckman DU spectrophotometer using 10-cm fused silica cells, an appropriate blank as reference and a slit-width of 0.05 mm. Beer's law was obeyed in this region and the molar absorptivity was found to be 729 l mole⁻¹ cm⁻¹, compared to about 730 reported elsewhere⁸.

The titanium reagent was prepared by dissolving 5 g of $K_2TiO(C_2O_4)_2 \cdot 2H_2O$ (Fisher, technical grade recrystallized from water) in 100 ml of sulfuric acid, warming to destroy oxalic acid and finally diluting to 500 ml with water.

To determine hydrogen peroxide in the electrolysis solution, a 10-ml portion of 0.1 *F* acetic acid–0.1 *F* sodium acetate was added to the cell, the potential of the mercury cathode was held at +0.2 V *vs.* S.C.E., and oxygen was bubbled through the solution for 10 min. The solution was then allowed to become quiescent for 2 min and a chronopotentiogram was recorded. The platinum anode, gas inlet tube and reference electrode were removed and the solution was removed with a pipette. The surface of the mercury was washed twice with *ca.* 3 ml of water. The process was repeated until reproducible chronopotentiograms were obtained. Then a trial was carried out in which the electrolysis was interrupted at some point on the chronopotentiogram and the solution and washings were added to 2.5 ml of the titanium reagent in a 25-ml volumetric flask. In this operation the platinum anode was removed very carefully to prevent any hydrogen peroxide reaching it and being oxidized by the oxidized platinum surface. The electrolysis product at the anode, molecular oxygen, was innocuous in the determination of hydrogen peroxide.

The absorbances were measured after each solution had been made up to volume with water. The absorbances ranged from 0.034–0.144. An absorbance of 0.007 was observed when the time of electrolysis was zero. This "blank", which was subtracted from all absorbances observed may have been due to a small amount of hydrogen peroxide formed by chemical interaction between oxygen and mercury prior to the electrolysis. The full visible spectrum of the electrolysis solution treated

with titanium reagent was indistinguishable from the spectrum obtained using authentic hydrogen peroxide.

THEORY

BERZINS AND DELAHAY¹ were the first workers to derive the transition-time equation for step-wise processes. They state that after the first transition time, "substance R_1 , which was produced in the first step of the electrolysis, diffuses toward the electrode at which it is reduced . . .". Subsequent authors^{3,4,5} essentially confirm this statement.

BERZINS AND DELAHAY, however, give the following equation for the flux of R_1 at the electrode surface after the first transition time,

$$D_{R_1} \left[\frac{\partial C_{R_1}(x, t)}{\partial x} \right]_{x=0} = \frac{i_0}{F} \left[\frac{1}{n_2} - \frac{n_1 + n_2}{n_1 n_2} \left(\frac{1}{2} + \frac{1}{\pi} \arcsin \frac{2\tau_1 - t}{t} \right) \right] \quad (4)$$

where D_{R_1} is the diffusion coefficient of R_1 , i_0 the current density, F the Faraday and t the time elapsed from the beginning of electrolysis. For certain values of t the flux of R_1 at the electrode surface is *negative*. This means that R_1 is diffusing *away* from the electrode, *i.e.*, there is net electrochemical formation of R_1 . For the case where $n_1 = n_2$, the flux is negative between the first transition time and $t = 2\tau_1$ at which point the

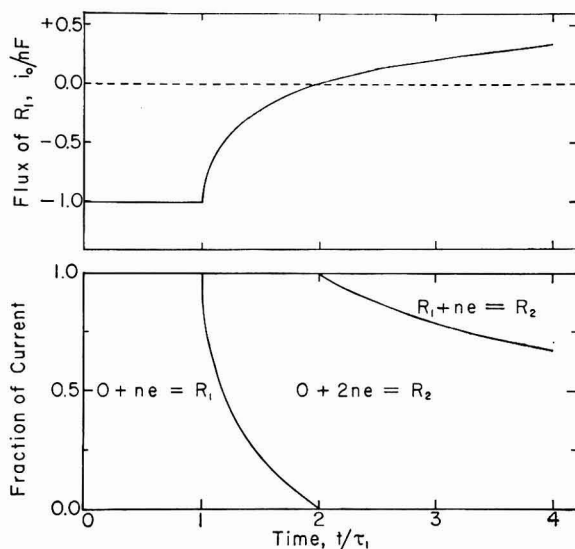


Fig. 1. Top: The flux of R_1 at the electrode surface in units of i_0/nF as a function of the time of electrolysis for the case where $n_1 = n_2$. Note that the flux is negative (R_1 diffusing away from electrode) up to $t/\tau_1 = 2$ and is positive (R_1 diffusing toward electrode) thereafter.

Bottom: Fraction of the electrolysis current due to the three overall electrode reactions as a function of the time of electrolysis for the case where $n_1 = n_2$. The reactions pertain to the area in which they are written. For example, at $t/\tau_1 = 0.75$ all the current is due to the n_1 -electron reduction of O while at $t/\tau_1 = 1.5$ about $1/4$ of the current is due to that reaction and $3/4$ to the $(n_1 + n_2)$ -electron reduction of O .

flux is zero. From that point on, the flux of R_1 at the electrode surface is positive, meaning that there is net reduction of R_1 to R_2 . The flux of R_1 as a function of time is given in Fig. 1 for the case where $n_1 = n_2$.

From the flux of R_1 , the current due to either its formation or consumption can be calculated. A graphical representation of the fraction of the total current due to reactions (1), (2) and (3) is given in Fig. 1 for the case where $n_1 = n_2$.

It is apparent from Fig. 1 that a considerable amount of R_1 is formed after the first transition time contrary to the commonly held view^{1,3-6} that the net formation of R_1 ceases at the first transition time. The time $2\tau_1$, a time during the chronopotentiogram the significance of which has not been previously recognized, is the time when the net formation of R_1 ends and its net reduction begins. Put in more meaningful physical terms, the net quantity of R_1 produced during chronopotentiometric electrolysis increases, reaching a maximum at $2\tau_1$, and declines thereafter. This point of maximum accumulation of R_1 , t_{\max} , depends on the ratio $n_1/(n_1 + n_2)$ and occurs at the time when the flux of R_1 at the electrode surface equals zero. Table 1 summarizes the calculated values of t_{\max} for various values of $n_1/(n_1 + n_2)$.

TABLE 1

CALCULATED VALUES OF THE TIME OF MAXIMUM ACCUMULATION OF R_1 , t_{\max}

n_1	n_2	$n_1/(n_1 + n_2)$	t_{\max}
3 6 etc.	1 2 }	3/4	1.17 τ_1
2 4 etc.	1 2 }	2/3	4/3 τ_1
1 2 etc.	1 2 }	1/2	2 τ_1
1 2 etc.	2 4 }	1/3	4 τ_1
1 2 etc.	3 6 }	1/4	6.82 τ_1

In a recent publication concerning the step-wise reduction of copper(II), PETERS AND CRUSER⁹ conclude on the basis of analogy with current-reversal chronopotentiometry that less than one-third of the copper(I), *i.e.*, R_1 , produced during the first step undergoes reduction in the second step. The net quantity of R_1 reduced in the second step can be calculated by integrating the flux of R_1 at the electrode surface over the time interval encompassed by the second step. Since the only electrochemical reaction during the first step is the formation of R_1 , the quantity of R_1 in moles formed up to τ_1 is simply $i\tau_1/n_1F$, where i is the constant current employed. Graphical integration of the flux of R_1 at the electrode surface demonstrates that $0.27 i\tau_1/n_1F$

additional moles of R_1 are formed between $t = \tau_1$ and $t = 2\tau_1$ and that $0.41 i\tau_1/n_1 F$ moles of R_1 are consumed between $t = 2\tau_1$ and $t = 4\tau_1$, the latter time being the second transition time when $n_1 = n_2$. Thus the overall consumption of R_1 during the second wave is $(0.41 - 0.27) i\tau_1/n_1 F = 0.14 i\tau_1/n_1 F$ which is clearly less than one-third the amount formed in the first step.

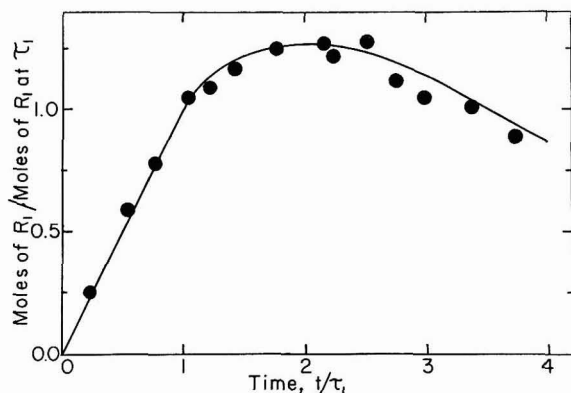


Fig. 2. The ratio of moles of R_1 present at any time to the moles of R_1 present at τ_1 as a function of electrolysis time. The solid curve is the theoretical curve obtained by integration of the curve, flux of R_1 vs. time (top of Fig. 1). Experimental points (taken from Table 2) pertain to the formation of hydrogen peroxide during the step-wise reduction of oxygen.

The net quantity of R_1 produced as a function of the time of electrolysis is given in Fig. 2. The curve rises linearly between $t = 0$ and $t = \tau_1$ since the production of R_1 is the only electrochemical reaction proceeding. The curve between $t = \tau_1$ and $t = 4\tau_1$ was calculated by graphical integration of the flux of R_1 for $n_1 = n_2$. No calculations can be made for times after $t = 4\tau_1$ (the second transition time) since the equation for the flux of R_1 does not hold after that point.

EXPERIMENTAL VERIFICATION

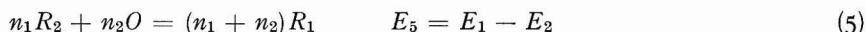
The best method of verifying the foregoing conclusions would be an analysis of the electrolysis products, R_1 and R_2 as a function of elapsed electrolysis time. The analysis could be either instantaneous in which the quantities of R_1 and R_2 would be monitored continuously or a batch analysis, where the electrolysis would be interrupted after various times of electrolysis and the resulting solutions analyzed for R_1 and R_2 . Since no simple instantaneous method of analysis is yet available (see, however, KUWANA, DARLINGTON AND LEEDY¹⁰) the batch analysis procedure was chosen.

An experimental difficulty in such an analysis is that the quantities of the electrolysis products formed in an ordinary chronopotentiometric electrolysis are very small. The concentration of R_1 in a solution resulting from electrolysis to a first transition time of 10 sec with the electroactive species at a concentration of $10^{-3} M$, a diffusion coefficient of $10^{-5} \text{ cm}^2/\text{sec}$ and $n_1 = 1$, would be only $8.9 \times 10^{-8} M$ with a 1-cm^2 planar electrode and a solution volume of 100 cm^3 . One way of increasing the

resulting concentration is to increase the area of the electrode while decreasing the solution volume, *e.g.*, the concentration of R_1 would be $8.9 \times 10^{-6} M$ with the same conditions as above except for an electrode area of 10 cm^2 and a solution volume of 10 cm^3 . Thus the optimal electrode configuration would consist of an electrode of large area covered by a thin layer of solution. The only constraints concerning the thickness of the solution layer are that it should be much greater than the thickness of the diffusion layer so that the condition of semi-infinite diffusion would obtain, and that it should be thick enough that the volume of solution would be sufficient for analysis.

The experimental arrangement chosen consisted of a cylindrical cell with a 25-cm^2 mercury pool covered by 4–6 mm layer of solution. The solution volume was thus 10–15 ml.

A second experimental difficulty concerns the electrochemical system to be studied. In most systems which have two-step chronopotentiograms, the standard reduction potential of reaction (1), E_1 , is more oxidizing (positive) than the standard reduction potential of reaction (2), E_2 . This is the case with copper(II) in chloride media⁹. It follows that the equilibrium constant for the reaction



is greater than one since $E_1 > E_2$. In the case of copper(II) in chloride media, metallic copper will react with copper(II) to produce copper(I). Thus, when the electrolysis is interrupted after the first transition time, copper(II) continuing to diffuse to the electrode will react with metallic copper on the electrode to form copper(I) and the quantity of copper(I) subsequently found by analysis will not represent the copper(I) actually formed by the electrolysis. Such a system could only be used if reaction (5) were very slow.

In other systems which have two-step chronopotentiograms, E_1 is less oxidizing than E_2 and two waves are obtained only because the reduction of R_1 is irreversible, *e.g.*, the reduction of uranium(VI) to uranium(V) to uranium(IV) in acid media^{11,12}. In these cases it follows that R_1 is unstable with respect to disproportionation, *i.e.*, the reverse of reaction (5) is favored. Such systems are also unsuitable because the R_1 found by analysis is less than the amount formed by the electrolysis. This problem can be circumvented if a system is found in which the disproportionation of R_1 is very slow. Such a case is the reduction of oxygen.

Dissolved oxygen produces a two-step chronopotentiogram by its reduction at a mercury cathode¹. The product during the first wave is hydrogen peroxide which disproportionates only very slowly in the absence of catalysts. Two waves are obtained because the reduction of hydrogen peroxide is very irreversible, the over-potential being of the order of 1–1.5 V. One problem with oxygen is its limited solubility, about $10^{-3} M$ in aqueous solutions with an oxygen pressure of one atmosphere. It was found, however, that this concentration was large enough to obtain adequate concentrations of hydrogen peroxide. One must also rely only on an analysis of R_1 since R_2 is the solvent itself (water) so that the amount formed by electrolysis cannot be ascertained.

BERZINS AND DELAHAY¹ used a neutral, unbuffered supporting electrolyte. This was avoided since hydroxide ion is produced in the electrolysis and the pH of the solution in the diffusion layer could be as great as 11 and the base-catalyzed disproportionation of hydrogen peroxide might become appreciable. Instead, an acetate

buffer (0.1 *F* acetic acid–0.1 *F* sodium acetate) was used to maintain a constant, acidic pH. The second wave is not sharply defined in this medium but the first transition time is unambiguous.

Two series of determinations were made, one at a temperature of 29.0° with an average τ_1 of 9.68 sec and one at a temperature of 25.4° with an average τ_1 of 10.07 sec. The pertinent data from these experiments are summarized in Table 2. The

TABLE 2

QUANTITY OF HYDROGEN PEROXIDE FORMED AS A FUNCTION OF TIME OF ELECTROLYSIS IN THE CHRONOPOTENTIOMETRIC REDUCTION OF OXYGEN

25-cm² mercury pool electrode, 0.1 *F* acetic acid–0.1 *F* sodium acetate satd. with oxygen, *i* = 7.5 mA. Theoretical values taken from Fig. 2.

Time of electrolysis, <i>t</i> (sec)	<i>t</i> / τ_1	Ratio of moles of <i>R</i> ₁ at <i>t</i> to moles of <i>R</i> ₁ at τ_1		Error (%)
		Obs.	Theor.	
2.31 ^a	0.23	0.25	0.23	+8.7
5.22 ^b	0.54	0.58	0.54	+7.4
7.77 ^a	0.77	0.78	0.77	+1.3
10.11 ^b	1.04	1.05	1.03	+1.9
12.27 ^a	1.22	1.09	1.13	-3.5
13.83 ^b	1.43	1.17	1.20	-2.5
17.85 ^a	1.77	1.25	1.26	-0.8
20.88 ^b	2.16	1.27	1.26	+0.8
22.53 ^a	2.24	1.22	1.26	-3.2
24.42 ^b	2.52	1.28	1.23	+4.1
27.81 ^a	2.76	1.12	1.19	-5.9
28.98 ^b	2.99	1.05	1.15	-8.7
34.08 ^a	3.39	1.01	1.05	-3.8
36.18 ^b	3.74	0.89	0.95	-6.3
			average	± 4.2

^a $\tau_1 = 10.07$ sec, temp. = 25.4°.

^b $\tau_1 = 9.68$ sec, temp. = 29.0°.

quantity of hydrogen peroxide formed was calculated from the absorbance of the titanium–peroxide species. The data of Table 2 are plotted in Fig. 2 in the form of *t*/ τ_1 (where *t* is the time of electrolysis) *vs.* ratio of peroxide found to the quantity present at the first transition time. The solid curve is the theoretical curve obtained by graphical integration of the flux of *R*₁ in the region $1 \leq t/\tau_1 \leq 4$. For values of *t*/ τ_1 < 1, the quantity of hydrogen peroxide expected increases linearly with *t*/ τ_1 since all the current is due to its formation.

It is clear that more hydrogen peroxide is formed after the first transition time and that the net quantity begins to decrease only after a time near $t = 2\tau_1$. The precision of the data does not permit the assignment of $t = 2\tau_1$ as the maximum point in the curve but such a value is consistent with the data. The experiment clearly demonstrates that statements made on the basis of the earlier conception that the formation of *R*₁ ceases at τ_1 , must be re-examined.

In an earlier communication, EVANS³ treated the case of step-wise reactions in chronopotentiometry in which the product of the first step is not further reducible once it is formed, although the original material can be reduced directly in the second

step. An example of such a system is the reduction of benzaldehyde which is reduced in the first step to hydrobenzoin and in the second step to benzyl alcohol. Hydrobenzoin is not electrochemically reducible to benzyl alcohol. To solve the diffusion problem for this system (the alternate path reaction), use was made of the equations for step current impulses in chronopotentiometry⁴. It was argued that since reaction (1) is the only current-producing reaction up to the first transition time and since reaction (3) is the only current-producing reaction after the first transition time (R_1 not being reducible to R_2), the situation is equivalent to a step current impulse at the first transition time since the electrode reaction changes from an n_1 -electron process to an $(n_1 + n_2)$ -electron process. The assumption made in this argument is the same as the erroneous assumption which was discussed above, *viz.*, the net formation of R_1 ceases at the first transition time and only the $(n_1 + n_2)$ -electron formation of R_2 takes place as well as the n_2 -electron reduction of R_1 when this is possible. From Fig. 1 it is apparent that this only approximates the truth. The net formation of R_1 continues after the first transition time. Thus the analogy to a step current impulse does not hold rigorously, a more gradual change being dictated by Fig. 1.

To what physical situation does the equation derived earlier³ pertain? It would apply to a system where (i) R_1 is not reducible to R_2 and (ii) where the net formation of R_1 ceases abruptly at τ_1 . The good agreement between this equation and the experimental transition time data for benzaldehyde reduction may mean that net formation of hydrobenzoin ceases at τ_1 . This is not the usual case as illustrated in Fig. 1.

What is the transition time equation for the case where (i) R_1 is not reducible to R_2 and (ii) the formation of R_1 continues after τ_1 in the normal fashion as shown in Fig. 1? This question can be answered by examining the lower part of Fig. 1. In such a case the current composition *vs.* time curve would be identical to what is shown up to $t = 2\tau_1$ for $n_1 = n_2$. This is the point where the forbidden reaction (3), the reduction of R_1 to R_2 , should begin. But since it cannot proceed, the reduction of solvent must commence to meet the demands of the constant current, *i.e.*, $t = 2\tau_1$ is the second transition time. Thus for linear diffusion with $n_1 = n_2$, τ_2 equals τ_1 in this more realistic picture, compared to $\tau_2 = 1.78\tau_1$ derived³ with the assumption that the net formation of R_1 ceases at τ_1 .

Can the experimental data obtained for benzaldehyde reduction³ be construed to agree with this equation? Because of the drawn-out nature of the second chronopotentiometric wave, the magnitude of the second transition time depends upon the method of locating the transition time. The time from the beginning of electrolysis to the inflection in the chronopotentiogram was taken as the transition time³. This method of locating the transition time yields longer second transition times and thus larger τ_2/τ_1 ratios than any of the other methods reviewed by RUSSELL AND PETERSON¹³. However, a re-study of the benzaldehyde data indicates that the ratio τ_2/τ_1 approaches 1.78 at short transition times no matter what method is used. The use of the inflection point method produces the best agreement for the dependence of the ratio on the transition time, an effect due to spherical diffusion.

The data for benzaldehyde reduction correspond to the simplified theory, *viz.*, that the formation of R_1 (hydrobenzoin) ceases abruptly at the first transition time. This conclusion could be tested by analyzing the electrolysis solutions for hydrobenzoin as was done for hydrogen peroxide in the present study. The chronopotenti-

metric reduction of benzaldehyde, however, was not satisfactory at mercury pool electrodes³ and the amounts of hydrobenzoin formed at the mercury-drop electrodes which were used would be difficult to detect.

ACKNOWLEDGEMENT

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SUMMARY

The relation between the amount of the first electrolytic product formed and the time of electrolysis for the case of step-wise processes in chronopotentiometry is extracted from a previously derived equation. The relation predicts that the net formation of the first electrolytic product continues beyond the first transition time and ceases at a time equal to twice the first transition time when $n_1 = n_2$. Beyond this time there is net consumption of the first electrolytic product. The theory was tested with the oxygen system in which the quantity of hydrogen peroxide formed was determined as a function of electrolysis time. The significance of this refinement for alternate path reactions in chronopotentiometry is discussed.

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MODIFICATION OF THE SURFACE AREA OF PLATINUM ELECTRODES BY THE APPLICATION OF SINGLE PULSES

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INTRODUCTION

Multipulse potentiodynamic sequences have been used in the study of a variety of adsorbates on platinum¹⁻⁴. It has been observed that the use of the appropriate pre-treatment sequence results in a highly reproducible surface in 1 *N* perchloric acid solution at temperatures of 30 or 60°^{1,2}. This reproducibility is evidenced by reproducibility of the hydrogen-deposition charge sQ_H ^{1,2}, the "oxygen-adsorption" charge, Q_0 ^{1,2}, and the electrode capacitance². The values of these quantities after a fraction of a second following pre-treatment can be reproduced within a few percent for over a year of use of the electrode, and upwards of one thousand operating cycles, for experiments performed only at the lower temperatures. Variations in these quantities following a pre-treatment sequence occurs in a manner indicative of electrode contamination¹.

Recently MPP measurements were attempted at temperatures of 90° or higher in solutions of both perchloric and phosphoric acids. Gradual "roughening" of the surface was observed, as evidenced by increases in both sQ_H and in Q_0 . The effect was slight, but observable at 90° in both acids, and quite pronounced in phosphoric acid at 120°. The investigation described below was undertaken to determine the origin of the electrochemical roughening of the surface observed at elevated temperatures.

EXPERIMENTAL

Glassware and electronic equipment have been described previously¹. The working electrode was a length of C.P. platinum wire 0.020 in. in diameter and of 0.064 cm² geometric area. The electrolyte was an 85% solution of A.R.-grade phosphoric acid. The test vessel was thermostatted at 120° in an air-bath.

Charges corresponding to hydrogen-deposition and to "oxygen adsorption" were measured by means of sequences I and II of Table I. Pulse sequences employed in the measurement of these charges are diagrammed in Fig. 1 (a and b). Figure 1 (c-g) are the repetitive signals rested for their effect on surface roughness.

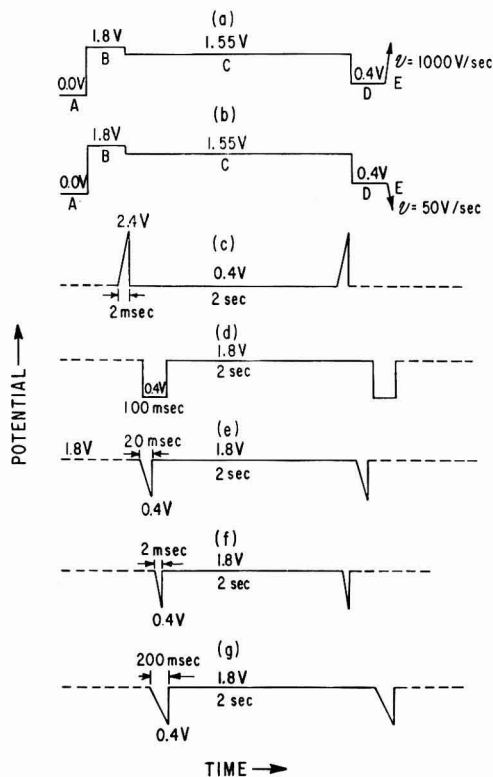


Fig. 1. Potential sequences used in this work.

RESULTS

I. Initial values of sQ_H , Q_0 and $R.F.$

Sequence II of Table I was employed for measurement of the charge corresponding to hydrogen-deposition, sQ_H . The application of step E of the sequence results in a hydrogen trace similar to that obtained at lower temperatures in perchloric acid¹. From this trace, sQ_H was obtained, as previously, by integrating the area under the trace, making approximate graphical correction for double-layer charging. The value of sQ_H obtained before alteration of the electrode surface was 0.31 mC/cm^2 . Assuming that 0.21 mC/cm^2 corresponds to a monolayer of hydrogen and a roughness factor, $R.F. = 1$, we calculated an original value of $R.F. = 1.47$ for the electrode.

Sequence I of Table I was employed in the measurement of the charge corresponding to "oxygen-adsorption". Trace 1 of Fig. 2 is the trace obtained initially by application of step E of sequence II. A charge, Q_0' was obtained from this trace by graphical integration of the area abcd. This charge includes a charge Q_0 , corresponding to oxidation of the surface and also a charge corresponding to double-layer charging². The choice of the location of point c of Fig. 2 must be somewhat arbitrary.

TABLE 1
 PULSE SEQUENCE APPLIED TO WORKING ELECTRODE

Sequence	Fig.	Step (refers to Fig. 1)	Procedure	Purpose
I	1a	A	1. Potential held at 0.0 V for 10 sec, with argon flowing and paddle-stirring.	1. To desorb foreign anions
		B	2. Stirring and argon flow continued while potential held at 1.8 V for 15 sec.	2. To remove impurities which oxidize and/or are repelled at high potentials.
		C	3. Stirring and argon flow continued for 0.5 min and solution allowed to become quiescent for 1.5 additional minutes. Potential held at 1.55 V throughout this step.	3. To sweep molecular oxygen produced during step B into the bulk and to restore concentrations of dissolved species near surface to bulk values.
		D	4. Potential of 0.4 V applied for time T_D	4. Surface is largely reduced within first few msec exposing a reproducible surface to the electrolyte.
		E	5. Apply linear anodic sweep E of speed $v = 1000$ V/sec and measure current-time trace	5. Q_0' may be determined from the trace.
II	1b	A-D	1-4. Same as sequence I, 1-4.	1-4. Same as sequence I, 1-4.
		E	5. Apply linear cathodic sweep E of speed $v = 50$ V/sec, and measure current-time trace.	5. sQ_H may be determined from the trace.

 TABLE 2
 VARIATION OF Q_0' WITH ELECTRODE PULSE-TREATMENT

Expt.	Signal (Fig.)	Q_0' Initial	Q_0' Final	Roughness factor Initial	Roughness factor Final	Total pulse time (min)	No. of cycles	Percentage change in Q_0' Total	Per cycle
1	1c	0.553	0.580	1.47	1.55	10	300	5.1	0.017
2	1d	0.580	0.960	1.55	2.55	10	300	64.7	0.216
3	1d	0.960	1.14	2.55	3.04	5	150	19.1	0.127
4	1e	1.43	0.98	3.83	2.62	5	150	-31.4	-0.210
5	1e	0.98	0.71	2.62	1.90	10	300	-27.6	-0.092
6	1f	0.71	1.07	1.90	2.85	10	300	50.0	0.166
7	1g	1.07	0.98	2.85	2.61	10	300	-8.45	-0.028
8	1e	0.98	0.74	2.61	1.96	10	300	-24.6	-0.082
9	1e	0.74	0.69	1.96	1.83	25	750	-7.2	-0.0096

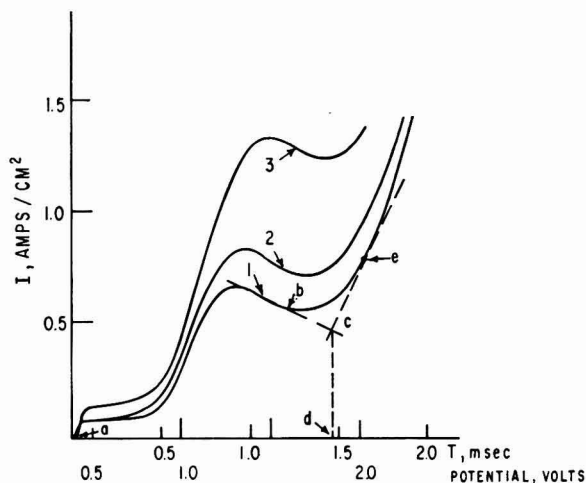


Fig. 2. "Oxygen adsorption" traces recorded: (1), initially; (2) and (3), after "roughening" the surface by pulsing.

To ensure standard conditions for the location of point *c*, and thereby, for the comparison of different values of Q_0' , point *c* was determined in the following way:

(1) The maximum current of the trace was determined. Point *e* was chosen as that point on the trace corresponding (arbitrarily) to 120% of the maximum current.

(2) A tangent to the trace was constructed at point *e*.

(3) A tangent was constructed to the trace at a point corresponding to a time half-way between that of the maximum current and that corresponding to point *e*.

(4) The intersection of the two tangents determines point *c*. The original value of Q_0' was found to be 0.553 mC/cm². After making approximate correction for double-layer charging on the assumption that the capacitance has a constant value of 70 μF/cm², $Q_0 = 0.43$ mC/cm² and $Q_0/2sQ_H = 0.69$ which is lower than the corresponding value at 30° in 1 *N* perchloric acid (0.9 according to Ref. 2) At least part of this decrease may be ascribed to the adsorption of phosphate ion which partially blocks surface oxidation⁴. Values of R.F. reported in Table 2 are calculated from Q_0' taking the original value of $Q_0' = 0.553$ to correspond to the R.F. of 1.47 and assuming that subsequent values of R.F. are directly equal to Q_0' .

II. ELECTRODE TREATMENTS LEADING TO NO CHANGE IN Q_0'

After a pre-treatment sequence similar to that of procedure 1, Table 1, the electrode was held at potentials of 0.4, 1.2, 1.55 and 1.8 V for 10 min. The particular potentials were chosen because they correspond to a variety of surface coverages with "oxygen"². Q_0' was found not to have varied at all at any of these constant potentials.

III. ELECTRODE TREATMENTS LEADING TO CHANGE IN Q_0'

Application of periodic pulses c, d and f of Fig. 1 lead to increase in Q_0' and hence in the calculated R.F. The reverse is true for pulses e and g. The results are summarized in Table 2. The change in Q_0' is compared with the preceding value of Q_0' by the expression:

$$\text{percentage change in } Q_0' = 100 \Delta Q_0/Q_0', \quad (1)$$

where $\Delta Q_0' = (\text{final value of } Q_0') - (\text{initial value of } Q_0')$. The value of Q_0' in the denominator of eqn. (1) is taken as the initial value. The change in Q_0' is also given on a "per cycle" basis by dividing expression (1) by the total number of cycles.

DISCUSSION

The results indicate that no change in R.F. occurs at any constant potential. According to Table 2, *increase* in R.F. is associated with signals c, d and f on Fig. 1, where the surface is oxidized and *rapidly* reduced during each cycle. A *decrease* in R.F. is noted when the surface is first oxidized and then *slowly* reduced as in signals e and g of Fig. 1. Hence roughening of the surface is correlated most directly with speed of reduction.

The rate at which the R.F. of the surface is increased by rapid reduction depends on the extent of previous exposure of the surface to oxidizing conditions. Hence Q_0' changes by only 0.02% per cycle when the surface is partially oxidized using a fast linear anodic sweep (Fig. 1, C), whereas the change is as large as 0.2% per cycle when the surface is first oxidized at 1.8 V for 2 sec and then rapidly reduced either by a step or a fast linear sweep (Fig. 1, d and f, respectively).

For the surface largely oxidized at 1.8 V, the rate of *decrease* of R.F. depends also on the speed of reduction. Hence in experiment 4, Table 2, signal 1e gave a rate of decrease of 0.2% per cycle during the first 5 min of pulsing whereas signal 1g gave an initial rate of change of only 0.03% per cycle. There is also evidence that a steady-state R.F. exists corresponding to signal 1e. In experiments 4, 5, 8 and 9, it is seen that the rate of change of Q_0' drops with decreasing R.F. The last value of R.F. measured in 2 cases (experiments 5 and 9) are approximately the same. It is possible that a steady-state value of R.F. may correspond to a variety of oxidation-reduction cycles. These effects may be of interest in preparing electrodes of desired R.F. in a reproducible manner.

Recently, HOARE⁶ examined "blackening" of platinum electrodes occurring at 25° upon application of 60 c/sec a.c. voltage signals. The extent of surface roughening encountered in the present work only leads to a slight dulling of the surface. Conditions are less severe than in HOARE's work in that relatively few (equivalent to only a few seconds of 60 c/sec a.c.) cycles are studied here. On the other hand, conditions are more severe in that the temperature chosen was higher (120° as compared with 25°). HOARE believes that roughening of the surfaces comes about through the action of deposited hydrogen. In this work, all reductions were made at potentials no lower than 0.4 V, under which condition there is no detectable hydrogen on the surface. Two general types of explanation of the observed phenomenon may be conceived:

(1) The rapid reduction of a relatively extensive "oxygen" or "oxide" film

does not allow time for the surface to "anneal" during reduction and this leads to progressive roughening of the surface.

(2) Some very slight rate of solution of the "oxide" occurs during some portion of each cycle. This, or subsequent reduction of dissolved platinum, leads to roughening. The author considers that the mechanism of the roughening process is still an entirely open question.

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SUMMARY

The application of a pulse sequence to a platinum electrode at elevated temperatures leads to variation in the estimated surface roughness, as calculated from hydrogen-deposition or "oxygen-adsorption" measurements. These variations are brought about during the reduction of surface "oxygen". Relatively rapid reduction causes an increase in roughness, whereas relatively slow reduction leads to a decrease in roughness. By use of the proper signal, it is possible to adjust the roughness factor of the surface to any value somewhat above 1.0 and below the values corresponding to platinum "blacks".

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ZUM MECHANISMUS DER KATHODISCHEN REDUKTION VON SAUERSTOFF AN EINER GLATTEN, AKTIVEN PLATINELEKTRODE IN ALKALISCHER LÖSUNG

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Die in früher von uns veröffentlichten Arbeiten^{1,2} enthaltenen Angaben bezüglich der kathodischen Reduktion von molekularem Sauerstoff an einer glatten, aktiven Platinelektrode in alkalischen Lösungen zeigten, dass Oberflächenoxyde des Platins die Reaktionsgeschwindigkeit dieses Prozesses stark beschleunigen. Die mit Hilfe der rotierenden Scheibenelektrode erhaltenen Strom-Spannungs-Kurven wiesen bei Rührgeschwindigkeiten der Elektrode $m > 300$ U/min anstelle des Diffusionsgrenzstromes bei einem Potential $\varphi_D \approx 0.5$ V ein Maximum auf. Der Stromabfall im Potentialbereich $\varphi_D = 0.5-0.1$ V konnte von uns auf die Hemmung der Reduktionsreaktion des sich bei der Sauerstoffionisation bildenden H_2O_2 zurückgeführt werden, die bedingt ist durch die Reduktion der sich an der Platinoberfläche befindlichen Platinoxyde. Die Wirkungsweise der Platinoberflächenoxyde und damit auch der Reaktionsmechanismus der kathodischen Sauerstoffreduktion ist heute, ungeachtet einer grossen Zahl von Arbeiten, die der Reduktion von Sauerstoff an Platin gewidmet sind, noch nicht aufgeklärt. Zur Deutung desselben muss man folgende in der Literatur vorhandene Angaben berücksichtigen, deren einseitige Interpretierung verschiedentlich zu falschen Ansichten führte^{3,4}.

1. Erhöhung des pH-Wertes der Lösung um eine Einheit führt zu einer Verschiebung des Halbwellenpotentials um 58 mV in negativer Richtung^{3,4}.

2. Sauerstoff und Platinoberflächenoxyde werden im gleichen Potentialbereich reduziert^{4,5,6}.

Übereinstimmung der Potentialbereiche der Reduktion von Sauerstoff und Platinoberflächenoxyden führte zur Entwicklung einer Theorie der Sauerstoffreduktion an Platin^{4,5}, nach der die Reduktion von Sauerstoff die elektrochemische Reduktion von Platinoberflächenoxyden darstellt, die sich ihrerseits durch chemische Reaktion von Sauerstoff mit Platin schnell regenerieren. So geben z.B. SAWYER AND INTERRANTE⁴ folgenden Mechanismus an:



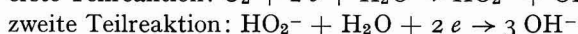
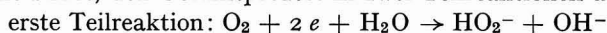
Zugunsten dieses Reaktionsmechanismus scheint auch die Tatsache zu

sprechen, dass Platinoberflächenoxyde den Reduktionsprozess von Sauerstoff stark beschleunigen.

Im Zusammenhang mit den letztgenannten experimentellen Befunden wurde deutlich, dass die Hauptaufgabe bei der Lösung der Frage des Sauerstoffreduktionsmechanismus in der Klärung der Rolle der Platinoxide besteht, was uns veranlasste, diese Frage etwas ausführlicher zu untersuchen.

Als Untersuchungsmethode wurde die rotierende Scheibenelektrode mit Ring angewandt^{1,7,8}, die es ermöglichte, hintereinander ablaufende Teilreaktionen zu trennen und einzeln zu untersuchen.

Die quantitative Bestimmung des sich bei der Sauerstoffreduktion bildenden H₂O₂ gestattete es, unter der Annahme, dass sich H₂O₂ als Reaktionszwischenprodukt bildet, den Gesamtprozess in zwei Teilreaktionen aufzuteilen⁸:



Als Beweis für die Richtigkeit unserer Annahme über die intermediäre Bildung von H₂O₂ und damit für die Gültigkeit der Teilung des Gesamtprozesses in zwei Teilreaktionen, kann man die Ähnlichkeit der Form der Polarisationskurven der Reduktion von Sauerstoff und H₂O₂ in 0.125 N KOH anführen (Abb. 1 und 2).

Wie in früher von uns veröffentlichten Arbeit^{1,2} gezeigt wurde, verläuft die 1. Teilreaktion in 0.125 N KOH im Potentialgebiet der Scheibenelektrode* $\varphi_D = 0.5-0$ V reversibel, während die 2. Teilreaktion infolge Reduktion der Platinoberfläche stark gehemmt ist. Für den Fall, dass H₂O₂ ein Zwischenprodukt der Sauerstoffreduktion ist, und nicht Endprodukt einer parallel zum Sawyerschen 4-Elektronenprozess ablaufenden Reaktion, sollte man deshalb erwarten, dass die Geschwindigkeit des Gesamtprozesses im Potentialbereich $\varphi_D = 0.5-0$ V durch die Geschwindigkeit der 2. Teilreaktion, d.h. der Reduktion von H₂O₂ zu OH⁻ bestimmt wird.

Aus diesem Grunde wurden einerseits die Geschwindigkeitskonstanten der 2. Teilreaktion ($k_{\text{H}_2\text{O}_2}$) mit Hilfe der Formel von LEWITSCH UND IWANOW^{7,8} und zum anderen die Geschwindigkeitskonstanten des Gesamtprozesses (k_{O_2}) aus der wirklichen kinetischen Strom-Spannungs-Kurve für die Potentiale +0.5 und +0.1 V berechnet. Die wahre kinetische Strom-Spannungs-Kurve wurde durch graphische Extrapolation der für konstante Potentiale bei verschiedenen Rührgeschwindigkeiten (m) ermittelten Ströme auf $m \rightarrow \infty$ erhalten. Die gute Übereinstimmung der Konstanten $k_{\text{H}_2\text{O}_2}$ und k_{O_2} (Tabelle 1) lässt den Schluss zu, dass die Reduktionsreaktion von Sauerstoff an Platin in alkalischen Lösungen über die intermediäre Bildung von H₂O₂ verläuft.

TABELLE 1

φ_D (V)	$k_{\text{H}_2\text{O}_2}$ (cm/sek)	k_{O_2} (cm/sek)
+0.5	$(8.9 \pm 0.8) \times 10^{-2}$	8.6×10^{-2}
+0.1	$(3.6 \pm 0.5) \times 10^{-2}$	3.5×10^{-2}

* Alle Potentiale beziehen sich auf die reversible Wasserstoffelektrode in der gleichen Lösung.

EINFLUSS VON OBERFLÄCHENOXYDEN AUF DIE GESCHWINDIGKEIT DER I. TEILREAKTION

Die Untersuchung des Einflusses von Oberflächenoxyden auf die Geschwindigkeit der 1. Teilreaktion war nur im Potentialgebiet des Anstiegs der Polarisationskurve möglich, da nur in diesem Potentialbereich die 1. Teilreaktion irreversibel verläuft.

Zur Klärung dieser Frage untersuchten wir die kathodische Reduktion von Sauerstoff in 0.125 N KOH an einer glatten Platinelektrode in Abhängigkeit von ihrer Oberflächenvorbehandlung. Im ersten Falle wurde die Elektrode abwechselnd anodisch und kathodisch bei Potentialen +1.8 bzw. -0.2 V polarisiert und danach 1 Min bei einem Potential von 1.3 V gehalten (gewöhnliche Aktivierung). Auf diese Weise erhielten wir eine leicht oxydierte Elektrode. Als reduzierte Elektrode bezeichneten wir eine solche, die nach gewöhnlicher Aktivierung 5 Min bei einem Potential von -0.2 V kathodisch polarisiert wurde. Die Polarisationskurven der Reduktion von Sauerstoff, die mit Hilfe dieser beiden Elektroden erhalten wurden, sind in Abb. 1 (Kurven 1 und 2) dargestellt.

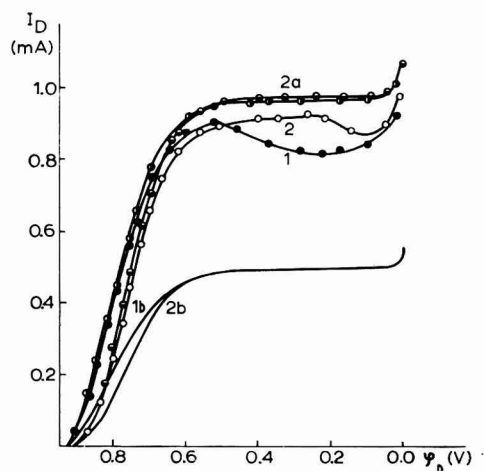


Abb. 1. Polarisationskurven der Reduktion von Sauerstoff an einer Platinelektrode: (1), reduziert; (2), oxydiert. (a), Polarisationskurven, die, nach Addierung der nicht zu OH^- reduzierten Menge H_2O_2 , erhalten wurden; (b), berechnete Strom-Spannungskurven der 1. Teilreaktion.

Die Berechnung der Stromspannungskurven für die 1. Teilreaktion, die auf Grund der Messungen mit Hilfe der rotierenden Scheibenelektrode mit Ring möglich war⁸ (Abb. 1, Kurven a und b), zeigt, dass das Halbwellenpotential der Reduktion von Sauerstoff zu H_2O_2 an der reduzierten Elektrode positiver ist, als an der leicht oxydierten Elektrode. Dieses Ergebnis weist darauf hin, dass Oberflächenoxyde die Geschwindigkeit der 1. Teilreaktion hemmen, d.h. die Oberflächenoxyde des Platins nicht an der Reduktionsreaktion von Sauerstoff teilnehmen. Damit ist bewiesen, dass

der von SAWYER UND INTERRANTE⁴ angegebene Reduktionsmechanismus in alkalischen Lösungen nicht zutreffend sein kann, weil sonst keine Verlangsamung dieser Reaktion durch Oberflächenoxyde zu erwarten gewesen wäre.

Da der von KRASILSCHTSCHIKOW UND ANDREJEW³ vorgeschlagene Mechanismus durch die Messungen von VIELSTICH⁹ ebenfalls widerlegt ist, bleibt nur die Möglichkeit anzunehmen, dass die 1. Teilreaktion eine rein elektrochemische ist, ähnlich der, wie sie für die Quecksilberelektrode gefunden wurde¹⁰.

Die Übereinstimmung der Potentialbereiche der Reduktion von Sauerstoff und Platinoberflächenoxyden ist dadurch bedingt, dass letztere den elektrochemischen Reduktionsprozess von Sauerstoff hemmen, und diese Reaktion nur an den Stellen der Oberfläche schnell verlaufen kann, die infolge kathodischer Reduktion frei von Oberflächenoxyden sind.

Die Bestimmung des geschwindigkeitsbestimmenden Schrittes der 1. Teilreaktion war wegen der starken Abhängigkeit ihrer Geschwindigkeit vom Oxydationsgrad der Platinoberfläche mit der von uns angewandten Methode nicht möglich. Die Abhängigkeit des Halbwellenpotentials der 1. Teilreaktion vom pH der Lösung gestattet es nicht, Aussagen über den geschwindigkeitsbestimmenden Schritt dieser Reaktion zu machen, da diese Gesetzmässigkeit nichts anderes als die Änderung des Potentialbereiches der Oberflächenoxydreaktion mit Änderung des pH der Lösung ausdrückt¹¹.

In Abhängigkeit von der Antwort auf die Frage: verläuft der kathodische Reduktionsprozess von Sauerstoff über die Zwischenbildung von Platinoxiden, oder entspricht der Mechanismus der 1. Teilreaktion dem von uns oben vorgeschlagenen, d.h. welcher Art ist die Reaktion der Sprengung der O–O-Bindung, klärt sich auch die Frage der Stellung von H₂O₂ im Reaktionsschema. Nach dem Reaktionsmechanismus von SAWYER UND INTERRANTE⁴ geschieht die Spaltung der O–O-Bindung durch die Bildung von Pt(OH)₂, H₂O₂ kann in diesem Falle kein Zwischenprodukt sein. Seine eventuelle Bildung müsste auf eine Parallelreaktion zurückgeführt werden. Wenn dagegen die 1. Teilreaktion ein elektrochemischer Prozess ist, ähnlich dem, wie er für die Quecksilberelektrode gefunden wurde¹⁰, muss die Reduktion von O₂ zu OH⁻ über die Zwischenbildung von H₂O₂ gehen.

EINFLUSS VON OBERFLÄCHENOXYDEN AUF DIE GESCHWINDIGKEIT DER 2. TEILREAKTION

In früher veröffentlichten Arbeiten^{1,2} konnten wir zeigen, dass Oberflächenoxyde die Geschwindigkeit der 2. Teilreaktion in alkalischen Lösungen stark beschleunigen. Einen Hinweis auf die Wirkungsweise der Oberflächenoxyde gibt die Tatsache, dass H₂O₂ schon in kleinen Konzentrationen (10⁻⁴ M) schnell mit Platinoxiden reagiert, wobei diese reduziert werden. Da diese Reaktion eine der Teilreaktionen des HABER–GRINBERG'schen Mechanismus¹² der katalytischen Zersetzung von H₂O₂ an Platin darstellt:



ist es naheliegend anzunehmen, dass sich H_2O_2 , das durch Diffusion zur Oberfläche gelangt, an dieser teilweise zersetzt, und die Reduktion von H_2O_2 die Reduktion des sich beim katalytischen Zerfall bildenden Sauerstoffs darstellt.

Wenn die Reaktionen (3), (4), (5) an der Scheibenelektrode tatsächlich ablaufen sollten, müsste sich molekularer Sauerstoff bilden, den man an der Ringelektrode nachweisen könnte.

Zur Bestimmung der an der Scheibe frei werdenden Sauerstoffmenge erwies es sich als notwendig, an der Ringelektrode aus platinierterm Platin die Differenz zwischen der Grösse des anodischen und kathodischen Diffusionsgrenzstromes bei konstantem Potential der Scheibe zu bestimmen. Der Unterschied zwischen beiden Grenzströmen ist dadurch bedingt, dass der an der Scheibe gebildete Sauerstoff durch den Flüssigkeitsstrom zum Ring transportiert wird und hier im Potentialbereich der kathodischen Reduktion von H_2O_2 reduziert wird, während er bei den Potentialen der anodischen Oxydation von H_2O_2 elektrochemisch inaktiv ist. Alle Versuche wurden in Stickstoffatmosphäre durchgeführt. Unter Berücksichtigung, dass mit der von uns verwendeten Scheibenelektrode mit Ring nur 41% der an der Scheibe gebildeten Sauerstoffmenge am Ring fixiert werden konnte, war es nicht schwer, auf der Grundlage dieser Messungen den Zersetzungsgrad von H_2O_2 zu berechnen.

Die Versuchsergebnisse zeigen, dass beim stationären Potential der Scheibenelektrode ($\varphi_{\text{st}} = 0.94 \text{ V}$) an der Ringelektrode Sauerstoff in einer Menge registriert wird, die völligem Zerfall des zur Scheibenelektrode diffundierenden H_2O_2 entspricht (Abb. 2). Die Menge des in die Lösung entweichenden Sauerstoffs verringert sich im Gebiet des Anstiegs der Polarisationskurve und wird beim Potential des Maximums (φ_{max}) der Polarisationskurve, bei dem der Strom diffusionsbedingt ist, null. Korrektur des kathodischen Stromes an der Scheibenelektrode auf die bei dem entsprechenden Potentiale entwichene Sauerstoffmenge ergibt in allen Fällen den Diffusionsgrenzstrom für H_2O_2 (Abb. 2, Kurve 2). Weitere Erhöhung der kathodischen Polarisation ($\varphi_D < \varphi_{\text{max}}$) führt zu einem erneuten Abfall des Stromes

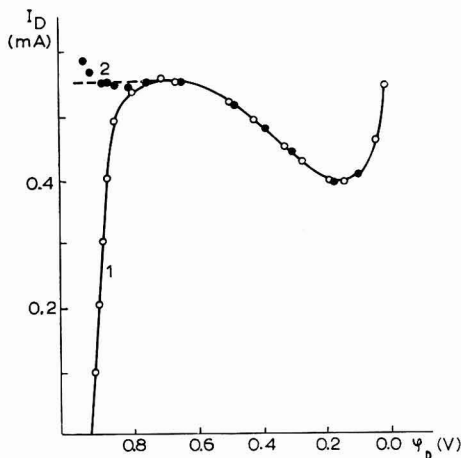


Abb. 2. (○), Polarisationskurve der Reduktion von H_2O_2 ; (●), Strom, der nach Addierung der freigewordenen Sauerstoffmenge zum Strome an der Scheibe berechnet wurde.

an der Scheibe, wobei zu bemerken ist, dass Sauerstoff bei diesen Potentialen nicht fixiert werden kann.

Diese Ergebnisse lassen den Schluss zu, dass die Reduktion von H₂O₂ an Platin in alkalischen Lösungen im Potentialgebiet $\varphi_D \geq \varphi_{\max}$ im wesentlichen der Reduktion des durch katalytischen Zerfall entstandenen Sauerstoffs entspricht. Die Geschwindigkeit der direkten elektrochemischen Reduktion von H₂O₂ ist in diesem Potentialgebiet klein.

Von BIANCHI *et al.*¹³ konnte gezeigt werden, dass der katalytische Zerfall von H₂O₂ an Platin durch Oberflächenoxyde stark beschleunigt wird. Der Stromabfall an der Scheibe bei $\varphi_D < \varphi_{\max}$, hervorgerufen durch Reduktion der Oberfläche, kann deshalb in Übereinstimmung mit unseren Versuchsergebnissen auf die Verringerung der Katalysegeschwindigkeit zurückgeführt werden. Während wir uns beim Potential des Maximums der Polarisationskurve im Sauerstoffgebiet der Ladekurve befinden, und die katalytische Zersetzung von H₂O₂ mit grosser Geschwindigkeit abläuft, ist im Minimum der Polarisationskurve an der Oberfläche kein Sauerstoff mehr vorhanden, und der katalytische Zerfallprozess deshalb stark gehemmt. Der gemessene Strom im Minimum der Polarisationskurve entspricht etwa dem Strom der direkten elektrochemischen Reduktion von H₂O₂ bei diesem Potential. Da dieser kleiner ist als der Diffusionsgrenzstrom, ist es verständlich, dass die durch kathodische Reduktion der Oberfläche bedingte Verringerung der Zerfallsgeschwindigkeit von H₂O₂ zu einem Absinken des Stromes bei $\varphi_D < \varphi_{\max}$ führen muss. Der erneute Stromanstieg bei $\varphi_D < +0.1$ V entspricht der Abhängigkeit der direkten elektrochemischen Reduktion von H₂O₂ vom Potential. Die Bestimmung des Faktors "b" der Tafelgleichung für den letztgenannten Prozess ergab einen Wert von ~ 0.4 V.

Interessant ist auch die Abhängigkeit der Form der kathodischen Polarisationskurve des H₂O₂ von der Art der Vorbehandlung der Elektrode. Merklichen Einfluss zeigt schon anodische Polarisation im Verlaufe von 15 Sek bei $\varphi_D = +1.8$ V

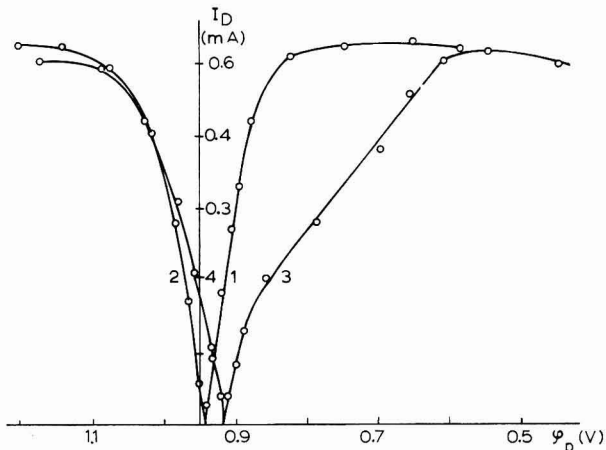
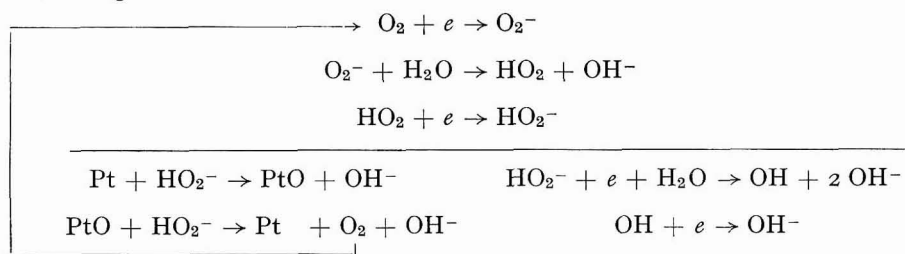


Abb. 3. Kathodische und anodische Polarisationskurven des H₂O₂: (1,2), gewöhnliche Aktivierung der Elektrode; (3,4), die Elektrode wurde nach der gewöhnlichen Aktivierung 15 Sek bei einem Potential von $\varphi_D = 1.8$ V gehalten.

(Abb. 3, Kurve 3). Eine derartige anodische Vorbehandlung passiviert noch nicht die Elektrode gegenüber den elektrochemischen Prozessen (direkte Reduktion und Oxydation von H_2O_2), wie aus Abb. 3 (Kurve 4) ersichtlich ist, sondern führt dagegen zu einer starken Abnahme der Zerfallsgeschwindigkeit von H_2O_2 . Unter diesen Bedingungen beträgt der bei φ_{st} gemessene Zersetzungsgrad nur etwa 40% des zur Oberfläche diffundierten H_2O_2 . Da der kathodische Prozess der Reduktion von H_2O_2 im Potentialbereich $\varphi_D \geq \varphi_{\text{max}}$ im wesentlichen der Reduktion des sich beim Zerfall an der Elektrodenoberfläche bildenden Sauerstoffs entspricht, ist es verständlich, dass eine Erniedrigung der Oberflächenkonzentration von Sauerstoff, infolge Erniedrigung der katalytischen Zerfallsgeschwindigkeit, zur Verringerung der Geschwindigkeit des Reduktionsprozesses von H_2O_2 führen muss. Der anodische Vorgang wird, wie auch zu erwarten war, durch leichte anodische Vorbehandlung beschleunigt.

Für den Reduktionsprozess von Sauerstoff an Platin kann man folgendes Schema angeben:



DANK

Schliesslich möchten wir unseren besten Dank Prof. A. FRUMKIN für seine Hilfe bei der Ausführung der Arbeit ausdrücken.

ZUSAMMENFASSUNG

Mit Hilfe der rotierenden Scheibenelektrode mit Ring konnte gezeigt werden, dass Platinoberflächenoxyde die Reduktionsreaktion von Sauerstoff zu H_2O_2 in alkalischen Lösungen hemmen, und diese Reaktion nur an den Stellen der Oberfläche schnell verlaufen kann, die frei von Oberflächenoxyden sind. Die beschleunigende Wirkung von Platinoberflächenoxyden auf die Reduktion von H_2O_2 erklärt sich aus den Besonderheiten des Mechanismus dieses Prozesses, der darin besteht, dass H_2O_2 , das zur Platinoberfläche diffundiert, sich an dieser teilweise katalytisch zersetzt, und die Reduktion von H_2O_2 die Reduktion des sich beim katalytischen Zerfall bildenden Sauerstoffs darstellt. Die beschleunigende Wirkung von Platinoberflächenoxyden ist dadurch bedingt, dass die Geschwindigkeit des katalytischen Zerfalls von H_2O_2 an einer oxydierten Platinelektrode grösser ist als an einer reduzierten.

SUMMARY

Using a rotating disk electrode with a ring, it can be shown that the surface

oxide of platinum retards the reduction of oxygen to H₂O₂ in alkaline solution, and that this reaction can occur rapidly only where the surface is free from the surface oxide. The accelerating action of the surface oxide of platinum on the reduction of H₂O₂ is explained by the singularity of this process, in that the H₂O₂ diffusing to the platinum surface is partially decomposed catalytically there, and the reduction of H₂O₂ is represented by the reduction of the oxygen formed in the catalytic decomposition. The accelerating action of the surface oxide of platinum therefore arises because the speed of the catalytic decomposition of H₂O₂ at an oxidized platinum electrode is larger than that at a reduced platinum electrode.

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THE DETERMINATION OF IONIC ZINC IN SEA-WATER BY ANODIC STRIPPING VOLTAMMETRY USING ORDINARY CAPILLARY ELECTRODES*

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INTRODUCTION

^{65}Zn plays an important role in the radio-active contamination of the marine system. It may be present as an induced radionuclide produced at the moment of a nuclear explosion, or introduced with the cooling water from nuclear reactors. It has a relatively long half-life (246 days) and is accumulated and concentrated by marine organisms: planktonic algae, benthic organisms and many fishes^{1,2}. Oysters are able to concentrate zinc to $5 \cdot 10^4$ or even $3 \cdot 10^5$ times the concentration in sea-water².

The biological importance of zinc as an essential constituent of living matter has been established. Many enzymatic systems, *e.g.*, the carbonic anhydrase of animals and plants, the alcohol-dehydrogenase of yeasts and the anserinase of fishes, have zinc as a co-factor³⁻⁷ and there is, therefore, a growing interest in this element in radio-ecology.

It is probable that zinc is present in sea-water as hydrated ions, and also as complexed zinc and zinc associated with soluble organic compounds or absorbed by suspended solid, but there is, as yet, no clear evidence on this subject.

A serious difficulty encountered in the analytical determination, especially of the stable isotopes in sea-water, is that practically all chemical reagents contain traces of zinc as impurity. These traces are difficult and laborious to remove⁹. Zinc in sea-water is usually determined by the classic method of measuring spectrophotometrically the extinction of the dithizone complex at a wavelength of 524 m μ after a preliminary separation. Zinc is separated from sea-water, for example, by extraction⁸ or by co-precipitation with other elements¹⁰. These methods afford sufficient sensitivity and reproducibility but are very laborious. In addition, zinc impurities in the reagents will contaminate the sample.

So far, no attempt had been made to determine zinc in sea-water by direct measurements on the sample, *e.g.*, by measuring the peak current with an oscillographic polarograph, although WHITNACK¹¹ has suggested this possibility. This method, which combines speed with precision, has the fundamental advantage that it does not require any treatment of the sample, as sea-water itself serves as supporting electrolyte. Our work has been concerned with investigating the possibility of developing such a method.

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Initially, we verified the statement made by WHITNACK that sea-water is a good supporting electrolyte for the determination of zinc at a concentration of about 50 $\mu\text{g/l}$. Zinc produces a peak at a potential of -0.95 V vs. the S.C.E. at a temperature of 18° . Under these conditions the peak current increases linearly with concentration, making possible the direct determination of zinc at about 50 $\mu\text{g/l}$. The concentration of zinc in our waters is of the order of 1 $\mu\text{g/l}$, and is not therefore detectable by the usual technique of oscillographic polarography. It was thus necessary to evolve a new technique to increase the sensitivity.

The data in Table 1 gives some idea of the zinc concentration in different seas, reported by various authors.

TABLE 1
ZINC CONCENTRATION IN $\mu\text{g/l}$ REPORTED IN LITERATURE^{8,9}

Author	Year	Sea	Concn. ($\mu\text{g/l}$)
BODANSKY	1920	Galveston, Texas, U.S.A.	7.5
KURODA	1940	Coast of Honshu, Japan	7
NODDACK AND NODDACK	1940	Coast of Sweden	14
SVERDRUP, JOHNSON AND FLEMING	1942		5
WATTENBERG	1943		5-30
VINOGRADOV	1944		50
BUCH	1944	Coast of Finland	4.5-23
LEGENDRE	1947		14
RANKAMA AND SAHAMA	1950		5-14
MORITA	1950	Tokyo Bay, Japan	2.8-11.7
BLACK AND MITCHELL	1952	Coast of Great Britain	9-21
ISHIBASHI	1955		5
GOLDBERG	1957		10
DIETRICH AND KALLE	1957		5
CHIPMAN <i>et al.</i>	1958	Beaufort, N. Carolina, U.S.A.	9-21
FUKAI AND MEINKE	1959		5
PARKER	1961	Redfish Bay, Texas, U.S.A.	6-8
FONSELIUS AND KOROLEFF	1963	Ligurian Sea, Monaco	3.3-86

EXPERIMENTAL

The anodic stripping technique

Recently, ARIEL AND EISNER¹² have determined zinc directly in Dead Sea brines at a concentration of 5.7×10^{-7} M taking advantage of the higher sensitivity obtained by using anodic stripping polarography. This technique consists in a pre-electrolysis of the solution for a well-defined time at a potential more negative than the reduction potential of the substance to be determined. This is necessary in order to concentrate, on the mercury drop, a quantity of substance large enough to make its corresponding anodic current measurable. Using this method, KEMULA *et al.*¹³ were able to determine traces of Pb, Cd and Cu in uranium salts at a concentration of about $5 \cdot 10^{-8}$ M. This suggested that it might be possible to apply the same method to sea-water; but the hanging drop electrode of KEMULA is very delicate, difficult to obtain, and moreover, cannot be synchronized. We have used a method, described below, using ordinary polarographic capillary electrodes which have a very long dropping period (~ 68 sec) and stirring the solution during the delay-time.

Instrument and cells

The instrument used in the measurements was a Cathode Ray Polarograph, Model 451 (AMEL, Milano), which can be used for anodic stripping polarography because the delay-time can be varied over a wide range. A feature of this instrument is the possibility of compensating the slope and the residual current. At very high sensitivity, the charge of the double-layer capacity becomes comparable with the peak current, and must be compensated. At the same time, the drop-growth contributes an increasing residual current and the slope of the polarogram must be reduced to obtain exact measurements. The dimensions of the capillary used in our measurements were 380 mm in length and 0.010 mm in diameter (supplied by AMEL). The mercury was distilled three times.

The cell, illustrated in Fig. 1, has a special structure, which increases the enrichment of the drop during pre-electrolysis. The enrichment of the drop depends on many parameters, particularly the stirring time and the position of the capillary with respect to the stirring bar. Precautions were taken, therefore, in order to obtain reproducible measurements, and a special frame was constructed to keep the capillary always exactly in the same position in relation to the stirrer. Stirring, at 146 rev./min, was carried out with a synchronous electric motor incorporated in the frame that supports the cell. The cell is maintained in a fixed position by a special casting (Fig. 2). Once the upper part of the cell is fixed, and the possibility of vertical and horizontal

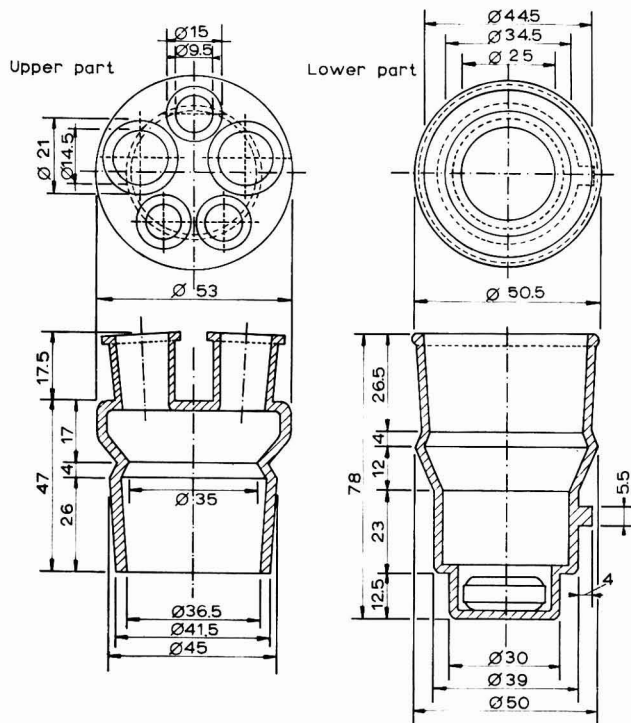


Fig. 1. Polarographic cell; measurements in mm.

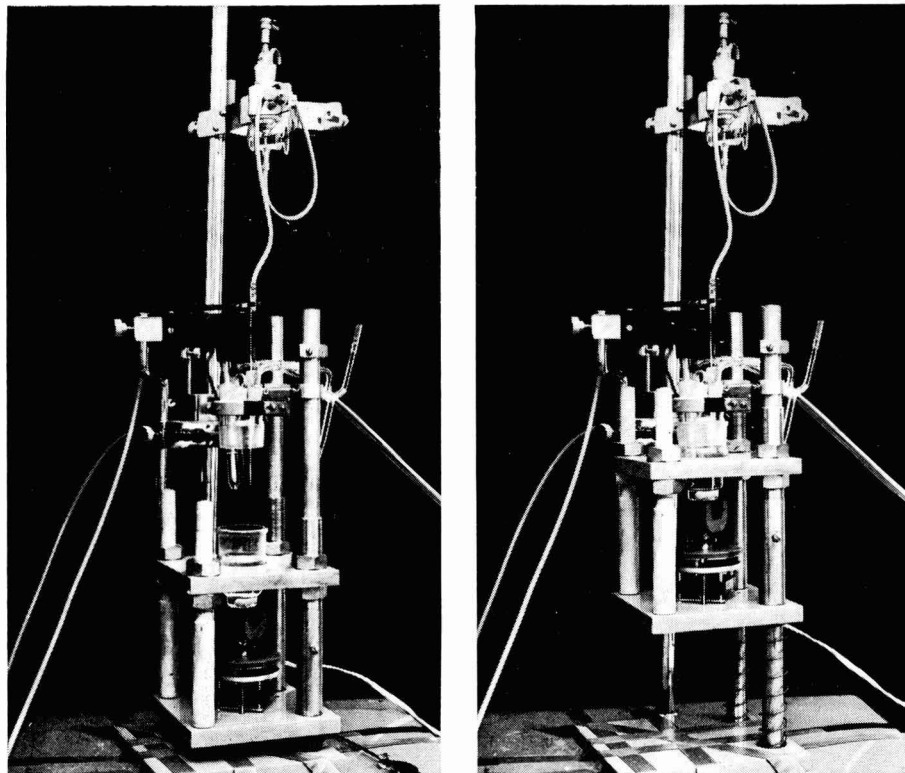


Fig. 2. Supporting frame with polarographic cell: (left), cell lowered for substitution; (right), cell in position for measurement.

displacement of the capillary reduced, an appropriate mechanism allows the agitator to be moved upwards, together with the lower part of the cell, in order to facilitate its substitution between successive determinations.

Technique

The sequence of the automatic operations performed by the apparatus is as follows: as soon as the mercury drop starts to develop and the solution is electrolysed, the stirrer begins to work for a time which is normally 50 sec, then the stirring stops for a period of 10 sec, at the end of which the anodic sweep starts and the measurement is made. A small magnetic hammer then knocks the capillary, causing the drop to fall; the formation of a new drop begins and the cycle starts anew. The sequence and synchronization of these operations is of fundamental importance for the reproducibility of measurements.

For the determination of zinc the pre-electrolysis potential was maintained at -1.3 V; the amplitude of sweep was 1 V, from -1.3 to -0.3 V; the scanning time was 4 sec. The zinc peak is at -1.00 V vs. S.C.E. All measurements were made at $+18^\circ$. All values are based on the average of 6 measurements. The advantage of

the new technique is that the repeated measurements are always synchronized; the operator always sees the same image and can measure directly on the screen of the oscillograph.

Sampling

The sea-water samples were collected about 15 miles off the coast of the "Cinque Terre" (La Spezia) with Van Dorn bottles made entirely of polyethylene and were kept in bottles of the same material. High purity nitrogen was used for de-aeration of the sample. Standard solutions were prepared by direct dilution of a solution containing an exactly weighed quantity of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$.

RESULTS AND DISCUSSION

Identification of the zinc peak

The peak obtained was verified as due to zinc and not to other metals present in sea-water; the potential of the peak (-1.00 V) was in perfect agreement with the peak potential of zinc as found by ARIEL AND EISNER¹² in Dead Sea brines, and the value of the peak current increased when solutions of zinc salts were added. Other metals do not interfere with the determination; as under the experimental conditions Co^{2+} , Ni^{2+} , Mn^{2+} , Cr^{3+} , Fe^{3+} and Al^{3+} , give no peak current although excessive

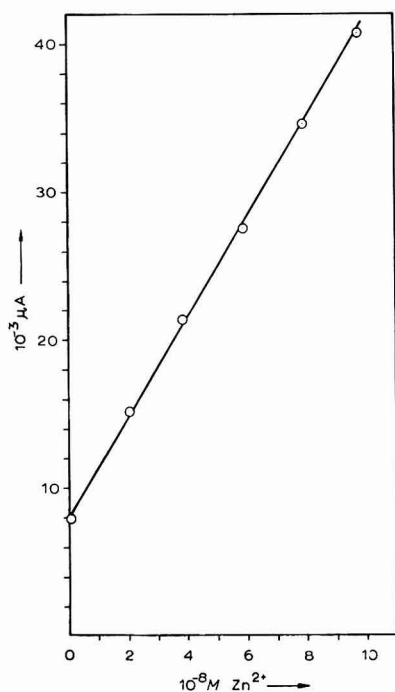


Fig. 3. Relation between peak current and concn. of zinc ion in sea-water.

concentration of Co^{2+} and Ni^{2+} (higher than 20 times the concentration of Zn^{2+}) may distort the base line. Cd^{2+} , Pb^{2+} and Cu^{2+} have a peak potential of -0.70 V, -0.52 V and -0.25 V respectively. However, chromium, iron and aluminium hydroxides and particulate matter have a tendency to absorb zinc ions. Therefore, a preliminary filtration of the samples is required.

Correlation between peak current and zinc concentration

The relationship between the peak current and the concentration of zinc in sea-water was investigated by adding successive known quantities of zinc to a 25-ml sample of sea-water. It can be seen from Fig. 3 that there is a linear relationship in the concentration range present. These data refer to one single determination, but other determinations under the same conditions confirmed the linearity.

Effect of stirring

Figure 4 shows the anodic curve, registered after the sample has been stirred for 50 sec. After the same delay-time, but without stirring, no peak was observed. Table 2 shows the variation in the height of the peak caused by changing the stirring time.

It was noticed that the position of the capillary electrode in relation to the stirring bar had a large effect on the peak height (see Table 3). NERNST'S diffusion layer theory can explain these experimental results, at least from a qualitative point of view¹⁴.

The limiting current, i_l , is given by:

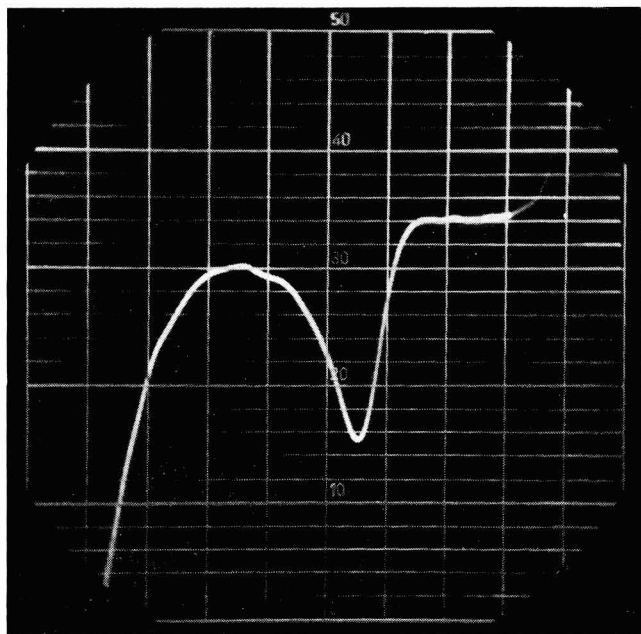


Fig. 4. The anodic curve: the concn. of Zn^{2+} in the sample of sea-water is 5.7×10^{-8} M (about $3.7 \mu\text{g/l}$).

TABLE 2

EFFECT OF THE STIRRING TIME ON THE HEIGHT OF THE PEAK

Initial potential, -1.3 V; peak potential, -1.00 V

Delay time (sec)	Stirring (sec)	Units
44	10	5
44	15	8
44	20	12
53	25	14.5
53	35	22.5

TABLE 3

VARIATION OF THE VALUE OF THE PEAK CURRENT WITH VARIATION IN THE CAPILLARY POSITION

These positions were obtained by moving the capillary each time about 5 mm nearer to the cell wall

Position	Reading units
1	24.9
2	28.4
3	30.7
4	34.6
5	36.2

$$i_1 = nFAD_z \frac{C^z}{\delta_z} \quad (1)$$

where C^z is the bulk concentration of zinc ions, n the number of electrons involved in the electrochemical reaction, F the Faraday constant, A the area of the electrode, D_z the diffusion coefficient of zinc ions and δ_z the thickness of the diffusion layer for zinc ions. This equation shows that, for a given solution, the limiting current increases either with increase of the electrode area or with decrease of the diffusion layer thickness. When the solution is stirred for a given period during the drop development, there is a decrease in the thickness of the diffusion layer and, consequently, a higher value of the limiting current is established.

The relationship between limiting current and speed of stirrer rotation can be expressed by an empirical equation of the form:

$$i_1 = pr^a \quad (2)$$

where, p is a constant, r rev./min and a a number depending on the system geometry. Clearly, the speed of the stirrer and the geometric dispositions of the electrolytic cells and working electrode should be identical in comparative measurements. When the position of the capillary in relation to the stirrer bar is maintained during the addition of standard solutions, it is possible to plot a calibration curve. However, if the cell is removed for cleaning and replaced, the position of the capillary in relation to the stirring bar must change and a calibration curve with a different slope will result. This does not affect determinations involving the addition of solutions, as during the process the capillary remains in a fixed position. In practice it is useful to keep the

sensitivity constant as under these conditions it is easier to detect contamination of the sample. The cell holder described in Fig. 2 was developed to ensure this.

Sensitivity and standard deviation

The sensitivity has been shown to depend on several factors: mode of stirring, time of stirring, geometry of the system; but in any case, the conditions necessary for optimum sensitivity must be established experimentally.

The system described above had a sensitivity of $3 \cdot 10^{-9} M$ /unit of scale, under the following conditions: the capillary, synchronized at 60 sec; stirring, maintained at 146 rev./min for a period of 50 sec; the capillary, fixed in a peripheral position and the measurements, taken at the maximum sensitivity of the apparatus. The sensitivity thus obtained enables zinc to be determined at a concentration of $1 \mu\text{g/l}$.

Forty-two determinations were made on a sample of sea-water containing zinc at a concentration of $3 \mu\text{g/l}$ with a coefficient of variability of 4.5%.

CONCLUSIONS

The results show that zinc can be directly determined in sea-water polarographically. The method gives a very high sensitivity and the coefficient of variability is of the order of 4.5%.

There are some difficulties in standardization, because the peak current depends on the position of the capillary in relation to the stirring bar but this can be overcome by appropriate cell construction.

The method is rapid (15 min for each analysis) and has the advantage that no chemical treatment of the sample is required thus eliminating the possibility of contamination of the sample by reagents. In addition the method is specific; under the stated experimental conditions Co^{2+} , Ni^{2+} , Mn^{2+} , Fe^{3+} , Cr^{3+} , Al^{3+} , Cd^{2+} , Pb^{2+} and Cu^{2+} do not interfere.

ACKNOWLEDGEMENTS

The author thanks Mr. P. CHAMARD for his help in making the measurements and is grateful to Dr. M. BERNHARD, Director of "Laboratorio per lo Studio della Contaminazione Radioattiva del Mare" (C.N.E.N. Fiascherino), for his interest in this investigation.

SUMMARY

Direct determinations, with an extremely high sensitivity, of zinc in samples of sea-water, have been carried out using a cathode-ray polarograph operating for anodic polarography. The apparatus is designed to use special capillary electrodes with a very long dropping time in order to obtain a pre-electrolysis of about 60 sec.

The persistence of the cathode-ray tube is long enough to facilitate synchronized operation which eliminates any difficulty with the time measurements.

Reproducible stirring conditions must be used during the pre-electrolysis to obtain a good enrichment of the drop with zinc. The apparatus allows for compensation of the current due to the double-layer charge and of the slope due to the growth

of the drop. A concentration of about $1 \mu\text{g/l}$ (about $1.5 \times 10^{-8} M$) can be measured reproducibly.

The measurements have been carried out on sea-water samples from the Ligurian Sea (Mediterranean).

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DETERMINATION OF MIXTURES BY SINGLE-SWEEP OSCILLOPOLAROGRAPHY

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The development of rapid, linear potential sweep polarography (single-sweep oscillopolarography) has led to analytical applications of the method^{1,2}. A commercial instrument, the Cathode Ray Polarograph, which can be used both with the dropping electrode as well as others³, is manufactured by Southern Analytical Limited in England and is an outgrowth of the work of RANGLES¹ and DAVIS AND SEABORN⁴. The general topic of the single-sweep method has been discussed by VOGEL and some experimental work at a dropping electrode is reported by VOGEL AND VALENTA^{5,6}. However, little quantitative data are given.

The voltage sweep methods have been extended by SHAIN and co-workers and KEMULA to *stripping analysis* procedures at the hanging mercury drop electrode^{7,8,9} where a pre-electrolysis concentrates the metallic ion as the metal, and the metal, which is deposited in the pendant mercury drop, is subsequently stripped by application of an anodic going voltage sweep. A recent application is that of ARIEL AND EISNER¹⁰. SHAIN has shown that there is difficulty in determining mixtures at the hanging mercury drop electrode due to the inability to separate the *tail* of the reduction of the more easily reduced (or oxidized) species from the peak current for the second reaction. A differential method utilizing two hanging mercury drops, in an effort to overcome the separation problem¹¹, was reported on by MARTIN AND SHAIN.

The present work describes the determination of mixtures and the determination of a minor constituent in the presence of a large excess of other interfering electroactive material using simple sweep procedures with one electrode. The applicability of anodic stripping procedures at a dropping electrode was also briefly investigated.

EXPERIMENTAL

The electronic apparatus is a multi-purpose instrument; details of this instrumentation will be published elsewhere¹². The sweep circuitry is essentially similar to that previously published¹³ except for the incorporation of an automatic compensating circuit. This compensating circuit effectively cancels out currents which arise as a result of a reaction taking place before the sweep is applied. When the dropping electrode is used, the drop is mechanically detached by an electrically operated solenoid-hammer (a doorbell chime) which is synchronized so that the sweep is initiated at some fixed time in the drop-life; the time is limited by the natural drop-life but may be varied at will.

The current measuring resistor used was 40 k Ω . The voltage is amplified 40-fold by a fixed gain amplifier following the measuring resistor. In the case of mixtures, the sweep was initiated at a potential in the diffusion current region of the electrode reaction preceding the one of interest so that the automatic compensation circuit permitted observation of a very small signal on top of a large diffusion limited current. The diffusion current is obviously not changed by application of the sweep. If the sweep is sufficiently rapid and applied late enough in the life of a slowly growing drop, the change in area of the drop during the interval in which the sweep is applied will be small.

Current-voltage curves were displayed on a Moseley Model 2D X-Y recorder or on a Tektronix 564 storage oscilloscope.

All chemicals used were analytical reagent-grade and were used without further purification. Standard stock solutions of electroactive materials were prepared by careful weighing; the more dilute solutions were prepared by volumetric procedures. All solutions were deaerated with argon containing approximately 4 p.p.m. of oxygen.

RESULTS AND DISCUSSION

Cadmium was determined in 0.1 *F* KNO₃ at a 0.04-cm² hanging mercury drop in the 10⁻⁵ *M* concentration range. Results are given in Table 1. The sweep was

TABLE 1

i_p vs. [Cd(II)]

Sweep rate 79.6 mV/sec; hanging Hg drop area, 0.04 cm²; 0.1 *F* KNO₃.

$[Cd(II)] \cdot 10^5$ (moles/l)	$i_p/C \cdot 10^{-5}$ ($\mu A-l/moles$)
1	0.233
2	0.224
3	0.238
4	0.242
5	0.241
6	0.231
7	0.247
8	0.248
9	0.247
10	0.246
	0.240 \pm 0.007

initiated several hundred millivolts before the reduction took place, and it is seen that the i_p/C ratio is constant to about an average deviation of 3%. At this slow sweep rate the Moseley X-Y recorder could be used. Table 2 presents data for cadmium reduction at a dropping mercury electrode applying a 431 mV/sec sweep approximately 8 sec into the drop life. The sweep was initiated at -400 mV against the S.C.E. Curves were recorded on the oscilloscope in the storage mode and photographed. In the range 3-20 $\cdot 10^{-7}$ *M*, linearity of peak current to concentration is

TABLE 2

 i_p vs. $[\text{Cd}^{2+}]$ Sweep rate 431 mV/sec; 0.1 F KNO_3 ; D.M.E.; sweep 8 sec after drop fall.

$[\text{Cd(II)}] \cdot 10^7$ (moles/l)	$i_p \cdot 10^9$ (A)	$i_p/C \cdot 10^{-4}$ ($\mu\text{A-l}/\text{moles}$)
3	7.15	2.4
4	9.1	2.3
5	11.05	2.2
6	14.3	2.4
7	15.6	2.2
8	17.6	2.2
9	21.5	2.4
10	22.8	2.3
12	27.3	2.3
15	35.8	2.4
20	48.7	2.4

excellent. At this concentration, however, the curves are on a base-line which is sloping upwards rather sharply due to the charging current.

Although the idea of initiating the sweep voltage from a potential on the diffusion plateau of a species undergoing reaction prior to the ion of interest was mentioned by RANGLES in his initial work, little notice appears to have been taken of this point; in fact, as previously mentioned, it is often stated that mixtures are difficult to determine with the voltage sweep method. The automatic current compensating feature of our apparatus facilitates elimination of the diffusion current arising from the prior reaction. Table 3 presents data for the determination of Cd(II)

TABLE 3

 i_p vs. $[\text{Cd}^{2+}]$ Sweep rate 431 mV/sec; $10^{-3} F$ Cu(II) ; 0.1 F KNO_3 ; D.M.E.

$[\text{Cd(II)}] \cdot 10^6$ (moles/l)	$i_p \cdot 10^9$ (A)	$i_p/C \cdot 10^{-3}$ ($\mu\text{A-l}/\text{moles}$)
1	42.5	43
2	80	40
3	130	43
4	182	45
5	220	44
6	252	42
7	297	42
8	367	46
9	402	45
10	425	43

in the micromolar region in the presence of millimolar copper. The potential at which the sweep was initiated was -400 mV, well on top of the copper diffusion plateau. Again, the current-voltage curves were photographed from an oscilloscope face. The constancy of i_p/C for cadmium is very good over the 10-fold concentration range;

TABLE 4

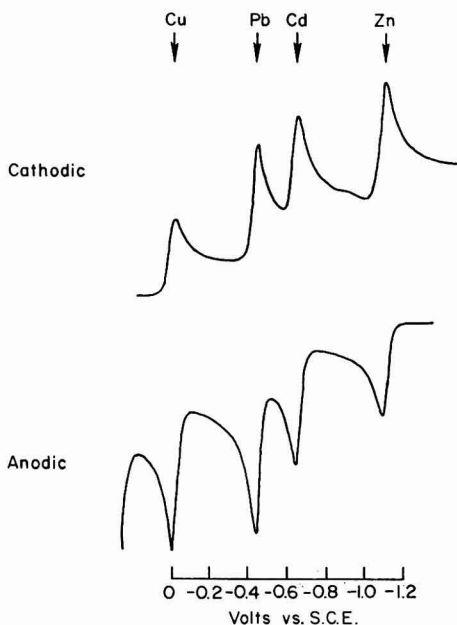
POTENTIAL SWEEP CHRONOAMPEROMETRIC ANALYSIS OF 4-COMPONENT SYSTEM

0.1 *F* KNO₃; D.M.E.; sweep rate, 431 mV/sec cathodic; 441 mV/sec anodic.

Zn(II) determined in presence of 10 ⁻⁴ <i>M</i> Cu(II), Pb(II), Cd(II).			Cd(II) determined in presence of 10 ⁻⁴ <i>M</i> Cu(II), 10 ⁻⁴ <i>M</i> Pb(II), 4 · 10 ⁻⁴ <i>M</i> Zn(II).		
[Zn(II)] · 10 ⁴	<i>i_p</i> /C (arbitrary units) Cathodic(1)	Anodic(2)	[Cd(II)] · 10 ⁴	<i>i_p</i> /C (arbitrary units) Cathodic(3)	Anodic(4)
1.00		1.99	0.97	1.46	2.01
1.98	1.51	1.92	1.97	1.44	1.98
2.94	1.51	1.90	2.83	1.45	1.94
3.88	1.51	1.87	3.74	1.42	1.82

Pb(II) determined in presence of 10 ⁻⁴ <i>F</i> Cu(II), 4 · 10 ⁻⁴ <i>F</i> Cd(II), 4 · 10 ⁻⁴ <i>M</i> Zn(II).			Cu(II) determined in presence of 10 ⁻⁴ <i>M</i> Zn(II), 10 ⁻⁴ <i>M</i> Pb(II), 10 ⁻³ <i>M</i> Cd(II).		
[Pb(II)] · 10 ⁴	<i>i_p</i> /C (arbitrary units) Cathodic(5)	Anodic(6)	[Cu(II)] · 10 ⁴	<i>i_p</i> /C (arbitrary units) Cathodic(7)	Anodic(8)
0.935	1.70	2.08	0.91	1.39	1.95
1.85	1.71	2.13	1.80	1.46	1.96
2.75	1.72	2.14	2.63	1.52	2.00
3.64	1.72	2.02	3.54	1.48	1.92

Sweep initiated at (mV vs. S.C.E.); (1), -700; (2), -1200; (3), -450; (4), -900; (5), -200; (6), -500; (7), +150; (8), -300.

Fig. 1. *i*-*E* trace for 4-component mixture; cathodic and anodic sweep (see text).

in this range the polarographic diffusion current due to copper reduction is about a hundred times greater than the peak current due to cadmium reduction.

Table 4 presents data for the determination of individual components in a four-component mixture of copper, lead, cadmium, and zinc. Figure 1 shows the 4 peaks observed when sweeps are made either cathodically or anodically. The anodic sweeps were obtained after 8 sec of plating during drop growth prior to the sweep. Each component was individually determined by starting at the diffusion plateau for the preciously reduced ion, in the case of cathodic sweeps, or on its own diffusion plateau, in the case of anodic sweeps. Again, the degree of precision appears reasonable as indicated by the constancy of the i_p/C ratios for both the cathodic and anodic determinations.

TABLE 5

i_p vs. area (proportional to drop-time^{2/3}); soln. $\sim 5 \cdot 10^{-3} M$ Tl(I) in 0.1 F KNO_3 ; 431 mV/sec.

$t^{2/3}(\text{sec}^{2/3})$	$i_p \cdot 10^6$ (A)	$i_p/t^{2/3}$
2.39	9.48	3.96
2.81	11.37	4.04
3.21	13.0	4.05
3.56	14.68	4.12
3.90	16.1	4.13
4.24	17.27	4.07
		4.06 ± 0.05

Table 5 indicates the proportionality between peak current and the two-thirds power of the drop time, which is proportional to the area of the drop. It can be seen that $i_p/t^{2/3}$ is quite constant to an average deviation of about 1%. As indicated previously, the charging current was found to be proportional to sweep rate, as expected, since i_c (at E) = C (at E) dE/dt and was also proportional to the area of the drop. The linearity of peak Faradaic current to the square root of sweep rate was verified, as expected.

The data supports the use of the dropping mercury electrode in the determination of multi-component systems and indicates the possibility of determining trace amounts of one component in large excesses of another, more easily reducible, component. The use of anodic sweeps following deposition into the drop is feasible in both single- and multi-component systems. In some instances, where cathodic waves are too close together, resolution may be achieved by anodic stripping.

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SUMMARY

Single-sweep oscillopolarography was used to analyze multi-component sys-

tems by initiating voltage sweeps from the diffusion plateau of the preceding reaction at a dropping mercury electrode. Both anodic and cathodic sweeps were employed. The procedure is applicable to the determination of a trace of a substance in the presence of a large excess of a more easily reduced substance.

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FILM FORMATION ON PYROLYTIC GRAPHITE ELECTRODES

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Pyrolytic graphite (PG)*, a type of graphite with an orderly arrangement of individual planes, is rapidly becoming a popular material for making solid electrodes²⁻⁹ for electrochemical measurements. In general, solid electrodes are of particular usefulness at potentials at which mercury is oxidized (~ 0 V vs. S.C.E., depending on the supporting electrolyte). It is well known that platinum, the most widely used solid electrode material, forms an oxide film when subjected to an anodic¹⁰⁻¹⁴ or a chemical^{10-12,15} treatment. The presence of such a film has a significant effect on the voltammetric behavior of the electrode.

This study was initiated to determine whether pyrolytic graphite, when subjected to oxidizing conditions, will form a film which changes the voltammetric characteristics of the electrode.

EXPERIMENTAL

Apparatus

Voltammeter. A controlled-potential voltammeter constructed at the Oak Ridge National Laboratory was used to obtain the voltammograms¹⁶.

Chronopotentiometer. Chronopotentiograms were obtained with a chronopotentiometer fabricated at the Oak Ridge National Laboratory¹⁷.

Electrolytic cell. A glass electrolytic cell containing two compartments separated by a porous glass plug was used for obtaining both the voltammograms and the chronopotentiograms. One compartment of the cell contained the working electrode and the reference electrode; the counter electrode was in the other compartment.

Pyrolytic graphite electrode. Much of the previous work with the pyrolytic graphite electrode in aqueous solutions was done with the pyrolytic graphite encased in epoxy resin³⁻⁶, but because the solution of Ce(IV) in 1.0 M sulfuric acid used in the present study oxidized the epoxy resin, the pyrolytic graphite was encased in KEL-F fluorocarbon resin (produced by the Minnesota Mining and Manufacturing Company).

Figure 1 is a diagram of the electrode. A solution-tight seal between the pyro-

* For a brief description of PG properties, see ref. 1.

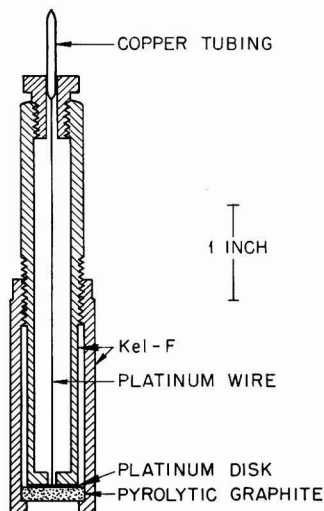


Fig. 1. Pyrolytic graphite electrode encased in KEL-F.

lytic graphite and the KEL-F assembly was obtained by pressure applied when the two major parts of the KEL-F assembly were screwed together. Electrical contact with the pyrolytic graphite was made with a platinum disk pressed against the graphite surface and brazed to a platinum wire. The geometrical area of the electrode was 1.27 cm². The area obtained from the electrochemical study of the oxidation of Fe(CN)₆⁴⁻ was 1.29 cm².

Reference electrode. A Beckman saturated calomel electrode with an asbestos fibre tip was used as a reference electrode.

Counter electrode. A piece of platinum foil served as the counter electrode.

Reagents. All chemicals used were of reagent grade.

Inert gases. When it was desirable to remove dissolved oxygen from the electrolysis solution, it was thoroughly flushed with helium and a layer of argon was kept over the solution during the electrochemical determinations.

Procedure

The effect of prior electrochemical oxidation as well as prior chemical oxidation (with Ce(IV) in 1 M H₂SO₄), on the electrochemical behavior of the PG electrode was studied in the following manner. To explore the effect of electrochemical oxidation, the potential of the PG electrode was controlled at some positive value for a given period of time; this treatment was followed by a cathodic voltammogram or chronopotentiogram. To study the effect of oxidation by Ce(IV), the electrode was immersed in a Ce(IV) solution for a given period of time; it was then removed from that solution, washed with the supporting electrolyte and placed in the electrochemical cell containing 1 M H₂SO₄; a cathodic voltammogram or chronopotentiogram was obtained.

RESULTS AND DISCUSSION

Cathodic voltammograms obtained in an oxygen-free solution at a non-anodized* PG electrode are shown in Fig. 2, curves 1 and 2. The reduction of oxygen (the solution was saturated with air) at a non-anodized electrode is also shown (Fig. 2, curve 3). Figure 2, curve 4, is the voltammogram obtained when the PG electrode is anodized at +1.5 V for 1.5 min in an oxygen-free solution. A voltammogram obtained under the same conditions as curve 4, but which includes

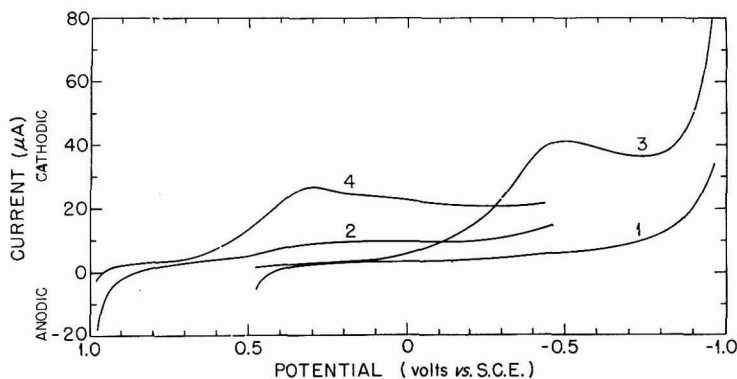


Fig. 2. Cathodic voltammograms in 1.0 M H_2SO_4 at the PG electrode: (1) and (2), background; (3), reduction of oxygen; (4), reduction of the film. Scan rate 0.5 V/min.

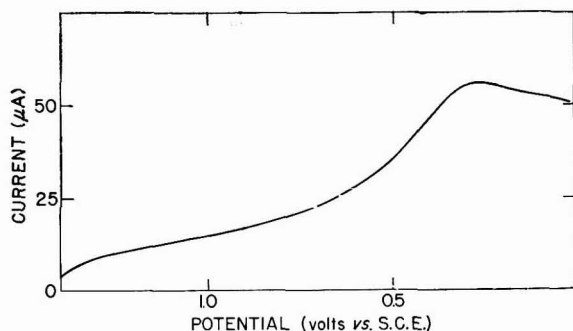


Fig. 3. Reduction of the film on PG electrode. Scan rate 1.0 V/min.

the potential interval +1.5—+1.0 V is shown in Fig. 3. The wave with $E_{p/2} = +0.48$ V is obviously caused by the anodic treatment; it will be referred to as the film wave. The reduction of the film probably proceeds irreversibly although the theory for an insoluble $O (+n e \rightleftharpoons R)$ has apparently not been developed.

* The term "non-anodized" implies that the electrode was not subjected to an anodic treatment immediately prior to the cathodic voltammogram; it has been found that anodization followed by one or two cathodic voltammograms results in an electrode surface which behaves similarly to a non-anodized electrode.

The experimental $E_p - E_{p/2} = -210$ mV. For a reversible charge transfer, $O + n e \rightleftharpoons R$, both O and R soluble, $E_p - E_{p/2} = -56.5/n$ mV at 25°C ¹⁸. When R deposits on the electrode, the charge transfer being reversible, $E_p - E_{p/2} = -20/n$ mV¹⁹.

A series of voltammograms corresponding to different initial anodic potentials and showing both the film and the oxygen waves are shown in Fig. 4. It is apparent that the peak potential of the film reduction becomes more negative and the peak potential of oxygen reduction becomes more positive with increasing initial anodic potentials.

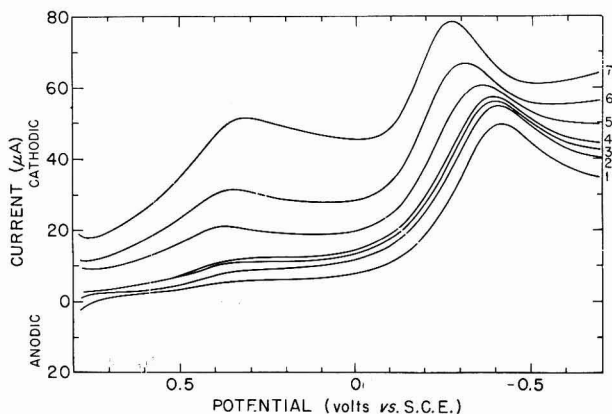


Fig. 4. Voltammograms of the reduction of the film on the PG electrode and the consecutive reduction of oxygen in $1.0 M \text{H}_2\text{SO}_4$. Scan rate 0.5 V/min . Prior to each run the electrode was anodized for 1 min at the following potentials: (1), no treatment; (2), $+1.1 \text{ V}$; (3), $+1.2 \text{ V}$; (4), $+1.3 \text{ V}$; (5), $+1.5 \text{ V}$; (6), $+1.6 \text{ V}$; (7), $+1.7 \text{ V}$.

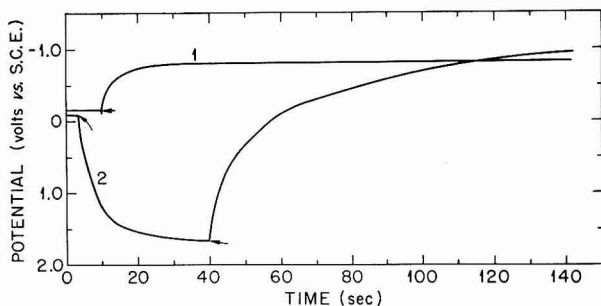


Fig. 5. Chronopotentiograms illustrating film formation on PG electrode in $1.0 M \text{H}_2\text{SO}_4$. (1): $i_{\text{cath}} = 5.0 \times 10^{-5} \text{ A}$; (2): $i_{\text{an}} = 2.37 \times 10^{-4} \text{ A}$ (2): $i_{\text{cath}} = 9.0 \times 10^{-5} \text{ A}$ (the current was applied at the time corresponding to the position of the arrow).

The chronopotentiograms illustrating the presence of the film are shown in Fig. 5. No well-defined potential-time curve corresponding to the reduction of the film was obtained; it is apparent, however, that in the case of the anodized electrode,

the potential corresponding to the reduction of the supporting electrolyte is approached gradually, rather than abruptly. Similar results are obtained when the electrode is exposed to Ce(IV) solution (the electrode is left overnight in $4.1 \times 10^{-3} M$ $Ce(SO_4)_2$ in $1.0 M$ H_2SO_4).

The voltammogram obtained with the PG electrode that has been kept in contact with $4.2 \times 10^{-2} M$ Ce(IV) in $1.0 M$ H_2SO_4 for 20.5 h, followed by a thorough washing with $1.0 M$ H_2SO_4 , in a deaerated $1.0 M$ H_2SO_4 solution, is shown in Fig. 6,

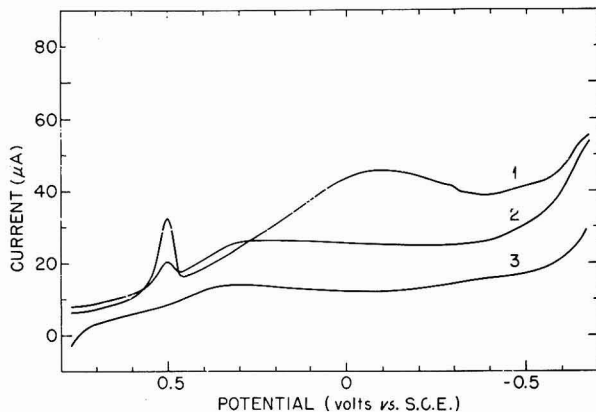


Fig. 6. Reduction of the film on PG electrode; film caused by treatment with Ce(IV) in $1.0 M$ H_2SO_4 . Voltammograms obtained: (1), after 20.5 h; (2), after 47 min; (3), immediately after (2). Scan rate = $0.5 V/min$.

curve 1. A sharp peak occurs at the potential corresponding to the anodically-formed film; the sharp peak is followed by a broad peak at $\sim 0 V$. Ce(IV) is reduced under these conditions at $+1.15 V$ vs. S.C.E.⁵

A voltammogram obtained after a much shorter exposure (47 min) to Ce(IV) is also shown (curve 2); curve 3 was obtained immediately after curve 2 without further treatment with Ce(IV). From a comparison of the voltammograms obtained after the chemical oxidation with those obtained after the anodic treatment, it appears that the nature of the film obtained by chemical oxidation is different from that of the anodically-formed film.

Attempts were made to study the surface film on pyrolytic graphite by electron diffraction. Three samples of pyrolytic graphite treated as indicated below, were examined by T. E. WILLMARTH*. Sample A was untreated; sample B was left in contact with a $4.1 \times 10^{-3} M$ Ce(IV) solution in $1.0 M$ H_2SO_4 for 9 days, and $4.1 \times 10^{-2} M$ Ce(IV) solution in $1.0 M$ H_2SO_4 for 3 days; sample C was anodized at $+2.0 V$ in $1.0 M$ H_2SO_4 for 80 min. The three reflection electron diffraction patterns were identical. High voltage electron diffraction was employed; low voltage diffraction, a much more sensitive technique for film studies, might have resulted in differences in

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the patterns obtained but the equipment for low voltage electron diffraction was not available.

In conclusion, a film is produced on pyrolytic graphite electrodes through anodic oxidation or treatment with a strong oxidant, such as Ce(IV). The film produced anodically differs electrochemically from the film produced chemically. This film (or films) is apparently reduced irreversibly. The nature of the film could not be ascertained in this study. Since the film is apparently conducting (reduction of Ce(IV) has been observed at the PG electrode), it is not likely that it is graphite oxide²⁰ or a layer of chemisorbed oxygen. Electrolytic lamellar compounds²⁰ of graphite are a possibility.

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We would like to thank Mr. RALPH E. MORTON for designing and fabricating the PG electrode encased in KEL-F.

SUMMARY

It has been shown that electrochemical or chemical oxidation with a strong oxidant, such as Ce(IV), results in the formation of a film on the surface of pyrolytic graphite. The film produced anodically differs electrochemically from the film produced chemically, although in both cases reduction of the film is observed at $\sim +.5$ V vs. the saturated calomel electrode. The reduction of the film apparently proceeds irreversibly. Attempts to study the film by high voltage electron diffraction were unsuccessful. The nature of the film has not been determined.

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UNEVEN CURRENT DISTRIBUTION ON THE SURFACE OF A DROPPING MERCURY ELECTRODE AND ITS POSSIBLE RELATION TO MAXIMA OF THE FIRST KIND

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INTRODUCTION

The dropping mercury electrode has proved to be extremely useful in analytical applications and also for the determination of the kinetics of electrode reactions. ILKOVIČ^{1,2} treated mass transport towards and from a concentrically growing mercury drop, and derived his well-known equation for the mass transfer limiting current, i_l :

$$\pm i_l = nFAc^*(7D/3\pi t)^{\frac{1}{2}} \quad (1)$$

$$A = 4\pi r_0^2 = 4\pi(3mt/4\pi d)^{\frac{2}{3}} \quad (2)$$

where A is the surface area and r_0 the radius of the (spherical) mercury drop as a function of Hg flow rate m , Hg density d and time t . Per particle, n electrons are involved in the electrode reaction, F is the faraday, c^* the bulk concentration of the reducible or oxidizable species and D its diffusion coefficient. The sign preceding i_l depends on the sign convention adopted and whether a reduction or an oxidation is considered; henceforth the sign of i_l will be omitted from the formulae. Equation (1) describes the polarographic experiments satisfactorily, but a number of corrections have been made to account for small deviations observed.

The *curvature* of the drop surface was accounted for in the differential equation of MACGILLAVRY AND RIDEAL³. In solving their eqn. (4) with the appropriate boundary conditions, however, these authors introduced approximations which reduced the problem to that of ILKOVIČ, whose result they thus "confirmed".

After a number of authors⁴⁻⁸ had given approximate treatments, KOUTECKÝ⁹ arrived at the complete solution.

A small amount of solution which is partially exhausted by electrolysis on a drop may remain near the orifice of the capillary after this drop has fallen off, and cause a lowering of current on the next drop, especially during the early stages of drop life. This *depletion effect*¹⁰⁻¹² may be reduced by using a capillary with a sharply drawn-out tip and by knocking off the drops¹³, or by using "alternate drops"¹⁴. It may be completely avoided by using so-called first drops¹¹⁻¹².

With blunt capillaries the top of the drop is less accessible to mass transfer than the bottom of the drop. This *shading effect*⁸ should be absent with a capillary with a fine point.

In the derivation of the Ilkovič equation the mercury flow rate, m , is assumed to be constant. Because the curved mercury–solution interface results in a surface pressure counteracting the pressure of the mercury head, and the magnitude of this *back pressure*^{15–20} changes with changing drop radius, m may vary during drop life. This results in a lowering of the current in the early stages of drop life. A large Hg head reduces the effect.

In this communication we will discuss still another complication, which is a consequence of the fact that the drop does not grow concentrically, but rather from a fixed point at its surface. We do not suggest that this effect is more important than any of the preceding ones, and in fact we will show that eqn. (1) is hardly affected if the more correct expansion of the drop is taken into account. However, it appears that the current is distributed rather unevenly over the surface of the Hg drop, and this may have some interesting consequences, see the discussion.

THE ILKOVIČ EQUATION

In the derivation of the Ilkovič equation it is assumed that the drop grows concentrically. This is visualized in Fig. 1, where we consider a concentrically growing drop (inner sphere) plus a constant volume of surrounding solution (outer sphere), at different stages in drop life.



Fig. 1. A concentrically growing Hg drop (inner sphere) plus a constant volume of surrounding solution (outer sphere), at different stages in drop life.

a drop plus a constant volume of solution. Points on the surfaces of both spheres move away from the center of the drop, but the two surfaces approach each other since the volume of incompressible solution between the two is fixed.

Quantitatively, the flux of incompressible solution through a surface of radius r around the center of the drop follows from the volume passing through it,

$$4\pi r^2 v_r t = mt/d \quad (3)$$

so that the radial velocity v_r of the solution is given by

$$v_r = m/4\pi r^2 d \quad (4)$$

The relative velocity v_x of solution towards the electrode surface at r_0 is then

$$v_x = v_r - v_{r_0} = \frac{m}{4\pi d} \left(\frac{1}{r^2} - \frac{1}{r_0^2} \right) \approx -\frac{2x}{3t} \quad (5)$$

for

$$x \equiv r - r_0 \ll r_0, \quad r_0 = (3mt/4\pi d)^{\frac{1}{2}}$$

Inserting eqn. (5) into the general equation for plane diffusion plus convection yields the Ilkovič differential equation²

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v_x \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial x^2} + \frac{2x}{3t} \frac{\partial c}{\partial x} \quad (6)$$

which we will solve here for the simple case of the limiting current⁺, which corresponds to the boundary conditions

$$c(x, 0) = c(\infty, t) = c^*, \quad c(0, t) = 0 \text{ for } t \geq 0 \quad (7)$$

with^{2,3,24} $\xi \equiv xt^{2/3}$, $\tau \equiv 3/7t^{7/3}$ and $u \equiv c - c^*$ we transform eqns. (6) and (7) into

$$\frac{\partial u}{\partial \tau} = D \frac{\partial^2 u}{\partial \xi^2} \quad (8)$$

$$u(\xi, 0) = u(\infty, \tau) = 0, \quad u(0, \tau) = -c^* \text{ for } \tau \geq 0 \quad (9)$$

Using the Laplace transform

$$\overline{f(\tau)} \equiv \int_0^\infty f(t) \exp[-p\tau] d\tau$$

we obtain

$$\frac{p\bar{u}}{D} = \frac{d^2 \bar{u}}{d\xi^2} \quad (10)$$

$$\bar{u}(\infty, p) = 0, \quad \bar{u}(0, p) = -\frac{c^*}{p} \quad (11)$$

From eqns. (10) and (11) it follows that

$$\bar{u} = -\frac{c^*}{p} \exp\left[-\xi \sqrt{\frac{p}{D}}\right] \quad (12)$$

$$\left(\frac{d\bar{u}}{d\xi}\right)_{\xi=0} = c^*(pD)^{-1/2} \quad (13)$$

Inverse Laplace transformation²¹ finally gives

$$u = c - c^* = c^* \operatorname{erfc}\left[\frac{\xi}{2}(D\tau)^{1/2}\right] = c^* \operatorname{erfc}\left[\frac{1}{2}x(7/3Dt)^{1/2}\right] \quad (14)$$

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} = t^{1/2} \left(\frac{\partial u}{\partial \xi}\right)_{\xi=0} = c^* t^{1/2} (\pi D\tau)^{-1/2} = c^* (7/3\pi Dt)^{1/2} \quad (15)$$

from which eqn. (1) follows, since

$$i_l = nFAD \left(\frac{\partial c}{\partial x}\right)_{x=0} \quad (16)$$

⁺ In view of the substantial contribution of convection to the total current, as reflected, for example, in the Ilkovič factor $(7/3)^{1/2}$ in eqn. (15), we prefer the term limiting current to the more commonly used "diffusion current".

THE EFFECT OF ECCENTRIC DROP GROWTH

We will now consider the effect of eccentric drop growth, leaving unaltered all other assumptions implicitly made in the derivation of the Ilkovič equation.

The expansion of a Hg droplet from a point at its surface may be represented by the radial expansion expressed by eqn. (4) plus an additional downward velocity of the center of the drop,

$$\frac{dr_0}{dt} = \frac{1}{3} (3 m/4\pi d)^{\frac{1}{3}} t^{-\frac{2}{3}} = m/4\pi r_0^2 d \quad (17)$$

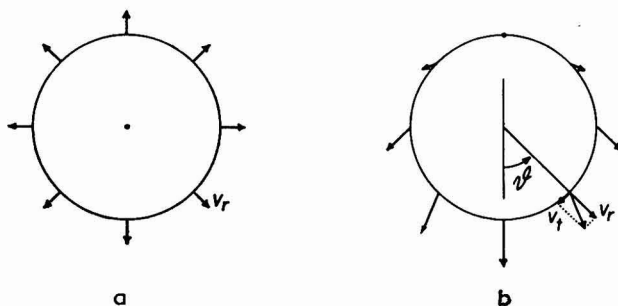


Fig. 2. The velocity of the drop surface, and its radial (v_r) and tangential (v_t) components; (a), concentric, (b), eccentric drop growth.

We assume, as before, that the solution moves in the direction in which it is pushed by the expanding surface of the drop, see Fig. 2. For the velocity component perpendicular to the surface of the drop we find, by adding eqn. (4) and the radial component of eqn. (17),

$$v_r = m(1 + \cos \vartheta)/4\pi r^2 d \quad (18)$$

and consequently for the relative velocity v_x of the solution towards the electrode

$$v_x = \frac{m(1 + \cos \vartheta)}{4\pi d} \left(\frac{1}{r^2} - \frac{1}{r_0^2} \right) \approx -\frac{2x}{3t} (1 + \cos \vartheta) \quad (19)$$

which may be compared with eqn. (5).

The differential equation substituting eqn. (6) is therefore

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} + \frac{2x}{3t} (1 + \cos \vartheta) \frac{\partial c}{\partial x} \quad (20)$$

which after substitution of

$$\xi \equiv xt^{2(1 + \cos \vartheta)/3}$$

$$\tau \equiv \frac{3t^{(7 + 4 \cos \vartheta)/3}}{7 + 4 \cos \vartheta}$$

$$u \equiv c - c^*$$

gives

$$\frac{\partial u}{\partial \tau} = D \frac{\partial^2 u}{\partial \xi^2} \quad (21)$$

Equation (21) has the same form as eqn. (8), although ξ and τ are defined differently. Since the corresponding boundary conditions have the form of eqn. (9), we obtain the solution for $(\partial c / \partial x)_{x=0}$ by analogy with eqn. (15), hence

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} = t^{2(1+\cos\vartheta)/3} \left(\frac{\partial u}{\partial \xi}\right)_{\xi=0} = c^* (7 + 4 \cos \vartheta)^{\frac{1}{3}} (3\pi Dt)^{-\frac{1}{2}} \quad (22)$$

The current density, I , as a function of ϑ is given by

$$I(\vartheta) = nFD \left(\frac{\partial c}{\partial x}\right)_{x=0} = nF \sqrt{\frac{(7 + 4 \cos \vartheta)D}{3\pi t}} \quad (23)$$

The total current i through the drop then follows as

$$i = \int_{\vartheta=0}^{\pi} 2\pi r_0^2 I(\vartheta) \sin \vartheta \, d\vartheta = 2\pi r_0^2 nF (D/3\pi t)^{\frac{1}{2}} \int_{\vartheta=0}^{\pi} (7 + 4 \cos \vartheta)^{\frac{1}{3}} \sin \vartheta \, d\vartheta$$

On substituting $z \equiv 7 + 4 \cos \vartheta$ so that $\sin \vartheta \, d\vartheta = -\frac{1}{4} dz$, we finally obtain

$$\begin{aligned} i &= \frac{1}{2} \pi r_0^2 nF (D/3\pi t)^{\frac{1}{2}} \int_{z=11}^3 z^{\frac{1}{3}} dz = 4 \pi r_0^2 nF (D/3\pi t)^{\frac{1}{2}} \frac{11^{\frac{4}{3}} - 3^{\frac{4}{3}}}{12} \\ &= 1.505 nFA (D/\pi t)^{\frac{1}{2}} \end{aligned} \quad (24)$$

When we compare the numerical coefficient 1.505 with that of eqn. (1), *viz.*

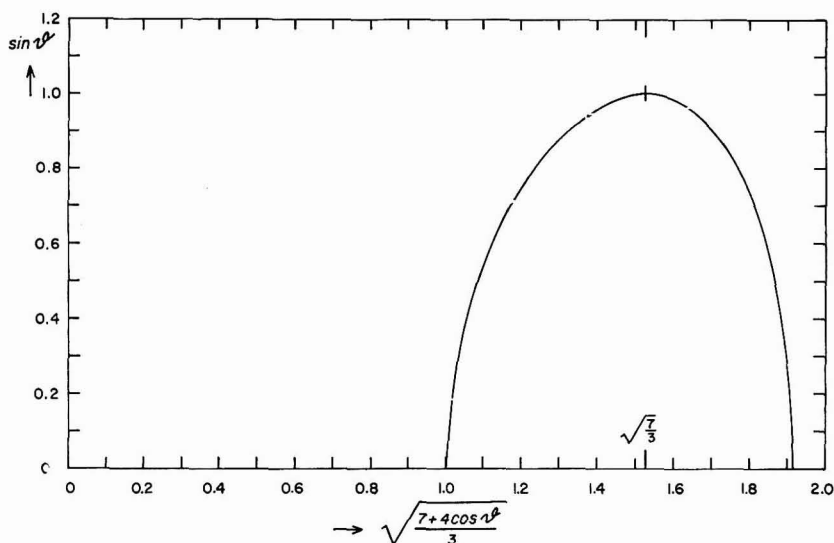


Fig. 3. The convection coefficient, $\{(7 + 4 \cos \vartheta)/3\}^{\frac{1}{3}}$, as a function of the weight factor, $\sin \vartheta$.

$(7/3)^{\frac{1}{2}} = 1.528$, we see that the eccentricity of the drop growth has a negligible effect on the total current flowing through the electrode. However, the current is not evenly distributed over the surface of the drop, as shown by eqn. (23). For the bottom of the drop, where the radial velocity is twice that of the Ilkovič treatment, we have $\vartheta = 0$ and consequently $I = nF(11D/3\pi t)^{\frac{1}{2}} = 1.915 nF(D/\pi t)^{\frac{1}{2}}$. For the top of the drop, which does not move, we have $\vartheta = \pi$, so $I = nF(D/\pi t)^{\frac{1}{2}}$, as one would expect. This shows that the current density at the bottom of the drop is almost twice that at the neck. Of course, the current densities at top and bottom are the two extremes, and a more realistic representation is given in Fig. 3, where we have plotted the numerical coefficient $\{7 + 4 \cos \vartheta/3\}^{\frac{1}{2}}$ of eqn. (23) versus the weight factor, $\sin \vartheta$. The Ilkovič treatment yields the numerical coefficient $(7/3)^{\frac{1}{2}}$, at which value the curve of Fig. 3 has its maximum.

DISCUSSION

(a) From the preceding calculations it follows that the limiting current is rather unevenly distributed over the surface of the growing mercury drop, even if the capillary has negligibly thin walls. It can easily be verified that the same applies to every point of the so-called "reversible waves", which are those polarographic waves for which the electrode reactions are so much faster than mass transport towards and from the electrode, that their rates may be considered to be infinitely fast.

If the rates of the electrode reactions must be taken into account, a similar derivation can be given along the lines of published treatments^{24,25}. However, the corresponding equations get very complicated, whereas the effect becomes relatively less important since mass transport is no longer the sole factor controlling the current. Moreover, with both fast and slow electrode reactions, a relatively simple mathematical treatment can only be given when the solution resistance is negligibly small, see (b). This is the main reason why such explicit formulae would be of little practical use, and are not given here.

However, even without a quantitative treatment one comes to the conclusion, that rate constants determined from polarographic measurements are often apparent rather than actual values. This is not too surprising since polarographic waves can often be described by relations²²⁻²⁵ for first-order electrode reaction and mass transfer even if the electrode processes are known to be more complicated. This may be illustrated by the system V^{3+}/V^{2+} in H_2SO_4 as studied by RANGLES²⁶ with both polarography and impedance measurements. The method used in the evaluation of his impedance measurements (his foot-note, p. 245) indicates that the system is more complicated, as is also borne out by the variation in the apparent transfer coefficient observed, see his Fig. 4. Nevertheless the analysis of the polarogram does not indicate any irregularity. The same applies to Ni^{2+}/Ni in $NaClO_4$ ²⁷, since Ni^{2+}/Ni is known^{28,50} to be a more complicated reaction in $NaClO_4$.

(b) In all cases in which the solution resistance cannot be neglected, uneven current distribution causes uneven potential distribution over the solution side of the electrode-solution interface. Consequently, in the region of larger mass transport, *i.e.*, near the bottom of the drop, the effective electrode potential is smaller than in regions of smaller mass transport. If the current density depends on the electrode

potential, as is the case in the region of the polarographic wave, this may either enhance or partially compensate the effect of uneven mass transport.

(c) Since the surface tension depends on potential, the uneven potential distribution will also cause differences in surface tension over the surface of the drop, which in turn may cause streaming (which in the solution may already originate in the tangential velocity $v_t = m \sin \vartheta / 4\pi r_0^2 d$ of the drop surface. The surface tension usually changes markedly with potential in the region of the polarographic wave if one or both electroactive species are specifically adsorbed at the interface^{29,30}, because in this region the concentrations at the interface of the oxidized and reduced form change abruptly with potential. Thus one may expect "maxima of the first kind" in such a case. In this respect we may note, as did HEYROVSKÝ *et al.*³⁴⁻³⁷ and recently BARKER AND FAIRCLOTH³², that strong specific adsorption seems to be present with a number of substances known to give pronounced maxima. Double-layer capacitance measurements³¹ indicated that the capacitance, and consequently the surface tension, change rapidly near the equilibrium potential of $\text{Hg}_2^{2+}/\text{Hg}$ in HClO_4 . Pb^{2+} was reported³² to be strongly specifically adsorbed in KCl-HCl , causing a pronounced lowering of the double-layer capacitance in a narrow region close to the half-wave potential of that system (ref. 32, Fig. 4) which must likewise be reflected in the surface tension. Also, BARKER AND FAIRCLOTH³² showed that the maxima of Pb^{2+} and Tl^+ disappear in media in which these ions are not strongly specifically adsorbed.

Drop weight measurements at potentials slightly more negative than those of the streaming maximum of O_2 in Na_2SO_4 solutions²⁹ suggest that H_2O_2 is adsorbed. (In the region of the maximum, the streaming apparently interferes with the relation between drop weight and surface tension³³, so that the drop-weight method cannot be used.)

(d) It should be noted that this tentative explanation of the origin of maxima reconciles the seemingly contradictory views of HEYROVSKÝ *et al.*³⁴⁻³⁷ and those of FRUMKIN AND BRUNS^{33,38}, ANTWEILER^{39,40} and VON STACKELBERG⁴¹⁻⁴³. HEYROVSKÝ *et al.*³⁴⁻³⁷ noted that maxima usually occur when strongly surface-active substances are reduced, and consequently based their explanation on the adsorption of electroactive substances. FRUMKIN AND BRUNS³⁸ showed that maxima at a stationary Hg drop were accompanied by intensive streaming of the solution in the vicinity of the electrode, and suggested that similar streaming phenomena might cause maxima at a dropping mercury electrode. Indeed ANTWEILER^{39,40} observed such streaming, and attributed it to changes in surface tension caused by uneven current distribution due to shielding by the capillary tip. However⁴⁰, he observed no difference in streaming between a blunt capillary and one which had a tip of only 80 μ external diameter, so that the region where shielding might have occurred would have been extremely small. Recently FLEMMING AND BERG⁴⁴ confirmed this observation with a capillary with extraordinarily thin walls.

The dependence of the maxima on the rate of mercury flow^{34-36*} and on the concentration of the electroactive substance^{34,36} cannot be explained by ANTWEI-

* However, this might be due to time-dependent accumulation of surface-active impurities.

LER's theory, neither can the observation that the occurrence of maxima may depend upon stirring of the solution³⁶. Moreover, ANTWEILER's theory does not give an explanation for the fact that the maximum usually breaks off as soon as the limiting current is reached, and the *ad hoc* explanation of VON STACKELBERG^{41,42} is not supported by any independent evidence.

If streaming is caused by the effect on surface tension of local variations of the concentration, at the interface, of a surface-active reducible substance, streaming must disappear in the region of the cathodic limiting current, where the concentration is zero everywhere at the interface. When the reduction product is surface active, its concentration at the interface changes very rapidly during the wave and much less in the region of the cathodic limiting current, and consequently in this case the maximum will usually be confined to the region of the wave also. For further comments the reader may consult ref. 45.

Finally we note that the explanation presented here for the occurrence of maxima of the first kind has some aspects in common with that given by LEVICH (summarized in ref. 46), in that the downward movement of the growing drop is taken into account. However, no external electrical field need be introduced in our explanation, and we see no difficulties in explaining the occurrence of only one maximum, in the region of the wave, usually breaking off as the limiting current is reached.

(e) We do not suggest that eccentric drop growth is the only possible origin of uneven current distribution, causing maxima of the first kind. Apparently other causes must be involved in maxima observed with suspended³⁸ and hanging⁴⁰ drops or Hg pools^{33,41}.

VON STACKELBERG AND DOPPELFELD⁴³ have pointed out that *e.g.* a reduction on a positively charged Hg electrode at rest may already constitute an unstable system.

Severe shielding occurs in the thin solution film usually formed between Hg and glass⁴⁷ (compare the creeping of solution between Hg and glass reported in ref. 41). Such shielding may be another cause of differences in surface tension leading to streaming of the interface.

In the experiments with large Hg pools^{33,41} non-uniform current distribution may easily have resulted from the relative positions of the electrodes⁴¹. (With a small Hg droplet, almost all solution resistance is confined to the region very close to the drop⁴⁸, and the position of the counter electrode is far less important.)

In view of the shape of the drop neck (*e.g.*, ref. 15) and the experiments of ANTWEILER⁴⁰ and FLEMMING AND BERG⁴⁴ mentioned under (d), it seems unlikely* that shielding³⁹⁻⁴³ (uneven current distribution resulting from a geometric constriction of current lines) or shading⁸ (geometric hindrance of mass transport) by the tip of the capillary can cause significant non-uniformity of the current under usual polarographic conditions. Since streaming of the solution enhances the non-uniformity of mass transport over the drop surface, the maximum will usually sustain itself even beyond the region where it would originate from drop growth or other causes. Consequently considerable hysteresis^{36,41} of the maximum may occur at stationary Hg surfaces. At the dropping mercury electrode such hysteresis is small or absent^{36,43}. Apparently the streaming is not so easily transferred from one drop to another.

* However, a more quantitative treatment is in order before a final conclusion can be drawn.

(f) The non-uniformity of mass transport towards a growing drop may severely complicate the quantitative description of double-layer effects as observed *e.g.*, with the reduction of anions (for a review see ref. 49), especially when experiments are made in very dilute solutions where variations in local *IR* drop be rather important (compare (a)).

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SUMMARY

The downward movement of a growing mercury drop electrode is taken into account in a treatment in which all other assumptions inherent in the Ilkovič treatment are retained. It is shown that the downward movement results in a non-uniform distribution of mass transport towards the electrode. On this basis, also taking into account specific adsorption, a tentative explanation is given for the origin of polarographic maxima of the first kind. Finally some difficulties with the polarographic determination of rates of electrode reactions are briefly discussed.

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SHORT COMMUNICATIONS

Polarographic studies of the pyridine complexes of zinc and cadmium in aqueous medium

HEYROVSKÝ AND ILKOVIČ¹ in 1935 were the first to recognize the possibility of using polarography for the study of complexes. This method, later discussed in detail by LINGANE², has a number of limitations, but DEFORD AND HUME³ extended the scope of polarography to the study of the composition and consecutive formation constants of a number of weak complex species of comparable stabilities present in solution, provided the reduction at D.M.E. is reversible. A number of studies using this approach have appeared in recent years. The present communication, describes the polarographic determination of the composition and stability of pyridine complexes of zinc and cadmium in aqueous medium.

Theory

It was shown by DEFORD AND HUME that the shift in half-wave potential due to complex formation can be expressed as

$$\Delta E_{\frac{1}{2}} = (E_{\frac{1}{2}})_c - (E_{\frac{1}{2}})_s = \frac{2.303 RT}{nF} \log_{10} f_M \frac{I_c}{I_s} \sum_0^N \frac{\beta_j \{x\}^j}{f_{Mx_j}} \quad (1)$$

where $(E_{\frac{1}{2}})_c$ and $(E_{\frac{1}{2}})_s$ are the half-wave potentials of the complex and simple metal ions, respectively; R , T and F have their usual significance; n denotes the number of electrons required for the electrode reaction; I_s and I_c are the experimental diffusion constants for simple and all complex ions, respectively; β_j is the over-all formation constant of the j -th complex; $\{x\}$ is the activity of the complexing ligand and f_M and f_{Mx_j} denote the activity coefficients at the electrode surface of the metal and complex species, respectively.

Equation (1) can be rearranged to define a function $F_0(x)$ such that

$$\begin{aligned} F_0(x) &= \text{antilog} \left(\frac{0.4343 nF}{RT} \cdot \Delta E_{\frac{1}{2}} + \log \frac{I_s}{I_c} \right) \\ &= f_M \sum_0^N \frac{\beta_j \{x\}^j}{f_{Mx_j}} \\ &= 1 + \beta_1(x) \frac{f_M f_x}{f_{Mx}} + \beta_2(x)^2 \frac{f_M (f_x)^2}{f_{Mx_2}} + \beta_3(x)^3 \frac{f_M (f_x)^3}{f_{Mx_3}} + \dots \end{aligned} \quad (2)$$

where (x) denotes the concentration of the complexing ligand and f_x the corresponding activity coefficient. It has been pointed out by IRVING⁴ that the activity coefficient term can be dropped to a good approximation for uncharged ligands. Values of $F_0(x)$ for different values of the concentration of the complexing ligand can be determined experimentally and eqn. (2) can then be solved graphically for β_1 , β_2 , β_3 etc. as suggested by DEFORD AND HUME³.

Further calculations show that the proportion of the uncomplexed metal ion and the various complex species, as a function of the ligand concentration, can be calculated using the following equations:

$$\frac{(M)}{C_M} = \frac{1}{F_0(x)} \quad (3)$$

$$\frac{(M_{x_j})}{C_M} = \frac{\beta_j(x)^j}{F_0(x)} \quad (4)$$

where (M) denotes the concentration of uncomplexed metal ions, (M_{x_j}) the concentrations of the j -th complex species and C_M the total metal ion added to the system.

Experimental

A LP-55 polarograph was used manually for obtaining the current-potential curves. Capillary characteristics for the open circuit were $m = 1.76$ mg/sec and $t = 4.2$ sec. A constant temperature of $30^\circ \pm 0.01^\circ$ was maintained by means of a Haake ultra thermostat. Purified nitrogen was used for removing oxygen from solutions.

Concentrations of Zn^{2+} and Cd^{2+} (as the nitrates) were kept constant at

TABLE 1

ANALYSIS OF THE PYRIDINE COMPLEXES OF ZINC IN AQUEOUS MEDIUM

No.	Pyridine Concn. (M)	$E_{\frac{1}{2}}$ vs. S.C.E. (V)	i_a (μA)	$F_0(x)$	$F_1(x)$	$F_2(x)$
1	0.0	-1.0008	5.65	1		
2	0.2	-1.0179	5.5	3.95	14.75	33.75
3	0.3	-1.0238	5.3	6.34	17.8	33.0
4	0.4	-1.0274	5.3	8.69	19.22	28.5
5	0.5	-1.0340	5.3	14.52	27.0	38.0
6	0.6	-1.0370	5.3	18.11	28.5	33.4
7	0.8	-1.0434	5.3	29.64	35.8	34.7
8	1.0	-1.0480	5.1	43.71	42.7	34.7

TABLE 2

ANALYSIS OF THE PYRIDINE COMPLEXES OF CADMIUM IN AQUEOUS MEDIUM

No.	Pyridine Concn. (M)	$E_{\frac{1}{2}}$ vs. S.C.E. (V)	i_a (μA)	$F_0(x)$	$F_1(x)$	$F_2(x)$	$F_3(x)$
1	0.00	-0.5795	6.10	1.0			
2	0.1	-0.5908	5.70	2.543	15.43		
3	0.2	-0.6033	5.35	7.041	30.2		
4	0.3	-0.6117	5.25	13.78	42.6		
5	0.4	-0.6201	5.15	26.58	63.9	102	75.8
6	0.5	-0.6257	5.10	41.18	80.4	115	84.0
7	0.6	-0.6293	5.05	54.83	89.7	111	70.0
8	0.8	-0.6375	4.85	107	132.5	137	81.2
9	1.0	-0.6436	4.75	174.4	173.4	150.4	78.4
10	1.5	-0.6541	4.20	440.7	293	180	72.0

$1 \cdot 10^{-3} M$ and a constant ionic strength, $\mu = 0.1$, was maintained using KNO_3 . An over-all concentration of 0.001% Triton X-100 was necessary for the suppression of maxima in both systems. Plots of $\log i/(i_d - i)$ vs. the applied potential were used to test the reversibility of the electrode reaction and also for obtaining the half-wave potentials. The analyses of the zinc-pyridine and cadmium-pyridine systems are given in Tables 1 and 2.

Results and discussions

Zinc-pyridine system. A plot of $F_0(x)$ vs. (x) is a smooth curve indicating the presence of more than one complex species, but $F_1(x)$ plotted against (x) gives a straight line with a slope and the $F_2(x)$ plot is a straight line parallel to the axis (concentration of pyridine) showing the presence of two complex species in solution, $[Zn(py)]^{2+}$ and $[Zn(py)_2]^{2+}$. The over-all formation constants for these complex ions

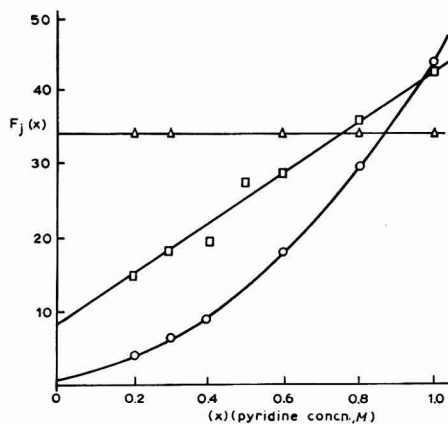


Fig. 1. $F_j(x)$ plots for the zinc-pyridine system. (○), $F_0(x)$; (□), $F_1(x)$; (△), $F_2(x)$.

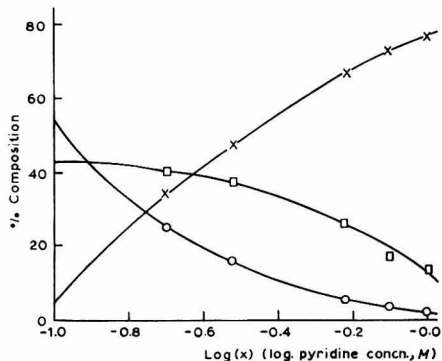


Fig. 2. Percentage composition for various species of the zinc-pyridine system. (○), Zn^{2+} ; (□), $[Zn(py)]^{2+}$; (×), $[Zn(py)_2]^{2+}$.

are $\beta_1 = 8.0 \pm 0.5$ and $\beta_2 = 34.0 \pm 1.0$. The $F_j(x)$ vs. (x) plots given in Fig. 1 show clearly that this method can be used to advantage for the study of very weak complexes. Recently MESARIC AND HUME⁶ have studied very weak complexes of Zn^{2+} , Cd^{2+} and Cu^{2+} with fluoride ions, using this method. The percentage compositions of Zn^{2+} , $[Zn(py)]^{2+}$ and $[Zn(py)_2]^{2+}$ are plotted against $\log(x)$ in Fig. 2.

Cadmium-pyridine system. The $F_j(x)$ vs. (x) plots (Fig. 3) for the cadmium-pyridine system show the presence of three complex species, $[Cd(py)]^{2+}$, $[Cd(py)_2]^{2+}$ and $[Cd(py)_3]^{2+}$. The over-all formation constants for these species are found to be, $\beta_1 = 23 \pm 2.0$, $\beta_2 = 72 \pm 5.0$ and $\beta_3 = 80 \pm 5.0$. A potentiometric study of the cadmium-pyridine system⁵ gave: $\beta_1 = 23 \pm 2$, $\beta_2 = 118 \pm 5$ and $\beta_3 = 574 \pm 15$.

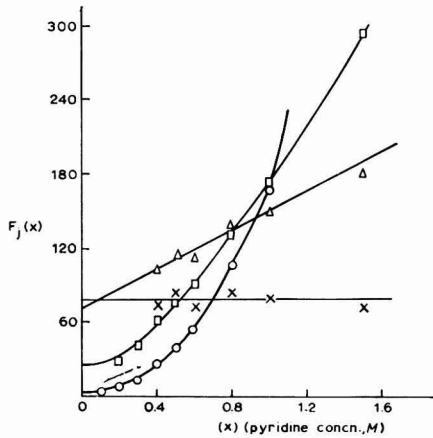


Fig. 3. $F_j(x)$ plots for cadmium-pyridine complexes. (\circ), $F_0(x)$; (\square), $F_1(x)$; (Δ), $F_2(x)$; (\times), $F_3(x)$.

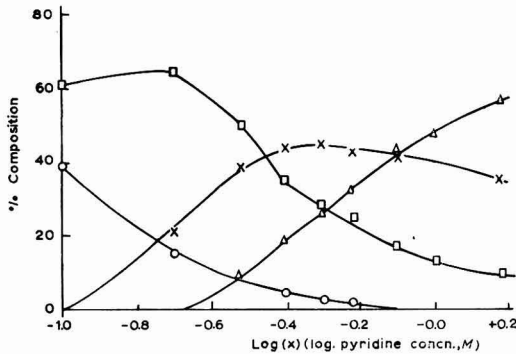


Fig. 4. Percentage composition of various species for the cadmium-pyridine system. (\circ), Cd^{2+} ; (\square), $[Cd(py)]^{2+}$; (\times), $[Cd(py)_2]^{2+}$; (Δ), $[Cd(py)_3]^{2+}$.

The first two values are of the same order as those obtained by us but the third differs considerably. In Fig. 4 the percentage compositions of the various species present in solution are plotted against $\log(x)$.

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POLAROGRAPHIC STUDIES OF THE PYRIDINE COMPLEXES OF ZINC AND CADMIUM IN AQUEOUS MEDIUM

Complexes of zinc and cadmium with pyridine have been studied polarographically using the method of DEFORD AND HUME. Two complex ions, $[\text{Zn}(\text{py})_2]^{2+}$ and $[\text{Zn}(\text{py})_3]^{2+}$, having over-all formation constants, $\beta_1 = 8.0 \pm 0.5$ and $\beta_2 = 34.0 \pm 1.0$, were detected in the zinc-pyridine system. In the case of the cadmium-pyridine system, three complex species, $[\text{Cd}(\text{py})]^{2+}$, $[\text{Cd}(\text{py})_2]^{2+}$ and $[\text{Cd}(\text{py})_3]^{2+}$, were found to be present, having constants $\beta_1 = 23 \pm 2.0$, $\beta_2 = 72 \pm 5.0$ and $\beta_3 = 80 \pm 5.0$. The percentage composition of the various complexed and uncomplexed ions for both systems are presented.

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The mechanism of charge transfer at electrodes

From 1935 until the late '50's, most treatments¹⁻⁵ of the charge transfer process have been analogous to those used in the quantum mechanics of chemical reactions. Stretching of ion-solvent and substrate-discharged ion bonds to give entities of equal energy have been the essential processes governing the rate of charge transfer. Such treatments allow the prediction of the effect of variables¹⁻⁷, *e.g.*, dielectric constant of the solvent, on the rate of charge transfer. They allow calculation of the symmetry factor of electrode reactions and its variation with potential⁶. However, such an ion-transfer model leaves implicit the motion of the electron itself, and omits to consider the charge distribution in the activated state.

Since 1958 several treatments⁸⁻¹⁰ of charge transfer have been made in which the basic model is that of redox processes in solution. In these treatments attention has been focused on the electron, tending to minimise the role played by ion-solvent and substrate-atom interactions. GERISCHER¹¹ has introduced a more general treatment based on the work of GURNEY¹². The above treatments of charge transfer lead to incorrect interpretations of the symmetry factor¹⁴. The significance of the crossing point of the potential energy surfaces, pertinent to the reaction, has not been fully recognized and the charge distribution in the activated state has either been neglected or given a false significance.

The potential energy profile for electron transfer, *e.g.*, in the discharge step,



of the hydrogen evolution reaction (h.e.r.) may be represented¹² by Fig. 1. The energy of the initial state, $\text{H}_3\text{O}^+ + \text{Me}^-$, with the reactants in their ground states, is represented by E_I . The energy of the neutralized state, $\text{M}-\text{H} + \text{H}_2\text{O}$ with the H atom in the position immediately after neutralization (not necessarily the ground state of the $\text{M}-\text{H}$) is represented by E_{II} .

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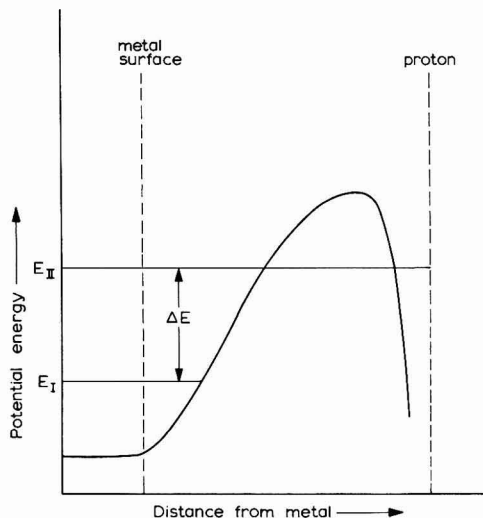
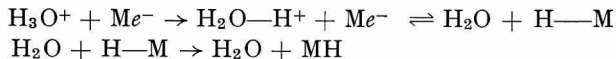


Fig. 1. Potential energy profile for electron transfer.

The probability of electron tunnelling from the metal to the H_3O^+ ion for an unactivated electron is zero, if there is no acceptor state for the electron. Thus, for neutralization of the H_3O^+ ion by an electron from the Fermi level of the metal, the energy ΔE (Fig. 1), equal to $(E_{\text{II}} - E_{\text{I}})$, must be decreased to zero. *This is brought about by activating the $\text{H}^+ - \text{OH}_2$ bond* by an amount of energy $\Delta\varepsilon$. Because stretching of the $\text{H}^+ - \text{OH}_2$ bond activates the initial state, but stabilizes the resultant neutralized state, $\Delta\varepsilon$ is equal to some fraction, β , of $\Delta\varepsilon$, where β is, general, a function of E . When the system is arranged so that $\Delta E = 0$, electron tunnelling from the metal to the proton can occur with some finite probability. The resulting H atom may then either relax into the ground state of the system $\text{MH} + \text{H}_2\text{O}$, or re-form a proton by electron tunnelling to the metal. The discharge step of the h.e.r. may then be written:



The activated state is comprised of *two resonant states*, with the same atomic, but different electronic configuration (*cf.* a similar conclusion by MARCUS⁸ for redox systems, reached by a different approach).

Consideration of the relative electron tunnelling probabilities, from H to H^+ and H to M, leads to the conclusion that the resonant states are equally probable, and that the *effective charge on the H nucleus in the activated state* is $1/2$ (*cf.* a similar conclusion due to HUSH⁹, attained for redox systems by a different approach).

Application of an electrical potential difference $\Delta\phi$, changes the energy gap, ΔE , to $\Delta E(\Delta\phi) = \Delta E + \Delta\phi F$ ($\Delta\phi$ being negative for cathodic potentials). The energy required to activate the $\text{H}^+ - \text{OH}_2$ bond is then $\beta\Delta E(\Delta\phi)$. Thus, the activation energy at a given $\Delta\phi$ is $\beta\Delta E(\Delta\phi)$ and the symmetry factor is β . Since for the purposes of calculating β , we are interested only in the energy required to stretch the $\text{H}_2\text{O}-\text{H}$ bond at a given $\Delta\phi$, then β may be obtained by the usual method of 'vertical shift'^{1,3,6,15}

and the symmetry factor is independent of the charge distribution in the activated state.

The symmetry factor at a given $\Delta\phi$ is thus the ratio of energy put into the $\text{H}^+ - \text{OH}_2$ bond to that put into closing the gap $\Delta E(\Delta\phi)$.

The present theory thus gives a tenable model for the electron movement in charge transfer⁸⁻¹³, but it relates this movement to that of the ion-solvent and atom-substrate¹⁻⁷. Means other than the above described mechanism, of closing the energy gap $\Delta E(\Delta\phi)$, such as electron activation, solvent activation, or activation of modes other than the $\text{H}^+ - \text{OH}_2$ stretching mode, will lead to higher energies of activation by virtue of the fact that $\Delta\varepsilon = \Delta E(\Delta\phi)$ for such processes. This suggests that, for all types of electrode processes the stretching of the ion-solvent (or anion-solvent) bond constitutes the rate-determining aspect of charge transfer at electrodes.

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REPORT**A RESUME OF THE EIGHTH CONFERENCE ON ANALYTICAL CHEMISTRY IN NUCLEAR TECHNOLOGY****ANALYSIS OF HIGH-PURITY NUCLEAR AND REACTOR MATERIALS**

More than 300 scientists, including 21 visitors from eight countries other than the U.S., attended the *Eighth Conference on Analytical Chemistry in Nuclear Technology*, which was held on October 6–8th, 1964, at Gatlinburg, Tennessee. This conference was sponsored by the Oak Ridge National Laboratory, operated by Union Carbide Corporation under the auspices of the U.S. Atomic Energy Commission.

Fifty-six technical papers were presented at nine sessions on the three days of the conference. In addition to the formal program, meetings were also held during the conference by three committees on specialized aspects of the subject. The best-known of these committees was the Sub-committee of the National Research Council on Radioactivity Standards. The other committees had met to discuss the results of analyses on exchange samples of beryllium and uranium.

The Eighth Conference emphasized the importance of the analysis of high-purity nuclear and reactor materials, particularly in the concentration ranges of parts per million and parts per billion. The discussion and comments of A. A. SMALES (UKAEA, Harwell, England) were of particular interest. He discussed the nature of the problems with which analytical chemists have to deal when they undertake the analysis of high-purity materials used in nuclear energy research, *i.e.* knowing what the engineer wants and then choosing a method which will yield the information in a reasonable time and at reasonable cost. He pointed out that the analytical chemist in his choice of a method must always consider the advantages of a number of methods and he gave a brief summary of his evaluation of a number of different methods of analysis considering sensitivity, accuracy, and freedom from contamination.

SMALES emphasized that the competent analytical chemist should be eager to learn new techniques or methods and be able to evaluate a proposed process and assign it to its proper place in the organization of a modern analytical laboratory.

Much of the success of many analytical laboratories is a consequence of the willingness of the laboratory staff to meet this challenge by discarding obsolete and sometimes revered methods of analysis which under careful scrutiny do not measure up to modern standards although they may have been the best available in the past.

After summarizing a wide range of available methods, SMALES commented briefly on the great interest shown in the use of techniques of spark-source mass spectrographic instruments of recent design, which were discussed earlier in the session in *Mass Spectrometric Methods of Analysis* by both W. FLETCHER (UKAEA, Capenhurst Works, England) and J. C. FRANKLIN (Y-12 Plant at Oak Ridge, Tennessee). In his opinion this instrumental technique holds great promise for future analysis of traces in high-purity materials.

When asked whether he thought the so-called "wet chemist" would disappear from analytical laboratories, he said he thought not, but commented, however, that this did not mean that old methods should be retained when new methods and techniques are more satisfactory.

SMALES also stressed the importance of good liaison between the analytical chemist and the engineer who submits the materials for analysis. Their cooperation could be very helpful especially in the early stages of development. These comments led to some discussion which in general favored his views.

In another session, the use of both radioactive ^{99}Tc and stable ^{139}La fission-products nuclides as burn-up monitors was discussed. A handicap in the accurate determination of burn-up values is the variation in the published values for a number of the physical constants needed such as fission yields and cross sections. J. E. REIN (Phillips Petroleum, Idaho Falls, Idaho) described their program which aims at a better understanding of these parameters. Their program is a long-range one, and the results will be of significance to all those who are interested in burn-up analysis.

At the session on nuclear methods of analysis, a number of specific analytical methods were described. At another session, general applications of liquid scintillation counting were presented, including a description of a method for the determination of noble gases by D. L. HORROCKS AND M. H. STUDIER (Argonne National Laboratory), and a technique for absolute assay of β -emitters of maximum energy greater than 200 keV, by G. GOLDSTEIN (Oak Ridge National Laboratory).

Several new or modified techniques were discussed in the session on the determination of carbon, hydrogen, oxygen and nitrogen. M. E. SMITH (Los Alamos Scientific Laboratory, Los Alamos, New Mexico) described a device for crushing pyrolytic carbon-coated uranium carbide particles in the inert atmosphere of the furnace prior to analysis for oxygen. M. S. W. WEBB (UKAEA, Woolwich, England) described an apparatus with which 27 steel samples could be analyzed spectrographically for oxygen. The sensitivity was $1\ \mu\text{g}$ of oxygen and analysis time was 2.5 min per sample.

W. E. DALLMAN (Iowa State University) presented a comparative study on the determination of gases in rare-earth metals. Inert-gas fusion, hot extraction, vacuum fusion and d.c. carbon-arc methods were discussed.

For the first time, a complete session of a major meeting was devoted to the analysis of trace impurities in the alkali metals. The impurities dealt with were oxygen, carbon and hydrogen. Methods discussed for the determination of oxygen were (i) a modification of the amalgamation technique which materially reduced the time per analysis; (ii) a distillation technique and (iii) a neutron activation method. A freezing-point method for the determination of oxygen in rubidium and cesium was also presented. Both wet- and dry-combustion methods were discussed for the determination of carbon, and thermal extraction and isotopic dilution technique were presented for the determination of hydrogen. The application of the modified amalgamation technique to the simultaneous determination of oxygen and hydrogen in the same sample was of particular interest.

The Ninth Conference in this series is provisionally scheduled to be held at the Mountain View Hotel, Gatlinburg, Tennessee, on October 12-14th, 1965.

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BOOK REVIEWS

Analytical Chemistry of Thallium, by I. M. KORENMAN, translated from the Russian by Z. LERMAN, Israel Program for Scientific Translations, 1964, vi + 138 pages, price \$6.00.

Thallium is one of the less common elements and few books deal in detail with its analytical chemistry. This volume in the series of monographs on the analytical chemistry of the elements, published by the V.I. Vernadskii Institute of Geochemistry and Analytical Chemistry of the Academy of Sciences of the U.S.S.R., is, therefore, particularly welcome.

The history, occurrence and general properties of thallium are dealt with in Chapter I and the remainder of the book deals in a conventional manner with the analytically important reactions of thallium, and its separation, identification and determination. A useful and rather unusual contribution to this type of book is a section on the detection of thallium in the systematic analysis of cations. An appendix lists pertinent physical and chemical properties of thallium and its compounds. In general, the treatment is detailed and thorough, although there are omissions and on some subjects contradictory information is given without comment.

The book is copiously referenced and 932 references are listed in the bibliography. However, many of these are in journals not generally available and 9% refer to pre-1900 literature. Of twelve references checked, five contain errors and one (ref. 402) does not appertain to the subject under discussion *i.e.*, the use of xanthates in group separations. It is just as important to avoid errors in references as in the main text and in view of the particular susceptibility of Russian translations to contain such errors, the practice of copying bibliographies *verbatim* from the original is to be deprecated. An inconspicuous and inconsistent system of section headings makes rapid consultation difficult. In spite of these failings however, this book is of very real value and can be strongly recommended for all those interested in the analytical chemistry of thallium.

B. L. TAYLOR (Harwell)

J. Electroanal. Chem., 9 (1965) 330

The Encyclopedia of Electrochemistry, edited by CLIFFORD A. HAMPEL, Reinhold Publishing Corp., New York, 1964, 1206 pages, \$35.00.

The destiny of directories, catalogues, dictionaries, and encyclopedias is to be never completely read; for these are tomes to be dipped into as need be. They are, however, expected to be unerring — a sort of ultimate authority. Does the present volume live up to this view of a work of reference, or is the view a mirage? The answer lies somewhere between these alternatives, but probably closer to the latter.

This new work is no handbook, for its page size is 10 in. \times 6 $\frac{3}{4}$ in. and it weighs five pounds. Appropriately, the paper and the binding are strong to withstand plenty of handling, and the type is consistently clear yet compact. The entries are in alpha-

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betical order, two columns to the page, and the title of the main article is prominent in the top corner of each page. There is the added convenience of an index of subject matter, and the text is liberally endowed with cross references, diagrams, and photographs. Thus, the rudimentary makings of a successful encyclopedia are all there.

The scope of the work is huge, since it embraces electrochemistry as the American Electrochemical Society knows it. This covers such fields as luminescence, electrothermics, and insulators, which are foreign ground to electrochemists nurtured on ions and electrolysis. Clearly the author of the article on *Electrochemistry* is reserved about the inclusion of these fields and disdains to justify the position when he writes: "While not strictly electrochemistry, electrothermics has come to be known as a branch of the subject". The character of the book is borne out in many ways. Of the 273 contributors, all but 30 come from the United States, and in the reviewer's judgement only about 25 contributors merit the designation "distinguished international expert" printed conspicuously on the dust cover. Fortunately, a contributor to an encyclopedia need not be so illustrious to produce an excellent article. Among the 412 articles are 48 biographies of "scientists whose lives influenced electrochemistry". No living person is the subject of a biography, and the great majority of the subjects are American. Four Nobel Prize winners figure in the biographies and rub shoulders, as it were, with others of surprisingly feeble qualification for inclusion. Absent are BJERRUM, BRONSTED, DONNAN, MAXWELL, and J. J. THOMSON. One of the curious but justified entries is the one-time Superintendent of Weights and Measures in the Philippine Islands, G. N. LEWIS. Delving through the biographical *bric-à-brac* one finds that NERNST invented a player piano, and the discover of Ohm's Law was apparently so pilloried that it cost him his job.

These are not the only curiosities in this erratically-edited book. For instance, there is no separate article on that very bastion of electrochemistry — the Faraday. The measurement of this fundamental constant is virtually an American tradition, yet here it is described unworthily, and there are at least seven different values from 96484 to 96501 scattered about the book. Other inconsistencies include three different symbols for the electron, and three symbols for the number of electrons participating in a reaction as written. Degrees Centigrade and Fahrenheit can be found mixed in the same article and on the same page. Notations for familiar ions wander among, for example, Fe^{+2} , Fe^{2+} , and Fe^{++} , or Ag^{+1} and Ag^+ . There are two separate lists of electrode potentials with minor numerical differences between them, and sign conventions are presented four times. Throwing power is described twice, both times ineffectively. Eight pages are devoted to electro-diagnosis, but only one page to pH as such; eleven pages are allotted to electron beam melting and welding, but none at all to galvanic cells. Under *Batteries, Dry Cells* is written, "... dry cell is a slight misnomer . . . If the cell were dry it would not work"; but shortly afterwards the workings of truly dry cells are described on part of three pages. The familiar battery reaction in which manganese dioxide takes part is given wrongly on one page and properly on the next. One contributor falls into ambiguity with the verb "electroplate", which in hasty hands can refer either to the metal deposited or to the metal deposited upon. The reader can come across other revealing usages: "corrosion is a phenomena"; "discreet metal particles"; "disappointment for EEG'ers"; and "thermo-galvano-magneto-electrical effects".

The book contains technical faults enough to ruin a teacher's confidence. On

page 345 there is the clear implication that ΔH for the ionization of water does not vary with temperature. It is also not clear that the first two diagrams in the book are accurate only at 25°C. Two laws are stated under "Faraday's Laws", but on page 309 the author of another article quotes a third. On page 582 a contributor writes that energy efficiency can be expressed as a percentage in electro-refining and attaches "prime importance" to this. It would be instructive to know how the calculation is done — if it is possible at all. In the article on copper electro-winning "Thompson's rule" is used. This perhaps refers to the archaic approximation $\Delta H \sim zEF$, but no confirmation could be found, and THOMSON (Lord KELVIN) has no biography. On page 346 Ostwald's Dilution Law is curtly mentioned, but no explanatory details were traced, even in OSTWALD's biography. Surely these could have had priority over the information given on page 1094 that replacement of atmospheric nitrogen by sulphur hexafluoride has not harmed albino rats.

Substantial articles will be found in this book on: askarel, zone refining, ferro-alloys, figure of merit, solion, ultraviolet lamps, nitrogen trifluoride, corrosion by liquid metals, plasma, and radiation pyrometry. There are no separate articles on indicators, ionic mobility, film formation, electrochemical equivalent, reversible electrode. "What is electrolysis?" — this book will not provide a specific answer! Splendid though certain of the articles are in this book, it contains too many imperfections to stand as a dominant work of authority on the library shelf.

E. C. POTTER, Water Research Association, Marlow

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