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SUMMARIES OF PAPERS PUBLISHED IN  
JOURNAL OF ELECTROANALYTICAL CHEMISTRY

Vol. 8, No. 5, November 1964

THE USE OF AMALGAM ELECTRODES IN BIAMPEROMETRY

Direct chelatometric titrations of lead with biamperometric indication produce fairly good results when lead amalgam electrodes are used.

H. L. KIES,

*J. Electroanal. Chem.*, 8 (1964) 325-331.

TRANSIENTS IN CONVECTIVE SYSTEMS

II. LIMITING CURRENT AND KINETICALLY COMPLICATED GALVANO-  
STATIC TRANSIENTS AT ROTATING DISC ELECTRODES

The shape of the limiting current transient at a rotating disc electrode is considered, limits in time being derived for the applicability of Fick's law and of the steady state, for its description. Interpretation of a galvanostatic transition time, determined when the depolariser takes part in a homogeneous "kinetic" or "catalytic" process, is less convenient in a convective than in a quiescent system if polarisation is affected by passage of a constant current through a solution containing a bulk concentration of the depolariser. When, however, polarisation is achieved by current reversal, the depolariser having been generated by a steady-state condition of the reverse direction of the electrode reaction, the convective system is more advantageous.

New functions are presented for the interpretation of steady-state limiting currents in kinetic and catalytic systems.

J. M. HALE,

*J. Electroanal. Chem.*, 8 (1964) 332-349.

THE RATE OF ELECTRODE OXIDE FORMATION DURING  
CHRONOPOTENTIOTRAGRAMS AT A PLATINUM ANODE

The formation of electrode oxide during anodic chronopotentiograms has been investigated for the oxidation of oxalic acid in 1 *F* sulfuric acid at a platinum anode. The amount of oxide on the electrode is found to be directly proportional to the anode potential above 0.7 *V* vs. S.C.E. The proportionality constant is 800  $\mu\text{C}/\text{cm}^2$  volt.

M. D. MORRIS,

*J. Electroanal. Chem.*, 8 (1964) 350-358.

## USE OF A "COULOAMPEROMETRIC" METHOD FOR KINETIC STUDIES OF FAST REACTIONS

A "couloamperometric" technique is proposed for microanalysis and fast kinetic investigations of bromine addition, substitution and oxidation-reduction reactions in solution. The technique requires a minimum amount of compound for investigation,  $10^{-8}$  moles normally being sufficient. Bromine is produced by electrolysis of a bromide in solution and its concentration is followed by means of the diffusion current measured between a fixed and a rotating platinum electrode. It has been found possible to make analytical determinations with only  $0.5 \mu\text{g}$  of compound which reacts rapidly with the " $\text{Br}_2\text{-Br}_3^-$ " system and rate constants of the order of  $5 \cdot 10^8 \text{ l mole}^{-1}\text{min}^{-1}$  (second order) can be determined with a satisfactory reproducibility.

J. E. DUBOIS, P. ALCAIS ET G. BARBIER,

*J. Electroanal. Chem.*, 8 (1964) 359-365.

## THEORY OF ANODIC STRIPPING VOLTAMMETRY WITH A PLANE, THIN MERCURY-FILM ELECTRODE

An approximate theory for anodic stripping voltammetry with a plane, thin ( $\leq 100$  micron) mercury-film electrode is presented. This approximate theory is valid only for slow rates of linear potential scan during the stripping of the reduced metal from the mercury, and for thin mercury films.

There are important differences between anodic stripping peaks obtained with a thin mercury-film electrode and the peaks obtained under the conditions of the Ševčík-Randles theory. In the latter case the peak potential and the peak width are independent of the rate of potential change  $v$ , and of the mercury-film thickness  $l$  (which is supposed to be infinite), but the peaks obtained with a mercury-film electrode show a variation of both the peak potential and the peak width with varying  $v$  and  $l$ . The peak width can be very small (ca. 40 mV), permitting a sharp separation of metals with closely adjacent half-wave potentials. For very thin mercury-films ( $\leq 25$  micron) the peak current is nearly proportional to the rate of potential change.

W. T. DE VRIES AND E. VAN DALEN,

*J. Electroanal. Chem.*, 8 (1964) 366-377.

## ON THE INCREASE OF SENSITIVITY IN OSCILLOPOLAROGRAPHY

*(Preliminary Communication)*

In supporting electrolytes containing a mixture of sulfuric acid, ammonium thiocyanate and thiourea or urotropine the sensitivity of the oscillopolarographic determination of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  is increased 10-50-fold. The same is found for the determination of  $\text{Tl}^+$  in acidified solutions of potassium iodide. The adsorption phenomena involved may also be utilised in stripping oscillopolarographic microanalysis.

R. KALVODA AND J. AI-CHUA,

*J. Electroanal. Chem.*, 8 (1964) 378-381.

## ON THE POLAROGRAPHY OF TECHNETIUM

### I. DIRECT CURRENT AND ALTERNATING CURRENT POLAROGRAPHIC INVESTIGATIONS OF PERTECHNETATE SOLUTIONS

Neutral and alkaline solutions of  $K^{99}TcO_4$  in the concentration range of  $10^{-3}$  to  $10^{-4}$  M have been investigated polarographically with direct and alternating current. Four steps and waves respectively have been observed. The first two steps of  $E_1 \approx -0.8$  V and  $\approx -1.1$  V correspond to electron transitions  $n \approx 2$  and  $\approx 3$ , whereas the third and fourth steps are influenced by catalytic effects. It may be specially pointed out that reduction first to Tc(V) takes place not only in alkaline but also in neutral solution.

Alternating current efficiencies of 70–90% for the wave  $E_r \approx -0.8$  V were obtained as a function of the type and concentration of the supporting electrolyte. From this follows the possibility of a.c. polarographic determination of technetium which is advantageous on account of its higher separation capacity in comparison to the direct current polarographic methods.

L. ASTHEIMER AND K. SCHWOCHAU,

*J. Electroanal. Chem.*, 8 (1964) 382–389.

### ELECTROCHEMICAL REDUCTION OF URANIUM(VI) AT MERCURY ELECTRODES IN CARBONATE SOLUTIONS. AN EXPERIMENTAL CHRONOPOTENTIOMETRIC STUDY

The chronopotentiometric technique has been used in studying the reduction of uranyl on mercury electrodes in sodium carbonate solutions. At 1 M of free carbonate no kinetic complications were observed at experimental conditions pertinent to galvanostatic techniques at quiescent solutions. At low free carbonate concentrations (0.10 M) the electrochemical reduction is followed by a second order chemical reaction the rate of which is dependent on the concentration of the free carbonate ion. The potential–time relation is a suitable means of studying the kinetics as dependent on the free ligand concentration and on the concentration of the electroactive uranyl ion. The data indicate that the uranyl tricarbonate complex undergoes reduction without dissociation, while the coupled chemical reaction (disproportionation) involves rearrangement in the transition of uranium(V) into the uranium(IV) and uranium(VI) carbonate complex forms.

J. ČAJA AND V. PRAVDIĆ,

*J. Electroanal. Chem.*, 8 (1964) 390–398.

### A SUPPLEMENTARY DEVICE TO A PEN-RECORDING POLAROGRAPH FOR DOUBLE-LAYER CAPACITY MEASUREMENTS

A new device for measuring the dependence of the double-layer capacity on the electrode potential is described. It uses the amplifier, potentiometer and recorder of a polarograph. The apparatus is fed from the sine wave voltage generator and the hanging mercury electrode acts as a cathode. The detailed electronic diagram of the new device and a description of the preparation of the hanging mercury drop electrode are given. The results of experiments which illustrate the performance of the device are presented.

Z. KOWALSKI AND J. SRZEDNICKI,

*J. Electroanal. Chem.*, 8 (1964) 399–405.

ELLIPSOMETRIC STUDY OF OXYGEN-CONTAINING FILMS  
ON PLATINUM ELECTRODES

*(Short Communication)*

A. K. N. REDDY, M. GENSHAW AND J. O'M. BOCKRIS,

*J. Electroanal. Chem.*, 8 (1964) 406-407.

FARADAIC IMPEDANCE OF STEP-WISE ELECTRODE  
REACTIONS

*(Short Communication)*

J. M. HALE,

*J. Electroanal. Chem.*, 8 (1964) 408-409.

POLAROGRAPHIC MEASUREMENTS WITH A MERCURY  
ELECTRODE WITH A CONSTANTLY RENEWED SURFACE  
THE AREA OF WHICH REMAINS CONSTANT

*(Short Communication)*

A. ROUELLE AND E. T. VERDIER,

*J. Electroanal. Chem.*, 8 (1964) 409-412.

## THE USE OF AMALGAM ELECTRODES IN BIAMPEROMETRY

H. L. KIES\*

*University of Connecticut, Storrs, Conn. (U.S.A.)*

(Received July 2nd, 1964)

## INTRODUCTION

So far, one-phase amalgam electrodes have found application only in potentiometry<sup>1</sup>, coulometry<sup>2</sup>, and polarography<sup>3,4</sup>. It can easily be deduced from current-potential relationships that there must be potentialities in biamperometry as well. Experiments have confirmed this prediction for the titration of lead, bismuth, and cadmium. This paper deals only with the chelatometric titration of lead, although the titration with oxalate was reasonably successful. Titration with E.D.T.A., however, shows a more prompt attainment of a stationary state, and is therefore to be preferred.

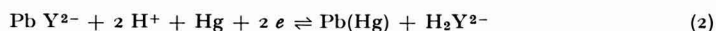
Earlier experiments<sup>5</sup> were carried out using two synchronised dropping amalgam electrodes. The application of perspex makes possible the construction of a more convenient cell.

*Theoretical discussion*

The course of the voltammograms at different stages of the titration, provided the electrode reactions be rapid, was outlined by CHARLOT *et al.* in Fig. 52 of their book<sup>6</sup>. According to the principles of biamperometric titrations<sup>7,8</sup>, the current which is already flowing at the starting point, diminishes on addition of the reagent. At the equivalence point it has completely vanished (but for a small residual current); an excess of reagent causes the current to return. Although the reaction



has to be considered as a very rapid one, as shown by the literature<sup>9</sup>, this is not true for the reaction:



The equilibrium tension corresponding to this reaction can easily be derived.

$$E = E_0 + \frac{RT}{2F} \ln \frac{C_{\text{Pb}^{2+}}}{C_{\text{Pb}}}$$

$$E = E_0 + \frac{RT}{2F} \ln \frac{C_{\text{PbY}^{2-}}}{C_{\text{Pb}}} \cdot \frac{K_c}{C_{\text{Y}^{4-}}}$$

$$E = E_0 + \frac{RT}{2F} \ln \frac{C_{\text{PbY}^{2-}}}{C_{\text{Pb}}} \cdot \frac{K_c}{K_3 K_4} \cdot \frac{(C_{\text{H}^+})^2}{C_{\text{H}_2\text{Y}^{2-}}}$$

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$K_c$  is the dissociation constant of the complex  $PbY^{2-}$  and  $K_3$  and  $K_4$  are the third and fourth dissociation constants of E.D.T.A., respectively.

The electrode tension in the presence of an excess of E.D.T.A. shifts by an amount, equal to

$$\frac{RT}{2F} \ln \frac{K_c}{K_3 K_4} \frac{(C_{H^+})^2}{C_{H_2Y^{2-}}} \text{ volts}$$

with respect to the electrode tension exhibited by the same amalgam electrode in an equally concentrated solution of free lead ions.

With the numerical values:  $K_c = 10^{-17.9}$ ,  $K_3 = 10^{-6.16}$ ,  $K_4 = 10^{-10.26}$ ,  $C_{H_2Y^{2-}} = 10^{-1}$ ,  $C_{H^+} = 10^{-4}$  and  $RT/2F = 0.030$  V this leads to a tension shift of  $-0.255$  V. Supposing the reaction mechanism to be a rapid one, the shift of the half-wave tension will be of the same order of magnitude. According to the literature<sup>10,11,12</sup>, the shift amounts to  $-0.600$  V. This considerable divergence indicates that the kinetics of reaction (2) must be more complicated. Further evidence for this conclusion is given in the literature<sup>13</sup>, in particular from the investigation of many analogous systems:  $PbX^{-14,15}$ ,  $CdX^{-14,16,17,18}$ ,  $CdY^{2-19}$ . It can be inferred from this behaviour that the amperogram will not show any current after the equivalence point has been reached.

#### Mathematical discussion

The starting point is the relationship existing between the current and the tension of an amalgam electrode in contact with a solution of the corresponding free metal ion. Application to this case of the well-known formula for a redox wave gives:

$$E_K = E_0 + \frac{RT}{2F} \ln \frac{(1-x)C_{Ox} - i/K_{Ox}}{C_R + i/K_R}$$

$E_0$  = normal tension of redox couple,

$C_{Ox}$  = initial concentration of the free metal ion in the aqueous phase,

$C_R$  = bulk concentration in amalgam phase,

$E_K$  = cathode tension,

$E_A$  = anode tension,

$i$  = numerical value of the current,

$\Delta$  =  $E_A - E_K$  = applied tension (assumed to be sufficiently low for reaction (2) not to interfere),

$K_{Ox}$  = proportionality factor between limiting current and concentration of the solution,

$K_R$  = analogous factor for the amalgam,

$x$  = degree of advancement of the titration.

The anode tension for the same numerical value of the current intensity is given by:

$$E_A = E_0 + \frac{RT}{nF} \ln \frac{(1-x)C_{Ox} + i/K_{Ox}}{C_R - i/K_R}$$

Subtraction of the two equations leads to:

$$\Delta = \frac{RT}{nF} \ln \frac{\{(1-x)C_{Ox} + i/K_{Ox}\} \cdot (C_R + i/K_R)}{\{(1-x)C_{Ox} - i/K_{Ox}\} \cdot (C_R - i/K_R)}$$

After introducing  $\Delta' = \exp nF \Delta/RT$ , we obtain a quadratic equation in  $i$ , which can readily be solved:



$$i = \frac{\Delta' + I}{\Delta' - I} \cdot \frac{K_{Ox}(1-x)C_{Ox} + K_R C_R}{2} \cdot \left[ I - \sqrt{\left\{ I - \frac{4K_{Ox}K_R(1-x)C_{Ox}C_R}{\{K_{Ox}(1-x)C_{Ox} + K_R C_R\}^2} \left( \frac{\Delta' - I}{\Delta' + I} \right)^2 \right\}} \right]$$

When the current during the titration is related to its initial value and  $q$  is written for  $K_{Ox}C_{Ox}/K_R C_R$ , the relative current  $j = i/i_{x=0}$  can be expressed as

$$j = \frac{(1-x)q + I}{q + I} \cdot \frac{I - \sqrt{\left[ I - \frac{4q(1-x)}{\{(1-x)q + I\}^2} \left( \frac{\Delta' - I}{\Delta' + I} \right)^2 \right]}}{I - \sqrt{\left\{ I - \frac{4q}{(f+I)^2} \left( \frac{\Delta' - I}{\Delta' + I} \right)^2 \right\}}}$$

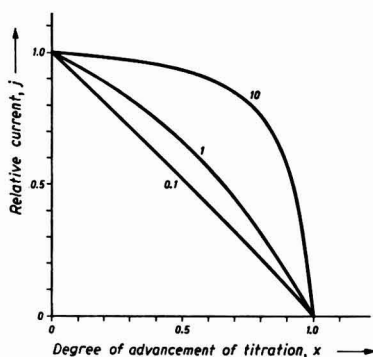


Fig. 1. Relative current intensity as function of the degree of advancement of the titration for different values of the parameter  $q$ . Applied tension 25.7/mV. Ohmic voltage drop in circuit assumed to be absent.

This function is shown in Fig. 1 for different values of the parameter  $q$ . The titration curve is almost independent of  $\Delta$  for low values of  $\Delta$ ; the slope near the equivalence point becomes steeper as the amalgam concentration is decreased. At very high amalgam concentrations the curve approaches to a straight line.

#### EXPERIMENTAL SET-UP

##### Titration cell

This was made of perspex; two grooves to contain the amalgam were machined in the bottom. Electrical contact was achieved by sealing platinum wires through the undersides of the grooves. In the centre of the bottom a small hole was made into which the spindle of the stirring bar fitted (Fig. 2).

Circular electrodes are much superior, from the hydrodynamical point of view, to the holes previously used when introducing mercury electrodes into biamperometry<sup>20</sup>. The electrode surface now remains fairly smooth. The vessel is closed by a cover having accommodation for the gas inlet tube and the burette tip.

Some experiments were performed with a cell of somewhat different construction, which made it possible to reduce the contents to about one-fifth.

### Electrical circuit

A fixed resistor of 2000  $\Omega$  and a variable resistor were connected in series with a 2 V accumulator. The tension over the variable resistor was applied to the cell *via* a galvanometer (Pye, 7901/S). In some cases the tension over the cell was measured with a high-impedance voltmeter (Philips G.M. 6020).

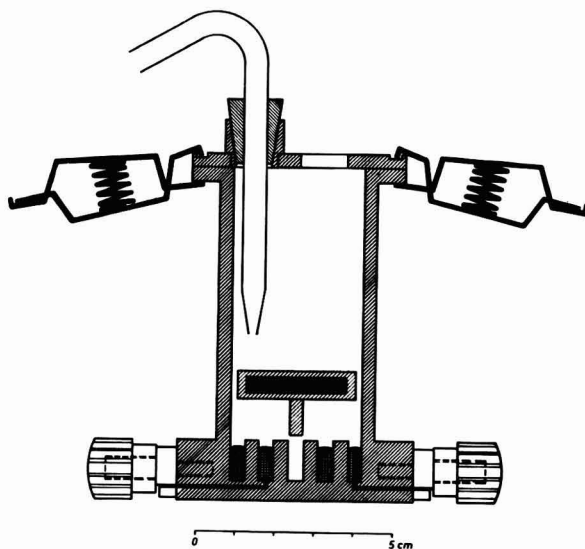


Fig. 2. Titration cell. Stirring bar shown in lifted position.

It was found that the residual current becomes more reproducible when the tension applied is not too low. At least 350  $\Omega$  should be switched in by the variable resistor. All experiments described were performed with 500  $\Omega$ , which corresponds to a tension of about 400 mV.

### REAGENTS

Lead nitrate and E.D.T.A. were both of Analar quality. The approximately 0.1 *M* solutions were standardized against one another by spectrophotometric titration.

[Procedure: 5 ml of  $\text{Pb}(\text{NO}_3)_2$ ; 25 ml of acetate buffer (1 *M* acetate, 1 *M* acetic acid, pH 5.0); 4 drops of 0.1% xylenol orange; 50 ml of  $\text{H}_2\text{O}$ ; light-path 3.5 cm; wave-length 580  $\text{m}\mu$ ; after the extinction has decreased by one-tenth, the titration is continued with 0.01 *M* E.D.T.A.] Both solutions are added by means of piston burettes (capacity 5 or 2 ml). The delivery of a pipette against a perspex wall involves uncertainties because the wall is not wetted by the solution.

The 0.5% lead amalgam is prepared by dissolving the calculated amount of lead in mercury with vigorous shaking. The volume remaining in the bottle over the amalgam is filled with a dilute solution of ascorbic acid. Every day, before use, the amalgam is washed several times with a fresh ascorbic acid solution. More dilute amalgams (0.05% and even 0.005%) have been used in preliminary experiments but although

0.05% amalgam can be used equally well, this is no longer the case for the 0.005% amalgam. Moreover, more concentrated amalgams will be less liable to change their concentration because of oxidation during storage.

The nitrogen used for removing the oxygen from the titration vessel is passed through a wash bottle containing an acidified vanadium(II) or chromium(II) sulfate solution. The presence of oxygen has a deleterious effect on the results.

The supporting electrolyte chosen was a buffered ascorbic acid solution<sup>21</sup> of the following composition: ascorbic acid 0.1 *M*, sodium acetate 0.25 *M*, potassium nitrate 1 *M*, adjusted to pH 5.0. The solution must be renewed every week.

#### PROCEDURE

25 ml of the supporting electrolyte is put into the titration cell, the cover is replaced and fixed by means of two spring clips. Oxygen is removed by a vigorous flow of nitrogen. After about 15 min, the grooves are filled with amalgam by means of a special pipette. It is advisable to keep the meniscus of the amalgam about 1 mm below the edge of the grooves, otherwise the surface will be disturbed by stirring and this might produce unsteady galvanometer readings. The gas inlet tube is now withdrawn from the solution, so that the nitrogen is sweeping out only the space above the solution. The sample is added and the stirring motor started. Any oxygen present in the sample is allowed to diffuse away for 10 min.

Before starting the titration proper, the stirring speed is reduced to such a rate that the galvanometer reading is quite steady.

As a rule, galvanometer readings are noted when the current begins to show a distinct decrease. The time needed for performing the titration is about 15 min. The end-point is obtained graphically by extrapolating the apparently rectilinear steep part of the titration curve and the horizontal line which originates from the residual current. This current shows some tendency to reduce when the time of waiting is slightly longer but as its intensity is, however, only a few per-cent of the initial value, its influence on the location of the end-point is negligible, especially as the other part of the titration curve is very steep.

#### RESULTS AND DISCUSSION

One of the titration curves is shown in Fig. 3, which gives also a detail on an enlarged scale. The numerical data are given in Table 1. The reproducibility proved to be fairly good. When the cell tension is plotted against the volume of the reagent, it is clear that even the very low resistance of the galvanometer (20  $\Omega$ ) produces a considerable voltage drop. The initial current intensity is almost wholly determined by the sum of the resistances of galvanometer and cell. This is due to the large electrode areas and the corresponding high current intensity, which causes a considerable ohmic voltage drop in the circuit. This phenomenon is always present in biamprometry to some degree, but here it is present to such an extent that this titration can be classed with polarovolttry. This intermediate type of titration is not so favourable when dealing with two rapid redox systems which show rather too small a difference in normal tension. In the present case it is even advantageous because of the steeper slope of the titration curve just before the end-point. The influence of the use of electrodes of unequal area has already been forecast by CHARLOT AND GAUGUIN<sup>7</sup> and investigated in practice by SONGINA AND SAVITSKAYA<sup>24</sup>. One of the statements of the latter authors

TABLE 1

$Pb(NO_3)_2$ taken (ml)	No. of detmn.	E.D.T.A. found (ml)		Difference		Stand. dev.		Max.	
		biamp.	spectroph.	ml	%	ml	%	ml	%
5 <sup>a,d</sup>	13	5.032	5.018	0.014	0.28	0.0052	0.10	0.015	0.30
5 <sup>b,d</sup>	12	5.030	5.018	0.012	0.24	0.0040	0.08	0.012	0.24
1 <sup>a,e</sup>	8	1.011	1.005	0.006	0.60	0.0026	0.26	0.005	0.50
0.5 <sup>c,e</sup>	15	0.5030	0.5024	0.0006	0.12	0.0004	0.08	0.002	0.40

<sup>a</sup> outer electrode as anode.

<sup>b</sup> inner electrode as anode.

<sup>c</sup> small scale titration cell of different construction.

<sup>d</sup> capacity of burettes ample 5 ml.

<sup>e</sup> capacity of burettes ample 2 ml.

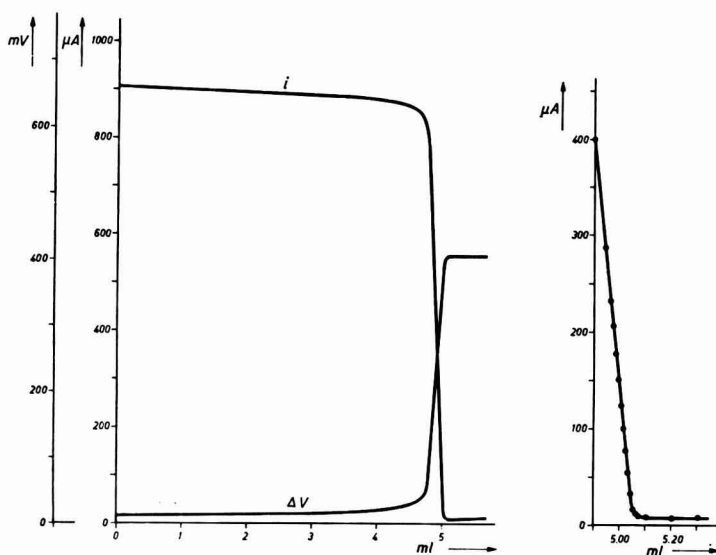


Fig. 3. Experimental curves for titration of 5 ml 0.1 M  $Pb^{2+}$  with 0.1 M E.D.T.A.:  $i$ , current;  $\Delta V$ , tension between electrodes. On enlarged scale, course of titrigrum near the end-point.

about the slope of the titration curve, *viz.*, that the electrode which determines the end-point of the titration should be large when a steep curve is desired, has also been corroborated by the present experiments, although the difference between the two electrode areas was not as large as theirs. Indeed, the slope of the titrigrum just before the end-point becomes more than twice as steep when the inner electrode is made the anode instead of the cathode. The reproducibility, however, does not improve appreciably, but when the small-scale titration cell is used, it becomes very important to choose the right electrode as the anode.

The results obtained with the end-points determined by biamperometry are always slightly in excess compared with those obtained in the spectrophotometric

titrations which are highly accurate. It is possible that small amounts of the aqueous solution adhering to the amalgam may introduce some dissolved lead into the titration vessel.

A possible extension of this titration is the determination of silver with E.D.T.A. The supporting electrolyte, of course, must not be reducing in character, and the reaction rate between lead amalgam and the silver ion should be sufficiently high.

#### ACKNOWLEDGEMENT

The author wishes to express his gratitude for Dr. J. T. STOCK's kind invitation and the financial support of the U.S. Atomic Energy Commission which enabled him to start this research at the University of Connecticut.

#### SUMMARY

Direct chelatometric titrations of lead with biampereometric indication produce fairly good results when lead amalgam electrodes are used.

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## TRANSIENTS IN CONVECTIVE SYSTEMS

## II\*. LIMITING CURRENT AND KINETICALLY COMPLICATED GALVANOSTATIC TRANSIENTS AT ROTATING DISC ELECTRODES

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Considerable importance is attached to the theoretical description of electrochemical experimental transients at the rotating disc electrode, partly because natural convection may be neglected in comparison with forced convection although its contribution to mass transfer might be greater than that arising from purely diffusional effects, and partly because it is necessary to achieve high rates of mass transfer to working electrodes when effects of reaction polarisation are to be studied. A rotating disc is unique among electrodes to which material is transported by a moving solution, in that its surface is uniformly accessible to the material<sup>1</sup>.

Convective mass transfer introduces into an experiment a degree of freedom, represented for example by the corresponding steady-state thickness of the diffusion layer at the electrode surface. This can be controlled through the rate of stirring, and can assume an important role in the study of electrode processes under steady-state conditions<sup>2,3</sup>. When a transient state of affairs is considered, however, the theoretical situation can be complicated by this extra degree of freedom to such an extent that experimental interpretation is made cumbersome. For example, in the case of potentiostatic polarisation of a rotating disc electrode, the shape of an experimental current-time transient depends not upon one parameter as in an unstirred solution, but inevitably upon two parameters, namely

$$\bar{\chi} = \frac{k_f \delta}{D} (1 + r \exp n f \eta) \quad \text{and} \quad \theta = \frac{Dt}{\delta^2}$$

Here  $\bar{\chi}$ , independent of time, is a rate parameter;  $\theta$  is the dimensionless time of polarisation;  $k_f$  is the forward rate constant of the electrode reaction;  $\delta$  is the above-mentioned thickness of the diffusion layer;  $D$  is the diffusion coefficient of the reacting species;  $r$  is the ratio of cathodic to anodic limiting currents appropriate to the magnitude of  $\delta$ ,  $t$  is the time of electrolysis;  $n$  electrons are involved in the electrode reaction, which takes place at a constant overpotential  $\eta$ , and  $f = F/RT$ , where  $F$  is the faraday,  $R$  the gas constant, and  $T$  the absolute temperature. This general prob-

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lem is not further considered in this paper, (an approximate solution was derived by SIVER<sup>3</sup>) but the most important and simplest case,  $\bar{\chi} \rightarrow \infty$ , is treated for the sake of completeness of the subject matter of this series.

Another example which typifies this theoretical complication, is provided by the galvanostatic polarisation of an electrode process modified by the reaction of one of its participants with another substance in the bulk of the solution. In the case of unstirred solutions experimental interpretation can be based upon one graphical or tabular relationship between experimental results and kinetic parameters<sup>4,5</sup>, but according to the treatment herein of the analogous situation at a rotating disc electrode, a number of such graphs or tables must be employed. Experimental analysis then requires one step more than the corresponding analysis when the solution is motionless.

It is sometimes possible, however, to choose experimental conditions such that there is no extra complication of this kind. The guiding principle is that one of the characteristic parameters of the experiment must be made trivial, so that experimentally accessible quantities can be expressed uniquely as a function of the unknown. When, in particular, the bulk concentration of a substance simultaneously involved in the electrode process and some homogeneous reaction is made zero, then in favourable circumstances such a formulation is feasible, and the consequent modification in the behaviour of the electrode allows the investigation of the kinetics of the homogeneous reaction. The method proposed and evaluated in this communication is suitable for the study of "kinetic" reactions of any order, but requires that the reaction be essentially irreversible. It makes use of the unique feature of a rotating disc, that electrolysis at its surface may be carried out under steady-state conditions. A time-independent concentration profile of the reduced species is established in solution, followed by current reversal, and measurement of the transition time for oxidation of the reduced species  $R$ . Fast decay of  $R$  evidently, will be reflected by a rather brief period of re-oxidation; indeed, it is found that the duration of this period is a unique function of the rate of decay. This method is therefore quite direct and convenient and has an advantage over the analogous method for unstirred solution<sup>6,7</sup> that the experimental result is not a function of the time of electrolysis before reversal of the current. It is unfortunate that the "irreversible" condition will be quite restrictive.

Previous theoretical work pertinent to the rotating disc has been thoroughly reviewed by LEVICH<sup>1</sup>. Its application to the investigation of the kinetics of homogeneous reactions, has been confined to an elucidation of the steady-state limiting current<sup>8</sup> (see Appendix), yet the extension of techniques to embrace the galvanostatic transition time is a natural one, since these measurements have been shown to be complementary in quiescent systems<sup>9</sup>. Thus the elucidation of the kinetics of a homogeneous reaction through its modification of electrode behaviour under limiting current and constant current conditions has been reviewed by DELAHAY<sup>9</sup>, and its influence upon the results of current reversal explored by KING AND REILLEY<sup>7</sup>, and by FURLANI AND MORPUGO<sup>6</sup>.

Simulation of the experiments described is achieved by solution of the appropriate convective diffusion equation and associated boundary conditions. Only diffusion and convection are considered as modes of mass transfer, so that experiments must be conducted in the presence of an excess of indifferent electrolyte in order that the

neglect of migration be permissible. Where necessary, KOUTECKÝ's method of solution is adopted, in which linear combinations of the concentration functions are employed, such that a problem involving a system of two simultaneous differential equations is preliminarily separated into individually soluble problems. This requires approximate equality of the diffusion coefficients of the diffusing species. Numerical methods are employed in the actual solution process, because of mathematical difficulties which prevent the application of more familiar analytical procedures. All parameters and functions are chosen in dimensionless form for economy of computation; indeed, other uses will be found for the same functions.

#### THE LIMITING CURRENT PROBLEM

The limiting current observable at an electrode is determined by the maximum rate of supply of reactant to the electrode surface, and is characterised by a vanishingly small concentration,  $C$ , of the depolariser at the electrode surface *i.e.*,

$$C = 0 \text{ at } x = 0 \text{ and } t > 0 \quad (1)$$

$x$  and  $t$  will represent the independent distance and time coordinates, the electrode is situated in the plane  $x = 0$ , and the start of electrolysis is taken as the origin of the time scale. There is an initial condition

$$C = C^b \text{ at } t = 0, x \geq 0 \quad (2)$$

and the usual condition upon the bulk concentration:

$$C = C^b \text{ at } x \rightarrow \infty, t \geq 0 \quad (3)$$

Because of the uniform accessibility of its surface, the concentration distribution at a rotating disc electrode is a solution of the convective diffusion equation in its one-dimensional form:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x} \quad (4)$$

$V$ , the velocity of the stirred fluid in the direction normal to the plane of the disc, is determined by the equations of hydrodynamics, and was evaluated by COCHRAN<sup>10</sup>. Equations (1)–(4) formulate a boundary value problem for the concentration distribution, which is most conveniently written in terms of the dimensionless dependent and independent variables:

$$u = C/C^b \quad (5)$$

$$z = \frac{1}{\delta} \int_0^x \exp \left[ \int \frac{V}{D} dx \right] dx \quad (6)$$

and

$$\theta = Dt/\delta^2 \quad (7)$$

where

$$\delta = \int_0^\infty \exp \left[ \int \frac{V}{D} dx \right] dx \quad (8)$$

The integral (8)  $\delta$ , the thickness of the diffusion layer in the steady state, was evaluated by LEVICH<sup>11</sup>, and more accurately by GREGORY AND RIDDIFORD<sup>12</sup>. The boundary value problem restated has the appearance:



$$\left. \begin{aligned} \frac{\partial u}{\partial \theta} &= a^2 \frac{\partial^2 u}{\partial z^2}, & 0 \leq z \leq 1 \\ u &= 0 \text{ at } z = 0; \quad u = 1 \text{ at } z = 1; \quad u = 1 \text{ at } \theta = 0 \end{aligned} \right\} \quad (9)$$

Here

$$a^2 = \exp \left[ 2 \int_0^x \frac{V}{D} dx \right] \quad (10)$$

is a function of  $z$  and was determined in the previous communication<sup>13</sup>.

The flux of reactant to the surface of the electrode is given by:

$$j = -D \left( \frac{\partial C}{\partial x} \right)_{x=0} \quad (11)$$

and contains no convective contribution because the fluid velocity is zero at the disc,  $V = 0$  at  $x = 0$ . If  $n$  faradays are transferred to one mole of the reactant in the course of the electrode reaction, then the limiting current may be expressed by:

$$i = nFAD \left( \frac{\partial C}{\partial x} \right)_{x=0} = \frac{nFADC^b}{\delta} \left( \frac{\partial u}{\partial z} \right)_{z=0} = i_s \left( \frac{\partial u}{\partial z} \right)_{z=0} \quad (12)$$

$A$  is the electrode area,  $F$  is the faraday, and  $i_s$  is the constant magnitude of the limiting current observed in the steady state. Defining the transient limiting current as:

$$i = \frac{nFADC^b}{\delta(t)} \quad (13)$$

we have

$$\frac{i}{(\partial u / \partial z)_{z=0}} = \frac{i_s}{i} = \frac{\delta(t)}{\delta} = g \quad (14)$$

Evidently  $i \rightarrow i_s$  and  $\delta(t) \rightarrow \delta = \delta(\infty)$  as  $\theta$  or  $t \rightarrow \infty$ , whilst  $\delta(t) = 0$  at  $\theta = 0$ ; hence the function  $g$  varies between zero and unity during the establishment of the steady state;  $g$  may be interpreted as a reduced time scale for potentiostatic problems at a rotating disc.

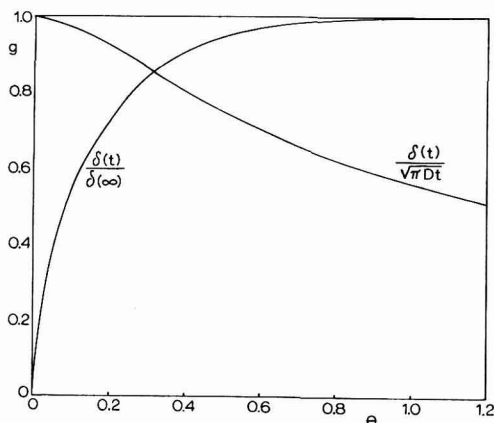


Fig. 1. Comparison of instantaneous thickness of the diffusion layer at a rotating disc electrode with the steady-state thickness, and with that at a stationary electrode.

$u(z, \theta)$  and hence  $[(\partial u / \partial z)_{z=0}]^{-1}$  were evaluated by the Crank-Nicholson<sup>14</sup> method, as previously described<sup>13</sup>, with the mesh having  $\Delta z = 0.1$  and  $\Delta \theta = 0.01$ . The function  $g$  is illustrated in Fig. 1 for the range of  $\theta$ ,  $0 < \theta \leq 1.2$ , and we find the interesting result that the steady state is virtually achieved for  $\theta > 1.0$ , *i.e.*,

$$t > \frac{2.6}{\omega} \left( \frac{\nu}{D} \right)^{\frac{1}{2}}$$

$\nu$  is the kinematic viscosity of the fluid and  $\omega$  is the rotation speed of the electrode. In aqueous solution the Prandtl number ( $\nu/D$ ) is of the order of magnitude  $10^3$ , whence for rotational frequencies of 100 radians/sec, this time limit is of the order of 0.3 sec.

In unstirred solutions the diffusion layer thickness is  $\sqrt{\pi D t}$ , and there is no steady state when natural convection is ignored. Also illustrated in Fig. 1 is the comparison between the thicknesses of the diffusion layer under convective and stationary conditions, and it follows that Fick's equation might be used for the description of transient experiments at the r.d.e. for times

$$\theta < \theta_{\max} \sim 0.01 \quad \text{i.e., } t < 3 \text{ msec}$$

LEVICH<sup>15</sup> has evaluated an approximate formula for  $\delta(t)$ , asymptotically correct at short times, by considering that convective effects appear as a small perturbation upon diffusional supply of reactant. He found:

$$\frac{\sqrt{\pi D t}}{\delta(t)} = 1 + 4.26 \sqrt{\pi} \theta^{\frac{1}{2}} + \dots \quad (15)$$

An approximate solution applicable to the whole range of  $\theta$  is obtained by making the approximation introduced in Part I, namely,  $a^2 = 1$ . An analytic solution of the boundary value problem (9) may then be derived and can be expressed in the form<sup>3</sup>:

$$\left( \frac{\partial u}{\partial z} \right)_{z=0} = 1 + 2 \sum_{n=1}^{\infty} \exp(-n^2 \pi^2 \theta) \quad (16)$$

which solution is about 8% lower than the numerical solution, at its worst.

#### GALVANOSTATIC POLARISATION IN THE PRESENCE OF KINETIC AND CATALYTIC PROCESSES

##### *Kinetic processes*

We determine the consequences of passage of a constant cathodic current,  $I$ , through a rotating disc electrode immersed in a reacting mixture. The reaction is pseudo first-order in one participant  $O$ , which is the only electro-reducible substance present within the potential-range of operation of the electrode.



As is usual in treatments of this kind, any other substance partaking in reaction (17) is present in excess, so that variations in its concentration are negligible; also, this concentration is included in the magnitude of one of the rate constants. The quantities measured are the transition time,  $\tau$ , (hence the current has to be greater than the steady-state limiting current at the electrode), and those parameters which enter

into the formula for the steady-state thickness of the diffusion layer,  $\delta$ , ( $\delta = 1.63 D^{1/2} \nu^{1/2} \omega^{-1/2}$ , see ref. 11).

At the electrode surface there is a time-independent gradient of concentration of species  $O$ , but no gradient of concentration of  $B$  because it is inactive at the electrode:

$$\frac{\partial C_O}{\partial x} = \frac{I}{nFAD_0} \quad \text{and} \quad \frac{\partial C_B}{\partial x} = 0 \quad \text{at} \quad x = 0 \quad (19a)$$

The initial and bulk conditions are similar to those of the limiting current problem:

$$C_O = C_O^b \quad \text{and} \quad C_B = C_B^b \quad \text{at} \quad t = 0 \quad \text{and} \quad x \rightarrow \infty \quad (19b)$$

Finally, within the domain  $0 \leq t \leq \infty$ ,  $0 \leq x \leq \infty$ , the concentration distributions satisfy the simultaneous continuity equations:

$$\left. \begin{aligned} \frac{\partial C_O}{\partial t} &= D_O \frac{\partial^2 C_O}{\partial x^2} - V \frac{\partial C_O}{\partial x} - k_1 C_O + k_2 C_B \\ \frac{\partial C_B}{\partial t} &= D_B \frac{\partial^2 C_B}{\partial x^2} - V \frac{\partial C_B}{\partial x} + k_1 C_O - k_2 C_B \end{aligned} \right\} \quad (19c)$$

Reformulation in terms of linear combinations of  $C_O$  and  $C_B$  is arranged in dimensionless form, for the convenience of the numerical method of solution. We employ the independent variables  $z$  and  $\theta$ , a rate parameter  $\lambda$  defined by:

$$\lambda = (1 + K)k_1\delta^2/D \quad (20)$$

where

$$K = k_2/k_1$$

and the functions  $u(\theta, z)$  and  $v(\lambda, \theta, z)$

$$u = \frac{nFAD}{I\delta} [C_O^b - C_O + C_B^b - C_B] \quad (21)$$

and

$$v = \frac{nFAD}{I\delta} [KC_B - C_O] \quad (22)$$

The diffusion coefficients of  $O$  and  $B$  are taken to be identical and given the symbol  $D$ .  $u$  and  $v$  satisfy the separate boundary value problems in the domain:  $0 \leq \theta \leq \infty$ ,  $0 \leq z \leq 1$

$$\left. \begin{aligned} \frac{\partial u}{\partial \theta} &= a^2 \frac{\partial^2 u}{\partial z^2} \\ \frac{\partial u}{\partial z} &= -1 \quad \text{at} \quad z = 0; \quad u = 0 \quad \text{at} \quad z = 1 \quad \text{and} \quad \theta = 0 \end{aligned} \right\} \quad (23)$$

and

$$\left. \begin{aligned} \frac{\partial v}{\partial \theta} &= a^2 \frac{\partial^2 v}{\partial z^2} - \lambda v \\ \frac{\partial v}{\partial z} &= -1 \quad \text{at} \quad z = 0; \quad v = 0 \quad \text{at} \quad z = 1 \quad \text{and} \quad \theta = 0 \end{aligned} \right\} \quad (24)$$

Evidently the problem (23) for  $u$  is merely a special case of (24), namely that with  $\lambda = 0$ , and therefore need not concern us further. The Crank-Nicholson method was

TABLE

$\theta$	$\lambda = 0$	$\lambda = 0.1$	$\lambda = 0.2$	$\lambda = 0.5$	$\lambda = 0.7$	$\lambda = 1$
$1 \cdot 10^{-3}$	$1.802 \cdot 10^{-2}$	$1.802 \cdot 10^{-2}$	$1.802 \cdot 10^{-2}$	$1.801 \cdot 10^{-2}$	$1.801 \cdot 10^{-2}$	$1.801 \cdot 10^{-2}$
2	3.196	3.196	3.195	3.195	3.194	3.193
3	4.508	4.507	4.507	4.505	4.504	4.502
4	5.643	5.642	5.641	5.638	5.636	5.633
5	6.641	6.640	6.639	6.634	6.631	6.627
6	7.534	7.532	7.530	7.524	7.520	7.515
7	8.342	8.339	8.337	8.329	8.325	8.317
8	9.082	9.079	9.076	9.067	9.061	9.052
9	9.767	9.763	9.760	9.749	9.742	9.732
$1 \cdot 10^{-2}$	$1.041 \cdot 10^{-1}$	$1.040 \cdot 10^{-1}$	$1.040 \cdot 10^{-1}$	$1.039 \cdot 10^{-1}$	$1.038 \cdot 10^{-1}$	$1.037 \cdot 10^{-1}$
2	1.499	1.498	1.497	1.494	1.492	1.489
3	1.875	1.873	1.871	1.865	1.861	1.855
4	2.186	2.183	2.180	2.171	2.165	2.156
5	2.456	2.452	2.448	2.435	2.427	2.415
6	2.699	2.694	2.688	2.672	2.661	2.645
7	2.921	2.914	2.907	2.887	2.873	2.853
8	3.126	3.118	3.109	3.084	3.068	3.044
9	3.318	3.308	3.298	3.268	3.249	3.220
$1 \cdot 10^{-1}$	3.516	3.486	3.475	3.440	3.417	3.384
2	4.920	4.773	4.743	4.658	4.599	4.517
3	5.927	5.784	5.730	5.575	5.476	5.334
4	6.707	6.556	6.477	6.250	6.107	5.904
5	7.329	7.165	7.059	6.761	6.575	6.314
6	7.831	7.650	7.519	7.152	6.926	6.613
7	8.237	8.039	7.885	7.454	7.192	6.832
8	8.567	8.352	8.175	7.687	7.393	6.993
9	8.835	8.604	8.407	7.867	7.545	7.112

found to be suitable for the determination of  $v(\lambda, \theta, z)$ , and was employed with  $\Delta z = 0.1$ . Unlike the linear time scale of the previous example, it was decided to evaluate  $v$  for several orders of magnitude of  $\theta$ , and the calculation was arranged with  $\Delta \theta$  equal to  $10^{-5}$ ,  $10^{-4}$ ,  $10^{-3}$  and  $10^{-2}$ , printing  $v$  at  $z = 0$  in every tenth line. Table 1 records the results of this computation, for several values of  $\lambda$ . The accuracy is likely to be of the order of 1% at low values of  $\lambda$ , but should fall off with increase in  $\lambda$  because the thickness of the reaction layer can become smaller than the mesh size at the electrode interface (it was shown in Part I that  $x \sim \delta$  at  $z \sim 0.85$ ; hence in the absence of kinetic complications, with  $\Delta z = 0.1$ , the region of most interest within the diffusion layer is divided into  $8\frac{1}{2}$  strips).

An approximate analytic solution may be derived by writing

$$v = y \exp(-\lambda \theta)$$

and taking  $a^2 = 1$  in the problem satisfied by  $y$ . Hence we solve:

$$\frac{\partial y}{\partial \theta} = \frac{\partial^2 y}{\partial z^2}$$

$$\frac{\partial y}{\partial z} = -\exp(\lambda \theta) \text{ at } z = 0; y = 0 \text{ at } z = 1 \text{ and } \theta = 0$$

and find for  $v(\lambda, \theta, 0)$

1

$\lambda = 2$	$\lambda = 5$	$\lambda = 7$	$\lambda = 10$	$\lambda = 20$	$\lambda = 50$	$\lambda = 70$
$1.800 \cdot 10^{-2}$	$1.798 \cdot 10^{-2}$	$1.796 \cdot 10^{-2}$	$1.793 \cdot 10^{-2}$	$1.785 \cdot 10^{-2}$	$1.759 \cdot 10^{-2}$	$1.743 \cdot 10^{-2}$
3.190	3.182	3.176	3.168	3.140	3.058	3.004
4.496	4.478	4.446	4.449	4.390	4.222	4.115
5.623	5.594	5.575	5.546	5.451	5.180	5.010
6.613	6.571	6.543	6.501	6.366	5.982	5.744
7.496	7.439	7.402	7.347	7.167	6.663	6.356
8.293	8.222	8.175	8.105	7.877	7.250	6.873
9.023	8.935	8.878	8.792	8.516	7.762	7.314
9.696	9.592	9.524	9.422	9.059	8.212	7.695
$1.032 \cdot 10^{-1}$	$1.020 \cdot 10^{-1}$	$1.012 \cdot 10^{-1}$	$1.000 \cdot 10^{-1}$	9.625	8.612	8.026
1.478	1.447	1.428	1.399	$1.309 \cdot 10^{-1}$	$1.089 \cdot 10^{-1}$	9.761
1.836	1.781	1.746	1.695	1.542	1.205	$1.048 \cdot 10^{-1}$
2.127	2.043	1.991	1.916	1.700	1.262	1.078
2.375	2.261	2.190	2.091	1.813	1.293	1.091
2.593	2.446	2.356	2.233	1.896	1.309	1.096
2.788	2.607	2.498	2.350	1.958	1.318	1.099
2.965	2.749	2.620	2.448	2.004	1.324	1.100
3.127	2.875	2.727	2.530	2.040	1.326	1.101
3.276	2.988	2.820	2.601	2.068	1.328	
4.261	3.637	3.314	2.930	2.159	1.345	
4.906	3.955	3.514	3.030	2.169		
5.312	4.104	3.590	3.058	2.170		
5.577	4.176	3.620	3.066	2.171		
5.752	4.211	3.632	3.069			
5.868	4.228	3.637	3.069			
5.945	4.237	3.639	3.070			
5.997	4.241	3.640				

$$v(\lambda, \theta, 0) = 2 \sum_{n=1}^{\infty} \frac{1 - \exp \left\{ - \left[ (2n-1)^2 \frac{\pi^2}{4} + \lambda \right] \theta \right\}}{(2n-1)^2 \frac{\pi^2}{4} + \lambda}$$

This solution would appear no more convenient, in the absence of an automatic computer, than the purely numerical result, but it does allow the direct evaluation of the relationship between  $v$  at constant  $\theta$ , and  $\lambda$  which is required in the analysis of experiment. Computation is made easier, upon noting that the steady-state value of  $v$  may be expressed in a hyperbolic form (see Appendix)

$$v(\lambda, \infty, 0) \approx 2 \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2 \frac{\pi^2}{4} + \lambda} \approx \frac{1}{\sqrt{\lambda}} \tanh \sqrt{\lambda}$$

Hence

$$v(\lambda, \theta, 0) = \frac{1}{\sqrt{\lambda}} \tanh \sqrt{\lambda} - 2 \sum_{n=1}^{\infty} \frac{\exp \left\{ - \left[ (2n-1)^2 \frac{\pi^2}{4} + \lambda \right] \theta \right\}}{(2n-1)^2 \frac{\pi^2}{4} + \lambda}$$

which converges rapidly for values of  $\theta$  of experimental interest. The numerical and analytic solutions are compared in Fig. 2 for the case  $\lambda = 10$ ; evidently there is a choice between the convenience but limited accuracy of the analytical solution, and the labour of interpolation within Table I.

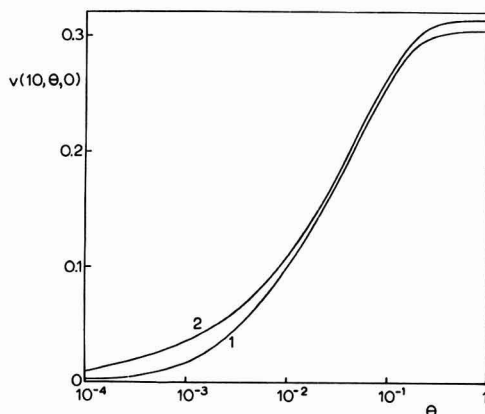


Fig. 2. Comparison of numerical (1) and analytic (2) approximations to  $v(10, \theta, 0)$ .

The dimensionless time  $\theta' = D\tau/\delta^2$  is calculated from experimental observables, then  $u(\theta', 0)$ , and  $v(\lambda, \theta', 0)$  as a function of  $\lambda$ , derived by one of the above methods. Because  $C_o(0) = 0$  at the transition time

$$\frac{nFADC_B(0)}{I\delta} = \frac{nFAD}{I\delta} (C_o^b + C_B^b) - u(\theta', 0)$$

which may be inserted into the expression derived from eqn. (22) for  $v(\lambda, \theta', 0)$

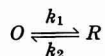
$$v(\lambda, \theta', 0) = \frac{nFADKC_B(0)}{I\delta} = \frac{nFADC_o^b}{I\delta} (1 + K) - Ku(\theta', 0) \quad (25)$$

This equation forms a basis for experimental interpretation, since the right-hand side is directly calculable, and hence  $\lambda$  may be interpolated from the plot of  $v(\lambda, \theta', 0)$  vs.  $\lambda$ . An accurate determination of  $k_1$ , and a test of the applicability of this reaction mechanism, is provided by the straight line plot of  $\lambda\theta'$  vs.  $\tau$  derived from measurements at various rotation speeds or current densities.

$$\lambda\theta' = k_1\tau(1 + K) \quad (26)$$

#### Catalytic processes

In this section we consider reaction systems of the type:



in which the oxidant is catalytically regenerated from the reductant in the bulk of the solution. Conditions and terminology will be identical to that adopted in the previous section.

Convenient linear combinations of the concentrations functions are found to be:

$$u = \frac{nFAD}{I\delta} (C_o^b - C_o + C_R^b - C_R) \quad (27)$$

and

$$v = \frac{nFAD}{I\delta} \left( \frac{KC_R - C_o}{1 + K} \right) \quad (28)$$

which may be demonstrated to satisfy:

$$\left. \begin{aligned} \frac{\partial u}{\partial \theta} &= a^2 \frac{\partial^2 u}{\partial z^2} \\ \frac{\partial u}{\partial z} &= 0 \text{ at } z = 0; u = 0 \text{ at } z = 1 \text{ and } \theta = 0 \end{aligned} \right\} \quad (29)$$

and

$$\left. \begin{aligned} \frac{\partial v}{\partial \theta} &= a^2 \frac{\partial^2 v}{\partial z^2} - \lambda v \\ \frac{\partial v}{\partial z} &= -1 \text{ at } z = 0; v = 0 \text{ at } z = 1, v = 0 \text{ at } \theta = 0 \end{aligned} \right\} \quad (30)$$

$\lambda$  is as given by eqn. (20).

The boundary value problem (29) has the trivial solution  $u(\theta, z) = 0$ , whilst the problem (30) for  $v(\lambda, \theta, z)$  is identical with (24) already solved. Further analysis is therefore unnecessary.

Conditions at the electrode surface at the transition time are such that:

$$C_R(0) = C_o^b + C_R^b$$

and

$$v(\lambda, \theta', 0) = \frac{nFADC_o^b}{I\delta} \quad (31)$$

Treatment of eqn. (31) is analogous to that of (25), except that its right-hand side is independent of the transition time — which is required only to select the possible values of  $v(\lambda, \theta', 0)$ . A plot of eqn. (26) can again be recommended.

#### CURRENT REVERSAL FROM A STEADY STATE

The principle of the electrochemical method analysed here, was described in the introduction. We consider two experimental situations, both of which may be reduced to single-parameter problems; these examples will serve, incidentally, to illustrate the usefulness of the numerical method of solution adopted.

##### *First-order decay of the product of electroreduction*

The reaction system is described by the equation



where, in order that this method should be useful, restriction is made to irreversible homogeneous reactions. Species  $R$  is supposed to be absent from the solution. Then,

in dimensionless form, the system of equations which determine the concentration distribution of species  $R$  during the period of *electro-oxidation* reads:

$$\left. \begin{aligned} \frac{\partial y}{\partial \theta} &= a^2 \frac{\partial^2 y}{\partial z^2} - \lambda y \\ \frac{\partial y}{\partial z} &= 1 \text{ at } z = 0; y = 0 \text{ at } z = 1 \end{aligned} \right\} \quad (32)$$

with  $y$  given initially by the solution of

$$\left. \begin{aligned} a^2 \frac{d^2 y}{dz^2} - \lambda y &= 0 \\ \frac{dy}{dz} &= -1 \text{ at } z = 0; y = 0 \text{ at } z = 1 \end{aligned} \right\} \quad (33)$$

Here

$$y = \frac{nFADC_R}{I\delta} \quad \text{and} \quad \lambda = \frac{k\delta^2}{D}$$

$I = |i|$ , the magnitude of the faradaic current, account having been taken of its sign in the formulation of the surface boundary condition.

The domain  $0 \leq z \leq 1$ ,  $\theta \geq 0$  was sub-divided into a mesh with  $\Delta z = 0.1$ ,  $\Delta \theta = 0.01$ . The ordinary differential equation was replaced by its direct finite difference equivalent<sup>14</sup>, the partial differential equation by its Crank-Nicholson form, and the gradient at the electrode surface by its central difference approximation. Computer simulation of the transient state of electro-oxidation was then programmed with a range of magnitudes of the parameter  $\lambda$ , continuing in each case until the value of  $y$  at  $z = 0$  became negative. By interpolation using Newton's divided difference method<sup>16</sup>, the "transition time"  $\theta'$ , corresponding to the situation  $y = 0$  at  $z = 0$  was then determined.  $\theta'$ , as noted in the introduction, is a function only of  $\lambda$ , and their relationship is tabulated in Table 2.

The recommended procedure for experimental analysis requires the measurement of a selection of transition times,  $\tau$ , either at various rotation speeds or at various current densities; the corresponding values of  $\theta'$  are computed ( $\theta' = D\tau/\delta^2$ ) and Table 2 employed for the interpolation of  $\lambda\theta'$ . A plot of  $\lambda\theta'$  vs.  $\tau$  yields the first-order homogeneous rate constant,  $k$ , through the relationship:

$$\lambda\theta' = k\tau$$

TABLE 2

DEPENDENCE OF  $\theta'$  UPON  $\lambda$  FOR FIRST-ORDER DECAY OF THE PRODUCT OF ELECTRO-REDUCTION

$\lambda \cdot 10^p$	$p = 2$	$p = 1$	$p = 0$	$p = -1$
1	2.056·10 <sup>-1</sup>	1.943·10 <sup>-1</sup>	1.218·10 <sup>-1</sup>	2.230·10 <sup>-2</sup>
2	2.043	1.829	8.359·10 <sup>-2</sup>	9.804·10 <sup>-3</sup>
3	2.030	1.726	6.279	7.635
4	2.017	1.633	4.989	6.229
5	2.005	1.548	4.137	5.207
6	1.992	1.470	3.469	4.415
7	1.980	1.399	3.028	3.778
8	1.967	1.333	2.730	3.253
9	1.955	1.273	2.466	2.814



Non-linearity of this result might be an indication of a more complicated reaction path than that upon which this analysis was modelled, but the possibility of interference by double-layer charging at current reversal should be investigated.

If the back reaction is appreciable or if the bulk concentration of  $R$  is not zero, analysis is similar to that of the previous section, and the current reversal method has no particular advantage.

### *Bimolecular decay reactions*

Homogeneous reaction systems of any order may be treated by numerical procedures, with very little extra complication, because finite difference methods do not suffer the restriction, as do analytical methods, to linear boundary value problems. As in the previous example, however, specification of irreversibility and of zero bulk concentration of the homogeneous reactant is necessary.

We consider the reaction system:



and employ the dimensionless quantities:

$$w = \frac{nFADC_R}{I\delta} \quad \text{and} \quad \eta = \frac{I\delta^3 k}{nFAD^2}$$

so that  $w$  satisfies the problem:

$$\left. \begin{aligned} \frac{\partial w}{\partial \theta} &= a^2 \frac{\partial^2 w}{\partial z^2} - \eta w^2 \\ \frac{\partial w}{\partial z} &= 1 \text{ at } z = 0; w = 0 \text{ at } z = 1, w = w_i \text{ at } \theta = 0 \end{aligned} \right\} \quad (35)$$

where:

$$\left. \begin{aligned} a^2 \frac{d^2 w_i}{dz^2} - \eta w_i^2 &= 0 \\ \frac{dw_i}{dz} &= -1 \text{ at } z = 0; w_i = 0 \text{ at } z = 1 \end{aligned} \right\} \quad (36)$$

Problem (36) for the initial distribution,  $w_i$ , was solved by an iterative finite difference procedure, with the range of  $z$  as usual divided into ten strips, and the differential equation replaced by the approximate relation:

$$f_{(k-1)} - \left( 2 + \frac{\eta(\Delta z)^2}{a_k} f_k \right) f_k + f_{(k+1)} = 0 \quad (37)$$

$k$  labels a point in the  $z$  domain, and  $a_k$ , the "convective coefficients", are the values of

$$a^2 = \exp \left[ 2 \int_0^x \frac{V}{D} dx \right]$$

at the points  $k$ . The electrode surface will be referred to by  $k = 0$ . In the case of ten strips,  $a_0$ - $a_{10}$  are as follows:  $a_0 = 1$ ,  $a_1 = 0.9946$ ,  $a_2 = 0.9848$ ,  $a_3 = 0.9599$ ,  $a_4 = 0.9097$ ,  $a_5 = 0.8260$ ,  $a_6 = 0.7051$ ,  $a_7 = 0.5451$ ,  $a_8 = 0.3512$ ,  $a_9 = 0.1438$ ,  $a_{10} = 0$ . To start the calculation an estimate is required of the  $f_k$  appearing in the parentheses. For the first value of  $\eta$  chosen, namely  $\eta = 0.01$ , this was approximated by its value

appropriate to  $\eta = 0$ , that is:

$$f = 1 - z$$

For successively larger values of  $\eta$  however, this estimate was taken as the steady-state distribution of  $f$  determined for the adjacent lower value of  $\eta$ . Then, the matrix of twelve simultaneous equations, (37) together with the boundary conditions

$$f_1 - f_{-1} = -2(\Delta z)$$

and

$$f_{10} = 0$$

or

$$\mathbf{A}\mathbf{f} = \mathbf{B}$$

was solved for  $\mathbf{f}$  by factorisation of  $\mathbf{A}$  into upper and lower triangle matrices<sup>14</sup>. In the second approximation, this column matrix  $\mathbf{f}$  was used for the calculation of the coefficients of  $f_k$  in (37), and so on, until successive estimates for  $f_0$  differed by less than 0.1%. In practice two or three iterations were enough when  $\eta < 1$ , whilst the procedure converged very slowly for  $\eta > 10$ .

Problem (35) was solved by a fully explicit method for simplicity and speed<sup>14</sup>. The finite difference equivalent of the partial differential equation was:

$$\frac{(w_k)_\theta - (w_k)_{\theta-\Delta\theta}}{\Delta\theta} = \left\{ \frac{a_k}{(\Delta z)^2} (w_{(k-1)} - 2w_k + w_{(k+1)}) - \eta w_k^2 \right\}_{\theta-\Delta\theta} \quad (38)$$

from which  $(w_k)$ , the value of  $w$  at the "point"  $k$ , the instant  $\theta$ , may be calculated directly, utilizing the distribution in the previous "line", at  $\theta - \Delta\theta$ .  $w_{-1}$  and  $w_N$  required in each line for the calculation of  $w_0$  and  $w_{(N-1)}$  respectively, are derived from the boundary conditions:

$$w_{-1} = w_1 - 2(\Delta z) \text{ and } w_N = 0$$

Finally,  $(w_k)_{\theta-\Delta\theta} = f_k$  in the first line of calculation.  $\Delta z$  was chosen, as in the previous computations, to be 0.1, but  $\Delta\theta$  was adjusted to be of the order of 1% of the transition time — an optimum between accuracy and speed of computation. This was achieved for each  $\eta$ , by taking the increment of  $\theta$  to be one two hundredth of the transition time found for the adjacent, lower value of  $\eta$ ; in the first case  $\eta = 0.01$ , the same fraction was taken of the transition time for  $\eta = 0$ , determined previously ( $\theta' = 0.207$ ). The oxidation simulation was continued therefore, until the function  $w$

TABLE 3

DEPENDENCE OF  $\theta'$  UPON  $\eta$  FOR SECOND-ORDER DECAY OF THE PRODUCT OF ELECTRO-REDUCTION

$\eta \cdot 10^p$	$p = 2$	$p = 1$	$p = 0$
1	2.060·10 <sup>-1</sup>	1.987·10 <sup>-1</sup>	1.534·10 <sup>-1</sup>
2	2.050	1.917	1.266
3	2.042	1.853	1.097
4	2.034	1.796	9.768·10 <sup>-2</sup>
5	2.026	1.743	8.862
6	2.018	1.695	8.147
7	2.010	1.650	7.571
8	2.003	1.608	7.086
9	1.995	1.570	6.675

became negative at the electrode surface. Interpolation was then effected, and the magnitude of  $\theta'$  recorded as a function of the rate parameter  $\eta$ . This relationship appears in Table 3, and may be used for experimental interpretation in the manner described for first-order reactions.

#### CONCLUSIONS

The interpretation of electrochemical transients in convective systems can be more cumbersome than the analogous interpretation of results from unstirred systems, unless there is a careful choice of experimental conditions. Numerical methods are ideally suitable for the solution of theoretical problems arising from these transient experiments, and can enable the elucidation of the kinetics even of multiple-order homogeneous reactions. A steady-state of electrolysis is attained more rapidly under potentiostatic, than under galvanostatic, conditions.

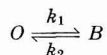
#### APPENDIX

##### STEADY-STATE LIMITING CURRENTS AT ROTATING DISC ELECTRODES IN THE PRESENCE OF KINETIC AND CATALYTIC COMPLICATIONS

KOUTECKÝ AND LEVICH<sup>17</sup> considered the magnitude of the limiting current at a rotating disc electrode, when the participants in the electrode process also enter into reactions in the bulk of the solution. Their method of solution was an approximate one, and an analysis of the consequent error shows that the reaction rate must be high for their results to be valid. Substitution of a numerical method of solution can remove this restriction in simple cases, and increases the usefulness of the disc electrode as a tool for the study of the kinetics of homogeneous reactions.

##### *First-order kinetic scheme*

Let  $i_l$  connote the magnitude of the limiting current observed at a rotating disc due to reduction of the substance  $O$ , which also enters into the homogeneous reaction



Not only does  $i_l$  vary with the position of equilibrium of this reaction, but also with the rate of the forward and backward reactions.

We define linear combinations of the concentration functions  $C_O$  and  $C_B$  of the species  $O$  and  $B$ , and assign the symbol  $D$  to the assumed common diffusion coefficient of these species:

$$u = \frac{nFAD}{i_l \delta} (C_{O^b} - C_O + C_{B^b} - C_B) \quad (A1)$$

and

$$v = \frac{nFAD}{i_l \delta} (KC_B - C_O) \quad (A2)$$

Then  $u$  and  $v$  satisfy:

$$\left. \begin{aligned} \frac{d^2 u}{dz^2} &= 0 \\ \frac{du}{dz} &= -1 \text{ at } z = 0; u = 0 \text{ at } z = 1 \end{aligned} \right\} \quad (\text{A3})$$

and

$$\left. \begin{aligned} a^2 \frac{d^2 v}{dz^2} - \lambda v &= 0 \\ \frac{dv}{dz} &= -1 \text{ at } z = 0; v = 0 \text{ at } z = 1 \end{aligned} \right\} \quad (\text{A4})$$

The terminology is that introduced in the text; for example,  $\lambda$  is given by eqn. (20)  $u(z)$  may be found directly from A3, and in particular,  $u(0) = 1$ .  $v(\lambda, z)$  was determined by a finite difference method with the range of  $z$  divided into one hundred strips;  $v(\lambda, 0)$  is recorded as a function of  $\lambda$  in Table 4.

TABLE 4  
TABLE OF  $v(\lambda, 0)$

$\lambda \cdot 10^p$	$p = 2$	$p = 1$	$p = 0$	$p = -1$	$p = -2$
1	0.997	0.964	0.745	0.310	0.0997
2	0.993	0.932	0.611	0.222	0.0704
3	0.989	0.902	0.527	0.182	0.0574
4	0.985	0.874	0.470	0.157	0.0497
5	0.982	0.848	0.427	0.141	0.0444
6	0.978	0.824	0.394	0.129	0.0405
7	0.975	0.802	0.367	0.119	0.0374
8	0.971	0.782	0.345	0.111	0.0350
9	0.968	0.763	0.326	0.105	0.0329

It may be demonstrated that KOUTECKÝ AND LEVICH'S approximation for  $v(\lambda, 0)$  is  $1/\sqrt{\lambda}$ , which is always greater than the true solution, by about 25% at  $\lambda = 1$ , 2% at  $\lambda = 10$ , and 0.3% at  $\lambda = 1000$ . A better approximation at small values of  $\lambda$  is

$$v(\lambda, 0) = \frac{1}{\sqrt{\lambda}} \tanh \sqrt{\lambda} \quad (\text{A5})$$

which is obtained upon making the approximation  $a^2 = 1$  in eqn. (A4).

Equations A1 and A2 yield for the electrode surface:

$$\frac{nFAD}{i_1 \delta} (C_B^b - C_B(0)) = 1 - \frac{nFADC_0^b}{i_1 \delta} \quad (\text{A6})$$

and

$$v = \frac{nFADC_0^b}{i_1 \delta} (1 + K) - K \quad (\text{A7})$$

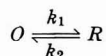
But  $nFADC_0^b/\delta = i_a$ , the purely diffusion-controlled limiting current at the same rotation speed and bulk concentration of  $O$ , so that

$$v(\lambda, 0) = \frac{i_a}{i_l} (1 + K) - K \quad (\text{A8})$$

Evaluation of the right-hand side of this equation and interpolation in Table 4 allows the determination of  $\lambda$ , and hence of  $k_1$ , the rate constant of the homogeneous reaction.

### Catalytic reactions

The reaction system:



was described in a corresponding section of the text. We employ the functions  $u$  and  $v$  of eqns. (27) and (28), which satisfy in the steady state:

$$\left. \begin{aligned} \frac{d^2 u}{dz^2} &= 0 \\ \frac{du}{dz} &= 0 \text{ at } z = 0 \text{ and } u = 0 \text{ at } z = 1 \end{aligned} \right\} \quad (\text{A9})$$

and

$$\left. \begin{aligned} a^2 \frac{d^2 v}{dz^2} - \lambda v &= 0 \\ \frac{dv}{dz} &= -1 \text{ at } z = 0 \text{ and } v = 0 \text{ at } z = 1 \end{aligned} \right\} \quad (\text{A10})$$

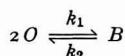
Evidently  $u(z) = 0$  and  $v(\lambda, z)$  is as determined in Table 4. Insertion of the condition for the limiting current, that  $C_o(0) = 0$  yields the equation upon which experimental interpretation may be based:

$$v(\lambda, 0) = \frac{i_a}{i_l} \quad (\text{A11})$$

The procedure for analysis follows the scheme outlined in the previous section.

### Bimolecular decay

KOUTECKÝ AND LEVICH<sup>17</sup> also treated the problem of the limiting current, which can be observed when the reducible substance can take part in a homogeneous bimolecular reaction of the form:



The approximations required for the analytical calculation of the limiting current were necessarily severe, because of the non-linearity of the differential equations descriptive of the process. LEVICH<sup>18</sup> has shown, however, that the derived result is asymptotically correct at high reaction rates. A numerical method of solution, on the other hand, is most suited to the complementary situation of low reaction rates, when the back reaction may be neglected.

We express the boundary value problem in terms of the quantities:

$$w = \frac{C_o^b - C_o}{C_o^b} \quad \text{and} \quad \xi = \frac{k\delta^2 C_o^b}{D}$$

and find that the solution is then required of

$$\left. \begin{aligned} a^2 \frac{d^2 w}{dz^2} + \xi (1 - w)^2 = 0 \\ w = 1 \text{ at } z = 0; w = 0 \text{ at } z = 1 \end{aligned} \right\} \quad (\text{A12})$$

Then

$$\left( \frac{dw}{dz} \right)_{z=0} = \frac{i_l}{i_d} = A$$

where  $i_l$  is the limiting current observed, and  $i_d$  is its value with pure diffusion control. As in the corresponding problem of the text, it is most convenient to linearise the difference equation:

$$w_{(k-1)} + \pi_k w_k + w_{(k+1)} = b_k \quad 1 \leq k \leq N - 1$$

where

$$\pi_k = -(2 + 2g_k - g_k w_k)$$

$$b_k = -g_k$$

$$g_k = \xi(\Delta z)^2/a_k$$

At the boundaries we have  $w_1 = 1$  and  $w_N = 0$ . The calculation was carried out with successively increasing values of  $\xi$  and with  $\Delta z = 0.1$ ,  $N = 10$ . When computing  $w_k$  for  $\xi = 0.01$ , the first value in the list, the coefficient  $\pi_k$  was estimated by substituting for  $w_k$  its value appropriate to  $\xi = 0$ , *i.e.*,

$$w = 1 - z$$

The set of elements,  $w_k$ , derived were then used to estimate a new  $\pi$ , and the procedure iterated until  $w_s$  was reproduced within 0.1%. A calculation of  $w$  appropriate to larger values of  $\xi$ , was started with the  $w_k$ 's calculated for the "previous"  $\xi$ . Two iterations were sufficient when  $\xi$  was less than 0.9, while the procedure failed to converge for  $\xi > 10$ . In other respects the method of calculation was as described for first-order processes.

For the numerical estimation of the gradient at the surface of the function  $w$ , GREGORY'S<sup>16</sup> forward difference formula was employed, truncated at the third term.

TABLE 5  
TABLE OF  $A(\xi)$

$\xi \cdot 10^p$	$p = +2$	$p = +1$	$p = 0$
1	0.998	0.978	0.805
2	0.995	0.956	0.655
3	0.993	0.935	0.533
4	0.991	0.915	0.428
5	0.989	0.895	0.336
6	0.987	0.876	0.252
7	0.984	0.858	0.714
8	0.982	0.840	0.0992
9	0.980	0.822	0.0264

Higher-order differences were found to have little effect. The function calculated in this manner is recorded in Table 5, and is immediately applicable to the identification of a second-order rate constant  $k$ , when the conditions and approximations of this section are appropriate.

## SUMMARY

The shape of the limiting current transient at a rotating disc electrode is considered, limits in time being derived for the applicability of Fick's law and of the steady state, for its description. Interpretation of a galvanostatic transition time, determined when the depolariser takes part in a homogeneous "kinetic" or "catalytic" process, is less convenient in a convective than in a quiescent system if polarisation is affected by passage of a constant current through a solution containing a bulk concentration of the depolariser. When, however, polarisation is achieved by current reversal, the depolariser having been generated by a steady-state condition of the reverse direction of the electrode reaction, the convective system is more advantageous.

New functions are presented for the interpretation of steady-state limiting currents in kinetic and catalytic systems.

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## THE RATE OF ELECTRODE OXIDE FORMATION DURING CHRONOPOTENTIOTRAGRAMS AT A PLATINUM ANODE

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When a platinum or other noble metal electrode is used as the working anode in chronopotentiometric experiments, correction is required for the increase in the transition time caused by oxidation of the electrode itself<sup>1-4</sup>. If the working electrode is undergoing oxidation, only a fraction of the observed current density pertains to the reaction of the diffusing material. The remainder is due to the oxidation of the electrode. Correspondingly, the observed transition time is longer than it would be if such electrode oxidation did not occur.

LINGANE<sup>2</sup> discovered empirically that the applied current density,  $i_0$  (A/cm<sup>2</sup>), can be corrected for oxide filming by a factor  $Q/\tau$ , where  $Q$  is the amount of electricity (C/cm<sup>2</sup>) consumed in oxidizing the electrode to the transition potential and  $\tau$  is the transition time (sec). Thus, the Sand equation becomes

$$(i_0 - Q/\tau)\tau^{1/2} = \frac{n\pi^{1/2}D^{1/2}FC}{2} \quad (1)$$

where  $n$  is the number of electrons involved in the oxidation of the diffusing material,  $D$  is its diffusion coefficient (cm<sup>2</sup>/sec),  $C$  is the bulk concentration of the diffusing material (moles/cm<sup>3</sup>) and  $F$  is the Faraday (C/equiv). If the chronopotentiogram is obtained under conditions of spherical or cylindrical diffusion, then  $i_0 - Q/\tau$  should be substituted for  $i_0$  in the appropriate transition time equation.

BARD<sup>4</sup> has recently proposed the same correction, in a slightly different mathematical form, to explain the enhancement of chronopotentiometric waves by concurrent electrode oxidation and/or double-layer charging. BARD plots  $i_0\tau$  against  $\tau^{1/2}$ , since, according to his treatment, the data should obey eqn. (2).

$$i_0\tau = \frac{n\pi^{1/2}D^{1/2}FC\tau^{1/2}}{2} + Q \quad (2)$$

$Q$  here represents the amount of electricity required to oxidize the electrode and/or charge the double layer to the transition potential. From the slope of the line obtained, BARD finds the concentration of the oxidizable or reducible material and from the intercept he obtains the amount of electricity necessary to film the electrode or charge

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the double layer. Division of eqn. (2) by  $\tau^{\frac{1}{2}}$  and rearrangement of terms brings it into the same form as eqn. (1).

As both LINGANE and BARD recognized, in order for eqn. (1) to be strictly valid, the current density due to oxide formation and/or double-layer charging must be constant throughout the duration of the electrolysis. However, it has long been known<sup>5</sup> that the double-layer charging current is proportional to the rate of change of potential. Hence the charging current is largest near the beginning of the chronopotentiogram and near the transition time, the regions where the slope of the potential-time curve is greatest. The charging current is very much smaller during the central part of the chronopotentiogram, when the rate of change of potential with time is relatively small. The nature of the oxide filming current is the subject of this communication.

Little is known about the rate of oxide film formation on anodes in the presence of another electrode reaction. GINER<sup>6</sup> showed that during the oxidation of oxalic acid on platinum in sulfuric acid solution, the major portion of the 1200  $\mu\text{C}/\text{cm}^2$  required to film the electrode completely was consumed after the oxalic acid transition time. ANSON AND SCHULTZ<sup>7</sup> state that most of the filming of the electrode (in acidic oxalic acid solutions) occurs after the oxalic acid transition time. They did no systematic investigation of the rate of formation of the platinum oxide film during the course of a chronopotentiogram.

#### EXPERIMENTAL PROCEDURE

Mallinckrodt Analytical Reagent grade oxalic acid dihydrate was used as received. Stock solutions of the acid were prepared with distilled water and stored in the dark. Dupont reagent-grade sulfuric acid, appropriately diluted with distilled water, was used as a supporting electrolyte.

The linear diffusion chronopotentiometric cell was fundamentally the same as that described in a previous communication<sup>8</sup>. For these experiments, a machined plug of Teflon was used instead of the Nylon plug previously described. Since Teflon undergoes some distortion under pressure, the area of each of the two foils employed was determined empirically by chronopotentiometric reduction of solutions of ferric chloride and thallos sulfate of known concentrations. From these measurements, the apparent areas of the two foils used were 0.145  $\text{cm}^2$  and 0.113  $\text{cm}^2$ .

The conventional electrolysis circuit described in ref. 2 was modified so that the clock was started when the electrolysis was begun and stopped when the current was reversed. Potential-time curves were recorded with a Tektronix Model 502 oscilloscope equipped with a Polaroid camera. A Sargent Model MR recording potentiometer was used for those experiments requiring a recorder. All measurements were made at  $25.0 \pm 0.1^\circ$ .

The rate of formation of platinum oxide films during the chronopotentiometric oxidation of oxalic acid in 1 *F* sulfuric acid was determined by reverse current chronopotentiometry. Neither oxalic acid nor its oxidation product, carbon dioxide, is reducible at a platinum cathode in this medium. The cathodic wave which is observed on current reversal is due to the reduction of the platinum oxide film on the working electrode. The product  $i_0\tau_{\text{cath}}$  is taken to be the amount of film on the electrode surface at the time of current reversal. By making current reversal measurements at a sufficiently large number of anodization times before the expected

transition time, the amount of oxide film on the electrode as a function of the time of anodizing can be determined.

The measuring techniques and the type of data obtained are illustrated by Fig. 1. A complete anodic chronopotentiogram for  $1.025 \times 10^{-3} F$  oxalic acid is presented as curve 1. Curve 2 is a current reversal chronopotentiogram recorded at the same

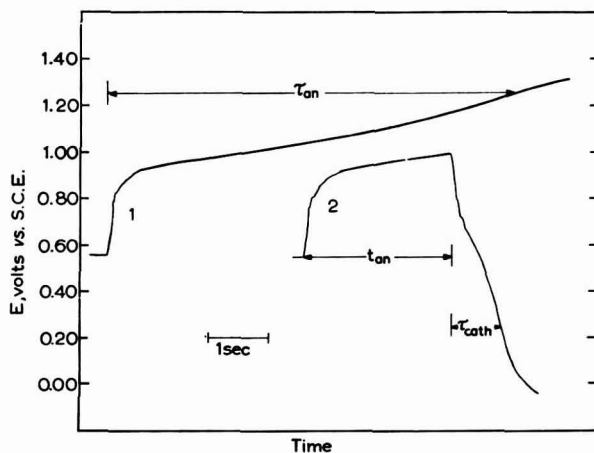


Fig. 1. An illustration of the current reversal technique used to study the rate of electrode oxide formation. curve 1, complete anodic chronopotentiogram for  $1.025 \times 10^{-3} F$  oxalic acid in  $1 F$  sulfuric acid at a current density of  $234 \mu A/cm^2$ ; curve 2, a current reversal chronopotentiogram run at the same current density. The current is reversed at time  $t_{an}$  and a cathode wave, due to the reduction of the electrode oxide film, is observed.

current density. After the electrolysis has proceeded for a time  $t_{an}$ , the current is reversed and a cathodic chronopotentiogram with transition time  $\tau_{cath}$  is obtained. The amount of oxide on the electrode at time  $t_{an}$  is  $i_0\tau_{cath}$ .

By this technique, the growth of the oxide film during chronopotentiometric oxidation of oxalic acid was measured at different current densities for three concentrations of oxalic acid,  $0.508 \times 10^{-3} F$ ,  $1.025 \times 10^{-3} F$  and  $4.86 \times 10^{-3} F$ .

In order to ensure reproducibility of the measurements a standard pre-treatment was evolved. Before each measurement, the electrode was anodized to oxygen evolution and then cathodized to hydrogen evolution. The solution, including that in the working electrode cavity, was stirred with nitrogen for about one minute and then allowed about one minute to become quiescent. The anodic transition time was checked several times during the course of a series of measurements to guard against any systematic variation or major change in its magnitude. The sequence of anodization times was random so that no systematic change in the behavior of the electrode could occur unnoticed.

The amount of oxide film on the electrode as a function of the anode potential was determined by comparison of complete anodic chronopotentiograms with the amount of oxide *versus* time-of-anodization measurements made at the same current density. Anodic chronopotentiograms were recorded with the recording potentiometer, but

cathodic transition times were short enough (0.05–2 sec) to require oscilloscopic measurement. By comparing the two sets of measurements, one does not rely on imprecise oscilloscopic potential measurements to find  $Q$  as a function of anode potential.

## EXPERIMENTAL RESULTS

The amount of oxide on the working electrode during the course of anodic chronopotentiograms is presented, for two concentrations of oxalic acid, in Figs. 2 and 3.

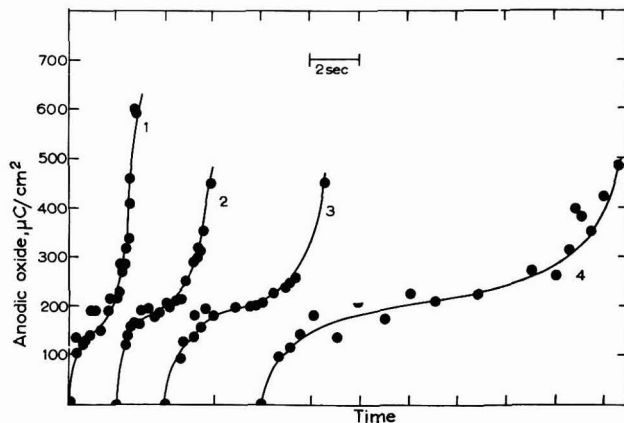


Fig. 2. The amount of oxide film on the anode as a function of electrolysis time for the oxidation of  $4.86 \times 10^{-3} F$  oxalic acid at  $25.0^\circ$ . curve 1,  $i_0 = 1720 \mu\text{A}/\text{cm}^2$ ; curve 2,  $i_0 = 1287 \mu\text{A}/\text{cm}^2$ ; curve 3,  $i_0 = 993 \mu\text{A}/\text{cm}^2$ ; curve 4,  $i_0 = 646 \mu\text{A}/\text{cm}^2$ . The transition times are, respectively,  $2.63 \pm 0.04$  sec,  $3.81 \pm 0.06$  sec,  $6.73 \pm 0.10$  sec, and  $14.31 \pm 0.05$  sec.

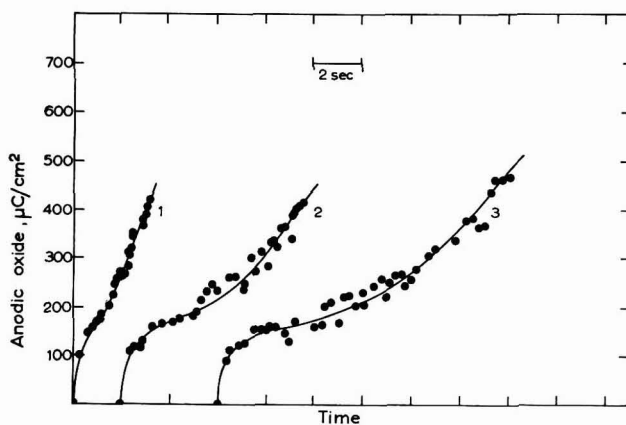


Fig. 3. The amount of oxide film on the electrode as a function of electrolysis time for the oxidation of  $1.025 \times 10^{-3} F$  oxalic acid in  $1 F$  sulfuric acid at  $25.0^\circ$ . curve 1,  $i_0 = 407 \mu\text{A}/\text{cm}^2$ ; curve 2,  $i_0 = 230 \mu\text{A}/\text{cm}^2$ ; curve 3,  $i_0 = 178 \mu\text{A}/\text{cm}^2$ . The transition times are, respectively,  $3.22 \pm 0.10$  sec,  $7.33 \pm 0.05$  sec and  $11.23 \pm 0.17$  sec.

The data represent the growth of the oxide film over a five-fold range of oxalic acid concentrations and over current densities corresponding to transition times ranging from 2.5 to 14 sec. Similar results were obtained for the growth of the oxide film during the electrolysis of  $0.508 \times 10^{-3} F$  oxalic acid<sup>9</sup>. The time-derivative of each curve represents the instantaneous rate of film formation for the conditions of measurement, but it is in the integrated form that the rate is susceptible to measurement by the techniques available.

Because it was impossible to obtain measurements at current reversal times much below 0.2 sec with the equipment employed, it was not considered worthwhile to attempt measurements under conditions where the anodic transition time is less than about 2.5 sec. In such cases, a large part of the electrode film forms before an elapsed time of 0.2 sec and its rate of formation could not be obtained.

Figure 4 shows plots of  $i_0\tau$  versus  $\tau^{1/2}$  for the oxidation of  $4.86 \times 10^{-3} F$  oxalic acid

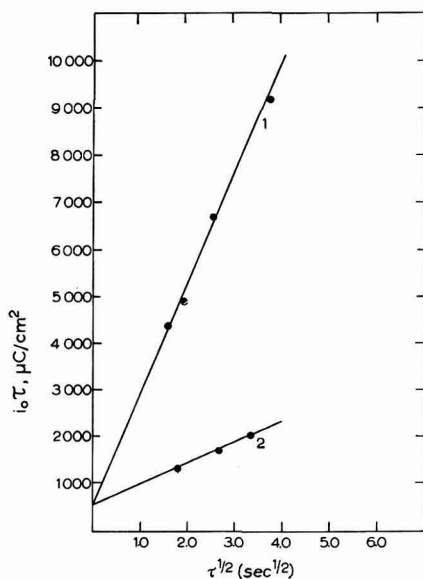


Fig. 4. Plots of chronopotentiometric data for the oxidation of oxalic acid in 1 *F* sulfuric acid. Curve 1,  $4.86 \times 10^{-3} F$  oxalic acid; from the slope of the line, the apparent chronopotentiometric constant is  $463 \text{ A sec}^{1/2} \text{ cm/mole}$ ; the intercept is  $450 \mu\text{C}/\text{cm}^2$ . Curve 2,  $1.025 \times 10^{-3} F$  oxalic acid; from the slope of the line the apparent chronopotentiometric constant is  $476 \text{ A sec}^{1/2} \text{ cm/mole}$ ; the intercept is  $450 \mu\text{C}/\text{cm}^2$ .

and  $1.025 \times 10^{-3} F$  oxalic acid in 1 *F* sulfuric acid at the current densities employed in this study. Extensive verification of the Lingane-Bard equations has been made<sup>2,4</sup> and this figure is presented to show that the data obtained in these experiments do indeed fit eqs. (1) or (2). If the diffusion coefficient of oxalic acid is taken to be  $1 \cdot 10^{-5} \text{ cm}^2/\text{sec}$ , then the chronopotentiometric constant for oxalic acid ( $n = 2$ ) is  $478 \text{ A sec}^{1/2} \text{ cm/mole}$ . The slopes of the lines in Fig. 4 are close to  $470 \text{ A sec}^{1/2} \text{ cm/mole} \cdot C$ . The intercept of each line is about  $450 \text{ C}/\text{cm}^2$ , quite close to the quantity of electricity

( $439 \pm 15 \mu\text{C}/\text{cm}^2$ ) required to film the electrode to the transition potential,  $+1.25 \text{ V vs. S.C.E.}$  The current densities and quantities of oxide film are expressed in terms of the apparent rather than the real, microscopic electrode area.

Figure 5 shows the relationship between the observed current density,  $i_0$ , the current density due to oxide formation,  $i_p$ , and the effective current density due to oxalic acid oxidation,  $i_r$ . The oxide formation current density,  $i_p$ , was obtained by graphical differentiation of curve 2 of Fig. 3. Similar curves are obtained by differentiation of the other  $Q$  versus time-of-anodizing plots.

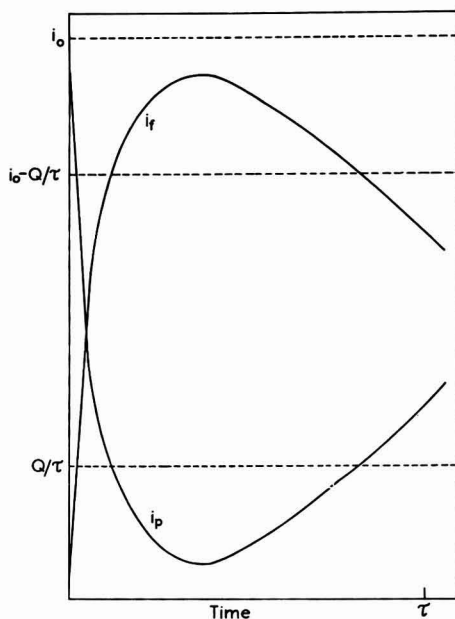


Fig. 5. The components of the observed current density,  $i_0$ , in a typical anodic oxidation of oxalic acid.  $i_r$  is the current density due to oxalic acid oxidation and  $i_p$  is the current density due to oxide film formation on the working anode. The average current density due to oxalic acid is  $i_0 - Q/\tau$ . The average filming current density is  $Q/\tau$ .

It is obvious that the oxide filming current density during anodic chronopotentiograms is far from constant. Inspection of Figs. 2, 3 and 5 suggests that the amount of oxide film on the electrode might be directly proportional to the anode potential. That this is so is demonstrated by Fig. 6, the variation of the amount of oxide film on the electrode with anode potential. For clarity only two sets of measurements have been included; the other points fall on the same line. Within the precision of the measurements, the quantity of oxide on the electrode is proportional to the anode potential above about  $0.7 \text{ V vs. S.C.E.}$  The proportionality constant is about  $800 \mu\text{C}/\text{cm}^2 \text{ volt}$ .

The initial potential of the reduced platinum electrode in the oxalic acid solutions used is between  $0.5$  and  $0.6 \text{ V vs. S.C.E.}$  This value is  $0.1$ – $0.2 \text{ V}$  more negative than

the potential at which electrode oxidation appears to begin. Oscilloscopic measurements show that  $2-5 \mu\text{C}/\text{cm}^2$  is consumed in traversing the interval from the initial potential to  $0.7 \text{ V}$ . Presumably the major process occurring in this potential interval is double-layer charging, which should require  $2-3 \mu\text{C}/\text{cm}^2$  per  $0.1 \text{ V}$  potential increase.

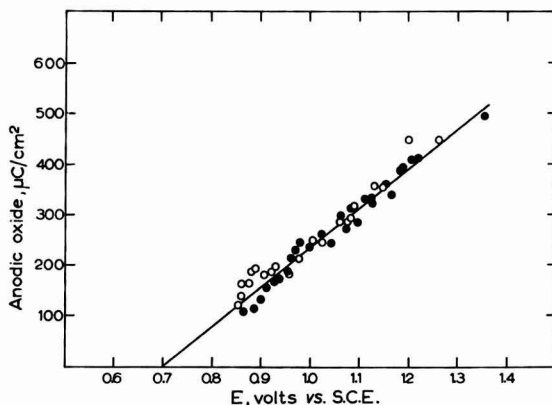


Fig. 6. The amount of oxide film on the anode as a function of anode potential for the oxidation of oxalic acid in  $1 \text{ F}$  sulfuric acid at  $25.0^\circ$ . The rate of increase of film is  $800 \mu\text{C}/\text{cm}^2 \text{ volt}$ .  
 $\circ$ ,  $4.86 \text{ mF H}_2\text{C}_2\text{O}_4$ ;  $i_0 = 1287 \mu\text{A}/\text{cm}^2$ .  $\bullet$ ,  $1.024 \text{ mF H}_2\text{C}_2\text{O}_4$ ,  $i_0 = 230 \mu\text{A}/\text{cm}^2$ .

Therefore, we feel justified in extrapolating our experimental results to an intercept at  $0.7 \text{ V vs. S.C.E.}$  although direct measurements of the amount of oxide on the electrode were not made at potentials more cathodic than  $0.85 \text{ V vs S.C.E.}$  It is suggested that in calculations employing the potential interval in which the chronopotentiogram occurs, the interval from  $0.7 \text{ V}$  to the transition potential ( $1.25 \text{ V}$ ) be used. This approximation is equivalent to subtracting from the transition time the time required to reach  $0.7 \text{ V}$  and normally introduces no appreciable error.

The data obtained in these experiments show that the oxide filming current density  $i_p$ , is proportional to the change in the anode potential. In other words, eqn. (3) is a good approximation to the filming current density except, perhaps, at the very beginning and at the very end of the chronopotentiogram.

$$i_p(t) = k \frac{dE}{dt} \quad (3)$$

The proportionality constant,  $k$ , here has the value  $800 \mu\text{C}/\text{cm}^2 \text{ volt}$  or  $800 \mu\text{F}/\text{cm}^2$ . This value of  $k$  agrees well with that obtained by LAITINEN AND ENKE<sup>10</sup> by potentiostatic formation of oxide films in perchloric acid solutions. Formally  $k$  is a capacitance and formally the oxide filming process is analogous to the charging of a capacitor. Thus we see why a correction of a given form will work equally well for both double-layer charging and oxide-film formation: the current resulting from each process should follow the same law in so far as the double-layer capacitance and the quantity  $k$  are independent of potential.

The value of  $k$  obtained from Fig. 6 contains a contribution from double-layer

charging. The double-layer capacitance is about  $25 \mu\text{F}/\text{cm}^2$ . Subtracting this value from  $k$  leaves a filming capacitance of  $770 \mu\text{F}/\text{cm}^2$ . However, what contributes to the enhancement of anodic transition times is not just oxide-film formation, although that is the dominant effect, but also double-layer charging. Therefore, if the aim of the investigation is to discover the nature of the enhancement and to correct for it, there is no reason to subtract the double-layer component of  $k$ .

As pointed out above, the observed current density,  $i_0$ , in anodic chronopotentiograms may be considered to contain two components,  $i_t$ , the current density due to oxidation of the diffusing species, and  $i_p$ , the current density due to oxide film formation or other parasitic processes. In this case, the boundary condition for chronopotentiometry may be written as

$$i_t(t) = i_0 - i_p(t) = nFD \left( \frac{\partial C}{\partial x} \right)_{x=0} \quad (4)$$

or, in view of eqn. (3)

$$i_0 - k \left( \frac{\partial E}{\partial t} \right) = nFD \left( \frac{\partial C}{\partial x} \right)_{x=0} \quad (5)$$

If the variation of  $i_p$  with time were known explicitly, it would be possible, in principle at least, to solve the diffusion equation with boundary condition (4) or (5) and arrive at a correction for film formation. However,  $E(t)$  is not known *a priori* for chronopotentiograms distorted by oxide-film formation and rigorous solution of the diffusion equation for this case is not possible. The difficulties involved in attempting to use the expression for the potential-time function in the absence of filming in arriving at an approximation to eqn. (4) have been discussed by MORRIS<sup>9</sup>. The difficulties arise from the fact that the usual expressions for the shape of a chronopotentiogram have infinite first derivatives at time  $t = 0$  and at the transition time and therefore predict infinite filming currents at these points.

Although it is impossible to provide a rigorous derivation of a transition-time equation corrected for the influence of oxide filming and/or double-layer charging, qualitative justification of eqns. (1) and (2) is possible.

It is obvious that if the filming current were strictly constant at the value  $Q/\tau$ , eqns. (1) and (2) would be strictly valid. During the first part of the chronopotentiogram, however,  $i_t$  is rising ( $i_p$  falling). This tends to make the transition time shorter than that expected at a constant  $i_t = i_0 - Q/\tau$  but longer than that expected at a current density of  $i_0$ . However, during the latter part of the chronopotentiogram,  $i_t$  decreases below  $i_0 - Q/\tau$ . This decrease tends to lengthen the transition time. Reference to Fig. 5 makes the relationship between  $i_t$  and  $i_0 - Q/\tau$  clear. It is the fact that  $i_t$  rapidly reaches a maximum and then decreases again which makes the transition time quite close to that which would be observed if  $i_t$  remained constantly at its average value of  $i_0 - Q/\tau$ .

#### ACKNOWLEDGEMENTS

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## SUMMARY

The formation of electrode oxide during anodic chronopotentiograms has been investigated for the oxidation of oxalic acid in 1 *F* sulfuric acid at a platinum anode. The amount of oxide on the electrode is found to be directly proportional to the anode potential above 0.7 V vs. S.C.E. The proportionality constant is 800  $\mu\text{C}/\text{cm}^2$  volt.

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## UTILISATION D'UNE MÉTHODE "COULOAMPÉROMÉTRIQUE" POUR L'ÉTUDE CINÉTIQUE DE RÉACTIONS RAPIDES

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Si jusqu'à ces dernières années la cinétique des réactions rapides n'avait été que peu étudiée, il n'en est pas de même actuellement, grâce aux progrès des techniques de mesure. En effet à côté des méthodes classiques où l'on suit la disparition ou l'apparition d'un réactif en fonction du temps, se sont développées des méthodes basées sur des perturbations d'un équilibre ou d'un état stationnaire (photolyse éclair, relaxation) ou sur une compétition entre deux processus chimique et physique (écoulement, polarographie)<sup>1</sup>.

Les techniques classiques de dosage ne permettent pas en général de mesurer des constantes de vitesse aussi élevées que celles qui sont atteintes par les techniques précédentes, surtout dans le cas de réaction du premier ordre. Cependant des mesures cinétiques très rapides du deuxième ordre peuvent être faites par des adaptations plus ou moins simples des méthodes électrochimiques classiques.

Elles sont toutes basées sur l'emploi de très faibles concentrations de réactifs.

On peut distinguer deux types principaux de méthodes:

(i) celles où l'on réalise, par voie physique ou chimique, l'état "quasi stationnaire" d'une concentration  $C_X$  d'un composé  $X$  en solution et où l'on mesure en fonction du temps la quantité  $X$  à apporter pour maintenir cet état quasi stationnaire;

(ii) celles où l'on suit d'une manière continue la variation de la concentration d'un composé  $X$  en solution.

L'exemple des réactions de bromation (addition du brome) et de bromuration (substitution du brome) permet de mettre en évidence les principes de ces méthodes.

On ne connaît qu'une seule méthode du premier type; elle a été proposée par DUBOIS et coll.<sup>2,3,4</sup>: elle consiste à maintenir la concentration en brome à une valeur constante par voie physique; le brome est produit par électrolyse à courant constant et les possibilités du premier appareil nommé "le concentrostat", permettaient de mesurer des constantes de vitesse du second ordre égales à  $5 \cdot 10^4$  l mole<sup>-1</sup> min<sup>-1</sup>.

Dans le second groupe on trouve des méthodes utilisant la potentiométrie ou l'ampermétrie pour suivre la variation de la concentration en brome<sup>5,6</sup>, ce réactif étant produit par des méthodes chimiques. Ces méthodes permettent d'atteindre des constantes expérimentales dont les valeurs s'élèvent jusqu'à  $10^4$  l mole<sup>-1</sup> min<sup>-1</sup>. Ce n'est

que par le jeu d'un asservissement chimique\* que des constantes supérieures peuvent être déterminées\*\*.

Les recoupements entre les différentes méthodes sont très rares; en effet, il est difficile de déterminer des valeurs absolues de constantes de vitesse très élevées<sup>7,8,9</sup>.

Dans les dernières années, les recoupements ont été facilités par l'extension des domaines d'application des diverses méthodes; DUBOIS ET MOUVIER<sup>10</sup> ont modifié le "concentrostat" et mesuré des constantes de vitesse  $k_2$  égales à  $3 \cdot 10^7$  l mole<sup>-1</sup> min<sup>-1</sup>. Par ailleurs, BELL<sup>11</sup> a étendu la possibilité de mesure directe par potentiométrie à des constantes  $k_2$  allant jusqu'à  $3 \cdot 10^8$  l mole<sup>-1</sup> min<sup>-1</sup>.

Parallèlement à ces développements, nous avons mis au point une méthode basée également sur l'emploi de très faibles concentrations de réactifs, de l'ordre de  $10^{-7}$  mole l<sup>-1</sup>. Des réactions du deuxième ordre, dont les constantes de vitesse atteignent  $5 \cdot 10^8$  l mole<sup>-1</sup> min<sup>-1</sup> peuvent ainsi être suivies<sup>14,15</sup>. La production du brome se fait par électrolyse à courant constant d'un bromure alcalin présent dans la solution, et sa disparition après introduction rapide de l'autre réactif est suivie par la mesure du courant limite correspondant, entre deux électrodes de platine.

La recherche des conditions expérimentales nécessaires à l'emploi de l'ampérométrie pour des concentrations aussi faibles,  $10^{-7}$  mole l<sup>-1</sup>, et la détermination de la sensibilité des électrodes à ces concentrations, nous ont conduit à tracer les réseaux des courbes "courant-tension" du système brome-bromure dans l'eau et le méthanol.

Nous envisagerons successivement:

- (i) les résultats obtenus dans l'étude des réseaux "courant-tension";
- (ii) la description de la méthode cinétique ainsi que la technique de calcul des constantes de vitesse.

#### COURBES COURANT-TENSION DU SYSTÈME BROME-BROMURE

Le montage classique de mesure des courbes courant-tension est un montage à trois électrodes (référence, auxiliaire et indicatrice) qui permet d'étudier le comportement anodique et cathodique des électrodes.

##### (1) *Montage expérimental et expérience type*

La cellule de réaction et les différents circuits sont les mêmes que ceux décrits dans l'exposé de la méthode cinétique.

Dans l'étude du système brome-bromure, avec deux électrodes de mesure en platine identiques (fil), il est préférable de tracer les courbes  $i = f(E_A - E_C)$  dans un montage à deux électrodes indicatrices dans les conditions des mesures cinétiques. Comme nous opérons avec un gros excès de bromure par rapport au brome, l'électrode positive se comporte comme une électrode de référence ayant un potentiel pratiquement constant.

Le brome est produit par électrolyse de la solution (50 ml de méthanol contenant  $0.2$  mole l<sup>-1</sup> de bromure alcalin). Les valeurs de  $i$  en fonction de  $E_A - E_C$  sont rassemblées dans le Tableau 1, pour différentes valeurs de la concentration en brome.

\* Maintien de la concentration d'un réactif à une valeur faible par le jeu d'un équilibre (acide-base par exemple).

\*\* Une nouvelle méthode a été proposée récemment que l'on peut classer dans le second groupe, bien que le brome soit produit de façon discontinue au cours de la réaction. La limite supérieure des mesures est alors  $k_2 = 10^7$  l mole<sup>-1</sup> min<sup>-1</sup> <sup>12,13</sup>.

TABLEAU 1

RÉSEAU  $i = f(E_A - E_C)$ Valeur de courant (en  $\mu\text{A}$ ) pour différentes valeurs de la tension et de la concentration en brome.

$E_A - E_C$ (V)	$[\text{Br}_2]$ (mole $l^{-1}$ )					
	0	$0.5 \cdot 10^{-6}$	$0.9 \cdot 10^{-6}$	$1.4 \cdot 10^{-6}$	$2 \cdot 10^{-6}$	$2.5 \cdot 10^{-6}$
0.1	0.06	0.53	0.87	1.30	1.80	2.22
0.2	0.10	0.57	0.92	1.30	1.81	2.29
0.3	0.15	0.57	0.93	1.33	1.87	2.29
0.4	0.21	0.57	0.96	1.33	1.87	2.32
0.5	0.49	0.69	1.06	1.46	2.01	2.42
0.6	1.46	1.65	1.93	2.16	2.70	3.10

## (2) Résultats

L'analyse des courbes obtenues dans nos conditions expérimentales (excès de bromure par rapport au brome, électrodes de platine de mêmes dimensions) montre qu'il est difficile d'attribuer à chaque partie de la courbe  $i = f(E_A - E_C)$  un système oxydo-réducteur propre; le palier peut être attribué au courant limite dû au brome.

Quinze réseaux de courbes ont été tracés avec les mêmes électrodes pour des concentrations en brome comprises entre  $0.5 \cdot 10^{-6}$  et  $3 \cdot 10^{-6}$  mole  $l^{-1}$ . Nous avons observé une bonne proportionnalité entre la concentration en brome et la valeur du courant limite malgré les causes d'erreurs possibles: adsorption de bromure<sup>16,17,18</sup> et action perturbatrice de l'oxygène (voir Tableau 2).

TABLEAU 2

Calcul du rapport  $\Delta[\text{Br}_2]/\Delta i$  pour  $E_A - E_C = 0.3$  V.

$[\text{Br}_2]$ (mole $l^{-1}$ )	$i_{\mu\text{A}}$	$\frac{\Delta[\text{Br}_2]}{\Delta i}$
0	0.15 <sup>a</sup>	
$0.5 \cdot 10^{-6}$	0.57 (0.42)	1.19
0.9	0.93 (0.78)	1.15
1.4	1.33 (1.18)	1.19
2.0	1.87 (1.72)	1.16
2.5	2.29 (2.14)	1.17

<sup>a</sup> Courant résiduel en l'absence de brome. Les valeurs entre parenthèse sont corrigées du courant résiduel et sont utilisées pour le calcul de  $\Delta[\text{Br}_2]/\Delta i$ .

La reproductibilité des courbes dépend essentiellement du traitement des électrodes et de la géométrie de la cellule de mesure. Si tous ces facteurs sont maintenus strictement identiques, la reproductibilité est de l'ordre de 5-10%; au contraire, dans les cas où l'un de ces facteurs varie, des écarts pouvant atteindre 100% ont été obtenus.

## (3) Application

Dans les conditions expérimentales que nous avons précisées, la limite inférieure en

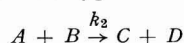
brome détectable dépend de deux facteurs: la teneur en oxygène dissous qui peut être réduit à la cathode\* et la réaction parasite du brome avec le solvant.

Dans la pratique il est possible de déceler des variations de concentrations en brome de  $10^{-7}$  mole  $l^{-1}$  avec une précision de quelques pour cent. Ceci permet le dosage de microquantités de réactifs, soit dans 50 ml, l'équivalent de  $5 \cdot 10^{-9}$  mole, d'un corps réagissant stœchiométriquement avec le brome. Nous avons pu ainsi déterminer des taux d'énols extrêmement faibles<sup>19</sup>. De plus la vitesse de réponse des électrodes s'est avérée suffisamment élevée pour autoriser leur emploi sans limitation apparente pour l'étude cinétique de telles réactions rapides.

#### MÉTHODE CINÉTIQUE

##### (1) Principe

Soit une réaction du second ordre du type



dont la vitesse est de la forme

$$v = -\frac{d[A]}{dt} = k_2[A][B]$$

Si on connaît, d'une part les concentrations initiales des deux réactifs  $A$  et  $B$  et d'autre part la variation en fonction du temps de la concentration de l'un des réactifs, on peut calculer  $k_2$ .

Dans le cas des réactions de bromation et de bromuration, la valeur du courant limite dû au brome entre les deux électrodes indicatrices, dans des conditions expérimentales données, permet de connaître à chaque instant la concentration en brome, car il lui est proportionnel. On obtient expérimentalement, en suivant la réaction, la courbe  $i = f(t)$  qui est en fait la représentation de  $[Br_2] = f(t)$ .

##### (2) Méthode expérimentale

(a) Montage. Nous utilisons une cellule Métrohm à doubles parois avec circulation d'eau maintenue à température constante, contenant 50 ml de solution; les schémas électriques sont les suivants (voir Fig. 1).

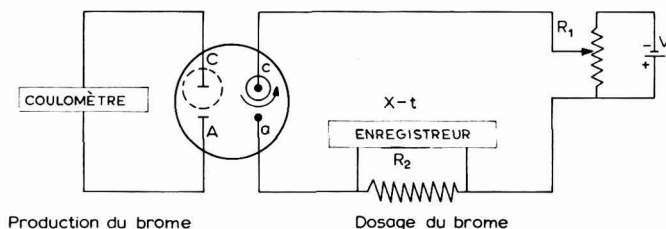


Fig. 1. Schéma du montage de mesure "couloampérométrique". A et a, anode; C et c, cathode.

*Circuit de coulométrie.* Il comprend deux électrodes Métrohm reliées à un coulomètre mis au point au laboratoire<sup>3</sup> et délivrant des courants compris entre 0.1 et 250 mA, stables à 0.1% près. Les électrodes (plaques de platine de 0.5 cm<sup>2</sup>) plongent dans la solution contenant du bromure de sodium en excès; la cathode est isolée de la solution

\* La solution n'est en effet soumise à aucun traitement préalable pour éliminer l'oxygène.

par un verre fritté; le temps d'électrolyse est mesuré avec un chronomètre Rochar type 927 B.

*Circuit d'ampérométrie.* Dans les expériences préliminaires on a utilisé deux électrodes de platine fixes (fil de 0.5 mm de diamètre et de 1 cm de longueur); l'emploi d'une électrode tournante a permis d'améliorer considérablement la stabilité du courant limite; cette électrode joue en même temps par sa forme le rôle d'agitateur (2 400 t/min). La tension constante appliquée entre les électrodes est de 340 mV; initialement, on enregistrait le courant limite en plaçant directement l'enregistreur Kipp du type BD 2 ou BD 3 en série dans le circuit, mais la détermination du zéro, nécessitant l'ouverture du circuit, entraînait une dépolarisation des électrodes. Pour remédier à cet inconvénient, nous avons intercalé une résistance  $R_2$  dans le circuit, ce qui permet la mesure de la chute de tension à ses bornes. On ajuste  $R_2$  de telle manière que la tension mesurée avec l'enregistreur précédent, soit inférieure à 2.5 mV.

(b) *Mode opératoire*

*Préparation des solutions.* Comme solvants ont été utilisés l'eau ou le méthanol soigneusement purifiés; l'eau permutée a été distillée avec du permanganate de potassium et de la potasse.

"*Saturation*". Après l'introduction de 50 ml de solution, on établit par coulométrie une certaine concentration en brome; dix minutes sont suffisantes pour assurer une saturation relative de la solution; en effet, initialement une quantité faible de brome (correspondant à environ  $2 \cdot 10^{-7}$  mole l<sup>-1</sup>) réagit immédiatement avec le solvant; elle est suivie d'une réaction de plus en plus lente, dont on doit tenir compte dans les calculs. Le solvant peut être caractérisé par les quantités de brome ainsi consommées.

*Détermination du rapport  $\Delta[\text{Br}_2]/\Delta i$ .* La moyenne des rapports (variation de concentration en brome divisée par la variation du courant limite) est déterminée sur plusieurs expériences.

Le corps à étudier est introduit rapidement à l'aide d'une microseringue et on suit en fonction du temps la variation du courant limite.

(c) *Calculs.* Pour une réaction du deuxième ordre, la constante de vitesse  $k_2$  est de la forme:

$$k_2 = \frac{2.3\alpha}{a - b}$$

$a$  et  $b$ : concentrations initiales en brome et en corps étudiés

$\alpha$ : pente de la droite représentant la fonction

$$\log \frac{a - x}{b - x} = f(t)$$

où  $a - x$  et  $b - x$  sont les concentrations en brome et en corps étudié au temps  $t$ .

Expérimentalement, deux cas différents se présentent selon les concentrations initiales respectives.

(i) Concentration en brome supérieure à celle en corps à bromer: la courbe expérimentale  $[\text{Br}_2] = f(t)$  permet de déterminer  $a - x$  et  $b - x$  pour différentes valeurs de  $t$ . La détermination de  $\alpha$  se fait alors graphiquement. D'autre part, la même courbe permet de déterminer également  $a - b$  qui est la concentration en brome en excès et il n'est pas nécessaire de connaître dans ce cas les concentrations initiales avec précision.

(ii) Concentration en brome inférieure à celle en corps à bromer: le principe du cal-

cul est le même avec la restriction qu'il est nécessaire de connaître  $a$  et  $b$ ; cependant la valeur de  $a - b$  peut être déduite par un micro-dosage en retour.

(d) *Domaine de mesure.* La principale limite quant à la mesure de constantes de vitesse élevées est l'importance du temps de mélange; ce temps dépend de la solubilité des réactifs et de leur vitesse de diffusion. Il est en général de l'ordre de 0.1 sec; or on admet, qu'une vitesse de réaction peut être mesurée, si le temps de demi-réaction est égal ou supérieur à dix fois le temps de mélange.

Ceci signifie que pour une réaction du premier ordre, si  $\tau(1/2)$  est le temps de demi-réaction on doit avoir

$$\tau(1/2) > 10 \text{ temps de mélange} = 1 \text{ sec}$$

$$k_1 < \frac{0.693}{\tau(1/2)} \simeq 42 \text{ min}^{-1}$$

Pour les constantes de vitesse du second ordre, la limite dépend à la fois du temps de mélange et des concentrations initiales des réactifs. On a en général  $c > 10^{-7}$  mole  $l^{-1}$ , d'où la limite théorique  $k_2 < 10^9$  l mole $^{-1}$  min $^{-1}$ . Seule une modification de la cellule réactionnelle permettrait d'atteindre des constantes plus élevées en réduisant le temps de mélange.

(e) *Exemple de détermination de constantes de vitesse.* Les résultats obtenus dans le cas de la réaction du système "Br $_2$  + Br $_3^-$ " sur l'énol de l'acétylacétate d'éthyle dans le méthanol à 25° avec 0.2 mole  $l^{-1}$  de bromure de sodium en solution figurent dans le Tableau 3.

Ces séries d'expériences permettent de calculer une valeur moyenne de  $k_2 = 4.97 \cdot 10^6$  l mole $^{-1}$  min $^{-1}$  et de déterminer l'écart type

$$\sigma \text{ (écart type)} = \sqrt{\frac{\sum \varepsilon_i^2}{n(n-1)}} = 0.03 \cdot 10^6$$

$$\varepsilon_i = [k - k_i] \quad n = \text{nombre d'expériences}$$

TABLEAU 3

Réaction de l'énol de l'acétylacétate d'éthyle et du système "Br $_2$ -Br $_3^-$ " dans le méthanol (0.2 mole  $l^{-1}$  BrNa) à 25°.

Cinétique N°	[Br $_2$ + Br $_3^-$ ] (mole $l^{-1}$ )	[Enol] (mole $l^{-1}$ )	$k_2$ (l mole $^{-1}$ min $^{-1}$ )
1	66.8 · 10 $^{-7}$	23.8 · 10 $^{-7}$	4.97 · 10 $^6$
2	62.8	43.4	5.03
3	57.8	33.2	4.80
4	26.9	58	5.12
5	57.5	35.6	4.90
6	62.9	34.1	4.85
7	63.2	43.3	4.97
8	32.0	67.8	4.80
9	60.8	40.4	4.93
10	63.8	23.3	5.51
11	54.4	28.0	4.97
12	39.2	20.0	4.86
13	39.2	25.0	5.00
14	39.8	20.0	4.98
15	39.7	20.1	5.08
16	36.0	18.0	4.85

Avec cette méthode, qui peut être appelée "couloampérométrie", on se heurte, pour mesurer des constantes de vitesse supérieures à  $5 \cdot 10^7$  l mole<sup>-1</sup> min<sup>-1</sup>, à des difficultés relatives aux impuretés des réactifs et du solvant; cependant dans le cas de l'action du brome sur le pentène-1 dans l'eau à 25°, une bonne reproductibilité a été obtenue, pour une valeur de la constante proche de la limite théorique calculée.

## RÉSUMÉ

On propose une méthode "couloampérométrique" de microdosage et de mesure cinétique rapide en solution, pour diverses réactions d'addition du brome: addition, substitution et oxydo-réduction. Le brome, dont de très faibles concentrations sont nécessaires (de l'ordre de  $10^{-7}$  mole l<sup>-1</sup>), est produit par électrolyse d'une solution de bromure de sodium; sa concentration analytique est connue par la valeur du courant limite dû au brome entre deux électrodes de platine, dont une tournante. On peut ainsi doser jusqu'à 0.5 µg de réactif réagissant rapidement avec le système "Br<sub>2</sub> - Br<sub>3</sub>-", et déterminer avec une reproductibilité satisfaisante, des constantes élevées de vitesse pouvant atteindre  $5 \cdot 10^8$  l mole<sup>-1</sup> min<sup>-1</sup> en 2ème ordre.

## SUMMARY

A "couloamperometric" technique is proposed for microanalysis and fast kinetic investigations of bromine addition, substitution and oxidation-reduction reactions in solution. The technique requires a minimum amount of compound for investigation,  $10^{-8}$  moles normally being sufficient. Bromine is produced by electrolysis of a bromide in solution and its concentration is followed by means of the diffusion current measured between a fixed and a rotating platinum electrode. It has been found possible to make analytical determinations with only 0.5 µg of compound which reacts rapidly with the "Br<sub>2</sub>-Br<sub>3</sub>-" system and rate constants of the order of  $5 \cdot 10^8$  l mole<sup>-1</sup> min<sup>-1</sup> (second order) can be determined with a satisfactory reproducibility.

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## THEORY OF ANODIC STRIPPING VOLTAMMETRY WITH A PLANE, THIN MERCURY-FILM ELECTRODE

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## INTRODUCTION

The theory of single-sweep voltammetry with linearly changing potential and with a plane electrode is well established<sup>1,2</sup>.

The theory of anodic stripping voltammetry with a mercury electrode and with linearly changing potential is analogous to that of single-sweep voltammetry. It has been shown<sup>3</sup> that the theory developed by REINMUTH<sup>4</sup> for a mercury drop electrode agrees well with experiment. This theory is valid only for electrodes with large volume, *i.e.*, the effect of finite electrode volume does not occur in the calculations.

Reported anodic stripping experiments with mercury electrodes of small volume and with slow rates of potential change<sup>5-7</sup>, as well as our own experiments (not published) with a mercury-film electrode, show that the effect of finite mercury volume can be appreciable. We have therefore developed a theory for anodic stripping voltammetry with a plane, thin mercury-film electrode.

The preparation, use, and advantages of the mercury-film electrode have been described recently<sup>8,9</sup>.

## PRELIMINARY REMARKS

SHAIN AND LEWINSON<sup>3</sup> have already remarked that an anodic stripping analysis consists experimentally of three steps:

1. *The pre-electrolysis.* During an accurately known time-interval the mercury-electrode is kept at a suitably chosen negative potential, and the metal to be determined is reduced at and collected into the mercury (it is assumed here that the metal forms an amalgam with mercury). If the pre-electrolysis time is not too long the flux of reduced metal into the mercury (expressed in moles  $\text{cm}^{-2} \text{sec}^{-1}$ ) is practically constant because the electrode is rotated or the solution is stirred. The pre-electrolysis time can vary from one minute to several hours.

2. *The rest period.* After the pre-electrolysis the rotation of the electrode is stopped and the solution is allowed to come to rest. During this rest period (which normally lasts 30-120 sec) the flux quickly decays to practically zero.

3. *The dissolution step.* The potential of the electrode is linearly changed with time



towards positive values, *i.e.*,  $E = E_i + vt$ . During this potential change the reduced metal is re-oxidized and a dissolution peak is registered.

It is convenient to discuss the theory of anodic stripping voltammetry along the same lines as the experimental procedure. First some calculations of the metal concentration in the mercury during the pre-electrolysis and the rest period are given. Such calculations have already been carried out for a mercury drop electrode by SHAIN AND LEWINSON<sup>3</sup>. Then an equation for the current-potential curve is derived, and the results of the numerical calculations are discussed.

Because actual mercury-film electrodes have a film thickness of the order of 10 micron<sup>8</sup> the numerical calculations have been carried out for mercury-film thicknesses of 4-100 micron, *i.e.*,  $4 \times 10^{-4} < l < 10^{-2}$  cm (see Fig. 1).

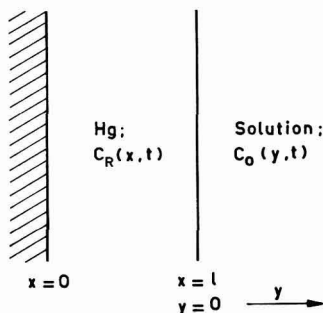


Fig. 1. Mercury-film electrode.

#### I. THE PRE-ELECTROLYSIS

When it is assumed that the equation for linear diffusion holds for the reduced metal in the mercury, and that complications such as inter-metallic compounds and solid amalgams are absent, then it is required to find the solution of

$$\frac{\partial}{\partial t} C_R(x, t) = D_R \cdot \frac{\partial^2}{\partial x^2} C_R(x, t) \quad (1)$$

with the following initial and boundary conditions (see also Fig. 1):

$$\begin{aligned} C_R(x, 0) &= 0, \quad 0 < x < l; \\ D_R \cdot \left( \frac{\partial C_R}{\partial x} \right)_{x=0} &= 0, \quad t > 0; \\ D_R \cdot \left( \frac{\partial C_R}{\partial x} \right)_{x=l} &= Q = \frac{i}{nFA}, \quad t > 0. \end{aligned}$$

$Q$  denotes the constant and positive flux, and  $l$  is the mercury-film thickness. The rest of the notation is conventional.

For an analogous problem in heat conduction, CARSLAW AND JAEGER<sup>10</sup> give the following solution:

$$\frac{C_R(x, t)}{Q} = \frac{t}{l} + \frac{l}{6D_R} \left\{ 3 \left( \frac{x}{l} \right)^2 - 1 \right\} - \frac{2l}{\pi^2 D_R} \sum_{j=1}^{\infty} \frac{(-1)^j}{j^2} \exp \left[ -\frac{D_R j^2 \pi^2 t}{l^2} \right] \cdot \cos j\pi \frac{x}{l}. \quad (2)$$

On substituting  $D_R = 1.8 \times 10^{-5} \text{ cm}^2\text{sec}^{-1}$ , and values for  $l$  (in cm) in the range indicated above, it is found that for small values of the pre-electrolysis time the  $\Sigma$ -term is already negligibly small. For the most unfavourable case, *i.e.*, when  $l = 10^{-2} \text{ cm}$ , for  $t = 2 \text{ sec}$  the following approximation can already be used:

$$C_R(x, t) = \frac{Qt}{l} + \frac{Ql}{6D_R} \left\{ 3\left(\frac{x}{l}\right)^2 - 1 \right\}; \quad (3)$$

this approximation will become more valid as  $t$  increases and  $l$  decreases.

During the pre-electrolysis the concentration function  $C_R(x, t)$  is thus essentially parabolic. It is to be noted that eqn. (3) satisfies eqn. (1).

## 2. THE REST PERIOD

After the pre-electrolysis the rotation of the electrode is stopped and the flux very quickly decays to practically zero. For the sake of mathematical simplicity we assume that the flux instantaneously becomes zero at the beginning of the rest period. Also, the time  $t$  is now counted from the beginning of the rest period.

If at  $t = 0$  there is a concentration function  $C_R(x, 0)$ , and if the concentration function  $C_R(x, t)$  is to be calculated, then eqn. (1) must be solved with the following initial and boundary conditions:

at  $t = 0$  there is a concentration function  $C_R(x, 0)$ ,  $0 < x < l$ ;

$$D_R \cdot \left( \frac{\partial C_R}{\partial x} \right)_{x=0} = D_R \cdot \left( \frac{\partial C_R}{\partial x} \right)_{x=l} = 0, \quad t > 0.$$

For this problem CARSLAW AND JAEGER<sup>11</sup> give the solution:

$$C_R(x, t) = \frac{1}{l} \int_0^l C_R(x, 0) dx + \frac{2}{l} \sum_{j=1}^{\infty} \exp \left[ \frac{-D_R j^2 \pi^2 t}{l^2} \right] \cdot \cos j\pi \frac{x}{l} \cdot \int_0^l C_R(x, 0) \cos j\pi \frac{x}{l} dx. \quad (4)$$

By substituting eqn. (3) into eqn. (4), *i.e.*, using

$$C_R(x, 0) = \frac{QT}{l} + \frac{Ql}{6D_R} \left\{ 3\left(\frac{x}{l}\right)^2 - 1 \right\},$$

where  $T$  denotes the duration of the pre-electrolysis, and carrying out the indicated integrations, there results:

$$\frac{C_R(x, t)}{Q} = \frac{T}{l} + \frac{2l}{\pi^2 D_R} \sum_{j=1}^{\infty} \frac{(-1)^j}{j^2} \exp \left[ \frac{-D_R j^2 \pi^2 t}{l^2} \right] \cdot \cos j\pi \frac{x}{l}. \quad (5)$$

Because the  $\Sigma$ -term in eqn. (5) is identical with that in eqn. (2), it can be neglected after  $t = 2 \text{ sec}$ . Therefore after 2 sec, and certainly after 30 sec (a common value for the rest period) the concentration of reduced metal in the mercury is practically homogeneous.

## 3. THE DISSOLUTION STEP

### (a) Formulation of the problem

We assume that there is equilibrium between the oxidized and reduced forms of

the amalgam-forming metal, and that the reaction  $M^0 \rightarrow M^{n+} + ne$  is reversible; see Fig. 1 for the definition of  $x$ - and  $y$ -coordinates.

In order to register the dissolution peak the potential of the electrode is changed linearly with time; again the time is counted anew from the beginning of the dissolution step. We have to solve eqn. (1) and

$$\frac{\partial}{\partial t} C_O(y, t) = D_O \cdot \frac{\partial}{\partial y^2} C_O(y, t) \quad (6)$$

with the following initial and boundary conditions:

$$\begin{aligned} C_R(x, 0) &= C^0, \quad 0 < x < l; \\ C_O(y, 0) &= \theta C^0, \quad y > 0, \quad \text{with } \theta = \frac{f_R}{f_O} \exp \left[ \frac{nF}{RT} (E_t - E^0) \right]; \\ D_R \cdot \left( \frac{\partial C_R}{\partial x} \right)_{x=0} &= 0; \\ D_R \cdot \left( \frac{\partial C_R}{\partial x} \right)_{x=l} &= D_O \cdot \left( \frac{\partial C_O}{\partial y} \right)_{y=0} = -q(t) = -\frac{i}{nFA}; \\ C_O(0, t) &= \theta \exp [\sigma t] \times C_R(l, t), \quad \text{with } \sigma = \left( \frac{nF}{RT} \right) vt; \\ \lim_{y \rightarrow \infty} C_O(y, t) &= \theta C^0. \end{aligned} \quad (7)$$

$C^0$  is the initial concentration of the reduced metal in the mercury.

We emphasize that it is assumed here that there is equilibrium with an uniform concentration of  $M^{n+}$  throughout the solution, although this is almost never true with an anodic stripping procedure. However, this assumption seems to have little influence on the accuracy of the final results, as indicated by the good agreement between theory and experiment for the case of semi-infinite spherical diffusion<sup>3,4</sup>.

### (b) Introduction of a simplifying assumption

An exact treatment of the problem formulated above proved to be very difficult and it was necessary to simplify the problem.

A simplification is suggested by the results of sections 1 and 2. These results indicate that for  $l \leq 10^{-2}$  cm, diffusion in this thin layer is relatively fast. Therefore it might be possible to approximate  $C_R(x, t)$  by a parabolic function also for the case when the flux is not constant, but a function  $q(t)$  of time.

Using this assumption it is easily verified that  $C_R(x, t)$  is given by

$$C_R(x, t) = C^0 - \frac{1}{l} \int_0^t q(\xi) d\xi - q(t) \cdot \frac{l}{6D_R} \left\{ 3 \left( \frac{x}{l} \right)^2 - 1 \right\}, \quad (8)$$

where the first term at the right-hand side represents the initial uniform concentration of the metal in the mercury; the second term gives the total amount of metal stripped from the mercury-film at time  $t$ ; the third term is the parabolic term due to the flux  $q(t)$ . Because the flux depends on time, eqn. (8) does not satisfy eqn. (1).

(c) *The assumption made plausible*

Equation (8) does not satisfy the equation for linear diffusion and therefore the above mentioned assumption might seem doubtful. The following reasoning, however, may serve to make it plausible.

For the sake of simplicity the anodic stripping peak is represented by a triangle. Until the flux has reached its maximum value in the top of the triangle it can be represented by

$$q(t) = kt. \quad (9)$$

Assuming an initial uniform concentration  $C^0$  of reduced metal in the mercury, the concentration of the remaining metal in the mercury (using the Laplace transformation) is found to be

$$C_R(x, t) = C^0 - kt \left[ 8 \sqrt{\frac{t}{D_R}} \left\{ \sum_{j=1}^{\infty} i^3 \operatorname{erfc} \frac{l(2j-1-x/l)}{2\sqrt{D_R t}} + \sum_{j=1}^{\infty} i^3 \operatorname{erfc} \frac{l(2j-1+x/l)}{2\sqrt{D_R t}} \right\} \right] = C^0 - kt \cdot R_{10}. \quad (10)$$

In this equation  $i^3 \operatorname{erfc}$  denotes the third repeated integral of the complementary error function<sup>12</sup>. Equation (10) is the *exact* expression for the concentration of the remaining metal in the mercury-film for the case of a linearly changing flux.

When eqn. (9) is substituted into eqn. (8) there results:

$$C_R(x, t) = C^0 - kt \left[ \frac{t}{2l} + \frac{l}{6D_R} \left\{ 3 \left( \frac{x}{l} \right)^2 - 1 \right\} \right] = C^0 - kt \cdot R_{11};$$

this equation is thus based upon the approximation of the true concentration function by means of a parabolic one.

The use of this approximation for the ascending segment of the triangular stripping

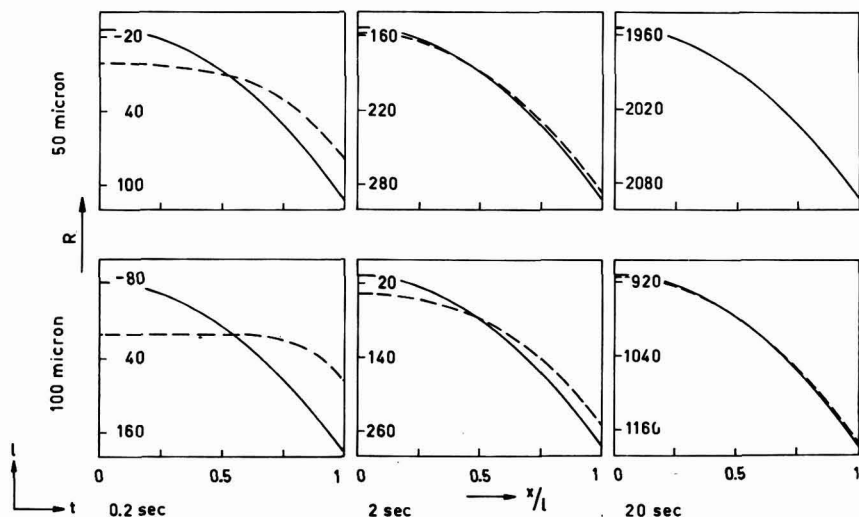


Fig. 2. Graphical representation of the rest-terms  $R_{10}$  (---) and  $R_{11}$  (—), for  $l = 5 \times 10^{-3}$  and  $10^{-2}$  cm, and  $t = 0.2, 2,$  and  $20$  sec.

peak is justified if  $R_{10}$  and  $R_{11}$  are equal or nearly equal. The  $R$ 's are calculated for  $l = 10^{-3}$ ,  $5 \times 10^{-3}$ ,  $10^{-2}$  cm, and  $t = 0.2, 2, 20$  sec ( $D_R = 1.8 \times 10^{-5}$  cm<sup>2</sup> sec<sup>-1</sup>).

For  $l = 10^{-3}$  cm the agreement between  $R_{10}$  and  $R_{11}$  is excellent for  $t \geq 0.2$  sec. The other cases ( $l = 50$  and  $100$  micron) are shown in Fig. 2.

It can be seen from this figure that eqn. (11) fails to represent the true concentration function as given by eqn. (10) for large  $l$  and small  $t$  (as is to be expected), and can even give rise to physical impossibilities (Fig. 2,  $t = 0.2$  sec). However, for small  $l$  and not too small  $t$ , eqn. (11) is a good approximation.

When it is now assumed that in the top of the stripping peak the concentration function is parabolic, one finds that on the descending segment the agreement between the true concentration function (which is somewhat analogous to eqn. (10)) and the parabolic approximation is subjected to precisely the same conditions as on the ascending segment.

We now extend these results and assume that eqn. (8) is valid with good approximation for functions  $q(t)$  as represented by experimentally obtained anodic stripping peaks.

(d) *The current-potential curve equation*

Putting  $x = l$  in eqn. (8) and using eqn. (7) one finds for  $C_0(0, t)$ :

$$C_0(0, t) = \theta C^0 e^{\theta t} - \frac{\theta e^{\theta t}}{l} \int_0^t q(\xi) d\xi - \frac{\theta l e^{\theta t}}{3D_R} \cdot q(t). \quad (12)$$

Using the Laplace transformation we can derive from eqn. (6) that

$$C_0(0, t) = \theta C^0 + \frac{1}{\sqrt{\pi D_0}} \int_0^t \frac{q(\xi)}{\sqrt{t-\xi}} d\xi. \quad (13)$$

Combination of eqns. (12) and (13) gives a non-linear Volterra integral equation of the second kind<sup>13</sup>, from which it follows that  $q(0) = 0$ . It is very difficult to solve this equation exactly for  $q(t)$  and therefore we have used a numerical method.

WAGNER<sup>14</sup> gives a short review of numerical methods for solving Volterra integral equations. We have used the simple but effective method of HUBER<sup>15</sup> which gives the following recursive current-potential curve equation (remembering that  $q(0) = 0$ ):

$$q_j = \frac{\theta C^0 (e^{j\theta\delta} - 1) - \frac{\delta\theta e^{j\theta\delta}}{l} \sum_{k=1}^{j-1} q_k - \frac{4}{3} \sqrt{\frac{\delta}{\pi D_0}} \cdot S_j}{\frac{4}{3} \sqrt{\frac{\delta}{\pi D_0}} + \left(\frac{\delta}{2l} + \frac{l}{3D_R}\right) \theta e^{j\theta\delta}}. \quad (14)$$

In this equation  $\delta$  is the width of the intervals into which the time axis is divided, and  $q_j$  is the flux  $q(t)$  at  $t = j\delta$ .  $S_j$  is given by

$$S_j = -q_{j-1} + \sum_{k=1}^{j-1} (q_k - q_{k-1}) \{ (j-k+1)^{3/2} - (j-k)^{3/2} \}. \quad (15)$$

(e) *The numerical calculations of the current-potential curves*

For the several constants occurring in eqn. (14), values representative for cadmium at a temperature of 25° are used (these values are also more or less applicable to

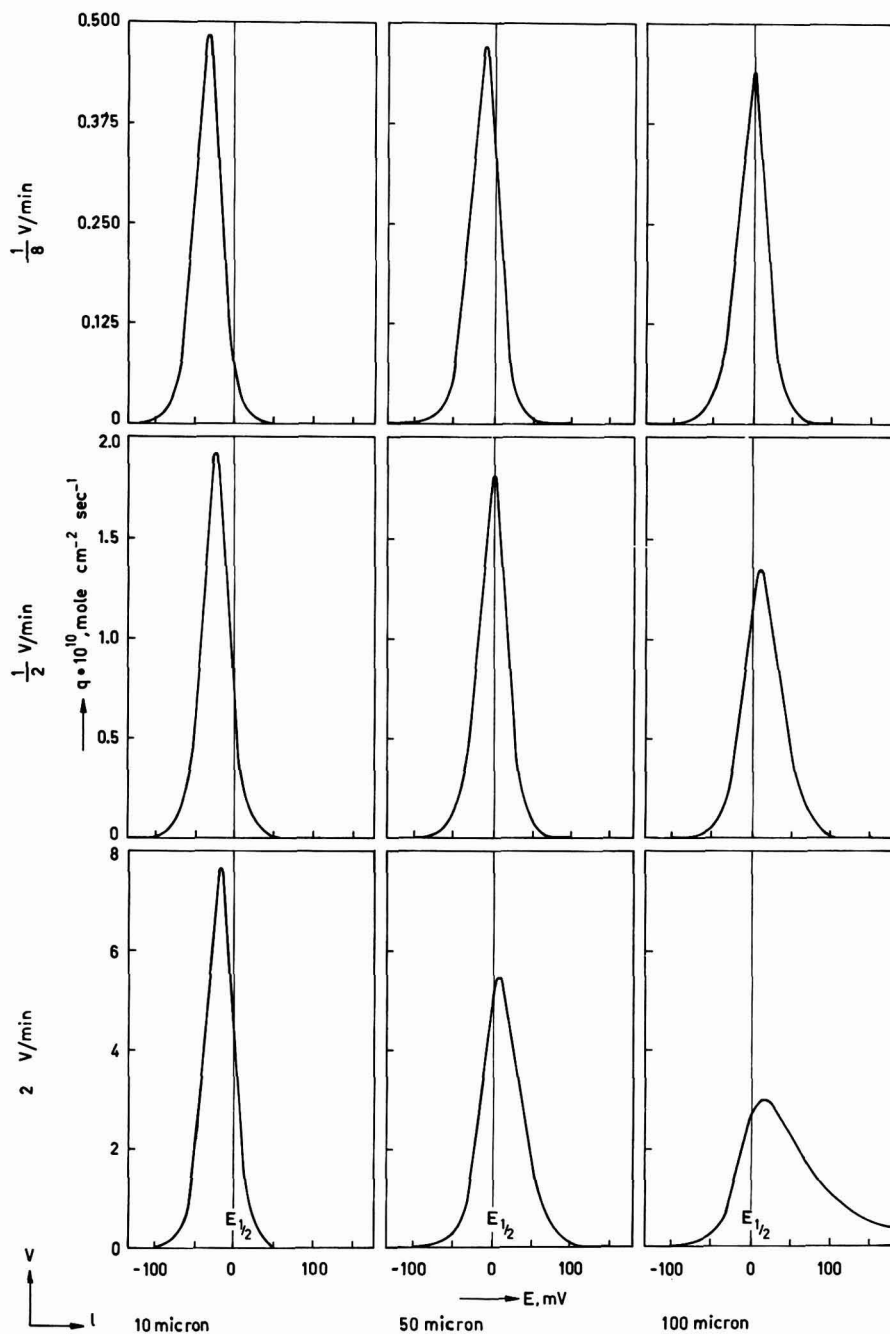
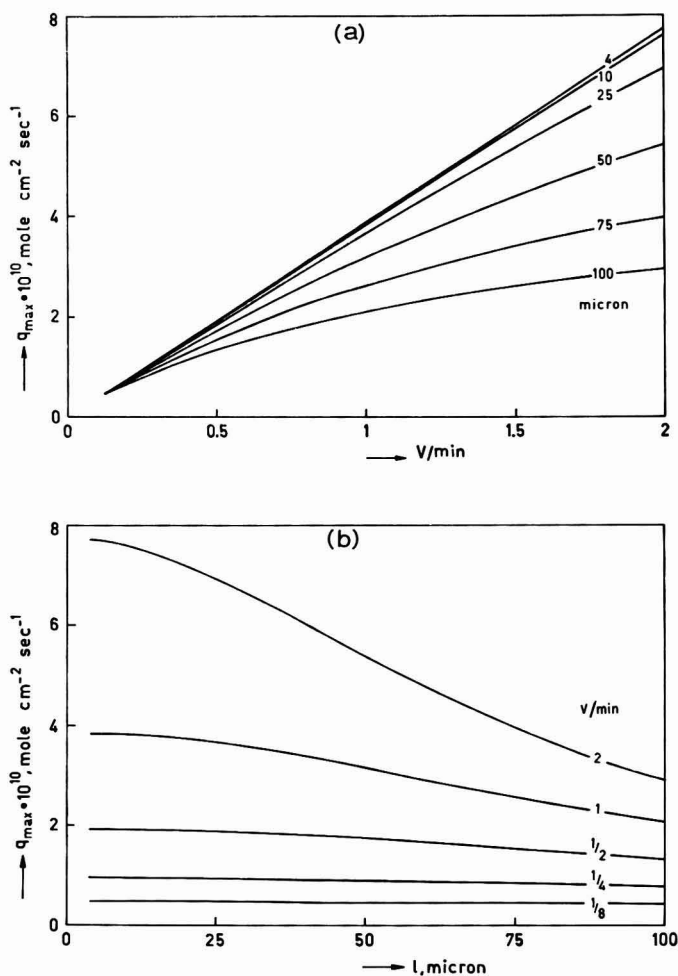


Fig. 3. General appearance of calculated current-potential curves obtained with a plane, thin mercury-film electrode, for several values of  $v$  and  $l$ .

lead). The values of these constants are given in the Appendix, together with some remarks on the calculations. The results of the calculations are summarized in Figs. 3-6.

It is to be noted that the concentration  $C^0$  varies inversely proportional to the mercury-film thickness; this means that for all values of  $l$  the amount of reduced metal in the mercury-film is the same. This is of course in agreement with actual practice, where the amount of metal reduced during the pre-electrolysis does not depend on the mercury-film thickness.

Our (unpublished) experiments have indicated that the concentrations used are representative for a  $10^{-6} M$  solution of Cd or Pb which is pre-electrolyzed during about 5-10 min. Also our calculations proved that  $q(t)$  is proportional to  $C^0$ , although this does not directly follow from eqn. (14).



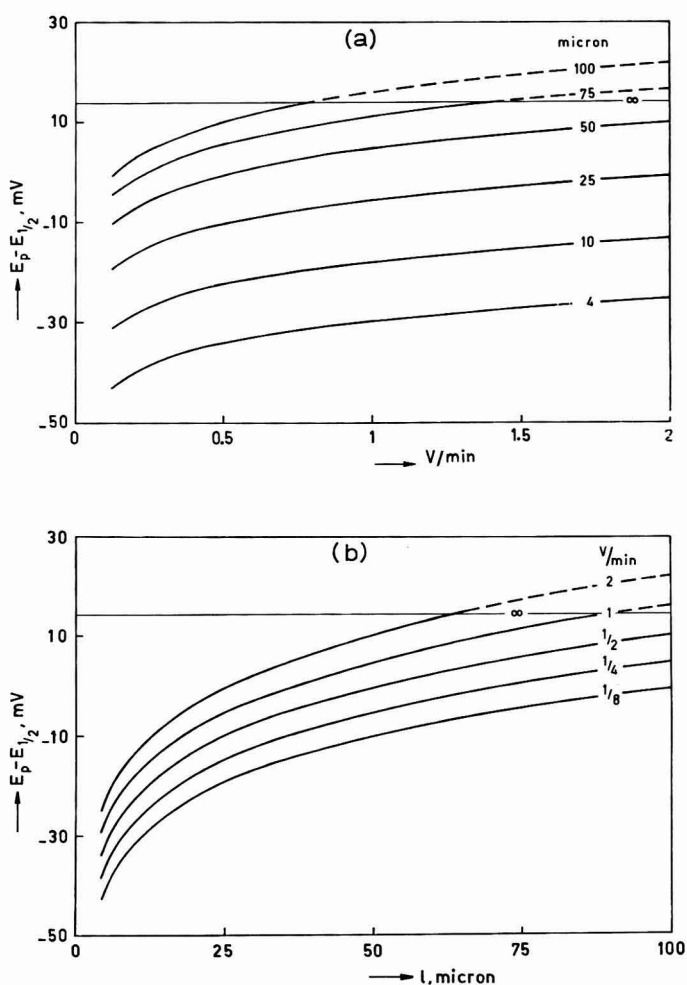
Figs. 4, (a) and (b). Dependence of the peak current on the rate of potential change  $v$  and the mercury-film thickness  $l$  respectively.

The most important features of the current-potential curves can be described by three parameters, *viz.*, the peak value of the flux  $q_{\max}$ , the peak potential  $E_p$  (referred to  $E_{1/2}$ ), and the width. As a measure for the width we have taken the width at half height  $b_{1/2}$ .

(f) Discussion of the results

Figure 3 shows the general appearance of the calculated current-potential curves for several values of  $v$ , the rate of potential change, and  $l$ , the mercury-film thickness. The three parameters mentioned above depend on both  $v$  and  $l$ . It is evident that with increasing  $v$  and  $l$  the values of  $E_p - E_{1/2}$  and  $b_{1/2}$  must approach those predicted by the theory of ŠEVČIK AND RANDLES *i.e.*, + 14.3 mV, and 101.9 mV<sup>16</sup> respectively.

In Fig. 4a,  $q_{\max}$  is plotted against  $v$ , with  $l$  as parameter. When the dependence of



Figs. 5, (a) and (b). Dependence of the peak potential (referred to  $E_{1/2}$ ) on  $v$  and  $l$  respectively.

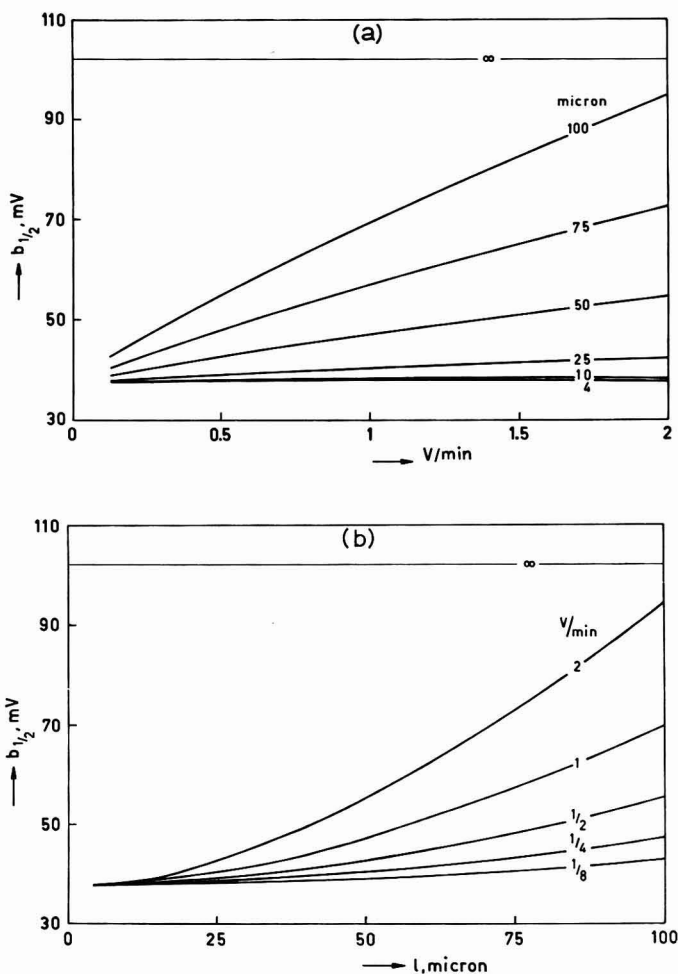


$q_{\max}$  is described with  $q_{\max} = \text{constant} \times v^\alpha$ , it is seen from the figure that for a very thin mercury-film  $q_{\max}$  is very nearly proportional to  $v$ , i.e.,  $\alpha \approx 1$ . But calculation of  $\alpha$  for  $v = 1.5$  V/min and  $l = 100$  micron gives a value 0.48, which is impossible, as the lowest possible value is 0.500<sup>1</sup>.

Figure 4b shows  $q_{\max}$  plotted against  $l$  with  $v$  as parameter. It is seen that for higher values of the rate of potential change,  $q_{\max}$  varies appreciably with the mercury-film thickness, while this variation is very slight for slow rates of potential change.

Figures 5a and 5b depict the dependence of  $E_p - E_{1/2}$  on  $v$  and  $l$ . It is to be noted that the position of the peak depends rather strongly on both parameters; also the figures show that our theory again fails for high values of both  $v$  and  $l$ .

In an analogous way the variation of  $b_{1/2}$  with  $v$  and  $l$  is represented in Fig. 6. It follows that the lowest possible width at half height is about 37 mV, and that for low values of one parameter the variation of  $b_{1/2}$  with the other is slight.



Figs. 6. (a) and (b). Dependence of the width at half height on  $v$  and  $l$  respectively.

From these results it follows that our theory fails when both  $v$  and  $l$  are large at the same time. This is of course to be expected, as the parabolic approximation of eqn. (8) is valid only for small  $l$  and large  $t$  (corresponding to slow rates of potential change).

However, our preliminary (unpublished) experiments indicate that the theoretical predictions are qualitatively quite correct, and that the quantitative agreement is rather close. We hope to publish some of these experiments later.

#### CONCLUSIONS

From the calculations reported above, it follows that there are important differences between the dissolution peaks in anodic stripping voltammetry obtained with a thin mercury-film electrode and the peaks obtained under the conditions of the theory of ŠEVČIK AND RANDES:

1. In the latter case the peak potential is independent of the rate of potential change, whereas in the case of a thin mercury-film electrode the peak potential depends on both the rate of potential change and the film thickness.
2. The peak width (as measured by the width at half height) is much smaller; also the peak width depends on both the rate of potential change and the mercury-film thickness. Because of the very small peak width a good separation of metals with closely adjacent half-wave potentials can be achieved.
3. For very thin mercury-films and slow rates of potential change the peak current is nearly proportional to the rate of potential change.
4. After its maximum the flux quickly decreases to zero, indicating that all the metal is quickly removed from the mercury during the dissolution step.

#### ACKNOWLEDGEMENTS

The authors are indebted to Prof. Dr. J. F. KOKSMA for helpful discussion on some of the mathematics of this paper; and to Mr. R. P. VAN DE RIET, who carried out most of the numerical calculations on the electronic computer XI of the Mathematical Centre, Amsterdam, the Netherlands.

#### APPENDIX

The values of the constants occurring in eqn. (14) refer to an electrode reaction  $M^0 \rightarrow M^{2+} + 2e$  at 25°.  $D_0 = 0.72 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ ,  $D_R = 1.8 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ ,  $\theta = e^{-10}$ , which corresponds to a pre-electrolysis potential 134 mV more negative than the half-wave potential of the metal. The values used for  $v = \sigma \times (RT/nF)$  are 2, 1, 1/2, 1/4, and 1/8 V/min. For  $l$  the values 4, 6, 8, 10, 20, 25, 40, 50, 60, 75, 80, and 100 microns are used,  $C^0 = 10^{-9}/l \text{ moles cm}^{-3}$ ,  $\delta = 1/(8 \times v \text{ in V/min}) \text{ sec}$ , which corresponds to an approximation of  $q(t)$  accurate to about 0.5–1%.

The numerical calculations have been programmed in ALGOL-60, and have been carried out on a digital electronic computer. Copies of the ALGOL-program are available from the authors.

#### SUMMARY

An approximate theory for anodic stripping voltammetry with a plane, thin ( $\leq 100$  micron) mercury-film electrode is presented. This approximate theory is valid only for slow rates of linear potential scan during the stripping of the reduced metal from the mercury, and for thin mercury films.

There are important differences between anodic stripping peaks obtained with a thin mercury-film electrode and the peaks obtained under the conditions of the Ševčík–Randles theory. In the latter case the peak potential and the peak width are independent of the rate of potential change  $v$ , and of the mercury-film thickness  $l$  (which is supposed to be infinite), but the peaks obtained with a mercury-film electrode show a variation of both the peak potential and the peak width with varying  $v$  and  $l$ . The peak width can be very small (ca. 40 mV), permitting a sharp separation of metals with closely adjacent half-wave potentials. For very thin mercury-films ( $\leq 25$  micron) the peak current is nearly proportional to the rate of potential change.

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## ON THE INCREASE OF SENSITIVITY IN OSCILLOPOLAROGRAPHY\*

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It has already been frequently observed that in alternating current oscillographic polarography<sup>1</sup> in some supporting electrolytes several ions or compounds show measurable incisions at concentrations up to 100 times smaller than usually noted on curves of  $dE/dt = f(E)$ . This effect is particularly marked when the electrode is polarized by single alternating current cycles. For example, under such conditions the incision corresponding to lead deposition is already apparent at a concentration of  $1 \cdot 10^{-5} M$   $Pb^{2+}$ , when  $1 M$   $KCl$  or  $Na_2SO_4$  is used as supporting electrolyte<sup>2</sup>. Similar incisions have been observed in the concentration range  $10^{-4}$ – $10^{-7} M$  in all cases in which the substance under examination is slightly soluble in the supporting electrolyte used (*e.g.*, atropine or papaverine in  $1 M$   $KOH$ ) and are recognized as due to adsorption. These incisions are deeper the later (after the drop is detached) the electrode is polarized. This is evidently connected with the specific adsorption of the substance on the electrode surface during the period of drop-life before the beginning of polarization<sup>3</sup>.

In complex supporting electrolytes containing mixtures of ammonium thiocyanate and urotropine in the presence of some bivalent ions such as  $Cd^{2+}$ ,  $Cu^{2+}$  or  $Ni^{2+}$  incisions are observed<sup>4,5</sup> even at a concentration of  $10^{-6} M$  and at continuous polarization. The incision corresponds to the reduction of a complex or addition particle adsorbed at the electrode surface.

These phenomena are studied here with the aim of increasing the sensitivity of the method and of simplifying the techniques of oscillographic microanalyses which make use of anodic stripping. The behaviour of some ions in complex-forming media has also been studied in order to increase the sensitivity of single-sweep oscillographic polarography.

## EXPERIMENTAL

*Apparatus*

The oscillographic polarograph 'Polaroscope P 576' (Kovo, Prague) was used with a display on the screen of  $dE/dt = f(E)$  curves;  $i = f(E)$  curves with single-sweep polarization were recorded with the OP 1 instrument (Academy of Sciences, Moscow). The dropping mercury electrode was used for oscillographic polarography and the hanging mercury drop electrode<sup>6</sup> for anodic stripping.

\* Preliminary communication.

## RESULTS

A marked increase of sensitivity in the determination of some metal ions has been observed in solutions of thiourea, ammonium thiocyanate and urotropine. Thus at a concentration of the order of  $5 \cdot 10^{-6} M$ ,  $Cu^{2+}$ ,  $Cd^{2+}$  or  $Pb^{2+}$  cathodic incisions were obtained in a mixture of  $0.1 M H_2SO_4$ ,  $0.1 M NH_4CNS$ , and  $0.01 M$  thiourea. Other ions of common metals show, under such conditions; incisions only when the concentration of the metal ion is of the order of  $1 \cdot 10^{-4} M$ . When polarization is carried out with a very small current (so that deposition of the cation of the supporting electrolyte does not occur), incisions of  $Cu^{2+}$  and  $Pb^{2+}$  can be observed even in  $5 \cdot 10^{-7} M$  solutions. An incision can be observed in  $10^{-5} M$  solutions of thallium when the supporting electrolyte consists of  $1.25 M KI$  and  $0.25 M H_2SO_4$ . This is due to the formation of an insoluble product at the surface of the electrode.

The above-mentioned supporting electrolytes also permit an increase in the sensitivity of stripping methods. For this purpose, solutions containing  $10^{-6}$ – $10^{-8} M$   $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$  or  $Tl^{+}$  were first electrolyzed for 1–2 min using d.c. and the hanging mercury drop electrode (Figs. 1 and 2). When such an electrolysis was carried out in

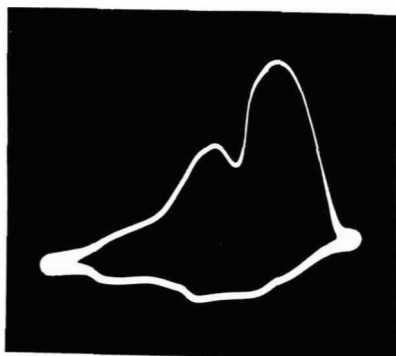


Fig. 1. The curve of  $dE/dt = f(E)$  in the micro-analytical determination of cadmium.  $1 \cdot 10^{-6} M$   $Cd^{2+}$  in  $0.02 M H_2SO_4$  was electrolyzed for 2 min; the amalgam was analyzed in a mixture of  $0.1 M H_2SO_4$ ,  $0.1 M NH_4CNS$  and  $0.01 M$  thiourea.

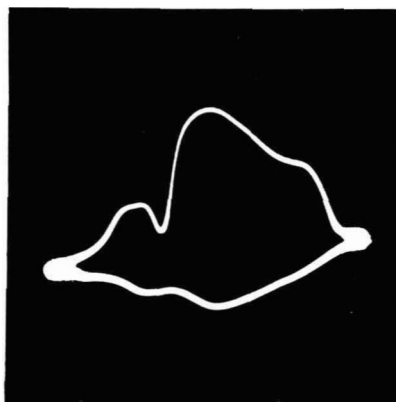


Fig. 2. The curve of  $dE/dl = f(E)$  in the micro-analytical determination of copper.  $1 \cdot 10^{-6} M$   $Cu^{2+}$  in  $0.02 M H_2SO_4$  was electrolyzed for 1 min; the amalgam was analyzed in a mixture of  $0.1 M NH_4NO_3$ ,  $0.1 M NH_4CNS$  and  $0.2 M$  urotropine.

the usual supporting electrolytes? and the electrode polarized subsequently by a.c., the amalgam formed was dissolved and the incision on the  $dE/dt = f(E)$  curve rapidly disappeared. For quantitative analysis it was necessary to photograph the curve immediately after switching over from the electrolysis to the anodic stripping. When an adsorbed complex or deposit is formed at the electrode surface in one of the supporting electrolytes mentioned, the solution of the amalgam is hindered and the depth of the stripping incision remains practically constant for a period of time (10 min) which allows measurement of the incision on the screen. For re-conditioning of the

\* Anodic incisions occur only at higher concentrations.

electrode it is sufficient to replace the electrolyzed solution by  $0.02\text{ M H}_2\text{SO}_4$  in which the amalgam is dissolved by a.c. polarization as shown by the disappearance of the incision. This drop electrode can then be used for subsequent determinations. Selective determination can be carried out in presence of other ions that form amalgams which are rapidly dissolved.

An increase in the sensitivity can also be achieved in some of these solutions when using single-sweep polarization of the dropping electrode. For example, a  $6 \cdot 10^{-6}\text{ M Cd}^{2+}$  solution containing  $0.1\text{ M NH}_4\text{NO}_3$ ,  $0.3\text{ M}$  urotropine and  $0.2\text{ M NH}_4\text{CNS}$  shows a peak on the current-voltage curve which is three times higher than that given by a  $6 \cdot 10^{-5}\text{ M Tl}^+$  solution containing the same mixture (Fig. 3a). With increasing rate of

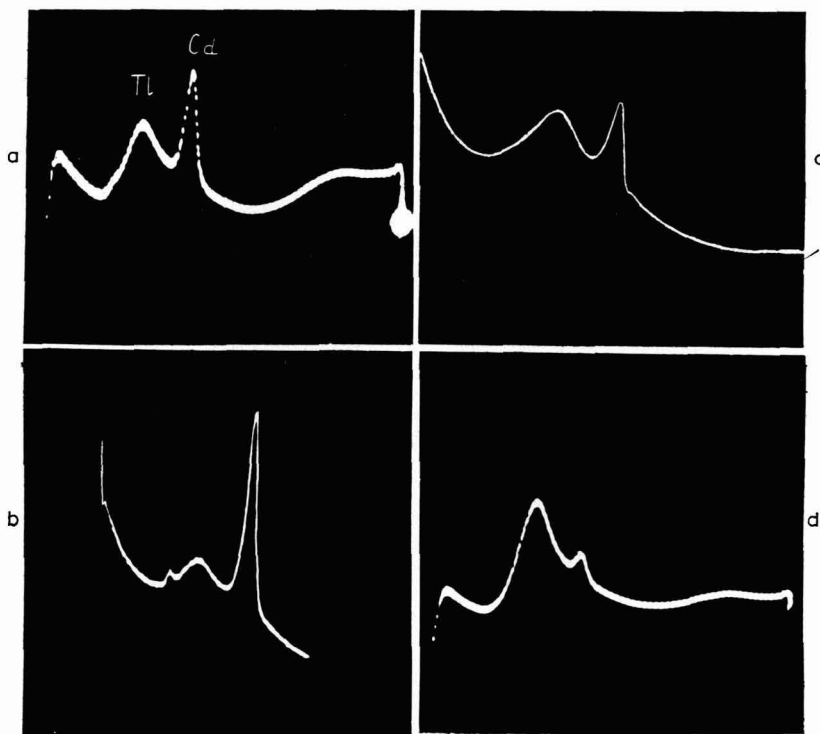


Fig. 3. The curves of  $i = f(E)$  of thallium and cadmium in  $0.1\text{ M NH}_4\text{NO}_3$ ,  $0.2\text{ M NH}_4\text{CNS}$  and  $0.3\text{ M}$  urotropine at different rates of voltage scanning: (a),  $6 \cdot 10^{-6}\text{ M Cd}^{2+} + 6 \cdot 10^{-5}\text{ M Tl}^+$  at  $0.5\text{ V sec}^{-1}$ ; (b), as (a) but  $12\text{ V sec}^{-1}$ ; (c),  $3 \cdot 10^{-6}\text{ M Cd}^{2+} + 3 \cdot 10^{-4}\text{ M Tl}^+$  at  $50\text{ V sec}^{-1}$ ; (d), as (c) but  $1\text{ V sec}^{-1}$ .

voltage scanning ( $dE/dt$ ) the electrolytic thallium peak decreases, whereas the cadmium peak increases (*cf.* Fig. 3b,c) and *vice versa* (*cf.* Fig. 3c,d). Such behaviour demonstrates the participation of adsorption in the electrode process and can be exploited for the determination of cadmium in a fifty-fold excess of thallium (Fig. 3c). A similar technique can also be used for the determination of traces of copper and can even be combined with the anodic stripping.

## SUMMARY

In supporting electrolytes containing a mixture of sulfuric acid, ammonium thiocyanate and thiourea or urotropine the sensitivity of the oscillopolarographic determination of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  is increased 10–50-fold. The same is found for the determination of  $\text{Tl}^+$  in acidified solutions of potassium iodide. The adsorption phenomena involved may also be utilised in stripping oscillopolarographic microanalysis.

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## ZUR POLAROGRAPHIE DES TECHNETIUMS

I. GLEICHSTROM- UND WECHSELSTROMPOLAROGRAPHISCHE  
UNTERSUCHUNGEN AN PERTECHNETAT-LÖSUNGEN

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## EINLEITUNG

Die bisherigen Publikationen<sup>1,2,3,4,5</sup> zur Gleichstrom-Polarographie des  $^{99}\text{TcO}_4^-$ -Ions enthalten hinsichtlich der beobachteten Stufenzahl und der zugehörigen Reduktionen teilweise widersprechende Angaben. Von verschiedenen Autoren werden für neutrale Lösungen eine bis drei Stufen, für alkalische zwei bis vier Stufen registriert. Insbesondere sind die Aussagen über die Ladungsänderungen in alkalischen Lösungen unterschiedlich. Die Reduktionsstufen wurden allein auf Grund der Auswertung von Gleichstrom-Polarogrammen sämtlich als irreversibel beschrieben. Eine Überprüfung der Verhältnisse erschien uns deshalb notwendig. Da in Säuren nach orientierenden Messungen nur schlecht ausgebildete, für Absolutbestimmungen ungeeignete Stufen auftreten, beschränkten wir uns auf systematische Untersuchungen neutraler und alkalischer Pertechnetat-Lösungen. Zur Ermittlung der Reversibilität haben wir erstmals die hierfür geeignetere Wechselstrom-Polarographie herangezogen.

## ARBEITSWEISE

Das für die Untersuchungen verwendete  $\text{K}^{99}\text{TcO}_4$  wurde durch Umsetzung von  $\text{NH}_4\text{TcO}_4$  mit der äquivalenten Menge Kalilauge gewonnen, gewaschen, umkristallisiert und bis zur Gewichtskonstanz getrocknet. Das Volumen der jeweils polarographierten Lösung betrug 20 ml, die Temperatur ( $25.0 \pm 0.1^\circ$ ). Durch Einleiten nachgereinigten Stickstoffs wurde der gelöste Sauerstoff entfernt. Zur Aufnahme der Gleichstrom- und Wechselstrom-Polarogramme verwendeten wir den Polarecord der Firma Metrohm in Verbindung mit der Tropfkontrollvorrichtung für Rapidpolarographie<sup>6</sup> und dem A.C.-Modulator<sup>7</sup>. Die Potentialangaben beziehen sich auf eine Ag/AgCl-Bezugselektrode in gesättigter KCl-Lösung. Der Grenz- und Spitzenstrom wurde gegen den Reststrom der Grundlösung vermessen. Die der Rapidpolarographie eigene geringe Tropfzeit betrug bei der Aufnahme der Gleichstrom- und Wechselstrom-Polarogramme 0.25 bzw. 0.20 sec. Auf die Zugabe von Maximadämpfern konnte verzichtet werden. Beispielsweise wirkt Gelatinezusatz sogar störend, indem teilweise eine erhebliche Überhöhung der Reduktionsstufen auftritt<sup>2</sup>.



## Gleichstrompolarographische Untersuchungen

Zur Charakterisierung der Reduktionsstufen wurde das Halbstufenpotential  $E_{\frac{1}{2}}$  graphisch ermittelt und nach der einfachen Ilkovič-Gleichung

$$i_a = 607 D^{\frac{1}{2}} m^{\frac{2}{3}} \tau^{\frac{1}{3}} n c \quad (1)$$

mit  $i_a$  = Grenzstrom ( $\mu A$ ),  $D$  = Diffusionskoeffizient ( $cm^2 sec^{-1}$ ),  $m$  = Quecksilbermassenfluss ( $mg sec^{-1}$ ),  $\tau$  = Tropfzeit (sec),  $n$  = Ladungsänderung und  $c$  = Konzentration (mM) die Ladungsänderung  $n$  berechnet. Als Diffusionskoeffizienten setzten wir den von uns bestimmten Wert  $D^0(^{99}TcO_4^-) = (1.48 \pm 0.01) \cdot 10^{-5} cm^2 sec^{-1} ein^8$ .

Orientierende Aufnahmen führten zu der Feststellung, dass vergleichende Untersuchungen an  $10^{-3}$  bis  $10^{-4}$  molaren  $KTcO_4$ -Lösungen in 0.1, 0.5 und 1.0 M NaOH- und LiCl-Grundelektrolyten besonders geeignet waren, um einen systematischen Überblick zum polarographischen Verhalten des  $TcO_4^-$ -Ions in alkalischer und neutraler Lösung zu gewinnen.

In Tabelle 1 ist ein Teil der Ergebnisse zusammengefasst; Abb. 1 veranschaulicht den charakteristischen Verlauf der Gleichstrom-Polarogramme.

TABELLE 1  
HALBSTUFENPOTENTIALE UND ELEKTRONENÜBERGÄNGE FÜR PERTECHNETAT-LÖSUNGEN IN  
ALKALISCHEN UND NEUTRALEN GRUNDELEKTROLYTEN

$C_{TcO_4^-}$ (mM)	1. Stufe		2. Stufe		3. Stufe		4. Stufe		1. Stufe	
	$E_{\frac{1}{2}}$ (V)	$n$	$E_{\frac{1}{2}}$ (V)	$n$	$E_{\frac{1}{2}}$ (V)	$n$	$E_{\frac{1}{2}}$ (V)	$n$	$E_{\frac{1}{2}}$ (V)	$n$
			0.1 M NaOH						0.1 M LiCl	
0.384	-0.81	1.9	-1.11	2.8	-1.55	21	-1.63	28	-0.82	2.2
0.576	-0.82	2.1	-1.15	2.9	-1.54	9.6	-1.66	10.0	-0.82	2.2
0.959	-0.81	1.9	-1.10	2.4	-1.53	6.2	-1.71	8.3	-0.81	1.9
			0.5 M NaOH						0.5 M LiCl	
0.324	-0.78	2.3	-1.06	3.0	-1.58	9.7	-1.70	17	-0.79	2.1
0.567	-0.78	2.4	-1.06	3.2	-1.56	7.8	-1.70	11	-0.78	2.2
0.810	-0.77	2.4	-1.08	3.1	-1.54	6.1	—	—	-0.78	2.1
			1.0 M NaOH						1.0 M LiCl	
0.413	-0.76	2.1	-1.04	2.8	-1.57	6.5	-1.76	10	-0.78	1.9
0.619	-0.76	2.4	-1.06	3.0	-1.54	5.8	—	—	-0.78	2.0
0.825	-0.76	2.4	-1.07	3.3	-1.54	5.6	—	—	-0.77	2.0

Die 1. Stufe bei  $E_{\frac{1}{2}} \approx -0.8 V$  ist von der Art und Konzentration des Grundelektrolyten weitgehend unabhängig. Die geringfügige Verschiebung des Halbstufenpotentials nach positiveren Werten bei steigender Grundelektrolyt-Konzentration wird auf die Herabsetzung des ohmschen Widerstandes der Lösungen zurückgeführt.

Die 2. Stufe bei  $E_{\frac{1}{2}} \approx -1.1 V$  wird dagegen sehr unterschiedlich durch den Grundelektrolyten beeinflusst. Sie setzt sich nur in alkalischer Grundlösung deutlich von der ersten Stufe ab; in neutraler Lösung äussert sie sich in einem breiten Stromanstieg.

Die 3. und 4. Stufe, die bei  $\approx -1.2$  und  $\approx -1.4 V$  beginnen, sind katalytischer

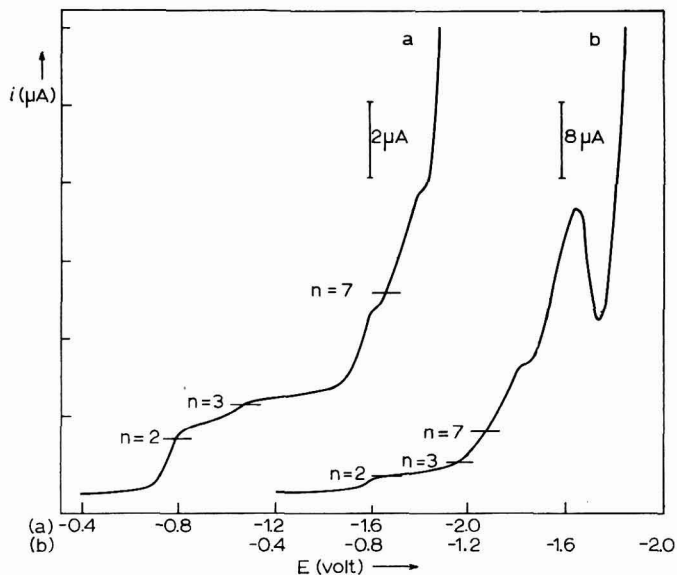


Abb. 1 Charakteristische Gleichstrom-Polarogramme des  $\text{TcO}_4^-$  in alkalischem und neutralem Grundelektrolyten. (a)  $0.206 \text{ mM KTcO}_4$  in  $1.0 \text{ M NaOH}$ ; (b) in  $1.0 \text{ M LiCl}$ . Die Eintragungen der Stromstärken für ganzzahlige  $n$ -Werte nach Gl. (1) verdeutlichen die unterschiedliche Ausbildung der Stufen in den beiden Medien.

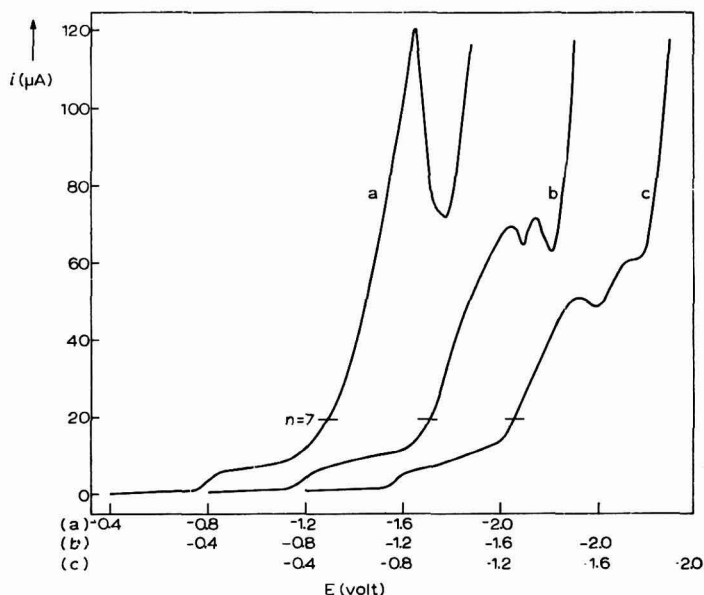


Abb. 2. Gleichstrom-Polarogramme von  $0.822 \text{ mM KTcO}_4$ : (a)  $0.1 \text{ M}$ ; (b)  $1.0 \text{ M}$ ; (c)  $2.0 \text{ M KCl}$ . Einfluss der Grundelektrolyt-Konzentrationen auf die Ausbildung der 3. und 4. Stufe des  $\text{TcO}_4^-$ . Die Eintragungen der Stromstärken für  $n = 7$  nach Gl. (1) verdeutlichen die Überhöhungen der 3. und 4. Stufe.

Natur. Bei konstanter Laugen-Konzentration nehmen die durch  $H^+$ -Entladung bedingten Überhöhungen der 3. und 4. Stufe mit wachsender  $TcO_4^-$ -Konzentration ab, während in  $LiCl$ -Lösungen eigentümlicherweise der umgekehrte Effekt festgestellt wurde. Steigende Grundelektrolyt-Konzentrationen wirken bei nahezu konstanter  $TcO_4^-$ -Konzentration ebenfalls verkleinernd auf die Überhöhungen der 3. und 4. Stufe; ähnliche Erscheinungen konnten auch in 0.1, 1.0 und 2.0  $M$   $KCl$  beobachtet werden (Abb. 2).

Für die 1. Reduktionsstufe mit  $E_{\frac{1}{2}} \approx -0.8$  V ergeben sich aus Tabelle 1  $n$ -Werte von  $\approx 2$ . Die Abweichungen von der Ganzzahligkeit sind besonders in alkalischer Lösung zum Teil erheblich. Wendet man zur Berechnung von  $n$  die verbesserte Ilkovič-Gleichung nach KOUTECKÝ<sup>9,10</sup>

$$i_a = 607 D^{\frac{1}{2}} m^{\frac{2}{3}} \tau^{\frac{1}{3}} n c (1 + 34 D^{\frac{1}{2}} m^{-\frac{1}{3}} \tau^{\frac{1}{3}}) \quad (2)$$

an, so nähern sich die Werte eher der Zahl 2 (vergl. Tabelle 2!).

Für die Stufe bei  $E_{\frac{1}{2}} \approx -1.1$  V folgen in 0.1, 0.5 und 1.0  $M$   $NaOH$  nach Gl. (1) Mittelwerte für den gesamten Elektronenübergang von  $\bar{n} = 2.8, 3.1$  bzw. 3.0.

TABELLE 2

MITTELWERTE  $\bar{n}$  VON JEWEILS SIEBEN EINZELWERTEN FÜR DIE 1. REDUKTIONSSTUFE DES  $TcO_4^-$  NACH GL. (1) UND (2)

Grund- elek- trolyt <i>NaOH</i> ( <i>M</i> )	$\bar{n}$		Grund- elek- trolyt <i>LiCl</i> ( <i>M</i> )	$\bar{n}$	
	nach Gl.(1)	nach Gl.(2)		nach Gl.(1)	nach Gl.(2)
0.1	2.1	1.9	0.1	2.2	2.0
0.5	2.4	2.2	0.5	2.1	1.9
1.0	2.3	2.1	1.0	2.0	1.8

Die für alkalische Lösungen in Tabelle 1 angeführten  $n$ -Werte der 3. und 4. Stufe zeigen, dass hier keine Proportionalität zwischen  $i_a$  und Depolarisatorkonzentration besteht; in neutralen Lösungen erhält man nur bei niedrigen  $TcO_4^-$ -Konzentrationen Stufenandeutungen, während für  $c > 0.3 \cdot 10^{-3}$   $M$  der Kurvenverlauf unregelmässig war. Über die bei diesen Reduktionen erzielten Wertigkeitszustände lassen sich keine verbindlichen Aussagen machen.

#### Wechselstrompolarographische Untersuchungen

Bisher wurde für die Reduktionsstufen des  $TcO_4^-$ -Ions aus der Neigung der Geraden  $\log i/(\bar{i}_a - i) = f(E)$  nur Irreversibilität festgestellt.

Wie jedoch Bauer und Elving<sup>11</sup> am Beispiel der polarographischen Reduktion des  $Bi(III)$  zeigen konnten, ist dieses Kriterium unzureichend. Bei der Anwendung von Gleichstrom kann auch bei irreversibler Reduktion die theoretische Höhe des diffusionsbedingten Grenzstromes erreicht werden. Überlagert man aber der sich kontinuierlich ändernden Gleichspannung eine Wechsellspannung konstanter Amplitude, so ist der experimentell ermittelte Spitzenstrom  $\bar{i}_{s,exp}$  dem Reversibilitätsgrad

der Elektrodenreaktion proportional<sup>12,13</sup>. Nach MATSUDA<sup>14</sup> gilt für den Spitzenstrom bei vollständiger Reversibilität  $\bar{i}_{s,rev}$  ( $\mu A$ ), phasenabhängiger Gleichrichtung und Messung der Wirkkomponente des Wechselstromes

$$\bar{i}_{s,rev} = 0.183 \bar{i}_a (\tau\omega)^{\frac{1}{2}} \frac{nF\Delta E}{2RT} \quad (3)$$

mit  $\bar{i}_a$  = Grenzstrom nach Gl. (2),  $\tau$  = Tropfzeit (sec),  $\omega$  = Frequenz (Hz),  $n$  = Ladungsänderung,  $F$  = Faradaysche Zahl ( $\mu C$ ),  $\Delta E$  = Amplitude (mV),  $R$  = Gaskonstante (mV $\cdot\mu C$ ) und  $T$  = Temperatur ( $^{\circ}K$ ).

Als Mass für die Reversibilität berechneten wir die Wechselstromausbeute  $\rho$  (%) nach

$$\rho = \frac{\bar{i}_{s,exp}}{\bar{i}_{s,rev}} \cdot 100 \quad (4)$$

Die Gesamtimpedanz des Stromkreises konnte vernachlässigt werden. Die Tabellen 3 und 4 und die Abb. 3 und 4 zeigen die Ergebnisse der wechselstrompolarographischen Untersuchungen.

TABELLE 3

SPITZENPOTENTIALE  $E_s$  FÜR 0.210 mM  $TcO_4^-$ -LÖSUNGEN BEI VERSCHIEDENEN GRUNDELEKTROLYT-KONZENTRATIONEN

Welle Nr.	Grundelektrolyt NaOH (M)	Spitzen- potential $E_s$ (V)	Grundelektrolyt LiCl (M)	Spitzen- potential $E_s$ (V)
1	0.1	-0.83	0.1	-0.84
	0.5	-0.79	0.5	-0.81
	1.0	-c.76	1.0	-0.78
2	0.1	-1.22	0.1	—
	0.5	-1.11	0.5	-1.06
	1.0	-1.03	1.0	-1.02
3	0.1	-1.58	0.1	—
	0.5	-1.57	0.5	-1.37
	1.0	-1.56	1.0	-1.29
4	0.1	-1.74	0.1	—
	0.5	-1.81	0.5	-1.75
	1.0	—	1.0	-1.65

Sowohl in alkalischer als auch in neutraler Grundlösung lassen sich vier Wellen beobachten. Die Spitzenpotentiale (Tabelle 3) liegen verglichen mit den Halbstufenpotentialen (Tabelle 1) meistens bei etwas grösseren negativen Werten. Die erste Welle ( $n \approx 2$ ) tritt bei allen Grundelektrolyt-Konzentrationen auf; die für sie nach Gl. (4) errechneten Wechselstromausbeuten (Tabelle 4) zwischen 70 und 90% zeigen im Unterschied zu früheren aus Gleichstrom-Polarogrammen gewonnenen Werten weitgehende Reversibilität.

Die 2. Welle mit der Reduktion  $Tc(V) \rightarrow Tc(IV)$  ist auch bei den Wechselstrom-

TABELLE 4

WECHSELSTROMAUSBEUTEN  $\varrho$  DER I. REDUKTIONSWELLE DES  $TcO_4^-$  MIT  $n \approx 2$  IN NaOH- UND LiCl GRUNDLÖSUNGEN. WEITERE MESSBEDINGUNGEN SIEHE ABB. 3 UND 4

$C_{TcO_4^-}$ (mM)	Grund- elektrolyt NaOH (M)	Wechselstrom- ausbeute $\varrho$ (%)	Grund- elektrolyt LiCl (M)	Wechselstrom- ausbeute $\varrho$ (%)
0.105	0.1	89	0.1	75
0.210	0.1	89	0.1	71
0.105	0.5	85	0.5	88
0.210	0.5	80	0.5	80
0.105	1.0	90	1.0	87
0.210	1.0	86	1.0	88

Polarogramme deutlicher in NaOH- als in LiCl Grundlösungen zu erkennen. In 0.5 und 1.0 M NaOH betragen die Wechselstromausbeuten  $\varrho$  90–100%.

Die bei der Besprechung der Gleichstrom-Polarogramme erwähnte starke Abhän-

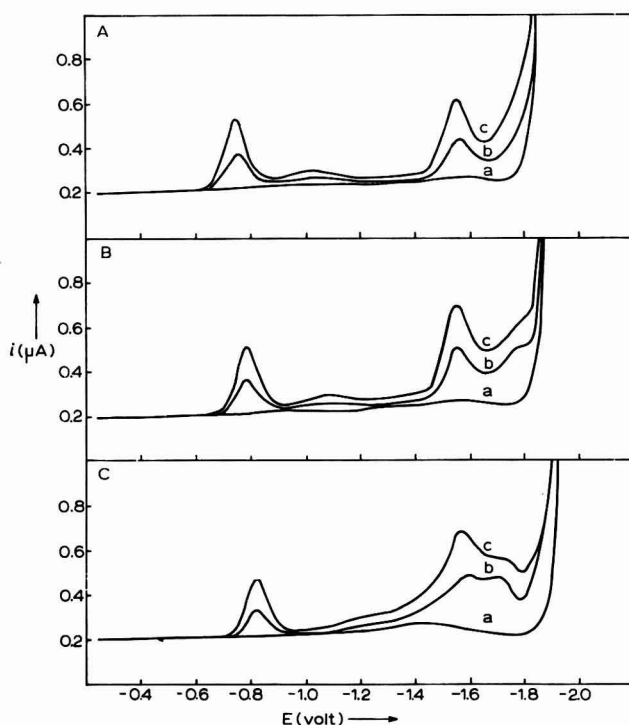


Abb. 3 Charakteristische Wechselstrom-Polarogramme des  $TcO_4^-$  in alkalischem Grundelektrolyten. Einfluss der  $TcO_4^-$ - und NaOH-Konzentrationen auf die Ausbildung der Wellen: (a) Grundelektrolyt; (b) 0.105 mM; (c) 0.210 mM  $KTcO_4$ . (A) 1 M; (B) 0.5 M; (C) 0.1 M NaOH. Frequenz 50 Hz, Wechselspannung 10 mV.

gigkeit der 3. und 4. Reduktionsstufe von Art und Konzentration des Grundelektrolyten wird auch bei der 3. und 4. Welle der Wechselstrom-Polarogramme festgestellt. Mit steigender Konzentration an NaOH und LiCl werden die Spitzenströme kleiner. Da zwischen der Depolarisator-Konzentration und  $\bar{i}_a$  hier keine Proportionalität besteht, lassen sich Wechselstromausbeuten nicht berechnen.

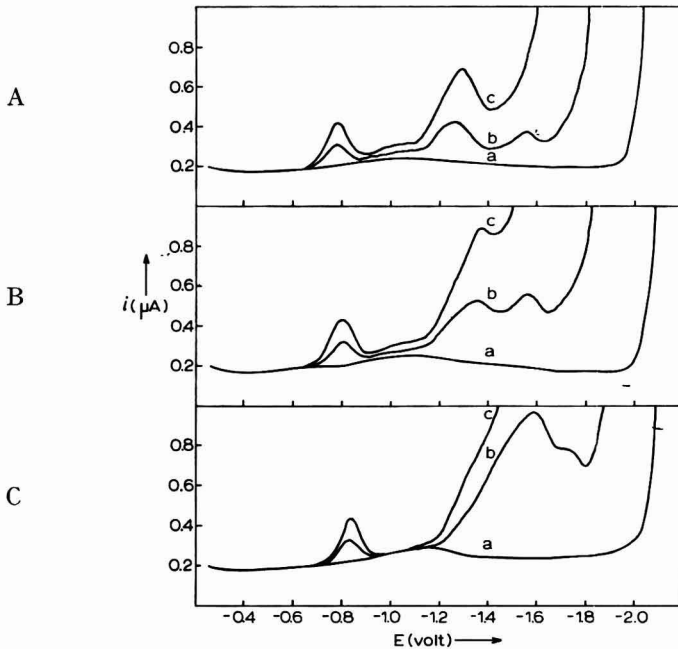


Abb. 4 Charakteristische Wechselstrom-Polarogramme des  $\text{TcO}_4^-$  in neutralem Grundelektrolyten. Einfluss der  $\text{TcO}_4^-$ - und LiCl-Konzentrationen auf die Ausbildung der Wellen: (a) Grundelektrolyt; (b) 0.105 mM; (c) 0.210 mM  $\text{KTcO}_4$ . (A) 1 M; (B) 0.5 M; (C) 0.1 M LiCl. Frequenz 50 Hz, Wechselspannung 10 mV.

Abschliessend sei noch erwähnt, dass auf Grund des hohen Reversibilitätsgrades der 1. Welle mit  $E_s \approx -0.8$  V die quantitative wechselstrompolarographische Bestimmung des Technetiums gegenüber den bereits bekannten analytischen Verfahren<sup>15,16</sup> sehr vorteilhaft sein kann. Über die Ergebnisse dieser Bestimmung des Technetiums neben verwandten Elementen soll an anderer Stelle berichtet werden.

#### DANK

Herrn Prof. W. HERR möchten wir für wertvolle Hinweise und sein förderndes Interesse verbindlich danken

#### ZUSAMMENFASSUNG

Neutrale und alkalische Lösungen von  $\text{K}^{99}\text{TcO}_4$  wurden im Konzentrationsbereich von  $10^{-3}$  bis  $10^{-4}$  M gleichstrom- und wechselstrompolarographisch untersucht. Vier Stufen bzw. Wellen konnten beobachtet werden. Den beiden ersten Stufen mit  $E_{1/2} \approx -0.8$  V und  $\approx -1.1$  V entsprechen die Elektronenübergänge  $n \approx 2$  und  $\approx 3$ , die

dritte und vierte Stufe werden durch katalytische Effekte beeinflusst. Es sei besonders darauf hingewiesen, dass nicht nur in alkalischer, sondern auch in neutraler Lösung die Reduktion zunächst zum Tc(V) erfolgt.

An der Welle mit  $E_s \approx -0.8$  V wurden als Mass für die Reversibilität Wechselstrom-Ausbeuten von 70–90% in Abhängigkeit von Art und Konzentration des Grundelektrolyten erhalten. Hieraus ergibt sich die Möglichkeit einer wechselstrompolarographischen Bestimmung des Technetiums, die auf Grund des höheren Trennvermögens gegenüber den gleichstrompolarographischen Verfahren von Vorteil ist.

## SUMMARY

Neutral and alkaline solutions of  $K^{99}TcO_4$  in the concentration range of  $10^{-3}$  to  $10^{-4}$  M have been investigated polarographically with direct and alternating current. Four steps and waves respectively have been observed. The first two steps of  $E_4 \approx -0.8$  V and  $\approx -1.1$  V correspond to electron transitions  $n \approx 2$  and  $\approx 3$ , whereas the third and fourth steps are influenced by catalytic effects. It may be specially pointed out that reduction first to Tc(V) takes place not only in alkaline but also in neutral solution.

Alternating current efficiencies of 70–90% for the wave  $E_s \approx -0.8$  V were obtained as a function of the type and concentration of the supporting electrolyte. From this follows the possibility of a. c. polarographic determination of technetium which is advantageous on account of its higher separation capacity in comparison to the direct current polarographic methods.

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# ELECTROCHEMICAL REDUCTION OF URANIUM(VI) AT MERCURY ELECTRODES IN CARBONATE SOLUTIONS

## AN EXPERIMENTAL CHRONOPOTENTIOMETRIC STUDY

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### INTRODUCTION

The reduction of uranium(VI) in aqueous solutions has been the subject of many studies since this system offers interesting features important in the elucidation of the kinetics of consecutive electrochemical and chemical reactions. The chemistry of uranium(VI) has also attracted a great deal of interest in view of its special importance in nuclear technology.

Polarographic measurements reported by KOLTHOFF AND HARRIS<sup>1</sup>, HEAL AND THOMAS<sup>2</sup> and ORLEMAN AND KERN<sup>3</sup> show that the reduction of uranium(VI) in acidic media of perchlorates, nitrates and chlorides is followed by a second-order chemical reaction, *i.e.*, disproportionation of uranium(V). It was postulated that this disproportionation, and therefore also the rate of the reduction, is dependent on the pH of the solution and on the total ionic strength.

In a more recent paper by FISCHER AND DRAČKA<sup>4</sup> galvanostatic electrolysis (chronopotentiometry) was used for the reduction of uranium(VI) in elucidating the effect of the coupled disproportionation reaction on the transition time. They found measurable effects on the transition time if the second-order constant was higher than  $50 \text{ mole}^{-1} \text{ sec}^{-1}$ . Actually the disproportionation of uranium(V) was found to be highly dependent on the ionic strength and on the pH. However no definite quantitative conclusions were made either in the sense of the equilibria involved, or on the supposed mechanism.

Much less is known about the electrochemistry of uranium(VI) in alkaline carbonate solutions. STABROVSKII<sup>5</sup> and later KOHMAN AND PEREC<sup>6</sup> investigated the polarographic behaviour of uranium(VI) in sodium and ammonium carbonate solutions. They defined the half-wave potentials for the reduction and reported two reduction waves in bicarbonate (low pH) solutions. More recently PRAVDIĆ, BRANICA AND PUČAR<sup>7</sup> studied the potentiostatic reduction of uranium(VI) at mercury pool electrodes in carbonate solutions and determined the current efficiency. BRANICA AND PRAVDIĆ<sup>8</sup> in a polarographic study of the reduction, oxidation and disproportionation of uranium ions in carbonate solutions, found that the diffusion currents are proportional to the concentrations of uranium(VI), uranium(V) and uranium(IV) over wide concentration ranges.



In the present paper the standard galvanostatic technique (chronopotentiometry) at the mercury pool electrode was used to study the reduction of uranium(VI) in sodium carbonate–bicarbonate solutions. The investigations show that *reference* conditions can be obtained by measuring the reduction of uranium(VI) at high free-carbonate concentrations where no subsequent chemical reaction was observed. This reference condition was used in the calculation of the diffusion coefficient for the uranium(VI) carbonate complex. At low concentrations of free carbonate the disproportionation reaction is moderately fast, and the influence of this reaction on the observed transition time can be studied.

## EXPERIMENTAL

The equipment for measuring potential against time at constant current was conventional in design<sup>9</sup>. The transition time in the range 4–64 sec was recorded on a strip-chart recorder with a chart speed of 12 in. per min. In this arrangement accurate calibration of the time axis was made by a coupled deatron-tube chronometer. Transition times below 3 sec and down to 50 msec were recorded photographically off the oscilloscope screen. In this case the calibrated time base of a Tektronix Type 541 oscilloscope was used in conjunction with mercury-wetted contact relays. A double cathode follower was used as the constant current source for currents between 30  $\mu$ A and 8 mA. An Elliot EBS mercury-wetted contact relay driven by the gate voltage of the oscilloscope was used for short pulses. The current was measured on a class 0.5 pointer microammeter allowing the current to flow through a dummy resistance matching the cell impedance. The scheme is shown in Fig. 1.

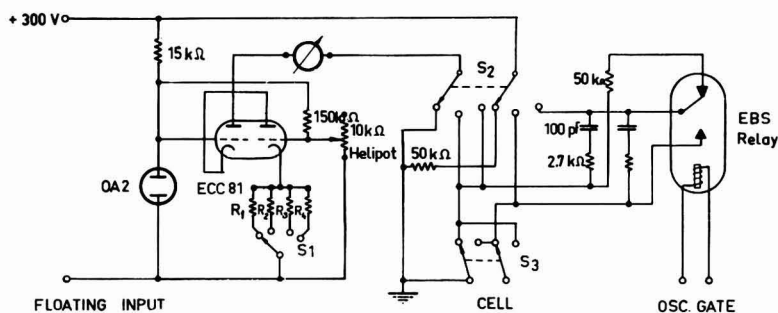


Fig. 1. The scheme of the double cathode follower used as the constant current source for currents of 30  $\mu$ A–8 mA. Current reversal is operated manually.

The all-glass cell was constructed following the pattern of STREULI AND COOKE<sup>10</sup>. The cup for the mercury-pool electrode of a carefully cleaned cell was treated with Silicone Repelcote Fluid and heated afterwards for several hours at 120°. The area of the electrode was determined by measuring the transition time for the reduction of Cd<sup>2+</sup>, as recommended by REILLEY *et al.*<sup>11</sup>. The standard error in the determination of the area of the mercury pool, taking 6 independent measurements, was about 2%.

Uranium(VI) carbonate solutions were prepared from reagent-grade ammonium diuranate and sodium carbonate and bicarbonate. Cadmium nitrate was used to

prepare  $\text{Cd}^{2+}$  solutions. Analyses on uranium and cadmium were carried out following standard gravimetric procedures<sup>12,13</sup>.

The method proposed by REINMUTH<sup>14</sup> for treating irreversible reactions was applied for evaluating the potential–time curves.

#### RESULTS AND DISCUSSION

##### 1. High concentration of free carbonate ion—a case of an electrochemical reaction without subsequent chemical kinetic complications

A typical potential–time curve for high concentrations of the free carbonate ion (1 M  $\text{Na}_2\text{CO}_3$ , pH 11.5) is shown in Fig. 2. There is only one cathodic potential step

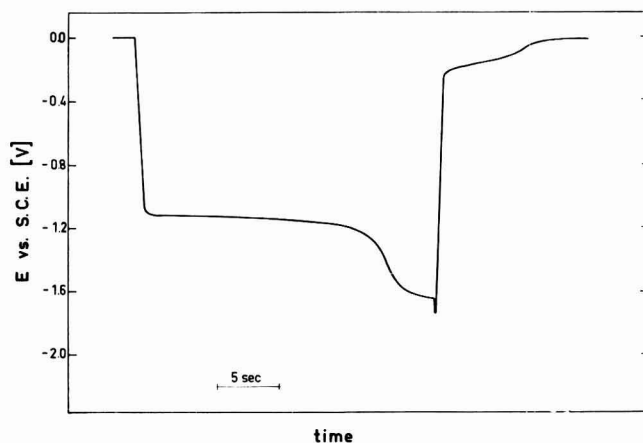


Fig. 2. The potential–time curve obtained for the electrolysis of 1 mM of uranium(VI) in 1 M  $\text{Na}_2\text{CO}_3$  (pH 11.5, temp. 25°) at the constant current density of 41.8  $\mu\text{A}/\text{cm}^2$ .

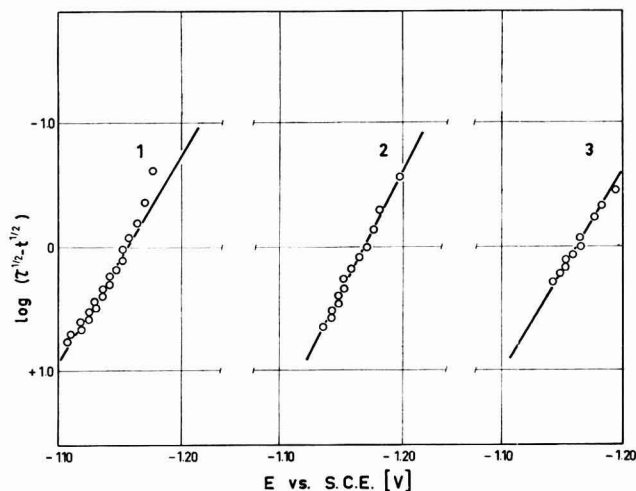


Fig. 3. The  $\log(\tau^1 - t^1)$  vs. potential relation for the reduction of 1 mM of uranium(VI) in 1 M  $\text{Na}_2\text{CO}_3$ , at pH 12.0 and temp. 25°, for three different current densities: (1), 21.7; (2), 27.1; (3) 62.6  $\mu\text{A}/\text{cm}^2$ .

indicating the reduction of uranium(VI) to uranium(V). In the re-oxidation step the oxidation of uranium(V) is observed. Inspection of the ratio of the transition times for the reduction and the re-oxidation shows that it is less than 3, this being a criterion of irreversible behaviour<sup>15</sup>. The high overpotentials encountered show that the electrochemical reaction can be classified as a completely irreversible one. In Fig. 3 the  $\log(\tau^{\frac{1}{2}} - t^{\frac{1}{2}})$  vs.  $E$  plots<sup>9</sup> are given for three different current densities. The overpotentials indicated, and the slopes of the lines do not change within the range of the current densities applied. The value of the overall transfer coefficient calculated from the slope of these and similar plots, taking 19 independent measurements, at different current densities was

$$\alpha = 0.95 \pm 0.06$$

In Fig. 4 the value of  $i\tau^{\frac{1}{2}}/C$  vs.  $i$ , the current density, is plotted for two concentrations of uranium(VI). The linear relationship and absence of deviations at low current densities indicates a purely diffusion-controlled electrochemical reaction. If any chemical reactions precede or follow the electron transfer reaction they must be in this case very fast or very slow, respectively.

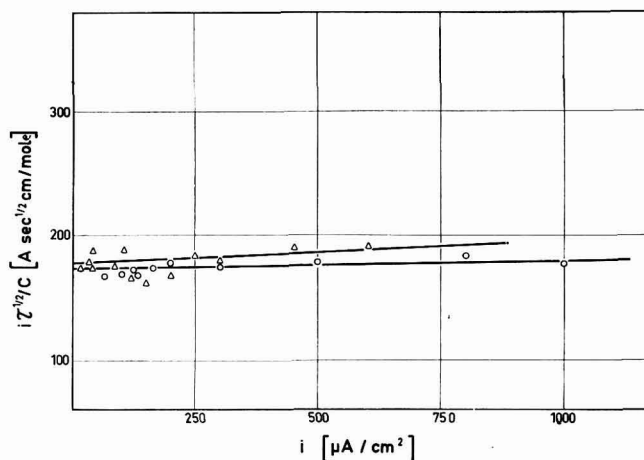


Fig. 4. The  $i\tau^{\frac{1}{2}}/C$  vs. current density plots of data for the reduction of 1 mM ( $\Delta$ ) and 3 mM ( $\circ$ ) of uranium(VI) in 1 M  $\text{Na}_2\text{CO}_3$  at pH  $11.4 \pm 0.2$  and temp.  $25^\circ$ . Data were corrected for double-layer charging taking  $15 \mu\text{C}/\text{cm}^2$ .

The value of the diffusion coefficient calculated from 18 independent measurements at 0.3, 1.0 and 3.0 mM of uranium(VI) yields

$$D_{25^\circ} = (4.35 \pm 0.43) \times 10^{-6} \text{ cm}^2/\text{sec}$$

From previous coulometric measurements<sup>16</sup> at a constant potential of  $-1.20$  V vs. S.C.E. the number of electrons involved in the overall electrochemical reaction at pH 11.5 was estimated as one.

The results of measurements of transition time shown in Fig. 4 were corrected for

the double-layer capacity. By plotting the data in the form<sup>17</sup>

$$i\tau/C = \frac{nF\pi^{1/2}D^{1/2}}{2}\tau^{1/2} + nFQ/C$$

using coordinates  $i\tau/C$  vs.  $\tau^{1/2}$ , an intercept corresponding to  $Q = 15 \mu\text{C}/\text{cm}^2$  was found. This corresponds to an integral capacity of approximately  $14 \mu\text{F}/\text{cm}^2$  which is in agreement with the data of GRAHAME<sup>18</sup> for  $\text{Na}_2\text{CO}_3$ .

2. Low concentrations of free carbonate ion—a case of electrochemical reactions followed by a second-order chemical reaction (disproportionation)

At low free-carbonate concentrations *i.e.*, in  $\text{NaHCO}_3$  solutions, pH 8.2–8.4, in the same potential range, two reduction steps were observed. This is shown in Fig. 5 where the potential–time curve is plotted for 5 mM of uranium(VI) in solutions of varying total carbonate concentration, but at constant ionic strength. On decreasing the carbonate concentration and increasing the perchlorate, the second reduction step becomes more pronounced. By inspecting the relative magnitudes of the transition times for the first and the second step it can be seen that both are one-electron transfer reactions. This follows from the ratio of the first and the second transition time  $\tau_1/\tau_2 = 1/3$ , which can be evaluated from the curves in Fig. 5.

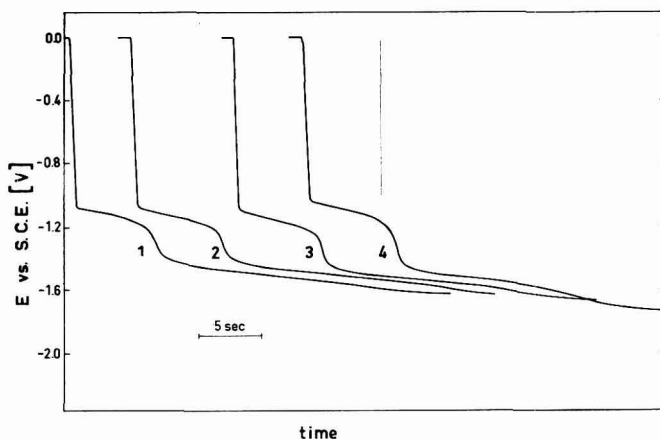
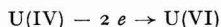


Fig. 5. The potential–time curves for the reduction of 5 mM of uranium(VI) in sodium bicarbonate–sodium perchlorate solutions (pH  $8.3 \pm 0.1$ ): (1), 0.7 M  $\text{NaHCO}_3$  + 0.3 M  $\text{NaClO}_4$ ,  $i = 418 \mu\text{A cm}^{-2}$ ; (2), 0.5 M  $\text{NaHCO}_3$  + 0.5 M  $\text{NaClO}_4$ ,  $i = 400 \mu\text{A cm}^{-2}$ ; (3), 0.3 M  $\text{NaHCO}_3$  + 0.7 M  $\text{NaClO}_4$ ,  $i = 400 \mu\text{A cm}^{-2}$ ; (4), 0.1 M  $\text{NaHCO}_3$  + 0.9 M  $\text{NaClO}_4$ ,  $i = 418 \mu\text{A cm}^{-2}$ .

Typical current reversal potential steps are shown in Fig. 6. The high overpotentials encountered indicate that the electrochemical reduction in this case is also an *irreversible* process. The importance of the potential for current reversal is manifested in the re-oxidation step as follows. When the current is reversed immediately after reaching the first transition time, two re-oxidation steps are observed. On prolonged reduction only a single re-oxidation step, presumably



is observed. Uranium(VI) is obtained by either one or both of the two possible reactions, (a) the reduction of uranium(V) by a one-electron transfer reaction, (b) and/or by the chemical reaction of disproportionation of uranium(V).

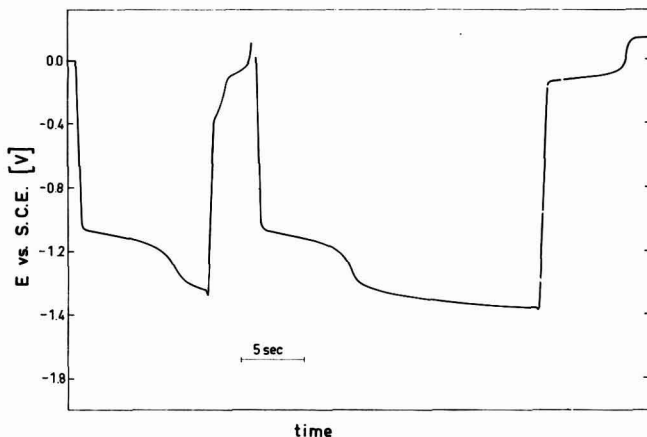


Fig. 6. The potential-time curves for the reduction and re-oxidation of 5 mM of uranium(VI) in 1 M NaHCO<sub>3</sub>, at pH 8.2, temp. 25°,  $i = 376 \mu\text{A cm}^{-2}$ . The curves differ with respect to the time of the current reversal.

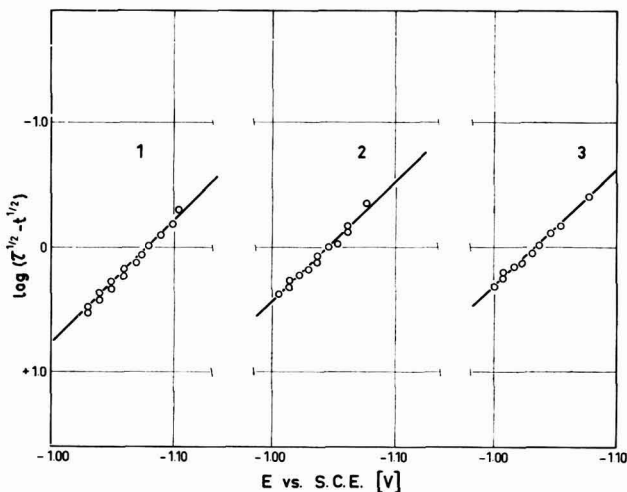


Fig. 7. The  $\log(\tau^1 - t^1)$  vs. potential relation for the reduction of 1 mM of uranium(VI) in 1 M NaHCO<sub>3</sub>, at pH 8.3 and temp. 25°, for three different current densities: (1), 43.0; (2), 55.0; (3), 66.7  $\mu\text{A cm}^{-2}$ .

From the slopes of the corresponding log plots (Fig. 7) a value for the overall transfer coefficient

$$\alpha = 0.49 \pm 0.05$$

is obtained. This value was calculated on the basis of 10 independent measurements of the reduction of 1 mM of uranium(VI) in 1 M NaHCO<sub>3</sub>, at current densities higher than 250 μA/cm<sup>2</sup>.

Inspection of the  $i\tau^{1/2}/C$  vs.  $i$  curves (Fig. 8) indicates that at low current densities an increase in the former value is obtained. The diagnostic criteria<sup>19</sup> and results reported earlier<sup>8</sup> indicate that this is due to the disproportionation of the electrochemically generated uranium(V). According to FISCHER AND DRAČKA<sup>4</sup>, if  $i\tau^{1/2}$  is plotted vs.  $i^{2/3}$ , the rate constant of the coupled chemical reaction may be computed from the slope of the steep part of the resulting plot. This has been done here for two

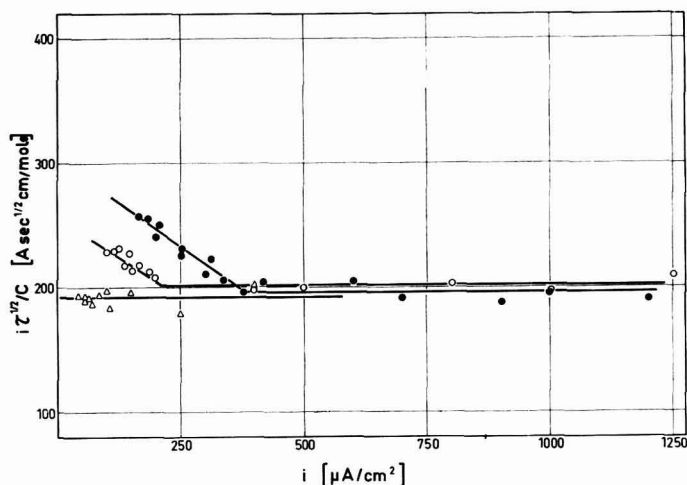


Fig. 8. The  $i\tau^{1/2}/C$  vs. current density plots for the reduction of uranium(VI) in 1 M NaHCO<sub>3</sub>, at pH 8.4 ± 0.2 and temp. 25°: ●, 5 mM; ○, 3 mM; △, 1 mM UO<sub>2</sub><sup>2+</sup>.

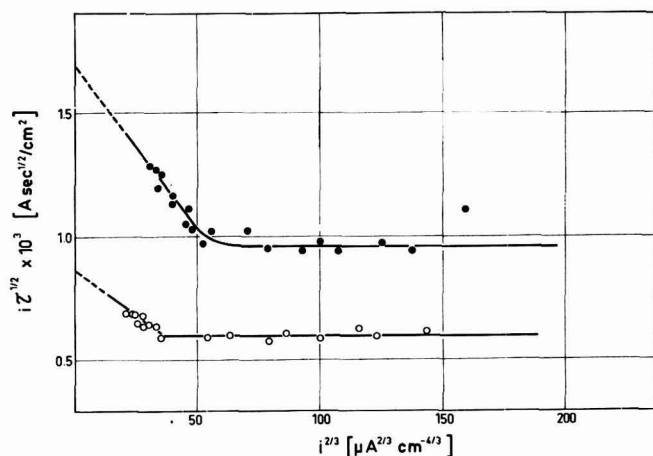


Fig. 9. The  $i\tau^{1/2}$  vs.  $i^{2/3}$  plots for the reduction of uranium(VI) in 1 M NaHCO<sub>3</sub>, at pH 8.4 ± 0.2 and temp. 25°: ●, 5 mM; ○, 3 mM UO<sub>2</sub><sup>2+</sup>.

concentrations of uranium(VI), 3 and 5 mM, in 1 M NaHCO<sub>3</sub> (pH 8.4). Typical plots are shown in Fig. 9.

Rate constants for the disproportionation of uranium(V) have been computed for the same concentrations of uranium(VI) in 1.0, 0.7, 0.5 and 0.3 M NaHCO<sub>3</sub>. In all solutions the ionic strength was kept constant by the addition of NaClO<sub>4</sub>. The apparent rate constants obtained were divided by the square of the concentration of the free carbonate ion. This was done on the basis of data obtained in the polarographic study of the disproportionation of uranium(V)<sup>8</sup>. A rationalized rate constant of the chemical reaction

$$k^+_{\text{galv.}} = 4.7 \times 10^{-3} \text{ M/sec at } 25^\circ$$

was obtained. The relative standard error in this value amounts to  $\pm 120\%$ . This value is, however, in agreement with the value obtained from polarographic measurements:

$$k^+_{\text{pol.}} = 5.7 \times 10^{-3} \text{ M/sec}$$

The apparent second-order rate constant of the disproportionation reaction in these experiments was 30 M<sup>-1</sup> sec<sup>-1</sup> in 1 M NaHCO<sub>3</sub> (pH 8.4) and approximately 200 M<sup>-1</sup> sec<sup>-1</sup> in 0.5 M NaHCO<sub>3</sub> (pH = 8.3). From the analysis of the dispersion of data at these two carbonate concentrations and the magnitudes of the rate constant, it seems that a minimum value of the latter experiment *i.e.*, 200 M<sup>-1</sup> sec<sup>-1</sup>, can be taken as the limit of applicability of galvanostatic techniques for the measurement of the rate of coupled second-order chemical reactions. This value is appreciably higher than the value of 50 M<sup>-1</sup> sec<sup>-1</sup> proposed by FISCHER AND DRAČKA<sup>4</sup> as a lower limit.

### 3. Comparison of electrochemical reactions at high and low-carbonate concentrations

The results of the measurements of transition times for the reduction of uranium(VI) in solutions of high concentration of free-carbonate ion indicated that there should be no preceding chemical step limiting the overall rate of reduction. Calculation of the formal rate constant for the electron transfer reaction<sup>20</sup>

$$k_{f,h} = \pi^{1/2} D_0^{1/2} / 2f_0(\tau^{1/2} - t^{1/2})$$

and extrapolating to  $E = 0$  N.H.E. in the expression:

$$\ln k_{f,h} = \ln k^o_{f,h} - (\alpha n F E / RT)$$

yields a significant difference in the rate constant for solutions of high and low concentrations of the free-carbonate ion:

$$\text{pH} = 11.5 \quad [\text{CO}_3^{2-}]_{\text{free}} = 0.94 \text{ M}: \quad \log k^o_{f,h} = -15.4 \pm 0.9$$

$$\text{pH} = 8.4 \quad [\text{CO}_3^{2-}]_{\text{free}} = 0.012 \text{ M}: \quad \log k^o_{f,h} = -11.4 \pm 0.8$$

for 25° and U(VI) concentrations in the range 0.3–5 mM. Although the precision of these data is low, it is highly probable that there are two different rate-determining steps depending on the concentration of the free-carbonate ion. According to the data available<sup>21</sup> uranium(VI) and uranium(V) are complexed as tricarbonates [UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>]<sup>4-</sup> and [UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>]<sup>5-</sup>, respectively. It seems probable that a more detailed analysis of the kinetics of the electrochemical reactions involved will reveal consecutive reactions of which at least one rate-determining step will depend on the dissociation rate and equilibrium of the carbonate complexes.

## SUMMARY

The chronopotentiometric technique has been used in studying the reduction of uranyl on mercury electrodes in sodium carbonate solutions. At 1 *M* of free carbonate no kinetic complications were observed at experimental conditions pertinent to galvanostatic techniques at quiescent solutions. At low free carbonate concentrations (0.10 *M*) the electrochemical reduction is followed by a second order chemical reaction the rate of which is dependent on the concentration of the free carbonate ion. The potential-time relation is a suitable means of studying the kinetics as dependent on the free ligand concentration and on the concentration of the electroactive uranyl ion. The data indicate that the uranyl tricarbonate complex undergoes reduction without dissociation, while the coupled chemical reaction (disproportionation) involves rearrangement in the transition of uranium(V) into the uranium(IV) and uranium(VI) carbonate complex forms.

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A SUPPLEMENTARY DEVICE TO A PEN-RECORDING POLAROGRAPH  
FOR DOUBLE-LAYER CAPACITY MEASUREMENTS

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The differential capacity of the double layer and the capacity component of an electrode reaction can be determined by using Grahame's alternating current bridge. This, however, although very accurate is a time-consuming method, particularly when measurements of the differential capacity of the double layer are required in a wide range of potentials. Very often, in the measurements of capacity changes caused by the adsorption of organic substances, speed of measurement as well as accuracy is desirable and obtaining the dependence directly in the form of a continuous curve is also of importance.

The present work describes a special additional device which works in conjunction with a sine wave voltage generator and a polarograph. It is an improvement on apparatus described previously<sup>1</sup>. Taking advantage of elements of the polarograph such as the amplifier, the potentiometer and the recorder one can markedly simplify the device in question. The Radiometer PO-4 polarograph was chosen for the experiments as it is the most suitable of available polarographs, but other types of polarograph could be used.

The continuous recording of capacity requires a highly sensitive and stable apparatus. The accuracy of the recorded values is closely dependent on the choice of the appropriate amplitude of the voltage feeding the circuit. This amplitude should be small enough to allow the capacity to remain constant over the range of potential given by the superposition of the alternating voltage on the constant polarization voltage. The greater the slope of the capacity dependence, the smaller should be the alternating voltage. On the other hand too small a voltage affects the sensitivity of the measurements and increases the effect of the interfering potentials which in turn lowers the accuracy of the measurements. In the present work an alternating voltage of 10 mV was used. The schematic diagram of the system is shown in Fig. 1.

The polarographic cell is polarized with the d.c. voltage from the polarograph (A—anode) and with the alternating voltage (from the GEN generator through the voltage divider consisting of the resistances  $R_1$  and  $R_2$ ), superimposed on it. The input resistance of the amplifier  $A_1$  is so high that the current in the polarographic cell flows almost entirely through the capacity  $C$  in the circuit of the negative feedback of the amplifier. Neglecting then the current,  $I_a$ , and assuming that the current

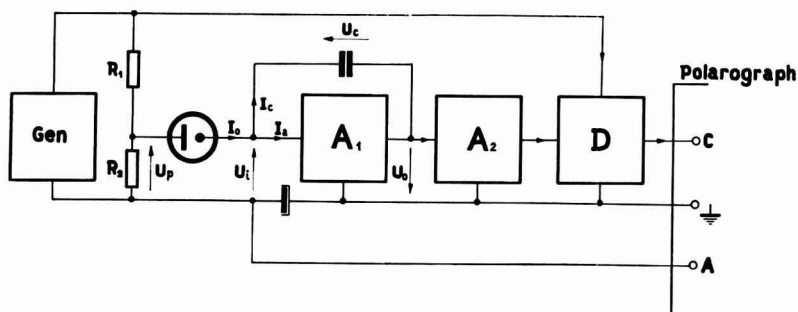


Fig. 1. The schematic diagram of the supplementary polarographic device for measurements of the double-layer capacity.

$I_o \approx I_c$ , the drop of the potential then equals;

$$U_c = U_i + U_o \approx -j \frac{I_o}{C\omega} \quad (1)$$

$\omega$  is the angular velocity of the polarizing a.c. voltage and  $U_i$  and  $U_o$  the input and output voltages of the amplifier,  $A_1$ , respectively.

$$U_i = -\frac{U_o}{K} \quad (2)$$

where  $K$  is the gain of the amplifier  $A_1$ . The output voltage of the amplifier,  $A_1$ , can be calculated from eqns. (1) and (2).

$$U_o \approx -j \frac{K}{K-1} \cdot \frac{I_o}{C\omega} \approx -j \frac{I_o}{C\omega} \quad (3)$$

The conductivity,  $Y_o$ , of the polarographic cell is the sum of conductance  $G_o$  and the capacitive conductivity  $C_o\omega$ :

$$Y_o = G_o + jC_o\omega \quad (4)$$

The polarographic cell current is:

$$I_o = Y_o(U_p - U_i) \quad (5)$$

From eqns. (2), (3) and (5) we obtain

$$I_o \approx \frac{Y_o U_p}{1 + j \frac{Y_o}{(K-1)C\omega}} \quad (6)$$

When  $|C\omega| \geq |Y_o|$  and the gain is high, the term  $+jY_o/(K-1)C\omega$  can be neglected and then from eqns. (3), (4) and (6) we get

$$U_o \approx U_p \left( \frac{C_o}{C} - j \frac{G_o}{C\omega} \right) \quad (7)$$

The a.c. output voltage  $U_o$  is directed, after the additional amplification by the amplifier  $A_2$ , to the phase detector D. The phase detector is controlled by the voltage in phase with  $U_p$  and hence the d.c. voltage obtained from the phase detector is proportional only to the real component of  $U_o$ , *i.e.*, to the ratio  $C_o/C$  and does not

depend on the imaginary component *i.e.*, on the ohmic resistance of the polarographic cell. The main advantage of the use of the amplifier with the negative feed-back is high stability of amplification.

The detailed scheme of the apparatus is shown in Fig. 2. The amplifier  $A_1$  (Fig. 1)

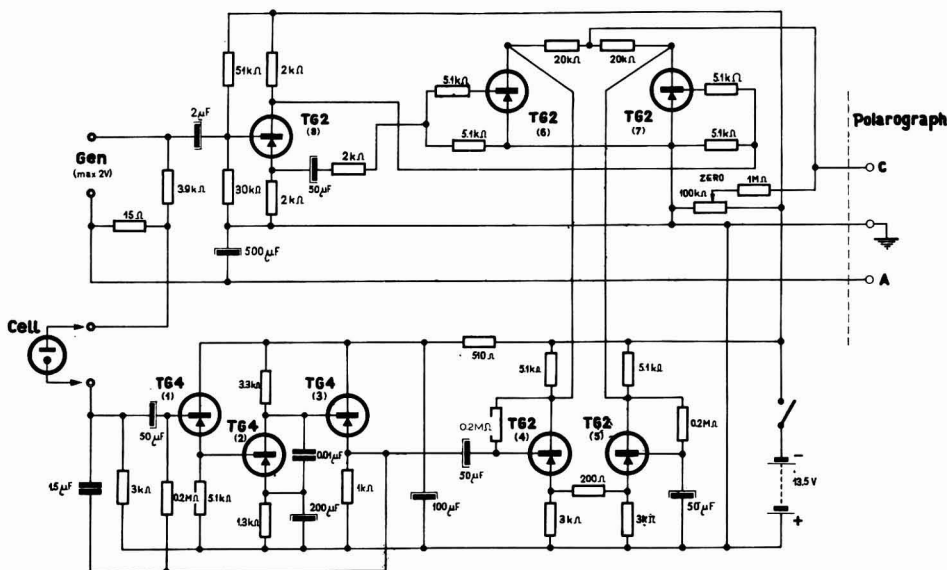


Fig. 2. The detailed diagram of the supplementary polarographic device.

consists of the transistors 1, 2 and 3 and the amplifier  $A_2$  of the transistors 4 and 5. At the output of  $A_2$  one obtains two potentials with a phase difference of  $180^\circ$  which control the phase detector constructed of transistors 6 and 7. The switching of this detector also requires two potentials with a phase difference of  $180^\circ$ . For this reason the generator is not connected directly to the phase detector but indirectly through the phase inverter — transistor 8 (not shown in the schematic diagram, Fig. 1). The whole system is fed from a battery of 13.5 V. Polish transistors of characteristics similar to the Philips transistors OC70 and OC71 were used.

The system described, works in the frequency range 20 c/sec–2 kc/sec when the capacity does not exceed  $1 \mu\text{F}$ . For greater capacities the upper limit of the frequencies would be correspondingly smaller.

The current sensitivity of the polarograph should be adjusted to the magnitude of the recorded capacity. Small changes of capacity can also be determined, using high sensitivities of the polarograph. In this case the deflections of the recorder are compensated with the potentiometer "zero" and the current sensitivity of the polarograph is raised. An example is given in Fig. 4, curve (b).

### The mercury electrode

A hanging mercury drop electrode was used in the apparatus described above. It was prepared by means of the device described previously<sup>2</sup> and the present work

describes a modification of this set-up (Fig. 3). The device suggested by KEMULA AND KUBLIK<sup>3</sup> which produces a hanging drop with a constant and reproducible surface can also be used in this apparatus.

The device for producing the hanging mercury drop consists of a capillary (internal

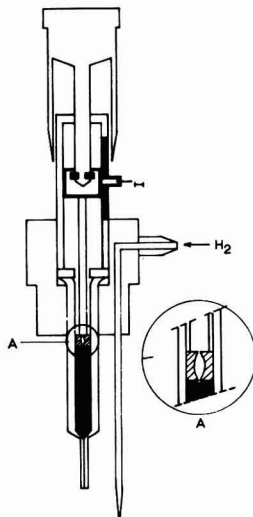


Fig. 3. The assembly for producing the hanging mercury drop electrode.

diameter, 2 mm) which is coated with silicone and provided with a conical inlet. Its outlet is connected with a capillary of 0.2 mm internal diameter fused into the first one and coated with silicone by heating. The capillary is placed inside the plastic stopper which is provided with a metal bushing to prevent the capillary moving inside the stopper. A steel rod is placed inside the capillary; its diameter is 5% smaller than the internal diameter of the capillary. The rod has, in its lower part, an incision the shape shown in Fig. 3 (see detail A) filled with PVC. The upper part of the steel rod is fastened to the guide connected with the micrometric screw. The guide bar placed in the guide which prevents rotation is connected at the same time with the voltage supply of the electrode. The steel rod can also be tightened with plastic wire insulation. The piston should move smoothly without friction and to obtain a good plasticity and a low friction of the PVC prior to its placing in the cavity, it is pressed for several minutes between two plates with talc. The excess talc is then removed. In order to fill the capillary with mercury a small amount of it is drawn into the capillary, the whole set-up turned through 180° and then shaken vigorously to obtain contact of mercury with the steel rod. The mercury should adhere to this without a meniscus which ensures that no air is present in the capillary. At the first filling of the capillary this procedure should be repeated several times. This method for producing a hanging mercury drop ensures complete removal of air from the capillary. This can be checked by inverting the assembly and watching the column of mercury in the capillary. The method gives good reproducibility of drops

and the piston is durable. The capillary can be exchanged or recoated with silicone several times without the need to change the piston.

This apparatus can also be used as a dropping mercury electrode if necessary.

### The measurements

The experiments presented below are examples to show the general character of the recorded relationships and the reproducibility of the results obtained. Fig. 4, curve (a) shows the capacity of the double layer as a function of the potential of the hanging

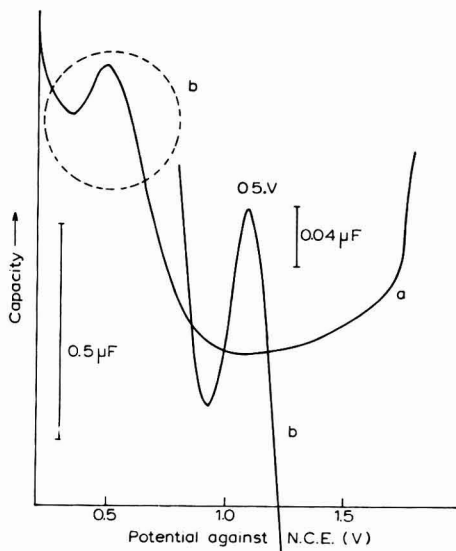


Fig. 4. The dependence of the double-layer capacity on the potential for an aqueous solution of KCl: (a), potential range 0.2–1.8 V, current sensitivity 7; (b), potential range 0.2–0.65 V, current sensitivity 2.

mercury electrode for an aqueous solution of KCl, in the potential range 0.2–1.8 V against N.C.E. A detail of this curve with the maximum at 0.5 V in the potential range 0.2–0.65 V for a current sensitivity 3.5 times higher, is shown in Fig. 4, curve (b). The surface area of the hanging mercury drop electrode was 2.16 mm<sup>2</sup> in all the cases described. Recording of the maximum is possible after a compensation with the potentiometer “zero” which increases the current sensitivity of the polarograph. By this means it is possible to estimate the adsorption of surface active compounds by measuring the decrease of the capacity of the maximum at minute concentrations of the active compounds.

Fig. 5 is a plot of the double-layer capacity against potential for the aqueous solution 1 M KCl containing 10% v/v of dioxane. The sharp maximum of adsorption is displayed very markedly in this figure together with the broad one of desorption. The plot for a pure solution of KCl is also shown here. The same dependence for a KCl solution containing dodecyltrimethylammonium bromide (DTAB)<sup>5</sup>, which shows a

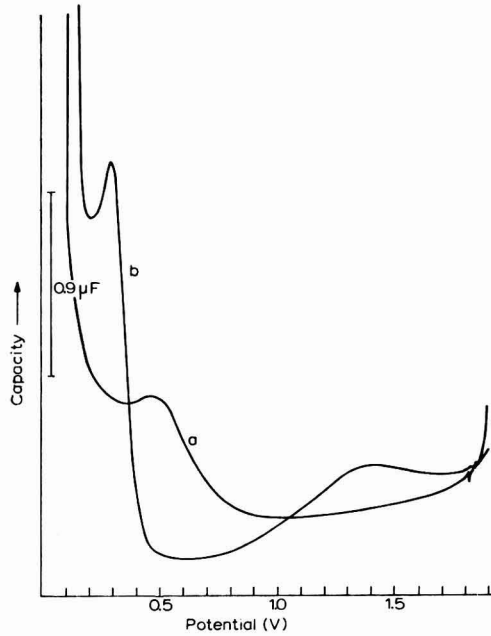


Fig. 5. The dependence of the double-layer capacity on the potential: (a), aqueous solution of KCl; (b), after the addition of dioxane.

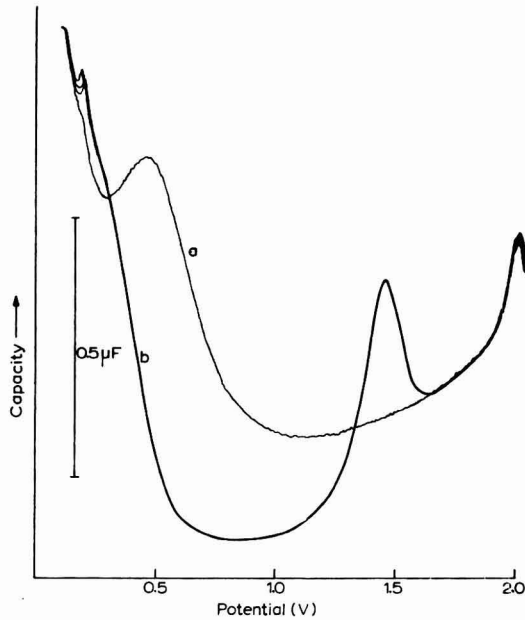


Fig. 6. The dependence of the double-layer capacity on the potential: (a), KCl solution; (b), after the addition of dodecyltrimethylammonium bromide.

much higher surface activity than dioxane, at a concentration of  $2.6 \times 10^{-5} N$ , is shown in Fig. 6. The maximum of adsorption is situated in this case at 0.2 V and the desorption maximum at 1.45 V. Fig. 6, curve (b), shows three successive runs for different mercury drops. The good agreement of these results illustrates the reproducibility of the measurements.

#### ACKNOWLEDGEMENT

We should like to express our sincere thanks to Prof. E. GÖRLICH for valuable discussions during the present work.

#### SUMMARY

A new device for measuring the dependence of the double-layer capacity on the electrode potential is described. It uses the amplifier, potentiometer and recorder of a polarograph. The apparatus is fed from the sine wave voltage generator and the hanging mercury electrode acts as a cathode. The detailed electronic diagram of the new device and a description of the preparation of the hanging mercury drop electrode are given. The results of experiments which illustrate the performance of the device are presented.

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*J. Electroanal. Chem.*, 8 (1964) 399-405

## Short Communications

### Ellipsometric study of oxygen-containing films on platinum electrodes

This brief communication describes the main results which have emerged from an ellipsometric study of the oxygen-containing films on bright platinum sheet-anodes in acid solutions ( $1\ N\ H_2SO_4$ ). Ellipsometry is a direct and *in situ* optical method of examining films on reflecting surfaces. It is based on a study of the changes which surface films produce on the polarization state of a light beam reflected from a metallic mirror.

The particular ellipsometric method used<sup>1</sup> is that of a quantitative study of films held in a steady-state condition by means of a potentiostat (Fig. 1). The parameters of the reflected elliptically polarized light were determined while maintaining the potential of a reflected platinum sheet-anode at various values. From these parameters, the thickness of the film was calculated using standard ellipsometric procedures<sup>2</sup>.

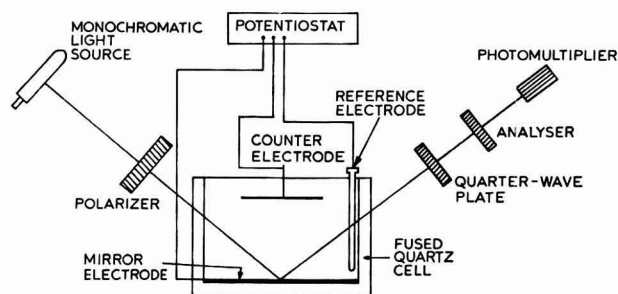


Fig. 1. Experimental arrangement.

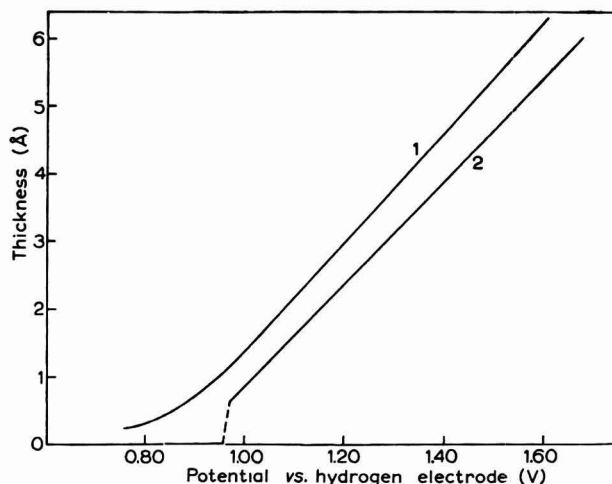


Fig. 2. Dependence of film thickness on potential: (1), typical coulometric curve; (2), ellipsometric curve.



The dependence of average film thickness on potential is shown in Fig. 2. The thickness-potential plot shows that: (i) at potentials less positive than about 0.98 V (*vs.* N.H.E.), there is no ellipsometric evidence of a film although the sensitivity of the technique is about 0.1 Å; (ii) a film (of average thickness  $\sim 0.2$  Å) "comes on" suddenly at about  $+0.980 \pm 0.010$  V; (iii) and thereafter the film thickness increases linearly with potential (a result which is in striking agreement with those of coulometry<sup>3-6</sup>).

Computer analysis of the ellipsometric data shows that the refractive index ( $n_F^*$ ) of the film is a complex quantity, *i.e.*,  $n_F^* = n_F + i\kappa$ . The real part ( $n_F$ ) of the complex refractive index is 3.3. The imaginary part is the absorption coefficient ( $\kappa$ ) which is a measure of the conductivity of the film at optical frequencies. The results indicate that this conductivity at optical frequencies (in the case of the film on platinum) is of the same order as that of a metal, judging from the order of magnitude of the same optical-frequency quantity for semi-conductors and metals<sup>7,8</sup>.

The ellipsometric detection of a surface film depends on the optical constants ( $n_F^*$ ) of the film being sufficiently different from those of the surrounding medium. It is suggested, therefore, that the difference between chemisorbed oxygen and water is too small to make a chemisorbed oxygen film register in the ellipsometer. When, however, platinum joins with oxygen to form a new phase, the optical constants between this "oxide" and the surrounding water are adequate to produce an ellipsometric effect. The average thickness of 0.2 Å of this platinum "oxide" film is interpreted in terms of a "partial" coverage of a mono-layer of oxide.

#### Acknowledgements

The authors thank Miss W. VISSCHER and Dr. M. A. V. DEVANATHAN for help and discussion in the preliminary experiments and the University Computer Center for their assistance. The financial support of the Aeronautical Systems Command and the National Aeronautics and Space Administration, Contract No. NSG-325 and U.S. Army Electronics Laboratories, Fort Monmouth, New Jersey, Contract No. DA 36-039 SC-88921 is gratefully acknowledged.

One of us (A.K.N.R.) thanks the Council of Scientific and Industrial Research, India, for the grant of a Leave of Absence.

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Received August 17th, 1964

### Faradaic impedance of step-wise electrode reactions

In a previous communication<sup>1</sup>, the properties of polarographic and chronopotentiometric waves of reversible multi-electron transfer electrode reactions involving one intermediate of appreciable stability were discussed. Equilibrium at the electrode surface of the intermediate,  $Z$ , was admitted with the oxidised,  $O$ , and reduced,  $R$ , species through the formation reaction (2), and with its dimer,  $D$ , through the association reaction (3)



It is also of interest to investigate the behaviour of this system, when the polarising current is a sinusoidal function of time. The magnitudes of the series resistance,  $R_s$ , and capacitance,  $C_s$ , in the circuit equivalent to the polarised cell are affected by the presence of the species  $Z$  and  $D$ , in a manner which follows from eqns. (51), (36) and (48) of the previous communication. We specify a current-time function of the form

$$I(t) = I_1 + I_2 \sin \omega t$$

where  $I_1$  might be transient but contains no periodic terms, and  $I_2$  and  $\omega$  are the amplitude and frequency, respectively, of the alternating modulation. When a steady state has been reached, *i.e.*, transient terms have tended to their constant limits, it is found by comparison of the expressions of the current-voltage characteristic of the faradaic and equivalent series circuit impedances, that:

$$R_s = \sigma / \sqrt{\omega}$$

$$C_s = 1 / \sigma \sqrt{\omega}$$

where

$$\sigma = \frac{1}{\sqrt{2FAa'}} \frac{n_2 i_1 + n_1 i_2}{n_1 + n_2} \frac{dE}{di}$$

and

$$a' = \sqrt{D_O C_O^b} + \sqrt{D_Z C_Z^b} + \sqrt{D_R C_R^b} + 2\sqrt{D_D C_D^b}$$

$D_r$  and  $C_r^b$  are the diffusion coefficient and the bulk concentration, respectively, of species  $r$ ;  $i_1$  and  $i_2$  are the limiting cathodic and anodic currents, and  $di/dE$  is the gradient of the polarographic wave.  $F$  is the faraday and  $A$  is the electrode area.

Evidently the dependence of the faradaic series resistance and capacity upon potential in this reversible system, is controlled by the total gradient of the current-voltage curve. This result and even its algebraic form, are also valid for single-step electrode reactions. Thus the Warburg impedance of the electrode,  $(R_s^2 + 1/\omega^2 C_s^2)^{1/2}$ , has two minima only when two waves can be distinguished in the polarographic

characteristic. The positions of these minima allow the calculation of the equilibrium constant of reactions (2) and (3) only in the case  $n_1 = n_2 = n$ , and with dimerisation of the intermediate either complete or absent<sup>2</sup>. It appears that the method of faradaic impedance is less useful in this system than the simpler method of d.c. measurement of current-voltage curves.

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*J. Electroanal. Chem.*, 8 (1964) 408-409

### Utilisation en polarographie d'une électrode à mercure à surface renouvelée, mais à aire constante

GRIFFITHS ET PARKER<sup>1</sup> ont signalé l'utilisation d'une électrode dont la superficie ne varie pas mais dont le mercure à la surface est néanmoins continuellement renouvelé. Cette électrode est constituée par un montage aussi simple qu'ingénieux: un tube capillaire étroit (diamètre intérieur 0.5 mm; parois 0.25 mm) placé à l'intérieur d'un tube plus large (diamètre intérieur 2 mm) assure l'arrivée du mercure alors que l'écoulement se fait par l'intermédiaire du capillaire plus large. Le mercure immédiatement au voisinage du ménisque formé au niveau de la surface supérieure du tube extérieur et qui est en contact avec la solution électrolysée est ainsi continuellement renouvelé, l'orifice du capillaire d'arrivée étant placé contre une des parois du tube plus large et à 1.5 mm au-dessous du niveau de la surface.

Cette électrode doit permettre d'éliminer sur les courbes courant-tension en polarographie les oscillations dues à la formation des gouttes tout en présentant les mêmes avantages qu'une électrode à gouttes. C'est pour cette raison qu'il paraissait intéressant d'étudier le comportement d'une telle électrode qui semblait devoir être d'une grande utilité<sup>2</sup> dans bien des mesures.

#### Reactifs et appareillage

Les produits utilisés étaient de qualité pure pour analyse et les courbes ont été enregistrées avec un polarographe Radiometer PO4.

Les dimensions géométriques des électrodes utilisées étaient exactement semblables à celle de GRIFFITHS ET PARKER, mais contrairement à celle-ci qui était en polyéthylène elles étaient en verre. Il est essentiel de recouvrir très soigneusement toute la surface intérieure de l'électrode d'une couche non mouillante pour empêcher la

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pénétration de la solution entre les parois de l'électrode et du mercure. Une solution de Rhodorsil 240 diluée à 10% dans du cyclohexane anhydre a été utilisée dans ce but.

Le réglage du débit de mercure est délicat et le montage de GRIFFITHS ET PARKER dépendant uniquement d'une petite différence de niveaux entre deux réservoirs de mercure ne permet pas un ajustage facile, aussi a-t-il été remplacé par deux capillaires reliant d'une part le tube d'arrivée à un réservoir de mercure à niveau variable et, d'autre part le tube extérieur de sortie à une surface de mercure (Fig. 1). En variant la hauteur du réservoir au-dessus de l'électrode, et de celle-ci par rapport au niveau du capillaire de sortie il est possible d'obtenir des électrodes dont le niveau reste constant avec des débits comparables à ceux utilisés en polarographie. Mais pour faciliter l'élimination des produits d'électrolyse, il est préférable d'avoir des débits rapides équivalents à une goutte toutes les 2 ou 3 sec.

Finalement, il est important<sup>1</sup> de régler le niveau du mercure de telle sorte que le ménisque soit maintenu au niveau de la surface du tube capillaire extérieur. Un cathétomètre a été utilisé pour suivre l'évolution du niveau au cours du temps et pendant l'enregistrement d'une courbe.

Il est à noter que s'il est facile de maintenir le niveau constant en dehors de toute électrolyse, il est beaucoup plus difficile d'assurer ceci durant une mesure à cause de la variation de la tension superficielle avec le potentiel.

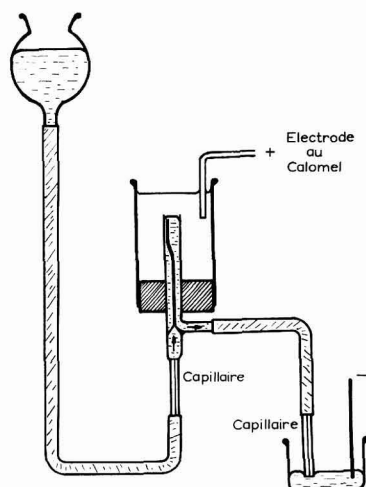


Fig. 1. Schéma du montage.

### Analyse des résultats

**Reproductibilité.** Il est très difficile d'atteindre une reproductibilité satisfaisante. Il faut pour cela maintenir le niveau du ménisque constant, assurer des débits suffisants et un siliconage parfait des électrodes. Seulement dans ces conditions peut-on obtenir des courbes aller et retour (à potentiel croissant ou décroissant) qui soient presque identiques et en partant d'un courant zéro assurer un retour à cette valeur.

**Forme des courbes.** Pour les métaux étudiés (Cd et Tl) les courbes courant-tension

obtenues présentent un maximum dont la forme est semblable à celle des courbes données par une goutte pendante (Fig. 2), le courant augmentant avec le potentiel d'abord puis décroissant lentement. Par ailleurs, pour un potentiel donné le courant diminue avec le temps. Dans aucun cas il n'a été possible d'obtenir des courbes présentant un palier comme l'indiquent GRIFFITHS ET PARKER pour l'antimoine et ceci quelles que soient les caractéristiques géométriques de l'électrode ou la présence de substances tensio-actives.

Le potentiel du maximum est le même que le potentiel normal de demi palier mais il dépend de la présence en solution d'un ion plus facilement réductible. Ainsi dans le cas du cadmium il est déplacé vers des potentiels plus négatifs en présence du thallium.

La hauteur du maximum est proportionnelle à la concentration de la substance réduite et le courant est donné, aux erreurs d'expériences près, par une équation<sup>3</sup> semblable à celle utilisée en polarographie oscillographique soit :

$$i = 217 A n^{\frac{3}{2}} V^{\frac{1}{2}} D^{\frac{1}{2}} C$$

où  $A$  = surface, en  $\text{mm}^2$  de l'électrode considérée comme une demi-sphère,

$n$  = nombre de Faradays,

$V$  = vitesse d'augmentation du potentiel (V/sec),

$D$  = coefficient de diffusion en  $\text{cm}^2/\text{sec}$ ,

$C$  = concentration en mole/l.

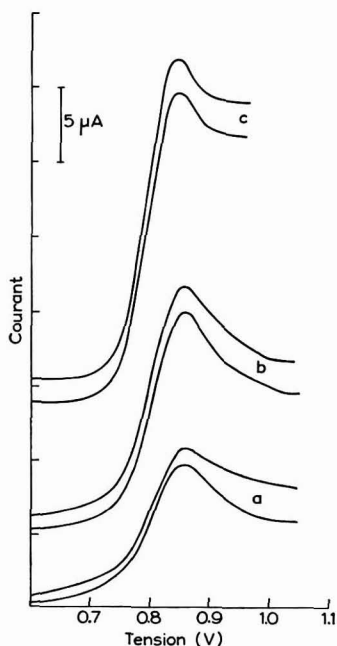


Fig. 2. Variation de la hauteur du maximum avec la concentration; 10 ml d'une solution 1 M  $\text{NH}_4\text{Cl}$ , 1 M  $\text{NH}_4\text{OH}$ ,  $\text{Na}_2\text{SO}_3$  et gelatine + (a), 0,5 ml; (b), 1 ml; (c), 1,5 ml  $10^{-2}$  M  $\text{CdSO}_4$ .

### Conclusions

Les résultats de GRIFFITHS ET PARKER semblent difficilement reproductibles et s'il est possible, dans certaines conditions, d'obtenir des courbes plus ou moins satisfaisantes, il n'en est pas moins vrai que l'électrode n'apporte pas assez d'avantages pour que son utilisation se généralise.

Les résultats obtenus sont en accord avec la théorie qui prévoit un courant limite indépendant du temps seulement dans le cas d'une diffusion vers une électrode sphérique ou alors avec une goutte renouvelée<sup>4</sup>.

En l'absence de paliers il n'y a pas lieu de postuler, comme l'ont fait certains auteurs<sup>5</sup> l'existence de conditions hydrodynamiques à l'électrode qui permettent de transférer le mouvement du mercure à la solution.

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Reçu le 17 juin 1964

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### Correction

The REPORT FOR DISCUSSION AND COMMENT which appeared in *J. Electroanal. Chem.*, 7 (1964) 417, should have the following title:

ABBREVIATED REPORT OF THE "ELECTROCHEMICAL NOMENCLATURE AND DEFINITIONS" COMMISSION OF C.I.T.C.E. AND OF THE "ELECTROCHEMICAL SYMBOLS AND TERMINOLOGY" SUB-COMMISSION OF I.U.P.A.C.

Other corrections are as follows:

- page 417, line 4 of (2): "the ratio  $w'/q$  tends to zero", read: "the ratio  $w'/q$  as  $q$  tends to zero";  
 page 418, line 1: "system must be", read: "system can be";  
 page 418, line 3: "in this report", read: "in this section";  
 page 419, line 2 of (19): "(see II6)", read: "[see III(6)]";  
 page 420, line 4 of (5): add: "Consider, for example, the Daniell cell";  
 page 420, 2nd reaction:  $2 e(1)$ , read:  $2 e(4)$ ;  
 page 421, line 7 of (7):  $2 \tilde{\mu}e^2$ , read:  $2 \tilde{\mu}e^1$ ;  
 page 421, line 9 of (8):  $\mu_{Cu^1}$ , read:  $\mu_{Zn^1}$ ;  $\mu_{Zn^4}$ , read:  $\mu_{Cu^4}$ ;  
 page 424, line 12/13: "divergence", read: "difference".

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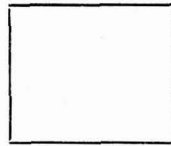
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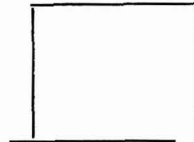


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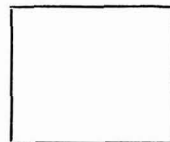


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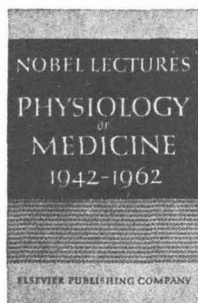
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