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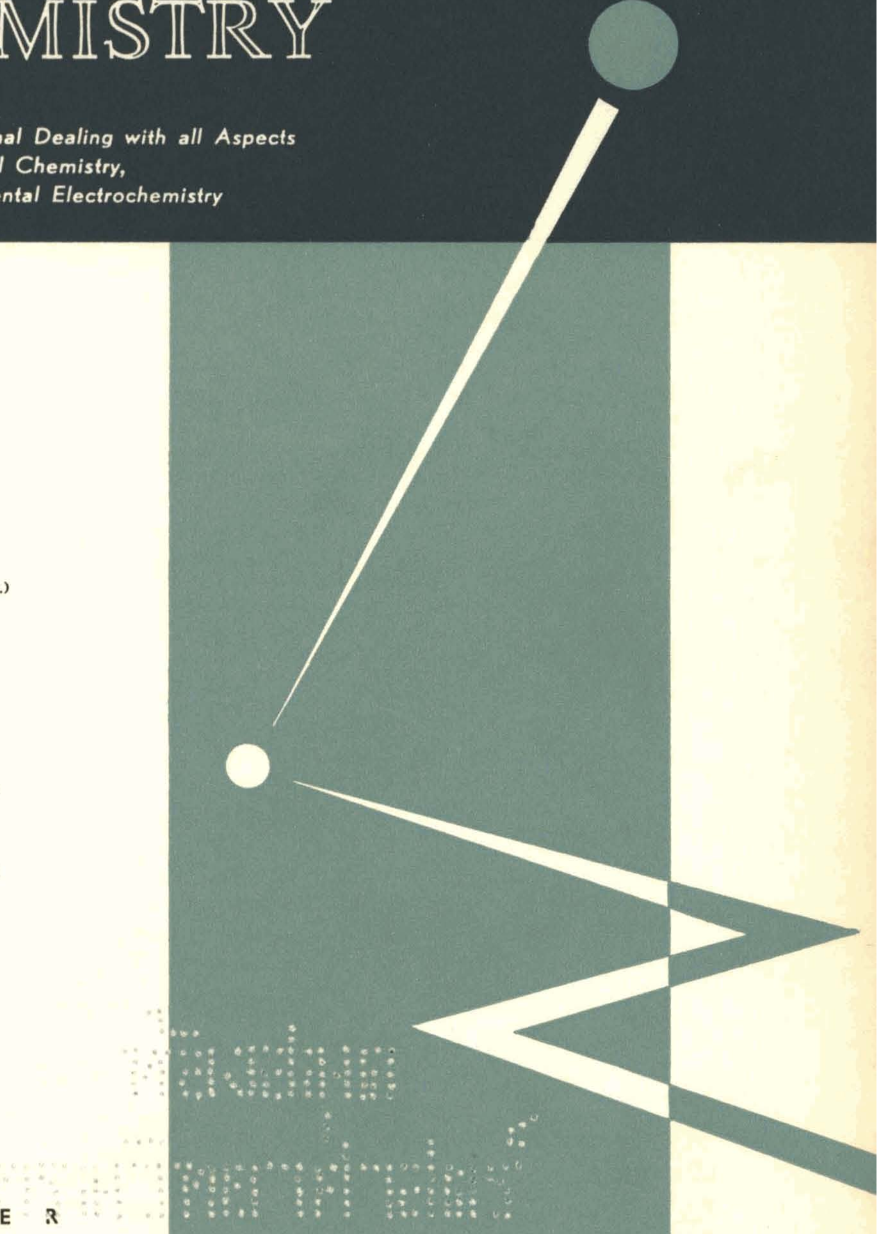

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SUMMARIES OF PAPERS PUBLISHED IN JOURNAL OF ELECTROANALYTICAL CHEMISTRY

Vol. 6, No. 6, December 1963

ALTERNATE PATH REACTIONS IN CHRONOPOTENTIOMETRY THE REDUCTION OF BENZALDEHYDE

The theory of alternate path reactions in chronopotentiometry is developed. Alternate path reactions differ from normal stepwise reactions of an electroactive substance in that the product of the first reaction does not react further during the second chronopotentiometric wave. This causes the second wave to be shorter than it is with normal stepwise reactions. The transition time equation for alternate path readtions at both planar and spherical electrodes is derived. The two-step reduction of benzaldehyde at the slow-dropping mercury electrode has been studied as an example of such a process since the product of the first reaction, hydrobenzoin, is not reducible to the product of the second step, benzyl alcohol.

D. H. EVANS,

J. Electroanal. Chem., 6 (1963) 419–425.

THE DETECTION OF OXYGEN BY GAS-PHASE POLAROGRAPHY AT LOW TEMPERATURES AND LOW PRESSURES

An oxygen detector based on gas phase polarography is described. Utilizing a buffered alcoholic solution of KCl as electrolyte, the detector is capable of operating at low temperature (–25°). The detector has a sensitivity range of 0.001% to 100% oxygen and can operate to pressures as low as 10 mm Hg. A 0.5-mil thick Teflon membrane was selected as the most suitable membrane after testing more than 60 types of commercially available materials. Possible interferences from N_2, A, CO_2, and O_3 were investigated.

G. HALPERT AND R. T. FOLEY,

J. Electroanal. Chem., 6 (1963) 426–433.

A POLAROGRAPHIC STUDY OF IRON(III)–NITRILOTRIACETIC ACID COMPLEX

A two-stepped kinetic wave was obtained above pH 4.1 in the reduction of an iron(III)–NTA complex in the presence of excess NTA in acetate buffer solution. The electrode process of the first wave which was controlled by the rate of dissociation of Fe(III)X complex, was reversible and represented a 1-electron change; the formation constant, K_{FeX}, was calculated to be $10^{16.01}$. The second wave was also kinetic and its electrode process was irreversible and represented a 2-electron change. A relation between the rate constant, g, of the electron transfer reaction, and potential was deduced and it was found that the Fe(II)HX complex would be reduced directly.

S. MISUMI AND Y. MASUDA,

J. Electroanal. Chem., 6 (1963) 434–442.

THE POLAROGRAPHY OF THE NICKEL(II)-ETHYLENEDIAMINE SYSTEM

STUDY OF THE ETHYLENEDIAMINE CATALYTIC HYDROGEN WAVE

The small wave observed above the diffusion limited plateau when Ni^{2+} is reduced in the presence of trace amounts of ethylenediamine has been investigated. The effects of ethylenediamine concentration, nickel ion concentration and pH on the wave, are described. The results of this investigation indicate that the wave is a catalytic hydrogen wave. It has been found that the wave can be employed for the determination of ethylenediamine at low concentrations. The optimum concentration range for the analyses is 3×10^{-5}–3×10^{-4} *M* ethylenediamine.

H. B. Mark, Jr. and H. G. Schwartz, Jr.

J. Electroanal. Chem., 6 (1963) 443–449.

POTENTIOMETRIC DETERMINATION OF TIN(II), IRON(II), FERROCYANIDE, ANTIMONY(III) AND ARSENIC(III) BY MANGANIC SULPHATE

The conditions for the estimation of iron(II), tin(II), antimony(III), arsenic(III) and ferrocyanide ion by manganic sulphate solution have been investigated. A bright platinum electrode was satisfactory for all these estimations except in the case of arsenic(III) where a platinum black electrode was found to be more useful. The titration of antimony (III) with manganic sulphate could be successfully carried out only in presence of hydrochloric acid (minimum concn. 0.6 *N*). The oxidation of arsenic(III), was slow and was therefore catalysed by the addition of minute amounts of potassium bromide or potassium chloride. The potentiometric titration curves for mixtures gave breaks for each of the constituents, but for mixtures of iron(II) and antimony(III) the titre values obtained for the first break were far removed from the theoretical values. For mixtures containing three metals ions the potentials attained at the equivalence points of the first and third breaks were approximately equal to the theoretical potentials but those for the second break were different from the theoretical values. Titrations for metals separately, and in mixtures were accurate to 0.1%.

W. U. Malik and M. Ajmal,

J. Electroanal. Chem., 6 (1963) 450–459.

POLAROGRAPHIC CHARACTERISTICS OF CHLORITE

Solutions of chlorite in buffered aqueous solution have been investigated polarographically over the pH range 1–10. Chlorite produces a well defined, diffusion-controlled, but irreversible wave at pH <4.5; in solutions of higher pH the wave becomes more drawn out, less concentration dependent and kinetically controlled. In the optimum pH range, 4.2–4.5, the diffusion-limited wave height is proportional to concentration from 0.2–2.0 m*M*; higher concentrations produce a large maximum on the top of the wave which is not removable by the ordinary suppressors. In solutions more acid than pH 4.2 chlorite decomposes too rapidly for polarographic analysis. On the basis of pH dependence of wave height and half-wave potential it is assumed that the overall electrode reaction is: $HClO_2 + 4e + 3H^+ \rightarrow Cl^- + 4H_2O$

A. M. Hartley and A. C. Adams,

J. Electroanal. Chem., 6 (1963) 460–464.

INFLUENCE OF THE POSITION OF THE CAPILLARY ON THE TRANSFER OF CONCENTRATION POLARIZATION IN POLAROGRAPHY

The polarographic capillary with the orifice in an inclined position — most conveniently at 45° — improves the properties of dropping-mercury electrode. It removes the effect of transfer of concentration polarization from one drop to the other, or the transfer of the products of electrolysis, and in this manner ensures the fulfilment of the basic condition for the polarographic diffusion current, namely, that the concentration of depolarizer in the time of drop-formation in the neighbourhood of the electrode is the same as in the bulk of solution. Accordingly, it gives the instantaneous current of theoretical shape. It is the only type of dropping-mercury electrode on which may be registered the mean polarographic current which is not influenced by transfer of concentration polarization and which satisfies the equation of diffusion current with the correction for spherical diffusion. It removes the disturbances that can be caused by the insoluble products of electrolysis collecting in the vicinity of the orifice. At potentials, where hydrogen is evolved at the electrode, the bubbles arising on the orifice can escape upwards. It lowers considerably the movement of electrolyte near the drop giving rise to the maximum of the second kind. It affords a reasonable short drop-time with small oscillations at a small rate of flow of mercury.

I. Smoler,

J. Electroanal. Chem., 6 (1963) 465–479.

REDOXOKINETIC AND IMPEDANCE TITRATIONS OF ZINC AND CADMIUM SALTS WITH POTASSIUM FERROCYANIDE

It has been shown that the techniques of redoxokinetic and impedance titrations can be successfully applied to the titration with potassium ferrocyanide of (i) zinc salts and (ii) cadmium salts, both in presence of traces of potassium ferricyanide to establish the redox system. The titrations have been carried out at elevated temperatures, and the results are compared with those obtained by conventional potentiometry.

K. S. Narayanan and C. P. Namboodiripad,

J. Electroanal. Chem., 6 (1963) 480–485.

CHARGE AND OUTER HELMHOLTZ POTENTIAL FOR A MERCURY ELECTRODE IN AQUEOUS NaF AT 25°

(Short Communication)

C. D. Russell,

J. Electroanal. Chem., 6 (1963) 486–490.

THE CURRENT–POTENTIAL EQUATION FOR LINEAR-SWEEP VOLTAMMETRY

(Short Communication)

W. T. de Vries, E. van Dalen,
J. Electroanal. Chem., 6 (1963) 490–493.

POLAROGRAPHY OF THALLOUS ION IN SOME SUPPORTING ELECTROLYTES

(Short Communication)

D. S. Jain, K. Zutshi and J. N. Gaur,
J. Electroanal. Chem., 6 (1963) 493–496.

ALTERNATE PATH REACTIONS IN CHRONOPOTENTIOMETRY THE REDUCTION OF BENZALDEHYDE

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(Received October 2nd, 1963)

INTRODUCTION

In the development of the theory of chronopotentiometry with stepwise reactions, it has quite generally been assumed that the product of the first electrochemical reaction is reducible during the subsequent chronopotentiometric wave. Such is the case with oxygen reduction[1] where the hydrogen peroxide formed during the first wave contributes to the current during the second step by its reduction to water. This communication develops the theory for the case where the product of the first reaction is not further reducible. Such a reaction scheme has been designated an *alternate path reaction*, since the product of the second reaction is formed by a reaction path not involving the product of the first. The reduction of benzaldehyde has been studied as an example of such a system.

EXPERIMENTAL

The chronopotentiometric cell was the same as one described previously[2]. The working electrode was a slow-dropping mercury electrode (S.D.M.E.) constructed from normal polarographic capillary tubing by forming a constriction a few cm above the end. The rate of flow (*m*) with a 36.5 cm head of mercury was 0.0365 mg/sec. The drop time at −1.0 V *vs.* S.C.E. in phosphate–citrate buffer, pH 4, was 203 sec.

The electrical circuit used was conventional[3] with one modification[4]. A simple polarizing unit maintained the potential of the working electrode at a value (−0.9–−1.0 V *vs.* S.C.E.) which was slightly more oxidizing than the potential of the first chronopotentiometric wave. This polarizing circuit was opened by the same relay which closed the constant current electrolysis circuit thus interrupting the polarization at the moment that the chronopotentiogram was initiated. This modification was made to eliminate the significant quantity of electricity required to change the potential of the electrode from its rest potential, *ca.* +0.2 V *vs.* S.C.E., to the potential of the first wave, −1.1 V *vs.* S.C.E.

The chronopotentiograms were photographed from a Dumont Model 403 oscilloscope and the transition times were measured from enlargements of the photographs[3] For illustrative purposes a chronopotentiogram was recorded with a Sargent Model

MR strip-chart recording potentiometer whose full scale response time was 1 sec.

Benzaldehyde was purified by distillation under nitrogen with reduced pressure. Chemicals for supporting electrolytes were reagent quality. Distilled water of specific conductance lower than $2 \cdot 10^{-6}\ \Omega^{-1}\ \text{cm}^{-1}$ was used to prepare all solutions. Prepurified nitrogen (99.98%) supplied by the Air Reduction Company was used to deaerate solutions. All experiments were carried out with the cell in a water thermostat the temperature of which was controlled to ± 0.1°.

THEORY

Two types of electrochemical processes can produce two chronopotentiometric waves with a solution containing only one electroactive material. They are represented by the following reaction schemes:

	Wave 1	*Wave 2*
Normal stepwise reduction	$O + n_1 = R_1$	$O + (n_1 + n_2) = R_2$ $R_1 + n_2 = R_2$
Alternate path reduction	$O + n_1 = R_1$	$O + (n_1 + n_2) = R_2$ R_1 not reducible

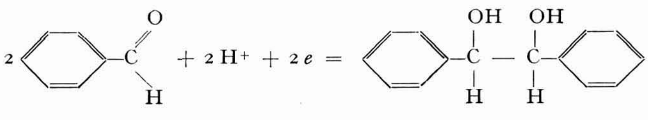
For the ordinary stepwise reduction of an electro-active material the ratio of chronopotentiometric transition times for a planar electrode is given by[1]

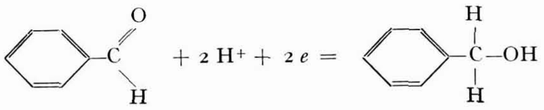
$$\frac{\tau_2}{\tau_1} = \left(\frac{n_1 + n_2}{n_1}\right)^2 - 1 \tag{1}$$

where τ_1 is the first transition time, τ_2 the second transition time (measured from τ_1 to the second potential break), and n_1 and n_2 are the number of Faradays per mole of electrochemical reaction for the first and second steps respectively. Thus for the case where $n_1 = n_2$ (*e.g.*, the stepwise reduction of oxygen), $\tau_2/\tau_1 = 3$.

After the first transition time, part of the constant current is due to the reduction of the product of the first step and part to the reduction of the original material which continues to diffuse to the electrode surface. In the special case where the product of the first step is not itself further reducible (alternate path reduction), the second transition time will be shortened since the only process contributing to the constant current is the $(n_1 + n_2)$ electron reduction of the original material which continues to diffuse to the electrode surface.

An example of such a process is the reduction of benzaldehyde, which is reduced with one electron per benzaldehyde molecule to produce hydrobenzoin in the first step and, at more reducing potentials, is reduced in a two-electron process to benzyl alcohol. The hydrobenzoin is not further reduced.


(2)



(3)

The reduction of benzaldehyde has been studied polarographically by several workers[5-7]. Two waves of equal height are observed in a buffered solution of pH between 3 and 5. Controlled potential electrolysis at a potential on the diffusion current plateau of the first wave, produced only hydrobenzoin. It is interesting to note that the polarographic method cannot distinguish between reductions in which the product of the first step is reducible (normal stepwise reduction) and those in which it is not (alternate path reduction), since both cases produce polarograms with two waves of equal height if $n_1 = n_2$.

The equation relating the transition times for the reduction of a substance by two alternate paths has not been reported as such. However, the relation can be obtained by a simple manipulation of the equation for the transition time in chronopotentiometry with step current impulses which has been derived by TESTA AND REINMUTH[8] and MURRAY AND REILLEY[9].

In the reduction of benzaldehyde, the flux of electroactive material at the electrode surface must satisfy the constant current flowing through the cell. That is,

$$D(\partial C/\partial x)_{x=0} = i_0/nF \tag{4}$$

where D is the diffusion coefficient of the electroactive substance, $(\partial C/\partial x)_{x=0}$ is the concentration gradient at the electrode surface, i_0 is the current density, F is the Faraday and n is the number of Faradays per mole of electrode reaction.

MURRAY AND REILLEY[9] have derived an equation for the transition time obtained when a current step impulse, i_1, is added to i_0 at time t_1. From eqn. (4) it is apparent that changing the flux by adding a current impulse of $-1/2\, i_0$ (*i.e.*, reducing the current to one-half the original value) is exactly equivalent to a change in the electrode reaction which doubles the value of n. That is precisely what occurs at the first transition time when the n-value for the reduction of benzaldehyde changes from one to two.

For step current impulses, the transition time equation is[9]

$$\tau^{\frac{1}{2}} + (i_1/i_0)\,(\tau - t_1)^{\frac{1}{2}} = \tau_u^{\frac{1}{2}} \tag{5}$$

where τ is the transition time finally observed after the current is increased from i_0 to $(i_0 + i_1)$ at t_1 and τ_u is the transition time which would have been observed if the current had not been altered.

For the general case of a change in electrode reaction from a n_1-electron process up to the first transition time to a $(n_1 + n_2)$-process after the first transition time, τ is replaced by $(\tau_1 + \tau_2)$, t_1 and τ_u by τ_1 and (i_1/i_0) by $-n_2/(n_1 + n_2)$*.

Equation (5) becomes,

$$(\tau_1 + \tau_2)^{\frac{1}{2}} - (n_2/(n_1 + n_2))\tau_2^{\frac{1}{2}} = \tau_1^{\frac{1}{2}} \tag{6}$$

---

* From eqn. (4) the flux after changing the n-value from n_1 to $(n_1 + n_2)$ would be $i_0/(n_1 + n_2)\,F$. To obtain the same flux by changing the current instead of the n-value we must have $(i_0 + i_1)/n_1F$ Equating these two fluxes $i_0/(n_1 + n_2)\,F = (i_0 + i_1)/n_1\,F$ or $(i_0 + i_1)/i_0 = n_1/(n_1 + n_2)$; so $i_1/i_0 = (n_1/(n_1+n_2)) - 1 = -\,n_2/(n_1 + n_2)$.

which on rearrangement gives,

$$\frac{\tau_2}{\tau_1} = 4\left(\frac{n_2^2 + n_1 n_2}{n_1^2 + 2n_1 n_2}\right)^2 = 4\left[\frac{\dfrac{n_1}{n_1 + n_2} - 1}{\left(\dfrac{n_1}{n_1 + n_2}\right)^2 - 2\left(\dfrac{n_1}{n_1 + n_2}\right)}\right]^2 \qquad (7)$$

The second form of eqn. (7) emphasizes what the first, simpler form does not, *viz.*, τ_2/τ_1 is a function of the ratio $n_1/(n_1 + n_2)$ and not a function of the absolute values of n_1 and n_2.

For the case of benzaldehyde reduction (alternate path reduction) where $n_1 = n_2 = 1$, $\tau_2/\tau_1 = 16/9$ or 1.78 according to eqn. (7). For the normal stepwise reduction (reducible intermediate) with $n_1 = n_2$, $\tau_2/\tau_1 = 3$ (*cf.* eqn. (1)).

Table 1 summarizes calculated ratios of transition times for various values of n_1 and n_2 for both ordinary two-step reduction (eqn. (1)) and alternate path reduction (eqn. (7)).

TABLE 1

CALCULATED RATIOS OF TRANSITION TIMES

n_1	n_2	$n_1/(n_1 + n_2)$	τ_2/τ_1 *Normal stepwise reduction, eqn. (1)*	τ_2/τ_1 *Alternate path reduction, eqn. (7)*
3 6 etc.	1 2	3/4	7/9 or 0.778	64/225 or 0.284
2 4 etc.	1 2	2/3	5/4 or 1.25	9/16 or 0.562
1 2 etc.	1 2	1/2	3	16/9 or 1.78
1 2 etc.	2 4	1/3	8	144/25 or 5.76
1 2 etc.	3 6	1/4	15	576/49 or 11.76

It is apparent from Table 1 that the two mechanisms produce τ_2/τ_1 ratios which are easily distinguishable for a wide variety of values of n_1 and n_2. The difference in ratios is relatively smaller for large values of the ratio, *i.e.*, when the second transition time is already many times longer than the first, the fact that the product of the first reaction is not reducible makes little difference in the magnitude of the second transition time.

RESULTS

It was found that mercury pool electrodes, amalgamated gold electrodes and mercury film (on platinum) electrodes were unsuitable for this reduction. Usually only the first chronopotentiometric wave was observed and when two waves were obtained, reproducibility was poor. However, with the slow-dropping mercury electrode two waves were always observed and the reproducibility was acceptable.

A typical chronopotentiogram for the reduction of 0.01 M benzaldehyde at the S.D.M.E. is presented in Fig. 1. The supporting electrolyte was a buffer of pH 4 composed of 0.0614 F (formula weight/l) citric acid and 0.0771 F Na_2HPO_4. The chronopotentiogram was started when the drop was 90 sec old.

A solution of pH 4 was found to give the best separation of the waves. In accordance with the known polarographic behaviour of benzaldehyde, the second wave was masked by hydrogen ion reduction in more acidic solutions and the first wave began to merge into the second when the pH became greater than about 5.

The effect of current density on the chronopotentiograms was also studied. Since eqn. (7) pertains only to a planar electrode, the ratio τ_2/τ_1 is not simply 1.78 for data obtained at the spherical S.D.M.E. The proper equation for τ_2/τ_1 can be obtained from the equation for chronopotentiometry with step-current impulses with spherical diffusion (eqn. (40). ref. 9) by the same procedure used to obtain eqn. (7). The result is

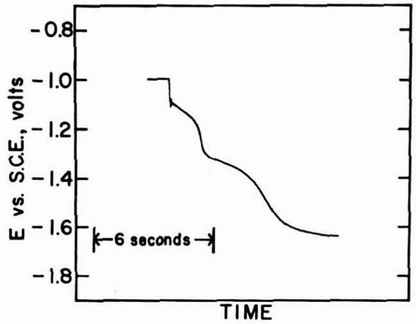


Fig. 1. Typical chronopotentiogram for benzaldehyde reduction at the slow-dropping mercury electrode: 0.01 M benzaldehyde in phosphate–citrate buffer, pH 4; temp., 25.0°; i, 34.05 μA; age of drop at start of chronopotentiogram, 90 sec.

$$\exp\left(\frac{D\tau_1}{r_0^2}\right)\operatorname{erfc}\left(\frac{D^{\frac{1}{2}}\tau_1^{\frac{1}{2}}}{r_0}\right) - \exp\left(\frac{D(\tau_1+\tau_2)}{r_0^2}\right)\operatorname{erfc}\left(\frac{D^{\frac{1}{2}}(\tau_1+\tau_2)^{\frac{1}{2}}}{r_0}\right) + \left(1-\frac{n_1}{n_1+n_2}\right)\exp\left(\frac{D\tau_2}{r_0^2}\right)\operatorname{erfc}\left(\frac{D^{\frac{1}{2}}\tau_2^{\frac{1}{2}}}{r_0}\right) = \left(1-\frac{n_1}{n_1+n_2}\right) \quad (8)$$

where D is the diffusion coefficient and r_0 is the radius of the electrode. For small values of $D^{\frac{1}{2}}\tau^{\frac{1}{2}}/r_0$, $\exp(D\tau/r_0^2)\operatorname{erfc}(D^{\frac{1}{2}}\tau^{\frac{1}{2}}/r_0)$ can be replaced by $1 - 2D^{\frac{1}{2}}\tau^{\frac{1}{2}}/\pi^{\frac{1}{2}}r_0$ and eqn. (8) reduces to eqn. (7).

Table 2 summarizes the results of these measurements. The transition time was taken at the inflection in the potential break. The radius of the electrode was calculated from m, the age of the drop (90 sec), and the density of mercury, assuming the drop to be a perfect sphere. Over the range of transition times studied, the area or the radius of the drop did not change significantly during the course of the electrolysis. The diffusion coefficient of benzaldehyde was estimated to be $8 \cdot 10^{-6}$ cm²/sec. Calculations from the Stokes–Einstein equation[10] for diffusion coefficients of uncharged substances yield a diffusion coefficient at infinite dilution for benzaldehyde of $8.6 \cdot 10^{-6}$ cm²/sec and the infinite dilution diffusion coefficient for the benzoate ion (a structurally similar species) is $7.1 \cdot 10^{-6}$ cm²/sec from conductance data. In any case τ_2/τ_1 from eqn. (8) is not a very sensitive function of D. For example, the ratio by is increased only 3.4% at $\tau_1 = 1$ sec, $r_0 = 0.0387$ cm, for an increase in D from $8 \cdot 10^{-6}$ cm²/sec to $1 \cdot 10^{-5}$ cm²/sec.

The observed and calculated values of τ_2/τ_1 are plotted in Fig. 2. The upper curve

TABLE 2

CHRONOPOTENTIOMETRIC REDUCTION OF BENZALDEHYDE

Measurements made with 0.01 *M* benzaldehyde in phosphate–citrate buffer, pH 4. Temp., 25.0°. Slow-dropping mercury electrode pre-polarized to −1.0 V *vs.* S.C.E. Transition times are averages of two trials; average deviation given in parentheses. τ_2 (calc.) and τ_2/τ_1 (calc.) obtained by solving eqn. (8) for the observed τ_1. $D = 8 \cdot 10^{-6}$ cm²/sec; $r_0 = 0.0387$ cm.

τ_1 *(sec)*	τ_2 *(sec)*	τ_2 *(calc.)* *(sec)*	τ_2/τ_1	τ_2/τ_1 *(calc.)*
1.50*	3.75	3.80	2.50	2.53
1.17 ± 0.02	2.75 ± 0.01	2.84	2.35 ± 0.03	2.43
0.750 ± 0.016	1.75 ± 0.04	1.71	2.33 ± 0.10	2.28
0.464 ± 0.012	1.01 ± 0.01	1.00	2.18 ± 0.08	2.16
0.401 ± 0.004	0.864 ± 0.008	0.856	2.15 ± 0.04	2.13
0.287 ± 0.009	0.620 ± 0.009	0.594	2.16 ± 0.10	2.07
0.202 ± 0.008	0.414 ± 0.009	0.408	2.05 ± 0.13	2.02
0.095 ± 0.002	0.187 ± 0.007	0.184	1.97 ± 0.11	1.94
0.079 ± 0.000	0.154 ± 0.001	0.152	1.95 ± 0.01	1.93
0.038 ± 0.001	0.071 ± 0.000	0.071	1.87 ± 0.05	1.88

* One trial only

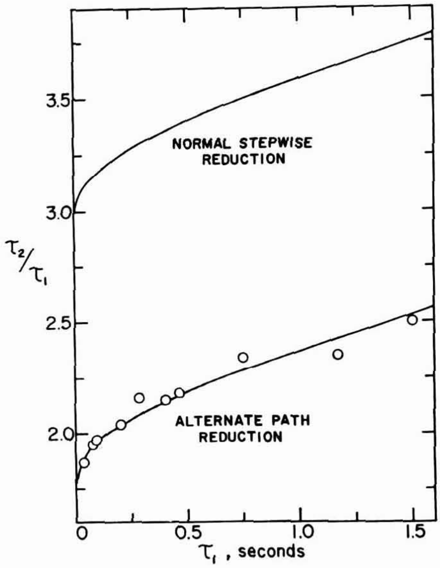


Fig. 2. Ratio of second transition time to first transition time as a function of the first transition time. Upper curve, theoretical curve for normal stepwise reduction; lower curve, theoretical curve for alternate path reduction; circles represent data for benzaldehyde reduction from Table 2. Theoretical curves calculated from eqns. (9) and (8) respectively with $n_1 = n_2$, $D = 8 \cdot 10^{-6}$ cm²/sec and $r_0 = 0.0387$ cm.

represents the theoretical values of the ratio for normal stepwise reduction at a spherical electrode. This equation is

$$\exp\left(\frac{D\tau_1}{r_0^2}\right)\operatorname{erfc}\left(\frac{D^{\frac{1}{2}}\tau_1^{\frac{1}{2}}}{r_0}\right)-\left(\frac{n_1}{n_1+n_2}\right)\exp\left(\frac{D(\tau_1+\tau_2)}{r_0^2}\right)\operatorname{erfc}\left(\frac{D^{\frac{1}{2}}(\tau_1+\tau_2)^{\frac{1}{2}}}{r_0}\right)=\left(1-\frac{n_1}{n_1+n_2}\right)$$

Equation (9) can be derived by means of response function additivity principles[9] or by the von Stackelberg diffusion layer model[11,12]. This equation reduces to eqn. (1) for small values of $D^{\frac{1}{2}}\tau^{\frac{1}{2}}/r_0$.

The data in Table 2 indicate that if benzaldehyde is first reduced to a free radical which then dimerizes to form hydrobenzoin, the half-life of this free radical is very short in this medium. If the free radical had a half-life greater than *ca.* 0.5 sec, τ_2/τ_1 in Table 2 would be expected to increase at short transition times, approaching a value of 3 as the transition time approached zero. This would be due to the fact at short transition times a significant portion of the radical intermediate could be reduced to benzyl alcohol before dimerization. The reaction scheme would then approximate to normal stepwise reduction (reducible intermediate).

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The author wishes to thank Professor JAMES J. LINGANE for helpful discussions as well as the Danforth Foundation and the National Institutes of Health for financial support.

SUMMARY

The theory of alternate path reactions in chronopotentiometry is developed. Alternate path reactions differ from normal stepwise reactions of an electroactive substance in that the product of the first reaction does not react further during the second chronopotentiometric wave. This causes the second wave to be shorter than it is with normal stepwise reactions. The transition time equation for alternate path reactions at both planar and spherical electrodes is derived. The two-step reduction of benzaldehyde at the slow-dropping mercury electrode has been studied as an example of such a process since the product of the first reaction, hydrobenzoin, is not reducible to the product of the second step, benzyl alcohol.

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THE DETECTION OF OXYGEN BY GAS-PHASE POLAROGRAPHY AT LOW TEMPERATURES AND LOW PRESSURES

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INTRODUCTION

The detection of oxygen has been widely accomplished by various electroanalytical and chemical methods. This paper describes an oxygen detector which uses the principle of gas-phase polarography. Oxygen detectors of this type are already known; the particular type discussed here, however, is also capable of operating at low temperatures (to −25°) and low pressures (10 mm Hg). The sensitivity range is from 0.001% to 100% oxygen.

In gas-phase polarography[1], as in conventional solution polarography, the cell contains a polarized micro-electrode and a reversible reference electrode in a suitable electrolyte. In gas-phase polarography, as distinct from conventional polarography, however, the diffusion layer is contained by a membrane which is held taut against the micro-electrode. In the polarographic oxygen detector described here, the gas mixture diffuses through the special semipermeable membrane and dissolves in the electrolyte. Oxygen in the electrolyte is electrochemically reduced at the polarized cathode in the usual polarographic sense. Apart from this membrane-diffusion process, gas-phase polarography is similar to ordinary polarography.

EXPERIMENTAL

Cell construction and assembly

The test cell shown in Fig. 1 is constructed with the use of special glass O-ring seals*. The polarized micro-electrode is a platinum inlay**. Pre-treatment of this electrode is accomplished by electro-reduction for 5–10 sec at 22.5 V d.c. in HCl solution containing a small amount of detergent. The reference electrode is of silver–silver chloride, made from silver wire wound spirally around the platinum-inlay electrode. The membrane is 0.5-mil Teflon***. The electrolytes are prepared with certified reagent-grade chemicals. Saturated KCl was used for the first part of the investigations, but for work at −25°, an alcoholic solution of potassium chloride is necessary. This solution consists of (by weight) 24% methanol, 5% KCl, and 71% H_2O; a phosphate buffer is added to maintain the pH at 6. The screen is an electroformed grid made of 40-mesh stainless steel †.

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* From Konte's Glass Co., Vineland, N.J.

** Beckman Electrode Catalog No. 39273.

*** E. I. Du Pont and Co., Wilmington, Delaware.

† Jelliff Co., Baltimore, Md.

The cell is assembled as follows.

1. The membrane and screen are set between glass O-ring connectors, using Viton-O-rings.
2. The cell container is half-filled with electrolyte and N_2 is bubbled through the cell for 10 min to eliminate oxygen in the electrolyte.
3. The electrodes are fixed in a rubber stopper and, after pre-treatment, inserted into a cell so that the platinum micro-electrode is pressed firmly against the membrane.
4. The cell is now ready for calibration. The test gases are nitrogen*, air, and calibrated mixtures of 1%, 0.1%, and 0.001% oxygen in prepurified nitrogen**.

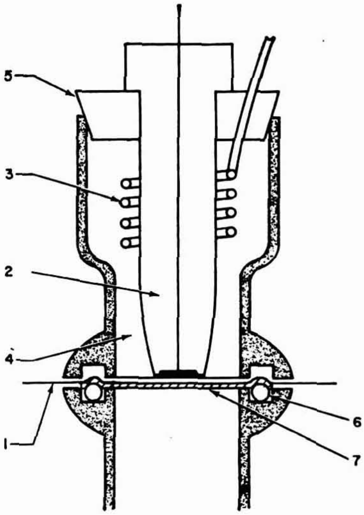

Fig. 1. Diagram of cell.
1, 0.5-mil Teflon membrane; 2, platinum inlay electrode; 3, silver–silver chloride reference electrode; 4, electrolyte; 5, Neoprene stopper; 6, Viton-O-ring; 7, screen.

Polarographic measurements

Polarographic measurements were made with a Leeds and Northrup Electrochemograph or a Fisher Scientific Co. Elecdropode. Because measurements are made in unstirred solutions, there should be a 2-min interval after the desired potential is applied to the cell before the current data are taken. For low oxygen concentrations which give very low current outputs, a circuit was devised consisting essentially of an ordinary dry cell with a voltage divider for applying potential and a galvanometer*** with a sensitivity of 0.0004 μA/div for current measurement. The schematic diagram is shown in Fig. 2.

Membrane study

The method of gas-phase polarography requires that the semi-permeable membrane be stretched tightly across the platinum electrode surface so that only a thin film of

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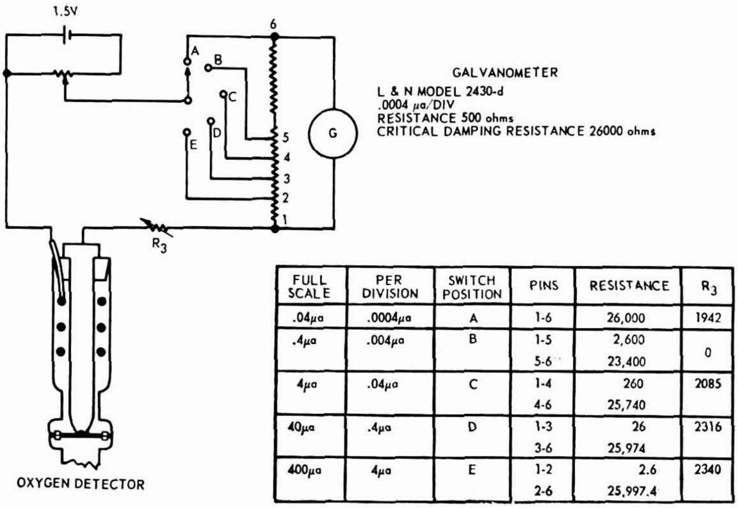
* Seaford grade.

** The Matheson Company, Inc., East Rutherford, New Jersey.

*** Leeds and Northrup No. 2430-d.

electrolyte separates the electrode from the interstices of the membrane. Diffusion of the gas containing molecular oxygen takes place through the membrane to the electrolyte. The significant properties of the membrane are: high oxygen permeability; insignificant porosity; high and low temperature stability; and physical strength.

High oxygen permeability is obviously desirable in order to achieve maximum sensitivity. The membrane must be permeable to oxygen, but not so porous that the electrolyte leaks out. There is therefore a fine distinction between permeability and porosity, and it is difficult to determine the optimum conditions. In the experiments, however, this becomes obvious.



FULL SCALE	PER DIVISION	SWITCH POSITION	PINS	RESISTANCE	R_3
.04μa	.0004μa	A	1-6	26,000	1942
.4μa	.004μa	B	1-5 5-6	2,600 23,400	0
4μa	.04μa	C	1-4 4-6	260 25,740	2085
40μa	.4μa	D	1-3 3-6	26 25,974	2316
400μa	4μa	E	1-2 2-6	2.6 25,997.4	2340

Fig. 2. Circuit diagram.

The membrane is required to maintain its characteristic permeability unimpaired at low temperatures (to —25°). Also, with respect to the particular application, the membrane must be capable of withstanding a temperature of 145° for 24 h.

Good physical strength, including burst and tear strength characteristics, is important because when the oxygen detector is operating al low pressures, the membrane must support a pressure difference greater than 750 mm.

A membrane with the specific characteristic of high oxygen permeability had to be chosen from the many commercially available materials. More than 60 types were tested, including polyethylene from Du Pont, Dow, and Visking Corp.; Teflon from Du Pont; silicone rubber from Norris Manufacturing Co. and Materials Testing, Inc.; cellophane, gum rubber, various silicone-coated fabrics, Saran, fibrous mixtures, "microporous" membranes, nylon, neoprene, Visqueen, Trycite, Trithene, Tedlar, and cellulose acetate from various manufacturers. Three of these, *viz.* polyethylene, Teflon, and silicone rubber, have the desired properties; and the tests confirmed results reported in the literature[2]. A high sensitivity is required, and because permeability is approximately a linear function of membrane thickness, only very thin membranes were used.

A polyethylene membrane (0.001 in. thick) proved to be too weak structurally. The results obtained using silicone rubber were not reproducible results[3]; this was attributed to its slow attack by KCl.

Teflon, in the form of a 0.5-mil thick membrane, has sufficient strength and oxygen permeability and the desired temperature characteristics.

RESULTS AND DISCUSSION

The reduction of oxygen at a micro-electrode in neutral solution takes place according to the following reaction:

$$\frac{1}{2}\,O_2 + H_2O + 2\,e \rightarrow 2\,OH^-$$

The half-wave potential *vs.* a saturated calomel electrode is reported to occur at 0.16 to 0.20 V, in solution, and the reduction wave is independent of pH for a pre-reduced or unconditioned electrode[4].

A polarographic wave, using the 0.5-mil Teflon membrane with saturated KCl electrolyte under atmospheric pressure and at room temperature, is shown in Fig. 3. The half-wave potential is 0.16 V and the diffusion current 15.0 μA for this typical gas-polarographic oxygen wave. From this starting point, the use of the polarographic oxygen detector was extended to the regions of low pressure and low temperature. Experiments were conducted to measure oxygen concentrations in gases at pressures down to 10 mm Hg and/or at temperatures as low as $-25°$.

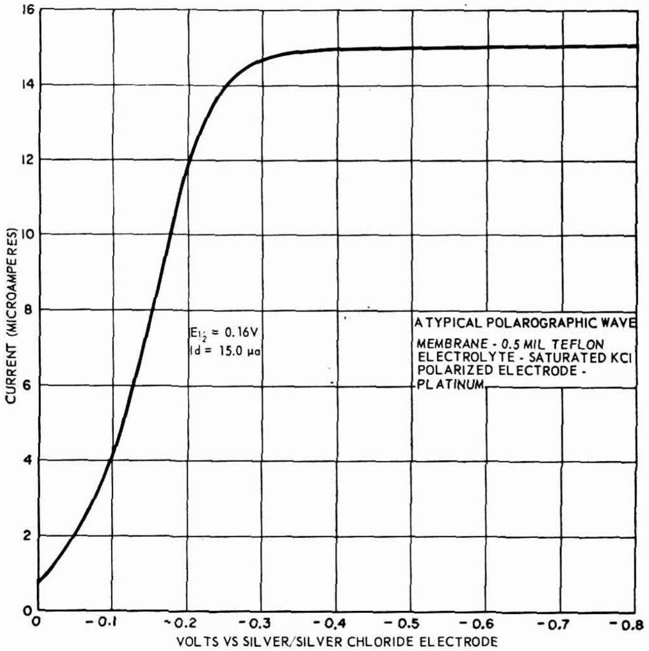


Fig. 3. Typical polarographic wave.

For low-pressure application, a screen was inserted beneath the membrane to prevent it from bulging outward and tearing. The screen was fabricated by electroforming techniques to avoid rough edges which might tear the membrane. The Teflon membrane has good tear and burst strength, even at the 0.5-mil thickness.

The diffusion-limited current, under atmospheric pressure and at room temperature, was always in the range −0.6 to −0.8 V, applied between the silver–silver chloride reversible electrode and the platinum-inlay electrode. It was therefore decided to work in this range during the entire experimental program.

Experiments that indicate sensitivities at low concentrations are shown in Fig. 4, but because Seaford nitrogen and pre-purified grades of nitrogen contain less than 0.002% oxygen as impurity there are difficulties in obtaining a suitable current

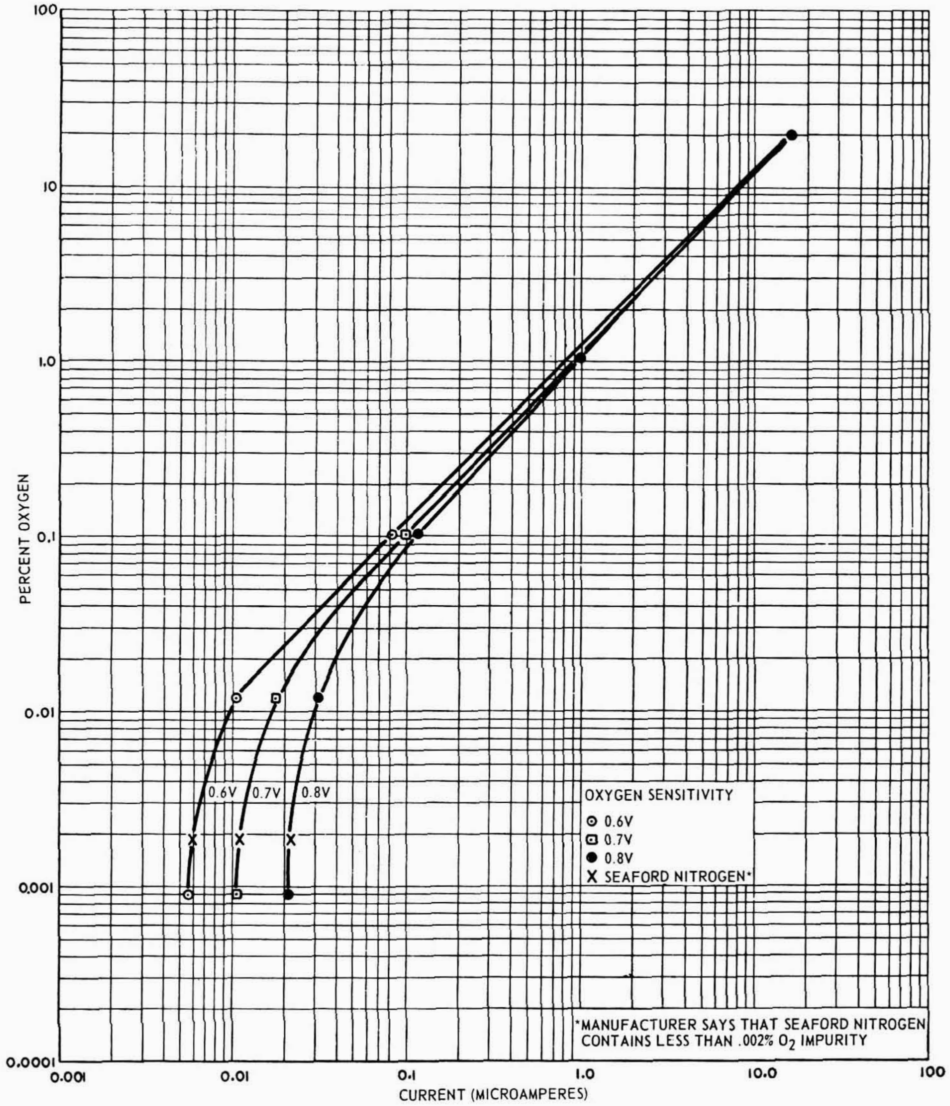


Fig. 4. Sensitivity.

background*. It can be seen from Fig. 4, that the sensitivity changes slightly on changing from 0.6 to 0.8 V. The current readings, however, are linear down to 0.01% oxygen but at this concentration slight deviations occur. Mixtures were used for these experiments and thus, it was possible to estimate the oxygen concentrations in the Seaford nitrogen gas from the calibration curve of the detector.

For O_2 determinations in which the temperature of the gas is below the freezing point of ordinary aqueous electrolytes such as KCl solutions, the composition of the electrolyte must be modified. This problem was given considerable attention. Polarography of dissolved gases was carried out using $CaCl_2$ and LiCl in absolute alcohols[5]. Various salt–solvent mixtures were investigated including KCl–glycol, KCl–glycol–water, LiCl–glycol–water, LiCl–methanol, LiCl–methanol–water, $CaCl_2$–methanol–water, KCl–methanol–water and KCl–ethanol–water. A mixture which was found to be suitable, consists (by weight) of 24% methanol, 71% water, and 5% KCl. The freezing point of this mixture is approximately −27°. Figure 5 shows the results of determinations of the gaseous oxygen mixture at 26°, 0°, and −20°. It can be seen that there is a reduction in sensitivity; even with this reduction, however, a distinguishable current measurement is observed at the low temperature.

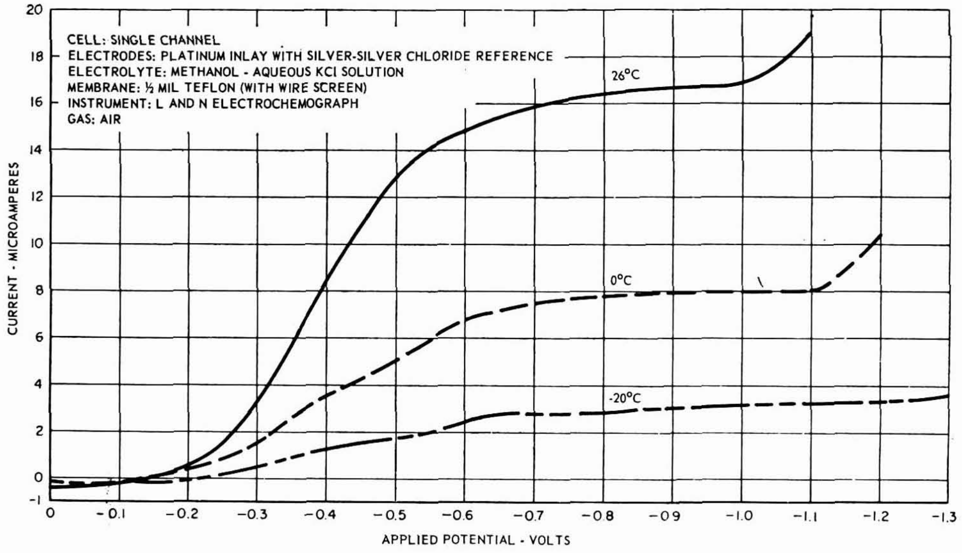


Fig. 5. Temperature sensitivity.

Although the oxygen detector is capable of working at low temperatures, the variation in temperature while monitoring must be considered. To reduce the effects caused by temperature variation, a thermistor circuit can be employed[6].

The sensitivity at low pressures is determined by filling the sample chamber with the desired gas concentration and evacuating to the desired pressure. Current readings were observed at a pressure as low as 1 mm of Hg but, in this lower-pressure range, the readings were not reliable. Figure 6 gives the results obtained at low pressures. A linear relationship is observed over the range of 1–76 mm Hg. The data were ob-

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* < 0.002 % O_2: manufacturer's specifications.

tained by proceeding from vacuum to increased pressure, and then from pressure to vacuum. In this way, any possible hysteresis effects would have been operative, but none has been observed. These results are significant because the electrolyte and inner parts of the cell were under 1 atm of pressure, while the outer side of the membrane was subjected to the reduced pressures.

Certain interferences were studied. Nitrogen and argon, as expected had no effect. One per-cent of CO_2 in nitrogen had a slight effect, but 0.1% of CO_2 caused no deviation. The effect of ozone was also investigated. Ozone was generated by an apparatus similar to that described by Hughes[7]. Only a comparatively large concentration of ozone (0.1%) could be detected, and this affected the readings only slightly.

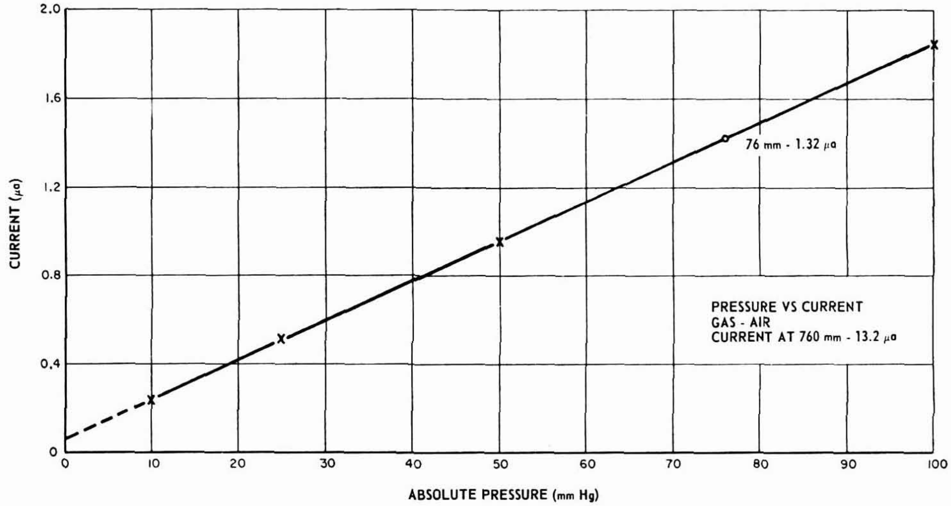

Fig. 6. Sensitivity at low pressure.

ACKNOWLEDGEMENTS

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SUMMARY

An oxygen detector based on gas phase polarography is described. Utilizing a buffered alcoholic solution of KCl as electrolyte, the detector is capable of operating at low temperature (−25°). The detector has a sensitivity range of 0.001% to 100% oxygen and can operate to pressures as low as 10 mm Hg. A 0.5-mil thick Teflon membrane was selected as the most suitable membrane after testing more than 60 types of commercially available materials. Possible interferences from N_2, A, CO_2 and O_3 were investigated.

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A POLAROGRAPHIC STUDY OF IRON(III)-NITRILOTRIACETIC ACID COMPLEX*

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INTRODUCTION

Complexes of some metals such as cadmium, lead(II) and manganese (II) with nitrilotriacetic acid (NTA) have been studied polarographically by KORYTA and his coworkers[1-6] and kinetics of their electrode processes in polarography reported. SCHWARZENBACH[7] found the iron(III)–NTA complex to be a 1 : 1 chelate complex (FeX, where X = NTA) and determined its stability constant ($\log K = 15.87 \pm 0.2$ at 20°). The object of this work was to study the polarography of the iron(III)–NTA complex in the presence of excess NTA, in acetate buffer solution ($\mu = 0.1$) and to describe the kinetics of its electrode process. The formation constant of K_{FeX} was also determined.

EXPERIMENTAL

Materials

Reagent-grade chemicals and Dotite's extra pure nitrilotriacetic acid were used without further purification. Iron(III) stock solution was prepared by dissolving iron(III) perchlorate in distilled water and was standardized gravimetrically. The concentration of the stock solution was 2.51×10^{-2} *M*. Nitrilotriacetic acid was dried at 80°, cooled over $CaCl_2$ in a desiccator, weighed precisely, suspended in water, neutralized with sodium hydroxide solution and diluted with water to 1 l. The concentration of the NTA stock solution was 0.1 *M*. Acetate buffer (CH_3CO_2H–CH_3CO_2Na) was used to adjust the pH of solutions within the range 4.0–6.2. Ionic strengths were adjusted appropriately with sodium perchlorate.

Apparatus

Polarograms were recorded using a Yanagimoto pen-recording polarograph P.A. 102-type. An H-type cell was used in a thermostat at 25.0 ± 0.1°. The capillary used had the following characteristics: $m = 0.809$ mg sec^{-1} at a height of 67.95 cm (corr.) Hg, drop time $t = 4.0$ and 3.2 sec at applied potentials of -0.20 V and -1.45 V *vs.* S.C.E., respectively. All potentials were corrected and referred to the saturated calomel electrode. A Hitachi glass electrode pH-meter EHM-1 type was used to measure pH .

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[*] Presented at the 9th Symposium on Polarography of the Chemical Society of Japan, Kyoto, Japan, October 27th, 1962.

Procedure

To a solution of iron containing an appropriate quantity of nitrilotriacetic acid, acetic acid–sodium acetate buffer was added to adjust the pH to the required value. Sodium perchlorate was also added to maintain an ionic strength (μ) of 0.1. The solution was prepared at 25.0 ± 0.1° and dissolved oxygen was removed by passing purified nitrogen gas through the solution for at least 20 min before the polarogram was recorded.

RESULTS AND DISCUSSION

Typical polarograms of iron–NTA complex ions in acetate buffer solutions are shown in Fig. 1.

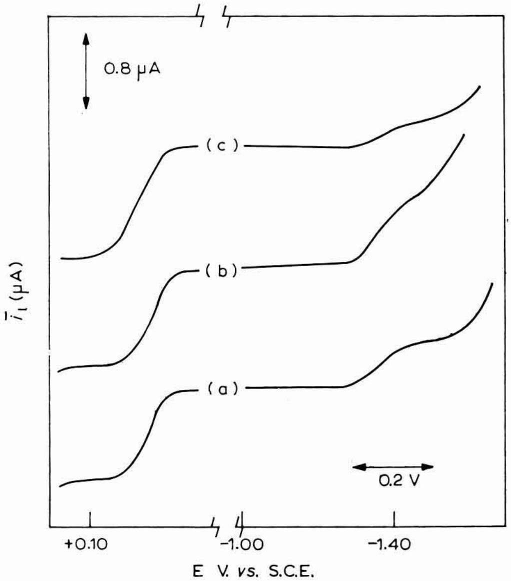

Fig. 1. Polarograms of Fe(III)–NTA complex in acetate buffer solution. 0.40 mM Fe^{3+}, 1 mM NTA, μ = 0.1 ($NaClO_4$). pH: (a), 5.40; (b), 5.50; (c), 5.70.

The two-stepped kinetic waves were obtained in the presence of an excess of NTA. The first wave is due to the reversible reduction of iron(III) ion dissociated from the FeX complex, and the second wave to the irreversible reduction of iron(II) hydrogen NTA complex, FeHX. The reversibility of the electrode process was verified by plotting log $\bar{i}/(\bar{i}_1 - \bar{i})$ *vs.* E. From the wave slope, the number of electrons, n, associated with the electrode reaction for the first wave was found to be 1 and for the second wave to be about 2 ($\alpha = 0.5$). It can be seen in Fig. 1, that the limiting current of the first wave increases and that of the second wave decreases with increasing pH.

From the relationship of the limiting currents of the first and second waves to the pressure of dropping mercury, it was calculated that the limiting currents were not proportional to the square roots of the heights of the mercury columns and that the product of the limiting current and the square root of the drop time for the first or the second wave was not constant but varied with the limiting current[8] as shown in Fig. 2. Accordingly, the limiting currents of the first and the second waves were shown to be kinetic above pH 4.1.

The effect of variation in pH on the first wave, the electrode process of which was

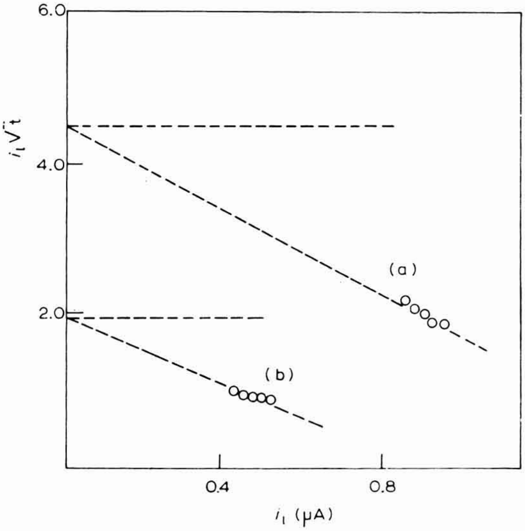

Fig. 2. Relation between the wave height and t. 0.4 mM Fe^{3+}, 1 mM NTA, pH 5.70, μ = 0.1 ($NaClO_4$). (a), the first wave; (b), the second wave.

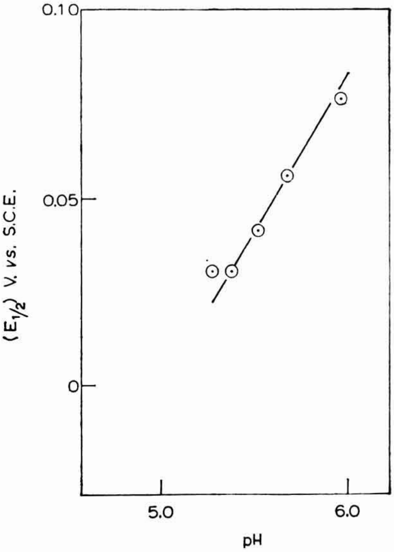

Fig. 3. Effects of pH on the half-wave potential of the first wave. 0.40 mM Fe^{3+}, 1 mM NTA, CH_3COOH–CH_3COONa buffer, μ = 0.1 ($NaClO_4$), $\left\{\frac{\partial (E_{\frac{1}{2}})_1}{\partial \text{pH}}\right\}_{[\text{NTA}]} = -0.062$ V *vs.* S.C.E.

reversible, are shown in Figs. 3 and 4. The half-wave potential of the first wave $(E_{\frac{1}{2}})_1$, shifted always to more negative values with increasing pH. That is,

$$(\partial(E_{\frac{1}{2}})_1/\partial \mathrm{pH})_{(C_X)} = -0.062 \text{ V } vs. \text{ S.C.E.}$$

was obtained in acetate buffer solution (see Fig. 3).

This showed that one proton took part in the electrode reaction and that the predominant species of NTA is HX^{2-} ion in the pH range 4.0–6.0 although iron(III)–NTA complex contains X^{3-} ion. The limiting current of the first wave $\bar{i}_{l_1}$ increased above pH 5.0 and that of the second wave $\bar{i}_{l_2}$ decreased above pH 4.8 (see Fig. 4).

The effect on the first wave changes in NTA concentration between $5 \cdot 10^{-4}$ M to $1 \cdot 10^{-3}$ M are shown in Figs. 5 and 6.

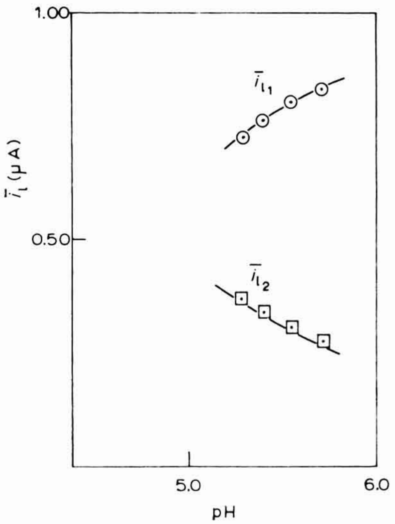

Fig. 4. Effects of pH on the limiting current. 0.40 mM Fe^{3+}, 1 mM NTA, CH_3COOH–CH_3COONa buffer, $\mu = 0.1$ ($NaClO_4$).

The half-wave potential of the first wave $(E_{\frac{1}{2}})_1$ shifted to a more negative value with increasing NTA concentration, in acetate buffer solution. That is,

$$(\partial(E_{\frac{1}{2}})_1/\partial \log C_X)_{[H^+]} = -0.055 \text{ V } vs. \text{ S.C.E.}$$

was obtained, which showed that one molecule of NTA would be contained in an iron–NTA complex ion. The limiting current of the first wave $\bar{i}_{l_1}$ was almost constant and that of the second wave $\bar{i}_{l_2}$ decreased with increasing concentration of NTA (see Fig. 6).

Iron ion usually forms a weak complex with acetate ion and it was observed that above an acetate concentration of 0.07 M, the half-wave potential began to shift to a more negative value; this shift resulted from the formation of a weak acetate complex ion in acetate buffer, in which the electrode process was still reversible. It is therefore necessary to consider the concentrations of both ligands, acetate and

NTA, in the kinetic current equation and moreover to use the fact that the iron complex with NTA is a 1 : 1 chelate complex as reported by SCHWARZENBACH[7].

The first wave is reversible and corresponds to the reduction of iron(III) aquo ion which is dissociated from a 1 : 1 iron–NTA complex in equilibrium with a weak acetate complex ion. Thus, the rate-determining step of this electrode process would be due to the following dissociation of an iron(III)–NTA complex.

$$\mathrm{FeX} \underset{k^-}{\overset{k^+}{\rightleftharpoons}} \mathrm{Fe^{3+}} + \mathrm{X^{3-}}$$

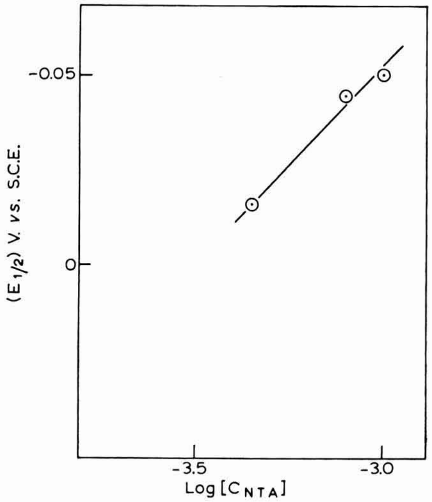

Fig. 5. Relation between the half-wave potential of the first wave and NTA concn. 0.40 mM Fe^{3+}, pH 5.70, μ = 0.1 (NaClO$_4$), $(\partial(E_{\frac{1}{2}})_1/\partial \log C_{\mathrm{NTA}})_{[\mathrm{H}^+]} = -0.055$ V *vs.* S.C.E.

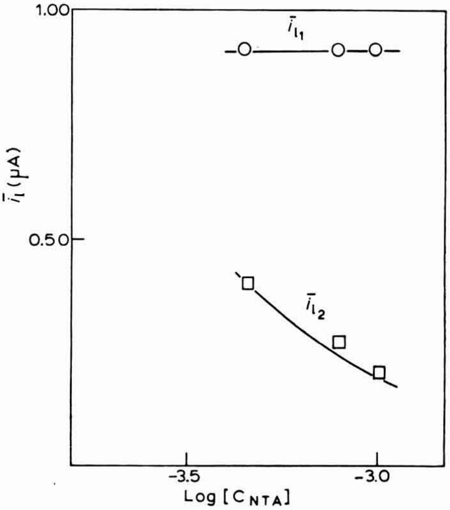

Fig. 6. Effects of change in NTA concn. on the limiting currents. 0.40 mM Fe^{3+}, pH 5.70, μ = 0.1 (NaClO$_4$).

where X^{3-} denotes the nitrilotriacetate anion which combines rapidly with a proton to give HX^{2-} which is predominant in the pH range 4.0–9.0 ($\mathrm{H^+ + X^{3-} \rightarrow HX^{2-}}$). If the equilibrium concentration of iron acetate complex is comparable to the total concentration of iron aquo ion, where this weak complex is in a complete mobile equilibrium with iron–NTA complex, from KORYTA's equation[3] the half-wave potential is given by

$$(E_{\frac{1}{2}})_c = E_0 + \frac{RT}{2F} \ln (D_{\mathrm{ox}}/D_{\mathrm{red}}) - \frac{RT}{F} \ln \left\{ \sum_{j=0}^{n} k_0 \ldots k_j[\mathrm{X}]^j + \sum_{j=1}^{p} k_1' \ldots k_j'[\mathrm{Y}]^j \right\} + \frac{RT}{F} \ln \frac{\bar{i}_d}{\bar{i}_1} \quad (1)$$

where [X] is the concentration of the complexing agent NTA, [Y] the concentration of the second ligand acetate, $\bar{i}_d$ and $\bar{i}_1$ the limiting currents without and with NTA ion respectively in acetate buffer solution, D the diffusion coefficient and k_j the consecutive formation constant. Assuming the diffusion coefficient of oxidant to be equal to that of reductant, the half-wave potential of iron ion in acetate buffer solution is almost equal to E^0. That is,

$$(E_{\frac{1}{2}})_{\mathrm{Fe}} = E_0 + \frac{RT}{2F} \ln (D_{\mathrm{ox}}/D_{\mathrm{red}}) \approx E^0$$

so that, from eqn. (1)

$$(E_{\frac{1}{2}})_c = (E_{\frac{1}{2}})_{\mathrm{Fe}} - \frac{RT}{F} \left\{ \sum_{j=o}^{n} k_0 \ldots . k_j[\mathrm{X}]^j + \sum_{j=1}^{p} k_1' \ldots . k_j'[\mathrm{Y}]^j \right\} + \frac{RT}{F} \ln \frac{\bar{i}_d}{\bar{i}_l} \qquad (2)$$

is obtained. The half-wave potential of iron ion in acetate buffer solution is given by eqn. (3),

$$(E_{\frac{1}{2}})_{\mathrm{Fe}} = E^0 - \frac{RT}{nF} \ln \left\{ \sum_{j=o}^{p} k_0' \ldots . k_j'[\mathrm{Y}]^j \right\} \qquad (3)$$

By substituting in eqn. (3) the values $n = 1$, the half-wave potential of iron(III) ion in acetate buffer solution $(E_{\frac{1}{2}})_{\mathrm{Fe,OAc}} = +0.015$ V *vs.* S.C.E. $= +0.261$ V *vs.* N.H.E.; and the standard oxidation potential $E^0 = +0.74$ V *vs.* N.H.E. ($\mathrm{Fe}^{3+} + e \rightleftharpoons \mathrm{Fe}^{2+}$),

$$\sum_{j=o}^{p} k_0' \ldots . k_j'[\mathrm{Y}]^j = 10^{8.10}$$

is obtained.

The diffusion current of iron(III) ion in acetate buffer solution without NTA, $\bar{i}_d$, is equal to 0.66 μA. HX^{2-} ion is predominant in the pH range 4.0–6.0 as described above but the complex ion contains X^{3-} ion. The formation constant of the iron(III)–NTA complex is expressed as $K_{\mathrm{FeX}} = [\mathrm{FeX}]/([\mathrm{Fe}^{3+}] \cdot [\mathrm{X}^{3-}])$, ($\mathrm{Fe}^{3+} + \mathrm{X}^{3-} \rightleftharpoons \mathrm{FeX}$) and the third dissociation constant of NTA, $k_3 = [\mathrm{X}^{3-}] \cdot [\mathrm{H}^+]/[\mathrm{HX}^{2-}]$ at 20° ($\mu = 0.1$) is $10^{-9.73}$ ($pk_3 = 9.73$), therefore

$$[\mathrm{X}^{3-}] = k_3 \cdot [\mathrm{HX}^{2-}]/[\mathrm{H}^+]$$

and

$$[\mathrm{FeX}]/[\mathrm{Fe}^{3+}] = K_{\mathrm{FeX}} \cdot k_3 \cdot [\mathrm{HX}^{2-}]/[\mathrm{H}^+]$$

are obtained. Accordingly, from eqn. (2) we can obtain,

$$(E_{\frac{1}{2}})_c = (E_{\frac{1}{2}})_{\mathrm{Fe}} - 0.0591 \log \left\{ K_{\mathrm{FeX}} \cdot [\mathrm{HX}^{2-}] \cdot k_3/[\mathrm{H}^+] + 10^{8.10} \right\} + 0.0591 \log \frac{\bar{i}_d}{\bar{i}_l} \qquad (4)$$

By substituting the known values of $[\mathrm{X}^{3-}]$, $(E_{\frac{1}{2}})_c$, $(E_{\frac{1}{2}})_{\mathrm{Fe}}$ and $\log \bar{i}_d/\bar{i}_l$ in eqn. (4), the formation constant of iron(III)–NTA complex could be calculated, as shown in Table 1. The mean value of the formation constant is given by $\log K_{\mathrm{FeX}} = 16.01$ (25°) which is a little larger than that obtained by SCHWARZENBACH AND HELLER[7] ($\log K_{\mathrm{FeX}} = 15.87$, at 20°).

The second wave is irreversible and corresponds to a 2-electron change. The limiting current decreased with increasing pH and increasing concentration of NTA. The dependence of the current on pH, concentration of NTA and potential is explained by using the rate constant g of the reduction. The current is controlled by the rate of the irreversible electron transfer reaction and also at the same time by the formation of a hydrogen complex. The value of g is constant at a certain potential and pH at various concentrations of NTA, so that the reducible complex has one NTA ion like the ligand. According to KORYTA[4], the value of g is obtained from the following equation,

$$\frac{g}{\sqrt{D}}\sqrt{t_1} = \frac{1}{\gamma}\cdot\frac{\bar{i}}{\bar{i}_d - \bar{i}} - \frac{1}{\gamma'}\cdot\frac{\bar{i}_1}{\bar{i}_d - \bar{i}_1}$$

where γ is a constant ($= 0.886$), t_1 the drop time and γ' a similar constant to γ concerning the value of $\bar{i}_1/(\bar{i}_d - \bar{i}_1)$.

In Fig. 7 are plotted the values of log $(g/\sqrt{D})$ *vs.* log $[H^+]$, *i.e.*, the dependence of the rate constant of the reducible complex in acetate buffer solution on the concentration of hydrogen ion, is shown. The values of $g/\sqrt{D}$ were calculated by assuming $\gamma = \gamma'$ ($=0.886$) and by using $\bar{i}/(\bar{i}_d - \bar{i}) = 1.78$, obtained from the eqn. $E = (E_{\frac{1}{2}})_{Fe} - (0.0591/\alpha n) \log \bar{i}/(\bar{i}_d - \bar{i})$ for $E - (E_{\frac{1}{2}})_{Fe} = -15$ mV and $t_1 = 3.2$ sec.

TABLE 1

FORMATION CONSTANT OF IRON–NTA COMPLEX

$[X]$ (M)	$(E_{\frac{1}{2}})_c - (E_{\frac{1}{2}})_{Fe}$	$\log \bar{i}_d/\bar{i}_1$	$\log K_{FeX}$
$5 \cdot 10^{-4}$	-0.526	-0.145	16.01
$8 \cdot 10^{-4}$	-0.538	-0.145	16.05
$1 \cdot 10^{-3}$	-0.540	-0.140	15.98

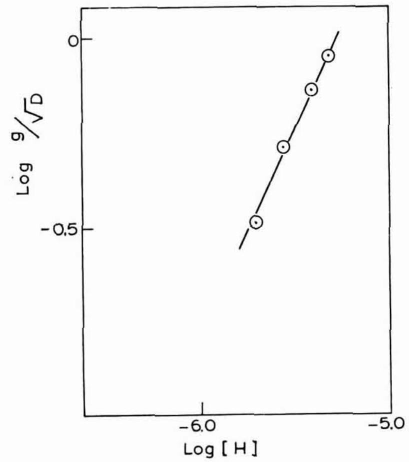

Fig. 7. Relation between the rate constant g and the hydrogen ion concn.; $E - (E_{\frac{1}{2}})_{Fe} = -15$ mV

It can be seen in Fig. 7, that the value of g decreases with increasing pH and $\partial \log g/\partial$ pH was found to be approximately equal to -1 (at pH > 5.2). This relation means that the value of g depends on the concentration of hydrogen ion and that the reducible complex is an hydrogen complex, Fe(II)HX, in acetate buffer solution. The formation constant of this iron(II) hydrogen complex is given by $K^{H}_{FeHX} = [FeHX]/$

($[\mathrm{FeX^-}]\cdot[\mathrm{H^+}]$) which is unknown and presumed to be extremely small. $K^{\mathrm{H}}_{\mathrm{FeHX}} \ll 1$, $\mathrm{FeX^-} + \mathrm{H^+} \rightleftharpoons \mathrm{FeHX}$.

Therefore, $K^{\mathrm{H}}_{\mathrm{FeHX}} \cdot [\mathrm{H^+}] = [\mathrm{FeHX}]/[\mathrm{FeX^-}]$.

Assuming only one complex ion to be formed by acetate ion,

$$g_1 = g_{1(0)} \exp\left[-\frac{\alpha n F(E - E^0)}{RT}\right] \tag{5}$$

is obtained, where $g_{1(0)}$ is a constant and E^0 the standard potential of iron ion.

Then according to KORYTA's equation[4], if $K^{\mathrm{H}}_{\mathrm{FeHX}} \ll 1$ is assumed, the rate constant g of the complex with NTA(X) and proton ($\mathrm{H^+}$) would also be given by eqn. (6).

$$g = g_{0(0)} + g_1 K^{\mathrm{H}}_{\mathrm{FeHX}} \cdot [\mathrm{H^+}] \tag{6}$$

where

$$g_{0(0)} = 0.$$

Hence, we can obtain eqn. (7)

$$g = g_{1(0)} K^{\mathrm{H}}_{\mathrm{FeHX}} \cdot [\mathrm{H^+}] \exp\left[-\frac{\alpha n F(E - E^0)}{RT}\right] \tag{7}$$

i.e., the value of g is shown to be an exponential function of potential where α is 0.5. By substituting this value of α and $n = 2$ in this equation, the logarithm of g is given by

$$\log g = \log g_{1(0)} + \log K^{\mathrm{H}}_{\mathrm{FeHX}} - \mathrm{pH} - \frac{(E - E^0)}{0.0591} \tag{8}$$

Therefore

$$\partial \log g/\partial\, \mathrm{pH} = -1 \tag{9}$$

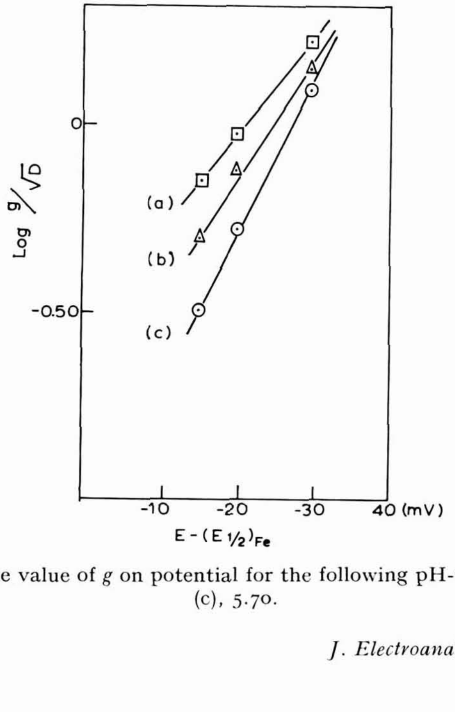

Fig. 8. Dependence of the value of g on potential for the following pH-values: (a), 5.30; (b), 5.50; (c), 5.70.

is obtained. As this value (eqn. 9) coincides with the approximate experimental value shown in Fig. 7, it is an indication that the reducible complex is the iron(II) hydrogen complex, FeHX, and the rate constant g decreases with increasing pH.

The relation between the value of $g/\sqrt{D}$ and potential for various pH-values are plotted in Fig. 8, using E_0 as the half-wave potential.

It can be concluded that the kinetic electrode process of the reduction of iron(III) complex with NTA in acetate buffer solution at a dropping mercury electrode is expressed in the following way at pH-values between 4.1 and 6.0.

Iron(III) ion dissociated from an iron(III)–NTA complex, Fe(III)X, is reduced reversibly in an equilibrium of iron acetate ion and then iron(II) hydrogen NTA complex, FeHX, formed by Fe(II)X ion taking one proton, is reduced irreversibly.

It is very interesting to note that below pH 4.1 the electrode process seems to approach gradually, with decreasing pH, to the diffusion-controlled system because of the faster dissociation of iron(III)–NTA complex ion in acetate buffer solution.

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SUMMARY

A two-stepped kinetic wave was obtained above pH 4.1 in the reduction of an iron(III)–NTA complex in the presence of excess NTA in acetate buffer solution. The electrode process of the first wave which was controlled by the rate of dissociation of Fe(III)X complex, was reversible and represented a 1-electron change; the formation constant, K_{FeX}, was calculated to be $10^{16.01}$. The second wave was also kinetic and its electrode process was irreversible and represented a 2-electron change. A relation between the rate constant, g, of the electron transfer reaction, and potential was deduced and it was found that the Fe(II)HX complex would be reduced directly.

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THE POLAROGRAPHY OF THE NICKEL(II)-ETHYLENEDIAMINE SYSTEM*

STUDY OF THE ETHYLENEDIAMINE CATALYTIC HYDROGEN WAVE

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INTRODUCTION

The polarographic reduction of Ni(II) at pH 7 in the presence of small quantities of ethylenediamine has been reported to exhibit a catalytic wave before the main free metal ion, $Ni(H_2O)_6{}^{2+}$, wave; this is probably the result of the reduction of a nickel–ethylenediamine complex[1,2]. It has been suggested that this pre-wave could be employed for the polarographic analysis of 10^{-3}–10^{-5} *M* ethylenediamine. Studies of nickel(II)-ethylenediamine solutions at pH 5 have revealed a new wave which occurs, in this case, after the main free metal ion wave. This post-wave, which was not observed at pH 7, is probably a catalytic hydrogen wave[3,4] resulting from the reduction of hydrogen ion associated in some way with ethylenediamine. Aliphatic amines apparently are not reduced at a dropping-mercury electrode (D.M.E.), but catalytic hydrogen waves are usually observed[3,4]. Similar waves have also been reported for organic sulfhydryl compounds[5-7].

This paper describes the effect of ethylenediamine and nickel(II) concentration on the characteristics of this catalytic hydrogen wave. The effects of pH are also discussed.

Catalytic hydrogen waves have been successfully employed in the analysis of organic sulfhydryl compounds, such as cysteine[6-11], and, as the catalytic hydrogen waves of ethylenediamine have similar characteristics to those observed for organic sulfhydryl compounds[7,9,10], the feasibility of employing this catalytic current for the determination of trace quantities of ethylenediamine has been investigated.

EXPERIMENTAL

Apparatus

The D.M.E. used in all experiments had a drop time of 3.70 sec at a height of 55.0 cm of mercury in a 0.125 *M* KCl solution with no applied potential .Under these

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conditions the outflow of mercury was 2.18 mg/sec. The electrolysis cell was a standard H-cell which contained a saturated calomel electrode (S.C.E.) used as the reference electrode. This electrode made electrical contact with the sample solution through an agar-agar KCl bridge (the salt bridge was separated from the sample solution by means of a medium sintered-glass frit).

A Sargent Model XV recording polarograph was used.

Preparation of samples

All solutions were prepared with distilled water and with reagent-grade chemicals.

Procedure

The sample solutions were de-aerated in the polarograph cell by bubbling nitrogen gas through the solution for 10 min prior to the determination and a nitrogen atmosphere was maintained over the surface of the sample solution during the actual determination.

Ca^{2+} was added to all sample solutions as a maximum suppressor for the free nickel on background wave[12-14]. The presence of calcium ion had no apparent effect on the shape or magnitude of the catalytic hydrogen wave.

All polarograms in this paper are drawn as the line through the maximum current obtained at the end of drop life. The pH of the solutions was adjusted to 5.00 ± 0.10 prior to each determination and 0.125 M KCl was used as supporting electrolyte. All potentials are reported with respect to the S.C.E. The temperature of the sample solutions was 25.0° ± 0.5°.

RESULTS AND DISCUSSION

The effects of nickel ion concentration, ethylenediamine concentration, and pH on he characteristics of the post-wave were studied in order to establish its catalytic nature and to investigate the possibility of using it as a basis for the determination of small amounts of ethylenediamine.

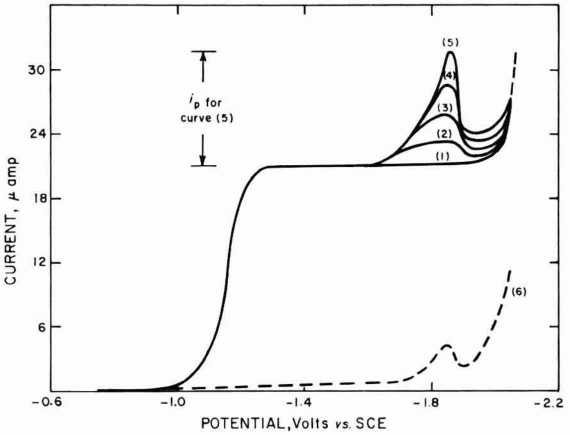

Fig. 1. Polarograms of a 2.5×10^{-3} M Ni^{2+}, 15×10^{-3} M Ca^{2+}, and 0.125 M KCl solution containing he following concentrations of ethylenediamine: (1), 0; (2), 3.0×10^{-5} M; (3), 8.8×10^{-5} M; 4), 15.1×10^{-5} M; (5), 24.0×10^{-5} M; (6), 30.0×10^{-5} M ($[Ni^{2+}] = 0$). Temp. 25 ± 0.5°, pH = 5.00 ± 0.05.

Effect of ethylenediamine and nickel concentrations

The polarograms of a 2.5×10^{-3} *M* Ni^{2+}, 15×10^{-3} *M* Ca^{2+}, and 0.125 *M* KCl solution containing different concentrations of ethylenediamine (0–3.0×10^{-4} *M*) are shown in Fig. 1. The polarograms of the solutions containing ethylenediamine exhibit a small wave on the $Ni(H_2O)_6{}^{2+}$ diffusion-limited plateau. This small wave reaches a maximum current value at about -1.85 V *vs.* S.C.E. and then decreases sharply to return again to a current value corresponding approximately to the $Ni(H_2O)_6{}^{2+}$ diffusion-limited current. The value of this peak current, i_p, (measured from the $Ni(H_2O)_6{}^{2+}$ diffusion limited plateau to the hydrogen wave peak, as indicated in Fig. 1) at -1.85 V increases with increasing ethylenediamine concentration. Curve 6 of Fig. 1 shows the polarogram of a 30×10^{-5} *M* ethylenediamine solution which is similar to the other solutions of Fig. 1 except that Ni^{2+} is absent. The wave appears to be catalytic with respect to ethylenediamine concentration because the peak current for the wave of a 30×10^{-3} *M* ethylenediamine solution is about 11 μA compared to a current of about 2.2 μA to be expected for a diffusion-controlled wave (calculated by means of the Ilkovič equation[15] using $n = 2$, $m = 2.18$ mg sec^{-1}, $t = 2$ sec, and an estimated diffusion coefficient of 5×10^{-6} cm^{2}sec^{-1} which is the value of the diffusion coefficient of similar types of organic compounds[16]). A small current peak is observed at -1.85 V even in the absence of Ni^{2+} ion; however, in this case, i_p is considerably less than that observed in curve 5 ([en] $= 24.0 \times 10^{-5}$ *M*). It appears, therefore, that the wave at -1.85 V is associated with ethylenediamine, and is probably a catalytic hydrogen wave[17] as aliphatic amines are not reduced at the D.M.E.[3,4]. Further evidence that the small post-wave is a hydrogen wave was

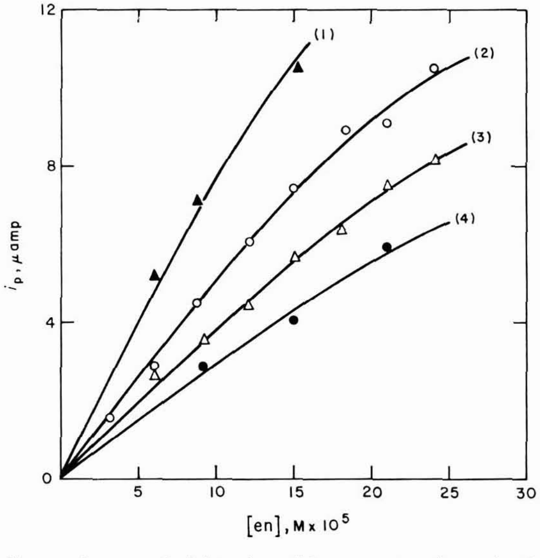

Fig. 2. Variation of the peak wave height, i_p, with concentration of ethylenediamine. Temp. 25 ± 0.5°, pH = 5.00 ± 0.05. (1), $[Ni^{2+}] = 5 \times 10^{-3}$ *M*, $[Ca^{2+}] = 30 \times 10^{-3}$ *M*, [KCl] = 0.125 *M*; (2), $[Ni^{2+}] = 2.5 \times 10^{-3}$ *M*, $[Ca^{2+}] = 15 \times 10^{-3}$ *M*, [KCl] = 0.125 *M*; (3), $[Ni^{2+}] = 1.0 \times 10^{-3}$ *M*, $[Ca^{2+}] = 7.6 \times 10^{-3}$ *M*, [KCl] = 0.125 *M*; (4), $[Ni^{2+}] = 0.50 \times 10^{-3}$ *M*, $[Ca^{2+}] = 3 \times 10^{-3}$ *M*, [KCl] = 0.125 *M*.

obtained by holding the potential at -1.85 V *vs.* S.C.E. for different periods of time. The pH of the solution was found to increase with electrolysis time. The enhancement of the catalytic current in this case by the presence of Ni^{2+} ion is similar to that observed for the catalytic hydrogen wave of the amino acid, cysteine (which contains an -SH group) by Co^{2+}, Co^{3+} or Ni^{2+} [7,9,10]. Also the actual shape of the Ni(II)–ethylenediamine polarograms of Fig. 1 are very similar to those reported by KOLTHOFF AND LINGANE[7] for the Co(II)–cysteine system which is further evidence that the ethylenediamine post-wave is also a catalytic hydrogen wave.

In Fig. 2, the peak height of the catalytic wave is plotted as a function of ethylenediamine and of Ni^{2+} ion concentration. The variation of the peak current with ethylenediamine is not linear, which is not inconsistent with a catalytic wave[18]. The fact that i_p for a given constant ethylenediamine concentration increases as the concentration of Ni^{2+} ion increases, indicates that the metal ion participates in some way in the electrode reaction .

Effect of pH

The polarograms of solutions containing 2.5×10^{-3} M Ni^{2+}, 15×10^{-3} M Ca^{2+}, 0.125 M KCl, and 3×10^{-5} M ethylenediamine were determined at pH-values between 3 and 7 (the pH was adjusted to desired value by the addition of HCl). The peak height of the catalytic wave at -1.85 V increased as the pH decreased as would be expected for a catalytic hydrogen wave[6]. At pH 7 no wave was observed at -1.85 V and at the lower pH-values, although the wave could be observed it was obscured by the H_3O^+ wave which becomes appreciable below pH 4. The catalytic hydrogen wave of ethylenediamine was therefore best defined at pH-values between 4.0 and 5.0.

Attempts were made to use an acetate buffer (pH 4.5) as the supporting electrolyte, but the background wave was shifted sufficiently in a positive direction (to about -1.7 V) to mask the catalytic hydrogen wave of ethylenediamine.

Analysis of ethylenediamine

Because the peak height, i_p, of the catalytic hydrogen wave in the Ni(II)–ethylenediamine system is quite sensitive to changes in ethylenediamine concentration, it was felt that it could be employed to determine small concentrations of ethylenediamine in the same manner as in the Co(II)–cysteine system for the determination of cysteine. A Ni^{2+} ion concentration of 2.5×10^{-3} M and a pH value of 5 were chosen as the solution conditions for the analysis because they gave the most well-defined waves. Because the variation of i_p with ethylenediamine concentration is not linear (see Fig. 1), it was necessary to construct a calibration curve with known solutions. Table I shows the results of some typical determinations of ethylenediamine. The range of ethylenediamine concentrations that can be conveniently analyzed under the above conditions is $3\text{–}30 \times 10^{-5}$ M; a precision of about $\pm 1.0 \times 10^{-5}$ was achieved. Concentrations of ethylenediamine as low as 5×10^{-6} M can be determined by increasing the nickel ion concentration to 1×10^{-2} M, although the accuracy and precision is poor at such low concentrations.

Because the peak current is dependent on the rate of a chemical regeneration reaction of the electroactive species, it is necessary to control all conditions, such as temperature, pH, and Ni^{2+} concentrations, very carefully to obtain accurate and precise results[2,19].

TABLE 1

DETERMINATION OF ETHYLENEDIAMINE

Solns. contain 2.5×10^{-3} *M* Ni^{2+}, 15×10^{-3} *M* Ca^{2+}, and 0.125 *M* KCl, pH = 5.00 ± 0.05, temp. = 25° ± 0.5

Number of determinations	*Concn. of ethylenediamine ($M \times 10^5$)*	
	Taken	*Found*
1	3.0	2.6
3	5.9	5.0–5.5
2	8.8	8.0, 8.5
2	12.2	12.0, 12.5
2	15.1	15.0, 15.0
1	18.1	19.0
1	21.0	19.9
3	24.0	23.5–24.4

CONCLUSIONS

This investigation demonstrates that ethylenediamine exhibits a catalytic hydrogen wave which is enhanced by the presence of Ni^{2+}. The peak current, i_p, of the catalytic wave can be employed for the polarographic analysis of ethylenediamine in the concentration range 10^{-5}–10^{-4} *M*. Although the sensitivity of this method is approximately the same as that of the method employing the catalytic polarographic prewave of the $Ni(en)_1^{2+}$ complex[2], the catalytic hydrogen wave has a distinct advantage for analytical purposes as it is considerably better defined.

The characteristic shape and the behaviour of the catalytic hydrogen wave of ethylenediamine examined in this investigation gives some insight into the mechanism involved in the process. Evidently, bonding of protons with the basic amine groups lowers the reduction overpotential to give a hydrogen wave at −1.85 V *vs.* S.C.E. Thus, the electroactive species is probably a protonated form of ethylenediamine (at pH 5 the equilibrium should favor most of the ethylenediamine being in the diprotonated form, as the $pK_{a_1} = 7.4$[20]). The protonated ethylenediamine reacts at the electrode to give hydrogen and to regenerate the free base form of ethylenediamine. The freed ethylenediamine can then react again with a proton donor such as water to regenerate the electroactive cation. Thus, a cyclic reaction takes place in the vicinity of the electrode to produce a current which is considerably greater than that which would be obtained for a process that was diffusion-controlled and which did not involve cyclic regeneration of the initial reactant. This type of cyclic mechanism was proposed by BRDIČKA[6] to explain the catalytic wave observed for the reduction of sulfhydryl compounds[7]. The sharp decrease of the current at potentials more negative than −1.85 V suggests that adsorption is involved in the mechanism. Probably both the diprotonated and free base forms are adsorbed on the mercury electrode surface and the cyclic regeneration reactions take place on the electrode surface at potentials more positive than −1.85 V *vs.* S.C.E. The current decrease at potentials more negative than -1.85 V probably results from desorption of the uncharged free base form of ethylenediamine. This would be expected to result in a decrease in the rate of the overall electrode reaction, as the freed ethylenediamine would diffuse away from the electrode and the protonation reaction would then take place in the bulk of solution rather than on the electrode surface. The mechanism for the sulfhydryl compound catalytic hydrogen wave, which also is a peaked wave, is thought to be complicated by adsorption[9,21]. The presence of ethylenediamine also partially suppressed the $Ni(H_2O)_6^{2+}$ maximum (when Ca^{2+} was absent) which is further evidence for adsorption of the diamine.

The role of the metal ion in the ethylenediamine catalytic hydrogen wave mechanism is difficult to understand as it appears to be quite different from than that in the cysteine catalytic hydrogen wave. BRDIČKA postulated that the function of the metal ion in the cysteine reaction was the formation of a co-ordination bond between the metal ion and the sulfhydryl group which weakens the S–H bond, lowering the hydrogen reduction overpotential[9,10]. However, this does not appear to be the case with the ethylenediamine wave although ethylenediamine is almost completely associated in the bulk of the solution (the stability constant of the $Ni(en)_1^{2+}$ complex is about 3.0×10^7 [20]). The wave-shape characteristics and the potential at which the current peak occurs are identical both in the presence and absence of Ni^{2+}, only i_p changes. Furthermore, if ethylenediamine were complexed with Ni^{2+}, the free electron pair of the nitrogens would not be available to bond with a proton and it must then be assumed that the formation of the complex has weakened an amino hydrogen which is, therefore, reduced at a lower overpotential. It does not seem likely, however, that the N–H bond would be weakened to this extent. The potentials of the catalytic waves for the reduction of an associated proton (in the absence of Ni^{2+}) would be expected to be different from that of an amino proton in the case of the metal complex. Thus, it seems more likely that ethylenediamine, associated with Ni^{2+} in the bulk of the solution, is freed when the $Ni(en)_1^{2+}$ complex is reduced (the $Ni(en)_1^{2+}$ is thought to reduce at a potential slightly more positive than that of the reduction of the $Ni(H_2O)_6^{2+}$ complex[2]) and is then adsorbed on the electrode surface. The adsorbed diamine then reacts with a proton donor to form the cationic species. At present the mechanism for the enhancement of the catalytic hydrogen wave by Ni^{2+} is not understood.

SUMMARY

The small wave observed above the diffusion limited plateau when Ni^{2+} is reduced in the presence of trace amounts of ethylenediamine has been investigated. The effects of ethylenediamine concentration, nickel ion concentration and pH on the wave, are described. The results of this investigation indicate that the wave is a catalytic hydrogen wave. It has been found that the wave can be employed for the determination of ethylenediamine at low concentrations. The optimum concentration range for the analysis is 3×10^{-5}–3×10^{-4} M ethylenediamine.

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POTENTIOMETRIC DETERMINATION OF TIN(II), IRON(II), FERROCYANIDE, ANTIMONY(III) AND ARSENIC(III) BY MANGANIC SULPHATE

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Manganese(III) compounds, in spite of their high oxidation potential, have found little use as analytical reagents. Among the relevant literature, is the earlier work of UBBELOHDE[1] on the use of manganic sulphate as an oxidizing titrant, and the investigations of BELCHER AND WEST[2] on the estimation of vanadium, nitrite, oxalate, peroxide, and of SAITO AND SATO[3] of arsenite, antimony etc., by means of manganic pyrophosphate. Recently, TSUBKI[4] studied the influence of hydrochloric acid on the determination of Fe(II) with manganic sulphate. The present authors also have used this compound for the spectrophotometric determination of ferrocyanide ions, Sn(II) and Fe(II)[5]. The use of Mn(III) compounds for the potentiometric estimation of metal ions, has however, escaped the attention of workers in this field. The present communication describes attempts to assess the usefulness of manganic sulphate as an analytical reagent for the estimation of metal ions separately and in their mixtures. It is expected that, when investigations have been succesfully completed, this reagent will replace the less effective, more expensive but more commonly used oxidizing titrant, ceric sulphate.

EXPERIMENTAL

Solutions

Manganic sulphate solution was prepared by the method recommended by UBBELOHDE[1] but with certain modifications. Manganous sulphate solution was prepared by dissolving 15.1 g of the A.R. salt in 1 l of 8 *N* sulphuric acid. To 50 ml of this solution (kept in a freezing mixture), 12 ml of 0.5 *N* potassium permanganate was added in 2-ml aliquot (with brisk shaking) at intervals of about 4 min. To ensure that a large excess of sulphuric acid was present at each stage of the oxidation of Mn(II), 4 ml of concentrated sulphuric acid was first added followed by two further additions each of 4 ml after 8 ml and 12 ml of potassium permanganate had been added. In this way the oxidation proceeded smoothly to manganic sulphate. The solution was stored in dark coloured bottles for at least four hours before use. The solution thus prepared was found to be quite stable and did not change in strength even on keeping for several weeks in coloured bottles.

UBBELOHDE[1] recommended the standardization of manganic sulphate by volumetric titration against ferrous ammonium sulphate, but it was not possible using

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this method to see a definite colour change by the addition of one drop at the end point. The solution was, therefore, standardized by titrating potentiometrically against ferrous ammonium sulphate. In this titration the addition of 0.1 ml of 0.06 N manganic sulphate to 15.0 ml of 0.016 N ferrous ammonium sulphate gave a potential change of 0.424 V at the equivalence point.

Antimony trichloride (T.T.) was dissolved in sulphuric acid and a little hydrochloric acid added; the strength of the solution was determined by titrating against potassium bromate[6] solution.

Sodium arsenite solution was prepared by the method of WILLARD AND YOUNG[7] and also standardized by titrating against potassium bromate[8].

Stannous chloride (B.D.H.) was dissolved in concentrated hydrochloric acid and the strength of this solution was determined iodometrically[9] after dilution with air-free distilled water. The solution was stored under an atmosphere of nitrogen and pieces of tin metal were kept in the bottom of the flask to check oxidation by atmospheric oxygen. A solution of ferrous ammonium sulphate was prepared by dissolving the salt (A.R., B.D.H.) in acidulated air-free double-distilled water.

Apparatus

A Pye Precision Vernier Potentiometer (Cat. No. 7568) was used for the titrations. A bright platinum wire (1 cm) fused into a pyrex tube was used as an indicator electrode and a calomel electrode as the reference electrode. A platinized electrode was used in the As(III) determinations.

Procedure

Varying amounts of the solutions to be estimated were placed in the cell. Nitrogen gas (purified by passing through alkaline pyrogallol and chromous chloride solution) was used for maintaining the inert atmosphere as well as for stirring the solution.

To prepare mixtures containing two metal ions, solutions of each ion of approximately the same strength were mixed in varying amounts (2.0 ml, 3.0 ml and 4.0 ml of one mixed with 4.0 ml, 3.0 ml and 2.0 ml of the other) and the total volume made upto 10.0 ml in each case. The mixtures of Sb(III) and Fe(II) were obtained in this way but it was found in the titrations that the first break corresponded to an amount of Fe(II) a little higher than that taken in the cell. The discrepancy appeared to be due to the close proximity of the E_0 values of the two systems, $Fe(III) + e \rightleftharpoons Fe(II)$, and $Sb(V) + 2e \rightleftharpoons Sb(III)$. To investigate the influence of the concentration of Fe(II) on the first break, equinormal solutions of both constituents were mixed in the following way: 9.0 ml, 8.0 ml, 7.0 ml, 6.0 ml, 5.0 ml, 4.0 ml, 3.0 ml, 2.0 ml and 1.0 ml of Sb(III) solution with 1.0 ml, 2.0 ml, 3.0 ml, 4.0 ml, 5.0 ml, 6.0 ml, 7.0 ml, 8.0 ml and 9.0 ml of Fe(II) solutions, keeping the total volume equal to 10.0 ml. Mixtures containing three metal ions were prepared by mixing equal volumes, *viz.*, 2.5 ml, 4.0 ml and 5.0 ml of each of the constituents and diluting to a total volume of 20.0 ml.

RESULTS AND DISCUSSION

In Sn(II) and Fe(II) determinations, the bright platinum electrode behaved quite satisfactorily. As expected, the inflexions were sharper for Sn(II) than for Fe(II) because of the large difference between the standard potentials of the stannous–stannic and ferrous–ferric couples. The theoretical potential values were almost realised in Fe(II) determinations (Table 1), but in the case of Sn(II) the potential at the equivalence point was higher than the theoretical potential (−0.596 V).

Micro quantities of ferrocyanide were successfully determined by potentiometric titration with Mn(III) at the platinum electrode. Well-pronounced breaks (Fig. 1) were obtained at the equivalence point the potential values almost reaching the theoretical potential (−0.933 V). The results of the estimations in each case were highly satisfactory.

TABLE 1

DETERMINATION OF IRON(II)

Concn. of soln. taken (N)	*Diff. between the concn. taken and found*	*Observed potential at the equivalence point (V)*	*Remarks*
0.1	nil	−0.840	The observed potential approximates to the theoretical value* (−1.09 V) at lower concn. of Fe(II) ions
0.05	nil	−0.950	
0.01	nil	−0.970	

* $E_e = \frac{bE_{01} + aE_{02}}{a+b}$ where E_e is the potential at the equivalence point, E_{01} and E_{02} are the standard potentials of the two couples involved in the system and a and b are the number of electrons used in the respective systems.

TABLE 2

DETERMINATION OF TIN(II)

Concn. of soln. taken (N)	*Diff. between the concn. taken and found*	*Observed potential at the equivalence point (V)*	*Remarks*
0.1800	nil	−0.880	Theoretical potential (−0.594 V) not realised, results very satisfactory
0.033	nil	−0.870	
0.0999	nil	−0.820	
0.00472	nil	−0.850	

TABLE 3

DETERMINATION OF FERROCYANIDE

Concn. of soln. taken (N)	*Diff. between the concn. taken and found*	*Observed potential at the equivalence point (V)*	*Remarks*
0.00296	nil	−0.900	The observed potential is equal to the theoretical potential (−0.933 V) at the equivalence point
0.0060	nil	−0.912	
0.000804	nil	−0.925	

It was expected that Sb(III), like Fe(II) would be oxidized completely to antimony-(V) by manganic sulphate, as the oxidation potentials of the two systems, Sb(V) +

$2\,e \rightleftharpoons \mathrm{Sb(III)}$ (-0.69 V), and $\mathrm{Fe(III)} + e \rightleftharpoons \mathrm{Fe(II)}$ (-0.68 V) in sulphuric acid medium[10], are almost equal. But it was observed that the reaction was comparatively slow and more so with dilute solutions of antimony trichloride (< 0.009 *N*). The bright platinum electrode was satisfactory for the titrations and equilibrium at the equivalence point was attained in about 2 min. The experimental results for Sb(III) estimations were slightly different from those in the preceding experiments. In the case of dilute solutions, the rate of the reaction could be increased by the addition of HCl (minimum concentration 0.6 *N* HCl). The theoretical potential value could be realised in almost all cases (see Table 4).

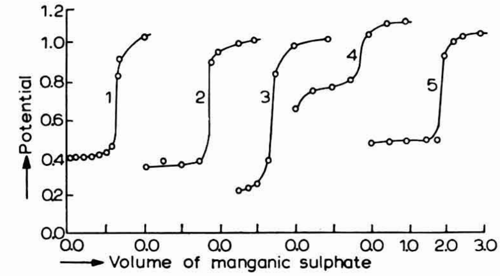

Fig. 1. Potentiometric titration curves for metal ions: curve 1, 0.1 *N* Fe(II) against 0.076 *N* Mn(III); curve 2, 0.00473 *N* Sn(II) against 0.0263 *N* Mn(III); curve 3, 0.00296 *N* ferrocyanide against 0.01 *N* Mn(III); curve 4, 0.009 *N* Sb (II) against 0.055 *N* Mn(III); curve 5, 0.01 *N* As(III) against 0.0423 *N* Mn(III).

TABLE 4

DETERMINATION OF ANTIMONY(III)

Concn. of soln. taken (N)	*Diff. between the concn. taken and found*	*Observed potential at the equivalence point (V)*	*Remarks*
0.203	nil	−0.950	Theoretical potential (−0.963 V) is almost realized for concns. ranging from micro to macro quantities; at lower concn., 0.6 *N* HCl is required for satisfactory results
0.055	nil	−0.960	
0.0209	nil	−0.960	
0.0099	nil	−0.970	

The oxidation by Mn(III) of trivalent to pentavalent arsenic should proceed almost to completion as evident from a consideration of the value of K, 1.6×10^{33}, the equilibrium constant for the reaction $2\,\mathrm{Mn(III)} + \mathrm{As(III)} \rightleftharpoons \mathrm{As(V)} + 2\,\mathrm{Mn(II)}$ calculated from the oxidation potentials of the two systems $\mathrm{Mn(III)} + e \rightleftharpoons \mathrm{Mn(II)}$ (-1.51 V) and $\mathrm{As(V)} + 2\,e \rightleftharpoons \mathrm{As(III)}$ (-0.56 V). Nevertheless the reaction did not proceed without the addition of foreign ions (catalyst). WILLARD AND YOUNG[7] and FURMAN[11] experienced the same difficulty while carrying out potentiometric titrations with ceric sulphate and sodium arsenite; they found that they could catalyse the reaction by the addition of iodine mono-chloride or potassium bromide. In the case under discussion, potassium bromide (minimum concentration 0.6 *M*) was also found useful for accelerating the reaction. It was further discovered that potassium chloride could replace potassium bromide in these studies although the minimum concentration required was higher (5.0 *M*). Moreover, the amount of potassium bromide required in manganic sulphate titrations was less than that used by WILLARD AND YOUNG for titrations with ceric sulphate (10 g for 10.0 ml of 0.1 *N* sodium arsenite solution) as the oxidizing titrant. The electrode material was also found to influence the titrations. A longer time was required for the attainment of equilibrium and lower potential values were realized

TABLE 5

DETERMINATION OF ARSENIC(III)

Concn. of soln. taken (N)	*Diff. between the concn. taken and found*	*Electrode material*	*Observed potential at the equivalence point (V)*	*Catalyst*	*Remarks*
0.0595	nil	Bright Pt	−0.590	KBr	Theoretical potential (−0.876 V) is almost realized at Pt black using KBr as catalyst. Lower potential values at bright Pt and more so when KCl used as catalyst. Error 0.1% both at bright Pt and Pt black
0.0595	nil	Bright Pt	−0.185	KCl	
0.0595	nil	Pt black	−0.800	KCl	
0.0595	nil	Pt black	−0.870	KBr	
0.0338	nil	Pt black	−0.950	KBr	
0.0100	nil	Pt black	−0.890	KBr	
0.0020	nil	Pt black	−0.860	KBr	

TABLE 6

MIXTURES OF IRON(II) AND ANTIMONY(III)

Concn. of solns. taken (N)			*Observed potential at the equivalence point (V)*	
Fe(II)	+	*Sb(III)*	*at 1st break*	*at 2nd break*
0.0	+	0.033	—	−1.03
0.0033	+	0.0297	−0.67	−1.01
0.0066	+	0.0254	−0.65	−0.98
0.0099	+	0.0231	−0.65	−1.02
0.0132	+	0.0198	−0.64	−1.01
0.0165	+	0.0165	−0.64	−1.02
0.0198	+	0.0132	−0.64	−1.00
0.0231	+	0.0099	−0.62	−0.99
0.0254	+	0.0066	−0.54	−0.95
0.0287	+	0.0033	−0.99	—
0.033	+	0.0	−0.95	—

Theoretical potential at the two breaks (−0.68 V for the 1st and −0.963 V for the 2nd) are almost realized for the mixtures containing varying proportions of the two constituents. Mixtures containing very small amount of Sb(III) (0.0033 *N*) could not be analysed. Vol. of Mn(III) at the 1st break does not give strength of Fe(II) due to the simultaneous oxidation of both constituents. Values calculated for the 2nd break give the total strength of the mixture.

at the equivalence point when using bright platinum; black platinum electrodes were satisfactory.

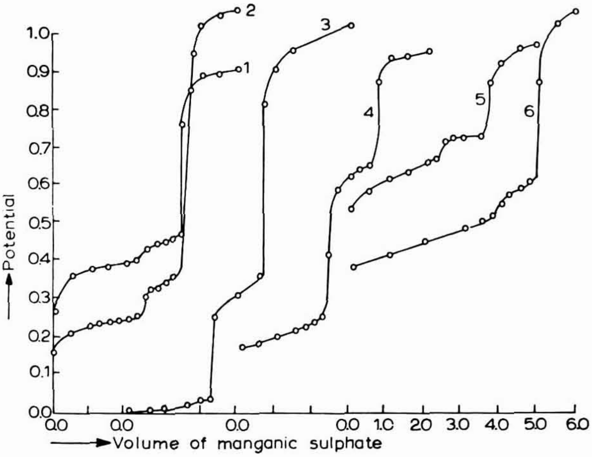

Fig. 2. Potentiometric titration curves for mixtures of two metal ions: curve 1, 0.0136 N Sn(II) + 0.0064 N Fe(II) against 0.0537 N Mn(III); curve 2, 0.0064 Fe(II) + 0.0136 N As(III) against 0.0537 N Mn(III); curve 3, 0.0128 N Sn(II) + 0.0068 N As (III) against 0.0537 N Mn(III); curve 4, 0.0128 N Sn(II) + 0.0066 N Sb(III) against 0.0537 N Mn(III); curve 5, 0.0066 N Sb(III) + 0.0136 N As(III) against 0.0537 N Mn(III); curve 6, 0.0254 N Fe(II) + 0.0066 N Sb(III) against 0.033 N Mn(III).

The behaviour of the mixtures of Sb(III) and Fe(II) was rather interesting. As the oxidation potentials of the two systems, Sb(V) + 2 $e \rightleftharpoons$ Sb(III) (−0.69 V) and Fe(III) + $e \rightleftharpoons$ Fe(II) (−0.68 V)[10] are almost equal, simultaneous oxidation was expected; but in all cases except one (where the concentration of Sb(III) was too low, − 0.0033 N) two definite breaks were obtained. However, the volume of manganic sulphate equivalent to iron(II) present in the mixture *i.e.*, at the first break, was far removed from the theoretical value, although it is interesting to note that potential values at both breaks were approximately theoretical (Table 6).

As expected, two breaks were obtained for mixtures of Sn(II) and Fe(II), and Sn(II)

TABLE 7

MIXTURES OF TIN(II) AND IRON(II)

Concn. of solns. taken (N) *Sn(II) + Fe(II)*	*Diff. between the concn. taken and found*	*Observed potential (V)* *at 1st break*	*at 2nd break*	*Remarks*
0.0136 + 0.0064	nil	−0.31	−0.85	Observed potential for the 1st break is equal to theoretical potential (−0.32 V); theoretical potential (−1.09 V) is almost reached for the 2nd break
0.0102 + 0.0096	nil	−0.32	−0.85	
0.0068 + 0.0128	nil	−0.32	−0.85	

and Sb(III) (Fig. 2). The first break obtained, corresponding to the oxidation of Sn(II) was sharper in the mixture with Sb(III) than in the mixture with Fe(II). The sharpness of the first break for Sn(II)–Sb(III) mixtures could be predicted from a comparison of theoretical potential values at the equivalence point. The value for Sn(II)–Sb(III) mixtures is higher (—0.415 V) than that for Sn(II)–Fe(II) mixtures (—0.32 V).

TABLE 8

MIXTURES OF TIN(II) AND ANTIMONY(III)

Concn. of solns. taken (N)		*Diff. between concn. taken and found*	*Observed potential (V)*		*Remarks*
Sn(II) +	*Sb(III)*		*at 1st break*	*at 2nd break*	
0.0128 +	0.0066	nil	−0.55	−0.890	The observed potentials at the 1st break are higher than the theoretical value (−0.415 V) and at the 2nd break are almost equal to the theoretical value (−0.963 V)
0.0096 +	0.0099	nil	−0.53	−0.900	
0.0064 +	0.0132	nil	−0.55	−0.940	

TABLE 9

MIXTURES OF TIN(II) AND ARSENIC(III)

Concn. of solns. taken (N)		*Diff. between concn. taken and found*	*Observed potential (V)*		*Remarks*
Sn(II) +	*As(III)*		*at 1st break*	*at 2nd break*	
0.0128 +	0.0068	nil	−0.31	−0.85	Observed potential values at 1st and 2nd breaks are equal to the theoretical values (−0.35 V at 1st and −0.876 V at 2nd)
0.0096 +	0.0102	nil	−0.34	−0.88	
0.0064 +	0.0136	nil	−0.34	−0.90	

The observed high potential values (—0.55 V) at the first break for Sn(II)–Sb(III) mixtures might be attributed to the presence of HCl in the Sb(III) solution which would be likely to catalyse the reaction.

The behaviour of As(III) in mixtures was found to be slightly different from that observed in the absence of other compounds; potassium bromide was not a satisfactory catalyst (Pt black as the indicator electrode) since only one break was obtained. On the other hand with potassium chloride as catalyst, both the constituents could be analysed within 0.1%.

Another important point in these titrations is that the break, representing the oxidation of As(III), was not in the same sequence for the three sets of mixtures used.

TABLE 10

MIXTURES OF ANTIMONY(III) AND ARSENIC(III)

Concn. of solns. taken (N)	*Diff. between concn. taken and found*	*Observed potential (V)*		*Remarks*
Sb(III) + As(III)		*at 1st break*	*at 2nd break*	
0.0066 + 0.0136	nil	−0.69	−0.925	Observed potential at 2nd break approximately reaches the theoretical value (−0.963 V), the value for the 1st break is higher than the theoretical values (−0.625 V)
0.0099 + 0.0102	nil	−0.70	−0.925	
0.0132 + 0.0068	nil	−0.71	−0.950	

TABLE 11

MIXTURES OF IRON(II) AND ARSENIC(III)

Concn. of solns. taken (N)	*Diff. between concn. taken and found*	*Observed potential (V)*		*Remarks*
Fe(II) + As(III)		*at 1st break*	*at 2nd break*	
0.0064 + 0.0136	nil	−0.43	−0.94	Theoretical potential (−0.60 V) not realized for the 1st break; observed potential almost equal to the theoretical value (−1.09 V) for the 2nd break
0.0096 + 0.0102	nil	−0.51	−0.99	
0.0128 + 0.0068	nil	−0.49	−0.98	

TABLE 12

MIXTURES OF TIN(II), ARSENIC(III) AND IRON(II)

Concn. of solns. taken (N)	*Diff. between concn. taken and found*	*Observed potential (V)*		
Sn(II) + As(III) + Fe(II)		*at 1st break*	*at 2nd break*	*at 3rd break*
0.011 + 0.009 + 0.0072	nil	−0.30	−0.50	−0.90
0.0176 + 0.0144 + 0.0116	nil	−0.32	−0.52	−0.92
0.022 + 0.018 + 0.0194	nil	−0.34	−0.55	−1.00

Remarks: The theoretical potential for the first (−0.35V) and third (−1.09 V) breaks are almost realized in all mixtures. The observed potential for the second break is slightly less than the theoretical value (−0.60 V).

For the mixtures containing Sn(II) and As(III), the second break represented the oxidation of As(III) while in the other two, namely Sb(III)–As(III) and Fe(II)–

As(III), the first break represented the oxidation of As(III). The probable cause of this anomalous behaviour is the fact that the E_0 value of the reaction As(V) + 2 $e \rightleftharpoons$ As(III) (−0.56 V) is less than those of the reactions Fe(III) + $e \rightleftharpoons$ Fe (II) (−0.68 V) and Sb(V) + 2 $e \rightleftharpoons$ Sb(III) (−0.69 V) with the result that As(III) is preferentially oxidized and the oxidation of Fe(II) and Sb(III) takes place at a later stage.

TABLE 13

MIXTURES OF TIN(II), ARSENIC(III) AND ANTIMONY(III)

Concn. of solns. taken (N)			*Diff. between concn. taken and found*	*Observed potential (V)*		
Sn(II)	*+ As(III)*	*+ Sb(III)*		*at 1st break*	*at 2nd break*	*at 3rd break*
0.011	+ 0.009	+ 0.0072	nil	−0.32	−0.560	−0.90
0.0176	+ 0.0144	+ 0.0116	nil	−0.34	−0.55	−0.94
0.022	+ 0.018	+ 0.0144	nil	−0.34	−0.56	−0.98

Remarks: The theoretical potential at the first (−0.35 V) and third (−0.96 V) breaks are almost realized in all three mixtures. The values of the observed potential for the second break are slightly less than the theoretical value (−0.625 V).

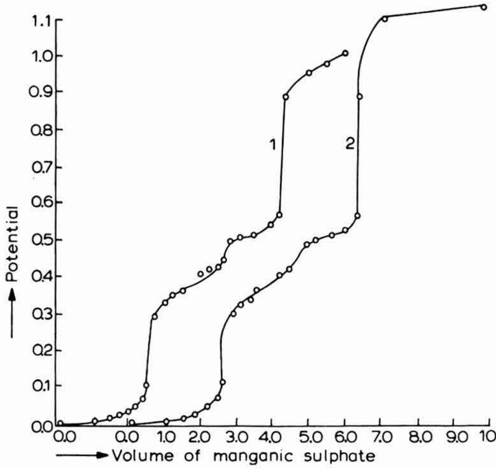

Fig. 3. Potentiometric titration curves for mixtures of three metal ions: curve 1, 0.011 *N* Sn(II) + 0.009 *N* As(III) + 0.0072 *N* Fe(II) against 0.086 *N* Mn(III); curve 2, 0.011 *N* Sn(II) + 0.009 *N* As(III) + 0.0072 *N* Fe(II) against 0.086 *N* Mn(III).

In mixtures of three metal ions, the breaks for each of the constituents could be obtained (Fig. 3). The potentials attained at the equivalence points of the first and third breaks were equal to the theoretical values, the potential values at the second breaks for the mixtures Sn(II)–As(III)–Fe(II), and Sn(II)–As(III)–Sb(III) were lower than the theoretical values (Tables 12 and 13).

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SUMMARY

The conditions for the estimation of iron(II), tin(II), antimony(III), arsenic(III) and ferrocyanide ion by manganic sulphate solution have been investigated. A bright platinum electrode was satisfactory for all these estimations except in the case of arsenic(III) where a platinum black electrode was found to be more useful. The titration of antimony(III) with manganic sulphate could be successfully carried out only in presence of hydrochloric acid (minimum concn. 0.6 *N*). The oxidation of arsenic-(III), was slow and was therefore catalysed by the addition of minute amounts of potassium bromide or potassium chloride. The potentiometric titration curves for mixtures gave breaks for each of the constituents, but for mixtures of iron(II) and antimony(III) the titre values obtained for the first break were far removed from the theoretical values. For mixtures containing three metal ions the potentials attained at the equivalence points of the first and third breaks were approximately equal to the theoretical potentials but those for the second break were different from the theoretical values. Titrations for metals separately and in mixtures were accurate to 0.1 %.

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POLAROGRAPHIC CHARACTERISTICS OF CHLORITE

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In connection with a study of the nature of peracid-stabilized chlorine dioxide solutions it became necessary to devise analytical methods for the several chlorine-containing species which could arise from redox and disproportionation reactions of this family. Perchlorate, chlorate, chloride, hypochlorite, and chlorine may be satisfactorily determined by a variety of methods. Solutions of chlorine dioxide or chlorite, however, failed to give reproducible results when subjected to reductive titration with any of the common reductants such as ferrous iron, iodide or ferrocyanide. Further, these several titrants did not give concordant results. In an effort to improve our understanding of the redox behaviour of chlorite and chlorine dioxide we have initiated a study of their electrochemical characteristics.

EXPERIMENTAL

Most of the polarographic characteristics were recorded with a Leeds and Northrup Electrochemograph E polarograph; a few polarograms were obtained with a Kelley–Jones–Fisher operational amplifier polarograph[2]. The latter instrument is identical with that described by KELLEY AND FISHER as ORNL Model Q-1988 except that the peak follower, derivative, and residual current compensator circuits were omitted. Since these circuit elements can be disconnected by switches in the original design, their omission in the present case has no effect on the polarograms obtained. A dropping-mercury electrode of conventional design with stand-tube and levelling-bulb connected to a 20-cm length of marine barometer tubing (Corning Glass Works), was used throughout this work. The open circuit characteristics of this capillary at a mercury column height of 50 cm were: $m = 1.85$ mg/sec; $t = 4.29$ sec. Polarographic solutions were contained in conventional H-cells in which both side-arms were filled with the polarographic solution, and connection to an external reference electrode (saturated calomel) was made *via* a flexible salt bridge of 10 mm Tygon tubing terminating in a medium porosity fritted-glass sealing tube. The total resistance of this polarographic cell was measured with a Fisher-Serfass Conductivity Bridge (Fisher Scientific Company) and found to be less than 200 Ω.

Solutions of sodium chlorite were prepared from reagent grade sodium chlorite (Mathieson Chemical Corp.). In alkaline or neutral solutions this substance is apparently stable for at least a month as measured by the reproducibility of polarograms;

TABLE 1

POLAROGRAPHIC CHARACTERISTICS OF CHLORITE IN VARIOUS SUPPORTING ELECTROLYTES

	Electrolyte	*pH*[a]	$E_{\frac{1}{2}}$ *(vs. S.C.E.)*	i_d *(μA)*
1.	0.1 *M* $HClO_4$ + 0.1 *M* $NaClO_4$	1.0	−0.31	5.7
2.	0.1 *M* Citrate[b]	3.5	−0.26	6.6
3.	0.1 *M* HOAc + 0.1 *M* NaOAc	4.5	−0.33	8.8
4.	0.1 *M* Citrate[b]	5.0	−0.99	7.9
5.	0.1 *M* Na_2HPO_4+0.1 *M* NaH_2PO_4	6.3	−0.49 (−0.98)	4.4 (1.0)[c]
6.	0.1 *M* NH_4OAc	7.0	−1.25	2.7
7.	0.1 *M* NH_4OH + 0.1 *M* NH_4Cl	9.0	no wave	—

[a] Approximate pH; actual solution pH was measured for each composition.
[b] Prepared from 0.1 *M* NaH_2Cit by adding NaOH to obtain the appropriate pH.
[c] In this solution 2 waves were observed, the first was unstable.

in solutions of pH less than 7, decomposition is rapid and is complete within a day if the acidity is greater than millimolar. Polarographic solutions were prepared immediately before use from the stable, neutral stock solutions and the appropriate buffer.

Buffer solutions were prepared from a variety of weak acid systems as shown in Table 1. In each case the buffers were first prepared to be approximately 0.2 *M* in respect of the buffer anion, and were then adjusted, using the glass electrode, to the desired pH.

Polarographic characteristics of chlorite ion

Solutions of sodium chlorite in the buffer systems given in Table 1 produce polarograms typified by that of Fig. 1. In solutions of pH less than 4.5 the single wave is

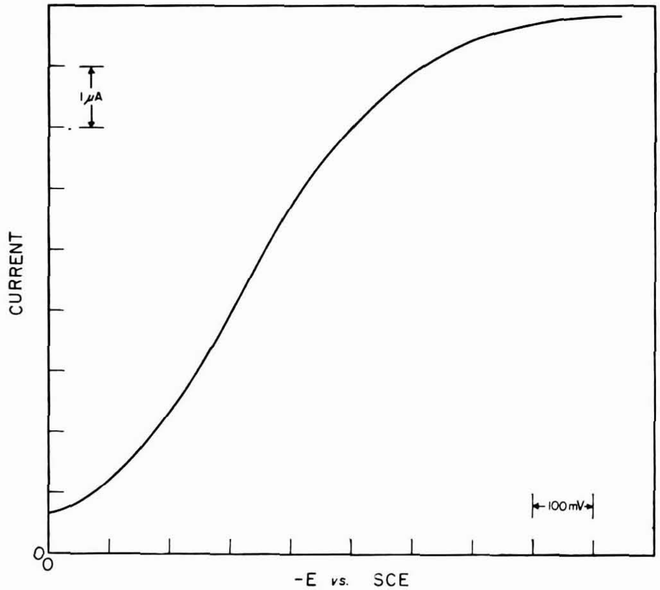

Fig. 1. Polarogram of 0.1 m*M* ClO_2^- in 1 : 1 HOAc–NaOAc (0.1 *M*) aqueous buffer.

well-defined although highly irreversible. As the pH is increased above 4.5, the wave becomes increasingly drawn out and the estimated half-wave potential, which was previously independent of pH, shifts radically to more negative potentials. In the more acid region where the wave is well-defined, the usable pH range is further narrowed by extensive decomposition in solutions more acid than pH 3. The optimum pH with regard to solution stability and wave definition is 4.2–4.5. Further, the limiting current increases steadily to a maximum in the acid region below pH 4.5, and then decreases with further increase in pH. This behaviour is illustrated by the disconnected line of Fig. 2.

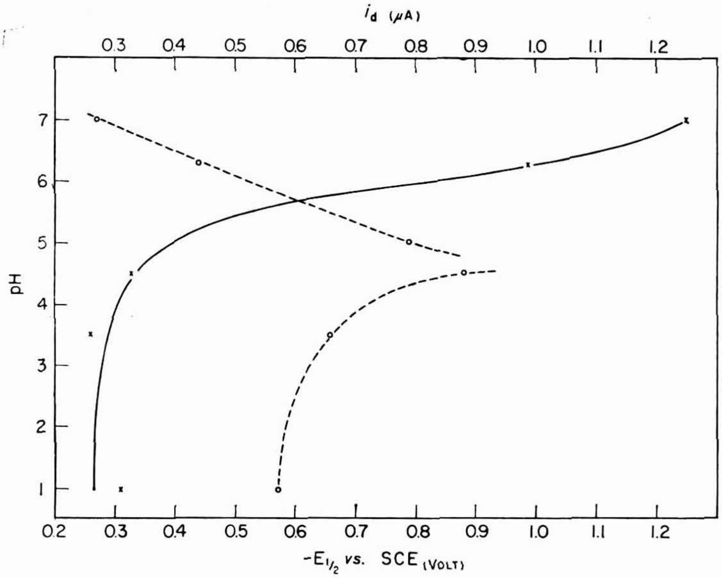

Fig. 2. Half-wave potential (X) and limiting current (O) as a function of pH for 0.1 mM ClO_2^- in buffered solution.

In solutions of optimum pH (4.5), which are easily prepared from equinormal solutions of sodium acetate and acetic acid, the half-wave potential (*vs.* S.C.E.) does not vary from -0.35 ± 0.01 V *vs.* S.C.E., within a concentration range of 0.2–2.0 mM, and the wave height is proportional to concentration. Investigation of the dependence of wave height upon the height of the mercury column shows the wave to be diffusion-controlled in this concentration range. Solutions more concentrated than 2 mM produce a maximum at the top of the wave which becomes more pronounced with increasing concentration and extends over a potential range of 0.2 V thus interfering with limiting current measurements. This maximum is not eliminated by the addition of the usual maximum suppressors such as methyl red, gelatin or Aerosol OT, in normal amounts (less than 0.01%).

The ill-defined waves obtained in solutions of higher pH show a decreasing concentration dependence with pH until, at pH 7, the wave becomes insensitive to further increase in concentration in the 0–2 mM range. Also, the limiting current becomes less sensitive to changes in the height of the mercury column; at pH 7 and above, the wave is apparently totally kinetically-controlled; this can only be estimated approximately because the wave becomes drawn out to the point of having no limiting current region above pH 7. Solutions more acid than pH 4.5 apparently give diffusion-controlled waves, but the measurements of mercury height dependence are unreliable because of the decomposition of the solutions during the time of measurement.

Plots of log $(I_d - I)/I$ against potential are linear for solutions of pH 4.5 over the logarithmic interval +1.0 to −1.0. The slopes of these plots show a tendency towards increasing irreversibility with increase in concentration.

DISCUSSION

The polarographic behaviour described above indicates that chlorite can be determined polarographically in the presence of the other oxy-anions of chlorine in the pH interval 4.2–4.5. The addition of chlorate to these solutions has no effect. Perchlorate is not polarographically reducible in the absence of specific catalysts[1]. Chlorine dioxide does apparently produce a wave in the region of −0.7 V *vs.* S.C.E. This observation is qualified because the only chlorine dioxide solutions available were stabilized with percarbonate or perborate and at present these solutions have not been investigated sufficiently to determine whether the wave is due to chlorine dioxide or to some complex species.

The behaviour of the half-wave potential and limiting current with changes in pH presents a conflicting pattern which defies a simple explanation. KONOPIK has investigated the polarographic behaviour of chlorite in strong (0.1–5 M) sodium hydroxide solution[3]. In this strongly basic solution chlorite exhibits a highly reversible, irregular wave at potentials more negative than −1.0 V *vs.* S.C.E. The wave is further characterized by a sudden desorption *dip* in the vicinity of −1.6 V. Controlled-potential electrolysis yields n-values of 4.2–4.4. The results of our experiments in acid solution can be explained on the basis of a reduction process involving a sluggish equilibrium between chlorite ion and its acid:

$$HClO_2 = ClO_2^- + H^+$$

In order for this to represent the solution chemistry defining the electrochemically active species it is necessary to postulate that the free acid is at least not reducible at a rate comparable to that of the anion. It is also necessary that the attainment of equilibrium between the acid and anion be rapid enough to establish bulk equilibrium conditions within the time of preparation of solutions, and yet slow enough to ensure that depletion of the anion at the electrode surface by reduction is not compensated by a shift of equilibrium concentrations at the electrode surface. MOELLER[4] estimates the pK_a of chlorous acid to be about 2 which is in agreement with an apparent maximum concentration of anion at pH 4.5 as measured by the diffusion current. This rationale is partially substantiated by the height dependence and change in log $(I_d - I)/I$ plot slopes with concentration. First, the diffusion-controlled character of the wave is evident in only a narrow region of pH, becoming kinetically-controlled with increase in pH. The increase in slope of the log-plot indicates a process which overall does require hydrogen ion but which does not reflect this requirement until the analytical concentration of chlorite anion becomes an appreciable fraction of the total available hydrogen ion concentration. This set of circumstances becomes apparent when either (a) the concentration of chlorite exceeds the analytical concentration of hydrogen ion in terms of normality expressed from the overall reaction or (b) when the pH is increased to the point that the hydrogen ion concentration is decreased below this limiting value at constant chlorite ion concentration. The best estimate of the overall reaction in the pH region 4.2–4.5, using the simple Ilkovic equation and diffusion coefficients of similar anions, leads to *n*-values of 4.2–4.8 depending upon the choice of diffusion coefficient. If these values reasonably reflect the true state of affairs then the overall reaction may be written:

$$ClO_2^- + 4\,e + 4\,H^+ \rightarrow Cl^- + 4\,H_2O$$

If this equation represents the overall reaction, then, regardless of possible intervening steps such as reaction between chlorite and chloride analogous to that between chlorate and chloride, the diffusion-limiting current would decrease with increasing pH because the successive steps requiring hydrogen ion become limited in rate by the available hydrogen ion at the electrode surface. The shift from diffusion-control to kinetic-control above pH 7 supports this view.

ACKNOWLEDGEMENT

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SUMMARY

Solutions of chlorite in buffered aqueous solution have been investigated polarographically over the pH range 1–10. Chlorite produces a well defined, diffusion-controlled, but irreversible wave at pH <4.5; in solutions of higher pH the wave becomes more drawn out, less concentration dependent and kinetically controlled. In the optimum pH range, 4.2–4.5, the diffusion-limited wave height is proportional to concentration from 0.2–2.0 mM; higher concentrations produce a large maximum on the top of the wave which is not removable by the ordinary suppressors. In solutions more acid than pH 4.2 chlorite decomposes too rapidly for polarographic analysis. On the basis of pH dependence of wave height and half-wave potential it is assumed that the overall electrode reaction is:

$$HClO_2 + 4\,e + 3\,H^+ \rightarrow Cl^- + 4\,H_2O$$

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INFLUENCE OF THE POSITION OF THE CAPILLARY ON THE TRANSFER OF CONCENTRATION POLARIZATION IN POLAROGRAPHY

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INTRODUCTION

The first attempt to use the polarographic capillary in another position than the usual, vertical position (with the orifice downwards) was made in 1943 by SCHWARZ[1], who patented a capillary which was bent obliquely upwards in order to prevent penetration of the solution into the orifice of the capillary. He did not, however, publish any reports on the results of his experiment. Later, in 1953, the present author proposed a bent capillary with the end in a horizontal position and found that it offers some advantages both from theoretical considerations and in practical polarography[2,3]. A capillary of this shape was used by subsequent investigators: *e.g.*, MARHA, for registering the curves in the Brdička reaction[4,5,6]; ŠERÁK, for the determination of oxygen consumption in living tissues[7]; KELLEY, in controlled-potential and derivative rapid polarography[8]; KALVODA AND SMOLER, for rapid polarography[9]; ZUMAN in order to remove the insoluble products of electrolysis from the vicinity of the electrode[10] and by others.

In this paper the present state of our knowledge is discussed partly on the basis of material already published, partly on new experimental evidence. A new type of capillary is proposed which satisfies the theoretical presumptions and is suitable for analytical use.

REVIEW OF PREVIOUS WORK

It has been found by numerous authors[11-15] that when using a vertical capillary the shape of the current–time curves on single drops follows neither the equation of the diffusion current derived by ILKOVIČ nor the equation of the diffusion current with the correction for spherical diffusion derived, for example, by KOUTECKÝ[16]. The current–time curve is distorted by the effect of transfer of concentration polarization from one drop to another.

The current–time curve, free from the influence of previous polarization and of the transfer of concentration polarization, can be obtained with the vertical capillary only at the so-called "first-drop", realized by applying the e.m.f. to the polarographic cell precisely at the instant when a new drop begins to grow[17,18]. The current on the first drop then corresponds to the equation of the diffusion current calculated with assumption of spherical diffusion[19-23].

The value of the correction term in this equation depends on the rate of flow of mercury, the drop-time and the diffusion coefficient. Under normal conditions (m = 2 mg/sec, t_1 = 4 sec and $D = 7 \cdot 10^{-6}$ cm²/sec) the increase of the current theoretically calculated above the value obtained from the Ilkovič equation (for a planar growing electrode) amounts to approximately 15%. The corresponding equation shows that the current–time curve is no longer parabolic; but for values of t that are neither too large nor too small it may be regarded as a parabola ($i = k \cdot t^{\beta}$) with the exponent $\beta = 0.190$[19–23].

The instantaneous current on the second drop (and on all subsequent drops) shows a decrease at the beginning of the drop-time due to depletion of the solution in the vicinity of the drop; the current–time curve represents a transition from a parabola to a hyperbola and in the purest solutions is a hyperbola — of a form $i = t/(a + bt)$. The mean current on the second drop is very variable and, according to the purity of the solution, shows a reduction of 5–20% compared with the current on the first drop; the reduction of current attains its largest value in solutions free from surface active substances[19,20].

The addition of a small quantity of gelatin does not generally affect the shape of the current–time curve on the first drop; on the second drop, the addition of gelatin considerably reduces the transfer of concentration polarization; hence the resulting mean value of current is increased (Fig. 1).

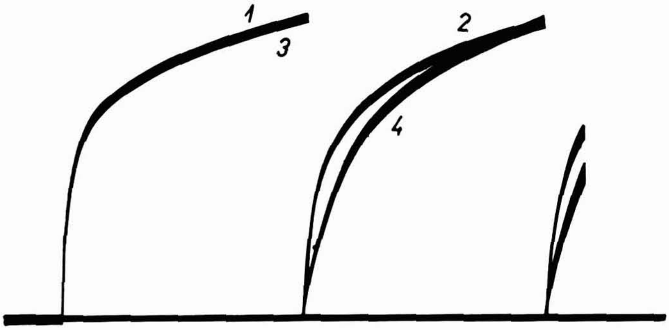

Fig. 1. Current–time curves recorded with the vertical capillary (III), time-beater 3.9 sec. The influence of gelatin on the transfer of concentration polarization, −0.8 V against S.C.E. Curves (1, 2), 0.005 M $CdSO_4$, 0.1 M K_2SO_4, 0.005% gelatin; curves (3, 4), 0.005 M $CdSO_4$, 0.1 M K_2SO_4, active carbon.

The mean polarographic current recorded with the usual vertical capillary consists of non-first drops only and, consequently, is lowered by transfer of concentration polarization. This lowering has an indefinite value varying from 5–20% and depends on the purity of the solution. An attempt was made[24] to express this lowering by a semi-empirical equation which, however, cannot be correct because it does not account for the presence of the surface-active substance, which exerts a very substantial influence on this effect. The depletion of the solution compensates more or less for the increase of current above the value according to the Ilkovič equation due to the effect of spherical diffusion (which under usual conditions amounts to about 15%). Thus, the resulting mean current approaches the value required by the Ilkovič equation. The addition of surface-active substance in small traces does not change these relations to any great extent.

The method of the first drop enables a theoretical current–time curve to be obtained on a single drop only, but it does not give mean current–voltage curves corresponding to theory. The recording of such *i–t* curves is possible only when the transfer of concentration polarization is prevented; this can be achieved by the use of properly positioned capillary.

The influence of the capillary position has been thoroughly studied[19] and it has been proved that the effects of concentration polarization do not appear with a horizontal capillary (or, generally, a capillary inclined at 45° or more) or with a capillary bent upwards according to SCHWARZ[1]. This can be demonstrated by the current–time curves which, in all these cases, have the same shape on the first drop as with subsequent drops. It is due to the fact that, as mercury drops fall, the fresh solution flows slowly around the orifice of the capillary and carries away from the orifice the solution depleted by previous polarization[19,20]. This motion of the solution can be observed by a microscope after the addition of a small quantity of powdered charcoal. Under these conditions the linear dependence of the height of the wave on the concentration as well as the linear dependence of the diffusion current on the square root of the height of the mercury reservoir is fully preserved. The curves obtained with a horizontal or an inclined capillary show very small oscillations which are due not only to the short drop-time but also to the fact that the value of the current after the fall of the drop is not further lowered by the depletion of the solution.

The use of a horizontal or an inclined capillary is advantageous, especially in recording rapid changes of current, *e.g.*, at maxima in derivative polarography, and in the so-called rapid polarography — with a rapid change of potential and high-speed recording[8,9].

As the horizontal capillary affords a means of obtaining a polarographic wave unaffected by the depletion of solution near the capillary, it would be possible to compare the curves obtained under these conditions with a curve recorded with a normal vertical capillary of the same characteristics. The difference in height of the limiting current, caused by the transfer of concentration polarization from one drop to another, could be thus determined experimentally.

However, the drop-time at the horizontal capillary is very different from the drop-time of the same capillary in the vertical position, and it is difficult to obtain the same characteristics for both positions. The capillary bent upward[1] can be conveniently used for this purpose. A capillary of this shape can be used either in the position with the orifice downwards, or with the orifice upwards. With the latter position it is possible by using a suitable inclination to obtain the same drop-time as in the position with the orifice downwards, with the same rate of flow. The conditions being perfectly comparable in both cases, the only difference is the absence of depletion effect in the case of capillary bent upwards. In this manner a current was obtained that was actually 14% larger than that recorded with the vertical capillary (see Fig. 2).

The capillary bent upward, however, is not convenient in practice because of its shape; moreover its drop-time is extremely sensitive to the inclination of the electrode and, therefore, its field of application will probably be limited.

The position of the capillary influences also the character of flow of mercury within the drop. In the case of a vertical capillary the stream of mercury out of the capillary passes through the centre of the drop and is divided in all directions upwards (see Fig. 3). Provided the rate of flow is greater than 2 mg/sec, under certain conditions the streaming of mercury is transferred to the solution in the neighbourhood of the drop and this results in a maximum of the second kind.

When the capillary is in an inclined position, the mercury streaming into the drop is directed in such a manner that the drop is kept in a rotating motion (see Fig. 3b).

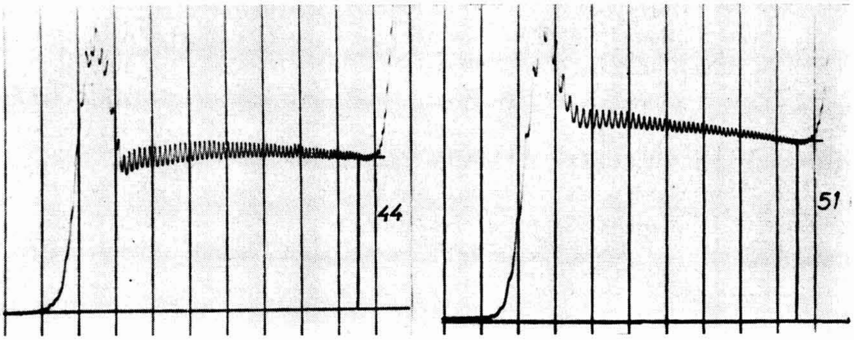

Fig. 2. Polarographic curves with a normal vertical capillary and with a capillary bent upward. t_1 = 4.2 sec in both positions, $4 \cdot 10^{-3}$ M Tl_2SO_4, 0.1 M K_2SO_4, MSE, from −0.2 V, 200 mV/absc, sens. 1/300.
Left — vertical capillary; right — capillary bent upward.

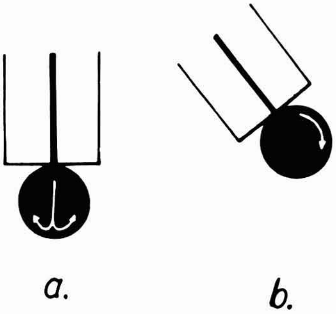

Fig. 3. The motion of mercury within the drop — the vertical capillary and the inclined capillary.

This motion is also transferred into the solution near the drop but here it has a laminar character and does not interfere with the concentration gradient in the solution. Under otherwise identical conditions the maximum of the second kind is much lower when using an inclined capillary than with a vertical capillary (Fig. 4b, c).

In order to avoid the effect of the motion of mercury within the drop, a capillary with a rate of flow of about 1 mg/sec should be used; here again the use of an inclined capillary is preferable because of a suitable drop time (see below).

The inclined capillary was also used[25] for studying the effect of the motion of mercury within the drop on the current–time curves in the cathodic deposition of a metal on to mercury and in the anodic dissolution of amalgams. The inclination of the capillary modifies the flow of mercury, or of the amalgam to the surface of the drop and thus also alters the value of the current in the cases where the concentration of the depolariser at the drop surface is different from that within the drop. In particular this is apparent on the limiting current of dissolution of amalgams, where the concentration of the amalgam on the surface approaches zero whilst fresh amalgam is streaming into the drop.

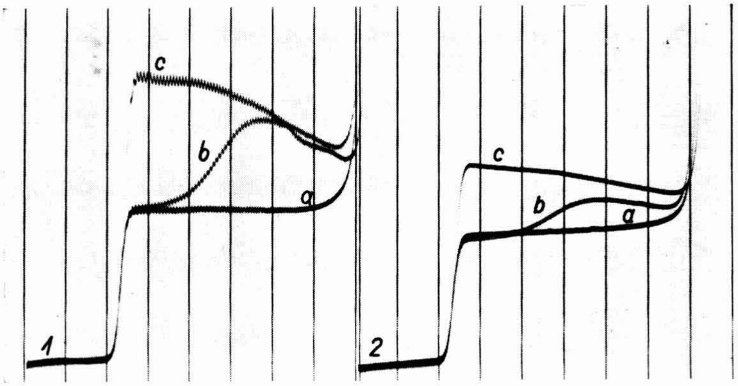

Fig. 4. The maxima of the second kind with a vertical and with an inclined capillary. 0.001 M $CdCl_2$, 4 M NaCl, S.C.E., 200 mV/absc, from −0.2 V, sens. 1/70, capillary (IV), m = 4 mg/sec. 1(a), vertical capillary, 0.005% gelatin; 1(b), vertical capillary, without gelatin; 1(c), vertical capillary, with active carbon; 2(a), capillary inclined at 45°, 0.005 gelatin; 2(b), capillary inclined at 45°, without gelatin; 2(c), capillary inclined at 45°, with active carbon.

If the position of the capillary is changed in steps when recording the current–time curves on the limiting current of dissolution of an amalgam, a still greater deviation from the theoretical shape of the curve is obtained. The magnitude of this effect depends on the rate of the flow of mercury, as would be expected. In this particular case, the shape of the curves obtained with the vertical capillary is closer to that predicted by theory. However, the inclined capillary is important from a theoretical point of view, as it proves that the irregularities on the current–time curves of amalgams are caused by the convection within the drop.

In cathodic polarization the difference of concentration of amalgam arises at the foot of the wave, where the value of the current is determined by the equilibrium between the concentration of depolariser in the surface layer of mercury and in the adjacent layer of the solution. Pure mercury flowing into the drop disturbs this equilibrium by convection. In this case also the influence of position of the capillary can be observed on the current–time curves registered at the foot of the wave; the effect is, however, not so striking as with the diffusion current of an amalgam.

It is obvious that convection does not exert such a disturbing influence in cathodic processes, because the phenomena occuring at the foot of the wave are of little consequence in polarography and are therefore not often studied. When working with amalgams, it is important to keep this fact in mind and to choose those conditions that ensure minimal convection within the drop — in the first instance a small rate of flow of mercury (about 0.5 mg/sec), which can be best achieved by narrowing the inner diameter of the capillary above the orifice.

In the preceding part of this paper attention has been focused on the horizontal capillary with its substantial advantages. This capillary is characterized, however, by a very short drop-time (about 1 sec) which is not the optimum drop-time in polarography; at more negative potentials the drop time is accelerated to such an extent that the dropping becomes irregular. In particular, the very short drop-time makes it impossible to compare the polarographic currents recorded with a horizontal capillary with those obtained using a usual vertical capillary.

The capillary inclined at 45° is much more appropriate from theoretical considerations as well as analytical application. It preserves all the advantages of the horizontal capillary, without showing the unfavourable qualities mentioned above. This kind of capillary was therefore chosen for the experiments described below.

EXPERIMENTAL

Four capillaries were used for these investigations: (I) the normal capillary of Jena glass, inner diameter 63 μ, rate of flow 1.14 mg/sec ($h = 70$ cm), drop-time ($E = -1.2$ V) 6 sec; (II) a capillary bent at 45°, inner diameter 60 μ, rate of flow 1.24 mg/sec ($h = 70$ cm), drop-time ($E = -1.2$ V) 2.75 sec; (III) a capillary of inner diameter 90 μ, constricted above its orifice to give a rate of flow of 0.5 mg/sec ($h = 70$ cm), drop-time ($E = -1.2$ V) 14 sec, and (IV) a capillary of inner diameter 87 μ and rate of flow 4 mg/sec. The rate of flow of mercury was determined with the orifice of the capillary immersed in mercury. The drop-time was measured in a solution of 0.1 *M* supporting electrolyte.

The capillary with the end inclined at 45° is simply made by bending the usual capillary in a narrow flame at 90°. Then it is cut at 45° in the middle of the bend. In this way two capillaries are obtained, each of the shape shown in Fig. 5. These capillaries can be used with all normal polarographic cells. The sharp edge of the capillary above the orifice should be ground away or rounded, so as to ensure the free flow of solution in the vicinity of the orifice.

Fig. 5. Capillary (II), bent at 45°, scale 1 : 1.

The most convenient characteristics are — inner diameter 55–60 μ, length 15–20 cm — which give a drop-time of 2.5–3.0 sec and a rate of flow of ~ 1 mg/sec.

For recording the current-time curves the inclined capillary with a longer drop-time may be preferred. This capillary can be made from a capillary tube with a larger diameter (*ca.* 100 μ) by constricting it above the orifice.

When the construction of the cell requires the introduction of the capillary in a horizontal position (*e.g.*, ref. 7), this can be realized with the same capillary and the orifice is inclined at 45° also in this case.

The same effect as with the capillary shown above can be obtained with the normal capillary, by inclining the polarographic cell. A modification of ŠERÁK's cell with a separated anode is suitable for this purpose[3]. Other types can also be used, provided that the platinum contact remains covered with mercury when the cell is inclined. It is then possible to use the same capillary alternatively in various positions; this procedure can sometimes be of importance, *e.g.*, when studying the effects connected with the transfer of concentration polarization without the use of a special synchronization device[17, 18] for the first drop. It must be mentioned, that in the latter case the effect of inclining the capillary (with the cell) is not so pronounced as in the case of the bent capillary (II) because the vertical flow of solution characteristic for the inclined capillary cannot be readily established in an inclined cell because of less favourable hydrodynamic conditions.

Polarographic curves were registered with the HEYROVSKÝ polarograph, type V 301 and a galvanometer with a sensitivity of 2.8. $\times 10^{-9}$ amp/mm (at 70 cm distance) and a period of 11 sec. The *i–t* curves were registered with a "Stylo" galvanometer (Kipp & Zonen), type A80, period 1/63 sec, sensitivity $4 \cdot 10^{-8}$ amp/mm at 70 cm, with the aid of a recording device, made from a gramophone chassis and a polarographic cylinder. The curves on the first drop were registered by means of a special synchronizing apparatus[18]. The oxygen was removed by passing nitrogen through the solution.

RESULTS

Using the cell which allows an arbitrary inclination of capillary (I), the dependence of the drop-time on the inclination of the capillary was observed at −1.0 V (M.S.E.) in a solution of $1 \cdot 10^{-3}$ *M* KCl open to air, on the limiting current of oxygen at potentials more negative than that of the maximum. The curve of the dependence of t_1 on the angle of inclination (Fig. 6) shows that the drop time is most sensitive to changes in inclination when the capillary is just in the position near to the vertical (0°). This is in agreement with statements in the literature[26], that the normal dropping electrode must be mounted so that it is within ± 5° of the vertical and that a greater degree of tilt produces erratic dropping. The curve of the change of drop-time with the angle had the same shape when measurements were carried out in 0.005 *M* $CdSO_4$ in. 0.1 *M* $HClO_4$ under nitrogen, where the drop-time was determined at −1.2 V (M.S.E.) on the diffusion current of cadmium.

The effect of the position of the capillary on the shape of polarographic waves is shown in Fig. 7. In the vertical position when the normal rate of voltage scanning (200 mV/absc) was applied, one drop falls every 33 mV and hence the curves are distorted. In the position inclined at 45° one drop falls every 13 mV and thus the curve possesses the regular theoretical shape (Fig. 7).

Obviously, vertical capillaries with a larger rate of flow can be used, but the danger that the motion of the solution may result in maxima of the second kind at too large rate of flow must be kept in mind.

The capillary bent at 45° enables perfectly reproducible current–time curves of the diffusion current to be obtained. In all cases these show a parabolic shape undisturbed by the transfer of concentration polarization from one drop to another or by turbulence, and within the limits of experimental error there is no difference between the first curve and the ones following; the curves obtained with a solution of cadmium are shown in Fig. 8.

The logarithmic plot of the current–time curves ($\log i - f(\log t)$) is almost linear; in fact it is usually very slightly curved as required by the equation derived by WEBER[27] for the current–time curve with the correction for spherical diffusion.

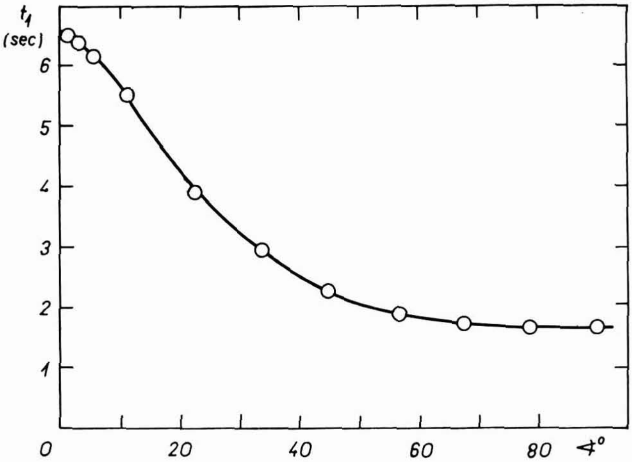

Fig. 6. The dependence of drop-time on the inclination of capillary (I). 0.0012 M KCl; $E = -1.0$ V; m = 1.14 mg/sec.

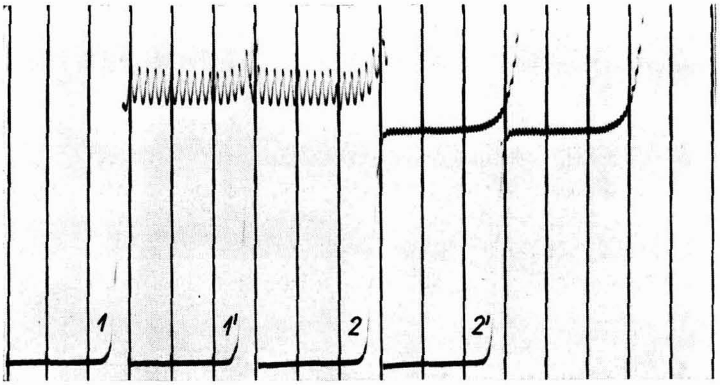

Fig. 7. The influence of the position of the capillary on the shape of the polarographic curve. Šeràk cell, M.S.E., from −0.4 V, 200 mV/absc, capillary (I), m = 1.14 mg/sec. Curves (1,1′), capillary in the vertical position, t_1 = 6.1 sec; curves (2,2′), the same capillary inclined at 45°, t_1 = 2.35 sec.

For the experimental determination of the exponent of such a curve a series of 12 curves was recorded with precisely defined and constant conditions using capillary II, m = 1.24, t_1 = 2.8 sec. By measuring the curves the average value 0.183 was found; the standard deviation of a single measurement was 0.003. By computing according to WEBER's equation[27] for t = 0.5 sec a value 0.182 was obtained in accordance with the experimental method used. By calculating according to the same equation in an integrated form a value of 0.184 was found.

The capillary bent at 45° as well as the capillary bent upwards allows the mean polarographic current affected by depletion of the solution in the vicinity of the drop to be compared with the theoretical mean current.

For comparison polarographic curves were recorded, first with capillary (III) inclined at 45° and then with the same capillary in a vertical position. The drop-time was adjusted (4 sec) in the latter case with mechanical regulation (a time beater) so that it was the same as that at the capillary in the inclined position. In this way exactly comparable conditions for the measurement of the diffusion current were obtained, at the same drop time and at the same rate of flow of mercury.

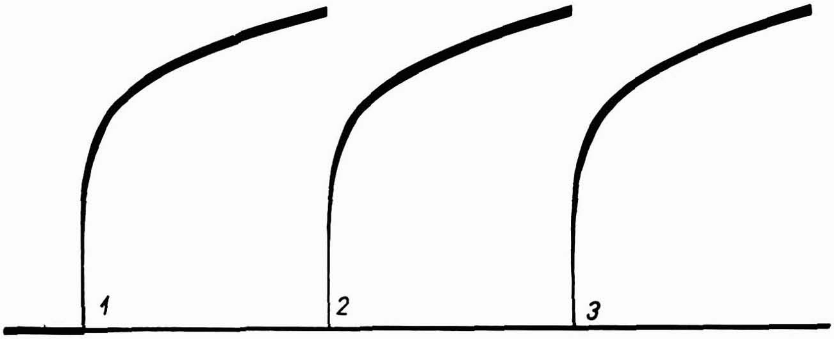

Fig. 8. Current–time curves with capillary (II) (bent at 45°). 1–3 drop, 0.005 *M* $CdSO_4$, 0.1 *M* $HClO_4$, M.S.E., −1.1 V, m = 1.24 mg/sec, drop-time 2.85 sec.

The shape of the current–time curves obtained using a device permitting the application of the voltage to the polarographic cell just at the moment when the drop has been knocked off by means of the time-beater was perfectly regular as shown with normal capillaries. Consequently, the mechanical control of the drop time does not disturb the electrode process. The current–time curves and the polarographic curves in a solution of cadmium were now recorded with both vertical and inclined capillaries. On the current–time curves recorded with the vertical capillary, the mean current on the second drop (measured by weighing the paper sheets cut out of the oscillogram) was equal to 91.5% of the mean current on the first drop. The same lowering was found also with the polarographic curve recorded with a vertical capillary (and a time-beater) compared with the polarographic curve, recorded with the same capillary in an inclined position (Fig. 9).

The current–time curves in a similar solution of cadmium were recorded also with capillary (I) (vertical, straight); in this case the mean current on the second drop was 15.5% lower than the mean current on the first drop (Fig. 10).

The actual value of the instantaneous current recorded with the capillary in the vertical position on the first drop was also compared with that obtained with the same capillary in the position inclined at 45°. It was found from a series of measurements that the instantaneous current measured with the inclined capillary is about 1% lower than the current measured at the corresponding moment with the first drop using a vertical capillary. The lowering is the same on subsequent drops.

This lowering can be explained by a greater degree of screening of the drop exerted by the glass of the tip of the capillary.

Polarographic curves in which the effect of concentration polarization is also cancelled out can be obtained also with the Tastpolarograph[30]. In this more complex instrument the polarographic circuit is connected in the last phase of drop-life where the current attains its maximum value; by this means the effect of depletion of the solution near the drop is excluded. In this case, however, the height of the wave does not correspond to the mean polarographic current.

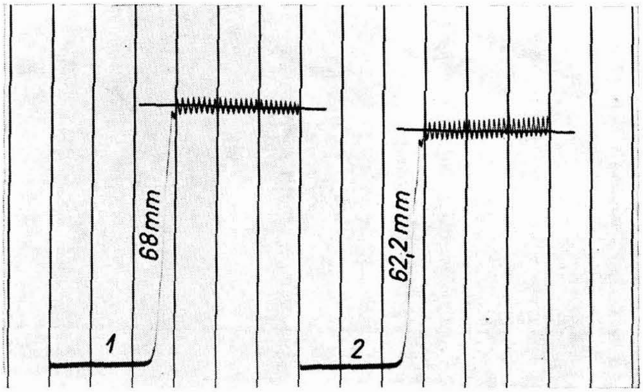

Fig. 9. 0.005 M $CdSO_4$, 0.1 N K_2SO_4, active carbon, M.S.E., from −0.4 V, 200 mV/absc, sens. 1/50, capillary (III) (0.5 mg/sec). Curve 1, capillary in inclined position, $t_1 = 4$ sec (at −1.4 V); curve 2, capillary in vertical position, time-beater 4 sec.

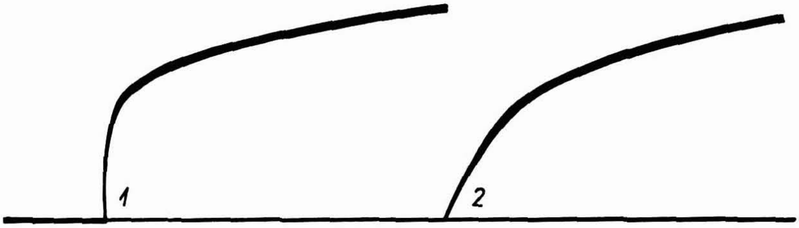

Fig. 10. Current–time curves with capillary (I), (h = 77 cm), 0.0057 M $CdSO_4$, 0.1 N Na_2SO_4, M.S.E., −1.0 V, sens. 1/10.

In addition to transfer of the concentration polarization from one drop to another, the products of electrolysis can be transferred too, but this effect also can be eliminated by using the inclined capillary. The study of glyoxalate anion in unbuffered solution is very instructive in this respect. OH^- ions that are liberated by the reduction of this substance catalyse the rate of dehydration[28]. A theoretical course of current is obtained only on the first drop or with the inclined capillary (Fig. 11, left), whilst on the second drop the OH^- ions that remain at the orifice of the capillary cause a considerable rise of current at the beginning of drop-life (Fig. 11, right). This behaviour was observed also to a minor extent when studying the reduction wave of formaldehyde in an unbuffered solution[29].

Sometimes the insoluble products of electrolysis collected beneath the vertical capillary are liable to stick to the orifice of the capillary thus causing disturbances. The motion of the solution at the inclined capillary helps to remove these products from the neighbourhood of the orifice[10].

The influence of the position of the capillary on the maximum of the first kind seems also to be of importance. The nature of the turbulent motion which causes these maxima is not influenced by the position of the capillary; the direction of the motion with respect to the drop and to the capillary remains unchanged. It is, however, turned in the space in the same sense as the capillary; the motion is more vigorous on the lower side of the capillary than on its upper side.

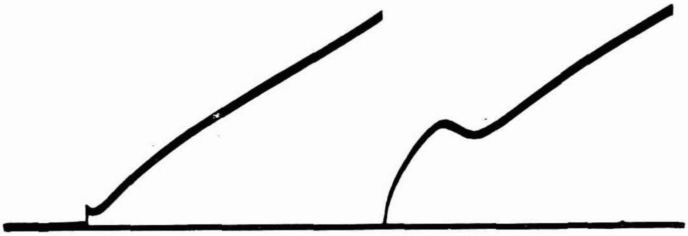

Fig. 11. Current–time curves. 3.64×10^{-3} *M* glyoxalate anion, 0.05 *N* NaCl, potential of limiting current, sens. 1/4, t_1 = 5 sec, temp. = 25°.

However, the difference arising from the position of the capillary lies in the fact that when negative maxima are recorded with a vertical capillary a drop in the current beneath the limiting diffusion current is often observed after the maximum, whereas with the inclined capillary this phenomenon does not occur. This fall of current was observed on negative maxima (Ni, Zn in ammoniacal solution, Co in ammoniacal buffer, Tl) and does not appear on positive maxima (O_2, Cu, Ag, Pb). This phenomenon was explained previously as due to a fall of current in the potential region before the limiting current is reached[31]. This explanation is in contradiction with the experiments obtained with the inclined capillary. With this capillary the fall below the diffusion current does not occur, although the potential of the dropping electrode cannot change with the inclination of capillary.

Further, this effect is a function of time. If the fall of the maximum on the polarographic curve is recorded and the voltage scanning is stopped at the moment when

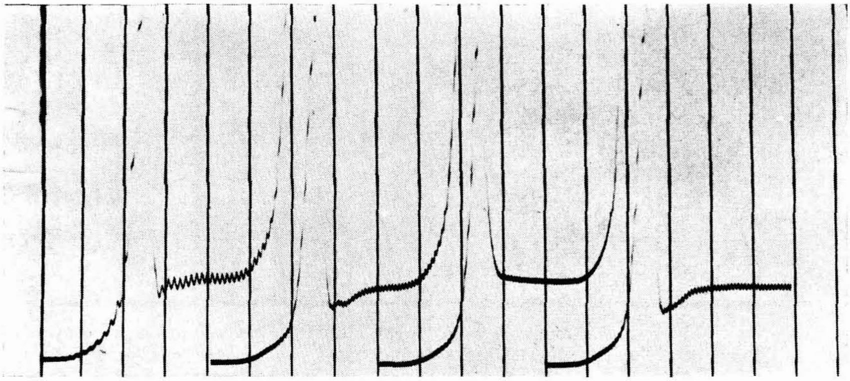

Fig. 12. 0.0025 *M* $CdSO_4$, 0.5 *M* NH_4Cl, 0.1 *M* NH_4OH, capillary (II) (bent at 45°), from −0.8 V, 200 mV/absc, sens. 1/150. Curves from left to right: 1, cap. with the end in vertical position; 2, cap. with the end in vertical position, time-beater 3 sec; 3, cap. with the end in inclined position (45°), without time-beater; 4, cap. with the end in vertical position, time-beater 3 sec; In this case the potentiometric drum stopped at the potential of the lowest point of the curve after the maximum; starting from this point the current is recorded at constant potential as a function of time.

the current attains its lowest value and the recording of the curve as a function of time at constant potential is continued, the curve after some 20 sec attains the value of the limiting current (Fig. 12, curve 4).

When the current–time curves are recorded on the falling portion of current after the maximum with a vertical capillary, the curve on the first drop after the e.m.f. has been applied corresponds in height to the maximum current; the height of further curves amounts to about one-third of the first one (Fig. 13a). After an interval of a few seconds the original series of curves can be repeated. With the inclined capillary under the same conditions, lowering of current on subsequent drops (after the first one) does not appear at all or only on every second drop (Fig. 13b).

All these effects can be satisfactorily explained by depletion of the solution within a larger distance from the drop which occurs because of an increased current at the maximum connected with the vigorous stirring of the solution by turbulent motion. At negative maxima the depleted solution is transferred by the motion upwards and accumulates under the front surface of the capillary in the vicinity of the drop. At positive maxima the depleted solution is carried away by the motion of the solution downwards and does not affect the current after the fall of the maximum. Because of the difficulty involved in reproducing the hydrodynamic conditions these effects are poorly reproducible.

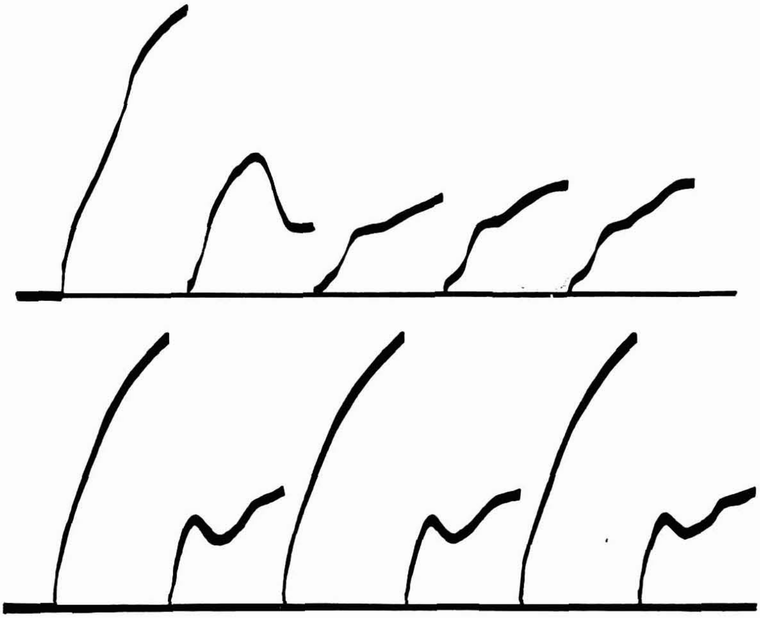

Fig. 13. a, Current–time curves. 0.0025 N CoSO$_4$, 0.25 M NH$_4$Cl, 0.1 M NH$_4$OH, capillary (II) (bent at 45°), the end in vertical position, time-beater 3 sec, − 1.3 V (on the falling portion of the maximum), sens. 1/25. b, as a, capillary with the end at 45°.

KRYUKOVA[31] remarks that maxima of this shape are obtained with a slowly increasing e.m.f., when the recording does not lag behind the change of e.m.f. — *e.g.*, when recording manually — whereas in the case of automatic recording this detail is often lost. This is not quite correct. When the current–potential curve is recorded slowly there is enough time to compensate for the depletion at the electrode and no lowering of the current beneath the limiting current occurs. Accordingly, this phenomenon is usually not recorded with a very slow drop but on the contrary will be very apparent with a quickly dropping capillary, as may be seen in Fig. 12.

The same behaviour was observed also with the maximum of thallium (Fig. 14). Here the height of the current with the vertical capillary was 87% of the current recorded with the inclined capillary.

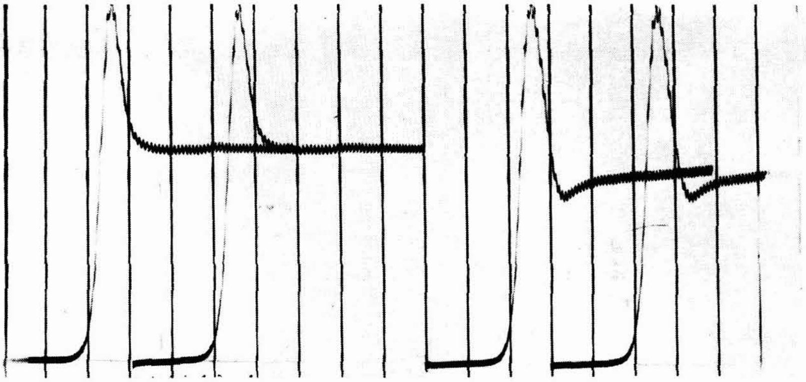

Fig. 14. 0.0025 *N* Tl_2SO_4, 0.1 *M* K_2SO_4, active carbon, M.S.E., capillary (I), from −0.2 V, 200 mV/absc, sens. 1/200. Curves left, capillary in inclined position, $t_1 = 2.1$ sec; curves right, capillary in vertical position, time-beater 2.1 sec.

The lowering of the diffusion current beneath the value of the limiting current as an effect of depletion of the solution can be observed also in Fig. 4.

A further effect can be observed in very pure solutions. This shows itself on the current–time curves of limiting diffusion current by a general increase of the current on the first and second drop both with the vertical and with the inclined capillary. This increase is proportional to the instantaneous value of current and does not alter the shape of the current–time curve; it amounts to about 10% of the value of the current.

A very small addition of gelatin (~ 0.01%) suffices to suppress entirely this increase of current (Fig. 15); further additions do not affect the value of the current. From this it may be concluded that the increase is caused by streaming of the solution

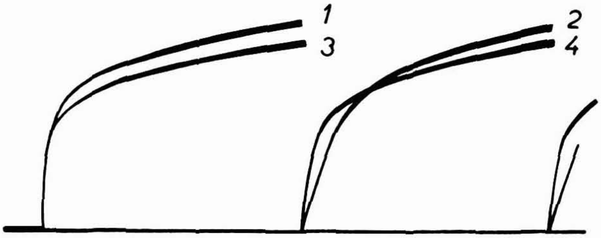

Fig. 15. Current–time curves recorded with usual vertical capillary; the influence of gelatin on the increase of the current (combined with exhaustion effect). $4 \cdot 10^{-3}$ *M* $CdSO_4$, 0.1 *M* K_2SO_4, −1.4 V against M.S.E., capillary (I), *h* = 70 cm. 1, first drop, without gelatin; 2, second drop, without gelatin; 3, first drop, 0.006% gelatin; 4, second drop, 0.006% gelatin.

near the drop, this streaming however, could not be observed directly with a microscope. Evidently, it is a tangential and very feeble. It differs from the streaming at the maxima of the first kind in that it arises on the limiting current, and from the maximum of the second kind in that it appears at low concentrations of indifferent electrolyte (0.01–0.1 M) and in its independence of the height of the mercury reservoir. It appears also at low rates of flow of mercury ($\approx$ 0.5 mg/sec).

This kind of motion of the solution does not influence the exhaustion of depolariser in the vicinity of the drop and mostly accompanies it. In such a case the addition of gelatin lowers the mean current on the first drop, whilst on the second drop the decrease of the current is partly compensated for by decrease in the exhaustion of the depolariser, the resulting change of current being given by a summation of both effects (Fig. 15).

A possible disadvantage of the use of the inclined capillary, could be that the drop on the inclined capillary adheres to the front surface of capillary and in this manner part of the surface of the drop is screened from contact with the solution. However, it has been confirmed experimentally, that the current–time curve with the inclined capillary corresponds nearly exactly to that with the first drop at the vertical capillary and has a precisely theoretical shape. This can be explained by the fact that the drop on the inclined capillary never attains the size of the drop on the vertical capillary. As long as the drop remains small, it retains its spherical shape sufficiently exactly and the surface of contact with the solution remains the same at the inclined capillary as with the vertical capillary. On the contrary, the drop on the vertical capillary is often liable to deformation towards the end of drop-life and acquires a pear-like shape with a correspondingly larger surface and so affects the regular course of current.

The mercury drop at the inclined capillary loses its spherical shape in the case when mercury adheres to glass. This phenomenon occurs in distilled water or in extremely diluted solutions (10^{-5} M). In this case, the electrokinetic potentials of the glass capillary and of mercury drop extend relatively far beyond the layer of firmly adhering liquid films[32]. When the electric charge of glass and of mercury have opposite signs the mercury is attached to the glass, the drop-time increases to 2 or 3 times the normal value and the drop takes an irregular shape. In solutions of electrolytes the double layers on glass and on mercury are compressed and do not extend beyond their firmly adhering liquid films and the attachment of mercury to glass does not occur. Accordingly, in conditions of polarographic work this adhering of mercury to glass is hardly to be expected.

ACKNOWLEDGEMENT

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SUMMARY

The polarographic capillary with the orifice in an inclined position — most conveniently at 45° — improves the properties of the dropping-mercury electrode. It removes the effect of transfer of concentration polarization from one drop to the other, or the transfer of the products of electrolysis, and in this manner ensures the fulfilment of the basic condition for the polarographic diffusion current, namely, that the concen-

tration of depolarizer in the time of drop-formation in the neighbourhood of the electrode is the same as in the bulk of solution. Accordingly, it gives the instantaneous current of theoretical shape. It is the only type of dropping-mercury electrode on which may be registered the mean polarographic current which is not influenced by transfer of concentration polarization and which satisfies the equation of the diffusion current with the correction for spherical diffusion. It removes the disturbances that can be caused by the insoluble products of electrolysis collecting in the vicinity of the orifice. At potentials, where hydrogen is evolved at the electrode, the bubbles arising on the orifice can escape upwards. It lowers considerably the movement of electrolyte near the drop giving rise to the maximum of the second kind. It affords a reasonable short drop-time with small oscillations at a small rate of flow of mercury

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REDOXOKINETIC AND IMPEDANCE TITRATIONS OF ZINC AND CADMIUM SALTS WITH POTASSIUM FERROCYANIDE

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INTRODUCTION

The techniques of redoxokinetic and impedance titrations are by now established analytical tools for various determinations[1-5]. In these techniques the redoxokinetic potential (the potential developed at an inert electrode in contact with a redox system in solution, when it is polarized by an alternating current), and the cell impedance are measured as functions of the volume of titrant added. The redoxokinetic potential which is related to kinetic factors like the exchange current density, and the symmetry factor, has been found to undergo a sudden change at the end point. The gross cell impedance across the cell also shows an inflexion corresponding to the end point, if the electrode is polarised by a constant alternating current. Various mathematical expressions for the redoxokinetic potential have been worked out by different workers[6-12]. However, the mechanism for these titrations has not yet been fully resolved.

The results of the following titrations are summarized in this paper:

(i) zinc salts *vs.* potassium ferrocyanide;

(ii) cadmium salts *vs.* potassium ferrocyanide;

both in presence of traces of potassium ferricyanide.

The results obtained by the above techniques have been compared with those from conventional potentiometric titrations.

EXPERIMENTAL

The circuit diagram is given in Fig. 1 which is self-explanatory. By use the of the variable series resistances R_1, R_2 and R_3, a constant current of 100 μA r.m.s. was maintained across the electrodes. The alternating current was measured by means of a vacuum tube voltmeter and a non-inductive standard resistance (R_5), included in the circuit. Only two electrodes have been used in this set-up, one of which is a platinum micro-electrode (E_1) and the other a platinum reference electrode having a large area (gauze electrode, E_2). The gauze electrode just surrounds the experimental micro-electrode thereby minimizing the *IR* drop across it. The electrodes were cleaned

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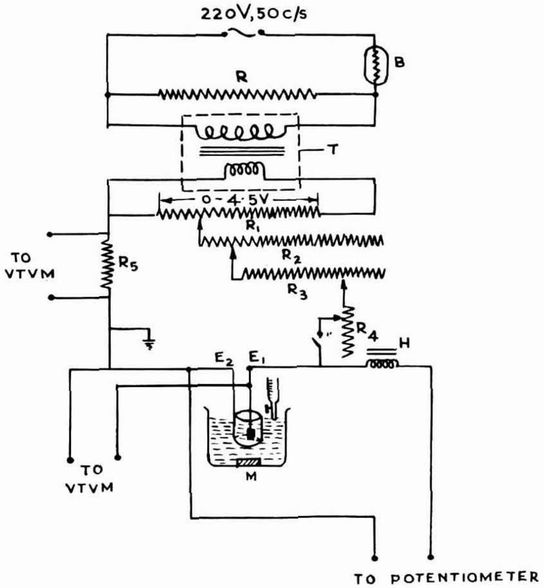

Fig. 1. Experimental set-up for redoxokinetic titration: B, current-stabilizing barretter (0.3 A); R, mains resistance (600 Ω, 20 W); T, step-down transformer (input 220 V, output 6 V); R_1, R_2, R_3 and R_4, potentiometers (total resistance 200 Ω, 40, 10 and 1 kΩ, 3 W); R_5 (100 Ω, 0.5 W); E_1, Pt micro-electrode (length 7.45 mm, mean diam. 0.48 mm); E_2, gauze electrode (mean diam. 10 mm, cylindrical height 11.7 mm).

Solution in the beaker

I Titration of zinc vs. potassium ferrocyanide

(a) 100 ml of 5 m*M* solution of zinc sulphate ($ZnSO_4 \cdot 7H_2O$) in 1.0 *M* potassium nitrate (supporting electrolyte) + 0.5 ml of an approximately 1% solution of potassium ferricyanide (temperature, 70 ±0.2°), see Fig. 2.

(b) 100 ml of 1 m*M* solution of zinc sulphate in 1.0 *M* potassium nitrate (supporting electrolyte) + 0.5 ml of an approximately 1% solution of potassium ferricyanide (temperature, 70 ±0.2°), see Fig. 3.

II Titration of cadmium vs. potassium ferrocyanide

(a) 100 ml of 5.17 m*M* cadmium acetate buffered with acetic acid (pH ~ 4.5) in 1.0 *M* potassium nitrate + 0.5 ml of an approximately 1% solution of potassium ferricyanide (temperature, 65 ±0.2°), see Fig. 4.

(b) 100 ml of 1.0 m*M* cadmium acetate ($Cd(CH_3COO)_2 \cdot 2H_2O$) buffered with acetic acid (pH ~ 4.5) in 1.0 *M* potassium nitrate + 0.5 ml of an approximately 1% solution of potassium ferricyanide (temperature, 65 ±0.2°), Fig. not given.

Solutions in the burette

0.05 *M* and 0.01 *M* freshly prepared potassium ferrocyanide solution.

After each addition, the solution was well-stirred by a magnetic stirrer. At each

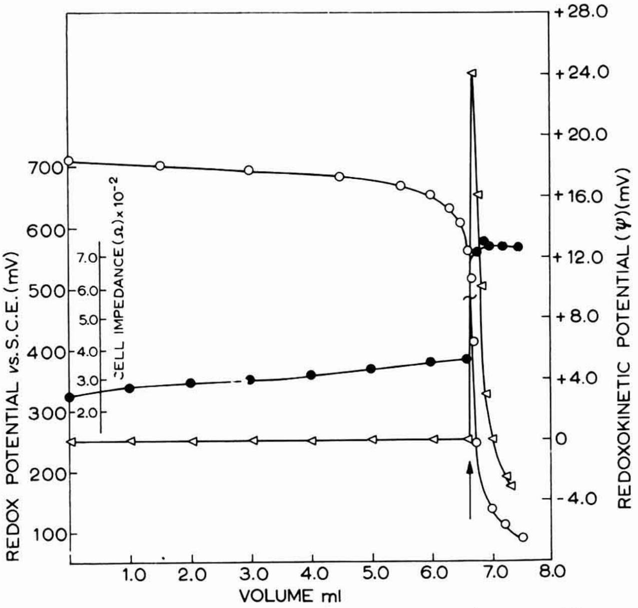

Fig. 2. Titration of 100 ml of 5 m*M* zinc *vs.* 0.05 *M* potassium ferrocyanide: ○, redox potential; △, redoxokinetic potential; ●, cell impedance.

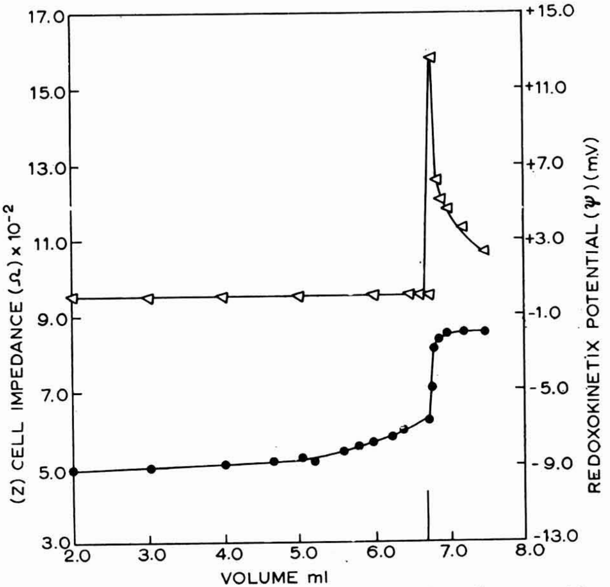

Fig. 3. Titration of 100 ml of 1 m*M* zinc *vs.* 0.01 *M* potassium ferrocyanide: △, redoxokinetic potential; ●, cell impedance.

stage the redoxokinetic potential between E_1 and E_2 was measured using a students' potentiometer (Kaycee), the a.c. having been blocked by an inductance. The a.c. potential across the electrodes were measured using a V.T.V.M. (Philips Type 6015). The gross cell impedance was calculated from the readings on V.T.V.M. and the constant current in the circuit.

The potentiometric titrations under unpolarized conditions were carried out independently for the sake of comparison. The redox potentials of the unpolarized electrode during the course of the titration were measured by means of a students' potentiometer (Kaycee), using a saturated calomel electrode as the reference electrode.

RESULTS

The values of the redoxokinetic potential (Ψ), the cell impedance (Z), and the redox potential during the course of various typical titrations are presented in Figs. 2–4. The arrows indicate the stoichiometric end points. Fig. 2 represents the titrations of zinc at a concentration of 5 mmoles/l. There is a striking coincidence in the values of the end points obtained by the three independent methods.

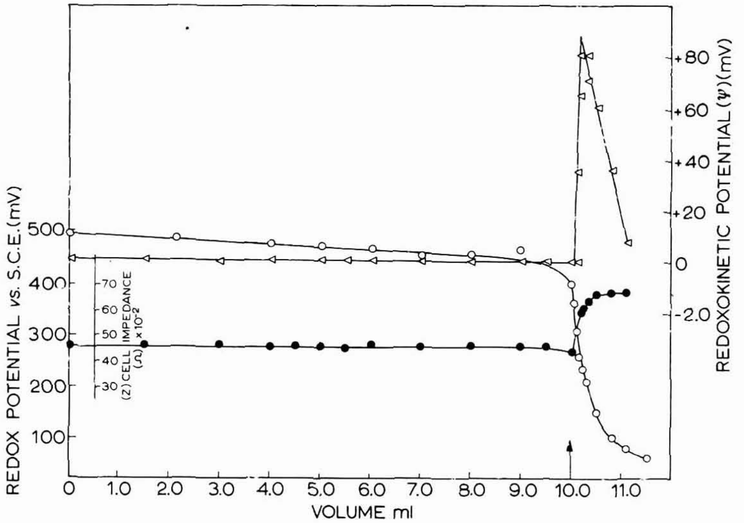

Fig. 4. Titration of 100 ml of 5.17 m*M* cadmium *vs.* 0.05 *M* potassium ferrocyanide: ○, redox potential; △, redoxokinetic potential; ●, cell impedance.

With more dilute solutions of zinc (1 mmole/l) potentiometry fails, whereas by redoxokinetic and impedance titrations (Fig. 3) the end point could be detected with a reproducibility within ± 2%.

When the concentration is reduced to 0.1 mmole/l or less all the discussed methods are unsuccessful. The irreproducibility is enhanced with dilution. Although the characteristic feature of these titrations is the sudden change in Ψ and Z at the end point, small variations in their values are unavoidable as kinetic parameters are involved and these are difficult to reproduce at solid surfaces. The equivalence point in the case of zinc corresponds to the formation of a precipitate of composition $K_2Zn_3[Fe(CN)_6]_2$, which is in agreement with previous findings[13,14].

Figure 4 shows the results obtained with a solution of cadmium of concentration 5.17 mmoles/l. Here again there is a good correspondence at the end point between the different methods. The error involved in the case of a dilute solution (1 mmole/l) is outside the range permissible for precision work. All the discussed methods fail if the concentration is reduced to 0.1 mmole/l or less. The equivalence point in the case of cadmium corresponds to the formation of a precipitate of composition $K_2Cd[Fe(CN)_6]$.

Table 1 presents the comparative data on precision in terms of the mean percentage deviation of reproducibility, obtainable in various titrations. The data for the percentage error represent the average of a large number of titrations.

TABLE 1

PRECISION OBTAINABLE IN VARIOUS TITRATIONS

Titration	*No.*	*Conc. of Zn(Cd) in mmoles/l*	*Precision obtainable (%)*			*Fig.*
			Potentiometry	*Redoxokinetic*	*Impedance*	
Zinc *vs.* potassium ferrocyanide	I(a)	5.0	± 0.5	± 0.2	± 0.5	2
	I(b)	1.0	> 5.0 unsuccessful	± 1.5	± 2.0	3
	I(c)	≤ 0.10		— unsuccessful —		
Cadmium *vs.* potassium ferrocyanide	II(a)	5.17	± 0.5	± 0.3	± 0.5	4
	II(b)	1.0	unsuccessful	± 3.0	± 3.0	—
	II(c)	≤ 0.1		— unsuccessful —		

It can be seen that in all cases the redoxokinetic and impedance technique give more accurate results than potentiometry. The end points shown in Fig. 2 correspond to exact stoichiometry. The end points in the titrations of cadmium and dilute solutions of zinc appear at values much higher than those predicted from stoichiometry. The discrepancy is more pronounced as the dilution increases. Ferrocyanide ions have been reported as adsorbing on such precipitates[15], as those obtained in the titrations described in this paper. The deviations observed in titrations of dilute solutions may therefore be a result of adsorption of this kind, which would predominate in dilute solutions because of the larger surface area offered by the precipitate.

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SUMMARY

It has been shown that the techniques of redoxokinetic and impedance titrations can be successfully applied to the titration with potassium ferrocyanide, of (i) zinc salts and (ii) cadmium salts, both in presence of traces of potassium ferricyanide to establish the redox system. The titrations have been carried out at elevated temperatures, and the results are compared with those obtained by conventional potentiometry.

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Short Communications

Charge and outer Helmholtz potential for a mercury electrode in aqueous NaF at 25°

The accompanying tables were compiled to facilitate the application of the theory of the electrical double layer to the study of electrode kinetics[1,2]. They were obtained by numerical interpolation and extrapolation from the data of GRAHAME[3] on the mercury–aqueous NaF interface at 25°, using a digital computor. The surface charge density q and the potential ψ of the outer Helmholtz plane *vs.* the solution are listed in Table 1 as a function of electrode potential (*vs.* S.C.E.) for various concentrations of NaF. ψ was calculated from the equation[2]

$$\psi = \left(\frac{2\,RT}{ZF}\right) \sinh^{-1} \left(\frac{\pi q^2}{2\varepsilon\, kTc}\right)^{\frac{1}{2}} \tag{1}$$

of the Gouy-Chapman theory with the assumption of no specific adsorption of sodium or fluoride ions. To enable the reader to assess the accuracy of the calculation, Grahame's reported data for 0.001 *M* NaF are given in Table 2 for comparison with the values calculated by extrapolation from his data for 0.01 *M* NaF. This was the least favourable extrapolation undertaken.

METHOD OF CALCULATION

A. Extrapolation

From Grahame's data for E *vs.* q at concentration c_1, a new table of potentials E' was calculated for concentration c_2 at the same values of q, by assuming that the change in E was the same as the change in ψ and calculating the change in ψ from eqn. (1). This is in accordance with Grahame's rule that the potential drop across the inner Helmholtz layer depends only on the surface charge[3]. Then q' was calculated at equal increments of potential by quartic Lagrangian inverse interpolation in the table of E' *vs.* q. The potential ψ was finally calculated from q' using eqn. (1)

B. Interpolation

This was similar to the extrapolation, but potentials E' were calculated from data at both higher and lower concentrations and a linearly weighted average taken. A quartic Lagrangian interpolation was used to obtain values of E at a common value of q for both higher and lower concentrations.

TABLE 1A

CALCULATED FROM DATA AT 0.01 *M*, *E* AND ψ IN VOLTS, q IN $\mu C/cm^2$

E vs. *S.C.E.*	0.00100 *M*		0.00150 *M*		0.00200 *M*		0.00300 *M*		0.00500 *M*		0.00750 *M*		0.0100 *M*	
	q	ψ	q	ψ	q	ψ	q	ψ	q	ψ	q	ψ	q	ψ
−1.850	−21.99	-0.245_{3}	−22.19	-0.235_{3}	−22.34	-0.228_{3}	−22.54	-0.218_{3}	−22.80	-0.205_{8}	−23.01	-0.195_{9}	−23.16	-0.188_{8}
−1.750	−20.13	-0.240_{7}	−20.32	-0.230_{8}	−20.45	-0.223_{8}	−20.64	-0.213_{8}	−20.88	-0.201_{3}	−21.08	-0.191_{4}	−21.22	-0.184_{3}
−1.650	−18.36	-0.236_{0}	−18.54	-0.226_{1}	−18.67	-0.219_{1}	−18.85	-0.209_{2}	−19.08	-0.196_{7}	−19.26	-0.186_{8}	−19.40	-0.179_{7}
−1.550	−16.65	-0.231_{0}	−16.83	-0.221_{1}	−16.95	-0.214_{1}	−17.13	-0.204_{3}	−17.35	-0.191_{8}	−17.53	-0.181_{9}	−17.66	-0.174_{9}
−1.450	−15.02	-0.225_{7}	−15.18	-0.215_{9}	−15.30	-0.208_{9}	−15.47	-0.199_{0}	−15.68	-0.186_{6}	−15.85	-0.176_{8}	−15.98	-0.169_{8}
−1.350	−13.43	-0.220_{0}	−13.60	-0.210_{2}	−13.71	-0.203_{2}	−13.88	-0.193_{5}	−14.08	-0.181_{1}	−14.25	-0.171_{3}	−14.37	-0.164_{4}
−1.250	−11.88	-0.213_{7}	−12.04	-0.204_{0}	−12.16	-0.197_{1}	−12.32	-0.187_{3}	−12.52	-0.175_{1}	−12.68	-0.165_{3}	−12.80	-0.158_{4}
−1.150	−10.29	-0.206_{3}	−10.46	-0.196_{7}	−10.58	-0.189_{9}	−10.74	-0.180_{3}	−10.95	-0.168_{2}	−11.12	-0.158_{6}	−11.24	-0.151_{8}
−1.050	− 8.70	-0.197_{7}	− 8.87	-0.188_{3}	− 8.98	-0.181_{6}	− 9.15	-0.172_{1}	− 9.36	-0.160_{2}	− 9.52	-0.150_{7}	− 9.64	-0.144_{0}
−0.950	− 7.05	-0.186_{9}	− 7.23	-0.177_{8}	− 7.35	-0.171_{3}	− 7.52	-0.162_{1}	− 7.74	-0.150_{5}	− 7.91	-0.141_{3}	− 8.04	-0.134_{7}
−0.850	− 5.29	-0.172_{2}	− 5.48	-0.163_{6}	− 5.61	-0.157_{5}	− 5.80	-0.148_{8}	− 6.03	-0.137_{7}	− 6.21	-0.128_{9}	− 6.34	-0.122_{7}
−0.750	− 3.46	-0.150_{4}	− 3.65	-0.142_{8}	− 3.78	-0.137_{3}	− 3.97	-0.129_{5}	− 4.21	-0.119_{6}	− 4.40	-0.111_{6}	− 4.54	-0.105_{9}
−0.650	− 1.74	-0.115_{7}	− 1.90	-0.109_{9}	− 2.01	-0.105_{7}	− 2.18	-0.099_{6}	− 2.40	-0.091_{7}	− 2.57	-0.085_{3}	− 2.70	-0.080_{7}
−0.550	− 0.61	-0.066_{0}	− 0.67	$-0{,}060_{9}$	− 0.71	-0.057_{5}	− 0.78	-0.053_{1}	− 0.89	-0.047_{9}	− 0.98	-0.044_{0}	− 1.05	-0.041_{3}
−0.450	0.10	0.014_{1}	0.13	0.015_{4}	0.16	0.015_{8}	0.20	0.015_{8}	0.24	0.015_{1}	0.28	0.014_{1}	0.31	0.013_{4}
−0.350	1.05	0.090_{8}	1.17	0.086_{4}	1.26	0.083_{1}	1.40	0.078_{2}	1.58	0.072_{0}	1.73	0.066_{9}	1.84	0.063_{3}
−0.250	2.65	0.136_{9}	2.85	0.130_{3}	3.00	0.125_{6}	3.21	0.118_{7}	3.48	0.110_{0}	3.70	0.103_{0}	3.86	0.097_{9}
−0.150	4.82	0.167_{4}	5.07	0.159_{6}	5.24	0.154_{0}	5.49	0.146_{0}	5.81	0.135_{9}	6.06	0.127_{8}	6.25	0.122_{0}
−0.050	7.28	0.188_{5}	7.54	0.180_{0}	7.73	0.173_{9}	8.00	0.165_{2}	8.34	0.154_{3}	8.60	0.145_{5}	8.80	0.139_{3}
0.050	9.88	0.204_{2}	10.16	0.195_{2}	10.35	0.188_{8}	10.63	0.179_{8}	10.99	0.168_{4}	11.27	0.159_{3}	11.48	0.152_{9}
0.150	12.62	0.216_{8}	12.92	0.207_{6}	13.13	0.201_{0}	13.43	0.191_{8}	13.82	0.180_{1}	14.12	0.170_{9}	14.35	0.164_{3}
0.250	15.61	0.227_{7}	15.94	0.218_{4}	16.18	0.211_{7}	16.52	$c.202_{4}$	16.96	0.190_{6}	17.31	0.181_{3}	17.57	0.174_{7}

TABLE 1B

CALCULATED FROM DATA AT 0.01 M AND AT 0.1 M, E AND ψ IN VOLTS, q IN μC/cm^2

E *vs. S.C.E.*	0.0150 M		0.0200 M		0.0300 M		0.0500 M		0.0750 M		0.100 M	
	q	ψ	q	ψ	q	ψ	q	ψ	q	ψ	q	ψ
−1.850	−23.37	-0.178_{9}	−23.52	-0.171_{9}	−23.74	-0.162_{0}	−24.01	-0.149_{5}	−24.24	-0.139_{6}	−24.42	-0.132_{7}
−1.750	−21.41	-0.174_{4}	−21.55	-0.167_{4}	−21.76	-0.157_{5}	−22.02	-0.145_{1}	−22.23	-0.135_{2}	−22.39	-0.128_{3}
−1.650	−19.58	-0.169_{8}	−19.72	-0.162_{8}	−19.91	-0.152_{9}	−20.15	-0.140_{5}	−20.35	-0.130_{7}	−20.50	-0.123_{8}
−1.550	−17.83	-0.165_{1}	−17.96	-0.158_{1}	−18.14	-0.148_{2}	−18.37	-0.135_{8}	−18.56	-0.126_{1}	−18.70	-0.119_{2}
−1.450	−16.15	-0.160_{0}	−16.27	-0.153_{0}	−16.44	-0.143_{2}	−16.67	-0.130_{9}	−16.84	-0.121_{2}	−16.98	-0.114_{3}
−1.350	−14.53	-0.154_{6}	−14.65	-0.147_{6}	−14.81	-0.137_{9}	−15.03	-0.125_{6}	−15.20	-0.116_{0}	−15.32	-0.109_{2}
−1.250	−12.96	-0.148_{7}	−13.07	-0.141_{8}	−13.23	-0.132_{2}	−13.44	-0.120_{0}	−13.60	-0.110_{4}	−13.72	-0.103_{7}
−1.150	−11.40	-0.142_{2}	−11.51	-0.135_{4}	−11.67	-0.125_{8}	−11.87	-0.113_{8}	−12.03	-0.104_{3}	−12.14	-0.097_{6}
−1.050	− 9.80	-0.134_{5}	− 9.92	-0.127_{8}	−10.08	-0.118_{4}	−10.28	-0.106_{6}	−10.44	-0.097_{3}	−10.56	-0.090_{8}
−0.950	− 8.20	-0.125_{5}	− 8.32	-0.118_{9}	− 8.48	-0.109_{7}	− 8.68	-0.098_{2}	− 8.83	-0.089_{2}	− 8.94	-0.082_{9}
−0.850	− 6.51	-0.113_{9}	− 6.63	-0.107_{6}	− 6.80	-0.098_{8}	− 7.00	-0.087_{8}	− 7.16	-0.079_{2}	− 7.26	-0.073_{1}
−0.750	− 4.72	-0.097_{8}	− 4.84	-0.092_{1}	− 5.01	-0.084_{0}	− 5.22	-0.073_{9}	− 5.37	-0.066_{1}	− 5.47	-0.060_{6}
−0.650	− 2.86	-0.074_{0}	− 2.98	-0.069_{3}	− 3.14	-0.062_{7}	− 3.32	-0.054_{4}	− 3.46	-0.048_{0}	− 3.55	-0.043_{7}
−0.550	− 1.15	-0.037_{7}	− 1.22	-0.035_{1}	− 1.32	-0.031_{4}	− 1.43	-0.026_{8}	− 1.51	-0.023_{4}	− 1.56	-0.021_{0}
−0.450	0.34	0.012_{2}	0.37	0.011_{3}	0.40	0.010_{1}	0.44	0.008_{6}	0.47	0.007_{5}	0.49	0.006_{7}
−0.350	1.99	0.058_{1}	2.10	0.054_{4}	2.26	0.049_{2}	2.44	0.042_{8}	2.58	0.037_{8}	2.68	0.034_{4}
−0.250	4.08	0.090_{8}	4.24	0.085_{7}	4.46	0.078_{5}	4.73	0.069_{5}	4.94	0.062_{5}	5.08	0.057_{5}
−0.150	6.50	0.113_{8}	6.68	0.107_{9}	6.93	0.099_{7}	7.24	0.089_{4}	7.48	0.081_{2}	7.66	0.075_{6}
−0.050	9.06	0.130_{5}	9.25	0.124_{3}	9.52	0.115_{5}	9.86	0.104_{5}	10.12	0.095_{8}	10.31	0.089_{7}
0.050	11.76	0.143_{8}	11.97	0.137_{3}	12.26	0.128_{3}	12.63	0.116_{9}	12.94	0.107_{9}	13.18	0.101_{7}
0.150	14.66	0.155_{0}	14.90	0.148_{5}	15.23	0.139_{3}	15.67	0.127_{8}	16.05	0.118_{7}	16.20	0.112_{0}

TABLE 1C

CALCULATED FROM DATA AT 0.1 M, 0.66 M AND 0.916 M, E AND ψ IN VOLTS, q IN μC/cm^2

E vs.S.C.E.	0.150 M		0.200 M		0.300 M		0.500 M		0.750 M		E vs.S.C.E.	1.00 M	
	q	ψ	q	ψ	q	ψ	q	ψ	q	ψ		q	ψ
−1.750	−22.59	-0.118_5	−22.73	-0.111_6	−22.94	-0.102_0	−23.22	-0.090_0	−23.45	-0.080_8	−1.850	−25.70	-0.078_4
−1.650	−20.69	-0.114_1	−20.82	-0.107_2	−21.01	-0.097_6	−21.26	-0.085_8	−21.47	-0.076_7	−1.750	−23.60	-0.074_4
−1.550	−18.87	-0.109_5	−19.00	-0.102_7	−19.18	-0.093_2	−19.40	-0.081_5	−19.60	-0.072_5	−1.650	−21.63	-0.070_5
−1.450	−17.15	-0.104_7	−17.26	-0.097_9	−17.43	-0.088_5	−17.64	-0.077_0	−17.82	-0.068_2	−1.550	−19.76	-0.066_4
−1.350	−15.48	-0.099_6	−15.59	-0.092_9	−15.75	-0.083_7	−15.94	-0.072_3	−16.12	-0.063_8	−1.450	−17.99	-0.062_3
−1.250	−13.87	-0.094_3	−13.97	-0.087_7	−14.12	-0.078_5	−14.29	-0.067_4	−14.46	-0.059_1	−1.350	−16.29	-0.058_1
−1.150	−12.28	-0.088_4	−12.39	-0.081_9	−12.52	-0.073_0	−12.68	-0.062_2	−12.84	-0.054_2	−1.250	−14.62	-0.053_7
−1.050	−10.70	-0.081_8	−10.80	-0.075_5	−10.94	-0.066_9	−11.09	-0.056_5	−11.24	-0.049_0	−1.150	−13.00	-0.049_1
−0.950	− 9.09	-0.074_2	− 9.19	-0.068_1	− 9.32	-0.060_0	− 9.47	-0.050_2	− 9.62	-0.043_3	−1.050	−11.40	-0.044_2
−0.850	− 7.41	-0.065_0	− 7.51	-0.059_4	− 7.64	-0.051_9	− 7.79	-0.043_0	− 7.93	-0.036_8	−0.950	− 9.78	-0.039_0
−0.750	− 5.62	-0.053_4	− 5.72	-0.048_5	− 5.85	-0.042_0	− 6.00	-0.034_5	− 6.12	-0.029_3	−0.850	− 8.08	-0.033_0
−0.650	− 3.68	-0.038_1	− 3.77	-0.034_3	− 3.89	-0.029_5	− 4.02	-0.024_0	− 4.13	-0.020_3	−0.750	− 6.24	-0.026_1
−0.550	− 1.63	-0.018_1	− 1.69	-0.016_2	− 1.75	-0.013_8	− 1.83	-0.011_2	− 1.89	-0.009_5	−0.650	− 4.21	-0.018_1
−0.450	0.51	0.005_7	0.52	0.005_1	0.53	0.004_3	0.54	0.003_3	0.54	0.002_7	−0.550	− 1.95	-0.008_5
−0.350	2.80	0.030_0	2.89	0.027_0	3.00	0.023_2	3.10	0.018_8	3.18	0.015_8	−0.450	0.56	0.002_4
−0.250	5.28	0.050_9	5.41	0.046_4	5.59	0.040_4	5.78	0.033_4	5.93	0.028_5	−0.350	3.26	0.014_1
−0.150	7.89	0.067_8	8.05	0.062_3	8.26	0.055_0	8.50	0.046_2	8.70	0.039_9	−0.250	6.05	0.025_4
−0.050	10.57	0.081_2	10.75	0.075_3	11.00	0.067_1	11.29	0.057_3	11.55	0.050_1	−0.150	8.88	0.035_9
0.050	13.48	0.092_9	13.69	0.086_7	13.97	0.078_0	14.28	0.067_4	14.56	0.059_4	−0.050	11.78	0.045_4
											0.050	14.92	0.054_5
											0.150	20.29	0.067_6

TABLE 2

DATA GIVEN BY GRAHAME[3] FOR 0.001 M NaF

E (*vs.* S.C.E.)	q ($\mu C/cm^2$)
−1.75	−20.12
−1.65	−18.34
−1.55	−16.64
−1.45	−15.00
−1.35	−13.43
−1.25	−11.88
−1.15	−10.32
−1.05	−8.72
−0.95	−7.05
−0.85	−5.15
−0.75	−3.48
−0.65	−1.81
−0.55	−0.54
−0.45	+0.14
−0.35	+1.05

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SUMMARY

Tables of double layer potentials were calculated from literature data.

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The current–potential equation for linear-sweep voltammetry

The theory of voltammetry with linearly changing potential ("linear-sweep polarography") for a reversible redox-system has been treated by ŠEVČIK[1] and RANDLES[2]. ŠEVČIK solved the diffusion equation for linear diffusion by using the Laplace transformation; RANDLES used a numerical method.

Their results can be summarized in the following current–potential equation:

$$i = \frac{n^{3/2} F^{3/2}}{R^{1/2} T^{1/2}} A C^0 v^{1/2} \left(\sqrt{D_0} + \frac{\sqrt{D_R}}{\theta}\right) \cdot P\left(\frac{nF}{RT} \cdot vt\right) . \qquad (1)$$

It is supposed here that the potential changes from positive towards negative values. The notation used in this communication is the same as in DELAHAY's book[3].

ŠEVČIK arrived at a convolution integral for the function P; this integral he evaluated by a summation. RANDLES evaluated P numerically only and his calculations were repeated and confirmed by NICHOLSON[4]. The numerical P-values of ŠEVČIK and RANDLES differ by as much as 25%. ŠEVČIK finds:

$$P_{\max.} = 0.361 \quad \text{at} \quad E = E_{\frac{1}{2}} - 1.6 \frac{RT}{nF},$$

while according to RANDLES and NICHOLSON

$$P_{\max.} = 0.452 \quad \text{at} \quad E = E_{\frac{1}{2}} - 1.1 \frac{RT}{nF}.$$

A better evaluation of P seemed justified and is described below.

We have verified the correctness of ŠEVČIK's convolution integral, which can be written in a slightly modified form as follows:

$$P = \frac{1}{4\sqrt{\pi}} \int_0^{\sigma t} \frac{1}{\sqrt{\sigma t - \sigma\xi}} \cdot \frac{1}{\cosh^2 \frac{1}{2}(\sigma t_{\frac{1}{2}} - \sigma\xi)} \, \mathrm{d}\sigma\xi . \tag{2}$$

From eqn. (2) it follows that P is a function of $\sigma t = (nF/RT)vt$ and this shows that the form of the current–potential curve is independent of the rate of potential change, although its height is proportional to $v^{\frac{1}{2}}$.

ŠEVČIK evaluated eqn. (2) by replacing the integration by a summation which gives:

$$P \approx \frac{1}{4\sqrt{\pi}} \sqrt{\frac{\sigma t}{n}} \sum_{k=0}^{n-1} \frac{1}{\sqrt{n-k}} \cdot \frac{1}{\cosh^2 \frac{1}{2}(\sigma t_{\frac{1}{2}} - \frac{k}{n}\sigma t)} . \tag{3}$$

Because the factor $\sqrt{\sigma t - \sigma\xi}$ occurs in the denominator of the function inside the integral (2) this function has a point at infinity. Therefore eqn. (3) gives P-values which are much too low, unless n is very large.

However, integrating eqn. (2) by parts results in the following expression;

$$P = \frac{1}{2\sqrt{\pi}} \left\{ \frac{\sqrt{\sigma t}}{\cosh^2 \frac{1}{2}\sigma t_{\frac{1}{2}}} + \int_0^{\sigma t} \sqrt{\sigma t - \sigma\xi} \cdot \frac{\operatorname{tgh} \frac{1}{2}(\sigma t_{\frac{1}{2}} - \sigma\xi)}{\cosh^2 \frac{1}{2}(\sigma t_{\frac{1}{2}} - \sigma\xi)} \, \mathrm{d}\sigma\xi \right\} . \tag{4}$$

The function inside the integral in eqn. (4) has no points at infinity, and is well suited for accurate evaluation by standard methods for numerical integration.

However, for $t < t_{\frac{1}{2}}$, *i.e.*, for $E < E_{\frac{1}{2}}$, a simpler way of computing P is possible. The hyperbolic cosine in eqn. (2) can be expressed in an infinite series, and performing two integrations by substitution gives:

$$P = -\sum_{n=1}^{\infty} (-1)^n \exp\left[-n(\sigma t_{\frac{1}{2}} - \sigma t)\right] \sqrt{n}\, \mathrm{erf} \sqrt{n\sigma t}\,. \tag{5}$$

Equation (5) was also derived by ŠEVČIK, but in a different way, and was not used for his numerical calculations.

For $t > t_{\frac{1}{2}}$, *i.e.*, for $E > E_{\frac{1}{2}}$, ŠEVČIK also derived an infinite series but the correctness of this series could however not be proved; moreover this series is divergent. It is possible to derive an infinite series for $t > t_{\frac{1}{2}}$ in the same way as eqn. (5) is derived, but its evaluation is more difficult than the evaluation of eqn. (4).

We have computed P-values with eqns. (4) and (5) and the results are given in Fig. 1. It appears that P is practically independent of the value of the parameter $\sigma t_{\frac{1}{2}}$; only the very first part of the curve is appreciably dependent of $\sigma t_{\frac{1}{2}}$. The given figure is constructed for $\sigma t_{\frac{1}{2}} = 10$. The origin of the potential axis is at $\sigma t_{\frac{1}{2}}$, which corresponds with the polarographic half-wave potential of the redox-system.

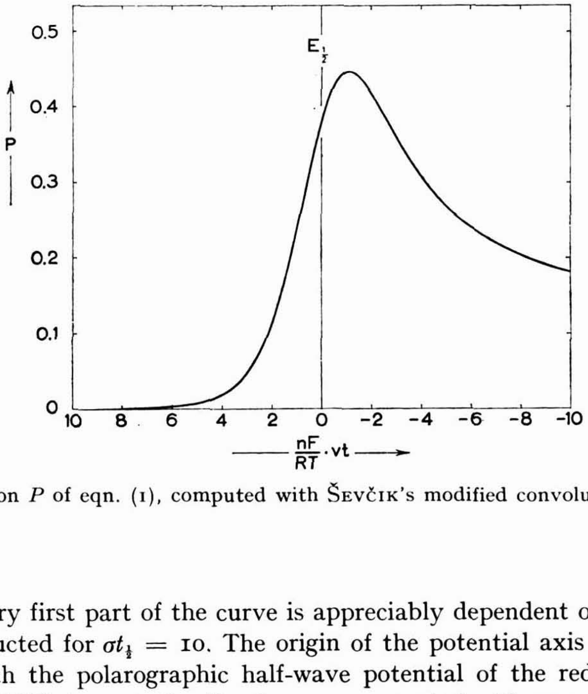

Fig. 1. The function P of eqn. (1), computed with ŠEVČIK's modified convolution integral.

For $10 \geqslant (nF/RT)vt \geqslant 0.5$, the P-values are computed with eqn. (5) for $\sigma t_{\frac{1}{2}} = 10$. For $0.5 \geqslant (nF/RT)vt \geqslant -10$, eqn. (4) is evaluated using Simpson's rule, with $\sigma t_{\frac{1}{2}} = 6$, and a division of the interval of integration into 50 intervals.

For the maximum of P we found:

$$P_{\mathrm{max.}} = 0.446 \quad \text{at} \quad E = E_{\frac{1}{2}} - 1.1 \frac{RT}{nF}\,.$$

In order to obtain some idea of the accuracy of our P-values we computed P for $\sigma t = -1$ with eqn. (4) and Simpson's rule, and with a division of the interval of integration into 100 intervals. The result was $P = 0.4454$, whereas with a division into 50 intervals we found $P = 0.4457$. Therefore we have reasons to assume that our P-values are accurate to well within 0.5%.

By modifying **Ševčik**'s original convolution integral we have thus obtained accurate *P*-values, which are in good agreement with those found by **Randles** and **Nicholson**, but which are probably more accurate.

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W. T. de Vries
E. van Dalen

1 A. Ševčik, *Collection Czech. Chem. Commun.*, 13 (1948) 349.
2 J. E. B. Randles, *Trans. Faraday Soc.*, 44 (1948) 327.
3 P. Delahay, *New Instrumental Methods in Electrochemistry*, Interscience Publishers, Inc., New York, 1954, Chapter 6.
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Received October 4th, 1963

Polarography of thallous ion in some supporting electrolytes

The polarography of thallous ion has been studied by **Heyrovský and Ilkovič**[1], **Lingane**[2] and **Klumpar**[3] in different supporting electrolytes *viz.*, KNO_3, KCl, NH_4Cl, NH_4OH, KOH and the common mineral acids. The $E_{\frac{1}{2}}$ of thallous ion in 1 *M* solutions of these supporting electrolytes is -0.475 ± 5 V *vs.* S.C.E. This paper deals with the reduction of thallous ion in $KHCO_3$, HCOONa, $NaNO_2$ and Na_2SO_4 solutions.

EXPERIMENTAL

All the chemicals used were reagent grade. The manual polarographic set-up used was the same as that described in an earlier paper[4]. The dropping-mercury electrode had the following characteristics: $m = 2.07$ mg/sec, $t = 3.45$ sec (at -1.0 V *vs.* S.C.E. in 0.1 *M* HCOONa). The temperature was kept constant at 18° and Triton X-100 was used as maxima suppressor. i_d was plotted against Tl^+ concentration to ascertain that the current was diffusion-controlled and the temperature coefficient of the diffusion current was also determined. The reversibility of the reduction was determined by plotting $\log i/(i_d - i)$ *vs.* $E_{\text{d.e.}}$ and also by $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ measurements. An H-type cell with a saturated KCl–agar-agar bridge was employed for all the measurements.

RESULTS

Polarograms for Tl^+ were recorded manually in all four supporting electrolytes. In all cases, in the presence of oxygen, a two-wave polarogram is observed which reduces to one wave after de-aeration (Fig. 1).

In the absence of a maxima suppressor, a maximum appears in each solution which is suppressed by Triton X-100 (0.001%), (Fig. 2). The wave height remains practically the same at all concentrations of all the supporting electrolytes except Na_2SO_4 in which the wave height decreases with increasing salt concentration (Fig. 3).

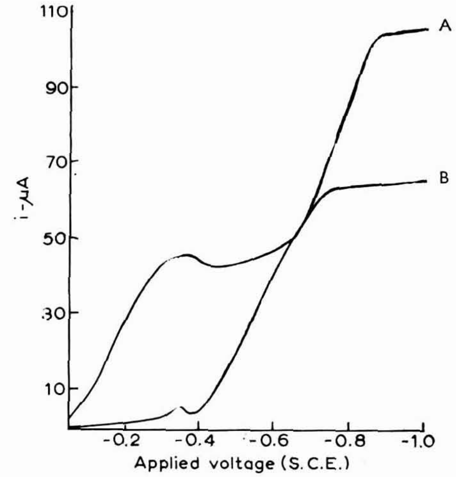

Fig. 1. Polarograms of 1 m*M* Tl^+ in 0.1 *M* $NaNO_2$: (a), with oxygen; (b), without oxygen.

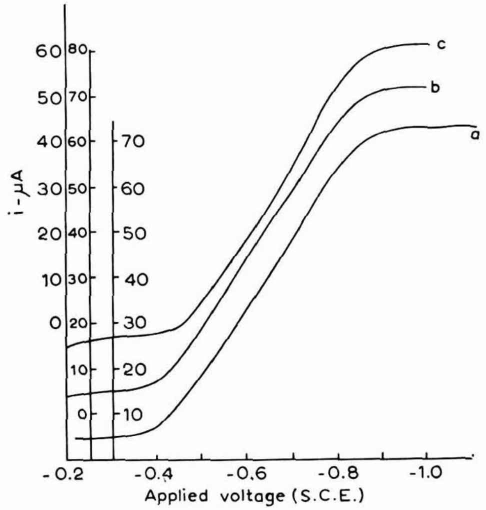

Fig. 2. Polarograms of 1 m*M* Tl^+ + 0.001% Triton X-100 in the following concns. of $NaNO_2$: (a), 0.1 *M*; (b), 0.5 *M*; (c), 1 *M*.

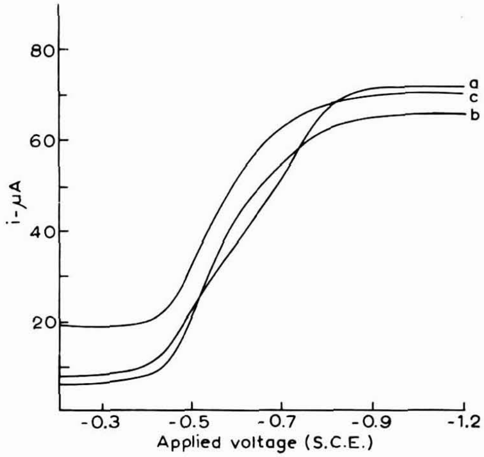

Fig. 3. Polarograms of 1 m*M* Tl^+ + 0.001% Triton X-100 in the following concns. of Na_2SO_4: (a), 0.1 *M*; (b), 0.5 *M*; (c), 1 *M*.

$E_{\frac{1}{2}}$ shifts towards the negative side with increasing concentrations of the supporting electrolytes except in the case of Na_2SO_4 in which a positive shift is observed (Table 1).

TABLE 1

Supporting electrolyte	*Concn. of supporting electrolyte (moles)*	$E_{\frac{1}{2}}$ *(V)*	*Slope (V)*	*Temp. coeff. of* i_d *(%)*
$KHCO_3$	0.1	−0.46	0.055	1.1
	0.5	−0.462	0.056	1.0
	1.0	−0.465	0.055	1.2
HCOONa	0.1	−0.45	0.056	1 2
	0.5	−0.45	0.056	1.2
	1.0	−0.452	0.056	1.2
	1.5	−0.455	0.056	1.15
$NaNO_2$	0.1	−0.45	—	1.2
	0.5	−0.453	—	1.2
	1.0	−0.46	—	1.25
Na_2SO_4	0.1	−0.62	—	3.0
	0.5	−0.58	—	2.8
	1.0	−0.55	—	2.8

Concn. of Tl^+ = 1.0 m*M*

The plot of i_d *vs.* Tl^+ concentration was linear, and passed through the origin for all the supporting electrolytes except Na_2SO_4 in which the current does not increase proportionately with concentration. The temperature coefficient of the diffusion current was found to be of the order of 1.2% in $KHCO_3$ $NaNO_2$ and HCOONa, but was much higher in Na_2SO_4.

The plot of $\log i/(i_d - i)$ *vs.* $E_{\mathrm{d.e}}$ was linear for $KHCO_3$ and HCOONa *only*. The slope of the graph was of the order of 0.056 V. The value of n was found to be unity. In the case of Na_2SO_4 and $NaNO_2$ the plot was not linear.

DISCUSSION

The reduction of Tl^+ is reversible for a one-electron reduction, in HCOONa and $KHCO_3$. In Na_2SO_4 and $NaNO_2$ the reduction was found to be irreversible. The current was diffusion-controlled in all the supporting electrolytes (except Na_2SO_4) showing that the Ilkovic equation is obeyed. This suggests that thallous ion can be estimated polarographically in these supporting electrolytes. The negative shift of $E_{\frac{1}{2}}$ with increasing ionic strength, in all the supporting electrolytes except Na_2SO_4 can be explained on the basis that the activity coefficient of the reducible metal ion decreases with increasing ionic strength. In Na_2SO_4 solution the $E_{\frac{1}{2}}$ of Tl^+ shifts to a more positive value with increasing concentration of the supporting electrolyte, the reduction is irreversible and the current is not diffusion-controlled. This behaviour may be explained on the basis that the electrode process comes into action in controlling the polarographic current and as this process may be slow the electrode equilibrium is not reached within the drop-time.

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1 I. HEYROVSKÝ AND K. ILKOVIČ, *Collection Czech. Chem. Commun.*, 7 (1935) 198.
2 J. J. LINGANE, *J. Am. Chem. Soc.*, 61 (1939) 2099.
3 I. KLUMPAR, *Collection Czech. Chem. Commun.*, 11 (1939) 459.
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Received October 11th, 1963

Book Reviews

Advances in Electrochemistry and Electrochemical Engineering; Volume 2, *Electrochemical Engineering*, edited by Charles W. Tobias, Interscience Publishers, New York and London, 1963, ix + 300 pages, 90 s.

This is the second volume in a series edited by Professors DELAHAY AND TOBIAS. Volume 1 was devoted to pure electrochemistry, Volume 2 deals with topics having a more immediate bearing on applied electrochemistry.

In an introductory chapter, CARL WAGNER defines the scope of *Electrochemical Engineering* and discusses the question of how it may be developed as a "science" rather than an "art". His survey although perhaps over-emphasizing mass-transfer problems, seems to me to give an admirable outline of the basic principles of this highly specialised branch of chemical engineering. It is therefore somewhat disappointing to find that subsequent articles do not really fit into the pattern that WAGNER suggests as most of them are confined too closely to rather narrow and isolated topics.

Chapter II on "Conduction in Heterogeneous Systems" by MEREDITH AND TOBIAS, is an exception, in that it deals with a problem of general interest; a wide range of readers will find it useful.

The remaining articles are more specialised and less definitive, though individually they are interesting and provide a valuable stimulus to further work. IBL discusses the formation of powdered metal deposits by electrolysis and KARDOS AND FOULKE describe recent work on electrodeposition on small scale profiles (including some reference to levelling and brightening in electrodeposition). In the final chapter, MORRIS EISENBERG discusses design and scale-up problems for fuel-cells. General principles are explained and are illustrated by calculations on certain aspects of hydrogen–oxygen cells (power requirements for circulating the electrolyte, net power output and some economic factors).

J. N. AGAR, The University, Cambridge

J. Electroanal. Chem., 6 (1963) 497

Catalysis and Catalysts, by MARCEL PRETTRE, Translated by DAVID ANTIN, Dover Publications, Inc., New York, 1963, $1.00.

This paper-back is a translation of the third (1961) edition of Professor PRETTRE's *Catalyse et Catalyseurs*, originally published in 1946. It is an excellent thing that this little book is now available in English; it serves as a very good introduction to the subject, and is a concise and interesting survey of a topic that is poorly treated in most general chemistry texts.

The book takes a broad definition of catalysis. Thus, initiation and inhibition of chain reactions by added substances are regarded, very properly, as coming within the scope of homogeneous catalysis and are given a whole chapter to themselves. There are two introductory chapters, one of which gives a useful summary of the main thermodynamic and kinetic characteristics of homogeneous and heterogeneous catalytic reactions. Then follow two chapters on homogeneous catalysis and two on heterogeneous catalysis. One of the latter is devoted to a description of catalysts and points out the importance of morphology and of electronic properties. There is a final, authoritative chapter on industrial applications which effectively illustrates the impact of catalysis on the modern world.

The title means what it says; there is a nice balance in the book between catalytic reactions and the modes of action of different types of catalyst. One exception is a page devoted to catalytic cracking where there is a good description of the catalyst and the technique of fluidization, but no details of the particular carbonium ion mechanism which is induced. Nothing of real importance, however, is omitted, and the chapters are refreshingly up-to-date. For example, there is reference to the stereospecific polymerisation of propylene and a substantial account of semi-conductor mechanisms in oxide catalysis, in spite of the limitations imposed by a mere 80 pages of text.

The book has been well translated and can be recommended as easy to read. It is good value for money and one may be sure that a wide public will be grateful to Dover Publications for their initiative.

FRANK S. STONE, The University, Bristol

J. Electroanal. Chem., 6 (1963) 497–498

Zone Electrophoresis in Blocks and Columns, by H. BLOEMENDAL, Elsevier Publishing Company, Amsterdam, 1963, viii + 219 pages, 40 s.

The phenomenon of the migration of particles in an electric field has been known for a long time and the pioneer work on this subject by workers such as HELMHOLTZ, SMOLUCHOWSKI, ABRAMSON and TISELIUS has proved its worth in the present day application of electrophoresis to the separation of many complex mixtures of biological materials. During the past two decades much ingenuity has been exercised in developing electrophoretic techniques either for separations using small quantities of material or for separation of materials as a continuous operation. As a result some complex mixtures can now be separated more easily and more completely than hitherto.

This little book by Dr. BLOEMENDAL gives an excellent account of the various methods of block and column electrophoresis which have been found successful in practice. The topics dealt with are: block electrophoresis (chapter 2), gel electrophoresis (chapter 3), continuous electrophoresis (chapter 4), column electrophoresis (chapter 5) and column electrophoresis in liquid density gradients (chapter 6). The emphasis is very much on the practical aspects and little theory is included.

However, the book does more than just review the literature. It is clearly written by an author who is very close to his subject and it is full of those practical hints and tips which make all the difference between an experiment being a success or a failure. Practical advice is given on powder packs, cooling devices, types of packing materials for columns, preparing gels and plates, cutting electrophoresis blocks, elution, etc.

The book is well printed on glossy paper and is profusely illustrated with high quality diagrams. Workers in this field will find this little book an invaluable "bench-side" companion.

R. H. OTTEWILL, Dept. of Colloid Science, Cambridge

J. Electroanal. Chem., 6 (1963) 498

Ions in Solution, by R. W. GURNEY, reprinted by Dover Publications Inc., New York, 1962, vii + 206 pages, $ 1.50.
Ionic Processes in Solution, by R. W. GURNEY, reprinted by Dover Publications Inc., New York, 1962, ix + 275 pages, $ 1.75.

The late RONALD GURNEY had the rare gifts of clarity of thought and expression, and the ability to explain in a simple and compelling manner the basic physical principles underlying the complex behaviour of ions in solution. In his writings on the physical chemistry of electrolyte solutions and electrode phenomena, he sought always to link the theory to that of the simpler situations studied by physicists, such as the behaviour of ions in gases and the contact potentials of metals.

This is a most useful approach and GURNEY's work has provided for many people a stimulating introduction to the basic concepts and theory of electrochemistry.

This is not to say, however, that his method of exposition is completely satisfactory. It is true that a chemist often finds difficulties in understanding concepts which are quite clear to a physicist. But the converse is also true. And sometimes in his writings GURNEY tends to dwell on familiar chemical facts at the expense of more interesting material. The first chapter of *Ionic Processes in Solution* is an example of this. A fairly elementary thermodynamic point about entropy changes accompanying ion solvation is treated, in what some would consider to be unnecessary detail. Similarly, his discussion in this book of energy changes in terms of unitary and communal ("cratic") components seems to be of more use for explaining physical chemistry to a physicist than to a student of electrochemistry. This terminology has not found much favour in the chemical literature.

The most valuable part of *Ionic Processes in Solution*, in the reviewer's opinion, is the discussion of ionic entropies and viscosities. We do not yet know the absolute entropy of H^+ in water solution, but until we do, GURNEY's estimate of -5.5 cal deg^{-1} mole^{-1} will continue to be quoted.

The earlier book, *Ions in Solution*, while again displaying GURNEY's grasp of the essentials of a problem and his gift for exposition, is now mainly of historical interest. It was written nearly 30 years ago, and electrochemistry has developed a great deal in that time. No introduction to the subject can be considered satisfactory for present use which does not contain, *inter alia*, accounts of modern theories of solvation, of the status of the Debye–Hückel method, electrode processes and above all a detailed analysis of the concept of electrical potential.

Physical chemists, and electrochemists in particular, are greatly in GURNEY's debt. The publishers of these reprinted editions, however, do his memory a disservice by their jacket descriptions of his books. *Ionic Processes in Solution*, valuable though it is, should *not* be called "probably the most important single work on this particular subject in any language' and *Ions in Solution* (reprinted unchanged from the 1936 edition) should *not*, in 1962, be called "the most thorough . . . introduction to this particular subject in the English language".

N. S. HUSH, The University, Bristol

Announcement

ELECTROANALYTICAL ABSTRACTS

According to an agreement with the Elsevier Publishing Company, the former "Abstracts Section" of the Journal of Electroanalytical Chemistry will be published by Birkhäuser Verlag (Elisabethenstrasse 19, Basel 10, Switzerland) under the title of "Electroanalytical Abstracts". The Editor of this new journal will remain, as formerly, Professor G. Milazzo, Istituto Superiore di Sanità, Rome, Italy.

The "Electroanalytical Abstracts" are conceived to cover the whole field of analytical electrochemistry, this intended in a broad sense, i.e. including all fundamental electrochemistry of, even potential, analytical interest and all applications of electroanalytical methods and techniques to the determination of physico-chemical constants (pH, pK, stability constants of complexes, transference number of electrolytes, electric tensions, etc.), to the characterization of compounds, to the solution of kinetic problems, etc.

The number of periodicals abstracted is about 500, they are abstracted by a worldwide staff of selected experienced abstractors. The number of abstracted papers is about 2000 yearly, divided in the following classes: Fundamental electrochemistry, Apparatus, Polarography, Amperometry, Potentiometry, Conductometry, Electrolysis, Coulometry, Electrophoresis, Various methods, Related topics, Book reviews.

The annual subscription rate is 150 Swiss francs (single issues 36 Sw.fr.); there will be six issues annually appearing bi-monthly. The format is 17.2 × 24.5 cm.

J. Electroanal. Chem., 6 (1963) 500

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BOOK REVIEWS

(after titles)

BOOK REVIEWS

(after authors)

New publication - Neue Zeitschrift - Périodique nouveau

ELECTROANALYTICAL ABSTRACTS

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VOL. 6 NO. 6 JOURNAL OF ELECTROANALYTICAL CHEMISTRY DECEMBER 1963

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Good wine needs no bush, and we therefore wish simply to announce that the second edition of "Chemistry of Carbon Compounds" will gradually be published during the coming years. The first edition was accorded such a favourable reception by organic chemists virtually all over the world that any further recommendation would be superfluous. As a recognition of the masterly way in which Dr. E. H. Rodd acted as editor, we have decided to entitle future editions

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