RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

January 1976

Translated from *Uspekhi Khimii*, 45, 3-28 (1976)

U.D.C. 543.257.1

Inversion Amalgam Chronopotentiometry

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The review deals with the theoretical principles of the method of inversion amalgam chronopotentiometry. The transition times and the potential-time relations for the electrochemical dissolution of amalgams under galvanostatic conditions are analysed and the applications of the method in electroanalytical practise, in the study of the kinetics of electrode processes and adsorption, in the determination of the numbers of electrons involved in the reaction and diffusion coefficients, and in the study of complex formation, corrosion of amalgams, etc. are examined in detail. The fundamentals of the theory of electrode processes complicated by preceding, subsequent, and simultaneous chemical reactions are described. The possibilities and advantages of the method of amalgam chronopotentiometry in relation to other electrochemical procedures are indicated.
The bibliography includes 86 references.

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I. INTRODUCTION

One of the promising methods for the determination of low concentrations of elements and for the investigation of the kinetics of electrode processes on amalgams is that of inversion amalgam chronopotentiometry (MIAC). The studies carried out hitherto have shown that this method is distinguished by the simplicity of the apparatus employed and of the mathematical treatment of the physicochemical relations. The latter factor makes it irreplaceable in the investigation of the chemical reactions accompanying the electrode process. The linear chronopotentiometric plot has already been used widely for these purposes, but the number of studies on the applications of inversion amalgam chronopotentiometry in the investigation of the kinetics of electrode processes and for the determination of microconcentrations of elements is still small. This is probably due to the novelty of the method (the first studies by this method were published in 1966) and the lack of a review dealing with the method.

II. THE METHOD OF INVERSION AMALGAM CHRONOPOTENTIOMETRY

The method of inversion amalgam chronopotentiometry (or simply amalgam potentiometry) is a variety of the galvanostatic method, the fundamental principles of which have been described[1,2]. In this method analysis of the transition times and of the shape of the potential-time

curve yields information about the presence of the depolariser in the amalgam and the physicochemical characteristics of the electrode process are determined.

The galvanostatic method was used for the first time to investigate the electrochemical dissolution of amalgams by Zbinden[3]. He demonstrated the possibility of determining copper at concentrations down to 10^{-6} M in the electrochemical dissolution of copper amalgam. The stepwise variation of the current and chemical dissolution on open circuit were used by Bruckenstein and Nagai[4] to determine thallium and lead at concentrations of 2×10^{-7} M. They obtained the amalgam at a rotating platinum electrode.

The method of inversion amalgam chronopotentiometry, which is essentially a new electrochemical procedure, has been put forward in a number of investigations[5-9]. Three stages must be distinguished in this method.

1. Preliminary electrolysis. The metal in the solution is concentrated in the mercury electrode at a specified potential with formation of an amalgam or a sparingly soluble deposit.

2. Period without stirring. After pre-electrolysis, the solution is allowed to stand for 30–60 s; the flux from the electrode then becomes virtually zero[10].

3. Electrochemical dissolution of the metal from the amalgam when a direct current is passed through the electrode. Under these conditions, the pen recorder draws the curve (chronopotentiogram) characterising the time variation of the electrode potential (Fig. 1).

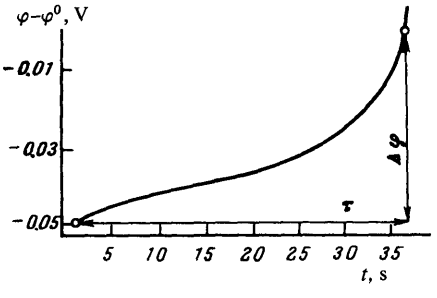


Figure 1. Theoretical chronopotentiometric curve.

If the electrochemical dissolution takes place in a stirred electrolyte, the system is allowed to stand until the attainment of the equilibrium (more precisely the initial) potential of the amalgam. The electrochemical-concentration and the solution-at-rest stages have been examined[10,11]. According to these investigations[10,11], a uniform distribution of the metal throughout the bulk of the electrode is observed towards the end of the second stage. This conclusion played an appreciable role in the formulation of the initial condition in the theory of inversion amalgam voltamperometry.

The usual circuit for galvanostatic measurements is assembled for recording chronopotentiometric curves in MIAC[1,2]. Two types of electrodes are used in the method: a mercury film electrode (stationary or rotating) and a stationary spherical mercury electrode consisting of a mercury drop with a radius not exceeding 0.1 cm. The mercury film electrode consists of a film of mercury between 4 and 20 μm thick deposited on a polished surface of the end-face of a silver wire 1–2 mm in diameter. The silver wire is pressed into a Teflon cylinder ($d \simeq$ 8 mm). A hermetically sealed three-electrode cell is used for the experiments. When a rotating disc electrode is employed, provision is made for a system regulating the rate of rotation (stepwise or continuous)[12]. The rates of rotation of the electrode employed usually do not exceed 10 000 rev min^{-1}.

III. THEORY OF THE METHOD IN THE ABSENCE OF KINETIC COMPLICATIONS

1. Expressions for the Transition Time

Suppose that a simple first-order electrochemical reaction

$$M(Hg) \rightleftarrows M^{z+} + ze$$

takes place at the electrode. We assume that there is an excess of an indifferent electrolyte in the solution, that the ψ_1 potential is negligibly small and independent of the cell potential, that there is no specific adsorption of the starting materials and products, and that the oxidised form of the electrochemically active substance is soluble in the electrolyte solution. We shall bear in mind that the reduced form of the electrochemically active substance diffuses under the conditions of restricted diffusion, i.e. during the measurement of the curve the diffusion layer extends throughout the entire volume of the electrode. The diffusion of the ions formed during the electrochemical dissolution of the amalgam from the surface of the electrode will occur under the conditions of a semi-infinite volume[13]. This is valid for $L_X \geq \sqrt{D_0 \tau}$, where L_X is the distance from the electrode surface to the wall of the electrolytic cell, D_0 the diffusion coefficient of the ions in solution, and τ the transition time. This condition is almost always fulfilled with the exception of thin-layer electrolysers.

In the electrochemical dissolution of the amalgam at a constant current density i the equations for the distribution of the concentration of the metal atoms are of the following form:

$$c^s_{R,f} = c^0_R - j_R\left[v_R + \frac{1}{3} - 2\sum_{n=1}^{\infty}\frac{\exp(-\mu_n^2 v_R)}{\mu_n^2}\right], \quad (1)$$

on the surface of the mercury film electrode[5,14], where $\mu_n = n\pi$, $n = 1, 2, 3, \ldots$, $v_R = D_R t/l^2$, and t the time;

$$c^s_{R,s} = c^0_R - j_R\left[3v_R + \frac{1}{5} - 2\sum_{n=1}^{\infty}\frac{\exp(-\bar{\mu}_n^2 v_R)}{\bar{\mu}_n^2}\right], \quad (2)$$

on the surface of a spherical mercury electrode[9], where $\bar{\mu}_n$ are the roots of the transcendental equation $\tan \bar{\mu}_n = \bar{\mu}_n$. In Eqns. (1) and (2) $j_R = q_R y_0/D_R$, $q_R = i/zF$, q_R is the flux from the electrode, z the number of electrons participating in the electrode process, F the Faraday, c^0_B the initial concentration of the metal in the amalgam, y_0 the characteristic dimension of the electrode ($y_0 = l$ for the mercury film electrode and $y_0 = r_0$ for the spherical electrode), and D_R the diffusion coefficient of metal atoms in mercury.

Eqns. (1) and (2) have been analysed in detail in a number of reports[14-16]. For large values of t, the exponential terms in these equations may be neglected. The following equations are valid (to within at most 1%)

for the mercury film electrode with $v_R \geq 0.35$ (when $D_R = 10^{-5}$ cm^2 s^{-1} and $l \leq 10^{-3}$ cm, we then have $t \geq 0.035$ s) and for the spherical electrode with $v_R \geq 0.14$ (when $r_0 \leq 5 \times 10^{-2}$ cm and $D_R = 10^{-5}$ cm^2 s^{-1}, we then have $t \geq 35$ s):

$$c^s_{R,f} = c^0_R - j_R\left(v_R + \frac{1}{3}\right) \quad (3)$$

and

$$c^s_{R,s} = c^0_R - j_R\left(3v_R + \frac{1}{5}\right). \quad (4)$$

When $v_R \geq 34$ (when $D_R = 10^{-5}$ cm^2 s^{-1} and $l \leq 10^{-3}$ cm, we have $t \geq 3.4$ s), Eqn. (3) reduces to

$$c^s_{R,f} = c^0_R - j_R v_R. \quad (5)$$

Since the time required to record chronopotentiograms is usually greater than 5 s, Eqn. (5) may be used.

The expression for the transition time τ is determined by the condition $c_R(1, v'_R) = 0$, where $v'_R = D_R\tau/y^2_0$. From Eqns. (3), (4), and (5), we obtain for the film electrode

$$\tau = \frac{zFlc^0_R}{i} - \frac{l^2}{3D_R}, \quad (6)$$

$$\tau = \frac{zFlc^0_R}{i}, \quad (7)$$

and for the spherical electrode

$$\tau = \frac{zFlc^0_R}{3i} - \frac{r^2_0}{15D_R}. \quad (8)$$

Analysis[14-16] of Eqns. (6)–(8) leads to the following conclusions: (1) the transition time for electrodes of both types is directly proportional to the concentration of the metal in the amalgam c^0_R (this relation is used in electroanalytical practise); (2) according to Eqn. (7), the product $i\tau$ is independent of current density and is proportional to the amount of metal in the amalgam; (3) the independence of $i\tau$ of current density constitutes a criterion of the absence of a preceding chemical stage; (4) Eqn. (8) may be used to find the diffusion coefficient of the metal atoms in the amalgam; (5) the form of the relation between τ and i makes it possible to investigate the adsorption of surface-active substances on the electrode.

Table 1. The transition times in inversion amalgam chronopotentiometry with film (τ_1) and spherical (τ_2) electrodes and in chronopotentiometry under the conditions of linear semi-infinite diffusion (τ_3) ($z = 2$, $l = 10^{-3}$ cm, $r_0 = 0.06$ cm, $D_R = 10^{-5}$ cm^2 s^{-1}; the degree of concentration of the metal in the mercury film electrode was assumed to be 1000*).

$10^{-7}c^0_0$, g-ion cm^{-3}	$10^{-5}i$, A cm^{-2}	τ_1, s	τ_2, s	τ_3, s	$\frac{\tau_1}{\tau_2}$	$\frac{\tau_1}{\tau_3}$
1	4	480	6	1.6	80	300
2	2	960	12	6.4	80	150
4	1	1920	24	25.6	80	75

* The degree of concentration of the metal in the mercury film electrode usually exceeds this value[14].

The expressions for the transition time in amalgam chronopotentiometry differ from those in the usual chronopotentiometry[1] (under the conditions of semi-infinite diffusion). Table 1 lists the calculated values of τ for chronopotentiometry under the conditions of restricted linear and spherical diffusion (amalgam chronopotentiometry) and semi-infinite linear diffusion. Evidently, other conditions being equal, the transition time in amalgam chronopotentiometry is much longer than in direct chronopotentiometry (under the conditions of semi-infinite diffusion), the difference decreasing with increasing concentration or with decreasing current density. Table 1 demonstrates the clear advantages of the mercury film electrode (in relation to analytical practise).

2. Equations of Chronopotentiometric Curves

For a reversible electrode process, the equation of the chronopotentiometric curve is (in terms of the diffusion overvoltage–time variables)[14-17]

$$\eta_d = \frac{2,3\,RT}{zF} L_O, \quad (9)$$

where

$$L^f_O = \lg[\nu'_R/(\nu'_R - \nu_R)]\,(1 + 2j_0 v_0^{1/2}/\pi^{1/2} c^0_O)$$

for the mercury film electrode ($v'_R \geq 3.4$), T is the absolute temperature, c^0_O the initial concentration of the metal ions in solution and

$$j_0 = \frac{il}{zFD_0}; \; v_0 = \frac{D_0 t}{l^2}.$$

For the spherical mercury electrode ($v'_R \geq 0.14$), we have

$$L^s_O = \lg\frac{(3v'_R + 0,2)}{3(v'_R - v_R)}\left[1 + \frac{i_0}{c^0_O}(1 - \exp v_0 \cdot \operatorname{erfc} v_0^{1/2})\right].$$

The plot of η_d against L_O is a straight line with a slope of $2.3RT/zF$. This serves as a criterion of the reversibility of the electrode process[17]; agreement between the theoretical and experimental values shows that the electrode process is reversible.

At high overvoltages ($\eta \gg RT/zF$) the irreversible electrochemical reaction $M(Hg) \rightarrow M^{Z+} + ze^-$ takes place and the equation of the chronopotentiometric curve simplifies greatly[14-17]:

$$\eta_{ir} = \frac{2,3\,RT}{\beta zF}\left(\lg\frac{i}{i_0} - L_{ir}\right), \quad (10)$$

where

$$L^f_{ir} = \lg\frac{v'_R - v_R}{v'_R} \text{ and } L^s_{ir} = \lg\frac{3(v'_R - v_R)}{(3v'_R + 0,2)}.$$

Hence the slope of the plot of η_{ir} against L_{ir} is βz; the exchange current density i_0 and hence the rate constant for the electrode process k_S may be found from the initial overvoltages taking into account the relation

$$k_S = \frac{i_0}{zF\,(c^0_O)^\beta\,(c^0_R)^\alpha}, \quad (11)$$

where α and β are the transfer coefficients for the cathodic and anodic processes respectively.

The main factors which determine the applicability of Eqns. (9) and (10) are the exchange current density, the overvoltage, and the transition time[14]. With decrease of i and η and with increase of τ, the processes shift towards reversibility and conversely.

A numerical estimate yields

$$4 \cdot 10^{-2} \geqslant k_S \geqslant 4 \cdot 10^{-5}. \quad (12)$$

The intermediate values of k_S correspond to a quasireversible (quasidiffusional) electrode process. A more detailed analysis of chronopotentiometric curves has been given elsewhere[14-17].

Some problems of amalgam chronopotentiometry at a mercury film electrode have also been examined by Igolinskii and Igolinskaya[18] and at a spherical mercury electrode by Galus[19] and Baranski[20].

All the above equations were obtained without taking into account the influence of the structure of the electrical double layer. In order to allow for the electrical double layer[21], the quantity ψ_1 must be introduced into the fundamental equation of electrochemical kinetics. If it is assumed that the electrode potential is distributed over the series-connected capacitances of the dense (C) and diffuse (C_d) components of the double layer and that the capacitance is independent of potential in the range of values of the latter corresponding to the chronopotentiometric curve, then

$$\psi_1 = \frac{C}{C_d}(\varphi - \varphi_0), \qquad (13)$$

where φ_0 is the zero-charge potential.

The method of cyclic chronopotentiometry[1] (with current reversal), which makes it possible to investigate both the anodic and cathodic processes, is convenient for the study of the kinetics of electrode processes. The theory of amalgam chronopotentiometry with current reversal has been discussed[22,23]. The equations were derived on the assumption that the direction of the current is reversed at the instant of attainment of the transition time and that the current density is not equal to that in the cell before reversal. If a reduction process takes place after an oxidation process, then analysis of the theoretical relations gives rise to the following expression, which is simplest when the current densities for the forward and reverse processes are equal:

$$\tau = \frac{4}{3}\tau_1, \qquad (14)$$

where τ_1 is the transition time of the oxidation process.

The characteristic points[23] on the cathodic branch of the chronopotentiometric curve in amalgam chronopotentiometry for a mercury film electrode are $\tau/4$ and 1.0716τ.

An interesting variety of the method of amalgam chronopotentiometry has been proposed[24-26], namely amalgam chronopotentiometry with a programmed current. Cases have been examined where the current was specified in the form of linear, exponential, and sinusoidal functions. The sinusoidal form of the specified current may find the greatest number of practical applications (under these conditions, the error in the determination of the transition time is fully excluded).

3. The Influence of the Charging of the Electrical Double Layer in Amalgam Chronopotentiometry

In the chronopotentiometric method a proportion of the charge supplied to the electrode is required to charge the electrical double layer (e.d.l.), which results in a discrepancy between the experimental and theoretical (obtained without allowance for the charging of the electrical double layer) relations[1]. Using the method of integral equations, de Vries[27] analysed theoretically the influence of the charging of the e.d.l. on chronopotentiometric curves for the electrochemical dissolution of amalgams from a mercury film electrode on the hypothesis that a diffusion-controlled process takes place at the electrode and that the e.d.l. capacitance is independent of the potential.

Using the Huber method, he solved the integral equation. The theoretical φ–t curves, calculated for certain values of K_C and h (see below), are presented in Fig. 2, while Table 2 lists the calculated shifts of the chronopotentiometric curves ($\Delta\varphi_{\tau/4}$) with and without allowance for the charging of e.d.l. Here $K_C = (RT/zF)C_d[c_R^0(\pi D_R\tau_\infty)^{1/2}]^{-1}$ is a parameter characterising the distortion of the chronopotentiometric curve, $h = l^2/D_R\tau$, $\lambda = t/\tau_\infty$, and τ_∞ is the transition time under the conditions of semi-infinite diffusion without allowance for the charging of e.d.l.

Table 2 shows that the error in the determination of the transition time is less than 4% for $h > 0.3$. This value of h characterises the applicability of the Delahay-Mattax method[1], which has been used here to determine the transition time. With decrease of h, the error in the determination of the transition time increases and the distorting influence of the e.d.l. capacitance becomes more appreciable (Fig. 2); the Delahay-Mattax method becomes unsuitable under these conditions. Fig. 2 shows that, with increase of the e.d.l. capacitance, the chronopotentiometric curves shift along the potential axis with a simultaneous change in the slope of the initial and final sections of the curve, the two being equal.

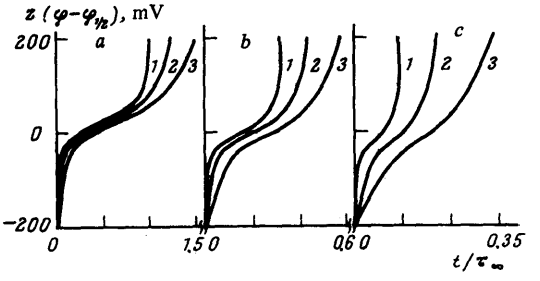


Figure 2. Theoretical φ–t curves for a mercury film electrode calculated taking into account the charging of the electrical double layer for different values of K_C [1) 0; 2) 0.003; 3) 0.0075] and three values of h [a) $h = \infty$; b) $h = 0.1$; c) $h = 0.01$].

De Vries[27] analysed in detail the case where $h \to 0$ (the case of thin films and large values of τ). The Delahay-Mattax graphical method may be applied in the potential range −200 – +200 mV subject to the condition that a horizontal line, parallel to the time axis, divides the distance between the initial and final sections of the curve in proportions of 0.382 : 0.618. The error in the measurement of the transition time under these conditions is not more than ±4% for $K_C \leq 0.01$ and $h \leq 0.1$.

The order of magnitude of the error due to the charging of the e.d.l. can be estimated approximately by Hirst's method[1]:

$$\frac{Q_C}{Q_\varphi} = \frac{C_d \Delta\varphi}{i\tau}, \qquad (15)$$

where $\Delta\varphi(V)$ is the width of the chronopotentiogram. Evidently the error is smaller the higher the current density and the concentration of the electrochemically active substance. For example, when $C_d = 20\ \mu F\ cm^{-2}$, $\Delta\varphi = 0.1V$, $D_R = 10^{-5}\ cm^2\ s^{-1}$, $z = 2$, and $c_R^0 = 10^{-6}$ g-atom cm^{-3}, the current density should not exceed 0.1 A cm^{-2} for a permissible error of 1%.

Table 2. The results of the calculation of the influence of the charging of the electrical double layer on the characteristics of the chronopotentiometric curves ($\Delta\varphi_{\tau/4}$ is the shift of the chronopotentiometric curve).

	$z\,(\Delta\varphi_{\tau/4})$, mV			Error in the determination of λ, %	
hK_c	0	0.003	0.0075	0.003	0.0075
	0	−1.7	−2.6	−1.7	1.9
$h=3$	−0.6	−2.4	−3.0	0	2.4
$h=1$	−5.6	−7.3	−7.9	0.5	3.5
$h=0.3$	−14.4	−15.8	−16.3	1.5	5.6

IV. APPLICATIONS OF THE METHOD OF AMALGAM CHRONOPOTENTIOMETRY

1. Oxidation of a Multicomponent Amalgam

If the chronopotentiometric half-wave potentials differ appreciably, several steps are observed on the potential–time curve. The system of equations describing the distribution of the concentrations of the elements at the surface of the mercury film electrode is[14-16,28-30]

$$\sum_{k=1}^{m} c_{R,k}^S = \sum_{k=1}^{m} \left\{ c_{R,k}^0 - j_{R,k}\left[v_{R,k} + \frac{1}{3} - 2S_1(v_{R,k}) \right] \right\}. \qquad (16)$$

We shall consider the electrochemical oxidation of a two-component amalgam, where the following reactions take place at the electrode:

$$M_1(Hg) \rightarrow M_1^{z_1+} + z_1 e,$$
$$M_2(Hg) \rightarrow M_2^{z_2+} + z_2 e.$$

The metal M_2 is oxidised at more positive potentials. When the transition time τ_1 is reached, M_2 begins to react, while M_1 continues to diffuse to the electrode surface, where it is oxidised simultaneously with M_2. If M_1 is fully oxidised during the time τ_1, then it has no influence on the transition time of M_2.

The fraction of the residual metal M_1 in the amalgam after the time τ_1 may be found from the formula[14,29]

$$p = \frac{il}{z_1 F c_R^0 D_R}. \qquad (17)$$

It follows from Eqn. (17) that the fraction of the residual metal in the mercury film increases with increasing film thickness and polarising current density. We shall estimate p for the following conditions: $i = 2 \times 10^{-4}$ A cm^{-2}, $l = 2 \times 10^{-3}$ cm, $S = 6 \times 10^{-2}\ cm^2$, $D_R = 10^{-5}\ cm^2\ s^{-1}$, and $c_R^0 = 2 \times 10^{-6}$ g-atom cm^{-3}, whereupon $p = 0.04$. Under the above conditions, $\tau = 5$ s. Usually $\tau > 5$ s and $l < 2 \times 10^{-3}$ cm and p is then less than 0.01.

Consequently when the curves are drawn by a pen recorder during the transition time, almost the entire metal dissolves from the mercury film. The constancy of $i\tau$ over a wide range of variation of the polarising current (from 7.5×10^{-7} to 1.4×10^{-5} A) has been demonstrated experimentally[14] in relation to the oxidation of cadmium (1 M KCl), lead (1 M KNO_3), and indium (0.5 M $HClO_4$) amalgams. This implies that, under the conditions of amalgam chronopotentiometry, the metal emerges almost completely from the mercury film.

Using the method of additive functions, Pnev and Zakharov[30] arrived at the following expression when they considered the oxidation of a two-component amalgam:

$$\tau_2 - \frac{2l^2}{D_R}[S_1(\tau_1 + \tau_2) - S_1(\tau_1)] = \frac{z_2 F l c_{R,2}^0}{i}, \qquad (18)$$

where

$$S_1(\tau_1 + \tau_2) = \sum_{n=1}^{\infty} \frac{\exp[-\mu_n^2(v_{R_1} + v_{R_2})]}{\mu_n^2};$$
$$S_1(\tau_1) = \sum_{n=1}^{\infty} \frac{\exp(-\mu_n^2 v_{R_1})}{\mu_n^2}.$$

It follows from the last equation that, for a fairly large value τ_1 (for $v'_R \geq 0.35$), when the sums $S_1(\tau_1 + \tau_2)$ and $S_1(\tau_1)$ may be neglected, the transition time for the oxidation of the succeeding element (M_2) is independent of the transition time for the oxidation of the previous element (M_1). For spherical diffusion, this conclusion is valid when $v'_R \geq 0.14$ (see above). The theoretical results obtained have been confirmed for the oxidation of thallium and lead amalgams in the presence of zinc and for a thallium amalgam in the presence of cadmium[14,28].

Table 3. Data for the determination of the number of electrons involved in the reaction by amalgam chronopotentiometry.

Element	$10^3 i\tau_{exp}$, C	$10^3 i\tau_{theor}$, C	z_{exp}	z_{theor}
Pb	2.65	2.80	1.9	2
Cd	2.87	2.92	2.0	2
In	2.02	2.2	2.8	3

Under the conditions of semi-infinite diffusion, the mutual influence of the elements is observed when they are present jointly in solution, which hinders their accurate quantitative determination[1].

2. Determination of the Number of Electrons Involved in the Electrode Reaction

Using Eqn. (7), it is possible to determine the number of electrons z and to reach appropriate conclusions concerning the mechanism of the electrode reaction. This method has been used in the determination of the number of electrons involved in the electrochemical oxidation of

lead (1 M KNO_3), cadmium (1 M KCl), and indium (0.5 M $HClO_4$) amalgams[14]. The observed values of z agree with the theoretical values (Table 3). The determination of the number of electrons from the chronopotentiometric curve is discussed below.

3. Determination of the Diffusion Coefficients of Metal Atoms in Mercury

As stated above, the diffusion coefficients of metal atoms in mercury can be found by analysing Eqn. (8)†.

According to Eqn. (8), the plot of τ against $1/i$ is a straight line, which makes an intercept $r_0^2/15D_R$ on the τ axis. Knowing r_0, it is possible to calculate the diffusion coefficient of metal atoms in mercury.

4. Investigation of the Kinetics of the Ionisation of Amalgams. The Use of the Rotating Disc Electrode

Eqns. (9) and (10) have been used[17] to investigate the electrochemical dissolution of thallium, lead, bismuth, and indium amalgams at a mercury film electrode. It was established that the electrochemical oxidation of thallium, bismuth, and lead amalgams in the corresponding supporting electrolytes (Table 4) is reversible, while that of indium and bismuth amalgams in perchloric acid solutions is irreversible (Table 5).

Table 4. The results of the study of the electrochemical dissolution of thallium, lead, and bismuth amalgams at a stationary mercury film electrode and a rotating mercury disc electrode (n_{rev} = 1200 rev min^{-1}) at 293 K.

Amalgam	Supporting electrolyte	φ^0, V	2.3 RT/zF, V		
			experimental values		Theoretical values
			stationary electrode	disc electrode	
Tl	1 M KNO_3	−0.484	0.060	0.059	0.058
Pb	1 M KNO_3	−0.374	0.030	0.029	0.029
Bi	1 M HNO_3	−0.008	0.020	0.0215	0.0194

Table 5. The results of the study of the kinetics of the electrochemical oxidation of bismuth and indium amalgams at a stationary mercury film electrode.

Amalgam	Supporting electrolyte	$10^5 c_O^0$, M	$10^5 i$, A	τ, s	$\frac{2.3RT}{\beta zF}$, V	βz	$10^4 i_0$, A cm^{-2}	k_S, cm s^{-1}
In	2 M $HClO_4$	1.0	0.9	20.0	0.0277	2.1	0.9	$4 \cdot 10^{-5}$
Bi	1 M $HClO_4$	1.0	1.3	25.0	0.0233	2.49	1.83	$2 \cdot 10^{-4}$

† In view of the small thickness of the mercury film electrode, the analogous Eqn. (6) is difficult to use for these purposes.

Kinetic studies can be carried out very conveniently at a rotating electrode[12], whereby it is possible to take into account exactly concentration polarisation. The rotating disc electrode has been used in inversion amalgam chronopotentiometry to investigate the kinetics of the electrochemical dissolution of amalgams[31]. It has been stated[32,33] that amalgam chronopotentiometry with a rotating disc electrode is distinguished by the simplicity of the interpretation of the results. If the treatment is based on the general kinetic discharge–ionisation equation[21], then the equation of the chronopotentiometric curve for the electrochemical dissolution of the metal from the amalgam on the rotating disc electrode is

$$\eta = \frac{2.3\,RT}{\beta zF}\left(\lg\frac{i}{i_0} - L_k\right), \qquad (19)$$

where

$$L_k = \lg\left[\frac{v_R' - v_R}{v_R'} - \left(1 + \frac{j_0}{c_O^0}\right)e^{-\frac{zF}{RT}\eta}\right] \qquad (20)$$

is the thickness of the boundary diffusion layer on the rotating disc, $j_0 = i\delta/zFD_O$, $\delta = 0.642\,D_O^{1/3}\nu^{1/6}n_{rev}^{-1/2}$), and n_{rev} the rate of rotation of the electrode (rev s^{-1}).

At fairly high overvoltages (but not such that an irreversible electrode process can occur), the $\eta - L_k$ curve becomes a straight line with a slope of 2.3 $RT/\beta zF$ (Fig. 3). Evidently, with increase of the rate of rotation of the electrode (with decrease of the parameter j_0/c_O^0), the curve is transformed into a straight line at lower overvoltages. The limiting case corresponds to $j_0/c_O^0 \ll 1$. This factor makes it possible to simplify the analysis of chronopotentiometric curves. Hence the advantage of amalgam chronopotentiometry using a rotating disc electrode is evident.

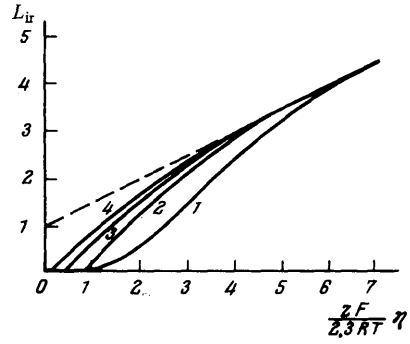


Figure 3. Variation of η with L_{ir} for a rotating mercury disc electrode corresponding to different values of j_0/c_O^0: 2) 4; 3) 1; 4) $\ll$ 1; β = 0.5. Curve *1* has been plotted for a stationary mercury film electrode.

For diffusion-controlled processes, the equation of the chronopotentiometric curve is

$$\eta_d = \frac{2.3\,RT}{zF}\left[\lg\left(1 + \frac{j_0}{c_O^0}\right) + L_O\right], \qquad (21)$$

where

$$L_O = \lg\frac{\tau}{\tau - t}.$$

It follows from this equation that the plot of η_d against L_O is a straight line with a slope of $2.3RT/zF$. It is appropriate here to compare the equation obtained with the analogous equation [Eqn. (9)] for a stationary mercury film electrode; the evident simplicity of Eqn. (21) can be easily seen. Analysis of Eqn. (21) shows that an increase of the rate of rotation of the electrode leads to a shift of the chronopotentiometric curves towards negative potentials, the maximum shift being observed when $j_0/c_O^0 \ll 1$.

Studies at a rotating mercury disc electrode showed that the electrochemical dissolution processes for thallium and lead amalgams (in 1 M KNO_3 as the supporting electrolyte) and bismuth amalgam (in 1 M HNO_3 as the supporting electrolyte) are diffusion-controlled (Table 4). The study of the ionisation of cadmium and zinc amalgams in the appropriate supporting electrolytes at a rotating disc electrode showed that the electrochemical dissolution of these metals from the amalgams is determined by mixed kinetics (Table 6). The kinetic parameters found by the method of amalgam chronopotentiometry agree with the literature[34-38].

Table 6. The results of the study of the kinetics of the electrochemical oxidation of zinc and cadmium amalgams at a rotating mercury disc electrode ($i = 1.2 \times 10^{-4}$ A cm^{-2}, $n_{rev} = 1200$ rev min^{-1}).

Amalgam	Supporting electrolyte	$10^4 c_0^0$, M	$\frac{2.3RT}{\beta z F}$, V	βz	$10^4 i_{0_2}$, A cm^{-2}	k_S, cm s^{-1}	
						experimental data	literature data
Zn	1 M KNO_3	1.0	0.050	1.16	1.1	$3.2 \cdot 10^{-3}$	$3.5 \cdot 10^{-3}$ [36,37]
Cd	1 M Na_2SO_4	0.1	0.040	1.45	1.2	$1.1 \cdot 10^{-2}$	$2.6 \cdot 10^{-2}$ [38] (0.5 M Na_2SO_4)

It is noteworthy that the methods used in the literature[35-38] are more complex as regards apparatus and the interpretation of the results than in amalgam chronopotentiometry.

5. Analytical Scope of the Method

Using Eqn. (15), we shall estimate theoretically the minimum concentration which can be determined by the method of amalgam chronopotentiometry. When the error introduced by the capacitance current is $m\%$, we have[28,39]

$$c_{O,\min}^0 = \frac{10^8 S C_d \Delta\varphi}{mzF\gamma V} \text{ (mole litre}^{-1}\text{)}, \quad (22)$$

for the film electrode and

$$c_{O,\min}^0 = \frac{1{,}26 \cdot 10^6 r_0^2 C_d \Delta\varphi}{mzF\gamma V} \text{ (mole litre}^{-1}\text{)}, \quad (23)$$

for the spherical electrode, where γ is the coefficient of consumption of the solution[40,41] and V the volume of the solution analysed.

After recalculation for a sample g (in grams), we have

$$a_{\min} = \frac{AV}{10\,g} c_{O,\min}^0, \quad (24)$$

where A is the atomic weight of the element to be determined and $a_{\min}$ the minimum impurity content which can be determined.

Numerical estimates yielded $c_{O,\min}^{0f} = 6.5 \times 10^{-9}$ M, $a_{\min}^f = 6.5 \times 10^{-8}\%$, $c_{O,\min}^{0S} = 6.7 \times 10^{-9}$ M, and $a_{\min}^S = 6.7 \times 10^{-8}\%$ for the following experimental conditions: $g = 1$ g, $A = 100$, $V = 1$ ml, $\gamma = 0.63$, $C_d = 20$ μF cm^{-2}, $D_R = 2 \times 10^{-5}$ cm^2 s^{-1}, $z = 2$, $m = 5\%$, $r_0 = 4 \times 10^{-2}$ cm, $\Delta\varphi = 0.080$ V (for lead) and $S = 0.025$ cm^2 (for the film electrode). These calculations have been confirmed by experimental data obtained in studies[6,7] where lead, copper, and zinc were determined at molar concentrations of $10^{-9}n$ ($n = 4$–8).

In the analysis of multicomponent amalgams a superposition of chronopotentiograms is possible (when the equilibrium potentials of the amalgams are similar). The problem therefore arises of the resolving capacity of the method. The resolving capacity may be[28] characterised approximately by the quantity $\Delta\varphi$ (Fig. 1). The lower the value of $\Delta\varphi$ the greater the number of elements which may be determined from a single chronopotentiogram. It has been shown theoretically[28] that, for reversible processes, $\Delta\varphi$ decreases with decrease of the concentration of the depolariser ions in solution and, for irreversible processes, $\Delta\varphi$ is independent of c_O^0 (Fig. 4). Experimental investigation of the electrochemical oxidation of lead and thallium amalgams in 1 M KNO_3 supporting electrolytes (reversible processes) and zinc amalgam in 1 M KNO_3 (irreversible process) confirmed the theoretical conclusions (Fig. 4). $\Delta\varphi$ is independent of the thickness of the mercury film, which is very convenient in analytical studies (there is then no need for an accurate determination of the film thickness, which may vary during the experiments).

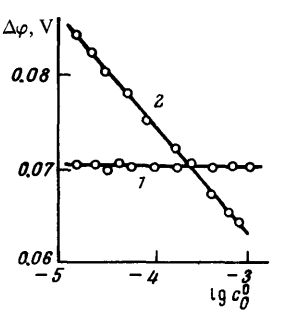


Figure 4. The influence of the depolariser concentration in solution on $\Delta\varphi$ for the electrochemical oxidation of zinc (curve *1*) and lead (curve *2*) amalgams.

The minimum value of $\Delta\varphi$ has been estimated[28] for bivalent elements, amounting to about 44 mV. For comparison, we may point out that the width of the polarographic wave for a dropping mercury electrode is about 72 mV and the width of the anodic peak in the method of amalgam polarography with accumulation is about 60 mV.

The possibility of the simultaneous determination of different elements with adequate resolution and accuracy makes the method of amalgam chronopotentiometry of potential value in analytical practise. The simplicity of the shape of the chronopotentiometric curve permits the application of the method in schemes for the automatic monitoring of continuously varying concentrations of

chemical elements[42-44]. A model of a digital chronopotentiograph has been constructed for the analysis of traces of elements by amalgam chronopotentiometry[43]. Other possible designs for chronopotentiometric apparatus have been described[45-47].

The use of a rotating mercury disc electrode yields more clear-cut chronopotentiograms (Fig. 5). This is achieved as a result of the alteration of the shape of the curve (the S-shaped curve at a stationary electrode is replaced by the "logarithmic" curve at a rotating disc electrode).

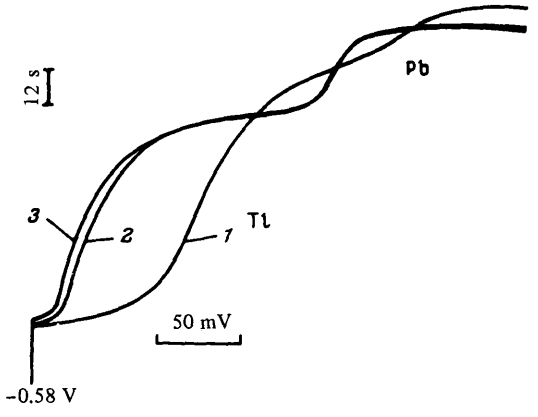


Figure 5. Chronopotentiometric curves for the ionisation of a thallium–lead amalgam at stationary (curve *1*) and rotating disc electrodes (curves *2* and *3*) for rates of rotation of 1200 and 3400 rev min^{-1} respectively.

6. Oxidation of Amalgams in the Presence of Oxygen

The interaction of the oxygen dissolved in the solution being analysed with amalgams makes a definite contribution to the dissolution of metals in the absence of a current[48]. Doronin and Kabanova[49] used the reaction of thallium amalgam with dissolved oxygen for the chronopotentiometric determination of both thallium and oxygen. The reduction of oxygen at a thallium amalgam in the absence of a current but in the presence of thallium ions in solution has been investigated[49,50].

The joint chronopotentiometric determination of thallium and oxygen is possible under certain conditions[49]. In the determination of oxygen the concentration of thallium in the amalgam should not be high, so that the rate of its dissolution in the reaction with oxygen can be measured. Preliminary electrolysis in the determination of oxygen yields the thallium amalgam and the concentration of oxygen is then found from the chronopotentiogram for the decomposition of the amalgam by the oxygen diffusion flux with the solution stirred in a specific manner. When the ratio of the concentrations of thallium and oxygen in solution is 10 : 1, oxygen can be determined at a concentration of 3×10^{-7} M or less.[49] Evidently the minimum concentration of oxygen which can be estimated is limited by the concentration of oxidants in solution, which may oxidise the metal in the amalgam to the ionic state. The possibility of determining traces of oxygen in gases or solutions by the chronopotentiometric method has also been pointed out[51].

Buffle et al.[48] examined theoretically the oxidation of metals in amalgams under chronopotentiometric conditions in the absence of a current. The following reaction then takes place at the electrode:

$$M(Hg) + \frac{z}{2n}O_2 \rightarrow M^{z+} + \frac{z}{n}O^{n-} + Hg.$$

The reduction of oxygen to water (O^{2-}) or hydrogen peroxide (O^-) depends on the nature of the metal[52,53] and the experimental conditions[50].

The equations of chronopotentiometric curves have been derived under the following conditions: (1) the expression for the spreading of concentration in the mercury drop in the presence of oxygen obeys Shain's equation[54]; (2) the flux of metal to the surface of the electrode is proportional to the flux of oxygen with the sign reversed and with the proportionality coefficient $z/2n$; (3) the chemical reaction between oxygen and the amalgam is assumed to be rapid compared with diffusion, so that one can put $c^S_{O_2} = 0$; (4) the solution is stirred vigorously and the flux of oxygen (q_{O_2}) to the electrode via a diffusion layer having a thickness δ_{O_2} is

$$q_{O_2} = \frac{zD_{O_2}c^0_{O_2}}{\delta_{O_2}}. \qquad (25)$$

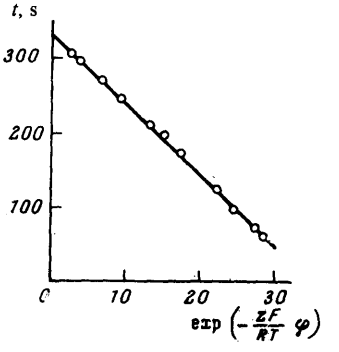


Figure 6. Relation between t and the potential in the electrochemical dissolution of a lead amalgam.

The equation of the chronopotentiometric curve (on the assumption that a reversible electrode process takes place) is[48]

$$\varphi = \varphi^0 + \frac{RT}{nF}\ln\left(zc^0_{O_2}\frac{D_{O_2}}{D_0}\right) - \frac{RT}{nF}\ln\left(c_R - \right.$$
$$\left. - \frac{3zc^0_{O_2}D_{O_2}t}{\delta_{O_2}r_0} - \frac{zc^0_{O_2}r_0D_{O_2}}{5D_R\delta_{O_2}} + \frac{2zc^0_{O_2}r_0}{D_R\delta_{O_2}}D_{O_2}S_{sph}\right), \qquad (26)$$

where

$$S_{sph} = \sum_{n=1}^{\infty}\frac{\exp(-\bar{\mu}_n^2 v_R)}{\bar{\mu}_n^2}.$$

Eqn. (26) was tested experimentally[43] in the oxidation of zinc, lead, and cadmium amalgams. The results of the test for lead amalgam are presented in Fig. 6 in terms

of a plot of t against $\exp(-zF\varphi/RT)$. Similar results were obtained for zinc and cadmium amalgams. The value of δ_{O_2} was calculated from the slope of the plot (Fig. 6). For $D_{Pb^{2+}} = 8.3 \times 10^{-6}$ cm^2 s^{-1}, $r_0 = 0.038$ cm, and $\varphi^0 = -0.120$ V, $\delta_{O_2} = 7.5 \times 10^{-4}$ cm was obtained, which agrees approximately with the literature ($\delta_{O_2} \simeq 10^{-3}$ cm).[55]

The expression for the transition time subject to the condition $v_R' \geq 0.14$ is

$$\tau = \frac{\delta_{O_2} r_0 c_R^0}{3 z c_{O_2}^0 D_{O_2}} - \frac{r_0^2}{15 D_R}. \quad (27)$$

Hence it follows that the transition time is inversely proportional to the O_2 content in solution. This relation has been used[48] to determine the content of oxygen in an acetate buffer (pH 4.7). The concentration obtained $c_{O_2}^0 = 8.23 \times 10^{-7}$ M corresponds to the solubility of O_2 in the test solution.

Thus, using the reaction of dissolved oxygen with amalgams, the method of amalgam chronopotentiometry can be applied for the determination of oxygen in gases or solutions.

7. The Study of Adsorption on Mercury

The simplicity of the chronopotentiometric method in the study of the adsorption of various substances on mercury has been increasingly frequently emphasised in the literature[56-58]. A planar mercury electrode is suitable for such purposes. When the substance in the form of a sparingly soluble compound or metal deposit is adsorbed on the surface of a mercury film, the transition time characterising the complete exhaustion of both the adsorbed and non-adsorbed depolariser is described by the equation

$$\tau = \frac{zFlc_R^0}{i} + \frac{zF\Gamma}{i}, \quad (28)$$

where Γ is the amount of adsorbed substance (mole cm^{-2}).

If the electrochemically active substance is insoluble in mercury (but is adsorbed on the surface of the electrode), Eqn. (28) reduces to

$$\tau_{ads} = \frac{zF\Gamma}{i}. \quad (29)$$

Using the values of τ_{ads}, it is possible to plot the adsorption isotherm. Ershler et al.[56] and Herman and Blount[59] analysed in detail various models for adsorption on mercury electrodes and the transition times. According to Herman and Blount[59], the method of chronopotentiometry with current reversal, whereby it is possible to investigate adsorption phenomena in both anodic and cathodic processes, is suitable for the study of adsorption.

8. Other Possible Applications of the Method and Some of Its Modifications

The method of amalgam chronopotentiometry can be used to determine the solubilities of sparingly soluble metals in mercury[17]. The essential feature of one of the modifications is as follows. A preliminary electrolysis is carried out for various concentrations of the element (whose solubility in solution is to be determined) during a period which is always the same and chronopotentiograms are recorded in each case. The transition time increases with increase in concentration up to a limit and then remains unchanged. This limiting transition time corresponds to the solubility of the metal in mercury. The above method yields correct results only when the solid phase formed dissolves at an infinitesimally low rate.

The above method can also be used to investigate chemical processes[60] which complicate the electrode process involving the dissolution of the amalgam (the formation of intermetallic compounds, complex formation). This problem is discussed in greater detail in the next section.

Using the method of the rotating disc electrode, it is possible to investigate the corrosion of amalgams under chronopotentiometric conditions.

An interesting version of amalgam chronopotentiometry—chronopotentiometry in the absence of a current or chronopotentiometry with a specified resistance—has been proposed[61-64]. In this method the electrochemical dissolution of the amalgam is measured with the aid of additional resistances introduced into the circuit.

Amalgam chronopotentiometry in a two-sided thin-film system has been examined[65]. The author[65] showed that the theoretical relations obtained by Christensen and Anson[66] for one-sided thin-film systems can be used in conjunction with this version of the method.

V. THEORY OF THE METHOD WHEN THE ELECTRODE PROCESS IS COMPLICATED BY CHEMICAL REACTIONS

In many cases electrode processes take place in several stages. In order to understand the mechanisms of the electrode process and particularly for a correct interpretation of experimental results, it is necessary to know the characteristics of chemical reactions at the surface of the electrode and the relations governing them.

The electrochemical dissolution of the amalgam may be complicated by chemical reactions occurring in the amalgam or in the solution. Certain metals are known to form with one another intermetallic compounds soluble in mercury[67]. In the electrochemical dissolution of such an amalgam the electrode process is complicated by the dissociation of the compound in the amalgam. If the metal ions formed on electrochemical dissolution of the amalgam react chemically with the components of the electrolyte or are involved in complex formation, the electrode process is complicated by the subsequent chemical reaction. The theory of inversion amalgam chronopotentiometry with kinetic complications has been largely described[14-16]. It is assumed that, in the presence of an excess of an indifferent electrolyte in solution, there are no adsorption effects, and that the electrolyte solution is not stirred.

1. Preceding Chemical Reactions

If the electrochemical dissolution of the amalgam is preceded by a chemical reaction (dissociation of the intermetallic compound), the electrode process can be represented schematically as follows[68,69]:

$$Y\,(Hg) \underset{k_2}{\overset{k_1}{\rightleftarrows}} M(Hg) + n M_1\,(Hg) \overset{ze}{\rightarrow} M^{z+},$$

where Y is the intermetallic compound soluble in mercury and M and M_1 are the metal atoms into which the substance Y dissociates. It is postulated that Y and M_1 are not oxidised at the potential of the electrochemical oxidation of M.

The expression for the distribution of the metal concentration at the surface of an electrode of any shape, subject to the condition $D_R = I_Y = D$, is

$$c_R^S = \frac{c_R^0 - j(S_1 + K_p S_2)}{1 + K_p}. \quad (30)$$

We have for the mercury film electrode ($v_R \geq 0.34$)

$$S_1 = v_R + \frac{1}{3}, \quad (31)$$

$$S_2 = \frac{1}{\sqrt{K}\tanh\sqrt{K}} - \frac{e^{-Kv_R}}{K}, \quad (32)$$

and for the spherical mercury electrode ($v_R \geq 0.14$)

$$S_1 = v_R + \frac{1}{15}, \quad (33)$$

$$S_2 = \frac{1}{3\sqrt{K}\coth\sqrt{K} - 1} - \frac{e^{-Kv_R}}{K}, \quad (34)$$

where $K = \lambda_1 + \lambda_2$, $\lambda_1 = k_1 y^2/D$, $\lambda_2 = k_2 y^2/D$, and K_p is the equilibrium constant for the chemical reaction. Hence we have the following expression for the transition time subject to the condition $c_R^S = 0$:

$$v_K' = v_R' - K_p S_2(v_K'), \quad (35)$$

where v_R' corresponds to the transition time in the limiting case where the chemical reaction is fast:

$$v_R' = \frac{c_R^0}{j} - \frac{1}{3}; \quad v_K' = \frac{D\tau}{l^2}.$$

It follows from Eqn. (35) that the kinetic effect may be observed [69] under the condition

$$K_p S_2(v_K') \geq 0.1 v_K'. \quad (36)$$

According to Eqn. (35), when account is taken of Eqn. (32) or (34), the plot of the relation is linear with the slope at low current densities

$$\frac{K_p}{\sqrt{K}\tanh\sqrt{K}}$$

for the mercury film electrode and

$$\frac{K_p}{3\sqrt{K}\coth\sqrt{K} - 1}$$

for the spherical mercury electrode. The value of K may be calculated from these relations when K_p is known. Since v_K' is proportional to concentration for constant j, the linear plot of v_K' against concentration may be extrapolated to $v_K' = 0$. S_2 may be determined from the intercept on the ordinate axis and K_p and K can then be calculated.

In order to derive the equations of chronopotentiometric curves, it is necessary to substitute in the kinetic equation the expressions for c_R^S and c_O^S. The formula for the distribution of the concentration c_O^S has been published [1]. The equations of chronopotentiograms are simpler [68,69] when $D_O = D_R$:

$$\varphi = \varphi_{1/2} - \frac{RT}{zF}\ln\frac{c_R^0 - jS_1 + K_p S_2}{(1 + K_p)c_O^S} \quad (37)$$

for reversible electrode processes, and

$$\varphi = \varphi^0 + \frac{RT}{\beta zF}\ln\frac{q}{k_S} - \frac{RT}{\beta zF}\ln\frac{c_R^0 - j(S_1 + K_r S_2)}{1 + K_p} \quad (38)$$

for irreversible electrode processes. The quantity $jK_pS_2/(1 + K_p)$ introduces a correction for the kinetic effect. Since $jK_pS_2/(1 + K_p) > 0$, the chronopotentiometric curve should shift towards positive potentials when there is a preceding chemical reaction.

2. Subsequent Chemical Reactions

The influence of the chemical reaction which follows electron transfer is manifested in processes with a reversible electrochemical stage. In irreversible processes the subsequent chemical reaction cannot have any influence on the kinetics of the electrode process. Therefore the occurrence of the subsequent chemical reaction can affect only the distribution of the metal concentration in solution. For the mechanism under consideration,

$$M(Hg) \overset{ze^-}{\rightleftarrows} M^{z+} + N \underset{k_2}{\overset{k_1}{\rightleftarrows}} Y,$$

where M is the metal in the amalgam, M^{Z+} the metal ions formed on electrochemical dissolution of the amalgam and then reacting with the excess of the substance N, and Y the substance formed as a result of the chemical reaction (Y is not reduced or oxidised in the potential range where M is oxidised), the equation of the chronopotentiometric curve corresponding to reversible electrode processes at a mercury film electrode is (subject to the conditions $v_R \geq 0.34$ and $D_I = D_O = D$) [14,70]

$$\varphi = \varphi_{1/2} - \frac{RT}{zF}\ln(v' - v) + \frac{RT}{zF}\ln P(v), \quad (39)$$

where

$$P(v) = \frac{1}{1 + K_p}\left(\frac{2v^{1/2}}{\pi^{1/2}} + \frac{K_p \operatorname{erf}\sqrt{Kv}}{\sqrt{K}}\right). \quad (40)$$

For a fairly long transition time (low current density), the second term in Eqn. (40) becomes negligibly small compared with the first. Under these conditions, K_p may be calculated from the chronopotentiometric half-wave potential (the case of a stable equilibrium in the chemical reaction).

Using Eqn. (40), it is then possible to calculate K and hence k_1 and k_2.

The quantity $K_p \operatorname{erf}\sqrt{Kv}/\sqrt{K}$ introduces a correction for the kinetic effect. Since it is positive, in the subsequent chemical reaction the chronopotentiometric curve shifts towards negative potentials:

$$\Delta\varphi_{\tau/2} = \varphi_{\tau/2,K} - \varphi_{\tau/2} = \frac{RT}{zF}\ln\frac{1}{1 + K_p}\left(1 + \frac{\pi^{1/2}K_p}{\sqrt{2}\sqrt{Kv'}}\operatorname{erf}\sqrt{\frac{Kv'}{2}}\right) \quad (41)$$

or in the limiting case (low current densities) we have

$$-\Delta\varphi_{\tau/2} = \frac{RT}{zF}\ln(1 + K_p). \quad (42)$$

Thus the shift of the chronopotentiometric half-wave potential, in which the current density becomes constant, does not change on further decrease of current density. Under this condition, it is fairly easy to calculate the equilibrium constant K_p.

At high current densities (low values of τ) the kinetic effect is vanishingly small and in this case Eqn. (39) assumes the form corresponding to the absence of kinetic complications.

For an irreversible chemical reaction, which occurs, for example, in the formation of many complexes, the equation of the chronopotentiogram simplifies [70]:

$$\varphi = \varphi_{1/2} - \frac{RT}{zF}\ln(v' - v) + \frac{RT}{zF}\ln\frac{\operatorname{erf}\sqrt{k_1 v}}{\sqrt{k_1}}. \quad (43)$$

If the rate of the chemical reaction is fairly high, we obtain the following expression from Eqn. (43) when $\sqrt{k_1 v} \geq 3$:

$$\varphi = \varphi_{1/2} - \frac{RT}{zF}\ln(v' - v) - \frac{RT}{2zF}\ln k_1, \qquad (44)$$

i.e. the electrode process becomes irreversible. k_1 may be determined by Eqn. (44) from the chronopotentiometric half-wave potential.

By analysing the $\varphi - t$ curves, Bakanov[14] derived the following criterion of the irreversibility of the electrode process followed by a chemical reaction:

$$k_f \ll \frac{v'\sqrt{k_1}}{\operatorname{erf}\sqrt{k_1 v'}}. \qquad (45)$$

Thus, when the rate constant for the chemical reaction k_1 is greater than k_f (k_f is the formal rate constant for the cathodic process), the electrode process becomes irreversible. This conclusion is consistent with the above hypothesis that the process is irreversible.

The equations of chronopotentiometric curves for a spherical mercury electrode are more complex. They have been analysed in detail together with a quasireversible electrode process for electrodes of both types[14,70].

Table 7. Criteria for the determination of kinetic mechanisms.

Kinetic mechanism	Logarithmic time function	Slope of linear section*	$i\tau$	$\Delta\varphi_{\tau/2}$, K
1) $M_{(Hg)} \rightleftarrows M^{z+} + ze$	$\frac{\tau}{\tau - t}\left(1 + \frac{2qt^{1/2}}{\pi^{1/2}D_o^{1/2}C_o^0}\right)$	$\frac{RT}{zF}$	const	0
2) $M_{(Hg)} \rightarrow M^{z+} + ze$	$\frac{\tau}{\tau - t}$	$\frac{RT}{\beta zF}$	const	0
3) $Y_{(Hg)} \underset{k_2}{\overset{k_1}{\rightleftarrows}} M_{\leftarrow} + nM_1 \rightleftarrows M^{z+} + ze$	$\frac{v' - v + K_p(S_2' - S_1)}{\frac{c_0^0}{j} + \frac{2}{\pi^{1/2}}v^{1/2}}$	$\frac{RT}{zF}$	f(i)	>0
4) $Y_{(Hg)} \underset{k_2}{\overset{k_1}{\rightleftarrows}} M_{\leftarrow} + nM_1 \rightarrow M^{z+} + ze$	$v' - v + K_p(S_2' - S_2)$	$\frac{RT}{\beta zF}$	f(i)	>0
5) $M_{(Hg)} \rightleftarrows M^{z+} + ze + N \underset{k_2}{\overset{k_1}{\rightleftarrows}} Y$	$\frac{S(v)}{v' - v}$	$\frac{RT}{zF}$	const	<0
6) $M_{(Hg)} \rightleftarrows M^{z+} + ze + N \overset{k_1}{\rightarrow} Y$	$\frac{\operatorname{erf}\sqrt{k_1 v}}{v' - v}$	$\frac{RT}{zF}$	const	<0

* The slope of the linear section is found from the time variation of the overvoltage.

3. Criteria for the Determination of Kinetic Complications in Amalgam Chronopotentiometry

Analysis of the transition times and of the time variation of the potential makes it possible to determine the kinetic mechanisms of electrode processes. If the electrochemical amalgam dissolution stage is preceded by a chemical stage, the quantity $i\tau$ depends on the current density and the kinetic parameters may be determined from the transition times. Indeed, we can put Eqn. (35) in the form

$$v_R' = \frac{c_R^0}{j} - K_p S_2(v_R') - b, \qquad (46)$$

where $b = 1/3$ for the mercury film electrode and $b = 1/15$ for the spherical mercury electrode. It follows from Eqn. (46) that

$$jv_R' = c_R^0 - j[K_p S_2(v_R') + b], \qquad (47)$$

whence it is seen that the product jv_R' depends on the current density; for short transition times, this relation is non-linear.

When the amalgam ionisation stage is followed by a chemical reaction and the preceding stage is merely diffusion in the amalgam, the product $i\tau$ is independent of current density, as in the absence of chemical reactions. Therefore in such cases the potential–time curves must be analysed in order to obtain kinetic data. The following criteria for the determination of kinetic mechanisms may be suggested: (1) a linear relation between the logarithm of the corresponding time function and potential; (2) dependence of the product $i\tau$ on current density; (3) a change in the half-wave potential of the chronopotentiometric curve $\Delta\varphi_{\tau/2}$ in the presence of kinetic complications. Table 7 illustrates the application of these criteria to certain electrode processes occurring in the electrochemical dissolution of amalgams at a mercury film electrode. All the relations indicated in Table 7 were analysed above in detail.

4. Application of Amalgam Chronopotentiometry in the Study of Complexes Formed During the Electrochemical Dissolution of Amalgams

The problems of inversion amalgam chronopotentiometry in relation to electrode processes complicated by complex formation have been examined[14,15,71–74]. If a reversible process takes place at the electrode with formation of equilibrium complexes in the presence of an excess of the ligand, then the composition and stability constant of the complex are determined from the dependence of the shift of the chronopotentiometric half-wave potential on ligand concentration[14]. The shift of the half-wave potential is described by the following equation on the assumption that the ligand concentrations at the electrode surface and in the bulk of the electrolyte are the same[75]

$$\Delta\varphi_{\tau/2,k} = -\frac{RT}{zF}\ln\sum_{n=0}^{p} K_n (c_X)^n, \qquad (48)$$

where K_n is the stability constant of the nth complex and c_X is the ligand concentration.

Since the dependence of $\varphi_{\tau/2,k}$ on $\lg c_X$ is similar to that in the polarographic method, Eqn. (48) can be analysed by the method of de Ford and Hume[76].

When only one type of complex is present in solution, Eqn. (48) reduces to

$$\Delta\varphi_{\tau/2,k} = -\frac{RT}{zF}\ln K_n - \frac{nRT}{zF}\ln c_X. \qquad (49)$$

According to this expression, the dependence of the chronopotentiometric half-wave potential on the logarithm of ligand concentration should be linear; the coordination number n may be determined from the slope of this relation and the stability constant K_n may be found from the intercept on the ordinate axis, where $c_X = 0$.

Complex formation in the presence of concentration polarisation with respect to the ligand has been examined[74]. As in the presence of an excess of the ligand, the quantity $\Delta\varphi_{\tau/2,k}$ is in this case defined by Eqn. (49).

Bakanov[14] and Bakanov and Zakharov[71] tested the theoretical conclusions in relation to the hydroxo- and chloro-complexes formed in the electrochemical oxidation of lead and cadmium amalgams respectively. The ionic strength of the solution was kept constant and equal to unity by varying the concentration of KNO_3. The concentration of lead ions in solution was 1×10^{-4} M. The experiments were performed at a mercury film electrode. It was established that in 1 M KOH as the supporting electrolyte lead forms the complex $Pb(OH)_3^-$. The slope of the relation between $\Delta\varphi_{T/2},_k$ and c_{OH^-} proved to 85.5 mV. $\lg K_n = 12.55$ was found from the intercept on the ordinate axis. The results agree well with those obtained in other studies[77-79]. Lingane[80] obtained $\lg K_n = 12.8$ and $n = 3$ at an ionic strength of 0.1.

In the electrochemical dissolution of a cadmium amalgam in 1 M (KCl + KNO_3) as the supporting electrolyte the complexes $CdCl^+$ and $CdCl_2$ are formed in succession[14]. Their stability constants were found to be 21.5 and 60.7 respectively, in good agreement with other results[79,80].

The method of amalgam chronopotentiometry has been applied[15,72] in the study of the kinetics of the electrochemical dissolution of the amalgam with participation of complex ions. The following mechanism was proposed:

$$z_R M(Hg) + p_2 X \rightarrow z_O MX_{p_2} + ze$$

with the subsequent attainment of the equilibrium

$$z_O MX_{p_2}^{(p_2 m-z)-} + (p - p_2)\, X^{m-} \rightleftarrows z_O MX_p^{(pm-z)-},$$

where P is the composition of the complex predominating in the solution, p_2 the composition of the intermediate complex formed directly in the electrochemical dissolution of the amalgam, z_O and z_R are the orders of the electrochemical reaction with respect to the oxidant and reductant respectively, and X is the ligand.

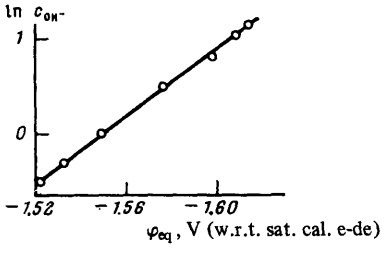


Figure 7. The dependence of the equilibrium potential of a zinc amalgam on OH^- concentration.

The general case has been analysed[15] on the hypothesis that a quasireversible electrode process takes place with subsequent complex formation. It was shown that the composition of the intermediate complex p_2 and the order of the electrochemical reaction may be determined from the exchange current density by means of the following relations:

$$\frac{\partial \ln i_O}{\partial \ln c_R^0} = \alpha z_R - \beta; \quad \frac{\partial \ln i_O}{\partial \ln c_O^0} = \beta z_O - \alpha;$$
$$\frac{\partial \ln i_O}{\partial \ln c_X} = p_2 - \beta p. \qquad (50)$$

The conclusions reached were tested in relation to the formation of zinc hydroxide and tartrate complexes formed in the electrochemical dissolution of a zinc amalgam[72]. The ionic strength was maintained at 3 by adding NaCl solution. The zinc hydroxide complexes were studied in a solution having the composition x M KOH + $(3 - x)$ M NaCl. To determine the composition of the complex predominating in solution, a study was made of the dependence of the equilibrium potential on the concentration of OH^- ions for a constant zinc concentration in solution and in the amalgam (Fig. 7). The slope of this relation pRT/zF proved to be 0.057, whence $p = 4$ ($z = 2$), in agreement with Vetter's data[81]. The values of i_O, z_R, and βz were determined from a plot of η against L_{ir} (Fig. 8): $i_O^0 = (1.75 \pm 0.3) \times 10^{-2}$; $\beta z = 0.48 \pm 0.02$; $z_R = 0.89 \simeq 1.0$. Here i_O^0 is the standard exchange current density. Using Fig. 7 and Eqns. (50), the composition of the complex $p_2 = 0.96 \simeq 1$ was determined. On the basis of the results, the ionisation of zinc amalgam can be represented as follows:

$$Zn(Hg) + OH^- \rightarrow Zn(OH)^+ + 2e + Hg,$$
$$Zn(OH)^+ + 3\,OH^- \rightleftarrows [Zn(OH)_4]^{2-}.$$

The conclusions reached agree well with the literature data[81].

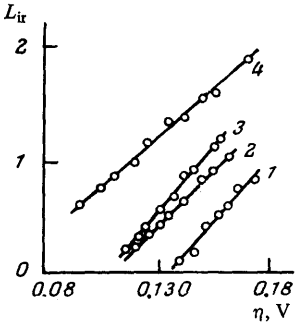


Figure 8. Variation of L_{ir} with $\eta_{Zn(Hg),Zn^{2+}}$ at different zinc amalgam concentrations (g-atom litre^{-1}): 1) 6.1×10^{-3}; 2) 1.3×10^{-2}; 3) 3.6×10^{-2}; 4) 5×10^{-2}.

Similar studies on zinc tartrate complexes showed that, in agreement with the literature[82], the complex Zn(tart) predominates in solution. It was established that $z_R = 1.0$, $\beta = 0.49 \pm 0.02$, $i_O^0 = (2.55 \pm 0.33) \times 10^{-2}$, and $p_2 = 0.13$. The value of p_O obtained leads to the conclusion that mainly hydrated zinc ions are involved in the ionisation of the amalgam.

The results quoted above have shown that the method of amalgam chronopotentiometry can be used to investigate complex formation.

5. Simultaneous Chemical Reactions in Amalgam Chronopotentiometry

When several electrochemically active substances whose standard potentials differ appreciably are present jointly in solution, a simultaneous amalgam oxidation reaction may occur. Chemical oxidation of the amalgam in the presence of oxygen has been investigated[7,83,84].

A quantitative treatment of this phenomenon for the spherical mercury electrode was described for the first time by Barański and Galus[85]. The authors began with the following mechanism:

$$M_1\,(Hg) \rightleftarrows M_1^{z_1+} + z_1 e$$
$$z_2 M_1\,(Hg) + z_1 Ox_2 \rightarrow z_2 M_1^{z_1+} + z_1 R_2,$$

where Ox_2 is the oxidised form of the reactant (it may consist either of the ions of a metal more electropositive than M_1 or of traces of dissolved oxygen) and R_2 is the reduced form of the reactant.

The electrode reaction is assumed to be reversible. If the rate of the chemical reaction is limited by the diffusion of Ox_2, the expression for the concentration can be obtained from the equation of Fick's Second Law. The quantitative treatment of the influence of the simultaneous chemical reaction on the electrode process involving the electrochemical dissolution of the amalgam was based by the authors[85] on the equality

$$i_0 = i + i_C,$$

where i_0 is the overall current in the circuit, i the electrode reaction current, and i_C the amalgam chemical oxidation current. The results of the study are expressed as the ratios of the transition times:

$$\frac{\tau_0}{\tau} = \frac{15\,D_{R_1}\tau_0}{15\,D_{R_1}\tau_0 + r_0^2} - \frac{6\,D_2^{1/2} z_2 c_2^0}{\pi^{1/2} z_1 r_0 c_{R_1}^0}\,\tau_0^{1/2} - \frac{3\,z_2 D_2 c_2^0}{z_1 r_0^2 c_{R_1}^0}\,\tau_0, \qquad (51)$$

where τ_0 is the experimental transition time, τ the transition time in the absence of a chemical reaction, and c_2^0 the initial concentration of Ox_2.

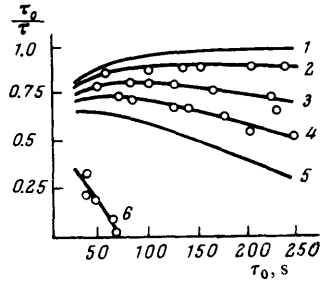


Figure 9. Theoretical $\tau_0/\tau - \tau_0$ relations for different values of $c_2^0/c_{R_1}^0$: 1) 0; 2) 0.013; 3) 0.04; 4) 0.067; 5) 0.1; 6) 0.33. The circles represent experimental data. Experimental conditions: 0.1 M KCl supporting electrolyte; $c^0_{Zn^{2+}} = 1.7 \times 10^{-5}$ M; $c^0_{Cd^{2+}} = 1.6 \times 10^{-5}$ (curves *2–4*); $c^0_{Cd^{2+}} = 1.6 \times 10^{-4}$ (curve *6*).

Fig. 9 presents curves calculated by Eqn. (51) for the following parameters: $r_0 = 0.043$ cm; $D_{R_1} = 2 \times 10^{-5}$ cm^2 s^{-1}; $D_2 = 7.9 \times 10^{-6}$ cm^2 s^{-1}; $z_1 = z_2$.

It follows from Eqn. (6) that, when $i \rightarrow 0$, then $\tau \rightarrow \infty$; however, owing to the chemical oxidation of the amalgam, in practise the transition time is always finite and equal to τ_C; it can be obtained from Eqn. (51) subject to the condition $\tau_0/\tau = 0$ (or can be found graphically). For example, when $c_2^0/c_{R_1}^0 = 0.33$, then $\tau_C = 70$ s, i.e. is equal to the maximum transition time in the chemical oxidation of the amalgam. When $c_2^0/c_{R_1}^0 \leqslant 0.01$, the error in the determination of the transition time due to the chemical oxidation of the amalgam may be neglected.

The experimental results obtained in the study of the electrochemical oxidation of a zinc amalgam in the presence of Cd^{2+} ions in solution are presented in Fig. 9 in the form of circles. Those on curves *2–4* and *6* correspond to different durations of preliminary electrolysis (240, 80, 40, and 90 s respectively). The satisfactory agreement between the experimental and theoretical curves is noteworthy.

Barański and Galus[85] described two methods of reducing the corrosion of amalgams in the presence of various impurities in solution: (1) by adding surface-active substances (which complicates the theoretical interpretation of the results) and (2) by additional preliminary electrolysis in an unstirred solution. A "diffusion barrier" is then created for Ox_2, as a result of which its concentration at the electrode surface falls. This procedure has been used[86] in a study of a multicomponent system under chronopotentiometric conditions.

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