Polarography with a Stationary Platinum Plate Electrode. Part I. The Time of Decay of the Diffusion Layer.

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Polarography with stationary platinum electrodes is developed. The time of decay of the diffusion layer is studied by a procedure in which the potential is applied intermittently to the electrode, and agrees with that obtained theoretically. By taking this time into consideration reproducible diffusion currents can be obtained which are directly proportional to the concentration.

Polarography with the dropping-mercury electrode is limited in anodic processes by dissolution of the metal (El Wakkad and Salem, *J. Phys. Chem.*, 1952, **56**, 621; Kolthoff and Miller, *J. Amer. Chem. Soc.*, 1941, **63**, 1405, 2732). Platinum electrodes can be used in the study of oxidation reactions up to +1·2 v *vs.* S.C.E. (El Wakkad and Emara, *J.*, 1952, 461) and several investigators tried to obtain reproducible polarograms with them (Laitinen and Kolthoff, *J. Phys. Chem.*, 1941, **45**, 1079; Miller, *Trudy Vesesoyuz. Konferentsii. Anal. Khim*, 1943, **2**, 551; Müller, *J. Amer. Chem. Soc.*, 1947, **69**, 2992; Skobets and Kacherova, *Zavodiskaya Lab.*, 1947, **13**, 133; Lyalikov and Karmazin, *ibid.*, 1948, **14**, 138, 144; Lyalikov and Glazer, *ibid.*, 1949, **15**, 909; Lyalikov, *ibid.*, 1950, **16**, 442). In voltammetry (Kolthoff and Lingane, "Polarography," Interscience, New York, 1946, p. 429 *et seq.*) with stationary electrodes, the diffusion layer is allowed to extend into the solution and a steady state is awaited. This takes a long time, beside giving irreproducible results.

In this Series it is intended to study the properties of the diffusion layer and the diffusion currents on a platinum plate electrode with the aim of arriving at a new procedure for polarography in which these difficulties are overcome. In this paper the time of decay of the diffusion layer is studied. No previous work on stationary platinum plate electrodes from the present standpoint has been published. For this purpose the potential is applied intermittently to the electrode, *i.e.*, electrolysis is allowed to proceed for a short time (about 3·5 sec.) and then the current is interrupted for the time required to destroy completely the diffusion layer and restore the initial conditions. This time, obtained experimentally, is found to be in agreement with that calculated theoretically. It is shown that by taking this time into consideration, reproducible results for the diffusion currents can be obtained which are directly proportional to the concentration.

Experimental

The electrical circuit used in applying the potential intermittently to the electrode is shown diagrammatically in Fig. 1. *S* was a geared, constant-speed, motor controlled by a suitable resistance. A light copper brush *B*, attached to its axle, rotated on an ebonite disc *D*, containing a quarter-segment of copper through which the electrical connection was made. The key T isolated the electrolytic cell *E*, so that, by omitting periodic cycles of the disc it was possible to obtain different ratios of the time of electrolysis to the time of interruption; and *A* was an accurate Sangamo Weston microammeter which gave direct readings to ±0·5 μA.

The known variable e.m.f. applied to the electrolytic cell was obtained from the accumulator *C* and the potential divider R_2. The total drop across the bridge was measured by the voltmeter *V*, and for convenience was adjusted by R_1 to be exactly 2 v.

The Pyrex electrolytic cell, of *ca.* 150 ml. capacity, was fitted with a rubber bung having four openings, for the platinum electrode, the syphon for the reference calomel electrode, an accurate thermometer, and an outlet for nitrogen which was introduced through two side openings to maintain an atmosphere of nitrogen over the solution during measurements. The platinum electrode was a platinum foil one face of which was covered with soda glass, thus exposing an area of 0·18 cm.^{2}. The other half cell was a saturated calomel electrode of relatively large surface area to minimise the polarisation effect. Most measurements were carried out in 2×10^{-3}, $1{\cdot}5 \times 10^{-3}$, $1{\cdot}0 \times 10^{-3}$, or $5{\cdot}0 \times 10^{-4}$M-silver nitrate in a supporting electrolyte of 0·1M-sodium nitrate, all prepared from "AnalaR" materials and conductivity water.

To perform an experiment, the platinum electrode was washed with nitric acid, conductivity water, and then with the solution to be studied. Pure nitrogen was passed through the solution for about 15 min. to remove dissolved oxygen. The nitrogen was then allowed to pass over the solution during the measurements and great care was taken to keep the solution undisturbed. Every experiment was carried out with a clean electrode and a fresh solution. All experiments were carried out at 25° ± 0·1°.

When the brush *B*, Fig. 1, made contact with the copper part of the disc *D*, a comparatively high instantaneous current—termed throughout this paper the maximum current—was found to pass. This current decreased gradually until the circuit was interrupted by the ebonite part of the disc.

RESULTS AND DISCUSSION

In Fig. 2 are shown the results obtained for the maximum currents recorded in 1·5 × 10^{-3}M-silver nitrate solution at potentials of 0·0 and −0·3 v *vs.* S.C.E. at one revolution per 13 sec. (*i.e.*, an electrolysis time of 3·25 sec.). The current falls off gradually towards a steady value, indicating that the time during which the electrolysis was interrupted was not enough to destroy completely the diffusion layer and so start each cycle from precisely the same conditions.

The minimum time required to destroy the diffusion layer which was built up during the electrolysis interval was obtained by increasing gradually the time of interruption of the process of electrolysis.

FIG. 1.

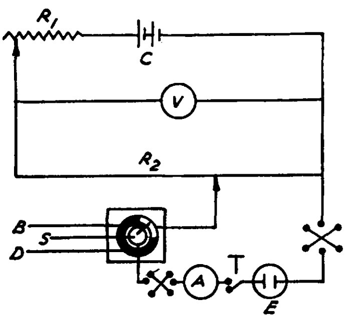
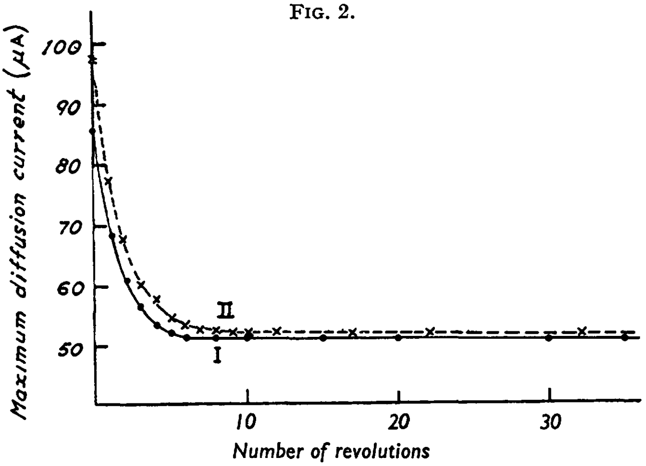


FIG. 2.



I, 0·0 v *vs.* S.C.E.; II, −0·3 v *vs.* S.C.E.

In Fig. 3 are shown the curves obtained for the maximum diffusion currents recorded as the time of interruption was increased. The black spot on each curve represents the initial diffusion current while the crosses show the values of the diffusion currents as the ratio between the time of electrolysis to the time of interruption was increased from 1 : 3 to 1 : 27 by manually operating key T. The diffusion currents retain their original values when the time of interruption has become 19—20 times that of electrolysis, *i.e.*, the minimum time required to destroy completely the diffusion layer which is built up during an electrolysis interval is 19—20 times as much as this electrolysis interval. These observations can be verified by taking into consideration the laws of linear diffusion as follows :

In the case of linear diffusion to a plane electrode, the distribution ϕ of the diffusing species near the electrode surface is given by the relation (MacGillavry and Rideal, *Rec. Trav. chim.*, 1937, **56**, 1013) :

$$\phi = c\,\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = \frac{2c}{\sqrt{\pi}}\int_0^{x/2\sqrt{Dt}} \exp\,(-\mu^2)\mathrm{d}\mu$$

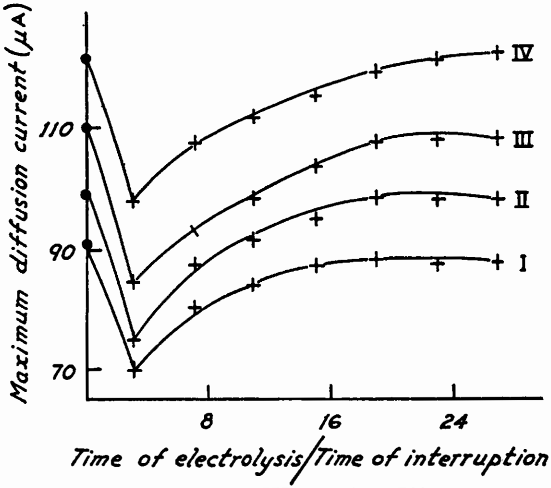
where erf represents the error function (cf. Glaisher, *Phil. Mag.*, 1871, **42**, 294), *c* is the bulk concentration of the diffusing material, *x* is the distance from the electrode surface, *t* is the time measured from the moment at which electrolysis commenced, D is the diffusion coefficient, and μ is an integration variable.

Von Stackelberg and Strehlove (*Z. Elecktrochem.*, 1950, **54**, 51) differentiated between the thickness of a differential diffusion layer δ and the thickness of an integral diffusion layer Δ (see Fig. 4):

$$\delta = c\left(\frac{\partial\phi}{\partial x}\right)^{-1}_{x=0} = c\left(\frac{\sqrt{\pi Dt}}{c}\right) = \sqrt{\pi Dt}$$

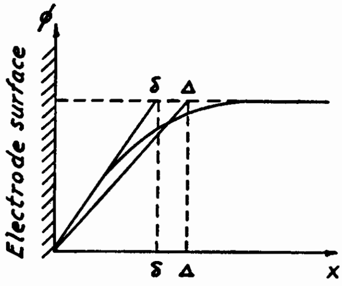
δ, therefore, corresponds to the layer that would be present if there was a linear fall in concentration with the distance.

FIG. 3.



I, 0·0 v; II, – 0·2 v; III, – 0·4 v; IV, – 0·6 v.
All *vs.* S.C.E.

FIG. 4. *Schematic representation of the differential and integral diffusion layer at a plane electrode (after Von Stackelberg and Strehlove,* loc. cit.).



The integral diffusion layer of thickness Δ is that corresponding to the same amount of ions actually reduced,

$$\Delta = \frac{2}{c}\int_0^\infty (c - \phi)\mathrm{d}x = 2\int_0^\infty \mathrm{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)\mathrm{d}x$$

where erfc stands for the complementary to the error function, or

$$\Delta = 4\sqrt{Dt/\pi}$$

for a plane electrode.

Let γ_1 stand for the total of reducible ions depleted through electrolysis in time t_1. It corresponds, therefore, to the amount of ions present in a layer of thickness Δ and cross sectional area A, *i.e.*,

$$\gamma_1 = Ac\Delta = 4Ac\sqrt{Dt_1/\pi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

When electrolysis is interrupted the amount of reducible materials required to compensate for that lost during electrolysis can be computed by Fick's first law of diffusion. Thus:

$$\gamma_2 = \int_0^{t_2} \mathrm{d}n = \int_0^{t_2} DA\left(\frac{\partial\phi}{\partial x}\right)_{x=\delta}\mathrm{d}t$$

where $\left(\frac{\partial\phi}{\partial x}\right)_{x=\delta}$ is the gradient of the distribution curve at the solution side of the differential diffusion layer and n is the number of moles of the diffusing material.

The gradient of the distribution curve at any point is given by :

$$\frac{\partial\phi}{\partial x} = \frac{c}{\sqrt{\pi Dt}} \exp\frac{-x^2}{4Dt}$$

It can be shown that the diffusion gradient has its mean value when $x = \sqrt{\pi Dt}$.

$$\therefore \quad \gamma_2 = \int_0^{t_2} DA\,\frac{c}{\sqrt{\pi Dt}} \exp\left(-\frac{\pi}{4}\right) = 2\exp\left(-\frac{\pi}{4}\right) Ac\sqrt{\frac{Dt_2}{\pi}} = 0{\cdot}912Ac\sqrt{Dt_2/\pi}\ . \quad (2)$$

FIG. 5.

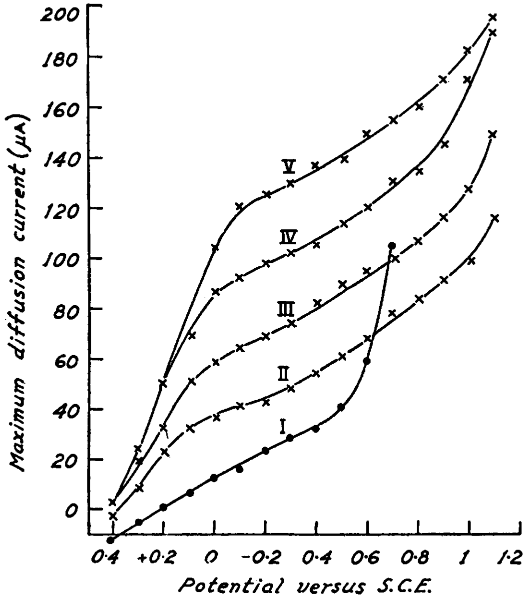


FIG. 6.

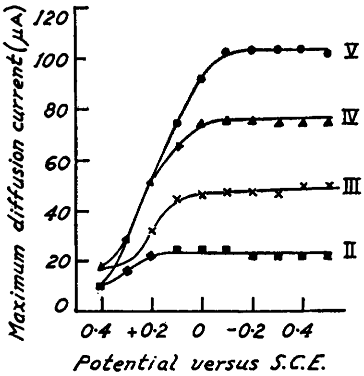
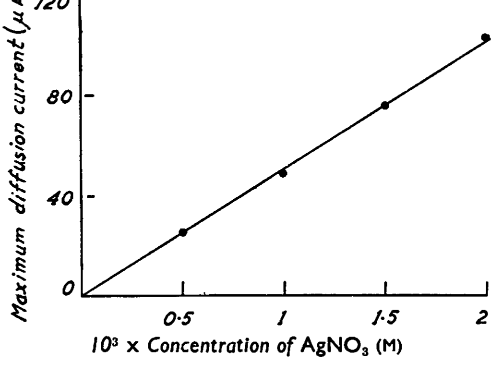


FIG. 5 and FIG. 6. I, Residual current; II, 0·5 × 10^{-3}M-AgNO$_3$; III, 1·0 × 10^{-3}M-AgNO$_3$; IV, 1·5 × 10^{-3}M-AgNO$_3$; V, 2·0 × 10^{-3}M-AgNO$_3$.

FIG. 7.



In order to start precisely from the same experimental conditions, the amount reduced in time t_1 must be equal to the amount diffusing in time t_2; *i.e.*, γ_1 must be equal to γ_2. Therefore, from equations 1 and 2, $t_2 = 19{\cdot}24t_1$. This theoretical conclusion indicates that the time of decay of a diffusion layer which has been built up during an electrolysis interval, is about 19 times this interval. This is in agreement with experiment. The same results have also been obtained experimentally during the electro-oxidation of ferrous iron.

By taking into consideration this time necessary for the complete decay of the diffusion layer the satisfactory and reproducible current–voltage curves shown in Fig. 5 were obtained for silver nitrate solutions of various concentrations between $5{\cdot}0 \times 10^{-4}$ and $2{\cdot}0 \times 10^{-3}$M. The residual current of the supporting electrolyte was determined with the same platinum electrode after it had been coated with silver, under the conditions of the experiments. When the residual current of the supporting electrolyte was taken into consideration, constant diffusion current regions were obtained (see Fig. 6). When these diffusion currents, which were obtained at different concentrations of silver nitrate, were plotted against the concentration of the solution a straight line passing through the origin (Fig. 7) was obtained.

This indicates clearly that, by taking into consideration the time necessary for the complete decay of the diffusion layer on a stationary platinum plate electrode, reproducible results for the diffusion currents can be obtained which are directly proportional to the concentration.

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