The Kinetics of the Anodic Processes at Very Low Current Density. Part I. The Anodic Dissolution of Copper and Mercury.*

By S. E. S. El Wakkad, T. M. Salem, and S. E. Khalafalla.

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A new approach to the kinetics of anodic processes is made by deducing an equation expressing the potential of an electrode dissolving at a very low anodic current in terms of the rate of the electrode reaction and the gradient of the potential-determining ions at the electrode surface. The equation has been applied to the anodic dissolution of copper, and the results of the rate constant for this process so obtained are compared with those obtained with small alternating potential. The measurements have been extended to the anodic dissolution of mercury, and the rate constant of this reaction is given.

In spite of recent advances in the study of electrode processes, little is known concerning the kinetics of the anodic processes. Generally, in any electrode process three factors can be considered to control the speed of the process, *viz.*, the rate of the electrode process itself, the rate of diffusion, and the ohmic resistance of the electrolyte (Bowden and Agar, *Proc. Roy. Soc.*, 1938, *A*, **169**, 206). Most of the previous work on electrode processes was on reactions in which the rate of the electrode process itself is very slow and thus the other two factors were neglected. Very few investigations of moderately rapid electrode processes have been made, and diffusion control has been either disregarded or minimised (Erdey-Grúz and Volmer, *Z. physikal. Chem.*, 1931, **157**, 165; Roiter, Polnyan, and Juza, *Acta Physicochim.*, 1939, **10**, 389, 845; Essin, *ibid.*, 1942, **16**, 102; Bonnemay, *J. Chim. phys.*, 1944, **41**, 218). Randles (*Discuss. Faraday Soc.*, 1947, **1**, 11; *Trans. Faraday Soc.*, 1952, **48**, 828) and Randles and Somerton (*ibid.*, p. 937) measured the rates of some rapid electrode reactions at the dropping-mercury electrode upon which an alternating potential of small amplitude was applied. The reactions studied were redox reactions of the type $M^{4+} + e = M^{3+}$, and the deposition of metal ions into dilute amalgams. The electrode reactions which can be studied by this technique are limited owing to the tendency of many ions to oxidise the mercury. Hillson (*ibid.*, 1954, **50**, 385) modified Randles's theoretical treatment to suit solid electrodes when a small alternating potential is superimposed on them. Hillson applied this procedure to the reaction at a Cu–Cu^{2+} electrode.

In this paper a new approach to the kinetics of anodic processes is made by deducing an equation expressing the potential of an electrode dissolving at a very low anodic current in terms of the rate of the electrode reaction and the gradient of the potential-determining ions at the electrode surface. The equation has been applied to the anodic dissolution of copper and the results of the rate constant for the dissolution of copper as obtained by our procedure are compared with those obtained with small alternating potential. The measurements have been extended to the anodic dissolution of mercury and the rate constant of such reaction is given.

The Theory of the Method.—The rate of dissolution is assumed to depend on the electrode potential according to the equation

$$\partial n/\partial t = Ake^{\alpha VzF/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where n represents the number of ions dissolving in time t, A the area of the electrode, k the rate constant of the electrode process, α the fraction of the extra potential helping the dissolution process, and V the difference between the electrode potential E and the standard electrode potential E_0.

If t represents the time in seconds counted from the moment at which electrolysis has started, then it/zF would represent the number of moles of ions dissolved in time t, i being the constant current passing and zF the charge per mole of ions. When the solution is originally free from the dissolving ions and contains a sufficient amount of an indifferent salt, the dissolving ions will diffuse away from the electrode surface. The differential equation describing this situation is $\partial c/\partial t = D(\partial^2 c/\partial x^2)$ subject to the initial condition $c = 0$ when $t = 0$, $x \geqslant 0$ and the boundary condition $c = it/z\mathbf{F}A\delta$, when $x = 0$, $t > 0$, where δ is the thickness of a monolayer of ions, and D the diffusion coefficient of the dissolving ions. The solution of this equation is given by Carslow and Jaeger ("Conduction of Heat in Solids," Oxford, 1947, p. 45) :

$$c_{x,t} = \frac{it}{z\mathbf{F}A\delta}\left\{\left(1 + \frac{x^2}{2Dt}\right)\operatorname{erfc}\frac{x}{2\sqrt{Dt}} - \frac{x}{\sqrt{\pi Dt}}\,\mathrm{e}^{-x^2/4Dt}\right\} \quad . \quad . \quad . \quad (2)$$

where x is the distance from the electrode surface, and erfc the complementary to the error function defined by

$$\operatorname{erfc} y = 1 - \operatorname{erf} y = 1 - \frac{2}{\sqrt{\pi}}\int_0^y \mathrm{e}^{-\mu^2}\mathrm{d}\mu$$

Differentiating (2) with respect to x and setting $x = 0$, one obtains

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} = -\frac{it}{z\mathbf{F}A\delta}\,\frac{2}{\sqrt{\pi Dt}}$$

The rate of diffusion as given by Fick's first law would be

$$\frac{\partial n}{\partial t} = -D\left(\frac{\partial c}{\partial x}\right)_{x=0} = \frac{2i}{z\mathbf{F}A\delta\sqrt{\pi}}\sqrt{Dt} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

At equilibrium, the rate of dissolution per unit area given by (1) must be equal to the rate of diffusion from the electrode surface given by (3); hence

$$ka_s\,\mathrm{e}^{\alpha Vz\mathbf{F}/\mathbf{R}T} = \frac{2i}{z\mathbf{F}A\delta\sqrt{\pi}}\sqrt{Dt}$$

$$\therefore\ V = \frac{\mathbf{R}T}{\alpha z\mathbf{F}}\ln i + \frac{\mathbf{R}T}{2\alpha z\mathbf{F}}\ln t + \frac{\mathbf{R}T}{\alpha z\mathbf{F}}\ln\frac{2D^{\frac{1}{2}}}{z\mathbf{F}\delta Aka_s\sqrt{\pi}} \quad . \quad . \quad . \quad . \quad (4)$$

This equation shows that the potential at the equilibrium state changes with time according to log t. This is a state of transient equilibrium slowly drifting with time. The factors which influence the value of V, as seen from equation (4), are i, k, and t, since all the other terms including D are constant for the same metal.

The plot of V against log i at corresponding times and at constant temperature should give a straight line, the slope of which is $2{\cdot}303\mathbf{R}T/\alpha z\mathbf{F}$ or $0{\cdot}060/\alpha z$ at 30°, from which α can be obtained and which makes an intercept with the V axis (where $\log i = 0$) of $(0{\cdot}060/\alpha z) \times \log 2D^{\frac{1}{2}}/z\mathbf{F}Aka_s\delta\sqrt{\pi}$; this enables the rate constant to be calculated. Again, the plot of V against log t should be linear with a slope of $2{\cdot}303\mathbf{R}T/2\alpha z\mathbf{F} = 0{\cdot}060/2\alpha n$ at 30°. This treatment is valid at very low current densities, where linear diffusion due to concentration gradient is expected to occur for a measurable time.

EXPERIMENTAL

The electrical circuit used in determining the potential of the electrode as it is dissolved anodically at very low current density incorporated a pentode valve as a constant-current device, so the current passing was largely independent of changes in the back e.m.f. of the electrode system. The current was supplied from 120-v dry battery. The electrolytic cell was of Pyrex glass of *ca.* 150 ml. capacity. It was fitted with a rubber bung having five openings; for the anode, the syphon for the reference saturated calomel electrode, an accurate thermometer, the cathodic compartment, and an outlet for the nitrogen which was introduced through a side opening.

The copper anode was prepared by electrodeposition from an acidified copper sulphate solution with a current of 4·0 mA per electrode for 10 min. on a platinum foil one face of which was covered with soda glass, thus exposing area of 0·21 cm.^{2}. The electrode was washed several times in conductivity water and then introduced directly into the electrolytic cell. Each experiment was carried out with a freshly prepared electrode.

The mercury anode was in the form of a circular disc of diameter 0·32 cm. and thus with an area of 0·080 cm.^{2}. This was prepared by introducing twice-distilled mercury in a cup provided with a platinum contact. The cathode was always a platinum spiral placed in its compartment in such a manner as to ensure uniform distribution of the polarising current at the anode surface.

The design of our cells, as shown before, led the more dense solution to the side of the less dense in the case of the copper electrode. In the case of mercury the denser part was below the solution. In both cases convection diffusion due to density gradients is not liable to occur in the early stages of the process. Comparison of the geometry of the diffusion processes shows that it is more difficult in the case of mercury (where the denser part was below the solution) to get convection diffusion than in the case of copper; accordingly, while constant potential was reached at about 3 min. with copper, it was not until 15 min. with mercury.

Measurements have been carried out in 0·1M-perchloric acid, and so the sole anodic process in such solution will be the dissolution of the metal (El Wakkad and Emara, *J.*, 1952, 461; El Wakkad and Salem, *J. Phys. Chem.*, 1952, **56**, 621). The solution in the cell was boiled before use and cooled in an atmosphere of pure nitrogen to remove dissolved oxygen.

FIG. 1.

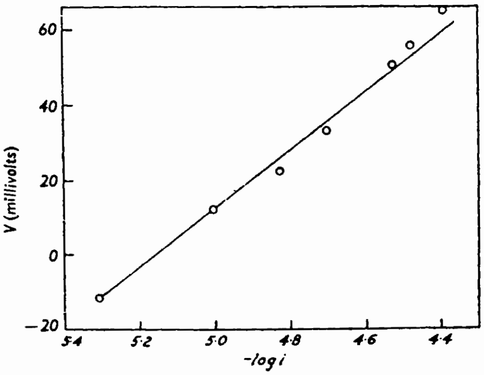
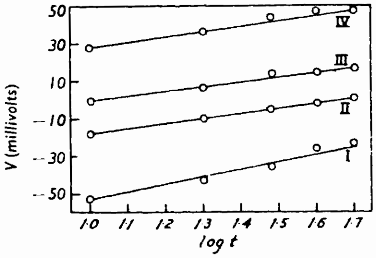


FIG. 2.



I, 5 μA. II, 10 μA.
III, 20 μA. IV, 30 μA.

Before starting each experiment the electrode was washed with conductivity water and dipped in the solution while a cathodic current was imposed on it. The cathodic polarisation was continued until a constant potential was recorded so as to ensure the reduction of any oxide present on the surface of the electrode during its preparation. The current was then adjusted to the required value, and reversed to start the anodic polarisation, and then the potential of the anode was recorded as a function of time.

All experiments, except when otherwise stated, were carried out in a water thermostat kept at 30° ± 0·1°. The reference half-cell was a saturated calomel electrode. The e.m.f. was measured with a valve potentiometer (Cambridge Instruments, England). Great care was taken to prevent the electrolytic cell from mechanical disturbances during measurements.

Results and Discussion.—Fig. 1 shows the plot of V at 1 min. against log i, for our copper electrode. The line has a slope of 0·078 which gives a value for α of 0·38. Hillson (*loc. cit.*) found $\alpha = ca.$ 1/3 for his copper electrode. The intercept with the V axis in Fig 1 has a value of 0·402$_5$. Using equation (4), one obtains

$$\frac{\boldsymbol{RT}}{2\alpha z\boldsymbol{F}}\ln t+\frac{\boldsymbol{RT}}{\alpha z\boldsymbol{F}}\ln\frac{2D^{\frac{1}{2}}}{z\boldsymbol{F}Ak\delta a_s\sqrt{\pi}}=0{\cdot}402_5$$

Using a value for the diffusion coefficient of Cu^{++} of 7·2 × 10^{-6} cm.^{2} sec.$^{-1}$ (Kolthoff and Lingane, " Polarography," Interscience, 1948, p. 45) and δ the thickness of a monolayer of Cu^{++} as 10^{-7} cm., we calculate k for the copper electrode to be 3·6 × 10^{-2} cm. sec.$^{-1}$. Randles and Somerton (*loc. cit.*) found 4·5 × 10^{-2} cm. sec.$^{-1}$ for M/1000-Cu^{++} in M-potassium nitrate.

Fig. 2 shows the plots of V against log t at different current densities: they are nearly parallel straight lines, as expected from the theory. The average slope of these lines is 0·039. The expected slope from the deduced equation is $2{\cdot}303\boldsymbol{R}T/2\alpha z\boldsymbol{F}$, which should be half of the slope of the V–log i straight line. The slope of the V–log i curve (Fig. 1) is 0·078 and accordingly the slope of the V–log t curve should be 0·039, which is in good agreement with the results represented in Fig. 2.

The intercept for the curve at 5 µA is found to be —0·092, and using equation (4) we have

$$-0{\cdot}092 = \frac{\boldsymbol{R}T}{\alpha z\boldsymbol{F}} \ln \frac{2iD^{\frac{1}{2}}}{z\boldsymbol{F}Ak\delta a_s\sqrt{\pi}}$$

This gives a value for k of $4{\cdot}52 \times 10^{-2}$ cm. sec.$^{-1}$ in good agreement with the value obtained from the V–log i curve.

Fig. 3 gives the plot of V against log i for the mercury anode at 30°; V was measured at 15 min. The slope of the line obtained is 0·037, which gives a value of 0·8 for α in the anodic dissolution of mercury. This line makes an intercept of 0·194 with the V axis. Applying equation (4) and using a value for the diffusion coefficient of Hg_2^{++} of $9{\cdot}2 \times 10^{-6}$ cm.^{2} sec.$^{-1}$ (Kolthoff and Lingane, *op. cit.*, p. 258), we obtain a value for k = 0·476 cm. sec.$^{-1}$.

FIG. 3.

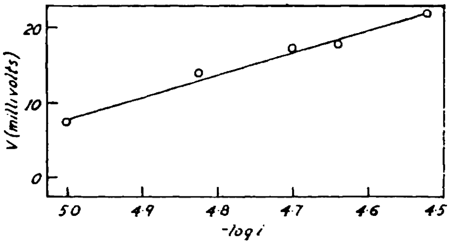
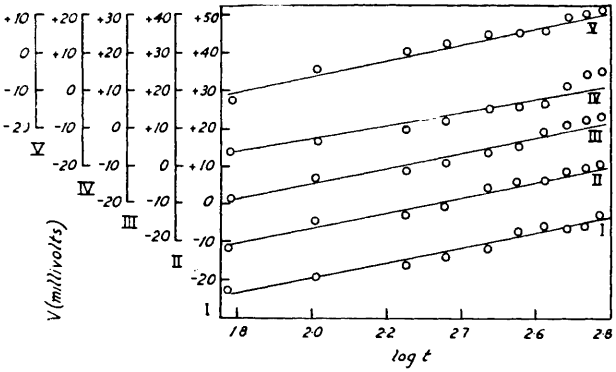


FIG. 4.



I, 10 µA. II, 15 µA. III, 20 µA. IV, 23 µA. V, 30 µA.

Fig. 4 shows the plot of V against log t at different current densities: it is a series of straight lines with an average slope of 0·021. The rate constant k can be also determined from the V–log t curves with the help of equation (4). Thus the intercept of the curve at 10 µA with the V axis has a value of —0·053, and by using equation (4) a value for k of 0·391 cm. sec.$^{-1}$ was obtained, in reasonable agreement with the results obtained from the V–log i curve.

From the above discussion it is clear that our new approach for the kinetics of anodic processes is in harmony with the results obtained experimentally. Thus the derived equation predicts a linear relation between V and log i when V is measured at the same time, and also a linear relation between V and log t at constant current i and temperature. This has been found experimentally for the dissolution of copper and mercury. From the slope and intercept of the curves we obtained for copper $\alpha = 0{\cdot}38$ and $k = 3{\cdot}6 \times 10^{-2}$ cm. sec.$^{-1}$, and for mercury $\alpha = 0{\cdot}8$ and $k = 0{\cdot}476$ cm. sec.$^{-1}$.

CAIRO UNIVERSITY, CAIRO, EGYPT.

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