Theory of Electrochemical Oscillations

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An explanation is given of the oscillations of current at constant external potential which are found in different electrode processes; this is based on the external resistance, the negative slope in the current potential curve, and the concentration polarization. A mathematical model, consisting of simplified expressions for these three properties, and an electronic analogue circuit show waveform and frequency dependence in agreement with experiments.

Oscillations of current or potential in connection with electrochemical processes have been known for more than a century. There is a great variety of electrochemical systems which can show oscillatory behaviour. Two examples are the iron anode in dilute sulphuric acid [1, 2] and the platinum anode, oxidizing molecular hydrogen dissolved in dilute sulphuric acid. [3, 4] Most electrochemical oscillations have been observed in anodic processes but cathodic oscillations are also known. [5] The waveforms of the current oscillations at constant external potential are often remarkably similar in different systems. The following four phases can usually be recognized in current oscillations (fig. 1). (i) The current increases rapidly to its maximum value. (ii) The current decreases at a decreasing rate. (iii) At a certain value the decrease accelerates and the current rapidly falls off to a low value. (iv) The current remains nearly constant at a low value until (i) reoccurs.

A general feature of electrodes which are capable of oscillations is that they have a region of negative slope in their current against potential curve. The phenomenon of decreasing current with increasing potential (i.e., negative resistance) is usually called passivation. This property plays a major role in the mechanism which brings forth the oscillations, but does not in itself explain the oscillations. A time-dependent function must also be involved. The current in an electrochemical reaction causes changes of concentrations in the electrolyte layer at the electrode surface, and such changes of concentrations cause a time dependence of the behaviour of the electrode. Franck [6] assumed the changes of hydrogen ion concentration in the electrolyte layer at the electrode surface to be the time-dependent function in the mechanism of the oscillations. The passivation potential is assumed to depend on the hydrogen ion concentration in such a way that the depletion of hydrogen ions due to a high current causes the electrode to become passive. The resulting low current allows the back diffusion of hydrogen ions and causes the electrode to become active again. This theory was elaborated by Franck and FitzHugh [7] for an iron anode in dilute sulphuric acid as an example. However, their analogue computer solution of the resulting differential equations failed to produce oscillations resembling those observed experimentally.

The similarity between the waveforms of current oscillations in different systems suggests that the oscillations may result from one general mechanism. The mechanism proposed by Franck for the iron anode is not generally applicable, since it depends

on the specific assumption that passivation is caused by a resistive layer of metal oxide formed according to the general equation

$$Me + nH_2O - 2ne \rightleftharpoons MeO_n + 2nH^+.$$
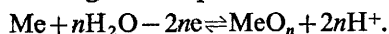
There is good evidence that this equation applies to the iron anode,[8] but its applicability to noble metal anodes is not so firmly established.[9] Even if it is assumed that the equation holds for a platinum anode, the oscillations of current during the oxidation of dissolved H_2 at a platinum anode cannot be explained by Franck's theory since an electrode reaction, exclusively producing hydrogen ions, can hardly be accompanied by a depletion of hydrogen ions at the electrode surface. It would also be difficult to reconcile Franck's theory with the cathodic oscillations.

FIG. 1.—Oscillations of current at constant external potential in different electrode processes. A : iron in 1N H_2SO_4 at $E_h = +0.49$ V ; B : gold in 4N HCl at $E_h = +1.8$V. C : zinc in 4N NaOH at $E_h = -1.1$V (redrawn after Franck and FitzHugh[7]). D : platinum anode oxidizing dissolved H_2 in 2N H_2SO_4. The solution was saturated with H_2 at 1 atm. Both anode and cathode were platinum wires of 0·2 mm diam., 4 mm and 22 mm long respectively. The external potential was 1·2V and the oscillation occurred when a resistance of 70 Kohm was inserted in series with the electrolysis cell.[11]
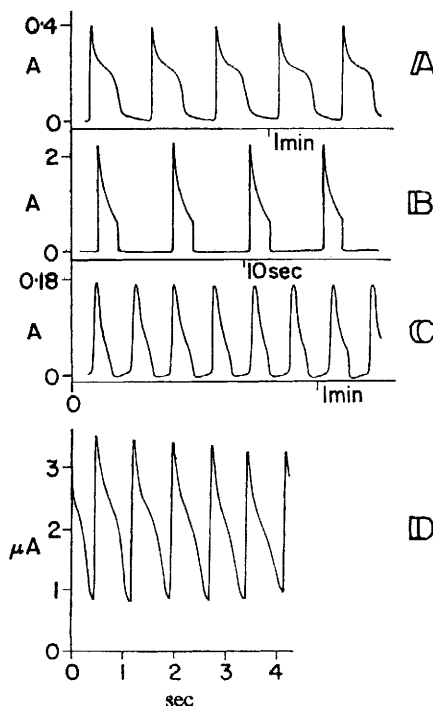
The purpose of this paper is to show that the electrochemical oscillations can be explained without any specific assumptions about the mechanism of the passivation process. The theory is based entirely on the following three conditions : (i) external resistance, (ii) a range of negative slope in the current/potential curve, and (iii) concentration polarization.

A characteristic of the theory is that changes of concentrations of substances involved in the primary electrode reaction are assumed to be responsible for the oscillations whereas in Franck's theory the change of concentration of a substance involved in the passivation process is responsible. Both theories assume phenomena which undoubtedly exist, and one theory does not exclude the other. The choice between the theories will therefore depend on their ability to predict experimental findings.

EXTERNAL RESISTANCE

If the potential of an electrode is measured with reference to a counter electrode when a current is flowing, the measured potential exceeds the true potential of the

electrode by a term RI, where R is the external resistance and I is the current. The most important contributions to the external resistance are the ohmic resistance of the electrolyte and the polarization resistance in the counter electrode. The internal resistance of the current source is also important. Although it does not affect the potential measurements it causes the potential of the source to vary with the current. In older electrochemical work the external resistance was usually minimized by the use of a large " unpolarizable " counter electrode and a current source with a low internal resistance. By such precautions the external resistance could be reduced to about 1 ohm.[2] While the external resistance cannot be made zero,[10] it can be further reduced by the use of a potentiostat. In connection with an electrode which can become passive even a small external resistance is significant because it can render the negative slope in the current/potential curve unmeasurable.[1]

PASSIVATION

It is usually assumed that passivation is caused by the deposition of a resistive layer on the electrode surface. The chemical composition of the passivating surface layer has been a matter of controversy.[9] A widely accepted theory is that the surface layer consists of metal oxide. However, this theory cannot apply to all cases of passivation. For example, a platinum anode oxidizing H_2 can become passive and show oscillations in a totally oxygen-free electrolyte, such as acetonitrile saturated with hydrogen chloride.[11] However, we shall adopt the surface layer theory without favouring any specific chemical interpretation.

Assume that the passivation is caused by a reaction of the form

$$A + S \rightleftharpoons (AS)^{n+} + ne,$$

where A is a substance, charged or uncharged, in the electrolyte, S is a site on the electrode surface which can accommodate an A, and $(AS)^{n+}$ is a site which is occupied by an A. The standard electrode potential due to the passivation reaction is

$$V = V^\circ - \frac{RT}{nF} \ln \frac{[A][S]}{[(AS)^{n+}]}, \tag{1}$$

where the concentrations are in moles per area unit and all activity coefficients are assumed to be one. The fraction θ of unoccupied sites as a function of the potential, at equilibrium in the passivation process, can be found from (1):

$$\frac{[S]}{[S_{max}]} = \theta = \frac{1}{1 + [A] \exp \dfrac{nF(V - V^\circ)}{RT}}. \tag{2}$$

If it is assumed that the current due to the primary electrode reaction is proportional to θ, eqn. (2) shows that the current will be a decreasing sigmoidal function of the potential, provided the potential is changed slowly enough to allow the passivation process to be at equilibrium.

In some cases, passivable electrodes exhibit a sigmoidal current/potential relationship in the range of negative resistance [12, 13] as predicted by (2), but in others the electrode changes abruptly from a fully passive to a fully active state as the potential is decreased below a well-defined limit, the Flade potential,[14] and similarly changes abruptly from active to passive as the potential is increased beyond a certain value which is usually not identical with the Flade potential.[2, 6] The observation of such abrupt changes indicates that the passivation process can approach the equilibrium rapidly. The occurrence of abrupt changes of the current instead of a smooth sigmoidal curve can be explained if the external resistance is taken into account.[1]

Consider an idealized electrode where the current increases linearly with the potential until a certain potential V'. At potentials higher than V', the current decreases linearly with the potential until a second potential V'' is reached where the current becomes zero. At higher potentials, the current is always zero (fig. 2a).
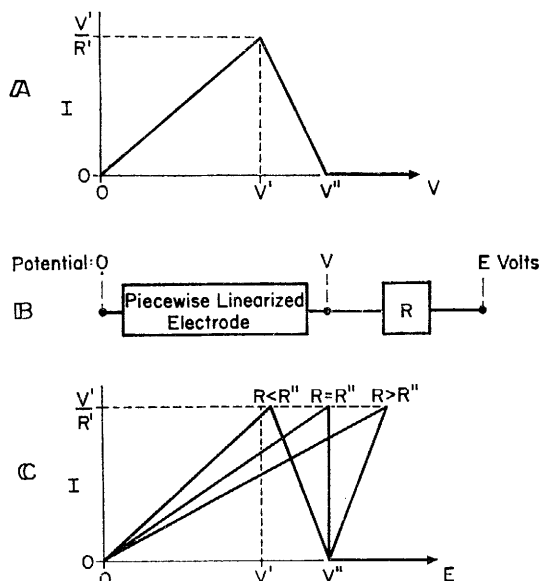

FIG. 2.—Distortion of current/potential curve by external resistance. Curve A is the current/ potential curve of an idealized, passivable electrode. It consists of three linear pieces with the slopes $1/R'$, $-1/R''$ and zero respectively. If the current/potential curve of the idealized electrode in series with a resistance R is measured for different values of R the curves C are obtained. If $R > R''$ the negative slope disappears and discontinuous jumps of the current take place.

The equation of the first linear section of the current/potential curve is

$$I = V/R' \quad \text{for } 0 \leqslant V \leqslant V'. \tag{3}$$

The second linear section is

$$I = -\frac{V}{R''} + V'\left(\frac{1}{R'} + \frac{1}{R''}\right), \qquad \text{for } V' \leqslant V \leqslant V'', \tag{4}$$

where $V'' = (1 + R''/R')V'$. The third linear piece is

$$I = 0, \quad \text{for } V > V''.$$

The quantities $1/R'$ and $-1/R''$ are the slopes of the first two linear sections.

We now examine the current/potential curve obtained if this idealized electrode is connected in series with a resistance R and the current is measured as a function of the potential E across the series (fig. 2b). If we let E increase, starting from zero, the current will increase proportionally according to

$$I = E/(R' + R). \tag{5}$$

Eqn. (5) will be followed until $V = V'$. Since $V = E - RI = ER'/(R' + R)$, the limit of validity, $V = V'$ of (5) is equivalent to $E = V'(1 + R/R')$. For this value of E, the current is equal to V'/R'. The current at the point where (5) ceases to be valid does not depend on R. By rewriting (4),

$$V = [(V'/I)(1 + R''/R') - R'']I, \tag{6}$$

and comparing with Ohm's law, we conclude that the resistance of the electrode, in the range where (4) is valid, is the quantity within the brackets of (6). Consequently the current is determined by

$$I = \frac{E}{(V'/I)(1 + R''/R') - R'' + R},$$

or

$$I = \frac{E}{R - R''} - \frac{V''}{R - R''}. \tag{7}$$

From (7) the slope of the second linear section of the current/potential curve is negative for $R < R''$. If $R = R''$ the slope is infinite. If $R > R''$, the slope is positive. The minimal value of E for which $I = 0$ is always V'', and does not depend on R.

Fig. 2c illustrates this treatment of a piecewise linearized electrode. When $R < R''$, the current is always a single-valued function of the potential. When $R > R''$ the current is a triple-valued function of the potential in the interval $V'' < E < V'(1 + R/R')$. If the current/potential curve is measured with increasing potential the current will jump discontinuously from the value V'/R' to zero, when the potential exceeds $V'(1 + R/R')$. However, if the potential is decreased the current will jump from zero to a point on the first linear piece of the curve when the potential is lowered below V''. V'' corresponds to the Flade potential of a real electrode.

The condition $(R > R'')$ for the appearance of discontinuous jumps of the current which was found for the piecewise linearized current/potential curve is also valid in the more realistic case where the current/potential curve has a sigmoidal shape in its range of negative slope. The condition is that the external resistance R must be larger than the negative reciprocal of the inclination at the steepest point of the negative slope.

The question now arises whether this condition was fulfilled in the cases where abrupt changes between the active and the passive states were reported. Unfortunately, the reports do not usually contain sufficient information. One exception is the paper by Bartlett and Stevenson,[2] who measured the initial current through an iron anode after the external voltage had been switched off for a short period of time. The charging of the double layer capacity was an insignificant part of the initial current. The curve depicting the initial current as a function of the potential is therefore the current/potential relationship which would be found if concentration polarization did not take place. If the initial current is extrapolated to the passivation potential a value of about 50 mA is obtained (fig. 4 in ref. (2)). Since the range of potential where passivation takes place is about 50 mV wide the slope of the current/potential curve in this range must be about -1 ohm. Since the external resistance was reported to be about 1 ohm the condition for abrupt changes derived above was fulfilled.

CONCENTRATION POLARIZATION

The current potential relationship of an electrode depends on time. Consider an electrode reaction

$$A \rightarrow B^+ + e.$$
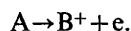
When an external current is flowing the utilization of A and the production of B^+ will cause depletion of A and an enrichment of B^+ in the electrolyte layer at the electrode surface. If the potential is kept constant the current will tend asymptotically to a limit value as the diffusion gradient of A and B^+ in the electrolyte layer at the surface tends to a stationary value. The stationary current depends on the rate of convection or stirring in the electrolyte. Likewise, if the current is kept constant

the potential will tend asymptotically to a limiting value. If the current is interrupted and the potential is measured it is different from the equilibrium potential of the electrode. The difference is the concentration overpotential. After the interruption of the current, the diffusion gradient will eventually disappear, and the potential of the electrode will return to the equilibrium potential.

Now the true electrode potential is RI less than the externally measured potential. When the external potential is kept constant the current is not constant and consequently the true electrode potential is not constant. The oscillation can be explained on this basis. If the external potential is fixed at a value which is higher than the passivation potential, there is initially no concentration polarization and the current is high. At the high current the RI term keeps the true electrode potential below the passivation potential. The current decreases with time because of the increasing concentration polarization and consequently the true electrode potential will increase with time. Eventually, the true electrode potential reaches a value where passivation takes place, and the current drops to a low value. The concentration polarization will now decrease with time. Consequently, the current will increase and the true electrode potential will decrease with time. Eventually, the true electrode potential will fall below the passivation potential and the electrode will become active again. Thereafter, the cycle will repeat itself.

SIMPLIFIED MATHEMATICAL MODEL

The concentration overpotential is observed as a potential which opposes the the external potential applied to the electrode and which increases with the charge transported through the system. We assume that the current is proportional to the fraction of unoccupied sites and to the difference between the true electrode potential V and the concentration overpotential P:

$$I = k_1\theta(V-P). \tag{8}$$

It is further assumed that the concentration overpotential increases linearly with the charge transported through the system and that the spontaneous degradation of the concentration overpotential is a first-order process:

$$dP/dt = k_2 I - k_3 P. \tag{9}$$

Eqn. (2) indicates that the current will decrease according to a sigmoidal curve with increasing potential. Instead of using (2) we here express the passivation by a polynomial approximation:

$$\theta = k_4/(k_5 V^2 + 1). \tag{10}$$

Assuming that the equilibrium in the passivation process is instantaneous, we combine (8) and (10) to yield an expression for I as a function of V and P:

$$I = k_1 k_4 (V-P)/(k_5 V^2 + 1). \tag{11}$$

The additional assumption that the external resistance R is ohmic yields

$$V = E - RI, \tag{12}$$

where E is the external potential.

Eqn. (9), (11) and (12) describe an electrode where only external resistance, passivity and concentration polarization are taken into account. All functions, except the passivation, are linearized.

GRAPHICAL SOLUTION

The concentration overpotential can be found as a function of the current from (11) and (12). For simplicity, $k_1 k_4$ and k_5 are assumed to be one.

$$P = -R^2 I^3 + 2ERI^2 - (E^2 + R + 1)I + E. \tag{13}$$

Graphical representations of this function were obtained on a digital computer for particular values of E, R and I. Fig. 3 shows some typical examples of the family of curves obtained.

For the particular case of $R = 30$ and $V = 10$ (fig. 4), if P increases from 0 to 10 the representative point will move from point A to the extremum B from which it jumps discontinuously to the point C, and finally ends at D. If P decreases from 10 to 0 the representative point moves from D to the extremum E from which it jumps to F and finally ends at A.
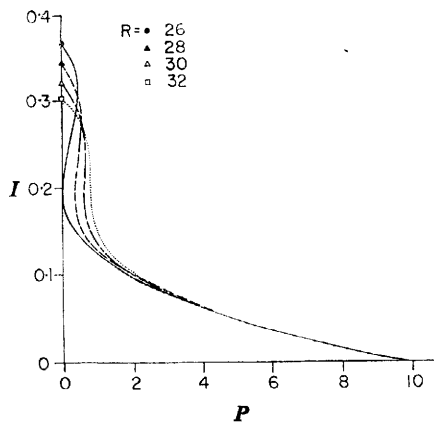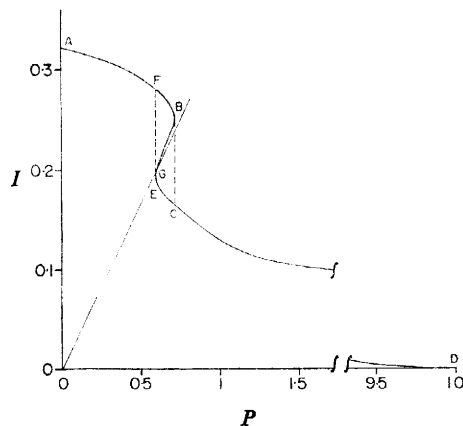

FIG. 3.

FIG. 4.

FIG. 3.—Relationship between the current I and the concentration overpotential P for the external potential $E = 10$ and different values of the external resistance R.

FIG. 4.—I/P curve for $E = 10$ and $R = 30$. The point of intersection G between the I/P curve and the straight line $I = k_3 P/k_2$ is the stationary point of the system. If the point of intersection is situated betwen B and G it is inaccessible and the representative point will describe the closed path FBCE.

From (9) we find that the condition for the stationary state is given by
$$k_2 I - k_3 P = 0. \tag{14}$$
Graphically the stationary point is found by the intersection of the curve given by (13) and the line
$$P = k_2 I/k_3, \tag{15}$$
given by (14). For $k_2/k_3 = 3$ the curves intersect between B and E, as shown in fig. 4, and the point of intersection G is inaccessible. Consequently, the representative point must cycle the closed curve FBCE.

An expression for dP/dt can be derived from (13). Substituting P and dP/dt into (9) gives
$$\frac{dI}{dt} = \frac{k_3(R^2 I^3 - 2ERI^2 + (E^2 + R + k_2/k_3 + 1)I + E)}{-3R^2 I^2 + 4ERI - E^2 - R - 1}. \tag{16}$$

An approximate graphical solution of (16) using the values of the parameters E, R and k_2/k_3 determined above, was obtained by computing dI/dt for a series of values of I, plotting the corresponding tangents in the I/t plane and drawing integral curves fitting the tangents as shown in fig. 5. The direction of motion along the curves are indicated by arrows and can be deduced by considering the initial states $P_{t=0} = 0$ and $P_{t=0} = 10$ respectively.

Following an integral curve in the direction of the arrow leads to a point where the slope of the curve is infinite. From this point the current jumps discontinuously to a point on the other integral curve. This curve is followed until its slope is infinite and the current jumps back to the first curve. The end points of the jumps can be
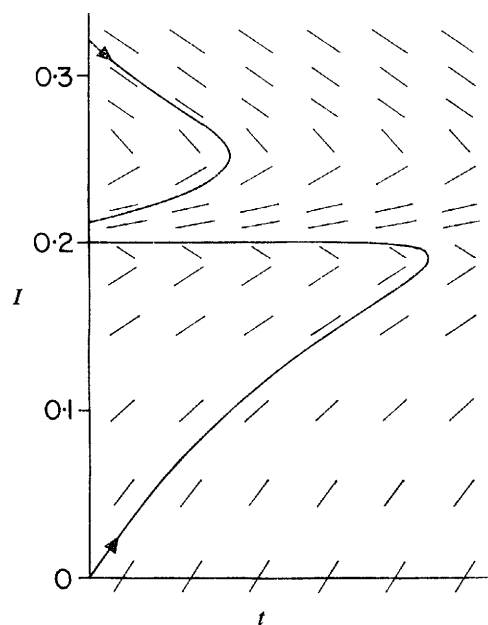
FIG. 5.—Graphical solution of the differential eqn. (16) obtained by fitting curves to tangents calculated from (16).
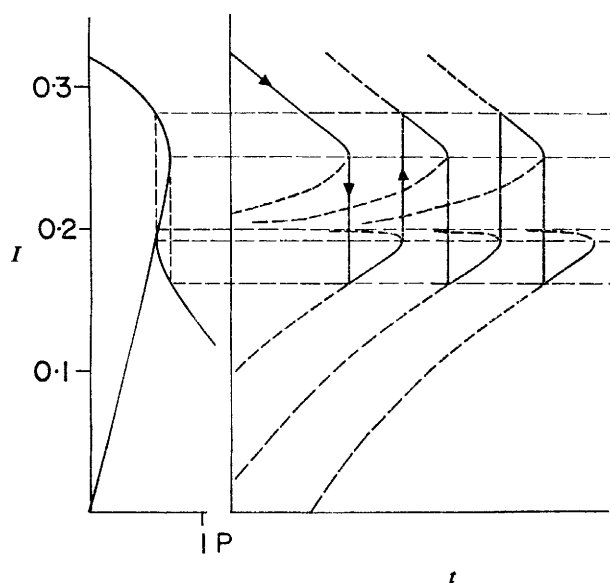
FIG. 6.—Periodic solution of the mathematical model constructed from the integral curves in fig. 5 and the I/P curve in fig. 4.

determined by the help of the I/P curve and a periodic solution can be constructed graphically as shown in fig. 6.

The graphical method yielded a particular set of the parameters for which the model will oscillate and an approximate solution for this set of parameters. The general condition for oscillation can be deduced from the particular example. The condition is that the parameters, which are always positive, should be adjusted so that the equation

$$dP/dI = -3R^2I^2 + 4ERI - E^2 - R - 1 = 0, \qquad (17)$$

has two positive roots I' and I'' ($I' < I''$). In addition, eqn. (14) which can be written as

$$R^2I^3 - 2ERI^2 + (E^2 + R + k_2/k_3 + 1)I + E = 0, \qquad (18)$$

must have one positive root I''' such that $I' < I''' < I''$. The left-hand sides of (17) and (18) are found respectively in the denominator and the numerator of (16).
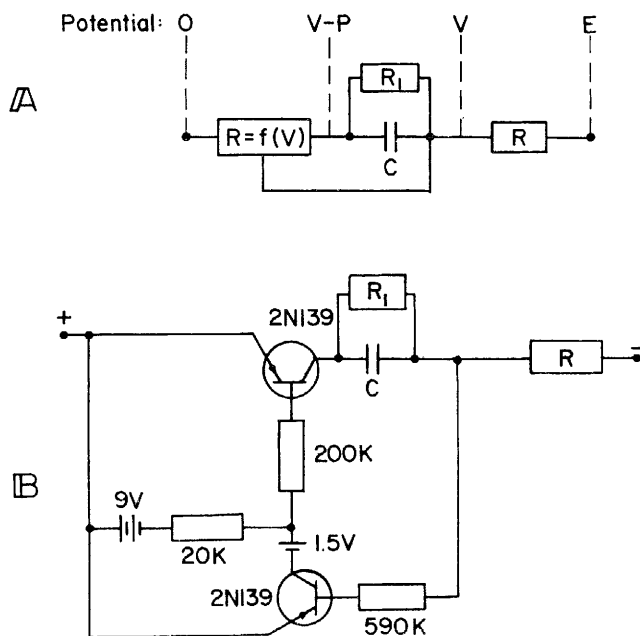

FIG. 7.—A: schematic analogue circuit of passivable electrode; B: realization of the circuit in A.

There appears to be no reason to work out these formal conditions in detail. The graphical method is considerably easier. Some information can, however, be derived from the above conditions. Since $dP/dI = 0$ must have two positive roots the polynomial approximation expressing the decrease of current with increasing potential must, at least, be quadratic. If a function containing only a first power of V is used instead of (10), dP/dI becomes linear and has only one root.

When the oscillatory solution of the mathematical model is compared with the experimental oscillations, the model predicts the four distinct phases which are found in a period of a real electrochemical current oscillation.

ELECTRIC ANALOGUE CIRCUIT

The assumptions expressed in the form of functions in the mathematical model can also be expressed in the form of function generators in an analogue circuit.

Fig. 7a shows such a circuit. The passivation is simulated by a function generator which acts as an ohmic resistance with respect to the voltage $(V-P)$ across it and the magnitude of this resistance increases according to a nonlinear curve $(R = f(V))$ with increasing V. The function generator simulating passivity must have three terminals since a channel which can convey the potential V to the function generator is needed. This information channel is the lower wire in the diagram which is supposed to carry a negligible current. The concentration polarization is simulated by the charging of a condenser, and the spontaneous degradation of the concentration polarization is effected by a resistance parallel to the condenser. Finally, the external resistance is simulated by an ohmic resistance.

The current in the analogue circuit is given by

$$I = P/R_1 + C\,\mathrm{d}P/\mathrm{d}t, \tag{19}$$

$$I = (V-P)/f(V), \tag{20}$$

$$E = V - RI. \tag{21}$$

These equations are identical with (9), (11), and (12) which constitute the mathematical model.

A function generator which simulates passivity can be built from two transistors. The circuit shown in fig. 7b approximates the above assumptions. By proper adjustment of R, R_1 and E, the circuit produces oscillations of a waveform indistinguishable
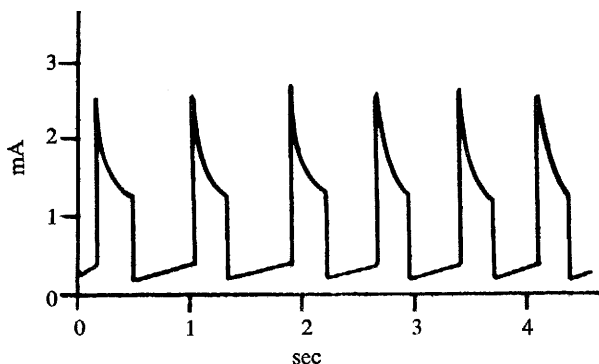

FIG. 8.—Oscillations of current at constant external potential of the circuit in fig. 7B. E, 8·2 V; R, 2·7 Kohm; R_1, 3·4 Kohm; C, 25 μF.

from electrochemical oscillations (fig. 8). The frequency of the oscillation decreases with increasing external potential, which is in accordance with experimental observations.[2] A discussion of oscillator circuits of the class to which the above analogue circuit belongs is given by Minorsky.[15]

DISCUSSION

We first gave a qualitative description of the usual waveform of current oscillations at constant external potential. The four phases in which a period was divided can now be ascribed to different processes.

Phase 1 is an increase of the current occurring when the electrode changes from the passive to the active state. In the model this increase is discontinuous. In the real electrode it must be a time-dependent process. However, the increase of current is so rapid compared to the overall time-scale of the oscillation that it is recorded as a vertical line. The assumption that the passivation process reaches equilibrium instantaneously is thus a good approximation in the case of phase 1. Phase 2 is a decrease of the current due to concentration polarization.

Phase 3 is a decrease of the current occurring when the electrode changes from the active to the passive state. In the experimental oscillations, phase 3 is sometimes recorded as a vertical line (fig. 1*b*) but in other cases it is not so rapid. It is concluded that the assumption of instantaneous passivation is a good approximation in some cases but in others the time dependence of the passivation process should be taken into account.

For phase 4 the model predicts an increase of the current due to decreasing concentration polarization. In the experimental oscillations the current increases during phase 4 in some cases (fig. 1*c*) but in others it decreases (fig. 1*a* and 1*d*). This discrepancy probably exists because the real passivation process is not instantaneous as assumed in the model. If the passivation is still in progress in phase 4 the current will be decreasing. However, the concentration polarization will still be decreasing as in the model and the passive state will eventually become unstable.

In his theoretical study of oscillating chemical reactions, Bonhoeffer [16] pointed out that oscillations can only be expected in systems which are described by at least two independent differential equations of the form

$$dx/dt = f(x, y),$$
$$dy/dt = g(x, y). \qquad (22)$$

However, the present model yielded only one first-order differential equation. This apparent discrepancy is due to the assumption that the equilibrium in the passivation process is instantaneous. If the time dependence of the passivation process were introduced the mathematical model would yield two differential equations of the form (22), which would have periodic solutions.

The present theory may also be applicable to the oscillation of voltage across an artificial lipid membrane separating two aqueous phases.[17] The membranes which show oscillatory electrokinetic behaviour have a range of negative slope in their current/potential curve.[18] Whether the other component of the present theory, concentration polarization, plays any role in the membrane systems is not yet known. The same mathematical model can also be used to account for the oscillations in the respiration of continuous cultures of *Klebsiella Aerogenes* reported by Harrison and Pirt.[19]

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