Electrochemical oscillators: their description through a mathematical model

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Abstract

A simple mathematical formalism is considered for the description of spontaneous oscillations in electrochemical systems. Emphasis is on the modelling of "cathodic" oscillators, i.e. those that involve a metal ion reduction which displays a potential-dependent catalysis or inhibition, resulting in a negative (differential) impedance. The model appears to be able to reproduce many of the essential features of the experimental oscillators. Some of the model's most severe approximations and assumptions are discussed and their possible improvements indicated.

INTRODUCTION

Spontaneous oscillations of current or potential have been observed in a wide variety of electrochemical systems [1]. Although there seems to be extensive experimental evidence, mathematical models that are both simple and physically reasonable as well as pertaining to some distinct and well-studied experimental system are still rare. Among them, the Franck and FitzHugh model [2] for spontaneous oscillations in the anodic dissolution of iron in sulphuric acid has become the classic reference. In this paper we hope to contribute to the current state of knowledge of electrochemical oscillators through the development of a simple mathematical model, which is especially intended to serve as a description of the indium/thiocyanate oscillator, studied in the preceding paper [3].

The conditions for an electrochemical system to bear the possibility of spontaneous oscillations can be divided into electrical and chemical conditions. Evidently, these two are related when referring to the impedance of a faradaic process. The most general condition is that of the existence of a (differential) negative impedance in the (equivalent) circuit, and it follows immediately from the Glansdorff–Prigogine stability criterion [4].
Somewhat more specific but still completely general statements can be derived from an analysis of the circuit of Fig. 1, which depicts an equivalent cell circuit containing the essential elements. The faradaic impedance \( Z_F \) in Fig. 1 should not be confused with a series connection of a charge transfer and Warburg impedance, as they have their usual meaning only when \( E \) is a sinusoidally oscillating function with a small amplitude. Rather, it is intended here only to indicate the two pathways of the electric current through the electrode/electrolyte interface. Clearly, any stationary state is characterized by \( E = \text{constant} \). If, in such a case, a small perturbation of potential produces an extra current which charges the double layer faster than \( R_s \) discharges it (thus if \( 1/|Z_F| < 1/R_s \)), and if this current flows in the "wrong" direction (\( Z_F < 0 \)), the stationary state becomes unstable. Thus, the instability conditions are given by:

\[
Z_F < 0 \quad |Z_F| < R_s
\]

This shows that a small enough external resistance will always stabilize the circuit. Although eqn. (1) may almost seem a trivial result, it is surprising to note that it has not been formulated in this way before, since in our opinion it is the only general statement that can be made of an electrochemical oscillator in terms of "equivalent" impedances. The second condition which \( R_s \) must obey is that it should not be too large to be able to create a potential drop which can oscillate exactly out of phase with \( E \), for the total state of the experiment is still potentiostatic.
A comment may be in order on two earlier theoretical investigations on the In/SCN oscillator that have appeared in the literature. In principle, the model that we will consider in the following may be regarded as both a simplification and an extension of the Keizer–Scherson model [5]. In our opinion, their model suffers from some shortcomings and we will address them whenever our derivation requires that. De Levie's investigation [6] was restricted entirely to the electrical properties of an electrochemical oscillator circuit which does not seem to yield much more information than our simpler approach above does. Furthermore, tackling the problem in this way seems to become quite hopeless (as de Levie frankly admits) when one actually tries to calculate current oscillation profiles.

THE MODEL SKELETON

Consider the circuit of Fig. 1. Conservation of current requires that

\[ i = A(j_c + j_F) \]  

(2)

where \( i \) is the current, \( j \) the current density and \( A \) the working electrode area. This can also be written as (after a rearrangement)

\[ \frac{dE}{dt} = \frac{V - E}{R_A C_d} - \frac{j_F}{C_d} \]  

(3)

Keizer and Scherson [5] take into account certain effects of a double-layer relaxation in eqn. (3) that we will not include. We are not convinced that it is necessary to account for such an effect (which is known to occur only at > 10 MHz in concentrated solutions [7]) in a qualitative model in which far more unreasonable assumptions like that of a linear diffusion layer of constant thickness and a potential-independent double-layer capacity are still present (as they are also in Keizer and Scherson's model).

For the time dependence of the surface concentration \( c_0 \) of the electroactive species, we will assume that it can be estimated from the simplified picture that the concentration gradient near the electrode can always be regarded as linear and the resulting diffusion layer, of constant thickness \( \delta \) [2]. From Fig. 2 it follows that the shaded area can be equated to the difference between the amount of matter that diffuses towards the electrode surface and the amount that reacts at the electrode surface:

\[ \frac{1}{2}(c_0(t + dt) - c_0(t))\delta = \frac{D(c_{\text{bulk}} - c_0)}{\delta} dt - k_F c_0(t) dt \]  

(4)

which is equivalent to the differential equation

\[ \frac{dc_0(t)}{dt} = -\frac{2k_F c_0(t)}{\delta} + \frac{2D}{\delta^2}(c_{\text{bulk}} - c_0(t)) \]  

(5)
Equations (3) and (5) will serve as the skeleton of the models that we will concentrate on in the next sections, where the exact mechanism of the kinetic process taking place at the electrode is expressed in the heterogeneous reduction rate constant $k_f$. Note that we have tacitly assumed that the complete double-layer structure can be ascribed to the inert electrolyte.

For mathematical convenience, we will non-dimensionalize eqns. (3) and (5). Introducing the dimensionless quantities

$$v = \frac{(F/RT)V}{e = (F/RT)E} \quad x = \frac{c_0}{c_{\text{bulk}}}$$

and rewriting the reaction constant $k_f$ as $k_f = \frac{1}{2}kk'$, in which $k$ represents the dimensionless, but variable (potential-dependent) part and the dimension (cm s$^{-1}$) is incorporated in the non-variable part $k'$, and next non-dimensionalizing time according to

$$t = \left(\frac{k' t}{\delta}\right)$$
(t denoting dimensionless time from now on), we obtain two dimensionless differential equations:

\[
\frac{de}{dt} = \frac{v - e}{r} - cx
\]

\[
\frac{dx}{dt} = -kx + d(1 - x)
\]

in which

\[ r = AC_d k'R_s/\delta \]

(dimensionless external resistance)

\[ c = nF^2c_{\text{bulk}} \delta k/2RTC_d \]

\[ d = 2D/\delta k' \]

The dimensionless current can be calculated from \( i = (v - e)/r \) (provided that \( A = \text{constant} \)).

A MODEL FOR THE In/SCN OSCILLATOR

Simplified (unrealistic?) model yielding analytical expressions

We now turn to a more specific formulation of the model for the In\(^{3+}\)/SCN\(^-\) oscillator. We will assume that the catalysis by SCN\(^-\) of the In(III) reduction at mercury conforms to the mechanism proposed by Pospisil and de Levie [8]:

\[
\text{In}^{3+} + 2 \text{SCN}_{\text{ads}} \quad \xrightarrow{\text{slow}} \quad \text{In(SCN)}^+_{2,\text{ads}}
\]

\[
\text{In(SCN)}^+_{2,\text{ads}} + 3 e^- \quad \xrightarrow{\text{fast}} \quad \text{In}^0 + 2 \text{SCN}_{\text{ads}}
\]

Following de Levie, we assume the first, chemical, step to be rate-determining in the overall process, which means that its rate is dictated by the potential-dependent value of the surface activity of the SCN\(^-\) ions. Consequently, we do not agree with the Butler–Volmer type expression that is assumed by Keizer and Scherson for the faradaic current. Apart from that, their model derived in this way leads (as they state) to the necessity of an (independent) adjustment of the transfer coefficients to obtain oscillations. This gives the impression of being a physically rather unreasonable condition. Consequently, we equate the change in the indium(III) surface concentration \( c_0 \) to

\[
\frac{dc_0}{dt} = -k_1 c_0 [\text{SCN}_{\text{ads}}^-]^2 = -k_1 c_0 \theta^2
\]

where

\[ \theta = [\text{SCN}_{\text{ads}}^-]/[\text{SCN}_{\text{ads}}^-]_{\text{max}} \]
and

\[ k_f = k_1 [SCN_{ads}]_{\text{max}} \]

Combining this with eqn. (6) leads to the following model equations:

\[
\begin{align*}
\frac{d\theta}{dt} &= \frac{v - e}{r} - cx\theta^2 \\
\frac{dx}{dt} &= -kx\theta^2 + d(1 - x)
\end{align*}
\]

(9)

\( \theta \) representing the relative surface activity of the thiocyanate.

(Based on the following not unreasonable values for several quantities: \( F = 96485 \) C/mol, \( \delta = 1 \times 10^{-2} \) cm, \( c_{\text{bulk}} = 1 \times 10^{-6} \) mol cm\(^{-3} \) \( k = 0.1, \ k' = 0.2 \) cm/s, \( R = 8.31 \) J K\(^{-1} \) mol\(^{-1} \), \( T = 300 \) K, \( A = 3 \times 10^{-2} \) cm\(^2\), \( D = 1 \times 10^{-5} \) cm\(^2\) s\(^{-1} \), \( C_d = 40 \) \( \mu \)F cm\(^{-2} \), one can obtain estimations for the model parameters: \( v \approx 35-45, r \approx 0.5-5, c \approx 10-15, d \approx 0.01-0.03. \)

Owing to specific adsorption and coulombic repulsion, the function \( \theta(E) \) varies between 1 at more positive potentials and 0 at far negative potentials. We will first consider the simplistic functional form suggested by Keizer and Scherson (Fig. 3):

\[
\theta = \begin{cases} 
1 & e \leq e_d \\
0 & e > e_d 
\end{cases}
\]

(10)

The "transition potential" \( e_d \) is not equal to zero as a result of the specific adsorption. Equation (10) also assumes that \( \theta \) always immediately adjusts to \( e \) and that its transition at \( e_d \) is infinitely fast.

Fig. 3. The relative surface activity \( \theta \) (of thiocyanate) described as a discontinuous function of the electrode potential \( e \).
We will refer to the $\theta = 1$ state as the "active" or "catalysed" state and the $\theta = 0$ state as the "passive" or "uncatalysed" one. Now for both the passive and the active state inhomogeneous linear differential equations result from eqn. (9):

passive: \[ \frac{\text{d}e}{\text{d}t} = \frac{v - e}{r} \quad \frac{\text{d}x}{\text{d}t} = d(1 - x) \]

active: \[ \frac{\text{d}e}{\text{d}t} = \frac{v - e}{r} - cx \quad \frac{\text{d}x}{\text{d}t} = -kx + d(1 - x) \]

the solutions of which read

passive: \[ x(t) = 1 - A_3 \exp(-dt) \]
\[ e(t) = v - A_4 \exp(-t/r) \]

active: \[ x(t) = \frac{d}{d + k} + A_1 \exp((-k - d)t) \]
\[ e(t) = v - \frac{rcd}{k + d} - \frac{cA_1}{-k - d + 1/r} \exp((-k - d)t) \]
\[ + A_2 \exp(-t/r) \]

where $A_1$, $A_2$, $A_3$ and $A_4$ are constants determined by the initial conditions.

From this it can be easily seen that a repetitive transition from passive to active and back again to passive can never take place if $e_d$ is regarded as a constant. This is the reason why Keizer and Scherson were forced to adopt a dependence of $e_d$ on $c_0 (x)$ to obtain oscillations. They tried to give this dependence some plausibility by noticing its equivalence to the pH dependence of the Flade potential, a dependence which Franck and FitzHugh [2] showed to be crucial for the occurrence of oscillations in anodic "corrosion" systems. The logarithmic dependence that Keizer and Scherson assume seems a bit unfortunate however, since it suggests some kind of thermodynamic relationship, which is only evident for the Flade potential. So here we will just suppose a linear relationship of the kind

\[ e_d = e_1 + e_2 x \]

We will need a physical justification of eqn. (16) other than some equivalence to a relationship of a completely different nature. One might think of some kind of co-adsorption effect, but this is not a very satisfying concept, since the $\text{In}^{3+}$ and SCN$^-$ concentrations near the electrode differ by almost five orders of magnitude. More acceptable is an $x$-independent hysteresis effect (not expressible by eqn. 16), i.e. $e_d$ different for adsorption and desorption (Fig. 4), for example as the result of some time-delayed nucleation and growth process or slow diffusion. This, however, introduces an internal inconsistency in our model because we assumed earlier by eqn. (10) the infinitely fast adjustment of $\theta$ to $e$. Therefore, the results of this section should be judged mainly on their "pedagogical" properties and on their ability to describe, after some reformulation perhaps and restoring eqn. (16)'s logarithmic functionality, anodic "corrosion" oscillators in a simplistic but lucid way.
The two-valued relative surface activity $\theta$ with different values for $e_{ads}$ (adsorption) and $e_{des}$ (desorption), as the result of, for instance, some hysteresis phenomenon, can cause oscillatory behaviour in the simplistically formulated model eqns. (9) and (10).

That a model consisting of eqns. (9), (10) and (16) can lead to oscillations can be illustrated most easily by means of phase plane analysis. We will divide the $e-x$ phase plane into two regions, passive ($\theta = 0$) and active ($\theta = 1$), bounded by eqn. (16). Stationary states will be given by the intersections of the nullclines of eqn. (11), which read

$$e = v \quad x = 1$$

passive:  
$$e = v - rcx \quad x = d/(k + d)$$

active: 
(17)

Both can be identified as stable nodes (see Appendix), provided they fall within the matching areas of the phase plane. Now four situations can be distinguished:

(a) there is only an intersection in the passive region (Fig. 5a);
(b) there is only an intersection in the active region (Fig. 5b);
(c) there are intersections in both regions (bistability, Fig. 5c); and
(d) there are no intersections (Fig. 5d).

The latter gives rise to limit-cycle oscillations. Obviously, situation (a) occurs if

$$v > e_1 + e_2$$  \hspace{1cm} (18)

for every value of $r$. Situation (b) occurs if

$$v < e_1 + \frac{de_2}{d+k} + \frac{rcd}{d+k}$$  \hspace{1cm} (19)

this means for relatively large $r$. Situation (c) occurs whenever both (18) and (19) are satisfied, and situation (d) whenever neither of them is satisfied. All this gives rise to the stability diagram of Fig. 6. Computed oscillation profiles for $x$, $e$ and $i$ for
distinct values of the model parameters are depicted in Fig. 7. They simply result from combining eqns. (12)–(15).

Although the model developed in this section has the charming property of being largely calculable in an analytical fashion, yielding oscillation profiles in fairly good agreement with the experimental ones (especially those of corrosion oscillators [2]), it still suffers from many shortcomings. The dependences of the amplitude and frequency on the potential and external resistance deviate somewhat from experiment [3], as do several properties of Fig. 6. Apart from these phenomenological reflections, from a fundamental point of view it seems a serious drawback (at least in the case of cathodic oscillators) that the model forces us to assume a variable transition potential $e_d$ without any reasonable physical background. In the next section we will see that fortunately this can be considered an artefact caused by a too simplistically formulated model.

_A more realistic formulation of the model_

Two improvements can be introduced that will contribute to the realistic character of our model. First we will assume, parallel to the pathway (7), that an
Fig. 6. Stability diagram of eqns. (11) (or eqns. 9 and 10) indicating the various parts of the $v-r$ parameter plane where the four situations of Fig. 5 occur (are stable).

Fig. 7. Computed oscillation profiles for $x$, $e$ and $i$ for model eqns (9) and (10) with parameter values $c = 12$, $d = 0.02$, $k = 0.1$, $e_d = 35 + 10x$, $v = 42$ and $r = 2$. 
additional process occurs at the electrode, being the “normal” uncatalysed irreversible reduction of indium(III). We will assume its dependence on the electrode potential \( e \) to be exponential. This leads to the new model equations

\[
\frac{de}{dt} = \frac{v - e}{r} - c_1 x \theta^2 - c_2 x \exp(n \alpha(e - e^\circ))
\]

and

\[
\frac{dx}{dt} = -k_1 x \theta^2 - k_2 x \exp(n \alpha(e - e^\circ)) + d(1 - x)
\]

\( e^\circ \) representing the (dimensionless) standard potential. In the following, we have equated \( n \alpha \) to 0.5. The influence of the back reaction is neglected on account of the reaction's irreversibility. Of course, \( k_2 \ll k_1 \).

The second improvement is the more important one and deals with the functionality of \( \theta(e) \). A more realistic dependence of \( \theta \) on \( e \) than the one assumed in eqn. (10) and Fig. 3 is shown in Fig. 8. Any numeric trial approximation to Fig. 8 will do, and we have chosen a kind of “Gaussian” shape expressed by

\[
\theta = \begin{cases} 
1 & e \leq e_d \\
\exp\left(-b(e - e_d)^2\right) & e > e_d 
\end{cases}
\]

We could just as well have chosen a function of the kind \( \theta(e) = 1/[1 + \exp(b(e - e_d))] \), for instance. The parameter \( b \) will determine the curve's steepness.

We have now obtained a formulation of the model in which it appears no longer to be necessary to assume a variable \( e_d \). Some typical limit-cycle oscillation profiles which can be computed by means of simple Runge–Kutta numerical integration techniques [9] are shown in Fig. 9. They are in reasonable agreement with those
Fig. 9. Computed oscillation profiles for $i$ for model eqns. (20) and (21) with parameter values $c_1 = 12$, $c_2 = 0.48$, $k_1 = 0.1$, $k_2 = 0.004$, $d = 0.02$, $e^o = 34$, $e_d = 35$, $b = 0.5$ and (from top to bottom): $u = 37/r = 0.5$, $u = 38/r = 1.1$, $u = 38/r = 1.3$.

Fig. 10. Stability diagram of eqns (20) and (21) with parameter values as in Fig. 9.
observed in experiment, as are the amplitude/frequency characteristics. A stability diagram is depicted in Fig. 10.

It is interesting to examine the model's bifurcation behaviour in somewhat more detail. Figure 11 shows four bifurcation diagrams, either as $i$ vs. $v$ or as $i$ vs. $r$ plots. These diagrams should be compared with Figs. 3 and 4 of our preceding paper [3], where the distance from the lower to the upper branch of the oscillatory regimes in Fig. 11 can be interpreted as the amplitude of oscillation, which is depicted in the experimental relationships of Figs 3 and 4 of ref. 3. In Fig. 11a ($r = 0.4$), the stationary state is globally stable for all $v$, so this diagram can be considered a polarogram under small external resistance conditions. At $r = 0.5$ (Fig. 11b, cf. Fig. 3 of ref. 3) we observe a supercritical Hopf bifurcation followed by a subcritical one, whereas at $r = 1.0$ (Fig. 11c) the former has turned into a subcritical Hopf and the latter into a SNIPER bifurcation. With $r$ serving as the bifurcation parameter first a SNIPER bifurcation (low $r$) and then a subcritical Hopf (higher $r$) are perceived (Fig. 11d, cf. Fig. 4 of ref. 3). In experiment, however, structures other than those mentioned are also present. In the In/SCN oscillator, as well as in many other electrochemical oscillators (see ref. 3 and refs. 14 and 17–20 cited therein), more complex bifurcation structures (mixed-mode oscillations, chaotic oscillations, probably caused by a homoclinic tangency to a saddle focus fixed point present in the system) take their place. These can be described mathematically only by at least

![Fig. 11. Bifurcation diagrams for model eqns. (20) and (21). (a) $r = 0.4$; (b) $r = 0.5$; (c) $r = 1.0$; (d) $v = 38$. (All other parameter values as in Fig. 9.)](image-url)
three autonomous differential equations. We hope that an extension of the present 
two-dimensional model may in the future be capable of reproducing this behaviour.

It should be noted that the properties of the model equations treated above are 
not very critically dependent on the assumed kinetic mechanism as long as the 
"apparent heterogeneous reduction rate constant" decreases sufficiently strongly 
with the negative-going electrode potential in some potential interval. In fact, 
detailed knowledge of the underlying molecular mechanism is redundant in our 
approach, and serves only to make the model chemically more appealing. All that 
we actually need is the rate constant's functionality on the electrode potential 
(which can partly be obtained from the dc polarogram, for instance). This function-
ality should then show the "wrong" potential dependence leading to the 
necessary negative impedance. The Pospisil–de Levie mechanism (where the ap-
parent rate constant equals $k_r \theta^2$) contains this property in both a chemically and a 
mathematically tractable way. Clearly, the qualitative features of the model will also 
not change much with the number of thiocyanate molecules involved in the slow 
rate-determining step of the mechanism (eqns. 7).

**Oscillations at a dropping mercury electrode**

For a mathematical description of the oscillations at a DME we have to replace 
the equality

$$i_c = AC_d \frac{dE}{dt}$$

(22)

that was used in eqn. (3) by the more general expression

$$i_c = \sigma(E) \frac{dA}{dt} + AC_d \frac{dE}{dt}$$

(23)

where $\sigma(E)$ is the electrode charge density. For a DME at constant flow rate of the 
mercury, the drop's surface area will conform to

$$A = A't^{2/3}$$

(24)

As we are still assuming a potential-independent double-layer capacity, eqn. (23) 
can be written as

$$i_c = \frac{2}{3}C_d EA't^{-1/3} + A'C_dt^{2/3} \frac{dE}{dt}$$

(25)

So for a DME eqn. (3) takes the form

$$\frac{dE}{dt} = \frac{V - E}{A'R_cC_d t^{2/3}} - \frac{j_F}{C_d} - \frac{\frac{2}{3}E}{t}$$

(26)

where we have assumed that the external resistance will dominate the ohmic cell 
resistance during every moment of the experiment. The dimensionless form of eqn.
Fig. 12. Computed oscillation profiles for a dropping mercury electrode for model eqns. (20) and (21) with “DME adjustment” eqn. (27). The rate of mercury flow was chosen in such a way that \( r'/t^{2/3} = r \) at \( t = 500 \). (a) \( v = 37, \ r = 0.5 \); (b) \( v = 38, \ r = 1.1 \). (All other parameter values as in Fig. 9.)

(26) will read

\[
\frac{de}{dt} = \frac{v - e}{r't^{2/3}} - cx - \frac{3e}{t}
\]

in which \( r' = A'C_d(k'/\delta)^{1/3}R_\delta \).

Some typical “chronoamperometric” relations that can be obtained in this formulation are shown in Fig. 12 for the more realistic version of the model. The oscillations exhibit the experimentally observed time, or rather drop size, dependence, but fail to reproduce the characteristic decreasing current amplitude, however [6]. This failure probably finds its origin in the growing drop and its effect on the diffusion layer thickness \( \delta \).
A MODEL FOR THE "INHIBITOR OSCILLATOR"

The formalism treated above can also be employed to formulate a model for what may be called the "inhibitor oscillator". This type of oscillator concerns the potential-dependent inhibition of some metal-ion reduction by an organic surface-active agent. A classic example is the copper(II) reduction inhibited by tribenzylamine [10]. All these oscillators show the characteristic negative impedance in their current–voltage relationships [11,12].

When we suppose the faradaic current to be proportional to the free, unoccupied area of the mercury electrode, and the rate of the reduction to conform to an exponential dependence on the electrode potential, this will lead to the following equations:

\[
\begin{align*}
\frac{dv}{dt} &= \frac{v - e}{r} - cx(1 - \theta) \exp(na(e - e^o)) \\
\frac{dx}{dt} &= -kx(1 - \theta) \exp(na(e - e^o)) + d(1 - x)
\end{align*}
\]

\[\text{(28)}\]

in which \( \theta = \frac{[\text{inh}_{\text{ads}}]}{[\text{inh}_{\text{ads}}]_{\text{max}}} \). We have neglected the back-reaction rate, the potential range of interest again being remote from the standard potential.

The relative occupancy \( \theta \) will meet a potential dependence of the general form depicted in Fig. 13. Again this phenomenology can be expressed by, for instance, a "Gaussian" fit function:

\[
\theta = \begin{cases} 
\theta_{\text{max}} & e \geq e_d \\
\theta_{\text{max}} \exp\left(-b(e - e_d)^2\right) & e < e_d
\end{cases}
\]

\[\text{(29)}\]

By choosing \( \theta_{\text{max}} \) to be unequal to 1 (0.95, for instance), we can take into account the fact that even at "maximum" coverage there will still be some faradaic current.

![Fig. 13. Relative occupancy \( \theta \) of the inhibitor given as a function of the electrode potential \( e \).](image)
Fig. 14. Computed oscillation profile for $i$ for model eqns. (28) and (29) with parameter values $c = 0.12$, $k = 0.1$, $d = 0.02$, $e^o = 15$, $e_d = 20$, $b = 0.5$, $v = 21$ and $r = 0.8$.

flowing (as can be seen from the polarograms [11]). A typical oscillation profile that can be obtained from eqns. (28) and (29) is given in Fig. 14.

DISCUSSION

It has been our purpose to show with the model presented above that it is possible to obtain limit-cycle oscillations on the basis of some simple mathematically expressed phenomenology pertaining to the oscillatory systems studied. When one is willing to simplify the picture to an extreme, it is even possible to obtain analytical expressions for the oscillation profiles, provided that an additional condition of a variable transition potential is assumed (eqn. 16). This may not be a very acceptable concept for cathodic oscillators, but it is the more so for corrosion oscillators. A striking merit of the model is its ability to show that, with a simple extension, it is not at all necessary to construct a dependence like that of eqn. (16) to obtain oscillations. In this way, we consider this model to be a substantial improvement on the Keizer–Scherson model, in which such an unsatisfying "ansatz" was assumed to be inevitable.

Our model is the result of some quite serious simplifications, and therefore next we wish to pay some attention to their validity. We will focus on three assumptions in particular:

1. the absence of relaxation in the adsorption of the catalyst or the inhibitor;
2. the potential independence of the double-layer capacity; and
3. the concept of the "at all times" linear diffusion layer of constant thickness.

The assumed time independence of $\theta$ may be quite reasonable in the case of the In/SCN oscillator, considering the very high thiocyanate concentration. For the inhibitor oscillator this seems far less plausible. It is probable that a kind of nucleation and growth process will cause a certain relaxative effect of $\theta$ on $e$, ...
eventually maybe even leading to hysteresis. In a previous section we have seen how hysteresis can play a role in producing oscillatory behaviour, and the possibility that this is indeed of importance in the inhibitor oscillator should not be overlooked. We have seen, however, that for the model it is not necessary to assume such an effect. Generally, any allowance for a time dependence of $\theta$ will lead to a third differential equation, which should account for the nucleation and growth of the surface layer and perhaps also for (slow) diffusion of the adsorbing species (in the case of very low concentrations).

A potential dependence of the double-layer capacity can easily be implemented. Assuming that the contribution of the Gouy–Chapman diffuse layer can be neglected because of the very high electrolyte concentration, we are left with a dependence of the Stern part of the double-layer capacity on the potential, in particular through the occupancy $\theta$. The well-known definition of the differential double-layer capacity will read as follows for the $C_d$ dependence on $\theta$:

$$C_d = \left( \frac{\partial \sigma}{\partial E} \right)_\theta + \left( \frac{\partial \sigma}{\partial \theta} \right)_E \left( \frac{d \theta}{d E} \right)$$

(30)

with $\sigma$ representing the charge density on the electrode. Expressing this dependence by using the Frumkin model, which supposes that

$$\sigma = \sigma_{\theta=0}(1 - \theta) + \sigma_{\theta=1}\theta$$

(31)

the double-layer capacity becomes

$$C_d = C_{d,\theta=0}(1 - \theta) + C_{d,\theta=1}\theta + (C_{d,\theta=1} - C_{d,\theta=0})E \frac{d \theta}{d E}$$

(32)

where we have assumed that $C_d$ depends only on $\theta$ and on $E$ merely via $\theta$. We have to be aware that the last term in eqn. (32) should always be positive in the case of the adsorption of neutral organic substances [7]. Since we have treated the normal sign convention somewhat inattentively in the preceding sections (for we are considering a cathodic process in reality), we have to make sure that the model formulation is brought into accordance with this restriction. Bearing this in mind, we obtain a “new” potential relaxation equation:

$$\left( \frac{d e}{d t} \right)_{\text{corrected}} = \frac{1}{D(\theta, e)} \left( \frac{d e}{d t} \right)_{\text{uncorrected}}$$

(33)

with

$$D(\theta, e) = 1 - \left( 1 - \frac{C_{d,\theta=1}}{C_{d,\theta=0}} \right) \left( \theta + e \frac{d \theta}{d e} \right)$$

(34)

The term $d\theta/de$ can be obtained from differentiating eqn. (21) or eqn. (29) with respect to $e$ and should be preceded by a minus sign in the case of the inhibitor oscillator.

All this may seem a bit punctilious or even redundant for the qualitative picture that we are aiming at so far. It is nevertheless encouraging to see that the model appears to be able to “survive” this correction. It will become an especially severe
Fig. 15. Computed oscillation profile for $i$ for model eqns. (28) and (29) with "differential double-layer" adjustment eqns. (33) and (34). $v = 21$, $r = 0.65$, $C_d(\theta = 1)/C_d(\theta = 0) = 0.1$. (All other parameter values as in Fig. 14.)

test for the inhibitor oscillator, where the ratio $C_{d,\theta=1}/C_{d,\theta=0}$ may be expected to have a value of roughly 0.1 [10]. Figure 15 shows a computed oscillation profile for the inhibitor oscillator with the "corrected" eqn. (33) incorporated in the model.

The most serious and doubtful assumption of the three that we have mentioned is that of the linear diffusion layer of constant thickness, as it is incorporated in the model through eqn. (5). This approximation is equivalent to

$$
\left( \frac{dc}{dx} \right)_{x=0} = \frac{c_{\text{bulk}} - c_{x=0}}{\delta}
$$

$x$ being the spatial coordinate here, and where $\delta$, the diffusion layer thickness, is supposed to be a constant. This can also be conceived by stating that no phase angle enters in the relation between $(dc/dx)_{x=0}$ and $c_{x=0}$. Clearly, in oscillatory electrode kinetics $\delta$ will most probably also be an oscillatory function of time. The circumstance in which we expect eqn. (5) to be especially lacking in correspondence with reality is that of (temporal) "passive" or "uncatalysed" electrode kinetics. Diffusion relaxative effects could make the initial slope of the concentration gradient near the electrode particularly small in that case, giving extremely large values for $\delta$.

The diffusion layer thickness $\delta$ used in eqn. (5) should thus be conceived as an average diffusion layer thickness. That such an average, eventually time-independent and stable diffusion layer thickness should exist for a HMDE follows from the Cottrell equation for the case of semi-infinite spherical diffusion. Consequently, from a mathematical point of view, our model does not permit stable oscillations at a planar electrode on account of the time dependence of the diffusion layer thickness for linear diffusion (neglecting, of course, the influence of natural convection).

Obviously, any realistic improvement of our model would have to incorporate Fick's second law together with the usual boundary conditions for the faradaic
current. However, it will be hard to lift such an attempt above the black-box level, and, consequently, the attractive mathematical simplicity of the model will be hopelessly lost.

SUMMARY

In this paper we have considered a simple mathematical model for an electrochemical oscillator and have discussed its merits and demerits to some extent. One of its merits is that in principle it is very easy to take into account additional processes that may be important in oscillatory electrode kinetics. As we have pointed out, however, the most desirable improvement of the model — a more sophisticated treatment of the diffusion problem — will involve considerably more computational effort and will detract from the mathematical transparency of the present model.

We wish to mention one extension of the model in particular which concerns the not yet existing mathematical model equations that are able to (re)produce chaotic electrochemical oscillations, as they have been observed in several (corrosion) experiments recently [13,14] (see also ref. 3 and refs. 14 and 17–20 cited therein). This necessitates at least one additional differential equation. In that context it would be particularly interesting to see what happens to the steady state to oscillatory state transition of the two-variable model, since experiments show that near these points an intriguing structure of dynamic behaviour appears on the scene [3,14].

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APPENDIX

This appendix will deal with some elementary nomenclature from the theory of non-linear differential equations, in order to make our articles more self-contained and to serve readers who are unfamiliar with these concepts. Attention is paid only to those concepts from stability and bifurcation theory that were used in this and in the preceding paper [3]. The treatise is necessarily brief and (too) simplified, so for more detailed and better accounts on the subject the reader is referred to recent textbooks. A very readable qualitative introduction (with some additional emphasis on numerical aspects) can be found in ref. 15. A mathematically more sophisticated treatment is given in ref. 16. Furthermore we would like to point out a nice appendix on the subject by Odell [17]. For more technical-mathematical details see ref. 18. The classical review by Wojtowicz [1] also contains a discussion on some of the aspects of the mathematics of non-linear oscillators.

Consider a set of two coupled differential equations (de’s):

\[
\frac{dX}{dt} = f_X(X, Y) \\
\frac{dY}{dt} = f_Y(X, Y)
\]  

(A1)
These de's are called *autonomous* whenever the right-hand side does not depend explicitly on the time $t$. The stationary states (fixed points) of eqns. (A1) are given by setting $f_x$ and $f_y$ equal to zero. Such stationary states can either be *stable* or *unstable*; i.e. they are reached asymptotically if time goes to infinity or if time goes to minus infinity, respectively. It is often convenient to study (A1)'s dynamic behaviour in a graphical representation called the $X$, $Y$ phase plane, which depicts the $X$, $Y$ trajectories parameterized by the time $t$. Three classes of stationary states can then be distinguished (spirals (foci), nodes and saddles [1]), together with another type of generic behaviour in a set of two de's: the limit-cycle. This is a closed trajectory in the phase plane which, when it is stable, attracts all neighbouring trajectories. $X$ and $Y$ are then oscillatory functions in time. It is an important result from the famous Poincaré–Bendixson theorem that these four types of singular behaviour are the only ones to be expected in a set of two de's describing dissipative motion (chemical reactions are always dissipative). More exotic kinds of behaviour (quasi-periodicity, period-doubling, deterministic chaos) can be encountered only in a set of three or more (non-linear) autonomous de's.

Usually (A1) will contain some kind of parameter $\mu$, which is not a variable of the system like $X$ and $Y$, but can be chosen since it represents, for instance, an experimentally adjustable quantity, like a potential, a flow rate, etc. Generally $\mu$ can be considered to represent some kind of effective force working on the system. The study of the solutions of (A1) for different values of $\mu$ is called bifurcation analysis. The specific value of $\mu$ where some kind of behaviour loses stability (and usually another gains stability) is called a bifurcation point. A kind of bifurcation point that is of most interest is the so-called Hopf bifurcation. This involves the transition of a stationary state called a spiral point (as the name suggests the trajectories reach this point in a rotational manner) into a limit-cycle (the spiral point becoming unstable;
the arrows accompanying the spiralling trajectories reverse direction). A graph showing the dependence of some scalar measure of $X$ or $Y$ on $\mu$ is called a bifurcation diagram. Usually, in a system displaying stationary and oscillatory states, one depicts the extrema of $X$ or $Y$ as a function of $\mu$. The two types of Hopf bifurcation (HB) are shown in Fig. A1 by means of their bifurcation diagram. They are called \textit{supercritical} and \textit{subcritical}. Note that the supercritical HB involves a "soft loss" of stability (i.e. starts with a zero oscillation amplitude), whereas the subcritical HB displays a "hard loss" (starts with a finite oscillation amplitude). The latter also shows a characteristic \textit{bistability} region (hysteresis).

Two other common mechanisms by which a stable limit-cycle can appear or disappear are the saddle-loop bifurcation, at which the separatrix of a saddle point is closed, and the saddle node infinite period (SNIPER) bifurcation, at the exact value of which the limit-cycle coalesces with a saddle-node point. Both are characterized by a so-called homoclinic connection to the fixed point and by an oscillation period going to infinity at the bifurcation value.

\textbf{REFERENCES}