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REACTIONS AND PERIODIC OCCURRENCES AT A PLATINUM
ANODE IN ALKALI SULPHIDE SOLUTIONS

H. Gerischer, Z. Elektrochem., 54 (1950) 540

Translated from German

by

K. Bartels*

FOREWORD
(by translator)

This translation was made to assist our own work in the study of the double-layer properties of sulphide minerals as applied to the beneficiation of sulphide ores; it was felt that it might be of interest to other Canadian workers in the field.

ABSTRACT

A platinum electrode, anodically polarized in a Na_2S solution, can take on adsorbents in three different regions of potential. In the lowest region, some type of polysulphide is formed and then sulphur is precipitated. In the next region, the main product, besides polysulphide and sulphate, is thiosulphate. In the uppermost region, sulphate is practically the only product. The existence of the upper potential regions is explained by the formation of a layer of oxygen on the electrode. With this formation, the periodic phenomena, which can be shown to be of three different types, can be derived from a basic concept. The periodic reaction mechanism is thoroughly discussed.

*Technologist, Physical Chemistry Group, Mineral Sciences Division,
Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

I. INTRODUCTION

Within the framework of investigating periodic reactions, and acting on a suggestion by Prof. Bonhoeffer, I have occupied myself with the so-called "phenomena of the reversible sulphur electrode", discovered by Küster(1). The questions here are the phenomena appearing on a platinum anode; periodic potential changes occur during deposition and dissolution of a distinctly visible layer of sulphur. It was already realized by Bohnholtzer and Heinrich(2) that the interpretation of the periodicity given by Küster was insufficient. The aim of this investigation was to explain the reaction mechanism leading to this periodic phenomenon.

II. EXPERIMENTAL ARRANGEMENT

Two groups of experiments were conducted. In the first arrangement, schematically reproduced in Figure 1, changes in current strength and electrode potential were observed by means of an oscilloscope. In this configuration, the recording of current-potential curves was also conducted, and a remelted platinum wire was used for these experiments. In the cases in which the electrode was to be observed microscopically, a round platinum disc was used, having the platinum exposed on one side only. The cathode was many times larger and consisted of a platinum cylinder arranged concentrically around the anode. The electrolyte was stirred so that it flowed in a linear fashion along the platinum wire. The potential measurements were made against a normal mercury-oxide electrode situated directly beside the anode. The electrolytes were Na_2S solutions of between 0.8 and 2.0 molarity. These were made by bubbling H_2S into NaOH solutions and then adding the equivalent

amount of NaOH to the resulting NaHS(3).

A second arrangement served for the analysis of the reaction products during electrolysis. These experiments were performed in a U-shaped vessel, in which separate anode and cathode compartments were formed by the use of a glass wool plug. The anode cell was filled with a known volume of Na_2S solution; the cathode cell was filled with NaOH solution. The current flow was measured with a coulometer; potentials were measured in the same fashion as in the first configuration. After electrolysis, the whole solution was poured into a flask and analysed.

III. CURRENT POTENTIAL CURVES

Bohnholtzer and Heinrich(2) had already obtained current-potential curves. However, if one plots the values of the current and potential that are obtained during the final equilibrium, one loses essential features of this system. One finds, for example, that the potential passes through a number of regions, after one initially turns on the current, before the potential finally reached equilibrium. Furthermore, with large variations in current strengths, completely different stationary potentials are reached at equilibrium, according as to whether one increases the current to its upper value gradually or whether one allows it to build up rapidly.

Thus, areas shaded in the i - P diagram (Figure 2) are those through which the system passes. In this case, "passing through" means that these are the areas in which the potential varies relatively slowly or attains distinct stationary values, whereas, in the hatched areas, only discrete transitions are allowed. As shown in Figure 2, one can distinctly define three different areas which must correspond to three special states of the electrode. The individual areas are marked as a, b, and c.

The stationary values for the current-potential curves that finally appear after a long time are shown in Figure 2 as heavy lines. The curves shown here are only examples. Their position is essentially dependent on the rate of stirring, the Na_2S concentration, the polysulphide content, and other factors that are very difficult to observe and whose individual effects are difficult to judge. However, the position of the potential regions is only minimally dependent on the size of these factors.

IV. ELECTROLYTIC PRODUCTS

When investigating the reaction products, it was considered especially important that the electrode remained at approximately the same potential while passing current through it; in every case it was at least ensured that it remained within an individual potential region. For this reason, it was always necessary to continually adjust the current intensity immediately after turning on the current. In this respect, my attempts are essentially different from similar measurements made by Fetzer(4), and by Bohnholtzer and Heinrich. This also explains the differing results.

The following analyses were made:

- 1) sulphide ions (5);
- 2) polysulphide sulphur (6);
- 3) thiosulphate (6); and
- 4) sulphate as BaSO_4 .

Fetzer, as well as Bohnholtzter and Heinrich analyzed for dithionate as well. Because they always found very low quantities of dithionate, I omitted this analysis. One can estimate the amount of dithionate formed, from the unreacted quantities, from the amount of reduced sulphide, and from the total current passed.

The results are compiled in Table 1. The results given have been converted to the percentage of current used. One should not place too much significance on the values because the analytical errors multiply during the conversion of current equivalents, especially with the oxygen-rich ions. However, the general trend is easily recognizable.

The Table is accordingly divided into three potential regions a, b, and c. In region a, practically only the polysulphide is formed and, in region c, practically only the sulphate. Region b, however, is interesting in that, with increasing potential, the formation of polysulphide obviously decreases, whereas the formation of sulphate increases; the main product is thiosulphate. In regions b and c, the unreacted remaining components would indicate $S_2O_6^{--}$ formation.

The appearance of $S_2O_3^{--}$ opposes the findings of Fetzer and those of Bohnholtzer and Heinrich. However, this discrepancy could be explained by the fact that these authors probably worked only in the regions a and c.

V. REACTIONS IN THE VARIOUS POTENTIAL REGIONS

One can develop a scheme of the expected reactions within each potential field by considering the results given in Sections III and IV. These are listed in Table 2. The respective end products are underlined.

An estimate of the normal potentials for the results of the potential-determining reactions; outlined in Column 2, in comparison with the values of Randall(7) for the free energies of these reactions, confirms this interpretation, at least in view of the sequence of the expected potentials.

TABLE 1

Electrolytic Reaction Products at Various Potentials

P (Volt)	i (mA)	Polysulphide	S ₂ O ₃ ⁻⁻	SO ₄ ⁻⁻	Remainder	Potential Region
0.13-0.19	~15	101%	--	--	+1%	a
0.16-0.26	~15	100%	--	--	±0%	
0.23-0.40	~30	102%	--	--	+2%	
0.55-0.60	~60	96%	3%	--	-1%	
1.27-1.33	~22	33%	36%	18%	-7%	b
1.24-1.38	~15	28%	47%	20%	-5%	
1.34-1.41	~20	47%	30%	15%	-8%	
1.41	24-36	33%	42%	19%	-6%	
1.41-1.60	37-45	30%	37%	26%	-9%	
1.50-1.63	29-47	34%	35%	30%	-1%	
1.55-1.62	~60	28%	30%	38%	-4%	
1.66-1.73	~30	16%	35%	42%	-7%	
1.65-1.85	~56	26%	22%	52%	±0%	
1.90-2.22	~113	0.8%	3%	92%	-4%	c
2.02-2.18	~225	4%	11%	83%	-2%	
2.18-2.40	~225	0.9%	0%	97%	-2%	

TABLE 2

Potential Region	Potential-Determined Reactions	Successive Reactions
a	$S_x^{--} \rightarrow \underline{xS} + 2e^-$	$S_x^{--} + S \rightarrow \underline{S_{x+1}^{--}}$
b	$S^{--} + 6.OH^- \rightarrow SO_3^{--} + 3H_2O + 6e^-$ $S_x^{--} + 6.OH^- \rightarrow \underline{S_2O_3^{--}} + 3H_2O + (x-2)S + 6e^-$	$2 SO_3^{--} \rightarrow \underline{S_2O_6^{--}}$ $SO_3^{--} + S \rightarrow \underline{S_2O_3^{--}}$ $2 S_2O_3^{--} \rightarrow S_4O_6^{--} + 2e^-$ $4.S_4O_6^{--} + 6.OH^- \rightarrow 5.S_2O_6^{--} + 2.S_3O_6^{--} + 3H_2O$ $S_3O_6^{--} + 2.OH^- \rightarrow \underline{S_2O_3^{--}} + \underline{SO_4^{--}} + H_2O$
c	$SO_3^{--} + 2.OH^- \rightarrow \underline{SO_4^{--}} + H_2O + 2e^-$ $S_2O_3^{--} + 2.OH^- \rightarrow \underline{SO_4^{--}} + H_2O + S + 2e^-$	—

VI. CONDITIONS FOR THE EXISTENCE OF THE VARIOUS ELECTRODE STATES

Interpretation of electrode processes has as yet not explained the existence of the various potential regions. The regions a, b, and c do not occur sequentially with increasing current densities but, instead, co-exist at common current densities. One thus cannot explain the transitions by the superseding of marginal current values for the various electrode processes. Instead, chemical changes of the electrode must effect such variable behaviour at similar current densities.

Küster assumed that the visible deposited layer of sulphur on the electrode was the reason for the occurrence of high electrode potentials. (From now on, the electrode will be considered as passive in the potential regions a and c and as active in the normal condition.)

However, the formation of the sulphur layer on the electrode explains **only the transition into the passive state**, whereas the electrode can be completely freed from sulphur after that and yet remain passive.

The passivation apparently proceeds in the following fashion. Sulphide ions are discharged at the electrode. The elemental sulphur thus formed could either be picked up by other sulphide ions or, if the precipitation rate is greater than the rate of dissolution, would precipitate on the electrode. This is to be expected after a certain current density is reached. The precipitated sulphur now acts as an insulator (dielectric) on the parts of the electrode covered by it. The effective current density must, however, keep increasing on the ever-decreasing available amount of uncovered electrode surface at a given constant potential. This will cause the electrode to reach potentials at which new electrode processes can commence.

First, OH^- discharge comes into play, by which oxidation reactions

are initiated that form the aforementioned reaction products in the passive phase.

Observations have already shown that, after the ensuing passivation, the layer of sulphur proceeds to dissolve again. The supposition of Bohnholtzer and Heinrich that an invisible colloidal layer of sulphur remains on the electrode is untenable, if one considers the diffusion and dissolution conditions at that time. If the electrode, nevertheless, remains passive, some other chemical condition dictating this passive state must be in force.

The only possibility that remains is the formation of an oxygen layer on the platinum, the formation of which is initiated by the discharge of OH^- and which now inhibits the discharging of sulphide ions.

The conditions allowing deposition of oxygen on the platinum are immaterial. Possibly involved here is a thin oxide layer, whose surface is covered by an adsorbed layer of oxygen. The important point is that the reactivity for the discharge reactions on the covered areas is strongly reduced. This, of course, can be assumed without further ado in the case of an oxygen layer.

The development of oxygen does not occur in the passive phase, because, after the formation of the O-layer, the OH^- ions arriving at the electrode to be discharged are used up in oxidizing the simultaneously discharging sulphide ions in the resulting high electrode potential.

On the other hand, the layer remains intact so long as as much oxygen is supplied to the electrode as is lost. Only when the oxygen supplied to the electrode becomes less than the losses of the layer, can the passivating oxygen layer disappear. During the lowering of applied potential, as is brought about by a reduction of the applied current, the OH^- discharge rate and, with it, the rate of O-supply is correspondingly reduced. The fact thus

remains that, with sufficient reduction in current, one can eliminate the passive state of the electrode.

Similarly, electrolyte variations at the electrode must also affect the rate of O-supply and thus influence the boundary of the passive state.

That the oxygen is responsible for the passive state of the electrode is further supported by two other observations.

1. Bubbles of oxygen were often observed on edges or cracks in the electrode in the passive phase; these detached themselves when the current was turned off.

2. On an electrode which was partly platinized, O₂ formation took place while the other shiny parts of the electrode remained passive.

The essential argument, however, that explains the periodic behaviour of the electrode, is the assumption that such periodicity is the result of an oxygen layer forming on the electrode. This will be shown in the next sections.

The passivating action of oxygen on platinum is well known. Thalinger and Vollmer(8) have shown this on a platinum-oxygen electrode. From oscillographic observations of potentials in the transition from anodic to cathodic polarization, Bowden(9) and Butler(10) concluded that there existed a surface layer of oxygen. Ershler(11) developed concepts of the passivation of platinum through an oxygen layer. Tödt(12) and co-workers also showed that oxygen is adsorbed on platinum. The formation of platinum oxides during anodic oxidation has already been known for a long time (eg., Altmann and Busch(13)). Finally, several authors assume O-coverage of the electrode surface to explain the oxygen over-voltage.

VII. PERIODIC PROCESSES

Under certain conditions, the passing of current through the anode does not result in the stationary state but, instead, in continuous periodic transitions between the various potential regions. One can relate the occurring periods to three types, shown in Figure 3. The individual types occur only within particular regions of current density. Type Ia generally undergoes a transition to Type Ib with increasing current density. Periods of Type II occur only in special areas at higher current densities.

VIII. REACTION MECHANISMS OF THE PERIODICITY

The active phase and the transition into the passive state have already been discussed in Section VI. The key to understanding the periodicity, however, lies in the reactions of the passive phase. It is now assumed that the passive phase is characterized by the existence of an oxygen layer. The formation conditions of such an O-layer must, therefore, be investigated.

In view of Figure 4, we want to compare the rate of formation of the O-layer on an electrode at constant current conditions with its dependence on the electrode potential. First of all, the upper part of the dot-dash line in Figure 4 shows the portion of the OH^- discharge with respect to current passed. The OH^- -discharge starts at a potential P_0 and increases steadily with increasing P . The S^{--} discharge reduces correspondingly.

One suspects that, with potentials above P_0 , the O_2 produced is at first not energetic enough to oxidize sulphide ions simultaneously; therefore, it will be adsorbed on the platinum, and the rate of OH^- discharge should correspond to the rate of O^{--} formation.

Only after a certain potential is reached, is it possible for the oxygen to oxidize the sulphide ions to sulphur. Now, a growing portion of the discharging oxygen, increasing with P , is used up in oxidation reactions. SO_3^{--} and $\text{S}_2\text{O}_3^{--}$ are now formed at the electrode. This results in a simultaneous reduction in the amount of oxygen available for the formation of the oxygen layer. The upper dashed line in Figure 4, which is supposed to show the rate of oxygen formation, turns away from the OH^- discharge curve and continues to fall with an increase in P . At even higher values of P , practically all the discharging sulphide ions are oxidized. From then on, the rate of O-formation reactions must again rise with an increase in OH^- discharge, until a new, oxygen-depleting electrode process is possible. At high electrode potentials, one expects the electrochemical oxidation of SO_3^{--} and $\text{S}_2\text{O}_3^{--}$ to SO_4^{--} to occur. With the initiation of these processes, the rate of oxygen formation must again fall, until these reactions, too, are proceeding at their maximum rate.

Of course, the oxygen layer also suffers losses. One has to assume, among other things, that the adsorbed oxygen can also react directly in a chemical fashion with sulphide ions or that molecular oxygen will form, which will be lost by diffusion. In the lower dashed line, the rate of the dissolution reactions within a large potential region has been assumed to be constant for simplicity's sake and is given a random value. For potentials below P_0 , reduction of the oxygen layer by local currents must occur and the rate of the dissolution reactions must increase correspondingly; with high potentials, O_2 evolution starts and leads to a rapid increase in O-losses.

If one combines the formation and dissolution reactions just discussed, the solid line in Figure 4 results. It shows the formation rate of the O-layer as a function of P . Because of the qualitative nature of the derivation, only the nature of the curve is substantiated and is characterized

by its two maxima and its one minimum.

For interpreting this diagram, it is essential that the rate of O-formation and the electrode potential are not large independently from each other. For stationary conditions, one can assume that, with an increase in the amount of coverage, the potential will also rise. Because of the growing thickness of the oxide layer over a period of time, one cannot expect a direct relationship between the potential and the amount deposited anymore, but one can still expect a relative connection in the aforementioned sense. The total, bound amount of oxygen stays small in any case, because of the certainty of a limited build-up of the oxide layer. For this reason, even small changes in the rate of O-formation can effect large changes of O-deposition and, by this effect, finally bring about large, very rapid changes in potential.

Therefore, only potentials can be maintained at the electrode, for which the O-deposition practically remains constant; i.e., the rate of formation of O is zero.

The curve in Figure 4, which assumes to show the rate of O-formation, cuts the abscissa in four places, G_1 to G_4 . The oxygen deposition is in equilibrium only at these points. It is easily shown that, of these four equilibrium conditions, only two are stable.

Let us assume the electrode to be in state G_1 or G_3 . Now, if the potential is raised a little, then the rate of O-formation becomes positive. The O-deposition will now grow and, following this, the potential will increase again. Reducing the potential will effect exactly the reverse. The electrode thus moves from equilibrium at an increasing rate with a small change in potential. These equilibria are thus unstable.

On the other hand, the equilibria in conditions G_2 and G_4 , try to re-establish themselves when imbalanced by a small change in potential as is

shown by an analogy similar to the one above. From this, one can conclude that stable equilibrium states occur only in those regions in which the curve O-formation rate versus P is decreasing.

The type of curve shown in Figure 4 has two decreasing regions. Accordingly, the electrode can become stationary only at potentials that belong to these regions. The experimental fact that the electrode can assume two stationary states in the passive condition is explained by the dropping rate of O-formation in these two regions.

In order to understand the periodicity, it is also necessary to discuss temporal changes in the passive phase and, especially, to explain how the passive state disappears.

In deriving the curve for the rate of O-production in Figure 4, (in future called the O-curve), the level of the curve was chosen purely at random. The height of the curve is dependent on several factors.

S-coverage reduces the losses of the layer. The rate of O-supply depends only on P and is, therefore, only minimally affected. The O-curve will therefore shift downwards with a reduction in the S-coverage.

Either an increase in the concentration of sulphide ions or a decrease in the OH^- concentration reduces the portion of OH^- discharge with respect to current **passed**. The first also increases the O-usage for the oxidation reactions. For this reason, the oxygen formation will be reduced through a change in this concentration in the direction mentioned, i.e., the O-curve shift downward.

Finally, the current strength is the main determining factor in fixing the position of the curve. With increasing current strength, the OH^- discharge and, with it, the rate of formation must rise considerably, especially at high potentials. The O-curve is thus raised, and increasingly so with increasing P.

During electrolysis at constant current, the deposited layer of sulphur on the active phase of the electrode, dissolves after passivation. Likewise, as one can readily see, the sulphide ion concentration increases at the electrode in the course of the formation of the passive phase and the OH^- concentration diminishes (during the course of passivation). Because of all these reactions and according to the aforementioned, a lowering of the O-curve occurs.

After the curve has dropped to such an extent that the second maximum lies below the abscissa, an equilibrium for the oxygen deposition no longer occurs in the potential region c. The electrode must, therefore, cross over to the stable equilibrium of the region b. If the O-curve drops even further, so that the first maximum also falls below the abscissa, the possibility for maintaining a layer of oxygen on the electrode disappears altogether. The oxide layer already present disappears rapidly, and the electrode returns to the active state. Thus, one can discuss the process of the periodic behaviour of the electrode by considering shifts in the O-curve which are brought about by changes at the electrode. O-deposition and the establishment of equilibrium with respect to P, occur more quickly than a shift in the position of the O-curve. The potential thus practically always follows the point of intersection of the O-curve with the abscissa, apart from the step-like transitions. From the displacement of the O-curve with increasing current strength, one can easily derive the abovementioned three period types as shown in the following section.

IX. DERIVATION OF THE THREE-PERIOD TYPES

The three types of periodicity are to be schematically developed and presented here. We will make the simple assumption that the shape of the O-curve is fixed by the current density and that its level is dependent only on the parameter s , upon whose increase the curve will move upwards in a parallel fashion. The significance of this term will be specially explained.

Furthermore, we will assume that the change in s with time will not only be dependent on the current density but on the potential and that it will take on the following relationship:

$$P < P_k: \frac{ds}{dt} > 0$$

$$P > P_k: \frac{ds}{dt} < 0$$

P_k corresponds to the potential at which the derivative of s changes sign.

This value of P_k moves to higher potentials with an increase in current density.

Figures 5, 6, and 7 show the periodic behaviour, between the potential and the rate of O-formation, with respect to the parameter s . The arrowed curves show the corresponding respective directions of periodicity. The thick arrows show the horizontal part of the change of potential with time; in other words, a slow rate of change; the dashed-arrow curves show the potential jumps which occur very rapidly.

The differential changes of P and s are also shown on these figures.

Type Ia

This type occurs when P_k becomes larger than P_0 , but, at the moment of passivation, the O-curve is so flat that its minimum is still under its abscissa. This is the case only at low current densities.

The parameter, s , essentially denotes the sulphur coverage of the electrode. Below P_k , sulphur is deposited: above P_k , the deposited layer dissolves again. At the same time, the S^{2-} and OH^- concentration at the electrode is described by s .

The formation and dissolution times for the sulphur layer determine the duration of the active and passive phases. This explains the longer duration of these phases.

Type Ib

With an increase in current density, the minimum of the O -curve for the s -value, shifts above the abscissa the moment the electrode is passive. The O -formation reaches equilibrium only in the potential region c. When the second maximum of the O -curve falls below the abscissa, ($s=s_m$), the potential jumps into the region b; when the first maximum falls under the abscissa ($s=s_\mu$), activation is achieved.

Periodic behaviour stops when P_k moves into the potential region b under the influence of increasing current density. This condition then becomes stationary.

The significance of the parameter, s , and the duration of the individual phases, is the same as that of the type Ia.

Type II

With a further increase in current density, the critical potential, P_k moves past the region b into the areas of increasing O -curves between b and c. Now, new periodic behaviour sets in, in which the potential oscillates between the regions b and c, and the parameter, s , oscillates between S_μ and s_m , as is shown in Figure 7.

Type Ia

Time-Dependent Behaviour of s and P

Phase	s	P
Switch on	$S_o \rightarrow S_k$	a
↓		
→ Passivation	S_k	a → b
↓		
passive	$S_k \rightarrow S_u$	b
↓		
Activation	S_u	b → a
↓		
→ active	$S_u \rightarrow S_k$	a

Type Ib

Time-Dependent Behaviour of s and P

Phase	s	P
Switch on	$S_o \rightarrow S_k$	a
↓		
→ Passivation	S_k	a → c
↓		
passive c	$S_k \rightarrow S_m$	c
↓		
Transition to b	S_m	c → b
↓		
passive b	$S_m \rightarrow S_u$	b
↓		
Activation	S_u	b → a
↓		
→ active	$S_u \rightarrow S_k$	a

Type II

Time-Dependent Behaviour of s and P

Phase	s	P
Switch on	$S_o \rightarrow S_k$	a
↓		
Passivation	S_k	a → c
↓		
passive c	$S_k \rightarrow S_m$	c
↓		
Transition to b	S_m	c → b
↓		
passive b	$S_m \rightarrow S_\ell$	b
↓		
Transition to c	S_ℓ	b → c
↓		
passive c	$S_\ell \rightarrow S_m$	c

The periodic interval is bounded, at the upper limit, by the current density at which P_k is again in the area of falling O-curves in the potential region c. The electrode will become stationary at this potential.

A layer of sulphur does not develop during this periodic behaviour. The parameter, s, will now be determined by the S^{--} and OH^- concentration. This explains the high frequency of the periodicity*.

*It is interesting that periods which were very much like those of Type II were observed also on the same electrode in a 1M Na_2SO_3 -solution. From this, one can conclude that the transition of $S_2O_4^{--}$ to $S_nO_6^{--}$ (where n could be 3 or 4) formation occurs on an O-layer as well and that these periods can be interpreted in the same way.

X. COMPARISON WITH OTHER PERIODIC REACTIONS

The method of the aforementioned investigations is based on analytical methods for simultaneously coupled reactions developed by Bonhoeffer. From these, one obtained a qualitative understanding of periodicity. The kinetics of the investigated reactions point to a surprising similarity with an anodic periodic behaviour in a completely different system (Cu in HCl), investigated by Bonhoeffer and the author.

In both cases, the deposition of a non-conducting substance caused very high resistive polarization of the electrode to occur, by which the formation of an electrically conducting but potential-determining (passivating) oxidizing layer was made possible. The oxide layer can be rebuilt only after considerable dissolution of the protective insulating layer which, in both cases, occurs very rapidly under the effect of local current. This type of periodicity is easily reproduced and apparently found in many instances.

With the Periodicity discussed heretofore, Type II, the role of the resistive polarization is replaced by a concentration polarization. The conditions for periodicity are very definite concentration changes, in other words, conditions of a very different nature. This, then, also explains the relatively poor reproducibility of this periodic behaviour. One suspects that many periodic phenomena of high frequency, which one often observes during electrolysis, are explained by this type.

In all cases discussed here, the decisive factor for the occurrence of periodic behaviour is the formation of a potential-determining oxide layer on the electrode. The general inclination of metals to form such oxide layers points to a close relationship between the often-occurring periodic behaviour during electrolysis and such oxide layer formation.

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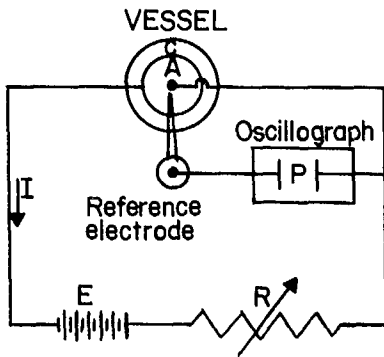


Figure 1. Circuitry (A = Anode, C = Cathode).

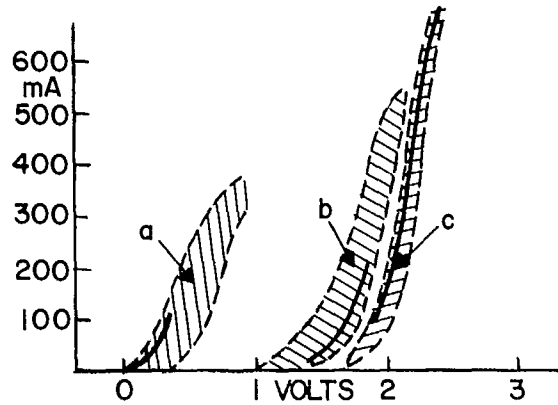


Figure 2. Electrode Potential Regions and Stationary Current-Potential Curves.

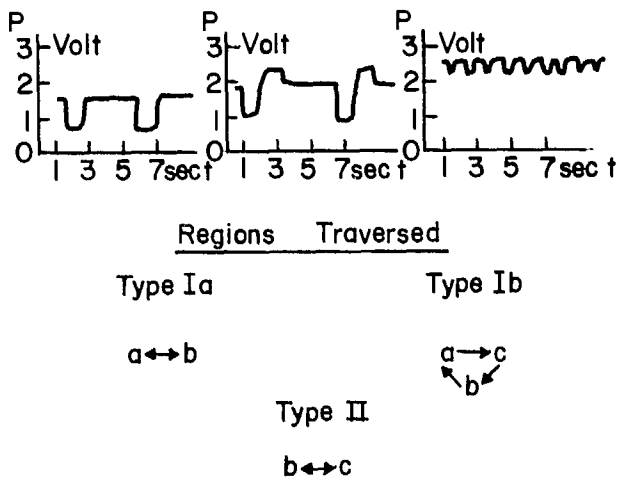


Figure 3. Comparison of the Three Period Types.

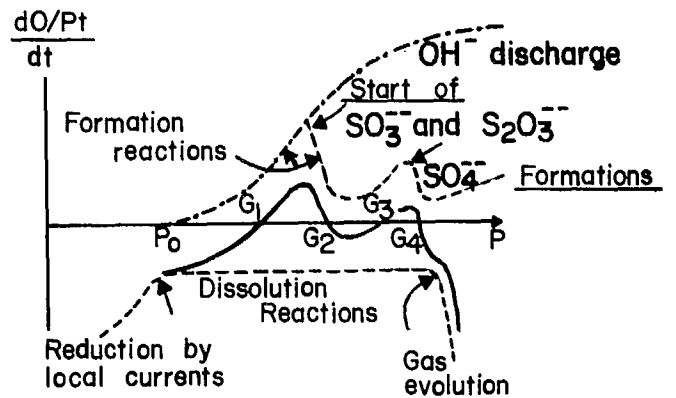


Figure 4. Growth Rate of the O-Layer as a Function of Potential.

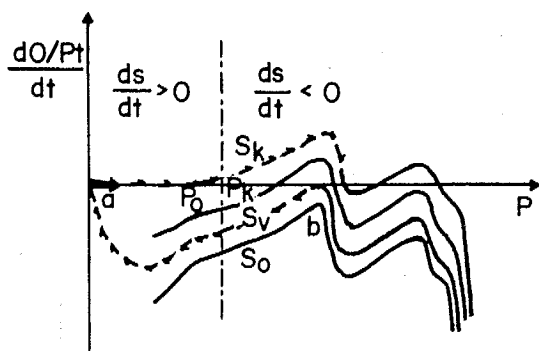


Fig. 5

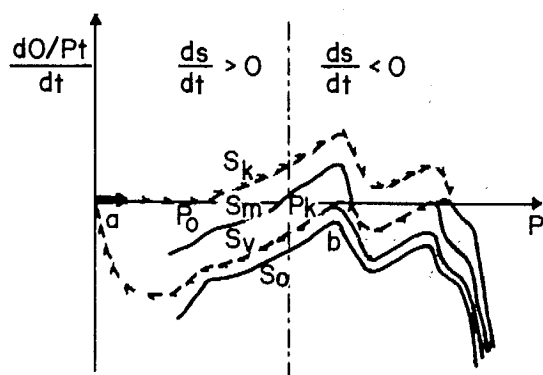


Fig. 6

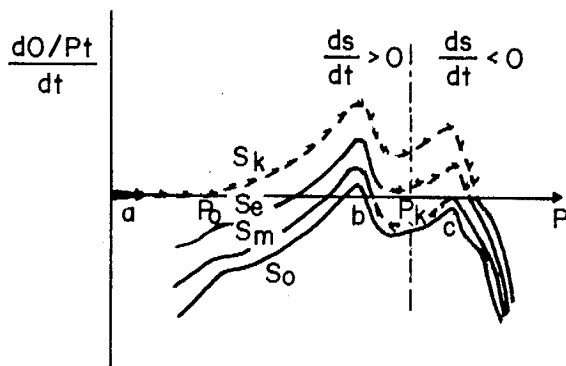


Fig. 7

Figure 5, 6, 7. Period Types Shown with Reference to Rate to O-Layer. Formation as a Function of Potential and the Parameter the Arrows Successive Periodic Reactions.