REVIEW AND INTERPRETATION OF RECENT EXPERIMENTS WHICH EXTEND AND ELUCIDATE THE DOMAIN OF THE PASSIVITY OF METALS.

(Translated from the German.)

Dr. G. Reichinstein (Zürich), who was prevented by indisposition from attending the meeting, communicated a "Review and Interpretation of Recent Experiments which Extend and Elucidate the Domain of the Passivity of Metals."

1. *Historical*.—Faraday* ascribes the discovery of the passivity to Keir,† who observed in 1790 that iron was not attacked in strong nitric acid, but assumed a "changed" state.

The problem was, however, investigated only in the thirties of the last century by Faraday and by Schönbein; the latter introduced the term "passivity." The difference of opinion between the two originators of the problem is of high historical interest. Faraday's views as to the nature of passivity were interpreted by Schönbein‡ to the effect as if Faraday saw the cause of the passive behaviour of a metal in the formation of a well-developed oxide on the metallic surface, and Faraday is still frequently being called the originator of the oxide theory of passivity. In my opinion Faraday may with equal right be regarded as the originator both of the oxide theory and of the most modern theories of gas charges and metal-oxygen alloys; and in this sense I regard the theory which I am going to present merely as a logical consequence of the views of Faraday.

In support of this statement I quote the beginning of a letter which Faraday addressed to R. Taylor§ on January 21, 1837: "DEAR SIR,—I am much obliged to you for a sight of Mr. Schoenbein's paper, the experiments and observations in which are excellent. The cause of the phænomena he has so well distinguished is indeed exceedingly difficult to be distinguished at present, and I was in hopes that the doubt on my mind when I ventured the view referred to would be evident from my words. My strong impression is," etc. (*Phil. Mag.*, vol. ix., p. 61, 1836). "Moreover, Mr. Schoenbein and also M. Alb. Mousson, in an attempt which he has made to explain the cause (*Bibliothèque Universelle de Genève*, 1836, p. 165), have not given my view clearly. I have said that my impression is that the surface of the metal is oxidized, or else that the superficial particles of the metal are in such relation to the oxygen of the electrolyte as to be equivalent to an oxidation, meaning by that, not an actual oxidation, but a relation. . . ."

Faraday further alludes to the researches of Nobili on the colours of thin plates, and he expresses the view that the latter went much further still in the opinion that skins of oxygen and acid may lastingly adhere to the surfaces of

* Faraday, Letter to Brayley, July 8, 1836, *Lond. and Edinb. Phil. Mag.*, 1836, vol. ix., p. 122.

† Keir, *Phil. Trans.*, 1790, pp. 374 and 379.

‡ Schönbein, *Pogg. Ann.*, 37, p. 390; 38, p. 444; 39, p. 342.

§ *Phil. Mag.*, vol. x., p. 175, 1837.

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platinum, iron, and steel without entering into chemical combination with the metal.

The above quoted letter by Faraday to Taylor further contains, near its end, the following words: "And my opinion of the cause of the phenomena as due to a relation of the superficial particles of the iron to oxygen. . . ."

From these views of Faraday has arisen the oxide theory of passivity which has been advocated up to the most recent days.*

The theory which I am going to develop is further connected with the views of M. Le Blanc,† who first expressed the idea that it is velocity phenomena which condition passivity. This assumption has successfully been developed and specialized by Fredenhagen,‡ who makes the occurrence of passivity dependent upon "a coherent, uniform gas charge"; finally Muthmann and Fraunberger§ have recognized that this gas charge has the character of an alloy.

The question now, which I put to myself, and which is not discussed by any of the actual theories, is how the transition is taking place from the active state of a metal into the passive state. This question is to receive an answer which can quantitatively be tested by calculations.

Before we pass to the discussion of this question, however, we have to acquaint ourselves with a series of experiments of the very latest dates, some of which have extended the domain of passive phenomena, while others are able to introduce us into the labyrinth of passivity.

2. *Chemical Polarization of Reversible Active Metallic Electrodes.*—Before the year 1910 all the metals were distinguished as active and passive, and if there was a tendency to look for the cause of passivity in slowly progressing chemical reactions, *i.e.*, in a slow rate of ion-formation, people held on the other side that with active metals anodically treated the formation of ions took place with infinite velocity, and that any polarization observed with active metals had to be designated a concentration polarization or a diffusion polarization, that is to say, a polarization which arose owing to the differences in the concentration of the electrolyte caused by the current flow, whilst diffusion tended to balance this difference in concentration.

I should like to emphasize in this place already that these definitions of chemical or of concentration polarization are inappropriate, and that they fail in complicated cases. For the occurrence of concentration differences is not characteristic for the diffusion polarization. With one and the same electrode different polarizations are observed, always as results of different concentrations of the substances in question. The point is rather, which process is opposing the differences in concentrations to which the electric current gives rise, *i.e.*, whether this compensation is of a chemical nature or a diffusion phenomenon. Hence it would, in my opinion, be appropriate to introduce a definition like the following: If in any observed polarization the substitution of a real process by an imaginary *chemical* process, proceeding at infinite velocity, would make the polarization vanish, we should have to deal with a *chemical polarization*; if a *diffusion* proceeding at infinite rate should have the same effect, we should have to deal with a *diffusion polarization*.

Now Le Blanc|| described in 1910 some experiments which have revolu-

* *E.g.*, by F. Haber and F. Goldschmidt, *Zschr. Elektrochem.*, **12**, p. 49, 1906.

† M. Le Blanc, *Zschr. Elektrochem.*, **6**, p. 476, 1900.

‡ Fredenhagen, *Zschr. Elektrochem.*, **11**, p. 857, and *loc. cit.*

§ Muthmann and Fraunberger, *Sitzber. Bayer. Akad. Wissensch., München: Math.-Phys. Kl.*, 1904, p. 236.

|| M. Le Blanc, *Die elektromotorischen Kräfte der Polarisation*, Halle, 1910, W. Knapp.

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tionized our conception of active and passive metals. Two proofs can be adduced that there is only a quantitative, not a qualitative, difference between active and passive metals and that there is, in active metals, a possibility not only of a diffusion polarization, but also of a chemical polarization.

These are the proofs:

In 1904 Thatcher observed that when quite small quantities of so-called poisons are added to an electrode, at which an electrolytic oxidation is taking place, the anode potential rises considerably, which indicates that slowly progressing chemical reactions are at play. Le Blanc and his assistants now demonstrated that an addition of poisons to the active electrode $\text{Cu} \mid \text{CuSO}_4$ called forth the same effect. Thus 1 cm.³ of a faintly acid solution of brucine sulphate (of 1 per cent.), added to 100 cm.³ of a solution of $1\text{N-CuSO}_4 + 1\text{N-H}_2\text{SO}_4$, raises the cathodic polarization from 29 to 148, and the anodic from 14 to 40 millivolts. Strychnine raised the cathode polarization by 115, the anode polarization by 18 millivolts, etc.

When we further compare the polarizations of two electrodes under conditions, as equal as possible, of temperature, current density, concentration of the ions, etc., and when we consider that the diffusion rates must, under those equal conditions, be of the same order of magnitude, we are entitled to conclude that large differences in the polarization values of the two electrodes can only arise owing to the chemical polarization of that electrode which possesses the higher polarization value.

Thus the system $\text{Hg} \mid 0.1\text{N-HgNO}_3 + 1\text{N-HNO}_3 \mid \text{Hg}$ gave, at a current density of 0.09 amp./cm.², a polarization of about 6 millivolts, whilst under the same conditions the system $\text{Cu} \mid 1\text{N-CuSO}_4 + 1\text{N-H}_2\text{SO}_4 \mid \text{Cu}$ gave, with electrodes of Cu quenched in methyl alcohol, 30 millivolts, and with Cu electrodes polished with emery 110 millivolts. Still higher polarizations, of the order of 500 millivolts, were obtained with the system—

The third proof for the existence of the chemical polarization of active electrodes was given by Haber and Zawadzki* in 1912, in a paper on the polarization of solid electrolytes. They found that "solid silver salts show, with a silver anode, a polarization which increases considerably with falling temperature and which, in the case of silver sulphate, becomes so pronounced at the temperature of solid carbon dioxide, that the silver anode behaves like an anode of platinum or graphite."

A further proof for the existence of the chemical polarization of active electrodes is afforded by the fact that additions of free sulphuric acid and of its salts to the $\text{Cu} \mid \text{CuSO}_4$ electrode much increase the cathodic polarization.† In order to keep the effect of an addition of a neutral salt quantitatively reproducible, the electrolyte should possess a certain minimum of H^+ ions; for below a certain H^+ ion concentration the cathodic current intensity-potential curve of the $\text{Cu} \mid \text{CuSO}_4$ electrode takes a qualitatively quite different course from the curve found above this minimum. That indicates that it is purely chemical processes which are responsible for the current intensity-potential curve. Since now all the neutral salts as well as the sulphuric acid itself have the same effect, the increased polarization is evidently due to the fact that the addition diminishes the concentration of the Cu ions in the electrolyte.

* Haber and Zawadzki, *Zschr. Physik. Chem.*, **78**, p. 241, 1912.

† R. Goebel, *Dissertation*, Dresden, 1912 (researches carried out under F. Foerster). Also D. Reichinstein, *Zschr. Electrochem.*, **19**, p. 520, 1913, and D. Reichinstein and A. Zieren, *ibid.*, p. 530. These two accounts do not yet contain the results of all the experiments made.

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What kind of a polarization is this then—a chemical or a diffusion polarization?

The first-mentioned case must not be confounded with another, in which the electrolyte contains the same small concentration of Cu^{++} ions, but in which the neutral salt and the noteworthy concentration of undissociated CuSO_4 are missing in the electrolyte.

In contrast to this simple case the more complicated case may be discussed as follows: Imagine an ideal case, in which the Cu electrode has a considerable concentration of the Cu ions (a), the required minimum of H^+ ions, and a very small concentration (practically none) of undissociated CuSO_4 molecules. At a certain current density at which the cathodic polarization is still zero, a large amount of some alkali salt is added to the electrolyte, in order to reduce the concentration of the Cu ions to $\frac{a}{10}$, e.g., and to set up a certain definite polarization at the same time. Let us further assume the existence of an electrode which, in the presence of the $\frac{a}{10}$ concentration of its ions (without, however, possessing the 0.9a concentration of the undissociated salt) will mark, *ceteris paribus*, the same polarization as the Cu electrode referred to. The comparison between this hypothetical electrode and the really existing Cu electrode would suggest: On the one hand (case 1) the polarization of the Cu electrode would be caused by a slow (i.e., secondary) transition of the ions into the metallic state; it is assumed that while the current is flowing the concentration of the ions is, by vigorous stirring, kept the same at the electrode surface as in the middle of the electrolyte. On the other hand (case 2) the polarization of the Cu electrode might be caused by the difference in the concentration near the electrode and in the middle of the electrolyte. The comparison between the Cu electrode and the hypothetical electrode now teaches: *The latter case (2) is only possible when the rate at which the spent Cu ions are replenished by the reaction $\text{CuSO}_4 \rightarrow \text{Cu}^{++} + \text{SO}_4^{--}$ is infinitely small compared with the rate of diffusion of the Cu ions from the middle of the electrolyte to the surface of the electrode.*

The following criteria enable us to distinguish between case 1 and case 2:

If we can find an electrode such that the concentration of its ions be only $a/10$, that it contain no undissociated salt, and that it do not display any polarization, *ceteris paribus*, then that Cu electrode would belong to case 1.

If we further succeed in constructing an electrode such that, with an ion concentration of $a/10$, it show *ceteris paribus* the same polarization as our Cu electrode, *but practically do not, in an electrolyte of the composition 0.1a concentration of its ions + 0.9a concentration of the undissociated salt, possess any polarization*, that would be our case 2. It should be added that case 1 represents a pure example of chemical polarization, whilst case 2 may be regarded as chemical polarization and as diffusion polarization as well. For, according to the definition formulated above, in case 2 the polarization would vanish: by substitution of the real rate of dissociation of the CuSO_4 by an infinitely rapid rate of dissociation, and also by substitution of the real rate of diffusion of the Cu ions by an infinitely rapid rate of diffusion.

These complicated polarization phenomena may probably be more easily investigated in practice than it would appear from this deduction; for I consider that the compensation process of case 2 will, in the predominating number of examples, practically be conditioned only by the dissociation of the undissociated salt. We shall thus either have case 1, or have case 2, in which the dissociation of an undissociated salt will represent the compensation

process. The further investigation of the Cu electrode, undertaken for the purpose of deciding the question whether the chemical polarization owes its existence to the dissociation process indicated, or perhaps to the reduction of the Cu ions (slow because of the small concentration of the latter), has suggested a solution of the problem in favour of case 1 (*loc. cit.*). This consideration is of principal importance for electrodes whose electrolytes consist of complex salts, *e.g.*, Ag | Ag(CN)₂K | electrode.

Interesting examples of chemical polarization, again not due to slow diffusion of the electrolyte, can be observed when the Cu electrode is rubbed with a little mercury. These cases will be explained lower down.

In looking for an example of an electrolysis which would supply a simple analogy to the described cases of chemical polarization, that is to say, which would render clear how chemical polarization can occur with an active electrode, without the metallic electrode losing its capacity of *primarily** furnishing ions—in looking for such an analogy (which has been found) a whole series of phenomena was recognized as exemplifying negative depolarization.

3. *Negative Depolarization.*†—What is a depolarizer? Imagine a circuit, consisting of a source of electric current having a constant e.m.f. independent of the load, and of a polarization cell, *e.g.*, of two platinum electrodes in clay cells charged with diluted sulphuric acid, these pots themselves immersed in a common beaker also filled with H₂SO₄. We close the circuit after the current intensity has reached its stationary value, and we add to the electrolyte about the kathode a solution of CuSO₄. Then a partly new process will set in at the kathode, and the current intensity will rise. Any material capable of producing these two effects simultaneously is usually called a depolarizer. The action of the depolarizer appears especially clear to us when it is soluble in the solvent which constitutes the electrolyte, and particularly when it does not chemically react with the electrolyte to which it is added, and does not disturb the state of this electrolyte.

Are there now such materials which, when added to the electrolyte, will not chemically react with it, and will diminish the current intensity instead of increasing it? In other words, are there any *negative* depolarizers? The reply to this question must decidedly be in the affirmative. Let the kathode of the described circuit consist, not of Pt, but of a Pd–H₂SO₄ electrode. When the electrode has, from the beginning, a small H₂ concentration, the electrolysis at not too high current densities will proceed in such a way that the whole hydrogen will be occluded by the electrode, and the polarization will be very small. We have probably to deal with a very rapid chemical compensation process constituted perhaps by the reaction between the Pd atoms and the primarily formed H atoms.

If we now add, during the electrolysis under suitable conditions, a zinc salt to the electrolyte, the polarization will increase, the current intensity in the circuit diminish, and a new process will set in: zinc is deposited on the kathode.‡

* By a primary electrochemical reaction we understand a reaction with which the passage of the current through the boundary electrode-electrolyte is connected, *e.g.*, the charging of a metallic atom with an electron, or the discharge of an ion. Since this reaction proceeds in synchronism with the electric current, it is more rapid than all chemical reactions (practically of infinite velocity). If the anodic formation of Cu ions progressed primarily, undisturbed, that would not cause any chemical polarization. The fact that chemical polarization does occur indicates that another primary reaction is proceeding, and that the Cu⁺ ion formation is secondary.

† Reichstein, *Zschr. Electrochem.*, **19**, p. 520, 1913.

‡ *Ibid.*, **16**, 1910.

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The surprising feature in this phenomenon is that, of all the possible processes, it is generally the more rapid which takes place. Which means in the case of the zinc addition that that process which occurs more easily will be impeded, namely, the deposition of hydrogen from the electrolyte by the zinc which would be deposited in minimal quantities (not to be determined by weighing), even at open circuit owing to local action. The zinc hence strengthens the chemical inertia of the reaction between the Pd and H atoms, and acts as a depolarizer in a negative sense. I should like to point out in this place already that, if we desire to explain the chemical polarization of a metallic electrode—let it scarcely be recognizable or, on the other hand, sufficiently marked to lead to a generation of oxygen at the anode (= passivity)—without denying to the metallic atoms the capability of forming primary ions, then the discharge of OH' ions, which with anodic treatment is simultaneous with the process of charging the atoms, may be regarded as the first step of a negatively depolarizing reaction. The analogy is patent; we need only build up the mechanism of the chemical polarization in a correct way.

The behaviour of real alloys on the anode may further be recognized as an example of negative depolarization. A. Bürger and I (*loc. cit.*) have anodically investigated the alloys Cu-Ag, Cu-Hg, Cd-Hg, and Cd-Ag.

The noble metals, in amounts as small as possible, are alloyed with the surface of the baser metals. All the alloys examined have qualitatively the same property: they raise the polarization whilst the equilibrium potential remains equal to that of the unalloyed, chemically pure electrode. Thus the polarization of a Cu electrode which has been rubbed with a little mercury rises *ceteris paribus* from 33 to 161 millivolts. The anodic current density-potential curve of the alloys shows under certain conditions a point of inflection. The alloy is decomposed when the electrolysis is prolonged, and the nobler constituent aggregates or drops down from the electrode.

Of special interest for all these alloys is a strange relation between the velocity of formation of the alloy and the degree of polarization attainable with the resulting alloy. The Cu electrode may simply be amalgamated by holding it horizontally, the surface free from paraffin facing upward, and pouring some mercury on it, finally adding a few drops of concentrated nitric acid. When the electrode is quickly rinsed with distilled water, a bright mercury surface is left; the nitric acid in this operation plays the part of the soldering liquid in the soldering process.

An electrode prepared in this way, however, hardly marks any greater polarization than the pure unamalgamated Cu electrode.

In order to prepare an electrode which will show the effect described of the amalgamated Cu electrode, every trace of HNO_3 must be avoided, and the greatest care be observed to deal with pure metals. The mercury is rubbed in the dry into the chemically pure copper surface; this is a tedious operation, and the slower the alloy formation, the higher will afterwards be the polarization realized under anodic treatment.

To the phenomena of negative polarization might perhaps be joined another class of phenomena. In the cathodic polarization of mixtures of nickel sulphate and zinc sulphate, of the sulphates of nickel and iron and of zinc and iron, the polarization rises frequently up to the value of the baser metal, and this latter metal is likewise deposited.* These processes are not pure

* A. F. Walter von Escher, *Kathodische Vorgänge bei der Elektrolyse gemischter Lösungen von Zink- und Eisensulfat*, Dissertation, Dresden, 1912. A full literature list will be found there. Cp. also F. Foerster, "General Electrochemical Behaviour of Metals," *Zschr. Elektrochem.*, 14, p. 153, 1908.

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examples of negative depolarization, however, because in the absence of the less noble metal the more noble one is deposited quantitatively, *i.e.*, with a current efficiency of 100 per cent.; at the same time hydrogen is generated. These cases are worthy of attention when one of the two metals at least in the salt mixture which is being electrolysed belongs to the cathodically passive metals.

To these experiments, which, as we shall see, introduce us into the ante-room of the passivity phenomena, others may be added, which initiate us directly into the secrets of passivity.

4. *Direct Experiments on the Passivation of Metals.*—Surprise has often been expressed at the fact that a metal turning passive does not, at higher current density, show at least that anodic solubility which belongs to it at small current density. Let a passive metal be dissolved anodically at a low current density a to the extent of 50 per cent., and let it liberate oxygen, so that its dissolution takes place at $\frac{a}{2}$ amp./cm.² of metallic surface. When we increase the current intensity tenfold, the dissolution will not proceed at the rate of $5a$ amp./cm.²; it does not even take place at the former rate $\frac{a}{2}$ amp., but at a much smaller rate. How is this to be interpreted chemico-kinetically? Let us assume that a passive metal Me generates primarily oxygen. Two reactions are possible:

The commencement of reaction (2) is designated "passivity." The example teaches us that passivity is not a result of two competing reactions, for both of which the velocity would increase with increasing oxygen concentration, but: *the passivity is caused by two reactions such that the velocity of the one reaction decreases with increasing O concentration, whilst the velocity of the second reaction regularly increases with increasing O concentration.*

In 1911 I set myself the task to investigate how the rate of increase of the anodic polarization potential accompanying the flow of continuous current through a Pt-H₂SO₄ electrode differs in the two cases when the Pt electrode is free from oxygen and when it has previously been charged with O₂.^{*} I made the following observations. A current impulse is imparted to the combination

in the direction of the arrow. Its anodical amplitude is 0.1 amp./cm.² of the Pt electrode, its duration 0.026 second. After the expiration of this period follows a spontaneous diminution in the electrode charge lasting 0.028 second. The rest of the anodic charge is then destroyed by short-circuiting the cell for 0.025 second. These three processes succeed one another. (The arrangement comprises a rotating commutator which closes the primary circuit, interrupts it, and closes the short-circuit; the latter could be opened and closed at will during an experiment with the aid of a cut-out.) In this way it was possible to obtain, on a photographic plate, oscillographs of the time-potential curves at open and at closed short-circuit.

At open short-circuit this time-potential curve rises steadily up to an asymptotic potential value, which is independent of the time. At closed short-circuit

^{*} Reichinstein, *Zschr. Elektrochem.*, **17**, p. 89 (1911), and **19**, p. 672 (1913).

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the curve marks a point of inflection corresponding to the moment 0.004 second after closing the circuit. This point is well marked on the oscillogram, and the experiment is easily to be reproduced. I have been able to show this with the aid of the oscillographs at different times to several scientists.

This point of inflection can only be interpreted as indicating that we have to deal with a chemical reaction, the velocity of which first increases and then decreases, as the current quantity (i.e., together with the oxygen concentration) is increasing. During a period which is smaller than 0.004 second the time-potential curve has the distinct tendency of approaching the time ordinate and a stationary value at low potentials. Every approach to a stationary condition now is connected with an increase in the velocity of the compensation process, i.e., of that process in the absence of which the stationary conditions could not be reached. Now we observe a point of inflection within 0.004 second after closing the circuit, when the potential rises; the velocity of the compensation process is beginning to fail.

Thus the curve velocity-oxygen concentration possesses a maximum.

The compensation process consists of the formation of platinum oxides (see below).

During a period which is smaller than 0.004 second, therefore, a Pt | H₂SO₄ electrode behaves, at a current density of 0.1 amp./cm.², like an inattackable electrode. The amount of Pt oxide which is formed per sq. cm., when the continuous current is not interrupted, is hence of the order of magnitude $0.004 \cdot 0.1/96540 = 4 \cdot 10^{-9}$ gramme-equivalent.

When afterwards the electrode is polarized for some time with the short-circuit closed, the electrode becomes covered with a yellowish layer which consists of Pt oxides. This does not occur when the short-circuit is open. We remember that platinum is dissolved with a high current yield in KCN solutions by alternating currents, but not by continuous currents. A combination, continuous currents superposed on alternating currents, is utilized in the gold industry.

A lucky accident has led us to the direct experimental recognition of the described maximum of the curve, in which the velocity is plotted as a function of the oxygen concentration.

In Russia a large amount of gold is gained by dissolving the ores in aqueous KCN solution in the presence of air as oxidizing agent. This process being very slow, there has been no lack of attempts of trying other oxidizing agents.

In this connection Andrejew* and later Michailenko and Meschterjakow† (on the instigation of Kistiakowsky) determined the rate of solution of gold in KCN in the presence of oxidizing agents. They all found that this dissolution takes place in such a manner that the rate first increases and then decreases with the concentration of the oxidizing agent. The velocity-concentration curve displays a well-marked maximum.

We may now pass to the exposition of the theories which aim at bringing all the cases of chemical polarization under one point of view.

5. *First Theory.*—The first theory was proposed at a time (1910–11) when the experiments of Le Blanc concerning the chemical polarization of active metal electrodes were already known, and when the palladium-zinc experiments were made in order to clear the matter up; the other experiments mentioned above were not yet known, however. The theory, therefore, aimed at devising a mechanism which would admit of chemical polarization without

* J. J. Andrejew, *Fourn. Russ. Phys. Chem. Soc.*, **39**, p. 1637 (1907); *Nachricht. Polyt. Inst., Petersburg*, **9**, p. 447 (1908); *Zschr. Elektrochem.*, **19**, p. 667 (1913).

† Michailenko and Meschterjakow, *Fourn. Russ. Phys. Chem. Soc.*, **44**, p. 567 (1912).

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denying the possibility that a system, and a passive metal-anode likewise, might primarily emit anodic ions. I should like to emphasize at this place already that this question is more satisfactorily answered by this first theory than by the second one.

The first theory* conceives a mechanism of the chemical polarization after the type of the Pd-Zn electrode. The rate of formation of the Pd-H alloy in the cathodic polarization of the Pd-H₂SO₄ electrode is given by the momentary concentration of the Pd and H atoms near the boundary of the solid electrode and of the liquid electrolyte. Let us now assume that the contact with the electrolyte at the boundary electrode/electrolyte is not formed by the solid metal, but by a solution (= alloy) of all those substances whose ions are represented in the electrolyte. The volume which this hypothetical alloy occupies in the electrode is designated the *electrode volume*.

When we add to the electrolyte of the Pd-H₂-H₂SO₄ electrode some Zn salt, some zinc will be deposited in the electrode volume already at open circuit, because the thermodynamical equilibrium demands that the potentials H₂-H⁺ ion and Zn-Zn⁺⁺ ion must finally be equal to one another.

We now make the assumption that the zinc entering the electrode volume diminishes the concentration of the Pd atoms there. When we now treat the electrode cathodically, the rate of formation of the Pd-H alloy will be smaller, and the polarization will be greater, than before. As a consequence some more zinc will be deposited on the electrode in accordance with the higher potential. The formation of the Pd-H alloy will proceed more slowly, and the polarization will finally rise so high that zinc alone is deposited.

Analogously a Cu electrode has a certain oxygen concentration in the electrode volume already before the current is turned on. The potentials of the systems Cu-Cu⁺⁺ ions and OH['] ions always remain equal to one another, with or without the current flowing. That may be supposed to become possible by the splitting of the electric current into two components: two primary processes are *simultaneously* taking place at the anode—

Whilst the first process depresses the concentration of the Cu atoms in the electrode volume, the second process raises the O concentration there, and it is therefore the electric current which maintains the equilibrium in the electrode volume. Both the reactions increase the polarization, and the purely chemical compensation processes oppose them. The process which is subject to chemical inertia is the oxidation of the massive copper by the aid of the oxygen in the electrode volume in the presence of the H['] ions of the electrolyte (any reaction between the oxygen of the electrode volume and the Cu atoms present in it is excluded, because there is equilibrium between the two systems, which, as we shall see, is a weak point of the first theory). When under special conditions the described oxidation takes place at a slow rate, the O concentration in the electrode volume and consequently the polarization rise to a high degree, until finally another compensation process sets in, for example, O₂ generation (= passivity). The equations of this theory may be deduced as follows:

Let there be: P₁, the electrolytic solution tension of the oxygen concentration in the alloy metal-oxygen, P₂, the electrolytic solution tension of its metal concentration, and p₁ and p₂ the corresponding concentrations of the ions in the electrolyte, which are assumed to be very high (= constant, prac-

* Reichinstein, *Zschr. Elektrochem.*, **17**, p. 699 (1911).

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tically not variable by small current densities). When the system tends to equilibrium, only P_1 and P_2 will change, and the conditions of equilibrium will be—

$$\frac{RT}{n_1 F} \ln \frac{P_1}{p_1} + \frac{RT}{n_2 F} \ln \frac{P_2}{p_2} = 0 \quad \dots \quad (1)$$

or—

$$\sqrt{\frac{n_1}{P_1}} = \sqrt{\frac{n_2}{P_2}} \quad \dots \quad (2)$$

In the most simple case where the chemical valencies n_1 and n_2 are equal we shall have—

$$P_1 P_2 = p_1 p_2 = K \quad \dots \quad (3)$$

where K is a constant. When we bear in mind that according to our assumption there is always (current flowing or not) equilibrium between the systems oxygen-oxygen ions and metal-metal ions, we may interpret equation (3) to mean that, when the solution tension of the metal decreases as the current flows because its concentration in the alloy is reduced, the solution tension of the oxygen must decrease at the same time. We therefore write—

$$\delta(P_1, P_2) = 0 \quad \dots \quad (4)$$

By differentiating (4) we obtain—

$$\frac{\delta P_1}{P_1} + \frac{\delta P_2}{P_2} = 0$$

$$-\frac{\delta P_1}{\delta P_2} = \frac{P_1}{P_2} \quad \dots \quad (5)$$

If we now send the quantity of electricity i in the direction electrode-electrolyte, the system O-OH' will transport the fraction r of the quantity of electricity which will discharge OH' ions and enrich the alloy in oxygen, whilst the electricity quantity $(i-r)$ will diminish the metal concentration in the alloy. The relation between these two quantities is the following: Let the potential of the alloy with regard to the electrolyte be π during a short interval, while the current is flowing. The work to be done in order to transport the quantity of electricity i from the electrode to the electrolyte will be—

$$\pi = r \frac{RT}{n_1 F} \ln \frac{P_1}{p_1} - (i-r) \frac{RT}{n_2 F} \ln \frac{P_2}{p_2} \quad \dots \quad (6)$$

The ratio of the increase in the oxygen concentration to the decrease in the metal concentration of the metal-oxygen alloy may be considered equal to the ratio of these two quantities of electricity; hence—

$$-\frac{\delta P_1}{\delta P_2} = \frac{r}{i-r} = \frac{P_1}{P_2} \quad \dots \quad (7)$$

and consequently—

$$r = \frac{P_1}{P_1 + P_2} \quad \dots \quad (8)$$

By combining (8) with (3) we find—

$$r = \frac{K}{K + P_2^2} \quad \dots \quad (9)$$

Or in words: *When with the anodic treatment of a metal its concentration in the*

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metal-oxygen alloy becomes small, then the system O-OH' will effect the whole transport of electricity : r therefore becomes equal to 1. The electrode now transports the electric current in a way, as if it were a highly noble metal ; its capability of primarily forming ions is completely suppressed, and it is limited to a secondary formation of ions.

Let us further assume that the total current in the anodic treatment of a copper electrode in the presence of H⁺ and of Cu⁺⁺ ions of high concentration be given by the reaction—

We will also suppose that the slow process of chemical compensation is defined by—

Let this process be much slower than the replenishing of the OH' ions which are consumed by the current. And finally let the experimental conditions be such that the rate of percentage rise in the Cu ion concentration at the electrode within the time t is so small that it may be neglected.

If, then—

x be the total oxygen concentration which the current has supplied up to the moment t ;

x_1 that concentration of the oxygen which has chemically been bound up to the moment t by Cu and H⁺ ions ;

$c = x - x_1$ the oxygen concentration on the electrode surface at the moment t ;

k_o the velocity coefficient of the reaction :

i_t a variable current intensity for which the same direction is, however, always maintained ;

and if, as stated, the oxygen concentration on the electrode surface at the moment t be—

$$c = x - x_1 \quad \dots \dots \dots (10)$$

then the concentration at the moment $(t+dt)$ will be—

$$c + dc = x + dx - (x_1 + dx_1) \quad \dots \dots \dots (11)$$

According to Faraday's law

$$dx = ki_o dt \quad \dots \dots \dots (12)$$

where k is a proportionality factor.

The velocity of the reaction—

$\left(\frac{dx_1}{dt}\right)$ is at any moment proportional only to the actual oxygen concentration because the concentration of the metallic copper is *eo ipso* constant, and the concentration of the H⁺ ions constant by hypothesis, and we obtain finally—

$$dc = (ki_o - k_o c) dt \quad \dots \dots \dots (13)$$

from which we find—

$$c = e^{-k_o t} \left(C_1 + \int_0^t k i_o dt \right) \quad \dots \dots \dots (14)$$

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where C_1 is the integration constant. From the initial condition (for which $t=0$) we see at once that the integration constant is dependent only upon that oxygen concentration which corresponds to the electrode when no current is flowing. This value of c is in our case given by the equilibrium potential of the copper electrode. If we now consider that the chemical polarization of a type of electrode such as we deal with in the copper electrode will, at small current density already, assume relatively large values, which differ strongly from the equilibrium potential of the base electrode, C_1 may be regarded as infinitely small with respect to the c values, and the equation may be written in the form—

$$c = ke^{-k_0 t} \int_0^t i_{(t)} dt \quad . . . . . (15)$$

This theory, which very satisfactorily characterizes the chemical polarization on condition that all the metals become primarily active as anodes, fails in many instances. Without entering into detail I will emphasize the consideration which will help us on to the right way.

We have seen that in the consideration of the anodic treatment of a metal the theory leads to quasi-secondary formation of ions, although in principle the theory starts from primary anodic formation of ions. That is just the desired result of the theory. This result is not arrived at, however, when we attempt to explain the cathodic chemical polarization by the aid of this theory. For if we imagine that the two chief components of the electrode volume consist, in the cathodic polarization of the Cu-CuSO₄ electrode, of Cu and of H atoms, then their quotient is constant, not their product, and the increase in the concentration of the one calls forth a simultaneous increase in the concentration of the other.

Further—and that is the chief drawback of the theory—we cannot, with its aid, come to the above-mentioned type of two reactions, of which the one is retarded by a rise in the O concentration whilst the second increases its velocity in a regular manner. This type of two reactions, we have recognized, can alone elucidate the phenomena of passivity. We can easily comprehend that we shall arrive at such a type of reaction if we imagine some reaction to take place within the electrode volume, *i.e.*, between its constituents. The first theory does not admit of that, because there is always equilibrium within the electrode volume; and all the compensation processes of which the first theory admits are indirect reactions. In order, therefore that we may imagine a larger number of possible compensation processes, the mechanism of the electrode volume should be so designed that there should not prevail equilibrium in it while the current is flowing. The entire current must be transported by *one* system from the electrode to the electrolyte.

We also saw that the prototype of the mechanism of chemical polarization, the Pd-Zn experiment, renders it necessary to ascribe to the zinc which enters the electrode volume a diminution of the concentration of the Pd atoms. How is this to happen? This effect is difficult to conceive if we regard the electrode volume as constant, and if we make no new hypothesis as to the mutual influences of the various constituents of the electrode volume. The simplest assumption which at once enables us to describe all the experiments mentioned is this: *The sum of the concentrations of all the constituents of the electrode volume is always constant, whether the current flows or not.*

6. *The Constant-Sum Hypothesis and the Second Theory.**—We presume

* Reichinstein, *Zschr. Elektrochem.*, **19**, p. 672, 1913.

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that the electrode volume is always fully saturated, and that any new constituent, possibly introduced by the electric current, ejects part of the old substances.

For the present I am not in a position to maintain the idea of a primary activity of all the systems. In view, however, of the fact that this theory satisfactorily answers all the questions concerning the chemical polarization, as well as those concerning the spontaneous solution of solid bodies in the presence of oxidizing agents, we may for the present rest satisfied with the assumption that in aqueous solutions the transport of the electric current across the boundary electrode/electrolyte is effected only by the OH' and the H' ions.

When a metal electrode is treated anodically the oxygen introduced pushes the metal atoms out of the electrode volume—the same will happen on the kathode by the H_2 introduced—and the chemical equilibrium prevailing before the current was flowing will be destroyed. The oxygen now begins to react with the metal atoms of the electrode volume. Let this reaction be of the form :

where Me and O are respectively an atom of the metal and of the oxygen of the hypothetical alloy, and H' concerns the electrolyte.

If the concentrations of the three substances reacting with one another are x , y , z , the velocity of the compensation process can be formulated as follows :

According to the hypothesis of the constant sum

$$x + y = a \quad \dots \dots \dots (16)$$

where a is a constant ; the velocity v

$$v = k_0 z^2 xy = k_0 z^2 y(a - y) \quad \dots \dots \dots (17)$$

when, in a special case, z is a constant, the $(v - y)$ curve has a maximum. Now—

$$v = k'(ay - y^2) \quad \dots \dots \dots (18)$$

from which—

$$\frac{dv}{dy} = ak' - 2k'y$$

and

$$\frac{d^2v}{dy^2} = -2k'.$$

The maximum corresponds to the value $y = \frac{a}{2}$.

When with a certain current density of the electrolysis the compensation process is so rapid that the oxygen concentration of the electrode volume does not rise above the value $\frac{a}{2}$ (which we may call the *critical concentration*), then there will be no reason to fear that another compensation process will set in, *e.g.*, generation of oxygen (= passivity). When, however, the critical concentration is exceeded, the compensation process will necessarily be retarded, and the O concentration will increase rapidly until a new compensation process sets in. Instead of the above-mentioned equation of the

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first theory, which defines the accumulation of the O concentration in the electrode volume after closing the circuit :

$$\frac{dy}{dt} = ki - k_0y,$$

where i is the current intensity of the continuous current, we have now—

$$\frac{dy}{dt} = ki - v \quad . . . . . (19)$$

and by combining (19) and (18)—

$$\frac{dy}{dt} = ki - k'ay + k'y^2 \quad . . . . . (20)$$

This equation gives us the above-discussed point of inflection for the y - t curve, that is to say, also for the curve which illustrates the rise of the polarization with time after closing the circuit.

We have now arrived at some point of reference enabling us to describe the experiments of Andrejew.

When we immerse a foil of gold in a solution of KCN which contains an oxidizing agent like O_2 , H_2O_2 or O_3 in solution, two purely chemical reactions will come into play :

I. The formation of the gold-oxygen alloy.

This process is missing in the electrolytic dissolution of metals because in their instance the oxygen is directly supplied by the primary discharge of OH' ions, whilst here the oxygen is supplied by a chemical reaction (=decomposition of the oxidizing agent). If the oxygen were not to disappear owing to the dissolution of the gold, we should finally arrive at an equilibrium between its concentration in the electrode volume and the concentration of the oxidizing agent in the aqueous KCN solution. We may suppose that in one and the same oxidizing agent these two concentrations will bear a rectilinear relation. Now the formation of the gold-oxygen alloy, we shall see, does not proceed at an infinitely rapid rate, yet not so slowly that this process should become decisive for the entire process of solving the gold. The CN' ions are, moreover, not in contact now with the compact gold metal, but in contact with the gold-oxygen alloy, and process II is taking place.

II. $2Au | O (alloy) + H_2O + CN' \longrightarrow 2Au(CN)'_2 + 2OH'$.

This process may, of course, proceed in several stages. When we increase the O concentration of the alloy by increasing the concentration of the oxidizing agent in the liquid phase, the critical O concentration will finally be exceeded, and the velocity of the process II will diminish more and more.

It should here be emphasized that there are many instances in which the rate of oxidation becomes smaller as the oxygen concentration is raised ; I will content myself with drawing attention to the table of these cases compiled by van't Hoff.*

The critical O concentration has now been exceeded, and, in accordance with what has been explained, a new chemical process (a second compensation process) must come into play. Such processes are the following : formation of H_2O_2 (observed by Bodländer), formation of gold peroxide.

We recognize that the occurrence of oxide layers must not be regarded as the cause of the delay in the solution of gold. The peroxide films are merely a concomitant feature, which indeed indicates that the O concentra-

* J. H. van't Hoff, *Vorlesungen über theoretische und physikalische Chemie*, No. 1, Braunschweig, 1898, p. 238.

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tion of the alloy has attained high values, but which must by no means be represented as the cause of the dissolution of gold. It is a symptom, like the rise of temperature in the diseased human body.

It is interesting to note that some investigators regard as cause of the passivity that in which other investigators see the consequence of the cause of passivity.

Thus, process I supplies oxygen to the alloy metal-oxygen, and temporarily increases its concentration, whilst process II tends to diminish this concentration. In the stationary condition, when the reactions proceed at a constant rate, the concentration of the oxygen in the alloy is dependent upon the two processes I and II; that is to say, the O concentration may be increased, not only by increasing the rate of process I, but also by diminishing the rate of process II. *Ceteris paribus*, therefore, the "critical O concentration" (in the process of dissolving gold in diluted KCN) may be exceeded with the aid of oxidation potentials of the oxidizing agents, which are so low that they would be ineffective at higher CN' ion concentration. This is in agreement with the experiments of Andrejew, according to which the characteristic film of gold peroxide appears in solutions of KCN ranging from 0.01 to 0.05 per cent., already when air acts as oxidizing agent, which demonstrates that process I is absolutely necessary. We may draw a comparison as to the spontaneous solution of passive and of active metals in the presence of oxidizing agents from this point of view. What could we predict as regards the spontaneous solution of copper and nickel in H_2SO_4 in the presence of oxidizing agents? We know that the latter of these two metals belongs to the so-called passive metals, *i.e.*, that the process of solution is slow. We should then expect, from what has been explained, that the critical O concentration of the nickel-oxygen alloy, and hence the retardation in the rate of solution of nickel, will, *ceteris paribus*, always occur at such oxidation potentials of the oxidizing agent at which this will not be attainable in the case of copper; and it is altogether doubtful whether the v maximum will experimentally be realized in the dissolution of copper.

Of especial interest from the standpoint of the new theory are the exposition of the cases of the palladium-zinc cathode and the behaviour of the alloys mentioned on the anode.

When a palladium electrode, to the electrolyte of which a zinc salt has been added, is treated cathodically, the current is carried by the H ions. Owing to the prevailing conditions of equilibrium, some zinc will enter the electrode volume and will push out some palladium, already before the circuit is established. When the current flows, the zinc acts as ballast, because it depresses the Pd concentration according to the hypothesis of the constant sum, and hence retards the rate of the compensation process. When the concentration of the zinc in the electrode volume is γ and the sum-constant is a , the maximum of the curve, which expresses the rate of the compensation process (Pd + H reaction) as a function of the H concentration, will correspond, not to the H value $\frac{a}{2}$, but to $\frac{a-\gamma}{2}$. Now, hydrogen accumulates more

and more in the electrode volume, and the polarization rises. It should be noted that the whole conception forces us to assume a chemical reaction between the H atoms and those Pd atoms which fill up the electrode volume—an assumption which was impossible according to the first theory of there being always equilibrium in the electrode volume. Thus quite generally any foreign substance entering into the electrode volume which will not take part in the compensation process may be regarded as ballast.

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A special interest attaches, from this point of view, to the behaviour of the real alloys forming on the anode. When, in the case of a purely active metal, the maximum of the curve O concentration/velocity cannot be attained, that maximum can, in the case of an alloy as described, be realized, owing to the ballast, at relatively low current density, and the curve will show an inflection. An alloyed anode, therefore, displays formally the properties of a passive metal. We may imagine the whole anodic process on the following lines. As regards the space distribution the electrode, at the beginning of the anodic treatment, has the appearance: *Electrolyte/hypothetical alloy/real alloy/compact base metal*. The anodic treatment carries oxygen into the hypothetical alloy, where it partly displaces both the metals, and the chemical reaction between the oxygen and the base metal sets in. (As a matter of fact the two metals enter into competition with regard to the oxygen; practically, however, the oxygen reacts with the less noble metal only.) The base metal, which has disappeared owing to the chemical reaction, is being replaced in the hypothetical alloy by both the metals of the real alloy. In which ratio? That depends upon the rate of diffusion of the base metal, or upon the rate of the alloy formation of the two metals. If this rate be small, then the concentration of the base metals in the hypothetical alloy (when the current is flowing) will also be small—the velocity of the compensation process will decrease, the polarization will rise, and finally will follow the decomposition of the real alloy; the electrode then will have the following spatial distribution: *Electrolyte/hypothetical alloy/thin layer of the noble metal/compact base metal*. The noble metal may then separate from the electrode. For this end, we know from galvanoplastic processes, a trace of impurity between the two metals will be sufficient.

In order to keep the rate of alloy formation alluded to small, we must, as has been pointed out already, exercise the greatest care as to the purity of the two metals in building up the real alloy. Certain foreign substances accelerate the alloy formation; nitric acid in particular should here be mentioned; it plays the part of the soldering liquid in soldering two metals.

APPENDIX ADDED NOVEMBER, 1913.

In order further to elucidate the researches I have added a few diagrams.

Fig. 1 represents the curves current density/potential. The abscissæ are the current densities in millivolts per 5 sq. cm., the free electrode surface of my experiments amounting to 5 sq. cm., the back and edges being coated with paraffin. The electrolyte was kept well stirred during the experiments. The ordinates are the polarization values in millivolts, *i.e.*, the differences between the electromotive forces of the electrode when the current was on and when off.

The lower portion of Fig. 1 concerns Section 2 of my paper. We see that curve 1—in which case *no free H₂SO₄ was added to the electrolyte*—differs qualitatively from curve 2, where the electrolyte contained 0·111 gramme-equivalent of free acid per litre. When the concentration of the free acid is raised to 1·975 gramme-equivalent per litre, the polarization increases as curve 3 indicates. The same effect can be realized by diminishing the concentration of the CuSO₄, as curve 4 exemplifies.

The upper portion of Fig. 1 illustrates Section 3 of the paper. The anodic polarization of a pure (not alloyed) Cu electrode (curve 3) is small, and that holds still more for the anodic polarization of the Cd electrode in a solution which is highly concentrated as regards H₂SO₄ (curve 5).

FIG. 1.

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As soon as we rub a little mercury into the electrode of base metal, everything changes. Curve 1 marks the polarization of the Cu electrode alloyed with Hg; curves 2 and 2a refer to the Cd electrode alloyed with Hg. The experiment represented by curve 2 was made by determining the polarization value corresponding to a certain density, interrupting the current and then raising the current density after a certain interval. When finally the current density of about 350 milliamps. per 5 sq. cm. had been reached, curve 2a resulted when the current density was reduced again, *without, however, altogether interrupting the current.*

FIG. 2.

The original oscillogram, which is reproduced in Fig. 2, refers to Section 4 of the paper and illustrates the time-potential curves of two Pt electrodes in H_2SO_4 , the one practically free of oxygen, and the other previously charged with oxygen. The abscissa marks the time, progressing from A to B; 1 mm. of the abscissa is equivalent to 0.00074 second. The ordinate indicates the potential, 1 mm. being equivalent to 0.0754 volt; 0 is the zero line of the oscillograph mirror, whose deflection indicates the potential; N is the datum line. The electric circuit is closed at A and flows until the moment B is reached; the length BC is the interval during which the electrode charge spontaneously decreases after interrupting the current; the length CD is the

FIG. 3.

period during which the cell remains short-circuited for the purpose explained. Curve I shows the time-potential relation when the short-circuit is not worked; curve II marks at X the point of inflection (mentioned in Section 4) observed when the cell is short-circuited in the interval CD. The resistance of the short-circuit was 2.05 ohms, that of the cell 1.40 ohms, and that of the leads for the short-circuiting 0.65 ohm.

Fig. 3 explains the general arrangement of the apparatus.

- Q is a battery of accumulators ;
- K a commutator ;
- W_1 and W_2 are resistances, free of self-induction ;
- A is a hot-wire galvanometer ;
- Z is the cell under test ;
- E is the sensitive loop of the oscillograph ;
- S_1, S_2, S_3 are keys ;
- L are the leads for standardizing the instruments.

U_1 and U_2 are two rotating interrupters, mounted on the shaft of the drum of the oscillograph and connected in the following way : When the terminals *c* and *d* of the commutator are joined to *a* and *b* and S_1 is closed, the current will flow from Q through the cell Z, as long as U_1 is closed ; during this period, and also for a little while after U_1 has been opened owing to the rotation of the drum, U_2 will not be in contact. As the drum continues to turn, U_2 will be closed, and the cell will be short-circuited ; during this period U_1 will, of course, be left interrupted.