

Classic Paper in Corrosion Science and Engineering with a Perspective by F. Mansfeld*

PERSPECTIVE

The paper, "On the Interpretation of Corrosion Processes Through the Superposition of Electrochemical Partial Processes and on the Potential of Mixed Electrodes," published in 1938 by Wagner and Traud is a milestone in the history of corrosion—in fact, it is the beginning of modern corrosion science as we know it today. The key point of this paper is the establishment of "mixed potential theory," which postulates that even without the assumption of the existence of local anodes and cathodes one can explain corrosion reactions by assuming that cathodic and anodic partial reactions occur at the phase boundary metal/electrolyte in constant change with random distribution of location and time of the individual reaction. In their paper, Wagner and Traud developed quantitative conclusions and substantiated them experimentally using the system zinc amalgam in acid solution.

It is interesting to note that Wagner and Traud point out in the introduction of their paper that "the special significance of 'local cells' under practical conditions has frequently led to interpreting every kind of metal dissolution and corrosion through the local cell concept." Despite their clear formulation of mixed potential theory and its successful application to basic corrosion processes, even today corrosion reactions are often explained solely by the local cell concept. In a frequently used textbook on corrosion for students of science and engineering, one can find as explanation of corrosion of a metal in an acid solution that "the microstructure of the metal causes it to act as its own anode and cathode."¹

The development of mixed potential theory has been clearly described by Kaesche in his book, "Die Korrosion der

EDITOR'S NOTE: This new series, "Classic Paper in Corrosion Science and Engineering," will feature reprints of defining papers that presented milestone advances in corrosion science and engineering. Each paper will be accompanied by a perspective written by a senior member of the corrosion research community. (Comments may be submitted via e-mail at PubsOnline@mail.nace.org or mailed to Dr. J.B. Lumsden, FNACE, CORROSION Technical Editor, Rockwell International, 1049 Camino Dos Rios, Thousand Oaks, CA 91360.) —Jesse B. Lumsden, Technical Editor

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Metalle,"² and its—somewhat flawed—English translation, "Metallic Corrosion," which was published by NACE International.³ Mixed potential theory explains the mechanism of cathodic and anodic corrosion inhibition in a simple manner. It also explains more complicated processes such as the passivation of Ti by small additions of noble metals, which was a hot topic in the 1950s. In this case, small amounts of Pd or Pt increase the rate of the hydrogen reaction, significantly causing a shift of the open-circuit potential into the passive region. The partial anodic reaction does not change due to alloying.^{4,5}

Another important contribution by Wagner and Traud is the discovery that the slope of the total potential-current curve at the mixed potential, E_m , can be used to calculate the rate of the corresponding electrochemical reaction at E_m , where $i = 0$. While this important conclusion was not applied to the determination of corrosion rates, it clearly points the way to the polarization resistance technique. The term "polarization resistance" was first used in 1951 by Bonhoeffer and Jena,⁶ following a suggestion by Lange to replace the previously used term "polarizability." They found an unambiguous correlation between the polarization resistance and corrosion rates for iron samples with different carbon content. K.F. Bonhoeffer was—as C. Wagner—a member of the influential "Göttingen School," who made his most important contributions in the difficult time after the Second World War. In 1957, Stern and Geary,⁷ based on the concept of mixed potential theory, derived an equation that quantitatively related the slope of a polarization curve at the corrosion potential, E_{corr} , to the corrosion current density, i_{corr} , thereby firmly establishing the polarization resistance technique that was reviewed in detail in 1976.⁸

Wagner and Traud also anticipated what today is called the "Tafel-extrapolation technique." Their approach to determine the mixed potential, E_m , and the partial anodic and anodic current densities at E_m is illustrated in Figures 3 and 4, which are probably the most reproduced figures in the corrosion literature. In the Tafel-extrapolation technique, the anodic or cathodic partial polarization curves—or both—are extrapolated to E_{corr} to determine i_{corr} .

In Paragraph 3, the concepts developed in the two previous paragraphs have been tested using the system zinc amal-

gam in acid. A very thorough description of the experimental approach and the analysis of the experimental data is given. The authors conclude that the amount of evolved H₂ and the amount of H₂ calculated based on Equation (3) agree quite well (Table 1). This agreement is considered to prove the assumption of the independent superposition of the partial polarization curves for zinc oxidation and hydrogen ion reduction.

The last part of the Wagner-Traud paper deals with Pt that is exposed simultaneous to H₂ and an oxidizing species. It was concluded that, in this case also, the general behavior of such a mixed electrode can be described by the superposition of the partial potential-current density curves of the individual redox systems. Finally, Wagner and Traud also tackle the problem of electrode poisons for the hydrogen electrode—a topic that became very hot in the 1960s and 1970s when electrochemists spent much effort studying “clean” Pt electrodes.

In summary, this paper is a testament to the genius of Carl Wagner, who unfortunately today still remains an under-ap-

preciated giant in the world of electrochemistry and corrosion. This new series, “Classic Paper in Corrosion Science and Engineering,” will hopefully bring well-deserved recognition to Carl Wagner and the many others who have made significant contributions to the establishment of modern corrosion science.

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On the Interpretation of Corrosion Processes Through the Superposition of Electrochemical Partial Processes and on the Potential of Mixed Electrodes

C. Wagner* and W. Traud*

1. STATEMENT OF THE PROBLEM

In the dissolution of metals in acids, e.g., $Zn + 2H^+ = Zn^{2+} + H_2$, it is now generally assumed that the preceding equation describes only the whole process, whereas actually consecutive electrochemical processes take place:



In particular, it is known that frequently H₂ evolution does not occur uniformly at all parts of the metal/acid interface but primarily at individual foreign metal inclusions where the hydrogen overvoltage is lowest while equivalent amounts of zinc go into solution at other places. The special significance of “local cells”^{1,(1)} under practical conditions has frequently led to interpreting each kind of metal dissolution and corrosion through the local cell concept. Although this concept can account for many phenomena encountered under usual conditions, it appears to be necessary to investigate corrosion reactions from a more general standpoint. A general electrochemical interpretation

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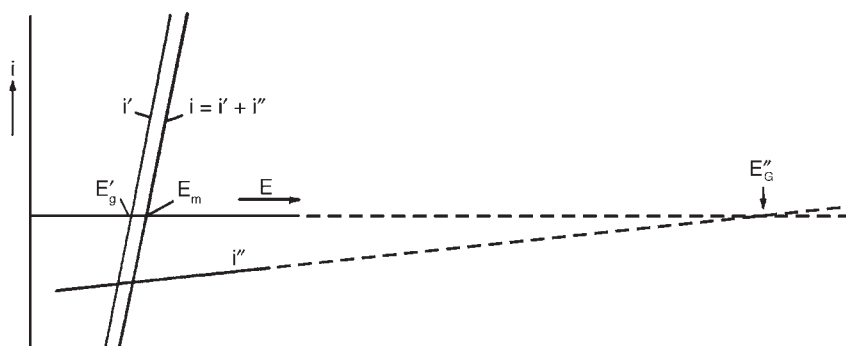


FIGURE 1. Schematic diagram of the current-potential curves for a metal dissolved in an acid. E —electrode potential; E'_g —metal equilibrium potential; E_m —mixed potential; the hydrogen equilibrium potential E''_g lies to the right outside the drawing. i' as a function of E : partial current-potential curve for the metal dissolution; i'' is the partial current-voltage curve for the $H_2 \rightleftharpoons 2H^+ + 2e^-$ process; $i = i' + i''$ as a function of E : total current-voltage curve. Current positive in the anodic direction, negative in the cathodic direction.

without local elements is possible if the assumption is made that consecutive cathodic and anodic partial processes occur alternately at the metal/liquid interface with a random distribution of the individual processes with regard to sites and time. It is the purpose of the present investigation to develop quantitative conclusions amenable to experimental tests on the basis of this working hypothesis and to substantiate them experimentally.

The principle of the superposition of partial current-potential curves² will serve as a general intellectual guide. Corrosion processes have already been treated on this basis by Masing, et al.³ Schematic curves for the dissolution of a metal in acid are given in Figure 1. (Current is taken positive in the anodic direction and negative in the cathodic.) The partial current-potential curves intersect the horizontal axis at the corresponding equilibrium potentials E'_g and E''_g . The intersection of the total current-potential curve lies between E'_g and E''_g and is called the mixed potential E_m . The partial currents corresponding to the mixed potential have equal amounts but opposite signs, $|i'(E_m)| = |i''(E_m)|$. Therefore, no current flows, and consequently, this case corresponds to an electrically insulated metal. According to our hypothesis, the corresponding chemical changes (Zn dissolution = H_2 evolution) are directly equivalent to the partial current intensities $i'(E_m)$ or $i''(E_m)$. If one of the partial current-potential curves (e.g., for metal dissolution) is very steep (practically without polarization) whereas the other partial current-potential curve (e.g., hydrogen evolution) is much less steep, then the mixed potential lies very close to the equilibrium potential of the former partial process, as is shown in Figure 1.

The general problem of the establishment of the potential of electrodes, which are not in complete equilibrium (more than one reduction-oxidation reaction on the same electrode = mixed electrode), has already been treated repeatedly. Hofmann and coworkers,⁴ Bodenstern,⁵ Aten and Zieten,⁶ and Ben-

newitz and Neumann,⁷ in particular, have investigated the behavior of a platinum electrode when hydrogen and oxygen are simultaneously present in the electrolyte. Furthermore, Biastoch⁸ and Bennewitz⁹ have studied the behavior of a platinum electrode with simultaneous presence of hydrogen and chlorine. These questions are of general importance, since mixed potentials have been measured in many cases and have been rejected until now as ill-defined, e.g., hydrogen electrodes with poisoning phenomena (see Sections 4 and 5), oxygen electrodes,¹⁰ redox potentials in biological systems.

As Hofmann and Ebert¹¹ as well as Bennewitz and Neumann have already shown for the catalytic formation of water on platinum, the mechanism of catalytic processes on the metal-aqueous solution interface can be elucidated. Special possibilities of an advance calculation of the reaction rate are discussed generally in Section 2 and are evaluated in Section 4 for individual systems.

2. POSSIBILITIES OF PROVING THE PRINCIPLE OF THE SUPERPOSITION OF ELECTROCHEMICAL PARTIAL PROCESSES AND GENERAL CONSEQUENCES

a) Measurements of Chemical Changes at an Applied Equilibrium Potential of a Redox System

The basis of the above working hypothesis is that a reduction-oxidation reaction between a strong oxidizing agent and a strong reducing agent does not occur directly but only through the intervention of electrochemical processes. Hence, if the mixed electrode is polarized by means of an external current source to the equilibrium potential of a redox (reducing agent + oxidizing agent) system, then the change in the concentrations of this redox system must be zero, since a finite rate of the reaction of the constituents of this redox system is electrochemically pos-

sible only if there is a deviation from the equilibrium potential. Inasmuch as a pure chemical reaction also occurs (hence, without electron exchange with the electrode), then a finite reaction rate should result even at the equilibrium potential. A reaction has not been found as yet for the systems investigated with an applied equilibrium potential (see Section 4[b]).

This principle of investigation is practically not applicable when a partial current-voltage curve is very steep, as in the case of zinc amalgam dissolving in an acid. Since the process $\text{Zn}^{2+} + 2\text{e}^- = \text{Zn}$ (in Hg) takes place practically without polarization, the total current-potential curve is almost vertical; hence, it is practically impossible to enforce the hydrogen equilibrium potential from an external current source because the required current would be exceedingly large. Of course, the total current-voltage curve must bend over at high current densities if concentration polarization sets in; however, no conclusions can be obtained about the reaction mechanism under these conditions, as will be illustrated in Section 2(c). On the other hand, in principle, it is easily possible to apply the zinc equilibrium potential. Because of the high slope of the Zn partial current-potential curve, significant quantities of zinc already dissolve anodically or are deposited cathodically if very small deviations of the applied potential from the Zn equilibrium exist. In practice, it is therefore not possible to prove with sufficient accuracy that the rate of the reaction zinc and zinc ions will actually be zero at the equilibrium potential.

b) Calculation of Reaction Rates from Current-Voltage Curves for Each Individual Redox System Under the Assumption of an Undistorted Superposition

The total current-potential curve in a system with two or more redox systems can be obtained directly in a well-known manner from simultaneous measurements of the potential and the total current intensity by using an ammeter. The partial current intensities of the individual processes can be determined only by means of a simultaneous determination of the corresponding chemical changes.

If the electrode material is not participating in the individual processes (Pt as the inert electrode or Hg as a solvent for less noble metals such as Zn), the simplest case to be considered is that the current-potential curve is determined only by the respective reducing and oxidizing agents for the individual partial process, but is independent of the presence of a second redox system. This assumption is certainly not generally valid, especially when films are formed (for example, Pt or Au oxides¹²). However, if our assumption is correct in a given case, then the current-voltage curve can be determined for each of the two individual processes by means of purely electrical measurements with the individual redox systems and

the mixed potential, and the corresponding total current-voltage curve can be derived for the simultaneous presence of both redox systems from a plot as shown in Figure 1. The dissolution of Zn amalgam in acid will be investigated as an example (see Section 3). In particular, the partial currents $|i'(E_m)| = |i''(E_m)|$ for $E = E_m$ can be determined directly from electrical measurements. Dividing by the electrochemical equivalent, $F = 96,500 \text{ C}$, one obtains the rate in equivalents \bar{n} divided by time t :

$$\frac{d\bar{n}}{dt} = \frac{1}{F} \times |i'(E_m)| = \frac{1}{F} |i''(E_m)| \quad (3)$$

c) Calculation of the Reaction Rates from the Slope of the Total Current-Potential Curves

The total current-potential curve at a mixed electrode can be determined experimentally and the slope $\frac{\partial i}{\partial E}$ can be established at the point $E = E_m$, $i = 0$. If certain assumptions concerning the shape of the partial current-potential curve can be made, then a calculation of the rate of the reduction-oxidation reaction is again possible from purely electrical data. In contrast to Section 2(b), it will no longer be assumed in the following that the partial current-potential curves of the individual redox system are superimposed without distortion in forming the mixed electrode; any shifts are permissible since the presuppositions refer only to the general shape of the partial current-potential curves but not to the values of individual parameters. We subdivided the investigation according to special assumptions as follows:

1. In accordance with Figure 1, the mixed potential E_m can be near the equilibrium potential of a redox system ($'$ superscript). Hence, $E'_g > E'_m$, i.e., the system ($'$) is less noble than the system ($''$). In the neighborhood of the mixed potential E_m , furthermore, the current-voltage curve for the first redox system is supposed to be much steeper than for the second redox system (see Section 1):

$$\frac{\partial i'}{\partial E} \gg \frac{\partial i''}{\partial E} \quad (4)$$

Moreover, we assume approximately rectilinear partial current-potential curves in the small range between E'_g and E_m so that we have in this range:

$$i' = (E - E'_g) \times \frac{\partial i'}{\partial E} \quad (5)$$

The quantity $\frac{\partial i'}{\partial E}$ can be expressed in terms of the directly measurable slope of the total current-voltage curve $\frac{\partial i}{\partial E}$ because of Equation (4):

$$\frac{\partial i}{\partial E} = \frac{\partial(i' + i'')}{\partial E} \cong \frac{i'}{E} \quad (6)$$

Hence, it follows from Equations (5) and (6) for equal and opposite partial-current intensities i' (E_m) and i'' (E_m) of equal amounts but opposite signs at the mixed potential E_m :

$$i'(E_m) = i''(E_m) \cong (E_m - E'_g) \times \frac{\partial i}{\partial E} \quad (7)$$

From the measurements of the mixed potential E_m , the equilibrium potential E'_g and the slope of the total current-voltage curve, a calculation of the partial current intensities i' (E_m) = i'' (E_m) is, therefore, possible under the assumption that $E_m \cong E'_g$ and, hence, a calculation is also possible of the reaction rate at a mixed electrode without a flow of current from Equation (3). The comparison with the direct measurements again leads to a proof of our working hypothesis that the redox reaction occurs exclusively by virtue of electrochemical partial processes. Experimental proofs are still lacking.

The relations for $E_m \cong E'_g$ and $\frac{\partial i''}{\partial E} \gg \frac{\partial i'}{\partial E}$ are obviously analogous.

2. Further conclusions are possible, if special assumptions can be made on the shape of the partial current-potential curves. We next treat the case that both partial current-voltage curves are determined exclusively by concentration polarization. This case has been investigated by Bodenstein,¹³ Bennewitz and Neumann,¹⁴ and others.¹⁵ We will assume local concentration depletion only for the substances consumed by the reaction at the mixed electrode (reducing agent of the less noble system [\cdot] with the symbol Red' , oxidizing agent of the nobler system [\cdot] with the symbol Ox''). The reaction products Ox' and Red'' are supposed to be present at sufficiently high concentrations so that the relative changes in their concentrations are insignificant. The following kind of function holds for the partial current-voltage curves of uncharged Red' or Ox'' molecules and, more generally, for charged particles in the presence of a large excess of an inert supporting electrolyte:

$$\frac{i'}{F} = \frac{q}{\Delta \xi} \times D_{\text{Red}'} \times v_{\text{Red}'} \times c_{\text{Red}'} \times \left\{ 1 - \exp\left(-\frac{v_{\text{Red}'} \times [E - E'_g]}{\varepsilon}\right) \right\} \quad (8)$$

$$\frac{i''}{F} = -\frac{q}{\Delta \xi} \times D_{\text{Ox}''} \times v_{\text{Ox}''} \times c_{\text{Ox}''} \times \left\{ 1 - \exp\left(-\frac{v_{\text{Ox}''} \times [E'_g - E]}{\varepsilon}\right) \right\} \quad (9)$$

The notation in Equations (8) and (9) follows: $\Delta \xi$ is the thickness of the diffusion layer at the electrode; q is the area of the electrode; $D_{\text{Red}'}$ and $D_{\text{Ox}''}$ are diffusion constants; $v_{\text{Red}'}$ and $v_{\text{Ox}''}$ are the numbers of the elementary charges that are involved in the oxidation of 1 molecule of Red' or in the reduction of 1 molecule of Ox'' ; $c_{\text{Red}'}$ or $c_{\text{Ox}''}$ are the concentrations mol/cm³ within the bulk solution; and $\varepsilon = RT/F$ is the factor in front of the logarithm of the Nernst potential formula.

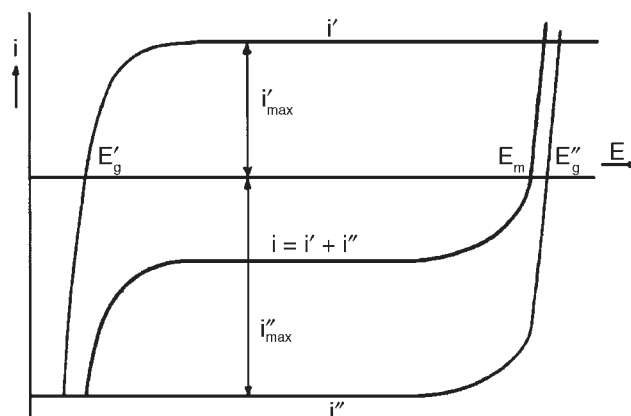


FIGURE 2. Schematic diagram of the current-voltage curves at a mixed electrode with exclusive polarization concentration. E —electrode potential E'_g and E''_g equilibrium potentials of the individual redox systems; E_m —mixed potential; i' and i'' as a function of E : partial current-voltage curves for the individual redox systems; $i = i' + i''$: total current-voltage curve.

We will assume that the equilibrium potentials E'_g and E''_g are far enough from each other or, more exactly, that $(E''_g - E'_g) \gg \varepsilon$. It is obvious from the graphical representation in Figure 2 that both the partial current-voltage curves as well as the total current-voltage curve have long horizontal sections (a saturation current).

The horizontal sections are determined by the magnitude of the diffusion rate. For $(E - E'_g) \gg \varepsilon$ the concentration of Red' directly at the electrode is small in comparison to that in the bulk concentration; hence, the difference in the concentration ($c_{\text{Red}'} - 0$) determines the magnitude of the diffusion rate in practice, and the maximum oxidation rate is also equivalent to the saturation current intensity i'_{max} for the oxidation of Red' . Corresponding relations hold for the reduction of the Ox'' with a current i''_{max} if $(E'_g - E) \gg \varepsilon$.

The mixed potential E_m lies either somewhere in the neighborhood of E''_g or in the neighborhood of E'_g (see diagram in Figure 2). An intermediate position of E_m is not realizable in practice, since, in the case of equal absolute values of the partial saturation currents, the middle section of the total current-potential curve coincides with the horizontal axis and thus a definite mixed potential E_m does not exist for $i = 0$. By and large, the mixed potential lies in the neighborhood of the equilibrium potential of that system whose partner diffuses more rapidly and is, consequently, in excess at the mixed electrode (see M. Bodenstein, loc. cit., K. Bennewitz and W. Neumann, loc. cit.):

$$E_m \cong E'_g \text{ for } D_{\text{Red}'} \times v_{\text{Red}'} \times c_{\text{Red}'} > D_{\text{Ox}''} \times v_{\text{Ox}''} \times c_{\text{Ox}''} \quad (10)$$

$$E_m \cong E''_g \text{ for } D_{\text{Red}'} \times v_{\text{Red}'} \times c_{\text{Red}'} < D_{\text{Ox}''} \times v_{\text{Ox}''} \times c_{\text{Ox}''} \quad (11)$$

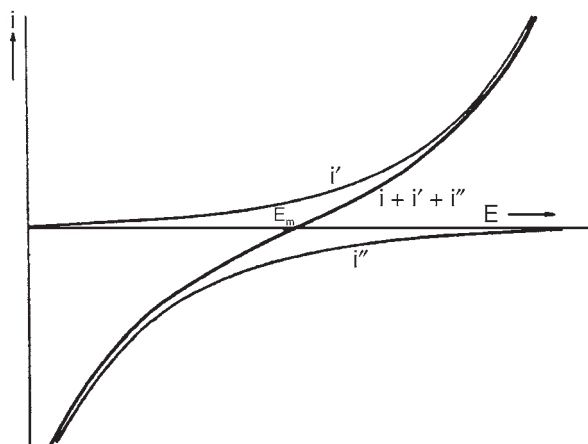


FIGURE 3. Schematic representation of the current-potential curves at a mixed electrode with activation polarization. Notation as in Figure 2.

Therefore, a jump from $E_m \cong E'_g$ to $E_m \cong E''_g$ occurs for a gradual change in the ratio of the concentrations of Red' and Ox'' if the limiting value corresponding to (11) and (12) is exceeded:

$$D_{\text{Red}'} \times v_{\text{Red}'} \times c_{\text{Red}'} = D_{\text{Ox}''} \times v_{\text{Ox}''} \times c_{\text{Ox}''} \quad (12)$$

This case is easy to understand and leads to very precise conclusions. However, if just one diffusion rate is controlling, then, by and large, it cannot be distinguished whether the redox reaction at the mixed electrode occurs by means of a sequence of electrochemical partial processes or by means of a direct chemical reaction. For this reason, both Bodenstein and Bennewitz and Neumann (loc. cit.) arrive at the conclusions stated in Equations (10), (11), and (12) without any special assumptions on the mechanism of the processes directly at the electrode surface and without using the principle of the superposition of partial current-voltage curves.

3. As a further case, we will assume that the partial current-potential curves of both redox systems are determined decisively by activation polarization without substantial polarization concentration. In this case, the following expression can be used according to Erdey-Grusz and Volmer¹⁶ and other authors:

$$i' = C' \times \left\{ \exp\left(\beta' \frac{E - E'_g}{\varepsilon}\right) - \exp\left(-\alpha' \times \frac{E - E'_g}{\varepsilon}\right) \right\} \quad (13)$$

$$i'' = C'' \times \left\{ \exp\left(\beta'' \frac{E - E''_g}{\varepsilon}\right) - \exp\left(-\alpha'' \times \frac{E - E''_g}{\varepsilon}\right) \right\} \quad (14)$$

The values C' and C'' in these equations are characteristic constants with the dimension of current; ε is an abbreviation of the factor in front of the logarithm

in the Nernst equation (see above). Moreover, α' and α'' as well as β' and β'' are dimensionless numbers between 0 and 1; in the case of an H^+ discharge, 1/2 has often been found as a special numerical value.

If E_m is far from E'_g and E''_g , or more exactly, if

$$E_m - E'_g \gg \varepsilon \quad (15)$$

$$E''_g - E_m \gg \varepsilon \quad (16)$$

(hence, $E''_g > E'_g$, i.e., the ['] system is less noble than the ['] system), then the second exponential function in Equation (8) as well as the first exponential function in Equation (9) practically vanish in the neighborhood of $E = E_m$. Figure 3 is the corresponding graphical representation. Hence, we have for the total current-potential curve:

$$i = C' \times \exp\left(\beta' \times \frac{E - E'_g}{\varepsilon}\right) - C'' \times \exp\left(-\alpha'' \times \frac{E - E''_g}{\varepsilon}\right) \quad (17)$$

If $i = 0$ and $E = E_m$ in Equation (17), we obtain a characteristic equation for the determination of the mixed potential E_m , which Bennewitz and Neumann (loc. cit.) have already given. This equation also explains the remarkably weak dependence of the mixed potential on the concentrations of the reactants and reaction products (exactly opposite to case 2).

Both terms of the right side become equal in the absence of current flow. If we polarize the mixed electrode either anodically or cathodically, then at a certain distance E_m ($|E - E_m| \gg \varepsilon$), either only the first or only the second term on the right-hand side of Equation (7) is decisive and, therefore, a linear dependence of $\log i$ as a function of E results. As Figure 4 shows, a semi-logarithmic plot can be used to determine the important quantities E_m and i' , ($E_m = i' = i''$). The linear portions of the total current-potential curves are to be extrapolated so that they intersect each other. The intercept has the meaning:

$$\log |i'| = \log |i''|, \text{ Hence } |i'| = |i''|, \text{ i.e., } E = E_m$$

We have found in the practical use of this procedure that frequently irreversible changes in the state of the electrode occur at strong polarizations so that an illustrating example cannot be presented.

4. An approximate evaluation of our Equation (17) for the total current-potential curve appears possible if the slope in the neighborhood of $E = E_m$ can be determined. Differentiation of Equation (17) yields:

$$\left(\frac{\partial i}{\partial E}\right)_{E=E_m} = \frac{C' \times \beta'}{\varepsilon} \times \exp\left(\beta' \times \frac{E_m - E'_g}{\varepsilon}\right) + \frac{C'' \times \alpha''}{\varepsilon} \times \exp\left(\alpha'' \times \frac{E_m - E''_g}{\varepsilon}\right) \quad (18)$$

Furthermore, we put $i = 0$ and $E = E_m$ in Equation (17). Then, the values of C' and C'' result from Equations (17) and (18) expressed in terms of the measurable quantities E_m and $\left(\frac{\partial i}{\partial E}\right)_{E=E_m}$. The values of C' and C'' thus obtained are substituted in Equations (13) and (14), respectively. Hence, partial currents of equal amount but opposite sign, $i'(E_m) = i''(E_m)$, at the electrically insulated mixed electrode are obtained:

$$i'(E_m) = |i''(E_m)| = \frac{E \times \frac{\partial i}{\partial E}}{\beta' + \alpha''} \quad (19)$$

If it is assumed that $\beta' = 1/2$ and $\alpha'' = 1/2$ (see above), then the denominator in Equation (19) becomes 1. This yields with Equation (3):

$$\frac{d\bar{n}}{dt} \cong \frac{\varepsilon}{F} \times \frac{\partial i}{\partial E} \text{ for } \beta' + \alpha'' \cong 1 \quad (20)$$

$$\frac{d\bar{n}}{dt} = \frac{\frac{\varepsilon}{F} \times \frac{\partial i}{\partial E}}{\alpha'' + \beta' + \left(\frac{\exp\left[-(\alpha' + \beta') \frac{E_m - E'_g}{\varepsilon}\right]}{1 - \exp\left[-(\alpha' + \beta') \frac{E_m - E'_g}{\varepsilon}\right]} \right) + \left(\frac{\exp\left[-(\alpha'' + \beta'') \frac{E''_g - E_m}{\varepsilon}\right]}{1 - \exp\left[-(\alpha'' + \beta'') \frac{E''_g - E_m}{\varepsilon}\right]} \right)} \quad (21)$$

Under the assumption that E_m lies far from E'_g and E''_g because of Equations (15) and (16), this form can be satisfactory for an order of magnitude estimate of the rate of the redox reaction, since the slope of the total current-potential curve is easy to measure while the methods suggested above (Sections 2[a] and 2[b]) can be used only under special conditions. See the results of the investigation in Section 4(c) for deviations.

A certain danger is to be noted in using Equation (20). Namely, if simultaneously $\beta' \ll 1$ and $\alpha'' \ll 1$, then the denominator in Equation (20) can assume values substantially smaller than 1, so that the simplified formula in Equation (20) yields a value of the rate of the redox reaction, which is decisively too low. This danger always exists when both concentration and activation polarization are controlling. It is easily noted that Equation (13) with $\beta' = 0$ is formally identical to Equation (8) for $v_{\text{Red}'} = 1$ and is valid for concentration polarization and, similarly, Equation (14) with $\alpha'' = 0$ is formally identical to Equation (9) for $v_{\text{Ox}''} = 1$.

If none of the exponential functions in Equations (13) or (14) can be neglected, Equation (21) follows by means of analogous intermediate computations as above.

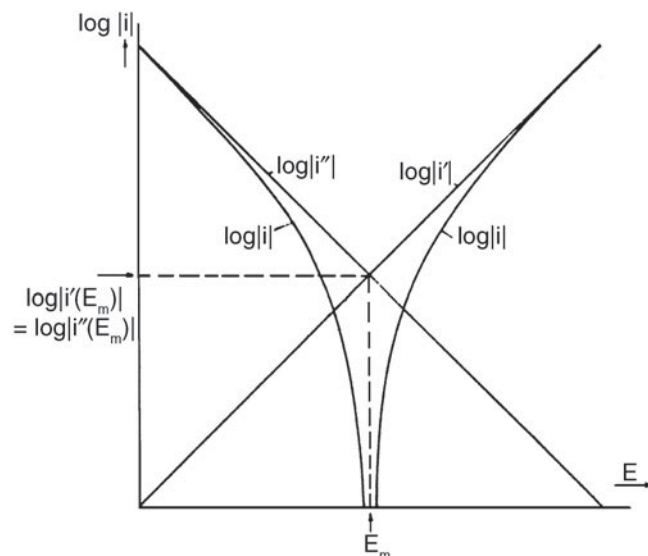


FIGURE 4. Logarithmic representation of the current-voltage curves at a mixed electrode (discharge processes determined for the polarization). Notation as in Figure 2.

This equation yields the simplified Equation (19) under the assumptions of Equations (15) and (16) or the simplified formula of Equation (7) under the assumptions $E_m - E'_g \gg \varepsilon$ and $E''_g - E_m \gg \varepsilon$.

3. THE DISSOLUTION RATE OF ZINC AMALGAM IN ACID

(a) Previous Work

The dissolution rate of amalgams in acid has already been investigated many times, above all by Fraenkel and coworkers,¹⁷ Klein,¹⁸ and Bronsted and Kan.¹⁹ It is known from these investigations that the dissolution rate of amalgams in fairly well reproducible, since a uniquely defined metal phase/acid solution interface is present. Local elements are not decisive according to the authors. In some cases (alkali and alkali earth amalgam + acid), diffusion processes are rate controlling. Fraenkel and Heinz have measured the potential during the dissolution process and have denoted it explicitly as a mixed potential, but no interpretation has yet been given in detail. Bronsted and Kane have found simple and clear-cut relations in the dissolution of sodium amalgam in buffer solutions. The dissolution rate is proportional to the square root of the Na concentration in the amalgam phase as well as a linear function of the concentration of proton donors such as C_6H_5OH or H_2PO_4 . Dronsted and Kane also assume electrochemical partial processes. In addition to the direct discharge of hydrogen ions, an electrochemical interface reaction of proton donors is supposed to occur, for example, $C_6H_5O^- + H$ (adsorbed). The dependence of the dissolution rate on the Na concentration of the amalgam phase has been in-

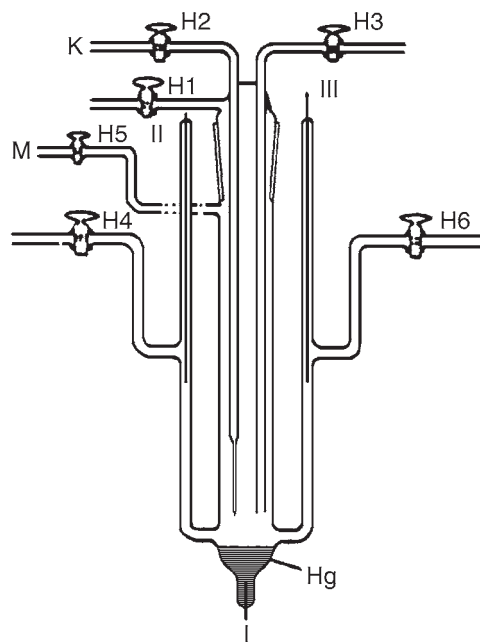


FIGURE 5. Reaction vessel for the dissolution of zinc amalgam in acid. I—Hg electrode. II and III—Ag/AgCl electrodes. K—Capillary to admit hydrogen. M—Open H₂O manometer with a separating stopcock; H1, H2, etc. stopcocks.

terpreted quantitatively by Frumkin.²⁰ In our notation, Frumkin sets the mixed potential E_m equal to the Na equilibrium potential. A change in the Na concentration of 10, therefore, means a shift in the potential of about 0.058 V. Furthermore, it is known from the work on the hydrogen overvoltage on mercury²¹ that a potential shift of 0.058 V corresponds to only about half a power of 10 of the current for cathodic H₂ development. Hence, a change in the Na concentration of one power of 10 corresponds to a change in the dissolution rate by about half a power of 10 if a single-valued relation between current and potential holds in accordance with the electrochemical working hypothesis, i.e., the dissolution rate is proportional to the square root of the Na concentration in the amalgam phase.

b) Plan and Method of the Experiments

The working hypothesis of the superposition of electrochemical partial processes was verified indirectly using the results obtained by Bronsted and Kane. The method outlined in Section 2 is to be used for direct proof. The following measurements are necessary:

1. The current-potential curve for the cathodic H₂ development from acid with Hg as electrode and without the presence of Zn or Zn²⁺ in the solution.
2. The current-potential curve for the process Zn (dissolved in Hg) = Zn²⁺ + 2e⁻ in a solution with the lowest possible acid concentration.
3. The potential and the reaction rate in the Zn-amalgam + Zn-salt solution system.

The following points were decisive for the choice of the composition of the electrolyte. An undistorted superposition of the partial current-potential curves of the individual systems is to be expected only if the electrolytic double layer at the metal solution interface is not altered substantially.²² Consequently, a total concentration of the monovalent cations [H⁺] + [K⁺] = 1.0 and a total concentration of the divalent cations [Ca²⁺] + [Zn²⁺] = 1.0 mol/L was used in all experiments (hence, [Cl⁻] = 3.0 mol/L is the anion concentration). The higher the H⁺ concentration in an experiment, the lower the K⁺ concentration; the higher the [Zn²⁺], the lower the [Ca²⁺].

All measurements were made in the vessel shown in Figure 5 in a thermostat at 25°C.

An appropriate quantity of mercury was weighed out as electrode I (surface: ~2.5 cm²; Hg purified by passage of air by means of a glass frit-gas distribution tube from Fa. Schott and Gen., filtration, and vacuum distillation). Then, the electrolyte for the determination of the current-potential curve for cathodic H₂ development without the presence of Zn or Zn²⁺ was poured in up to the stopcocks H4 and H6. The ground cap was greased slightly only in the upper part in order to avoid contamination of the system. The vessel was evacuated through stopcock H1 (the remaining stopcocks closed) and pure hydrogen was admitted through H₂. This procedure was repeated many times in order to remove residual air. Simultaneously, the air in the manometer M beneath stopcock H5 was also removed by means of flushing with H₂. In order to remove the rest of the oxygen and the Hg-salts in the solution, the Hg-electrode I was made a cathode with a current of about 10⁻³ A for several hours. The current was varied between 10⁻³ A and 10⁻⁶ A for the determination of the current-potential curves (first with decreasing, then with rising current within the Ag/AgCl^{II} electrode as anode; current supply from a 16-V battery with a resistance of 10⁴ Ω to 10⁷ Ω in series; current measurements by means of a reflecting galvanometer + shunt). The potential of the Hg-electrode I relative to the Ag/AgCl-electrode III was measured with the acid of a compensating potentiometer. The vessel was shaken in the same way as in the rate measurements (see below). The current-potential curves were determined with the same mercury charge for solutions involving various H⁺-concentrations. In conclusion, the first solution was sometimes again investigated in order to check the constancy of the surface condition of the mercury.

For further investigations, the solution was spilled out through stopcock H3 and zinc amalgam was prepared directly in the reaction apparatus (saturated ZnSO₄ solution as electrolyte, a zinc rod as anode). Current-potential curves for the process Zn (dissolved in Hg) = Zn²⁺ + 2e⁻ in an acetate solution buffer were determined with this zinc amalgam. In this buffer the dissolution of zinc under H₂ solution is negligible.

Then, the same solution as for the determination of the hydrogen overvoltage curves was poured in with the addition of ZnCl_2 and a correspondingly lower concentration of CaCl_2 , and the air was replaced by hydrogen as before. The rate of H_2 evolution was determined with the help of the open H_2O -manometer M (Figure 5) as a measure of the rate of the reaction $\text{Zn} + 2\text{H}^+ = \text{Zn}^{++} + \text{H}_2$. The same readings were taken at a twin vessel with the same dimensions in order to eliminate external pressure changes as well as eventual temperature fluctuations. The difference in both the manometer readings is decisive for the actual rate; a 1-mm shift of the H_2O meniscus on one side corresponded to an evolution of 0.82×10^{-6} mol $\text{H}_2 = 1.64 \times 10^{-6}$ equivalent. The reaction vessel and the twin vessel were shaken back and forth horizontally over 9 cm 30 times per minute in order to accelerate the gas liberation from the solution. Values obtained during the first hours were rejected until a steady state had satisfactorily been reached. The concurrent concentration changes of the amalgam and electrolyte were practically negligible. Simultaneously, the potential of electrode I was measured in a compensation circuit vs. the reference electrode III. Rate measurements were carried out with the same amalgam filling in solutions of different H^+ and Zn^{++} concentrations. Finally, the first solution was investigated again as a check. In some cases, furthermore, the total current-potential curve for the mixed electrode was determined with the circuit already described above.

c) Experimental Results

Figure 6 and Table 1 give a selection of the experimental results; parallel experiments gave practically the same results.

Essentially, a linear relation between $\log i$ and E , as shown in Figure 6, was obtained for the current-potential curves for hydrogen evolution, which is in agreement with the results of Tafel, Baars, Erdey-Grusz and Volmer, Bowden, St. von Naray-Szabo, Lewina and Sarinsky,²¹ etc. A simple law for the dependence on hydrogen ion concentration was not obtained (see also Section 3[d]).

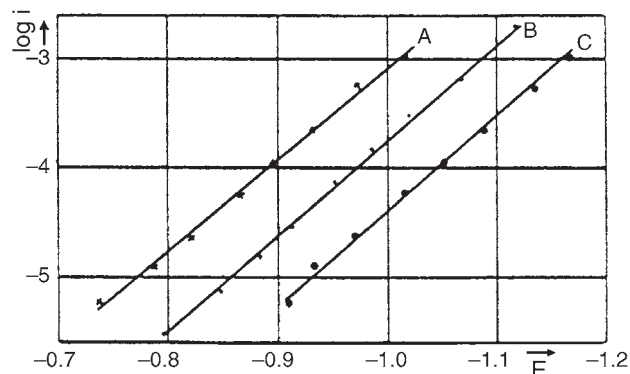


FIGURE 6. Current-potential curves for the cathodic H_2 evolution on mercury electrolyte: (a) \times 1.0 M CaCl_2 + 1.0 M HCl . (b) \bullet 1.0 M CaCl_2 + 0.1 M HCl + 0.9 M KCl . (c) \circ 1.0 M CaCl_2 + 0.01 M HCl + 0.99 M KCl . E is the potential of the mercury vs. the Ag/AgCl reference electrode.

The potential E of the mixed electrode can be called the Zn-equilibrium potential E'_g in practice, since the partial current-potential curve for the process Zn (dissolved in Hg) = $\text{Zn}^{++} + 2e^-$ (in an acetate buffer) is as extraordinarily steep as the total current-voltage curve (Figure 7) and, hence, the change in potential amounts to only a few millivolts even at the highest values of i' (E_m). Moreover, the changes in $E_m = E'_g$ correspond to the requirements of the Nernst formula if the Zn concentration in the amalgam and the Zn^{++} concentration in the solution is changed. The H^+ concentration is without an essential influence, except in 1.0 m HCl (a change in the activity coefficient with the transition from 0.9 m KCl + 0.1 m HCl to 1.0 m HCl).

The current i' (E_m) corresponding to the mixed potential E was interpolated from the measured current-potential curves and the equivalent rate of H_2 evolution was calculated using Equation (3). (Column 8 of Table 1 calculated for time in hours). These values are, in general, in good agreement with the observed rates (column 7 of the Table 1). The assumption of an undistorted superposition of the current-

TABLE 1
Dissolution of Zinc Amalgam in Acid

No. 1	Wt% Zn in Hg 2	$[\text{H}^+]$ 3	$[\text{Zn}^{++}]$ 4	E_m 5	$i'' (E_m)$ 6	Rate (Equiv./h)	
						Observed 7	Calculated 8
1	0.4	0.10	0.10	-1.023	3.2×10^{-4}	1.23×10^{-5}	1.19×10^{-5}
2	0.4	0.01	0.10	-1.023	0.63×10^{-4}	0.25×10^{-5}	0.23×10^{-5}
3	0.4	0.10	0.01	-1.051	6.0×10^{-4}	2.40×10^{-5}	2.24×10^{-5}
4	0.4	0.10	0.10	-1.023	3.2×10^{-4}	1.15×10^{-5}	1.19×10^{-5}
5	1.6	0.10	0.10	-1.041	4.9×10^{-4}	1.81×10^{-5}	1.83×10^{-5}
6	1.6	0.01	0.10	-1.041	0.87×10^{-4}	0.36×10^{-5}	0.32×10^{-5}
7	1.6	0.10	0.01	-1.067	8.7×10^{-4}	3.00×10^{-5}	3.24×10^{-5}
8	1.6	1.00	0.10	-1.038	14.4×10^{-4}	5.67×10^{-5}	5.36×10^{-5}
9	1.6	0.10	0.10	-1.041	4.9×10^{-4}	1.81×10^{-5}	1.83×10^{-5}

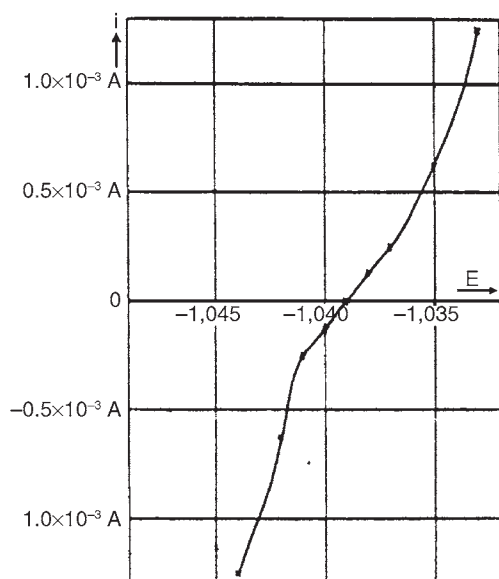


FIGURE 7. Total current-potential curve of a mixed electrode (1.6% by weight Zn in Hg; electrolyte: 0.9 M CaCl₂ + 0.1 M HCl + 0.9 M KCl) (Potential *E* vs. the Ag/AgCl reference electrode).

potential curves of the individual systems is confirmed to hold. The reaction rate of the overall $\text{Zn} + 2\text{H}^+ = \text{Zn}^{2+} + \text{H}_2$ can be described quantitatively with the aid of the superposition of the electrochemical partial processes (1) and (2).

d) Dissolution Rate of Zinc Amalgam as a Function of the Concentrations of the Reactants

As already mentioned, the potential of the mixed electrode is essentially equal to the zinc equilibrium potential, i.e., is given by:

$$E = E_0(\text{Zn in Hg, Zn}^{2+}) + \frac{RT}{2F} \ln \frac{[\text{Zn}^{2+}]}{[\text{Zn (in Hg)}]} \quad (22)$$

Here, $E_0(\text{Zn in Hg, Zn}^{2+})$ is the standard electrode potential for $[\text{Zn}^{2+}] = 1$ and $[\text{Zn (in Hg)}] = 1$.

Furthermore, the following approximation can be made for the hydrogen current-potential curve according to Equation (14) with $\alpha'' = 1/2$ and for $-(E - E'_g) \gg \epsilon$:

$$i'' = C \times [\text{H}^+] \times e^{-\frac{1}{2} \times \frac{EF}{RT}} \quad (23)$$

The proportionality between the current intensity *i* and the hydrogen ion concentration H^+ has been established theoretically by Frumkin²³ and experimentally by Lewina and Sarinsky.²⁴ This relation, however, holds only if changes in the potential difference across the diffused double layer are avoided by a sufficient excess of an inert-supporting electrolyte. This condition is not entirely realized in our investigations. Especially recommended is the addition of electrolytes with trivalent cations, for example, LaCl₃ according

to Lewina and Sarinsky. Substitution of Equation (22) into Equation (23) gives the partial current of the hydrogen evolution at the mixed electrode, hence the rate according to Equation (3):

$$\frac{d\bar{n}}{dt} = [\text{H}^+] \times \sqrt[4]{\frac{[\text{Zn (in Hg)}]}{[\text{Zn}^{2+}]}} \times \left\{ \frac{C}{F} \times \exp\left(-\frac{E_0(\text{Zn in Hg, Zn}^{2+}) \times F}{2RT}\right) \right\} \quad (24)$$

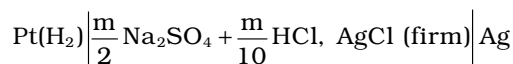
The dependence thus established for the rate as a function of the concentrations of the reactants is only reached approximately in our investigations, since the assumption $\alpha'' = 1/2$ as well as the assumption of a proportionality between *i* and H^+ is satisfied only approximately.

4. THE REACTION BETWEEN HYDROGEN AND OXIDIZING AGENTS AT PLATINUM

a) Experimental Method

A very weakly platinized platinum sheet (4 by 4 cm² with a total surface of 32 cm²) was placed in a solution with a definite H^+ concentration (0.5 m: Na₂SO₄ + 0.1 m HCl, i.e., an HSO₄⁻/SO₄²⁻ buffer). This solution contains H₂ on the one hand (corresponding to $P_{\text{H}_2} = 1$ atm in the gas phase) and an oxidizing agent on the other hand, either persulfate or nitrobenzol or arsenic acid. The platinum electrode and the solution are in the vessel shown in Figure 8, which is shaken in a thermostat at 25°C in order to have a H₂ equilibrium between the gas phase and the solution. The H₂ consumption by reduction of the oxidizing agent (catalyzed by Pt) is read at the open H₂O manometer M. Corresponding readings on a twin vessel were taken as in Section 3(b) to eliminate changes in external pressure; a 1-mm shift of the H₂O meniscus on one side corresponded to 1.06×10^{-6} mol/H₂, which equals 2.12×10^{-6} equivalents.

Furthermore, two Ag/AgCl electrodes are in the test apparatus, one of which is the counter electrode in the polarization of the Pt electrode while the other is used as the reference electrode for the potential measurements of the Pt electrode. The (emf) of the cell:



under equilibrium conditions was determined to -0.403 V at 25°C.

b) Rate Measurements at an Insulated Electrode and an Electrode to Which the Hydrogen Equilibrium Potential Is Enforced

The rate at an insulated Pt electrode and the rate for an applied hydrogen equilibrium potential E'_g were

measured in correspondence with the procedure outlined in Section 2(a). The current intensities necessary for the polarization are relatively low (Table 2). We are convinced, in view of auxiliary experiments and calculations, that no essential depletion of the oxidizing agent occurs at the Pt/solution interface. As Table 2 shows, the rate of H_2 consumption is zero within the limits of error if the hydrogen equilibrium potential shift less than E'_g is enforced (manometer shift less than 1 mm in 4 h for No. 1 or in 10 h for Nos. 2 and 3). Hence, it follows that hydrogen consumption under our conditions results essentially by electrochemical partial processes.

c) Investigation to Calculate Rates from the Slope of the Total Current-Potential Curves

Furthermore, the slope of the total current-potential curve at $E = E_m$ was determined for the above-mentioned hydrogen + oxidizing agent system (current supplied from a 16-V battery with a $10^4 \Omega$ to $10^7 \Omega$ shunt; potential measurements of the Pt electrode I vs. the Ag/AgCl reference electrode III). Although we went only to a maximum deviation of $E - E_m = 0.025$ V in determining the slope of the total current-potential curve, polarization potentials tended to definite values only with great delay. Extrapolation to a definite initial value does not appear to be possible. Therefore, all the potential readings were taken after a flow of current lasting 3 min when a certain terminal state was reached. As Table 3 shows, the exchange calculated using Equation (20) as an approximation is in agreement with the exchange found experimentally in order of magnitude. The values found experimentally lie about half a power of ten higher. According to the results of Section 4(b), the superposition principle of partial current-potential

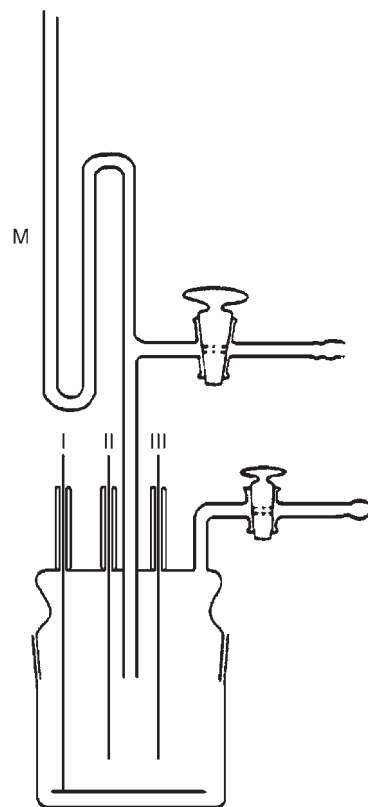


FIGURE 8. Reaction vessel for the reaction between hydrogen and oxidizing agents. I Pt electrode, II and III Ag/AgCl electrodes; M open H_2O manometer.

curves is indeed not to be doubted. The deviations between the calculations and the direct experimental results can possibly be related to the gradual time adjustment of the polarization potential (corresponding to a change in the surface state of the Pt electrode?).

TABLE 2

Measurements of the Reaction Rate Between Hydrogen and Oxidizing Agents for an Insulated Electrode and at an Applied Hydrogen Equilibrium Potential E'_g (25°C). Buffer Mixture: $m/2 Na_2SO_4 + m/10 HCl$

No.	Oxidizing Agent	$E_m - E'_g$ Volt	Rate of H_2 Consumption for $E = E_m$ (Equiv/s)	Average Current for Polarization at $E = E'_g$	Rate of H_2 Consumption for $E = E'_g$
1	$m/100 K_2S_2O_8$	0.60	7×10^{-9}	6.4×10^{-3}	$<0.14 \times 10^{-9}$
2	$m/100 C_6H_5NO_2$	0.36	1.2×10^{-9}	1.7×10^{-3}	$<0.06 \times 10^{-9}$
3	$m/100 H_3AsO_4 + m/100 As_2O_3$	0.32	0.6×10^{-9}	5.5×10^{-5} to 0.5×10^{-5}	$<0.06 \times 10^{-9}$

TABLE 3

Investigation to Calculate the Reaction Rates of Hydrogen and an Oxidizing Agent from the Slope of the Total Current-Voltage Curve (25°C). Buffer Mixture: $m/2 Na_2SO_4 + m/10 HCl$

No.	Oxidizing Agent	$E_m - E'_g$ Volt	$\frac{dI}{dE}$ for $E = E_m$ (Amp/Volt)	Reaction Rate in Equiv./s	
				Observed	Calculated ¹⁹
1	$m/100 K_2S_2O_8$	0.60	0.010	8×10^{-9}	2.6×10^{-9}
2	$m/100 C_6H_5NO_2$	0.36	0.0011	1.2×10^{-9}	0.3×10^{-9}
3	$m/100 H_3AsO_4 + m/100 As_2O_3$	0.32	0.0004	0.6×10^{-9}	0.15×10^{-9}

TABLE 4

Potential Changes of a Hydrogen Electrode in the Presence of H_2S and O_2 (25°C). Electrolytic Hydrogen Freed from O_2 Over Copper at 950°C; the Hydrogen Stream was Charged in a Wash Flask with a H_2S Buffer Mixture of 0.5 M $B(OH)_3$ + 0.25 M Na_2S with about 1% H_2S ; O_2 from an Electrolyzer. 12-h Waiting Time for Each Potential Value. E = Potential Difference of the Pt Electrode vs. a $Ag/AgCl$ Reference Electrode.

% O_2	Electrolyte: m/1 HCl		Electrolyte: 0.0267 m KH_2PO_4 + 0.04 m Na_2HPO_4 + m/10 KCl (pH = 6.97)	
	E without H_2S	E with 1% H_2S	E without H_2S	E with 1% H_2S
0.00	-0.356	-0.356	-0.693	-0.693
0.25	-0.235	-0.114	-0.344	-0.400
0.50	-0.188	-0.076	-0.275	-0.361
0.75	-0.149	-0.068	-0.256	-0.351
1.00	-0.119	-0.065	-0.256	-0.347

5. REMARKS ON THE CONTAMINATION OF THE HYDROGEN ELECTRODE

It is known that the establishment of the equilibrium potential at a hydrogen electrode is disturbed by a great number of substances (for example, H_2S , As_2O_3). Many times a "poisoning" of the electrode is spoken of.²⁵ This way of expression (by analogy with heterogeneous catalysis) leads to the conception that the poisons work by covering the electrode surface or, at least, the active sites. Hence, the reaction rates can indeed be diminished; however, the shift of a true equilibrium condition is not possible. The well-known "poisons" are partially typical oxidizing agents (for example, O_2 , Fe^{+++} , Hg^{++} , I_2) or reducing agents (for example, SO_2). In this case, a typical mixed potential is obtained instead of the hydrogen equilibrium potential of which the examples in Section 4 are proof.

The interpretation of contamination by substances such as H_2S and As_2O_3 is somewhat different. A.H.W. Aten and coworkers²⁶ have shown that an electrode with pure hydrogen still shows an equilibrium potential in the presence of As_2O_3 while deviations occur in the presence of oxygen. However, for equal oxygen concentrations, deviations from the equilibrium potential are considerably greater in the presence of As_2O_3 than without As_2O_3 . Starting from the concept of Tafel²⁷ on the overvoltage ($2H \rightarrow H_2$ process time-determined for a cathodic hydrogen production), Aten and his coworkers assumed that the presence of As_2O_3 strongly delays the $H_2 \rightarrow 2H$ process while the reaction between H and O_2 is influenced less, i.e., the stationary concentration in the H atoms is decreased on the electrode surface and the potential is shifted toward the positive side according to the general Nernst formula.

We have been able to supplement the observations by Aten and coworkers with H_2S as a contaminating substance. A thinly platinized sheet shows the same potential in H_2 (pure) as in $H_2 + 1\% H_2S$. An increase in the potential in both H_2 and $H_2 + 1\% H_2S$ results from the addition of oxygen. Details of the

measurements are shown in Table 4. Especially notable is that the presence of H_2S in a chloride solution amplifies the potential shift due to the presence of O_2 and weakens it, however, in a phosphate buffer.

In the sense of our general representation, we give the following limiting cases for the interpretation of the increase in the mixed potential E_m by means of the nonoxidizing substances such as As_2O_3 and H_2S , the O_2 concentration being held constant.

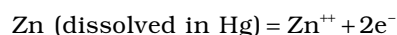
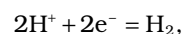
1. The addition of the poison lowers the slope of the hydrogen current-potential curve (for example, by covering especially active centers) while the oxygen current-voltage curve is not changed essentially. The changes in the slope of the hydrogen current-voltage curve for the addition of As_2O_3 have been proven by the detailed investigations of Volmer and Wick.²⁸

2. The addition of poison raises the slope of the oxygen current-voltage curve (catalysis of the gross process $O_2 + 4H^+ + 4e^- = 2H_2O$) while the hydrogen current-voltage curve is not shifted essentially.

The first limiting case corresponds to the Aten interpretation if we disregard details of the mechanism. The second limiting case is a new possibility, which has a certain probability, especially for H_2S contamination; thus, H_2S can be oxidized to H_2S_2 by means of the O_2 , and this substance can enter into the electrochemical reaction as an oxidizing agent at a higher rate than the O_2 .

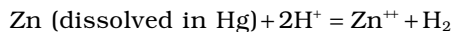
CONCLUSIONS

❖ Dissolution of a metal (for example, zinc amalgam) solution in acid is possible without local elements in which the cathodic and anodic partial processes:



follow each other in steady rotation with a random distribution of site and time of the individual process. The behavior of the hydrogen-zinc amalgam mixed electrode can be interpreted quantitatively by means

of an undistorted superposition of partial current-potential curves. The rate of the reaction:



can be calculated in advance from the electrode potential and the current-voltage curve for cathodic H₂ evolution. A comparison between calculated and observed rates gives a satisfactory agreement.

❖ A platinum sheet exposed simultaneously to hydrogen and an oxidizing agent (persulfate or nitrobenzol or arsenic acid) is generally not in complete equilibrium. The hydrogen is slowly oxidized to H₂O and the oxidizing agent is reduced. Hence, there results a so-called mixed potential of the second redox system. If the electrode is polarized to the hydrogen equilibrium potential by means of an external current supply, then the rate of hydrogen consumption is zero within the limits of error. Hence, it follows that the reaction between hydrogen and the oxidizing agent proceeds essentially by virtue of electrochemical partial processes. The general behavior of such a mixed electrode can be described by means of the superposition of partial current-potential curves of the individual redox systems. The potential of the mixed electrode without external current is given entirely by the condition that the anodic partial current should equal the cathodic partial current.

❖ Under certain assumptions on the shape of the partial current-potential curves the rate of the reaction between different redox systems at a mixed electrode can be determined approximately from the total current-potential curve and especially from the slope.

❖ The potentials of contaminated hydrogen electrodes are to be interpreted as mixed potentials.

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