This paper is in a collection of

"Historic Publications in Electrochemistry"

which is part of

Electrochemical Science and Technology Information Resource (ESTIR)

(http://electrochem.cwru.edu/estir/)

JOURNAL of the Electrochemical Society

WA



Volume 104, Nos. 1-12 January-December 1957

Published by THE ELECTROCHEMICAL SOCIETY, INC. 1860 Broadway, New York 23, N. Y. aqueous reaction to form the hydrated fluorides which are subsequently dehydrated at elevated temperatures in an atmosphere of HF gas. Extensive studies were made of the conditions for the preparation of high-purity ZrF_4 , and pilot plant equipment is described which was used to prepare 100 lb batches of the fluorides.

The reduction step was investigated thoroughly, particularly for Zr, and those factors which affect metal quality and yield were determined. Reduction yields of 96% were obtained with both Zr and Hf. After arc-melting, the sponge Zr had a hardness of 40-45 Rockwell A and was readily cold-rolled into sheet. Zr metal thus prepared had a purity of about 99.8%.

Hf metal, similarly prepared, had a hardness of 69 Rockwell A and was hot-rolled but was too brittle to be easily cold worked. The Hf was low in metallic impurities, but contained considerable amounts of C, N, and oxygen.

ACKNOWLEDGMENTS

The authors are especially grateful to J. W. Starbuck for his valuable contribution in the experimental reduction studies, to B. A. LaMont and co-workers for the chemical analyses, and to C. Lentz and associates for the spectrographic analyses.

Manuscript received February 23, 1956. Contribution No. 480. Work was performed in the Ames Laboratory of the A.E.C.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1957 JOURNAL.

REFERENCES

- 1. K. A. WALSH, U. S. A.E.C. Report No. AECD-3640,
- 2. D. PETERSON AND H. A. WILHELM, Unpublished work, Ames Laboratory, Iowa State College, (1950). 3. F. J. LAMBERT, P. J. HAGELSTON, AND R. O. HUTCHI-
- son, Oak Ridge National Lab. Report No. Y-595, (1950)
- 4. J. L. WILLIAMS AND B. WEAVER, U. S. A.E.C. Report No. AECD-3329, (1950).
- 5. M. U. COHEN, Rev. Sci. Instr., 6, 68, (1936).
- 6. R. M. TRECO, J. Metals, 5, 344, (1953). 7. R. A. FOOS AND H. A. WILHELM, U. S. A.E.C. Report ISC-693, (1956).

Electrochemical Polarization

I. A Theoretical Analysis of the Shape of Polarization Curves

M. STERN AND A. L. GEARY

Metals Research Laboratory, Electro Metallurgical Company, A Division of Union Carbide and Carbon Corporation, Niagara Falls, New York

ABSTRACT

At low overvoltage values, deviations from Tafel behavior for a noncorroding electrode are due primarily to the reverse reaction of the oxidation-reduction system, and at high overvoltages to concentration and/or resistance polarization. It is shown further that the practice of placing straight lines through a few experimental points is extremely hazardous, while the indiscriminate introduction of "breaks" is contrary to the electrode kinetics described.

Further complexities arising from a corroding electrode are described. In this instance, the forward and reverse reactions of both of the oxidation-reduction systems forming the corrosion couple must be considered. This representation of the local polarization diagram of a corroding metal is more fundamental than that used previously in the literature, and thus provides a clearer picture of the various factors which affect the corrosion rate and the shape of polarization curves.

A region of linear dependence of potential on applied current is described for a corroding electrode by treating it in a manner analogous to that for a noncorroding electrode. An equation is derived relating the slope of this linear region to the corrosion rate and Tafel slopes. This relation provides an important new experimental approach to the study of the electrochemistry of corroding metals since, in some instances, interfering reactions prevent determination of Tafel slopes at higher current densities.

Polarization measurements are an important research tool in investigations of a variety of electrochemical phenomena. Such measurements permit studies of the reaction mechanism and the kinetics of corrosion phenomena and metal deposition. In spite of their wide applicability and extensive use, considerable uncertainty in the interpretation of polarization measurements still exists. Some of the uncertainties include the proper method of plotting

data and the correct interpretation of "breaks" in polarization curves. Abrupt changes in slope of overvoltage vs. log current have been given considerable significance in the past few years. Logan (1) examined various methods of plotting cathodic polarization measurements to evaluate the correspondence between current required for complete cathodic protection of a system and current flow at the potential break. He reported that the potential break

method indicated a different current requirement than that indicated by other criteria. In addition, breaks could be obtained regardless of whether the potential was plotted as a linear or logarithmic function of applied current. However, examination of the data presented indicates that there is no real experimental evidence pointing toward existence of breaks. In most cases, the plots would best have been considered smooth curves rather than a series of straight lines. Schwerdtfeger and McDorman (2) presented a theory which permitted calculation of the corrosion rate of a metal from its polarization characteristics. The calculation was based on plotting both anodic and cathodic polarization as linear functions of current and using currents at the potential "breaks" in a formula derived essentially from trigonometric considerations. Again, however, experimental evidence for the existence of breaks was not clear-cut. Still another discussion of potential "breaks" was presented recently by Johnson and Babb (3) who used irreversible thermodynamics to derive Pearson's (4) equation for the relation between the corrosion current and potential breaks. Data presented by these investigators for the corrosion of Fe in KCl solutions indicate that a great deal of imagination must be used when drawing the curves in order to obtain "breaks".

Changes in slope rather than a sharp break can be obtained in H activation overvoltage measurements as a result of the H being discharged by two different ratedetermining reactions. Parsons (5) discussed a dual mechanism of H discharge and from energy considerations calculated the potential ranges where more than one ratedetermining step might be expected. However, he did not imply that a "break" should be found. Bockris and Conway (6) found the cathodic overvoltage vs. $\log i$ plots for Ag in 0.1-7.0N HCl solutions showed a marked change in slope at current densities which depended on acid concentration. They attribute the change in slope to a change in symmetry of the energy barrier at the electrode interface rather than to a dual discharge mechanism. Here again a sharp break was not found, the two linear portions of the plot being connected by a curve over a short range of overvoltage values.

The purpose of this discussion is to analyze the shape of polarization curves in terms of modern concepts of electrochemistry. It is shown that many of the reported breaks in polarization curves are not real, and result either from attempts to apply activation overvoltage theory to data obtained under conditions where other types of overvoltage are included in the measurements, or from a combination of insufficient data and an erroneous assumption that a break must exist. In such a presentation, it is convenient to consider first the shapes of polarization curves for a noncorroding electrode, then to extend the analysis to include further complexities which arise from local action currents.

A NONCORRODING ELECTRODE SYSTEM

Consider a substance Z in a solution containing its ions $Z^{+,1}$ In such a system at equilibrium, the rate of oxidation

¹ This might be Cu in equilibrium with Cu⁺. The same analysis also applies to an inert electrode in an oxidationreduction system such as Pt in a ferrous-ferric solution or in a reducing acid solution saturated with H gas.



FIG. 1. Relationship between overvoltage and current for the anodic and cathodic reactions of a single electrode system.

of Z is equal to the rate of reduction of $Z^+(Z^+ + e \leftrightarrows Z)$. The reaction rate and current flow are directly related according to Faraday's Law. If $\overline{\imath}_z$ is defined as the current in the forward (reduction) direction $(Z^+ + e \rightarrow Z)$ and $\overline{\imath}_z$ as the current in the reverse (oxidation) direction $(Z \rightarrow Z^+ + e)$, the electrode equilibrium may be expressed in the form

$$\vec{\imath}_z = \vec{\imath}_z = i_{o,z} \tag{I}$$

where $i_{o,z}$ is commonly called the exchange current. When the reaction rate is controlled by a slow step requiring an activation energy, the dependence of current on overvoltage may be expressed as²

$$\vec{\imath}_z = i_{o,z} \exp\left(-\frac{\eta}{\beta'_z}\right)$$
(II)

$$\bar{\imath}_z = i_{o,z} \exp\left(+\frac{\eta}{\beta_z''}\right)$$
(III)

where the overvoltage, η , is the difference between the potential of the working electrode and the equilibrium potential of the reaction being studied, and β'_z and β''_z are constants. For a system with a symmetrical energy barrier at the electrode interface, β'_z is equal to β''_z . Therefore, Eq. (II) and (III) may be written as

$$\eta = -\beta_z \log \frac{\dot{t}_z}{\dot{t}_{o,z}} \,. \tag{IV}$$

$$\eta = +\beta_z \log \frac{\bar{i}_z}{i_{o,z}} \tag{V}$$

where $\beta_z = 2.3 \ \beta'_z = 2.3 \ \beta''_z$.

To aid in visualizing the relations given by Eqs. (IV) and (V), they have been plotted on Fig. 1 by arbitrarily giving β_z a value of 0.100 v and $i_{o,z}$ a value of 1.0 μ a. These

² Other investigators have expressed these equations in more fundamental terms. They are simplified here in order not to detract from the main purpose of the discussion. Excellent literature reviews and discussions on the subject are presented by Bockris (7, 8) and Vetter (9).

are of the same order of magnitude commonly found by experiment; exchange current values generally vary from 10^{-4} to 100 μ a and β values from 0.03 to 0.30 v.

Fig. 1 illustrates the relationship between the oxidation and reduction rates and the exchange current at the equilibrium potential and the effect of overvoltage on these rates. When the electrode equilibrium is disturbed by external polarization, the reaction rates change in accord with the curves in Fig. 1. Experimentally, however, the individual oxidation or reduction rates cannot be measured. The external current used for polarization actually is a measure of the difference between the two rates. For example, if the electrode under discussion (Fig. 1) is cathodically polarized from its equilibrium potential to an overvoltage of -0.1 v, the rate of reduction is equivalent to 10 μ a while the rate of oxidation is $0.1 \ \mu a$. The external current required to polarize to this potential is the difference between i_z and i_z , or 9.9 μa . If the absolute difference between the forward and the reverse reaction currents is defined as i_x so that

$$\vec{i}_z - \vec{i}_z = \vec{i}_x \tag{VI}$$

then $\bar{\imath}_x$ is the external cathodic current when the electrode is polarized to some overvoltage value, η . It is evident that $\bar{\imath}_x$ approaches $\bar{\imath}_z$ at overvoltage values sufficiently removed from the reversible potential. It is important to emphasize again that experimentally the only factors measured directly are η and $\bar{\imath}_x$ or $\bar{\imath}_x$. The individual rate of oxidation or reduction cannot be measured. Although theory shows that there is a linear (Tafel) relationship between η and log $\bar{\imath}_z$ or log $\bar{\imath}_z$, only η vs. log $\bar{\imath}_x$ is measured and plotted. Therefore, substituting Eq. (VI) in Eq. (IV), the theoretical relationship between overvoltage and the logarithm of the external cathodic current is obtained.

$$\eta = -\beta_z \log \frac{\vec{i}_x + \vec{i}_z}{i_{o,z}}$$
(VII)

Using the same arbitrary values for the constants β_z and $i_{o,z}$ as indicated previously, and knowing the relation between η and $\bar{\imath}_z$ (Eq. V), a plot of the variation of η with log $\bar{\imath}_x$ may be constructed. This is shown in Fig. 2.³ Note that deviation from a Tafel slope exists at the low values of applied current. Only when the reverse (oxidation) current, $\bar{\imath}_z$, becomes insignificant in comparison to the forward or reduction current can a true Tafel relation be expected. Further, Tafel slopes cannot be obtained until applied currents reach magnitudes of several times $i_{o,z}$. If it is assumed that experimental verification of a linear relationship between η and log $\bar{\imath}_x$ requires linearity over a range of about two logarithmic cycles of current, reliable estimates of the Tafel constants β_z and $i_{o,z}$ require measurements in the region of 1000 times $i_{o,z}$.

³ Points shown on this figure and all subsequent figures are not experimental. They are calculated from the derived equations and are included to illustrate the need for considerable data to define accurately the shape of a polarization curve. It is quite evident, on inspection of several of the figures, that insufficient data might lead to a series of straight lines.





FIG. 2. Relationship between overvoltage and applied cathodic current for a single electrode system.



FIG. 3. Effect of concentration polarization on the relationship between overvoltage and applied cathodic current for a single electrode system.

The measurement of activation overvoltage may be complicated by two interfering phenomena—concentration polarization and resistance drop effects—when the value of the exchange current is large. Concentration polarization occurs when the reaction rate or the applied external current is so large that the species being oxidized or reduced cannot reach the surface at a sufficiently rapid rate. The solution adjacent to the electrode surface becomes depleted of the reacting ions, and the rate then is controlled by the rate at which the reacting species can diffuse to the surface. The electrode potential changes sharply in this region until a potential is reached where a new reaction proceeds. The change in potential caused by

ment of the slope of η vs. log i_x in the Tafel region, while $i_{o.x}$ is found by extrapolation of the Tafel region to the reversible potential.

Vol. 104, No. 1

$$\eta_{\text{conc.}} = 2.3 \frac{RT}{n\mathbf{F}} \log \frac{i_L - \bar{i}_z}{i_L}$$
 (VIII)

where i_L is the limiting diffusion current for the forward reaction, R the gas constant, T the absolute temperature, and \mathbf{F} Faraday's constant. When i_z approaches 0.1 i_L , concentration polarization starts to become significant experimentally. The shape of a curve, including both activation and concentration polarization, is illustrated in Fig. 3. For the purpose of this illustration, i_L has arbitrarily been selected as 5000 μ a. The limiting diffusion current is a function of the concentration of the reacting species, the stirring rate of the solution, and all the other factors which influence the maximum rate at which an ion can approach a surface.⁶

Examination of Fig. 3 shows that deviation from Tafel behavior caused by concentration polarization is guite marked and illustrates the difficulties in overvoltage measurements when working near the limiting diffusion current. Note that it would be quite convenient to separate an experimental curve of this type into at least three distinct straight line regions and then to attempt to interpret the breaks theoretically. Such complicating interpretations are obviously unnecessary. Stern (13) illustrated the interference which occurs when H overvoltage measurements are conducted in the region where concentration polarization becomes significant. Both Stern (14) and King (15) criticized the recent work of Schuldiner (16), pointing out that the breaks in the reported H overvoltage curves on Pt were caused by concentration polarization effects. In addition, King pointed out that corrections for concentration polarization cannot be made quantitatively without accurate data for ion diffusion rates. Unfortunately, however, concentration polarization appears to have been overlooked again in more recent work with Pd (17). It is interesting to note that more than 25 years ago Bowden (18, 19) recognized the possibility that concentration polarization was the cause of breaks which he obtained during H overvoltage measurements on Hg.

Resistance between the reference electrode and the polarized electrode contributes still a third term to the total overvoltage measured. This is a linear function of current and can be expressed as $\eta_{\rm res} = \tilde{\iota}_x K_r$. If the resistance term K_r^7 is arbitrarily given a value of 10 ohms, the resulting deviation from Tafel behavior appears as illustrated in Fig. 4. Note here again that it is not only a sim-

⁵ Tobias, Eisenberg, and Wilke (10, 11) and Petrocelli (12) have presented extensive discussions on concentration polarization.

⁷ The resistance is a function of solution conductivity, distance between the reference electrode and the sample, and the geometry of the system. Barnartt (20) has presented an analysis of the magnitude of the *IR* drop expected as a function of both the current density and the solution conductivity. K_r may actually be a function of applied current if the conductance of the solution adjacent to the electrode interface changes (21).



FIG. 4. Effect of resistance polarization on the relationship between overvoltage and applied cathodic current for a single electrode system.

ple matter to draw a break in this curve, but that there is considerable latitude in choice of the break position.

CORRODING ELECTRODE SYSTEM

One additional factor is responsible for deviations from Tafel linearity in the low-current region: corrosion or local action current. When shifting from a noncorroding to a corroding system, many complicating factors arise. Two co-existing electrochemical reactions now appear: the previously discussed oxidation reduction system, $Z^+ + e \rightleftharpoons Z$, and the oxidation reduction system of the metal, $M^+ + e \rightleftharpoons M$. Each of these systems has its own exchange current and Tafel slope so that the steady-state potential of the corroding metal occurs where the total rate of oxidation equals the total rate of reduction. Thus at the steady-state corrosion potential,

$$\vec{\imath}_z + \vec{\imath}_m = \vec{\imath}_z + \vec{\imath}_m \tag{IX}$$

where i_m is the rate of reduction of M⁺ and i_m is the rate of oxidation of metal M, and $\bar{\imath}_z$ and $\bar{\imath}_z$ are the rates of reduction and oxidation of species Z, respectively. Since the corrosion rate by definition is $\bar{\iota}_m - \bar{\iota}_m$, it is evident that the rate may also be defined as $i_z - \bar{i}_z$ at the corrosion potential. When the corrosion potential is sufficiently removed from the equilibrium potentials of the reactions, i_m and i_z become insignificant in comparison to i_z and i_m . Thus the corrosion rate becomes equal to \vec{i}_z or \vec{i}_m . This has been used directly by Stern (13) to calculate corrosion rates of Fe from H overvoltage measurements, and indirectly by Elze and Fisher (22) to determine corrosion rates in inhibited acid environments. Fig. 5 illustrates the potential-current relationships for such a mixed electrode system. The metal oxidation reduction system has been drawn assuming an $i_{o,m}$ of 0.1 μ a, a β_m value of 0.060 v, and a reversible potential of -0.160 v. The Tafel constants for the Z oxidation reduction system are as previously described. Thus, equations for the various reaction

⁶ The limiting diffusion current for H ion reduction in HCl containing an indifferent electrolyte and stirred by natural convection is approximately 100 μ a/cm² at pH 3.1, 1000 μ a/cm² at pH 2.1, and 10,000 μ a/cm² at pH 1.1 (13).



FIG. 5. Relationship between overvoltage and current for a corroding electrode system consisting of two coexisting electrochemical reactions.

rates, using the equilibrium potential of the Z species reaction as a zero reference, are as follows:

Z Reduction

$$\eta = -\beta_z \log \frac{\vec{i}_z}{\vec{i}_{o,z}} = -0.100 \log \frac{\vec{i}_z}{1.0}$$
 (X)

Z Oxidation

$$\eta = +\beta_z \log \frac{\tilde{i}_z}{\tilde{i}_{o,z}} = +0.100 \log \frac{\tilde{i}_z}{1.0}$$
 (XI)

Metal Reduction

$$\eta = -0.160 - \beta_m \log \frac{\vec{i}_m}{\vec{i}_{o,m}} = -0.160 - 0.060 \log \frac{\vec{i}_m}{0.1}$$
 (XII)

Metal Oxidation

$$\eta = -0.160 + \beta_m \log \frac{\overline{i}_m}{\overline{i}_{o,m}} = -0.160 + 0.060 \log \frac{\overline{i}_m}{0.1}$$
 (XIII)

The constants are all arbitrary values. At any given potential, the rate of each reaction is indicated in Fig. 5. As already discussed, the corrosion potential is closely approximated by the potential at which $\bar{i}_z = \bar{i}_m$. This current is labeled i_{corr} in Fig. 5. It is quite important to note both the similarities and differences between this diagram of the electrochemistry of a corroding metal and that commonly used in the earlier literature (23, 24). Since the various oxidation reduction reactions occur at a finite rate even at the equilibrium potentials, it is apparent that the usual simplified polarization diagrams which have a linear current ordinate starting at zero are not strictly valid. Although the diagram in Fig. 5 is more in accord with modern electrochemical principles, its greatest value lies in the ease with which it permits an understanding of the shape and nature of experimental polarization curves. An expression describing the shape of the experimental cathodic polarization curve of a corroding electrode may be derived in the following manner. The external applied cathodic current, $\bar{\imath}_x$, is equal to the difference between the sum of the rates of all the reduction reactions and the sum of the rates of all the oxidation reactions. Thus,

$$\vec{i}_x = (\vec{i}_z + \vec{i}_m) - (\vec{i}_z + \vec{i}_m)$$
 (XIV)

Since the local action current during cathodic polarization may be defined as

$$i_{la} = \bar{i}_m - \bar{i}_m \tag{XV}$$

$$\vec{i}_x = \vec{i}_z - \vec{i}_z - i_{la}$$
 (XVI)

 \mathbf{but}

$$\eta = -\beta_z \log \frac{\overline{i_z}}{\overline{i_{o,z}}} \tag{X}$$

therefore,

$$\eta = -\beta_z \log \frac{\vec{i}_x + \vec{i}_z + i_{la}}{i_{o,z}}$$
(XVII)



FIG. 6. Relationship between overvoltage and applied cathodic current for a corroding electrode system.



FIG. 7. Effect of concentration polarization and resistance polarization on the relationship between overvoltage and applied cathodic current for a corroding electrode system.

Since the variations of \tilde{i}_z and i_{la} with η are known [Eq. (XI), (XII), and (XIII)], Eq. (XVII) permits a calculation of the potential change as a function of applied cathodic current. A similar equation may be derived for anodic polarization and would be of the form:

$$\eta = -0.160 + \beta_m \log \frac{\tilde{i}_x + i_{la} + \tilde{i}_m}{i_{o,m}} \quad (XVIII)$$

Fig. 6 shows the expected curve for the overvoltage as a function of the applied cathodic current, $(\bar{\imath}_x)$, for the system described above. This should be compared with Fig. 2 which shows the corresponding cathodic polarization curve for a noncorroding electrode with the same Tafel constants. Note that deviation from Tafel behavior occurs at much higher polarizing currents for the corroding electrode. True Tafel behavior is not evident until polarizing currents of the order of several times the corrosion current are applied.

If concentration polarization and resistance drop effects are included in the measurements, Eq. (XVII) becomes

$$\eta = -\beta_z \log \frac{\overline{i_x + \overline{i_z} + i_{la}}}{i_{o,z}} + 2.3 \frac{RT}{n\mathbf{F}} \log \frac{\overline{i_L} - \overline{i_x} - \overline{i_{la}}}{i_L} - \overline{i_x} K_r$$
(XIX)

For the same values of i_L and K_r used previously, Fig. 7 shows the effect of external applied cathodic current, \bar{i}_x , on the measured potential, η . Fig. 7 contains only a very short region which exhibits the Tafel slope, β_z . This is, of course, due to the choice of numbers used in this example. An increase in the corrosion current or in K_r and a decrease in i_L would completely eliminate any observable Tafel behavior. It is worth emphasizing here again that with a curve such as Fig. 7 a variety of straight line sections may be drawn with breaks placed at convenient positions. Obviously, such a treatment would be quite incorrect and contrary to the electrode kinetics described.

LINEAR VS. TAFEL POLARIZATION BEHAVIOR

In addition to the problem of polarization breaks, the question arises continually as to whether polarization should be a linear or logarithmic function of applied current. For example, Straumanis, Shih, and Schlechten (25, 26) have found Tafel behavior for H overvoltage on Ti in HCl, HBr, and H₂SO₄, but report a linear dependence of overvoltage on applied current in HF. In addition, these authors show that the linear relation is maintained if the Ti dissolves, while the Tafel relation holds if the Ti ceases to dissolve because of fluoride additions. That these results are in accord with the electrode kinetics described above is illustrated here.

A Noncorroding Electrode

Butler and Armstrong (27) have shown that the overvoltage of a reversible electrode is a linear function of applied current for values of overvoltage only slightly removed from the reversible potential. Proof of this can be found in the following derivation. Rearrangement of Eqs.



FIG. 8. Linear relationship between overvoltage and applied current for a single electrode system at overvoltage values only slightly removed from the reversible potential.

(IV) and (V) and substitution of these into Eq. (VI) yields

$$i_x = i_{o,z} [10^{-\eta/\beta_z} - 10^{+\eta/\beta_z}]$$
 (XX)

For small values of η/β_z where $10^{-\eta/\beta_z}$ may be approximated by $1 - \eta/\beta_z$ (2.3) and $10^{+\eta/\beta_z}$ may be approximated by $1 + \eta/\beta_z$ (2.3), Eq. (XX) reduces to

$$i_x = -(2)(2.3)(i_{o,z})\eta/\beta_z$$
 and (XXI)

$$\left. \frac{d\eta}{d\tilde{\imath}_x} \right)_{\eta \to 0} = - \frac{\beta_z}{\dot{\imath}_{o,z}(2)(2.3)} \tag{XXII}$$

Thus, measurements of overvoltage close to the reversible potential will yield results in accord with Eq. (XXII). For the system $Z^+ + e \rightleftharpoons Z$ where $\beta_z = 0.100$ and $i_{o,z} = 1.0 \ \mu a$ (Fig. 1), Eq. (XXII) indicates that $\frac{d\eta}{d\tilde{\imath}_x}\Big|_{\eta\to 0} = -0.0217 \ v/\mu a$. Fig. 8 is a plot of η as a function of $\tilde{\imath}_x$ calculated from Eq. (VII) for small values of η . Note that the linear relation predicted by Eq. (XXII) applies for η values up to about 20 mv.

Corroding Electrode

The same analysis may be applied to a corroding electrode where the corrosion potential is determined by the intersection of two logarithmic polarization curves. The corrosion current in this case is analogous to the exchange current of a noncorroding electrode. Thus⁸

$$\vec{i}_x = -2.3 \ i_{\text{corr}} \ \epsilon \left(\frac{\beta_z + \beta_m}{\beta_z \beta_m} \right) \text{ and }$$
 (XXIII)

$$\frac{d\epsilon}{d\tilde{t}_x}\bigg)_{\epsilon \to 0} = - \frac{\beta_z \beta_m}{(2.3) (i_{\text{corr}})(\beta_z + \beta_m)} \quad (XXIV)$$

For the mixed electrode system described earlier and illustrated in Fig. 5,

$$\left(\frac{d\epsilon}{d\bar{t}_x}\right)_{\epsilon \to 0} = -0.0040 \text{ v}/\mu a$$

Fig. 9 is a plot of ϵ as a function of $\tilde{\tau}_x$ calculated from Eq. (XVII) for small values of ϵ . Here again a linear relation between electrode potential and applied current is found. It is important to note that the linear behavior extends to

 ${}^{s}\epsilon$ is the difference between the polarized potential and the corrosion potential.



FIG. 9. Linear relationship between potential and applied current at potentials only slightly removed from the corrosion potential. ϵ is the difference between the polarized potential and the corrosion potential.

applied current values higher than the corrosion current. As stated previously, Tafel behavior would not be indicated until applied current values approximately ten times i_{corr} are reached.

In the data reported by Straumanis (25, 26) for the linear dependence of H overvoltage on applied current for Ti in HF, the region where Tafel behavior would be expected to appear had not been reached experimentally because of the high corrosion current under the conditions of test. For example, the corrosion rate of Ti in 1N HF has been reported as equivalent to 85 ma/cm² (28), while the overvoltage measurements were not carried farther than 50 ma/cm².

Eq. (XXIV) is valuable from both a theoretical and an experimental point of view, since it relates the corrosion rate and the Tafel slopes to polarization measurements close to the corrosion potential. Thus, low current polarization measurements combined with corrosion rate data permit a calculation of one of the Tafel slopes if the other is known. This is of great value when concentration polarization or IR drop effects interfere with measurements are made close to the corrosion potential, thus climinating any surface changes which may result from high current polarization.

ADDITIONAL CAUSES FOR TAFEL DEVIATION

The Tafel constants for Fig. 5 have been picked conveniently to yield a single Tafel relation at the currents illustrated in Fig. 6. Inspection of Fig. 5, however, reveals that \vec{i}_m becomes significant in respect to \vec{i}_z at very high current values. In this current region, the Tafel slope of Fig. 6 will gradually change from β_z to β_m . When $\tilde{\imath}_m \gg \tilde{\imath}_z$, a new Tafel slope exists with a value of β_m . A plot of the overvoltage curve for this situation is presented in Fig. 10. Obviously, a different choice of β_z , β_m , $i_{o,z}$, and $i_{o,m}$ could create this shift in Tafel slope at lower currents and smaller values of overvoltage. It is important to note that the change in slope takes place gradually and results in a curve which is only "Tafel-like" in nature over a considerable range of current. It would be a simple matter, although incorrect, to draw several Tafel lines through this curve. Thus, it is evident that real Tafel behavior will not be ob-



served in a potential range where two or more reduction reactions occur at similar rates.

A further extension of the concepts presented here shows that an improvement in the efficiency of reducing M^+ at any given potential may be achieved by increasing β_z , decreasing β_m , increasing $i_{o,m}$, decreasing $i_{o,z}$, or by reducing the difference between the reversible potentials of the two oxidation reduction systems. Thus, the analysis presented here is important in the study of metal plating efficiency as well as corrosion phenomena.

DISCUSSION

The picture of a mixed electrode presented above could be made more extensive by including even a third oxidation reduction system.⁹ It is doubtful whether a detailed discussion of such a system would be of benefit at the present, but it will be included in a future publication. It is worth noting in passing, however, that the polarization curves would be even more complex than those discussed here.

This analysis has illustrated several important concepts which are worth listing for emphasis.

1. The representation of a corroding metal by polarization diagrams should be extended to include the reverse reactions of the various oxidation reduction systems which are operative.

2. Deviations from Tafel behavior may be caused by local action currents, concentration polarization, and IR drop effects, and by a change in the predominant electrode reaction.

3. An experimental polarization curve may show a linear dependence of potential on applied current for small amounts of polarization.

4. An equation has been derived which relates the slope of the linear region of a polarization measurement to the corrosion rate and the Tafel slopes. This equation will prove valuable when interfering reactions prevent the determination of the Tafel constants at higher currents.

5. The shape of an experimental electrochemical polarization curve, either cathodic or anodic, can be analyzed

⁹ An example of this would be Fe corroding in acid with a depolarizer such as oxygen or ferric ion.

Vol. 104, No. 1

if sufficient data are obtained to permit an accurate description of the curve. Placing straight lines through four or five experimental points is hazardous, while the indiscriminate introduction of "breaks" is contrary to modern electrochemical concepts. Sufficient information concerning the system should be available to estimate whether concentration polarization or resistance drop effects have been included in the measurements.

Although this analysis contains only calculated polarization curves, a subsequent discussion will illustrate how experimental measurements comply with the electrode kinetics described.

The picture of a corroding metal presented here is consistent with the concept or theory of mixed potentials originally treated by Wagner and Traud (29) and subsequently discussed by Petrocelli (30). The concept of discrete anodic and cathodic areas in electrochemical corrosion may be considered a special case of this theory.

Manuscript received Feb. 24, 1956.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1957 JOURNAL.

LIST OF SYMBOLS USED

i_z	= Cathodic or reduction current of Z oxidation
*	reduction system.
ι_m	= Cathodic or reduction current of M oxidation
÷	reduction system.
ι_z	= Anodic or oxidation current of Z oxidation
÷	reduction system.
ι_m	= Anodic or oxidation current of M oxidation
	reduction system.
1 o , z	= The exchange current of the Z reaction. This
	is equal to the oxidation or reduction cur-
	rent at equilibrium
i _{0,m}	= The exchange current of the M reaction. This
	is equal to the oxidation or reduction cur-
	rent at equilibrium
β,	= The Tafel slope or $\frac{d\eta}{d\eta}$ for the Z oxidation
	$d \log i$
	reduction system.
ß.,,	= The Tafel slope or $\frac{d\eta}{d\eta}$, for the M oxidation
	$d \log i$
	reduction system.
\overline{i}_x	= The external applied cathodic current.
\overline{i}_x	= The external applied anodic current.
η	= Overvoltage or difference in potential between
	a polarized electrode and an electrode at
	equilibrium for the same reaction.
ηconc	= Concentration overvoltage.
η _{res}	= Resistance overvoltage.
i_L	= Limiting diffusion current.
i_{la}	= Local action current.
icorr	= Corrosion current or the local action current
	at the corrosion potential.

- = Resistance factor for calculating the IR drop K_r included in polarization measurements. This factor includes the solution conductivity and the system geometry.
 - = The difference between the potential polarized by applied current and the corrosion potential.

= The slope of the overvoltage vs. current curve for

small overvoltage values.

= The slope of the ϵ vs. current curve for small values of ϵ .

REFERENCES

- 1. K. H. LOGAN, Corrosion, 10, 206 (1954).
- 2. W. J. SCHWERDTFEGER AND O. N. MCDORMAN, This Journal, 99, 407 (1952).
- 3. P. A. JOHNSON AND A. L. BABB, Ind. Eng. Chem., 46, 518 (1954).
- J. M. PEARSON, Trans. Electrochem. Soc., 81, 483 (1942). 4
- 5. R. PARSONS, J. Chim. Phys., 49, C 82 (1952).
- 6. J. O'M. BOCKRIS AND B. E. CONWAY, Trans. Faraday Soc., 48, 724 (1952). J. O'M. BOCKRIS AND E. C. POTTER, This Journal, 99,
- 169 (1952).
- 8. J. O'M. BOCKRIS, "Modern Aspects of Electrochemistry," Academic Press Inc., New York (1954).
- 9. K. J. VETTER, Z. Elektrochem., 59, 435 (1955).
- 10. C. W. TOBIAS, M. EISENBERG, AND C. R. WILKE, This Journal, 99, 395C (1952).
- 11. C. R. WILKE, M. EISENBERG, AND C. W. TOBIAS, ibid., 100, 513 (1953).
- J. V. PETROCELLI, *ibid.*, **98**, 187 (1951).
 M. STERN, *ibid.*, **102**, 609, 663 (1955).
 M. STERN, *ibid.*, **102**, 356 (1955).

- 15. C. V. KING, ibid., 102, 193 (1955)
- 16. S. SCHULDINER, ibid., 101, 426 (1954).
- 17. J. P. HOARE AND S. SCHULDINER, ibid., 102, 485 (1955).
- F. P. BOWDEN, Trans. Faraday Soc., 24, 473 (1928).
 F. P. BOWDEN, Proc. Roy. Soc., 126A, 107 (1930).
- 20. S. BARNARTT, This Journal, 99, 549 (1952)
- 21. J. N. AGAR AND F. P. BOWDEN, Proc. Roy. Soc., 169A, 206 (1938).
- 22. J. ELZE AND H. FISHER, This Journal, 99, 259 (1952)
- 23. U. R. EVANS, "Metallic Corrosion, Passivity, and Protection," p. 350, Longmans Green and Co., New York (1948).
- 24. H. H. UHLIG, ed., "Corrosion Handbook," p. 436, J. Wiley & Sons, Inc., New York (1948).
- 25. M. E. STRAUMANIS, S. T. SHIH, AND A. W. SCHLECH-TEN, J. Phys. Chem., 59, 317 (1955).
- 26. M. E. STRAUMANIS, S. T. SHIH, AND A. W. SCHLECH-TEN, This Journal, 102, 573 (1955)
- 27. J. A. V. BUTLER AND G. ARMSTRONG, J. Chem. Soc., 1934, 743.
- 28. M. E. STRAUMANIS AND P. C. CHEN, This Journal, 98, 234 (1951).
- 29. C. WAGNER AND W. TRAUD, Z. Elektrochem., 44, 391 (1938)
- 30. J. V. PETROCELLI, This Journal, 97, 10 (1950).