CHAPTER

NINE

MODERN THEORY—PRINCIPLES

9-1 Introduction

In this chapter the modern electrochemical theory of aqueous corrosion is introduced and described. Although the presentation is necessarily simplified and brief, all generalizations and simplifications are clearly indicated. Equation derivations have been omitted for clarity and brevity. The principles described in this chapter differ from classic corrosion theories in that no mention is made of local anodes and cathodes. These concepts are not in conflict with classic corrosion theories, but represent a different approach to the problem of understanding the electrochemical behavior of corrosion reactions. We have chosen to utilize this particular approach since it has proved to be an unusually useful method for understanding and controlling corrosion as evidenced by the recent numerous advances in the corrosion field. Anodic protection, noble metal alloying, and methods for rapidly measuring corrosion rates by electrochemical measurements have been developed in the past 20 years by application of modern electrode kinetic principles.

This chapter is divided into two main sections: thermodynamic principles and electrode kinetics. Applications of these principles are described in Chap. 10.

THERMODYNAMICS

Thermodynamics, the science of energy changes, has been widely applied to corrosion studies for many years. Below, the principles applicable to corrosion phenomena and their limitations are reviewed.

9-2 Free Energy

The change in free energy ΔG is a direct measure of the work capacity or maximum electric energy available from a system. If the change in free energy accompanying the transition of a system from one state to another is negative, this indicates a loss in free energy and also the spontaneous reaction direction of the system. That is, if no external forces act on the system, the system will tend to transform to its lowest energy state. If the change in free energy is positive, this indicates that the transition represents an increase in energy, and this requires that additional energy be added to the system. These principles are illustrated in Fig. 9-1 by a mechanical analogy. If the ball moves from position 1 to position 2, this represents a decrease in free energy. The transition from position 1 to position 2 is the spontaneous direction for this particular system. The reverse transformation—from position 2 to position 1—is not a spontaneous direction and requires the application of energy.

The change in free energy is a state function and is independent of the reaction path. This is illustrated in Fig. 9-2, which is similar to Fig. 9-1 except that there are two possible reaction paths *A* and *B*. For either path, free-energy change for the transition from state 1 to state 2*A* or 2*B* is exactly the same. It is obvious, however, that the transformation along path *B* will require more time and will be slower than along path *A*. Chemical and corrosion reactions behave in exactly the same fashion. It is not possible to accurately predict the velocity of a reaction from the change in free energy. This parameter reflects *only* the direction of reaction by its sign, and any predictions of velocity based on the magnitude of the change in free energy may be erroneous, as illustrated in Fig. 9-2.

The free-energy change accompanying an electrochemical reaction can be calculated by the following equation:

$$\Delta G = -nFE \tag{9.1}$$

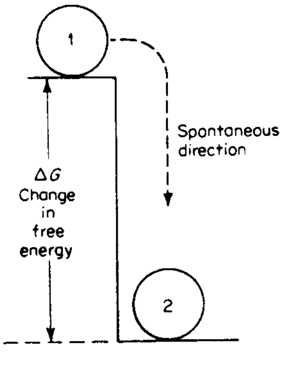

Figure 9-1 Mechanical analogy of free-energy change.

where ΔG is the free-energy change, n is the number of electrons involved in the reaction, F is the Faraday constant, and E equals the cell potential. Below we shall discuss how cell potential E is determined.

9-3 Cell Potentials and the EMF Series

The change in free energy accompanying an electrochemical or corrosion reaction can be calculated from a knowledge of the cell potential of the reaction. Since there has been considerable confusion regarding sign conventions in electrochemistry, we shall use actual electrode potentials in all discussions.

To illustrate the principle of a reversible cell potential, consider the replacement reaction between copper and zinc occurring at equilibrium:

$$\mathrm{Cu} + \mathrm{Zn}^{2+} = \mathrm{Cu}^{2+} + \mathrm{Zn} \tag{9.2}$$

The above reaction is written with an equal sign to indicate an equilibrium reaction. Considering zinc and copper electrodes in equilibrium with their ions, it is apparent that Eq. (9.2) represents their summation. Thus

$$\begin{array}{rr}
\mathrm{Cu} = \mathrm{Cu}^{2+} + 2e & (9.3) \\
+\,\mathrm{Zn}^{2+} + 2e = \mathrm{Zn} & (9.4) \\
\hline
\mathrm{Cu} + \mathrm{Zn}^{2+} = \mathrm{Cu}^{2+} + \mathrm{Zn} & (9.2)
\end{array}$$

To study the free-energy change associated with the above reaction, we can construct an electrochemical cell containing copper and zinc electrodes in equilibrium with their ions separated by a porous membrane to retard mixing, as illustrated in Fig. 9-3. For purposes of simplicity, the concentrations of metal ions are maintained at unit activity; each solution contains approximately 1 gram-atomic weight of metal ion per liter. It is necessary that both electrodes be at equilibrium. That is, the reactions in each compartment are represented by Eqs. (9.3) and (9.4), and the rates of metal dissolution and deposition must be the same; there is no net change in the system. This is illustrated in Fig. 9-4. At certain points on the metal surface,

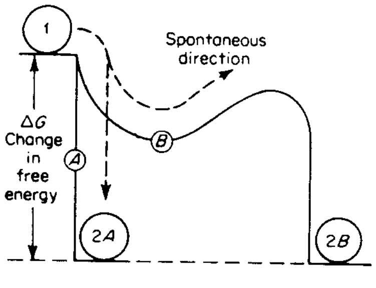

Figure 9-2 Effect of reaction path on reaction rate.

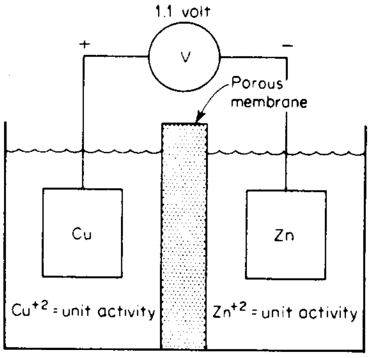

Figure 9-3 Reversible cell containing copper and zinc in equilibrium with their ions.

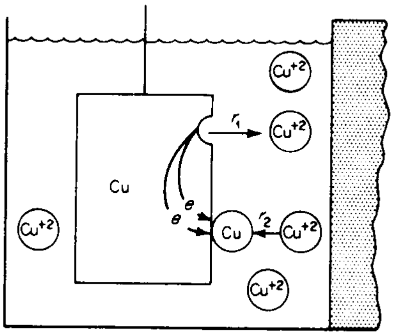

Figure 9-4 Reversible copper electrode.

copper atoms are oxidized to cupric ions, and at other points cupric ions are reduced to metallic copper. Equilibrium conditions dictate that the rates of both of these reactions r_1 and r_2 be equal. Similar restrictions apply to the zinc electrode. These equilibrium electrodes are called *half-cells*, and when the concentrations of all reactants are maintained at unit activity, they are termed *standard half-cells*.

If a high-resistance voltmeter is connected between the copper and zinc electrodes, a potential difference of approximately 1.1 volts is observed. This is the cell potential that is used in determining the free energy of the overall electrochemical reaction. The positive terminal of the voltmeter must be connected to the copper electrode, and the negative terminal must be connected to the zinc electrode to have the voltmeter read on scale.

Any electrochemical reaction can be studied as described above. For example, consider the replacement reaction between copper and silver:

$$Cu + 2Ag^+ = Cu^{2+} + 2Ag \tag{9.5}$$

To study this reaction, reversible electrodes of copper and silver can be established as shown in Fig. 9-5, and the potential difference between the two electrodes is 0.45 volt. In this cell, copper is negative with respect to silver.

Although it is usually possible to establish a reversible electrochemical cell for any given reaction, the fact that there is an infinite number of combinations makes both the experimental measurements and tabulations of such data almost impossible. To simplify the representation and calculations of cell potentials, the concept of half-cell potentials has been developed. An arbitrary half-cell reaction is used as a reference by defining its potential as zero, and all other half-cell potentials are calculated with respect to this zero reference. Although any half-cell reaction can be chosen for this standard reference point, the hydrogen-hydrogen ion reaction ($2H^+ + 2e = H_2$) is universally accepted, since it is relatively easy to establish a reversible hydrogen electrode. Consider for example the reaction between zinc and hydrogen ions:

$$Zn + 2H^+ = Zn^{2+} + H_2 \tag{9.6}$$

This reaction can be divided into two half-cell reactions:

$$Zn = Zn^{2+} + 2e \tag{9.7}$$

$$2H^+ + 2e = H_2 \tag{9.8}$$

Since it is not possible to make an electrode from hydrogen gas, an inert electrode is used. As shown in Fig. 9-6, a reversible divided cell between zinc and its ions and hydrogen gas and hydrogen ions is established by using zinc and platinum electrodes. The platinum electrode acts as an inert substrate for the electrochemical reaction as shown in Fig. 9-7. At different points on the platinum electrode, hydrogen ions are reduced to hydrogen gas and hydrogen gas is oxidized to hydrogen ions, with electron transfer occurring between these points. It is important to note that the platinum

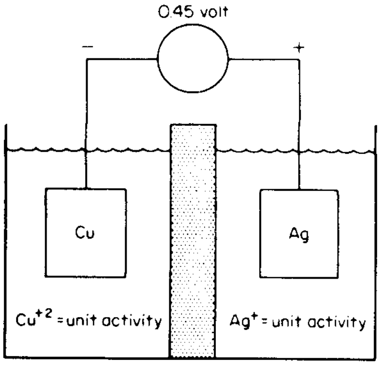

Figure 9-5 Reversible cell containing copper and silver in equilibrium with their ions.

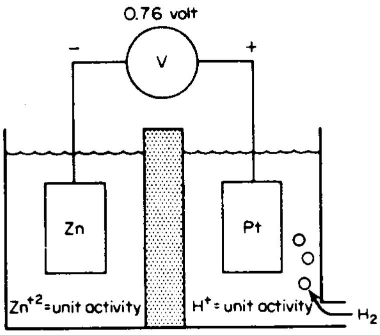

Figure 9-6 Cell containing reversible zinc and hydrogen electrodes.

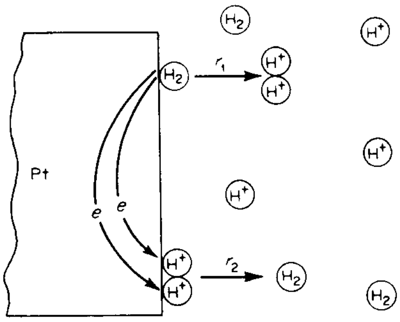

Figure 9-7 Hydrogen electrode on platinum.

electrode does not take part in this reaction but merely serves as a solid interface at which this reaction can occur. Many metals function as reversible hydrogen electrodes; platinum is usually preferred due to its inertness and the ease with which electron transfer occurs on its surface. As with other half-cell electrodes, the concentration of hydrogen ions is maintained at unit activity, and the solution is saturated with hydrogen gas at 1 atmosphere pressure.

The cell as shown in Fig. 9-6 has a potential of 0.763 and zinc is negative with respect to the hydrogen electrode. Using the above convention, the hydrogen electrode is defined as having a potential of zero, and it follows that the potential of the zinc half-cell is -0.76 volt. In a similar fashion, other half-cell potentials can be calculated. Table 9-1 lists the half-cell potentials for some electrochemical reactions.* This table is frequently called the emf series, half-cell, or oxidation-reduction potentials. The latter

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*For a very complete and accurate list of half-cell potentials, see the reference noted in Table 9-1.

term is frequently abbreviated as *redox* potentials. It is important to note that in all cases these potentials refer to electrodes in which all reactants are at unit activity and at 25°C.

From the data presented in Table 9-1, it is possible to calculate the cell potential for numerous electrochemical reactions. Note that the absolute potential difference between the copper electrode and zinc electrode is approximately 1.1 volts and that the copper electrode is positive with respect

Table 9-1 Standard oxidation-reduction (redox) potentials

25°C, volts vs. normal hydrogen electrode*

$Au = Au^{3+} + 3e$	+1.498
$O_2 + 4H^+ + 4e = 2H_2O$	+1.229
$Pt = Pt^{2+} + 2e$	+1.2
$Pd = Pd^{2+} + 2e$	+0.987
$Ag = Ag^+ + e$	+0.799
$2Hg = Hg_2^{2+} + 2e$	+0.788
$Fe^{3+} + e = Fe^{2+}$	+0.771
$O_2 + 2H_2O + 4e = 4\ OH$	+0.401
$Cu = Cu^{2+} + 2e$	+0.337
$Sn^{4+} + 2e = Sn^{2+}$	+0.15
$2H^+ + 2e = H_2$	0.000
$Pb = Pb^{2+} + 2e$	−0.126
$Sn = Sn^{2+} + 2e$	−0.136
$Ni = Ni^{2+} + 2e$	−0.250
$Co = Co^{2+} + 2e$	−0.277
$Cd = Cd^{2+} + 2e$	−0.403
$Fe = Fe^{2+} + 2e$	−0.440
$Cr = Cr^{3+} + 3e$	−0.744
$Zn = Zn^{2+} + 2e$	−0.763
$Al = Al^{3+} + 3e$	−1.662
$Mg = Mg^{2+} + 2e$	−2.363
$Na = Na^+ + e$	−2.714
$K = K^+ + e$	−2.925

*Electrode potential values are given and are invariant (e.g., $Zn = Zn^{2+} + 2e$, and $Zn^{2+} + 2e = Zn$, are identical and represent zinc in equilibrium with its ions with a potential of −0.763 volts vs. normal hydrogen electrode).

Source: A. J. de Bethune and N. A. S. Loud, *Standard Aqueous Electrode Potentials and Temperature Coefficients at 25°C*, Clifford A. Hampel, Skokie, Ill., 1964.

to the zinc. Likewise, the potential difference between the copper and silver electrode is 0.45 volt and copper is negative with respect to silver. Thus, the use of redox potentials greatly simplifies the calculation of cell potentials.

To determine the potential of a system in which the reactants are not at unit activity, the familiar Nernst equation can be employed; that is,

$$E = E_0 + 2.3\frac{RT}{nF}\log\frac{a_{\text{oxid}}}{a_{\text{red}}} \tag{9.9}$$

where E is the half-cell potential, E_0 the standard half-cell potential, R is the gas constant, T is absolute temperature, n is the number of electrons transferred, F is the Faraday constant, a_{oxid} and a_{red} are the activities (concentrations) of oxidized and reduced species. As indicated in the above equation, half-cell potential becomes more positive as the amount of oxidized species increases. For each tenfold increase in oxidized reactant, the half-cell potential increases by 59 mV for a single electron reaction.

9-4 Applications of Thermodynamics to Corrosion

As discussed above, there is a definite relation between the free-energy change and the cell potential of an electrochemical reaction. In most instances, the actual magnitude of the free-energy change is relatively unimportant in corrosion applications. The most important factor is the sign of the free-energy change for a given reaction, since this indicates whether or not the reaction is spontaneous. Hence, although Eq. (9.1) forms the basis for thermodynamic calculations, it is rarely used in studying corrosion phenomena. However, a simple rule derived from Eq. (9.1) is used to predict the spontaneous direction of any electrochemical reaction. This rule can be simply stated as: *In any electrochemical reaction, the most negative or active half-cell tends to be oxidized, and the most positive or noble half-cell tends to be reduced.* Considering Table 9-1 and applying this rule, the spontaneous direction of the zinc-copper replacement reaction given in Eq. (9.2) is toward the oxidation of zinc and the deposition of copper. Similarly, in the copper-silver replacement reaction, Eq. (9.5), copper tends to be oxidized and the silver ions tend to be reduced, indicating that the spontaneous direction of this reaction is to the right, as written.

Redox potentials are very useful in predicting corrosion behavior. From the above rule it follows that all metals with reversible potentials more active (negative) than hydrogen will tend to be corroded by acid solutions. Copper and silver, which have more noble potentials, are not corroded in acid solutions. Although copper and silver are not corroded by acid solutions, if dissolved oxygen is present there is a possibility of oxygen reduction. Table 9-1 indicates that in the presence of oxygen, copper and silver tend to corrode spontaneously. For example:

$Cu + H_2SO_4 = \text{no reaction}$ $\quad (Cu/Cu^{2+} \text{ more} + \text{than } H_2/H^+)$

$2Cu + 2H_2SO_4 + O_2 \rightleftarrows 2CuSO_4 + 2H_2O$ $\quad (O_2/H_2O \text{ more} + \text{than } Cu/Cu^{2+})$

As the reversible potential of a metal becomes more noble, its tendency to corrode in the presence of oxidizing agents decreases. Hence, the metals at the uppermost part of the redox series, such as platinum and gold, are very inert, since there will be no tendency to corrode except in the presence of extremely powerful oxidizing agents. It is important to note that all of the above discussions refer to systems at unit activity. Since half-cell potentials change with concentration, Nernst calculations must be made before making predictions about spontaneous direction at concentrations other than unit activity.

Thermodynamics or, more specifically, half-cell potentials can be used to state a criterion for corrosion. *Corrosion will not occur unless the spontaneous direction of the reaction indicates metal oxidation.* As mentioned above, it is important to remember that although the spontaneous direction of a reaction may be in the direction of metal corrosion, this does not necessarily indicate that corrosion will occur. If the reaction proceeds at a negligible rate, then the metal will be essentially inert. Hence, the major use of thermodynamic calculations is a negative one. That is, thermodynamics can indicate unambiguously that corrosion will not occur. However, corrosion may or may not occur if the reaction direction indicates metal oxidation.

The applications of thermodynamics to corrosion phenomena have been further generalized by means of potential-pH plots. These are frequently called Pourbaix diagrams, after Dr. M. Pourbaix who first suggested their use. The potential-pH diagram for iron is shown in Fig. 9-8. Such diagrams are constructed from calculations based on the Nernst equation (9.9 and

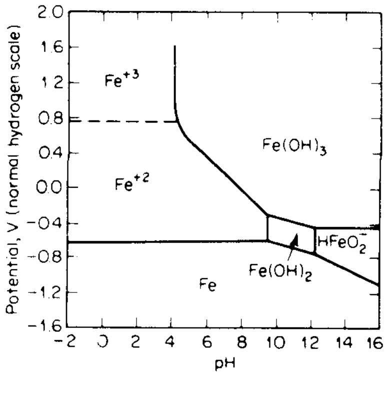

Figure 9-8 Simplified potential-pH diagram for the Fe-H_2O system. (*M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions*, pp. 307–321, Pergamon Press, New York, 1966.)

solubility data for various metal compounds. As shown, it is possible to delineate areas in which iron, iron hydroxide, ferrous ions, etc., are thermodynamically stable. That is, these forms represent states of lowest free energy.

The main uses of these diagrams are (1) predicting the spontaneous direction of reactions, (2) estimating the composition of corrosion products, and (3) predicting environmental changes that will prevent or reduce corrosive attack. For example, the large region in Fig. 9-8 labeled Fe indicates that iron is inert under these conditions of potential and pH.

Potential-pH diagrams are subject to the same limitations as any thermodynamic calculation. They represent equilibrium conditions and should never be used to predict the velocity of a reaction. Unfortunately, many investigators have ignored this limitation, which has been repeatedly stated by Pourbaix, and have attempted to use these plots to predict reaction kinetics. Similar diagrams have been prepared for other metals (see Suggested Reading at the end of Sec. 9-11).

ELECTRODE KINETICS

From an engineering standpoint, the major interest is in the kinetics or rate of corrosion. Corroding systems are not at equilibrium, and therefore thermodynamic calculations cannot be applied. Essentially, we are interested in what happens when cells such as have been described above are short-circuited, as illustrated in Fig. 9-9. In this instance a vigorous reaction occurs: the zinc electrode rapidly dissolves in the solution and simultaneously a rapid evolution of hydrogen is observed at the platinum electrode. Electrons released from the zinc-dissolution reaction are transferred through the connecting wire to the platinum electrode where they are consumed in the hydrogen-reduction reaction. The process that occurs in Fig. 9-9 is exactly the same process that occurs when zinc metal is immersed in a hydrogen-

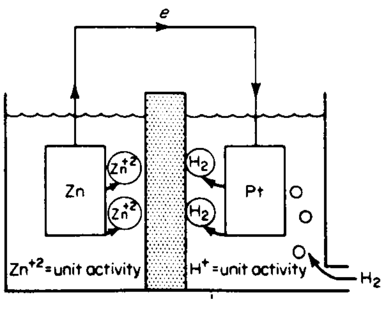

Figure 9-9 Short-circuited cell containing zinc and hydrogen electrodes.

saturated acid solution containing zinc ions, as shown in Fig. 9-10. In both instances the overall reaction is the dissolution of zinc and the evolution of hydrogen. In the divided cell shown in Fig. 9-9, the reactions occur on separate electrodes, whereas in Fig. 9-10 these reactions occur on the same metal surface. In both instances, the free-energy change for the reaction is exactly the same, since the platinum metal does not participate in the reaction.

Before proceeding with discussions of electrode-kinetics principles, several useful terms should be defined. *Anode* refers to an electrode at which a net oxidation process occurs, and *cathode* refers to an electrode at which a net reduction reaction occurs. Referring to Fig. 9-9, the zinc electrode is the anode, and the platinum or hydrogen electrode is the cathode in this particular cell when the terminals are short-circuited. Similarly, *anodic reaction* is synonymous with an oxidation reaction and *cathodic reaction* is synonymous with a reduction reaction. When a cell such as is shown in Fig. 9-9 is short-circuited, and net oxidation and reduction processes occur at the electrode interfaces, the potentials of these electrodes will no longer be at their equilibrium potential. This deviation from equilibrium potential is called *polarization*. Polarization can be defined as the displacement of electrode potential resulting from a net current. The magnitude of polarization is frequently measured in terms of *overvoltage*. Overvoltage, usually abbreviated as η, is a measure of polarization with respect to the equilibrium potential of an electrode. That is, the equilibrium potential of an electrode is considered as zero, and the overvoltage is stated in terms of volts or millivolts plus or minus with respect to this zero reference.

To illustrate overvoltage, consider that the zinc electrode which is coupled to the platinum electrode in Fig. 9-8 has a potential after coupling of -0.66 volt. Thus, its overvoltage is $+100$ mV or $+0.10$ volt. The terminology described above will be used consistently throughout the rest of this chapter and in Chap. 10.

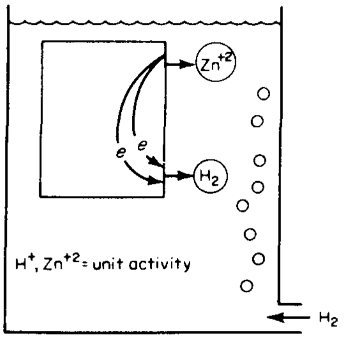

Figure 9-10 Corroding zinc, shown schematically.

9-5 Exchange Current Density

Consider the reversible hydrogen electrode established on platinum as shown in Fig. 9-7. Equilibrium conditions dictate that the rate of oxidation and reduction, r_1 and r_2 respectively, must be equal. Hence, at an equilibrium hydrogen electrode there is a finite rate of interchange between hydrogen molecules and hydrogen ions in solution. By plotting electrode potential versus reaction rate as shown in Fig. 9-11, it is possible to establish a point corresponding to the platinum-hydrogen electrode. This point represents the particular exchange reaction rate of the electrode expressed in terms of moles reacting per square centimeter per second. Note that there is no net reaction, since both the oxidation and reduction rates are equal; the exchange reaction rate is equal to the rate of oxidation and reduction. The exchange reaction rate can be more conveniently expressed in terms of current density. Since two electrons are consumed during the reduction of the two hydrogen ions, and since two electrons are released during the oxidation of the single hydrogen molecule, the reaction rate can be expressed in terms of current density. More precisely, the relationship between exchange reaction rate and current density can be directly derived from Faraday's law:

$$r_{\text{oxid}} = r_{\text{red}} = \frac{i_0}{nF} \tag{9.10}$$

where r_{oxid} and r_{red} are the equilibrium oxidation and reduction rates and i_0 is the exchange current density; n and F have been defined previously.

Exchange current density i_0 is the rate of oxidation and reduction reactions at an equilibrium electrode expressed in terms of current density. Exchange current density is a misnomer since there is no net current. It is merely a convenient way of representing the rates of oxidation and reduction at equilibrium. It is observed that the exchange current density varies depending on the metal electrode as shown in Fig. 9-12. In this figure, a logarithmic current-density scale is used to permit a wide range of points to be plotted. Note that the exchange current density for platinum is approximately 1 mA/cm^2, and that for mercury it is approximately 10^{-12} A/cm^2.

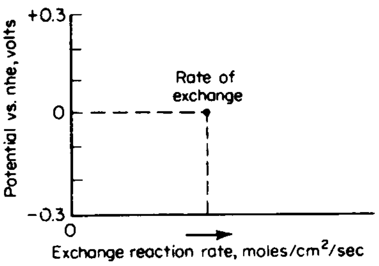

Figure 9-11 Hydrogen-hydrogen-ion exchange on platinum.

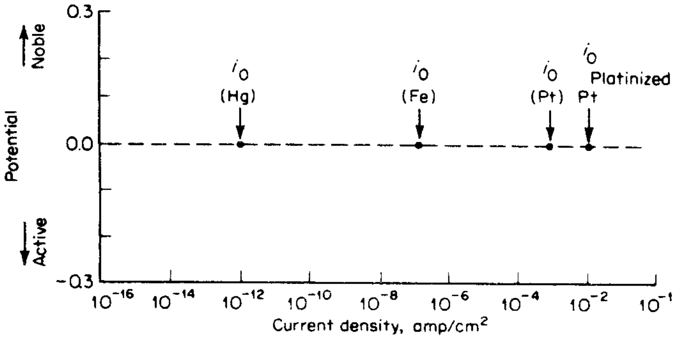

Figure 9-12 Hydrogen-hydrogen-ion exchange current densities.

Table 9-2 lists some experimentally determined exchange current densities. The magnitude of exchange current density is a function of several variables. First, it is a specific function of the particular redox reaction. Further, as shown in Fig. 9-12 and Table 9-2, it is also related to electrode composition. Like reversible potentials, exchange current densities are influenced by the ratio of oxidized and reduced species that are present and by the temperature of the system. There is no thereotical way of precisely

Table 9-2 Exchange current densities

Reaction	Electrode	Solution	i_0, A/cm²
$2H^+ + 2e = H_2$	Al	$2N$ H_2SO_4	10^{-10}
$2H^+ + 2e = H_2$	Au	$1N$ HCl	10^{-6}
$2H^+ + 2e = H_2$	Cu	$0.1N$ HCl	2×10^{-7}
$2H^+ + 2e = H_2$	Fe	$2N$ H_2SO_4	10^{-6}
$2H^+ + 2e = H_2$	Hg	$1N$ HCl	2×10^{-12}
$2H^+ + 2e = H_2$	Hg	$5N$ HCl	4×10^{-11}
$2H^+ + 2e = H_2$	Ni	$1N$ HCl	4×10^{-6}
$2H^+ + 2e = H_2$	Pb	$1N$ HCl	2×10^{-13}
$2H^+ + 2e = H_2$	Pt	$1N$ HCl	10^{-3}
$2H^+ + 2e = H_2$	Pd	$0.6N$ HCl	2×10^{-4}
$2H^+ + 2e = H_2$	Sn	$1N$ HCl	10^{-8}
$O_2 + 4H^+ + 4e = 2H_2O$	Au	$0.1N$ NaOH	5×10^{-13}
$O_2 + 4H^+ + 4e = 2H_2O$	Pt	$0.1N$ NaOH	4×10^{-13}
$Fe^{3+} + e = Fe^{2+}$	Pt		2×10^{-3}
$Ni = Ni^{2+} + 2e$	Ni	$0.5N$ $NiSO_4$	10^{-6}

Source: J. O'M. Bockris, Parameters of Electrode Kinetics, *Electrochemical Constants*, NBS Circular 524, U.S. Government Printing Office, Washington, D.C., pp. 243–262, 1953.

determining the exchange current density for any given system; it must be determined experimentally.

Exchange current density is usually expressed in terms of projected or geometric surface area, and as a consequence it is dependent on surface roughness. The greater exchange current density of platinized platinum relative to bright platinum is a result of its greater surface area. Exchange current densities for the H^+-H_2 system are markedly reduced by the presence of trace impurities such as arsenic, sulfur, and antimony-containing ions.

9-6 Activation Polarization

Electrochemical polarization is divided into two main types—activation and concentration polarization. Activation polarization refers to electrochemical reactions that are controlled by a slow step in the reaction sequence. As discussed in Chap. 2, this slow step during hydrogen evolution might be the electron-transfer step or the formation of hydrogen molecules: The relationship between reaction rate and overvoltage for activation polarization is:

$$\eta_a = \pm \beta \log \frac{i}{i_0} \tag{9.11}$$

where η_a is overvoltage, β is a constant, and i is the rate of oxidation or reduction in terms of current density. Equation (9.11) is called the Tafel equation, and β is frequently termed "β slope" or Tafel constant.* Equation (9.11) is graphically illustrated in Fig. 9-13. If a logarithmic current scale is

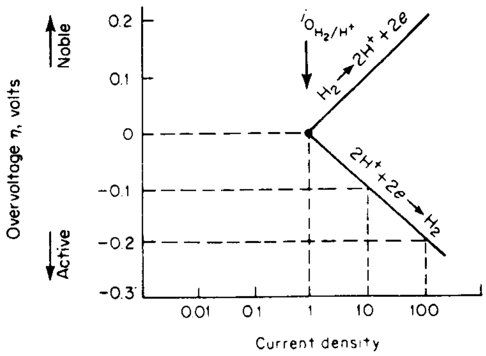

Figure 9-13 Activation-polarization curve of a hydrogen electrode.

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[*] β represents the expression $2.3RT/\alpha nF$, where R, T, n, and F are as before, and α is the symmetry coefficient, which describes the shape of the rate-controlling energy barrier. See Bockris for a detailed derivation of the Tafel equation (Suggested Reading at end of Sec. 9-11).

used, the relationship between overvoltage or potential and current density is a linear function.* The value of β for electrochemical reactions ranges between 0.05 and 0.15 volt. In general, the value of β is usually 0.1 volt. The significance of this parameter can be seen upon examination of Fig. 9-13. Here the oxidation and reduction reactions corresponding to a hydrogen electrode are plotted with a beta value of 0.1 volt. Note that the reaction rate changes by one order of magnitude for each 100-mV, or 0.1-volt, change in overvoltage. This illustration shows that the reaction rate of an electrochemical reaction is very sensitive to small changes in electrode potential. Further, it can be seen that at all potentials more noble than the reversible potential a net oxidation process occurs, and that at all potentials more active or more negative than the reversible potential a net reduction occurs. At the reversible potential, or at zero overvoltage, there is no net rate of oxidation or reduction since both rates are equal at this intersection point.

9-7 Concentration Polarization

To illustrate the phenomenon of concentration polarization, consider the hydrogen-evolution reaction. As shown schematically in Fig. 9-14, at low reduction rates the distribution of hydrogen ions in the solution adjacent to the electrode surface is relatively uniform. At very high reduction rates the region adjacent to the electrode surface will become depleted of hydrogen ions. If the reduction rate is increased further, a limiting rate will be reached that is determined by the diffusion rate of hydrogen ions to the electrode

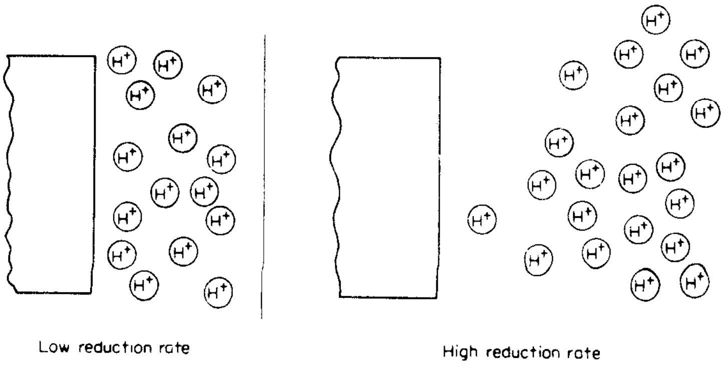

Figure 9-14 Concentration gradients during hydrogen evolution, shown schematically.

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*This applies only at overvoltages greater than approximately ±50 mV. However, since polarization during corrosion reactions is usually greater than ±50 mV, a linear relationship can be generally assumed.

surface. This limiting rate is the *limiting diffusion current density* i_L. It represents the maximum rate of reduction possible for a given system; the equation expressing this parameter is

$$i_L = \frac{DnFC_B}{x} \tag{9.12}$$

where i_L is the limiting diffusion current density, D is the diffusion coefficient of the reacting ions, C_B is the concentration of the reacting ions in the bulk solution, and x is the thickness of the diffusion layer.*

Equation (9.12) shows that limiting diffusion current is a function of the diffusion coefficient, the concentration of reacting ions in solution, and the thickness of the diffusion layer. Changes that affect these parameters influence the limiting diffusion current. It is generally observed that there is a linear relationship between the concentration of reactive ions in solution and the limiting diffusion current density, as indicated in Eq. (9.12). The diffusion layer thickness is influenced by the shape of the particular electrode, the geometry of the system, and by agitation. Agitation tends to decrease the diffusion layer thickness because of convection currents and consequently increases the limiting diffusion current density. Limiting diffusion current density is usually only significant during reduction processes and is usually negligible during metal-dissolution reactions. Hence, limiting diffusion current density can be ignored during most metal-dissolution reactions. The reason for this is, simply, that there is an almost unlimited supply of metal atoms for dissolution. Although the limiting diffusion current density of a particular system is precisely defined by Eq. (9.12), the magnitude of the diffusion layer thickness is extremely difficult to calculate except for very simple systems. The value of the diffusion layer thickness must be determined by empirical experimental measurements. Although this may seem to limit the application of these concepts, it should be noted that many useful qualitative predictions and correlations can be achieved merely by the knowledge of the relationship between limiting diffusion current density and various other factors of the particular system. These factors are discussed in detail below and also in Chap. 10.

If we consider an electrode in which there is no activation polarization, then the equation for concentration polarization is

$$\eta_c = 2.3 \frac{RT}{nF} \log\left(1 - \frac{i}{i_L}\right) \tag{9.13}$$

where the terms are as defined in Eqs. (9.9) and (9.12). A graphical representation of the Eq. (9.13) is shown in Fig. 9-15. Concentration polarization does not become apparent until the net reduction current density approaches the

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*See Glasstone and Potter for the derivation of this equation (Suggested Reading at end of Sec. 9-11).

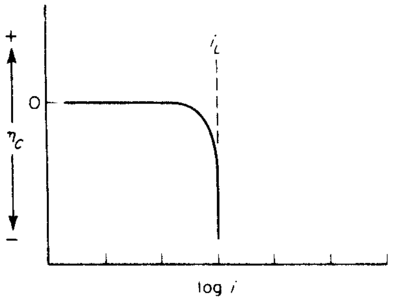

Figure 9-15 Concentration polarization curve (reduction process).

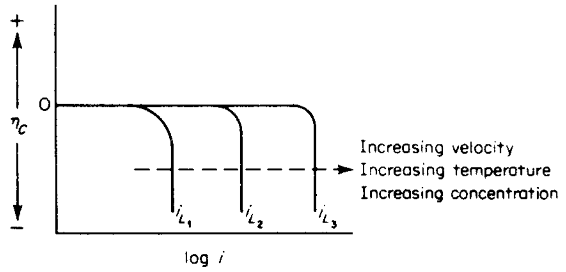

Figure 9-16 Effect of environmental variables on concentration polarization curve.

limiting diffusion current density. The net reduction current asymptotically approaches the limiting diffusion current density. Examination of Eq. (9.13) indicates that when the net reduction current is equal to the limiting diffusion current, overvoltage is equal to infinity.

Figure 9-16 illustrates the effects of changing limiting diffusion current on the shape of the polarization curve encountered during concentration polarization. As the solution velocity, concentration, or temperature are increased, limiting diffusion current increases since all of these factors exert an influence, as indicated in Eq. (9.12).

9-8 Combined Polarization

Both activation and concentration polarization usually occur at an electrode. At low reaction rates, activation polarization usually controls, whereas at higher reaction rates concentration polarization becomes controlling. The total polarization of an electrode is the sum of the contributions of activation polarization and concentration polarization:

$$\eta_T = \eta_a + \eta_c \tag{9.14}$$

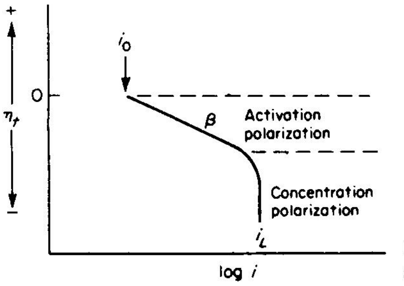

Figure 9-17 Combined polarization curve—activation and concentration polarization.

where η_T is total overvoltage. During anodic dissolution, concentration polarization is not a factor as mentioned above, and the equation for the kinetics of anodic dissolution is given by:

$$\eta_{\text{diss}} = \beta \log \frac{i}{i_0} \tag{9.15}$$

See Eq. (9.11). During reduction processes such as hydrogen evolution or oxygen reduction, concentration polarization becomes important as the reduction rate approaches the limiting diffusion current density. The overall reaction for a reduction process is given by combining Eqs. (9.11) and (9.13) with appropriate signs:

$$\eta_{\text{red}} = -\beta \log \frac{i}{i_0} + 2.3 \frac{RT}{nF} \log\left(1 - \frac{i}{i_L}\right) \tag{9.16}$$

Equation (9.16) is graphically illustrated in Fig. 9-17.

The importance of Eqs. (9.15) and (9.16) cannot be overemphasized since they are the basic equations of all electrochemical reactions. Equation (9.16) applies to any reduction reaction, and Eq. (9.15) applies to almost all anodic dissolution reactions. Exceptions to Eq. (9.15) are metals which demonstrate active-passive behavior; these discussed in detail below. Using only three basic parameters, namely, β, i_0 and i_L, the kinetics of virtually every corrosion reaction can be precisely described. Equations (9.15) and (9.16) represent an outstanding simplification of the complex phenomena observed during corrosion reactions. The use and application of these two equations are described below and also in greater detail in Chap. 10.

9-9 Mixed-Potential Theory

Although the concepts utilized in the mixed-potential theory were known before 1900, the first formal presentation of this theory is usually attributed to Wagner and Traud in 1938. The mixed-potential theory consists of two simple hypotheses:

1. Any electrochemical reaction can be divided into two or more partial oxidation and reduction reactions.
2. There can be no net accumulation of electric charge during an electrochemical reaction.

The first hypothesis is quite obvious, and it can be experimentally demonstrated that electrochemical reactions are composed of two or more partial oxidation or reduction reactions. The second hypothesis is merely a restatement of the law of conservation of charge. That is, a metal immersed in an electrolyte cannot spontaneously accumulate electric charge. From this it follows that *during the corrosion of an electrically isolated metal sample, the total rate of oxidation must equal the total rate of reduction.*

The mixed-potential theory, together with the kinetic equations described above, constitute the basis of modern electrode-kinetics theory.

9-10 Mixed Electrodes

The utilization of the mixed-potential theory can be best demonstrated by considering mixed electrodes. A mixed electrode is an electrode or metal sample that is in contact with two or more oxidation-reduction systems. To illustrate, let us consider the case of zinc immersed in hydrochloric acid. Under these conditions the zinc is rapidly corroded by the hydrochloric acid, and the electrochemical reactions occurring can be represented as in Fig. 9-18. If we consider a zinc electrode in equilibrium with its ions, it would

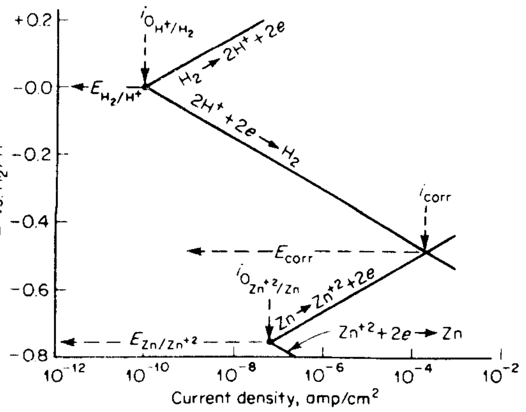

Figure 9-18 Electrode kinetic behavior of pure zinc in acid solution, shown schematically.

be represented by a reversible potential corresponding to the zinc–zinc-ion electrode reaction, and a corresponding exchange current density. Likewise, if we consider the hydrogen-electrode reaction occurring on a zinc surface under equilibrium conditions, then this particular equilibrium state would be represented by the reversible potential of the hydrogen electrode and the corresponding exchange current density for this reaction on a zinc metal surface. However, if a piece of zinc is inserted in hydrochloric acid containing some zinc ions, the electrode cannot remain at either of these two reversible potentials but must lie at some other potential. Zinc, since it is metallic, is an excellent conductor, and its entire surface must be at a constant potential. This potential is achieved when the second hypothesis of the mixed-potential theory is satisfied; that is, the total rate of oxidation must equal the total rate of reduction.

Examination of Fig. 9-18 illustrates this principle graphically. The only point in this system where the total rates of oxidation and reduction are equal is at the intersection represented by a "mixed" or corrosion potential E_{corr}. At this point the rate of zinc dissolution is equal to the rate of hydrogen evolution expressed in terms of current density.* For every zinc ion released, two electrons are utilized in forming a hydrogen molecule. Only at this point is charge conservation maintained. The current density corresponding to this point is usually called corrosion current density, i_{corr}, since it represents the rate of zinc dissolution. It should be noted that i_{corr} also corresponds to the rate at which hydrogen gas is evolved. If the β values and exchange current densities for this system are known, it is possible to predict the corrosion rate of zinc in hydrochloric acid from electrochemical data. For purposes of comparison, a current density of 1 $\mu A/cm^2$ roughly corresponds to a corrosion rate of 1 mpy for most metals. The exact relationship between dissolution current density and corrosion rate can be calculated utilizing Faraday's law. However, for general comparison purposes the above estimation is reasonably accurate.

To illustrate the importance of kinetic factors in determining the corrosion behavior of a metal let us examine the corrosion behavior of iron in dilute hydrochloric acid solution. Figure 9-19 qualitatively represents this particular system. The two reactions occurring are iron dissolution($Fe \rightarrow Fe^{2+} + 2e$) and hydrogen evolution ($2H^+ + 2e \rightarrow H_2$). The steady state of this particular system occurs at the intersection between the polarization curves for iron dissolution and hydrogen evolution. Although the free energy for the dissolution of iron is lower than that of zinc (the cell potential for iron and the hydrogen electrode under standard conditions is 0.440 volt as con-

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*Note that the reverse reactions, zinc deposition ($Zn^{2+} + 2e \rightarrow Zn$) and hydrogen oxidation ($H_2 \rightarrow 2H^+ + 2e$), do not occur since the corrosion potential lies between 0.0 and −0.76 volt. Zinc deposition can only occur at potentials more negative than −0.76, and hydrogen oxidation only occurs at potentials more positive than 0.00 volt.

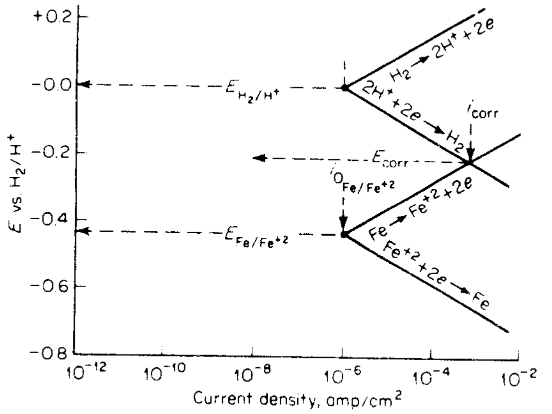

Figure 9-19 Schematic representation of electrode kinetic behavior of pure iron in acid solution.

trasted to 0.76 volt for zinc), the corrosion rate of iron is greater than that of pure zinc when exposed to identical concentrations of hydrochloric acid. This is due to the very low exchange current density for the hydrogen-evolution reaction on zinc surfaces. Thus, although the free-energy change for the corrosion of zinc is negative and greater than that for iron, the corrosion rate of zinc is less than that of iron. This illustrates the error that may be introduced by assuming that free-energy change and corrosion rate are proportional.

The system illustrated in Fig. 9-18 represents one of the simplest corrosion systems, a metal in contact with a single redox system. Under many actual corrosion conditions the environment is more complicated. Consider the corrosion behavior of a metal M in an acid containing ferric salts. This system is schematically illustrated in Fig. 9-20. Note that reversible potentials are indicated for the three redox systems, metal-metal ion, hydrogen ion - hydrogen gas, and ferric-ferrous ions. These can be assumed since all ferric salts contain traces of ferrous ions, and trace amounts of hydrogen gas and metal ion are present in this medium. The basic principles of the mixed-potential theory also apply to this more complex system. At steady state, the total rate of oxidation must equal the total rate of reduction. To determine steady-state conditions, the total rate of oxidation is determined by summing the individual oxidation currents corresponding to metal dissolution, hydrogen-gas oxidation, and ferrous-ion oxidations at constant potentials. As shown in Fig. 9-20, the total rate of oxidation follows the metal-dissolution rate until the reversible hydrogen potential is reached and an increase is noted because of the addition of hydrogen-oxidation currents. In a similar fashion, the total rate of reduction is determined by summing the total reduction currents corresponding to ferric-ion reduction, hydrogen-ion

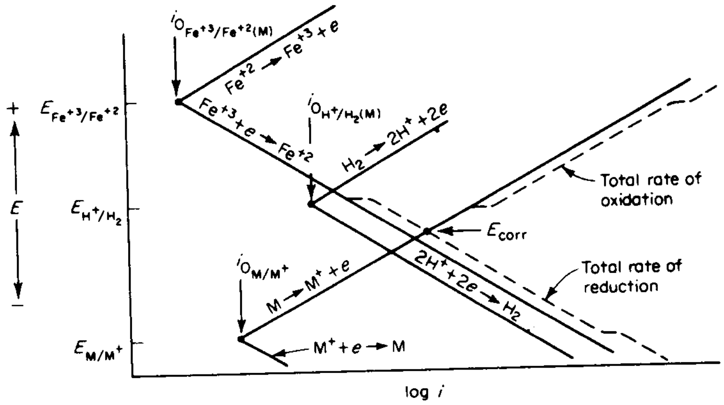

Figure 9-20 Behavior of metal M in acid solution containing ferric salts showing determination of E_{corr}.

reduction, and metal-ion reduction, as shown in Fig. 9-20. The point at which the total rate of oxidation equals the total rate of reduction is the mixed or corrosion potential of this system. The rates of the individual processes which are occurring in this system are illustrated in Fig. 9-21. A horizontal line is drawn at E_{corr} since the metal is equipotential. The rate of metal dissolution or the corrosion current is given by i_{corr}, the rate of ferric-ion reduction is equal to $i_{(Fe^{3+} \rightarrow Fe^{2+})}$, and the rate of hydrogen evolution is given by $i_{(H^+ \rightarrow H_2)}$. Note that this graphical construction leads to the equation

$$i_{corr} = i_{(Fe^{3+} \rightarrow Fe^{2+})} + i_{(H^+ \rightarrow H_2)} \tag{9.17}$$

Equation (9.17) satisfies the charge conservation principle of the mixed-potential theory.

Figure 9-21 illustrates some interesting principles concerning the corrosion of a metal in acid solutions containing oxidizers. In the absence of oxidizers, the corrosion rate of metal M is given by the intersection of the hydrogen-reduction and metal-dissolution polarization curves. The addition of an oxidizer, such as ferric ions, shifts the corrosion potential to E_{corr} and consequently increases corrosion rate from i'_{corr} to i_{corr} and decreases hydrogen evolution from i'_{corr} to $i_{(H^+ \rightarrow H_2)}$. Note that in oxidizer-free acids i_{corr} = rate of H_2 evolution. Experimentally, it is usually observed that the rate of hydrogen evolution is decreased markedly by the addition of oxygen or oxidizing agents to acid solutions. This phenomenon has often been termed *depolarization* and is assumed to be the result of interactions between the oxidizing agents and hydrogen gas on the surface. Figure 9-21 indicates that this is not the case; the reduction in hydrogen-evolution rate is a direct result of the shift in corrosion potential and is completely independent of the chemical character of the oxidizing agent.

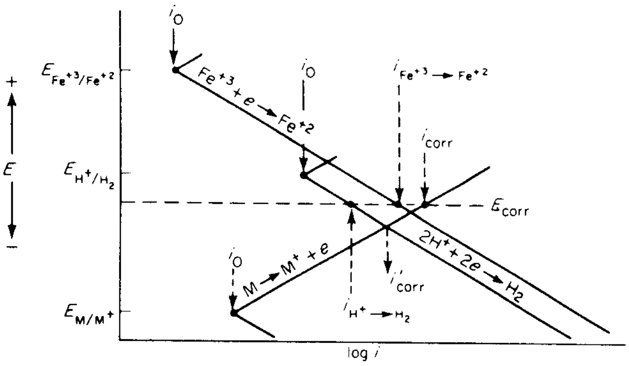

Figure 9-21 Behavior of metal M in acid solution containing ferric salts showing calculations of reaction rates.

The effect of an oxidizing agent is dependent both on its redox potential and its particular reduction kinetics. In the example shown above, the addition of ferric ions causes a pronounced change because of the relatively noble redox potential of the ferric-ferrous half-cell and its relatively high exchange current density of the surface of metal M. Figure 9-22 illustrates the importance of kinetic factors in determining the effect of an oxidizing-agent condition. In this figure, the exchange current density for the ferric-ferrous half-cell on metal M is considered to be very small. Reduction currents influence the total reduction rate only if they are within one order of magnitude of the major reduction process. As shown in Fig. 9-22, the addition of ferric ions produces no change in the corrosion potential and corrosion rate

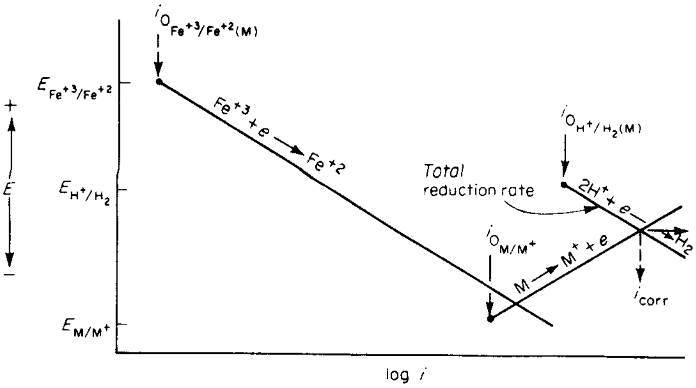

Figure 9-22 Behavior of metal M in acid solution containing ferric salts showing effect of oxidizer exchange current density.

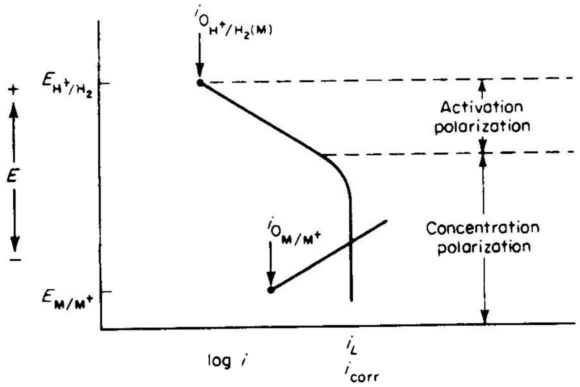

Figure 9-23 Corrosion of metal M under reduction-diffusion control.

of the system. This example serves to illustrate that not only is the redox potential of a particular oxidizing agent important, but also its exchange current density on the particular metal surface involved. This same kind of analysis can be applied to more complex systems; for example, a metal immersed in an acid solution containing several oxidizers such as ferric ion, cupric ion, and oxygen. Further, as we will see later, it can also be applied to the corrosion of two different metals immersed in contact in the same electrolyte. In all cases the analysis is exactly the same. The total rates of oxidation and reduction are determined, and the resulting corrosion potential of the system is graphically located. From this, the dissolution rate and the rates of the individual processes can be determined.

All of the above examples were shown with systems under activation polarization. The same principles can be applied to systems where one or more of the reduction processes are under diffusion control. Such an example is shown in Fig. 9-23, which represents the corrosion of a metal M in a weak acid solution where the reduction process is under diffusion control. In this example, the metal M follows the typical anodic dissolution reaction under activation control as given in Eq. (9.15). The reduction process follows Eq. (9.16). Initially, the reduction rate of hydrogen ions is under activation control; at higher reduction currents it is controlled by concentration polarization. The corrosion rate of this system is equal to i_{corr} or i_L and, as before, is determined by the intersection between the total reduction rate and total oxidation rate.

The graphical analyses presented here are probably new to many readers. Familiarity with these techniques can be readily gained by making similar analyses of hypothetical systems on semilogarithmic paper.

9-11 Passivity

Passivity is an unusual phenomenon observed during the corrosion of certain metals and alloys. Simply, it can be defined as a loss of chemical reactivity under certain environmental conditions. This is a very simple statement—we shall see later that it is possible to define this phenomenon more precisely by electrochemical parameters. To illustrate the nature of passivity, let us consider some of the very earliest experiments conducted by Faraday in the 1840s with the corrosion of iron in nitric acid. This particular series of experiments can be readily and simply accomplished in the laboratory and illustrates both the spectacular and unusual behavior of the passive state. If a small piece of iron or steel is immersed in nitric acid of approximately 70% concentration at room temperature, no reaction is observed. Weight loss determinations indicate that the corrosion rate of the iron in this system is extremely small, approaching zero. This experiment is illustrated in Fig. 9-24*A*. If water is now added, diluting the nitric acid approximately 1 to 1, no change occurs. The iron sample remains inert as shown in Fig. 9-24*B*. However, if the iron is scratched with a glass rod or if the beaker is shaken violently so that the sample strikes the sides, a violent reaction occurs. The iron rapidly goes into solution, and large volumes of nitrogen oxide gases are released (Fig. 9-24*C*). A similar effect occurs if the iron is directly introduced into diluted nitric acid.

Figures 9-24*B* and *C* illustrate the phenomenon of passivity. Both systems are identical. In one, the iron is almost inert, while in the other it corrodes at an extremely rapid rate. The difference in rates is of the order of about 100,000 to 1. In Fig. 9-24*B* the iron is considered to be in the passive state; in Fig. 9-24*C* the iron is in the so-called active state.

The above simple experiments demonstrate several important points concerning passivity. First, in the passive state, the corrosion rate of a metal is very low. Frequently the reduction in corrosion rate accompanying the transition from active to passive state will be of the order of 10^4 to 10^6. Secondly, the passive state often is relatively unstable and subject to damage

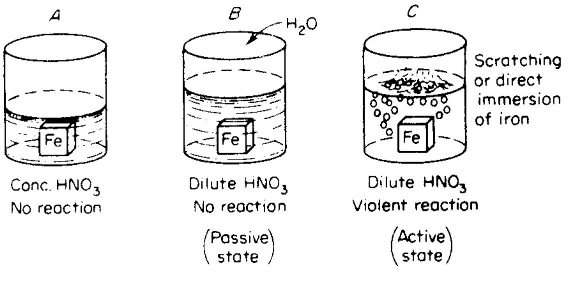

Figure 9-24 Schematic illustration of Faraday's passivity experiments with iron.

as shown by the effect of scratching in the above experiments. Hence, from an engineering viewpoint, passivity offers a unique possibility for reducing corrosion, but it must be used with caution because of the possibility of a transition from the passive to active state. The unusual characteristics of passivity, together with the possibility of utilizing this during engineering applications, explain why this subject has been studied extensively since its first observation more than 120 years ago.

The experiments described above, and numerous others, indicate that passivity is the result of a surface film. It is estimated that the film is only approximately 30 angstroms or less in thickness, contains considerable water of hydration and, as noted above, is extremely delicate and subject to changes when removed from a metal surface or when the metal is removed from the corrosive environment. Hence, the nature of the passive film, and consequently the basic nature of passivity, still remains an unsolved problem. Electrochemical studies conducted during the past 10 years have led to numerous and significant developments in the field of corrosion based on an increased knowledge of passivity. These studies do not give information concerning the nature of the passive film, but rather, are completely independent of the mechanism.

Iron, chromium, nickel, titanium and alloys containing major amounts of these elements demonstrate active-passive transitions. There are several other metals and alloys which also demonstrate passivity, but for our purposes we are primarily interested in the above metals since they are important materials of construction. Figure 9-25 schematically illustrates the typical behavior of an active-passive metal. The metal initially demonstrates behavior similar to nonpassivating metals. That is, as electrode potential is

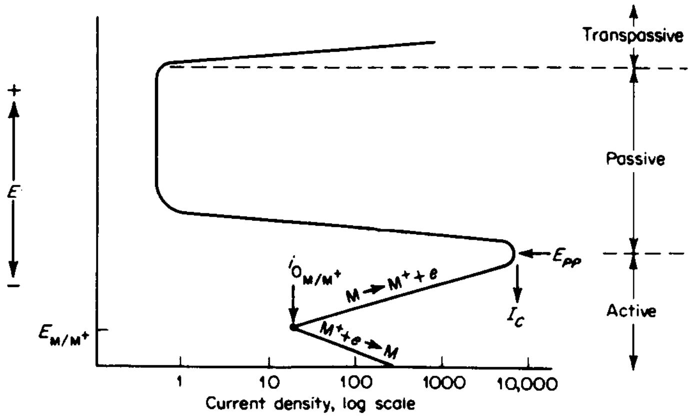

Figure 9-25 Typical anodic dissolution behavior of an active-passive metal.

made more positive, the metal follows typical Tafel behavior, and dissolution rate increases exponentially. This is the active region. At more noble potentials, dissolution rate decreases to a very small value and remains essentially independent of potential over a considerable potential region. This is termed the passive region. Finally, at very noble potentials, dissolution rate again increases with increasing potential in the transpassive region. As discussed below, one of the important characteristics of an active-passive metal is the position of its anodic current density maximum characterized by the primary passive potential E_{pp} and the critical anodic current density for passivity I_c. Electrode potential can be crudely equated to the oxidizing power of a medium, and hence a similarity between Fig. 9-25 and those shown previously in Chap. 2 is evident.

Figure 9-25 presents very useful information. First, it provides a method for defining passivity. A passive metal or alloy is one which demonstrates the typical S-shaped dissolution curve shown.* Further, it also illustrates the decrease in dissolution rate accompanying the active-to-passive transition. This decrease in dissolution rate just above the primary passive potential is the result of film formation at this point. The transpassive region where dissolution rate again increases with increasing potential is apparently due to the destruction of the passive film at very positive potentials.

Figure 9-26 illustrates the effect of increasing temperature and acid concentration on the behavior of an active-passive metal. Both temperature and hydrogen-ion concentration tend to increase the critical anodic current density and usually have relatively little effect on the primary passive potential and passive dissolution rate. A similar effect is noticed upon increasing

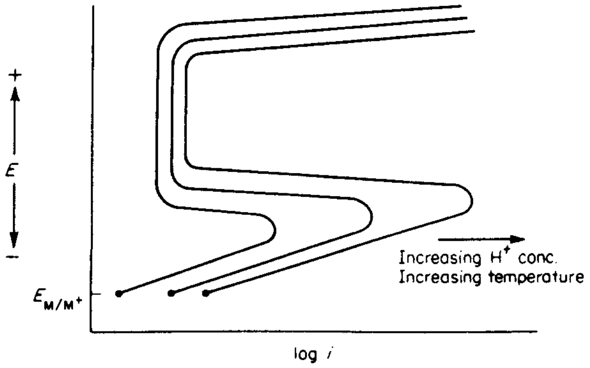

Figure 9-26 Effect of temperature and acid concentration on anodic dissolution behavior of an active-passive metal.

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*Titanium is an exception; it does not possess a transpassive region.

chloride additions in the case of stainless steels and other ferrous-base alloys. Additional information concerning the effect of environmental variables on the characteristic of active-passive metals can be found in the sources listed at the end of this section.

When considering mixed electrodes involving an active-passive metal, the peculiar S-shaped anodic polarization curves of these metals often leads to unusual results. Figure 9-27 illustrates three possible cases that may occur when an active-passive metal is exposed to a corrosive environment such as an acid solution. Reduction processes under activation polarization control are shown in Fig. 9-27. However, it should be noted that the cases shown here are general and apply regardless of the shape of the reduction polarization curve. Figure 9-27 shows a single reduction process such as hydrogen evolution with three different possible exchange current densities. In case 1 there is only one stable intersection point, point *A*, which is in the active region, and a high corrosion rate is observed. Case 1 is characteristic of titanium in dilute, air-free sulfuric or hydrochloric acid. Under these conditions, titanium corrodes rapidly and cannot passivate. Case 2 is particularly interesting since there are three possible intersection points at which the total rate of oxidation and total rate of reduction are equal. These are points *B*, *C*, and *D*. Although all three of these points meet the basic requirements of the mixed-potential theory (rates of oxidation and reduction are equal), point *C* is electrically unstable and, as a consequence, the system cannot exist at this point. Hence, both points *B* and *D* are stable; *B* is in the active region corresponding to a high corrosion rate, while *D* is in the passive region with a low corrosion rate. This system may exist in either the active or passive state. Chromium in air-free sulfuric acid and iron in dilute nitric acid are typical of this behavior. That is, both active and passive states are stable under identical environmental conditions. The unusual transition described for iron in dilute nitric acid upon scratching the surface, is due to a passive-to-active transition (point *D* to point *B*).

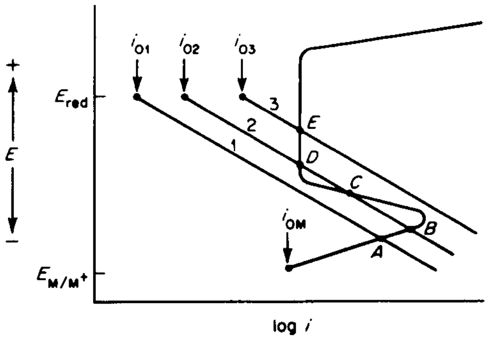

Figure 9-27 Behavior of an active-passive metal under corrosive conditions.

In case 3 there is only one stable point, in the passive region at point *E*. For such a system, the metal or alloy will spontaneously passivate and remain passive. This system cannot be made active and always demonstrates a very low corrosion rate. The system represented by case 3 is typical of stainless steels and titanium in acid solutions containing oxidizers such as ferric salts or dissolved oxygen and also iron in concentrated nitric acid (Fig. 9-24*A*).

From an engineering viewpoint, case 3 is the most desirable. This system will spontaneously passivate and corrode very slowly. Although in case 2 the passive state is possible, this particular situation is not desirable. In fact, it is the least desirable of the three cases, since an unexpected transition from the passive to active state as a result of surface damage or similar factors could lead to rapid attack. Case histories of such failure are quite common, the most common being stainless steels exposed to aerated acid solutions or acid solutions containing traces of oxidizers. During preliminary corrosion testing where specimens are handled carefully, it is frequently observed that all specimens exist in the passive state. However, when a chemical plant or component is fabricated from the material and installed, damage to the surface may result in a transition from the passive to active states. Case 1 is not particularly desirable, since the corrosion rate is usually quite high. However, since the corrosion rate is constant, predictions based on laboratory and pilot-plant tests are more accurate than those obtained with a system similar to case 2.

Considering Fig. 9-27, it is readily apparent why the position of the current maximum or "nose" of the anodic polarization curve is important. Spontaneous passivation only occurs if the cathodic reduction process clears the tip of the nose of the anodic dissolution curve as shown in case 3. More precisely, at the primary passive potential, the cathodic reduction rate must be equal to or greater than the anodic dissolution rate for spontaneous passivation to occur. It follows that a metal or alloy will be more readily passivated if it has a small critical anodic current density and an active primary passive potential. From this it is easy to see that a knowledge of the anodic dissolution behavior of a metal or alloy can be used to quantitatively determine its ease of passivation and consequently its ultimate corrosion resistance. This method of evaluating the corrosion resistance of a metal or alloy is discussed in greater detail in Chap. 10.

Suggested Reading

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