

The Fundamentals of Corrosion Science and Engineering: Equilibrium Theory and Its Meaning

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Abstract Corrosion is basically the oxidation of metals, where electrons are transferred between oxidant and reductant. Therefore, corrosion is generally composed of redox reactions and should be analyzed from the viewpoint of electrochemistry. In this chapter, we describe the basic concept of electrochemistry and how various corrosion aspects can be explained by this discipline. We focus particularly on the equilibrium side because it could suggest possibilities that might be useful for corrosion prediction. The close relationship between redox reactions and corrosion are explained and stressed qualitatively and quantitatively.

1 Introduction

As mentioned in the introductory chapter, metals were originally combined with oxygen, sulfur, and other non-metallic components to form minerals. From the viewpoint of thermodynamics, the state of compounds has lower energy and is more stable than that of metals themselves. It means that we generally need to add energy in order to produce metals. Since we could consider corrosion to be a reverse reaction of metal production, it is a very natural chemical reaction that occurs spontaneously in nature (Fig. 1). At this point, we already know that corrosion is basically an oxidation reaction. Therefore, corrosion (as a redox reaction) can be analyzed from the viewpoint of electrochemistry. Here we can see the fundamental aspect of electrochemistry as it relates to corrosion.

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Fig. 1 Metal production and corrosion phenomena

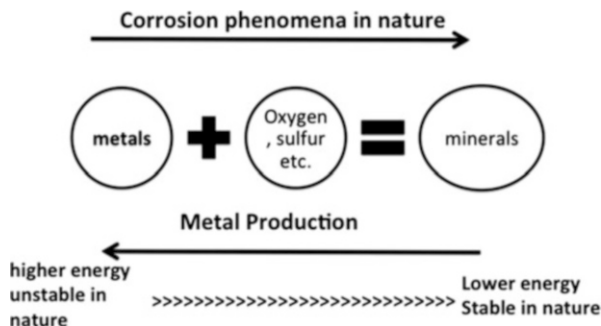
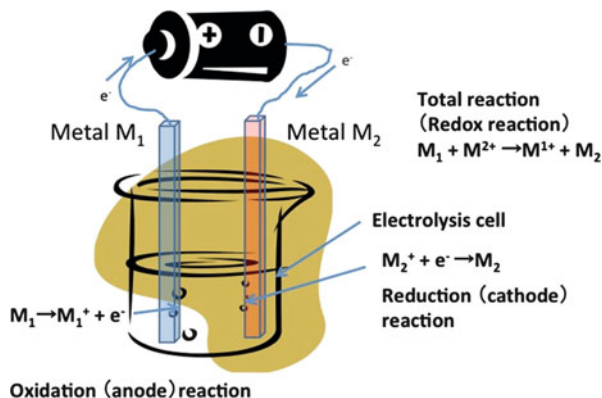


Fig. 2 Schematic illustration for electrolysis



2 Faraday's Law

Electrolysis is a fundamental phenomenon not only for corrosion, but also for electric cells, plating, electrolysis, synthesis, etc. Figure 2 shows the schematic illustration for electrolysis. Two electrodes are immersed in the electrolytic bath. One is an anode and the other is the cathode. At the anode, anodic reactions occur where electrons are released, as shown in Eq. (1).



M: electrode metal, n: electric charge number, e: electron

On the other hand, electrons are bound with ions at the cathode. If the aqueous solution is acid, the main cathode reaction might be the reduction of hydrogen ion to produce hydrogen gas, shown in Eq. (2).



Electrolysis generally occurs this way. In 1833, Michael Faraday discovered that electrolysis obeys a certain law. Actually, it can be divided into two laws.

One of them is the relation between the amount of electrolyzed matter and electric charges consumed during electrolysis. The amount of matter produced by electrolysis is proportional to the electric charge used for it. The relation can be formulated as shown in Eq. (3).

$$m = K \times I \times t = K \times Q \quad (3)$$

m : the amount of matter produced or decomposed during electrolysis

K : electrochemical equivalent, I : current [A], t : time [s], Q : charge of electricity, electric charge [Q]

$$n = \frac{m}{M} = \frac{It}{zF} \quad (4)$$

n : the amount of substance [mol], m : mass [g], M : Molecular weight [g/mol], I : current [A], t : time [s], z : valence of ion,

F : Faraday constant $9.6485 \times 10^4 [C/mol]$

The law expressed mathematically in Eq. (4) is called Faraday's second law. This law makes certain that the electrochemical equivalent is compatible with the chemical equivalent. See Eq. (4).

It means that the amount of electrical charge needed to precipitate 1 g equivalent of a substance is always constant, regardless of the kind of matter. The constant value is usually denoted as F and called the Faraday constant. Faraday found the relations in the nineteenth century, when people did not know about the existence of electrons at all. However, the laws suggested it very strongly. From the viewpoint, it could open an important door to the quantum mechanics world in the twentieth century.

The equation could be changed in the following way.

$$v = \frac{dm}{dt} = \frac{n}{t} = \frac{I}{zF} \quad (5)$$

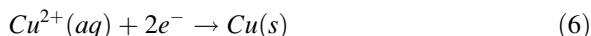
v means the production rate of a substance through electrolysis. Therefore, Eq. (5) suggests that the current could control the production rate of a substance during electrolysis.

3 The Electric Cell and Its Electric Motive Force

Figure 2 shows the case where the external electric force would drive the electrochemical reaction and produce the electric current as a result. On the other hand, we could think of a similar system without the external electric force. In this case, the electrochemical reactions would occur within the internal system and produce the flow of electrons as a result. We could take the electrical energy from the system and use it. The system is often called an electric cell. The system is shown in Fig. 3 schematically.

Historically, the Daniel Cell has been very well-known for the fundamental electric cell system. The schematic structure is shown in Fig. 4.

Two electrodes are immersed in aqueous sulfuric acid solution. One of the electrodes is zinc and the other one is copper. A barrier membrane is placed between the two electrodes. It could block the passage of cations, while it could allow anions to move through it freely. The copper is precipitated onto the zinc electrode. The color changes to dark brown, while the color of the solution (blue) gradually gets pale. This suggests that the copper ions in the aqueous solution precipitate onto the zinc electrode, as shown in Eq. (6).



Here, (aq) means an aqueous solution and (s) means the element exists as a solid. At the other electrode (zinc electrode), the following reaction (7) occurs.



The overall reaction could be written as the sum of the Eqs. (6) and (7) in the following way, Eq. (8).

Fig. 3 Conversion of the energy from chemical reactions to electrical energy

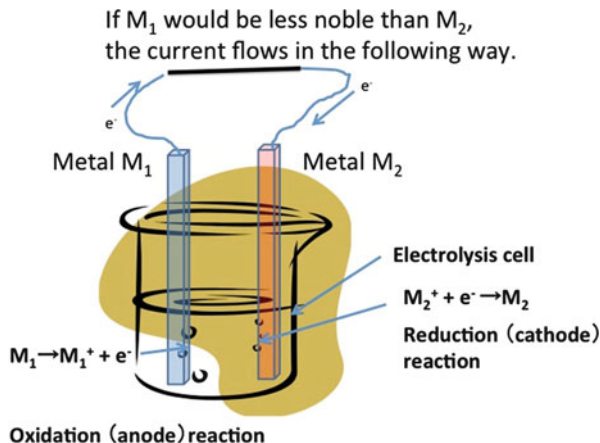
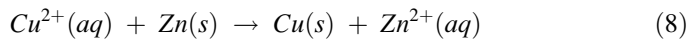
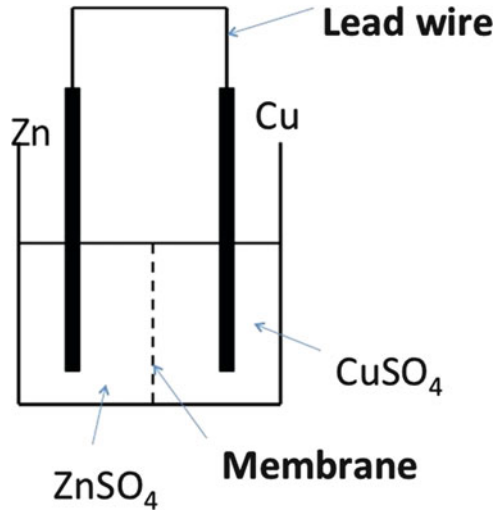


Fig. 4 Daniel Cell and its structure



Electric Cells are usually expressed in the following way, Eq. (9), from the viewpoint of cell structure.



The symbol, “|”, corresponds to the interface between two different phases, such as solid/liquid. The other symbol, “||”, corresponds to the membrane.

At the interface, the potential difference generally appears. If the right potential difference would be E_r and the left one E_l , the electromotive force, E_e , can be defined as follows Eq. (10).

$$E_e = E_r - E_l \quad (10)$$

The left electrode, $\text{Zn} | \text{Zn}^{2+}$, is less noble and the right one, $\text{Cu}^{2+} | \text{Cu}$, is noble. The two electrodes (couple) constitute the Daniel cell.

As described above, the potential difference generally appears at the interface between the two different phases. Each interface where an anodic or a cathodic reaction occurs has its own potential defined by the Nernst Equation. The corresponding reaction is always a part of the whole Redox reaction. It is called a “half-cell reaction”. Some examples are shown in Table 1. Using such a table, one can get the potential for a half-cell reaction. Then one can estimate the electromotive force for the couple of electrodes, using Eq. (10).

Table 1 Some representative half-cell reactions and their potentials [1]

Redox reaction	E (V)	Redox reaction	E(V)
$Li^+ + e^- \leftrightarrow Li$	-3.05	$AgCl + e^- \rightleftharpoons Ag + Cl^-$	0.22
$K^+ + e^- \leftrightarrow K$	-2.92	$Hg_2Cl_2 + e^- \rightleftharpoons Ag^+ Cl^-$	0.27
$Ba^{2+} + 2e^- \rightleftharpoons Ba$	-2.90	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	0.34
$Ca^{2+} + 2e^- \rightleftharpoons Ca$	-2.76	$Ca^+ + e^- \rightleftharpoons Cu$	0.52
$Na^+ + e^- \rightleftharpoons Na$	-2.71	$I_2 + 2e^- \rightleftharpoons 2I^-$	0.54
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	-2.38	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	0.77
$Al^{3+} + 3e^- \rightleftharpoons Al$	-1.67	$Ag^+ + e^- \rightleftharpoons Ag$	0.80
$Mn^{2+} + 2e^- \rightleftharpoons Mn$	-1.03	$Br_2 + 2e^- \rightleftharpoons 2Br^-$	1.09
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	-0.83	$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	1.23
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0.76	$MnO_2 + 4H^+ + 4e^- \rightleftharpoons Mn + 2H_2O$	1.28
$Cr^{3+} + 3e^- \rightleftharpoons Cr$	-0.74	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	1.33
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	-0.44	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	1.36
$PbSO_4 + 2e^- \rightleftharpoons Pb + SO_4^{2-}$	-0.36	$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons PbSO_4 + 2H_2O$	
$Fe^{3+} + 3e^- \rightleftharpoons Fe$	-0.04	$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	1.78
$2H^+ + 2e^- \rightleftharpoons H_2$	0	$F_2 + 2e^- \rightleftharpoons 2F^-$	2.87

4 Redox Potential and Chemical Reaction [2, 3]

In the previous section, we used electrode potential without any strict definition. However, it should be defined in advance, in order to better understand it. Originally, the electrode potential was closely related to Gibbs free energy change of a reaction at the interface (electrode). It is also related to chemical affinity. In this electrochemical case, we might say that the electrode reaction should be related to electrochemical affinity. So what is electrochemical affinity? To answer this question and others would lead to a complete understanding of what electrode potential is and what it really means. We would like to introduce the concept of inner potential for the explanation.

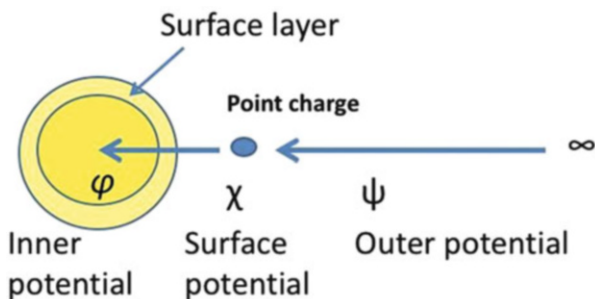
Let's think over the case shown in Fig. 5. A metallic electrode is placed in a vacuum. In the same vacuum phase, a point charge is placed. Here we postulate that the original distance of the point charge is separated enough from the electrode surface. When the point charge is moved from the infinite distance gradually ("gradually" means keeping the equilibrium state!), the work, W_t , can be expressed as follows.

$$W_t = W_\chi + W_i \quad (11)$$

Here W_χ is the work to move the point charge from the infinite distance to a very close point to the electrode surface. The special point (Point B) would be the limitation one where the image force available in the very close area to the electrode surface would not affect the moving of a point charge. On the other hand, the extra work would be required for the point charge to move into the inside phase (Point C) from point B. The work would be used for the point charge to overcome the very complicated potential barrier composed of dipole molecules, absorbed ones, etc. It corresponds to W_i . We can define the potential corresponding to the work. Therefore, the following Eq. (12) would be available.

$$\phi^i = \psi^i + \chi^i \quad (12)$$

Fig. 5 Inner potential, surface potential, and outer potential



ϕ_i is called the inner potential of phase i, ψ_i is the outer potential of phase i and χ_i is the surface potential. Essentially the inner potential is closely related to the electric potential.

Now we postulate that the different two phases, α and β , would be in contact with each other. The inner potentials corresponding to each phase can be described as ϕ^α and ϕ^β , respectively. Here we can define two types of potential differences. One of them is called the Galvani potential difference and is shown in the following Eq. (13).

$$\Delta\phi = \phi^\beta - \phi^\alpha \quad (13)$$

Another one is called the Volta potential difference or contact potential difference, as shown in Eq. (14).

$$\Delta\psi = \psi^\beta - \psi^\alpha \quad (14)$$

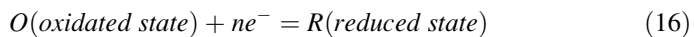
From (12) and (13), a Galvani potential difference can be described as follows (16).

$$\Delta\phi = (\psi^\beta - \psi^\alpha) + (\chi^\beta - \chi^\alpha) = \Delta\psi + \Delta\chi \quad (15)$$

The Volta potential difference can be measured in fact, while the Galvani potential difference could not be measured due to the complicated states of surface potentials and their difficult estimation. The potential difference at the interface between two contact phases corresponds to the Volta potential difference.

The potential difference is closely related to the difference of the electrochemical potential based on the electrochemical affinity. If we could measure $\Delta\phi$ directly, we could organize the table of electromotive forces based on the Galvani potential difference. However, $\Delta\phi$ is generally hard to measure. We always need a reference electrode to measure the half cell potential at an electrode. When a certain electrode is coupled with a reference electrode, then the electromotive force can be measured. Since we usually use some reference electrodes as standards, the electromotive force is defined as the equilibrium potential of the reaction. The table was made in such a way and the hydrogen reference electrode was used to measure and calculate potentials for the half cell reactions.

Now, we postulate the following Redox reaction at equilibrium.



When the potential is measured, based on a reference electrode such as a hydrogen reference electrode, the potential E has a certain relation with the electrochemical potential as follows.

$$nFE = -(\mu_R - \mu_O) \quad (17)$$

Here, μ_R and μ_O are the electrochemical potentials for the oxidant and reductant, respectively. When we describe the activities for O and R as a_O and a_R , respectively, the electrochemical potentials for the two substances can be shown as follows.

$$\mu_O = \mu_O^0 + RT \ln a_O \quad (18)$$

$$\mu_R = \mu_R^0 + RT \ln a_R \quad (19)$$

μ_O^0 and μ_R^0 are the electrochemical potentials when the activities of the substances are the unit.

From the Eqs. (17), (18) and (19), the following equation can be obtained.

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_O}{a_R} \quad (20)$$

Here E_0 is the equilibrium potential when both a_0 and a_1 are the units.

The Eq. (20) is called Nernst Equation.

5 Potential: pH Diagram

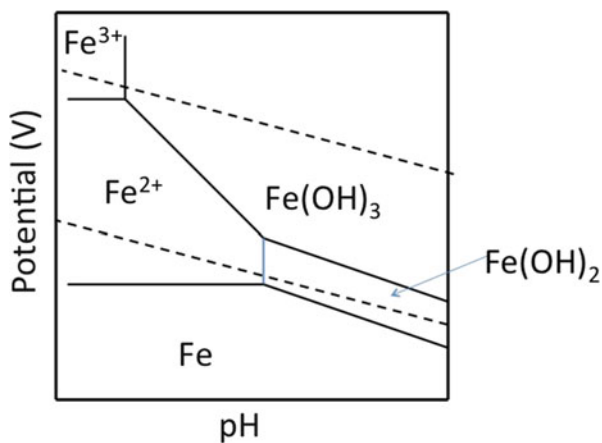
In the previous section, we described how to estimate the electromotive force for a couple of electrodes. Actually, the estimation is often needed to evaluate the possibility, if a type of corrosion would occur or not. As explained in the next chapter, corrosion can occur by one or more local cells formed on a material's surface. Therefore, it would be important from the viewpoint of corrosion prediction and analysis to evaluate the electromotive force for a combination of some reactions.

In the same way, a potential – pH diagram, is often used for estimations. The diagram has a potential axis (vertical one) and a pH axis (horizontal one). This diagram is also called a Pourbaix diagram after the original creator's name.

Figure 6 is an example for the case of iron. The figure is a schematic one. Using the reactions and the Nernst equation, the figure can be obtained for any metals. The dotted lines correspond to the decomposition of water. Therefore, the area between the two dotted lines is the stable area for water. Each area is surrounded by lines in the diagram. The areas where divalent or trivalent iron ions are stable correspond to corrosion ones. On the other hand, the areas where iron hydroxides are stable suggest that the thin oxide layers form on the iron surface to protect the substrate from corrosion. This schematic figure indicates that iron would be vulnerable to corrosion in acidic solutions or environments, while it has stronger corrosion resistance in alkaline solutions/environments.

In this chapter, we focused on the electrochemical potential, E , rather than the current. The potential can be used to predict the possibility of electrical potential.

Fig. 6 Schematic potential – pH diagram for iron



As for the kinetic aspect based on the current, we will explain it in the following chapters.

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Corrosion Control and Surface Finishing

Environmentally Friendly Approaches

Kanematsu, H.; Barry, D.M. (Eds.)

2016, XII, 302 p. 155 illus., 56 illus. in color., Hardcover

ISBN: 978-4-431-55955-9