# Part One

# Electrochemical Fundamentals and Active–Passive Corrosion Behaviors

# Chapter 1

# Fundamentals of Electrochemical Corrosion

## Overview

The thermodynamic tendency to corrosion and Gibbs free-energy change, $\Delta G = -nFE$, are discussed. The double layer is described and the Nernst equation is deduced to describe electrode potentials. Strong and weak electrolytes as well as Faraday laws are mentioned. The activity and conductance of the electrolyte are explained and the constant of dissociation and coefficients of dissociation and activity are defined.

Popular types of electrodes are examined and explained. The general approach to electrochemical cells is given and used to better explain the most frequently encountered corrosion cells. A classification of electrochemical cells and corrosion cells is then given. Electrochemical reactions are defined, such as those in which free electric charges, or electrons, participate. They are classified as micro- and macroelectrochemical cells (inseparable anode/cathode areas and separable anode/cathode areas). Corrosion chemical reactions, such as metal dissolution in liquid medium, can be described by the absence of charge transport in an electrolyte or a formed film at the interface in a metal–solvent reaction or at a metal–gas interface. A study of corrosion phenomena principally covers the corrosion product, the material, the medium, and the interface.

## A. THERMODYNAMIC CONSIDERATIONS OF CORROSION

Corrosion of metals is mainly due to an irreversible oxidation–reduction reaction, where an oxidizing agent in an environment attacks the metal. An electrochemical reaction is a chemical transformation that implies charge transport at the interface from a metallic conductor (electrode) to an ionic conductor (electrolyte). These are dependent on the thermodynamic and physical properties of the electrode and the activities of the different species in solution at the interface. The properties of the interface are dependent on temperature variation, bulk solution properties, convection, diffusion, and so on. In addition, metallurgical and mechanical properties of the electrode and microbiological organisms in solution or at the interface can cause corrosion alone or increase corrosion rates by a synergetic effect with electrochemical corrosion. In other limited conditions of corrosion, chemical reactions, such as the dissolution in liquid metals and some solvent media and

*Corrosion Resistance of Aluminum and Magnesium Alloys: Understanding, Performance, and Testing* By Edward Ghali

metal–gas free interface reactions, can cause corrosion alone or assist an electrochemical reaction.

## 1.1. ELECTROLYTIC CONDUCTANCE

Electrons are the current carriers in solids while ions are the only means of charge transport in a solution. An ion is an atom that has lost or gained electrons; if it lost some, it is a positive ion and called a cation, while if it gained some, it is a negative ion and called an anion. An ion can be a simple ion or a complex one. However, ions can be monovalent, divalent, trivalent, and so on (e.g., $Na^+$, $Mg^{2+}$, $Al^{3+}$) or complex ions (e.g., $SO_4{}^{2-}$, $PO_4{}^{3-}$, $Fe(CN)_6{}^{4-}$). The strength of attraction between sodium and chloride ions inside the crystal is $F = qq'/r^2$ ($q$ is the charge and $r$ is the distance between two ions from center to center). Once the sodium chloride is added to water as a solvent, the strength of attraction between sodium and chloride ions becomes $F = qq'/Dr^2$, where $D$ corresponds to the dielectric constant of water, which is close to 80 in centimeter-gram-second (CGS) units. The attraction therefore becomes 80 times smaller and the crystal separates into ions even at room temperature.

A solvated ion is an ion that fixes more closely one or several molecules of solvent. If the solvent is water, one says that the ion is hydrated. Many ions in aqueous solutions are hydrated such as given for HCl:

$$HCl + (n + m)H_2O \rightarrow H^+ \cdot nH_2O + Cl^- \cdot mH_2O$$

The values of $n$ and $m$ of $H_2O$ are not exactly known. The hydrated ions can conduct current, while liquid hydrochloric acid and pure water are bad conductors. The properties of hydrated or solvated ions in general are critical to conduction and corrosion.

Molten salts can be good electrolytes, such as potassium chloride that undergoes thermal agitation till melting. As the temperature rises, the strength of crystalline cohesion goes down. Once the resulting liquid at the point of fusion is reached, the $Cl^-$ and $K^+$ ions are relatively free to transport the charge and this can form a good electrolyte if the forces of attraction between differently charged ions do not dominate.

Under the effect of a sufficiently powerful outside electric field, one can produce a migration of ions of a solid salt in two opposite directions according to their signs. This is not the case of potassium chloride (KCl) and numerous other salts but this is the situation of several halides, such as silver bromide or iodide. AgI is considered a strong electrolyte but most solid electrolytes are weak. In the case of gas as an electrolyte, ions can form but their life span is very short and they recombine immediately to give the corresponding neutral molecules. It is necessary to use an outside energy source as the electric spark, and a plasma is helpful in separating and characterizing the ions separately for fundamental studies. Otherwise, there are many applications of plasma in the area of corrosion; for example, various plasma applications are emerging for anodizing (anodic oxidation) to protect Al or Mg alloys by forming their respective oxides.

All electrolytes are dissociated into ions independently of the passage of the current. Electrolytes can be divided into two groups:

1. *Strong electrolytes* dissociate almost completely in spite of the electrostatic attractions between oppositely charged ions. Their dissociation is almost total: $AB \rightarrow A^+ + B^-$.
2. *Weak electrolytes* are dissociated imperfectly or their dissociation is reversible: $AB \Leftrightarrow A^+ + B^-$.

In aqueous solution, with some exceptions, bases (e.g., NaOH) and salts (e.g., NaCl) are strong electrolytes. However, acids such as $CH_3COOH$ and $H_2S$ or bases such as $NH_4OH$ are weak. In the molten state, one considers a salt like KCl to be dissociated completely, while some melted salts undergo the phenomenon of association because of thermal agitation and attraction between positive and negative ions driving the formation of a weak mobile complex or even nonionized molecule. In this case, the molten electrolyte is considered weak. Many compounds, notably organic, are not ionized or hardly ionized in the melted state. It is interesting to note that acetic and hydrochloric acids in the pure liquid state don't drive the current.

### 1.1.1. Faraday Laws

The following three laws of Faraday apply for electrolysis and corrosion:

1. In electrolysis, products of the electrochemical decomposition appear on the electrodes and not within the electrolyte.
2. The metals of salts and bases and the hydrogen of acids appear at the cathode; remainders of the molecule and/or its products of decomposition appear at the anode.
3. The mass $m$ of deposited metal on the cathode by electrolysis is proportional to the quantity of current ($I$) crossing the cell and to the atomic mass of metal and inversely proportional to the valence of the metal:

$$m = \frac{1}{F} \times \frac{A}{n} \times I \times t$$

$F$ is called the Faraday constant and is $\sim$96,500 coulombs/mole if the current $I$ is expressed in amperes, the time $t$ is given in seconds, the atomic mass is in grams/mole, and $n$ is the electrovalence of an ion (sometimes expressed as $z$). The electrovalence of an ion should correspond to the number of electrons either gained or lost in the electrochemical reaction. Reactions of reduction occur at the cathode (gain of electrons) and reactions of oxidation occur at the anode (loss of electrons). The experience shows that a coulomb deposits 1.118 mg of silver. The atomic mass can be deposited by $107.88/0.001118 = 96{,}494$ coulombs, while the coulometer to iodine gives for 1 equivalent 96,514 coulombs (electrode of platinum and iridium using a solution of 10% KI). The quantitative law of Faraday applies to secondary reactions, that is, chemical reactions that follow electrochemical reactions.

Figure 1.1 shows a zinc–copper cell in a corrosive aqueous environment (exothermic reaction). By convention, in a cell, the polarity of the anode is negative and that of the cathode is positive (Figure 1.1). However, for electrolysis, the polarity of the anode is positive and that of the cathode is negative. In this case, the sign is imposed by the external electric current.

#### 1.1.1.1. Primary and Secondary Reactions

The reaction that involves a gain or a loss of electrons is considered the primary reaction. Often the remainder that appears at the anode is not chemically stable in solution such as the OH product species of a primary reaction that leads to the evolution of oxygen by the

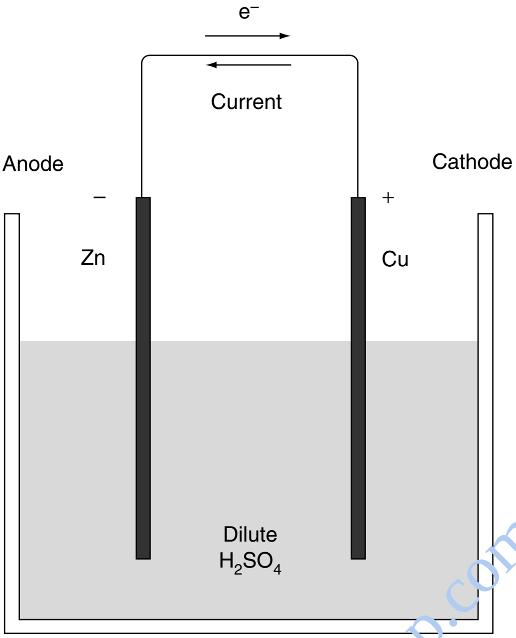

**Figure 1.1** Zn–Cu cell in dilute sulfuric acid ($H_2SO_4$).

reaction; the same applies for $SO_4$ and $SiF_6$. This reaction is called a *secondary reaction*. The primary and secondary reactions are dependent on the nature, composition, and microstructure of the electrode, the composition of the electrolyte, and the properties at the interface. The secondary reactions could produce the electrochemically active ion by dissociation of a complex, for example, or involve the substances formed by the primary reactions. The secondary reaction mechanism is often composed of one or more hypotheses that are very frequently based on the properties of the metal or material, the electrolyte at the interface, thermodynamic considerations, and kinetic approaches. The existence of some transient species could also be proved experimentally [1]. The primary and secondary reactions are indicated in the following for oxygen evolution in acidic nitrate solution:

$$\begin{array}{ll}
2NO_3^- \rightarrow 2NO_3 + 2e^- & \text{Primary reaction} \\
\left.\begin{array}{l} 2NO_3 + H_2O \rightarrow 2HNO_3 + \frac{1}{2}O_2 \\ 2HNO_3 \rightarrow 2H^+ + 2NO_3 \end{array}\right] & \text{Secondary reactions} \\
\hdashline
H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^- & \text{Total reaction}
\end{array}$$

## 1.2. TENDENCY TO CORROSION

The change in the Gibbs free energy, frequently designated as free enthalpy, or Gibbs function can be calculated from the equation $\Delta G = \Delta H + T\,\Delta S$, where $H$ is the enthalpy, $T$ is the absolute temperature, and $S$ is the entropy. The tendency for any chemical or electrochemical corrosion reaction is governed by the Gibbs free-energy change $\Delta G$. The $\Delta G$ of a corrosion reaction can be considered in its reduction form for magnesium and aluminum:

$$\mathrm{Al}^{3+} + 3\mathrm{e}^- \rightarrow \mathrm{Al}, \quad \Delta G = 481.374\ \mathrm{kJ}$$

$$\mathrm{Mg}^{2+} + 2\mathrm{e}^- \rightarrow \mathrm{Mg}, \quad \Delta G = 457.348\ \mathrm{kJ}$$

$$(F = 96,487\ \mathrm{C}, E^\circ(\mathrm{Al}) = -1.663\ \mathrm{V},\ \text{and}\ E^\circ(\mathrm{Mg}) = -2.37\ \mathrm{V})$$

The $\Delta G^\circ$ (standard free-energy change) of the reduction reaction corresponds to the difference of enthalpy between the oxidized products and the reactants in the standard states. Since the law of physics or nature is that the most stable state is the one with the lowest free energy, the reaction is exothermic when $\Delta G$ is negative. The more negative the value of $\Delta G^\circ$, the greater the tendency to corrosion. The positive value of the reduction potential of a gold reaction indicates the stability of this metal in water saturated with atmospheric oxygen [2]. When $\Delta G^\circ$ is equal to zero, there is no change in free energy of the reaction in each direction and this represents the equilibrium condition. It is assumed that every system reacts in a manner to offset any driving force and equilibrium is eventually obtained when $\Delta G^\circ = 0$. It should be emphasized that the tendency to corrode is not a measure of reaction rate. A large negative $\Delta G$ may or may not be accomplished by a high corrosion rate. If $\Delta G$ is negative, the reaction rate may be rapid or slow, depending on various kinetic factors and corrosion mechanisms. For chemical reactions it is convenient to make use of the van't Hoff equation: $\Delta G^\circ = -RT \ln K$, where $K$ is the product of the activities of reactants (in moles) at the state of equilibrium.

The net electrical work performed by a reaction giving a potential $E$ and supplying a quantity of electricity $Q$ equals $EQ$, but $Q = nF$, where $n$ is the number of equivalents, and so the net electrical work is $nFE$. However, any work by a cell can be accomplished only at the expense of a decrease in free energy occurring within the cell. The decrease in free energy must equal the electrical work done, and so $\Delta G = -nFE$. This equation of free energy is the bridge between thermodynamics and electrochemistry. Spontaneous reactions necessitate a positive potential and negative $\Delta G$; nonspontaneous reactions require negative potential and positive $\Delta G$. Every cell is composed of two individual single electrodes, such that their algebraic sum is equal to the total electromotive force (emf) of the cell [3]. In view of the electrochemical mechanism of corrosion, the tendency for a metal to corrode can also be expressed in terms of the electromotive force of the corrosion cells that are an integral part of the corrosion process. Since electrical energy is expressed as the product of volts and coulombs (joules, J), the relation between $\Delta G$ in joules and emf in volts, $E$, is defined by $\Delta G = -nFE$, where $n$ is the number of electrons (or chemical equivalents) taking part in the reaction, and $F$ is the Faraday constant (96,500 C/eq). The term $\Delta G$ can be converted from calories to joules by making use of the conversion 1 cal = 4.184 absolute joules. Thus the greater the value of $E$ for any cell, the greater is the tendency for the overall reaction of the cell to proceed [2].

## 1.3. THE ELECTROCHEMICAL INTERFACE

The passage of a current in a metallic conductor means that there is circulation of electrons: that is, the transported electricity is always negative. It is necessary to underline that the free electrons don't penetrate in electrolytes. In an electrolytic solution, for example,

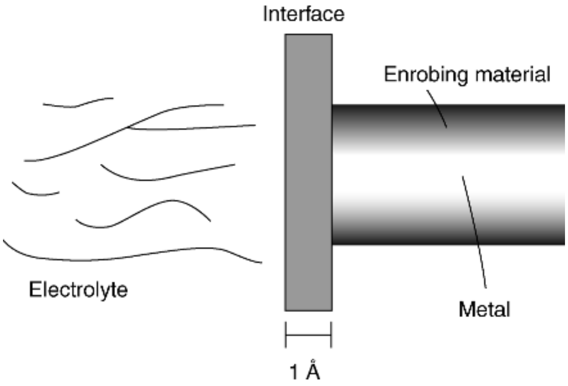

**Figure 1.2** Schematic of a round metallic sample (1 $cm^2$) in contact with an electrolyte or corrosive medium held in an isolated resin and frequently polished and connected electrically for electrochemical studies.

an aqueous solution or a molten salt of sodium chloride, the passage of an electric current is done by the positive ions and the negative ions. At the solid–electrolyte interface, there is a zone of exchange of electrons. The products of electrochemical decomposition appear at the interface of the electrode and not in the mass of the electrolyte (first law of Faraday). This zone of interface is not thick and is on the order of 1 Å. It has the particular physicochemical properties that permit the exchange of electrons (Figure 1.2). This interface can vary rapidly because of its thickness and its dynamic change in chemical composition, properties and concentrations can control the kinetics of the reaction and sometimes can dictate the dominant reaction.

### 1.3.1. Electric Double Layer

A metal immersed in a solvent can have a tendency to pass into solution and the passage of ions takes place until their concentration at the neighborhood of the metal is large enough to cancel the tendency of metal ions to pass into solution and an equilibrium between the metal and its ions occurs.

$$M^{n+} + ze^- \Leftrightarrow M$$

where $z$ ($n$) is the electrovalence of the considered ion. Excess electrons in the metal move to make an equal and oppositely charged layer to the one found in the solvent at the metallic interface. The atom or the crystal is electrically neutral, with equal positive and negative charges. In spite of their kinetic energy, electrons cannot move more than 2 nm from the crystal, because of the strength of attraction of the positive charge (Nernst double layer, internal and external Helmholtz planes).

However, unsymmetrical, polar $H_2O$ molecules (H atoms positive, O atoms negative in the molecule) are attracted to the conductive surface, forming an oriented solvent layer, which prevents close approach of a charged species (ions) from the bulk solution. Charged ions also attract their own sheath of polar water-solvent molecules, which further insulate them from the conducting surface. The plane of closest layer of positively charged cations to the negatively charged metal surface is often referred to as the *outer Helmholtz plane*, as indicated in Figure 1.3 [4,5].

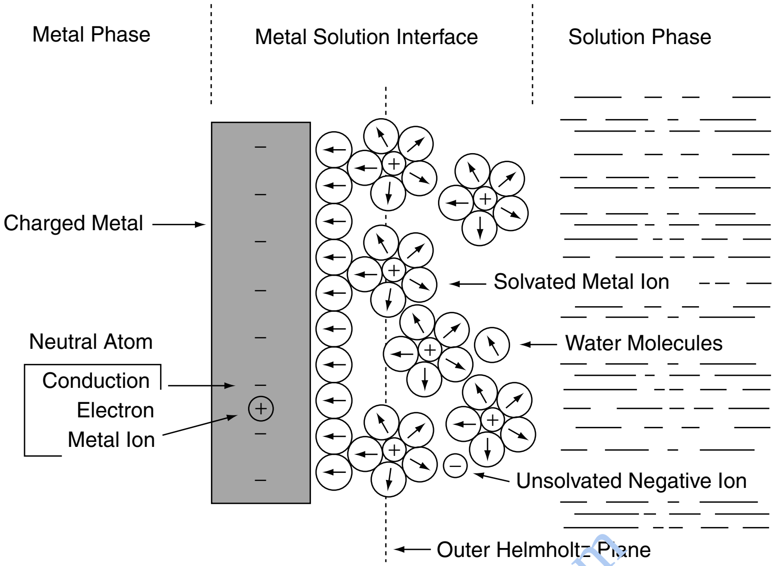

**Figure 1.3** Schematic of the complete double layer of the metal–solution interface. (Adapted from Refs. 4 and 5.)

Because of the strength of attraction of solvated ions of opposite sign and the strength of repulsion of those with identical sign, there is a diffusion of cations between anions in the total mass of the solution in a state of equilibrium (diffuse layer). The ions do not occupy a stationary position in the plane of Helmholtz because of the thermal agitation; instead, they are arranged according to a Boltzmann distribution in a zone situated very close to the surface, called the double diffuse layer or Gouy–Chapman layer. The Stern model is a combination of the Helmholtz and Gouy–Chapman models and this represents the complete double layer (Figure 1.4) [6].

### 1.3.2. Equivalent Circuit of the Electric Double Layer

The electric double layer at the interface behaves as a charged capacitor connected in parallel with a resistance (Figure 1.5a) and this limits electrochemical reactions at the surface. The electric circuit indicates that a continuous current can cross the interface. This current, called the current of charge transfer or Faraday current, provokes an electrochemical reaction at the electrode–electrolyte interface. Some electrodes—called ideally polarizable electrodes—do not contain any reactive species and permit one to vary the potential on a large scale without producing an electrochemical reaction or giving a measurable Faraday current. This is the case for an electrode of mercury immersed in a weak solution of salt, such as NaCl or NaF. Mercury, which is liquid at ambient temperature, is particularly interesting for double layer studies (Figure 1.5b) [6].

## 1.4. NERNST EQUATION

Let’s consider the following general reaction occurring in a cell:

$$l\mathrm{L} + m\mathrm{M} \rightarrow q\mathrm{Q} + r\mathrm{R}$$

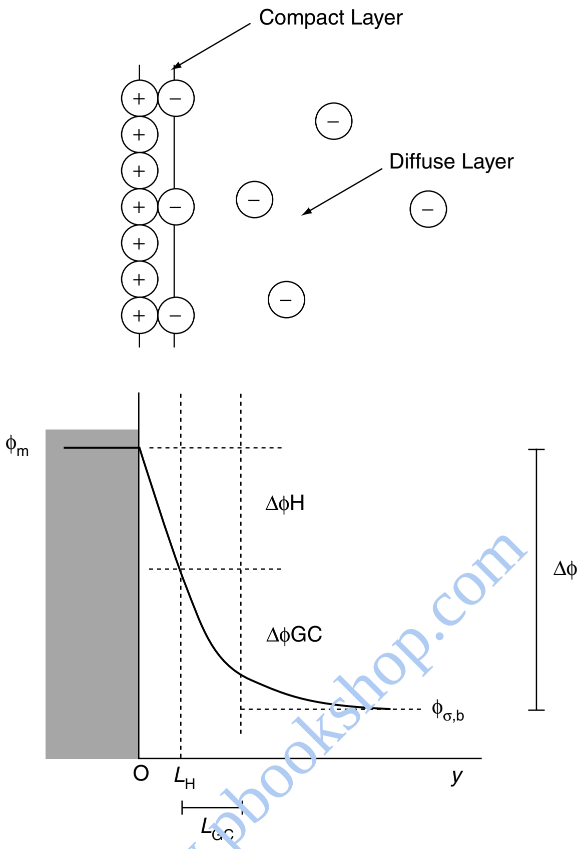

**Figure 1.4** Stern model for the double layer [6] showing the potential evolution at the interface.

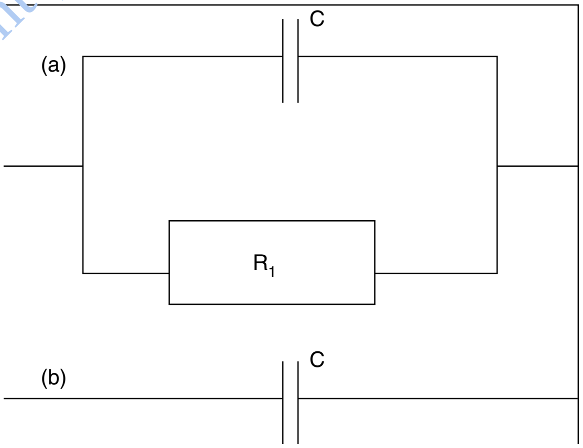

**Figure 1.5** Equivalent circuit of the interface for (a) corrodible metal and (b) ideally polarizable metal [6].

where $l$ moles of substance L and $m$ moles of M react to form $q$ moles of Q and $r$ moles of R. The change of the free enthalpy, $\Delta G$, for this reaction is given by the difference of the free energy between products and reactants:

$$\Delta G = (qG_{\mathrm{Q}} + rG_{\mathrm{R}}) - (lG_{\mathrm{L}} + mG_{\mathrm{M}})$$

At the arbitrary state of reference or equilibrium,

$$\Delta G^{\circ} = (qG_{\mathrm{Q}}^{\circ} + rG_{\mathrm{R}}^{\circ}) - (lG_{\mathrm{L}}^{\circ} + mG_{\mathrm{M}}^{\circ})$$

All concentrations or pressures of the different substances should be replaced by their activities considering the coefficient of activity in every case; the difference of the free energy of L in a certain state and its standard state is

$$l(G_{\mathrm{L}} - G_{\mathrm{L}}^{\circ}) = lRT \ln a_{\mathrm{L}} = RT \ln a_{\mathrm{L}}^{1}$$

where $R$ is the perfect gas constant (8.31441 J · K$^{-1}$ · mol$^{-1}$) and $T$ the absolute temperature in (K = °C + 273.16). By subtraction,

$$\Delta G - \Delta G^{\circ} = RT \ln \frac{a_{\mathrm{Q}}^{q} \times a_{\mathrm{R}}^{r}}{a_{\mathrm{L}}^{l} \times a_{\mathrm{M}}^{m}}$$

At equilibrium, the reaction is stationary and $\Delta G = 0$; so

$$K = \frac{a_{\mathrm{Q}}^{q} \times a_{\mathrm{R}}^{r}}{a_{\mathrm{L}}^{l} \times a_{\mathrm{M}}^{m}}$$

where $K$ is the constant of equilibrium of the reaction. By substitution,

$$\Delta G^{\circ} = -RT \ln K$$

Since $\Delta G = -zFE$, by substitution we have

$$-zEF = -RT \ln K + RT \ln \frac{a_{\mathrm{Q}}^{q} \times a_{\mathrm{R}}^{r}}{a_{\mathrm{L}}^{l} \times a_{\mathrm{M}}^{m}}$$

$$E = \frac{RT}{zF} \ln K - \frac{RT}{zF} \ln \frac{a_{\mathrm{Q}}^{q} \times a_{\mathrm{R}}^{r}}{a_{\mathrm{L}}^{l} \times a_{\mathrm{M}}^{m}}$$

Then the Nernst equation is

$$E = E^{\circ} - \frac{RT}{zF} \ln \frac{a_{\mathrm{Q}}^{q} \times a_{\mathrm{R}}^{r}}{a_{\mathrm{L}}^{l} \times a_{\mathrm{M}}^{m}}$$

where $z$ is the number of electrons considered in the electrochemical equation and $F$ is the Faraday constant.

At 25°C, the coefficient of the logarithmic term is $2.303RT/zF = 0.0592/z$. Then

$$E = E^\circ + \frac{0.0592}{z} \log \frac{\text{Reduced form}}{\text{Oxidized form}}$$

where

$$E^\circ = -\frac{\Delta G^\circ}{zF} = \frac{RT}{zF} \ln K$$

For example, to calculate the potential of reduction of zinc, we have

$$Zn^{2+} + 2e^- \rightarrow Zn$$

$$E_{Zn} = E^\circ_{Zn^{2+}/Zn} - \frac{RT}{zF} \ln \frac{a_{Zn}}{a_{Zn^{2+}}}$$

$$E = E^\circ_{Zn^{2+}/Zn} + \frac{RT}{2F} \ln a_{Zn^{2+}}$$

where $a_{Zn^{2+}}$ represents the activity of zinc and corresponds to the product between the molality (concentration in moles per 1000 g of water) and activity coefficient $\gamma$ as a function of concentration and temperature. With regard to solid materials or metals, it is a normal practice to assign to them an activity of unity, that is, to consider them in their standard state at all temperatures, under atmospheric pressure.

The equilibrium potential of metals corresponds to the formation of a complete double layer. This involves equilibrium between metal/interface/solution. According to the standard scale of comparison of every metal in a solution containing 1 M activity of its ions, it is clear that some metals do not reach this state of equilibrium, for example, the alkali metals such as sodium in water. The state of balance therefore exists completely on the left, while for noble metals such as gold, the balance exists on the other side.

## 1.5. STANDARD POTENTIALS OF ELECTRODES

### 1.5.1. Standard States in Solution

The chemical potential of a species A is $\mu_A = \mu^\circ(p, T) + RT \ln a_A$, where the activity $a_A = f_A x_A$ is the product between activity coefficient $f_A$ and the molar fraction of the species A, $x_A$. Note that $\mu^\circ$ is the chemical potential in the standard state when $x_A \rightarrow 1, f_A \rightarrow 1$, so that the standard state is also the reference state (the state where the activity coefficient goes to a defined limit, i.e., unity). For many electrolytes, the symmetrical system described above is inconvenient, partly because salts and solvents are often not completely miscible. It is therefore more common to use systems based on molality or concentration. The former has the advantage that it is independent of temperature. Our equation remains valid for the solute but the activity is given by $a_A = \gamma_A(m_A/m^\circ)$.

Although it is indispensable to note a difference of the potential between a metal and a solution of its ions, there is no absolute means to measure this potential. The convenient measurements give a difference of potential and require a complete circuit with another metal–solution interface (standard is arbitrarily gold) at the same temperature as the hydrogen electrode.

## 1.5.2. Hydrogen Electrode

By convention, the half-cell potential of the hydrogen reaction under standard conditions is zero at all temperatures: that is, $E^\circ = E^\circ_{H^+/H_2,\,Pt}$ "reduction" $= E^\circ_{Pt,\,H_2,/H^+}$ "oxidation" $= 0$ and the corresponding reaction,

$$2H^+(aq) + 2e^- \rightarrow H_2(gas),\ E^\circ = 0.000\ V$$

When the proton activity of the hydrogen ion (aq) $a_+ = 1$ or the hydrogen fugacity is not equal to unity, the electrode potential is given by the appropriate form of the Nernst equation:

$$E^\circ = -(RT/2F)\ \ln f_{H_2} + (RT/F)\ \ln\ a_{H^+}$$

where $f$ is the fugacity of hydrogen gas and $a_{H^+}$ is the proton activity. The effect of nonideal behavior of hydrogen gas may normally be ignored at ambient pressure but becomes significant at high pressure [7].

Applying the Nernst equation, and considering that the ionization constant of water at 298.15 K according to the equation $H_2O = H^+ + OH^-$ is equal to $K = 1.008 \times 10^{-14}$, the potentials of the hydrogen electrode in pure water ($10^{-7}$ M) and in molal hydroxide solution are −0.414 V and −0.828 V, respectively. When the fugacity (atmospheric pressure) is equal to unity, the Nernst equation at 25 °C becomes

$$E = -0.0592\ pH - 0.4144\ V$$

since E° is equal to zero and $pH = -\log a_{H^+}$. The reversible electrode to hydrogen is essentially composed of one electrode of platinized platinum immersed in a solution containing ions of hydrogen and saturated with the hydrogen gas, under atmospheric pressure. The platinized surface is especially prepared with a coating of very finely divided platinum, giving an important geometric surface that is multiplied by a factor of a few hundred. Platinized platinum reacts as a source of electrons for the discharge of hydrogen ions and, at the same time, adsorbs the formed atomic hydrogen. These molecules of hydrogen at the surface are also transformed subsequently into ions.

## 1.5.3. Positive and Negative Signs of Potentials

The potential sign of a reaction $E^\circ$ denotes the potential at equilibrium under standard conditions, all relative to the standard hydrogen electrode (SHE). The sign or polarity of the electrode (i.e., M, $M^{n+}$) is determined basically by the difference between the work required to move unit positive charge from infinity to the metal, M, and the work required for transport to the SHE. The electrode requiring the greater amount of work in moving the unit positive charge from infinity will be at a higher potential and is said to be positive relative to the second electrode, which is called the negative electrode. If the electrodes are connected externally through a conductor, conventional positive current, $I$, will flow from the positive to the negative electrode, although the actual carriers are electrons flowing in the opposite direction.

The International Union of Pure and Applied Chemistry, in 1953, declared that the reduction potential of one electrode is called the potential ($E^\circ$). It is compliant with the definition of potential by physicists as the necessary work to bring a unit positive charge to the point where the potential is determined ($Zn^{2+} \rightarrow Zn - 2e^-$). It also has the advantage of corresponding in sign to the polarity of a metal in relation to the electrode of hydrogen. For example, zinc has a negative potential of reduction and it is the negative electrode (anode) in a galvanic cell when we consider the standard electrode of hydrogen as the cathode. Practically, the polarity of the electrode whose potential is being measured relative to the SHE is given by the polarity of the terminal of a high-impedance voltmeter or electrometer that must be attached to the electrode to obtain a positive meter reading. Thus if M spontaneously oxidizes to $M^{n+}$ when coupled to the SHE, the M electrode will be negative relative to the SHE, and $E'_{M,M^{n+}}$ will be negative for the half-cell reaction [4], $M = M^{n+} + ne^-$.

It is important to realize that the standard half-cell potential, $E^\circ$, or the half-cell potential at other than standard conditions, $E'$, is sign invariant with respect to how the equilibrium reaction is written or considered; for example, $E^\circ_{Fe,Fe^{2+}} = -440\,\text{mV(SHE)}$ for both $Fe = Fe^{2+} + 2e$ and $Fe^{2+} + 2e = Fe$ [4]. When applying the Nernst equation we always consider oxidized species (ions) as reactants and reduced agents as products (metals) independent of the stoichiometric presentation of the electrochemical equation [6]. These measurements are usually made with an electrometer ($>10^{14}$ ohms internal resistance). The potentiometer (used frequently) is a variable potential device that is attached to the cell and adjusted until the current flow is zero. At this condition, the potentiometer is applying a potential to the cell that just equals the cell potential, for example, 440 mV for $Fe = Fe^{2+} + 2e$ with the negative terminal of the potentiometer connected to the Fe electrode, that is, $E^\circ_{Fe,Fe^{2+}} = -440\,\text{mV(SHE)}$ [4].

In applying the Nernst equation for unit activities,

$$E = E^\circ - \frac{RT}{nF}\ln\frac{a_{\text{products}}}{a_{\text{reactants}}}$$

for an electrochemical cell such as $Zn/Zn^{2+}||H^+/H_2,Pt$; following the reaction $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$, the emf of this cell is 0.763 V. On the other hand, for the reaction of the cell $Pt,H_2/H^+||Zn^{2+}/Zn$, following the equation $Zn^{2+} + H_2 \rightarrow Zn + 2H^+$, the emf is −0.763 V (|| indicates a bridge between the two electrodes).

### 1.5.4. Graphical Presentation

It is common practice to present reactions of reduction and oxidation on the internationally accepted scale of reduction, on the vertical or horizontal scales. These scales (vertical or horizontal) are employed often for curves of polarization in corrosion and can show the dominant or more exothermic reactions or less endothermic in every case. Figure 1.6 shows the basics of a frequently used vertical reduction scale in electrochemical studies.

# B. ACTIVITY AND CONDUCTANCE OF THE ELECTROLYTE

## 1.6. ACTIVITY OF THE ELECTROLYTE

### 1.6.1. Constant and Degree of Dissociation

Let us consider a weak electrolyte AB dissociated reversibly following the equation

$$AB \Leftrightarrow A^+ + B^-$$

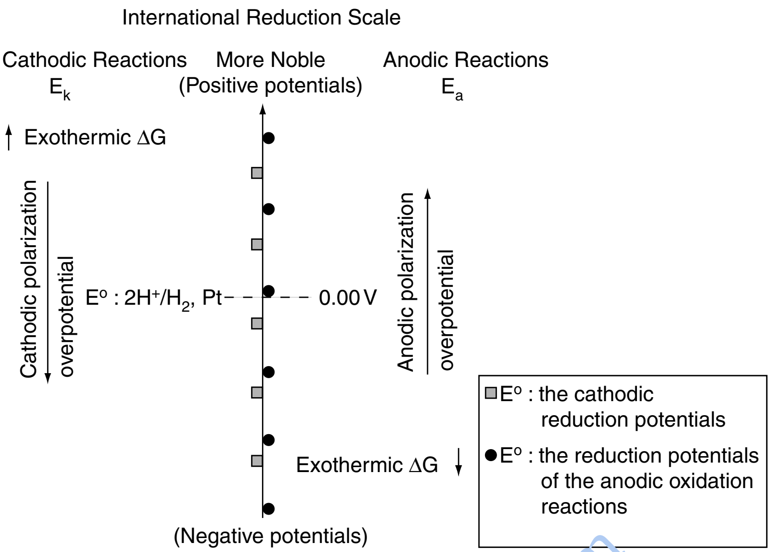

**Figure 1.6** Schematic of the potential for reduction and oxidation reactions on the internationally accepted scale of reduction indicating positive and negative potential values.

One has the relation provided by the law of mass action of Guldberg and Waage in considering that the solution is sufficiently diluted:

$$\frac{|A^+||B^-|}{|AB|} = K_{\mathrm{diss}}(T)$$

$K_{\mathrm{diss}}$ or $K_c$ (dependent on the temperature) is called the constant of dissociation of the electrolyte. The coefficient or degree of dissociation, $\alpha$ is expressed by

$$\alpha = \frac{|A^+|}{|A^+| + |AB|} = \frac{|B^-|}{|B^-| + |AB|}$$

In the case of a strong electrolyte, the constant of dissociation $K_c$ is therefore infinite and $\alpha$ is equal to 1. $K_c$ is often very weak, on the order of several negative powers of 10; it is advantageous to describe it by

$$pK = -\log K_c$$

### *1.6.1.1. Variation of $\alpha$ with the Concentration*

If we consider that $n$ molecules of AB give $\alpha n$ ions $|A^+|$ and $\alpha n$ ions $|B^-|$, while $n(1-\alpha)$ molecules of AB remain nondissociated in solution, one can get the following equation for a determined temperature:

$$\frac{\frac{n\alpha}{V} \times \frac{n\alpha}{V}}{\frac{n(1-\alpha)}{V}} = K_c$$

$$\frac{n\alpha^2}{V(1-\alpha)} = K_c$$
$$\frac{C\alpha^2}{1-\alpha} = K_c$$

This relation between the degree of dissociation of one weak electrolyte and its concentration constitutes the *law of Ostwald dilution*:

$$\begin{aligned} &\alpha \to 0 \quad \text{when } C \to \infty \\ &\alpha \to 1 \quad \text{when } C \to 0 \end{aligned}$$

### 1.6.2. Activity and Concentration

The ionic strength is the electrostatic strength between two ions. The ionic strength between two ions with double charges is four times stronger than the one between two ions with one charge each:

$$\mu = \frac{1}{2}\sum_i m_i z_i^2$$

The ionic strength $\mu$ is therefore equal to half of the global sum of the molar concentration of every ion multiplied by the square of the electrovalence ($z^2$) for every ion ($i$). The law of mass action, expressed in concentrations, only constitutes a first valid approximation if concentrations remain weak. The mainly electrostatic interactions between the elementary particles of the electrolyte are considered negligible in this situation.

Taking into consideration the interactions between particles, Lewis suggested the term *particle activity* instead of concentration. The law of dissociation can then be expressed as

$$\frac{a_{A^+}a_{B^-}}{a_{AB}} = K(T)\left(\frac{\text{mole}}{\text{dm}^3}\right)$$

$a_{A^+}$ and $a_{B^-}$ are the activities of the ions $A^+$ and $B^-$ and $a_{AB}$ corresponds to the activity of the nondissociated molecules. The activity of an ion $A^+$ is expressed as $a = \gamma_\pm C$; $\gamma_\pm$ is generally considered arbitrary, since it is different from $\gamma_+$ specially if there is an important difference in mobilities between the cation and the anion. If dilution is sufficiently important (ionic force $\mu < 0.01$), one can apply the Debye–Hückel limiting law:

$$\begin{aligned} \log \gamma_\pm &= -Az_+z_-\mu^{1/2} \\ A &= \frac{1}{2.303}\frac{1}{2}\frac{e^2}{DkT}\sqrt{\frac{8\pi e^2 N\rho_0}{1000DkT}} \end{aligned}$$

where

Dielectric constant of water: $D = 78.54$ (1 for vacuum)

Electron charge: $e = 4.803 \times 10^{-10}$ esu

Avogadro number: $N = 6.02252 \times 10^{23}$ mole$^{-1}$

Boltzmann constant: $k = 1.38054 \times 10^{-16}$ erg · degree$^{-1}$

$A = 0.5091$ for water at 25°C ($\rho_0 = 0.997$ in these conditions) [3]

For an electrolyte $A_xB_y \Leftrightarrow xA^{y+} + yB^{x-}$, the average coefficient of activity is

$$\gamma_\pm = (\gamma_+^x \gamma_-^y)^{1/(x+y)}$$

For example, the average coefficient of activity of a solution of 1 M of Fe $Cl_2$ is

$$\mathrm{FeCl_2} \rightarrow \mathrm{Fe}^{2+} + 2\mathrm{Cl}^-\text{: } \gamma_\pm = (\gamma_+^1 \gamma_-^2)^{1/(1+2)} = (\gamma_+ \gamma_-^2)^{1/3}.$$

Generally, $K_c$ is given when considering concentrations and not activities. However, even for a weak acid (e.g., acetic acid) having $K_c = 1.81 \times 10^{-5}$, where electrostatic attractions between ions are negligible, $K_{\text{thermodynamic}}$ was calculated and found to be slightly different and equal to $1.72 \times 10^{-5}$ M at 25°C. To calculate $K_{\text{thermodynamic}}$, $\alpha$ can be considered to be 0.04165 from the equation $K_c = C\alpha^2/(1-\alpha)$ and applying the Debye–Hückel limit law to determine the activities of the ions [8].

## 1.6.3. Theory of More Concentrated Solutions

There is a natural interest to develop a theory that is applicable to solutions that are more concentrated than those for which the Debye–Hückel theory is valid. This is one of the main nonsolved problems of physical chemistry. In the case of a molecule such as HCl in water, there are two fundamental parameters to consider:

1. Speeds with which molecules or the complex split up and reform themselves from ions in solution are very high. The average longevity of a complex or an ion can be on the order of only $10^{-10}$ second, instead of 1 second as in a gas. In this short lapse of time, few ions become really free and the likeliest phenomenon after separation is nearly an immediate recombination.
2. The dissociation of a molecule to give the hydrated ions requires the separation of ions having opposite charge. The electrostatic attraction between these two ions decreases relatively slowly when they separate, so that they are always associated more or less even though they are separated by a distance of several molecular diameters.

There are then two parameters to add to the Debye–Hückel limiting law to make it apply to more concentrated solutions:

1. The action of the repulsive forces at short distances between charged ions that results from the physical dimensions of the ion, since the charge is distributed on the surface and not concentrated at a simple point. This consideration has the tendency to reduce the electrostatic interactions. In a dilute solution, one can disregard the diameter of an ion in relation to the ionic atmosphere. On the other hand, when the concentration is close to 0.1 mole, the radius of the ionic atmosphere becomes very close to that of an ion, which is on the order of $2 \times 10^{-8}$ cm. In such solutions, Debye and Hückel stated an improved theory that considers the finite dimensions of the ions. The expression of the activity coefficient is as follows:

$$\log \gamma_\pm = -\frac{A_{z_+z_-}\sqrt{\mu}}{1 + Bd\sqrt{\mu}}$$

where $B$ is a constant $= \sqrt{8\pi Ne^2\rho_0/1000DkT}$ and $d$ is the average efficient diameter of the ions (Figure 1.7).

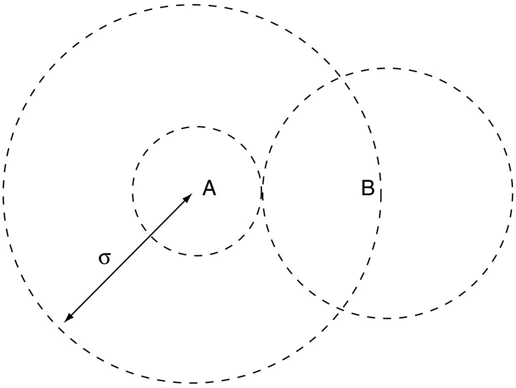

**Figure 1.7** Average efficient ionic diameters.

2. The action of ions on molecules of the solvent probably has an even bigger importance. It is admitted that ions are hydrated or solvated. The phenomenon of salting out indicated that the addition of electrolytes reduces the solubility of some nonelectrolytes. For example, the solubility at 25°C of the ethyl oxide in pure water is 0.91 $\text{mol}\cdot\text{L}^{-1}$ while it is only 0.13 $\text{mol}\cdot\text{L}^{-1}$ in a solution containing 15% of NaCl. Then, another correction should be added to the Debye–Hückel equation:

$$\log \gamma_{\pm} = -\frac{A_{z_+z_-}\sqrt{\mu}}{1+Bd\sqrt{\mu}} + C'\mu$$

   $C'$ is called the *salting out constant* and this equation is called the Hückel equation.

*Example of Application of Hückel Equation* Calculate the average coefficient of activity of 0.005 $\text{mol}\cdot\text{L}^{-1}$ of zinc chloride at 25°C using (a) the Debye–Hückel limit law and (b) the Hückel equation considering $d = 2.55\times10^{-8}$ cm (at 25°C, $B = 0.3286\times10^{8}$) and $A = 0.509$ for $H_2O$ at $T = 25°C$.

$$\begin{array}{ccc} \text{ZnCl}_2 & \Rightarrow & \text{Zn}^{2+} + 2\text{Cl}^- \\ 0.005 & & 0.005 \quad\; 0.01 \end{array}$$

(a)
$$\mu = \frac{1}{2}\sum m_i z_i^2 = 0.015$$
$$\log\gamma_{\pm} = -Az_+z_-\mu^{1/2};\ \gamma_{\pm} = 0.7504$$

(b)
$$\log\gamma_{\pm} = \frac{-0.509\times2\times1\times\sqrt{0.015}}{1+(0.3286\times10^{8}\times2.55\times10^{-8}\sqrt{0.015})}$$
$$\gamma_{\pm} = 0.7708$$

It is obvious that even for this dilute solution there is a difference in the activity coefficient in applying the correction of the Debye–Hückel limit law. If the electrolyte is weak enough (e.g., $K < 10^{-2}$), concentrations in free ions are very weak and one can admit that the coefficient of ion activity is always equal to 1. The limit law with and

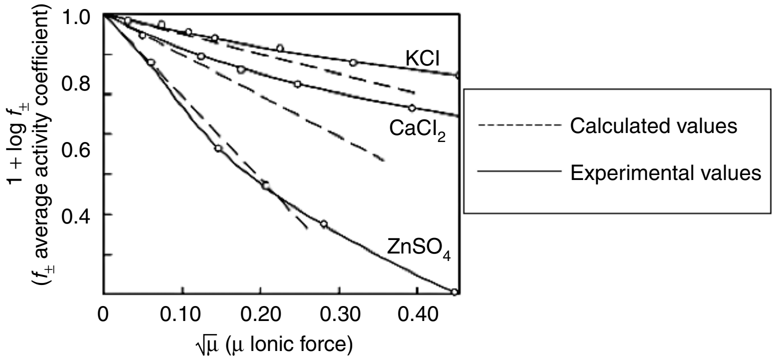

**Figure 1.8** Evaluation of Debye–Hückel theory for more concentrated solutions (From Ref. 3).

without the two mentioned corrections for more stronger electrolytes can be applied to achieve the real activity of the ions in solution.

It is important to mention that the theory of ion association developed independently by Bjerrum, Fuoss, and Krauss gives a more lucid physical representation of what can happen in more concentrated solutions. When the concentration of solutions increases, it is likely that definite ion pairs of opposite sign, associated by electrostatic attraction, are formed. This tendency to form ion pairs is much more marked when the dielectric constant of the solvent is lower and the radius of ions is smaller. The degree of association can become very substantial, even in a higher dielectric constant solvent such as water. Bjerrum and co-workers calculated that a normal aqueous solution of one electrolyte to two univalent ions, having a diameter $D$ of 2.82 Å, has 13.8% of associated pairs; for $D = 1.76$ Å there are 28.6% associated ions. For solvents having a lower $D$ than water, the proportion of associated ions will be even more important. This association of ions as pairs must decrease the values of ionic activity coefficients [3]. One can admit then that in the case of concentrated solutions (when the ionic strength is considerably over 0.1), the non-ideal behavior of the solution is not merely electrostatic in nature and it is useless to determine ideal behavior by a simple adjustment to the Debye–Hückel theory [8]. Practical measurements by selective electrodes, chemical cells with and without transport, and concentration cells with and without transport should be used and compared to some electrolytes with standard activities. Figure 1.8 shows the deviation from the theory for some frequently used electrolytes.

### 1.6.4. Electrolytic Conduction

The term *conductance* expresses the ratio of current to potential difference, while *conductivity* expresses the specific conductance of the electrolyte, $k$, considering 1 cm$^2$ of electrode surface and 1 cm$^3$ of solution between the electrodes [9].

## 1.7. MOBILITY OF IONS

For simple considerations, the ion is supposed to be spherical, with bigger measurements than that of particles of the solvent. The electric field $E$ is assumed to be constant and the resistance created by the medium obeys Stokes law.

$$\text{Force of resistance}: \; F_{\mathrm{r}} = \sigma\pi\eta r v = Kv$$

where $\sigma$ is conductivity, $\eta$ is the coefficient of viscosity, $r$ is the radius of the ion, $v$ is the speed of the ion, and $K$ is a constant for certain conditions.

At the instant where one applies the $E$ field, the ion is going to be displaced by a moving force:

$$F_{\mathrm{m}} = neE$$

where $n$ is the valence of the ion, $e$ is the charge of the electron, and $E$ is the electric field strength.

The force of resistance should be equal to $F_{\mathrm{m}}$ such that the resultant force acting on the moving ion is zero and the speed of the ion is uniform without acceleration:

$$\begin{aligned} F_{\mathrm{r}} &= F_{\mathrm{m}} \\ Kv &= neE \\ v &= \frac{ne}{K}E \end{aligned}$$

The speed limit $v$ settles in a very short time and is considered to be the speed of the ion. $v$ is proportional to the electric field and $K$ is constant. The units for electric field are $\mathrm{V \cdot cm^{-1}}$ while $\mathrm{cm \cdot s^{-1}}$ are the units for speed. Generally, the mobility $u$ of an ion is defined as the speed of that ion in an electric field $E$ and can be expressed as

$$\begin{aligned} &v = u \;\; E \\ &v = u \;\; \text{for} \;\; E = 1\,\mathrm{V \cdot cm^{-1}} \end{aligned}$$

$v^-$ and $u^-$ are used for an anion, and $v^+$ and $u^+$ for a cation.

As an example, $u$ values in aqueous solution (0.1 M) are $20 \times 10^{-4}\,\mathrm{cm \cdot s^{-1}}$ for $\mathrm{OH^-}$, and $30 \times 10^{-4}\,\mathrm{cm \cdot s^{-1}}$ for $\mathrm{H^+}$.

### 1.7.1. Law of Additivity of Kohlrausch

"The conductance limits of a binary strong electrolyte is the sum of two terms, that of the anion and that of the cation, for a determined solvent and at a certain temperature." The law of additivity is assigned to the ionic conductivity of an equivalent. Applying the law for some electrolytes, we have

$$\begin{aligned} \Lambda_0(\mathrm{KCl}) &= \lambda_0(\mathrm{K^+}) + \lambda_0(\mathrm{Cl^-}) \\ \Lambda_0(\mathrm{CaCl_2}) &= \lambda_0(\tfrac{1}{2}\mathrm{Ca^{2+}}) + \lambda_0(\mathrm{Cl^-}) \\ \Lambda_0(\mathrm{BaSO_4}) &= \lambda_0(\tfrac{1}{2}\mathrm{Ba^{2+}}) + \lambda_0(\tfrac{1}{2}\mathrm{SO_4}^{2-}) \end{aligned}$$

In Table 1.1, the values $\lambda_0$(cation) and $\lambda_0$(anion) of some ions at concentration zero (infinite dilution) in aqueous solution at 25°C are given. These values are valid as long as the degree of dissociation $\alpha$ is equal to one. The equivalent conductance is expressed in $\mho \cdot \mathrm{cm^2} \cdot \mathrm{equivalent^{-1}}$.

From Table 1.1, it is clear that the ions $\mathrm{H^+}$ and $\mathrm{OH^-}$ have very high values of $\lambda_0$ as compared to that of the average of other ions, which is between 50 and 75. The law of

**Table 1.1** Values of $\lambda_0$ at 25°C

| Cation | $\lambda_0$ | Anion | $\lambda_0$ |
|---|---|---|---|
| $H^+$ | 349.80 | $OH^-$ | 198.60 |
| $Na^+$ | 50.11 | $Cl^-$ | 76.34 |
| $Ag^+$ | 61.90 | $Br^-$ | 78.10 |
| $^1/_2Ba^{2+}$ | 63.60 | $^1/_2SO_4^{2-}$ | 80.00 |
| $^1/_2Ca^{2+}$ | 56.60 | $ClO_4^-$ | 67.30 |

Kohlrausch permits one to calculate $\Lambda_0$ or $\Lambda_\infty$ for the weak electrolytes, such as organic acids, from measured conductivities of their salts, which are strong electrolytes.

$$\Lambda_0(\mathrm{CH_3COOH}) = \Lambda_0(\mathrm{CH_3COONa}) + \Lambda_0(\mathrm{HCl}) - \Lambda_0(\mathrm{NaCl})$$

The equivalent conductance and mobility are

$$\begin{aligned}\Lambda_c &= \alpha Ne(u^+ + u^-)\\ &= \alpha F(u^+ + u^-)\\ &= \alpha(\lambda_+ + \lambda_-)\\ \Lambda_\infty &= (\lambda_+)_\infty + (\lambda_-)_\infty\end{aligned}$$

### 1.7.2. Ion Transport Number or Index

The contribution of every ion to the transport of the current is a function of its mobility and concentration. The transport number is defined as the fraction of total current, which is carried by an ion.

$$t_+ = \frac{u_+}{u_+ + u_-} \qquad t_- = \frac{u_-}{u_+ + u_-}$$

$$t_+ = \frac{\lambda_+}{\lambda_+ + \lambda_-} \qquad t_- = \frac{\lambda_-}{\lambda_+ + \lambda_-}$$

The transport numbers of positive and negative charge in a cell are evidently between 0 and 1 for the transport of 1 faraday in the cell. The sum of the transport number of positive and negative charges that are carried by the electrolyte should be equal to 1 in order to preserve the neutrality of the electrolyte. This does not mean that half of the current is carried by the positive ions or by the negative ions. To determine the transport number, Hittorf developed a method that is based on the measurement of concentration changes provoked in the neighborhood of electrodes by the passage of a current through the electrolyte, that is, in the anolyte and catholyte solutions [10].

The Hittorf method for the determination of the transport number considers an electrolytic cell divided into three compartments as in Figure 1.9 [3]. The disposition of ions before the passage of a current is represented schematically in Figure 1.9a, where the + or − sign means an equivalent of the corresponding ion. Now, suppose that the mobility of the positive ion is triple that of the negative ion, $U_+ = 3U_-$ and that 4 faradays of electricity is carried across the cell. This means that four equivalent negative ions should be carried at the surface of the anode and four equivalent positive ions at the cathode (Figure 1.9a). Three faradays of electricity is transported by the positive ions across the

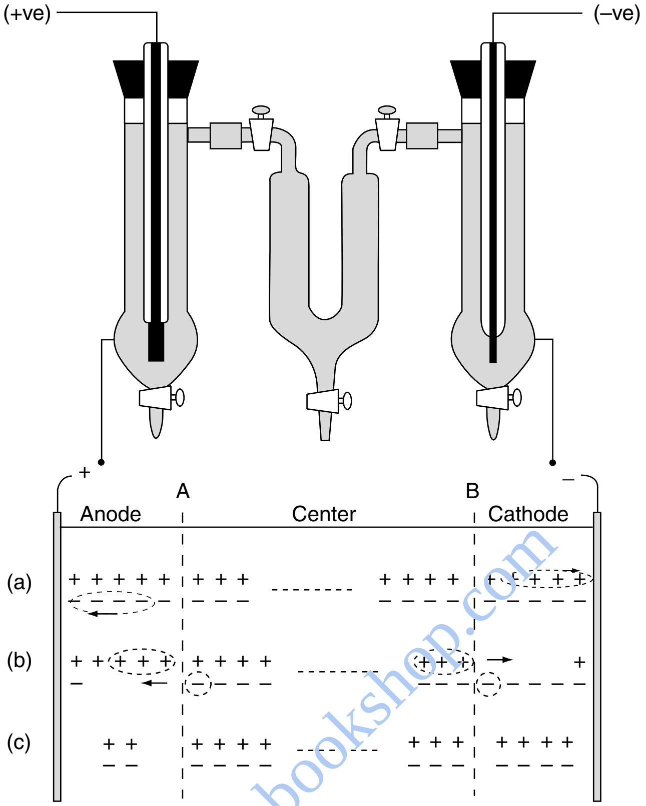

**Figure 1.9** Determination of the transport number of an ion [3].

plane P on the right while only 1 faraday is transported on the left by the negative ions (Figure 1.9b). There is a variation of the number of equivalents in the neighborhood of the anode ($\Delta n_a = 5 - 2 = 3$) and in the neighborhood of the cathode ($\Delta n_c = 5 - 4 = 1$) (Figure 1.9c) [10]. The change in concentration in the anodic and cathodic compartments in equivalents can be expressed as follows:

$$
\begin{aligned}
\Delta n_a &= \frac{q}{F} - t_- \times \frac{q}{F} = 4 - 0.25 \times 4 = 3 \\
\Delta n_c &= 4 - 0.75 \times 4 = 1
\end{aligned}
$$

The report of these concentration variations is inevitably equal to the report of ions mobilities [10]:

$$\frac{\Delta n_a}{\Delta n_c} = \frac{u_+}{u_-} = 3 \quad t_+ = 0.75 \quad t_- = 0.25$$

Then the variation of the concentration at the anodic or cathodic compartments is a function of the mobility of the ions in solution:

$$\Delta n_c = \frac{q}{F} - t_+ \frac{q}{F} = \frac{q}{F}(1 - t_+) = \frac{q}{F} t_-$$

Thus

$$t_- = \frac{\Delta n_c}{q/F} \quad \text{and} \quad t_+ = \frac{\Delta n_a}{q/F}$$

In the last example, the electrodes are inert, while in other cases, electrodes can dissolve in the solution giving positive ions. For example, for a silver anode in a solution of silver nitrate, when an electric current crosses the cell, the number of electrolyte equivalents increases in the neighborhood of the anode to equal the number of incoming silver equivalents in solution in the anodic compartment, less the number of silver equivalents moving to the cathodic compartment.

## 1.8. CONDUCTANCE

The conductance of one electrolyte is a function of the nature and the number of present ions. The resistance $R$ of a conductor is directly proportional to the length and inversely proportional to the area:

$$R = \rho \frac{l}{A}$$

A conductor's resistance for a section 1 $\text{cm}^2$ and a length of 1 cm is $R = \rho$. The constant $\rho$ is characteristic of every conductor and is called the *specific resistance* or *resistivity.* $\rho$ is measured in units of $\Omega \cdot \text{cm}$. The conductance is the inverse of the resistance and is frequently used. For such a system, that means the specific conductance or conductivity is

$$k = \frac{1}{\rho} = \frac{l}{RA} \Leftrightarrow \rho = \frac{RA}{l}$$

$k$ is expressed in $\Omega^{-1} \cdot \text{cm}^{-1}$ (mho/cm), and the values of $k$ and $\rho$ are dependent on the concentration of the electrolyte. The electrolytic conductivity is therefore better compared if one considers it in relation to a unit of concentration for all electrolytes, as in $\text{mol} \cdot \text{L}^{-1}$ or in $\text{equivalents} \cdot \text{L}^{-1}$. The equivalent conductance is therefore

$$\text{Equivalent conductance} = \frac{\text{Conductivity for a certain concentration}}{\text{Equivalent per cm}^3 \text{ of electrolyte}}$$

This is the most frequently used unit to characterize the conductance of electrolytes.

$$\Lambda_c = \frac{1\,000k}{zC} = \frac{1\,000\,\text{L}}{RA\,zC} = \frac{\Omega^{-1} \cdot \text{cm}^3 \cdot \text{cm}}{\text{cm}^2 \cdot \text{equivalent}} = \Omega^{-1} \cdot \text{cm}^2 \cdot \text{equivalent}^{-1}$$

The equivalent conductance $\Lambda_c$ varies to a certain extent with the temperature and the concentration. At constant temperature, the value $\Lambda_c$ increases when the concentration decreases and in several cases it is possible to define the value of $\Lambda_c$ for a concentration of zero ($\Lambda_0$) or for infinite dilution ($\Lambda_\infty$).

According to Kohlrausch, this value is determined better if one draws the equivalent conductance against the root of the normality of the electrolyte. It is clear that the determination of $\Lambda_0$ is not possible for weak electrolytes by this method.

Arrhenius explained that the growth of the equivalent conductance according to the decrease of the concentration is due to the increase of the degree of dissociation of the electrolyte in ions. One can suppose therefore that, at concentration zero, the dissociation of the electrolyte is complete. The degree of dissociation ($\alpha$) at $C$ concentration could be determined from the relation $\Lambda_c/\Lambda_0$. This point of view is correct for weak electrolytes but not acceptable for strong electrolytes, especially when concentrations are high. One can apply the Debye–Hückel theory therefore for weak concentrations of strong electrolytes by taking account of the electrostatic attractions to determine the coefficient of activity rather than the coefficient of dissociation. It is interesting to note that generally the equivalent conductance increases 2% by 1°C for temperatures below 40°C, and 3% by 1°C for temperatures above 40°C.

### 1.9. POTENTIAL OF DECOMPOSITION

To generalize Ohm's law, the $V = E + RI$ relation is introduced, where $E$ is the minimal potential of decomposition necessary for visible electrolysis. In the case of electrolytes, the current is transported by ions and the passage of the current could heat the electrolyte and vary the resistance. In addition, the electrolysis, accompanied by the passage of the current, could result in an impoverishment of ions at the interface or the formation of a nonconductor (passive) film such as aluminum oxide on an aluminum anode.

## C. THE DIFFERENT TYPES OF ELECTRODES

### 1.10. GAS ELECTRODES

A gas electrode consists of bubbling a gas about an inert or noble metal in the form of a wire or a foil immersed in a solution that contains ions for which the gas is reversible. Among gas electrodes are the hydrogen electrode reversible to hydrogen ions, the chlorine electrode reversible to chlorine ions, and the oxygen electrode whose emf depends on the activity of hydroxyl ions. Although hydrogen and chlorine electrodes can be made reversible, no material has been found to establish the state of equilibrium between the oxygen and hydroxyl ions. The precise information on the potential of this electrode is then deduced from free-energy data and not from direct emf measurements.

In the case of the hydrogen electrode ($H^+ + e^- \rightarrow \frac{1}{2}H_2$), the function of the metal, normally platinized platinum foil or wire, is to facilitate the state of equilibrium between hydrogen gas and its ions and to serve as the electric contact. The activity of hydrogen ions in the solution and the pressure of hydrogen around the electrode determine the potential of the hydrogen electrode:

$$E_{H^+/H_2,Pt} = E^\circ_{H^+/H_2,Pt} - \frac{RT}{F}\ln\frac{\sqrt{P_{H_2}}}{a_{H^+}}$$

However, $E^\circ_{H^+/H_2,Pt} = 0$ when the atmospheric pressure and the activity of ions are equal to 1:

$$
\begin{aligned}
E_{\mathrm{H^+/H_2,Pt}} &= -\frac{RT}{F}\ln\frac{\sqrt{P_{\mathrm{H_2}}}}{a_{\mathrm{H^+}}} \\
&= \frac{RT}{F}\ln a_{\mathrm{H^+}} - \frac{RT}{2F}\ln P_{\mathrm{H_2}} \\
&= \frac{RT}{F}\ln a_{\mathrm{H^+}} = -0.0592\,\mathrm{pH}\ \text{at } 25^\circ\mathrm{C} \text{ and atmospheric pressure}
\end{aligned}
$$

The chlorine electrode shows the same behavior. The reaction of reduction is

$$\tfrac{1}{2}\mathrm{Cl_2} + \mathrm{e^-} \rightarrow \mathrm{Cl^-} \quad \text{and} \quad E_{\mathrm{Cl_2/Cl^-}} = E^\circ_{\mathrm{Cl_2/Cl^-}} - \frac{RT}{F}\ln\frac{a_{\mathrm{Cl^-}}}{\sqrt{P_{\mathrm{Cl_2}}}}$$

The standard $E^\circ_{\mathrm{Cl_2/Cl^-}}$ is 1.3595 at 25°C and atmospheric pressure, and $-1.3595\,\mathrm{V}$ corresponds to the potential of the oxidation reaction.

## 1.11. METAL–METAL ION ELECTRODES

These electrodes are considered reversible to their ions, meaning that the potential of each electrode is a function of the activities of its own ions in solution.

$$\mathrm{M}^{n+} + ne^- \rightarrow \mathrm{M}$$

The Cu/CuSO$_4$ electrode is a robust and economic electrode and often used for field measurements of potentials as in soil for cathodic protection; however, it is less precise than the calomel and silver electrodes. This electrode has a potential of 0.316 V due to the weak activity of copper ions in saturated solution since $E^\circ = 0.337\,\mathrm{V}$ for $\mathrm{Cu^{2+}} + 2\mathrm{e} \rightarrow \mathrm{Cu}$. Solid crystals of copper sulfate are added to keep the solution saturated and the potential steady with a temperature coefficient of $0.7\,\mathrm{mV}\cdot{}^\circ\mathrm{C}^{-1}$.

### 1.11.1. Alloyed Electrodes

Alloying a noble metal with a more active one can give a new solid solution with an intermediate potential more noble and stable than that of the active one. The amalgam electrodes are a good example. Electrodes of amalgams of metals, more active than mercury, behave essentially like the pure metal with a lower activity because of the dilution with mercury and become more reversible. Currently, for environmental considerations, some laboratories decrease the use of mercury appreciably.

The standard Weston cell has an amalgam electrode Cd(Hg) and a reference electrode. The reaction is $\mathrm{Cd^{2+}} + 2\mathrm{e^-} + \mathrm{Hg} \rightarrow \mathrm{Cd\ (Hg)}$ and the potential of this electrode is

$$E_{\mathrm{a}} = E^\circ_{\mathrm{Cd^{2+}/Cd(Hg)}} - \frac{RT}{2F}\ln a_{\mathrm{Cd(Hg)}} + \frac{RT}{2F}\ln a_{\mathrm{Cd^{2+}}}$$

Where $E^\circ_{\mathrm{a}}$ is the standard potential for a given amalgam with a certain composition and equals

$$E^\circ_{\mathrm{a}} = E^\circ_{\mathrm{Cd^{2+}/Cd(Hg)}} - \frac{RT}{2F}\ln a_{\mathrm{Cd(Hg)}}$$

The $E_a^\circ$ value can be determined by measuring the emf of a cell composed of the amalgam and the pure metal electrodes, immersed in the same solution containing $Cd^{2+}$ ions.

## 1.12. METAL–INSOLUBLE SALT OR OXIDE ELECTRODES

### 1.12.1. Metal–Insoluble Salt Electrodes

These are frequently called reference electrodes and can be used for ambient and high-temperature conditions. Reference electrodes such as calomel electrodes, silver–silver chloride electrodes, lead–lead sulfate electrodes, and silver–silver bromide electrodes are examples of metal–insoluble salt electrodes. This kind of electrode is composed of metal in one of its almost insoluble salts and a solution containing the ion present in the salt. The reaction of these electrodes is composed of a chemical dissociation reaction combined with an electrochemical one. The two most used reference electrodes are silver and calomel electrodes in chloride media. The silver electrode should be checked periodically because of a gradual change on aging. Sulfate ions can replace chlorides for both electrodes for metal or system interfaces sensitive to chloride ions.

#### *1.12.1.1. Silver–Silver Chloride Electrodes*

The reaction of reduction ($Cl^-$/AgCl, Ag) is

$$\begin{array}{r}
\mathrm{AgCl} \Leftrightarrow \mathrm{Ag}^+ + \mathrm{Cl}^- \\
\mathrm{Ag}^+ + \mathrm{e}^- \Leftrightarrow \mathrm{Ag} \\
\hline
\mathrm{AgCl} + \mathrm{e}^- \Leftrightarrow \mathrm{Ag} + \mathrm{Cl}^-
\end{array}$$

The potential of the electrode corresponding to the reduction reaction ($Cl^-$/AgCl, Ag) or AgCl/Ag is

$$E = E^\circ - \frac{RT}{F}\ln a_{\mathrm{Cl}^-}$$

The inverse reaction is that of oxidation corresponding to $\mathrm{Ag} + \mathrm{Cl}^- \Leftrightarrow \mathrm{AgCl} + \mathrm{e}^-$ and has the negative sign of potential. The value of the standard reduction potential $E^\circ = 0.223$ V from numerous determinations, and for a solution of 0.1 N KCl it is 0.288 V. The temperature coefficient for this concentration is $-4.3 \times 10^{-4}$ V/°C. Knowing that the $K_c$ of AgCl is equal to $1.8 \times 10^{-10}$, it is easy to calculate the value of the standard potential $E^\circ$ of the silver–silver chloride electrode in a 1 M KCl solution from the Nernst equation directly:

$$\begin{aligned}
E &= E^\circ + 0.0592 \log a_{\mathrm{Ag}^+} \text{ (reaction of reduction)} \\
&= 0.7996 + 0.0592 \log(1.8 \times 10^{-10}), \text{ where } a_{\mathrm{Ag}^+} = \frac{K}{a_{\mathrm{Cl}^-}}
\end{aligned}$$

Or we can use the method that considers the sum of the two free energies of the chemical and electrochemical reactions, respectively, at 25°C as follows:

$$\begin{aligned}
\Delta G_1 &= -nRTK = -0.0592\,F\log(1.8 \times 10^{-10}) \\
\Delta G_2 &= -nE^\circ F = -0.7996\,F \\
E^\circ &= -\frac{\Delta G}{nF} = 0.223\text{ V}
\end{aligned}$$

**Table 1.2** Calomel Electrode Potential at Different Concentrations of KCl

| Concentration of KCl | $Hg_2Cl_2/2Hg$, $E$ (volts) | Temperature coefficient (V/°C) |
|---|---|---|
| 0.1 N | +0.3337 | $-0.88 \times 10^{-4}$ |
| 1.0 N | +0.2800 | $-2.75 \times 10^{-4}$ |
| Saturated | +0.2415 | $-6.60 \times 10^{-4}$ |

The external pressure-balanced reference electrode has been used in high-temperature and high-pressure electrochemistry studies, however, the Ag/AgCl as an internal reference electrode is one of the most accurate and serviceable and has been used for pH measurements for supercritical temperatures. Under every condition, the potential of the Ag/AgCl electrode can be calculated or calibrated against a hydrogen cell that has to be installed separately inside the autoclave [11].

### *1.12.1.2. Calomel Electrodes*

The reaction of reduction ($KCl/Hg_2Cl_2$, Hg) is

$$\begin{array}{r}
Hg_2Cl_2 \Leftrightarrow Hg_2^{2+} + 2Cl^- \\
Hg_2^{2+} + 2e^- \Leftrightarrow 2Hg \\
\hline
Hg_2Cl_2 + 2e^- \Leftrightarrow 2Hg + 2Cl^-
\end{array}$$

$$E^{\circ}_{Hg_2Cl_2/Cl^-} = 0.268\ \mathrm{V}$$

Three concentrations of potassium chloride are frequently used, as shown in Table 1.2 [2].

The more convenient solution to prepare is the saturated one, but its response to temperature is somewhat more sluggish [2]. For some corrosion studies, it is preferable to use reference electrodes based on sulfate ions ($K_2SO_4/Hg_2SO_4$, Hg) instead of chloride ions, which may cause or accelerate localized or pitting corrosion. If $K_2SO_4$ is saturated instead of potassium chloride, the potential of this electrode is 0.64 V (the reduction potential).

When the measurement is done, for example, against a saturated calomel electrode at 25°C, there are graphical and/or equation methods that can be used to calculate the measured potential with respect to the standard hydrogen electrode scale as explained (Figure 1.10) for a relatively more or less active potential than that of the reference calomel electrode.

## 1.12.2. Metal–Insoluble Oxide Electrodes

These are similar to the metal–insoluble salt electrodes. Some of them are also used as reference electrodes at high temperatures. The mercury–mercuric oxide electrode Pt, $H_2$ |KOH(aq)|HgO, Hg has a potential of 0.9256 V and is widely applied as a reference electrode in alkaline medium [11]. The reaction of the electrode is $HgO + H_2O + 2e^- \Leftrightarrow Hg + 2OH^-$ (International Union of Pure and Applied Chemistry (IUPAC) 1985). It is evident that for given water activity and pH, the equilibrium potential depends on the standard potential of the internal reference couple as Hg/HgO following the equation

$$HgO + 2H^+ \Leftrightarrow Hg + H_2O$$

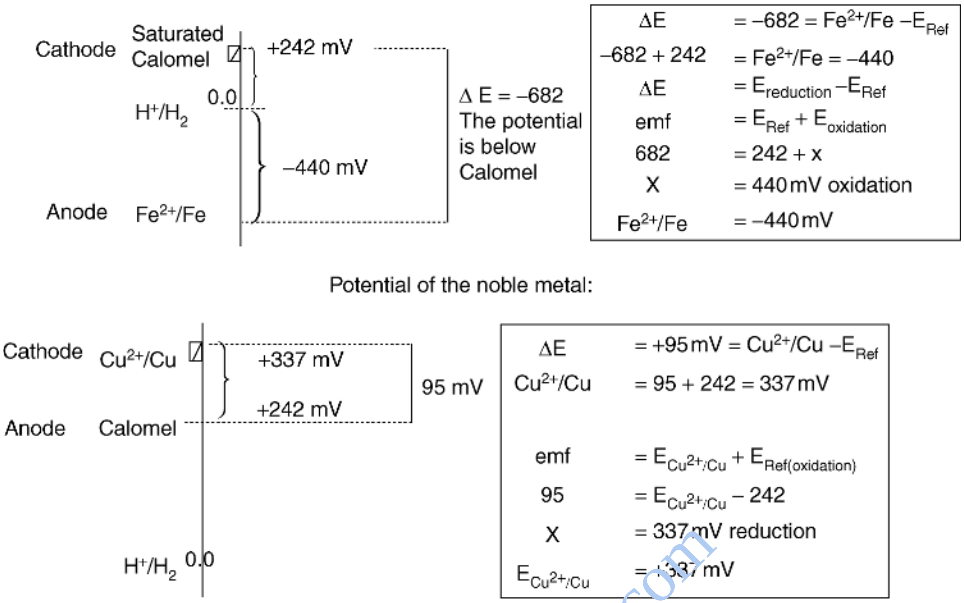

**Figure 1.10** Deduction of the electrode potential values to the standard hydrogen scale instead of other reference electrode measurements.

Another example is the antimony–antimony trioxide electrode, $Sb,Sb_2O_3|OH^-$. The antimony rod covered with a thin layer of oxide is dipped in solution containing $OH^-$ ions that is reversible to hydroxide ions according to the equation

$$Sb + 3OH^- \rightarrow \tfrac{1}{2}Sb_2O_3 + \tfrac{3}{2}H_2O + 3e^-$$

Since $OH^-$ and $H^+$ ions can establish a rapid equilibrium, this electrode is also reversible to $H^+$ ions. The potential of this electrode for the cubic oxide is 0.152 V. It can be useful in nonaqueous solutions [8,11].

The silver–silver oxide electrode has been investigated for high-temperature measurements and the emf of the cell $Ag,Ag_2O|$ KOH(aq)|HgO, Hg was found to be $0.2440 \pm 0.005$ V at 25°C. The temperature coefficients were obtained between 0°C and 90°C, the value being $-0.000198 \pm 0.000003\,V \cdot deg^{-1}$. This leads to $E = 1.1700$ V at 25°C [11].

## 1.13. ELECTRODES OF OXIDATION–REDUCTION

This designates a potential created on the surface of an electrode by two forms of ions of a substance in two stages of oxidation [3]. When a platinum wire or an inert metal is immersed in a solution containing, for example ferrous–ferric, cerous–ceric, stannous–stannic, or manganous–permanganate ions, the wire picks up a specific potential for every couple. This corresponds to the tendency of a free-energy decrease of ions in one state to another more stable state. The general reaction is $A^{n_1}(a_1) + ne^- \rightarrow A^{n_2}(a_2)$, where $a_1$ is the valence in the superior state of oxidation, $a_2$ is the valence in the inferior state and $n = n_1 - n_2$.

For example, for $Fe^{3+} \rightarrow Fe^{2+}$ or the $Fe^{2+}, Fe^{3+}/Pt$ electrode,

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+},\ E^{\circ} = 0.771\ \mathrm{V}$$

$$E = E^{\circ} - \frac{RT}{nF}\ln\frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}$$

This is an exothermic reaction that can create serious corrosion problems such as when atmospheric oxygen facilitates the cathodic reaction of steel corrosion; this can also initiate microbiological corrosion or can be used as a corrosion inhibitor to deplete oxygen. The oxidation reaction of ferrous to ferric has a potential of −0.771 V and can be designated as $Fe^{2+} \rightarrow Fe^{3+}$ or the $Fe^{2+}, Fe^{3+}/Pt$ electrode.

Another example is the $Ce^{+3}, Ce^{+4}/Pt$ electrode:

$$Ce^{+4} + e^{-} \rightarrow Ce^{+3},\ E^{\circ} = 1.61\ \mathrm{V}$$

## 1.14. SELECTIVE ION ELECTRODES

Some selective electrodes for certain ions are very useful in the field of corrosion science and technology, for example, selective electrodes for hydrogen ions, chloride ions and oxygen.

### 1.14.1. Glass Electrodes

Some glasses in fine membranes separating two different solutions can achieve a potential difference between the faces in contact with the two different solutions, which depends on the pH difference between the two solutions. How a tension on the glass electrode is established is not known for certain. However, if the surface of glass is in contact with a solution containing some $H^+$ ions, an exchange occurs between the alkali ions of the glass and the $H^+$ ions of the solution. This exchange is so weak that it does not alter the composition of the glass. At the interface, there is then no exchange of electrons, but only of ions. Since $H^+$ ions are more mobile than sodium ions, a double layer is built up on the glass membrane interface in contact with every solution. It is possible to measure the potential of the membrane electrode with the help of an external electrode with known potential. If one of these solutions is standard with known hydrogen activity or pH, the other pH ($-\log a_{H^+}$) can be deduced from measurement of the emf of the cell (Figures 1.11 and 1.12) [12].

It is possible to have electrodes of different shapes. Some permit one to measure the pH of just one drop of solution, while most require 5 mL in general to cover the appreciable part of the electrode completely. The deduced potential of the membrane electrode is

$$\begin{aligned} E &= \frac{RT}{F}\ln\frac{a_{H^+\,\mathrm{Soln}C_1}}{a_{H^+\,\mathrm{Soln}C_2}} \\ &= 2.3\frac{RT}{F}(\log a_{H^+C_1} - \log a_{H^+C_2}) \\ &= 2.3\frac{RT}{F}(\mathrm{pH}_2 - \mathrm{pH}_1) \end{aligned}$$

$$E = \frac{RT}{F} \ln \frac{a_x \cdot \text{Solu } C_1}{a_x \cdot \text{Solu } C_2}$$

$$= 2.3 \frac{RT}{F} (\log a_x \cdot C_1 - \log a_x \cdot C_2)$$

$$= 2.3 \frac{RT}{F} (\text{pH}_2 - \text{pH}_1)$$

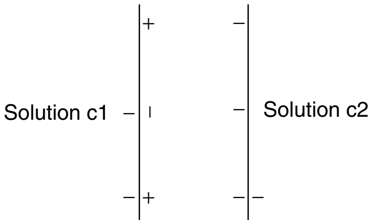

**Figure 1.11** Membrane of glass in contact with two different pH solutions.

### 1.14.2. Copper Ion-Selective Electrodes

Solid-state copper ion-selective electrodes are usually equipped with membranes containing a divalent copper ions with Nernstian slope of 29.6 mV/decade at 25°C in wide concentration ranges down to $10^{-8}$ M. This can result in good selectivity, short response time, and long lifetime, allowing a variety of successful analytical applications [13]. This extremely sensitive selective electrode can be influenced by the presence of chloride ions in concentrations higher than ~0.1 M [14]. Such electrodes are useful in certain corrosion studies where conventional measurements in corrosion and prevention investigations are difficult to conduct [15–17].

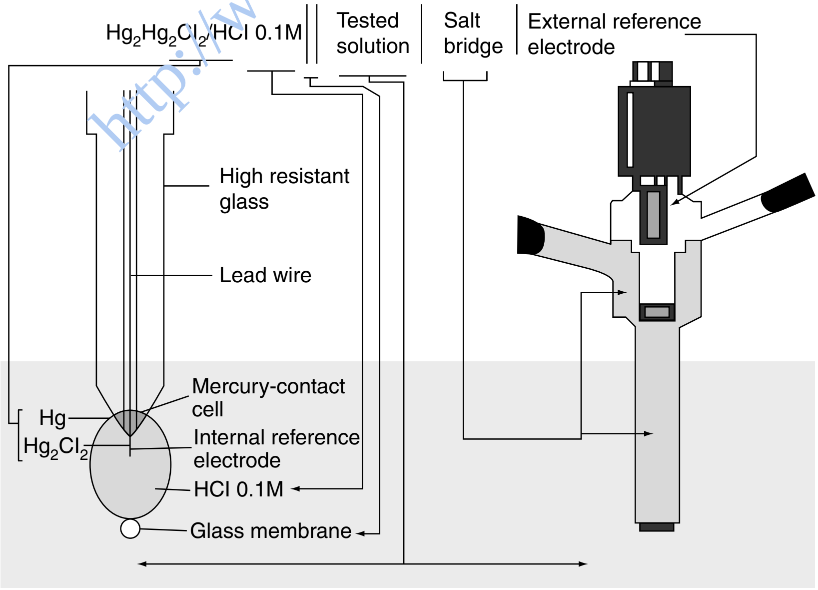

**Figure 1.12** Glass electrode and its reference electrode (Adapted from Ref. 12).

# D. ELECTROCHEMICAL AND CORROSION CELLS

The electrochemical cells can be divided into chemical and concentration cells. Corrosion cells are treated as electrochemical cells, unless specific features of corrosion mechanisms, such as solvent corrosion cells, are present, in that case they are treated separately. The chemical cell results because of a difference in potential between different electrodes, while the concentration (activity) cell is formed because of the difference in activity of species in the electrodes or in the electrolytes.

## 1.15. CHEMICAL CELLS

These can be divided into chemical cells with transport and chemical cells without transport.

### 1.15.1. Chemical Cell with Transport

A current cell of corrosion is composed frequently of two different electrodes with electric contact immersed in a solution containing their dissociated ions such as zinc and steel (iron). This corresponds to a frequently engineered cell in corrosion protection that consists of a zinc coating on a steel rod. The zinc is the sacrificial electrode (anode) and the steel rod (iron) acts as a cathode. In this cell, zinc is corroding, giving zinc ions and electrons. On the surface of the steel, the electrons should be gained to complete the cell, whether through the reduction of zinc ions, which is a highly endothermic reaction, or through the reduction of hydrogen ions (still slightly endothermic reaction, $\Delta G$ is positive), or through the reduction of hydrogen ions accelerated (depolarized) by oxygen in atmospheric conditions (exothermic reaction at pH 3–5 depending on the locality and acid rain pH) (Figure 1.13).

A single vertical bar represents a phase boundary between solid, gas, or aqueous solution, while a dashed vertical bar represents the presence of a junction between miscible liquids, and the cell is written as follows:

$$\mathrm{Zn(s)|Zn^{2+}(aq)\vdots Cd^{2+}(aq)|Cd(s)}$$

The emf of the cell is $E = E_1 + E_2 + \cdots + E_j$. The potential of the junction, $E_j$, depends on the mobility and concentration of cations to the cathode and anions to the anode.

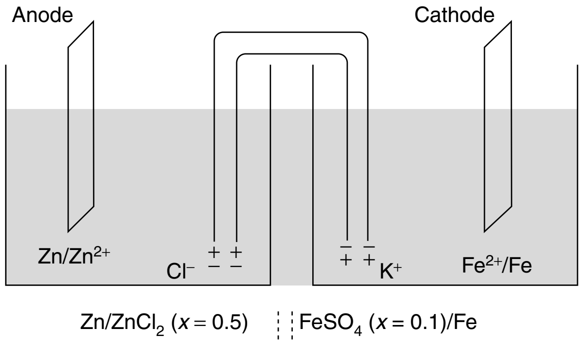

**Figure 1.13** Salt bridge in a chemical cell with transport.

Normally, one adds a salt bridge as a saturated solution or 1 N of KCl between the two solutions; the salt bridge is supposed to reduce the junction potential to a minimum. The mobilities of the $K^+$ and $Cl^-$ ions are nearly equal, and thus there will be two junction potentials with opposite signs at the two ends of the KCl bridge that nearly cancel each other. By convention, a double dashed vertical line represents the presence of a salt bridge at the junction of miscible liquids:

$$\mathrm{Zn(s)|Zn^{2+}(aq)} \vdots\vdots \mathrm{Fe^{2+}(aq)|Fe(s)}$$

The emf of the cell is

$$E = E^\circ - \frac{RT}{2F}\ln\frac{a_{Zn^{2+}}}{a_{Cd^{2+}}}$$

The certainty of the calculated emf of this cell with respect to the measured one depends on the coefficient of activity of the cations $\gamma_+$ (not $\gamma_\pm$ of both cations) and on $E_j \approx 0$.

Many measurements have also been made in cells, which have an explicit liquid junction. For example,

$$\mathrm{Cu|Hg(l)|Hg_2Cl_2(s)|HCl(sat)} \vdots \mathrm{CuSO_4(aq)|Cu}$$

The Nernst equation for such a cell may be written

$$E = E^\circ - (RT/2F)\ln \geq (1/a_{Cu^{2+}}a^2_{Cl^{-1}}) + E_{LJ}$$

where it must be noted that the activities of $Cu^{2+}$ and $Cl^-$ are in different solutions. Measurements in a cell of this type are usually done by varying the electrolyte concentration in the right-half of the cell while keeping that in the left-half constant. In such measurements $a_{Cu^{2+}}$ and $E_{LJ}$ (the liquid junction potential) vary. Neither of these quantities is independently variable, but when one side of the junction consists of saturated KCl and the other an electrolyte of substantially lower concentration, the theory of liquid junctions suggests that $E_{LJ}$ is small and reasonably constant [7].

The *Daniell battery* is an example of a battery with a liquid junction. This battery consists of a copper electrode in a copper sulfate solution, and zinc electrode in a zinc sulfate solution, containing a liquid junction.

$$\mathrm{Zn/ZnSO_4, H_2O} \vdots \mathrm{CuSO_4, H_2O/Cu}$$

A porous system, such as fritted glass, separates the two electrolytes. It prevents the mixture of the two solutions, while letting ions migrate from one solution to the other. For most electrochemical batteries, the junction potential is only on the order of a few millivolts. This increases with the difference of concentration and mobility between ions of the two solutions [6].

### *1.15.1.1. Chemical Corrosion Cells on the Same Metal Surface*

In corrosion, the chemical electrode cell between two different electrodes is easy to identify and control, but for electrodes of the same metal it is more difficult to assess. The potential

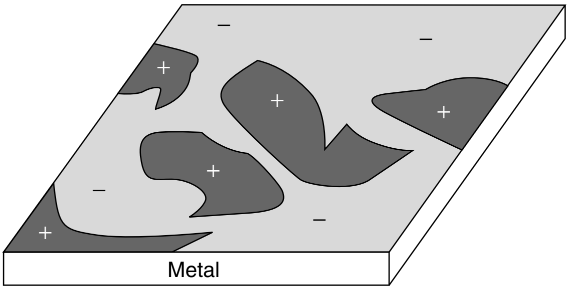

**Figure 1.14** Metal surface enlarged, showing schematic arrangement of anodic and cathodic sites of a chemical cell [2].

difference on the same electrode exists due to geometrical, mechanical, and microstructural properties or different phases. Also, any contamination with different conducting particles can act as a different electrode. A deformed metal or cold-worked metal next to the same metal, grains in contact with joint grains, and a monocrystal with an orientation in contact with another crystal with a different orientation are examples of mixed electrodes. A mixed electrode is a metallic surface that possesses some local cells having anodic and cathodic sites (Figure 1.14). The corrosion potential $E_{corr}$ is the open circuit potential, where anodic and cathodic currents are equal: $i_a = -i_c = i_{corr}$. The reaction of the cell can be the dissolution of the metal or alloy and the cathodic reaction can be any other reduction reaction or even an oxidoreduction reaction.

## 1.15.2. Chemical Cell Without Transport

In order to construct a chemical cell without transport, two electrodes and one electrolyte are chosen so that one electrode is reversible for the cation and the other is reversible for the anion. This is typical of a reference electrode such as

$$Cu(s)|Pt(s)|H_2(g)|HCl(aq)|AgCl(s)|Ag(s)|Cu(s)$$

The total reaction of the cell is

$$\tfrac{1}{2}H_2(P_{H_2}) + AgCl(s) \leftrightarrow Ag(s) + H^+(a_{H^+}) + Cl^-$$

It is possible to write the emf of this cell according to the Nernst equation by considering the potentials ($E^\circ$) of the two electrodes and the chemical activities of all reagents:

$$E_{anode} + E_{cathode} = E^\circ - \frac{RT}{F}\ln\frac{a_{H^+}a_{Cl^-}}{\sqrt{P_{H_2}}}$$

This cell is useful to determine experimentally the coefficient of activity of the electrolyte because of its precise emf.

### 1.15.2.1. *The Weston Standard Cell*

This is a good example of a chemical cell without transport (Figure 1.15). This battery has two stable electrodes: the amalgam electrode and the reference electrode. Its symbol and

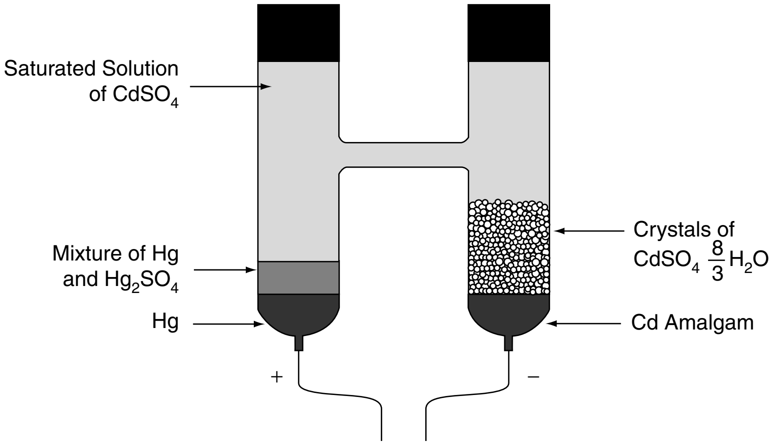

**Figure 1.15** Weston standard cell.

reaction are

$$Cd(Hg)|CdSO_4 \cdot \tfrac{8}{3}H_2O|CdSO_4(\text{saturated solution})|Hg_2SO_4,\ Hg,\ 12.5\%\text{ of Cd in Hg}$$

$$\begin{aligned}
\text{Anodic reaction :}\quad & Cd(Hg) \rightarrow Cd^{2+} + 2e^- + Hg \\
\text{Cathodic reaction :}\quad & Hg_2SO_4 + 2e^- \rightarrow SO_4^{2-} + 2Hg \\
& Cd(s) + Hg_2SO_4(s) + \tfrac{8}{3}H_2O \rightarrow CdSO_4 \cdot \tfrac{8}{3}H_2O(s) + 2Hg
\end{aligned}$$

The emf of the cell is

$$E = 1.01485 - 4.05 \times 10^{-5}(T - 20) - 9.5 \times 10^{-7}(T - 20)^2 \text{ V}$$

Then, $E = 1.01485$ V at 20°C and 1.01463 V at 25°C. The weak temperature coefficient of the emf of this battery is a good advantage. The emf can be slightly different from one battery to another and as a function of time, and so these must be verified periodically.

Other examples are

$$Pt, H_2(P_{H_2})|H_2SO_4(a_{H_2SO_4})|Hg_2SO_4, Hg$$

and

$$Cd|CdSO_4(a_{CdSO_4})|Hg_2SO_4(s), Hg$$

## 1.16. CONCENTRATION CELLS

The change of concentration can occur in either the electrode or the electrolyte. These cells are known as concentration cells, although the correct term should be *activity cells* since it is the activity and not the concentration that is responsible for the emf of the cell.

### 1.16.1. Concentration Cell with Difference of Activity at the Electrode and Electrolyte

One finds examples of concentration change in gas with different gas pressures or different concentrations of a given metal in an alloy (e.g., amalgam). An example for the gas electrode cell is

$$\mathrm{Pt, H_2(P_{H_2} = P_1)|H^+(a_{H^+})|H_2(P_{H_2} = P_2), Pt\ (P_1 > P_2)}$$

The reaction is $\frac{1}{2}\mathrm{H_2}(P_1) \rightarrow \frac{1}{2}\mathrm{H_2}(P_2)$.

For a metallic electrode such as

$$\mathrm{Zn(Hg)}(a_{\mathrm{Zn}} = a_1)|\mathrm{Zn}^{2+}(a_{\mathrm{Zn}^{2+}})|\mathrm{Zn(Hg)}(a_{\mathrm{Zn}} = a_2)\ (a_1 > a_2)$$

the emf is

$$E = -\frac{RT}{2F}\ln\frac{P_2}{P_1} \qquad E = -\frac{RT}{2F}\ln\frac{a_2}{a_1}$$

For the two cells, the emf is due to the transference of hydrogen from the electrode having higher pressure or from the amalgam with a higher activity $a_1$ to the other electrode, and the cell will stop in both cases when the two electrodes in every cell become equal in activity.

Two identical electrodes immersed in the same solution but with different concentrations exist in a concentration cell with a difference in electrolyte concentration. This cell has a liquid junction, and a junction potential therefore, except in the absence of matter transfer between the catholyte and anolyte. The electromotive strength here is not a function of a chemical reaction, but depends on the transfer of one electrode solution from anodic to cathodic compartments or vice versa. A typical example of these cells is $\mathrm{Cu|H_2SO_4}(a_1)\vdots\,\mathrm{H_2SO_4}(a_2)|\mathrm{Cu}$ (Figure 1.16) [6]. The copper electrode immersed in the less concentrated (active) solution will act as an anode.

The reactions of the cell considering the ion transport are as follows:

Anodic reaction : $\mathrm{Cu} \Rightarrow \mathrm{Cu}^{2+} + 2e^-$

Cathodic reaction : $\mathrm{Cu}^{2+} + 2\mathrm{e}^- \Rightarrow \mathrm{Cu}$

---

Total reaction : $\mathrm{Cu}^{2+}_{(\mathrm{C2})} \Rightarrow \mathrm{Cu}^{2+}_{(\mathrm{C1})}$

At the junction of the two liquids, there is the following exchange:

$$t_-\,\mathrm{SO}^{2-}_{4(\mathrm{C2})} \Rightarrow t_-\,\mathrm{SO}^{2-}_{4(\mathrm{C1})}$$
$$t_+\,\mathrm{Cu}^{2+}_{(\mathrm{C1})} \Rightarrow t_+\,\mathrm{Cu}^{2+}_{(\mathrm{C2})}$$

The sum of the reactions at the electrodes and due to the ion transport gives

$$\mathrm{Cu}^{2+}_{(\mathrm{C2})} + t_-\,\mathrm{SO}^{2-}_{4(\mathrm{C2})} + t_+\,\mathrm{Cu}^{2+}_{(\mathrm{C1})} \Rightarrow \mathrm{Cu}^{2+}_{(\mathrm{C1})} + t_-\,\mathrm{SO}^{2-}_{4(\mathrm{C1})} + t_+\,\mathrm{Cu}^{2+}_{(\mathrm{C2})}$$
$$(t_+ + t_-)\mathrm{Cu}^{2+}_{(\mathrm{C2})} + t_-\,\mathrm{SO}^{2-}_{4(\mathrm{C2})} + t_+\,\mathrm{Cu}^{2+}_{(\mathrm{C1})} \Rightarrow (t_+ + t_-)\mathrm{Cu}^{2+}_{(\mathrm{C1})} + t_-\,\mathrm{SO}^{2-}_{4(\mathrm{C1})} + t_+\,\mathrm{Cu}^{2+}_{(\mathrm{C2})}$$
$$t_-\,\mathrm{CuSO}_{4(\mathrm{C2})} \Rightarrow t_-\,\mathrm{CuSO}_{4(\mathrm{C1})}$$

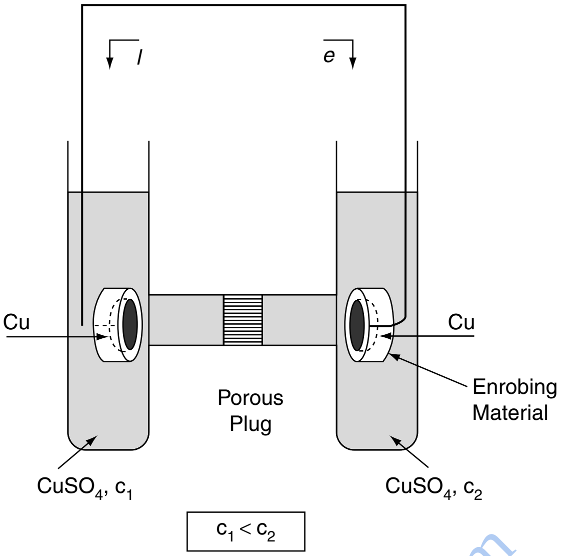

**Figure 1.16** Copper concentration cell with transport [6].

The emf of this cell is

$$E = -\frac{RT}{F}\ln\frac{a_1^{t_-}}{a_2^{t_-}}$$

Suggesting that $t_-$ is 0.6, we find the emf of this cell can be on the order of 25 mV if $a_1$ is 0.1 M and $a_2$ is 0.5 M and that can initiate pitting corrosion in certain circumstances.

$$\text{FEM} = -t_-\frac{RT}{zF}\ln\frac{[(a_{\text{Cu}^{2+}})(a_{\text{SO}_4^{2-}})]_{\text{C1}}}{[(a_{\text{Cu}^{2+}})(a_{\text{SO}_4^{2-}})]_{\text{C2}}}$$

#### 1.16.1.1. Oxygen Differential Cell

Two different electrolytes at the interface may create a concentration cell. The oxygen differential cell is one of the most important ones in corrosion. This can include two iron electrodes in a dilute solution of sodium chloride (NaCl); the electrolyte around an electrode is well aerated (cathode) while the oxygen around the other solution is expelled by nitrogen bubbling in the solution (anode) (Figure 1.17).

A small quantity of oxygen reaches the metallic surface below the iron oxide (rust), which slows its diffusion (Figure 1.18). The water line corrosion, caused by a differential oxygen cell and observed very frequently on ships in seawater or even boats in river water is illustrated in Figure 1.19. The underground corrosion, caused by a differential oxygen cell, is illustrated in Figure 1.20. The oxygen flux is stronger at the top than that on the bottom. This creates a differential aeration cell with higher oxygen at the surface of the pipe as compared to that of the bottom. The latter with less oxygen plays as anode. Frequently,

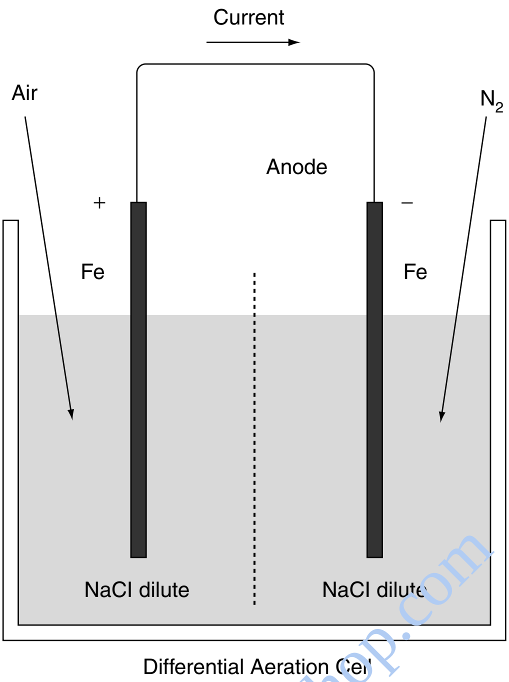

**Figure 1.17** Oxygen differential cell.

careful inspection should identify pitting corrosion at the bottom of the pipe rather than on the surface. The main reason explaining the importance of this cell in corrosion is that the cathodic reaction of $2H^+ + \frac{1}{2}O_2 + 2\,e^- \rightarrow H_2O$ is much more exothermic than that of hydrogen $2H^+ + 2\,e^- \rightarrow H_2$, with almost 1200 mV at unity activity of hydrogen ions at 25°C under atmospheric pressure.

### 1.16.2. Junction Potential

The junction potential ($E_j$) is the difference between the total emf of the cell and the sum of the reactions at the anode and cathode. A typical example to calculate the junction potential is to consider the reaction at the cell (Figure 1.21), where $a_2 > a_1$:

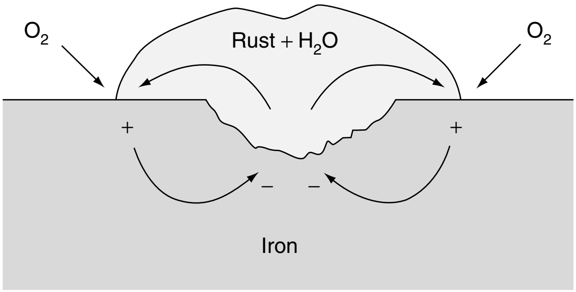

**Figure 1.18** Corrosion differential aeration cell formed by rust on iron.

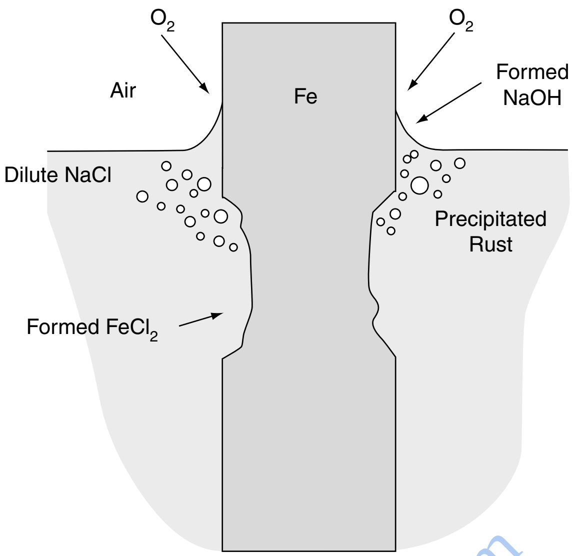

**Figure 1.19** Corrosion differential aeration cell at the waterline.

$$\underset{\boxed{\text{anode}}}{\text{Pt, H}_2(1\text{ atm})|\text{HCl}(a_1)} \vdots \underset{\boxed{\text{cathode}}}{\text{HCl}(a_2)|\text{H}_2(1\text{ atm}),\text{Pt}}$$

The sum of the reactions at the two electrodes is

$$\text{H}^+(a_2) \leftrightarrow \text{H}^+(a_1)$$

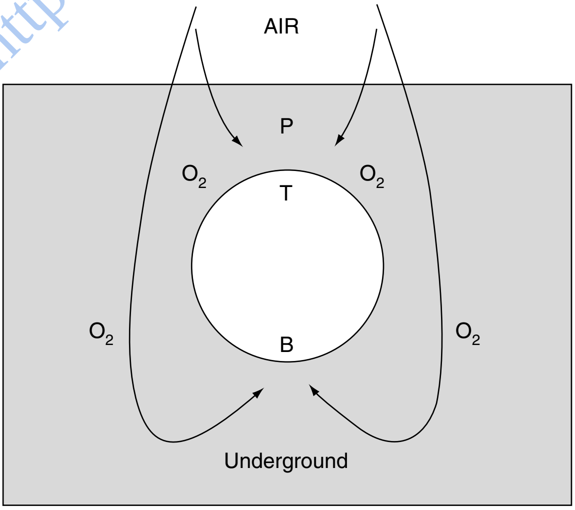

**Figure 1.20** Corrosion differential aeration cell of buried pipe [17].

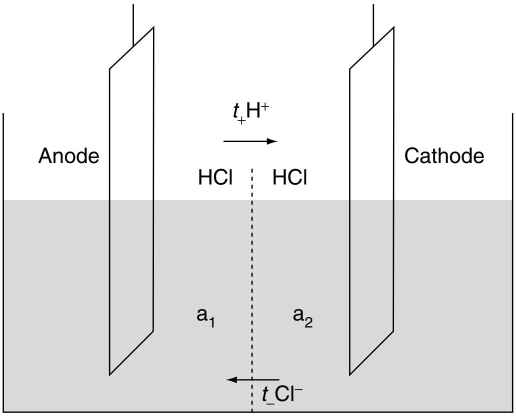

**Figure 1.21** Corrosion cell with transport.

The emf due to the reaction at the electrodes is

$$E_1 + E_2 = -\frac{RT}{F}\ln\frac{(a_{H^+})_1}{(a_{H^+})_2}$$

$$E_1 + E_2 = \frac{RT}{F}\ln\frac{(m_{H^+}\gamma_{H^+})_2}{(m_{H^+}\gamma_{H^+})_1}$$

$$E_{\text{total}} = \frac{2t_-RT}{F}\ln\frac{m_2\gamma_2}{m_1\gamma_1}$$

$$E_{\text{LJ}} = \frac{2t_-RT}{F}\ln\frac{m_2\gamma_2}{m_1\gamma_1} - \frac{RT}{F}\ln\frac{(m_{H^+}\gamma_{H^+})_2}{(m_{H^+}\gamma_{H^+})_1}$$

Considering the two approximations $(m_{H^+}) \approx \mathrm{m}_1$, and $(\gamma_{H^+}) = \gamma_1$,

$$E_{\text{LJ}} = (t_- - t_+)\frac{RT}{F}\ln\frac{m_2\gamma_2}{m_1\gamma_1}$$

In the case of a cell reversible to the anion, Ag,AgCl(s) |HCl($a_1$)¦HCl($a_2$) |AgCl(s), Ag, the liquid junction potential is

$$E_{\text{LJ}} = (t_+ - t_-)\frac{RT}{F}\ln\frac{m_1\gamma_1}{m_2\gamma_2}$$

It can be observed that in this case $a_1 > a_2$ for a spontaneous exothermic reaction in this direction of the cell.

Since the electromotive strength of these batteries involves the transport number, such batteries can be used to determine the transport number or the coefficient of activity in measuring the emf of the battery and knowing the $t$ or the $\gamma$ of the studied cation or anion.

The liquid junction potential is the difference between the transport numbers of the cations and anions of the electrolyte. In the case of potassium chloride, the value of $t_+ - t_-$ is equal to 0.02; therefore the junction potential is on the order of 1 mV between two concentrations of KCl, 0.001 N and 0.01 N, at a temperature of 25°C. This is the origin of the current use of a KCl salt bridge since $t_+ = 0.51$ and $t_- = 0.49$. $E_j$ could be ~ zero, positive,

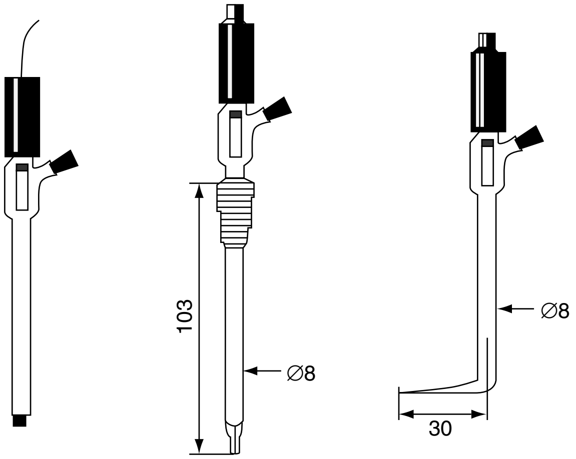

**Figure 1.22** Different shapes of reference electrodes, one with a junction bridge. The dimensions are given in millimeters (Tacussel Company electrode configurations, France).

or negative (Figure 1.22). The hydrochloric acid has a very elevated value for $2t_+ - 1 = t_+ - t_-$, roughly equal to 0.65; the junction potential between two concentrations of HCl, 0.001 N and 0.01 N, is on the order of 39 mV. This emf can initiate a local corrosion cell that can lead to pitting corrosion.

When the liquid on each side of the junction is different, the potential is complex and difficult to determine and, in most cases, is function of the geometric features of the junction. For numerous electrochemical batteries, the junction potential is on the order of a few millivolts and increases with the difference of concentration and mobility between ions of the two solutions [6].

In only one general case—a liquid junction between two liquids with the same concentration where all the ions are monovalent, and there is a common ion such as NaCl and KCl solutions—the potential of the liquid junction is independent of the structure of the border and equal to

$$E_{\mathrm{j}} = \frac{2.303RT}{F}\log\frac{\Lambda_1}{\Lambda_2}$$

where $\Lambda_1$ and $\Lambda_2$ are the equivalent conductance of the two electrolytes, respectively. It is clear from this equation that when the values of $\Lambda$ are very close, the potential of the junction becomes very weak. For example, the liquid junction between a solution of 0.1 N of KCl and a solution of NaCl at 25°C is on the order of

$$E_{\mathrm{j}} = 0.0592\log\frac{128.96}{106.74} = 0.0049\ \mathrm{V}$$

On the other hand, when the junction is between hydrochloric acid 0.1 N, where the $\mathrm{H}^+$ ions are very mobile, and 0.1 N sodium chloride, the potential of junction is important at 25°C:

$$E_{\mathrm{LJ}} = 0.0592\log\frac{391.32}{106.74} = 0.0333\ \mathrm{V}$$

In practice, one could reduce $E_j$ appreciably by means of a bridge composed of a narrow tube full of a solution saturated with potassium chloride or ammonium nitrate.

There is a concentration cell without transport that is in reality a combination of two chemical cells that can monitor the emf of the cell without any interference of the junction potential. This kind of concentration cell is useful to determine the activity coefficient or to deduce the junction potential:

$$\mathrm{Pt}, \mathrm{H_2}(1\ \mathrm{atm})|\mathrm{HCl}(a_1)|\mathrm{AgCl(s)}, \mathrm{Ag} - \mathrm{Ag}, \mathrm{AgCl(s)}|\mathrm{HCl}(a_2)|\mathrm{H_2}(1\ \mathrm{atm}), \mathrm{Pt}$$

and the reaction is

$$\tfrac{1}{2}\mathrm{H_2}(1\ \mathrm{atm}) + \mathrm{AgCl(s)} - \tfrac{1}{2}\mathrm{H_2(g)}(1\ \mathrm{atm}) - \mathrm{AgCl(s)} \leftrightarrow \mathrm{Ag(s)} + \mathrm{HCl}(a_1) - \mathrm{Ag(s)} - \mathrm{HCl}(a_2)$$

$$\mathrm{HCl}(a_2) \leftrightarrow \mathrm{HCl}(a_1)$$

The emf is

$$E = E_1 - E_2$$

## 1.17. SOLVENT CORROSION CELLS

This type of electrochemical cell depends on the surface properties, atomic structure, and potential level of the electrode, its chemical reactivity with respect to the species in solution (metallic or complex ions), or on some stray electrical current in the electrolyte.

### 1.17.1. Cathodic Oxidoreduction Reaction

This is a type of cell where its existence depends on an exothermic oxidoreduction electrode reaction. The ferric–ferrous reaction, the most abundant one in this category, has been exploited for chemical machining of highly precise steel instruments or for bacterial leaching of sulfide minerals. In the absence of oxygen, the iron and the divalent ion can coexist at equilibrium states. However, in the presence of oxygen and/or at higher temperatures than ambient, the trivalent ion can be formed and corrosion of iron can be accelerated according to

$$\mathrm{Fe} + 2\mathrm{Fe}^{3+} \rightarrow 3\mathrm{Fe}^{2+}$$

Table 1.3 gives the potential standard of different reactions between dissolved species. It shows that the oxygenated water and the dichromate ions are particularly powerful oxidizers. The oxidizing power of the dissolved oxygen decreases with an increase of the pH [6].

### 1.17.2. Displacement Cell

The most frequent corrosion reaction of active metals occurs in a liquid environment when ions of a more cathodic metal (e.g., copper) are plated out of solution onto a more anodic one (e.g., aluminum or magnesium alloy). This type of reaction is very serious for aluminum

**Table 1.3** Standard Oxidoreduction Potentials

| Reaction | $E°$ (V) |
|---|---|
| $H_2O_2 + 2\,H^+ + 2\,e^- = 2\,H_2O$ | 1.763 |
| $Ce^{4+} + e^- \rightarrow Ce^{3+}$ | 1.61 |
| $Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- = 2\,Cr^{3+} + 7\,H_2O$ | 1.36 |
| $2\,H^+ + 0.5\,O_2 = H_2O$ at 25°C and atmospheric pressure = 1.23 – 0.0592 pH | |
| $Fe^{3+} + e^- = Fe^{2+}$ | 0.771 |
| $Fe(CN)_6^{3-} + e^- = Fe(CN)_6^{4-}$ | 0.361 |
| $TiO^{2+} + 2\,H^+ + e^- = Ti^{3+} + H_2O$ | 0.100 |
| $TiO^{2+} + 2\,H^+ + 2\,e^- = Ti^{2+} + H_2O$ | –0.135 |
| $Cr^{3+} + e^- = Cr^{2+}$ | –0.424 |

*Source:* Reference [6].

and magnesium alloys in the active state, since they are the most active structural materials and so the deposited metallic impurities create active galvanic cells and more frequently pitting corrosion. It is called *deposition corrosion*, which is a combination of pitting and galvanic corrosion.

In the area of hydrometallurgy, a very useful and desired reaction is *cementation*, such as to cement a noble metal like gold or copper onto the surface of an active metal

$$2Au^+ + Fe \rightarrow 2Au + Fe^{+2} \quad \text{or} \quad Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu$$

## 1.17.3. Complexing Agent Cells

The presence of a complexing agent influences the potential of metals since it replaces the molecules of hydration or solvatation of the dissolved ion. Some powerful complexing ions are chloride, cyanide, and ammonia. The complexing chloride ions for copper and gold, the ammonia ions for copper, and the cyanide ions for gold, iron, and copper are all examples of exothermic corrosion reactions as seen in Table 1.4. They lower the potential standard of reactions of metal dissolution and facilitate corrosion. At the time of the dissolution of a metal, the presence of complexants encourages the formation of ions, the oxidization state of which correlates to the most stable formation of the complex. For example, in the case of copper, monovalent ions $CuCl_2^-$ and $Cu(CN)_2^-$ are formed in the presence of complexing

**Table 1.4** Standard Potentials of Electrode Reactions Implying Complexing Agents

| Reaction | $E°$ (V) |
|---|---|
| $Fe(CN)_6^{4-} + 2\,e^- = Fe + 6\,CN^-$ | –1.56 |
| $Fe(CN)_6^{3-} + 3\,e^- = Fe + 6\,CN^-$ | –0.92 |
| $Au(CN)_2^- + e^- = Au + 2\,CN^-$ | –0.595 |
| $Cu(CN)_2^- + e^- = Cu + 2\,CN^-$ | –0.44 |
| $Ag(CN)_2^- + e^- = Ag + 2\,CN^-$ | –0.31 |
| $CuCl_2^- + e^- = Cu + 2\,Cl^-$ | –0.225 |
| $Cu(NH_3)_2^+ + e^- = Cu + 2\,NH_3$ | –0.10 |
| $AuCl_4^- + 3\,e^- = Au + 4\,Cl^-$ | 1.002 |

*Source:* Reference [6].

ions $Cl^{-1}$ and $CN^{-}$, respectively, while its dissolution in a noncomplexing medium produces the bivalent ion $Cu^{2+}$. These should be identified carefully in every situation since they can initiate general and more severe forms of localized corrosion and even stress corrosion cracking such as in copper in solutions containing ammonia [6].

### 1.17.4. Stray Current Corrosion Cell

A stray current corrosion cell results from an induced electrical current and is basically independent of the environmental factors such as oxygen concentration or pH that influence other forms of corrosion. A current leaves the intended path because of poor electrical connections within the circuit due to poor insulation around the intended conductive material. It then passes through soil, water, or any other suitable electrolyte to find a low-resistance path, such as a buried metal pipe or some other metal structure, and flows to and from that structure, causing accelerating corrosion. Sources of stray currents include induction from adjacent lines, leakages, variable ground voltages, electric railway systems, grounded electric direct-current power, electric welders, cathodic protection systems, and electroplating plants.

Stray current effects are common on underground cast iron or steel pipelines that are located close to electrical supply lines. Stray currents cause corrosion at the point where they leave the metal (e.g., lead pipe or lead cable sheathing can undergo severe corrosion). Most soils, especially those containing sulfates, will frequently produce graphitic corrosion (a form of dealloying of cast iron) of unprotected gray and nodular cast iron. Tantalum electrically coupled to a less noble metal, such as low-carbon steel, in the presence of stray current may become a cathode and consequently may absorb and become embrittled by atomic hydrogen in the electrolytic galvanic cell [18].

## 1.18. TEMPERATURE DIFFERENTIAL CELLS

These cells are formed by a difference in the temperature. The constituents of these cells are made of the same metal immersed in one electrolyte with an equal initial composition but each is subjected to a different temperature. The importance theoretical basis of these cells are less obvious than for previous cells. These corrosion cells can be observed in heating elements and furnaces.

In a solution of copper sulfate at an elevated temperature, the copper plays the role of the cathode, while in the same solution at a lower temperature the copper plays the role of the anode. It is important to note that this cell depends on the metal, the medium, and the acceleration of cathodic reactions relative to that of the anodic ones.

## 1.19. OVERLAPPING OF DIFFERENT CORROSION CELLS

Any classification of corrosion cells cannot be based solely on interdependence of the parameters of these cells. However, it is useful to identify the main initiating reasons of corrosion in case histories.

1. Sometimes, the electrode itself for different concentrations of the same solution could be passive or active and so there is a chemical cell at the beginning that can create two different solutions. This can initiate a concentration cell or accelerate corrosion by acidity, for example.

2. The presence of two identical electrodes immersed in the same solution but with different concentrations can create a cell that depends not only on the charge transport but also on diffusion laws, convection, and temperature and density considerations.
3. Frequently, in the case of corrosion cells, a difference of temperature of the same material, such as copper in contact with the same solution at different temperatures, can give a difference in the electrode potentials as well as a difference in the activities of the corroding solutions.

## E. CHEMICAL AND ELECTROCHEMICAL CORROSION

Chemical reactions are governed by the laws of mass action, solubility product, and chemical equilibrium such as those involving oxidation–reduction processes. Electrochemical reactions are defined as those in which free electric charges, or electrons, participate. If a piece of iron is connected to a piece of zinc metal in seawater, zinc dissolves and liberates electrons and becomes an anode while iron can be protected completely by acting as a cathode in accepting these electrons to reduce water in the presence of oxygen on its surface.

## 1.20. DEFINITION AND DESCRIPTION OF CORROSION

There is a wide range of construction materials—metals and alloys, plastics, rubber, ceramics, composites, wood, and so on—and the selection of an appropriate material for a given application is the responsibility of the designer. Corrosion is not the sole factor of importance in material selection, however corrosion is frequently considered as the most neglected factor by the design engineer. Corrosion is a major factor in assessing the performance of structural materials. Evans [19] considers that corrosion may be regarded as a branch of chemical thermodynamics or kinetics, such as the outcome of electron affinities of metals and nonmetals, the short-circuited electrochemical cells, or the demolition of the crystal structure of a metal. However, this concerns electrochemical corrosion only. Fontana and Staehle [20] have stated that corrosion includes the reaction of metals, glasses, ionic solids, polymeric solids, and composites with environments that embrace liquid metals, gases, nonaqueous electrolytes, and other non-aqueous solutions.

In the early beginning of corrosion science, corrosion in aqueous solutions was defined as wet corrosion, while corrosion in the absence of water was called dry corrosion. A "wet" reaction of iron in an oxygenated aqueous medium can be represented by the equation

$$\mathrm{Fe} + 0.5\,\mathrm{H_2O} + 0.75\,\mathrm{O_2} \rightarrow 0.5\,\mathrm{Fe_2O_3} \cdot \mathrm{H_2O}$$

A "dry" corrosion of iron where water or aqueous solutions are not involved can be expressed as

$$\mathrm{Fe} + 0.75\,\mathrm{O_2} \rightarrow 0.5\,\mathrm{Fe_2O_3}$$

If the mechanism of the reaction is considered, our present knowledge of corrosion phenomena shows that wetting of solids by mercury, for example, should be considered a wet reaction in spite of the absence of aqueous solution. Liquid-metal corrosion should then be classified as "wet." On the other hand, the mechanism of corrosion in a wet solution, such as the case of the interior boiler drum corroding in dilute caustic soda at high temperature and high pressure, is best interpreted in terms of a dry corrosion mechanism. Similarly, the reaction of high-temperature water with aluminum and zirconium has been found to show a conventional dry corrosion mechanism [21].

## 1.21. ELECTROCHEMICAL AND CHEMICAL REACTIONS

If we look profoundly for the mechanism of the majority of wet and dry reactions, we can consider that the interfaces in both reactions involve anodic and cathodic sites. Wet corrosion (Figure 1.23)[21] can be considered as

$$\begin{aligned}\text{Anodic reaction}: &\quad \mathrm{M}_{\text{lattice}} + \mathrm{H_2O} \rightarrow \mathrm{M}^{z+}_{\text{aqueous}} + ze\\ \text{Cathodic reaction}: &\quad \tfrac{1}{2}\mathrm{O_2} + \mathrm{H_2O} + 2\,\mathrm{e} \rightarrow 2\,\mathrm{OH}^-\\ &\quad \text{or}\quad \tfrac{1}{2}\mathrm{O_2} + 2\,\mathrm{H}^+ + 2\,\mathrm{e} \rightarrow \mathrm{H_2O}\end{aligned}$$

Similarly, a dry reaction can be divided into two anodic and cathodic reactions (Figure 1.24):

$$\text{Anodic reaction}: \ \mathrm{M} \rightarrow \mathrm{M}^{z+} \bullet/0 + z\,\mathrm{e} \bullet/0$$

where $M^{z+}$ • represents a cation vacancy, e • a positive hole, and/0 the metal–oxide interface. At the gas–oxide interface the gas ionizes.

$$\text{Cathodic reaction}: \ (\tfrac{1}{2}\mathrm{O_2}/\text{ads}) + 2(\mathrm{e}/\mathrm{X}) \rightarrow (\mathrm{O}^{2-}/\text{ads})$$

where/X indicates the gas–oxide interface [21].

The formation of a hydrated ion is obligatory in a wet reaction. However, the hydration reaction of most metal ions in a wet reaction is very quick and thus facilitates ionization. The dry reaction involves a direct ionization of oxygen.

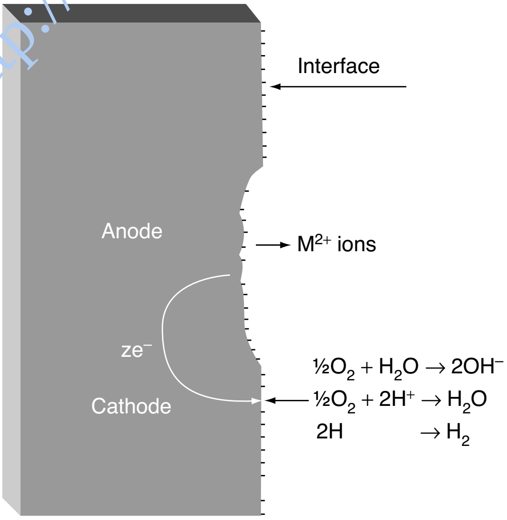

**Figure 1.23** Example of electrochemical aqueous corrosion of an active metal in an oxygenated aqueous solution [21].

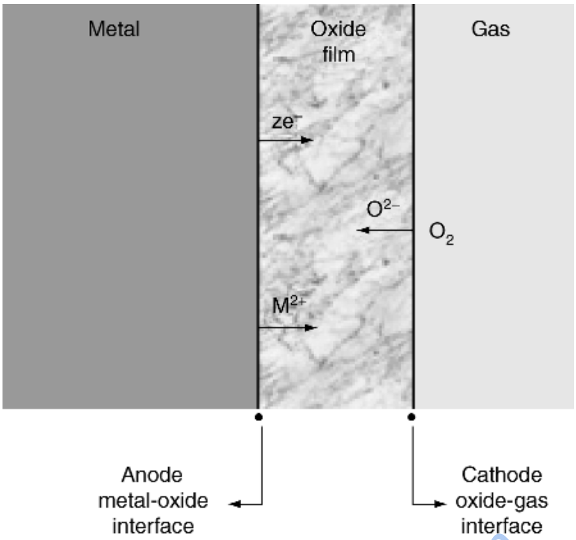

**Figure 1.24** An electrochemical reaction at high temperature: corrosion reaction diagram [21].

Shreir [21] suggested that the main types of corrosion reactions could be divided into electrochemical reactions and film-free chemical interactions.

### 1.21.1. Electrochemical Corrosion

Electrochemical reactions can be divided further into three categories: microelectrochemical cells (inseparable anode/cathode), macroelectrochemical cells (separable anode/cathode areas), and interfacial anode/cathode type.

#### *1.21.1.1. Microelectrochemical Cells (Inseparable Anode/Cathode Areas)*

The general uniform dissolution reactions of metals in acid, alkaline, or neutral solutions like zinc in hydrochloric acid or in caustic soda (wet reactions) are typical examples. The anodes and cathodes cannot be distinguished by experimental methods, although their theoretical presence is postulated. It can be admitted that the cathodic and anodic sites are interchangeable. The corrosion current of passive metals, like that of stainless steel in aqueous solutions, is a typical example of mobile anodic sites, although the corrosion rate is very low.

#### *1.21.1.2. Macroelectrochemical Cells (Separable Anode/Cathode Areas)*

Certain areas of the metal can be distinguished experimentally as predominantly anodic or cathodic, although the separation distances of these areas may be as small as a fraction of a millimeter. Typical examples could be the general attack of certain regions (localized corrosion), the reaction of iron containing a discontinuous magnetite scale with oxygenated water, crevice corrosion, water-line attack, or “long-line” corrosion of buried iron pipes.

### *1.21.1.3. Interfacial Anode/Cathode Type*

This group includes all metal oxidation reactions in which the charge is transported through a film of reaction product on the metal surface. With parabolic, logarithmic, or asymptotic growth rates, a film can be rate determining, while linear growth rates cannot be rate determining. These reactions are generally considered dry reactions (Figure 1.24). This group also includes the metal–solution reactions, where the uniform formation and growth of a film of reaction product are observed. This includes the reaction of metals with high-temperature water and the reaction of copper with sulfur dissolved in carbon disulfide. Then the reaction of iron with oxygen at room temperature or with oxygen or water at high temperatures is an interfacial electrochemical reaction. For example, in the oxidation of iron at high temperature, the Fe–oxide interface can be considered an anode while the oxide–$O_2$ interface can be considered a cathode. Reactions with fused salts or nonaqueous solutions (e.g., organic solvent/metal) can be electrochemical in nature. A typical example is the corrosion of copper in a molten salt of ammonium nitrate and bromine in alcohol. In certain cases of uniform general corrosion of metals in acids (e.g., aluminum in hydrochloric acid or iron in reducible acids or alkalis), a thin film of oxide is present on the metal surface. Although the film is not rate determining these reactions cannot be considered film-free ones.

Landolt [6] has characterized the kinetics of corrosion at high temperatures by three parameters:

1. In the absence of an aqueous solution, reactions remain electrochemical in nature (see Figure 1.24).
2. At high temperatures, the volume diffusion and the diffusion at joint grains constitute the basic mechanism of transport in the oxide films. Consequently, the film thickness can be measured in micrometers. In aqueous media, the oxide growth takes place by ionic conduction at high field, limiting the formed film to a thickness of a few nanometers.
3. Since the energy of activation of the electrochemical reaction is superior to that of diffusion phenomenon at high temperatures, an important increase in the corrosion rate occurs with temperature. Equilibrium can be achieved due to the increase in diffusion rate, which becomes sufficiently important. At room temperature, the reaction rate is frequently controlled by the charge transport to the interface.

## 1.21.2. Film-Free Chemical Interactions

There is a direct chemical reaction of a metal with its environment. The metal remains film-free and there is no transport of charge. The metal–gas reaction forms a volatile oxide or compound, like the reaction of molybdenum with oxygen or the reaction of iron or aluminum with chlorine (dry reactions). The reactions of solid metals with liquid metals like the dissolution of aluminum in mercury and the corrosion of metals in their fused halides (e.g., lead in lead chloride) can be considered chemical reactions. In the same way, the dissolution of metals in nonaqueous solutions (e.g., reaction of aluminum in carbon tetrachloride) can be integrated into this group of chemical reactions.

The first step in the identification of this type of corrosion reaction should then be followed as far as possible by:

1. Corrosion behavior: active or active–passive behavior.
2. Corrosion form, mode, and corrosion type.
3. Material properties.
4. Media description.
5. Corrosion product.
6. Corrosion kinetics and mechanisms.
7. Corrosion testing standards and/or equivalent procedures.

These will be described in detail in the following chapters of this book with special reference to aluminum and magnesium alloys.

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