

Chapter 2

ELECTROCHEMISTRY

2.1 INTRODUCTION

The goal of this chapter is to elucidate the fundamental characteristics and technological significance of electrochemical cells. A comprehensive review on the subject is excluded since the intention hereafter is to describe the principles of electrochemistry, which should provide the reader with relevant key definitions and concepts on metal reduction and metal oxidation in galvanic couplings. Thus, the principles of anodic protection and cathodic protection become uncomplicated or unproblematic to understand and comprehend suitable applications of electrochemistry for preventing localized corrosion and general corrosion on metallic structures. In general, electrochemistry deals with the chemical response of an electrode/electrolyte system to an electrical stimulation and the electrochemical behavior of species (ions) can be assessed, including concentration, kinetics, and reaction mechanisms.

Electrochemical galvanic cells involve electron transfer from a metal (electrode) surface to a environment (electrolyte). This metal is treated as the anode due to its ability to oxidize by losing electrons and becoming electron-deficient atoms called cations. On the other hand, the metal receiving or gaining electrons is the cathode since its cations in solution reduce or deposit on the cathode surface as atoms. Therefore, an electric field must exist in the electrolyte due to the presence of charge particles represented by ions [1]. If an electrochemical cell produces energy it is known as a galvanic cell and if it consumes energy it is an electrolytic cell. Nonetheless, an electrochemical process is treated as an electroanalytical technique associated with electricity and chemistry so that electrical quantities are measured in order to quantify chemical changes in a cell. Chemical measurements normally involve heterogeneous bulk solutions and electrochemical processes are analyzed according to the ionic interactions at the electrode-electrolyte interface.

The applications of electrochemistry is broad. Simply stated, metal ions can be reduced into atoms on an electrode surface by chemical and electrochemical

processes. The former process does not involve any current flow to drive a redox reaction, but the latter does. Eventually, metal reduction starts at a nanoscale forming atom agglomerates or nanoparticles [13-16] and it may proceed to a microscale as in thick film formation or macroscale as in electrowinning technology for recovering, say, copper from solution. Nowadays, nanotechnology is gaining acceptance in the scientific community.

2.2 ELECTRICAL POLES

Assume that electrical conductors, such as aqueous solutions containing charged particles known as ions, exists in a static electrochemical system and that there exists an infinitesimal current flow. Thus, an electric field strength vector $\vec{E}$ at a point P in space and an inner electric potential ϕ of the system are defined below, respectively [1]

$$\vec{E} = \vec{F}/Q \quad (2.1a)$$

$$\phi = \lim_{Q \rightarrow 0} \frac{W}{Q} \quad (2.1b)$$

where $\vec{F}$ = Electric force vector (N)
 Q = Electric charge (C = Coulomb)
 W = Electric work (J)

In fact, Q depends on the type of ions, which are treated hereafter as poles, and it is related to **Faraday's constant** F . Both F and Q are defined by

$$F = q_e N_A \simeq 96,500 \text{ C/mol} \quad (2.1c)$$

$$Q = zFX_i \quad (2.1d)$$

where q_e = Electron charge = $(1.6022 \times 10^{-19} \text{ C/ions})$
 N_A = Avogadro's number = $(6.02213 \times 10^{23} \text{ ions/mol})$
 X_i = Mole fraction (mol)
 z = Valence or oxidation number
 $\text{C/mol} = \text{A} \cdot \text{s/mol} = \text{J/mol} \cdot \text{V}$

The Cartesian electric field strength components in a three-dimensional scheme are defined as follows

$$\begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} = -\nabla\phi = - \begin{bmatrix} \partial\phi/\partial x \\ \partial\phi/\partial y \\ \partial\phi/\partial z \end{bmatrix} \quad (2.2a)$$

$$\begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} = \lambda Q \begin{bmatrix} x^{-2} \\ y^{-2} \\ z^{-2} \end{bmatrix} \quad (2.2b)$$

where $\epsilon_o = 8.854 \times 10^{-12} \frac{C}{Nm^2}$ = Permittivity of vacuum
 $\lambda \approx 1/(4\pi\epsilon_o) = 9 \times 10^9 \frac{Nm^2}{C^2}$

MONOPOLE: Let ϕ be defined at a point P in space around a charge Q^+ in an electrical monopole $Q^+ - P$ path shown in Figure 2.1a. Integrating eq. (2.2a) yields the inner electric potential in the x-direction

$$\phi_x = \int_0^r E_x dx = \frac{\lambda Q}{r} \quad (2.3)$$

Equation (2.3) gives the definition of the monopole potential due to a point charge Q . This is a simple definition of an internal potential between two points located at a relatively short distance. Otherwise, $\phi \rightarrow 0$ as $r \rightarrow \infty$. On the other hand, when $\phi \rightarrow \infty$ as $r \rightarrow 0$ an electric potential “singularity” can be established for ϕ in the order of r^{-1} as predicted by eq. (2.3).

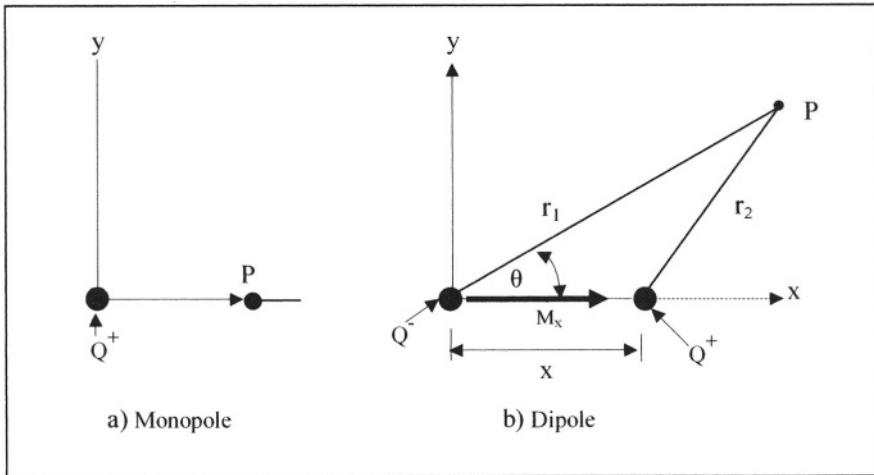


Figure 2.1 Schematic electrical poles in aqueous phase.

Consider an electrolyte or a metal as a single electrical conductor phase in equilibrium. In this case, current flow does not occur and the electric field at all points in the phase is zero. In fact, a non-infinitesimal current is an irreversible process since heat is generated by the current flowing in the phase [1]. At equilibrium, eq. (2.2b) gives $E_x = E_y = E_z = 0$, which means that the electric potential ϕ is constant in the bulk phase so that $\phi \neq 0$ and the current is $I = 0$.

This can be analyzed by using eq. (2.2a) since $\partial\phi/\partial x = 0$, but $\int \partial\phi = 0$ gives $\phi + C = 0$ where $C = \text{constant}$; therefore, $\phi \neq 0$, which implies that it is a net electrical charge being uniformly distributed over the surface of the phase; otherwise, the repulsive force of like charges will not allow diffusion (motion) of charges to the phase surface [1].

DIPOLE: Consider the charge couple shown in Figure 2.1b, in which the negative and positive charges are separated by a distance $x \ll r_i$, making an electrical dipole for which the electrical dipole moment has a magnitude of $M_x = xQ$. Suppose that the charged particles and the point P in space make **1) a right triangle Q^-PQ^+** . Thus, an extension of the single charge case described by eq. (2.3) can provide the internal electric potential ϕ . Using eq. (2.3) along with $M_x = xQ$ yields

$$\phi = \int_0^r E_x dx = \int_0^r E \cos \theta dx = \int_0^r \frac{\lambda Q \cos \theta}{r^2} dx \quad (2.4)$$

$$\phi = \frac{\lambda M_x \cos \theta}{r^2} \quad \text{for } r \gg x \quad (2.5)$$

2) If Q^-PQ^+ make an **oblique triangle**, then the electric potential is

$$\phi = \int_{r_2}^{r_1} E dr = \int_{r_2}^{r_1} \frac{\lambda Q}{r^2} dr = \lambda Q \left(\frac{1}{r_2} - \frac{1}{r_1} \right) \quad (a)$$

$$\phi = \lambda Q \left[\frac{r_1^2 - r_2^2}{r_1 r_2 (r_1 + r_2)} \right] \quad (b)$$

Using the law of cosines and assuming that $r_i \gg x$ yields

$$r_2 = r_1^2 + x^2 - 2xr_1 \cos \theta \quad (c)$$

$$r_2 \approx r_1^2 - 2xr_1 \cos \theta \quad \text{since } r_i \gg x \quad (d)$$

$$r_1^2 - r_2^2 \approx 2xr_1 \cos \theta \quad (e)$$

Substituting eq. (e) and $M_x = xQ$ into (b) gives

$$\phi \simeq \lambda M_x \left[\frac{2 \cos \theta}{r_2 (r_1 + r_2)} \right] \quad (f)$$

Now, letting $r \simeq r_1 \simeq r_2$ in eq. (f) the electric potential becomes [1]

$$\phi \simeq \frac{\lambda M_x \cos \theta}{r^2} \quad \text{for } r \gg x \quad (2.5)$$

The electric potential ϕ "singularity" is in the order of r^{-2} since $\phi \rightarrow \infty$ as $r \rightarrow 0$. Thus, the electric field strength according to eqs. (2.3) and (2.5) are, respectively

$$E_x = -\frac{\partial\phi}{\partial r} = \frac{\lambda Q}{r^2} \quad (\text{Monopole}) \quad (2.6a)$$

$$E_\theta = -\frac{\partial\phi}{\partial r} = \frac{2\lambda M_x \cos\theta}{r^3} \quad (\text{Dipole}) \quad (2.6b)$$

Notice that the E “singularity” is in the order of r^{-2} for the monopole and r^{-3} for the dipole cases. This brief introduction of the source of the electric field strength of a phase is for the reader to notice that a phase has been treated as an electrically neutral thermodynamic system, which is not the case for a heterogeneous electrochemical cell. In addition, this section serves the purpose of comparison with the proceeding electrochemical treatment.

Example 2.1 Let an electrolyte contain a net charge due to 10^{-11} moles of nickel cations (Ni^{+2}). Calculate the surface electric potential ϕ at a distance of 7 cm from the solid electrode-electrolyte interface in the x -direction. Will this calculated potential value differ from the electric potential difference ($\Delta\phi$) between electrodes? Explain.

Solution:

from eq. (2.1d),

$$Q = x_i(zF) = (10^{-11} \text{ mol}) (2)(96,500 \text{ C/mol}) = 1.93 \times 10^{-6} \text{ C}$$

But,

$$\lambda = 1/(4\pi\epsilon_0) = 9 \times 10^9 \frac{\text{Nm}^2}{\text{C}^2}$$

$$r = 0.05 \text{ m}$$

Thus, inserting these values into eq. (2.3) gives the electric potential

$$\phi = \lambda Q/r \simeq 0.25 \times 10^6 \text{ V} \quad \left(\frac{\text{Nm}}{\text{C}} = \frac{\text{Nm}}{\text{J/V}} = \frac{\text{JV}}{\text{J}} = \text{V} \right)$$

This large amount of volts does not represent a typical difference in electric potential between electrodes of a practical electrochemical system. Normally, a few volts are needed to operate a simple electrochemical system. Conclusively, $\phi \gg \Delta\phi$.

2.3 ELECTROCHEMICAL CELLS

First of all, corrosion is basically an electrochemical process that involves ionic interactions leading to metal dissolution or surface deterioration. Thus, the theory of corrosion requires thorough understanding of the electrochemical events

within a particular metal-electrolyte system for mitigating corrosion. This dictates that the driving force for electrochemical events must be known in order to classify the type of electrochemical cells to be characterized either to recover metals from solution (see Chapter 7) or prevent corrosion (Chapter 8).

In general, electrochemical cells have four basic components called

- The **electrolyte** is an electrical conductive fluid or moist soil.
- The **anode electrode** is a metal in contact with the electrolyte allowing anodic reactions to take place.
- The **cathode electrode** is a metal in contact with the electrolyte allowing reduction reactions to occur on the surface.
- The **power supply** which is connected to the anode and cathode electrodes, providing the potential to the electrochemical system for reduction reactions (electrolysis) or current through the anode to protect the cathode from corrosion.

Furthermore, an electrochemical system can be classified according to the schematic cells depicted in Figure 2.2. The electrochemical cells are described below.

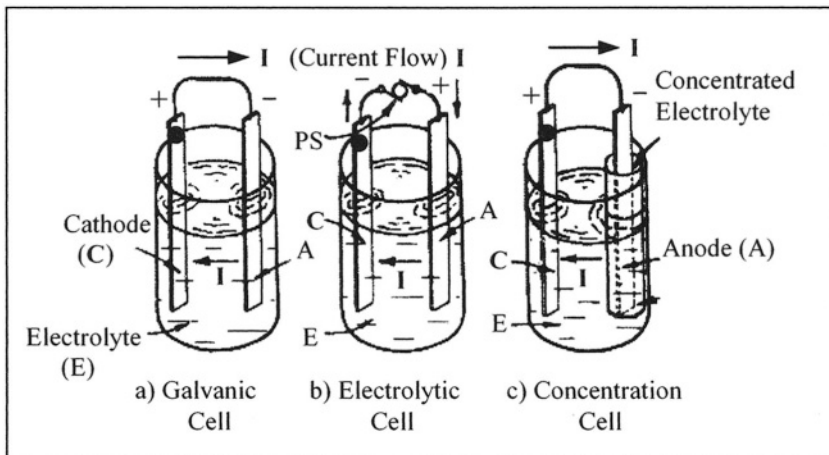


Figure 2.2 Type of electrochemical cells. PS = Power supply [20].

1) **Galvanic cell**, which is a bimetallic cell since it has different metallic electrodes, but current flows clockwise as indicated in Figure 2.2a by the arrows. This electrochemical event produces electric energy from the stored chemical energy in the metallic anode. Consequently, current flows from the cathode to the anode through the metallic circuit and electric power, $P = EI$, is

produced. Faraday's law of electrolysis is obeyed for forming electrochemical reaction reactions under the principles of electrochemical stoichiometry so that the redox reaction occurs spontaneously without the aid of an external power supply. The subject of electrolysis will be dealt with in Chapter 7.

2) **Electrolytic Cell**, in which current flows clockwise as shown in Figure 2.2b, but the source of power is external. The cell has bimetallic or mono-metallic electrodes. This cell consumes power, $P = EI$, and the cell reactions are driven in the reverse direction as opposed to galvanic ; that is, the galvanic spontaneous reactions are driven backwards. This is possible if the applied potential is greater than the galvanic potential. This type of cell is very useful in the electrometallurgy field for recovering metals from oxide ores by electroplating the metal ions on cathodes. Hence, if current flows, then the principles of electrochemical stoichiometry is used for producing electrochemical reactions through the process of electrolysis and metal ions are deposited on a cathode surface. Electrolysis stands for an electrochemical process in which the redox reaction is forced (non-spontaneous) to occur by passing a direct current (dc) through the electrolyte. Therefore, $E_{\text{electrolytic}} > E_{\text{galvanic}}$, but the measurable cell potential difference in an electrolytic or galvanic cell can be influence by the Ohm's potential ($E = IR$) drop. Table 2.1 lists comparison between galvanic and electrolytic cells.

Table 2.1 Comparison of electrochemical cells

Galvanic Cell	Electrolytic Cell
Produces Chemical Energy	Provides Electrical Energy
Chemical $\longrightarrow$ Electrical energy	Electrical $\longrightarrow$ Chemical energy
$\Delta G^\circ < 0$ and $E^\circ > 0$	$\Delta G^\circ > 0$ and $E^\circ < 0$
Spontaneous Redox Reaction	Forced Redox Reaction
Positive Cathode	Negative Cathode
Negative Anode	Positive Anode
Dry Batteries	Electroplating, Cathodic Protection

3) **Concentration Cell**, which has mono-metallic electrodes, but the anode is immersed in a concentrated region of the electrolyte as shown in Figure 2.2c. This cell has the electrodes made of the same metal and it is similar to a galvanic with respect to the electrode polarity and current flow direction. The electrodes are immersed in a nonhomogeneous electrolyte, but the anode is within the concentrated portion of the electrolyte where the concentration of species j is $C_j(\text{anode}) > C_j(\text{cathode})$.

Figure 2.3 shows two galvanic cells indicating metal dissolution at the anode (left electrode) and the direction of current flow. Figure 2.3a shows metals M_1 and M_2 as the anode and cathode, respectively. Both are immersed in their own sulfate-base electrolyte. Each $M_1 - M_1SO_4(aq)$ and $M_2 - M_2SO_4(aq)$

constitute what is known as anodic half-cell and cathodic half-cell, respectively. Subsequently, the electrochemical galvanic cell is composed of these two half-cells if current flows as shown in Figure 2.3a. On the other hand, Figure 2.3b shows a chemical galvanic cell due to the lack of current flow, but electron flow occurs from the anode to the cathode through the wires.

Recall that $M_1SO_4(aq)$ and $M_2SO_4(aq)$ are in their ionic state in solution (aqueous). Both metals are externally connected to an electrical circuit in order to measure the potential difference between them. In other words, the circuit is used to measure the galvanic cell potential by a voltmeter (V). This measurable cell potential is current/resistance dependent. If current ceases to flow, then the cell potential is known as the open-circuit potential or standard potential (E°), which are illustrated in Figure 2.2 for pure metal reduction. The standard potential is also known as the electromotive force (emf) under equilibrium conditions: unit activity, $25^\circ C$, and $1\ atm$ ($101\ kPa$) pressure.

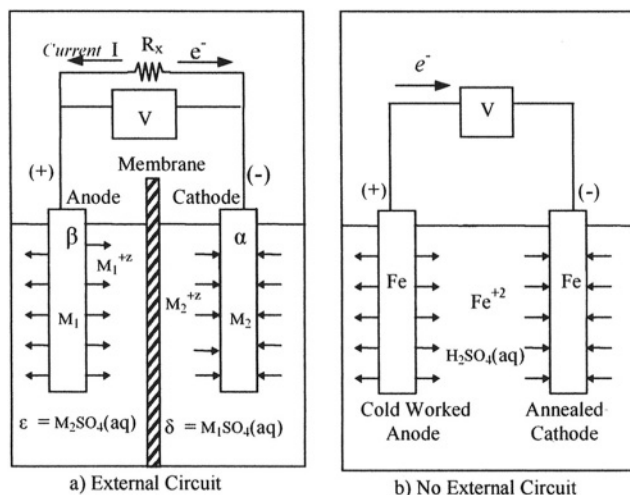


Figure 2.3 a) Electrochemical galvanic cell and b) Galvanic chemical cell.

Figure 2.3b, on the other hand, shows an iron (Fe) galvanic cell composed of a cold worked electrode (anode) and an annealed electrode (cathode). The former electrode becomes the anode due to a high microstructural defects, such as dislocation density, and internal (residual) stresses introduced during the cold working (plastic deformation) process. The latter electrode is stress relieved during annealing and the dislocation density is nearly zero or eliminated.

The assessment of Fe -base couplings to form galvanic cells can be elucidated using two cases. According to the galvanic series in Figure 2.2, Fe is located between copper (Cu) and zinc (Zn). Suppose that a steel plate is coated with Zn and another with Cu . Consequently, Fe is the anode for Cu and the cathode for Zn couplings. In the latter case, Zn becomes a sacrificial anode, which is the principle of coupling for galvanized steel sheets and pipes.

On the other hand, if Cu coating breaks down, steel is then exposed to an electrolyte and becomes the anode, and therefore, it oxidizes. These two cases are schematically shown in Figure 1.6. The cell potential of each coupling case is determined by adding the standard potentials, but the sign of $E_{Fe}^{\circ} = +0.44\text{ V}$ and $E_{Zn}^{\circ} = +0.763\text{ V}$ are reversed since they act as anodes. Recall that Figure 2.2 illustrates standard potentials for reduction reactions. Hence,

- a) $Fe - Cu$ coupling: $E_{cell}^{\circ} = E_{Fe}^{\circ} + E_{Cu}^{\circ} = +0.44\text{ V} + 0.337\text{ V} = 0.777\text{ V}$
 b) $Fe - Zn$ coupling: $E_{cell}^{\circ} = E_{Fe}^{\circ} + E_{Zn}^{\circ} = -0.44\text{ V} + 0.763\text{ V} = 0.323\text{ V}$

The above standard state (Table 2.2) conforms to the convention adopted by the International Union of Pure and Applied Chemistry (IUPAC), which requires that all tabulated electromotive force (emf) or standard electrode potential values (E°) be so with respect to the standard hydrogen electrode (SHE) for reduction reactions of pure metals, such as $M^{+z} + ze^{-} = M$. In addition, Table 2.3 illustrates standard potentials for some compounds.

Table 2.2 *Standard potential for metal reduction [5-6].*

	Reduction Reaction	$E^{\circ} (V_{SHE})$
Noble ↑	$Au^{+3} + 3e^{-} = Au$	+1.498
	$O_2 + 4H^{+} + 4e^{-} = 2H_2O$	+1.229
	$Pt^{+2} + 2e^{-} = Pt$	+1.200
	$Pd^{+2} + 2e^{-} = Pd$	+0.987
	$Ag^{+} + e^{-} = Ag$	+0.799
	$Cu^{+2} + 2e^{-} = Cu$	0.337
↓ Active	$Re^{+3} + 3e^{-} = Re$	0.300
	$2H^{+} + 2e^{-} = H_2$	0.000
	$Fe^{+3} + 3e^{-} = Fe$	-0.036
	$Pb^{+2} + 2e^{-} = Pb$	-0.126
	$Sn^{+2} + 2e^{-} = Sn$	-0.136
	$Ni^{+2} + 2e^{-} = Ni$	-0.250
	$Co^{+2} + 2e^{-} = Co$	-0.277
	$Cd^{+2} + 2e^{-} = Cd$	-0.403
	$Fe^{+2} + 2e^{-} = Fe$	-0.440
	$Cr^{+3} + 3e^{-} = Cr$	-0.744
	$Zn^{+2} + 2e^{-} = Zn$	-0.763
	$Ti^{+2} + 2e^{-} = Ti$	-1.630
	$Al^{+3} + 3e^{-} = Al$	-1.662
	$Mg^{+2} + 3e^{-} = Mg$	-2.363
	$Na^{+} + e^{-} = Na$	-2.714
	$K^{+} + e^{-} = K$	-2.925
	$Li^{+} + e^{-} = Li$	-3.045

Thus, *Cu* atoms coat the *Zn* rod or sediment to the bottom of the beaker. Eventually, this redox (overall) reaction produces chemical energy, which is dissipated as heat. This, then is a source of chemical energy that can be converted to useful work by adequately designing a device called electrochemical cell as schematically shown in Figure 2.3a and 2.4. In fact, this cell is assumed to contain charged species, but at least one electrically charged specie cannot penetrate all the phases of the system, and a difference in electric potential will be developed between phases.

Table 2.3 Standard potentials for compounds [6].

	Reduction Reaction	E° (V_{SHE})
Anodic ↑	$O_3 + 2H^+ + 2e^- = O_2 + H_2O$	+2.070
	$H_2O_2 + 2H^+ + 2e^- = 2H_2O$	+1.776
	$MnO_2 + 4H^+ + 4e^- = Mn^{+2} + 2H_2O$	+1.230
	$O_2 + 4H^+ + 4e^- = 2H_2O$	+1.229
	$AuCl_4^- + 3e^- = Au + 4Cl^-$	0.994
	$TiO_2 + 4H^+ + 4e^- = Ti + 2H_2O$	0.860
	$NiO_2 + 2H_2O + 2e^- = Ni(OH)_2 + 2(OH^-)$	0.760
	$Ag_2SO_4 + 2e^- = 2Ag + SO_4^{-2}$	0.653
	$AgNO_2 + e^- = Ag + NO_2^-$	0.590
	$O_2 + 2H_2O + 4e^- = 4(OH^-)$	0.401
	$Ag_2O + H_2O + 2e^- = 2Ag + 2(OH^-)$	0.342
	$AgCl + e^- = Ag + Cl^-$	0.222
	$Pt(OH)_2 + 2e^- = Pt + 2(OH^-)$	0.40
	$Pd(OH)_2 + 2e^- = Pd + 2(OH^-)$	0.100
	$2H^+ + 2e^- = H_2$	0.000
	$AgCN + e^- = Ag + CN^-$	-0.020
	$WO_2 + 4H^+ + 4e^- = W + 2H_2O$	-0.120
↓ Cathodic	$Cu(OH)_2 + 2e^- = Cu + 2(OH^-)$	-0.224
	$PbSO_4 + 2e^- = Pb + SO_4^{-2}$	-0.359
	$Ni(OH)_2 + 2e^- = Ni + 2(OH^-)$	-0.660
	$Co(OH)_2 + 2e^- = Co + 2(OH^-)$	-0.730
	$Fe(OH)_3 + 3e^- = Fe + 3(OH^-)$	-0.771
	$2H_2O + 2e^- = H_2 + 2(OH^-)$	-0.828
	$Fe(OH)_2 + 2e^- = Fe + 2(OH^-)$	-0.877
	$Mn(OH)_2 + 2e^- = Mn + 2(OH^-)$	-1.470

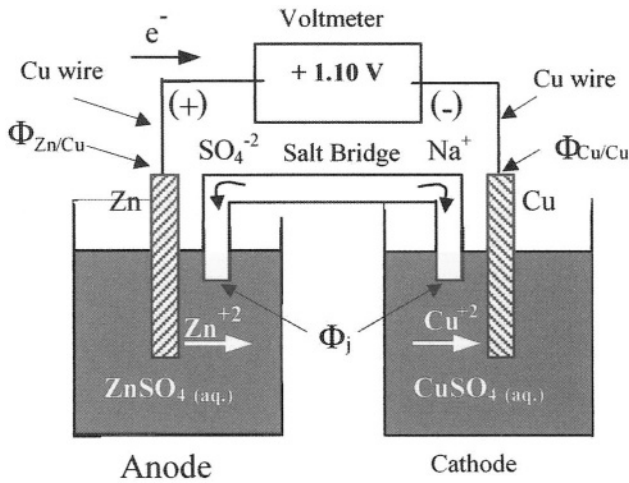


Figure 2.4 The Zn/Cu galvanic (voltaic) cell.

Furthermore, either Figure 2.3a or 2.4 can be used as the point of departure for developing the thermodynamics of electrochemical systems, which is referred to as electrochemical cells containing phases that are electrical conductors, which are known as electrolytes. Thus, electrolytes are needed for the proper development of a potential difference. In a conventional electrochemical cell set up, the cathode is the most positive electrode kept on the right hand side and the anode is the most negative electrode [2]. Thus, electron flow occurs from left to right through the terminals in the above Figures 2.3 and 2.4, which are schematic representations of galvanic cells or voltaic cells.

In general, an electrochemical cell can be used to drive or be driven by an external electrical system or device, such as an incandescent light or motor-generator, respectively. A motor-generator can drive or be driven by an electrochemical cell, depending on the cell potential or on the applied potential, respectively.

With regard to Figure 2.4, $\Phi_{\text{Zn/Cu}}$ and $\Phi_{\text{Cu/Cu}}$ are contact potentials and Φ_j is the liquid junction potential. The measurable standard cell potential for Figure 2.4 is a measure of interfacial potentials

$$E_{\text{cell}}^{\circ} = (E_{\text{Zn}}^{\circ} + E_{\text{Cu}}^{\circ}) + [\Phi_{\text{Zn/Cu}} + \Phi_{\text{Cu/Cu}} + \Phi_j] \quad (2.7a)$$

In real cases, nonstandard conditions exist and the cell potential can be predicted by

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} + [E_{\text{Nernst}} - E_{\text{Ohmic}} - \eta] \quad (2.7b)$$

where E_{Nernst} , E_{Ohmic} and η are potential terms for correcting the standard potential expression, eq. (2.7a). These terms will be dealt with in a later section.

The system shown in Figure 2.4 is a galvanic cell known as a voltaic cell, which consists of two different solids called anodic **Zn** electrode and cathodic **Cu** electrode. In summary, this electrochemical coupling has several events which can be described as follows:

1) Zinc (**Zn**) is immersed in aqueous zinc sulfate [**ZnSO₄(aq)**] so that **Zn** – **ZnSO₄(aq)** becomes the anodic half-cell. Similarly, copper in copper sulfate, **Cu** – **CuSO₄(aq)**, is the cathodic half –cell.

2) **Zn** – **Cu** cell $\equiv$ **Zn** – **ZnSO₄(aq)** half cell + **Cu** – **CuSO₄(aq)** half cell.

3) **ZnSO₄(aq)** and **CuSO₄(aq)** are solutions known as electrolytes, which are phases like **Zn** and **Cu** electrodes and are electrical conductors as well.

4) **Cu** wire is used to connect the **Zn** and **Cu** electrodes so that no potential difference develops between the wires, which are called terminals.

5) The salt bridge or porous membrane is used to connect both electrolytes and allow the migration of ions to maintain electrical neutrality of the cell.

6) If a salt bridge is not used, both half-cells become isolated and electrical neutrality is lost since the **Zn** electrode becomes more positive as **Zn⁺²** cations are produced and the **Cu** electrode becomes more negative as **Cu⁺²** are removed from solution and deposited as **Cu** atoms on the electrode surface. Thus, the **Zn⁺²** cations (positively charged particle) and sulfate **SO₄⁻²** anions (negatively charged) migrate through the salt bridge in the opposite direction.

7) The terminals are connected to a voltmeter to complete the well-known electrochemical galvanic cell circuit.

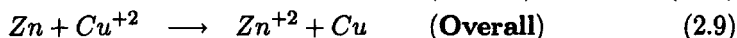
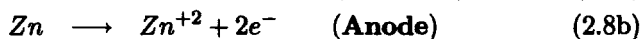
8) The galvanic cell (like a battery) converts chemical energy to electrical energy due to electron flow from the anode to the cathode through the terminals.

9) The voltmeter is used to measure the potential difference between the **Zn** and **Cu** electrodes at equilibrium.

2.3.1 OPEN-CIRCUIT CONDITION

This is the case when the voltmeter is removed leaving an open-circuit. A summary of events are outlined below for Figure 2.4.

1) Due to instability of the galvanic cell, **Cu⁺²** cations diffuse into the **ZnSO₄(aq)** solution through the salt bridge. Diffusion is slow, but **Cu⁺²** ions will come in contact with the **Zn** electrode. Consequently, the zinc anode oxidizes and the copper cations reduce to form atoms as shown below. The redox reaction results by adding both the anodic and cathodic reactions



2) A spontaneous redox reaction occurs without electron flow. Eventually, the **Zn** electrode will go into solution or simply dissolves.

3) The redox reaction indicates that **Zn** oxidizes in **ZnSO₄(aq)** solution and **Cu** reduces in **CuSO₄(aq)** solution. Eventually, the cell would be destroyed.

4) In order to avoid destruction of the cell, just connect a resistor like a voltmeter to the terminals. This will keep **Cu⁺²** cations away from the **ZnSO₄(aq)** solution due to the electric field force in the **CuSO₄(aq)** solution.

2.3.2 CLOSED-CIRCUIT CONDITION

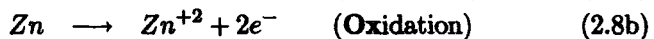
This is the case when a voltmeter (resistor) is connected to the galvanic cell for operation purposes, so that the potential difference between the **Zn** and **Cu** electrodes is measured as $E_{cell}^{\circ} = +1.10 \text{ V}$. What happens when the cell is operating, say, at standard condition ($P = 1 \text{ atm.}$, $T = 25^{\circ}\text{C}$, 1 mol/liter)?

1) The **Cu** – **Zn** junction potential $\Phi_{Zn/Cu}$ is lower than the **Cu** – **Cu** junction $\Phi_{Cu/Cu}$. Since $\Phi_{Zn/Cu} < \Phi_{Cu/Cu}$ electrons will flow from the lowest electric potential reservoir (anodic half-cell) to the highest reservoir (cathodic half-cell) through the external wires or terminals.

2) The electrical work is $W = Q\Delta\phi = QE_{cell} > 0$ for electron flow to occur as negative charges. Here, $\Delta\phi$ is the cell potential difference.

3) If $W > 0$, then positive charges flow from low to high potential reservoirs (from **Cu** to **Zn** electrodes).

4) Consequently, the following reactions occur



The electrons (e^{-}) arriving at the **CuSO₄(aq)** electrolyte combine with **Cu⁺²** cations in solution and deposit as **Cu** atoms on the **Cu** electrode surface. This **Cu** deposition is called electroplating.

5) An electric potential difference is developed since **CuSO₄(aq)** electrolyte becomes depleted of **Cu⁺²** cations and **ZnSO₄(aq)** electrolyte becomes enriched with **Zn⁺²** cations.

6) Once $\Delta\phi = E_{cell}$ is developed, positive ions flow through the solution from **Zn** to **Cu** electrodes, provided that the half-cells are separated by a porous membrane or salt bridge (Figure 2.3). According to Ohm's Law, the change in inner potential is $\Delta\phi = IR$.

7) The salt bridge is filled with an agar gel (polysaccharide agar or polymer gel) and concentrated aqueous salt (**NaCl** or **KCl**) solution in order to maintain electrical neutrality between the half cells (Figure 2.3). The gel allows diffusion of ions, but eliminates convective currents [1].

8) The maximum potential difference and the corresponding cell diagram (Figure 2.5) for Figure 2.4 are given below

$$E_{cell} = (E_{Zn}^{\circ} + E_{Cu}^{\circ}) + [\Phi_{Zn/Cu} + \Phi_{Cu/Cu} + \Phi_j] \quad (2.7a)$$

$$E_{cell} \simeq E_{Zn}^{\circ} + E_{Cu}^{\circ} \simeq 1.10 \text{ V}_{SHE} \quad (2.7b)$$

since $[\Phi_{Zn/Cu} + \Phi_{Cu/Cu} + \Phi_j] \approx 0$.

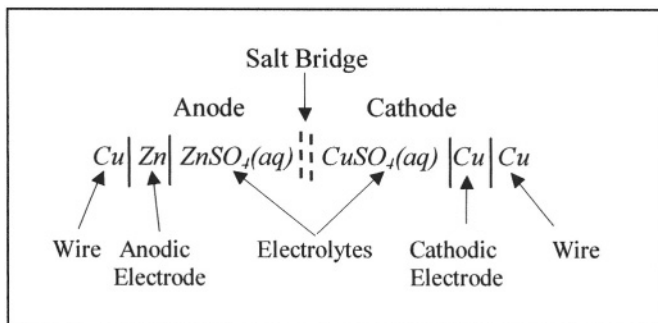


Figure 2.5 Galvanic cell diagram for Figure 2.4.

Vertical lines represent phase boundaries. A salt bridge is symbolized by two vertical lines and has two liquid junctions of insignificant potentials.

Now that an electrochemical galvanic cell has been described in details, it is convenient at this moment to expand the thermodynamic of electrochemistry in terms of chemical energy, which in turn, will be converted to electrical energy. The subsequent analytical procedure leads to the derivation of the Nernst equation, which is suitable for determining the cell electric potential when ion activities are less than unity as nonstandard conditions.

2.3.3 APPLICATION OF GALVANIC CELLS

The $Zn - Cu$ electrochemical galvanic cell being described so far (Figure 2.3) is a chemical energy source capable of producing 1.10 volts, which is a relatively low energy output. This energy source capacity can be enhanced by connecting several cells in series. A common application of galvanic cells is in the production of batteries for flashlights, radios, automobiles and so on. For instance, the production of lead-sulfuric acid ($Pb - H_2SO_4$) automobile batteries include lead anodes and lead oxide cathodes immersed in sulfuric acid solution. A brief description of these type of batteries is included in Chapter 1, section 1.4. Furthermore, a single $Pb - H_2SO_4$ galvanic cell produces 2 volts, but six (6) cells coupled in series produce 12 volts. If the cell is coupled in parallel, the total potential is 2 volts, but the total current is 6 times that of a single cell. The lifetime of these $Pb - H_2SO_4$ automobile batteries can be prolonged by supplying an external current provided by an alternator. In this case, the oxidation

and reduction reactions are reversed and the battery is maintained charged for some time. Table 2.4 lists alloy galvanic series.

Table 2.4 Galvanic series of metal and alloys in sea water [7].

Noble ↑ ↓ Active	Zinc (Zn)
	Low carbon steels
	Alloy steels
	Cast iron
	Stainless steels
	α -brass
	Aluminum brass
	Red brass
	Copper (Cu)
	Aluminum bronze
	<i>Cu – Ni</i> alloys
	Nickel (Ni)
	Inconel
	Monel
	Hastelloy C
	Titanium

2.4 THERMODYNAMICS

Using Figure 2.3a as the basic cell, the thermodynamics involved is treated below in a general case. Remove the salt bridge and treat each cell as isolated systems. Let metal *M* rod be the α phase being immersed in an aqueous solution (electrolyte), which is the ϵ phase (MSO_4). Let z^+ and z^- be the valence of the cations (M^{+z}) and the anions ($X^{-z} = SO_4^{-2}$). Let ϕ^α be the electric potential of the metallic α phase and ϕ^ϵ the electric potential of the ϵ phase. Once the α phase is in contact with the ϵ phase, an exchange of charged particles between α and ϵ phases causes a change in the total energy of the system, which consists of the negatively charged α phase as electrons are discharged into the electrolyte. The altered total energy is due to the change in electrostatic potential energy of the phases involved, specifically at the metal-electrolyte interface where a strong electric field exists and a double layer of charged particles disturbs the charge on the interface. This double layer is a normal balance (equal number) of positive and negative ions, which diffuse to the interface causing such as disturbance in energy [4]. Eventually, the system will reach the state of equilibrium within the electrolyte.

The entropy change (dS), the electrical energy change (dE), and the change of charge (dq) for a α - ϵ coupling, in which α is the metallic phase and ϵ is the electrolyte phase are, respectively

$$dS = dS^\alpha + dS^\epsilon \quad (2.10)$$

$$T^\alpha dS^\alpha = dU^\alpha + P^\alpha dV^\alpha - [(\mu^\alpha d\eta^\alpha)_M + (\mu^\alpha d\eta^\alpha)_e] \quad (2.11)$$

$$T^\epsilon dS^\epsilon = dU^\epsilon + P^\epsilon dV^\epsilon - (\mu^\epsilon d\eta^\epsilon)_{M+z} \quad (2.12)$$

$$dE = dU^\alpha + dU^\epsilon + \phi^\alpha dq^\alpha + \phi^\epsilon dq^\epsilon \quad (2.13)$$

$$dq = dq^\alpha + dq^\epsilon = z_e F (d\eta^\alpha)_e + z F (d\eta^\epsilon)_{M+z} \quad (2.14)$$

where μ = Chemical potential

P = Pressure

U = Internal energy

V = Volume

S = Entropy

T = Temperature

q_e = Electron charge

η = Number of moles

ϕ = Electric potential

F = Faraday's constant

For an isolated $\alpha - \epsilon$ thermodynamic system, the following constraints can be used to develop equilibrium conditions and the Gibbs free energy change (ΔG) [3]

$$(d\eta^\alpha)_{M+z} = -(d\eta^\alpha)_M \quad (a)$$

$$dV^\epsilon = -dV^\alpha \quad (b)$$

$$dV = 0 \quad (c)$$

$$dE = 0 \quad (d)$$

$$dq = 0 \quad (e)$$

Hence, combining eq. (e) and (2.14) and the resultant expression with eq. (a) yields

$$(d\eta^\alpha)_e = +(d\eta^\epsilon)_e \quad \text{since } z_e = -1 \quad (f)$$

$$(d\eta^\alpha)_e = -z (d\eta^\alpha)_M \quad \text{since } z \geq 1 \quad (g)$$

The physical interpretation of these constraints, eqs. (f) and (g), and eq. (2.14) implies that adding $(d\eta^\alpha)_e$ and $(d\eta^\epsilon)_{M+z}$ moles to the α phase and the ϵ phase, respectively, the change in electron charges becomes [3]

$$dq^\alpha = -F (d\eta^\alpha)_e \quad (h)$$

$$dq^\epsilon = +zF (d\eta^\epsilon)_{M+z} \quad (i)$$

Substituting eqs. (a) and (f) into (2.14) and (2.14) into (2.13) yields

$$dU^\alpha + dU^\epsilon + zF (\phi^\alpha - \phi^\epsilon) (d\eta^\alpha)_M = 0 \quad (j)$$

$$dU^\epsilon = -[dU^\alpha + zF(\phi^\alpha - \phi^\epsilon)(d\eta^\alpha)_M] \quad (k)$$

Substituting eqs.(a) through (k) into (2.11) and (2.12) and the resultant expressions into (2.10), and subsequently, collecting terms yields the entropy change of the $\alpha - \epsilon$ system

$$\begin{aligned} dS = & \left[\frac{1}{T^\alpha} - \frac{1}{T^\epsilon} \right] dU^\alpha + \left[\frac{P^\alpha}{T^\alpha} - \frac{P^\epsilon}{T^\epsilon} \right] dV^\alpha \\ & + \left[-\frac{(\mu^\alpha)_M}{T^\alpha} + \frac{z(\mu^\alpha)_e}{T^\alpha} - \frac{(\mu^\epsilon)_{M+z}}{T^\epsilon} + \frac{(zF)(\phi^\epsilon - \phi^\alpha)}{T^\epsilon} \right] (d\eta^\alpha)_M \end{aligned} \quad (2.15)$$

At equilibrium, $dS = 0$ and the following is deduced from eq. (2.15) [3]

1) For thermal equilibrium,

$$\left[\frac{1}{T^\alpha} - \frac{1}{T^\epsilon} \right] = 0 \text{ since } T^\alpha = T^\epsilon \quad (2.16)$$

2) For mechanical equilibrium,

$$\left[\frac{P^\alpha}{T^\alpha} - \frac{P^\epsilon}{T^\epsilon} \right] = 0 \text{ since } P^\alpha = P^\epsilon \quad (2.17)$$

3) For electrochemical equilibrium, $T^\alpha = T^\epsilon$ and

$$(\mu^\alpha)_M - [z(\mu^\alpha)_e - (\mu^\epsilon)_{M+z}] + zF(\phi^\alpha - \phi^\epsilon) = 0 \quad (2.18)$$

$$(\mu^\alpha)_M - [z(\mu^\alpha)_e - (\mu^\epsilon)_{M+z}] = -zF(\phi^\alpha - \phi^\epsilon) \quad (2.19)$$

$$\Delta G^\alpha = (\mu^\alpha)_M - [z(\mu^\alpha)_e - (\mu^\epsilon)_{M+z}] \quad (2.20a)$$

$$\Delta G^\alpha = -zF(\phi^\alpha - \phi^\epsilon) \quad (2.20b)$$

Thus, $(\mu^\alpha)_M - [z(\mu^\alpha)_e - (\mu^\epsilon)_{M+z}]$ is the affinity for $M^\alpha = (M^{+z})^\epsilon + (ze^-)^\epsilon$ and ΔG^α is the Gibbs free energy change for the $\alpha - \epsilon$ system.

In addition, the potential difference $(\phi^\alpha - \phi^\epsilon)$ between two phases in a half-cell at equilibrium cannot be measured. Instead, two electrodes are connected as shown in Figure 2.3a to measure the electric potential difference between the electrodes. This can be done by connecting, say, $\beta - \delta$ system to the previous $\alpha - \epsilon$ system using a salt bridge or porous membrane. Thus, the electric potential difference between the β and α electrodes is $E = (\phi^\alpha - \phi^\beta)$. Recall that the salt bridge is a glass tube filled with an electrolyte that allows charge transfer between the cell electrolytes without disturbing the equilibrium state.

Apply the generalized expression given by eq. (2.19) to the galvanic cell shown in Figure 2.3a. Thus, the anodic and cathodic reactions and their respective energy change expressions are, respectively

$$M_1^\alpha = (M_1^{+z_1})^\epsilon + (z_1 e^-)^\alpha \quad (\text{Anode}) \quad (2.21)$$

$$(M_2^{+z_2})^\delta + (z_2 e^-)^\beta = M_2^\beta \quad (\text{Cathode}) \quad (2.22)$$

$$\Delta G^\alpha = -z_1 F (\phi^\alpha - \phi^\epsilon) \quad (\text{Anode}) \quad (a)$$

$$\Delta G^\beta = -z_2 F (\phi^\delta - \phi^\beta) \quad (\text{Cathode}) \quad (b)$$

In order to balance the number of electrons in eqs. (2.21) and (2.22), multiply eq. (2.21), as well as eq. (a), by z_2/z_1 and add them up to get the redox reaction and its energy change as

$$\frac{z_2}{z_1} M_1^\alpha + (M_2^{+z_2})^\delta = \frac{z_2}{z_1} (M_1^{+z_1})^\epsilon + M_2^\beta \quad (2.23)$$

$$\Delta G = \frac{z_2}{z_1} \Delta G^\alpha + \Delta G^\beta \quad (a)$$

$$\Delta G = -z_2 F (\phi^\alpha - \phi^\beta) \quad (b)$$

$$\Delta G = -z_2 F E \quad (2.24)$$

where $(z_1 e^-)^\alpha = (z_2 e^-)^\beta$, $(\mu^\beta)_e = (\mu^\alpha)_e$, $\phi^\epsilon = \phi^\delta$ and $E = (\phi^\alpha - \phi^\beta)$.

In general, the equilibrium and no-equilibrium energy change expressions are, respectively

$$\Delta G^o = -z F E^o \quad (2.25)$$

$$\Delta G = -z F E \quad (2.26)$$

Using the argument for deriving eq. (2.19), the standard Gibbs free energy change can be defined in a general form as

$$\Delta G = \sum \nu_i \mu_i = \left(\sum \nu_i \mu_i \right)_{\text{product}} - \left(\sum \nu_i \mu_i \right)_{\text{reactants}} \quad (2.27)$$

where ν_i = Number of ions or molecules in an reaction

i = Specie involved in the reaction

Combining eqs. (2.26) and (2.27) yields the standard electric potential in terms of standard chemical potential

$$E = -\frac{\sum \nu_i \mu_i}{z F} \quad (2.28)$$

Table 2.5 illustrates standard chemical potentials for some metals, ions, and molecules. A more complete data can be found in Pourbaix work [18-19]. Applying eq. (2.28) to the redox reaction given eq. (2.23) yields

$$E = -\frac{1}{z_2 F} \left\{ \left[\frac{z_2}{z_1} (\mu_{M_1^{+z_1}})^\epsilon + (\mu_{M_2})^\beta \right] - \left[\frac{z_2}{z_1} (\mu_{M_1})^\alpha + (\mu_{M_2^{+z_2}})^\delta \right] \right\} \quad (2.28a)$$

Table 2.5 Standard chemical potentials [18].

Name	μ° (kJ/mol)	Name	μ° (kJ/mol)
Al	0	Cu	0
Al ₂ O ₃	-1576.41	CuO	-127.19
Al(OH) ₃	-1137.63	Cu(OH) ₂	-356.90
Al ⁺³	-481.16	CuSO ₄	-661.91
AlO ₂ ⁻	-839.77	Cu ⁺²	+64.98
Cr	0	Fe	0
Cr(OH) ₂	-587.85	Fe(OH) ₂	-483.54
Cr(OH) ₃	-900.82	Fe(OH) ₃	-694.54
Cr ⁺³	-215.48	FeSO ₄	-829.69
CrO ₂ ⁻	-835.93	Fe ⁺²	-84.94
H ₂ (g)	0	Fe ⁺³	-10.59
H ⁺	0	Zn	0
OH ⁻	-157.30	Zn(OH) ₂	-559.09
H ₂ O	-237.19	Zn ⁺²	-147.21

Example 2.2 Let's apply the above generalized procedure to the galvanic cell shown in Figure 2.4. Assume that the cell is in equilibrium and that the cell phases are $M_1^\alpha = \text{Zn}^\alpha$ with $z_1 = +2$, $\epsilon = \text{ZnSO}_4(\text{aq})$, $M_2^\beta = \text{Cu}^\beta$ with $z_2 = +2$, and $\delta = \text{CuSO}_4(\text{aq})$. Will the redox reaction occur?

Solution:

Using eqs. (2.23) and (2.24) along with $E^\circ = E_{\text{Zn}}^\circ + E_{\text{Cu}}^\circ = 0.763 \text{ V} + 0.337 \text{ V} = 1.10 \text{ V}$ (Figure 2.4) and $z_1 = z_2 = z = 2$ yields

$$\begin{aligned} \text{Zn}^\alpha + (\text{Cu}^{+2})^\delta &= (\text{Zn}^{+2})^\epsilon + \text{Cu}^\beta \\ \Delta G^\circ &= -zFE^\circ = (2)(96.50 \text{ kJ/mol V})(1.10 \text{ V}) \\ \Delta G^\circ &= -212.30 \text{ kJ/mol} \end{aligned}$$

Therefore, the redox reaction occurs spontaneously as written since $\Delta G^\circ < 0$.

Example 2.3 Let the anodic phases be $M_1^\alpha = \text{Cr}^\alpha$ with $z_1 = +3$ and $\epsilon = \text{CrSO}_4(\text{aq})$, whereas the cathodic phases are $M_2^\beta = \text{Cu}^{+2}$ with $z_2 = +2$,

and $\delta = \text{CuSO}_4(\text{aq})$. a) Determine the redox reaction using eq. (2.23) and b) calculate the Gibbs free energy change. Will the redox reaction occur?

Solution:

a) From, eq. (2.23),

$$\begin{aligned}\frac{2}{3}\text{Cr}^\beta + (\text{Cu}^{+2})^\epsilon &= \frac{2}{3}(\text{Cr}^{+3})^\delta + \text{Cu}^\alpha \\ \text{Cr}^\beta + \frac{3}{2}(\text{Cu}^{+2})^\epsilon &= (\text{Cr}^{+3})^\delta + \frac{3}{2}\text{Cu}^\alpha \\ 2\text{Cr}^\beta + 3(\text{Cu}^{+2})^\epsilon &= 2(\text{Cr}^{+3})^\delta + 3\text{Cu}^\alpha\end{aligned}$$

b) According to Figure 2.3a, the cell potential is

$$E^\circ = E^\circ_{\text{Cr}/\text{Cr}^{+2}} + E^\circ_{\text{Cu}^{+2}/\text{Cu}} = 0.774 \text{ V} + 0.337 \text{ V} = 1.08 \text{ V}$$

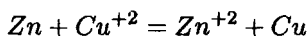
and from eq. (2.24), the standard free energy change is

$$\begin{aligned}\Delta G^\circ &= -z_2 F E^\circ = (2)(96.50 \text{ kJ/mol V})(1.08 \text{ V}) \\ \Delta G^\circ &= -208.44 \text{ kJ/mol}\end{aligned}$$

Therefore, the redox reaction occurs spontaneously as written since $\Delta G^\circ < 0$.

Example 2.4 Use the data given in Table 2.5 to determine the half-cells and the redox standard potentials for the galvanic cell shown in Figure 2.4. Compare the results with the data given in Table 2.2.

Solution:



From eq. (2.28) and Table 2.5,

$$\begin{aligned}E^\circ_{\text{Cu}^{+2}/\text{Cu}} &= -\frac{(\nu\mu^\circ)_{\text{Cu}} - (\nu\mu^\circ)_{\text{Cu}^{+2}}}{zF} \\ E^\circ_{\text{Cu}^{+2}/\text{Cu}} &= -\left[\frac{(1)(0) - (1)(+64.98 \text{ kJ/mol})}{(2)(96.50 \text{ kJ/mol} \cdot \text{V})}\right] = +0.337 \text{ V} \\ E^\circ_{\text{Zn}/\text{Zn}^{+2}} &= -\frac{(\nu\mu^\circ)_{\text{Zn}^{+2}} - (\nu\mu^\circ)_{\text{Zn}}}{zF} \\ E^\circ_{\text{Zn}/\text{Zn}^{+2}} &= -\left[\frac{(1)(-147.21 \text{ kJ/mol}) - (1)(0)}{(2)(96.50 \text{ kJ/mol} \cdot \text{V})}\right] = +0.763 \text{ V}\end{aligned}$$

These results are exactly the same as given in Table 2.2. Thus, eq. (2.7b) yields the standard cell potential

$$E^{\circ} = E_{\text{Cu}^{+2}/\text{Cu}}^{\circ} + E_{\text{Zn}/\text{Zn}^{+2}}^{\circ} = +1.10 \text{ V}$$

In addition, the activity a_j of a specie j for a redox reaction can be determined by considering the change in free energy

$$dG = -SdT + V_j dP \quad (2.29)$$

For an isothermal ($T = \text{constant}$) and isometric ($V_j = \text{constant}$) system, eq. (2.29) yields

$$\int_{\Delta G_j^{\circ}}^{\Delta G_j} dG = V_j \int_{P_o}^P dP \quad (\text{a})$$

$$G_j - G_j^{\circ} = V_j (P - P_o) \quad (\text{b})$$

or

$$\exp \left[\frac{\Delta G_j - \Delta G_j^{\circ}}{RT} \right] = \exp \left[\frac{V_j (P - P_o)}{RT} \right] \quad (\text{c})$$

where $P = \text{Pressure}$

$P_o = \text{Standard pressure} = 1 \text{ atm,}$

$R = 8.314510 \text{ J mol}^{-1} \text{ K}^{-1}$ (Universal gas constant)

$T = \text{Absolute temperature } (^{\circ}\text{K})$

Thus, the activity $a_j = [j]$ is defined as

$$a_j = \exp \left[\frac{G_j - G_j^{\circ}}{RT} \right] = \exp \left[\frac{V_j (P - P_o)}{RT} \right] \quad (2.29a)$$

At standard conditions, $T = 25^{\circ}\text{C}$, $P = P_o = 1 \text{ atm}$ and $a_j = 1 \text{ mol/l}$. Table 2.6 illustrates some important definitions, which are needed to solve electrochemical problems.

Table 2.6 Some useful definitions for solving electrochemical problems.

$a_i = [j] = \gamma_j x_j$ (Henry's law) $C_j = a_j A_{w,j}$ $a_j = \text{Activity (mol/l)}$ $a_j = 1 \text{ mol/l}$ for solids and molecules $C_j = \text{Concentration (g/l)}$ $V_j = \text{Molar volume (l)}$ $P_j = \text{Pressure (MPa)}$	$a_j = P_j/P_o$ $\gamma_j = \text{Activity coefficient}$ $A_w = \text{Atomic weight (g/mol)}$ $X_j = \text{Mole fraction}$ $P_o = 1 \text{ atm} = 101 \text{ kPa}$
Dissociation of water: $H_2O = H^+ + OH^-$ $K_w = [H^+][OH^-] = 10^{-14}$ $pH = -\log[H^+]$ $pH = 14 + \log[OH^-]$	

Now, the equilibrium constant K for eq. (2.23) can be defined in terms of activities as follows:

$$K = \frac{\sum a_{\text{Product}}}{\sum a_{\text{Reactants}}} = \frac{\sum [\text{Product}]}{\sum [\text{Reactants}]} \quad (2.30a)$$

$$K = \frac{[(M_1^{+z_1})^\epsilon]^{z_2/z_1} \cdot [M_2^\beta]}{[M_1^\alpha]^{z_2/z_1} \cdot [(M_2^{+z_2})^\delta]} \quad (2.30b)$$

Using eqs. (2.29a) and (2.30a) for a redox reaction yields

$$K = \exp\left(\frac{\Delta G - \Delta G^\circ}{RT}\right) \quad (2.30c)$$

Solving eq. (2.30c) for the no-equilibrium energy change ΔG gives

$$\Delta G = \Delta G^\circ + RT \ln(K) \quad (2.31a)$$

At standard conditions, $\Delta G = 0$ and eq. (2.31a) becomes

$$\Delta G^\circ = -RT \ln(K) \quad (2.31b)$$

Thus, the equilibrium constant K can be determined from measurements of the electric potential (E°) or chemical potential (μ°).

Substituting eqs. (2.25) and (2.26) into (2.31a) yields the **Nernst Equation** for calculating the nonequilibrium electric potential (E) of an electrochemical cell. Hence,

$$E = E^\circ - \frac{RT}{zF} \ln(K) \quad (2.32)$$

The interpretation of the Nernst equation suggests that the current resulting from the change of oxidation state of the metals M_1 and M_2^{+z} is known

as **Faradaic current**, which is a measure of the rate of redox reaction. The term zF in eq. (2.32) stands for the number of coulombs needed for reacting 1 mol of an electroactive specie. Therefore, eq. (2.32) embodies the Faraday's law of electrolysis since the redox reaction involves electron transfer between phases having different electric potential. For instance, electrochemical equilibrium is achieved if current flow ceases in a reversible galvanic cell (Figure 2.3). Despite that the Nernst equation is derived assuming thermodynamic equilibrium of a reversible cell, K in eq. (2.32) is not exactly the same as the chemical equilibrium constant due to a current flow. The Nernst equation gives the open-circuit potential difference (emf) for a reversible galvanic cell and excludes liquid junction potentials [see eq. (2.7a)], which are always present, but small in magnitude. For example, the liquid junction potential difference for the cell in Figure 2.4 is $\phi_j = \phi_{CuSO_4(aq)} - \phi_{ZnSO_4(aq)} \approx 0$, but it is not completely eliminated after a salt bridge is connected.

From a macroscale, the Nernst equation is graphically depicted in Figure 2.6, which elucidates a simple calculus plot. The intercept is just the standard potential (E°) at $25^\circ C$ and the slope, $b = -RT/zF$, is the energy/charge ratio.

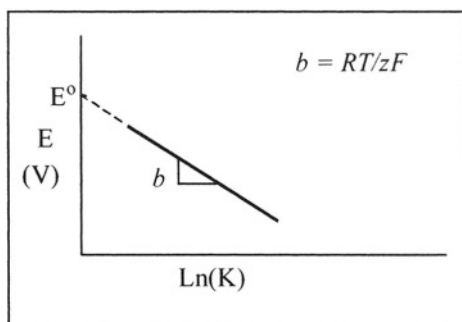


Figure 2.6 Nernst plot.

Example 2.5 Apply the preceding procedure to the galvanic cell shown in Figure 2.4 or to the cell diagram in Figure 2.5 at a temperature of $25^\circ C$ for determining a simplified expression for the equilibrium constant K and the Nernst cell potential E .

Solution:

From eq. (2.30b),

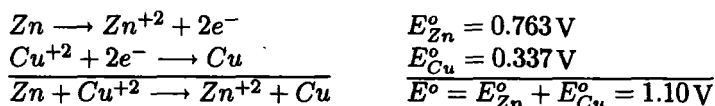
$$K = \frac{[Cu][Zn^{+2}]}{[Cu^{+2}][Zn]} = \frac{[Zn^{+2}]}{[Cu^{+2}]}$$

since $[Cu] = [Zn] = a$ (solids) = a (molecules) = 1 mol/liter. Thus, the cell potential defined by eq. (2.32) along with $z_1 = z_2 = z = 2$ and $E = E^\circ = 1.10 V$ (Figure 2.4) becomes

$$\begin{aligned}
 E &= E^\circ - \frac{RT}{zF} \ln \frac{[Zn^{+2}]}{[Cu^{+2}]} \\
 E &= E^\circ - \frac{2.303RT}{zF} \log \frac{[Zn^{+2}]}{[Cu^{+2}]} \\
 E &= 1.10 \text{ V} - (0.0296 \text{ V}) \log \frac{[Zn^{+2}]}{[Cu^{+2}]}
 \end{aligned}$$

Example 2.6 Derive the Nernst equation, eq. (2.32), using the anodic and cathodic reactions for Figure 2.4.

Solution:



Then,

$$E = E_{Zn} + E_{Cu} \quad (\text{a})$$

$$E = \left[E^\circ_{Zn} - \frac{RT}{zF} \ln \frac{[Zn^{+2}]}{[Zn]} \right] + \left[E^\circ_{Cu} - \frac{RT}{zF} \ln \frac{[Cu]}{[Cu^{+2}]} \right] \quad (\text{b})$$

$$E = (E^\circ_{Zn} + E^\circ_{Cu}) + \frac{RT}{zF} (\ln [Cu^{+2}] - \ln [Zn^{+2}]) \quad (\text{c})$$

$$E = E^\circ + \frac{RT}{zF} \ln \frac{[Cu^{+2}]}{[Zn^{+2}]} \quad (\text{d})$$

Example 2.7 The application of eq. (2.32) is suitable for determining the activity of Cu^{+2} ions when the $Zn-ZnSO_4(aq)$ anodic half-cell is mechanically kept replenished so that $a_{Zn^{+2}} = [Zn^{+2}] = 1 \text{ mol/l}$. If current ceases to flow in the galvanic cell shown in Figure 2-4, calculate the activity and the concentration of copper ions $[Cu^{+2}]$ in g/l at 25°C .

Solution:

From eq. (2.32) and Example 2.5,

$$E = E^\circ + \frac{RT}{zF} \ln \frac{[Cu^{+2}]}{[Zn^{+2}]} = 1.10 \text{ V} + (0.0296 \text{ V}) \log [Cu^{+2}] = 0$$

Solving for $a_{Cu^{+2}}$ yields

$$a_{Cu^{+2}} = [Cu^{+2}] = 6.20 \times 10^{-38} \text{ mol/l}$$

From Table 2.6, the concentration of Cu^{+2} is

$$\begin{aligned} C_{Cu^{+2}} &= (a_{Cu^{+2}})(A_w) = (6.20 \times 10^{-38} \text{ mol/l})(63.55 \text{ g/mol}) \\ C_{Cu^{+2}} &= 3.95 \times 10^{-36} \text{ g/l} \end{aligned}$$

which is very low.

An electrochemical cell can be used to measure the entropy change (ΔS) and the enthalpy change (ΔH) of a reversible reaction. This can be accomplished by measurements of the Nernst potential (E) as a function of temperature. At constant pressure, the free energy change (ΔG), ΔS and ΔH are defined by

$$\Delta G = -zFE \quad (2.26)$$

$$\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_p \quad (2.33)$$

$$\Delta H = \Delta G + T\Delta S \quad (2.34)$$

Differentiating eq. (2.26) with respect to the temperature T yields

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = -zF\left(\frac{\partial E}{\partial T}\right)_p \quad (2.35)$$

Then, the entropy change becomes

$$\Delta S = zF\left(\frac{\partial E}{\partial T}\right)_p \quad (2.35)$$

The reversible thermal energy (heat) is defined by

$$Q = -T\Delta S = -zFE - \Delta H \quad (2.36)$$

Substituting eqs. (2.33) and (2.26) into (2.34) yields

$$\Delta H = zF\left[T\left(\frac{\partial E}{\partial T}\right)_p - E\right] \quad (2.37)$$

The heat capacity at constant pressure (P) is defined by

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p \quad (2.38)$$

From eq. (2.35),

$$C_p = zFT \left(\frac{\partial^2 E}{\partial T^2} \right)_p \quad (2.39)$$

Using an electrochemical cell to measure the cell potential, eq. (2.32), as a function of temperature at constant pressure leads to curve fitting an empirical function, usually a polynomial. One particular polynomial is of the form [5]

$$E = a + b(T - T_o) + c(T - T_o)^2 + d(T - T_o)^3 \quad (2.40)$$

$$\frac{\partial E}{\partial T} = b + 2c(T - T_o) + 3d(T - T_o)^2 \quad (2.41)$$

$$\frac{\partial^2 E}{\partial T^2} = 2c + 6d(T - T_o) \quad (2.42)$$

where T_o = Reference temperature (K)

a, b, c, d = Curve fitting coefficients

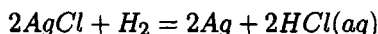
Now, the above thermodynamic state functions can be defined in terms of temperature. Thus,

$$\Delta G = -zF [a + b(T - T_o) + c(T - T_o)^2 + d(T - T_o)^3] \quad (2.43)$$

$$\Delta S = zF [b + 2c(T - T_o) + 3d(T - T_o)^2] \quad (2.44)$$

$$C_p = zFT \cdot [2c + 6d(T - T_o)] \quad (2.45)$$

Example 2.8 Levine [5] applied eq. (2.40) as continuous function in the closed temperature interval [0°C, 90°C] or [273.15 K, 363.15 K] for plating silver (Ag) from silver chloride (AgCl) according to the following redox (overall) reaction



The curve fitting coefficients at $P = 1$ atm and $T_o = 273.15$ K are

$$\begin{aligned} a &= 0.2366 \text{ V} & b &= -4.8564 \times 10^{-4} \text{ V / K} \\ c &= -3.4205 \times 10^{-6} \text{ V / K}^2 & d &= 5.8690 \times 10^{-9} \text{ V / K}^3 \end{aligned}$$

Calculate a) E° , ΔG° , ΔS° , ΔH° , Q , and C_p° at $T = 25^\circ\text{C}$ and b) use the Rolle's theorem to determine if the functions $E = f(T)$ and $\Delta G = (T)$ are differentiable in the open temperature interval [273.15 K, 363.15K].

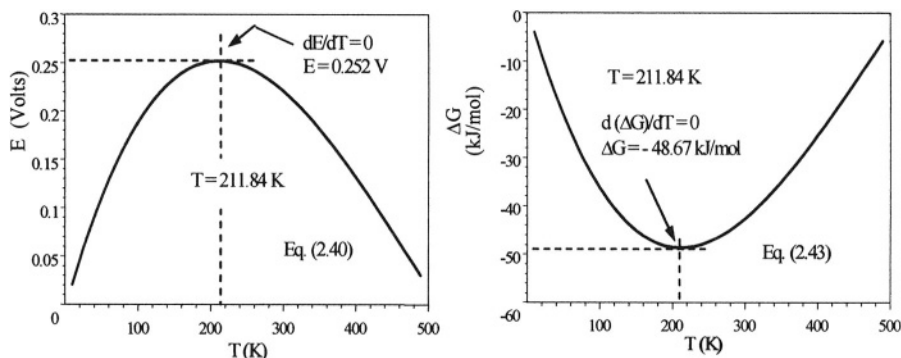
Solution:

a) If $T = 25\text{ }^{\circ}\text{C} = 298.15\text{ K}$, $(T - T_o) = 25\text{ K}$, $z = 2$ and $F = 96,500\text{ C/mol} = 96,500\text{ J/mol V}$, then the following results

$$\begin{aligned} \text{From eq. (2.40),} \quad & E^{\circ} = 0.222\text{ V} \\ \text{From eq. (2.43),} \quad & \Delta G^{\circ} = -42,926\text{ J/mol} < 0 \\ \text{From eq. (2.44),} \quad & \Delta S^{\circ} = -124.61\text{ J/mol}\cdot\text{K} < 0 \\ \text{From eq. (2.37),} \quad & \Delta H^{\circ} = -80,000\text{ J/mol} < 0 \\ \text{From eq. (2.86),} \quad & Q_{\text{irrev}} = -37,152.47\text{ J/mol} < 0 \\ \text{From eq. (2.45),} \quad & C_p^{\circ} = 343\text{ J/mol}\cdot\text{K} \end{aligned}$$

These results indicate that **Ag** can be plated at $T = 25\text{ }^{\circ}\text{C}$ since $E^{\circ} > 0$, $\Delta G^{\circ} < 0$, $\Delta S^{\circ} < 0$, $\Delta H^{\circ} < 0$, and $Q_{\text{rev.}} < 0$. Notice that the calculated value for $E^{\circ} = 0.222\text{ V}$ matches with the value given in Table 2.3.

b) The required plots, $E = f(T)$ and $\Delta G = f(T)$ are shown below as per eq. (2.40) and (2.43), respectively. According to Rolle's theorem the derivatives are $\partial E/\partial T = 0$ and $\partial \Delta G/\partial T = 0$ and, $E = 0.252\text{ V}$ and $\Delta G = -48.67\text{ kJ/mol}$ at $T = 211.84\text{ K}$. The condition $E(a) = E(b)$ and $\Delta G(c) = \Delta G(d)$ are met in the open interval $[273.15\text{ K}, 363.15\text{ K}]$. For instance, $E(100) = E(343.36) = 0.19\text{ V}$ and $\Delta G(100) = \Delta G(343.36) = -36.22\text{ kJ/mol}$. Therefore, both functions are continuous and differentiable.



Example 2.8b

2.5 STANDARD ELECTRIC POTENTIAL

In this section, a procedure to carry out measurements of the electromotive force (emf) is described. This emf is known as the standard potential (E°) already introduced in Table 2.2. The standard hydrogen electrode (*SHE*) is used as the reference electrode in conducting these measurements. In general, a reference electrode one selects to measure E° of a metal has to be reversible since classical

thermodynamics applies to all reversible processes. The SHE cell diagram for the potential E_M° measurement is shown in Figure 2.7 and the schematic cell is shown in Figure 2.8.

Nonetheless, the *SHE* is a gas electrode that consists of a platinum foil suspended in sulfuric acid solution having H^+ unit activity ($a_{H^+} = 1 \text{ mol/l}$) at 1 atm and 25 °C. In order to maintain $a_{H^+} = 1 \text{ mol/l}$ purified hydrogen (H_2) gas is injected into the anodic half-cell in order to remove any dissolved oxygen. The platinum foil is an inert material in this solution and it allows the hydrogen molecules to oxidize, providing the electrons needed by the metal M^{+z} ions to be reduced on the cathode surface. The concentration of M^{+z} ions are also kept at unit activity. By convention, the standard hydrogen electrode potential is zero; $E_H^\circ = 0$.

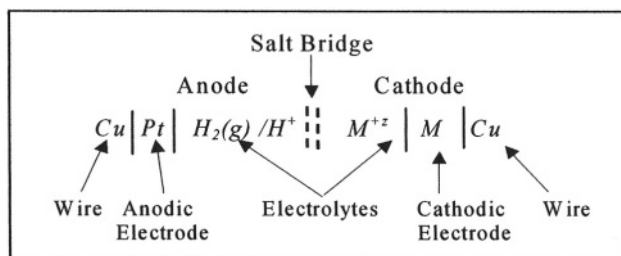


Figure 2.7 Metal/SHE standard cell diagram.

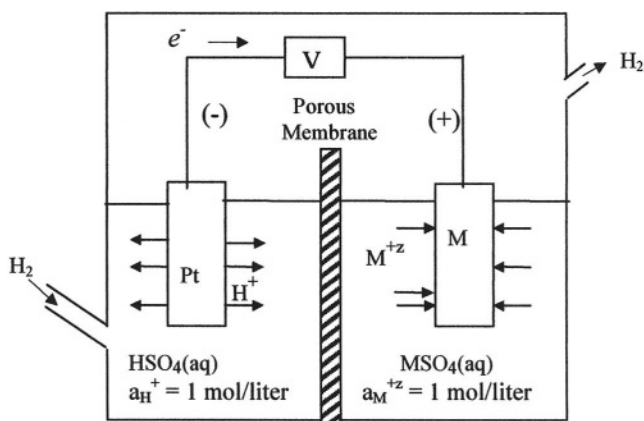


Figure 2.8 Schematic metal/SHE cell.

In addition, Table 2.7 lists some conversion of potential vs. SHE and half-cell reactions for secondary reference electrodes used for measuring corrosion potentials of metals and alloys in specific applications.

Table 2.7 Secondary reference electrode potentials [5].

Name	Half-cell reaction	$E(V)$ vs. SHE
Mercury Sulfate	$HgSO_4 + 2e^- = 2Hg + SO_4^{2-}$	0.615
Copper Sulfate	$CuSO_4 + 2e^- = 2Cu + SO_4^{2-}$	0.318
Saturated Colomel	$Hg_2Cl_2 + 2e^- = 2Hg + 2Cl^-$	0.241
Silver Chloride	$AgCl + e^- = Ag + Cl^-$	0.222
Standard Hydrogen	$2H^+ + 2e^- = H_2$	0.000

Example 2.9 If the potential of a metal M with respect to the saturated colomel electrode (SCE) is -0.541 V, convert this measured potential to SHE potential.

Solution:

If $E = -0.541$ V_{SCE}, then $E = E_{measured} + E_{Table\ 2.7}$

$$E = (-0.541 + 0.241) V_{SHE} = -0.30 V_{SHE}$$

As can be seen in Figure 2.8, the metal M is coupled with the platinum (Pt) electrode and the electric potential of M at the surface is measured against the SHE. Recall that this potential is the resultant of several interfacial potentials described by eq. (2.7a). The junction potentials of the Pt and M electrodes are small, equal, and apposite so that they cancel out. The liquid junction potential is also small and negligible. The cell potential is also known as the **interfacial cell potential**, which depends on the chemical potential of the species (ions) in solution at equilibrium and it is predicted by eq. (2.28). The electrons flow toward the cathodic electrode M , where the metal cations M^{+z} gain these electrons and enter the electrode lattice. This is a reduction process that strongly depends on the chemical potential of the M^{+z} cations.

The spontaneous redox reaction in Figure 2.8 is



and the standard cell potential using Table 2.5 is

$$E_{M^{+z}/M}^{\circ} = \frac{1}{zF} \left\{ \begin{aligned} &[(1)\mu_M^{\circ} + (2)\mu_{H^+}^{\circ}] \\ &- [(1)\mu_M^{\circ} + (1)\mu_{H_2}^{\circ}] \end{aligned} \right\} \quad (\text{b})$$

$$E_{M^{+z}/M}^{\circ} = \frac{\mu_{M^{+z}}^{\circ}}{zF} \quad \text{since } \mu_M^{\circ} = \mu_{H^+}^{\circ} = \mu_{H_2}^{\circ} = 0 \quad (\text{c})$$

For instance, if $M^{+z} = Cu^{+2}$, then

$$E_{Cu^{+2}/Cu}^{\circ} = \frac{+64.98 \text{ kJ/mol}}{(2)(96.50 \text{ kJ/mol} \cdot V)} = +0.337 \text{ V} \quad (\text{e})$$

This is exactly the result given in Table 2.2.

2.6 POURBAIX DIAGRAMS

Potential-pH plots are known as Pourbaix diagrams since they were first made by Pourbaix in 1938. A compilation of these diagrams is available in the *Atlas of Electrochemical Equilibria in Aqueous Solutions* [9]. In practice, Pourbaix diagrams are suitable for studies of corrosion, electrowinning, electroplating, hydrometallurgy, electrolysis, electrical cells, and water treatment since they are electrochemical maps indicating the domain of stability of ions, oxides and hydroxides [9]. This map provides the oxidizing power in an electrochemical field measured as potential and the acidity and alkalinity of species measured as pH. Thus, any reaction involving hydroxyl (OH^-) ions should be written in terms of H^+ ion concentration, which in turn is converted into pH. The conversion factor is given in Table 2.6. Besides the possible reactions that may occur in an electrochemical system, a simplified Pourbaix diagram gives important areas for designing and analyzing electrochemical systems. These areas are known as corrosion, passivation, and immunity. However, a Pourbaix diagram does not include corrosion rate, which is essential in kinetic studies.

2.6.1 DIAGRAM FOR WATER AND OXYGEN

The construction of the E-pH Pourbaix diagram for water and oxygen is straightforward. Consider the hydrogen evolution reaction at standard conditions ($T = 25^\circ\text{C}$, $P_o = 1 \text{ atm}$)



for which the equilibrium constant is

$$K = \frac{a_{H_2}}{a_{H^+}} = \frac{[H_2]}{[H^+]^2} = \frac{P_{H_2}/P_o}{[H^+]^2} \quad (a)$$

$$\log [K] = \log (P_{H_2}) - 2 \log [H^+] \quad (b)$$

From eq. (2.32), the Nernst equation gives the hydrogen potential as

$$E_H = E_{H^+/H_2}^\circ - \frac{2.303RT}{zF} \log [K] \quad (c)$$

$$E_H = \frac{b}{2} [2pH - \log (P_{H_2})] \quad (2.47)$$

where $b = \text{slope} = -2.303RT/F = -0.0592\text{V}$, $Z = 2$, $E_{H^+/H_2}^\circ = 0$, and $pH = -\log [H^+]$.

Figure 2.9 shows the plot for eq. (2.47) labeled H_2 .

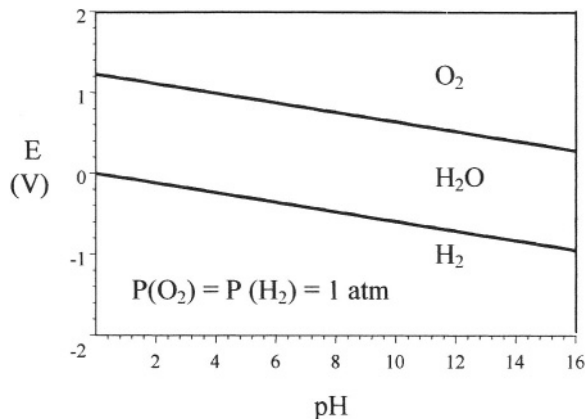


Figure 2.9 Pourbaix diagram for water and oxygen

For oxygen in an acid solution,



where

$$K = \frac{[H_2O]^2}{[O_2][H^+]^4} = \frac{1}{[P_{O_2}/P_o][H^+]^4} \quad (b)$$

$$\log [K] = -\log (P_{O_2}) - 4 \log [H^+] \quad (c)$$

$$\log [K] = -\log (P_{O_2}) + 4pH \quad (d)$$

Using eq. (2.32) along with $Z = 4$ yields

$$E_{O_2} = E_{O_2}^\circ - \frac{2.303RT}{zF} \log [K] \quad (e)$$

$$E_{O_2} = 1.229 \text{ V} + \frac{b}{4} [4pH - \log (P_{O_2})] \quad (2.48)$$

Plotting eq. (2.48) yields a straight line as shown in Figure 2.9. Notice that the slope $b = -0.0592 \text{ V}$ does not change if P_{H_2} and P_{O_2} change. Usually, these straight lines are superimposed on a metal $M - H_2O$ diagram for comparison purposes.

Analysis of Figure 2.9:

@ $P_{H_2} < 1 \text{ atm}$, water is unstable and decomposes to hydrogen gas H_2 . Thus, $H_2O + 2e^- = H_2 + 2(OH^-)$

@ $P_{H_2} = 1 \text{ atm}$, eq. (2.47) becomes $E_H = -0.0592(pH)$ and establishes the limit of predominance between H_2O and H_2 , but H_2 predominates.

@ $P_{H_2} > 1 \text{ atm}$, water is stable

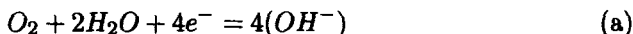
@ $P_{O_2} < 1 \text{ atm}$, water is stable

@ $P_{O_2} = 1 \text{ atm}$, eq. (2.48) becomes $E_{O_2} = 1.229 \text{ V} - 0.0592 \text{ V} (pH)$ and it establishes the limit of predominance between O_2 and H_2O , but O_2 predominates.

@ $P_{O_2} > 1 \text{ atm}$, O_2 predominates.

Example 2.10 Drive eq. (2.48) for an alkaline solution and compute the E_H and E_{O_2} for a $pH = 10$ under standard conditions.

Solution:



from which

$$K = \frac{[OH^-]^4}{[O_2]} = \frac{[OH^-]^4}{P_{O_2}/P_o} \quad (b)$$

$$\log(K) = 4 \log [OH^-] - \log(P_{O_2}) \quad (c)$$

From Table 2.6,

$$pH = 14 + \log [OH^-] \quad (d)$$

Then, eq. (c) becomes

$$\log(K) = 4(pH - 14) - \log(P_{O_2}) \quad (e)$$

From eq. (2.32) with $b = -2.303RT/F = -0.0592 \text{ V}$ and $Z = 4$, E_{O_2} becomes

$$E_{O_2} = E_{O_2}^\circ - \frac{2.303RT}{zF} \log(K) \quad (f)$$

$$E_{O_2} = 0.401 \text{ V} + \frac{b}{4} [4(pH - 14) - \log(P_{O_2})] \quad (g)$$

$$E_{O_2} = 1.229 \text{ V} + \frac{b}{4} [4pH - \log(P_{O_2})] \quad (2.48)$$

It can be concluded that eq. (2.48) gives the same result if either acid or alkaline solution is selected.

2.6.2 POURBAIX DIAGRAM FOR A METAL M

Below is a brief description on how to construct a Pourbaix diagram for a metal $M - H_2O$ electrochemical system. Figure 2.10 shows a schematic and yet, simple $M - H_2O$ Pourbaix diagram, which includes the water and oxygen lines for comparison purposes. The construction of the diagram consists of determining the potential E for lines 1 and 3 using the Nernst equation, and the pH for lines 2 and 4 using known equilibrium constant K . The range of metal ion concentration can be $10^{-6} \text{ mol/l} \leq a(M^{+z}) \leq 1 \text{ mol/l}$, but $a(M^{+z}) = 10^{-6} \text{ mol/l}$ is chosen hereafter in order to simplify the procedure for constructing the diagram. Otherwise, several vertical and incline lines would be generated. If $a(M^{+z}) = 1 \text{ mol/l}$, the electrochemical corrosion process is unrealistic [5]. The procedure is as follows

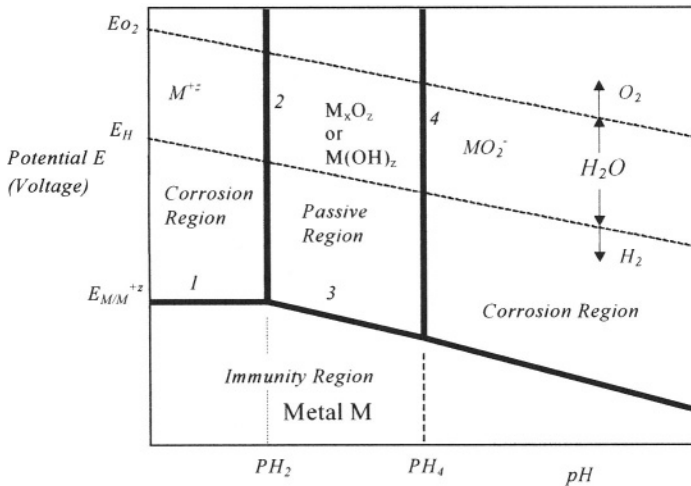


Figure 2.10 Schematic Pourbaix diagram for a metal M, water and oxygen.

1) Horizontal Line 1:



$$K = \frac{[M^{+z}]}{[M]} = [M^{+z}] \quad (b)$$

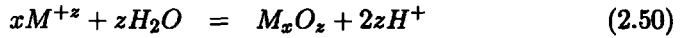
This reaction involves electron transfer only. Thus, the Nernst equation, eq. (2.32), with $[M^{+z}] = 10^{-6} \text{ mol/l}$ and $T = 298 \text{ K}$ becomes

$$E_1 = E_{M/M^{+z}}^o - \frac{2.303RT}{zF} \log [M^{+z}] \quad (c)$$

$$E_1 = E_{M/M^{+z}}^o - \frac{0.3552}{z} \quad (2.49)$$

The value for the standard potential $E_{M/M^{+z}}^{\circ}$ is given in Table 2.2, provided that the metal M is known. Thus, eq. (2.49) plots a horizontal line shown in Figure 2.10 as line 1.

2) Vertical Line 2:



$$K = \frac{[H^+]^{2z}}{[M^{+z}]^x} \quad (a)$$

This reaction involves a fixed hydrogen concentration only, the equilibrium constant K for this reaction must be known so that

$$\log(K) = 2z \log[H^+] - x \log[M^{+z}] \quad (b)$$

$$\log(K) = -2z(pH_2) - 6x \quad (c)$$

$$pH_2 = -\frac{1}{2z} [\log(K) + 6x] \quad (2.51)$$

Therefore, a straight line is drawn starting at $E_1 - pH_2$ point. This is shown in Figure 2.10 as line 2. It should be mentioned that the metal oxide M_xO_z can be replaced by a metal hydroxide $M(OH)_2$ or $M(OH)_3$ depending on the chosen metal. Thus, eq. (2.50) should be balanced accordingly. Hence,

3) Incline Line 3:

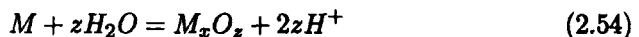


$$K = [H^+]^{2z} \quad (a)$$

Notice that this reaction involves both hydrogen and electron transfer. Then, the Nernst equation becomes

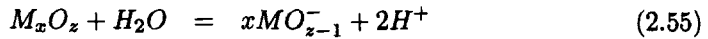
$$E_3 = E_{M/M_xO_z}^{\circ} - 0.0592(pH) \quad (2.53)$$

The standard potential $E_{M/M_xO_z}^{\circ}$ must be known. In Figure 2.10, Line 2 and line 3 intersect at a pH value given by eq. (2.51). Above this pH, a passivation process takes place on the metal surface according to the following reaction



where M_xO_z is a passive film compound. This reaction is reversed below the pH given by eq. (2.52).

4) Vertical Line 4:



$$K = a(H^+)^2 a(MO_{z-1}^-)^x \quad (a)$$

Letting $[MO_{z-1}^-] = 10^{-6} \text{ mol/l}$ in eq. (a) yields

$$\log(K) = 2\log a(H^+) + x\log a(MO_{z-1}^-) \quad (b)$$

$$\log(K) = -2(pH_4) - 6x \quad (c)$$

Solving for pH gives

$$pH_4 = -0.5[6x + \log(K)] \quad (2.56)$$

Subsequently, a vertical line 4 is drawn at this pH_4 value.

2.7 ELECTRICAL DOUBLE LAYER

When a metal M is immersed in a suitable electrolyte, initially its atoms oxidize at a relatively high rate, and subsequently, the oxidation (dissolution) process gradually ceases and eventually stops due to a negative charge build-up on the metal surface. Thus, the dynamic equilibrium is attained, provided that no other complex electrochemical reactions take place. In this process, metal atoms are removed from their lattice sites to ionize as cations (M^{+z}) into the electrolyte, forming a negatively charged metal surface. If polar water (H_2O) molecules and hydrogen cations (H^+) are in the electrolyte, they are attracted by the negatively charged metal surface to form an ionic structure (layer), which prevent other ions from the bulk solution to be part of it. This structure is a complex ionic arrangement in an electric field and has a limited thickness. Eventually, metal dissolution ceases if there is no external current flow, but it proceeds until the ionic structure is dense enough to protect and prevent the metal from reacting any further until equilibrium is reached. With respect to the metal-layer-bulk within which there must exist an electric potential decay. The ionic structure is known in the literature as the electrical double-layer (*EDL*). This *EDL* seems to limit the continuous electrochemical reactions at the metal surface due to the lack of charge transfer.

One finds in the literature [10-12] different models for explaining the interfacial structure of the electrical double layer. This layer is referred to as the Helmholtz layer which behaves like a charged capacitor. Figure 2.11 shows a schematic electrical double-layer model.

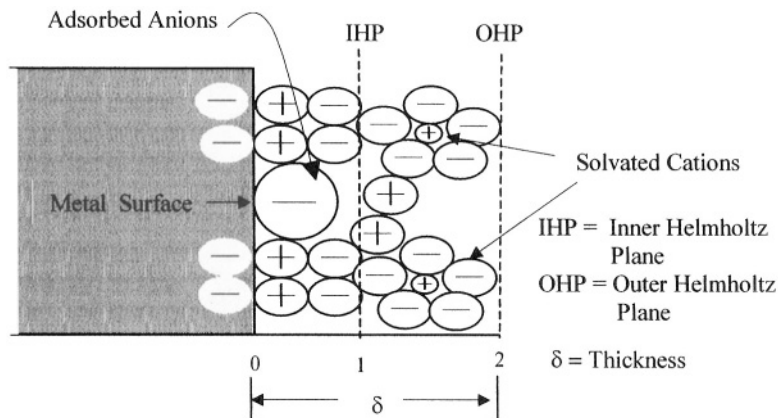


Figure 2.11 Schematic electrical double layer.

This model indicates that some negatively charge ions are adsorbed on the metal electrode surface and polar water covers the rest of this surface, forming a protective layer. The positively charged hydrogen is in contact with the negatively charge metal surface. Thus, one can conclude that

1) The **Inner Helmholtz Plane (IHP)** is an ionic layer that consists of adsorbed dipole H_2O molecules. The majority of the anions do not penetrate this layer, some do as indicated in Figure 2.11. The inner potential on the boundary of this ionic plane is ϕ_1 .

2) The **Outer Helmholtz Plane (OHP)** consists of a plane of adsorbed ions due to electrostatic forces in contact with a diffuse ionic layer at a inner potential ϕ_2 .

3) The **Diffuse Layer (DL)** is a thick layer located in a region of diffusely ions in contact with the OHP and the bulk of solution at a potential range of $\phi_1 < \phi_{Diffuse} < \phi_3$. Thus, the diffuse layer/bulk boundary is at $\phi_3 = \phi_b$.

The distribution of the inner electric potential ϕ in solution is shown in Figure 2.12 and defined by [4]

$$\phi(x) = \phi_o \exp(-\lambda x) \quad (2.57)$$

where λ = constant and x = distance from the metal surface.

In fact, this mathematical model represents an electric potential decay since

$$\phi(x) = \phi_o \longrightarrow \phi_{\max} \text{ when } x \longrightarrow 0 \quad (a)$$

$$\phi(x) = \phi_b \longrightarrow 0 \text{ when } x \longrightarrow \infty \quad (b)$$

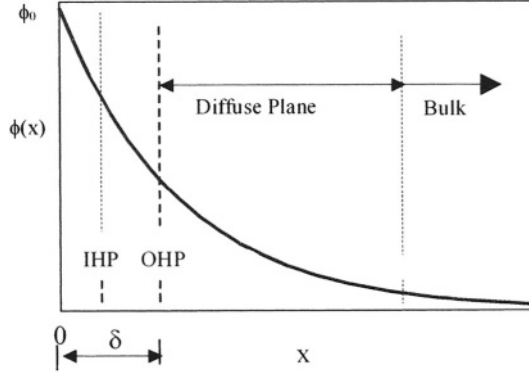


Figure 2.12 Schematic inner electrical potential distribution.

The concentration of the oxidized species, $C(x)$, may be predicted using the Nernst equation, eq. (2.32). In this case, the potential E is replaced by ϕ . Thus, for a species j the interfacial potential within the electrolyte is defined by

$$\phi(x) = -\frac{RT}{zF} \ln [K] \quad (2.58)$$

$$\phi(x) = -\frac{RT}{zF} \ln \left[\frac{C(x)}{C_o} \right] \quad (2.59)$$

where $K = C(x)/C_o$

K = Rate constant

$C(x)$ = Concentration (activity) at $x > 0$

C_o = Concentration (activity) at $x = 0$

Solving eq. (2.59) for $C(x)$ yields the concentration decay function, which is dependent on both interfacial potential $\phi(x)$ and temperature T

$$C(x) = C_o \exp \left[-\frac{zF\phi(x)}{RT} \right] \quad (2.60)$$

For small values of $\phi(x)$, eq. (2.60) can be linearized by expanding the exponential function using Taylor's series. Hence,

$$C(x) = C_o \left[1 - \frac{zF\phi(x)}{RT} \right] \quad (2.60a)$$

The resultant expression implies that there is a linear relationship between $C(x)$ and $\phi(x)$.

2.8 DEGREE OF DISSOCIATION

Since electrolytes transport charge in the solid, aqueous or vapor state, it is worthwhile mentioning that the degree of dissociation of a compound added to a solvent can be estimated by the degree of dissociation parameter α_1 . Electrolytes hereafter are treated as aqueous electrolytes (solutions) unless otherwise stated. In general, if $\alpha_1 < 1$, the solution is a weak electrolyte and if $\alpha_1 \geq 1$ the solution is a strong electrolyte since the compound being added to a solvent completely dissociates into ionic components, such as cations and anions.

Consider the following reaction for a salt M_xO_y dissolved in a solvent



where M is a metal and O is an oxide or hydroxide. The ionic components are metal M^{+z} cations and oxide or hydroxide O^{-z} anions.

The standard free energy change for chemical equilibrium and the equilibrium constant are, respectively

$$\Delta G^\circ = -RT \ln(K) \quad (2.62)$$

$$K = \frac{[M^{+z}]^x [O^{-z}]^y}{[M_xO_y]} \quad (2.63)$$

The activity or molar concentration a_i , the degree of dissociation α_1 , and the total molar activity $[C_T]$ are defined as follows [3]

$$[M^{+z}] = x\alpha_1 [C_T] \quad (2.64a)$$

$$[O^{-z}] = y\alpha_1 [C_T] \quad (2.64b)$$

$$[M_xO_y] = (1 - \alpha_1) [C_T] \quad (2.64c)$$

Substituting eq. (2.64) into (2.63) yields

$$K = (x^x y^y) \left[\frac{\alpha_1^{x+y} [C_T]^{x+y-1}}{1 - \alpha_1} \right] \quad (2.65)$$

If $\alpha_1 \ll 1$, then eq. (2.65) becomes

$$K = (x^x y^y) \left[\alpha_1^{x+y} [C_T]^{x+y-1} \right] \quad (2.66)$$

from which

$$\alpha_1 = (K x^{-x} y^{-y})^{1/(x+y)} [C_T]^{-1+1/(x+y)} \quad (2.67)$$

This expression indicates that the degree of dissociation increases with increasing concentration; that is, $\alpha_1 \uparrow$ as $[C_T] \uparrow$. Further, if $\alpha_1 \ll 1$, a hydroxyl ion activity $[OH^-]$ is related to a hydrogen ion activity $[H^+]$ through the dissociation of water. Hence, the dissociation constant for water is

$$K_w = \frac{[H^+][OH^-]}{[H_2O]} = [H^+][OH^-] = 10^{-14} \quad (2.68)$$

For a neutral solution, $[H^+] = [OH^-] = 10^{-7}$. Also, the acidity or alkalinity of a solution is defined by the pH

$$pH = -\log [H^+] \quad (2.69)$$

Hence,

$$[H^+] = 10^{-pH} \quad (2.70)$$

$$[OH^-] = K_w / [H^+] = 10^{-14} / 10^{pH} \quad (2.71)$$

This hydroxyl concentration may be used in the dissociation of a metal hydroxide compound, such as $Ag(OH)$. An example can make this procedure very clear.

Example 2.11 Determine the amount of silver hydroxide $Ag(OH)$ needed to make one liter of silver-containing electrolyte having a $pH = 11.6$ at $25^\circ C$ and 1 atm. The dissociation constant of $Ag(OH)$ is 1.10×10^{-4} . The atomic weight of silver is 107.87 g/mol and the molecular weight of $[Ag(OH)]$ is 124.87 g/mol.

Solution:

In this problem, the silver hydroxide is assumed to dissolve to an extent in pure water. The reactions of interest are



$$K = \frac{[Ag^+][OH^-]}{[Ag(OH)]} \quad (b)$$

$$K = [Ag^+][OH^-] = 1.10 \times 10^{-4} \quad (c)$$

and



$$K_w = \frac{[H^+][OH^-]}{[H_2O]} \quad (e)$$

$$K_w = [H^+][OH^-] = 10^{-14} \quad (f)$$

From eq. (2.70) and 2.71),

$$\begin{aligned}
[H^+] &= 10^{-pH} = 10^{-11.6} = 2.51 \times 10^{-12} \text{ mol/l} \\
[OH^-] &= K_w/a(H^+) = 10^{-14}/10^{-11.6} = 3.98 \times 10^{-3} \text{ mol/l} \\
C_{H^+} &= (2.51 \times 10^{-12} \text{ mol/l}) (A_w)_H = (2.51 \times 10^{-12} \text{ mol/l}) (1 \text{ g/mol}) \\
C_{H^+} &= 2.51 \times 10^{-12} \text{ g/l} \\
C_{OH^-} &= (3.98 \times 10^{-3} \text{ mol/l}) (A_w)_{OH} = (3.98 \times 10^{-3} \text{ mol/l}) (17 \text{ g/mol}) \\
C_{OH^-} &= 0.068 \text{ g/l}
\end{aligned}$$

From eq. (2.66) with $x = y = 1$, the total silver concentration in solution is predicted by

$$[C_T] = K/\alpha_1^2 \quad (g)$$

Solving for $[Ag^+]$ in eq. (c) yields

$$[Ag^+] = \frac{K}{[OH^-]} = \frac{K[H^+]}{K_w} = 2.76 \times 10^{-2} \text{ mol/l} \quad (h)$$

From eq. (2.64b),

$$[OH^-] = \alpha_1 [C_T] \quad (i)$$

$$\alpha_1 = \frac{[OH^-]}{[C_T]} \quad (j)$$

Substituting eq. (j) into (g) gives

$$\begin{aligned}
[C_T] &= \frac{[OH^-]^2}{K} = \frac{(3.98 \times 10^{-3} \text{ mol/l})^2}{1.10 \times 10^{-4}} = 0.144 \text{ mol/l} \\
C_{Ag(OH)} &= [C_T] A_w = (0.144 \text{ mol/l}) (124.87 \text{ g/mol}) \\
C_{Ag(OH)} &= 17.98 \text{ g/l}
\end{aligned}$$

From eq. (j),

$$\alpha_1 = \frac{[OH^-]}{[C_T]} = \frac{3.98 \times 10^{-3} \text{ mol/l}}{0.144 \text{ mol/l}} = 0.03$$

which implies that the solution is a weak electrolyte since $\alpha_1 < 1$. The total weight of $Ag(OH)$ added to water solvent is

$$W = VC = (1 \text{ liter}) (17.98 \text{ g/liter}) = 17.98 \text{ grams}$$

Therefore, add 17.98 grams of solid $Ag(OH)$ to one liter of pure water, stir until a homogeneous electrolyte is attained. This electrolyte can be used for silver plating purposes.

2.9 SUMMARY

It has been shown that the potential difference of an electrochemical galvanic cell is $E = \phi^\beta - \phi^\alpha$, where both ϕ^β and ϕ^α are the inner surface potentials and the sum of the junction potentials was assumed to be very small. Thus, the repulsive forces of like charged particles (ions) in an electrical polypole system allow diffusion of these particles to the phase surfaces. This is a significant electrochemical process to convert chemical energy into electrical energy as in the case of a battery flash light. In principle, electrical energy can be converted into chemical energy as in the case of electrolysis of copper ion reduction where the cell potential is $E > |\phi^\beta - \phi^\alpha|$.

In addition, $E = \phi^\beta - \phi^\alpha$ can be predicted by the Nernst equation, eq. (2.32). If the standard hydrogen electrode (SHE) is coupled with a pure metal electrode, the standard metal electrode potential is $E_m = \phi_M^\beta - \phi_H^\alpha = \phi_M^\beta$ since $\phi_H^\alpha = 0$. Moreover, the inner surface potential is $\phi(x) = f(x)$, where x is the distance from the metal electrode surface. It is assumed that $\phi(x)$ decays linearly through the Helmholtz double layer ($0 \leq x \leq \delta$) and exponentially in the diffuse layer and bulk ($\delta \leq x \leq \infty$).

An electrochemical cell can be used to determine thermodynamic energy changes like the change in entropy (ΔS), change in enthalpy (ΔH), change in Gibbs free energy (ΔG), the heat capacity at constant pressure (C_p) and the reversible thermal energy (heat) Q .

Also, Pourbaix diagrams being electrochemical maps of ionic species can be constructed using electrochemical cells containing water as the solvent at a constant temperature. These diagrams are potential-pH plots that show areas known as corrosion, passivation, and immunity. In spite of the usefulness of these diagrams for characterizing electrochemical systems, kinetics parameters, such as corrosion rate, cannot be predicted from such diagrams.

Electrolytes can be classified as strong or weak solutions through the degree of dissociation parameter α_1 . Thus, if $\alpha_1 < 1$, then the electrolyte is weak; otherwise, strong if $\alpha_1 \geq 1$.

2.10 PROBLEMS/QUESTIONS

2.1 Define the galvanic electrode potential for the cell shown in Figure 2.4 using the interfacial potentials involved in the electrochemical process.

2.2 Describe what happens in the galvanic cell shown in Figure 2.4 when electrons leave the Cu terminal at the Cu-Zn interface.

2.3 Explain why an electrode potential difference occurs in Figure 2.4.

2.4 Why are Cu^{+2} cations electroplated on the Cu electrode surface in Figure 2.4?

2.5 Calculate the standard potential for the formation of ferric hydroxide $Fe(OH)_3$ (brown rust). [$E^\circ = 1.172 \text{ V}$].

2.6 Consider the following electrochemical cell $|Cu^{+2}, Cu| |H_2, H^+| Pt$ to calculate the maximum activity of copper ions Cu^{+2} in solution due to oxidation of a copper strip immersed in sulfuric acid H_2SO_4 at 25°C , 101 kPa and $pH = 2$. [Solution: $a_{Cu^{+2}} = [Cu^{+2}] = 4.04 \times 10^{-16} \text{ mol/l}$].

2.7 Consider a galvanic cell $|Zn| 0.10 \text{ M } ZnSO_4 | 0.10 \text{ M } NiSO_4 | Ni |$. Calculate the cell potential using the Nernst equation at 25°C . [Solution; $E^\circ = 0.513 \text{ V}$].

2.8 The dissociation of silver hydroxide, $AgOH$, is 1.10×10^{-4} at 25°C in an aqueous solution. a) Derive an expression for the degree of dissociation as a function of total activity $[C_T]$ and plot the resultant expression for $0 < [C_T] < 0.50 \text{ mol/l}$, b) calculate the degree of dissociation constant α_1 when the molar concentration is $[C_T] = 0.144 \text{ mol/l}$, and c) determine the Gibbs free energy change ΔG° . [Solutions: b) $\alpha_1 = 0.028$, $\Delta G^\circ \approx -22.58 \text{ kJ/mol}$].

2.9 Calculate a) the concentration of $AgOH$, Ag^+ and OH^- at 25°C and b) the pH if $[C_T] = 0.144 \text{ mol/l}$ and $\alpha_1 = 0.028$. [Solutions: a) $C_{OH^-} = 6.85 \times 10^{-2} \text{ g/l}$, $C_{Ag^+} = 0.43 \text{ g/l}$, $C_{AgOH} = 17.48 \text{ g/l}$ and b) $pH = 11.61$].

2.10 If an electrochemical copper reduction reaction at 25°C and 101 kPa occurs at an infinitely low current density calculate a) the Gibbs free energy change ΔG° as the driving force, b) the equilibrium constant K and c) the copper ion concentration $[Cu^{+2}]$ in g/l . [Solutions: a) $\Delta G^\circ \approx -65 \text{ kJ/mol}$, b) $K = 2.52 \times 10^{11}$, c) $C_{Cu^{+2}} = 2.52 \times 10^{-10} \text{ g/l}$].

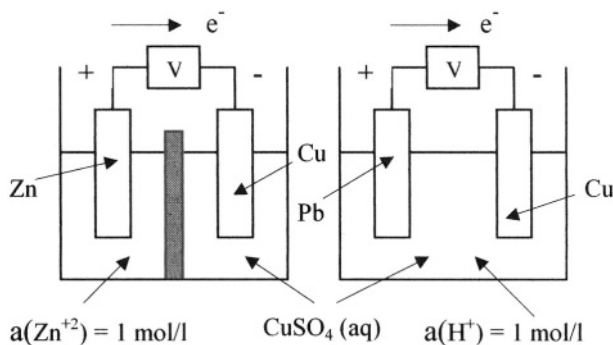
2.11 Use the electrochemical cell $|Cd| 0.05 \text{ M } Cd^{+2} | 0.25 \text{ M } Cu^{+2} | Cu |$ to calculate a) the temperature for an electric potential of 0.762 V_{SHE} , and b) ΔS , ΔG , ΔH , and Q . [Solutions: a) $T \approx 44^\circ\text{C}$ and b) $\Delta S = 13.38 \text{ J/(mol K)}$, $\Delta G \approx -147 \text{ kJ/mol}$, $\Delta H \approx -143 \text{ kJ/mol}$, $Q \approx -4.24 \text{ kJ/mol}$].

2.12 Pure copper and pure cobalt electrodes are separately immersed in solutions of their respective divalent ions, making up a galvanic cell that yields a cell potential of $0.65 V_{SHE}$. Calculate a) the cobalt activity if the activity of copper ions is 0.85 mol/l at 25°C and b) the change in entropy ΔS° and Gibbs free energy ΔG° . [Solutions: a) $[Co^{+2}] = 0.053 \text{ mol/l}$ and b) $\Delta S^\circ \approx 23 \text{ J/mol K}$ and $\Delta G^\circ = -125.45 \text{ kJ/mol}$].

2.13 Show that the activities are $[M_1^{+2}] = [M_2^{+2}]$ in a galvanic cell, provided that the potentials is $E = E^\circ$.

2.14 Show that $\Delta S = -R \ln K$ in a galvanic cell at constant pressure.

2.15 Derive an expression for $\ln [Cu^{+2}] = f(T)$ for the given cells below. Assume that the current ceases to flow and that the cells are not replenished with fresh solutions. Plot the expressions for a temperature range of $0^\circ\text{C} \leq T \leq 60^\circ\text{C}$, and draw some suitable conclusions to explain the electrochemical behavior based on the resultant trend. [Solutions: a) $\ln [Cu^{+2}] = -2.55 \times 10^4/T$ and b) $\ln [Cu^{+2}] = -7.89 \times 10^3/T$].



2.16 Explain why care must be exercised in using the galvanic series illustrated in Table 2.2?

2.17 If zinc and copper rods are placed in salt water, a direct chemical reaction may slightly corrode zinc. Why?

2.18 Is the cell potential a surface potential? If so, why?

2.19 Prove eq. (2.59).

2.20 Assume a solution containing a concentrations of $[Cu^{+2}] \ll 1 \text{ mol/l}$ and $[H^+] = 1 \text{ mol/l}$ at 25°C . Determine the concentration of copper ions for hydrogen evolution to occur. [Solution: $[Cu^{+2}] \leq 3.97 \times 10^{-12} \text{ mol/l}$].

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