VI. Electrochemistry

A. Definitions

1. Introduction

Electrochemistry is the study of a special kind of electron-transfer reaction that can be carried out in such a way that the electron transfer takes place in an electrical circuit outside the reaction medium. The connections between the reaction medium and the outside circuit are by means of electrodes. Two kinds of electrochemical cells are envisaged. In one kind, the electrolytic cell, electrons are forced through the reaction medium by an electromotive force in the outer circuit. In the second kind of electrochemical cell, the galvanic cell, electrons are forced through the outer circuit driven by chemical reaction in the cell itself. Electrolytic cells are used widely for both the plating of metals on surfaces and for the production of chemicals, especially aluminum and fluorine. Galvanic cells are the familiar batteries that we use to power a wide variety of electrical appliances. Rechargeable batteries are electrochemical cells that are galvanic cells during discharge and electrolytic cells during recharge.

We will see that much chemistry can be learned from the study of electrochemical cells in which there is no flow of charge at all; in which the electromotive force generated by the cell reaction is just balanced by an electromotive force generated in the outside circuit. By slightly reducing or slightly increasing the external electromotive force, it is possible to cause the chemical reaction in the cell to take place reversibly in either direction.

2. Electrical units

The fundamental element of electrical charge is the charge on the electron (e), whereas the fundamental unit of charge in the SI system is the coulomb (C). The charge on a single electron is $1.602 \times 10^{-19}$ C, while the total charge of Avogadro's number of electrons, called the faraday (F), is 96,485 C mol$^{-1}$.

The rate of flow of charge is measured in amperes (A), where 1 A = 1 C s$^{-1}$.

The electric potential at a point r, $\phi(r)$, is the work done ($w$) per unit charge in moving a tiny positive charge ($q$) from infinity to the point r. In the SI system, this work is measured in volts, where 1 V = 1 J C$^{-1}$. If

$$\phi(r) = \frac{w(\infty \rightarrow r)}{q}$$

and

$$\phi(r') = \frac{w(\infty \rightarrow r')}{{q}} = \frac{w(\infty \rightarrow r)}{{q}} + \frac{w(r \rightarrow r')}{{q}}$$

where $q$ is a tiny charge, then, the potential difference,

$$\Delta \phi = E = \phi(r') - \phi(r) = \frac{w(\infty \rightarrow r')}{q} - \frac{w(\infty \rightarrow r)}{q} = \frac{w(r \rightarrow r')}{q}$$
As indicated, we will use $E$ to designate the electric potential difference between two points. It is defined as the work required to move a unit positive charge from one point to the other. As also indicated, the electric potential difference is measured in volts in the SI system.

To relate the electric potential difference to the thermodynamics of electrochemical cells, we first recognize that the amount of work done in moving a charge from one point to another should be the electric potential difference times the charge. Then, we recall that in a system in which there is only $pV$ work and electrical work, the maximum amount of electrical work done for such a process is the Gibbs free energy after the movement minus the Gibbs free energy before the movement (because the Gibbs free energy difference is the maximum non-$pV$ work possible). We will write

$$\Delta G = -nFE$$

in which $n$ is the number of moles of electrons transferred in the cell reaction, $F$ is the Faraday constant, and $E$ is the cell potential, the electric potential difference between the cell electrodes for the situation in which the cell supplies no current (so that the cell reaction is reversible). The minus sign determines the choice of sign for $E$, which is discussed below.

B. Galvanic cells

1. Cell reactions

An example of a cell reaction (the Daniell cell) is

$$\text{Cu}^{2+}(aq) + \text{Zn}(s) \rightarrow \text{Cu}(s) + \text{Zn}^{2+}(aq)$$

In this reaction, each Zn atom spontaneously transfers two electrons to a Cu$^{2+}$ ion. If we arrange the reaction vessel so that the two electrons are transferred through an outer circuit, we have an electrochemical cell. In this case, the reaction can pump electrons through the outer circuit, so we have a galvanic cell.

The cell reaction just given could be written as two half-reactions, as follows:

$$\text{Cu}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Cu}(s)$$

and

$$\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2\text{e}^-$$

Neither of these half reactions is capable of occurring by itself, but the two half-reactions work well together to produce the full reaction.

In the half reaction involving Cu the Cu$^{2+}$ ion accepts two electrons and is converted to solid Cu. We say that the Cu$^{2+}$ ion has been reduced (it has actually gained electrons, but its oxidation number has been reduced). Correspondingly, each Zn atom gives up two electrons to form a Zn$^{2+}$...
ion. The Zn has been oxidized (it has lost electrons, but its oxidation number has been increased). These are examples of the more general concept of reduction and oxidation, which is usually based on the concept of decrease or increase in oxidation number, respectively.

According to the definition of oxidation number,

a) The sum of the oxidation numbers of a neutral species is zero.

b) The sum of the oxidation numbers of an ion is the charge on the ion.

The remaining rules are variously stated, but one can work reasonably well from the rules given in *Further Information 7* in the Atkins text (pp 464-465).

To write a balanced chemical equation from the two half reactions, it is only necessary to multiply each of the reactions by an appropriate factor so that the number of electrons involved in each reaction is the same. Then, summing the two half reactions cancels the electrons and produces a balanced cell reaction.

For example, consider the following two half reactions:

$$\text{Fe}(s) = \text{Fe}^{3+}(aq) + 3 \text{e}^-$$

$$\text{Cu}^{2+}(aq) + 2 \text{e}^- = \text{Cu}(s)$$

Multiplication of the first reaction by 2 and the second reaction by 3, followed by addition of the two reactions, yields the balanced equation,

$$2 \text{Fe}(s) + 3 \text{Cu}^{2+}(aq) = 2 \text{Fe}^{3+}(aq) + 3 \text{Cu}(s)$$

2. Electrodes

The interface between the outside circuit and the electrochemical cell is by means of electrodes. For the reactions just discussed, the metals Fe and Cu may be dipped into appropriate solutions of Fe$^{3+}$ and Cu$^{2+}$ ions and serve as electrodes in a galvanic cell. These electrodes are connected to the wires that make up the outer electrical circuit. As the reaction proceeds to the right, electrons are taken from the Fe electrode releasing Fe$^{3+}$ ions into the solution. The electrons travel through the external circuit and reenter the cell through the Cu electrode where they combine with Cu$^{2+}$ ions to form Cu metal.

The electrode at which the Fe($s$) is converted to Fe$^{3+}(aq)$ is called the anode, while the electrode at which the Cu$^{2+}(aq)$ is converted to Cu($s$) is called the cathode. The rule is that oxidation (i.e., increase in oxidation number) occurs at the anode, while reduction (i.e., decrease in oxidation number) occurs at the cathode.
A metal/metal ion electrode is symbolized as follows for the Fe(s), Fe\(^{3+}(aq)\) electrode:

\[ \text{Fe}(s) \mid \text{Fe}^{3+}(aq) \]

The vertical line symbolizes a phase boundary.

Other types of electrodes exist. The *gas electrode* consists of a strip of unreactive metal (typically, Pt) which comes into contact with bubbles of a reactive gas. An example is the H\(_2(g)\) electrode in which hydrogen gas is bubbled over a Pt electrode (the Pt electrode is usually treated in a special way to catalyze the dissociation of the hydrogen gas molecules). This electrode is symbolized, as follows:

\[ \text{Pt} \mid \text{H}_2(g) \mid \text{H}^+(aq) \]

In this case there are two phase boundaries: one between the platinum metal and the hydrogen gas; and one between the hydrogen gas and the water solution.

A third type of electrode is the insoluble-salt electrode, an example of which is the following:

\[ \text{Hg}(l) \mid \text{Hg}_2\text{Cl}_2(s) \mid \text{Cl}^-(aq) \]

This is the *calomel* electrode, which often serves as a standard electrode because it can be constructed reproducibly and the electrochemical potential associated with the use of this electrode has been measured to high accuracy.

An electrochemical cell is symbolized by the junction of two electrodes, one written backwards. For example,

\[ \text{Hg}(l) \mid \text{Hg}_2\text{Cl}_2(s) \mid \text{Cl}^-(aq), \text{H}^+(aq) \mid \text{H}_2(g) \mid \text{Pt} \]

In this case, a single solution, of H\(^+\) and Cl\(^-\) ions, serves as the cell solution. Sometimes, it is necessary to separate the two solutions used for the left and right hand electrodes. The two solutions are joined by a *salt bridge*, which consists of an inverted U-shaped glass tube filled with a saturated solution of a salt (for technical reasons, usually KCl) that is thickened with a gel such as agar (the salt solution should remain in the U-tube). The salt bridge, which insures a continuous solution path between the electrodes, creates an additional voltage difference, but with careful construction, a salt bridge like the one described may contribute only 1-2 mV to the potential difference between the electrodes.

The salt bridge is symbolized by two vertical lines. For example, for the Daniell cell,

\[ \text{Zn}(s) \mid \text{Zn}^{2+}(aq) \mid \text{Cu}^{2+}(aq) \mid \text{Cu}(s) \]

The reason for the salt bridge in this case is that if the Zn\((s)\) could come into contact with the Cu\(^{2+}(aq)\) ions, the cell reaction would proceed directly inside the solution without any transfer of
electrons through the electrodes. Some separation of the two solutions is essential for operation of this device as an electrochemical cell.

3. The cell reaction

The most common convention for writing the cell reaction for an assumed cell is the following (we use the Daniell cell as an example):

a) Write the half-reaction for the right-hand electrode as a reduction:

\[ Cu^{2+}(aq) + 2e^- = Cu(s) \]

b) Write the half-reaction for the left-hand electrode as a reduction:

\[ Zn^{2+}(aq) + 2e^- = Zn(s) \]

c) Multiply one or the other or both of the half-reactions by integers so that the number of electrons in each reaction is the same. In this case, no multiplication is needed.

d) Subtract the half-reaction for the left-hand electrode from the half-reaction for the right-hand electrode to obtain the cell reaction (the electrons should cancel):

\[ Cu^{2+}(aq) + Zn(s) = Cu(s) + Zn^{2+}(aq) \]

e) The Gibbs free energy change for this reaction is given by the usual expression (the implied 1 mol is included for later use):

\[ \Delta G = \Delta G^0 + (1 \text{ mol}) \times RT \ln Q \]

where for the Daniell cell

\[ \Delta G^0 = \Delta G_f^0 \left( Zn^{2+}(aq) \right) + \Delta G_f^0 \left( Cu(s) \right) - \Delta G_f^0 \left( Zn(s) \right) - \Delta G_f^0 \left( Cu^{2+}(aq) \right) \]

and

\[ Q = \frac{a(Cu(s))a(Zn^{2+}(aq))}{a(Zn(s))a(Cu^{2+}(aq))} \]

Of course, in this case, the standard Gibbs free energies of formation of elemental copper and elemental zinc are zero and the activities of these substances are both 1 (because they are elements in their standard reference states). The standard Gibbs free energies of the two ions can be found in tables, and the activities of the two ions should be known to the person who set up the cell. Therefore, \( \Delta G \) can be calculated.
f) When the Gibbs free energy change is calculated, the zero-current cell potential can be obtained from

\[ \Delta G = -nFE \]

where \( n \) is the number of electrons that was canceled in the subtraction of the left-hand half-reaction from the right-hand half reaction (In this case, \( n = 2 \)). The \( F \) is the Faraday constant, 96,485 C mol\(^{-1}\).

We recall that when \( \Delta G < 0 \), the reaction is spontaneous in the forward direction. Apparently, \( E > 0 \) means that the cell reaction is spontaneous in the forward direction.

If the activities of all of the reactants and products in the cell reaction are 1, then \( Q = 1 \), and \( \Delta G = \Delta G^0 \), the standard Gibbs free energy change. The cell potential under these conditions is called the standard cell potential and is symbolized by \( E^0 \). Then,

\[ \Delta G^0 = -nFE^0 \]

g) We will use the reaction for the Daniell cell, which is known from experiment to be spontaneous in the forward direction for any reasonable concentrations of the ions, to determine the directions of electron and current flow in the outer circuit for the case of \( E > 0 \).

As the reaction for the Daniell cell proceeds in the forward direction, Zn metal gives up electrons and Cu\(^{2+} \) ions receive them. If this electron transfer takes place through the outer circuit, then electrons evidently flow from left to right in the outer circuit. Thus, the electrons flow from the anode (electrode at which oxidation takes place) to the cathode (electrode at which reduction takes place). Also, the Zn anode is the negative electrode and the Cu cathode is the positive electrode (since electrons must flow from the negative to the positive electrode). Therefore, if \( E > 0 \), the anode is at the left and the cathode is at the right for a galvanic cell that is diagrammed according to our convention. If \( E < 0 \), the anode is at the right, the cathode is at the left, and the electrons flow from right to left in the outer circuit.

Current flow, as defined by electrical engineers, is in the opposite direction to electron flow. That is, current flows from the positive electrode to the negative electrode. Thus, if \( E > 0 \) for a galvanic cell in our convention, current flows from the right-hand electrode to the left-hand electrode.
C. Thermodynamics of cell reactions

1. The Nernst equation

To derive the Nernst equation, we start with

$$\Delta G = \Delta G^o + (1 \text{ mol}) \times RT \ln Q$$

and substitute $\Delta G = -nF \epsilon$ and $\Delta G^o = -nF \epsilon^o$. Then, we divide by $-nF$ to obtain

$$E = E^o - \frac{RT}{(n / \text{ mol})F} \ln Q$$

Atkins defines $\nu = n/\text{mol}$, so that $\nu$ moles is the number of moles of electrons transferred in the cell reaction ($\nu$ is unitless). Then,

$$E = E^o - \frac{RT}{\nu F} \ln Q$$

which is the Nernst equation. At 25 °C,

$$E = E^o - \frac{25.7 \text{ mV}}{\nu} \ln Q = E^o - \frac{59.2 \text{ mV}}{\nu} \log_{10} Q$$

2. Standard reduction potentials

The standard reduction potential for a given electrode is defined to be the zero-current potential for the galvanic cell that contains the standard hydrogen electrode (SHE) as the left-hand electrode and the given electrode as the right-hand electrode. All of the reacting species must be at unit activity. For example, for the Zn | Zn^2+ electrode, the cell is

$$\text{Pt} | \text{H}_2(g, 1 \text{ bar}) | \text{H}^+(aq, a = 1) || \text{Zn}^{2+}(aq, a = 1) | \text{Zn(s)}$$

The reaction for this cell is obtained by the rules, as follows:

right

$$\text{Zn}^{2+}(aq, a = 1) + 2 e^- = \text{Zn(s)}$$

left

$$\text{H}^+(aq, a = 1) + e^- = \frac{1}{2} \text{H}_2(g, 1 \text{ bar})$$

right $- 2 \times$ left

$$\text{Zn}^{2+}(aq, a = 1) + \text{H}_2(g, 1 \text{ bar}) = \text{Zn(s)} + 2 \text{H}^+(aq, a = 1).$$
Similarly, the zero-current potential for the cell,
\[ \text{Pt} \mid H_2(g, 1 \text{ bar}) \mid H^+(aq, a = 1) \parallel Cu^{2+}(aq, a = 1) \mid Cu(s) \]
is the standard reduction potential for the \( Cu \mid Cu^{2+} \) electrode. The reactions for this cell are as follows:

right \[ Cu^{2+}(aq,a=1) + 2 e^- = \text{Cu}(s) \]
left \[ H^+(aq,a=1) + e^- = \frac{1}{2} H_2(g,1 \text{ bar}) \]
right \(-2 \times\) left \[ Cu^{2+}(aq,a=1) + H_2(g,1 \text{ bar}) = \text{Cu}(s) + 2 H^+(aq,a=1). \]

If the Pt electrodes of these two cells are connected together to make a combined cell as follows:
\[ \text{Zn}(s) \mid \text{Zn}^{2+}(a = 1) \parallel H^+(a = 1) \parallel H_2(1 \text{ bar}) \parallel Pt \mid H_2(1 \text{ bar}) \parallel H^+(a = 1) \parallel Cu^{2+}(a = 1) \mid Cu(s) \]
Then, because the potential of the Zn cell is reversed and the potentials of the two cells add, we must have
\[ E = E^0(\text{Cu}^{2+},\text{Cu}) - E^0(\text{Zn}^{2+},\text{Zn}) \]

If the reaction for the defining cell for the standard Zn \( \mid \text{Zn}^{2+} \) electrode is subtracted from the corresponding cell reaction for the \( Cu \mid Cu^{2+} \) cell, the result will be found to be the cell reaction for the Daniell cell. This is consistent with the fact that in the center of the combined cell, \( H^+ \) is reduced to \( H_2 \) and then oxidized back to \( H^+ \). We could therefore leave these cancelling half-reactions out of the cell to give the Daniell cell, as follows:
\[ \text{Zn}(s) \mid \text{Zn}^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s) \]

What we have discovered is that to obtain the standard potential for an electrochemical cell from the cell diagram, it is only necessary to subtract the standard reduction potential for the left-hand electrode from the standard reduction potential for the right-hand electrode. That is,
\[ E^0 = E^0(\text{right}) - E^0(\text{left}) = E^0_R - E^0_L \]

If this rule is applied to the defining cell for the standard reduction potential for the Zn \( \mid \text{Zn}^{2+} \) electrode, we find that
\[ E^0 = E^0(\text{Zn}^{2+},\text{Zn}) - E^0(\text{H}^+,\text{H}_2) \]

But this \( E^0 = E^0(\text{Zn}^{2+},\text{Zn}) \). Evidently, our definition of the standard reduction potential is equivalent to defining the standard reduction potential for the \( Pt \mid H_2 \mid H^+ \) electrode to be zero. This can be seen another way by setting up the defining cell for the standard reduction potential
for this cell. The right-hand and left-hand electrodes of this cell are the same, so the cell potential must be zero. That is, by definition,

\[ E^0(H^+, a=1, H_2(g), 1 \text{ bar}) \equiv 0 \]

It is worth noting that the standard potential for a cell is obtained by simple subtraction of the standard reduction potential for the left-hand electrode from the standard reduction potential for the right-hand electrode. There is no multiplication by integers to make the number of electrons equal, as is required to obtain the cell reaction. The reason for this is that electrode potentials are defined to be *intensive* properties, like the density and the molar volume, rather than *extensive* properties, like the enthalpy, entropy, and free energy (note the \( n \) in the equation, \( \Delta G^o = -nFE^0 \)).

The rule that \( E^0 = E_R^0 - E_L^0 \) is consistent with considerations of Gibbs free energy changes also, if we make one more definition. We write for

\[
\text{Zn}^{2+}(aq, a=1) + 2 e^- = \text{Zn}(s)
\]

\( \Delta G_L^o = \Delta G_f^o(\text{Zn}(s)) - \Delta G_f^o(\text{Zn}^{2+}(aq)) \)

and for

\[
\text{Cu}^{2+}(aq, a=1) + 2 e^- = \text{Cu}(s)
\]

\( \Delta G_R^o = \Delta G_f^o(\text{Cu}(s)) - \Delta G_f^o(\text{Cu}^{2+}(aq)) \)

We have ignored the effect of the electron in writing the Gibbs free energy changes. This can be done because the electrons cancel when the equations are combined. Since subtracting the left-hand equation from the right-hand equation gives the cell reaction, it must be true that

\[
\Delta G^o = \Delta G_R^o - \Delta G_L^o
\]

Then, since \( \Delta G^o = -nFE^o \), \( \Delta G_R^o = -nFE_R^o \), and \( \Delta G_L^o = -nFE_L^o \), it must be true that

\[ E^o = E_R^o - E_L^o. \]

Another instructive example is provided by the cell,

\[ \text{Pt} | \text{Fe}^{2+}, \text{Fe}^{3+} | \text{Zn}^{2+} | \text{Zn} \]

(The \( aq \) and \( s \) indications have been omitted for simplicity.) For this cell, the electrode reactions and standard Gibbs free energy changes are

\[ \text{Fe}^{3+} + e^- = \text{Fe}^{2+} \quad \Delta G_L^o = -1FE_L^o \]

and
because the number of electrons in the first reaction is 1, while the number of electrons in the second reaction is 2. To form the cell reaction, we must multiply the \( \text{Fe}^{3+} , \text{Fe}^{2+} \) reaction by 2 before it is subtracted from the \( \text{Zn}^{2+} , \text{Zn} \) reaction in order to eliminate electrons during the subtraction of the first reaction from the second. Therefore, the Gibbs free energy change for the cell is given by

\[
\Delta G^\circ = \Delta G_R^\circ - 2\Delta G_L^\circ
\]

After substitution of the electrode potentials,

\[
-2FE^0 = -2FE_R^0 - 2(-FE_L^0)
\]

or

\[
E^\circ = E_R^\circ - E_L^\circ
\]

Therefore, even when the two electrode reactions have differing numbers of electrons, the overall cell potential is still the simple difference of the electrode potential for the right-hand electrode minus the electrode potential for the left-hand electrode. This shows again that electrode potentials are intensive properties (independent of the amount of substance), while Gibbs free energies are extensive properties (proportional to the amount of substance).

3. Calculation of cell potentials

The tables of standard reduction potentials simplify calculation of electrode potentials. We use a simple example to show two ways of carrying out the calculation. Consider the following cell

\[
\text{Zn}(s) | \text{Zn}^{2+}(aq,a=0.02) | \text{Fe}^{2+}(aq,a=0.05),\text{Fe}^{3+}(aq,a=0.10) | \text{Pt}
\]

For this cell, the reaction for the right-hand electrode, written as a reduction, is

\[
\text{Fe}^{3+}(aq,a=0.10) + e^- = \text{Fe}^{2+}(aq,a=0.05)
\]

while the reaction for the left-hand electrode, also written as a reduction, is

\[
\text{Zn}^{2+}(aq,a=0.02) + 2e^- = \text{Zn}(s)
\]

For the cell reaction, we first multiply the equation for the right-hand (RH) electrode by 2 to balance the number of electrons in left-hand (LH) electrode reaction. Then, we subtract the LH reaction from the RH reaction to obtain

\[
2\text{Fe}^{3+}(aq,a=0.10) + \text{Zn}(s) = 2\text{Fe}^{2+}(aq,a=0.05) + \text{Zn}^{2+}(aq,a=0.02)
\]

The activity quotient for this reaction is
\[ Q = \frac{a(Fe^{2+})^2 \cdot a(Zn^{2+})}{a(Fe^{3+})^2 \cdot a(Zn)} = \frac{(0.05)^2 \cdot (0.02)}{(0.10)^2 \cdot (1)} = 0.0050 \]

Then, to obtain the cell potential we need the Nernst equation in one of the forms,

\[ E = E^o - \frac{25.7 \text{ mV}}{V} \ln Q = E^o - \frac{59.2 \text{ mV}}{V} \log_{10} Q \]

We use \( E^o = E^o_R - E^o_L \) to obtain \( E^0 \) and obtain the standard reduction potentials from a table such as Table 6.1 in Atkins text.

\[ E^o_R = E^o(Fe^{3+}, Fe^{2+}) = 0.77 \text{ V} \]

and

\[ E^o_L = E^o(Zn^{2+}, Zn) = -0.76 \text{ V} \]

so that

\[ E^o = 0.77 - (-0.76) = 1.53 \text{ V} \]

Then, since \( \nu = 2 \) for the cell reaction (after multiplication of the RH reaction by 2, both electrode reactions contained 2 e\(^-\)),

\[ E = 1.53 \text{ V} - \frac{25.7 \times 10^{-3} \text{ V}}{2} \ln(0.005) = 1.598 \text{ V} \]

A second technique allows one to bypass writing the cell reaction. Only the electrode reactions have to be written (or examined in a table of reduction potentials, such as Table 6.1 in Atkins text). We write for the right-hand electrode reaction

\[ E_R = E^o_R - \frac{RT}{V_R F} \ln Q_R = E^o_R - \frac{0.0257 \text{ V}}{V_R} \ln Q_R \]

The right-hand electrode reaction for our example is

\[ Fe^{3+}(aq,a=0.10) + e^- = Fe^{2+}(aq,a=0.05) \]

for which \( E^o_R = 0.77 \text{ V} \), \( V_R = 1 \), and

\[ Q_R = \frac{a(Fe^{2+})}{a(Fe^{3+})} = \frac{0.05}{0.10} = 0.50 \]

so that
Now, for the left-hand electrode reaction,

\[ E_L = E_L^o - \frac{RT}{\nu_L} \ln Q_L = E_L^o - \frac{0.0257 \, \text{V}}{\nu_L} \ln Q_L \]

The left-hand electrode reaction in our example is

\[ \text{Zn}^{2+}(aq, a=0.02) + 2 \, \text{e}^- = \text{Zn}(s) \]

for which \( E_L^o = -0.76 \, \text{V}, \nu_L = 2 \), and

\[ Q_L = \frac{a(\text{Zn})}{a(\text{Zn}^{2+})} = \frac{1}{0.02} = 50 \]

so that

\[ E_L = -0.76 \, \text{V} - \frac{0.0257 \, \text{V}}{2} \ln(50) = -0.810 \, \text{V}. \]

Then,

\[ E = E_R - E_L = 0.788 \, \text{V} - (-0.810 \, \text{V}) = 1.598 \, \text{V} \]

which is the same as the result obtained by the first method.

D. **Special galvanic cells**

1. **Concentration cells**

Examination of the Nernst equation,

\[ E = E^o - \frac{25.7 \, \text{mV}}{\nu} \ln Q, \]

shows that if all the cell reactants and products are in their standard states (i.e., all activities = 1), then the cell potential is equal to the standard cell potential.

By contrast, if the left-hand and right-hand electrode reactions are the same, then \( E^o = 0 \) and

\[ E = - \frac{25.7 \, \text{mV}}{\nu} \ln Q \]

Furthermore, the activity quotient \( Q \) will have the activities of the same species in the numerator and denominator. If the corresponding activities in the numerator and denominator are the same,
$Q = 1$, and $E = 0$. But, if the activities of the species in the right-hand electrode compartment are different from the activities of the species in the left-hand compartment, then $E \neq 0$. This type of cell is known as a concentration cell.

If such a cell is composed of simple metal/metal ion electrodes,

$$M(s) | M^+(aq,a=a_L) | M^+(aq,a=a_R) | M(s)$$

Then,

$$Q = \frac{a_L}{a_R}$$

If $a_R > a_L$, then $E > 0$. This follows by Le Chatelier's Principle, because if $a_R > a_L$, then a reduction process in the right-hand compartment is more likely and our convention is such that if reduction occurs in the right-hand compartment (i.e., the cathode is in the right-hand compartment), then $E > 0$.

2. Thermodynamic data from cell potentials

a) Equilibrium constants from standard reduction potentials

If the activities of the reactants and products in the cell reaction are such that the cell reaction is at equilibrium, then $Q = K$, the equilibrium constant. But, also, $\Delta G = -nFE = 0$, so $E = 0$. In this case,

$$0 = E^o - \frac{RT}{\nu F} \ln K$$

or

$$\ln K = \frac{\nu F E^o}{RT}$$

This equation can be used to determine the equilibrium constant for the cell reaction from $E^o$ data obtained from a table.

b) Thermodynamic data from cell potentials

Consider the following cell:

$$Ag(s) | Ag^+(aq,a=1) | Br^-(aq,a=1) | AgBr(s) | Ag(s)$$

The electrode reactions and the cell reaction are

RH

$$AgBr(s) + e^- = Ag(s) + Br(aq)$$

LH

$$Ag^+(aq) + e^- = Ag(s)$$
\[ \text{RH} - \text{LH} \quad \text{AgBr}(s) = \text{Ag}^{+}(aq) + \text{Br}^{-}(aq) \]

The equilibrium constant for the cell reaction (RH–LH) is the solubility product constant for AgBr. But, as shown in the previous section, the equilibrium constant for the cell reaction can be determined from the standard cell potential. Now, the standard cell potential \( E^{\circ} \) in this case is the experimentally measurable potential \( E \) of the cell diagrammed, because all of the activities are 1. By repeating the cell potential measurement at several temperatures, the equilibrium constant is obtained at several temperatures. We showed earlier in the term that measurement of an equilibrium constant at several temperatures can be used to obtain the standard Gibbs free energy change as a function of temperature, which can be used in turn to obtain the standard enthalpy and standard entropy changes for the reaction.

3. **pH from cell potential measurements**

The standard method of measurement of pH is to use a pH meter, which uses a specialized cell potential measurement made after dipping two special electrodes in the desired solution. To show how this might work, consider the following cell

\[ \text{Pt} | \text{H}_2(g,p) | \text{H}^+(aq,a) | \text{Cl}^-(aq,a=1) | \text{Hg}_2\text{Cl}_2(s) | \text{Hg}(l) \]

For this cell,

\[ E = E_{cal}^{\circ} - E_L \]

where \( E_{cal}^{\circ} \) is the standard electrode potential for the so-called calomel electrode. Calomel electrodes are made with various concentrations of Cl\(^-\), usually from KCl. The potentials for these electrodes have been carefully measured and they are often used for reference electrodes.

For the cell just diagrammed, the electrode reaction for the left-hand electrode is

\[ \text{H}^+(aq,a) + \text{e}^- = \frac{1}{2} \text{H}_2(g,p) \]

For this electrode,

\[ E_L = E_{cal}^{\circ} - \frac{RT}{F} \ln Q_L \]

where

\[ Q_L = \frac{a(H_2)^{1/2}}{a(H^+)} = \left( \frac{p_{H_2}/1\text{ bar}}{a(H^+)} \right)^{1/2} \]

The standard electrode potential for the H\(^+\)/H\(_2\) reaction is zero by definition. Also, if the pressure of hydrogen is 1 bar,
\[ \frac{RT}{F} \ln Q_L = -\frac{RT}{F} \ln a(H^+) = 59.2 \text{ mV} \times \text{pH} \]

where the constant 59.2 mV = (ln 10) \( RT/F \) at 25 °C. Thus, the measured cell potential for the cell diagrammed at the beginning of this section is

\[ E = E_{cal}^o - 59.2 \text{ mV} \times \text{pH} \]

if the hydrogen gas is supplied to the cell at 1 bar pressure. This shows how a galvanic cell could be used to measure pH. The need for hydrogen gas makes this an inconvenient cell for routine pH measurement, so other more convenient pH-sensitive electrodes have been developed. The various manufacturers each have their own proprietary cell for this purpose.

E. Applications of standard electrode potentials

1. The direction of an oxidation-reduction reaction

The direction of reaction for an oxidation/reduction process for reactions involving species with near unit activity can be predicted from the standard electrode potentials of the two half reactions that make up the overall reaction. The rules for these predictions can be given in various ways. In Atkins text a rule is

"A species with a low reduction potential has a thermodynamic tendency to reduce a species with a high reduction potential."

Thus, the reduced form of a species with a low reduction potential is a strong reducing agent. The opposite is also true: the oxidized form of a species with a high reduction potential is a strong oxidizing agent.

Application of this rule is easy when a Table such as Table 6.1 in Atkins text is available. The electrode reactions, written as reductions, are printed in decreasing order of their standard electrode potential. In this table, cell reactions combine two electrode reactions in a clockwise direction if the species are present in near unit activity.

For example, two entries in the table are the following:

\[ \text{MnO}_4^- + 8 \text{H}^+ + 5 \text{e}^- = \text{Mn}^{2+} + 4 \text{H}_2\text{O} \quad E^o = 1.51 \text{ V} \]

\[ \text{I}_2 + 2 \text{e}^- = 2 \text{I}^- \quad E^o = 0.54 \text{ V} \]

The upper reaction goes right as the lower reaction goes left. The motion is clockwise. To obtain the overall reaction, first balance the number of electrons (in this case, multiply the upper
equation by 2 and the lower equation by 5). Then, subtract the lower equation from the upper. In this case, the result is

$$2 \text{ MnO}_4^- + 16 \text{ H}^+ + 10 \text{ I}^- = 2 \text{ Mn}^{2+} + 8 \text{ H}_2\text{O} + 5 \text{ I}_2$$

The standard electrode potentials predict a strong tendency for this reaction to go the right.

For those who have trouble remembering the rule, it is useful to commit one cell reaction to memory. A convenient reaction for this purpose is the Daniell cell reaction, obtained from

$$\text{Cu}^{2+} + 2 \text{ e}^- = \text{Cu} \quad E^0 = 0.34 \text{ V}$$

$$\text{Zn}^{2+} + 2 \text{ e}^- = \text{Zn} \quad E^0 = -0.76 \text{ V}$$

Metallic zinc displaces Cu from Cu$^{2+}$ solution, so the Cu reaction goes right while the Zn reaction goes left, a clockwise motion. One remembered reaction gives the rule for the entire table.

2. **The Electrochemical series**

Just as we have seen that Zn metal reduces Cu$^{2+}$ ion, it is possible to arrange the metals in decreasing order of reducing power (note that this is the opposite order of the arrangement in decreasing electrode potential). Of the common elements this puts K at the top followed by Ca, Na, Mg, etc., with Ag, Pt, and Au at the bottom. A more complete series is shown in Table 6.2 in the Atkins text. In this table, the metals at the top tend to reduce the ions of the metals below them. Thus, Al can reduce Ni$^{2+}$.

Hydrogen is normally placed in the electrochemical series and metals above hydrogen (more negative electrode potentials) can reduce H$^+$ to H$_2$. There are some practical limitations to the prediction of which metals will react with H$^+$ to produce H$_2$. One limitation is that H$^+$ is normally present in very low concentration ($1 \times 10^{-7}$ in pure water). This decreases the standard electrode potential required to produce hydrogen gas (the effect is 0.41 V in pure water). A second practical complication is the phenomenon of overvoltage, which is a surface effect that decreases the apparent reducing power of many metals. Overvoltage is a rate effect in that some step in the electrode reaction is slow.