Chapter 19

Electrochemistry

Concept Check 19.1
If you were to construct a wet cell and decided to replace the salt bridge with a piece of copper wire, would the cell produce sustainable current? Explain your answer.

Solution
No sustainable current would flow. The wire does not contain mobile positively and negatively charged species that are necessary to balance the accumulation of charges in each of the half-cells.

Concept Check 19.2
Let us define the reduction of I\(_2\) to I\(^-\) ions, I\(_2\)(s) + 2e\(^-\) \rightarrow 2I\(^-(aq)\), as the standard reduction reaction with \(E^\circ = 0.00\) V. We then construct a new standard reduction table based on this definition.

a. What would be the new standard reduction potential of H\(^+\)?

b. Would using a new standard reduction table change the measured value of a freshly prepared voltaic cell made from Cu and Zn? (Assume you have the appropriate solutions and equipment to construct the cell.)

c. Would the calculated voltage for the cell in part b be different if you were using the values presented in Table 19.1? Do the calculations to justify your answer.

Solution
a. Standard reduction potentials are measured against some arbitrarily chosen standard reference half-reaction. Only differences in potentials can be measured. A voltaic cell made from H\(_2\) and I\(_2\), and corresponding solutions, will have the same voltage, regardless of the choice of the reference cell. If the I\(_2\)/I\(^-\) half-reaction is assigned a value of \(E^\circ = 0.00\)
V, then the H₂/H⁺ half-reaction must have a voltage of \( E^\circ = -0.54 \) V to keep the overall voltage the same.

b. The voltage of a voltaic cell made from Cu and Zn, and corresponding solutions, will have the same measured voltage, regardless of the choice of the reference half-reaction.

c. The calculated voltage is 1.10 V and is the same either way.

**Concept Check 19.3**

Consider the voltaic cell, \( \text{Fe}(s) \| \text{Fe}^{2+}(aq) \| \text{Cu}^{2+}(aq) \| \text{Cu}(s) \), being run under standard conditions.

a. Is \( \Delta G^\circ \) positive or negative for this process?

b. Change the concentrations from their standard values in such a way that \( E_{\text{cell}} \) is reduced.

Write your answer using the shorthand notation of Section 19.3.

**Solution**

a. Using the standard reduction potentials in Table 19.1, you see that the voltage for this cell is positive, suggesting that \( \Delta G^\circ \) is negative.

b. In order to reduce \( E_{\text{cell}} \), you change the concentrations in a manner to increase the value of Q, where

\[
Q = \frac{[\text{Fe}^{2+}]}{[\text{Cu}^{2+}]} \]

For example: \( \text{Fe}(s)\|\text{Fe}^{2+} (1.10 \text{ M})\|\text{Cu}^{2+}(0.50 \text{ M})\|\text{Cu}(s) \).

**Concept Check 19.4**

Keeping in mind that seawater contains a number of ions, explain why seawater corrodes iron much faster than freshwater.

**Solution**

Many of the ions contained in seawater have very high reduction potentials – higher than \( \text{Fe}(s) \). This means that spontaneous electrochemical reactions will occur with the \( \text{Fe}(s) \) causing the iron to form ions and go into solution, while at the same time, the ions in the sea are reduced and plate out on the surface of the iron.

**Conceptual Problem 19.25**

Keeping in mind that aqueous Cu²⁺ is blue and aqueous Zn²⁺ is colorless, predict what you would observe over a several day period if you performed the following experiments.

a. A strip of Zn is placed into a beaker containing aqueous Zn²⁺.
b. A strip of Cu is placed into a beaker containing aqueous Cu\textsuperscript{2+}.
c. A strip of Zn is placed into a beaker containing aqueous Cu\textsuperscript{2+}.
d. A strip of Cu is placed into a beaker containing aqueous Zn\textsuperscript{2+}.

**Solution**

a. Since there is no species present to donate or accept electrons other than zinc, you would expect no change.
b. Since there is no species present to donate or accept electrons other than copper, you would expect no change.
c. According to the table of standard reduction potentials, the Cu\textsuperscript{2+} would undergo reduction and the Zn would undergo oxidation. You would expect the Zn strip to dissolve as it becomes Zn\textsuperscript{2+}, the blue color of the solution to fade as the Cu\textsuperscript{2+} becomes Cu, and the formation of the solid copper precipitate.
d. According to the table of standard reduction potentials, since Zn\textsuperscript{2+} cannot oxidize Cu, you would expect no change.

**Conceptual Problem 19.26**

You are working at a plant that manufactures batteries. A client comes to you and asks for a 6.0-V battery that is made from silver and cadmium. Assuming that you are running the battery under standard conditions, how should it be constructed?

**Solution**

You could construct the battery by hooking together, in series, five individual cells, each with $E^\circ = 1.20 \text{ V}$.

**Conceptual Problem 19.27**

The composition of the hull of a submarine is mostly iron. Pieces of zinc, called “zincs”, are placed in contact with the hull throughout the inside of the submarine. Why is this done?

**Solution**

The Zn is a sacrificial electrode, keeping the hull from undergoing oxidation by the dissolved ions in sea water. Zn works because it is more easily oxidized than Fe.
Conceptual Problem 19.28
You place a battery in a flashlight in which all of the electrochemical reactions have reached equilibrium. What do you expect to observe when you turn on the flashlight? Explain your answer.

Solution
When an electrochemical reaction reaches equilibrium, $E_{\text{cell}} = 0$, which means no current will flow and nothing will happen when you turn on the flashlight. This is typically what has occurred when you have a dead battery.

Conceptual Problem 19.29
The difference between a “heavy-duty” and a regular zinc-carbon battery is that the zinc can in the heavy-duty battery has thicker walls. What makes this battery heavy-duty in terms of output?

Solution
Since there is more zinc present, the oxidation-reduction reactions in the battery will run for a longer period of time. This assumes that the zinc is the limiting reactant.

Conceptual Problem 19.30
From an electrochemical standpoint, what metal, other than zinc, would be a reasonable candidate to coat a piece of iron to prevent corrosion (oxidation)?

Solution
Any metal that has a more negative standard reduction potential (Mg, Al, etc.) could be used, keeping in mind that group IA metals that fall into this category are too reactive to be of practical use.

Conceptual Problem 19.31
Pick a combination of two metals from the Standard Reduction Potential table (Table 19.1 or Appendix I) that would result in a cell with a potential of about $+0.90 \text{ V}$. For your answer, write both the half-reactions, write the overall balanced reaction, and calculate the cell potential for your choice.
Solution

One possible combination using two metals is a cell constructed from a Zn²⁺|Zn cathode with a voltage of -0.76 V, and an Al|Al³⁺ anode with a voltage of 1.66 V. The appropriate half-reactions are

\[
\begin{align*}
\text{Al}(s) & \rightarrow \text{Al}^{3+}(aq) + 3 \text{e}^- \quad E^{\circ}_{\text{ox}} = 1.66 \text{ V} \\
\text{Zn}^{2+}(aq) + 2 \text{e}^- & \rightarrow \text{Zn}(s) \quad E^{\circ}_{\text{red}} = -0.76 \text{ V}
\end{align*}
\]

The overall balanced reaction and cell potential is

\[
2 \text{ Al}(s) + 3 \text{ Zn}^{2+}(aq) \rightarrow 2 \text{ Al}^{3+}(aq) + 3 \text{ Zn}(s) \quad E^{\circ}_{\text{cell}} = 0.90 \text{ V}
\]

Conceptual Problem 19.32

You have 1.0 M solutions of Al(NO₃)₃ and AgNO₃ along with Al and Ag electrodes to construct a voltaic cell. The salt bridge contains a saturated solution of KCl. Complete the picture associated with this problem by

a. writing the symbols of the elements and ions in the appropriate areas (both solutions and electrodes).

b. identifying the anode and cathode.

c. indicating the direction of electron flow through the external circuit.

d. indicating the cell potential (assume standard conditions, with no current flowing).

e. writing the appropriate half-reaction under each of the containers.

f. indicating the direction of ion flow in the salt bridge.

g. identifying the species undergoing oxidation and reduction.

h. writing the balanced overall reaction for the cell.
Solution

(parts a to f) The completed diagram with all parts labeled is shown below.

![Diagram showing the cell with labeled parts and reaction equations]

Al (anode) → Al\(^{3+}\) + 3e\(^-\)

Ag\(^+\) + e\(^-\) → Ag

Ag\(^+\) + e\(^-\) → Ag

salt bridge

2.46 V

E\(^\circ\)\(_{\text{cell}}\) = E\(^\circ\)\(_{\text{cathode}}\) - E\(^\circ\)\(_{\text{anode}}\) = 0.80 V - (-1.66 V) = 2.46 V

g. The species undergoing oxidation is Al(s), and the species undergoing reduction is Ag\(^+\)(aq).

h. The balanced overall reaction is

Al(s) + 3 Ag\(^+\)(aq) → Al\(^{3+}\)(aq) + 3 Ag(s)

Conceptual Problem 19.33

The zinc–copper voltaic cell shown with this problem is currently running under standard conditions. How would the intensity of light from the bulb change if you were to

a. dissolve some additional CuSO\(_4\)(s) in the CuSO\(_4\) solution?

b. dissolve some additional Zn(NO\(_3\))\(_2\)(s) in the Zn(NO\(_3\))\(_2\) solution?
c. add H₂O to the CuSO₄ solution?
d. remove the salt bridge?

Solution

The effect of the various changes on the intensity of the light can be determined using the Nernst equation,

\[ E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{n} \log Q \]

For this reaction, \( E_{\text{cell}}^{\circ} = 1.10 \text{ V} \), \( n = 2 \), and \( Q \) is the reaction quotient.

\[ Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \]

If \( Q > 1 \), \( \log Q \) is positive, and the net result will be a decrease in cell potential and a decrease in the intensity of light. If \( Q < 1 \), \( \log Q \) is negative, and the net result will be an increase in cell potential and an increase in the intensity of light. At the start, both \([\text{Zn}^{2+}]\) and \([\text{Cu}^{2+}]\) are 1.0 \( M \), so \( Q = 1 \), and \( \log Q = 0 \), so \( E_{\text{cell}} = E_{\text{cell}}^{\circ} \).

a. If more CuSO₄(s) is dissolved in the CuSO₄ solution, \([\text{Cu}^{2+}]\) would be greater than 1, so \( Q < 1 \). The effect is to increase the intensity of light.

b. If more Zn(NO₃)₂(s) is dissolved in the Zn(NO₃)₂ solution, \([\text{Zn}^{2+}]\) would be greater than 1, so \( Q > 1 \). The effect is to decrease the intensity of light.
c. If $\text{H}_2\text{O}$ is added to the $\text{CuSO}_4$ solution, $[\text{Cu}^{2+}]$ would be less than 1, so $Q > 1$. The effect is to decrease the intensity of light.

d. If the salt bridge is removed, the circuit would not be complete, and the cell potential would be zero. No current would flow.

**Conceptual Problem 19.34**

The development of lightweight batteries is an ongoing research effort combining many of the physical sciences. You are a member of an engineering team trying to develop a lightweight battery that will effectively react with $\text{O}_2(\text{g})$ from the atmosphere as an oxidizing agent. A reducing agent must be chosen for this battery that will be lightweight, have nontoxic products, and react spontaneously with oxygen. Using data from Appendix I, suggest a likely reducing agent, being sure the above conditions are met. Are there any drawbacks to your selection?

**Solution**

The most important consideration in battery design is the spontaneity of the cell reaction since this determines the cell voltage. The half-reactions for the reduction of oxygen gas given in Appendix I are

\[
\begin{align*}
\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- & \rightarrow 4\text{OH}^- & E^\circ &= +0.40 \text{ V} \\
\text{O}_2 + 4\text{H}^+ + 4\text{e}^- & \rightarrow 2\text{H}_2\text{O} & E^\circ &= +1.23 \text{ V}
\end{align*}
\]

These represent the reduction of oxygen under basic and under acidic conditions. Thus, in basic solution, we would require an oxidation half-reaction (anode half-reaction) with a potential greater than -0.40 V to obtain a spontaneous reaction.

The density of the reducing agent is the next-most-important consideration. Hydrogen, the element with the lowest density, should certainly be considered. It does have some drawbacks, however. Because it is a gas, some method of storage needs to be developed. Liquid storage and metal hydride storage have been investigated. Storage of liquid hydrogen presents problems of safety and weight. Storage of hydrogen as a hydride is used in nickel-hydride cells presently available for portable computers, cellular phones, etc. (These batteries are rechargeable but do not use oxygen.) The metal hydride obviously adds weight to the battery. Other elements you might consider are $\text{Na}$, $\text{Li}$, $\text{Al}$, $\text{K}$, $\text{Ca}$, and $\text{Zn}$, which have favorable power-to-mass ratios. Lithium and sodium might present some disposal problems since they are very reactive metals. Batteries using aluminum with atmospheric oxygen are available.