19

Oxidation–Reduction Equilibria and Electrochemistry

Charge!

James Brudenell (Lord Cardigan)
Balaclava, 25 October 1854

T he current market prices for ancient coins are not dictated entirely
by the value of the gold, silver, or copper in them, or by the relative
scarcity of the individual issues. A gold stater of Croesus or a silver
teradrachm of Alexander, 2500 years after they were struck, can be
miniature art masterpieces in a physical condition that belies their age.
In contrast, a typical bronze or copper coin of the same period will be
corroded, pitted, and ugly, especially if it has been near moisture or damp
earth for a long time. Why does copper corrode, whereas silver and gold do
not? The answer lies in the different affinities of the three metals for their
electrons.

Under certain circumstances, a person with both gold inlays and
silver amalgam fillings in his teeth is in trouble. Every time he bites and
brings the two metals into contact, he receives a shock, which makes eating
unpleasant. Why the shock? Again, it is a matter of the different affinities
that substances have for electrons, and a flow of electrons from where they
are not particularly wanted to where they are wanted.

In this chapter we shall discuss ways in which chemical reactions can
be divided into two physically separated parts: one that gives up electrons
easily, and one that accepts them easily. If we can catch the electrons as
they flow "downhill" (to use a gravitational analogy), we may be able to
use this flow to do outside work. This is the principle of the **galvanic cell**.
Moreover, if we can find ways to push the electrons "uphill" from regions

where they are wanted to regions where they are not wanted, then we can either store the energy that this requires, for later use, or make chemical reactions take place that are normally not spontaneous. This is the principle of **electrolytic cells**.

As in previous chapters, we are interested in the concepts of spontaneity and equilibrium. Only this time, we have added a new dimension to spontaneity, that of electron flow.

19-1   HARNESSING SPONTANEOUS REACTIONS

If we open a tank of hydrogen gas at 10 atm pressure and allow the gas to escape, it will do so spontaneously. No useful work is obtained in this experiment. However, if we connect the outlet tube to a plastic bag or a piston we can lift weights, or if we place a pinwheel or windmill in the path of the outrushing gas we can convert the stored energy of the gas into mechanical work (Figure 19-1). The overall reaction is
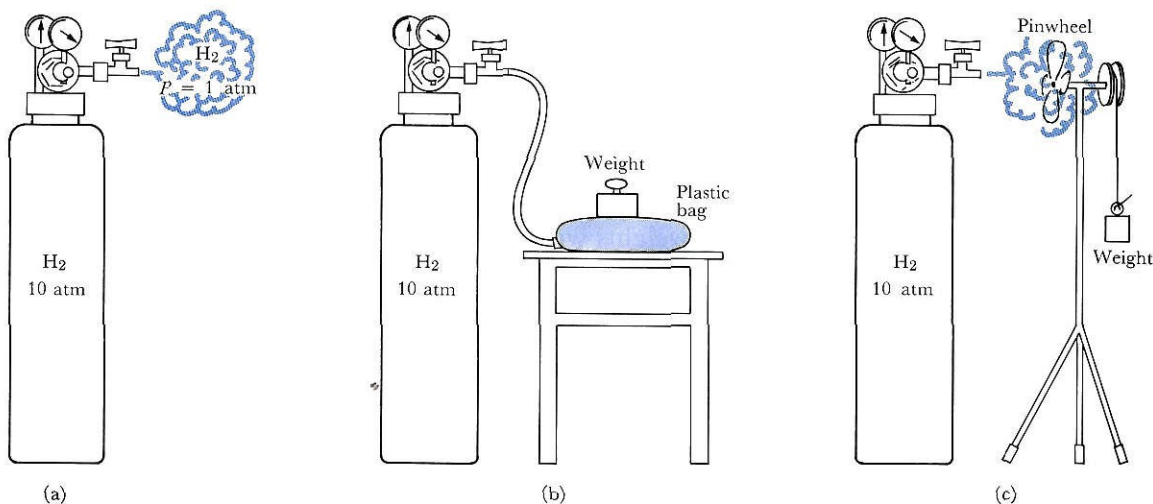
$$H_2(g, 10 \text{ atm}) \rightarrow H_2(g, 1 \text{ atm})$$
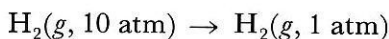

Figure 19-1   Nonproductive and productive use of the free energy stored in hydrogen gas at 10 atm pressure. (a) Expansion to 1 atm with dissipation of energy. (b) Use of part of the available free energy to lift a weight by inflating a plastic bag. (c) Use of part of the free energy to lift a weight by turning a pinwheel or windmill.

and from Chapter 16, we know the maximum free energy obtainable per mole of H_2 to be

$$\Delta G = \Delta G^0 + RT \ln (p_2/p_1)$$
$$\Delta G = 0 + RT \ln (1/10) = -RT \ln (10) = -5.706 \text{ kJ mole}^{-1}$$

(The standard free energy change for the reaction $H_2(g) \rightarrow H_2(g)$ obviously is zero.) This free energy decrease of 5.706 kJ mole^{-1} represents the *maximum* work obtainable when the process is carried out reversibly, an impractical upper limit that would take forever to reach. For any real, spontaneous, finite-time process, somewhat less than 5.706 kJ mole^{-1} of useful work will be available.

There is another way to harness the free energy of the escaping gas: through the so-called pressure cell (Figure 19-2). Although it may seem to be a somewhat artificial device, it will lead us directly to other kinds of chemical cells. The pressure cell shown in Figure 19-2 carries out the same reaction in two steps. In the left tank, hydrogen gas at 10 atm is "taken apart" into protons and electrons; in the right tank, hydrogen at 1 atm is "reassembled" from electrons and protons. However, the overall reaction still is

$$H_2(g, 10 \text{ atm}) \rightarrow H_2(g, 1 \text{ atm})$$
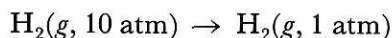
and the overall free energy yield likewise must be unchanged.
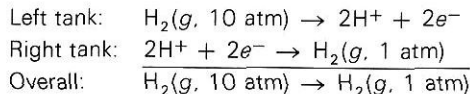
Since an excess of electrons is produced at the left electrode, and reaction at the right electrode cannot proceed without electrons, a flow of electrons from left to right occurs if the two terminals are connected with a wire. (This is analogous to opening the valve on a tank of compressed gas: high-pressure gas is converted to low-pressure gas without doing any useful work.) This tendency for electrons to flow, or this electron "pressure," is measured by a voltage difference between the two terminals. If we want to prevent electrons from flowing, we must supply an opposing voltage equal to the voltage developed by the pressure cell. Alternatively, we can use this electron "pressure" to carry out some useful task (the pressure-cell analogue of lifting weights with a windmill). In terms of the driving force for doing work, the pressure of compressed hydrogen gas has been converted into a voltage difference between an electron-rich terminal and an electron-poor terminal. For this particular cell the voltage is quite small: 0.0296 volt (V) or 29.6 millivolts (mV). Thus it is not a very useful type of cell.

Example 1

A pressure cell is set up as shown in Figure 19-2, with 10 atm pressure of H_2 on the left and 2 atm pressure on the right. Calculate the free energy change for this reaction. If cell voltage is proportional to the free energy difference, what is the voltage of this pressure cell? What would the voltage be if the H_2 pressures were 5 atm on the left and 1 atm on the right?
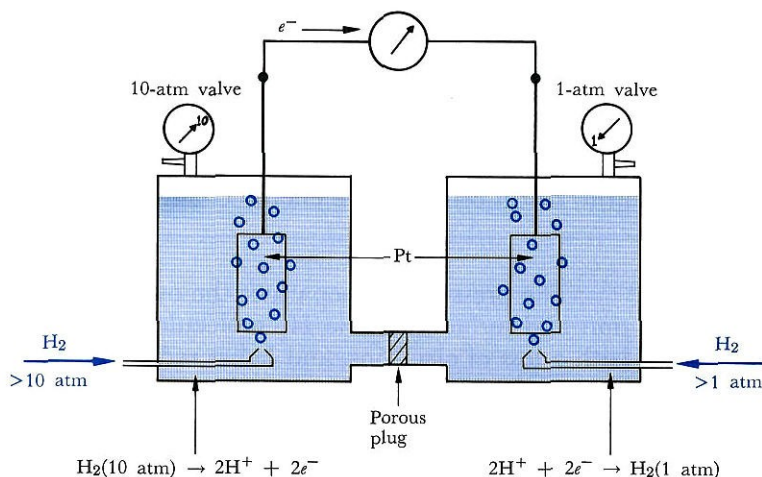
Figure 19-2   A hydrogen pressure cell for converting the free energy of expansion of H_2 at 10 atm into useful work. Two platinum electrodes are immersed in pure water (hydrogen ion concentration of 10^{-7} mole liter^{-1}) in two tanks that are connected by a channel with a porous plug, which permits ion flow but enables a pressure difference to be maintained. Hydrogen gas is bubbled over each electrode, and bleed-off valves and regulators maintain the H_2 pressure at 10 atm in the left tank and 1 atm in the right. In operation, the following reactions occur spontaneously:

Left tank: $H_2(g,\ 10\ \text{atm}) \rightarrow 2H^+ + 2e^-$

Right tank: $\underline{2H^+ + 2e^- \rightarrow H_2(g,\ 1\ \text{atm})}$

Overall: $H_2(g,\ 10\ \text{atm}) \rightarrow H_2(g,\ 1\ \text{atm})$

Electrons produced in the left-tank reaction flow through the external circuit to the right electrode, where they are used to react with hydrogen ions. (The dial with the arrow in the external electrical circuit symbolizes any current-measuring or work-producing device.) Hydroxide ions diffuse slowly through the porous plug from right to left to maintain electrical neutrality, and combine with the protons produced in the left tank.

Solution

$$\Delta G = \Delta G^0 + RT \ln \left(\frac{p_2}{p_1} \right)$$

$$= 0 + RT \ln \left(\frac{2}{10} \right)$$

$$= -3.99 \text{ kJ mole}^{-1}$$

The cell voltage is

$$\mathscr{E} = \frac{3.99 \text{ kJ}}{5.706 \text{ kJ}} \cdot 29.6 \text{ mV} = 20.7 \text{ mV}$$

Since the pressure ratio in the 5 atm/1 atm cell is the same as in the 10 atm/2 atm cell, the free energy change and voltage also will be the same.

The pressure cell separates the overall reaction into two parts: oxidation and reduction. The H_2 molecule is oxidized to H^+ in the left tank, with a loss of electrons, and H^+ is reduced to H_2 in the right tank, with a gain of electrons. The two terminals or electrodes are named according to whether electrons flow into them or out of them as observed from outside the system. Electrons flow away from the right electrode into the solution during reduction,* therefore this electrode is called the **cathode**. (*Cata-* means "away from," as in *catapult*.) Conversely, during oxidation electrons flow from the solution into the left electrode, which thus is called the **anode**. (*Ana-* means "back." For those of us for whom Greek is not a second tongue, it is easier to remember that *anode* and *oxidation* both begin with a vowel, and *cathode* and *reduction* begin with a consonant.)
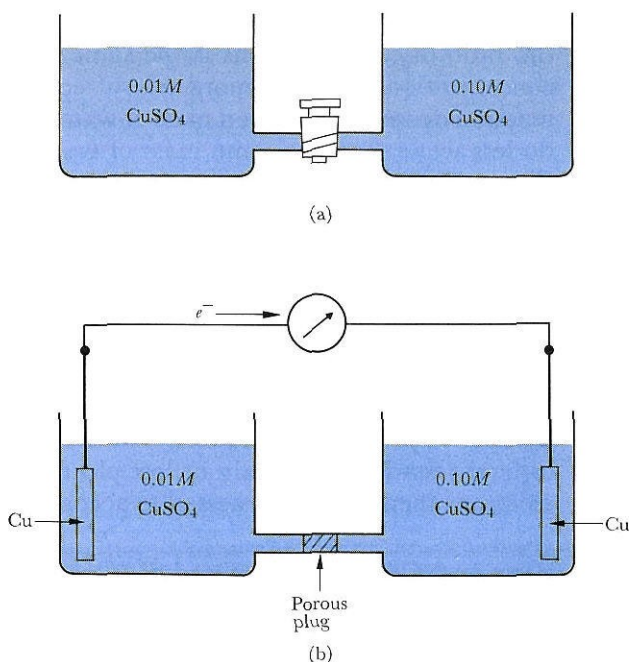
Concentration Cells

The pressure cell is a kind of concentration cell; it can generate an external flow of electrons because the concentrations of H_2 gas in the two electrode compartments are different. We can make a similar concentration cell using Cu and $CuSO_4$. If two solutions of different concentrations of copper sulfate are placed in contact, they will mix spontaneously (Figure 19-3a). We can harness this spontaneous reaction by setting up a cell such as that shown in Figure 19-3b. In the left compartment with a dilute solution, the copper electrode will be eroded slowly as copper is oxidized to form more Cu^{2+} ions. Hence, the left electrode is the anode, and it accumulates an excess of electrons. In the right compartment, with a high Cu^{2+} concentration, some of these copper ions will be reduced and Cu will deposit on the copper cathode. If the two electrodes are connected, electrons will flow from left to right through the wire, and sulfate ions will diffuse from left to right through the porous plug to maintain electrical neutrality. The dilute left compartment becomes more concentrated in $CuSO_4$, and the concentrated right compartment becomes more dilute, just as in a free-mixing process. When the two compartments reach equal concentration, electron flow stops.
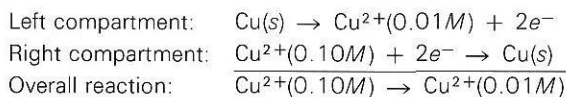
The overall reaction

$$Cu^{2+}(0.10M) \rightarrow Cu^{2+}(0.01M)$$

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*In the sense that either a negative ion is formed from a neutral substance, or a positive ion combines with the electrons and is neutralized.

(a)

(b)

Figure 19-3   Copper sulfate concentration cell. (a) When the connecting stopcock is opened, the concentrated and dilute solutions mix without yielding any useful work. (b) Concentration cell for converting the free energy of mixing into useful work. Two copper electrodes are immersed in the $0.01M$ and $0.10M$ $CuSO_4$ solutions, which are connected by a porous plug that permits slow ion flow without bulk mixing of the solutions. The following reactions occur spontaneously:

Left compartment:	$Cu(s) \rightarrow Cu^{2+}(0.01M) + 2e^-$
Right compartment:	$Cu^{2+}(0.10M) + 2e^- \rightarrow Cu(s)$
Overall reaction:	$Cu^{2+}(0.10M) \rightarrow Cu^{2+}(0.01M)$

Electrons produced in the left compartment flow through the external circuit to the right, where they react with copper ions. The solution in the left compartment gradually becomes more concentrated, and that in the right compartment, more dilute. When the concentrations become equal, no further electron flow occurs.

has a free energy change that can be calculated from the expression

$$\Delta G = \Delta G^0 + RT \ln (c_2/c_1)$$

in which c_2 and c_1 are final and initial concentrations in moles liter^{-1}. For this example,

$$\Delta G = 0 + RT \ln (0.01/0.10) = -5.706 \text{ kJ mole}^{-1}$$

The free energy change is the same as for the 10 atm H_2 pressure cell because the ratio of concentrations is the same. As the reaction proceeds and the concentrations become more nearly equal, the free energy per mole of reaction decreases. (A given mass of water dropped over a 2-ft-high dam can do less work than the same mass of water dropped over a 20-ft dam. See Figure 17-1.) The initial voltage or potential difference between electrodes is 29.6 mV, as in the H_2 cell, and gradually falls to zero as the Cu^{2+} concentrations in the two compartments become equal and the cell runs down.

19-2   ELECTROCHEMICAL CELLS

The two reactions in an electrochemical cell need not be the reverse of one another to produce a useful cell. All that is required is two substances with different tendencies to gain or lose electrons. This difference in affinity for electrons then can be harnessed to accomplish useful work.

Zinc and Copper: The Daniell (Gravity) Cell

If a piece of slightly impure zinc is placed in a solution of copper sulfate, it will slowly be pitted and eroded away. At the same time, copper will be deposited on the zinc surface as a spongy brown coating, and the characteristic blue color of the copper sulfate solution will gradually fade. The zinc spontaneously replaces the copper ions in solution by the reaction

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

because copper ions in solution have a greater affinity for electrons than do zinc ions.

Useful work can be obtained if we separate these two substances in a simple cell, as shown in Figure 19-4a. Zinc is oxidized spontaneously at the anode (left), and copper ions are reduced to the metal, which deposits on the cathode. Electrons flow through the external circuit from anode to cathode with a potential difference of 1.10 V if each of the solutions is $1M$. Anions diffuse left through the porous barrier to maintain electrical neutrality.

With a little reflection it should be apparent that neither the $ZnSO_4$ nor the copper rod is essential. Copper metal will deposit at the cathode on any other good conductor, such as a platinum wire, and the zinc sulfate solution in the anode compartment can be replaced by any other conducting salt that does not react with the zinc anode, such as sodium chloride. The porous barrier has a relatively high resistance to ion diffusion, and hence sets up a relatively high electrical resistance, which cuts down the current that can be drawn from the cell. A better method is to use a **salt bridge**, which is a glass U-tube containing an electrolyte such as KNO_3 mixed with agar or gelatin to hold it in place (Figure 19-4b).
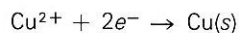
The best setup for a cell that will not be moved is to let gravity separate the solutions, with no internal barrier at all (Figure 19-4c). In this cell a

(a)

(b)   (c)
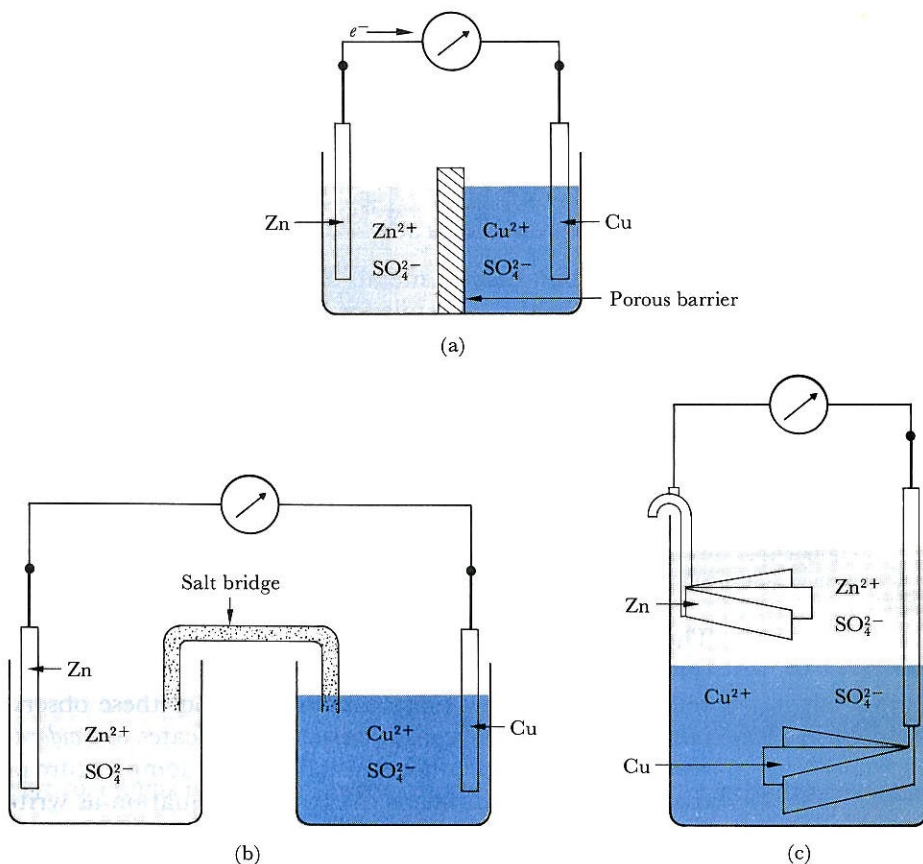
Figure 19-4   Three versions of a simple zinc—copper cell. In each case the oxidation reaction at the
                       anode at the left is

$$Zn(s) \rightarrow Zn^{2+} + 2e^-$$
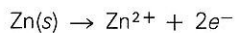
and the reduction at the cathode at the right is
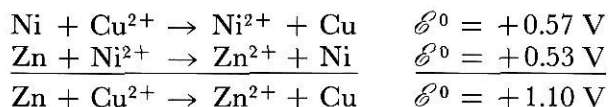
$$Cu^{2+} + 2e^- \rightarrow Cu(s)$$

The zinc anode is eaten away as copper deposits on the cathode. If $ZnSO_4$ and $CuSO_4$
are present in $1M$ concentrations, this cell develops a potential or emf of $+1.10$ V.
(a) Two solutions separated by a porous barrier. (b) Solutions separated by a salt bridge.
(c) Solutions separated by gravity in a Daniell cell, taking advantage of different solution
densities.

dilute solution of zinc sulfate is layered carefully over a concentrated, more dense copper sulfate solution. In the absence of motion or vibration the cell works quite well. Its internal resistance of almost zero makes it possible for large currents to be drawn from it. This Daniell cell was once used widely as a stationary power source in telegraph offices and for home appliances such as doorbells.

The Hydrogen Electrode

Other combinations of metals can be used in a cell similar to that shown in Figure 19-4b. If the metals are nickel and copper, nickel is oxidized at the anode, Cu^{2+} ions are reduced at the cathode, and the cell has a voltage or **electromotive force (emf)** of 0.57 V. If zinc and nickel are used, zinc is oxidized and Ni^{2+} ions are reduced, with an emf of 0.53 V (providing that the ions are at $1M$ concentration). Notice that the cell emf's are additive in the same way that the reactions are:

$$\begin{array}{ll} Ni + Cu^{2+} \rightarrow Ni^{2+} + Cu & \mathscr{E}^0 = +0.57 \text{ V} \\ \underline{Zn + Ni^{2+} \rightarrow Zn^{2+} + Ni} & \underline{\mathscr{E}^0 = +0.53 \text{ V}} \\ Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu & \mathscr{E}^0 = +1.10 \text{ V} \end{array}$$

The sum of these two cell reactions is the Zn–Cu reaction of the Daniell cell, and the sum of the two cell potentials gives the potential of the Daniell cell. (We shall draw more conclusions from these observations later.) The symbol $\mathscr{E}^0$, with the zero superscript, indicates a *standard* potential with all reacting ions at $1M$ concentrations* and a temperature of 298 K. The positive sign of the emf means that the cell equation as written is spontaneous from left to right.

An electrode reaction need not involve a metal; metals are merely particularly easy substances to shape and machine. Figure 19-5 shows a cell in which the cathode reaction is the liberation of hydrogen gas:

$$2H^+ + 2e^- \rightarrow H_2(g)$$
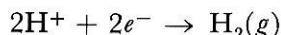
For a cell with the overall reaction

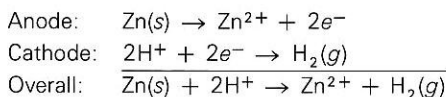$$Zn(s) + 2H^+ \rightarrow Zn^{2+} + H_2(g)$$
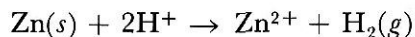
the standard emf is $+0.76$ V. If the Zn anode is replaced by Cu, and $ZnSO_4$ by $CuSO_4$, electrons flow in the other direction, from right to left, because copper ions have more of an affinity for electrons than hydrogen ions have. Copper ions are reduced spontaneously at the left electrode, which therefore becomes the cathode:

$$\text{Cathode:} \quad Cu^{2+} + 2e^- \rightarrow Cu(s)$$

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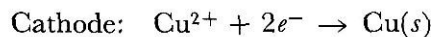
*Because solutions do not behave ideally when concentrated, the activity (or "effective concentration") really should be used instead of molarity. Standard potentials are actually defined at unit activity, rather than unit molarity. But because our goal is an understanding of basic principles rather than of laboratory technique, we shall ignore the difference between activity and molarity in this chapter.
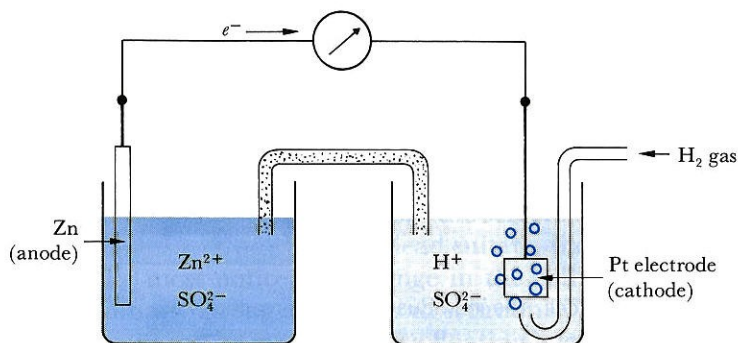
Figure 19-5 Cell with a hydrogen electrode. The two cell reactions are

Anode: $Zn(s) \rightarrow Zn^{2+} + 2e^-$
Cathode: $2H^+ + 2e^- \rightarrow H_2(g)$
Overall: $\overline{Zn(s) + 2H^+ \rightarrow Zn^{2+} + H_2(g)}$

The same overall reaction could be obtained less productively by immersing a strip of zinc in sulfuric acid. The metal would be eaten away (as at the anode in this cell) and bubbles of hydrogen gas would be given off (as at the cathode).
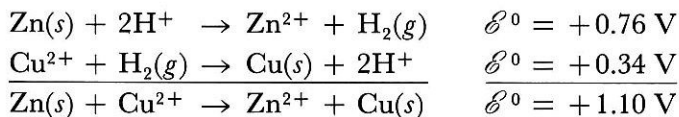
Hydrogen gas is oxidized at the anode on the right to form hydrogen ions:

Anode: $H_2(g) \rightarrow 2H^+ + 2e^-$
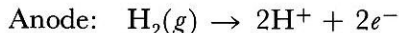
The overall spontaneous reaction is

$Cu^{2+} + H_2(g) \rightarrow Cu(s) + 2H^+$
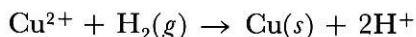
and the standard potential of this cell is $\mathscr{E}^0 = +0.34$ V. Once again, notice the additivity of cell potentials. These two hydrogen-electrode reactions can be added to produce the Daniell cell reaction, and the sum of their emf's is the emf of the Daniell cell:

$$Zn(s) + 2H^+ \rightarrow Zn^{2+} + H_2(g) \qquad \mathscr{E}^0 = +0.76 \text{ V}$$
$$\underline{Cu^{2+} + H_2(g) \rightarrow Cu(s) + 2H^+ \qquad \mathscr{E}^0 = +0.34 \text{ V}}$$
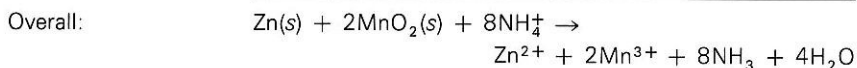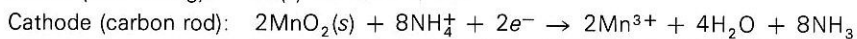$$Zn(s) + Cu^{2+} \rightarrow Zn^{2+} + Cu(s) \qquad \mathscr{E}^0 = +1.10 \text{ V}$$

The Dry Cell

Any cell that involves liquids is difficult or impossible to use in a situation involving motion. (Try to imagine a flashlight powered by a Daniell cell!) The dry cell, shown in Figure 19-6, is particularly convenient because its components are either solids or moist pastes, which are sealed tightly from the environment. The anode is the zinc casing of the dry cell itself. Around the carbon-rod cathode is a paste composed of MnO_2, NH_4Cl, and H_2O.
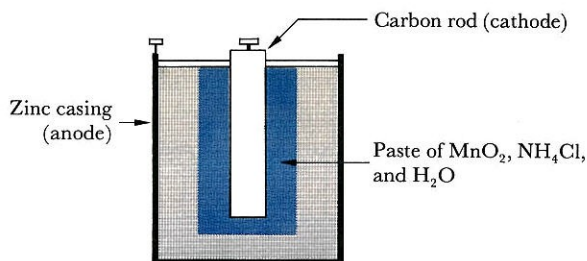
Figure 19-6

Dry cell. The individual electrode reactions are

Anode (zinc casing): $Zn(s) \rightarrow Zn^{2+} + 2e^-$

Cathode (carbon rod): $2MnO_2(s) + 8NH_4^+ + 2e^- \rightarrow 2Mn^{3+} + 4H_2O + 8NH_3$

Overall: $Zn(s) + 2MnO_2(s) + 8NH_4^+ \rightarrow$
$$Zn^{2+} + 2Mn^{3+} + 8NH_3 + 4H_2O$$

All chemical components are either solid or in the form of a paste, and the cell as a whole is sealed (hence the cell's name). Therefore, it is a highly useful cell for flashlights, radios, and other portable units.

At the anode zinc is oxidized to Zn^{2+} ions, and at the cathode MnO_2 is reduced to a mixture of several compounds of Mn in its $+3$ oxidation state. If the cell is used rapidly, ammonia, which is produced by the cathode reaction, can decrease the cell current by forming an insulating layer of gas around the carbon rod. With slower usage, zinc ions from the anode diffuse toward the cathode and combine with the ammonia to form complex ions such as $Zn(NH_3)_4^{2+}$. This is why apparently "dead" flashlight batteries sometimes can recover if allowed to rest.

Reversible Cells: The Lead Storage Battery

Most of the cells mentioned so far are reversible; that is, if a voltage greater than the cell voltage is applied from the outside, the cell reactions can be reversed, and electrical energy can be stored in the cell for withdrawal later. Thus in Figure 19-3b, if electrons are driven from right to left by an outside voltage, the $CuSO_4$ in the left compartment is made even more dilute, and the $CuSO_4$ in the right compartment is made more concentrated. In Figure 19-4c, an external voltage can cause additional Zn to deposit on the left terminal of the Daniell cell, and more copper from the right terminal to go into solution. Thus the free energy of the cell is brought to an even higher state, and at some later time this extra free energy can be released as useful work. Unfortunately, the commercial dry cell cannot be recharged in this way. The Zn^{2+} produced at the anode diffuses away, and the ammonia gas from the cathode reaction complexes with it. There is no convenient

mechanism for breaking this complex ion and sending each component back to its original position.

What is needed for rechargeability is a cell in which the electrode products stay in place at the electrodes, ready to be reconverted as the cell is charged. An example of such a cell is the lead storage battery, shown in Figure 19-7. The anode is a spongy lead screen, and when the lead is oxidized to lead sulfate, it remains in place in the screen. Similarly, when lead oxide in the cathode is reduced, also to lead sulfate, the reduction products stay in place. The most noticeable change in the cell as it discharges is a dilution of the initially strong sulfuric acid solution. Therefore, the state of charge of the battery can be measured by a floating hygrometer. This instrument records the density of the battery fluid, and hence the strength of the sulfuric acid solution. The emf of this cell is 2 V, but several cells can be connected in series to produce 6-V and 12-V storage batteries.

When the cell has run down, it can be recharged by applying an external voltage in excess of the normal emf of 2 V per cell. The reactions shown in the caption of Figure 19-7 are reversed, and the lead sulfate is converted to lead and lead oxide. If the lead sulfate fell to the bottom of the tank as the cell discharged, this reverse reaction would be impossible. But it does not; it remains in place on the grid, ready for reconversion. Therefore, the lead storage battery is a convenient device for storing electrical energy in the form of chemical free energy.
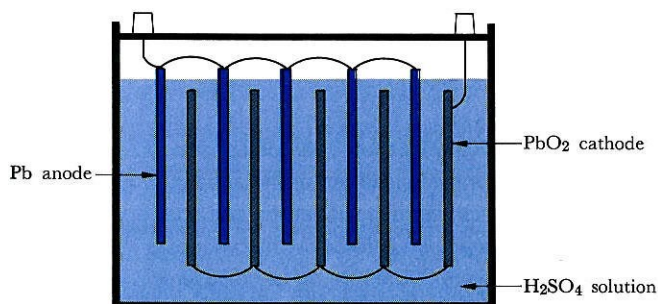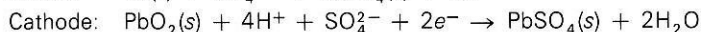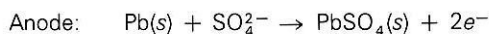

Figure 19-7   Lead storage battery. The electrode reactions are

Anode: $Pb(s) + SO_4^{2-} \rightarrow PbSO_4(s) + 2e^-$
Cathode: $PbO_2(s) + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4(s) + 2H_2O$

This battery is reversible (chargeable) since the product of the cell reaction, lead sulfate at both electrodes, adheres to the plates rather than diffusing or falling away. One cell of a lead storage battery, shown here, delivers approximately 2 V, and 6- or 12-V batteries have three or six cells connected in series.

Electrolytic Cells

The cell shown in Figure 19-8 can be used to produce high-purity copper if an external battery or other current source is used to drive the cell in a direction that it would not take spontaneously. An ingot of impure "blister" copper, which is prepared from the reduction of copper oxide (CuO) by coke (C), is suspended in a copper sulfate solution along with a "core" wire of very pure copper. Current is passed through the cell in the direction that makes the ingot the anode, and the pure wire the cathode. The ingot is eaten away, and copper ions plate out as very pure copper metal on the cathode, with the impurities settling to the bottom of the tank below the anode.

Other kinds of electrolytic cells can be used to plate gold or silver over base metals in jewelry, or to make accurate copies of engraving plates for printing. Our U.S. paper money is printed in plates of 12 notes. The engraver makes only one master engraving on steel, which is hardened and then copied by the electroplating process shown in Figure 19-9. The electrodeposited copy, called an *alto* since the engraved lines are now in relief, is then electrocopied to produce a *basso* whose intaglio lines are an exact copy of the grooves on the engraved master plate. These basso copies then are assembled into a 12-note plate that can be used either directly for printing or for making one-piece printing plates by repeating the electrocopying process.

Cells such as these, in which an external current source is used, are called *electrolytic* cells; those such as we discussed previously, which use internal chemical reactions to produce an electric current, are called *galvanic* cells. In both types of cells, the terminal at which oxidation occurs is the anode, and the cathode is the site of reduction.

Figure 19-8   Electrolytic purification of crude copper. Impure copper is oxidized at the anode, and pure copper deposits at the cathode. Impurities accumulate below the anode as "anode slime." The rare metals recovered from the anode slime, such as gold, silver, and platinum, are often valuable enough to pay for the cost of the purification process.
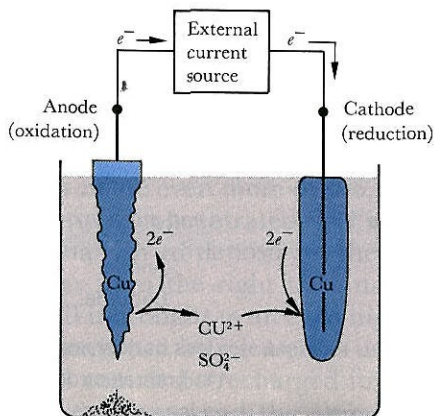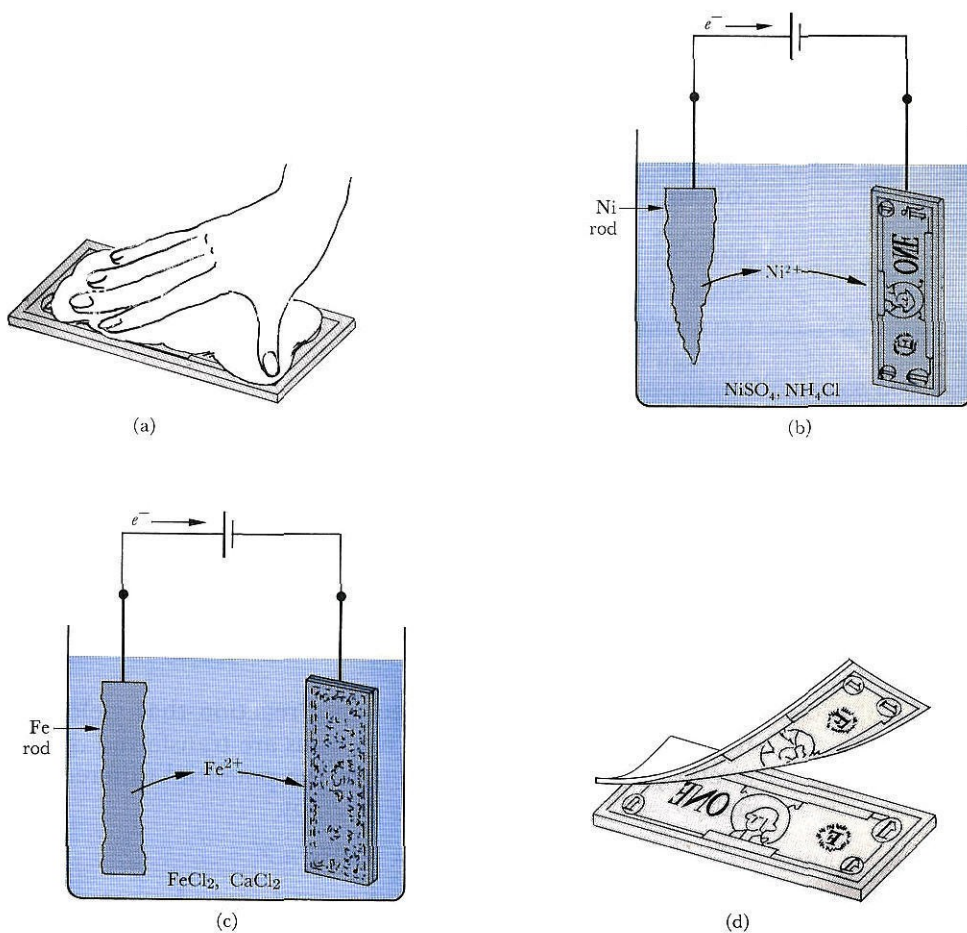
Figure 19-9   Reproducing engraved plates for U.S. currency by electrodeposition. (a) The engraved steel master plate is rubbed thoroughly with wet graphite powder and washed clean. The minute graphite coating aids electrodeposition and will make it possible to separate the master plate from the plated copy at the end. (b) The master is plated with a 0.025-mm layer of nickel during a 10-hour period. (The vertical tall and short lines at the top are the conventional sign for a battery, with the short line being the electron source—the battery anode. (c) The nickel layer is backed with a 0.1-mm layer of iron for strength, during a 14-hour electrodeposition. (d) The electrodeposited reverse image is peeled away and soldered to a steel plate. The process is repeated, starting with the reverse plate just produced, to yield a copy of the master that can be recopied or used for printing banknotes.

19-3   CELL emf AND FREE ENERGY

When a charge, q, moves spontaneously through a potential drop of $\mathscr{E}$ volts, the external electrical work that can be done on its surroundings is $w_{\text{ext}} = q\mathscr{E}$. Therefore, from equation 16-13, the free energy change of the system containing the moving electrical charge is

$$\Delta G = -w_{\text{ext}} = -q\mathscr{E} \qquad (19\text{-}1)$$

Since the electron has a negative charge, it will move spontaneously from a region of low potential to one of high potential. For one electron moving through a potential increase of $\mathscr{E}$, the free energy change is

$$\Delta G = -e\mathscr{E}$$

For a mole of electrons,

$$\Delta G = -Ne\mathscr{E} = -\mathscr{F}\mathscr{E}$$

where N is Avogadro's number and $\mathscr{F} = Ne$ is the charge on 1 mole of electrons, 96,485 coulombs or 1 faraday. In a reaction involving n electrons per molecule of reaction, or n faradays per mole, the free energy change is

$$\Delta G = -n\mathscr{F}\mathscr{E} \qquad (19\text{-}2)$$

If a galvanic cell is based on a reaction that yields ΔG kJ mole^{-1} of free energy, and if n moles of electrons are transferred through the external circuit per mole of reaction, then the potential difference between terminals, $\mathscr{E} = \mathscr{E}_{\text{cathode}} - \mathscr{E}_{\text{anode}}$ is given by

$$\mathscr{E}_{\text{cathode}} - \mathscr{E}_{\text{anode}} = \mathscr{E} = -\Delta G / n\mathscr{F}$$
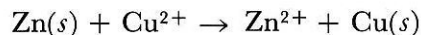
Since 1 volt-coulomb equals 1 J, equation 19-2 can be written

$$\Delta G(\text{kJ}) = -96.5\, n\mathscr{E}\,(\text{volts})$$

The pressure cell discussed in Section 19-1, for which the two-electron reaction had a standard free energy of -5.706 kJ mole^{-1}, therefore has a standard cell potential of

$$\mathscr{E}^0 = -\frac{-5.706 \text{ kJ mole}^{-1}}{2 \times 96.5 \text{ kJ mole}^{-1} \text{ V}^{-1}} = +0.0296 \text{ V}$$

The Daniell cell reaction,

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

has a standard cell potential of $+1.10$ V. Therefore, the standard free energy of this reaction must be

$$\Delta G = -2(96.5)(+1.10) = -212.3 \text{ kJ mole}^{-1}$$

In this expression $n = 2$ because two electrons are transferred per ion. You can calculate the standard free energies of other cells that we have discussed.

Example 2

Calculate the standard free energies of the Ni–Cu, Zn–Cu, and Zn–Ni cells discussed in Section 19-2. Demonstrate that the free energies are additive in the same way that the reactions and the potentials are.

Solution

$$\text{Ni–Cu cell:} \quad \mathscr{E}^0 = +0.57 \text{ V}; \Delta G = -110 \text{ kJ mole}^{-1}$$
$$\text{Zn–Ni cell:} \quad \mathscr{E}^0 = +0.53 \text{ V}; \Delta G = -102 \text{ kJ mole}^{-1}$$
$$\text{Zn–Cu cell:} \quad \mathscr{E}^0 = +1.10 \text{ V}; \Delta G = -212 \text{ kJ mole}^{-1}$$

As you can see, for a cell to deliver even $1V$ of potential difference between terminals requires a cell reaction that has a large free energy change. Since the free energies must be additive (by the first law of thermodynamics), it should not be surprising that emf's are additive also, as was explained in Section 19-2.

This additivity of emf's is represented in Figure 19-10. Recall from the discussion of free energy in Chapter 16 that we do not need to tabulate the free energy change for every possible reaction. Having once tabulated the free energy change for a certain kind of reaction, namely, the formation of
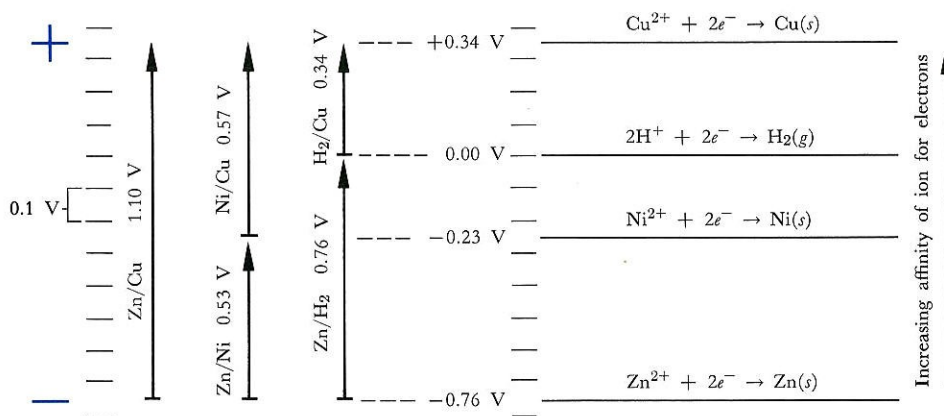

Figure 19-10   Since the potentials for the various cells involving Zn, Cu, Ni, and H_2 that we discussed previously are additive, they can be represented as additive distances along a vertical axis measured in volts. The choice of a zero potential along this axis is arbitrary, but once made, all voltages can be specified relative to this zero point. In this figure, the hydrogen electrode has been selected as the reference zero voltage. This is the standard convention in tables, although Ni, Zn, or any other electrode, could have been chosen.

Table 19-1

Standard Reduction Potentials in Acid Solution[a] at 298 K

Half-reaction (couple)	$\mathscr{E}^0$ (volts)
$F_2 + 2e^- \rightarrow 2F^-$	2.87
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.49
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21
$Br_2(l) + 2e^- \rightarrow 2Br^-$	1.09
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91
$Ag^+ + e^- \rightarrow Ag$	0.80
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56
$I_2 + 2e^- \rightarrow 2I^-$	0.54
$Cu^+ + e^- \rightarrow Cu$	0.52

[a]Values from the *Handbook of Chemistry and Physics*, 1978–9, 59th ed., Chemical Rubber Co., Cleveland, Ohio.

each compound from elements in their standard states, we can then calculate the free energy change for any reaction involving these compounds, because of the additivity of free energies. Similarly, we do not need to tabulate the potential of every conceivable cell, or of every conceivable combination of anode and cathode reactions. Instead, we need only tabulate voltages of cells in which all electrode reactions are paired with one standard electrode. This amounts to choosing an arbitrary zero in Figure 19-10. We can divide a cell reaction into two half-reactions, one at the anode and the other at the cathode, and we can assign to each half-reaction the voltage that would be observed in a cell if that half-reaction were paired with

$$H_2(g) \rightarrow 2H^+ + 2e^-$$
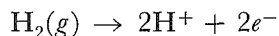
This is the basis for the scale of reduction potentials in Tables 19-1 and 19-2.

Table 19-1 continued

Standard Reduction Potentials in Acid Solution at 298 K

Half-reaction (couple)	$\mathscr{E}^{\,0}$ (volts)
$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.34
$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$2H^+ + 2e^- \rightarrow H_2$	0.00
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.41
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.41
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$Mn^{2+} + 2e^- \rightarrow Mn$	−1.03
$Al^{3+} + 3e^- \rightarrow Al$	−1.71
$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$La^{3+} + 3e^- \rightarrow La$	−2.37
$Na^+ + e^- \rightarrow Na$	−2.71
$Ca^{2+} + 2e^- \rightarrow Ca$	−2.76
$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$K^+ + e^- \rightarrow K$	−2.92
$Li^+ + e^- \rightarrow Li$	−3.05

19-4   HALF-REACTIONS AND REDUCTION POTENTIALS

The reduction potentials in Table 19-1 are the potentials that would be observed if the reduction equation as written were paired with the oxidation of hydrogen:

$$H_2(g) \rightarrow 2H^+ + 2e^-$$
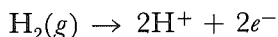
A positive sign indicates that the cell reaction will go spontaneously in the direction indicated. A negative sign means that the reverse reaction will occur; that is, the particular substance will be oxidized and protons will be reduced to hydrogen gas. The more positive the reduction potential, the greater the tendency for the substance to accept electrons and become reduced. A large negative reduction potential indicates a strong favoring of

Table 19-2

Standard Reduction Potentials in Basic Solution at 298 K

Half-reaction (couple)[a]	$\mathscr{E}^0$ (volts)
$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$	0.87
$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$	0.59
$O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$	0.40
$Co(NH_3)_6^{3+} + e^- \rightarrow Co(NH_3)_6^{2+}$	0.10
$HgO + H_2O + 2e^- \rightarrow Hg + 2OH^-$	0.10
$MnO_2 + H_2O + 2e^- \rightarrow Mn(OH)_2 + 2OH^-$	−0.05
$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$	−0.08
$Cu(NH_3)_2^+ + e^- \rightarrow Cu + 2NH_3$	−0.12
$Ag(CN)_2^- + e^- \rightarrow Ag + 2CN^-$	−0.31
$Hg(CN)_4^{2-} + 2e^- \rightarrow Hg + 4CN^-$	−0.37
$S + 2e^- \rightarrow S^{2-}$	−0.51
$Pb(OH)_3^- + 2e^- \rightarrow Pb + 3OH^-$	−0.54
$Fe(OH)_3 + e^- \rightarrow Fe(OH)_2 + OH^-$	−0.56
$Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^-$	−0.76
$SO_4^{2-} + H_2O + 2e^- \rightarrow SO_3^{2-} + 2OH^-$	−0.92
$Zn(NH_3)_4^{2+} + 2e^- \rightarrow Zn + 4NH_3$	−1.03
$Zn(OH)_4^{2-} + 2e^- \rightarrow Zn + 4OH^-$	−1.22
$Mn(OH)_2 + 2e^- \rightarrow Mn + 2OH^-$	−1.47
$Mg(OH)_2 + 2e^- \rightarrow Mg + 2OH^-$	−2.67
$Ca(OH)_2 + 2e^- \rightarrow Ca + 2OH^-$	−3.02

[a]Couples involving ions not affected by changing pH (such as $Na^+|Na$) have the same potential in acid or base.

the oxidized state. (These are *standard* values, which means a $1M$ concentration for all reacting ions and 1 atm partial pressure for gases at 298 K.)
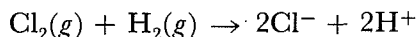
Example 3

If chlorine gas at 1 atm is bubbled over one platinum electrode in a solution of hydrochloric acid, and hydrogen gas at 1 atm is bubbled over a similar electrode, what will be the overall reaction and what will be the emf of the resulting cell?

Solution

The standard reduction potential for the reaction

$$Cl_2(g) + 2e^- \rightarrow 2Cl^-$$
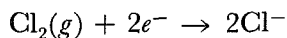
is $\mathscr{E}^0 = +1.36$ V. This means that when combined with the hydrogen electrode, the chlorine electrode is the cathode (where reduction occurs) and the hydrogen electrode is the anode. The overall reaction

$$Cl_2(g) + H_2(g) \rightarrow 2Cl^- + 2H^+$$

is spontaneous from left to right and has a standard free energy change of

$$\Delta G^0 = -n\mathscr{F}\mathscr{E}^0 = -2(96.5)(+1.36) = -262 \text{ kJ mole}^{-1} \text{ Cl}_2 \text{ or } \text{H}_2$$
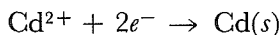
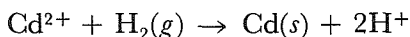Verify this free energy value from the data in Appendix 3.

Example 4

What is the spontaneous reaction when a cadmium electrode and a hydrogen electrode are paired in acid solution? What is the cell potential?

Solution

The standard reduction potential for the half-reaction

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

is -0.40 V. Thus, the overall reaction

$$\text{Cd}^{2+} + \text{H}_2(g) \rightarrow \text{Cd}(s) + 2\text{H}^+$$

is spontaneous *in reverse,* from right to left. Cadmium will be oxidized spontaneously to ions at the anode, and hydrogen ions will be reduced to hydrogen gas at the cathode. The cell potential is $+0.40$ V.

Example 5

Will a piece of cadmium, dropped into a $1M$ acid solution, produce bubbles of hydrogen gas? What about a piece of silver?

Solution

From the previous example, the reaction

$$\text{Cd}(s) + 2\text{H}^+ \rightarrow \text{Cd}^{2+} + \text{H}_2(g)$$
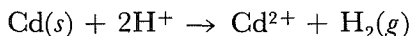
is spontaneous under standard conditions, so bubbles of hydrogen gas will escape as the cadmium metal is etched away by the acid solution. In contrast, silver has a positive reduction potential and a stronger tendency to remain reduced than hydrogen has. Thus silver, when dropped into a weak acid solution, will remain unaffected. The "nobility" of the noble metals gold, silver, and platinum is primarily a consequence of their large, positive reduction potentials.

Cell Potentials from Reduction Potentials of Half-Reactions

To find the potential of a cell in which a given reaction is occurring, first break the reaction up into its two half-reactions. Choose one of these half-reactions to be a reduction reaction at the cathode, and the other half-reaction to be an oxidation reaction at the anode. Write the second reaction in reverse, as an oxidation. Then find the standard reduction potentials for these two half-reactions and reverse the sign of $\mathscr{E}^0$ for the reaction that has

been taken as the oxidation. Add the two half-reactions as a check to be sure that you obtain the original overall reaction, and add the two half-reaction potentials at the same time. After finishing, if you have a positive overall potential, the reaction as written is spontaneous. If the overall potential is negative, you made the wrong assumption about the anode and the reverse reaction is spontaneous.
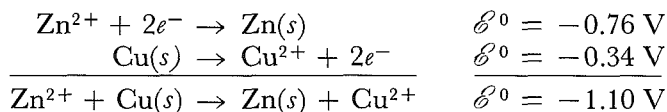
Example 6

Find the emf of a cell made up of a Zn electrode in $ZnSO_4$ and a Cu electrode in $CuSO_4$. Which is the anode and which is the cathode?

Solution

This is just the Daniell cell, and you know the answer already: the Zn electrode is the anode. But assume that you did not know this, and guessed (wrongly) that the Cu electrode was the anode. The two half-reactions are

$$Zn^{2+} + 2e^- \rightarrow Zn(s) \qquad \mathscr{E}^0 = -0.76 \text{ V}$$
$$Cu^{2+} + 2e^- \rightarrow Cu(s) \qquad \mathscr{E}^0 = +0.34 \text{ V}$$
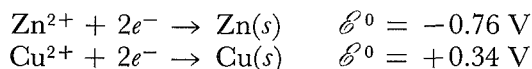
It is obvious that by reversing the Zn reaction and changing the sign of its emf we obtain a positive overall emf. Nevertheless, let's assume that the copper electrode is the anode. The two reactions to be added then are

$$Zn^{2+} + 2e^- \rightarrow Zn(s) \qquad\qquad \mathscr{E}^0 = -0.76 \text{ V}$$
$$\underline{\phantom{Zn^{2+} + 2e^-}Cu(s) \rightarrow Cu^{2+} + 2e^- \qquad\qquad \mathscr{E}^0 = -0.34 \text{ V}}$$
$$Zn^{2+} + Cu(s) \rightarrow Zn(s) + Cu^{2+} \qquad \mathscr{E}^0 = -1.10 \text{ V}$$

The negative potential tells us that the reverse reaction is spontaneous, and that the cell thus set up will have an emf of $+1.10$ V. This method is foolproof against errors in the original assumption about anode and cathode.
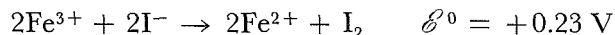
Example 7

What is the spontaneous direction in a cell made up of a ferrous–ferric ion electrode and an iodine–iodide ion electrode? What is the cell emf?

Solution

The half-reactions are

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad \mathscr{E}^0 = +0.77 \text{ V}$$
$$I_2 + 2e^- \rightarrow 2I^- \qquad \mathscr{E}^0 = +0.54 \text{ V}$$
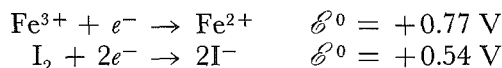
It is obvious that the way to obtain a positive overall voltage is to subtract the second half-reaction from the first, thereby reversing the sign of the 0.54-V term. The spontaneous overall reaction is

$$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2 \qquad \mathscr{E}^0 = +0.23 \text{ V}$$

In the preceding example, we had to multiply the first equation by 2 before subtracting the second equation from it because one electron was involved, whereas the iodine equation involved two. If we were subtracting free energies we would multiply the standard free energy change for the iron half-reaction by 2 before subtracting. Should we multiply the potential, $+0.77$ V, by 2 also? No, because the number of electrons has already been taken into account by n in the expressions

$$\Delta G^0 = -n\mathscr{F}\mathscr{E}^0 \qquad \text{and} \qquad \mathscr{E}^0 = -\Delta G^0/n\mathscr{F}$$

Half-cell potentials are already on a "per electron" basis and can be combined directly. To use our hydrostatic analogue again, these potentials are electron "pressures" rather than energy quantities. The pressure of water behind a dam of specified height does not depend on whether we take the water from the bottom in 1- or 2-gallon batches, but the work or energy obtained per batch does.

The factor of 2, for two electrons, will be taken into account as soon as we calculate free energy changes. For the iron half-reaction,
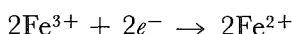
$$2Fe^{3+} + 2e^- \rightarrow 2Fe^{2+}$$
$$\Delta G^0 = -2\mathscr{F}\mathscr{E}^0 = -2(96.5)(+0.77) = -149 \text{ kJ}$$

For the iodine half-reaction,
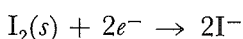
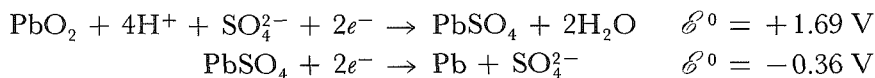$$I_2(s) + 2e^- \rightarrow 2I^-$$
$$\Delta G^0 = -2\mathscr{F}\mathscr{E}^0 = -2(96.5)(+0.54) = -104 \text{ kJ}$$

Subtracting the second half-reaction from the first, and the second free energy change from the first, we get

$$\Delta G^0 = -149 \text{ kJ} + 104 \text{ kJ} = -45 \text{ kJ}$$

As a check, verify that the value of this free energy change leads to the overall cell potential, using $\Delta G^0 = -n\mathscr{F}\mathscr{E}^0$.

Any half-reaction with a higher positive reduction potential will dominate over a half-reaction with a lower reduction potential, and send the latter in the reverse direction if the two half-reactions are coupled in a cell. Thus the two half-reactions for the lead storage battery are

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O \qquad \mathscr{E}^0 = +1.69 \text{ V}$$
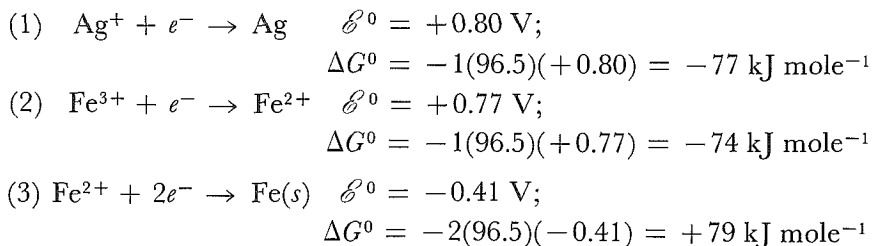$$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-} \qquad \mathscr{E}^0 = -0.36 \text{ V}$$

Since the first reaction has the higher reduction potential, it will take place at the cathode, and the reverse of the second reaction will occur at the anode. The overall cell potential will be

$$\mathscr{E}^0 = (+1.69 \text{ V}) - (-0.36 \text{ V}) = +2.05 \text{ V}$$

Ions of any metal in the reduction potential table will become reduced in the presence of a metal lower in the table. Thus silver from a silver nitrate solution will precipitate in the presence of zinc, iron, cadmium, or even

copper or mercury. In the presence of Ag^+ will iron be the ferrous ion, Fe^{2+}, or the ferric ion, Fe^{3+}?

The half-reactions from Table 19-1 are

(1) $Ag^+ + e^- \rightarrow Ag \quad \mathscr{E}^0 = +0.80$ V;

$$\Delta G^0 = -1(96.5)(+0.80) = -77 \text{ kJ mole}^{-1}$$

(2) $Fe^{3+} + e^- \rightarrow Fe^{2+} \quad \mathscr{E}^0 = +0.77$ V;

$$\Delta G^0 = -1(96.5)(+0.77) = -74 \text{ kJ mole}^{-1}$$

(3) $Fe^{2+} + 2e^- \rightarrow Fe(s) \quad \mathscr{E}^0 = -0.41$ V;

$$\Delta G^0 = -2(96.5)(-0.41) = +79 \text{ kJ mole}^{-1}$$

But why is no reaction listed for the reduction of Fe^{3+} to metallic iron? The reaction we want,

$$Fe^{3+} + 3e^- \rightarrow Fe(s)$$
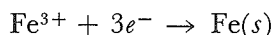
can be obtained by adding half-reactions 2 and 3. Can we find the potential by adding the potentials of these two reactions?

$$\mathscr{E}^0 = +0.77 - 0.41 = +0.36 \text{ V}$$

The answer is no; we cannot. The emf of the reduction of Fe^{3+} to $Fe(s)$ is not $+0.36$ V. It is legitimate to subtract one half-cell *potential* from another when the corresponding half-cell *reactions* are subtracted to form a correct overall cell reaction with proper balancing of electron gain and loss. It is not legitimate to add the potentials of a one-electron half-reaction and a two-electron half-reaction to obtain the potential of the resulting three-electron half-reaction.
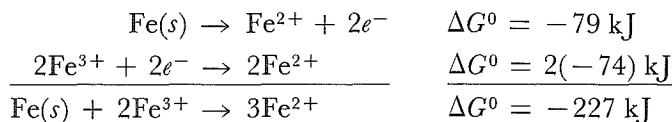
It is always safe to work with free energies, which is why we bothered to calculate free energies for the three half-reactions. In calculating free energies from cell potentials, explicit counts of electrons involved are made via the factor n in the expression $\Delta G^0 = -n\mathscr{F}\mathscr{E}^0$. Since the desired half-cell reaction is the sum of half-reactions 2 and 3, the overall free energy is the sum of the two free energies:

$$Fe^{3+} + 3e^- \rightarrow Fe(s) \quad \Delta G^0 = -74 + 79 = +5 \text{ kJ mole}^{-1}$$
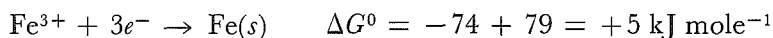
The standard emf can now be found by dividing by $-3\mathscr{F}$, since this is a three-electron reaction:
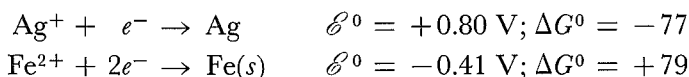
$$\mathscr{E}^0 = \frac{+5}{-3(96.5)} = -0.02 \text{ V}$$

But this is not a realistic half-reaction. If both Fe^{3+} and metallic iron were present together, they would combine spontaneously to produce Fe^{2+}, as the free energies indicate:

$$\begin{array}{ll} Fe(s) \rightarrow Fe^{2+} + 2e^- & \Delta G^0 = -79 \text{ kJ} \\ \underline{2Fe^{3+} + 2e^- \rightarrow 2Fe^{2+}} & \underline{\Delta G^0 = 2(-74) \text{ kJ}} \\ Fe(s) + 2Fe^{3+} \rightarrow 3Fe^{2+} & \Delta G^0 = -227 \text{ kJ} \end{array}$$

This is a highly spontaneous reaction with a strongly negative standard free energy change. Since a Fe–Fe^{3+} half-cell is physically unrealistic, its potential is not tabulated.

We have now answered the original question. When silver plates out from an Ag$^+$ solution in the presence of metallic iron, the iron goes into solution as Fe^{2+}. If some Fe^{3+} were present, it immediately would combine with metallic iron by the preceding reactions to make more Fe^{2+}. Thus, the two electrochemical reactions involved are
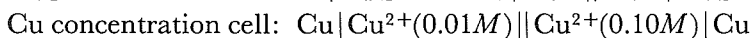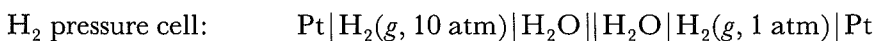
$$Ag^+ + e^- \rightarrow Ag \qquad \mathscr{E}^0 = +0.80 \text{ V}; \Delta G^0 = -77$$
$$Fe^{2+} + 2e^- \rightarrow Fe(s) \qquad \mathscr{E}^0 = -0.41 \text{ V}; \Delta G^0 = +79$$

Handling of electrode potentials can often be confusing. A safe guideline: *When in doubt, work with free energies.*

Shorthand Notation for Electrochemical Cells

In the usual abbreviated notation for a cell, the reactants and products are listed from left to right in the form

Anode│Anode solution║Cathode solution│Cathode

A single vertical line indicates a change of phase: solid, liquid, gas, or solution. A double vertical line indicates a porous barrier or salt bridge between two solutions. Thus, some of the cells we discussed would be written as follows:

H$_2$ pressure cell: Pt│H$_2$(g, 10 atm)│H$_2$O║H$_2$O│H$_2$(g, 1 atm)│Pt

Cu concentration cell: Cu│Cu^{2+}(0.01M)║Cu^{2+}(0.10M)│Cu

Daniell cell:
(in which x and y
are the molarities of
the ionic solutions)
Zn│Zn^{2+}(xM)║Cu^{2+}(yM)│Cu

Lead storage battery: Pb│H$_2$SO$_4$(aq)│PbO$_2$
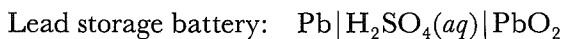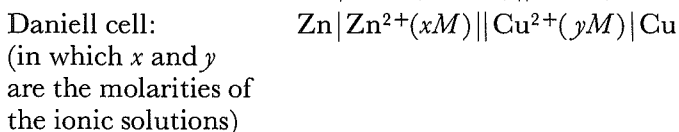
19-5 THE EFFECT OF CONCENTRATION ON CELL VOLTAGE: THE NERNST EQUATION

The reduction potentials that we have been working with so far all have been standard potentials, that is, with the concentrations of all solutes at 1 mole liter^{-1} and all gases at 1 atm partial pressure,* and at 298 K. Does the emf of a cell change with concentration? It does, for the same reasons that the free energy of the cell reaction changes. We saw special examples of this change at the beginning of this chapter in connection with concentration cells, and now we will derive a more general relationship.

*To be absolutely-correct, with all substances at unit activity.

The relationship between free energy and concentration was given by equation 16-26:

$$\Delta G = \Delta G^0 + RT \ln Q$$

in which the reaction quotient, Q, is the ratio of products to reactants, each raised to its proper stoichiometric power. We can convert this into a cell-voltage equation, using $\Delta G = -n\mathscr{F}\mathscr{E}$, to yield

$$\mathscr{E} = \mathscr{E}^0 - \frac{RT}{n\mathscr{F}} \ln Q$$

This is called the **Nernst equation** after Walther Nernst, who first proposed it in 1881. In it $\mathscr{E}^0$ is the standard cell potential, Q is the ratio of concentrations under the conditions of a given experiment, and $\mathscr{E}$ is the cell voltage measured under these same conditions. For the copper concentration cell discussed at the beginning of this chapter,

$$\Delta G = 0 + RT \ln (c_2/c_1) \;\; = 5.706 \log_{10} (c_2/c_1) \qquad \text{at 298 K}$$

$$\mathscr{E} = 0 - \frac{RT}{2\mathscr{F}} \ln (c_2/c_1) = -\frac{5.706}{2\mathscr{F}} \log_{10} (c_2/c_1)$$

The quantity $RT/\mathscr{F}$ at 298 K is encountered so often that it should be evaluated first:

$$RT/\mathscr{F} = \frac{8.314 \text{ J K}^{-1} \times 298 \text{ K}}{96{,}485 \text{ coulombs}} = 0.0257 \text{ J coulomb}^{-1}$$

$$RT/\mathscr{F} = 0.0257 \text{ V}$$

$$2.303 \, RT/\mathscr{F} = 0.0592 \text{ V}$$

The general expression then is

$$\mathscr{E} = \mathscr{E}^0 - \frac{0.0592}{n} \log_{10} Q$$

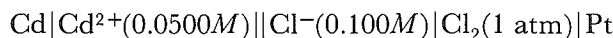and the emf of the copper concentration cell is

$$\mathscr{E} = -0.0296 \log_{10} (c_2/c_1)$$

As we calculated previously, for a concentration ratio of $1:10$ the emf is $+0.0296$ V or 29.6 mV. This value is true for *any* two-electron concentration cell with a $1:10$ concentration ratio, no matter what the chemical reaction actually is. Thus, the same voltages were calculated previously for the hydrogen cell and for the copper concentration cell. For a ratio of $1:5$ the emf of the cell is
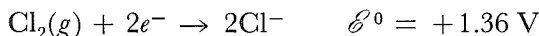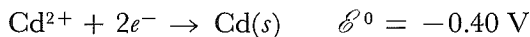
$$\mathscr{E} = +29.6 \log_{10} (5) = +20.7 \text{ mV}$$

Example 8

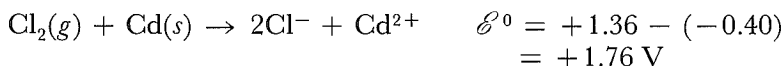What are the emf and free energy change for the cell

$$\text{Cd} | \text{Cd}^{2+}(0.0500M) \, || \, \text{Cl}^-(0.100M) | \text{Cl}_2(1 \text{ atm}) | \text{Pt}$$

Solution

The half-reactions are

$$Cd^{2+} + 2e^- \rightarrow Cd(s) \qquad \mathscr{E}^0 = -0.40 \text{ V}$$
$$Cl_2(g) + 2e^- \rightarrow 2Cl^- \qquad \mathscr{E}^0 = +1.36 \text{ V}$$

A positive overall voltage will be obtained by taking the $Cd|Cd^{2+}$ electrode to be the anode, where oxidation occurs, and subtracting it from the Cl_2 reaction to yield

$$Cl_2(g) + Cd(s) \rightarrow 2Cl^- + Cd^{2+} \qquad \begin{aligned}\mathscr{E}^0 &= +1.36 - (-0.40) \\ &= +1.76 \text{ V}\end{aligned}$$

The cell voltage at other than standard conditions is found from the expression

$$\mathscr{E} = +1.76 - \frac{0.0592}{2} \log_{10} \frac{[Cl^-]^2[Cd^{2+}]}{1 \cdot 1}$$

Chlorine gas at 1 atm and solid Cd both are in their standard states, thereby giving unit activities in the denominator. Hence,

$$\begin{aligned}\mathscr{E} &= +1.76 - 0.0296 \log_{10} [(0.100)^2(0.0500)] \\ &= +1.76 - 0.0296 \log_{10} (0.000500) \\ &= +1.76 + 0.0296(3.301) = +1.86 \text{ V}\end{aligned}$$
$$\Delta G = -2\mathscr{F}\mathscr{E} = -193(1.86) = -359 \text{ kJ}$$

Single-Electrode Potentials

It is often more convenient to deal with the concentration dependence of each half-reaction separately, and then to combine the results. The Nernst equation can be broken up by imagining that each half-reaction, oxidation and reduction, is coupled with the standard hydrogen reaction,

$$2H^+(1.0M) + 2e^- \rightarrow H_2(g, 1 \text{ atm}) \qquad \mathscr{E}^0 = 0.000 \text{ V}$$
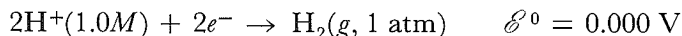
in which both H^+ and H_2 have unit activities. Thus for the $Zn^{2+}|Zn(s)$ half-reaction,

$$\mathscr{E} = -0.76 - 0.0296 \log_{10} \frac{1}{[Zn^{2+}]}$$

since the activity of solid zinc in the numerator is 1. The emf of the hydrogen electrode, $H^+|H_2(g)$, depends upon pH. If the pressure of the hydrogen gas is maintained at 1 atm then this dependence is

$$\mathscr{E} = 0.000 - 0.0592 \text{ pH}$$

(Prove to yourself that this is true.) For the half-reaction $Fe^{3+}|Fe^{2+}$,

$$\mathscr{E} = +0.77 - 0.0592 \log_{10} \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

And for the reaction

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

$$\mathscr{E} = +1.49 - 0.0118 \log_{10} \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

$$= +1.49 - 0.0118 \log_{10} \frac{[Mn^{2+}]}{[MnO_4^-]} - 0.0947 \text{ pH}$$
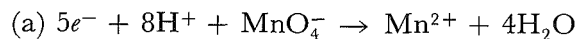
(Notice the division of 0.0592 by 5 to yield 0.0118, and the remultiplication by 8 at the right.) Therefore, any factors that affect ion concentrations will affect electrode potentials.

These individual half-reaction equations, once written properly with respect to concentrations of ions, then can be combined to form the Nernst equation for the cell as a whole.

Example 9

Write a balanced equation and calculate K_{eq} for the reaction involving the $Fe^{3+}|Fe^{2+}$ and $H^+, MnO_4^-|Mn^{2+}$ couples.
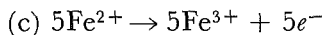
Solution   (a) $5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O$

$$\mathscr{E} = 1.49 - \frac{0.0592}{5} \log_{10} \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

(b) (reversed) $Fe^{2+} \rightarrow Fe^{3+} + e^-$
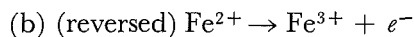
$$\mathscr{E} = -0.77 - \frac{0.0592}{1} \log_{10} \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

To provide enough electrons for a balanced equation with the manganese reaction, we must multiply the iron reaction by 5:
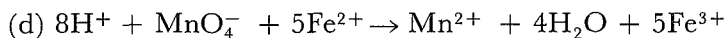
(c) $5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^-$

$$\mathscr{E} = -0.77 - \frac{0.0592}{5} \log_{10} \frac{[Fe^{3+}]^5}{[Fe^{2+}]^5}$$

Notice how the coefficients in the Fe equations have been treated in the denominator of the 0.0592 term and in the exponents within the logarithm. Recall that

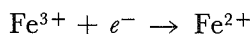$$\frac{1}{n} \log a^n = \log a$$

Now add (a) and (c):

(d) $8H^+ + MnO_4^- + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

$$\mathscr{E} = 0.72 - \frac{0.0592}{5} \log_{10} \frac{[Mn^{2+}][Fe^{3+}]^5}{[H^+]^8[MnO_4^-][Fe^{2+}]^5}$$

At equilibrium, $\mathscr{E} = 0$, and

$$\mathscr{E}_{cell}^0 = 0.72 \text{ V} = \frac{0.0592}{5} \log_{10} K_{eq}$$

$$K_{eq} = 6 \times 10^{60} = \frac{[Mn^{2+}][Fe^{3+}]^5}{[H^+]^8[MnO_4^-][Fe^{2+}]^5}$$

Notice that in considering the half-reaction

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$

the magnitude of the potential is independent of the number of times we use it in the balanced equation:

$$\mathscr{E} = \mathscr{E}^0 - 0.0592 \log_{10} \frac{[Fe^{2+}]}{[Fe^{3+}]} = \mathscr{E}^0 - \frac{0.0592}{5} \log_{10} \frac{[Fe^{2+}]^5}{[Fe^{3+}]^5}$$

Range of K_{eq} for Oxidation–Reduction Reactions

If we examine the reduction potentials in Tables 19-1 and 19-2, we find that they range from about $+3$ to -3 V. A difference of 6 V in half-reaction potentials corresponds to an equilibrium constant of 10^{100n}, in which n is the number of electrons transferred in a redox process:

$$\mathscr{E}^0 = \frac{0.0592}{n} \log_{10} K_{eq} = 6.0$$

$$\log_{10} K_{eq} \simeq 100n$$
$$K_{eq} \simeq 10^{100n}$$

This is an immensely large equilibrium constant in comparison with the maximum K_{eq} value of about 10^{14} encountered in proton-transfer reactions in aqueous solution. This large range of equilibrium-constant values within a redox potential range of 6 V means that *the chance of two half-cell potentials being close enough to establish equilibrium with significant quantities of both reactants and products present is small.* An equilibrium constant as large as 10^{20} would require only a redox potential difference of 0.59 V for a two-electron reaction. Redox reactions tend to be all-or-nothing processes, with either reactants or products present in significant amounts, but not both. For such reactions, cell emf measurements provide a convenient, practical way of determining equilibrium constants.

19-6   SOLUBILITY EQUILIBRIA AND POTENTIALS

One of the difficulties in measuring solubility products directly is that for slightly soluble salts, such as AgCl, the concentrations at equilibrium are too low to measure accurately. However, the half-reaction

$$Ag^+ + e^- \rightarrow Ag$$
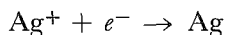
for which

$$\mathscr{E} = 0.80 - 0.0592 \log_{10} \frac{1}{[Ag^+]} = 0.80 + 0.0592 \log_{10} [Ag^+]$$
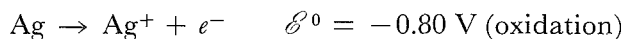
can be used to measure solubility. For example, if the silver ion concentration were as low as $10^{-30}M$ the silver electrode potential still would be -1.0 V, which is clearly within the measurable range.
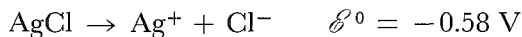

Example 10

Calculate the solubility product constant, K_{sp}, for AgCl at 298 K from appropriate couples in Table 19-1.

Solution

Begin with the two half-reactions:

$$AgCl + e^- \rightarrow Ag + Cl^- \qquad \mathscr{E}^0 = 0.22 \text{ V (reduction)}$$
$$Ag \rightarrow Ag^+ + e^- \qquad \mathscr{E}^0 = -0.80 \text{ V (oxidation)}$$

Add the reactions to obtain the equation for the solution of AgCl:

$$AgCl \rightarrow Ag^+ + Cl^- \qquad \mathscr{E}^0 = -0.58 \text{ V}$$

$\mathscr{E}^0$ is negative since the reaction goes spontaneously to the left for $1M$ Ag^+ and Cl^-. For the net reaction,

$$\Delta G^0 = -RT \ln K_{sp} = -n\mathscr{F}\mathscr{E}^0$$

($\mathscr{E}$ in the Nernst equation is zero at equilibrium.)

$$\ln K_{sp} = -\frac{1\mathscr{F}}{RT}(0.58)$$
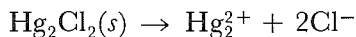
$$\log_{10} K_{sp} = -\frac{0.58}{0.0592} = -9.8$$

$$K_{sp} = 1.6 \times 10^{-10}$$

Example 11

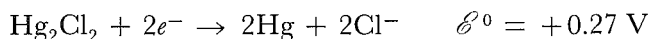Calculate K_{sp} for Hg_2Cl_2 at 298 K from data in Table 19-1.
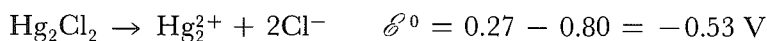
Solution

The solubility equilibrium is

$$Hg_2Cl_2(s) \rightarrow Hg_2^{2+} + 2Cl^-$$
$$K_{sp} = [Hg_2^{2+}][Cl^-]^2$$

The half-reactions for this equilibrium are

$$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^- \qquad \mathscr{E}^0 = +0.27 \text{ V}$$
$$Hg_2^{2+} + 2e^- \rightarrow 2Hg \qquad \mathscr{E}^0 = +0.80 \text{ V}$$

Adding the first half-reaction to the reverse of the second, we obtain

$$Hg_2Cl_2 \rightarrow Hg_2^{2+} + 2Cl^- \qquad \mathscr{E}^0 = 0.27 - 0.80 = -0.53 \text{ V}$$

The solubility product expression is

$$0 = -0.53 - \frac{0.0592}{2} \log_{10} K_{sp}$$
$$\log_{10} K_{sp} = -17.9$$
$$K_{sp} = 1.3 \times 10^{-18}$$

An interesting consequence of the effect of solubility on electrode potentials is revealed when we consider the reaction between silver ion and iodide ion. Table 19-1 "predicts" that silver ion should oxidize iodide ion according to the reaction

$$2Ag^+ + 2I^- \rightarrow 2Ag + I_2$$
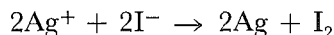
If a cell is made of the two half-reactions working separately, silver plates on the cathode and iodine forms at the anode, as predicted. However, if the two ions are mixed directly, the only reaction observed is the formation of insoluble silver iodide:

$$Ag^+ + I^- \rightarrow AgI(s)$$
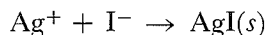
From the Nernst equation, we can show that since K_{sp} of AgI is about 10^{-16}, the potential of the $Ag^+|Ag$ couple is decreased by 16×0.0592 or nearly 1.0 V in a $1.0M$ I^- solution, whereas the $I_2|I^-$ couple has its potential increased by nearly the same amount in a $1.0M$ Ag^+ solution. Since the $I_2|I^-$ couple is only about 0.25 V below $Ag^+|Ag$, these two changes are more than enough to reverse the position of the couples in the table.

Complex-Ion Formation and Reduction Potentials

Consider the equilibrium between silver ion and cyanide ion:

$$Ag^+ + 2CN^- \rightarrow Ag(CN)_2^-$$
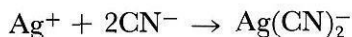
The equilibrium expression is

$$K_{eq} = \frac{[Ag(CN)_2^-]}{[Ag^+][CN^-]^2} \qquad \text{or} \qquad [Ag^+] = \frac{[Ag(CN)_2^-]}{K_{eq}[CN^-]^2}$$
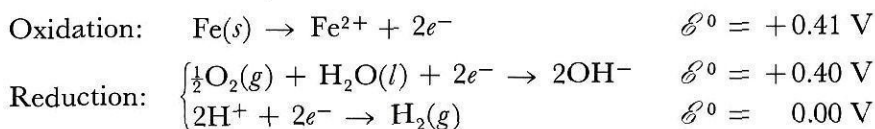
For a silver electrode immersed in a solution containing $0.01M$ silver ion with an excess of cyanide ion, virtually all of the silver ion is complexed. The potential is

$$\mathcal{E} = 0.80 + 0.0592 \log_{10} \frac{[Ag(CN)_2^-]}{K_{eq}[CN^-]^2}$$

$$= 0.80 - 0.1184 - 0.0592 \log_{10} K_{eq} - 0.1184 \log_{10} [CN^-]$$

Such relationships are used in the study of equilibria involving complex ions.

19-7   REDOX CHEMISTRY GONE ASTRAY: CORROSION

Corrosion of metals is a redox process. For example, iron can be oxidized either by molecular oxygen or by acid, if sufficient moisture is present for the chemical reactions to proceed at an appreciable rate.

Oxidation:	$Fe(s) \rightarrow Fe^{2+} + 2e^-$	$\mathcal{E}^0 = +0.41$ V
Reduction:	$\begin{cases} \frac{1}{2}O_2(g) + H_2O(l) + 2e^- \rightarrow 2OH^- \\ 2H^+ + 2e^- \rightarrow H_2(g) \end{cases}$	$\begin{aligned} \mathcal{E}^0 &= +0.40 \text{ V} \\ \mathcal{E}^0 &= 0.00 \text{ V} \end{aligned}$

When iron rusts, metallic iron is oxidized to the $+2$ state, and it is deposited as flakes of FeO or other iron oxides. Aluminum corrodes even more vigorously:

$$Al(s) \rightarrow Al^{3+} + 3e^- \qquad \mathcal{E}^0 = +1.66 \text{ V}$$
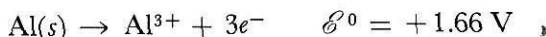
On the reduction-potential scale, aluminum is more susceptible to oxidation than iron. Yet we think of aluminum as relatively inert to corrosion, whereas the rusting of iron and steel is a serious and expensive problem. Why?

We find out why only when we look at the crystal structures of aluminum, iron, and their oxides. The unit-cell or packing distances in aluminum and its oxide are very similar to one another; thus the aluminum oxide formed at the surface of the metal can adhere tightly to the uncorroded aluminum beneath it. The oxidized surface provides a protective layer that prevents oxygen from getting to the metal beneath. "Anodized" aluminum kitchenware has had a particularly tough oxide layer applied to

it by placing the aluminum object in a situation where corrosion is especially favored—by making it the anode in an electrochemical reaction.

In contrast, the packing dimensions of metallic iron and FeO are not particularly close; thus there is no tendency for an iron oxide layer to adhere to metallic iron. The curse of rust is not that it forms, but that it constantly flakes off and exposes fresh iron surface for attack (Figure 19-11). One way to prevent rusting is to keep moisture and oxygen away from the surface of an iron object by giving it an artificial coating such as paint. A good paint adheres better than FeO does, but it still is not permanent.

Another, and more effective, method is to make electrochemistry work for you. Just as aluminum can be made to form an oxide film by making it the anode in an electrochemical cell, so iron can be *prevented* from oxidizing by making it the cathode. One way to do this is to coat it or plate it with a more reactive metal, yet one that itself forms a protective oxide coating. Aluminum would be a possible candidate. If iron and aluminum are in contact, the iron will behave as the cathode and the aluminum as the anode, as their reduction potentials indicate:

$$Fe^{2+} + 2e^- \rightarrow Fe(s) \qquad \mathscr{E}^0 = -0.41 \text{ V}$$
$$Al^{3+} + 3e^- \rightarrow Al(s) \qquad \mathscr{E}^0 = -1.66 \text{ V}$$
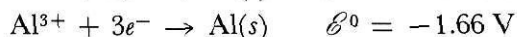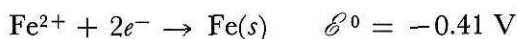
Aluminum will prevent the iron from becoming oxidized, and its own oxide will protect aluminum from continual destructive corrosion.

But if you are going to aluminum-plate iron, you might as well make the objects out of aluminum to begin with, thereby having the advantage of light weight. Unfortunately, aluminum is expensive. An earlier, and cheaper, alternative has been to "galvanize" iron, that is, to give it a thin coat of zinc. You can see from Table 19-1 that the principle is the same, although the reduction potentials of zinc and iron are closer. A galvanized steel bucket is corrosion-free, not merely because zinc shields iron as paint would, but because zinc electrochemically prevents iron from being re-
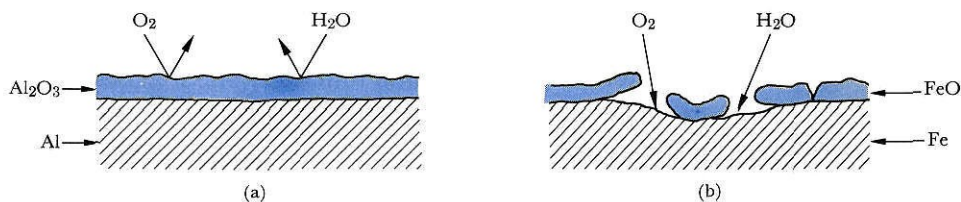

Figure 19-11 (a) A layer of aluminum oxide, once formed, adheres to the surface of the aluminum metal and protects it against further corrosion. (b) Unfortunately, iron oxide does not adhere as well to an iron surface. It continually flakes away as rust and exposes a clean surface to further attack by oxygen and moisture. Iron and steel objects must have their surfaces protected by some artificial method.
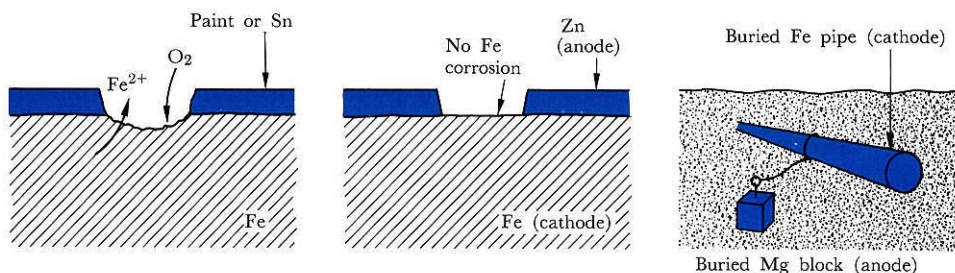
Figure 19-12   One protection for an iron object is an airtight coating of paint or of another metal such as tin. This works as long as the coating is intact, but when a pit or scratch develops, corrosion begins. A zinc coating provides additional electrochemical protection because iron has a higher reduction potential, and tends to remain reduced while zinc is oxidized. Similarly, magnesium can protect iron pipe by corroding in place of it. In these applications zinc and magnesium are called *sacrificial metals*.

duced. Scratch a galvanized pail and the scratched pail will not corrode; in principle the iron object does not even have to be completely covered.

Tin is another story. A "tin can" is tin-plated iron. You can see from Table 19-1 that Sn lies above Fe in reduction potential; thus the Sn^{2+} ion has a greater tendency to become reduced to the metal than does Fe^{2+}. The tin coating actually *encourages* oxidation, and hence corrosion, of the iron. A tin can is protected from corrosion only as long as the entire tin surface is intact. Scratch a tin can and it most certainly will rust. The tin plating functions only as a particularly tough and adhesive "superpaint." This is perhaps fortunate for our environment. Tin cans eventually self-destruct, whereas aluminum cans do not.

The same electrochemical trickery can be used to keep iron pipes from corroding in moist ground, or steel ship hulls from corroding in salt water. Magnesium rods driven into the ground periodically alongside an iron pipeline and connected electrically to it will make the pipe cathodic and prevent it from corroding. The magnesium itself will corrode, but it is easier and cheaper to replace magnesium rods than to dig up and replace the pipeline (Figure 19-12). Blocks of magnesium attached to a ship's hull in seawater perform the same function. The magnesium is called a "sacrificial" metal; its corrosion is acceptable as an alternative to corrosion of the iron object.

Summary

Some atoms and ions attract electrons more strongly than others. When we allow electrons to flow from the less attracting ions or atoms to more attracting ones, a more stable situation develops and energy is released. If

no special precautions are taken, this energy is dissipated as heat, or as an increase in disorder (entropy). But if the electron-releasing and electron-accepting half-reactions can be separated physically, then the flow of electrons from one place to another can be harnessed to do electrical work. This is the principle of all electrochemical cells.

The electron-losing substance is **oxidized**, and the electrode where this occurs is the **anode**. The electron-accepting substance is **reduced** at the **cathode**. The "pressure" that these electrons exert, measured between anode and cathode, is the **cell voltage** or **electromotive force (emf)**. A positive cell voltage means that the cell reaction will proceed spontaneously, with electron flow from the anode to the cathode. A negative cell voltage means that the reverse reaction is spontaneous. The cell voltage is related to the free energy of the cell reaction by the expression

$$\Delta G = -n\mathscr{F}\mathscr{E}$$

An overall cell reaction can be separated into two half-reactions that represent the processes at the anode and cathode. Each of these half-reactions can be assigned its own half-cell potential, defined as the potential that would be observed if the half-reaction were paired with the hydrogen half-cell,

$$2H^+ + 2e^- \rightarrow H_2(g)$$
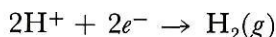
(This amounts to defining the voltage of the hydrogen half-reaction as $\mathscr{E}^0 = 0.000 \ldots$ V.) By convention, half-cell reactions are written as **reductions**, and the corresponding **reduction potential** measures the relative tendency for that reduction to take place. (Some older books use oxidations and oxidation potentials. The oxidation potential is the negative of the reduction potential.) A high positive reduction potential indicates a strong tendency toward reduction, and a low negative reduction potential indicates a strong tendency toward the oxidized state. When one half-reaction is subtracted from another to build a complete cell reaction, the corresponding reduction potentials are subtracted. Although one half-cell reaction may have to be multiplied by a stoichiometric constant to make the total number of electrons cancel in the overall reaction, the corresponding reduction potential is not multiplied by the constant. Reduction potentials are effective "electron pressures," and are already on a one-electron basis. Stoichiometry is taken care of by the quantity n in the expression

$$\Delta G = -n\mathscr{F}\mathscr{E}$$

If the concentrations of all ionic species are $1M$, and all gases are at 1 atm partial pressure, this is the **standard state** for the emf designated $\mathscr{E}^0$ (analogous to the standard free energy, ΔG^0, with a superscript zero). If the reactants and products are not all in their standard concentrations, then the cell voltage is given by the **Nernst equation**,

$$\mathscr{E} = \mathscr{E}^0 - \frac{RT}{n\mathscr{F}} \ln Q$$

which is the electrochemical analogue of the free energy versus concentration equation discussed in Chapters 16 and 17. Just as an overall cell reaction can be divided into two half-reactions, Nernst equations can be written separately for each half-cell process.

One remarkable feature of redox reactions, in contrast to most other chemical reactions, is that they occur over such a wide range of equilibrium-constant values. For a two-electron reaction, a cell voltage of 6 V corresponds to an equilibrium constant of $K_{eq} = 10^{200}$! This means that only rarely will two half-reactions have half-cell potentials so similar that the equilibrium constant for the overall reaction will be of moderate size. Most redox reactions either go to completion (effectively) or do not go at all. However, electrochemical methods can be used to study equilibrium, solubility product, and complex-ion formation in circumstances where one or another component at equilibrium is present in quantities far too small to be detected by standard analytical methods.

Using what we know about electrochemistry, we can design and build cells and batteries that deliver electrical power in small amounts in convenient places, and can use electrical power to bring about desirable chemical reactions. Electroplating and the refining of aluminum are examples. We also can use electrochemical principles to halt corrosion of susceptible metals that have low reduction potentials. What we cannot do yet is produce a cheap, lightweight storage battery with a high-energy density, or an electrochemical fuel cell that will operate with commonly available fuels.

Self-Study Questions

1. Which of the two electrodes, anode or cathode, is associated in all electrochemical cells with oxidation? Which with reduction?
2. What is the driving force that creates a potential in a concentration cell?
3. What would happen if you replaced the semipermeable barrier in a concentration cell by an impermeable one? If you removed the barrier altogether?
4. How is cell potential related to concentrations in a concentration cell?
5. How is a Daniell cell constructed, and what is the source of its electrical potential? Why is it unsuitable for powering flashlights or electric cars?
6. Why is a dry cell more suitable than the Daniell cell for flashlights and electric cars? What chemical reactions take place in a dry cell? Which reaction produces electrons, and how are they used up? Which reaction takes place at the anode, and which at the cathode?
7. How is cell potential related to the free energy of the cell reaction? What is the standard potential?
8. Are the free energies of half-cell reactions always additive? Are the half-cell potentials always additive? Outline the conditions under which

the free energies and potentials will be additive, and the conditions under which they will not.

9. Does a high positive reduction potential for a half-cell reaction indicate a strong tendency for the redox couple to reduce other substances?

10. Given two half-cell reactions with different half-cell potentials, how do we obtain the overall cell voltage? If the resulting cell voltage is positive, what does this indicate about the cell reaction?

11. The two manganese half-reactions with standard reduction potentials of $+1.68$ V and $+1.21$ V, in Table 19-1, can be added to produce a third reaction, listed in that table with a potential of $+1.49$ V. Explain why the reduction potential of this third reaction is not the sum of the other two; that is, not $+1.68$ V $+ 1.21$ V $= +2.89$ V. Account for the observed value of $+1.49$ V in terms of the tabulated potentials of the first two reactions.

12. What is the Nernst equation, and how does it relate cell potentials to concentrations?

13. Why is the first term of the Nernst equation zero for a concentration cell?

14. Why do concentration cells with the same ratio of concentrations always have the same cell potential, no matter what chemical substances are involved in the reaction?

15. How can oxidation–reduction measurements yield the solubility of a substance when the dissolved substance is not present in large enough amounts to be detected by ordinary analytical methods?

16. How is corrosion of iron impeded by a layer of paint? A layer of zinc metal? A layer of tin metal? Why is coating unnecessary with aluminum? What is meant by a "sacrificial metal" in preventing corrosion?
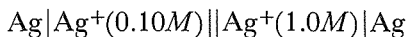
Problems

Data necessary for these problems can be found in Tables 19-1 and 19-2, and in the *Handbook of Chemistry and Physics* or similar references.

Concentration cells

1. A standard $Cl_2|Cl^-$ half-cell has been coupled to a $Cl_2(1.00 \text{ atm})|Cl^-(0.010M)$ half-cell. What is the cell voltage? Determine ΔG_{298} for the reaction.

2. The following cell

$$Ag|Ag^+(0.10M)||Ag^+(1.0M)|Ag$$

is a concentration cell and is capable of electrical work. (a) What is the cell potential? (b) Which side of the cell is the cathode, and which is the anode? (c) What is ΔG in joules for the spontaneous cell reaction?

3. Two copper electrodes are placed in two copper sulfate solutions of equal concentration and connected to form a concentration cell. What is the cell voltage? One of the solutions is diluted until the concentration of copper ions is one-fifth its original value. What is the cell voltage after dilution?

4. Consider the following perpetual motion device built around a concentration cell: (a) Two copper electrodes are placed in copper sulfate solutions of equal concentration and connected to form a concentration cell. Initially there is no voltage in the cell. Assume that each electrode contains more copper than is present in either solution. (b) Solution A is diluted until its Cu^{2+} concentration is cut in half, at which point the cell has a potential, $\mathscr{E}$. The cell is run and useful work is done on the surroundings until the concentrations in the two solutions are equalized, at which time the cell voltage has fallen to zero again. (c) Solution B is diluted until its Cu^{2+} concentration is halved, at which time the cell has the same potential, $\mathscr{E}$, as before, but in the opposite direction. Again the cell is run, and work is done until the concentrations in solutions A and B are the same. (d) Steps (b) and (c) are repeated, diluting first one solution and then the other by halving its Cu^{2+} concentration after equilibrium has been attained in the previous step. Since neither concentration ever falls to zero by the halving process, we can maintain this process as long as we like and take an infinite amount of work out of the cell. The operation of the cell actually helps us, for it *raises* the concentration of the solution that we had just diluted. What is wrong with this analysis?

Work and free energy

5. Determine the amount of useful work done when a mole of zinc powder is allowed to react with a $1.00M$ solution of $Cu(NO_3)_2$ in a constant-temperature calorimeter. If the reaction were carried out reversibly, how much useful work could be accomplished? ΔH^0_{298} for the reaction is -215 kJ. Calculate the heat liberated when the reaction is carried out reversibly.

Spontaneity

6. Assuming unit activities for all substances, determine which of the following reactions will be spontaneous:
   a) $Zn + Mg^{2+} \rightarrow Zn^{2+} + Mg$
   b) $Fe + Cl_2 \rightarrow Fe^{2+} + 2Cl^-$
   c) $4Ag + O_2 + 4H^+ \rightarrow 4Ag^+ + 2H_2O$
   d) $2AgCl \rightarrow 2Ag + Cl_2$

Half-cell potentials

7. What are the potentials for the following cells or half-cells?
   a) $\mathscr{E}^0$ for the cell
   $$Zn(s)|Zn^{2+}||Cu^{2+}|Cu(s)$$
   b) $\mathscr{E}$ for the half-cell
   $$Zn(s)|Zn^{2+}(0.0010M)$$
   c) $\mathscr{E}$ for the half-cell
   $$Cu^{2+}(10^{-36}M)|Cu(s)$$

8. What are the standard potentials, $\mathscr{E}^0$, for the following half-cells?
   a) $S^{2-}|CuS(s)|Cu(s)$
   b) $NH_3(aq), Zn(NH_3)_4^{2+}|Zn(s)$

Cell potentials and electron flow

9. Consider the cell
   $$Ag(s)|Ag^+(1.0M)||Cu^{2+}(1.0M)|Cu(s)$$
   a) Write the chemical reaction that takes place in this cell. In which direction will the reaction proceed spontaneously?
   b) What is $\mathscr{E}^0$ for the cell?
   c) Do electrons flow from Ag to Cu in the external circuit, or the other way?

10. Consider the following cell:

$$Ni\,|\,Ni^{2+}(0.010M)\,||\,Sn^{2+}(1.0M)\,|\,Sn$$
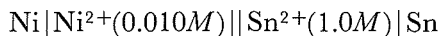
(a) Predict the direction in which spontaneous reactions will occur. (b) Which metal, Ni or Sn, will be the cathode and which the anode? (c) What is $\mathscr{E}^0$ for the cell? (d) What will $\mathscr{E}$ be for the cell with the specified concentrations at 25°C?

11. Consider the cell

$$Sn\,|\,SnCl_2(0.10M)\,||\,AgCl(s)\,|\,Ag$$
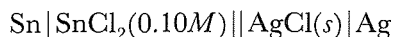
(a) Will electrons flow spontaneously from Sn to Ag, or in the reverse direction? (b) What is the standard potential, $\mathscr{E}^0$, for the cell? (c) What will the cell potential, $\mathscr{E}$, be at 25°C?
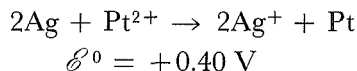
12. Use the line notation of the previous problems to represent a cell that uses the following half-reactions:

$$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$$
$$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$$
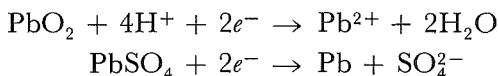
a) Which is the reaction at the cathode of the cell? Which way do electrons flow in an external circuit?

b) What is $\mathscr{E}^0$ for this cell?

Half-reaction zero conventions

13. The following two reactions have the $\mathscr{E}^0$ values given:

$$2Ag + Pt^{2+} \rightarrow 2Ag^+ + Pt$$
$$\mathscr{E}^0 = +0.40\ V$$

$$2Ag + F_2 \rightarrow 2Ag^+ + 2F^-$$
$$\mathscr{E}^0 = +2.07\ V$$
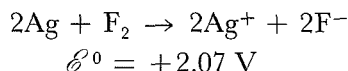
If the potential for the reaction $Pt \rightarrow Pt^{2+} + 2e^-$ is assigned a value of zero, calculate the potentials for the following half-reactions:

a) $Ag \rightarrow Ag^+ + e^-$
b) $F^- \rightarrow \frac{1}{2}F_2 + e^-$
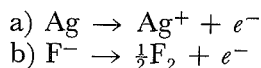
Competing reactions

14. Find the missing standard reduction potentials for these following half-reactions from Table 19-1:

| Half-reaction	$\mathscr{E}^0$ (V)
$MnO_4^- + 8H^+ + 5e^- \rightarrow$ $Mn^{2+} + 4H_2O$	+1.49
$Au^{3+} + 3e^- \rightarrow Au(s)$	+1.42
$Cl_2 + 2e^- \rightarrow 2Cl^-$	?
$AuCl_4^- + 3e^- \rightarrow$ $Au(s) + 4Cl^-$	?
$4H^+ + NO_3^- + 3e^- \rightarrow$ $NO + 2H_2O$	?

If we assume that all reactants and products are at unit activity, (a) which substance in the half-reactions given is the best oxidizing agent? Which is the best reducing agent? (b) Will permanganate oxidize metallic gold? (c) Will metallic gold reduce nitric acid? (d) Will nitric acid oxidize metallic gold in the presence of Cl^- ion? (e) Will metallic gold reduce pure Cl_2 gas in the presence of water? (f) Will chlorine oxidize metallic gold if Cl^- ion is present? (g) Will permanganate oxidize chloride ion?

Cell reactions and K_{eq}

15. From the data in Tables 19-1 and 19-2: (a) Will Fe reduce Fe^{3+} to Fe^{2+}? (Assume unit activities.) (b) Calculate the equilibrium constant, K_{eq}, for the reaction at 25°C,
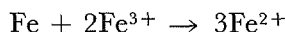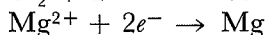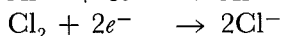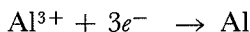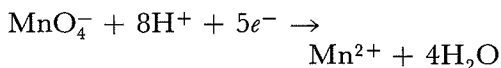
$$Fe + 2Fe^{3+} \rightarrow 3Fe^{2+}$$

16. Find the standard reduction potentials for the following half-reactions:

$$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$$
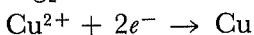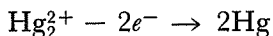$$Ag^+ + e^- \rightarrow Ag$$
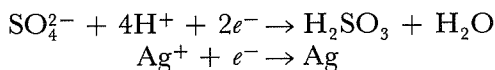
(a) Write the balanced overall reaction for a successful cell made from these two couples. (b) Write the line notation for the cell. (c) What is $\mathscr{E}^0$ for the cell? (d) What is the equilibrium constant for the cell reaction at 25°C? (c) Calculate the ratio of activities of products and reactants, Q, that will produce a cell voltage of 0.51 V.

Cell potentials

17. Find the standard reduction potentials for the following half-reactions:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow$$
$$Mn^{2+} + 4H_2O$$
$$Al^{3+} + 3e^- \rightarrow Al$$
$$Cl_2 + 2e^- \rightarrow 2Cl^-$$
$$Mg^{2+} + 2e^- \rightarrow Mg$$

(a) Which is the strongest reducing agent? Which is the strongest oxidizing agent? (b) Write the overall reaction for a successful cell made from the Mg and Cl_2 couples. (c) Write the line notation for this cell. (d) Which is the anode of the cell, and which is the cathode? (e) What is $\mathscr{E}^0$ for the cell? (f) What is the equilibrium-constant expression for this cell reaction? Calculate the numerical value of the equilibrium constant at 25°C.

18. Find the standard reduction potentials for the following half-reactions:

$$Hg_2^{2+} - 2e^- \rightarrow 2Hg$$
$$Cu^{2+} + 2e^- \rightarrow Cu$$

(a) Write the overall reaction for a successful cell made from these two half-reactions. (b) Write the line notation for

the cell. Which material, Hg or Cu, is the anode? (c) What is $\mathscr{E}^0$ for the cell? (d) What is the equilibrium constant for the cell? (e) What is the voltage of the cell when $[Hg_2^{2+}] = 0.10M$ and $[Cu^{2+}] = 0.010M$?

Le Chatelier's principle

19. For an electrochemical cell in which the spontaneous reaction is

$$3Cu^{2+} + 2Al \rightarrow 2Al^{3+} + 3Cu$$
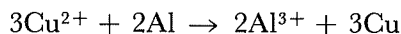
what will be the qualitative effect on the cell potential if we add ethylenediamine, a ligand that coordinates strongly with Cu^{2+} but not with Al^{3+}?

20. A copper–zinc battery is set up under standard conditions with all species at unit activity. Initially, the voltage developed by this cell is 1.10 V. As the battery is used, the concentration of the cupric ion gradually decreases, and that of the zinc ion increases. According to Le Chatelier's principle, should the voltage of the cell increase or decrease? What is the ratio, Q, of the concentrations of zinc and copper ions when the cell voltage is 1.00 V?

Nernst equation

21. A galvanic cell consists of a rod of copper immersed in a $2.0M$ solution of $CuSO_4$ and a rod of iron immersed in a $0.10M$ solution of $FeSO_4$. Using the Nernst equation and the reduction potentials for

$$Fe^{2+} + 2e^- \rightarrow Fe$$
$$Cu^{2+} + 2e^- \rightarrow Cu$$
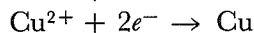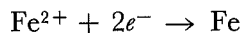
calculate the voltage for the cell as described.

22. What voltage will be generated by a cell that consists of a rod of iron immersed in a $1.00M$ solution of $FeSO_4$ and a rod of

manganese immersed in a $0.10M$ solution of $MnSO_4$?

Concentration and voltage

23. Consider the cell

    $$Zn|Zn^{2+}(0.0010M)||Cu^{2+}(0.0010M)|Cu$$

    for which $\mathscr{E}^0 = +1.10$ V. Does the cell voltage, $\mathscr{E}$, increase, decrease, or remain unchanged when each of the following changes is made? (a) Excess $1.0M$ ammonia is added to the cathode compartment. (b) Excess $1.0M$ ammonia is added to the anode compartment. (c) Excess $1.0M$ ammonia is added to both compartments at the same time. (d) H_2S gas is bubbled into the Zn^{2+} solution. (e) H_2S gas is bubbled into the Zn^{2+} solution at the same time that excess $1.0M$ ammonia is added to the other solution.

24. Consider the galvanic cell

    $$Zn|Zn^{2+}||Cu^{2+}|Cu$$
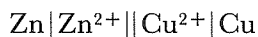
    Calculate the ratio of $[Zn^{2+}]$ to $[Cu^{2+}]$ when the voltage of the cell has dropped to 1.05 V, 1.00 V, and 0.90 V. Notice that a small drop in voltage parallels a large change in concentration. Therefore, a battery that registers 1.00 V is quite "run down."

Competitive reactions

25. Show that hydrogen peroxide is thermo-dynamically unstable and should disproportionate to water and oxygen.

Voltage and pH

26. A silver electrode is immersed in a $1.00M$ solution of $AgNO_3$. This half-cell is connected to a hydrogen half-cell in which the hydrogen pressure is 1.00 atm and the H^+ concentration is unknown. The voltage of the cell is 0.78 V. Calculate the pH of the solution.

Solubility product

27. Using half-reactions, show that Ag^+ and I^- spontaneously form $AgI(s)$ when mixed directly at unit initial activity. Show that K_{sp} for AgI is 10^{-16}.

28. A standard hydrogen half-cell is coupled to a standard silver half-cell. Sodium bromide is added to the silver half-cell, causing precipitation of AgBr, until a concentration of $1.00M$ Br^- is reached. The voltage of the cell at this point is 0.072 V. Calculate the K_{sp} for silver bromide.

Corrosion

29. Chrome-plated automobile trim contains an iron core coated by a thick layer of nickel that is coated by a layer of chromium. Arrange the metals in order of ease of oxidation. What is the purpose of the chromium layer? Of the nickel layer?

Suggested Reading

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C. A. VanderWerf, *Oxidation–Reduction*, Van Nostrand Reinhold, New York, 1961.