CHAPTER TWENTY-ONE

Electrochemistry: Chemical Change and Electrical Work

Electrochemistry is the study of the relationship between chemical change and electrical work.

21.1 REDOX REACTIONS AND ELECTROCHEMICAL CELLS

Whether an electrochemical process releases or absorbs free energy, it always involves the movement of electrons from one chemical species to another in an **oxidation-reduction** (**redox**) reaction.

A Quick Review of Oxidation-Reduction Concepts

- o   Oxidation is the loss of electrons,
- o   Reduction is the gain of electrons,
- o   An oxidizing agent is the species that does the oxidizing, taking electrons from the substance being oxidized.
- o   A reducing agent is the species that does the reducing, giving electrons to the substance being reduced.

Keep in mind three key points:

- ➢   Oxidation always accompanies reduction.

➢ The oxidizing agent is reduced, and the reducing agent is oxidized.

➢ The total number of electrons gained by the atoms/ions of the oxidizing agent always equals the total number lost by the atoms/ions of the reducing agent.

Figure 21.1 presents these ideas for the aqueous reaction between zinc metal and a strong acid.

PROCESS	$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$	
OXIDATION • One reactant loses electrons. • Reducing agent is oxidized. • Oxidation number increases.	Zinc **loses** electrons. Zinc is the reducing agent and becomes **oxidized**. The oxidation number of Zn **increases** from 0 to +2.	
REDUCTION • Other reactant gains electrons. • Oxidizing agent is reduced. • Oxidation number decreases.	Hydrogen ion **gains** electrons. Hydrogen ion is the oxidizing agent and becomes **reduced**. The oxidation number of H **decreases** from +1 to 0.	

Figure 21.1 A summary of redox terminology. In the reaction between zinc and hydrogen ion, Zn is oxidized and H^+ is reduced.

Half-Reaction Method for Balancing Redox Reactions

The following steps are used in balancing a redox reaction by the half-reaction method:

Step 1. Divide the skeleton reaction into two half-reactions, each of which contains the oxidized and reduced forms of one of the species.

Step 2. Balance the atoms and charges in each half-reaction.

➢ Atoms are balanced in order: atoms other than O and H, then O, and then H.

➢ Charge is balanced by adding electrons (e⁻).

Step 3. If necessary, multiply one or both half-reactions by an integer to make the number of e⁻ gained in the reduction equal the number lost in the oxidation.

Step 4. Add the balanced half-reactions, and include states of matter.

Step 5. Check that the atoms and charges are balanced.

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Balancing Redox Reactions in Acidic Solution

Let's balance the redox reaction between dichromate ion and iodide ion to form

chromium(III) ion and solid iodine, which occurs in acidic solution (Figure 2 1.2) .
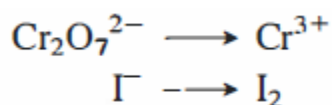

Figure 21.2 The redox reaction between dichromate ion and iodide ion. When $Cr_2O_7^{2-}$ (*left*) and I^- (*center*) are mixed in acid solution, they react to form Cr^{3+} and I_2 (*right*).

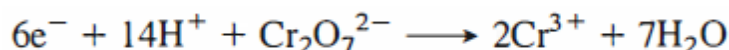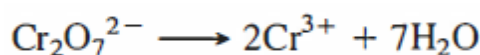The skeleton ionic reaction shows only the oxidized and reduced species:

$$Cr_2O_7^{2-}(aq) + I^-(aq) \longrightarrow Cr^{3+}(aq) + I_2(s) \qquad \text{[acidic solution]}$$
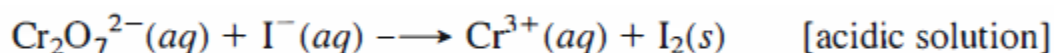
Step 1. Divide the reaction into half-reactions,

$$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$$
$$I^- \longrightarrow I_2$$

Step 2. Balance atoms and charges in each half-reaction.

➢ For the $Cr_2O_7^-/Cr^{3+}$ half-reaction:

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$$

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

$$14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

$$6e^- + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$
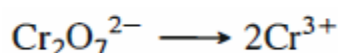
➢ For the I^-/I_2 half-reaction:

$$2I^- \longrightarrow I_2$$

$$2I^- \longrightarrow I_2 + 2e^-$$
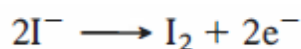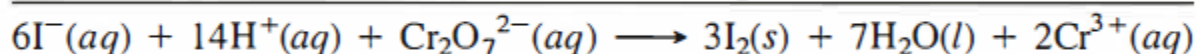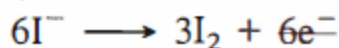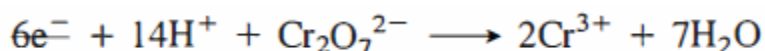
Step 3. Multiply each half-reaction, if necessary, by an integer so that the number of e⁻ lost in the oxidation equals the number of e⁻ gained in the reduction.
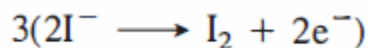
$$3(2I^- \longrightarrow I_2 + 2e^-)$$
$$6I^- \longrightarrow 3I_2 + 6e^-$$

Step 4. Add the half-reactions together:

$$6e^= + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$
$$6I^- \longrightarrow 3I_2 + 6e^=$$

$$6I^-(aq) + 14H^+(aq) + Cr_2O_7^{2-}(aq) \longrightarrow 3I_2(s) + 7H_2O(l) + 2Cr^{3+}(aq)$$

Step 5. Check that atoms and charges balance:

Reactants (6I, 14H, 2Cr, 7O; 6+) $\longrightarrow$ products (6I, 14H, 2Cr, 7O; 6+)

Balancing Redox Reactions in Basic Solution

As Sample Problem 21.1 shows, only one additional step is needed to balance a redox equation that takes place in basic solution. After both half-reactions have first been balanced as if they took place in acidic solution we add one OH⁻ ion to both sides of the equation for every H⁺ ion present. The H⁺ ions on one side are combined with the added OH⁻ ions to form H_2O, and OH⁻ ions appear on the other side of the equation.

SAMPLE PROBLEM 21.1 Balancing Redox Reactions by the Half-Reaction Method
Problem Permanganate ion is a strong oxidizing agent, and its deep purple color makes it useful as an indicator in redox titrations. It reacts in basic solution with the oxalate ion to form carbonate ion and solid manganese dioxide. Balance the skeleton ionic equation for the reaction between $NaMnO_4$ and $Na_2C_2O_4$ in basic solution:

$$MnO_4^-(aq) + C_2O_4^{2-}(aq) \longrightarrow MnO_2(s) + CO_3^{2-}(aq) \quad \text{[basic solution]}$$
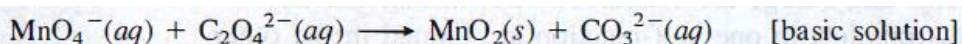
Plan We proceed through step 4 as if this took place in acidic solution. Then, we add the appropriate number of OH^- ions and cancel excess H_2O molecules (step 4 Basic).

Solution

1. Divide into half-reactions.

$$MnO_4^- \longrightarrow MnO_2 \qquad\qquad\qquad C_2O_4^{2-} \longrightarrow CO_3^{2-}$$

2. Balance.

a. Atoms other than O and H,	a. Atoms other than O and H,
Not needed	$C_2O_4^{2-} \longrightarrow 2CO_3^{2-}$
b. O atoms with H_2O,	b. O atoms with H_2O,
$MnO_4^- \longrightarrow MnO_2 + 2H_2O$	$2H_2O + C_2O_4^{2-} \longrightarrow 2CO_3^{2-}$
c. H atoms with H^+,	c. H atoms with H^+,
$4H^+ + MnO_4^- \longrightarrow MnO_2 + 2H_2O$	$2H_2O + C_2O_4^{2-} \longrightarrow 2CO_3^{2-} + 4H^+$
d. Charge with e^-,	d. Charge with e^-,
$3e^- + 4H^+ + MnO_4^- \longrightarrow MnO_2 + 2H_2O$	$2H_2O + C_2O_4^{2-} \longrightarrow 2CO_3^{2-} + 4H^+ + 2e^-$
[reduction]	[oxidation]
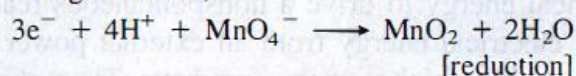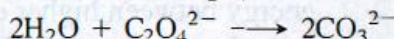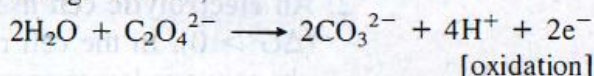
3. Multiply each half-reaction, if necessary, by some integer to make e^- lost equal e^- gained.

$$2(3e^- + 4H^+ + MnO_4^- \longrightarrow MnO_2 + 2H_2O) \qquad 3(2H_2O + C_2O_4^{2-} \longrightarrow 2CO_3^{2-} + 4H^+ + 2e^-)$$
$$6e^- + 8H^+ + 2MnO_4^- \longrightarrow 2MnO_2 + 4H_2O \qquad 6H_2O + 3C_2O_4^{2-} \longrightarrow 6CO_3^{2-} + 12H^+ + 6e^-$$
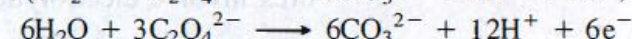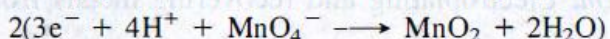
4. Add half-reactions, and cancel substances appearing on both sides.
The six e^- cancel, eight H^+ cancel to leave four H^+ on the right, and four H_2O cancel to leave two H_2O on the left:

$$6e^- + 8H^+ + 2MnO_4^- \longrightarrow 2MnO_2 + 4H_2O$$
$$\underline{2\ 6H_2O + 3C_2O_4^{2-} \longrightarrow 6CO_3^{2-} + 4\ 12H^+ + 6e^-}$$
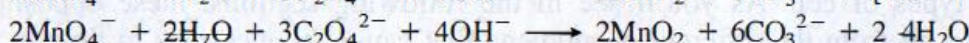$$2MnO_4^- + 2H_2O + 3C_2O_4^{2-} \longrightarrow 2MnO_2 + 6CO_3^{2-} + 4H^+$$
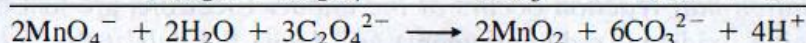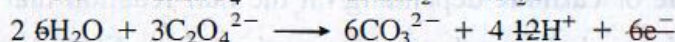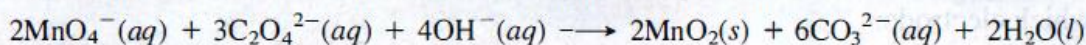
4 Basic. Add OH^- to both sides to neutralize H^+, and cancel H_2O.
Adding four OH^- to both sides forms four H_2O on the right, two of which cancel the two H_2O on the left, leaving two H_2O on the right:

$$2MnO_4^- + 2H_2O + 3C_2O_4^{2-} + 4OH^- \longrightarrow 2MnO_2 + 6CO_3^{2-} + [4H^+ + 4OH^-]$$
$$2MnO_4^- + 2H_2O + 3C_2O_4^{2-} + 4OH^- \longrightarrow 2MnO_2 + 6CO_3^{2-} + 2\ 4H_2O$$

Including states of matter gives the final balanced equation:

$$2MnO_4^-(aq) + 3C_2O_4^{2-}(aq) + 4OH^-(aq) \longrightarrow 2MnO_2(s) + 6CO_3^{2-}(aq) + 2H_2O(l)$$

5. Check that atoms and charges balance.

$$(2Mn, 24O, 6C, 4H; 12-) \longrightarrow (2Mn, 24O, 6C, 4H; 12-)$$

Comment As a final step, we can obtain the balanced *molecular* equation for this reaction by noting the number of moles of each anion in the balanced ionic equation and adding the correct number of moles of spectator ions (in this case, Na^+) to obtain neutral compounds.

Thus, for instance, balancing the charge of 2 mol of MnO_4^- requires 2 mol of Na^+, so we have $2NaMnO_4$. The balanced molecular equation is

$$2NaMnO_4(aq) + 3Na_2C_2O_4(aq) + 4NaOH(aq) \longrightarrow$$
$$2MnO_2(s) + 6Na_2CO_3(aq) + 2H_2O(l)$$
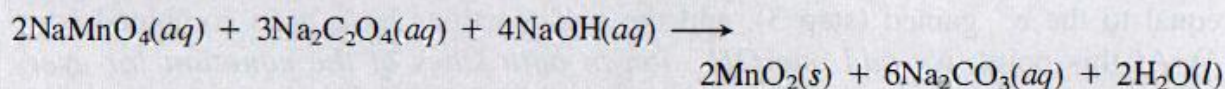
FOLLOW-UP PROBLEM 21.1 Write a balanced molecular equation for the reaction between $KMnO_4$ and KI in basic solution. The skeleton ionic reaction is

$$MnO_4^-(aq) + I^-(aq) \longrightarrow MnO_4^{2-}(aq) + IO_3^-(aq) \quad \text{[basic solution]}$$
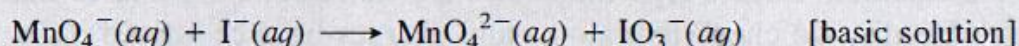
An Overview of Electrochemical Cells

We distinguish two types of electrochemical cells based on the general thermodynamic nature of the reaction:

1. A voltaic cell (or **galvanic cell**) uses a spontaneous reaction ($\Delta G < 0$) to generate electrical energy. This energy is used to operate the load-flashlight bulb, CD player, car starter motor, or other electrical device. In other words, the system does work on the surroundings. All batteries contain voltaic cells.

2. An electrolytic cell uses electrical energy to drive a nonspontaneous reaction ($\Delta G > 0$). Electroplating and recovering metals from ores involve electrolytic cells.
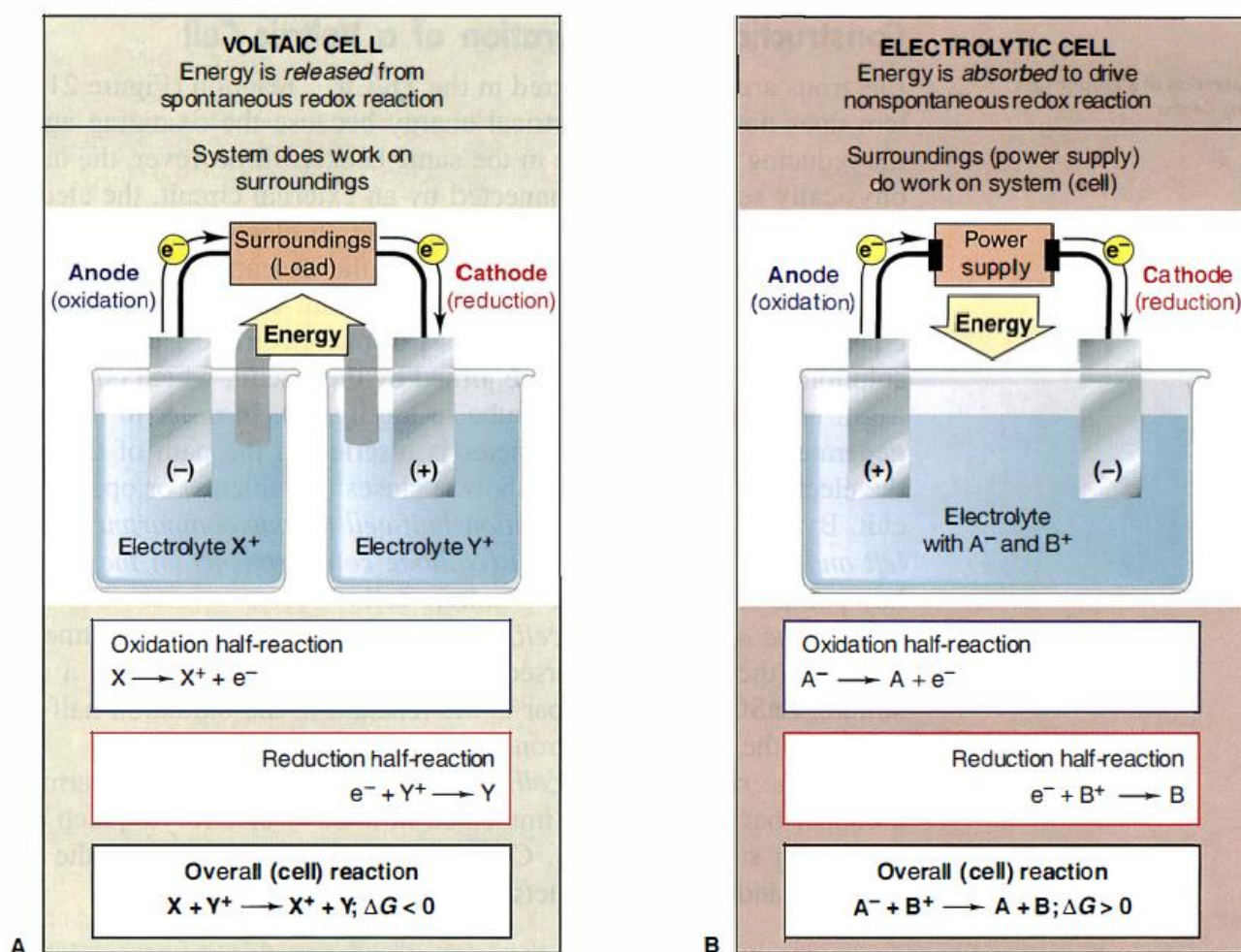
Figure 21.3 General characteristics of voltaic and electrolytic cells. A voltaic cell (**A**) generates energy from a spontaneous reaction ($\Delta G < 0$), whereas an electrolytic cell (**B**) requires energy to drive a nonspontaneous reaction ($\Delta G > 0$). In both types of cell, two electrodes dip into electrolyte solutions, and an external circuit provides the means for electrons to flow between them. Most simportant, notice that oxidation takes place at the anode and reduction takes place at the cathode, but the relative electrode charges are opposite in the two cells.

The two types of cell have certain design features in common (Figure 21.3).

- o Two **electrodes**, which conduct the electricity between cell and surroundings, are dipped into an **electrolyte**, a mixture of ions (usually in aqueous solution) that are involved in the reaction or that carry the charge.

- o An electrode is identified as either **anode** or **cathode** depending on the half-reaction that takes place there:

  - ➢ *The oxidation half-reaction occurs at the anode*. Electrons are lost by the substance being oxidized (reducing agent) and leave the cell at the anode.

  - ➢ *The reduction half-reaction occurs at the cathode*. Electrons are gained by the substance being reduced (oxidizing agent) and enter the cell at the cathode.

- o As shown in Figure 21.3, the relative charges of the electrodes are opposite in the two types of cell. As you'll see in the following sections, these opposite charges result from the different phenomena that cause the electrons to flow.

Here are some memory aids to help you remember which half-reaction occurs at which electrode:

1. The words anode and oxidation start with vowels; the words cathode and reduction start with consonants.

2. Alphabetically, the A in anode comes before the C in cathode, and the O in oxidation comes before the R in reduction.

3. Look at the first syllables and use your imagination:

ANode, OXidation; REDuction, CAThode ⇒ AN OX and a RED CAT

21.2 VOLTAIC CELLS: USING SPONTANEOUS REACTIONS TO GENERATE ELECTRICAL ENERGY

If you put a strip of zinc metal in a solution of Cu^{2+} ion, the blue color of the solution fades as a brown-black crust of Cu metal forms on the Zn strip (Figure 21.4). Judging from what we see, the reaction involves the reduction of Cu^{2+} ion to Cu metal, which must be accompanied by the oxidation of Zn metal to Zn^{2+} ion. The overall reaction consists of two half-reactions:

$$Cu^{2+}(aq) + 2e^- \dashrightarrow Cu(s) \qquad \text{[reduction]}$$
$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \qquad \text{[oxidation]}$$
$$\overline{Zn(s) + Cu^{2+}(aq) \dashrightarrow Zn^{2+}(aq) + Cu(s)} \qquad \text{[overall reaction]}$$

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$
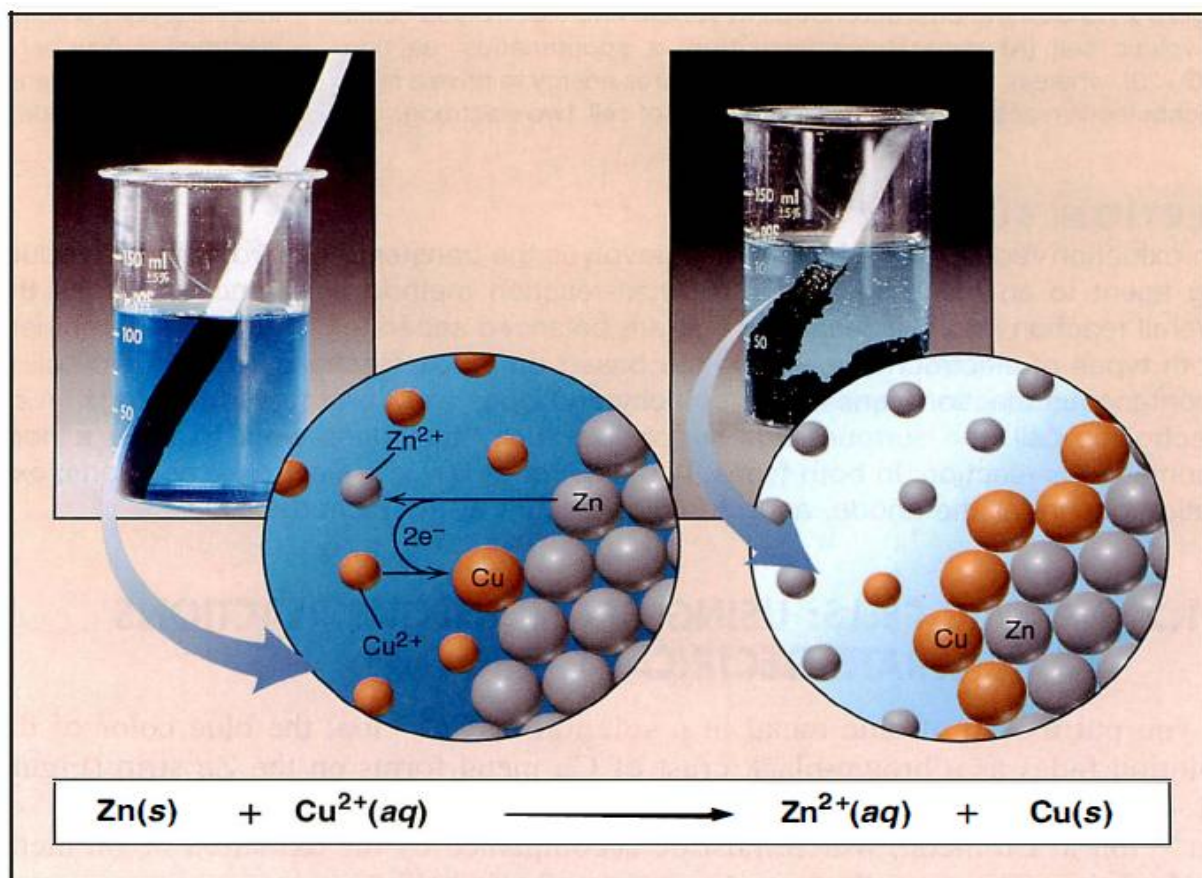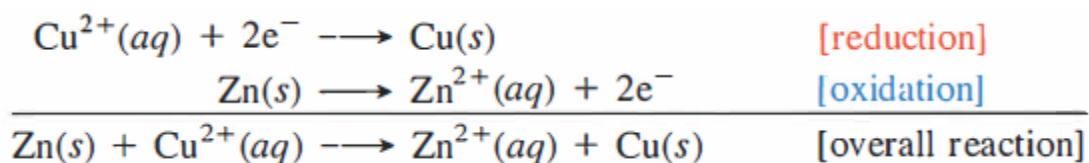
Figure 21.4 The spontaneous reaction between zinc and copper(II) ion. When a strip of zinc metal is placed in a solution of Cu^{2+} ion, a redox reaction begins (*left*), in which the zinc is oxidized to Zn^{2+} and the Cu^{2+} is reduced to copper metal. As the reaction proceeds (*right*), the deep blue color of the solution of hydrated Cu^{2+} ion lightens, and the Cu "plates out" on the Zn and falls off in chunks. (The Cu appears black because it is very finely divided.) At the atomic scale, each Zn atom loses two electrons, which are gained by a Cu^{2+} ion. The process is summarized with symbols in the balanced equation.

Construction and Operation of a Voltaic Cell

Electrons are being transferred in the Zn/Cu^{2+} reaction (Figure 21.4), but the system does not generate electrical energy because the oxidizing agent (Cu^{2+}) and the reducing agent (Zn) are in the same beaker.

If, however, the half-reactions are physically separated and connected by an external circuit, the electrons are transferred by traveling through the circuit and an electric current is produced.

This separation of half-reactions is the essential idea behind a voltaic cell (Figure 21.5A).

Figure 21.5 A voltaic cell based on the zinc-copper reaction. A, The anode half-cell (oxidation) consists of a Zn electrode dipping into a Zn^{2+} solution. The two electrons generated in the oxidation of each Zn atom move through the Zn bar and the wire, and into the Cu electrode, which dips into a Cu^{2+} solution in the cathode half-cell (reduction). There, the electrons reduce Cu^{2+} ions. Thus, electrons flow left to right through electrodes and wire. A salt bridge contains unreactive Na^+ and SO_4^{2-} ions that maintain neutral charge in the electrolyte solutions: anions in the salt bridge flow to the left, and cations flow to the right. The voltmeter registers the electrical output of the cell. B, After the cell runs for several hours, the Zn anode weighs less because Zn atoms have been oxidized to aqueous Zn^{2+} ions, and the Cu cathode weighs more because aqueous Cu^{2+} ions have been reduced to Cu metal.

➤ The components of each half-reaction are placed in a separate container, or half-cell, which consists of one electrode dipping into an electrolyte solution.

➤ The two half-cells are joined by the circuit, which consists of a wire and a salt bridge (the inverted U tube in the figure).

➤ In order to measure the voltage generated by the cell, a voltmeter is inserted in the path of the wire connecting the electrodes. A switch (not shown) closes (completes) or opens (breaks) the circuit.

➤ By convention, the oxidation half-cell (anode compartment) is shown on the left and the reduction half-cell (cathode compartment) on the right.

Here are the key points about the Zn/Cu^{2+} voltaic cell:

1. The oxidation half-cell

In this case, the anode compartment consists of a zinc bar (the anode) immersed in a Zn^{2+} electrolyte (such as a solution of zinc sulfate, $ZnSO_4$). The zinc bar is the reactant in the oxidation half-reaction, and it conducts the released electrons out of its half-cell.

2. The reduction half-cell

In this case, the cathode compartment consists of a copper bar (the cathode) immersed in a Cu^{2+} electrolyte [such as a solution of copper(II) sulfate, $CuSO_4$] . Copper metal is the product in the reduction half reaction, and the bar conducts electrons into its half-cell.

3. Relative charges on the electrodes

In this cell, zinc atoms are oxidized at the anode to Zn^{2+} ions and electrons. The Zn^{2+} ions enter the solution, while the electrons enter the bar and then the wire. The electrons flow left to right through the wire to the cathode, where Cu^{2+} ions in the solution accept them and are reduced to Cu atoms. Therefore, the anode has an *excess of electrons and a negative charge* relative to the cathode. In any voltaic cell, *the **anode is negative** and **the cathode is positive***.
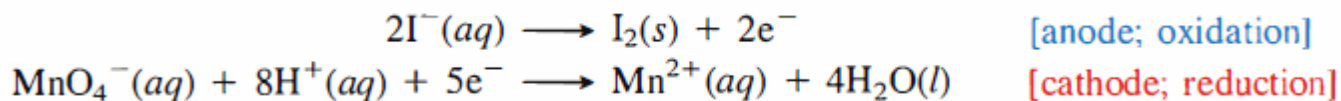
4. The purpose of the salt bridge.

✓ The cell cannot operate unless the circuit is complete.

✓ The oxidation half-cell originally contains a neutral solution of Zn^{2+} and SO_4^{2-} ions, but as Zn atoms in the bar lose electrons, the solution would develop a net positive charge from the Zn^{2+} ions entering.

✓ Similarly, in the reduction half-cell, the neutral solution of Cu^{2+} and SO_4^{2-} ions would develop a net negative charge as Cu^{2+} ions leave the solution to form Cu atoms.

✓ A charge imbalance would arise and stop cell operation. To avoid this situation and enable the cell to operate, the two half-cells are joined by a salt bridge, which acts as a "liquid wire," allowing ions to flow through both compartments and complete the circuit.

✓ To maintain neutrality in the reduction half-cell, Na^+ ions move from the salt bridge into the solution (and some SO_4^{2-} ions move from the solution into the salt bridge).

✓ Similarly, to maintain neutrality in the oxidation half-cell, SO_4^{2-} ions move from the salt bridge into that solution (and some Zn^{2+} ions move from the solution into the salt bridge). Thus, as Figure 21.5A shows, the circuit is completed as electrons move left to right through the wire, while anions move right to left and cations move left to right through the salt bridge.

5. Active vs. inactive electrodes

As the cell operates, the mass of the zinc electrode gradually decreases, and the $[Zn^{2+}]$ in the anode half-cell increases. At the same time, the mass of the copper electrode increases, and the $[Cu^{2+}]$ in the cathode half-cell decreases; we say that the Cu^{2+} "plates out" on the electrode. Look at Figure 21.5B to see how the electrodes look, removed from their half-cells, after several hours of operation.

For many redox reactions, *there are no reactants or products capable of serving as electrodes*, *so inactive electrodes are used*. Most commonly, inactive electrodes are rods of graphite or platinum; they conduct electrons into or out of the half-cells but cannot take part in the half-reactions. In a voltaic cell based on the following half-reactions, for instance, the reacting species cannot act as electrodes:

$$2I^-(aq) \longrightarrow I_2(s) + 2e^- \qquad \text{[anode; oxidation]}$$
$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l) \qquad \text{[cathode; reduction]}$$

Therefore, each half-cell consists of inactive electrodes immersed in an electrolyte
solution that contains all the reactant species involved in that half-reaction (Figure
21.6). In the anode half-cell, I^- ions are oxidized to solid I_2, The electrons that are released
flow into the graphite anode, through the wire, and into the graphite cathode. From there, the
electrons are consumed by MnO_4^- ions, which are reduced to Mn^{2+} ions. (a KNO_3 salt bridge
is used.)

Oxidation half-reaction
$$2I^-(aq) \longrightarrow I_2(s) + 2e^-$$

Reduction half-reaction
$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$$

Overall (cell) reaction
$$2MnO_4^-(aq) + 16H^+(aq) + 10I^-(aq) \longrightarrow 2Mn^{2+}(aq) + 5I_2(s) + 8H_2O(l)$$
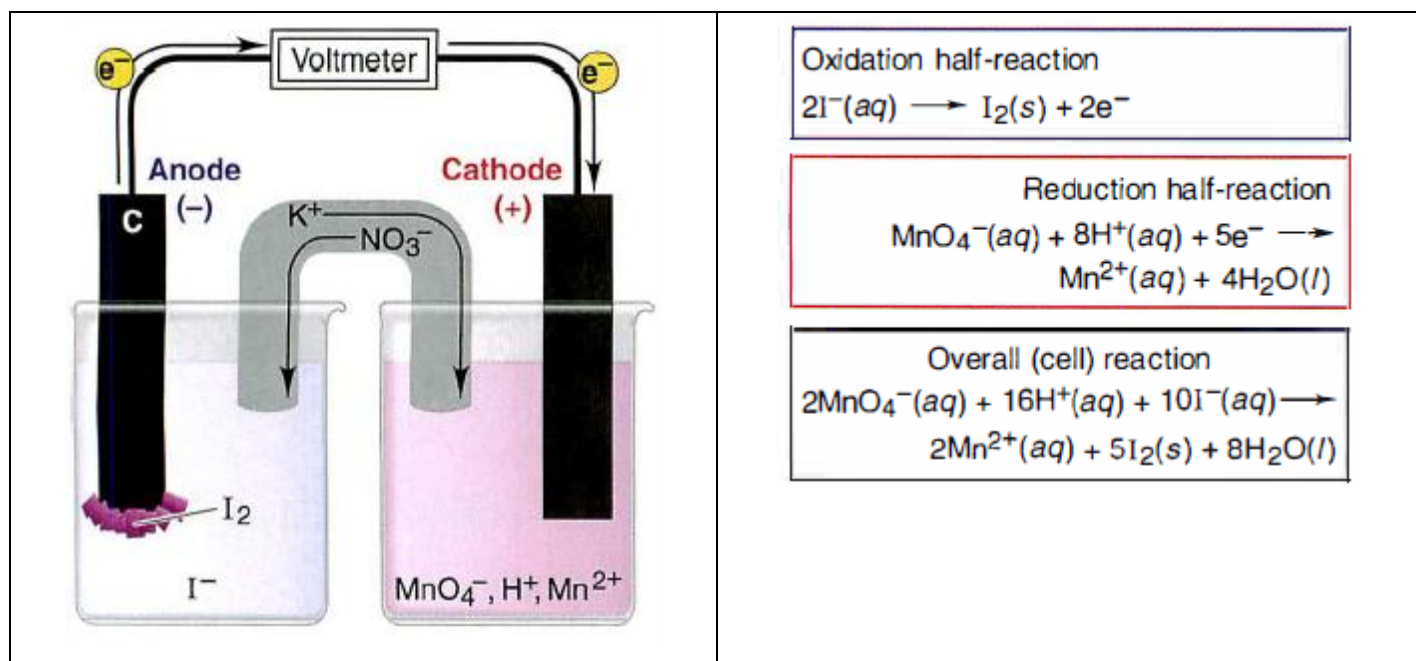
Figure 21.6 A voltaic cell using inactive electrodes. The reaction between I^- and
MnO_4^- in acidic solution does not have species that can be used as electrodes, so
inactive graphite (C) electrodes are used.

Notation for a Voltaic Cell

A useful shorthand notation describes the components of a voltaic cell. For example,
the notation for the Zn/Cu^{2+} cell is

$$Zn(s) \,|\, Zn^{2+}(aq) \,\|\, Cu^{2+}(aq) \,|\, Cu(s)$$
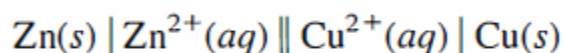
> ➤ A double vertical line indicates the separated half-cells and represents the phase boundary on either side of the salt bridge.
>
> ➤ The components of the anode compartment (oxidation half-cell) are written to the left of the components of the cathode compartment (reduction half-cell).
>
> ➤ A single vertical line represents a phase boundary. For example, Zn(s) I Zn^{2+}(aq) indicates that the solid Zn is a different phase from the aqueous Zn^{2+}.

A comma separates the half-cell components that are in the same phase. For example, the notation for the voltaic cell housing the reaction between land MnO_4^- shown in Figure 21.6 is

$$graphite \,|\, I^-(aq) \,|\, I_2(s) \,\|\, H^+(aq), MnO_4^-(aq), Mn^{2+}(aq) \,|\, graphite$$
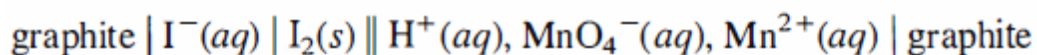
That is, in the cathode compartment, H^+ , MnO_4^- , and Mn^{2+} ions are all in aqueous solution with solid graphite immersed in it.

Often, we specify the concentrations of dissolved components; for example, if the concentrations of Zn^{2+} and Cu^{2+} are 1 M, we write

$$Zn(s) \,|\, Zn^{2+}(1\ M) \,\|\, Cu^{2+}(1\ M) \,|\, Cu(s)$$

SAMPLE PROBLEM 21.2 Describing a Voltaic Cell with Diagram and Notation

**Problem** Draw a diagram, show balanced equations, and write the notation for a voltaic cell that consists of one half-cell with a Cr bar in a $Cr(NO_3)_3$ solution, another half-cell with an Ag bar in an $AgNO_3$ solution, and a KNO_3 salt bridge. Measurement indicates that the Cr electrode is negative relative to the Ag electrode.

Plan From the given contents of the half-cells, we can write the half-reactions. We must determine which is the anode compartment (oxidation) and which is the cathode (reduction). To do so, we must find the direction of the spontaneous redox reaction, which is given by the relative electrode charges. Electrons are released into the anode during oxidation, so it has a negative charge. We are told that Cr is negative, so it must be the anode; and, therefore, Ag is the cathode.

Solution Writing the balanced half-reactions. The Ag electrode is positive, so the half-reaction consumes e^-:

$$Ag^+(aq) + e^- \longrightarrow Ag(s) \qquad \text{[reduction; cathode]}$$
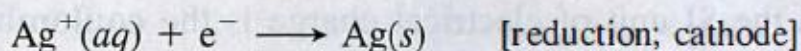
The Cr electrode is negative, so the half-reaction releases e^-:

$$Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^- \qquad \text{[oxidation; anode]}$$
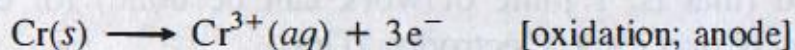
Writing the balanced overall cell reaction. We triple the reduction half-reaction to balance e^- and then combine the half-reactions to obtain the overall reaction:

$$Cr(s) + 3Ag^+(aq) \longrightarrow Cr^{3+}(aq) + 3Ag(s)$$

Determining direction of electron and ion flow. The released e^- in the Cr electrode (negative) flow through the external circuit to the Ag electrode (positive). As Cr^{3+} ions enter the anode electrolyte, NO_3^- ions enter from the salt bridge to maintain neutrality. As Ag^+ ions leave the cathode electrolyte and plate out on the Ag electrode, K^+ ions enter from the salt bridge to maintain neutrality. The diagram of this cell is shown in the margin. Writing the cell notation:

$$Cr(s) \mid Cr^{3+}(aq) \parallel Ag^+(aq) \mid Ag(s)$$
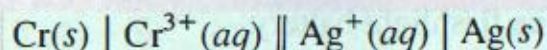
Check Always be sure that the half-reactions and cell reaction are balanced, the half-cells contain *all* components of the half-reactions, and the electron and ion flow are shown. You should be able to write the half-reactions from the cell notation as a check.

Comment The key to diagramming a voltaic cell is to use the direction of the spontaneous reaction to identify the oxidation (anode; negative) and reduction (cathode; positive) half-reactions.

FOLLOW-UP PROBLEM 21.2 In one compartment of a voltaic cell, a graphite rod dips into an acidic solution of $K_2Cr_2O_7$ and $Cr(NO_3)_3$; in the other compartment, a tin bar dips into a $Sn(NO_3)_2$ solution. A KNO_3 salt bridge joins them. The tin electrode is negative relative to the graphite. Draw a diagram of the cell, show the balanced equations, and write the cell notation.

21.3 CELL POTENTIAL: OUTPUT OF A VOLTAIC CELL

✓ The purpose of a voltaic cell is to convert the free energy change of a spontaneous reaction into the kinetic energy of electrons moving through an external circuit (electrical energy).

✓ This electrical energy is proportional to the difference in electrical potential between the two electrodes, which is called the cell potential (E_{cell}), also the voltage of the cell or the electromotive force (emf).

✓ Electrons flow spontaneously from the negative to the positive electrode. Thus, when the cell operates spontaneously, there is a positive cell potential:

$$E_{cell} > 0 \text{ for a spontaneous process}$$

✓ The more positive E_{cell} is, the more work the cell can do, and the farther the reaction proceeds to the right as written.

✓ A negative cell potential, on the other hand, is associated with a nonspontaneous cell reaction.

✓ If $E_{cell} = 0$, the reaction has reached equilibrium and the cell can do no more work.

✓ The SI unit of electrical potential is the volt (V), and the SI unit of electrical charge is the coulomb (C). By definition, for two electrodes that differ by 1 volt of electrical potential, 1 joule of energy is released

$$1 \text{ V} = 1 \text{ J/C}$$

Table 21.1 Voltages of Some Voltaic Cells	
Voltaic Cell	**Voltage (V)**
Common alkaline flashlight battery	1.5
Lead-acid car battery (6 cells = 12 V)	2.0
Calculator battery (mercury)	1.3
Lithium-ion laptop battery	3.7
Electric eel (~5000 cells in 6-ft eel = 750 V)	0.15
Nerve of giant squid (across cell membrane)	0.070

Standard Cell Potentials

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✓ The measured potential of a voltaic cell is affected by changes in concentration as the reaction proceeds and by energy losses due to heating of the cell and the external circuit.

✓ The standard cell potential (E^o_{cell}) is the potential measured at a specified temperature (usually 298 K) with no current flowing and all components in their standard states: 1 atm for gases, 1 M for solutions, the pure solid for electrodes.

e.g. When the zinc-copper cell that we diagrammed in Figure 21.5 begins operating under standard state conditions, that is, when $[Zn^{2+}] = [Cu^{2+}] = 1$ M, the cell produces 1.10 V at 298 K (Figure 21.7):

$$Zn(s) + Cu^{2+}(aq; 1\ M) \longrightarrow Zn^{2+}(aq; 1\ M) + Cu(s) \qquad E^o_{cell} = 1.10\ V$$
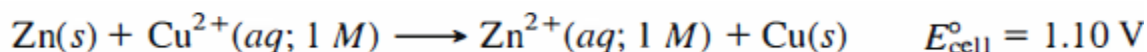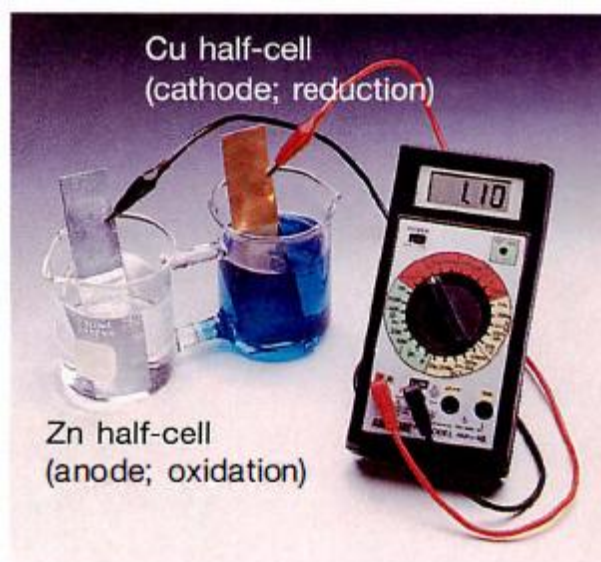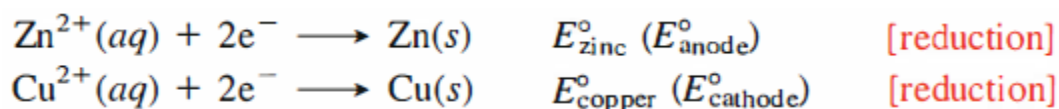
Figure 21.7 Measurement of a standard cell potential. The zinc-copper cell, operating at 298 K under standard-state conditions, produces a voltage of 1.10 V.


Standard Electrode (Half-Cell) Potentials

✓ The standard electrode potential ($E^o_{half\text{-}cell}$) is the potential associated with a given half-reaction (electrode compartment) when all the components are in their standard states.

✓ By convention, a standard electrode potential always refers to the half reaction written as a reduction.

$$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s) \quad E^\circ_{zinc} \; (E^\circ_{anode}) \quad \text{[reduction]}$$
$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \quad E^\circ_{copper} \; (E^\circ_{cathode}) \quad \text{[reduction]}$$

✓ The overall cell reaction involves the oxidation of zinc at the anode, not the reduction of Zn^{2+}, so we reverse the zinc half-reaction:

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \quad \text{[oxidation]}$$
$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \quad \text{[reduction]}$$
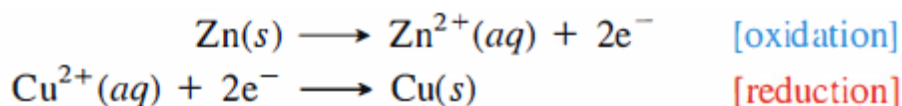
The overall redox reaction is the sum of these half-reactions:

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

$$E^\circ_{cell} = E^\circ_{copper} - E^\circ_{zinc}$$

✓ We can generalize this result for any voltaic cell

$$E^\circ_{cell} = E^\circ_{cathode \; (reduction)} - E^\circ_{anode \; (oxidation)}$$

For a spontaneous reaction at standard conditions, $E^\circ_{cell} > 0$.

Determining $E^\circ_{half-cell}$: The Standard Hydrogen Electrode

How can we know half-cell potentials if we can only measure the potential of the complete cell?

✓ Half-cell potentials, such as E°_{zinc} and E°_{copper} are not absolute quantities, but rather are values relative to that of a standard.

✓ This standard reference half cell has its standard electrode potential defined as zero ($E^\circ_{reference} = 0.00$ V). **The standard reference half-cell is a standard hydrogen electrode**, which consists of a specially prepared platinum electrode immersed in a 1 M aqueous solution of a strong acid, H^+ (aq) [or H_3O^+ (aq)] , through which H_2 gas at 1 atm is bubbled. Thus, the reference half-reaction is

$$2H^+(aq; 1\,M) + 2e^- \rightleftharpoons H_2(g; 1\,atm) \quad E^\circ_{reference} = 0.00\,V$$
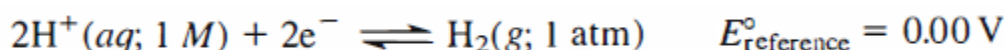
Now we can construct a voltaic cell consisting of this reference half-cell and another half-cell whose potential we want to determine. With $E^\circ_{reference}$ defined as zero, the overall E°_{cell} allows us to find the unknown standard electrode potential, $E^\circ_{unknown}$.
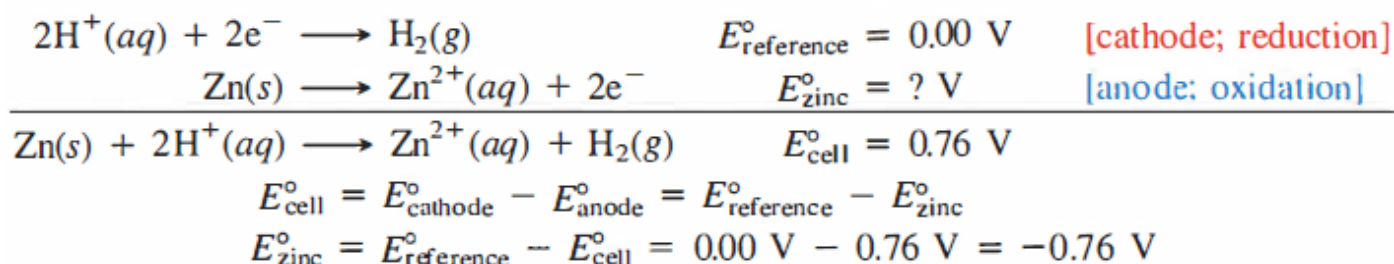
> ➤ When H_2 is oxidized, the reference half-cell is the anode, and so reduction occurs at the unknown half-cell:

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode} = E^{\circ}_{unknown} - E^{\circ}_{reference} = E^{\circ}_{unknown} - 0.00\,V = E^{\circ}_{unknown}$$

> ➤ When H^+ is reduced, the reference half-cell is the cathode, and so oxidation occurs at the unknown half-cell:

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode} = E^{\circ}_{reference} - E^{\circ}_{unknown} = 0.00\,V - E^{\circ}_{unknown} = -E^{\circ}_{unknown}$$

Figure 21.8 shows a voltaic cell that has the Zn/Zn^{2+} half-reaction in one compartment and the H^+/H_2 (or H_3O^+/H_2) half-reaction in the other. The zinc electrode is negative relative to the hydrogen electrode, so we know that the zinc is being oxidized and is the anode. The measured E°_{cell} is +0.76 V, and we use this value to find the unknown standard electrode potential, E°_{zinc}:

$$
\begin{array}{lll}
2H^+(aq) + 2e^- \longrightarrow H_2(g) & E^{\circ}_{reference} = 0.00\,V & \text{[cathode; reduction]} \\
\quad\quad Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- & E^{\circ}_{zinc} = ?\,V & \text{[anode: oxidation]} \\
\hline
Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g) & E^{\circ}_{cell} = 0.76\,V &
\end{array}
$$

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode} = E^{\circ}_{reference} - E^{\circ}_{zinc}$$

$$E^{\circ}_{zinc} = E^{\circ}_{reference} - E^{\circ}_{cell} = 0.00\,V - 0.76\,V = -0.76\,V$$

Now let's return to the zinc-copper cell and use the measured value of E°_{cell} (1.10 V) and the value we just found for E°_{zinc} to calculate E°_{copper}:

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode} = E^{\circ}_{copper} - E^{\circ}_{zinc}$$

$$E^{\circ}_{copper} = E^{\circ}_{cell} + E^{\circ}_{zinc} = 1.10\,V + (-0.76\,V) = 0.34\,V$$

By continuing this process of constructing cells with one known and one unknown electrode potential, we can find many other standard electrode potentials.
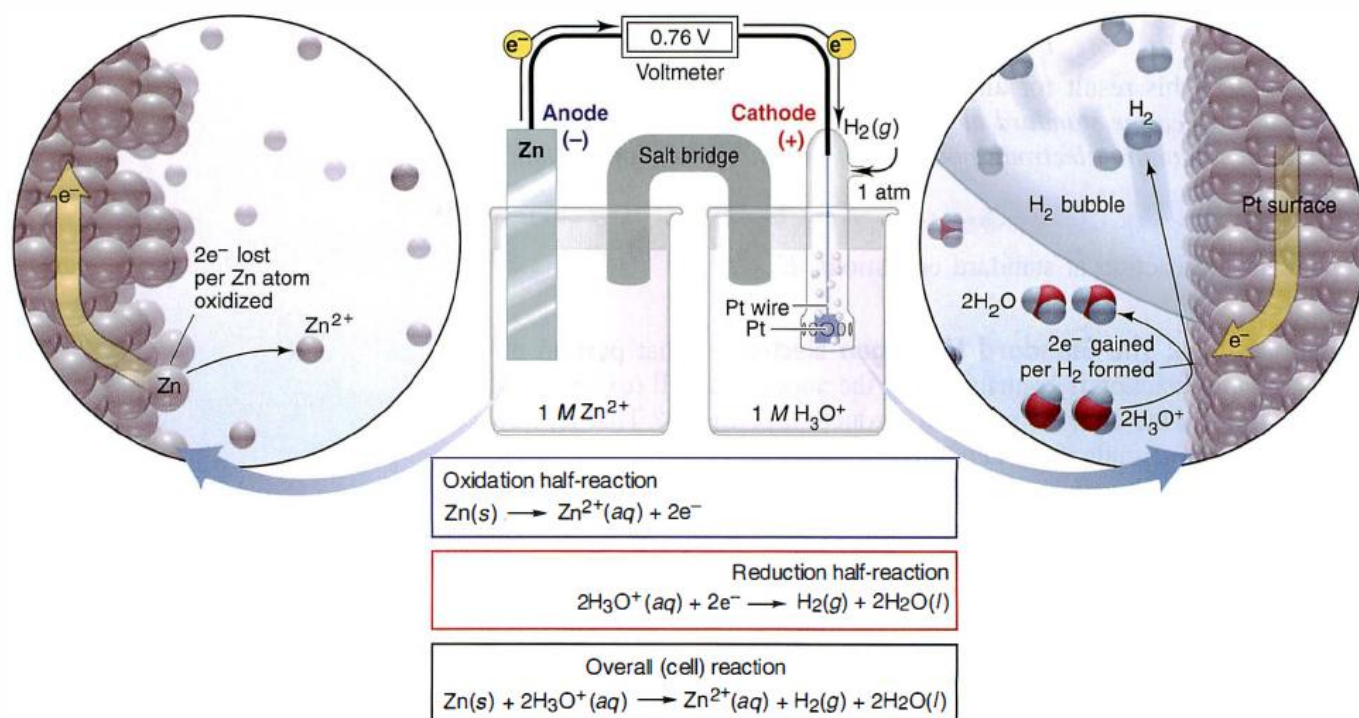
Figure 21.8 Determining an unknown $E_{half-cell}$ with the standard reference (hydrogen) electrode. A voltaic cell has the Zn half reaction in one half-cell and the hydrogen reference half-reaction in the other. The magnified view of the hydrogen half-reaction shows two H_3O^+ ions being reduced to two H_2O molecules and an H_2 molecule, which enters the H_2 bubble. The Zn/Zn^{2+} half-cell potential is negative
(anode), and the cell potential is 0.76 V. The potential of the standard reference electrode is defined as 0.00 V, so the cell potential equals the negative of the anode potential; that is,

$$0.76 \text{ V} = 0.00 \text{ V} - E^{\circ}_{zinc} \qquad \text{so} \qquad E^{\circ}_{zinc} = -0.76 \text{ V}$$

SAMPLE PROBLEM 21.3 Calculating an Unknown $E^{\circ}_{half-cell}$ from E°_{cell}

Problem A voltaic cell houses the reaction between aqueous bromine and zinc metal:

$$Br_2(aq) + Zn(s) \longrightarrow Zn^{2+}(aq) + 2Br^-(aq) \qquad E^{\circ}_{cell} = 1.83 \text{ V}$$
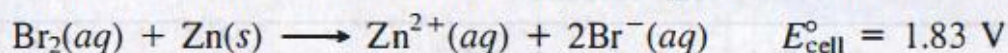
Calculate $E^{\circ}_{bromine}$, given $E^{\circ}_{zinc} = -0.76$ V.
Plan E°_{cell} is positive, so the reaction is spontaneous as written. By dividing the reaction into half-reactions, we see that Br_2 is reduced and Zn is oxidized; thus, the zinc half-cell contains the anode. We use Equation 21.3 to find $E^{\circ}_{unknown}$ ($E^{\circ}_{bromine}$).
Solution Dividing the reaction into half-reactions:

$$Br_2(aq) + 2e^- \longrightarrow 2Br^-(aq) \qquad E^{\circ}_{unknown} = E^{\circ}_{bromine} = ? \text{ V}$$
$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \qquad E^{\circ}_{zinc} = -0.76 \text{ V}$$
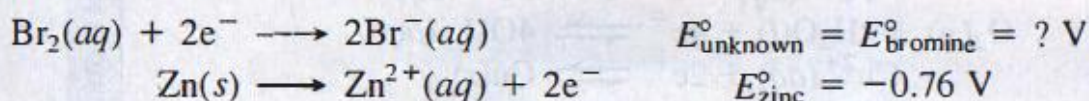
Calculating $E^{\circ}_{bromine}$:

$$E°_{cell} = E°_{cathode} - E°_{anode} = E°_{bromine} - E°_{zinc}$$
$$E°_{bromine} = E°_{cell} + E°_{zinc} = 1.83 \text{ V} + (-0.76 \text{ V})$$
$$= 1.07 \text{ V}$$

Check A good check is to make sure that calculating $E°_{bromine} - E°_{zinc}$ gives $E°_{cell}$: 1.07 V − (−0.76 V) = 1.83 V.

Comment Keep in mind that, whichever is the unknown half-cell, reduction is the cathode half-reaction and oxidation is the anode half-reaction. Always subtract $E°_{anode}$ from $E°_{cathode}$ to get $E°_{cell}$.

FOLLOW-UP PROBLEM 21.3 A voltaic cell based on the reaction between aqueous Br_2 and vanadium(III) ions has $E°_{cell} = 1.39$ V:

$$Br_2(aq) + 2V^{3+}(aq) + 2H_2O(l) \longrightarrow 2VO^{2+}(aq) + 4H^+(aq) + 2Br^-(aq)$$

What is $E°_{vanadium}$, the standard electrode potential for the reduction of VO^{2+} to V^{3+}?

Relative Strengths of Oxidizing and Reducing Agents

One of the things we can learn from measuring potentials of voltaic cells is the relative strengths of the oxidizing and reducing agents involved.
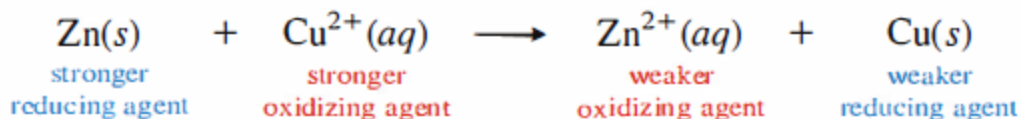

Table 21.2 Selected Standard Electrode Potentials (298 K)

Half-Reaction	$E°_{half-cell}$ (V)
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$	+1.23
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$N_2(g) + 5H^+(aq) + 4e^- \rightleftharpoons N_2H_5^+(aq)$	−0.23
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.44
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	−0.83
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.05

Strength of oxidizing agent (increasing upward)

Strength of reducing agent (increasing downward)
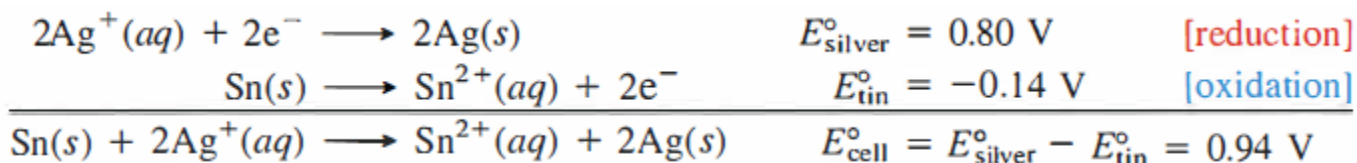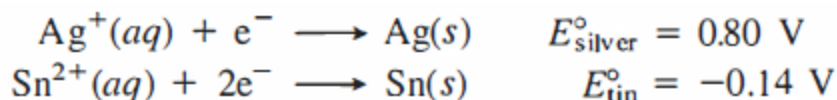
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Writing Spontaneous Redox Reactions

- o Every redox reaction is the sum of two half-reactions, so there is a reducing agent and an oxidizing agent on each side.

In the zinc-copper reaction:

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

stronger reducing agent   stronger oxidizing agent   weaker oxidizing agent   weaker reducing agent

- o Based on the order of the E^0 values in Appendix D, the stronger oxidizing agent (species on the left) has a half-reaction with a larger E^o value, and the stronger reducing agent (species on the right) has a half-reaction with a smaller E^o value.
- o Therefore, a spontaneous reaction ($E^o_{cell} > 0$) will occur between an oxidizing agent and any reducing agent that lies below it in the list.

Example

$$\text{Ag}^+(aq) + e^- \longrightarrow \text{Ag}(s) \qquad E^\circ_{silver} = 0.80 \text{ V}$$
$$\text{Sn}^{2+}(aq) + 2e^- \longrightarrow \text{Sn}(s) \qquad E^\circ_{tin} = -0.14 \text{ V}$$

$$2\text{Ag}^+(aq) + 2e^- \longrightarrow 2\text{Ag}(s) \qquad E^\circ_{silver} = 0.80 \text{ V} \qquad [\text{reduction}]$$
$$\text{Sn}(s) \longrightarrow \text{Sn}^{2+}(aq) + 2e^- \qquad E^\circ_{tin} = -0.14 \text{ V} \qquad [\text{oxidation}]$$
$$\overline{\text{Sn}(s) + 2\text{Ag}^+(aq) \longrightarrow \text{Sn}^{2+}(aq) + 2\text{Ag}(s) \qquad E^\circ_{cell} = E^\circ_{silver} - E^\circ_{tin} = 0.94 \text{ V}}$$
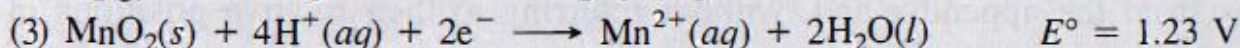
Notice that

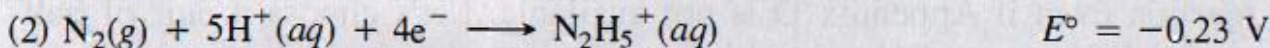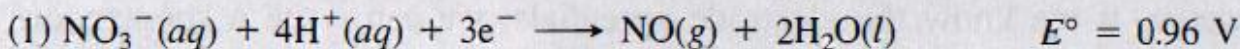- ✓ changing the balancing coefficients of a half- reaction does not change the E^o value. The reason is that a standard electrode potential is an intensive property, one that does not depend on the amount of substance present.
- ✓ When a half-reaction is reversed, the sign of $E_{half\text{-}cell}$ is not reversed because the minus sign in Equation 21.3 ($E^o_{cell} = E^o_{cathode} - E^o_{anode}$) will do that.
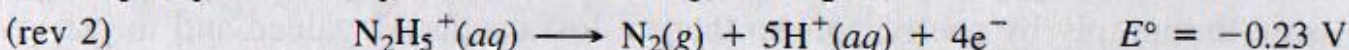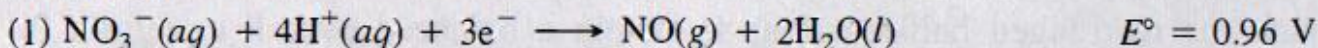
SAMPLE PROBLEM 21.4 Writing Spontaneous Redox Reactions

Problem Combine the following three half-reactions into three balanced equations (A, B, and C) for spontaneous reactions, and calculate $E°_{cell}$ for each.

(1) $NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O(l)$ $E° = 0.96$ V
(2) $N_2(g) + 5H^+(aq) + 4e^- \longrightarrow N_2H_5^+(aq)$ $E° = -0.23$ V
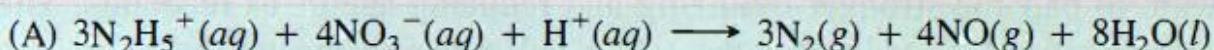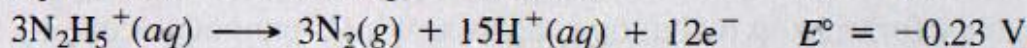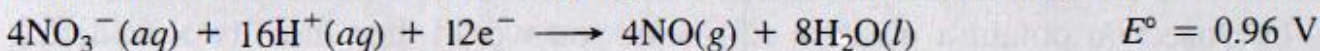(3) $MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O(l)$ $E° = 1.23$ V

Plan To write the redox equations, we combine the possible pairs of half-reactions: (1) and (2), (1) and (3), and (2) and (3). They are all written as reductions, so the oxidizing agents appear as reactants and the reducing agents appear as products. In each pair, we reverse the reduction half-reaction that has the smaller (less positive or more negative) $E°$ value to an oxidation to obtain a positive $E°_{cell}$. We make e⁻ lost equal e⁻ gained, without changing the magnitude of the $E°$ value, add the half-reactions together, and then apply Equation 21.3 to find $E°_{cell}$.

Solution Combining half-reactions (1) and (2) gives equation (A). The $E°$ value for half-reaction (1) is larger (more positive) than that for (2), so we reverse (2) to obtain a positive $E°_{cell}$:
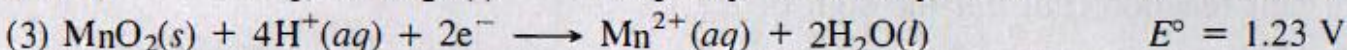
(1) $NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O(l)$ $E° = 0.96$ V
(rev 2) $N_2H_5^+(aq) \longrightarrow N_2(g) + 5H^+(aq) + 4e^-$ $E° = -0.23$ V

To make e⁻ lost equal e⁻ gained, we multiply (1) by four and the reversed (2) by three; then add half-reactions and cancel appropriate numbers of common species (H⁺ and e⁻):

$4NO_3^-(aq) + 16H^+(aq) + 12e^- \longrightarrow 4NO(g) + 8H_2O(l)$ $E° = 0.96$ V
$3N_2H_5^+(aq) \longrightarrow 3N_2(g) + 15H^+(aq) + 12e^-$ $E° = -0.23$ V

(A) $3N_2H_5^+(aq) + 4NO_3^-(aq) + H^+(aq) \longrightarrow 3N_2(g) + 4NO(g) + 8H_2O(l)$

$$E°_{cell} = 0.96 \text{ V} - (-0.23 \text{ V}) = 1.19 \text{ V}$$

Combining half-reactions (1) and (3) gives equation (B). Half-reaction (1) must be reversed:

(rev 1) $NO(g) + 2H_2O(l) \longrightarrow NO_3^-(aq) + 4H^+(aq) + 3e^-$ $E° = 0.96$ V
(3) $MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O(l)$ $E° = 1.23$ V
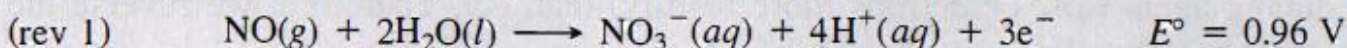
We multiply reversed (1) by two and (3) by three, then add and cancel:

$2NO(g) + 4H_2O(l) \longrightarrow 2NO_3^-(aq) + 8H^+(aq) + 6e^-$ $E° = 0.96$ V
$3MnO_2(s) + 12H^+(aq) + 6e^- \longrightarrow 3Mn^{2+}(aq) + 6H_2O(l)$ $E° = 1.23$ V

(B) $3MnO_2(s) + 4H^+(aq) + 2NO(g) \longrightarrow 3Mn^{2+}(aq) + 2H_2O(l) + 2NO_3^-(aq)$

$$E°_{cell} = 1.23 \text{ V} - 0.96 \text{ V} = 0.27 \text{ V}$$

Combining half-reactions (2) and (3) gives equation (C). Half-reaction (2) must be reversed:

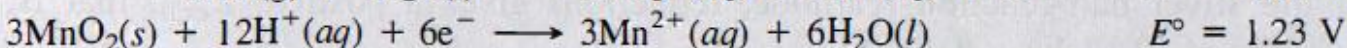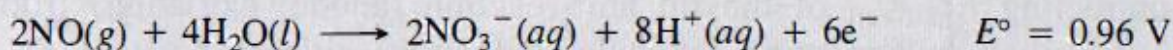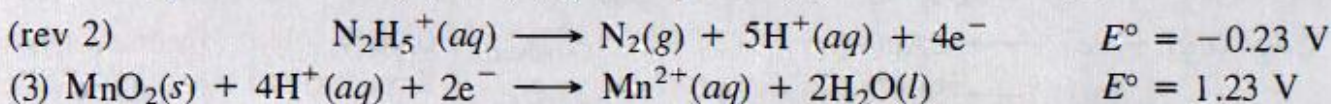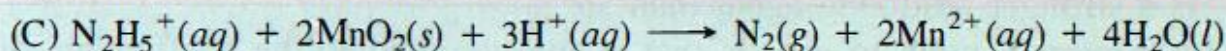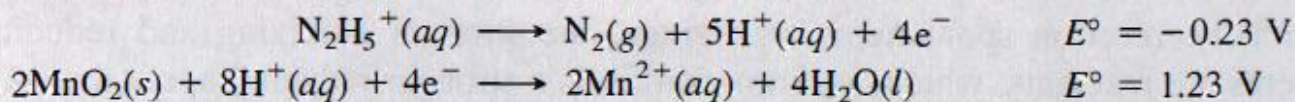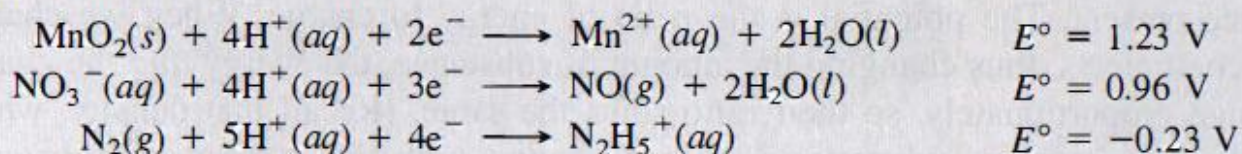$$\text{(rev 2)} \quad N_2H_5^+(aq) \longrightarrow N_2(g) + 5H^+(aq) + 4e^- \qquad E^\circ = -0.23 \text{ V}$$
$$\text{(3) } MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O(l) \qquad E^\circ = 1.23 \text{ V}$$

We multiply reaction (3) by two, add the half-reactions, and cancel:

$$N_2H_5^+(aq) \longrightarrow N_2(g) + 5H^+(aq) + 4e^- \qquad E^\circ = -0.23 \text{ V}$$
$$2MnO_2(s) + 8H^+(aq) + 4e^- \longrightarrow 2Mn^{2+}(aq) + 4H_2O(l) \qquad E^\circ = 1.23 \text{ V}$$

$$\text{(C) } N_2H_5^+(aq) + 2MnO_2(s) + 3H^+(aq) \longrightarrow N_2(g) + 2Mn^{2+}(aq) + 4H_2O(l)$$

$$E^\circ_{cell} = 1.23 \text{ V} - (-0.23 \text{ V}) = 1.46 \text{ V}$$

Check As always, check that atoms and charge balance on each side of the equation. A good way to check that the reactions are spontaneous is to list the given half-reactions in order of decreasing E° value:

$$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O(l) \qquad E^\circ = 1.23 \text{ V}$$
$$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O(l) \qquad E^\circ = 0.96 \text{ V}$$
$$N_2(g) + 5H^+(aq) + 4e^- \longrightarrow N_2H_5^+(aq) \qquad E^\circ = -0.23 \text{ V}$$

Then the oxidizing agents (reactants) decrease in strength going down the list, so the reducing agents (products) decrease in strength going up. Each of the three spontaneous reactions (A, B, and C) should combine a reactant with a product that is lower down on this list.

FOLLOW-UP PROBLEM 21.4 Is the following reaction spontaneous as written?

$$3Fe^{2+}(aq) \longrightarrow Fe(s) + 2Fe^{3+}(aq)$$
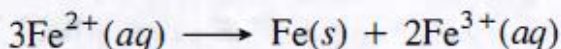
If not, write the equation for the spontaneous reaction, calculate E°_{cell}, and rank the three species of iron in order of decreasing reducing strength.

Relative Reactivities of Metals

1. Metals that can displace H_2 from acid.

If E°_{cell} for the reduction of H^+ is **more positive** for metal A than it is for metal B, metal A is a stronger reducing agent than metal B and a more active metal.

$$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^- \qquad E^\circ = -0.44 \text{ V} \quad \text{[anode; oxidation]}$$
$$2H^+(aq) + 2e^- \longrightarrow H_2(g) \qquad E^\circ = 0.00 \text{ V} \quad \text{[cathode; reduction]}$$
$$Fe(s) + 2H^+(aq) \longrightarrow H_2(g) + Fe^{2+}(aq) \qquad E^\circ_{cell} = 0.00 \text{ V} - (-0.44 \text{ V}) = 0.44 \text{ V}$$

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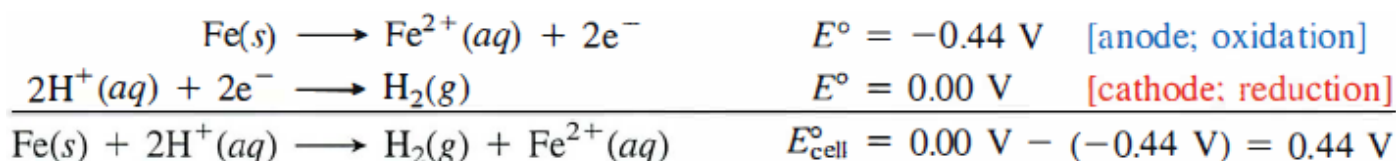
2. Metals that cannot displace H_2 from acid.

Metals that are above the standard hydrogen (reference) half-reaction cannot reduce H^+ from acids.

$$\begin{array}{lll} Ag(s) \longrightarrow Ag^+(aq) + e^- & E^\circ = 0.80 \text{ V} & \text{[anode; oxidation]} \\ 2H^+(aq) + 2e^- \longrightarrow H_2(g) & E^\circ = 0.00 \text{ V} & \text{[cathode: reduction]} \\ \hline 2Ag(s) + 2H^+(aq) \longrightarrow 2Ag^+(aq) + H_2(g) & E^\circ_{cell} = 0.00 \text{ V} - 0.80 \text{ V} = -0.80 \text{ V} \end{array}$$
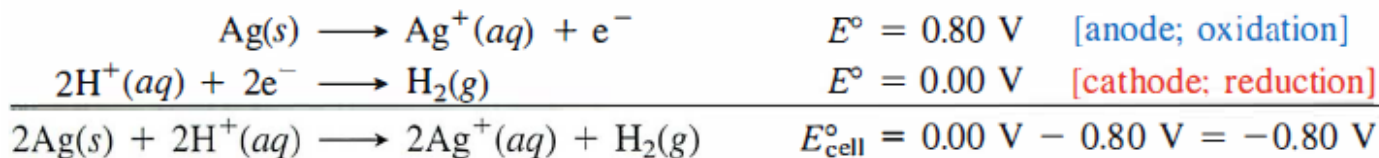
3. Metals that can displace H_2 from water.

Metals active enough to reduce H_2O lie below that half-reaction:
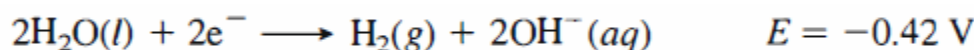
$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \qquad E = -0.42 \text{ V}$$

consider the reaction of sodium in water;

$$\begin{array}{lll} 2Na(s) \longrightarrow 2Na^+(aq) + 2e^- & E^\circ = -2.71 \text{ V} & \text{[anode; oxidation]} \\ 2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) & E = -0.42 \text{ V} & \text{[cathode; reduction]} \\ \hline 2Na(s) + 2H_2O(l) \longrightarrow 2Na^+(aq) + H_2(g) + 2OH^-(aq) \\ \qquad\qquad E_{cell} = -0.42 \text{ V} - (-2.71 \text{ V}) = 2.29 \text{ V} \end{array}$$
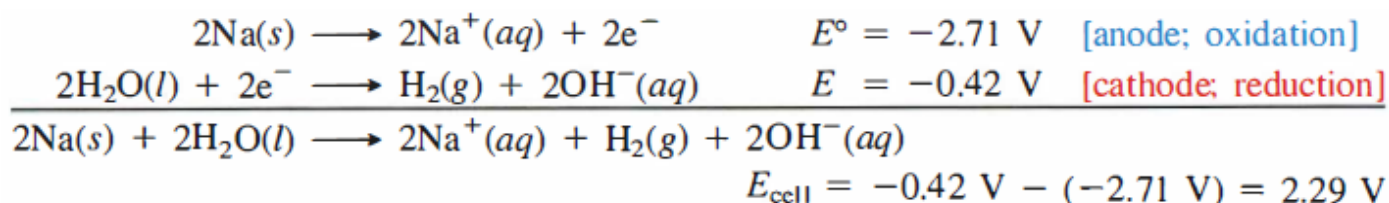
4. Metals that can displace other metals from solution.

We can also predict whether one metal can reduce the aqueous ion of another metal. Any metal that is lower in the list in Appendix D can reduce the ion of a metal that is higher up, and thus displace that metal from solution. For example, zinc can displace iron from solution:

$$\begin{array}{lll} Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- & E^\circ = -0.76 \text{ V} & \text{[anode; oxidation]} \\ Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s) & E^\circ = -0.44 \text{ V} & \text{[cathode; reduction]} \\ \hline Zn(s) + Fe^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Fe(s) & E^\circ_{cell} = -0.44 \text{ V} - (-0.76 \text{ V}) = 0.32 \text{ V} \end{array}$$
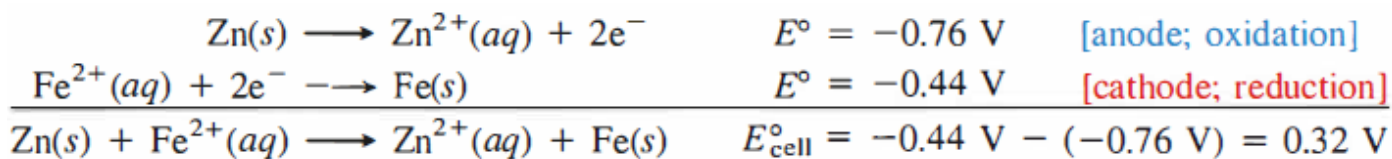
21.4 FREE ENERGY AND ELECTRICAL WORK

Standard Cell Potential and the Equilibrium Constant

As you know from Section 20.3 , a spontaneous reaction has a negative free energy

change ($\Delta G < 0$), and a spontaneous electrochemical reaction has a positive cell potential ($E_{cell} > 0$).

These two indications of spontaneity are related to each other:

$$\Delta G = -nFE_{cell}$$

n is the number of moles of electrons transferred, F is **Faraday constant** (96,485 C/mol e⁻).

When all of the components are in their standard states, we have

$$\Delta G^{\circ} = -nFE^{\circ}_{cell}$$

Using this relationship, we can relate the standard cell potential to the equilibrium constant of the redox reaction:

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

$$-nFE^{\circ}_{cell} = -RT \ln K$$

$$E^{\circ}_{cell} = \frac{RT}{nF} \ln K$$

$$E^{\circ}_{cell} = \frac{0.0592 \text{ V}}{n} \log K \quad \text{or} \quad \log K = \frac{nE^{\circ}_{cell}}{0.0592 \text{ V}} \quad \text{(at 298.15 K)}$$
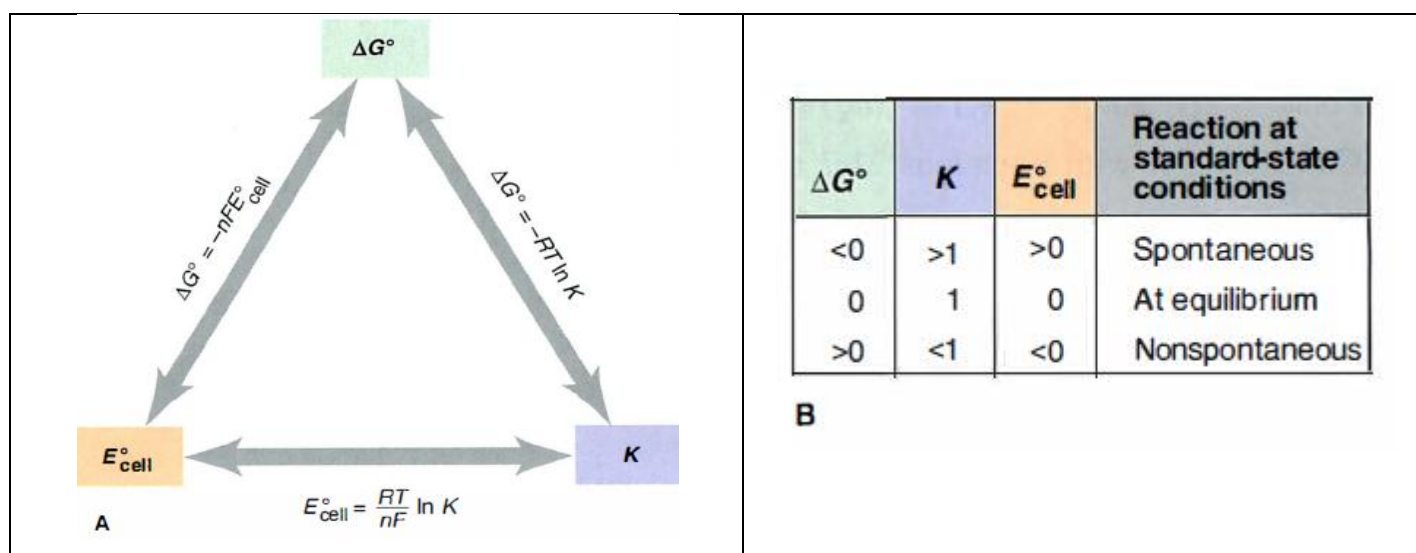

ΔG°	K	E°_{cell}	Reaction at standard-state conditions
<0	>1	>0	Spontaneous
0	1	0	At equilibrium
>0	<1	<0	Nonspontaneous

Figure 21.10 The interrelationship of ΔG°, E°_{cell}> and K. A, Any one of these three central thermodynamic parameters can be used to find the other two. B, The signs of ΔG° and E°_{cell} determine the reaction direction at standard-state conditions.

SAMPLE PROBLEM 21.5   Calculating K and $\Delta G°$ from $E°_{cell}$

Problem Lead can displace silver from solution:

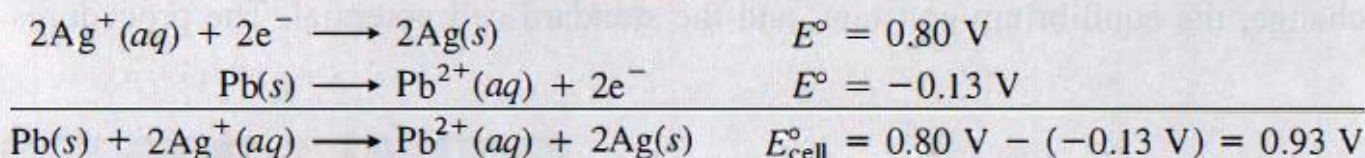$$Pb(s) + 2Ag^+(aq) \longrightarrow Pb^{2+}(aq) + 2Ag(s)$$

As a consequence, silver is a valuable by-product in the industrial extraction of lead from its ore. Calculate K and $\Delta G°$ at 298.15 K for this reaction.

Plan We divide the spontaneous redox equation into the half-reactions and use values from Appendix D to calculate $E°_{cell}$. Then, we substitute this result into Equation 21.8 to find K and into Equation 21.6 to find $\Delta G°$.

Solution Writing the half-reactions and their $E°$ values:

(1) $Ag^+(aq) + e^- \longrightarrow Ag(s)$ $E° = 0.80$ V
(2) $Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$ $E° = -0.13$ V
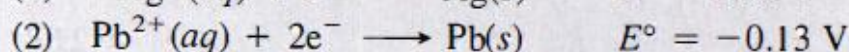
Calculating $E°_{cell}$: We double (1), reverse (2), add the half-reactions, and subtract $E°_{lead}$ from $E°_{silver}$:

$$2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s) \qquad\qquad E° = 0.80 \text{ V}$$
$$Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^- \qquad\qquad E° = -0.13 \text{ V}$$

$\overline{Pb(s) + 2Ag^+(aq) \longrightarrow Pb^{2+}(aq) + 2Ag(s) \quad E°_{cell} = 0.80 \text{ V} - (-0.13 \text{ V}) = 0.93 \text{ V}}$

Calculating K with Equations 21.7 and 21.8:

$$E°_{cell} = \frac{RT}{nF} \ln K = 2.303 \frac{RT}{nF} \log K$$

The adjusted half-reactions show that 2 mol of e^- are transferred per mole of reaction as written, so $n = 2$. Then, performing the substitutions for R and F that we just discussed with the cell running at 25°C (298.15 K), we have

$$E°_{cell} = \frac{0.0592 \text{ V}}{2} \log K = 0.93 \text{ V}$$

So, $\log K = \dfrac{0.93 \text{ V} \times 2}{0.0592 \text{ V}} = 31.42$ and $\boxed{K = 2.6 \times 10^{31}}$

Calculating $\Delta G°$ (Equation 21.6):

$$\Delta G° = -nFE°_{cell} = -\frac{2 \text{ mol } e^-}{\text{mol rxn}} \times \frac{96.5 \text{ kJ}}{\text{V} \cdot \text{mol } e^-} \times 0.93 \text{ V} = \boxed{-1.8 \times 10^2 \text{ kJ/mol rxn}}$$

Check The three variables are consistent with the reaction being spontaneous at standard-state conditions: $E°_{cell} > 0$, $\Delta G° < 0$, and $K > 1$. Be sure to round and check the order of magnitude: in the $\Delta G°$ calculation, for instance, $\Delta G° \approx -2 \times 100 \times 1 = -200$, so the overall math seems right. Another check would be to obtain $\Delta G°$ directly from its relation with K:

$$\Delta G° = -RT \ln K = -8.314 \text{ J/mol rxn} \cdot \text{K} \times 298.15 \text{ K} \times \ln (2.6 \times 10^{31})$$
$$= -1.8 \times 10^5 \text{ J/mol rxn} = -1.8 \times 10^2 \text{ kJ/mol rxn}$$

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FOLLOW-UP PROBLEM 21.5 When cadmium metal reduces Cu^{2+} in solution, Cd^{2+} forms in addition to copper metal. Given that $\Delta G° = -143$ kJ, calculate K at 25°C. What is $E°_{cell}$ of a voltaic cell that uses this reaction?

The Effect of Concentration on Cell Potential

Recall from Chapter 20 (Equation 20.13) that:

$$\Delta G = \Delta G° + RT \ln Q$$

$$-nFE_{cell} = -nFE°_{cell} + RT \ln Q$$

Dividing both sides by -nF, we obtain the **Nernst equation**:

$$E_{cell} = E°_{cell} - \frac{RT}{nF} \ln Q$$

- When $Q < 1$ and thus [reactant] > [product], $\ln Q < 0$, so $E_{cell} > E°_{cell}$.
- When $Q = 1$ and thus [reactant] = [product], $\ln Q = 0$, so $E_{cell} = E°_{cell}$.
- When $Q > 1$ and thus [reactant] < [product], $\ln Q > 0$, so $E_{cell} < E°_{cell}$.

The equation can be rewritten as:

$$E_{cell} = E°_{cell} - \frac{0.0592 \text{ V}}{n} \log Q \quad \text{(at 298.15 K)}$$

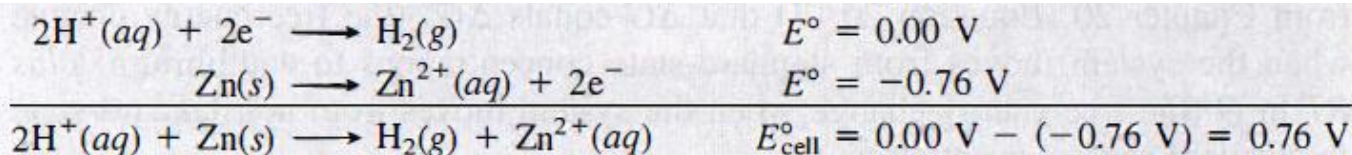**SAMPLE PROBLEM 21.6** Using the Nernst Equation to Calculate E_{cell}

Problem In a test of a new reference electrode, a chemist constructs a voltaic cell consisting of a Zn/Zn^{2+} half-cell and an H_2/H^+ half-cell under the following conditions:

$$[Zn^{2+}] = 0.010 \text{ M} \qquad [H^+] = 2.5 \text{ M} \qquad P_{H_2} = 0.30 \text{ atm}$$

Calculate E_{cell} at 298.15 K.
Plan To apply the Nernst equation and determine E_{cell}, we must know $E°_{cell}$ and Q. We write the spontaneous reaction, calculate $E°_{cell}$ from standard electrode potentials (Appendix D), and use the given pressure and concentrations to find Q. (Recall that the ideal gas law allows us to use P at constant T as another way of writing concentration, n/V.) Then we substitute into Equation 21.10.
Solution Determining the cell reaction and $E°_{cell}$:

$$2H^+(aq) + 2e^- \longrightarrow H_2(g) \qquad\qquad E° = 0.00 \text{ V}$$
$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \qquad\qquad E° = -0.76 \text{ V}$$

$$2H^+(aq) + Zn(s) \longrightarrow H_2(g) + Zn^{2+}(aq) \qquad E°_{cell} = 0.00 \text{ V} - (-0.76 \text{ V}) = 0.76 \text{ V}$$

Calculating Q:

$$Q = \frac{P_{H_2} \times [Zn^{2+}]}{[H^+]^2} = \frac{0.30 \times 0.010}{2.5^2} = 4.8 \times 10^{-4}$$

Solving for E_{cell} at 25°C (298.15 K), with $n = 2$:

$$E_{cell} = E°_{cell} - 2.303\frac{RT}{nF}\log Q = E°_{cell} - \frac{0.0592 \text{ V}}{n}\log Q$$

$$= 0.76 \text{ V} - \left[\frac{0.0592 \text{ V}}{2}\log(4.8\times10^{-4})\right] = 0.76 \text{ V} - (-0.0982 \text{ V}) = \boxed{0.86 \text{ V}}$$

Check After you check the arithmetic, reason through the answer: $E_{cell} > E°_{cell}$ (0.86 > 0.76) because the log Q term was negative, which is consistent with $Q < 1$; that is, the amounts of products, P_{H_2} and $[Zn^{2+}]$, are smaller than the amount of reactant, $[H^+]$.

FOLLOW-UP PROBLEM 21.6 Consider a voltaic cell based on the following reaction: $Fe(s) + Cu^{2+}(aq) \rightleftharpoons Fe^{2+}(aq) + Cu(s)$. If $[Cu^{2+}] = 0.30 \text{ M}$, what must $[Fe^{2+}]$ be to increase E_{cell} by 0.25 V above $E°_{cell}$ at 25°C?