

20 • Electrochemistry

20.3 - 20.4 Voltaic Cells and Cell EMF

Electrons spontaneously flow from one species to another—and through the wire from the anode to the cathode of a voltaic cell—because of a difference in potential energy, or a *potential difference*. The potential difference between two electrodes is measured in volts. One volt is equal to one joule per coulomb.

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

The potential difference that drives electrons through the wire in a voltaic cell is called the **electromotive force** or **emf**. For a voltaic cell the emf is denoted E_{cell} and referred to as the **cell potential**.

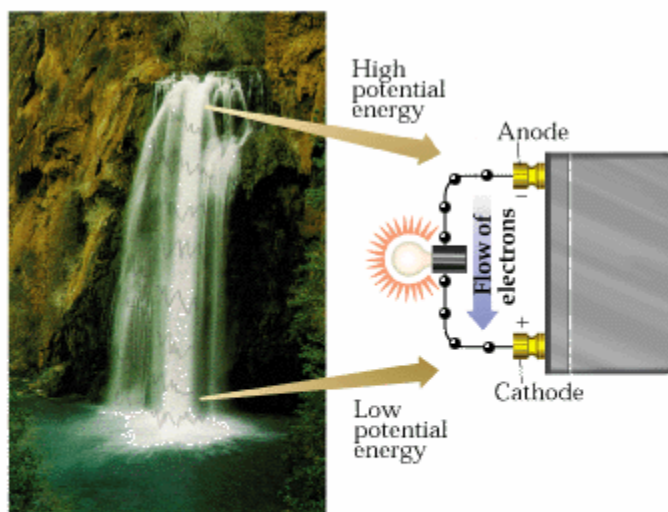
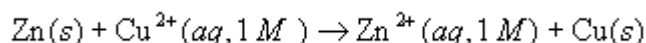


Figure 20.9. The flow of electrons from the anode to the cathode of a voltaic cell can be likened to the flow of water over a waterfall. Water flows over the waterfall because its potential energy is lower at the bottom of the falls than at the top. Likewise, if there is an electrical connection between the anode and cathode of a voltaic cell, electrons flow from the anode to the cathode in order to lower their potential energy.

The value of a cell potential depends on what half-reactions are taking place in the two compartments of the cell. The cell potential measured under standard conditions, E°_{cell} (25°C, 1 M concentrations, and 1 atm pressures), is the **standard cell potential** or **standard emf**. For the zinc and copper voltaic cell in Figure 20.5, E°_{cell} is 1.10 V. That is for the reaction



at 25°C, where the concentrations of copper and zinc ions are both 1 M.

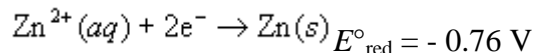
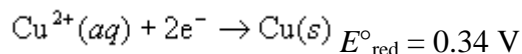
Such potentials can be measured experimentally, but many of them can be calculated from tabulated **standard reduction potentials**, E°_{red} values.

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}}(\text{cathode}) - E^{\circ}_{\text{red}}(\text{anode})$$

Table 20.1 gives some standard reduction potentials.

TABLE 20.1 Standard Reduction Potentials in Water at 25°C	
Standard Potential (V)	Reduction Half-Reaction
+2.87	$\text{F}_2(\text{g}) + 2\text{e}^- \longrightarrow 2\text{F}^-(\text{aq})$
+1.51	$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$
+1.36	$\text{Cl}_2(\text{g}) + 2\text{e}^- \longrightarrow 2\text{Cl}^-(\text{aq})$
+1.33	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$
+1.23	$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}(\text{l})$
+1.06	$\text{Br}_2(\text{l}) + 2\text{e}^- \longrightarrow 2\text{Br}^-(\text{aq})$
+0.96	$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \longrightarrow \text{NO}(\text{g}) + \text{H}_2\text{O}(\text{l})$
+0.80	$\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$
+0.77	$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$
+0.68	$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{H}_2\text{O}_2(\text{aq})$
+0.59	$\text{MnO}_4^-(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + 3\text{e}^- \longrightarrow \text{MnO}_2(\text{s}) + 4\text{OH}^-(\text{aq})$
+0.54	$\text{I}_2(\text{s}) + 2\text{e}^- \longrightarrow 2\text{I}^-(\text{aq})$
+0.40	$\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \longrightarrow 4\text{OH}^-(\text{aq})$
+0.34	$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cu}(\text{s})$
0	$2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{H}_2(\text{g})$
-0.28	$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ni}(\text{s})$
-0.44	$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Fe}(\text{s})$
-0.76	$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Zn}(\text{s})$
-0.83	$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$
-1.66	$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Al}(\text{s})$
-2.71	$\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Na}(\text{s})$
-3.05	$\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Li}(\text{s})$

In order to calculate the value of E°_{cell} for the Zn/Cu cell, we locate the pertinent half-reactions on the table. (Note that all of the half-reactions are tabulated as reductions, even though when two are coupled, one must occur in the reverse sense as an oxidation.)



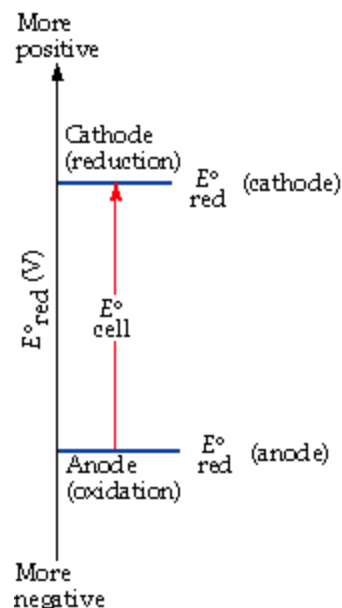
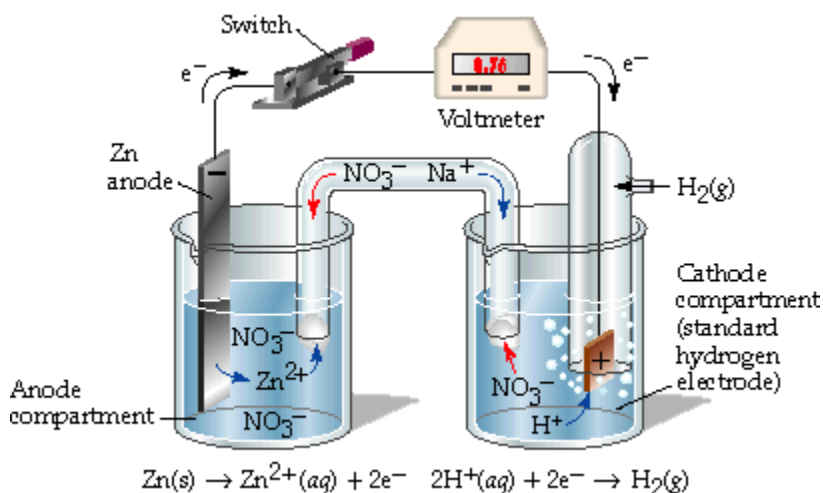
We have already seen that in this cell, oxidation occurs at the zinc electrode, making it the anode. The copper electrode is the cathode.

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}}(\text{cathode}) - E^\circ_{\text{red}}(\text{anode})$$

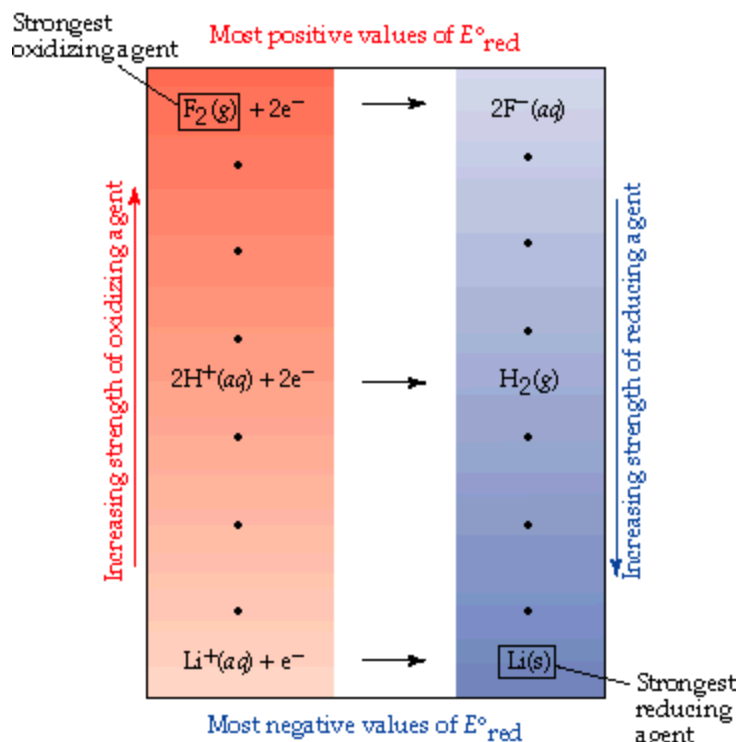
$$E^\circ_{\text{cell}} = 0.34 \text{ V} - (-0.76 \text{ V}) = 1.10 \text{ V}$$

The more positive the standard cell potential, the greater the driving force for electrons to flow from the anode to the cathode. Because the cathode of a voltaic cell is always the half-reaction with the more positive (or less negative) standard reduction potential, the standard cell potential of a voltaic cell is always positive.

The standard reduction potentials for the various half-reactions are measured against a **standard hydrogen electrode** (SHE). The half-reaction of interest and the SHE, both under standard conditions, are made into a voltaic cell, as shown in Figure 20.11, and the cell potential is measured experimentally. The standard potential of the standard hydrogen electrode's half-reaction is arbitrarily assigned a value of zero, so the measured potential corresponds to the half-reaction being evaluated.

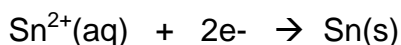
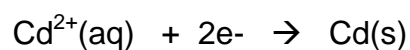


The standard reduction potentials in Table 20.1 can be used to compare the oxidizing power or reducing power of a substance. The more positive the value of E°_{red} for a species, the more readily it undergoes reduction and the better *oxidizing agent* it is. As E°_{red} becomes more negative, the species on the right side of the arrow becomes a stronger *reducing agent*.



Voltaic Cell and EMF Questions

1. A voltaic cell is based on the following two standard half-reactions:

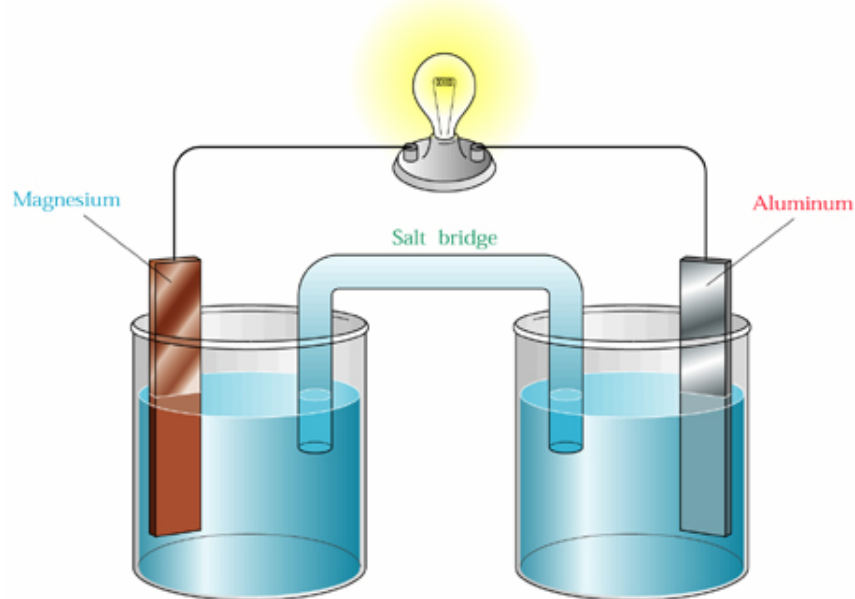


By using data in Appendix E, determine:

(a) the half-reactions that occur at the cathode and anode

(b) the standard cell potential

2. In the galvanic cell depicted below, which electrode would serve as the anode?



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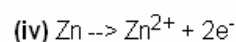
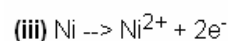
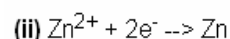
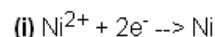
- ☐ No answer can be given, because this arrangement cannot act as a galvanic cell.
- ☐ The aluminum electrode is the anode.
- ☐ The magnesium electrode is the anode.

3. Solid lead(II) sulfide reacts with oxygen in the air at high temperatures to form lead(II) oxide and sulfur dioxide. Which substance is a reductant (reducing agent) and which is an oxidant (oxidizing agent)?

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- ☐ PbS, reductant; O₂, oxidant
- ☐ PbS, oxidant; SO₂, reductant
- ☐ PbS, reductant; no oxidant
- ☐ PbS, reductant; SO₂, oxidant
- ☐ Pb²⁺, reductant; S²⁻ oxidant

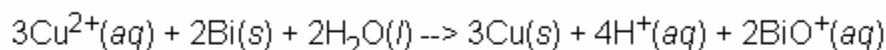
4. A voltaic cell similar to that shown in Figure 20.5 is constructed. One electrode compartment consists of a zinc strip placed in a solution of Zn(NO₃)₂, and the other has a nickel strip placed in a solution of NiCl₂. Which one of the following occurs at the anode and which at the cathode?



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- ☐ i anode, iv cathode
- ☐ i anode, ii cathode
- ☐ i cathode, iv anode
- ☐ i cathode, iii anode
- ☐ i anode, iii cathode

5. Using standard reduction potentials, calculate the standard emf for the following reaction:



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- ☐ +0.02 V
- ☐ +0.38 V
- ☐ -0.38 V
- ☐ -0.02 V

6. Using standard reduction potentials, calculate the standard emf for the following reaction:



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- ☐ -0.674 V
- ☐ -0.368 V
- ☐ 0.674 V
- ☐ 0.368 V

7. Cu metal displaces $\text{Ag}^+(\text{aq})$ from an aqueous solution. Which of the following is correct?

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- ☐ Ag is easier to oxidize than Cu.
- ☐ Ag^+ is easier to reduce than Cu^{2+} .
- ☐ Ag is a better reducing agent than Cu.
- ☐ Cu^{2+} is a better oxidizing agent than Ag^+ .

8. Which of the following is the best oxidizing agent according to the table below?

Selected Standard Electrode Potentials at 25°C

E° , V

$\text{Mg}^{2+}(\text{aq})$	+	2e^-	\rightarrow	$\text{Mg}(\text{s})$	-2.356
$\text{Fe}^{2+}(\text{aq})$	+	2e^-	\rightarrow	$\text{Fe}(\text{s})$	-0.440
$\text{Pb}^{2+}(\text{aq})$	+	2e^-	\rightarrow	$\text{Pb}(\text{s})$	-0.125
$2\text{H}^+(\text{aq})$	+	2e^-	\rightarrow	$\text{H}_2(\text{g})$	0.0
$\text{Cu}^{2+}(\text{aq})$	+	2e^-	\rightarrow	$\text{Cu}(\text{s})$	+0.337
$\text{I}_2(\text{s})$	+	2e^-	\rightarrow	$2\text{I}^-(\text{aq})$	+0.535
$\text{Fe}^{3+}(\text{aq})$	+	e^-	\rightarrow	$\text{Fe}^{2+}(\text{aq})$	+0.771
$\text{Ag}^+(\text{aq})$	+	e^-	\rightarrow	$\text{Ag}(\text{s})$	+0.800
$\text{O}_2(\text{g})$	+	$4\text{H}^+(\text{aq}) + 4\text{e}^-$	\rightarrow	$2\text{H}_2\text{O}(\text{l})$	+1.229
$\text{Cl}_2(\text{g})$	+	2e^-	\rightarrow	$2\text{Cl}^-(\text{aq})$	+1.358
$\text{F}_2(\text{g})$	+	2e^-	\rightarrow	$2\text{F}^-(\text{aq})$	+2.866

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- ☐ F^-
- ☐ Ag^+
- ☐ Cl_2
- ☒ Cu^{2+}
- ☐ Fe^{3+}

9. Which of these statements about a galvanic cell are *not* true?

- i. The cathode carries a positive sign.
- ii. The anions migrate toward the cathode.
- iii. The electrons are released through the anode.
- iv. Reduction occurs at the anode.

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- ☐ i and ii
- ☐ ii and iv
- ☐ ii and iii
- ☐ i and iii
- ☐ iii and iv

10. For each of the following pairs of substances, use data in Appendix E to choose the one that is the stronger oxidizing agent.

(i) $\text{Br}_2(l)$ or $\text{I}_2(s)$

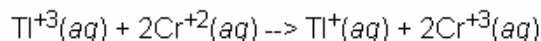
(ii) $\text{Ag}^+(aq)$ or $\text{AgCl}(s)$

(iii) $\text{Cl}_2(g)$ or $\text{Ce}^{4+}(aq)$

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- ☐ I_2 , Ag^+ , Ce^{4+}
- ☐ Br_2 , Ag^+ , Ce^{4+}
- ☐ Br_2 , AgCl , Cl_2
- ☐ I_2 , AgCl , Cl_2
- ☐ Br_2 , Ag^+ , Cl_2

11. A voltaic cell that uses the reaction



has a measured standard cell potential of 1.19 V. What is E°_{red} for the reduction of $\text{Ti}^{3+}(aq)$ to $\text{Ti}^{+}(aq)$?

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- ☐ 0.59 V
- ☐ 0.78 V
- ☐ 1.19 V
- ☐ -0.78 V
- ☐ 1.60 V

