

5.4: Day 39- Voltaic Cells, Half-Cell Potentials

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D39.1 Voltaic Cell Potential

When a voltaic cell is connected to a load, such as a light bulb, an electric current flows because there is a difference in electrical potential between the two electrodes. That electrical potential difference can be measured with a potentiometer (that is, a voltmeter). For an accurate measurement, the voltmeter must have a very high resistance so that no current flows; otherwise the voltage would drop from its highest possible value.

The voltaic cell shown in Figure 1, involves the spontaneous reaction

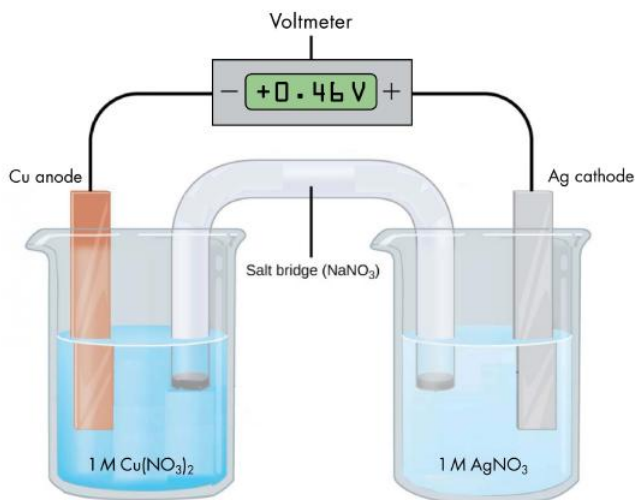
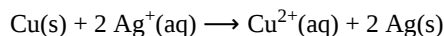


Figure 1. In this voltaic cell, an electrical potential difference between the electrodes is being measured with a voltmeter. When the concentrations of both solutions are 1 M, the potential difference for this cell is 0.46 V.

According to the reaction equation, copper loses electrons and is oxidized to copper(II) ions, so the half-cell with the copper electrode in Figure 1 is the anode. According to the reaction equation, silver ions gain electrons and are reduced to silver, so the half-cell with the silver electrode is the cathode. The copper electrode is more negative than the silver electrode.

When the more negative copper electrode is connected to the negative terminal of the voltmeter and the more positive silver electrode is connected to the positive terminal of the voltmeter, the meter reads +0.46 V. This reading is called the **cell potential**, E_{cell} . It is a measure of the energy per unit charge available from a redox reaction ($\text{V} = \text{J/C}$). A positive cell potential indicates how much electrical work a spontaneous reaction in a voltaic cell can do per unit electric charge moving through the circuit.

Under standard-state conditions (1 bar or 1 M, such as the 1-M concentrations in Figure 1), the cell potential is the standard cell potential, E°_{cell} (pronounced “E-standard-cell”). Thus, based on the voltmeter reading, $E^{\circ}_{\text{cell}} = 0.46 \text{ V}$

A meter like the one in Figure 1 measures the difference in electrical potential between its positive terminal and its negative terminal. Because the positive meter terminal is on the right, the cell potential is the difference in electrical potential between the right-hand half-cell and the left-hand half-cell, and we can write,

$$E_{\text{cell}} = E_{\text{right half-cell}} - E_{\text{left half-cell}}$$

In Figure 1, all concentrations are 1 M (standard-state conditions), so we can also write,

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{right half-cell}} - E^{\circ}_{\text{left half-cell}}$$

If the wire connections are reversed, a typical voltmeter would read -0.46 V . This provides an experimental way to determine which half-cell is the cathode and which is the anode: a positive voltmeter reading indicates that the meter’s negative terminal is

connected to the anode and the positive terminal is connected to the cathode; a negative voltmeter reading indicates the negative terminal is connected to the cathode and the positive terminal is connected to the anode.

The cell potential of a voltaic cell depends on the substances in each half-cell and the concentrations of solutions and partial pressures of gases involved in the half-cell. The half-cell potential does not depend on whether a half-reaction is occurring or on the direction in which the half-reaction goes. That is, the potential of the half cell involving silver ions and silver is the same whether silver is oxidized to silver ions or silver ions are reduced to silver.

A salt bridge must be present to complete an electric circuit. In the salt bridge when the cell generates electric current, anions move toward the anode and cations move toward the cathode.

D39.2 Cell Notation

Drawing a diagram, like Figure 1 above, to define a voltaic cell takes a lot of time. **Cell notation** is an abbreviation that summarizes the important information about a voltaic cell. In cell notation, a vertical line, |, denotes a phase boundary and a double line, ||, a salt bridge. The anode electrode is written to the left, followed by the anode solution, then the salt bridge, then the cathode solution, and, finally, the cathode electrode to the right. Figure 2 shows how the cell notation for a voltaic cell relates to various components of the cell.

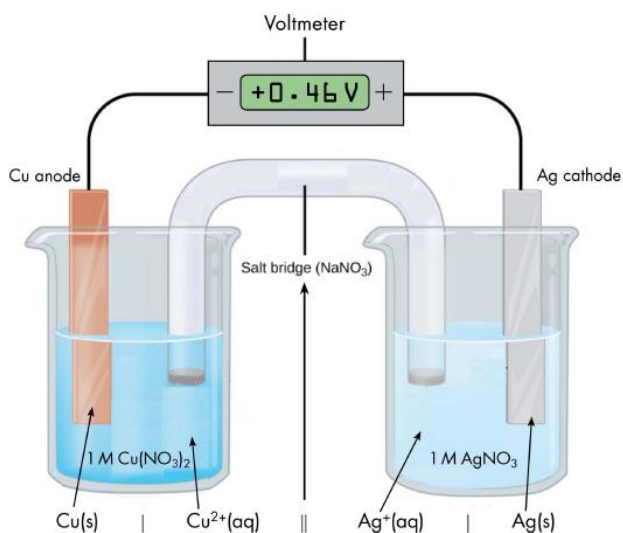


Figure 2. The cell notation, $\text{Cu(s)} | \text{Cu}^{2+}(\text{aq}) || \text{Ag}^{+}(\text{aq}) | \text{Ag(s)}$, is related to the diagram of the voltaic cell.

Note that spectator ions, such as NO_3^- , are not included in the cell notation, and if there are coefficients in a half-reaction the coefficients are not included (that is, the coefficients of 2 in the silver half-reaction are do not appear in the cell notation). When known, the initial concentrations of ions are usually included in the cell notation, so a more complete cell notation for the cell in Figure 2 is $\text{Cu(s)} | \text{Cu}^{2+}(\text{aq}, 1 \text{ M}) || \text{Ag}^{+}(\text{aq}, 1 \text{ M}) | \text{Ag(s)}$.

Some redox reactions involve species that are poor conductors of electricity, such as gases or ionic solids. For such substances, an inert electrode, that does not participate in the reactions, is used. An example of such a voltaic cell is shown in Figure 3.

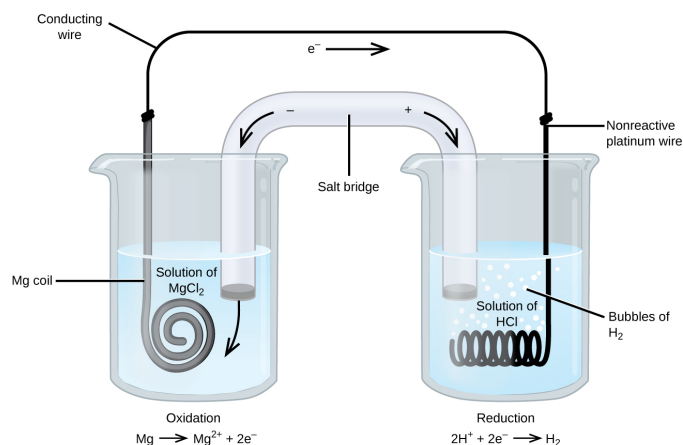


Figure 3. The oxidation of magnesium to magnesium ion occurs in the beaker on the left side in this apparatus; the reduction of hydrogen ions to hydrogen occurs in the beaker on the right. A nonreactive (inert) platinum wire conducts electrons into the right beaker.

The redox reaction involved is:

Oxidation (anode):	Mg(s)	→	Mg ²⁺ (aq) + 2e ⁻
Reduction (cathode):	2H ⁺ (aq) + 2e ⁻	→	H ₂ (g)
overall:	Mg(s) + 2H ⁺ (aq)	→	Mg ²⁺ (aq) + H ₂ (g)

This voltaic cell uses an inert platinum wire for the cathode, so the cell notation is:

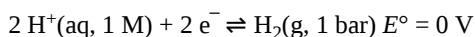


The magnesium electrode is an **active electrode** because it *participates in the redox reaction*. **Inert electrodes**, like the platinum electrode in Figure 3, *do not participate in the redox reaction* but must be present so that there is a complete electrical circuit. Platinum and gold are among the least reactive metals so they are good choices for inert electrodes. Graphite, also inert to many chemical reactions, is another common option.

D39.3 Standard Half-Cell Potentials

The cell potential in Figure 1 (+0.46 V) results from the *difference* in the electrical potential between the half-cells. It is not possible to measure directly the potential of a single half-cell; one half-cell has to be connected to another half-cell to measure a voltage.

However, it is useful to tabulate potentials for individual half-cells, such that the potential for a voltaic cell constructed from any two half-cells can be calculated from the values in the table. To create such a table, all half-cell potentials need to be measured relative to the same reference half-cell. That half-cell is the **standard hydrogen electrode (SHE)** (Figure 4), which consists of hydrogen gas at 1 bar pressure bubbling through a 1 M H⁺(aq) solution (platinum is used as the inert electrode):



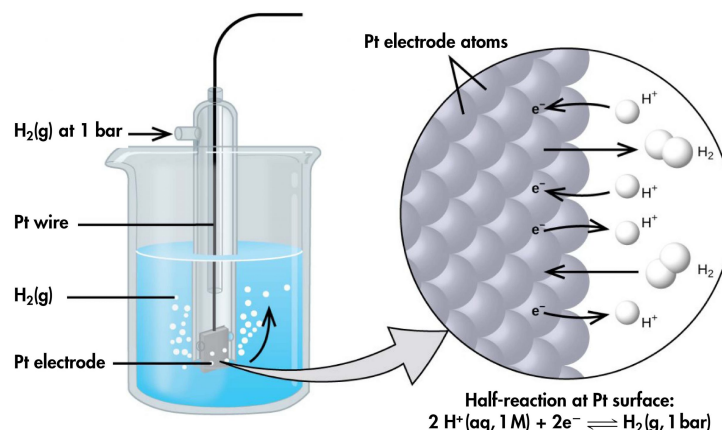


Figure 4. Hydrogen gas at 1 bar is bubbled through 1 M HCl solution. Platinum, which is inert to the action of the 1 M HCl, is used as the electrode. Electrons on the surface of the electrode combine with H^+ in solution to produce hydrogen gas.

If a cell is set up with the SHE on the left and the half-cell whose potential we want to measure on the right, with all concentrations 1 M and all gas partial pressures 1 bar, then the reading on the voltmeter is E° , the **standard half-cell potential**, for the half-cell on the right. (Unless specified, the temperature is typically assumed to be 25 °C.) For highly accurate measurements the voltmeter must not allow any current to flow; that is, no chemical reaction takes place.

For example, a voltaic cell consisted of a SHE and a $Cu^{2+} | Cu(s)$ half-cell (Figure 5) can be used to determine the standard half-cell potential for $Cu^{2+} | Cu(s)$.

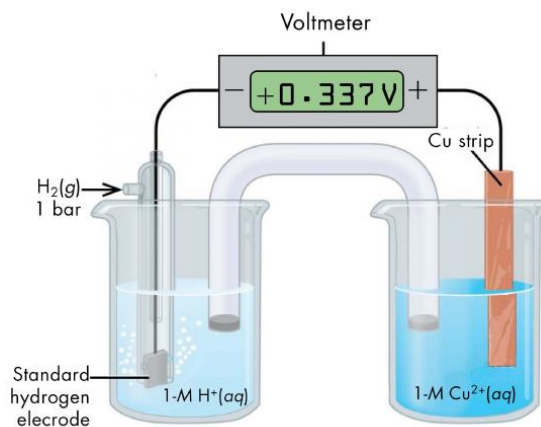
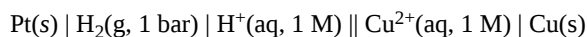


Figure 5. A voltaic cell involving the standard hydrogen electrode can be used to determine the standard half-cell potential of $Cu^{2+} | Cu(s)$.

The cell notation for this voltaic cell is:



As we noted in Section D39.1, the cell potential, E°_{cell} , measured by the voltmeter, is the difference between the potential of the right-hand half-cell and the left-hand half-cell:

$$E^\circ_{\text{cell}} = E^\circ_{\text{right half-cell}} - E^\circ_{\text{left half-cell}}$$

From the measured $E^\circ_{\text{cell}} = +0.337 \text{ V}$ and the defined potential of zero for the $Pt(s) | H_2(g, 1 \text{ bar}) | H^+(aq, 1 \text{ M})$ half-cell, we can calculate E° of the $Cu^{2+}(aq, 1 \text{ M}) | Cu(s)$ half-cell:

$$+0.337 \text{ V} = E^\circ_{Cu^{2+}|Cu} - E^\circ_{H^+|H_2} = E^\circ_{Cu^{2+}|Cu} - 0 = E^\circ_{Cu^{2+}|Cu}$$

Sometimes, when a cell is set up with the SHE on the left, the reading on the voltmeter is negative. That is, for some half-cells the standard half-cell potential is lower than the potential for the $Pt(s) | H_2(g, 1 \text{ bar}) | H^+(aq, 1 \text{ M})$ half-cell. Consider the cell shown in Figure 6, with cell notation

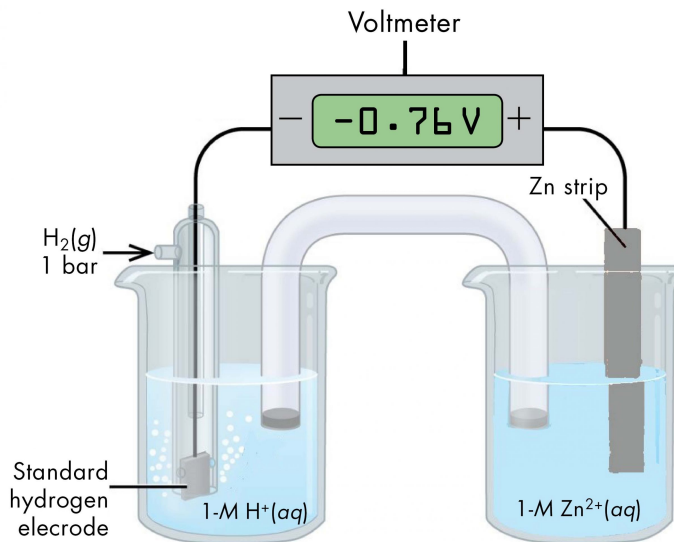
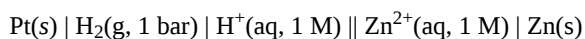


Figure 6. This voltaic cell can be used to determine the standard half-cell potential of the $\text{Zn}^{2+}(\text{aq}, 1 \text{ M}) \mid \text{Zn(s)}$ half-cell. The SHE on the left has a standard half-cell potential of zero.

Following the same reasoning as for the $\text{Cu}^{2+}(\text{aq}, 1 \text{ M}) \mid \text{Cu(s)}$ half-cell, E° of the $\text{Zn}^{2+}(\text{aq}, 1 \text{ M}) \mid \text{Zn(s)}$ half-cell can be calculated.

$$E^\circ_{\text{cell}} = E^\circ_{\text{right half-cell}} - E^\circ_{\text{left half-cell}}$$

$$-0.76 \text{ V} = E^\circ_{\text{Zn}^{2+} \mid \text{Zn}} - E^\circ_{\text{H}^+ \mid \text{H}_2} = E^\circ_{\text{Zn}^{2+} \mid \text{Zn}} - 0 = E^\circ_{\text{Zn}^{2+} \mid \text{Zn}}$$

It may seem strange that the standard half-cell potential is negative. This just reflects the fact that the electrical potential of the $\text{Zn}^{2+}(\text{aq}, 1 \text{ M}) \mid \text{Zn(s)}$ half-cell is smaller than the electrical potential of the $\text{Pt(s)} \mid \text{H}_2(\text{g}, 1 \text{ bar}) \mid \text{H}^+(\text{aq}, 1 \text{ M})$ half-cell. The potential of a half-cell depends only on the composition of the half-cell and does not depend on the direction of either a half-reaction or an overall reaction.

The standard hydrogen electrode is rather dangerous because $\text{H}_2(\text{g})$ is very flammable. Hence, it is rarely used in the laboratory. Its main significance is that it establishes the “zero” for standard half-cell potentials. Most standard half-cell potentials are measured by setting up a voltaic cell with one half-cell of known standard potential and one half-cell of unknown (to be measured) standard potential.

D39.4 Using Standard Half-Cell Potentials

Based on the methods described in the preceding section, [standard half-cell potentials](#) have been determined for many half-cells. The table below gives half-cell potentials for selected half-cells. Click on the table to open a version that can be enlarged or printed.

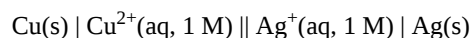
Standard Half-Cell Potentials in Aqueous Solution at 25 °C			
Reduction Half-Reaction	Half-Cell	E° (V)	
$\text{F}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{F}^-(\text{aq})$	$\text{F}_2(\text{g}) \text{F}^-(\text{aq}) \text{Pt}$	+2.87	
$\text{H}_2\text{O}_2(\text{aq}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow 2 \text{H}_2\text{O}(\ell)$	$\text{H}_2\text{O}_2(\text{aq}), \text{H}^+(\text{aq}), \text{H}_2\text{O}(\ell) \text{Pt}$	+1.763	
$\text{PbO}_2(\text{s}) + \text{SO}_4^{2-}(\text{aq}) + 4 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 2 \text{H}_2\text{O}(\ell)$	$\text{PbO}_2(\text{s}) \text{SO}_4^{2-}(\text{aq}), \text{H}^+(\text{aq}) \text{PbSO}_4(\text{s}) \text{Pb}$	+1.690	
$\text{Au}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Au}(\text{s})$	$\text{Au}^{3+}(\text{aq}) \text{Au}(\text{s})$	+1.52	
$\text{MnO}_4^-(\text{aq}) + 8 \text{H}^+(\text{aq}) + 5 \text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\ell)$	$\text{MnO}_4^-(\text{aq}), \text{H}^+(\text{aq}), \text{Mn}^{2+}(\text{aq}) \text{Pt}$	+1.51	
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^+(\text{aq}) + 6 \text{e}^- \rightarrow 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O}(\ell)$	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}), \text{H}^+(\text{aq}), \text{Cr}^{3+}(\text{aq}) \text{Pt}$	+1.36	
$\text{Cl}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{Cl}^-(\text{aq})$	$\text{Cl}_2(\text{g}) \text{Cl}^-(\text{aq}) \text{Pt}$	+1.358	
$\text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O}(\ell)$	$\text{O}_2(\text{g}) \text{H}^+(\text{aq}) \text{Pt}$	+1.229	
$\text{Br}_2(\ell) + 2 \text{e}^- \rightarrow 2 \text{Br}^-(\text{aq})$	$\text{Br}_2(\ell) \text{Br}^-(\text{aq}) \text{Pt}$	+1.066	
$\text{NO}_3^-(\text{aq}) + 4 \text{H}^+(\text{aq}) + 3 \text{e}^- \rightarrow \text{NO}(\text{g}) + 2 \text{H}_2\text{O}(\ell)$	$\text{NO}_3^-(\text{aq}), \text{H}^+(\text{aq}) \text{NO}(\text{g}) \text{Pt}$	+0.96	
$\text{OCl}^-(\text{aq}) + \text{H}_2\text{O}(\ell) + 2 \text{e}^- \rightarrow \text{Cl}^-(\text{aq}) + 2 \text{OH}^-(\text{aq})$	$\text{OCl}^-(\text{aq}), \text{Cl}^-(\text{aq}), \text{OH}^-(\text{aq}) \text{Pt}$	+0.89	
$\text{Hg}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Hg}(\ell)$	$\text{Hg}^{2+}(\text{aq}) \text{Hg}(\ell)$	+0.8535	
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	$\text{Ag}^+(\text{aq}) \text{Ag}(\text{s})$	+0.7991	
$\text{Hg}_2^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow 2 \text{Hg}(\ell)$	$\text{Hg}_2^{2+}(\text{aq}) \text{Hg}(\ell)$	+0.7960	
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	$\text{Fe}^{3+}(\text{aq}), \text{Fe}^{2+}(\text{aq}) \text{Pt}$	+0.771	
$\text{I}_2(\text{s}) + 2 \text{e}^- \rightarrow 2 \text{I}^-(\text{aq})$	$\text{I}_2(\text{s}) \text{I}^-(\text{aq}) \text{Pt}$	+0.535	
$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\ell) + 4 \text{e}^- \rightarrow 4 \text{OH}^-(\text{aq})$	$\text{O}_2(\text{g}) \text{OH}^-(\text{aq}) \text{Pt}$	+0.401	
$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu}(\text{s})$	$\text{Cu}^{2+}(\text{aq}) \text{Cu}(\text{s})$	+0.340	
$\text{Sn}^{4+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Sn}^{2+}(\text{aq})$	$\text{Sn}^{4+}(\text{aq}), \text{Sn}^{2+}(\text{aq}) \text{Pt}$	+0.15	
$2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g})$	$\text{H}^+(\text{aq}) \text{H}_2(\text{g}) \text{Pt}$	0	
$\text{Sn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Sn}(\text{s})$	$\text{Sn}^{2+}(\text{aq}) \text{Sn}(\text{s})$	-0.1375	
$\text{Ni}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Ni}(\text{s})$	$\text{Ni}^{2+}(\text{aq}) \text{Ni}(\text{s})$	-0.25	
$\text{PbSO}_4(\text{s}) + 2 \text{e}^- \rightarrow \text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq})$	$\text{PbSO}_4(\text{s}) \text{SO}_4^{2-}(\text{aq}) \text{Pb}(\text{s})$	-0.3505	
$\text{Cd}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cd}(\text{s})$	$\text{Cd}^{2+}(\text{aq}) \text{Cd}(\text{s})$	-0.403	
$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Fe}(\text{s})$	$\text{Fe}^{2+}(\text{aq}) \text{Fe}(\text{s})$	-0.44	
$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Zn}(\text{s})$	$\text{Zn}^{2+}(\text{aq}) \text{Zn}(\text{s})$	-0.763	
$2 \text{H}_2\text{O}(\ell) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$	$\text{H}_2\text{O}(\ell), \text{OH}^-(\text{aq}) \text{H}_2(\text{g}) \text{Pt}$	-0.8277	
$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Al}(\text{s})$	$\text{Al}^{3+}(\text{aq}) \text{Al}(\text{s})$	-1.676	
$\text{Mg}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Mg}(\text{s})$	$\text{Mg}^{2+}(\text{aq}) \text{Mg}(\text{s})$	-2.356	
$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	$\text{Na}^+(\text{aq}) \text{Na}(\text{s})$	-2.714	
$\text{K}^+(\text{aq}) + \text{e}^- \rightarrow \text{K}(\text{s})$	$\text{K}^+(\text{aq}) \text{K}(\text{s})$	-2.925	
$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	$\text{Li}^+(\text{aq}) \text{Li}(\text{s})$	-3.045	

Figure 7. Standard half-cell potentials in aqueous solutions at 25 °C, in volts versus the standard hydrogen electrode (highlighted in peach). Half-cell reactions in basic solutions are highlighted in blue. (Data from Bard, A. J., Parsons, R., and Jordan, J. *Standard Potentials in Aqueous Solution*. New York: Marcel Dekker: 1985. International Union of Pure and Applied Chemistry Commission on Electrochemistry and Electroanalytical Chemistry.)

There are several important aspects to note:

- The oxidizing agent is on the left (reactant) side of a reduction half-reaction equation.
- The **strongest oxidizing agents** (the substances most easily reduced) have the largest positive E° values and **are at the top of the table**. (For example, $F_2(g)$ is a very strong oxidizing agent.)
- The reducing agent is on the right (product) side of a reduction half-reaction equation.
- The **strongest reducing agents** (the substances most easily oxidized) have the most negative E° values and **are at the bottom of the table**. (For example, $Li(s)$ and $K(s)$ are very strong reducing agents.)
- A redox reaction is product-favored when a stronger oxidizing agent reacts with a stronger reducing agent. This results in a positive value for E°_{cell} when the oxidation half-reaction is combined with the reduction half-reaction.
- Half-cell reactions are reversible and the direction a half-cell reaction goes depends on the potential of the other half-cell to which it is connected in a cell.

The table of standard half-cell potentials can be used to determine the E°_{cell} for any voltaic cell and predict whether a specific redox reaction is product-favored. For example, for the cell:



$$E^\circ_{\text{cell}} = E^\circ_{\text{right half-cell}} - E^\circ_{\text{left half-cell}} = E^\circ_{Ag^+/Ag} - E^\circ_{Cu^{2+}/Cu} = 0.7991 V - 0.340 V = 0.459 V$$

Because the value of E°_{cell} is positive, the redox reaction corresponding to this cell notation is product-favored and the voltaic cell can produce electrical energy. The overall reaction can be obtained from the cell notation by writing the oxidation and the reduction half-reactions, multiplying each half-reaction by an appropriate number to balance electrons, and summing the two half-reactions:

Oxidation (left):	$Cu(s)$	\rightarrow	$Cu^{2+}(aq) + 2e^-$	$E^\circ_{\text{anode}} = +0.340 V$
Reduction (right):	$2 \times (Ag^+(aq) + e^-)$	\rightarrow	$Ag(s)$	$E^\circ_{\text{cathode}} = +0.7991 V$
Overall:	$Cu(s) + 2Ag^+(aq)$	\rightarrow	$Cu^{2+}(aq) + 2Ag(s)$	$E^\circ_{\text{cell}} = +0.459 V$

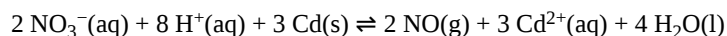
Note that:

- Even though the reduction half-reaction is multiplied by 2, the E°_{cathode} is not multiplied by 2 when E°_{cell} is calculated. This is because electrical potential is a ratio of energy per coulomb of charge transferred ($V = J/C$). If the half-reaction is doubled, both energy and charge transferred are doubled, leaving the ratio constant.
- The oxidation half-reaction is the reverse of the reaction as shown in the half-cell potential table, but E°_{right} is not multiplied by -1. The cell potential does not depend on the direction of a half-reaction; it depends only on the composition of the half-cell.

E° for many half-cells are included in the [appendix](#). Tables like these make it possible to determine the E°_{cell} for many redox reactions. Moreover, by comparing the standard potentials, we can discern which species is easier to reduce/harder to oxidize/is a stronger oxidizing agent (higher/more positive E°) and which species is easier to oxidize/harder to reduce/is a stronger reducing agent (lower/more negative E°).

Podia Question

Use data from the table of standard half-cell potentials to determine whether this redox reaction is product-favored.



Two days before the next whole-class session, this Podia question will become live on [Podia](#), where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use [this link](#) to report them. A similar link will be included in each day's material. We appreciate your comments.

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