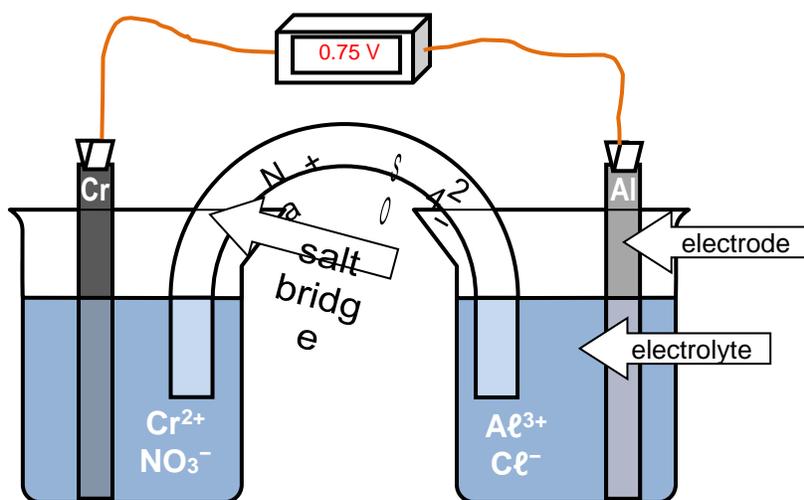


Voltaic Cells

A **voltaic** (or **galvanic**) **cell** is used to harness the energy released in a spontaneous redox reaction and transform that energy into electrical work. It does this by separating the reactants from direct contact with each other while providing a pathway for the electrons to flow between them.

A voltaic cell has two compartments, each containing an ionic solution (an **electrolyte**) and an **electrode**; a **salt bridge** (or porous glass disc between the compartments) and a wire connecting the electrodes. The electrons travel through the conducting wire between the two electrodes. A voltmeter can be connected to the wire to measure the potential of the reaction.

The compartments are called **half-cells**. In each half-cell a **half-reaction** takes place: a **half-reaction** is half of the overall redox reaction. One half-reaction will be the oxidation and one half-reaction will be the reduction.



Let's study the spontaneous reaction of chromium metal with aluminum in a voltaic cell. In the lab, our two half-cells are beakers. The left beaker holds a 1 M chromium nitrate solution and a chromium metal electrode. The right beaker has a 1 M aluminum chloride solution and an aluminum metal electrode. The salt bridge consists of an aqueous salt solution that will not interfere with the redox reaction (Na_2SO_4 in this case) and keeps the ionic solution in each half-cell electrically neutral.

For this cell, there's a chromium half-reaction: $\text{Cr}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cr}(\text{s})$, and an aluminum half-reaction: $\text{Al}(\text{s}) \rightarrow \text{Al}^{3+}(\text{aq}) + 3 \text{e}^-$. Notice that in half-reactions electrons are shown; a complete redox reaction for a cell *must not* have any electrons in it.

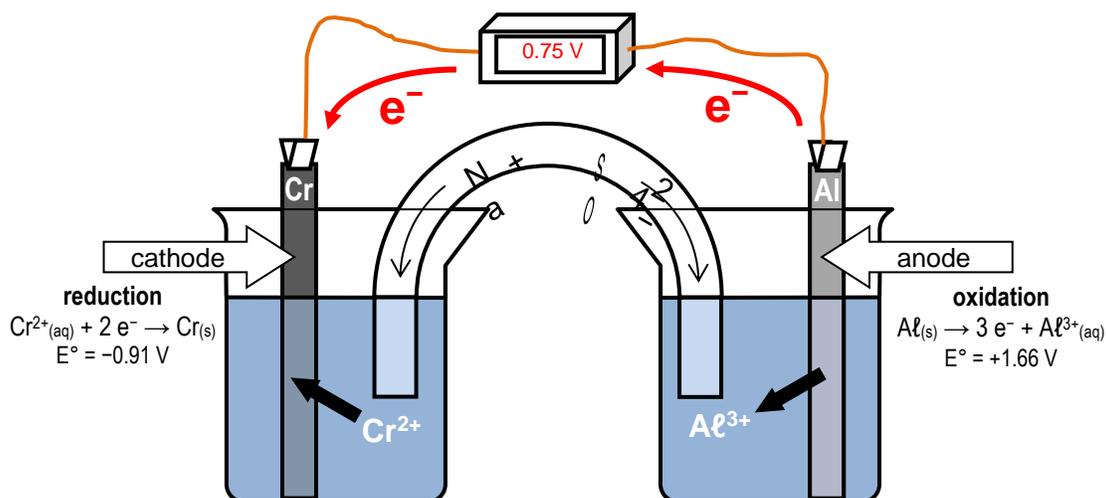
How do we know which metal will be reduced and which oxidized? It depends on which species wants the electrons more. The measure of attraction of charged particles, like



electrons, between two places is called voltage (**potential**, or **electromotive force**). For a galvanic cell, it has the symbol E .

The list of **standard reduction potentials** (E°_{red}) is given for many half-reactions at standard conditions in your textbook. The half-reaction with the more positive E°_{red} value will be reduced. The half-reaction with the more negative E°_{red} value will be oxidized; this half-reaction will be written backwards from the way it appears in the table in the final cell reaction equation.

Since E°_{red} for Cr^{2+} is greater than Al^{3+} ($-0.91 > -1.66$), the Cr^{2+} ion will be reduced, and $\text{Al}_{(s)}$ will be oxidized. The electrode at which reduction takes place is the **cathode**. The electrode where oxidation takes place is the **anode**. (Think: RED CAT at AN OX).



In oxidation of $\text{Al}_{(s)}$, electrons will flow from the anode to the cathode through the wire and $\text{Al}^{3+}_{(aq)}$ will build up in the solution. The aluminum electrode will start losing mass slowly as it dissociates into ions. The electrons that flow through the wire to the cathode react with Cr^{2+} ions in solution to plate $\text{Cr}_{(s)}$ onto the cathode. The chromium cathode will start to gain mass.

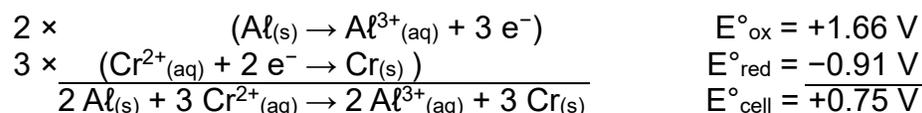
Any build-up of positive charge or negative charge in the ionic solution stops the flow of electrons through the wire. The negative sulphate ions from the salt bridge are drawn into the aluminum half-cell to balance the positive charge build-up of Al^{3+} ions. Similarly, as Cr^{2+} ions become a solid, the negative nitrate ions in solution are balanced by sodium cations from the salt bridge flowing in. The ions in the salt bridge complete the flow of charge in the cell and complete the circuit.

Example 1: A voltaic cell is constructed of two half-cells. One half-cell contains a copper electrode and a solution of $\text{Cu}(\text{NO}_3)_2$. The other half-cell contains a silver electrode and a solution of AgNO_3 . Identify the two half-reactions, which species is oxidized, and write the overall cell reaction.

Solution: The half-reaction of copper: $\text{Cu}_{(s)} \rightarrow \text{Cu}^{2+}_{(aq)} + 2e^-$. The half-reaction of silver: $\text{Ag}^{+}_{(aq)} + e^- \rightarrow \text{Ag}_{(s)}$. Since E°_{red} for this silver half-reaction is greater than the copper half-reaction ($0.80 > 0.34 \text{ V}$), Ag^{+} will be reduced and $\text{Cu}_{(s)}$ will be oxidized. The overall reaction is $2\text{Ag}^{+}_{(aq)} + \text{Cu}_{(s)} \rightarrow 2\text{Ag}_{(s)} + \text{Cu}^{2+}_{(aq)}$.



The aluminum/chromium cell we've been discussing is under **standard-state conditions**, meaning 1.00 M for all solution concentrations, and 1.00 atm for all pressures. The overall cell potential can be determined by adding the E° values for the two half-reactions. The *reduction* potential for the Al half-reaction is -1.66 V, but Al is being oxidized here, so the sign of the potential is reversed: $+1.66$ V. The oxidation potential is always the negative of the reduction potential.



The cell potential is $+0.75$ volts. (Notice that although we need to multiply each half-reaction to balance the electrons for the complete redox reaction, we do not multiply the potentials.) Because the E_{cell} is positive, we know that this is a spontaneous reaction, and current will flow.

The potential is low in a cell of this design because the aluminum and chromium are close to equilibrium in these concentrations. (A 1.00 M concentration for the aluminum ions means there's already a lot of products around, which slows the rate reaction down.) We can increase the cell potential by altering the concentrations of the electrolytes, or by altering the temperature of the cell's environment.

The equation for calculating the cell potential under non-standard conditions (called the **Nernst equation**) is:

$$E = E^\circ - \frac{RT \ln Q}{nF}$$

where R is the gas constant, $8.314 \text{ J/K}\cdot\text{mol}$,
 T is the temperature in kelvins,
 Q is the reaction quotient,
 n is the number of electrons exchanged in the reaction,
and F is Faraday's constant, $9.649 \times 10^4 \text{ C/mol}$

Example 2: Determine the cell potential of the aluminum/chromium cell at 25°C if the concentration of $[Al^{3+}]$ is now 0.0100 M .

Solution: The value for E° is still 0.75 V . According to the balanced half-reactions 6 electrons are exchanged, so $n = 6$. The temperature is 298 K . Q is calculated the same way as K , but there's no guarantee of the mixture being at equilibrium. (If it was, the cell would have no electrical potential and $E = 0$.)

$$Q = \frac{[\text{products}]}{[\text{reactants}]} = \frac{[Al^{3+}]^2}{[Cr^{2+}]^3} = \frac{(0.0100 \text{ M})^2}{(1.00 \text{ M})^3} = 0.0001$$

$$E = 0.75 \text{ V} - \frac{(8.314)(298)(\ln 0.0001)}{6(9.694 \times 10^4)} = 0.7894 \dots \approx +0.79 \text{ V}$$

It is possible to use a voltaic cell as a pH meter, so we often use \log_{10} instead of \ln , and we work at room temperature, 298 K . Under these conditions, the Nernst equation can be simplified to:

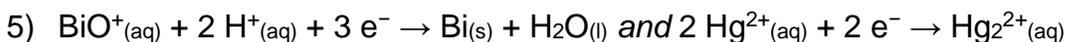
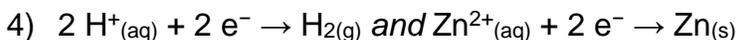
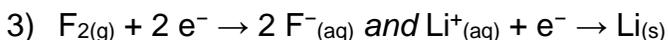
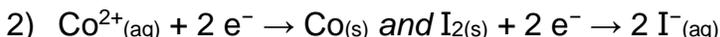
$$E = E^\circ - \frac{0.0592 \text{ V} \cdot \log Q}{n}$$



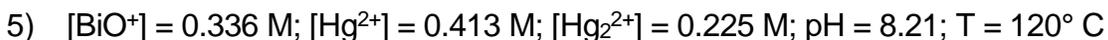
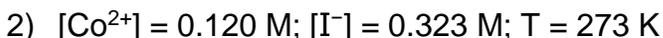
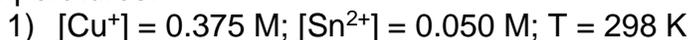
EXERCISES

A. Verify the answer to Example 1 by using the modified equation for E.

B. For each pair of reduction half-reactions, use your textbook to determine (a) the E°_{red} values for each, (b) which species undergoes oxidation in a voltaic cell, and (c) the E°_{cell} for the resulting voltaic cell.



C. For each of the pairs of half-reactions in B, (a) write the overall cell reaction, and (b) calculate the E for the cells with the following concentrations, pressures and temperatures.



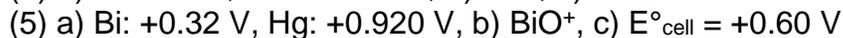
D. Notice that the voltaic cell that resulted when the concentration of aluminum was changed in Example 2 had a potential that was quite close to the unaltered potential (0.75 vs. 0.79). What would have to change in the design of the cell to increase its potential more dramatically?

E. Voltaic cells are essentially batteries — sources of electrical power. If the electrochemical reaction that's generating the power reaches equilibrium, how do we commonly describe the battery?

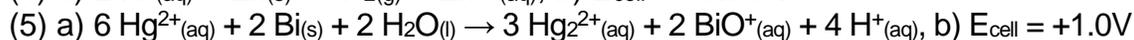
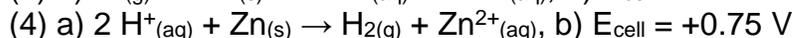
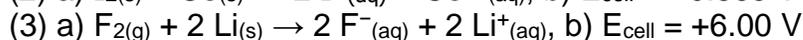
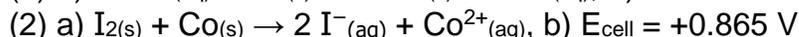
SOLUTIONS

A: Yes, it still works!

B: (Using the values from Chemistry: The Central Science, 10th ed.)



C: (1) a) $2 \text{Cu}^+_{(\text{aq})} + \text{Sn}_{(\text{s})} \rightarrow 2 \text{Cu}_{(\text{s})} + \text{Sn}^{2+}_{(\text{aq})}$, b) $E_{\text{cell}} = +0.67 \text{ V}$



D: Choose two half-reactions whose E°_{red} values are further apart in the table.

E: A dead battery

