

- 5a. Define the term *electromotive force* and the unit *volt*.

The electromotive force (abbreviated emf), denoted E_{cell} , is the 'driving force' or 'electrical pressure' which is responsible for the movement of electrons from the anode towards the cathode in a voltaic cell.

The volt is the standard unit of measuring the electromotive force in an electrochemical cell. By definition, it requires 1 joule of energy to transport 1 coulomb of electrical charge across a potential of 1 volt.

- b. How is the emf in an electrochemical cell measured?

The emf of an electrochemical cell can be measured using a voltmeter. A voltmeter is used to measure the potential difference, or the difference in electrical potential between the two half-reactions occurring in the electrochemical cell. The greater the difference between the electrical potential of the two half-reactions, the greater the voltage.

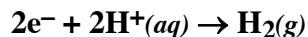
- 6a. Define the term *standard emf* and explain the importance of a reference half-reaction. Write the reference half-reaction discussed in lecture and its emf.

The potential of a voltaic cell depends on several factors. These include the nature of the chemical reaction, the concentration of all ions, and the pressure of any gases and the temperature at which the measurement is taken. A standard state emf is measured under a specific set of conditions. They are

- 1) All ions in solution are at a concentration of 1 M.
- 2) All gases are at a pressure of 1 atmosphere.
- 3) The temperature is 25 °C.

Under these conditions the cell potential is referred to a E° .

Standard emfs are measurements of the difference between the electrical potential of two half-reactions. So the E° for a reaction provides a relative measure of the reducing or oxidizing power of a chemical reaction. To organize the relative emf of a series of half-reactions, a reference half-reaction is defined and all other half-reactions are measured relative to it. The accepted reference half-reaction is,



The E° for this reaction is defined as 0.0.... volts.

b. Using the table of Standard Reduction Potential shown below, identify,

- i) the substance most likely to be oxidized **Li(s)**
 - ii) the substance most likely to be reduced **F₂(g)**
 - iii) the strongest oxidizing agent **F₂(g)**
 - iv) the strongest reducing agent **Li(s)**
- +E° the reaction is spontaneous**
-E° the reaction is nonspontaneous

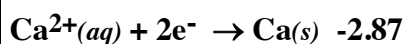
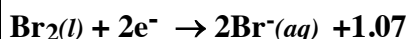
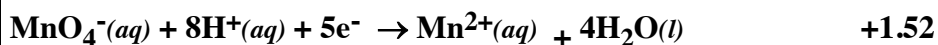
Standard Reduction Potentials at 25 °C	
<u>Half-Reaction</u>	<u>E°</u>
$\text{Li}^+(\text{aq}) + 1\text{e}^- \rightarrow \text{Li}(\text{s})$	-3.05 v
$\text{K}^+(\text{aq}) + 1\text{e}^- \rightarrow \text{K}(\text{s})$	-2.93 v
$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ca}(\text{s})$	-2.87 v
$\text{Na}^+(\text{aq}) + 1\text{e}^- \rightarrow \text{Na}(\text{s})$	-2.71 v
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mg}(\text{s})$	-2.37 v
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76 v
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.25 v
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}(\text{s})$	-0.136 v
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$	-0.126 v
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{s})$	0.00 v
$\text{AgCl}(\text{s}) + 1\text{e}^- \rightarrow \text{Ag}(\text{s}) + \text{Cl}^-(\text{aq})$	+0.22 v
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.34 v
$\text{I}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{I}^-(\text{aq})$	+0.53 v
$\text{Ag}^+(\text{aq}) + 1\text{e}^- \rightarrow \text{Ag}(\text{s})$	+0.80 v
$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \rightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	+0.96 v
$\text{Br}_2(\text{l}) + 2\text{e}^- \rightarrow 2\text{Br}^-(\text{aq})$	+1.07 v
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	+1.23 v
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	+1.33 v
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$	+1.36 v
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	+1.52 v
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	+1.77 v
$\text{F}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{F}^-(\text{aq})$	+2.87 v
$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83 v

7. Using the table of Standard Reduction Potential complete the following problems.

a. Which of the following species is the strongest oxidizing agent, MnO_4^- (in acidic solution), $\text{Br}_2(l)$, or $\text{Ca}^{2+}(aq)$?

An oxidizing agent is any substance which is reduced. To determine which of the three is the strongest oxidizing agent, the reduction half-reactions must be written and the magnitude of the E° 's compared. The highest positive value of E° corresponds to the reaction that occurs most readily.

$E^\circ(\text{volts})$

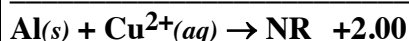
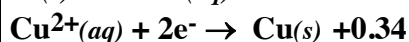
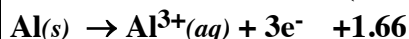


$\text{MnO}_4^-(aq)$ in acidic solution is the strongest oxidizing agent.

b. Will aluminum displace Cu^{2+} ion from an aqueous solution of $\text{Cu}(\text{NO}_3)_2$?

The reaction must be translated into the corresponding half-reactions. Whether a reaction will occur depends on whether E° is positive or negative. In this problem, the question wants to know if aluminum will displace Cu^{2+} from aqueous solution. This means aluminum is oxidized and Cu^{2+} is reduced. The half-reactions are,

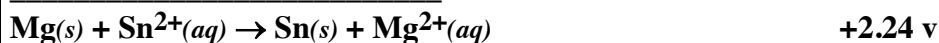
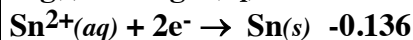
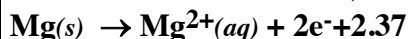
$E^\circ(\text{volts})$



Since E° is positive, Al will displace Cu^{2+} from solution.

c. Will Mg displace Sn^{2+} from an aqueous solution of tin (II) nitrate?

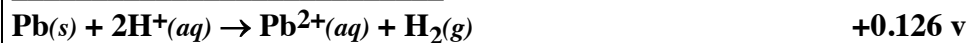
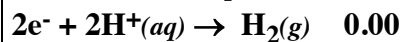
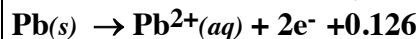
$E^\circ(\text{volts})$



Yes, Mg will displace Sn^{2+} from solution.

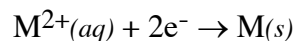
d. Will lead metal dissolve in 1 M HCl?

E° (volts)



Yes, lead will dissolve in 1 M HCl.

e. From the following information estimate the E° for



i) the metal, M, dissolves in 1 M HNO_3 but not in 1 M HCl. It will displace $\text{Ag}^+(aq)$, but not $\text{Cu}^{2+}(aq)$.

If a metal dissolves in 1 M HNO_3 but not in 1 M HCl, the E° for the oxidation of the metal must range from -0.1 to -0.95 v. (The metal is oxidized by the NO_3^- ion, not the H^+ .) If the same metal is expected to displace Ag^+ but not Cu^{2+} from solution, the range will be narrowed to -0.337 to -0.799 v. Looking at a list of standard reduction potentials, the metal could be Hg.