Chapter 20 - Electrochemistry

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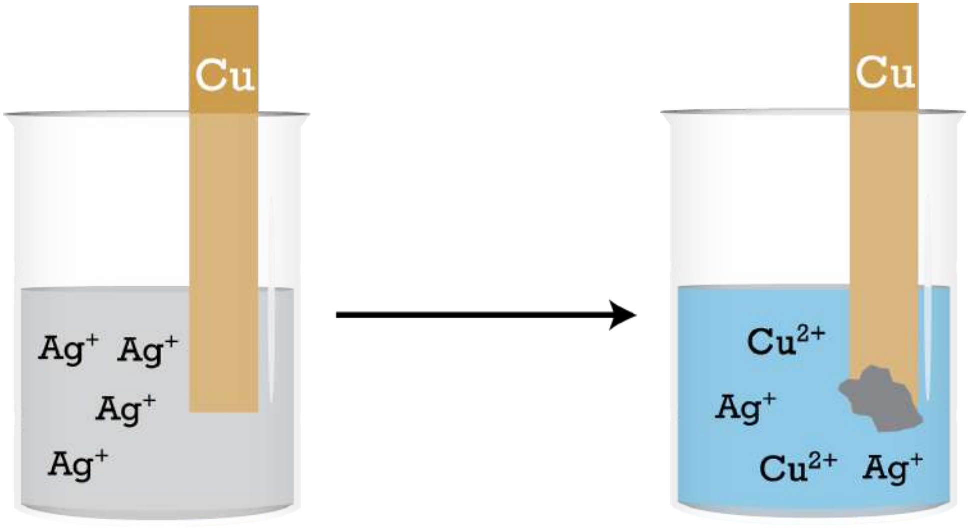
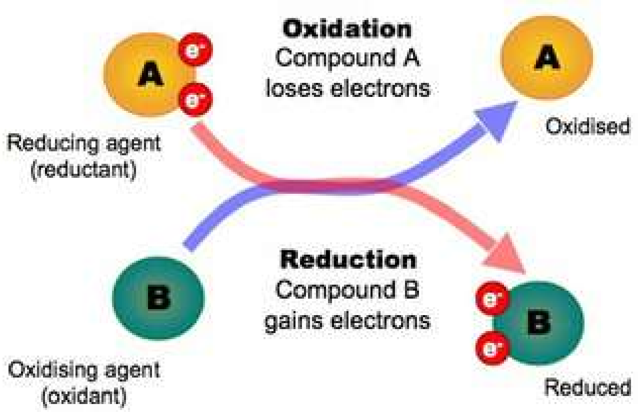
Section 20.1 – Oxidation States and Oxidation-Reduction Reactions

- Oxidation is loss of electrons.
- Reduction is gain of electrons.
- Electrochemistry is the study of the relationships between electricity and chemical reactions.



Redox Reactions

- In any redox reaction, both oxidation and reduction must occur.
- The substance that makes it possible for another substance to be oxidized is called the oxidizing agent.
- The substance that makes it possible for another substance to be reduced is called the reducing agent.



Sample Exercise 20.1

- The nickel-cadmium (nicad) battery, a rechargeable “dry cell” used in battery-operated devices, uses the following redox reaction to generate electricity:

$$Cd_{(s)} + NiO_{2(s)} + 2H_2O_{(l)} \rightarrow Cd(OH)_{2(s)} + Ni(OH)_{2(s)}$$

Identify the substances that are oxidized and reduced, and indicate which is the oxidizing agent and which is the reducing agent.

Practice Exercise

- Identify the oxidizing and reducing agents in the oxidation-reduction reaction

$$2H_2O_{(l)} + Al_{(s)} + MnO_4^-{}_{(aq)} \rightarrow Al(OH)_4^-{}_{(aq)} + MnO_{2(s)}$$

Section 20.2 – Balancing Oxidation-Reduction Reactions

- When balancing redox reactions, we must balance the atoms and the CHARGE.
- Electrons are added to the reaction to help balance charge.
- Half-reactions show either oxidation or reduction alone.

$$\begin{array}{ll}
\mathrm{Fe}^{2+} \rightarrow \mathrm{Fe}^{3+} + \mathrm{e}^{-} & \text{(oxidation half - reaction)} \\
\mathrm{Ce}^{4+} + \mathrm{e}^{-} \rightarrow \mathrm{Ce}^{3+} & \text{(reduction half - reaction)} \\
\cline{1-1}
\mathrm{Fe}^{2+} + \mathrm{Ce}^{4+} \rightarrow \mathrm{Fe}^{3+} + \mathrm{Ce}^{3+} &
\end{array}$$

Balancing Redox Reactions (Acidic)

- When balancing an oxidation-reduction reaction in an acidic aqueous solutions, follow these steps:

1. Separate the reaction into the 2 half-reactions.
2. Balance all elements other than O and H.
3. Balance O by adding H_2O as needed.
4. Balance H by adding H^+ as needed.
5. Balance charge by adding e^- as needed.

Balancing Redox Reactions (Acidic)

6. Multiply the half-reactions by integers, if necessary, so that the number of e$^-$ will cancel out in the half-reactions.

7. Add the two half-reactions.

$$5\,(\mathrm{Fe} \longrightarrow \mathrm{Fe}^{2+} + 2\,e^-)$$

$$\underline{2\,(\mathrm{MnO_4}^- + 8\,\mathrm{H}^+ + 5\,e^- \longrightarrow \mathrm{Mn}^{2+} + 4\,\mathrm{H_2O})}$$

$$2\,\mathrm{MnO_4}^- + 5\,\mathrm{Fe} + 16\,\mathrm{H}^+ \longrightarrow 2\,\mathrm{Mn}^{2+} + 5\,\mathrm{Fe}^{2+} + 8\,\mathrm{H_2O}$$

Sample Exercise 20.2

- Complete and balance this equation by the method of half-reactions:

$$Cr_2O_7^{2-} + Cl^- \rightarrow Cr^{3+} + Cl_2 \quad \text{(acidic)}$$

Practice Exercise

- Complete and balance the following equations using the method of half-reactions. Both reactions occur in acidic solutions.

a. $Cu + NO_3^- \rightarrow Cu^{2+} + NO_2$

b. $Mn^{2+} + NaBiO_3 \rightarrow Bi^{3+} + MnO_4^-$

Balancing Redox Reactions (Basic)

- When balancing oxidation-reduction reactions in a basic solution, you start balancing the way we did in acidic solution.
- After you balance the H^+ and the e^-, then you add the same number of OH^- as H^+ on both sides of the reaction.
- The side of the reaction that has both H^+ and OH^- will form water.

$$8\,OH^-_{(aq)} + 2\,H_2O_{(l)} + CH_3OH_{(aq)} + 6\,MnO^-_{4(aq)} \rightarrow CO^{2-}_{3(aq)} + 6\,MnO^{2-}_{4(aq)} + 8\,H^+_{(aq)} + 8\,OH^-_{(aq)}$$

$$8\,OH^-_{(aq)} + 2\,H_2O_{(l)} + CH_3OH_{(aq)} + 6\,MnO^-_{4(aq)} \rightarrow CO^{2-}_{3(aq)} + 6\,MnO^{2-}_{4(aq)} + 8\,H_2O_{(l)}$$

Sample Exercise 20.3

- Complete and balance this equation for a redox reaction that takes place in basic solution:

$$CN^- + MnO_4^- \rightarrow CNO^- + MnO_2 \quad \text{(basic)}$$

Practice Exercise

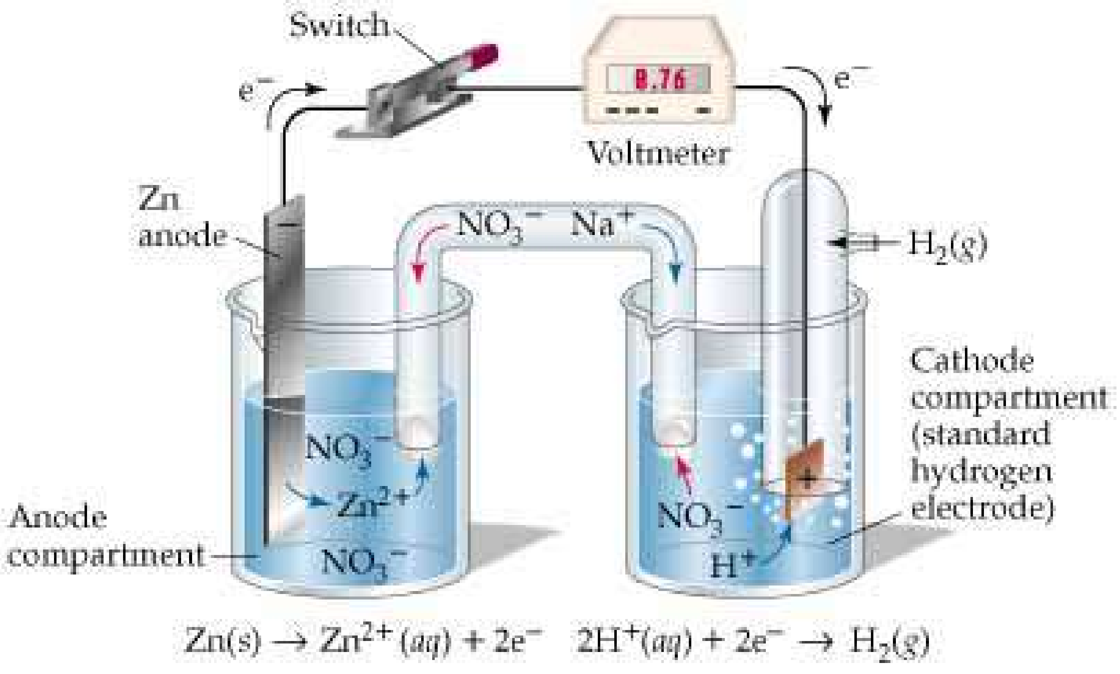
- Complete and balance the following equations for oxidation-reduction reactions that occur in basic solutions:

a. $NO_2^- + Al \rightarrow NH_3 + Al(OH)_4^-$

b. $Cr(OH)_3 + ClO^- \rightarrow CrO_4^{2-} + Cl_2$

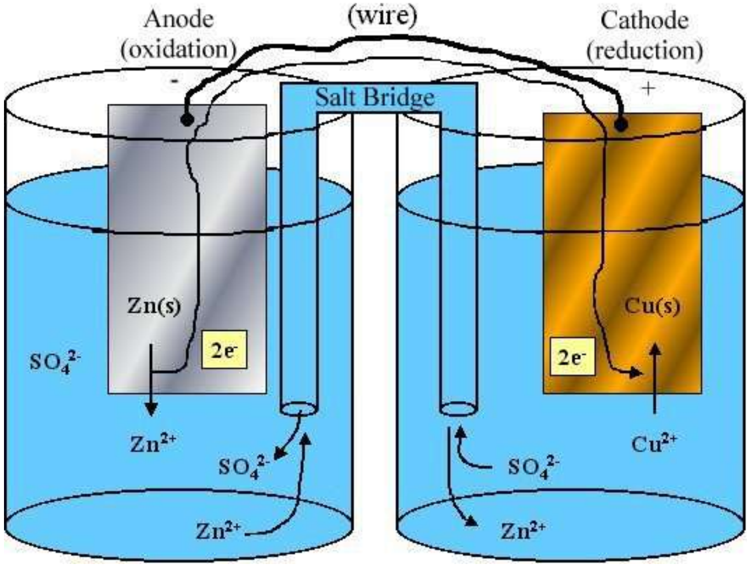
Section 20.3 – Voltaic Cells

- A voltaic/galvanic cell is a device in which the transfer of electrons takes place through an external pathway rather than directly between reactants.



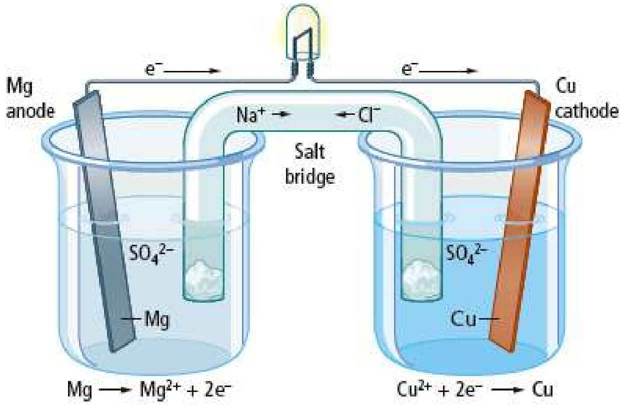
Voltaic Cells

- The two solid metals that are connected by the external circuit are called electrodes.
- The anode (-) is the location for oxidation.
- The cathode (+) is the location for reduction.



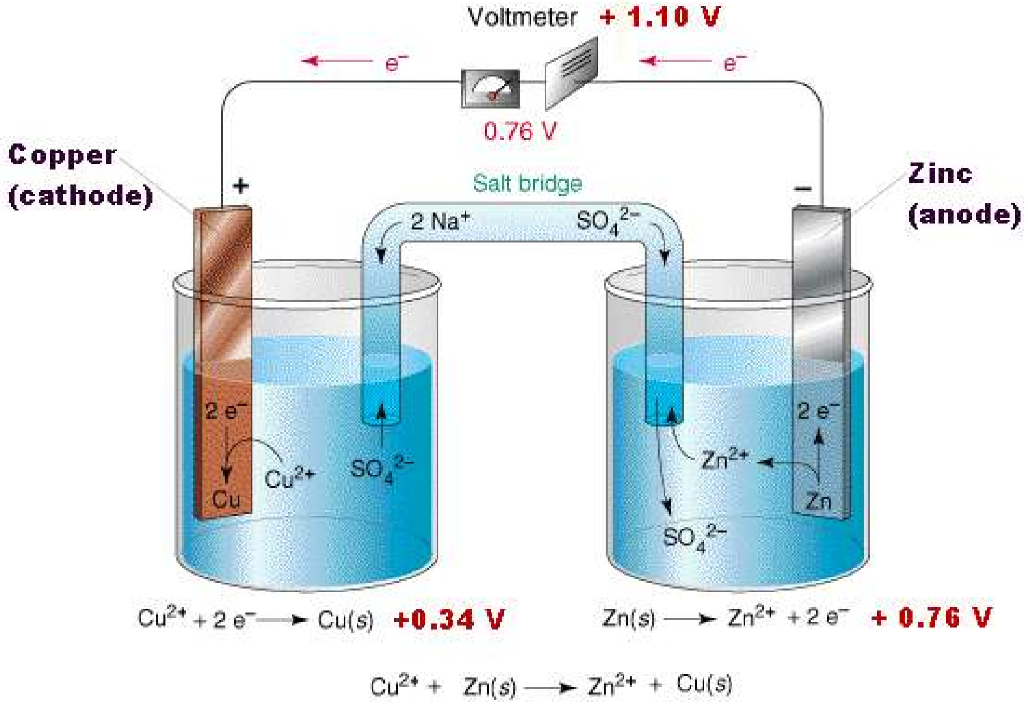
Voltaic Cells

- Each compartment of the voltaic cell is called the half-cell.
- When the voltaic cell has a current, the electrons are flowing from the anode to the cathode.
- For the cell to work, both half-cells must remain neutral. A salt bridge that contains spectator ions allows both solution to remain neutral.



Voltaic Cells

- As the reaction occurs, the cations migrate toward the cathode and the anions migrate toward the anode.



Sample Exercise 20.4

- The oxidation-reduction reaction

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

is spontaneous. A solution containing $K_2Cr_2O_7$ and H_2SO_4 is poured into one beaker, and a solution of KI is poured into another. A salt bridge is used to join the two beakers. A metallic conductor that will not react with either solution (such as platinum foil) is suspended in each solution, and the two conductors are connected with wires through a voltmeter or some other device to detect and electric current.

Sample Exercise 20.4 con’t

- The resultant voltaic cell generates an electric current. Indicate the reaction occurring at the anode, the reaction at the cathode, the direction of electron migration, the direction of ion migration, and the signs of the electrodes.

Practice Exercise

- The two half-reactions in a voltaic cell are

$$Zn \rightarrow Zn^{2+} + 2e^-$$

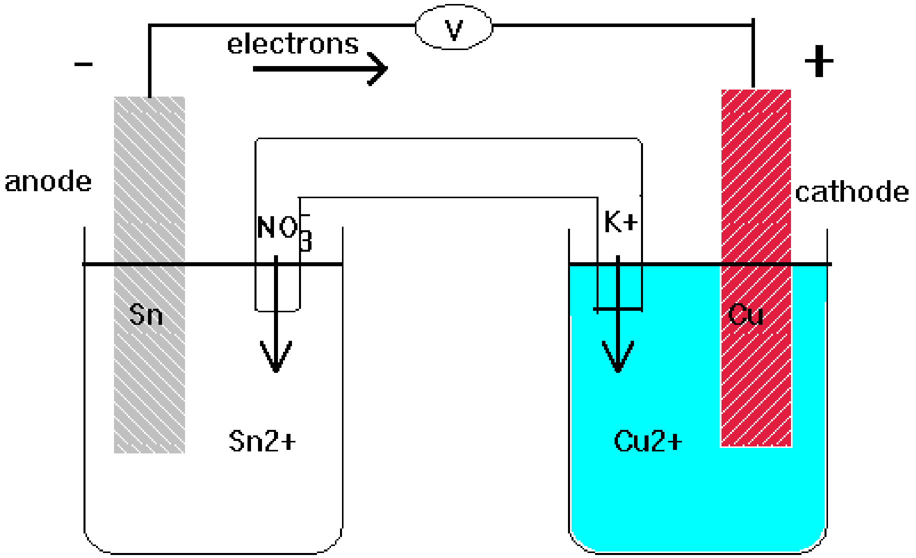
$$ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O$$

a. Indicate which reaction occurs at the anode and which at the cathode.
b. Which electrode is consumed in the cell reaction?
c. Which electrode is positive?

Section 20.4 – Cell EMF Under Standard Conditions

- Electrons flow from the anode to the cathode because of a difference in potential energy.
- The difference in potential energy per electrical charge (the potential difference) between two electrodes is measured in volts.

1 V = 1 J/C

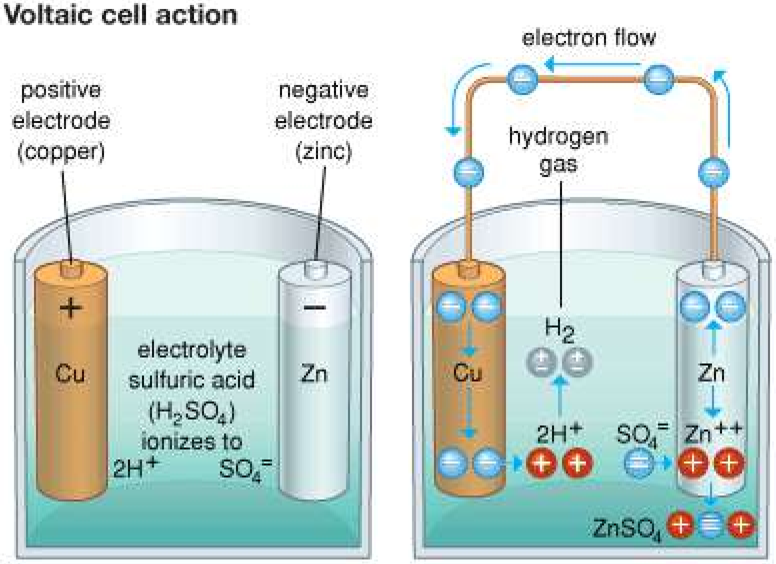


EMF

- The potential difference is called the electromotive force (emf).
- The emf of a cell, E_{cell}, is called the cell potential or cell voltage.
- For any spontaneous reaction, the E_{cell} will be positive.
- Standard emf is E°cell.
- The degree sign

  indicates standard

  conditions.



Voltaic cell action

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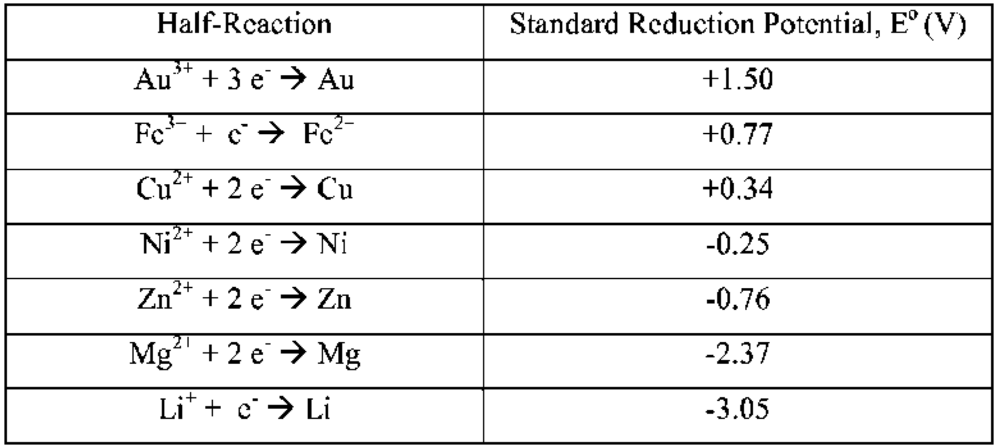
Reduction Potentials

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

- These standard reduction potentials can be found in Table 20.1 p. 857.
- Whenever we assign an electrical potential, we write the reaction as a reduction.



Half-Reaction	Standard Reduction Potential, E^o (V)
$Au^{3+} + 3e^- \rightarrow Au$	+1.50
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$Ni^{2+} + 2e^- \rightarrow Ni$	-0.25
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76
$Mg^{2+} + 2e^- \rightarrow Mg$	-2.37
$Li^+ + e^- \rightarrow Li$	-3.05

Reduction Potentials

- If a half-reaction is flipped, then the E changes sign.
- If a half-reaction is multiplied or divided by an integer, the E does not change because the ratio of energy to charge does not change.

Sample Exercise 20.5

- For the Zn-Cu^{2+} voltaic cell shown in Figure 20.5, we have

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu \qquad E^{o}_{cell} = 1.10V$$

Given that the standard reduction potential of Zn^{2+} to Zn is -0.76V, calculate the E^{o}_{red} for the reduction of Cu^{2+} to Cu:

$$Cu^{2+} + 2e^{-} \rightarrow Cu$$

Practice Exercise

- A voltaic cell is based on the half-reactions

$$In^+ \rightarrow In^{3+} + 2e^-$$

$$Br_2 + 2e^- \rightarrow 2Br^-$$

The standard emf for this cell is 1.46V. Using the data in Table 20.1, calculate E^o_{cell} for the reduction of In^{3+} to In^+.

Sample Exercise 20.6

- Using the standard reduction potentials listed in Table 20.1, calculate the standard emf for the voltaic cell described in Sample Exercise 20.4, which is based on the reaction

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

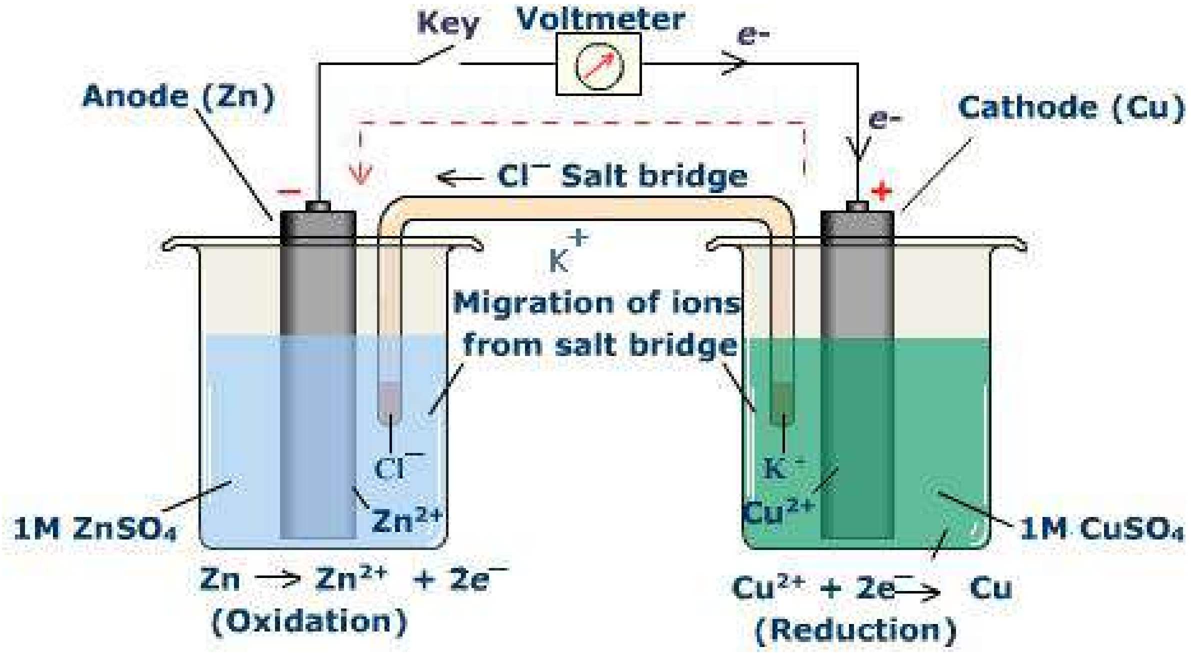
Practice Exercise

- Using date in Table 20.1, calculate the standard emf for a cell that employs the following overall cell reaction:

$$2Al + 3I_2 \rightarrow 2Al^{3+} + 6I^-$$

Reduction Potentials

- The more positive the value of E^o_{red}, the greater the diving force for reduction under standard conditions.
- The reaction at the cathode will have a more positive value than the reaction at the anode.



Sample Exercise 20.7

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

$$Cd^{2+} + 2e^{-} \rightarrow Cd$$

$$Sn^{2+} + 2e^{-} \rightarrow Sn$$

By using the date in Appendix E, determine:

a. The half-reactions that occur at the cathode and anode.
b. The standard cell potential.

Practice Exercise

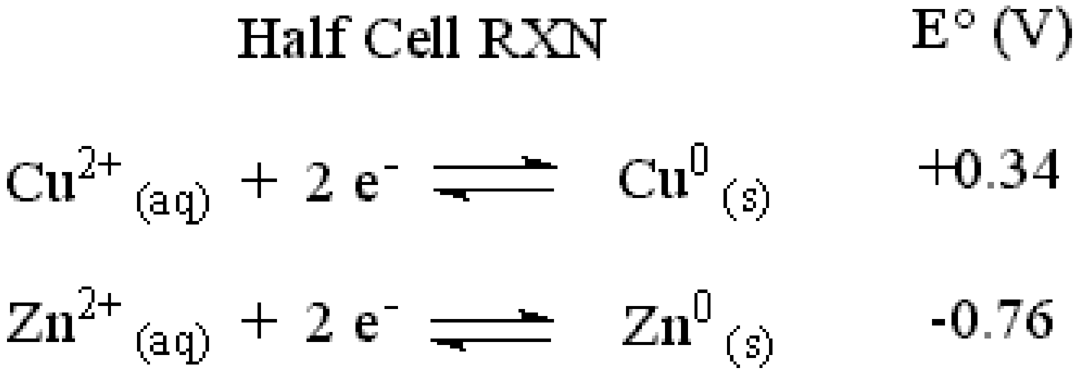
- A voltaic cell is based on a Co^{2+}/Co half-cell and an $AgCl/Ag$ half-cell.

a. What half-reaction occurs at the anode?

b. What is the standard cell potential?

Strengths of Oxidizing and Reducing Agents

- The more positive the E^{o}_{red} value for a half-reaction, the greater the tendency for the reactant of the half-reaction to be reduced, and therefore, to oxidize another species.
- The half-reaction with the smallest reduction potential is more easily reversed as oxidation.



Half Cell RXN	E° (V)
$Cu^{2+}_{(aq)} + 2\,e^{-} \rightleftharpoons Cu^{0}_{(s)}$	+0.34
$Zn^{2+}_{(aq)} + 2\,e^{-} \rightleftharpoons Zn^{0}_{(s)}$	-0.76

Sample Exercise 20.8

- Using Table 20.1, rank the following ions in order of increasing strength as oxidizing agents: NO_3^-, Ag^+, and $Cr_2O_7^{2-}$.

Practice Exercise

- Using Table 20.1, rank the following species from the strongest to the weakest reducing agent: I^-, Fe, and Al.

Section 20.5 – Free Energy and Redox Reactions

$$E^{o} = E^{o}_{red}(\text{reduction}) - E^{o}_{red}(\text{oxidation})$$

A positive value of E indicates a spontaneous process, and a negative value of E indicates a nonspontaneous process.

Sample Exercise 20.9

- Using standard reduction potentials in Table 20.1, determine whether the following reactions are spontaneous under standard conditions:

a. $Cu + 2H^+ \rightarrow Cu^{2+} + H_2$

b. $Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$

Practice Exercise

- Using the standard reduction potentials listed in Appendix E, determine which of the following reactions are spontaneous under standard conditions:

a. $I_2 + 5Cu^{2+} + 6H_2O \rightarrow 2IO_3^- + 5Cu + 12H^+$

b. $Hg^{2+} + 2I^- \rightarrow Hg + I_2$

c. $H_2SO_3 + 2Mn + 4H^+ \rightarrow S + 2Mn^{2+} + 3H_2O$

EMF and ΔG

$$\Delta G^o = -nFE^o$$

ΔG^o = Gibb's Free Energy

n = moles of electrons transferred

F = Faraday's constant (96,485 J/V·mol)

E^o = cell potential

If E^o is positive, then ΔG^o is negative, and the reaction is spontaneous.

Sample Exercise 20.10

a. Use the standard reduction potentials listed in Table 20.1 to calculate the standard free-energy change, ΔG^o, and the equilibrium constant, K, at 298K for the reaction.

$$4Ag + O_2 + 4H^+ \rightarrow 4Ag^+ + 2H_2O$$

Sample Exercise 20.10 con't

b. Suppose the reaction in part a was written

$$2Ag + 1/2O_2 + 2H^+ \rightarrow 2Ag^+ + H_2O$$

What are the values of E°, ΔG°, and K when the reaction is written this way?

Practice Exercise

- For the reaction

  $3Ni^{2+} + 2Cr(OH)_3 + 10OH^- \rightarrow 3Ni + 2CrO_4^{2-} + 8H_2O$

a. What is the value of n?

b. Use the data in Appendix E to calculate ΔG^o.

c. Calculate K at T = 298K.

Section 20.6 – Cell EMF Under Nonstandard Conditions

- Nernst Equation:

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

This allows you to solve for E using nonstandard conditions for Q.

Sample Exercise 20.11

- Calculate the emf at 298K generated by the cell described in Sample Exercise 20.4 when $[Cr_2O_7^{2-}]$ = 2.0M, $[H^+]$ = 1.0M, $[I^-]$ = 1.0M, and $[Cr^{3+}]$ = 1.0×10^{-5}M.

Practice Exercise

- Calculate the emf generated by the cell described in the practice exercise accompanying Sample Exercise 20.6 when $[Al^{3+}] = 4.0 \times 10^{-3}M$ and $[I^-] = 0.010M$.

Sample Exercise 20.12

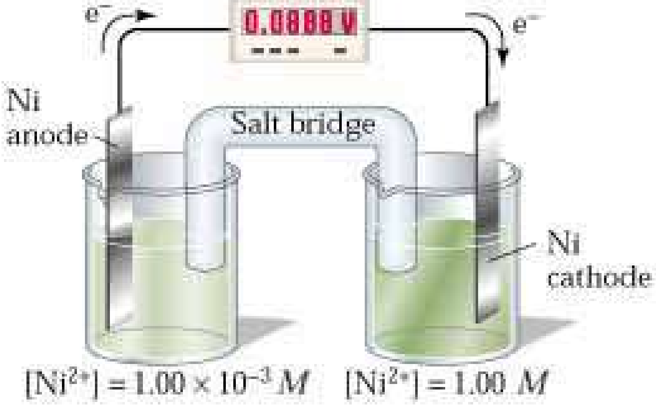
- Is the voltage of Zn-H^+ cell (like that in Figure 20.11) is 0.45V at 25°C when $[Zn^{2+}]$ = 1.0M and P_{H2} = 1.0atm, what is the concentration of H^+?

Practice Exercise

- What is the pH of the solution in the cathode compartment of the cell pictured in Figure 20.11 when P_{H2} = 1.0atm, [Zn^{2+}] in the anode compartment is 0.10M, and the cell emf is 0.542V?

Concentration Cell

- A concentration cell is a cell based solely on the emf generated because of a difference in concentration of the two half-cells.
- The cell will operate until the concentrations are equal.



Sample Exercise 20.13

- A voltaic cell is constructed with two hydrogen electrodes. Electrode 1 has P_{H2} = 1.00atm and an unknown concentration of $H^+_{(aq)}$. Electrode 2 is a standard hydrogen electrode ($[H^+]$ = 1.00M, P_{H2} = 1.00atm). At 298K the measured cell voltage is 0.211V, and the electrical current is observed to flow from electrode 1 through the external circuit to electrode 2. Calculate $[H^+]$ for the solution at electrode 1. What is the pH?

Practice Exercise

- A concentration cell is constructed with two Zn-Zn^{2+} half-cells. The first half-cell has $[Zn^{2+}] = 1.35M$, and the second half-cell has $[Zn^{2+}] = 3.75 \times 10^{-4}M$.

a. Which half-cell is the anode of the cell?

b. What is the emf of the cell?

THE END