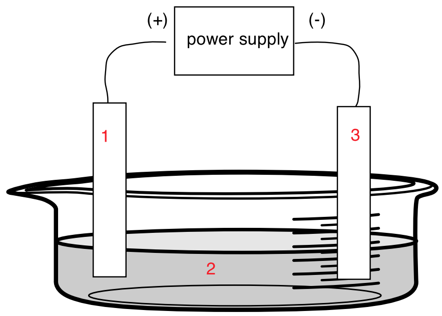
Objective 14. Apply oxidation-reduction reaction principles to electrolytic cells.
Key ideas: An electrolytic cell converts electrical energy to chemical energy.
An electrolytic involves a non-spontaneous chemical reaction ($\Delta G > 0$). Electrical energy is supplied to make the non-spontaneous reaction occur.
In an electrolytic cell, a power supply, e.g., battery, supplies electrons to the cathode where reduction occurs. At the anode, oxidation occurs.
Do not need to separate the anode from cathode.
Use Table of standard reduction potentials to calculate cell voltage.
Electrolytic cell: electrolytic cell: draw cell diagram (anode, cathode, half reactions, and overall reaction), Ecell.

Quiz Practice problems solutions:
1. Electroplating and thermodynamics.
a. You have Cr metal, Cr^{3+} (aq), Fe metal, and Fe^{2+} (aq).
(i) You place Cr metal into the Fe^{2+} (aq). This reaction will occur. Look up the reduction half reaction and reduction potential in the Standard Reduction Potential Table. Look up the oxidation half reaction and reduction potential in the Standard Reduction Potential Table. Add the two half reactions to give an overall reaction. Calculate E for the overall reaction (should be a positive E). Then, calculate ΔG for this reaction (should be less than 0).
(ii) You place Fe metal ino the Cr^{3+} (aq). Will a reaction occur? Calculate E and ΔG for this reaction.
b. You want to chrome plate a steel car part, e.g., wheels. In other words, you want to plate a more active metal (Cr) onto a a less active metal (Fe).
(i) This electroplating reaction uses a ____ (voltaic or electrolytic) cell. The electroplating reaction is _____ and has a ΔG __ 0.
(ii) The anode is the electrode at which oxidation occurs. Should the anode be the steel car part or chromium?
The cathode is the electrode at which reduction occurs. Should the cathode be the steel car part or chromium?
(iii) What would you use as the electrolyte?
What is the minimum voltage required to plate chrome onto the car part?
(iv) 100 mA of current is passed through the cell for 30 min. Calculate the mass of Cr that is plated onto the car part.
Formulas to use: I = Q/t and Q = n F
Answers:
a.
(i) You place Cr metal into the Fe^{2+} (aq).
$Fe^{2+} + 2\ e^- \text{-->} Fe$ $\quad E_{reduction} = -0.44$ V
$Cr^{3+} + 3\ e^- \text{-->} Cr$ $\quad E_{reduction} = -0.74$ V
Cr is more active than Fe so Cr should oxidize (anode) and Fe^{2+} should reduce (cathode) on the surface of the Cr metal.
$Cr + Fe^{2+} \text{-->} Cr^{3+} + Fe$
To balance the overall reaction, the number of electrons gained by Fe^{2+} = the number of electrons lost by Cr.
Multiply $Fe^{2+} + 2\ e^- \text{-->} Fe$ by 3.
Multiply $Cr^{3+} + 3\ e^- \text{-->} Cr$ by 2.
Overall reaction: $2\ Cr + 3\ Fe^{2+} \text{-->} 2\ Cr^{3+} + 3\ Fe$. So 6 electrons are transferred.
$E_{cell} = E_{cathode} - E_{anode}$ = = -0.44 V – (-0.74 V) = +0.30 V.
ΔG = - nFE = -(6 moles of electrons)(96,500 C/mole)(+0.30 V) = -174,000 J.
(ii) You place Fe metal ino the Cr^{3+} (aq). A reaction will not occur.
$2\ Cr^{3+} + 3\ Fe \text{-->} 2\ Cr + 3\ Fe^{2+}$
E = -0.30 V. (reverse the sign of E from (i))
ΔG = +174,000 J. (reverse the sign of ΔG from (i))

2. Use an electrolytic cell to gold plate an iron ring. Draw a cell diagram to show how to plate the ring with gold. Label the anode and cathode. Write the half reaction that occurs at each electrode. Specify an electrolyte. Calculate the minimum voltage for this cell to work.
Answers:
Oxidation reaction occurs at the anode. Reduction reaction occurs at the cathode.
In an electrolytic cell, energy is supplied from a power supply, e.g., battery, to make a non-spontaneous reaction occur.
The negative (-) terminal of the power supply supplies electrons to the cathode.
NOTE: the anode and cathode do NOT have to be separated in an electrolytic cell.

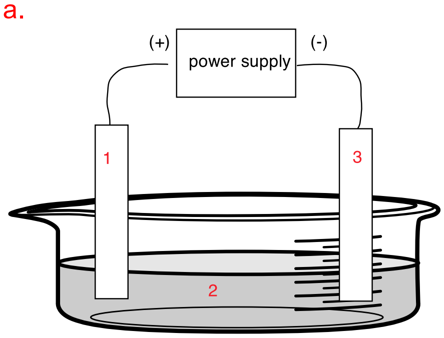


1 = Au anode, 2 = Au^{3+} (aq) solution for electrolyte, 3 = iron ring cathode
At Au anode: Au --> Au^{3+} + 3 e^-. Au metal is oxidized to Au^{3+} (aq)
At iron ring cathode: Au^{3+} + 3 e^- --> Au. Au^{3+} (aq) is reduced to Au metal on the surface of the iron ring. The electrons come from the (-) terminal of the power supply.
Overall reaction: Au + Au^{3+} ---> Au^{3+} + Au.
All substances cancel out so mininum voltage = 0 V.
Note: due to resistance in the cell, there will be a non-zero voltage at which gold starts to plate onto the iron ring.
Since this reaction is not spontaneous ($\Delta G > 0$), E (the cell voltage) is negative. ($\Delta G = -nFE$)

3. Hydrogen may be the fuel of the next generation. One way to produce hydrogen is by the electrolysis of water.
a. Draw an electrochemical cell that can be used for the electrolysis of water. Use an inert material such as C or Pt for each electrode. Label the anode and cathode. Write the reactions that occur at each electrode. You have the following choices for half reactions (some of which may <u>not</u> be balanced):

H^+ (aq) + e^- ---> H_2 (g)
2 H_2O (l) + 2 e^- ---> H_2 (g) + OH^- (aq)
O_2 (g) + 4 H^+ (aq) + 2e^- ---> 2 H_2O (l)
O_2 (g) + 4 H_2O (l) + 4 e^- ---> 2 OH^- (aq)

Write the net (overall) reaction. State what you will use as the electrolyte (choose prudently; more than one reaction may occur at each electrode). Calculate E^o_{cell}. At which electrode will H_2 be produced?
b. How can you make the electrolysis of water reaction go faster?
Answers:
a.



1 = Pt or C anode, 2 = H_2SO_4 (aq) or NaOH (aq) solution for electrolyte, 3 = Pt or C cathode,
Using acidic conditions (electrolyte = H_2SO_4 (aq))
At anode (oxidation): 2 H_2O (l) ---> O_2 (g) + 4 H^+ (aq) + 4 e^- $E_{oxidation}$ = -1.23 V
At cathode (reduction): 2H^+ (aq) + 2 e^- ---> H_2 (g) $E_{reduction}$ = 0 V
Multiply cathode reaction by 2 so # of electrons transferred is conserved.
Overall reaction: 2 H_2O (l) ---> 2 H_2 (g) + O_2 (g) $E_{cell} = E_{oxidation} + E_{reduction}$ = -1.23 V + 0 V = -1.23 V

Using basic conditions: (electrolyte = NaOH (aq))
At anode (oxidation): 4 OH^- (aq) ---> O_2 (g) + 2 H_2O (l) + 4 e^- $E_{oxidation}$ = -0.40 V
At cathode (reduction): 2 H_2O (l) + 2 e^- ---> H_2 (g) + 2 OH^- (aq) $E_{reduction}$ = -0.83 V
Multiply cathode reaction by 2 so # of electrons transferred is conserved.
Overall reaction: 2 H_2O (l) ---> 2 H_2 (g) + O_2 (g) $E_{cell} = E_{oxidation} + E_{reduction}$ = -0.40 V + (-0.83) V = -1.23 V

H_2 (g) is produced at the cathode. O_2 (g) is produced at the anode.

b. Make electrolysis reaction go faster by increasing the current. Current is the # of electrons passed through the cell per second (I = Q/time)
If voltage is increased, other substances in the solution could be oxidized or reduced. See Standard Reduction Potential Table.

4. Hydrogen is thought to be the fuel of the 21st century. It will be used in a fuel cell rather than combusted in a car engine. You need hydrogen for a hydrogen fuel cell. You have two carbon rods, one 1 V and one 1.5 V battery, NaOH pellets, water, some wire, and a 250 ml beaker.
a. Draw an electrochemical cell that can be used to split water. Label the anode and cathode. Write the half reaction that occurs at each electrode and the overall reaction.
b. Which battery would you use to split water? Give reasons.
c. You are impatient and want your cell to split water faster. What variable do you change?
d. How much energy in V is produced by a hydrogen fuel cell? Then, use E = QV to convert your energy from V to kJ/mole. What is K_{eq} for this reaction?
e. Hydrogen undergoes combustion in a heat engine. What is ΔG for the combustion of H_2? At what T will this reaction not occur?
f. Explain why H_2 is used in fuel cells and not in car engines. Hint: see work in a hydrogen combustion reaction.
What is the function of a proton exchange membrane (PEM) in a fuel cell?
Answers:
a. See Problem 3a.
b. 1.5 V battery because 1.23 V is required to split water.
c. Current. See Problem 3b.
d. E_{cell} = -1.23 V for 2 H_2O (l) ---> 2 H_2 (g) + O_2 (g)
so E_{cell} = +1.23 V for 2 H_2 (g) + O_2 (g) ---> 2 H_2O (l)
E = QV = (96,500 C/mole of electrons)(2 moles of electrons/1 mole H_2)(1.23 V) = 238,000 J/mole H_2 = 238 kJ/mole H_2
Note: 1 J = 1 C V (Coulomb Volt)
e. Use Hess' law to calculate ΔG for 2 H_2 (g) + O_2 (g) ---> 2 H_2O (l)
ΔG = 2(-237 kJ/mole) – [2(0) + 2 (0)] = -474 kJ for 2 moles of H_2 or -237 for 1 mole of H_2.
$\Delta G = -RT \ln K_{eq}$
Solve for K_{eq} = e^-(ΔG/RT) = e^-(-238000/(8.31)(298)) = 3.9×10^{41}.
f. H_2 is used in fuel cells and not in car engines because the H_2 combustion reaction does not produce work.
2 H_2 (g) + O_2 (g) ---> 2 H_2O (l) Δn = 0 – 3 = -3 so ΔV is negative and w = -pΔV is positive ==> supply work.

In a fuel cell, H_2 (g) is oxidized to H^+ at the anode: H_2 (g) ---> 2H^+ (aq) + 2 e^-
The proton exchange membrane (PEM) separates the the two electrodes and allows protons (H^+) to pass from the anode to cathode.
At the cathode, O_2 (g) reacts with H^+ and is reduced to water: O_2 (g) + 4 H^+ (aq) + 4 e^- ---> 2 H_2O (l)
Overall reaction: 2 H_2 (g) + O_2 (g) ---> 2 H_2O (l) produces 1.23 V of electricity.