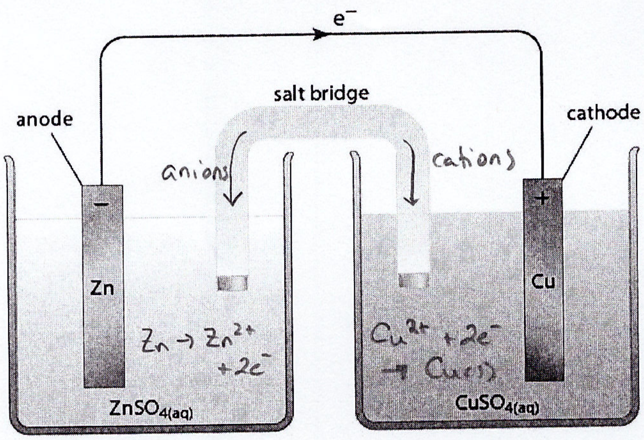
Electrolytic Cells

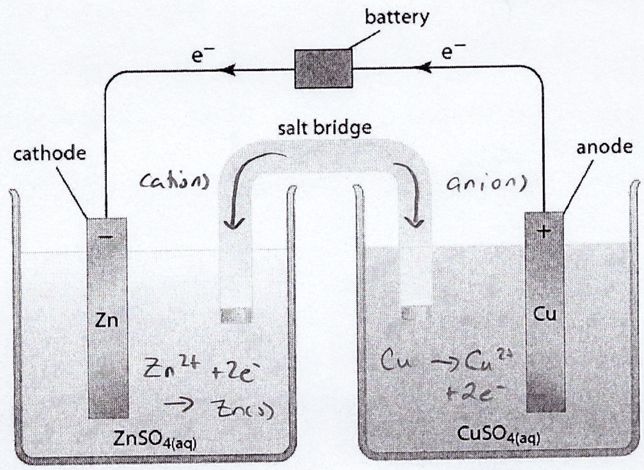
- Voltaic cells are *spontaneous* redox reactions which convert chemical energy to electrical energy. Voltaic cells are essentially batteries. requires a battery
- * A cell that uses an external source of electrical energy to drive a *non-spontaneous* redox reaction is called an **electrolytic cell**
- **Electrolysis** is the process that takes place in a electrolytic cell and it literally means to "break apart"
- * Since electrolytic cells are non-spontaneous, the reducing agent must be higher than the oxidizing agent on the table on pg. 7 of data booklet (weak agents)
- Let's compare a voltaic cell to an electrolytic cell

* no battery required



voltaic cell

*
↙ required



electrolytic cell

- Zn is SRA
- Zn has more "−" electric potential ($E°$)

- Cu^{2+} is SOA
- Cu^{2+} has more "+" electric potential ($E°$)

- Zn^{2+} is the more "−" $E°$
- Zn^{2+} is weak OA

- $Cu_{(s)}$ is the more "+" $E°$
- $Cu_{(s)}$ is weak RA

- The cell potential ($E°_{cell}$) for an electrolytic cell is calculated the same way as a voltaic cell. All voltaic cells will have a positive cell potential and all electrolytic cells will have a negative cell potential.

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

Voltaic

$E°_{cell} = 0.34V - (-0.76V)$

$E°_{cell} = 1.10V$

Electrolytic

$E°_{cell} = (-0.76V) - (0.34V)$

$E°_{cell} = -1.10V$

- Comparing a voltaic cell to an electrolytic cell

Voltaic Cell	**Electrolytic Cell**
spontaneous	non-spontaneous
converts chemical energy to electrical energy	converts electrical energy to chemical energy
is a battery	requires a battery
anions move to anode and cations move to cathode	anions move to anode and cations move to cathode
electrons flow into cathode	electrons flow into cathode
▪ oxidation at anode ▪ more negative electrical potential (E^o) at anode ▪ strongest reducing agent at anode	▪ oxidation at anode ▪ more positive electrical potential (E^o) at anode ▪ weakest reducing agent at anode
▪ reduction at cathode ▪ more positive electrical potential (E^o) at cathode ▪ strongest oxidizing agent at cathode	▪ reduction at cathode ▪ more negative electrical potential (E^o) at cathode ▪ weakest oxidizing agent at cathode
positive cell potential (E^o_{cell})	negative cell potential (E^o_{cell})

*****Now try Practice Problems*****

Practice Problems: Electrolytic Cells

1. Consider the following *un-balanced* redox reactions:
   a. $I_2 + Cl^- \rightarrow I^- + Cl_2$
   b. $MnO_4^-{}_{(aq)} + Br^-{}_{(aq)} \rightarrow Br_{2(l)} + Mn^{2+}{}_{(aq)}$ (acidic conditions)

   For each *un-balanced* redox reaction above:
   i. indicate if the reaction is spontaneous or not
   ii. write out the half-reaction at the anode
   iii. write out the half-reaction at the cathode
   iv. write out the balanced redox reaction
   v. calculate the cell potential
   vi. indicate if it is a redox reaction that can take place in a voltaic cell or electrolytic cell

2. Oxidation takes place at what electrode in a voltaic cell?

3. Oxidation takes place at what electrode in an electrolytic cell?

4. An electrolytic cell and a voltaic cell can look very similar except for the presence or absence of what?

5. In a voltaic cell, electrons flow out of which electrode?

6. In an electrolytic cell, electrons flow out of which electrode?

7. Why does a voltaic cell have the strongest oxidizing agent at the cathode while an electrolytic cell has the weakest oxidizing agent at the cathode?

8. Consider an electrolytic nickel-cadmium cell.
   i. Identify the anode and cathode.
   ii. Write out the oxidation half-reaction, the reduction half-reaction, and the net redox reaction.
   iii. Calculate the cell potential.

9. Consider a voltaic nickel-cadmium cell.
   i. Identify the anode and cathode.
   ii. Write out the oxidation half-reaction, the reduction half-reaction, and the net redox reaction.
   iii. Calculate the cell potential.

Electrolytic Cells Practice Problems (Solutions)

1.) a. $\overbrace{I_2 + Cl^- \rightarrow I^-}^{\text{reduced}} + Cl_2$

$\quad\ 0 \qquad -1 \qquad -1 \qquad 0$

$\underline{OA} \quad \underline{RA} \quad \text{oxidized}$

I.) non-spontaneous

II.) anode: $2Cl^-_{(aq)} \rightarrow Cl_{2(s)} + 2e^-$

III.) cathode: $I_{2(s)} + 2e^- \rightarrow 2I^-_{(aq)}$

IV.) $2Cl^-_{(aq)} + I_{2(s)} \rightarrow Cl_{2(s)} + 2I^-_{(aq)}$

V.) $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$E^\circ_{cell} = +0.54V - (+1.36V) = \boxed{-0.82V}$

VI.) Electrolytic cell

b.) I.) spontaneous

II.) anode: $2Br^-_{(aq)} \rightarrow Br_{2(l)} + 2e^-$

III.) cathode: $MnO_4^-{}_{(aq)} + 8H^+_{(aq)} + 5e^- \rightarrow Mn^{2+} + 4H_2O_{(l)}$

IV.) $5Br^-_{(aq)} + 2MnO_4^-{}_{(aq)} + 16H^+ \rightarrow 5Br_{2(l)} + 2Mn^{2+} + 8H_2O_{(l)}$

V.) $E^\circ_{cell} = E^\circ_{cathode} - E_{anode}$

$E^\circ_{cell} = +1.51V - (-1.07V) = \boxed{0.44V}$

VI.) Voltaic cell

2.) anode

3.) anode

4.) an electrolytic cell requires a battery/power source

5.) anode

6.) anode

7.) In both a voltaic and an electrolytic cell, the oxidizing agent needs to be at the cathode (i.e. where reduction occurs). An electrolytic cell requires a weak OA so that no spontaneous redox rxns occur. A voltaic cell requires a strong OA so that a spontaneous rxn occurs.

8.) i.) anode is $Ni_{(s)}$ & cathode is $Cd_{(s)}$

ii.) oxidation: $Ni_{(s)} \longrightarrow Ni^{2+}_{(aq)} + 2e^-$

reduction: $Cd^{2+}_{(aq)} + 2e^- \longrightarrow Cd_{(s)}$

net: $Ni_{(s)} + Cd^{2+}_{(aq)} \longrightarrow Ni^{2+}_{(aq)} + Cd_{(s)}$

iii.) $E^\circ_{cell} = -0.40\,V - (-0.26\,V)$

$\boxed{E^\circ_{cell} = -0.14\,V}$

9.) i.) anode is $Cd_{(s)}$ & cathode is $Ni_{(s)}$

ii.) oxidation: $Cd_{(s)} \longrightarrow Cd^{2+}_{(aq)} + 2e^-$

reduction: $Ni^{2+}_{(aq)} + 2e^- \longrightarrow Ni_{(s)}$

net: $Cd_{(s)} + Ni^{2+}_{(aq)} \longrightarrow Cd^{2+}_{(aq)} + Ni_{(s)}$

iii.) $E^\circ_{cell} = -0.26\,V - (-0.40\,V)$

$\boxed{E^\circ_{cell} = +0.14\,V}$

- If electrolysis means to break apart, let's consider the electrolysis of water. The equation that represents the breaking apart of water is as follows:

oxidized

$$\overset{+1\ -2}{2H_2O_{(l)}} \rightarrow \overset{0}{2H_{2(g)}} + \overset{0}{O_{2(g)}}$$

reduced

The half-reactions that are involved are found on the table in pg. 7 of the data book based off the reactants and products of the electrolysis process.

reduction: (cathode) $\overset{4}{\cancel{2}}e^- + \overset{4}{\cancel{2}}H_2O_{(l)} \rightarrow 2H_{2(g)} + \overset{4}{\cancel{2}}OH^-_{(aq)}$ $\times 2$

oxidation: (anode) $2H_2O_{(l)} \rightarrow 4e^- + 4H^+_{(aq)} + O_{2(g)}$

net : $6H_2O_{(l)} \rightarrow 2H_{2(g)} + \underbrace{4H^+_{(aq)} + 4OH^-_{(aq)}}_{4H_2O} + O_{2(g)}$

$\therefore\ 2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)}$

Calculation for cell potential:

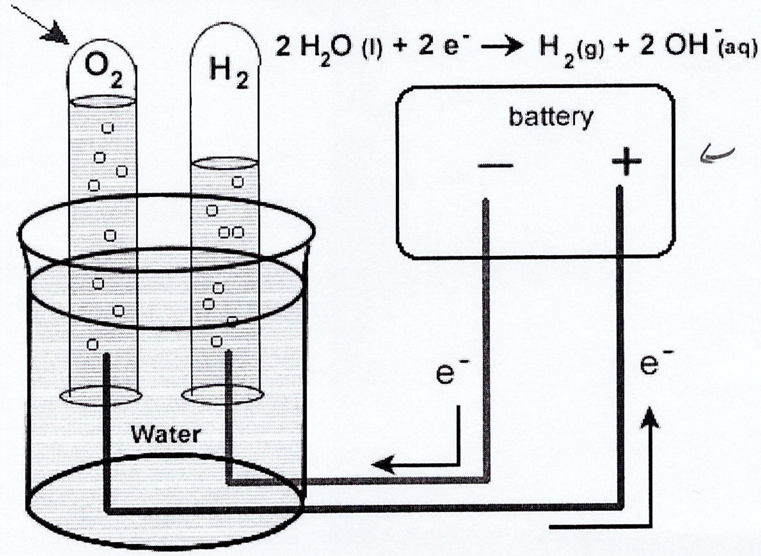
$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = -0.83V - (+1.23V)$

$\boxed{E^\circ_{cell} = -2.06V}$

* not spontaneous

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ anode

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ cathode



← electrolytic cell

$2H_2O_{(l)} \rightarrow \underline{2H_{2(g)}} + O_{2(g)}$

↳ twice as much as oxygen!

↗ liquid form

EXAMPLE: Consider the electrolysis of molten sodium chloride.

The equation that represents the breaking apart of $NaCl_{(l)}$ is a follows:

net redox: $2NaCl_{(l)} \rightarrow 2Na_{(l)} + Cl_{2(g)}$

The half-reactions that are involved are:

reduction (cathode): $Na^{+}_{(l)} + e^{-} \rightarrow Na_{(l)}$

oxidation (anode): $2Cl^{-}_{(l)} \rightarrow Cl_{2(g)} + 2e^{-}$

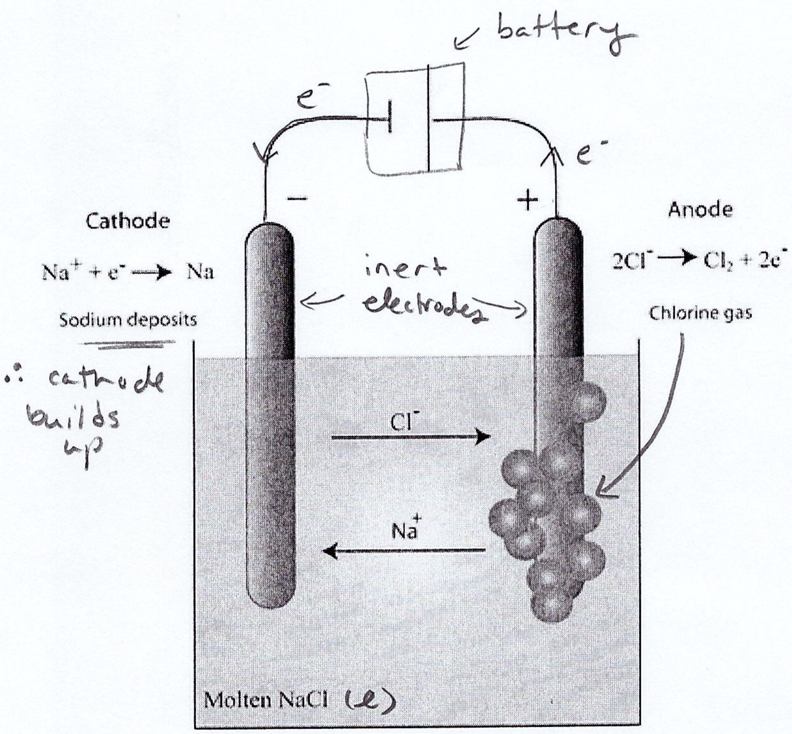
* not spontaneous due to spontaneity rule

Calculation for cell potential

$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$

$E^{\circ}_{cell} = -2.71\,V - (+1.36\,V)$

$\boxed{E^{\circ}_{cell} = -4.07\,V}$



- We need to be careful with the electrolysis of aqueous solutions. Consider the electrolysis of aqueous sodium chloride, $NaCl_{(aq)}$.
  - If we know electrolysis is the process of "breaking down" we would expect the half-reactions for this process to be as follows:

reduction (cathode): $Na^{+}_{(aq)} + e^{-} \rightarrow Na_{(s)}$

oxidation (anode): $2Cl^{-}_{(aq)} \rightarrow Cl_{2(g)} + 2e^{-}$

- * This would be incorrect because we are ignoring the presence of water and the fact that water is both an oxidizing and reducing agent

- We first need to list all substances present and identify them as oxidizing or reducing agents. We will use the agents in half-reactions to create the net redox reaction. The main redox reaction is the reaction that requires the least cell potential/voltage.

$\underset{}{\overset{RA}{Cl^-_{(aq)}}}$, $\underset{OA}{Na^+_{(aq)}}$, $\underset{OA}{\overset{RA}{H_2O_{(l)}}}$

Possibility #1

$2Cl^-_{(aq)} \rightarrow 2e^- + Cl_{2(s)}$ anode

$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$ cathode

$2Cl^-_{(aq)} + 2H_2O_{(l)} \rightarrow H_{2(g)} + 2OH^-_{(aq)} + Cl_{2(s)}$ net

$H_{2(g)}$ & $Cl_{2(g)}$ get produced!

$E^\circ_{cell} = -0.83V - (+1.36V)$

$E^\circ_{cell} = -2.19V$

* main rxn as it requires the least cell potential!

Possibility #2

$Na^+_{(aq)} + e^- \rightarrow Na_{(s)}$ (x4) cathode

$2H_2O_{(l)} \rightarrow 4e^- + O_{2(g)} + 4H^+_{(aq)}$ anode

$2H_2O_{(l)} + 4Na^+_{(aq)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + Na_{(s)}$ net

$E^\circ_{cell} = -2.71V - (+1.23V)$

$E^\circ_{cell} = -3.94V$

Now try pg. 508 #7, 8, pg. 510 #17, 18, 20 &pg. 513 #1, 3, 6

Helpful Hint to Determine the Anode and Cathode

VOLTAIC CELL

- **Cathode:** reduction half-reaction/ strong oxidizing agent $\longrightarrow$ therefore, needs a half-reaction with a *more positive* reduction potential (E^o)
- **Anode:** oxidation half-reaction/ strong reducing agent $\longrightarrow$ therefore, needs a half-reaction with a *more negative* reduction potential (E^o)

ELECTROLYTIC CELL (just the opposite rules)

- **Cathode:** reduction half-reaction/ weak oxidizing agent $\longrightarrow$ therefore, needs a half-reaction with a *more negative* reduction potential (E^o)
- **Anode:** oxidation half-reaction/ weak reducing agent $\longrightarrow$ therefore, needs a half-reaction with a *more positive* reduction potential (E^o)