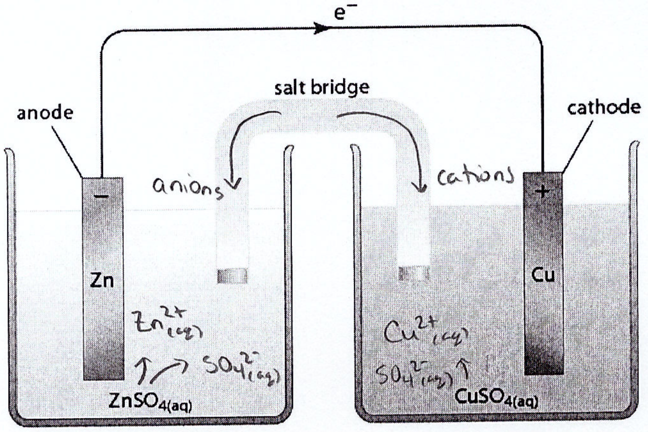
Electrolytic Cells

↗ O.A. higher than R.A.

- Voltaic cells are ***spontaneous*** redox reactions which convert chemical energy to electrical energy. Voltaic cells are essentially batteries. → can run an electronic device
- A cell that uses an external source of electrical energy to drive a ***non-spontaneous*** redox reaction is called an **electrolytic cell** ⇝ requires a battery!
- ✳ 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
- Let's compare a voltaic cell to an electrolytic cell



voltaic cell

(anode side)

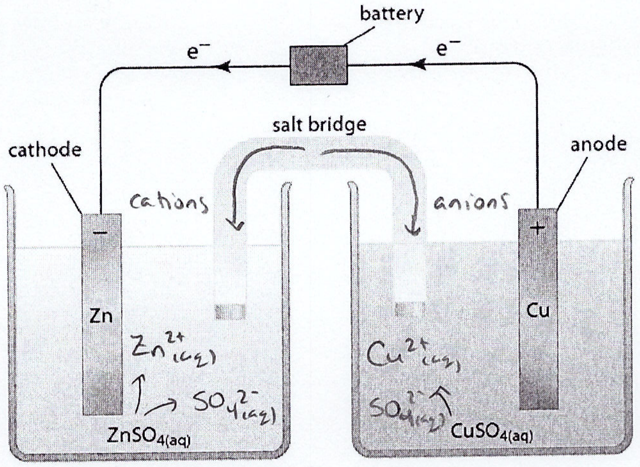
Strongest R.A. = $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

(cathode side)

strongest O.A. = $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

redox: $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

Presence of battery = electrolytic cell



electrolytic cell

(anode side)

R.A. = $Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$

(cathode side)

O.A = $Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$

redox: $Zn^{2+}_{(aq)} + Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + Zn_{(s)}$

- 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.

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

<u>Voltaic</u>

$E^\circ_{cell} = 0.34V - (-0.76V)$

$E^\circ_{cell} = 1.10V$

<u>Electrolytic</u>

$E^\circ_{cell} = -0.76V - 0.34V$

$E^\circ_{cell} = -1.10V$

- 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°) at anode ▪ strongest reducing agent at anode	▪ oxidation at anode ▪ more positive electrical potential (E°) at anode ▪ "strongest" reducing agent at anode
▪ reduction at cathode ▪ more positive electrical potential (E°) at cathode ▪ strongest oxidizing agent at cathode	▪ reduction at cathode ▪ more negative electrical potential (E°) at cathode ▪ "strongest" oxidizing agent at cathode
positive cell potential (E°_{cell})	negative cell potential (E°_{cell})

*****Now try Practice Problems #1-8*****

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. 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.

8. 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.

$$\underset{\underset{\text{OA}}{0}}{I_2} + \underset{\underset{\text{RA}}{-1}}{Cl^-} \longrightarrow \underset{-1}{I^-} + \underset{0}{Cl_2}$$

reduced

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

IV.) $10Br^-_{(aq)} + 2MnO_4^-{}_{(aq)} + 16H^+ \longrightarrow 5Br_{2(l)} + 2Mn^{2+} + 8H_2O_{(l)}$

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 rxn occurs. A voltaic cell requires a strong OA so that a spontaneous rxn occurs.

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

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

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

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

- **Electrolysis** is the process that takes place in a electrolytic cell and it literally means to "break apart"
- An **electrochemical cell** simply means voltaic or electrolytic.

EXAMPLE: Consider the electrolysis of $KI_{(aq)}$.

a. Identify and write out the half-reactions that occur at the anode and cathode.
b. Write out the redox reaction that occurs in the electrolysis process.
c. Label the diagram below.

a.) List all species

$\overset{\text{O.A.}}{K^+_{(aq)}}$, $\underset{\text{R.A. strongest}}{I^-_{(aq)}}$, $\underset{\text{R.A}}{\overset{\text{strongest O.A.}}{H_2O_{(l)}}}$

* O.A. needs to be lower than R.A. to have non-spontaneous rxn, but still need to choose the "strongest"

R.A.
Oxidation (anode side): $2I^-_{(aq)} \longrightarrow I_{2(s)} + 2e^-$

O.A.
reduction (cathode side): $2H_2O_{(l)} + 2e^- \longrightarrow H_{2(g)} + 2OH^-_{(aq)}$

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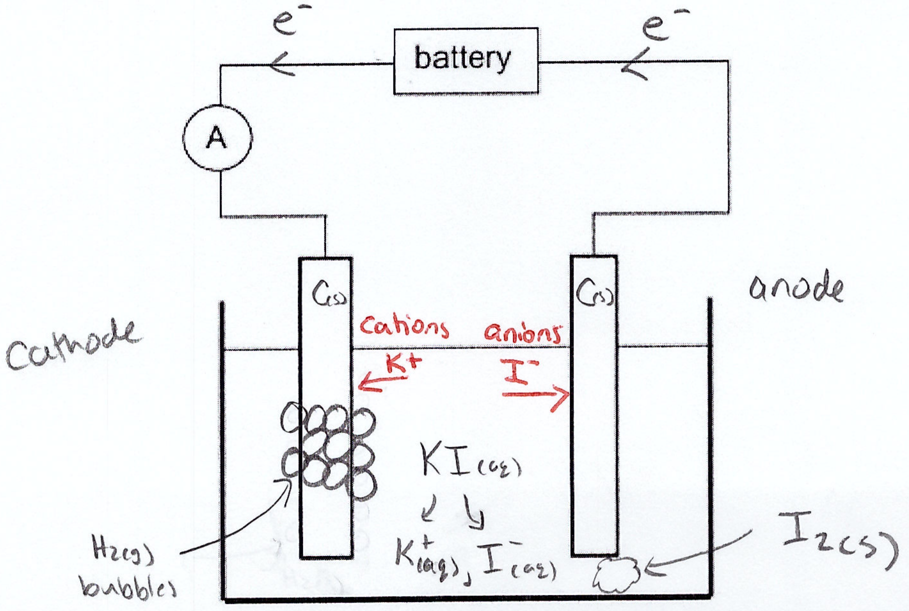
redox: $2I^-_{(aq)} + 2H_2O_{(l)} \longrightarrow I_{2(s)} + H_{2(g)} + 2OH^-_{(aq)}$



- Sometimes the predicted reactions do not always occur in electrolysis.
  - * The **chloride anomaly** occurs in aqueous solutions in which chloride ions are present. In these electrolytic reactions, even though $H_2O_{(l)}$ is the stronger reducing agent, the half-reaction with $Cl^-_{(aq)}$ will actually take place.

$$\underset{R.A.}{2Cl^-_{(aq)}} \longrightarrow Cl_{2(g)} + 2e^-$$

oxidation half-rxn occuring at anode

EXAMPLE: Consider the electrolysis of $NaCl_{(aq)}$.

a. Identify and write out the half-reactions that occur at the anode and cathode.

b. Write out the redox reaction that occurs in the electrolysis process.

c. Label the diagram below.

List all species present: $\overset{O.A.}{Na^+_{(aq)}}, \underset{R.A.}{Cl^-_{(aq)}}, \overset{\text{strongest } O.A.}{\underset{R.A. \text{ strongest}}{H_2O_{(l)}}}$

but need to use Cl^- anomoly

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

reduction: $2H_2O_{(l)} + 2e^- \longrightarrow H_{2(g)} + 2OH^-_{(aq)}$
(cathode side)

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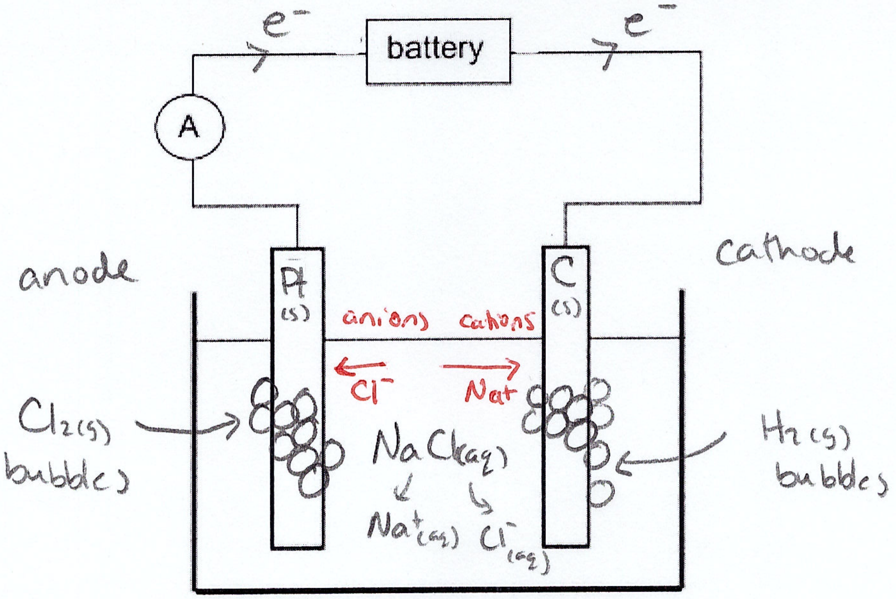
redox: $2Cl^-_{(aq)} + 2H_2O_{(l)} \longrightarrow Cl_{2(g)} + 2OH^-_{(aq)} + H_{2(g)}$



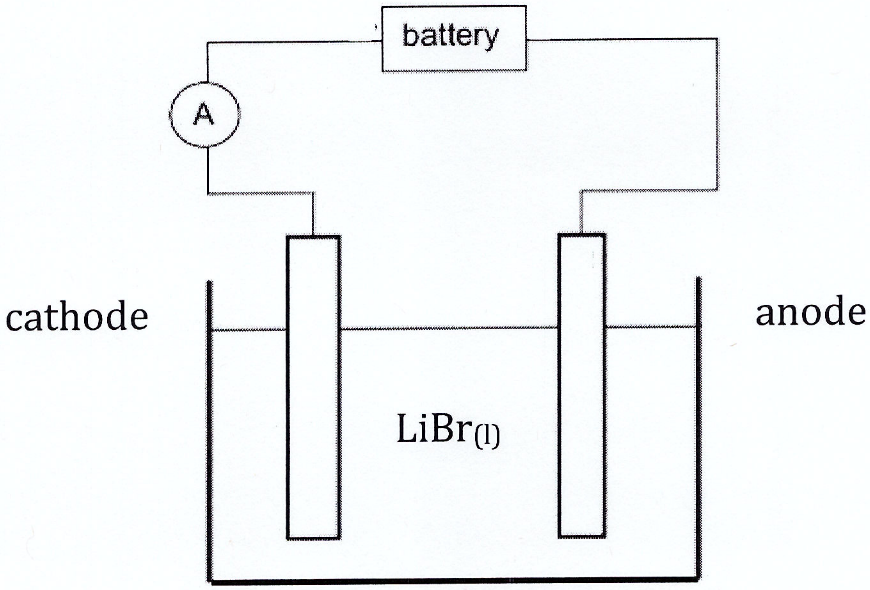
*****Now try pg. 508 #5, 7, 8 & Practice Problems #1-4*****

Practice Problems

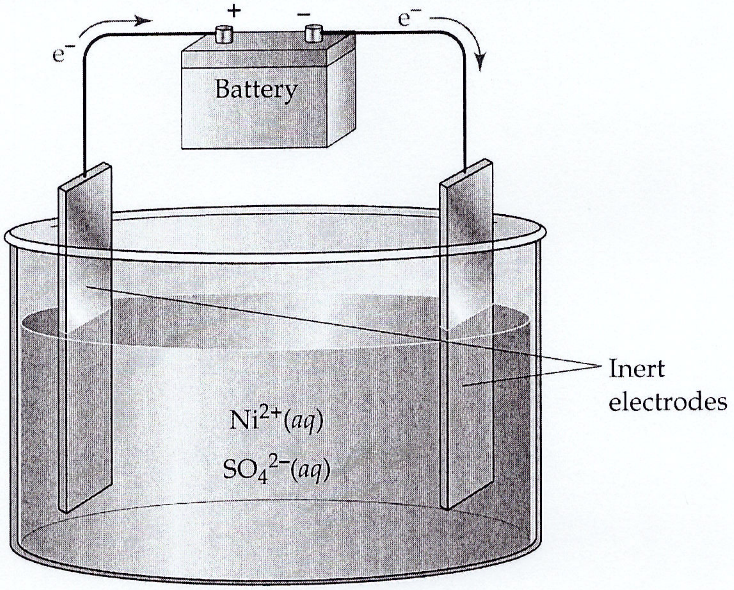
1. Predict whether the following reaction would take place in a voltaic cell or an electrolytic cell.
    a. $2\ Ag^{+}_{(aq)}\ +\ H_2SO_{3(aq)}\ +\ H_2O_{(l)}\ \rightarrow\ 2\ Ag_{(s)}\ +\ SO_4{}^{2-}{}_{(aq)}\ +\ 4\ H^{+}_{(aq)}$
    b. $FeI_{2(aq)}\ \rightarrow\ Fe_{(s)}\ +\ I_{2(s)}$

2. In the electrolysis of water, identify the gas produced at the anode and identify the gas produced at the cathode.

3. Consider the electrolysis of molten lithium bromide, $LiBr_{(l)}$.
    a. Write the half-reactions that take place at the anode and the cathode.
    b. What voltage is required for this electrolysis purpose?
    c. Will the mass of the cathode increase or decrease?
    d. Correctly label the diagram below with the direction of electron flow and the location $Br_{2(l)}$ forms.



4. Consider the picture of the following electrochemical cell.



a. Is the cell electrolytic or voltaic?

b. What side is the anode located (left or right)?

c. Write the half-reaction that takes place at the anode and cathode.

d. Calculate the cell potential.

Answers

1.
   a. Voltaic cell
   b. Electrolytic

2. $O_{2(g)}$ at anode and $H_{2(g)}$ at cathode.

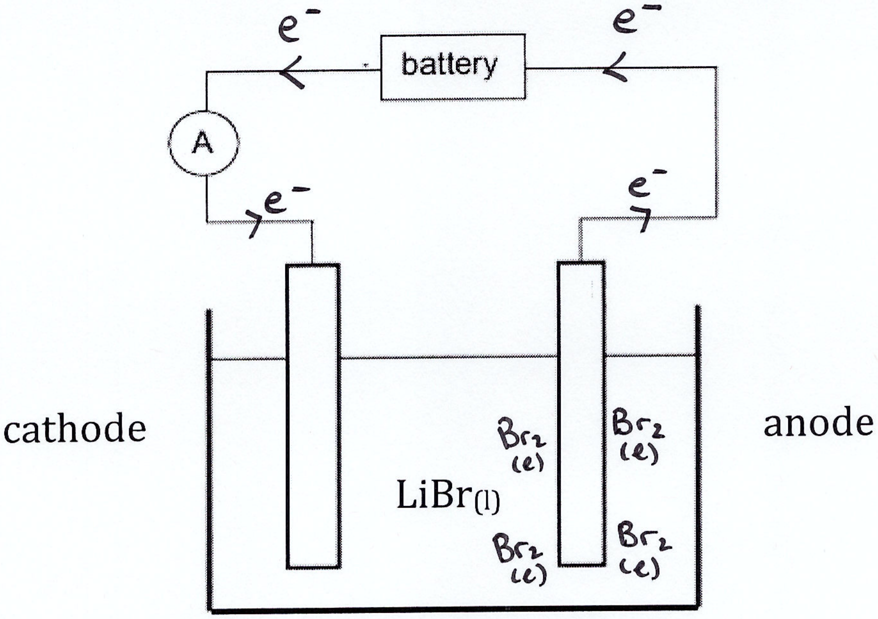
3.
   a. Anode: $2\ Br^{-}_{(l)} \rightarrow 2Br_{2(l)} + 2\ e^{-}$

   Cathode: $Li^{+}_{(l)} + e^{-} \rightarrow Li_{(l)}$

   b. Increase

   c. – 4.11 V

   d.



4.
   a. Electrolytic

   b. Left

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

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

   d. – 1.49 V

Helpful Hints to Determine the Anode and Cathode

VOLTAIC CELL (spontaneous rxn, therefore O.A. is ***higher*** than R.A.)

- **Cathode:** reduction half-reaction/ strong oxidizing agent ⟶ therefore, needs a half-reaction with a *more positive* reduction potential (E°)
- **Anode:** oxidation half-reaction/ strong reducing agent ⟶ therefore, needs a half-reaction with a *more negative* reduction potential (E°)

ELECTROLYTIC CELL (non-spontaneous rxn, therefore O.A. is ***lower*** than R.A.)

- **Cathode:** reduction half-reaction/ "strongest" oxidizing agent ⟶ therefore, needs a half-reaction with a *more negative* reduction potential (E°)
- **Anode:** oxidation half-reaction/ "strongest" reducing agent ⟶ therefore, needs a half-reaction with a *more positive* reduction potential (E°)