Electrochemistry = the branch of chemistry that deals with the relationships between electricity and chemical reactions.
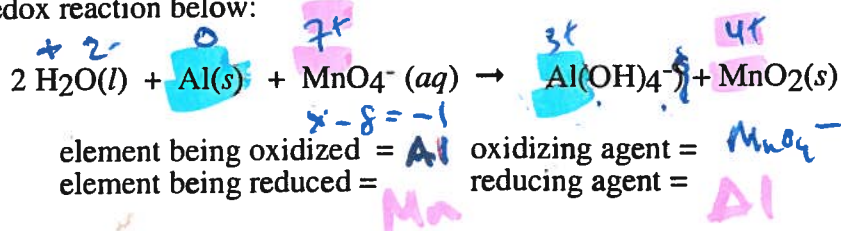
Oxidation-reduction reactions = reactions where one or more substances change oxidation states.

Oxidation = loss of electrons
Reduction = gaining of electrons
Oxidizing agent = removes electrons from another substance by acquiring them itself, the oxidizing agents is reduced.
Reducing agent = a substance that gives up electrons, thereby being reduced, the oxidizing agent, and the reducing agent in the redox reaction below:

$$2\ H_2O(l)\ +\ Al(s)\ +\ MnO_4^-\ (aq)\ \rightarrow\ Al(OH)_4^-\ +\ MnO_2(s)$$

$$x - 8 = -1$$

element being oxidized = Al oxidizing agent = MnO_4^-
element being reduced = Mn reducing agent = Al

BALANCING REDOX REACTIONS BY THE HALF-REACTION METHOD:

(5) Steps in balancing a redox reaction in an acidic solution:

Step 1: Write the oxidation and the reduction half-reactions
Step 2: Balance..
   a) the elements other than H and O
   b) balance the oxygen by adding water and balance the hydrogen by adding H^+.
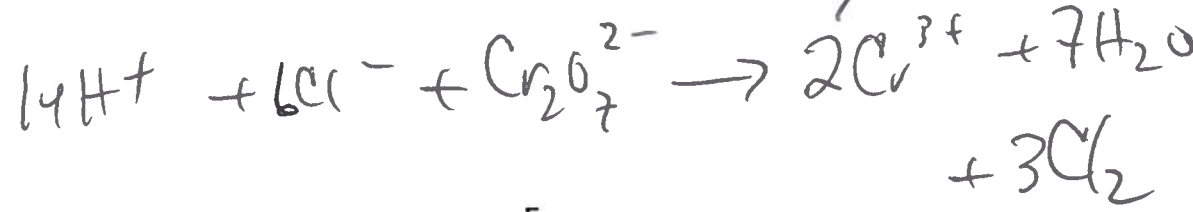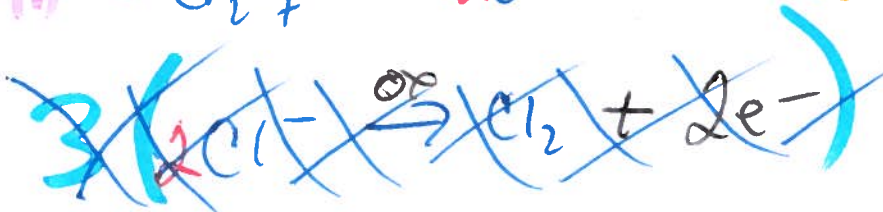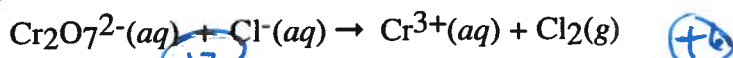   c) balance the charges by adding e- to the more positive side.
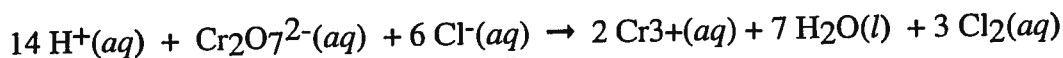Step 3: Make sure the e- lost = electrons gained by multiplying one or both reactions by an integer.
Step 4: Add and simplify the 2 reactions.
Step 5: Double check that the atoms and charges are balanced!

Example: Complete and balance the following redox reaction in an acidic solution:

$$Cr_2O_7^{2-}(aq) + Cl^-(aq) \rightarrow Cr^{3+}(aq) + Cl_2(g)$$

$$6e^- + 14H^+ + Cr_2O_7^{2-} \xrightarrow{RED} 2Cr^{3+} + 7H_2O$$

$$3(2Cl^- \xrightarrow{OX} Cl_2 + 2e^-)$$

$$6Cl^- \rightarrow 3Cl_2 + 6e^-$$

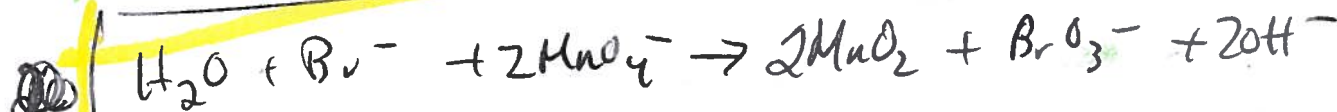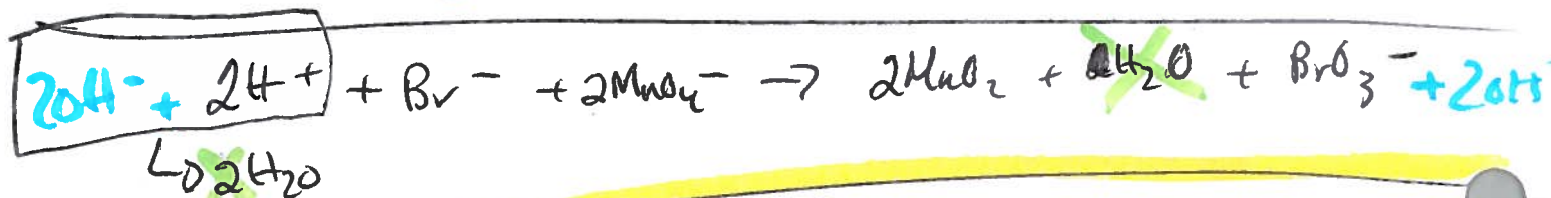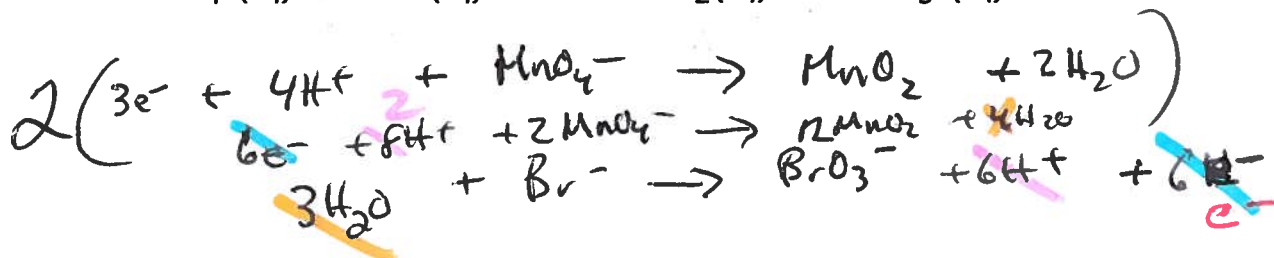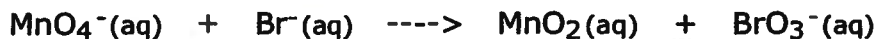$$14H^+ + 6Cl^- + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O + 3Cl_2$$

If you were asked to balance the previous redox reaction in a basic solution, you would first balance the reaction in an acidic solution and then add enough OH^- ions to both sides in order to cancel out the H^+ ions. Combine the OH^- ions and H^+ ions to form water. Then, simplify the equation. The previous equation was balanced in an acidic solution as follows

$$14\ H^+(aq)\ +\ Cr_2O_7{}^{2-}(aq)\ +6\ Cl^-(aq)\ \rightarrow\ 2\ Cr^{3+}(aq)+7\ H_2O(l)\ +3\ Cl_2(aq)$$

Now add 14 OH^- to both sides, form water, and simplify!

$$MnO_4{}^-(aq)\ +\ Br^-(aq)\ ----> \ MnO_2(aq)\ +\ BrO_3{}^-(aq)$$

$2\left(3e^- + 4H^+ + MnO_4{}^- \rightarrow MnO_2 + 2H_2O\right)$

$6e^- + 8H^+ + 2MnO_4{}^- \rightarrow 2MnO_2 + 4H_2O$

$3H_2O + Br^- \rightarrow BrO_3{}^- + 6H^+ + 6e^-$

$2OH^- + 2H^+ + Br^- + 2MnO_4{}^- \rightarrow 2MnO_2 + 4H_2O + BrO_3{}^- + 2OH$

$\downarrow 2H_2O$

$$H_2O + Br^- + 2MnO_4{}^- \rightarrow 2MnO_2 + BrO_3{}^- + 2OH^-$$

"Bob! You fool ... Don't plug that thing in!"

6

Section 20.3 Voltaic Cells

Itaic cell (or galvanic cell) = a device which uses a spontaneous redox reaction to generate electricity. The oxidation half-reaction and the reduction often occur in separate compartments, each of which contain a solid surface called an electrode. The electrode at which oxidation occurs is called the anode, and the electrode at which the reduction occurs is called the cathode. The electrons released at the anode flow through an external circuit (where they can do work) to the cathode. Electrical neutrality in the solution is maintained by the migration of ions between the two compartments through a device such as a salt bridge. See the diagram below:

Anode (oxidation)	$Zn(s) \dashrightarrow Zn^{2+}(aq) + 2e-$
Cathode (reduction)	$Cu^{2+}(aq) + 2e- \dashrightarrow Cu(s)$

Overall reaction: $Cu^{2+}(aq) + Zn(s) \dashrightarrow Cu(s) + Zn^{2+}(aq)$

$E^{\circ}_{ox} = +.76V$
$E^{\circ}_{Red} = .34V$
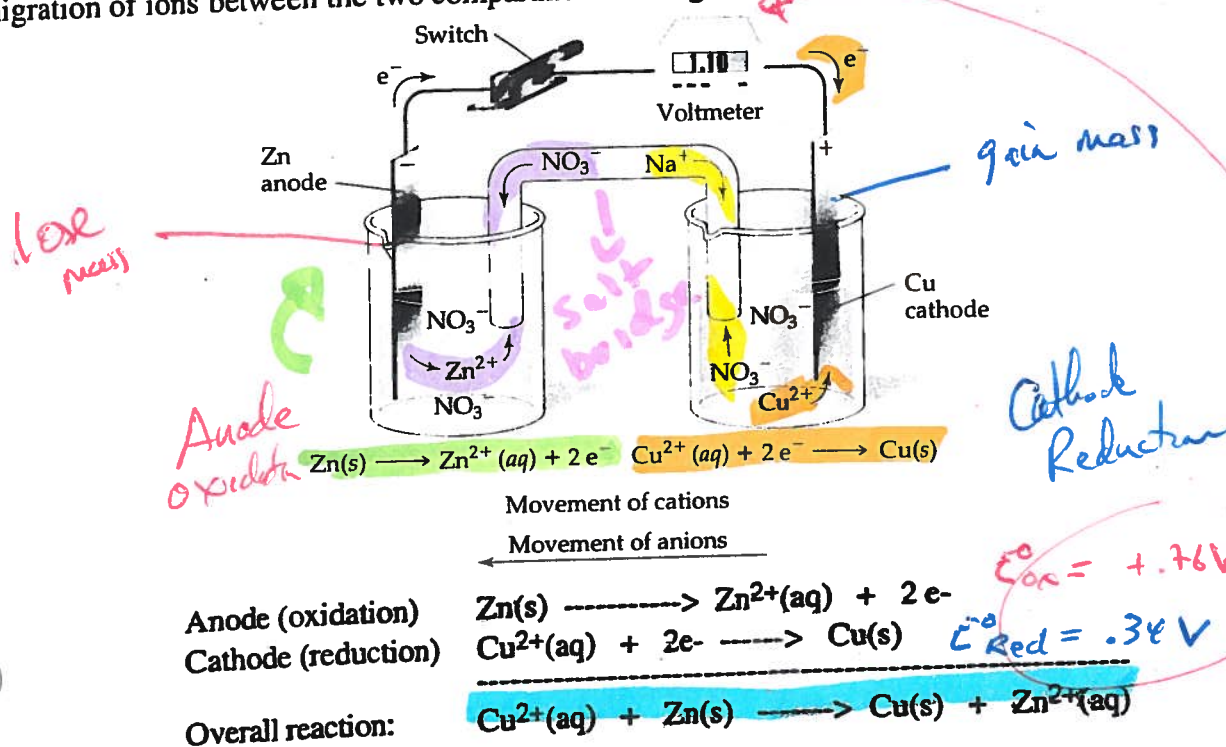
Notes: * As the zinc metal is oxidized (at the anode), e- are made available and flow through the external circuit to the cathode. The electrons are consumed by the Cu^{2+} ions.
* The zinc electrode loses mass (due to the formation of Zn^{2+} ions) and the CU electrode gains mass due to the "plating" of the copper.

* This reaction will not spontaneously continue to take place as there is no means made available to neutralize the positive charge in the zinc compartment or the negative charge in the copper compartment. This is the purpose of a *salt bridge.*

* The salt bridge consist of an electrolyte (i.e. aqueous $NaNO_3$). The ions of this electrolyte migrate to the cell compartments in order neutralize the charge in the compartments. The cations of the electrolyte will migrate towards the the cathode and the anions will migrate toward the anode. The presence of these ions will neutralize the charge in the respective compartments of the cell and allow the electrical circuits to be completed.

20.24 A voltaic cell similar to that shown in Figure 20.5(P. 857) is constructed. One electrode compartment consists of an Al strip placed in a solution of $Al(NO_3)_3$, and the other has a nickel strip and a solution of $NiSO_4$. On a separate sheet do the following:

A. Draw the cell similar to that of the drawing above.
. Write the two half reactions that occur in the two electrode compartments and the overall equation.
C. What is being oxidized and what is being reduced?
D. Which electrode is the anode, and which is the cathode?
E. Describe how the electrons flow in the cell.
F. In which directions do the cations and anions migrate through the solution.

7

please see the attached

Section 20.4 Cell EMF

electromotive force (emf) = a measure of the driving force for the completion of an electrochemical reaction; emf is measured in volts (1 V = 1 J/C) emf is also called **cell potential**. The emf helps explain exactly <u>why</u> electrons are transferred during a redox reaction.

* The electrons in anodes have higher PE than do electrons in cathodes which is why electrons spontaneously flow from the anode to the cathode. The potential difference between two electrodes of a voltaic cell is called the emf of the cell, E_{cell}.

*For any cell reaction that proceeds spontaneously (like that in voltaic cells), the cell potential is positive!

*Standard emf or **standard cell potential** ($E°_{cell}$) is the emf measured under standard conditions. Standard conditions are 25°C, 1 M solutions, 1 atm for gases.

*It is impossible to measure directly the emf generated by an oxidation or a reduction half-reaction, but we can easily measure the potential difference between a cathode and an anode by using a voltaic cell. The cell emf is simply the potential difference between the cathode and the anode.

*The cell potential, $E°_{cell}$, is given by ....$E°_{cell} = E°_{red}(cathode) - E°_{red}(anode)$; $E°_{cell} = E°_{RED} + E°_{ox}$

*By convention we have assigned a zero potential to a reference electrode system in involving hydrogen:

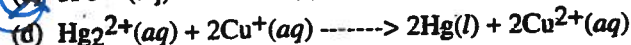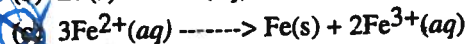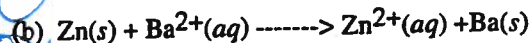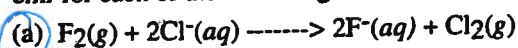$$2 H^+(aq)(1 M) + 2 e^- \longrightarrow H_2(g)(1 atm) ; E°_{red} = O \text{ volts at } 25°C$$
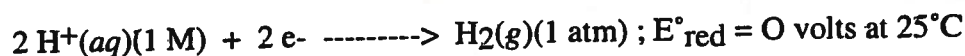
This electrode system is called **SHE (standard hydrogen electrode!)**

***Standard reduction potentials** ($E°_{red}$) = the potential of a reduction half-reaction under standard conditions, measured relative to the standard hydrogen electrode. A fairly extensive list is provided for you in appendix E of your text. A standard reduction potential is called a **standard electrode potential.**

*The standard reduction potential of Zn^{2+} to Zn is -0.76 V and it's determination is shown for you in figure 20.11 on page ~~765~~.
862

~~20-26~~
(20.34) Using data in Appendix E, calculate the standard emf for each of the following reactions:

    (a) $F_2(g) + 2Cl^-(aq) \longrightarrow 2F^-(aq) + Cl_2(g)$

    (b) $Zn(s) + Ba^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Ba(s)$

    (c) $3Fe^{2+}(aq) \longrightarrow Fe(s) + 2Fe^{3+}(aq)$

    (d) $Hg_2^{2+}(aq) + 2Cu^+(aq) \longrightarrow 2Hg(l) + 2Cu^{2+}(aq)$

$$E°_{Total} = E°_{RED} - E°_{RED}$$
$$\text{Cathod} \quad \text{anothe}$$
$$= E°_{Red} + E°_{ox} \quad \text{Anode}$$

Potential Difference: this is the "driving force" or electrical pressure that allows electrons through the external circuit.

Volt: One volt(V) is the potential difference required to impart one Joule of energy to a charge of one Coulomb(C).
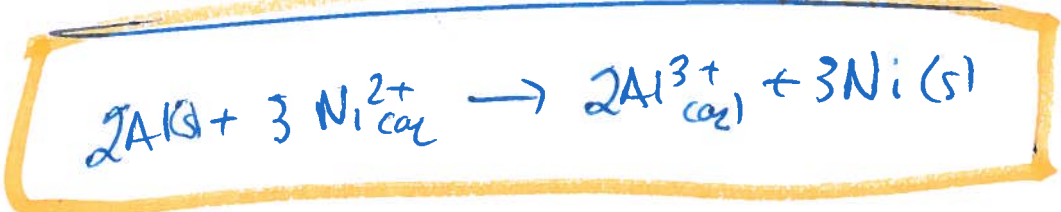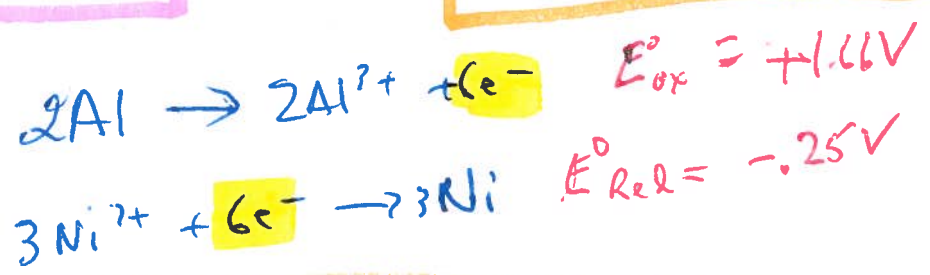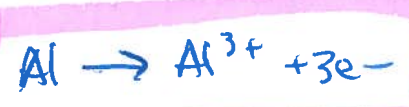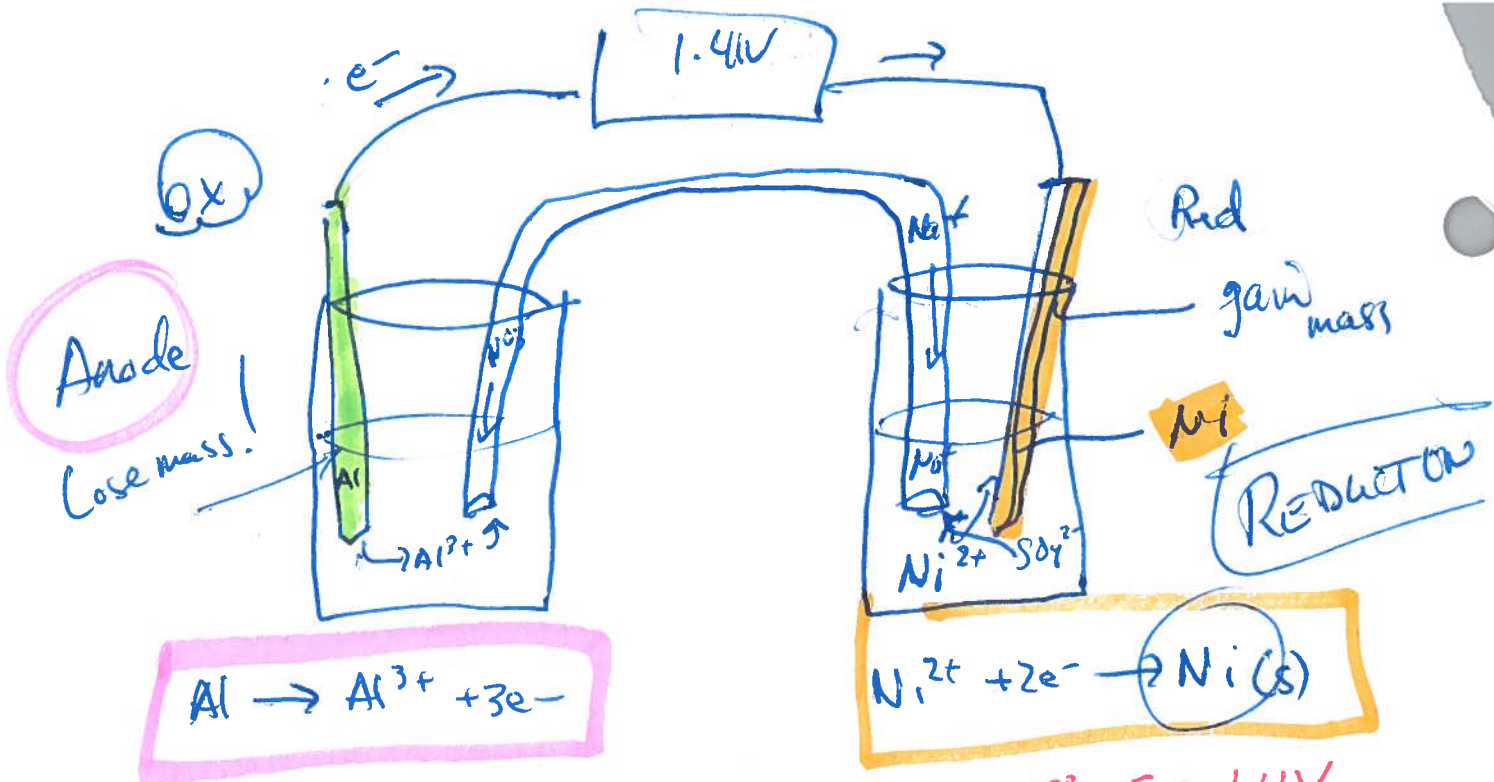
The half cell potential for a reduction is = in magnitude but opposite in sign to the half cell potential for the same reaction written as an oxidation. That is $E_{red} = -E_{ox}$

Electrode potentials are intensive properties so changing the stoichiometric coefficient in a half reaction does not affect the value of the electrode potential. The electrode potential does depend on the concentration of reactants and products.

The best oxidizing agents are substances that are easily reduced and the best reducing agents are substances that are easily oxidized.

A.   Four common oxidizing agents are O_2, F_2, Cl_2, Br_2 .

B.   Four common reducing agents are $Li, K 8, Cs, Rb$.

Ox

Anode
(lose mass!)

$e^- \rightarrow$

1.41V $\rightarrow$

Na$^+$

Red
gain mass

Ni

REDUCTION

Ni^{2+} SO$_4^{2-}$

$Al \rightarrow Al^{3+} + 3e^-$

$Ni^{2+} + 2e^- \rightarrow Ni_{(s)}$

$2Al \rightarrow 2Al^{3+} + 6e^-$ $E^o_{ox} = +1.66V$

$3Ni^{2+} + 6e^- \rightarrow 3Ni$ $E^o_{Red} = -.25V$

$$2Al_{(s)} + 3Ni^{2+}_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3Ni_{(s)}$$

$E^o_{Total} = E^o_{RED} - E^o_{RED}$

$= -25V - (-1.66V)$

$= \boxed{1.41V}$

- e^- flow from anode to cathode
- Salt bridge NO_3^- migrates to the Anode compartment
- "   "   Na$^+$ "   "   " Cathode compartment
      (cations)

4

Half-reaction			$E°$(V)
$F_2(g) + 2e^-$	$\rightarrow$	$2F^-$	2.87
$Co^{3+} + e^-$	$\rightarrow$	Co^{2+}	1.82
$Au^{3+} + 3e^-$	$\rightarrow$	$Au(s)$	1.50
$Cl_2(g) + 2e^-$	$\rightarrow$	$2Cl^-$	1.36
$O_2(g) + 4H^+ + 4e^-$	$\rightarrow$	$2H_2O(l)$	1.23
$Br_2(l) + 2e^-$	$\rightarrow$	$2Br^-$	1.07
$2Hg^{2+} + 2e^-$	$\rightarrow$	Hg_2^{2+}	0.92
$Hg^{2+} + 2e^-$	$\rightarrow$	$Hg(l)$	0.85
$Ag^+ + e^-$	$\rightarrow$	$Ag(s)$	0.80
$Hg_2^{2+} + 2e^-$	$\rightarrow$	$2Hg(l)$	0.79
$Fe^{3+} + e^-$	$\rightarrow$	Fe^{2+}	0.77
$I_2(s) + 2e^-$	$\rightarrow$	$2I^-$	0.53
$Cu^+ + e^-$	$\rightarrow$	$Cu(s)$	0.52
$Cu^{2+} + 2e^-$	$\rightarrow$	$Cu(s)$	0.34
$Cu^{2+} + e^-$	$\rightarrow$	Cu^+	0.15
$Sn^{4+} + 2e^-$	$\rightarrow$	Sn^{2+}	0.15
$S(s) + 2H^+ + 2e^-$	$\rightarrow$	$H_2S(g)$	0.14
$2H^+ + 2e^-$	$\rightarrow$	$H_2(g)$	0.00
$Pb^{2+} + 2e^-$	$\rightarrow$	$Pb(s)$	-0.13
$Sn^{2+} + 2e^-$	$\rightarrow$	$Sn(s)$	-0.14
$Ni^{2+} + 2e^-$	$\rightarrow$	$Ni(s)$	-0.25
$Co^{2+} + 2e^-$	$\rightarrow$	$Co(s)$	-0.28
$Cd^{2+} + 2e^-$	$\rightarrow$	$Cd(s)$	-0.40
$Cr^{3+} + e^-$	$\rightarrow$	Cr^{2+}	-0.41
$Fe^{2+} + 2e^-$	$\rightarrow$	$Fe(s)$	-0.44
$Cr^{3+} + 3e^-$	$\rightarrow$	$Cr(s)$	-0.74
$Zn^{2+} + 2e^-$	$\rightarrow$	$Zn(s)$	-0.76
$2H_2O(l) + 2e^-$	$\rightarrow$	$H_2(g) + 2OH^-$	-0.83
$Mn^{2+} + 2e^-$	$\rightarrow$	$Mn(s)$	-1.18
$Al^{3+} + 3e^-$	$\rightarrow$	$Al(s)$	-1.66
$Be^{2+} + 2e^-$	$\rightarrow$	$Be(s)$	-1.70
$Mg^{2+} + 2e^-$	$\rightarrow$	$Mg(s)$	-2.37
$Na^+ + e^-$	$\rightarrow$	$Na(s)$	-2.71
$Ca^{2+} + 2e^-$	$\rightarrow$	$Ca(s)$	-2.87
$Sr^{2+} + 2e^-$	$\rightarrow$	$Sr(s)$	-2.89
$Ba^{2+} + 2e^-$	$\rightarrow$	$Ba(s)$	-2.90
$Rb^+ + e^-$	$\rightarrow$	$Rb(s)$	-2.92
$K^+ + e^-$	$\rightarrow$	$K(s)$	-2.92
$Cs^+ + e^-$	$\rightarrow$	$Cs(s)$	-2.92
$Li^+ + e^-$	$\rightarrow$	$Li(s)$	-3.05

Section 20.5 - Spontaneity of Redox Reactions

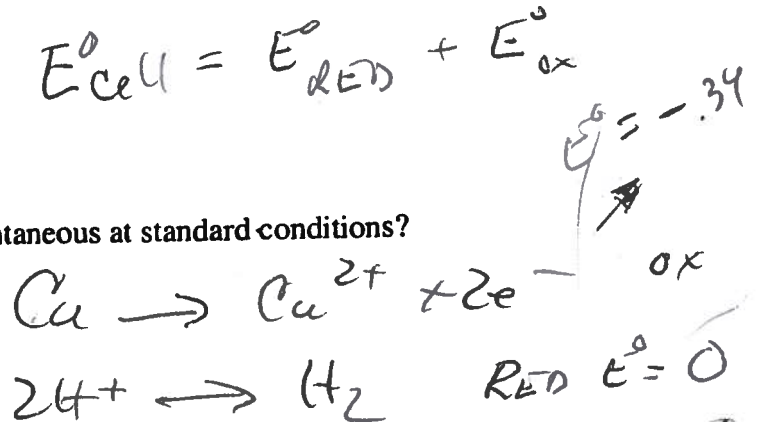$$E° = E°_{red}(reduction) - E°_{red}(oxidation)$$

Cathode   Anode

*This can be used to calculate the E° for any redox reaction and not just for voltaic cells as the "cell" has been dropped out of the E°cell from the equation...

$$E°cell = E°_{red}(cathode) - E°_{red}(anode).$$
$$= 0 - .34V$$

positive E° = spontaneous reaction
negative E° = non spontaneous reaction

example: Is $Cu(s) + 2H^+(aq) \longrightarrow Cu^{2+}(aq) + H_2(g)$ spontaneous at standard conditions?

$$E°cell = E°_{RED} + E°_{ox}$$
$$E° = -.34$$

$$Cu \longrightarrow Cu^{2+} + 2e^- \quad ox$$

$$+ 2e^- + 2H^+ \longrightarrow H_2 \quad RED \ E° = 0$$

Non spontaneous $E°_{Total} = -.34V$

EMF and Free-Energy Change

$$\Delta G = -nFE \quad or \quad \Delta G° = -nFE°$$

voltage

n = # of electrons transferred
F = Faraday's constant = 96,500 C/mol or 96,500 J/V - mol; Faraday's constant is the charge on one mole of e-

$$C = \frac{J}{V}$$

$$\Delta G° = -nFE$$
$$= -(2\ mole)\left(\frac{96,500\ J}{V\cdot mole}\right)(-.34V)$$
$$= + 65620\ J$$
$$= 65.6\ kJ$$

20.46 (20.48) For each of the following reactions, write a balanced equation, calculate the emf, and calculate $\Delta G°$ at 298 K. (a) Aqueous iodide ion is oxidized to $I_2(s)$ by $Hg_2^{2+}(aq)$. (b) In acidic solution copper (I) ion is oxidized to copper (II) ion by nitrate ion. (c) In basic solution $Cr(OH)_3(s)$ is oxidized to $CrO_4^{2-}(aq)$ by $ClO^-(aq)$

Section 20.6: Effect of Concentration on EMF

$$2I^- \longrightarrow I_2 + 2e^- \quad \text{non spontaneous}$$
$$2e^- + Hg_2^{2+} \longrightarrow HgCl_2 \ (.79) \quad -.53 \ E°_{ox}$$
$$E°_{red}$$
$$E°_{Total} = .26V$$

The Nernst Equation

$$E_{cell} = E°_{cell} - \frac{RT}{nF}\ln Q \quad or \quad E_{cell} = E°_{cell} - \frac{0.0592}{n}\log Q$$

The **Nernst Equation** is used when calculating the emf generated by a cell under non-standard conditions, or when the concentrations of the reactants/products are not 1.0 M!!

$$\Delta G° = (-2)\left(\frac{96,500\ kJ}{mol\ V}\right)(.26V)$$

Derivation of the Nernst Equation.....
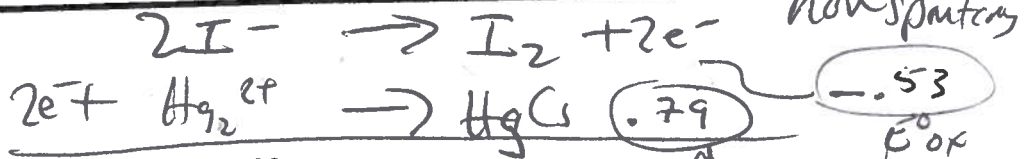
9

$$E_{cell} = E^\circ_{cell} - \frac{.0592}{n} \log \frac{[Al^{3+}]}{[Ag^+]^3}$$

20.50 (20.58) A voltaic cell utilizes the following reaction:

$Al(s) + 3Ag^+(aq) \rightarrow Al^{3+}(aq) + 3Ag(s)$

What is the effect on the cell emf of each of the following changes? (a) Some $Al(NO_3)_3$ is added to the anode compartment, increasing the concentration of Al^{3+} ions. (b) The size of the aluminum electrode is increased. (c) Additional water is added to the cathode compartment. (d) A solution of $AgNO_3$ is added to the cathode compartment, increasing the quantity of Ag^+ but not changing its concentration.
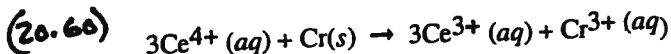
(a) $E_{cell} \downarrow$

(b) No change

(c) $\downarrow$

20.52 (20.60) A voltaic cell utilizes the following reaction and operates at 298K:

$3Ce^{4+}(aq) + Cr(s) \rightarrow 3Ce^{3+}(aq) + Cr^{3+}(aq)$

(a) What is the emf of this cell under standard conditions?
(b) What is the emf of this cell when $[Ce^{4+}] = 1.5\ M$, $[Ce^{3+}] = 0.010\ M$, and $[Cr^{3+}] = 0.010\ M$
(c) What is the emf of the cell when $[Ce^{4+}] = 0.55\ M$, $[Ce^{3+}] = 0.85\ M$, and $[Cr^{3+}] = 1.2\ M$?
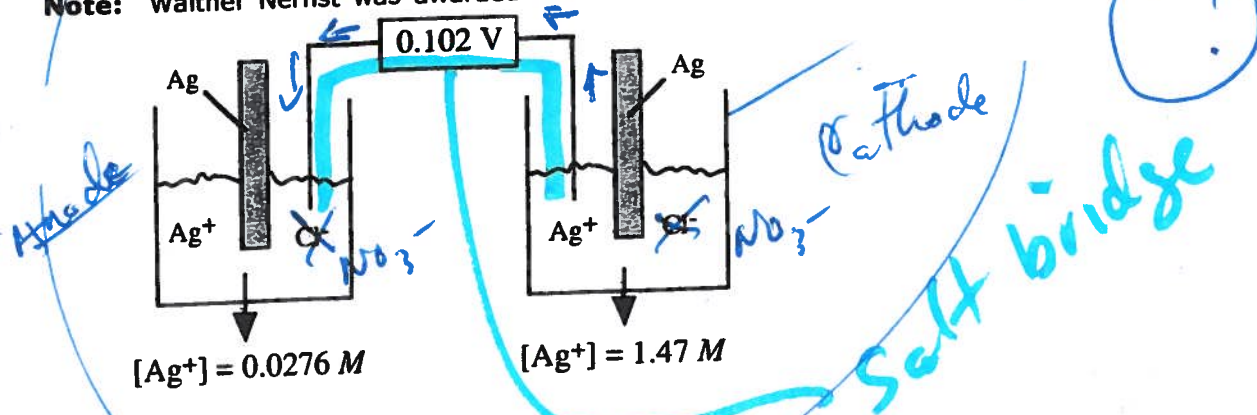
Red
Cathode
Ag^+/Ag

OX
Anode
Al/Al^{3+}

Concentration Cells: a voltaic cell containing the same electrolyte and the same electrode material, emf generated due to difference in concentrations of electrolyte solutions.

• Solve for emf by using NERNST EQUATION as you will h ave non-standard condtions!

• ANODE = half-cell with the more DILUTE solution

• CATHODE = half-cell with the more CONCENTRATED solution

Note: As a voltaic cell is discharged, emf falls until E = 0; then the cell is dead. When the [reactants] increases the emf Increases; when [products] increases the emf decreases. As a cell opereates, [reactants] decreases and [products] increases.

Note: Walther Nernst was awarded a Nobel Prize in his work in electrochemistry.

0.102 V

Ag   Ag

Anode   Cathode

Ag^+ Cl^- NO_3^- Ag^+ Cl^- NO_3^-

Salt bridge

$[Ag^+] = 0.0276\ M$ $[Ag^+] = 1.47\ M$

What is the emf for the above cell?

Relationship Between EMF & Equilibrium

O at Equilb

At Equilib E = 0

$$E = E° - \frac{0.0592}{n} \log Q$$

at equilibrium...

$$O = E° - \frac{0.0592}{n} \log K$$

rearranged...

$$\log K = \frac{nE°}{0.0592} \text{ at 25°C}$$

$$E° = \frac{.0592}{n} \log k$$

$$K = 10^{\left(\frac{nE°}{.0592}\right)}$$

Example:

(similar to 20.53)

A cell exhibits a standard emf of 0.147 V at 298 K. What is the value of the equilibrium constant if $n = 2$?

$E°$

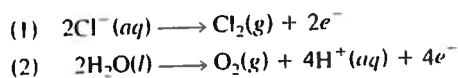9.25×10^4

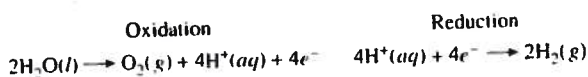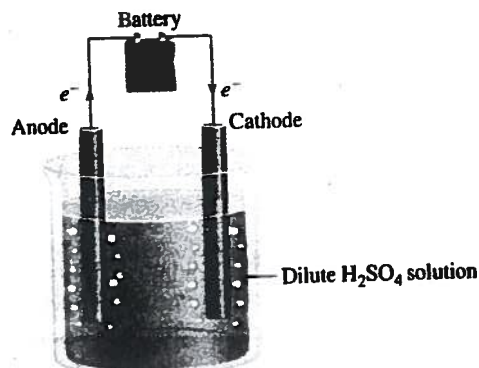$$K = 10^{\left(\frac{nE°}{.0592}\right)}$$

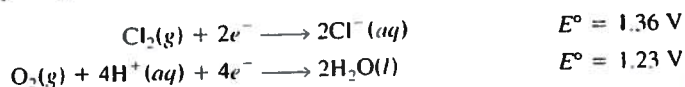$$K = 10^{\left(\frac{(2)(.147)}{.592}\right)}$$

$$K = 10$$

$$= 9.25 \times 10^4$$

11

Electrolysis of an Aqueous Sodium Chloride Solution

This is the most complicated of the three examples of electrolysis considered here because aqueous sodium chloride solution contains several species that could be oxidized and reduced. The oxidation reactions that might occur at the anode are
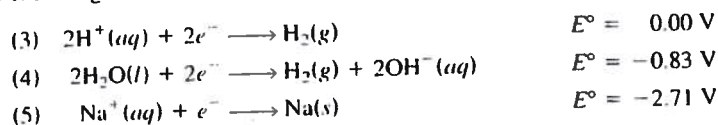

Oxidation
$$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$$

Reduction
$$4H^+(aq) + 4e^- \longrightarrow 2H_2(g)$$

(1) $\quad 2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$

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

Referring to Table 19.1. we find

$$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq) \qquad E° = 1.36 \text{ V}$$
$$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l) \qquad E° = 1.23 \text{ V}$$

The standard reduction potentials of (1) and (2) are not very different, but the values do suggest that H_2O should be preferentially oxidized at the anode. However, by experiment we find that the gas liberated at the anode is Cl_2, not O_2! In studying electrolytic processes, we sometimes find that the voltage required for a reaction is considerably higher than the electrode potential indicates. The *overvoltage* is *the difference between the electrode potential and the actual voltage required to cause electrolysis.* The overvoltage for O_2 formation is quite high. Therefore, under normal operating conditions Cl_2 gas is actually formed at the anode instead of O_2.
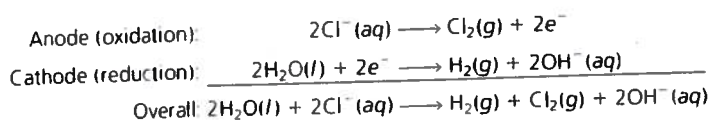
> Because Cl_2 is more easily reduced than O_2, it follows that it would be more difficult to oxidize Cl^- than H_2O at the anode.

The reductions that might occur at the cathode are

(3) $\quad 2H^+(aq) + 2e^- \longrightarrow H_2(g) \qquad\qquad E° = \quad 0.00 \text{ V}$

(4) $\quad 2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \qquad E° = -0.83 \text{ V}$

(5) $\quad Na^+(aq) + e^- \longrightarrow Na(s) \qquad\qquad E° = -2.71 \text{ V}$

Reaction (5) is ruled out because it has a very negative standard reduction potential. Reaction (3) is preferred over (4) under standard-state conditions. At a pH of 7 (as is the case for a NaCl solution), however, they are equally probable. We generally use (4) to describe the cathode reaction because the concentration of H^+ ions is too low (about 1×10^{-7} M) to make (3) a reasonable choice.

Thus, the half-cell reactions in the electrolysis of aqueous sodium chloride are

Anode (oxidation): $\qquad 2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$

Cathode (reduction): $\quad \underline{2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)}$

Overall: $2H_2O(l) + 2Cl^-(aq) \longrightarrow H_2(g) + Cl_2(g) + 2OH^-(aq)$

As the overall reaction shows, the concentration of the Cl^- ions decreases during electrolysis and that of the OH^- ions increases. Therefore, in addition to H_2 and Cl_2, the useful by-product NaOH can be obtained by evaporating the aqueous solution at the end of the electrolysis.

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From Dr. Chang's Text !!!

<div align="center">

Class Notes Section 20.9:   Electrolysis

</div>

Electrolysis Reaction - a reaction in which a nonspontaneous redox reaction is brought about by the passage of a current using an external voltage source; electrolysis reactions occur in electrolytic cells.

galvanic

Differences and Similarities Between Voltaic and Electrolytic Cells

Similarities

- oxidation occurs at the anode and reduction occurs at the cathode

Differences

- the redox rx's in voltaic cells are spontaneous; the redox rx's in electrolytic cells need an outside source to "force" e⁻ to flow

- signs of cathode and anode are opposite

	Voltaic	Electrolytic
anode	-	+
cathode	+	-

- the electrolytic cell is considered part of the external circuit (not so in a voltaic cell)

OX (Anode) or RED (cathode)

Example:
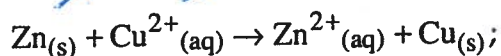
$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)};$$ $$E°cell = +1.10$$

This equation describes the reaction in a voltaic cell as the cell potential is positive and therefore spontaneous! If we connect the same cell to a battery which produced a voltage of > 1.10 V, the flow of e⁻ is reversed!

Zn   1.0 M $Zn(NO_3)_{2(aq)}$ Salt Bridge   Battery   1.0 M $Cu(NO_3)_{2(aq)}$ Cu
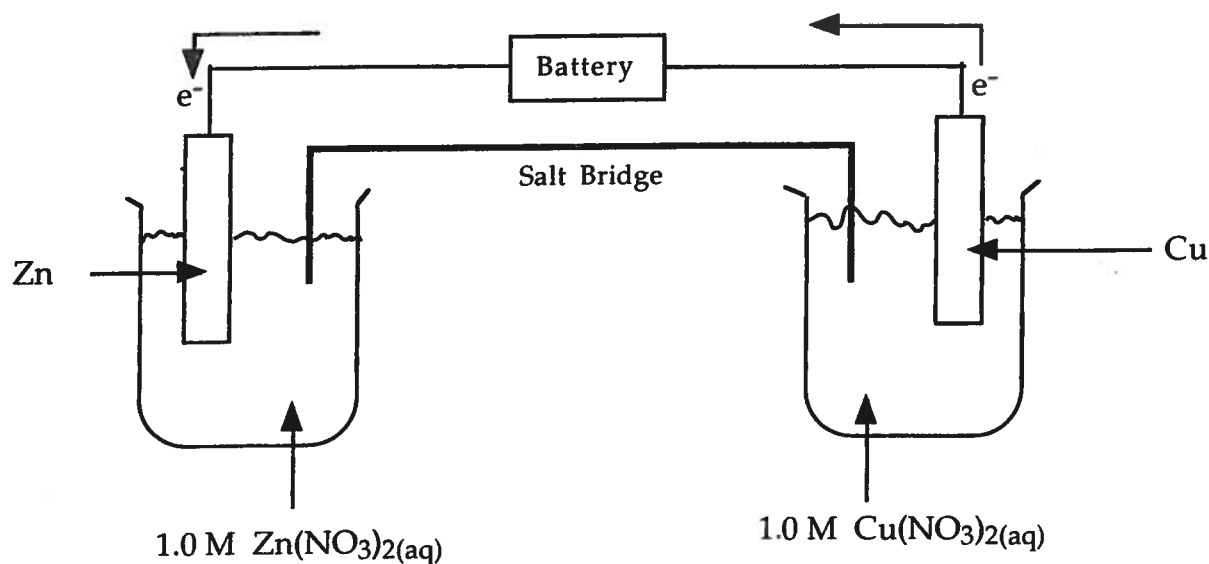
Electrolysis of Aqueous Solutions:
The electrolysis of aqueous solutions can become a little complicated as water may go through reduction and oxidation reactions instead of the salt. Consider the following example.

Electrolysis of **MOLTEN** Sodium fluoride: $NaF(s) \rightarrow Na(s) + F_2(g)$
Oxidation: $2 F^- \rightarrow F_2(g) + 2e^-$
Reduction: $2 Na^+ + 2e^- \rightarrow 2 Na(l)$

Electrolysis of **AQUEOUS** sodium fluoride: (now you must consider 2 oxidation and 2 reduction 1/2 reactions!)

Oxidation: $2 F^- \rightarrow F_2(g) + 2e^-$ $E^O_{red} = 2.87 V$
         $2H_2O(l) \rightarrow O_2(g) + 4H^+ + 4e^-$ $E^O_{red} = 1.23V^*$

Reduction: $2 Na^+ + 2e^- \rightarrow 2 Na(s)$ $E^O_{red} = -2.71 V$
         $2 H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-$ $E^O_{red} = -0.83 V^*$

The reduction potentials indicate that the $H_2O(l)$ is both easier to reduce and oxidize than the ions. In this case, the salt (NaF) would only serve as an electrolyte and not be reduced or oxidized.

Notes and Hints about Electrolysis:
* Remember you want the E^O_{cell} to be negative(non-spontaneous).
* Oxidation still takes place at the anode and reduction at the cathode.
* At the anode and cathode there will be a formation of **elements or diatomic molecules** and **water** may be oxidized or reduced or both!
* In salt hydrolysis both the salt and water are available to participate in the oxidation and reduction reactions. Write the possible half reactions that could occur at each cell, then choose the most positive value for each half reaction. For each half reaction water may be reduced(at Cathode) and/or oxidized(at Anode).
* Electroplating is when you use an external energy source to plate a thin layer of a metal onto another metal to make it more appealing or to prevent corrosion.
* Let's look at the 2005 Electrolysis Free Response.

Quantitative Aspects of Electrolvsis:
Conversion factors:
1.00 Coulomb = 1.00 amp(A) x Sec   1.00 volt(V) = 1.00 J/C
1.00 watt(W) = 1.00 J/sec 96,500 C = 1 mole e⁻(this is the charge on 1 mole of e⁻)

Example 1:
Determine the mass of copper that is plated out when a current of 10.0 amps is passed through a Cu^{2+} (aq) solution for 30 minutes.

$$\frac{30.0\,min}{} \left| \frac{60\,sec}{min} \right| \frac{C}{amp \cdot sec} \left| \frac{10.\,amps}{(i)} \right| \frac{mol\,e^-}{96,500\,C} \left| \frac{mol\,Cu}{2mol\,e^-} \right| \frac{63.55g}{mol\,Cu}$$

$$Cu^{2+} \rightarrow 2e^- + Cu \qquad 14 \qquad = \boxed{5.93g\,Cu}$$

Example 2:
How long must a current of 5.00 A be applied to a solution of Ag^+(aq) to produce 10.5 grams of Ag metal?

20.7 (Batteries and Fuel Cells)

NOTES:
* "A battery is a portable, self-contained electrochemical power source that consists of one or more voltaic cells."
* In an **ALKALINE BATTERY** used in flashlights, the Anode is composed of Zn and KOH and the Cathode is manganese dioxide.
* Rechargeable batteries are: Nickel-Cadmium, Nickel-Metal-Hydride and Lithium ion and a **Nickel-Cadmium battery** has Nickel oxidized at the anode and Nickel oxyhydroxide [NiO(OH)] reduced at the cathode.

A LEAD STORAGE BATTERY ...
* Is found in cars and consists of one or more voltaic cells connected in series.
* 12-Volt has six 2 V cells
* The ANODE is lead and the cathode is lead(IV) oxide on a metal grid.
* This is Redox reaction is acidified with sulfuric acid
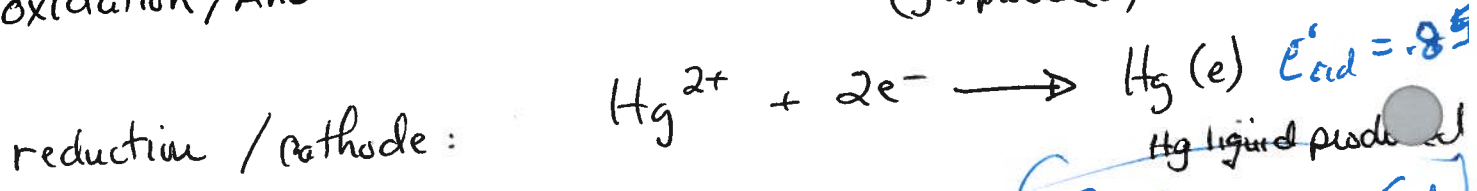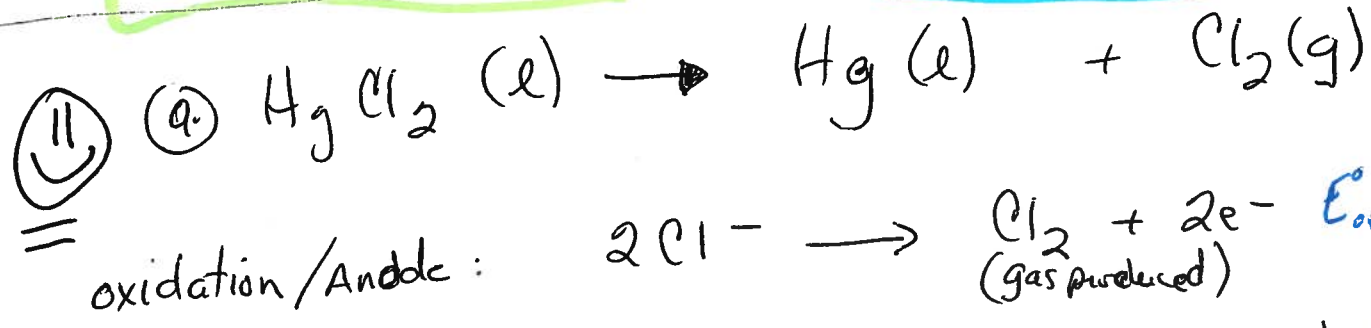* Most Car batteries are sealed to prevent electrolysis from occurring.

20.8 (Corrosion)

* These are undesirable REDOX reactions.
* A metal is attacked by some other metal in the environment (Na attacks iron)
* All metals EXCEPT Au and Pt undergo oxidation
* To prevent corrosion of Fe, coat Fe with Zn. "Protecting a metal from corrosion by making it the cathode in an electrochemical cell is known as **cathodic protection**. The metal that is oxidized while protecting the cathode is known as the **sacrificial anode.**"
* A great sacrificial anode is a metal(like zinc) that is easily oxidized or has a very negative reduction potential.
* NOTE: Electrical work ... $\Delta G = -nFE$ **so** $W_{max} = -nFE$ If the cell emf, E, is positive then W_{max} will be negative which means work is done on the surroundings by the system(voltaic cell).

Electrolysis Practice

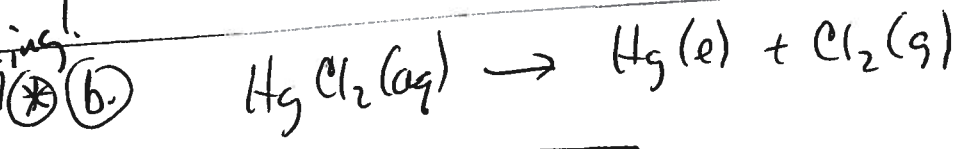What is produced at the anode and cathode through the electrolysis of:

(a.) Liquid $HgCl_2$
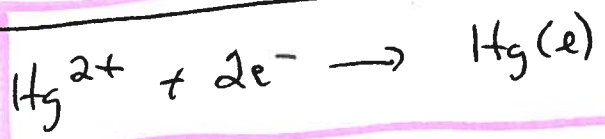
(b.) aqueous $HgCl_2$ (Electrolysis)

☺ (a.) $HgCl_2 (l) \longrightarrow Hg(l) + Cl_2(g)$

oxidation / Anode: $2Cl^- \longrightarrow Cl_2 + 2e^- \quad E_{ox}^o = -1.36$ (gas produced)

reduction / Cathode: $Hg^{2+} + 2e^- \longrightarrow Hg(l) \quad E_{red}^o = .85$
Hg liquid produced

$E_{total}^o = -.51$

you also have water available

More challenging! ✱ (b.) $HgCl_2(aq) \longrightarrow Hg(l) + Cl_2(g)$

2 Possible Reduction ½ Rxns:

E_{Red}^o

Cathode

$Hg^{2+} + 2e^- \longrightarrow Hg(l) \quad 0.85V$ ✱ $Hg(l)$ is produced (More positive)

$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \quad -0.83v$
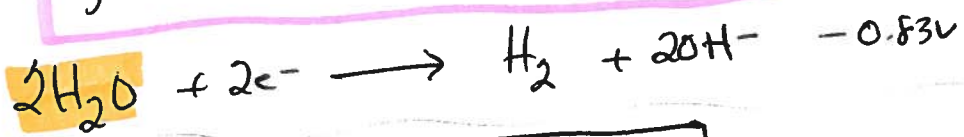
Just Begin w/ H_2O

2 Possible Oxidation ½ Rxns $\cancel{E_{ox}^o}$

E_{ox}^o

$2Cl^- \longrightarrow Cl_2 + 2e^- \quad -1.36V$ (More positive!)

$2H_2O(l) \longrightarrow O_2(g) + 4H^+ + 4e^- \quad -1.23$ ✱ $O_2(g)$ is produced!

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Note: The ½ Rxns that will occur will be the most positive!! or least negative