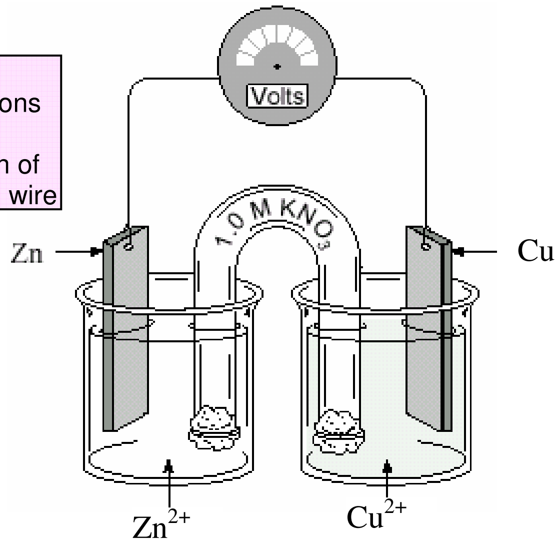
Cations + flow (migrate) toward the **cat**hode
And **An**ions – flow toward the **an**ode
} In the salt bridge

Show with arrows the direction of flow of all ions (Zn^{2+}, NO_3^-, K^+, Cu^{2+})
Also show the direction of flow of electrons in the wire



Identifying the anode and cathode

- Look at the **reduction table**
- All half-rx's are reversible (can go forward or backward)
- All are written as **reductions** (GERC)
- Their reverse would be **oxidations** (LEOA)
- The half-rx with the greater potential to be reduced is **higher** on the table (higher reduction potential E^o)

So the **higher** half-rx is the **cathode** (**HIC**)

(Notice $Cu^{2+} + 2e^- \rightarrow Cu$ is **higher** than $Zn^{2+} + 2e^- \rightarrow Zn$ so Cu gets to be the **cathode**)

Also notice that the **Anode** reaction Is **Reversed** (**AIR**)

(Anode rx: $Zn \rightarrow Zn^{2+} + 2e^-$)

Question. Fill in the following table. Use your reduction table:

Metal/ion	Metal/ion	Cathode (HIC)	Cathode Half-rx	Anode	Anode (AIR) Half-rx
Ag/Ag^+	Fe/Fe^{2+}	Ag (higher)	$Ag^+ + e^- \rightarrow Ag$	Fe (lower)	$Fe \rightarrow Fe^{2+} + 2e^-$
Zn/Zn^{2+}	Pb/Pb^{2+}	Pb	$Pb^{2+} + 2e^- \rightarrow Pb$	Zn	$Zn \rightarrow Zn^{2+} + 2e^-$
Ni/Ni^{2+}	Al/Al^{3+}	Ni	$Ni^{2+} + 2e^- \rightarrow Ni$	Al	$Al \rightarrow Al^{3+} + 3e^-$
Au/Au^{3+}	Ag/Ag^+	Au	$Au^{3+} + 3e^- \rightarrow Au$	Ag	$Ag \rightarrow Ag^+ + e^-$
Mg/Mg^{2+}	H_2/H^+	H_2	$2H^+ + 2e^- \rightarrow H_2$	Mg	$Mg \rightarrow Mg^{2+} + 2e^-$
Co/Co^{2+}	Sn/Sn^{2+}	Sn	$Sn^{2+} + 2e^- \rightarrow Sn$	Co	$Co \rightarrow Co^{2+} + 2e^-$

Summary of Electrochemical Cells (ECC's) so far…

1) Electrochemical cells convert chemical energy into electrical energy.
2) The Anode is the electrode where oxidation occurs.
3) Electrons are lost at the anode.
4) The cathode is the electrode where reduction occurs.
5) In the half-rx at the cathode, e^-'s are on the left side of the equation.
6) Electrons flow from the anode toward the cathode in the wire
7) Cations ((+) ions) flow from the anode beaker toward the cathode beaker through the saltbridge
8) Anions ((-) ions flow from the cathode beaker to the anode beaker through the saltbridge
9) The higher half-rx on the table is the one for the cathode and is not reversed.
10) The lower half-rx on the table is the one for the anode and **is** reversed.
11) Electrons do not travel through the salt bridge only through the wire
12) Ions (cations & anions) do not travel through the wire but only through the salt bridge
13) The salt bridge can contain any electrolyte
14) The anode will lose $_{\text{gains/loses)}}$ mass as it is oxidized$_{\text{(oxidized/reduced)}}$.
15) The cathode will gain mass as it is reduced $_{\text{(oxidized/reduced)}}$.

Read SW p. 215 - 217 in SW.
Ex 34 a-e & 35 a-e p.217 SW.

Standard reduction potentials and voltages

Voltage – The tendency for e^-'s to flow in an electrochemical cell. (Note: a cell may have a high voltage even if no e^-'s are flowing. It is the tendency (or potential) for e^-'s to flow.

-Can also be defined as the **potential energy per coulomb**. (Where 1C = the charge carried by 6.25×10^{18} e^-) **1 Volt = 1 Joule/Coulomb**

Reduction potential of half-cells

-The tendency of a half-cell to be reduced. (take e^-'s)

Voltage only depends on the difference in potentials not the absolute potentials.

The **voltage** of a cell depends only on the **difference in reduction potentials** of the two half-cells.

e.g.)

	$ before buying calculator	$ after buying calculator	Difference
Mrs. A	$2000	$1980	$20
Mrs. B	$50	$30	$20

-Both people spent $20 on the calculator.

-Relative potentials of half-cells can only be determined by connecting with other half-cells and reading the voltage.

E.g.) How good a basketball team is can only be determined by playing with other teams and looking at points (scores).

p.30

Example:

A cell is constructed using Nickel metal and 1M nickel (II) nitrate along with Fe metal and 1M Iron (II) nitrate.

a) Write the equation for the half-rx at the **cathode** (with the E^o)

$Ni^{2+} + 2e^- \rightarrow Ni$ -0.26 v

b) Write the equation for the half-rx at the **anode** (with the E^o)

$Fe \rightarrow Fe^{2+} + 2e^-$ + 0.45 v

c) Write the balanced equation for the **overall reaction** (with the E^o)

$Ni^{2+} + Fe \rightarrow Fe^{2+} + Ni$ E^o = 0.19 v

d) What is the **initial cell voltage**? 0.19 V

Another example:

A cell is constructed using aluminum metal, 1M $Al(NO_3)_3$ and lead metal with 1M $Pb(NO_3)_2$. Use the method in the last example to write the overall redox reaction and find the initial cell voltage.

Cathode: $3(Pb^{2+} + 2e^- \rightarrow Pb)$ E^o = - 0.13 v

Anode: $2(Al \rightarrow Al^{3+} + 3e^-)$ E^o = 1.66 v

Overall redox reacti: $3\ Pb^{2+} + 2\ Al \rightarrow 3\ Pb + 2\ Al^{3+}$

Initial cell voltage: 1.53 volts.

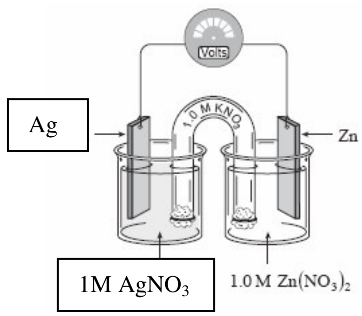
p.31

Example

A student has 3 metals: Ag, Zn and Cu; three solutions: $AgNO_3$, $Zn(NO_3)_2$, and $Cu(NO_3)_2$, all 1M. She also has a salt bridge containing $KNO_{3\,(aq)}$ wires and a voltmeter.

a) Which combination of 2 metals and 2 solutions should she choose to get the **highest** possible voltage?
Metal: Ag Solution: $AgNO_3$
Metal: Zn Solution: $Zn(NO_3)_2$

b) Draw a diagram of her cell labeling metals, solutions, salt bridge, wires, and voltmeter.



c) Write an equation for the half-rx at the **cathode**. (with E°)
$Ag^+ + e^- \rightarrow Ag$ E° = 0.80 v

d) Write an equation for the half-rx at the **anode** (with E°)
$Zn \rightarrow Zn^{2+} + 2e^-$ E° = 0.76 v

e) Write a balanced equation for the **overall redox reaction** in the cell (with E°)

$2Ag^+ + Zn \rightarrow 2Ag + Zn^{2+}$ E° = 1.56 v

f) The initial voltage of this cell is 1.56 volts.
g) In this cell, e^-'s are flowing toward which metal?_Ag In the wire
h) Positive ions are moving toward the $AgNO_3$ solution in the salt bridge
i) Nitrate ions migrate toward the $Zn(NO_3)_2$ solution in the salt bridge
j) Ag metal is gaining mass
Zn metal is losing mass } As the cell operates.

The student now wants to find the combination of metals and solutions that will give the **lowest** voltage.

k) Which metals and solution should she use?

Metal Ag Solution $AgNO_3$
Metal Cu Solution $Cu(NO_3)_2$

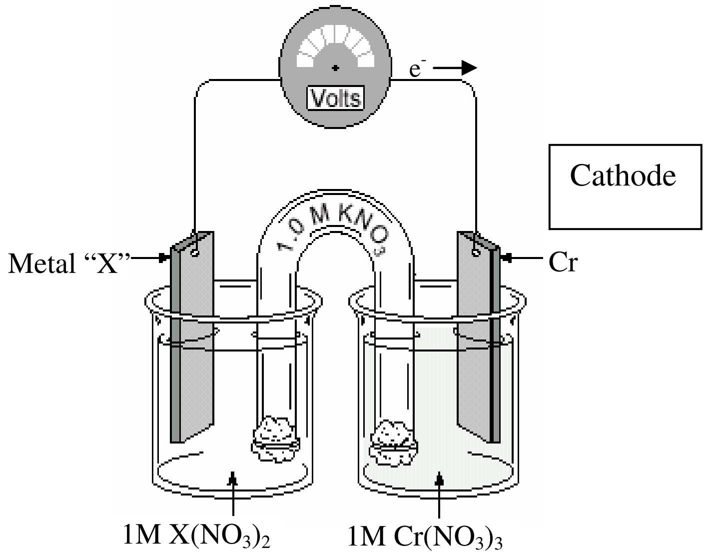
l) Find the **overall redox equation** for this cell.
$2(Ag^+ + e^- \rightarrow Ag)$ E° = 0.80 v
$Cu \rightarrow Cu^{2+} + 2e^-$ E° = -0.34 v

$2Ag^+ + Cu \rightarrow 2Ag + Cu^{2+}$ E° = 0.46 v

m) Find the **initial cell voltage** of this cell 0.46 v

p.32

Consider the following cell:



The voltage on the voltmeter is 0.45 volts.

a) Write the equation for the half-reaction taking place at the anode. Include the E°.

$X \rightarrow X^{2+} + 2e^-$ E°: = 1.19 v

b) Write the equation for the half-reaction taking place at the cathode.

$Cr^{3+} + 3e^- \rightarrow Cr$ E° = - 0.74 v

c) Write the balanced equation for the redox reaction taking place as this cell operates. Include the E°.

$3\,X + 2\,Cr^{3+} \rightarrow 3\,X^{2+} + 2\,Cr$ E° = 0.45 v

d) Determine the reduction potential of the ion X^{2+}.

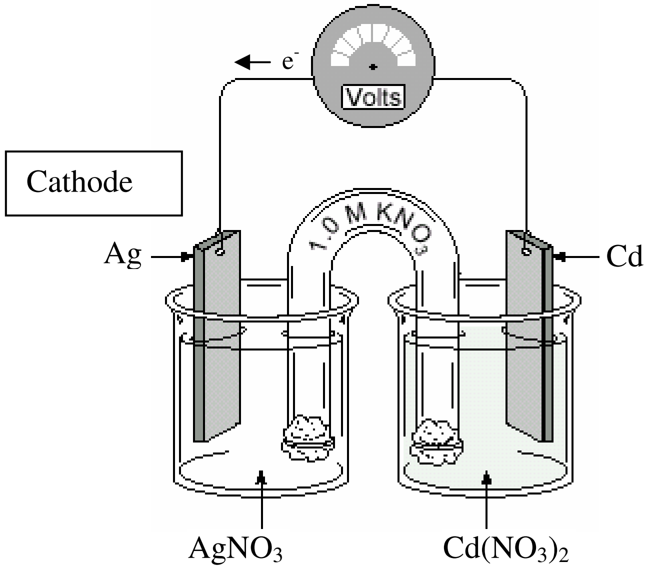
E°: - 1.19 v

e) Toward which beaker ($X(NO_3)_2$) or ($Cr(NO_3)_3$) do NO_3^- ions migrate?

$X(NO_3)_2$

f) Name the actual metal "X" Manganese

P33.
Consider the following cell:



The initial cell voltage is 1.20 Volts

a) Write the equation for the half-reaction which takes place at the cathode. Include the E°

$Ag^+ + e^- \rightarrow Ag \quad E^o = 0.80$ v

b) Write the equation for the half-reaction taking place at the anode:

$Cd \rightarrow Cd^{2+} + 2e^- \quad E^o = 0.40$ v

c) Write the balanced equation for the overall redox reaction taking place. Include the E°.

$2\,Ag^+ + Cd \rightarrow 2\,Ag + Cd^{2+} \quad E^o = 1.20$ v

d) Find the oxidation potential for Cd: $E^o = 0.40$v

e) Find the reduction potential for Cd^{2+}: $E^o = -0.40$v

f) Which electrode gains mass as the cell operates? Ag

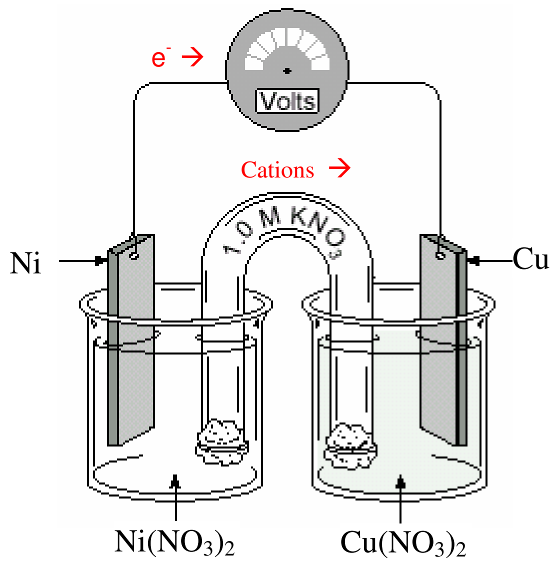
g) Toward which beaker ($AgNO_3$ or $Cd(NO_3)_2$) do K^+ ions move? $AgNO_3$

h) The silver electrode and $AgNO_3$ solution is replaced by Zn metal and $Zn(NO_3)_2$ solution.

What is the cell voltage now? 0.36v__Which metal now is the cathode? Cd

p. 34

Consider the following electrochemical cell:



a) Write the equation for the half-reaction taking place at the nickel electrode. Include the E°

$Ni \rightarrow Ni^{2+} + 2e^-$ E° = 0.26 v

b) Write the equation for the half-reaction taking place at the Cu electrode. Include the E°.

$Cu^{2+} + 2e^- \rightarrow Cu$ E° = 0.34 v

c) Write the balanced equation for the redox reaction taking place.

$Ni + Cu^{2+} \rightarrow Ni^{2+} + Cu$ E° = 0.60 v

d) What is the initial cell voltage? 0.60 v

e) Show the direction of electron flow on the diagram above with an arrow with an "e⁻" written above it. Show the direction of flow of cations in the salt bridge using an arrow with "Cations" written above it.

Voltages at non-standard conditions

Note: When cells are first constructed, they are **not at equilibrium**. All the voltages calculated by the reduction table are **initial voltages**.

-As the cells operate, the concentrations of the ions change:

eg) For the cell: $Cu(NO_3)_2/Cu//Zn/Zn(NO_3)_2$

the cathode ½ reaction is: $Cu^{2+} + 2e^- \rightarrow Cu$ $E^o = +0.34$ v

the anode ½ reaction is: $Zn \rightarrow Zn^{2+} + 2e^-$ $E^o = +0.76$ v

the overall reaction is: $Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$ $E^o = +1.10$ v

All electrochemical cells are exothermic (they give off energy) strong tendency to form products →

Initially: $Cu^{2+} + Zn \leftrightarrows Cu + Zn^{2+}$ + energy Voltage = 1.10 v

- As the cell operates $[Cu^{2+}]$ **decreases** (reactants used up) & $[Zn^{2+}]$ **increases** (products formed). Both these changes tend to push the reaction to the **left** (LeChateliers Principle)

  $Cu^{2+} + Zn \leftrightarrows Cu + Zn^{2+}$ + energy Voltage < 1.10 v

  Eventually, these tendencies will be **equal**. At this point, the cell has reached equilibrium. At **equilibrium** the cell voltage becomes **0.00 v.**

Question: A cell is constructed using $Cr/Cr(NO_3)_3$ and $Fe/Fe(NO_3)_2$ with both solutions at 1.0 M and the temperature at 25 °C.

a) Determine the **initial cell voltage**.

$3(Fe^{2+} + 2e^- \rightarrow Fe)$ $E^o = -0.45$ v

$2(Cr \rightarrow Cr^{3+} + 3e^-)$ $E^o = 0.74$ v

$3\,Fe^{2+} + 2\,Cr \rightarrow 3\,Fe + 2\,Cr^{3+}$ $E^o = 0.29$ v

Answer: 0.29 v

b) What is the **equilibrium cell voltage**?

Answer: 0.00 v

c) Write the balanced equation for the overall reaction taking place. Write the word "energy" on the right side and make the arrow double.

$3\,Fe^{2+} + 2\,Cr \leftrightarrows 3\,Fe + 2\,Cr^{3+}$ + energy

Using the equation in (c), predict what will happen to the cell voltage when the following changes are made:

i) More $Cr(NO_3)_3$ is added to the beaker to **increase** the $[Cr^{3+}]$

Cell voltage: decreases (shift left)

ii) The $[Fe^{2+}]$ ions is **increased**.

Cell voltage increases (shift right)

iii) A solution is added to precipitate the Fe^{2+} ions

The $[Fe^{2+}]$ will decrease & cell voltage will decrease (shift left) p.36 $3\ Fe^{2+} + 2\ Cr \leftrightharpoons 3\ Fe + 2\ Cr^{3+}$ + energy

iv) Cr^{3+} ions are removed by precipitation. Voltage: increases (shift right)

v) The surface area of the Fe electrode is increased (see "conclusion near middle of page 223 SW: voltage remains constant. Surface area does not affect voltage

vi) The salt bridge is removed. Voltage drops to 0

Predicting spontaneity from E° of a redox reaction

If E° for any redox (overall) reaction is > 0 (positive) the reaction is **Spontaneous**.

If E° is < 0 (negative) the reaction is **Non-spontaneous**

When a reaction is **reversed** the **sign** of E° changes

Example:

a) Find the standard potential (E°) for the following reaction:

$$2MnO_4^- + 4H_2O + 3Sn^{2+} \rightarrow 2MnO_2 + 8OH^- + 3Sn^{4+}$$

b) Is this reaction as written (forward rx) spontaneous? ______

c) Is the reverse reaction spontaneous? ______ E° = ______

Solution:

a) Find the two half-rx's which add up to give this reaction. Write them so what's on the **left** of the overall rx is on the **left** of the half-rx. (& what's on **right** is on the **right**) The half-rx for $MnO_4^- \rightarrow MnO_2$ in basic soln. is at + 0.60. To keep MnO_4^- on the left, this ½rx is written as it is on the table.

$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$ E°= +0.60

The rest of the overall rx involves Sn^{2+} changing to Sn^{4+}. The ½ reaction for that must be reversed as well as its E°. Since Sn^{2+} must stay on the left side, the half-rx on the table must be reversed as well as its E°.

$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$ E° = -0.15 V

-Now, add up the 2 ½-rx's to get the overall (Multiply by factors to balance e^-'s –and add up E°s.

$(MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-)\ 2$	E° = + 0.60 v
$(Sn^{2+} \rightarrow Sn^{4+}\ 2e^-)\ 3$	E° = -0.15 v
$2MnO_4^- + 4H_2O + 3Sn^{2+} \rightarrow 2MnO_2 + 8OH^- + 3Sn^{4+}$	E° = +0.45 V

So E° for the overall redox reaction = **+ 0.45 v**

b) Since E° is positive, this reaction is **spontaneous** as written.

The E° for the reverse reaction would be **– 0.45 v** so the **reverse reaction** is **non-spontaneous**.

p. 37

Question

a) Calculate E° for the reaction: $3N_2O_4 + 2Cr^{3+} + 6H_2O \rightarrow 6NO_3^- + 2Cr + 12H^+$

$3(N_2O_4 + 2H_2O \rightarrow 2NO_3^- + 4H^+ + 2e^-)$ E° = -0.80 v

$2(Cr^{3+} + 3e^- \rightarrow Cr)$ E° = - 0.74 v

$3N_2O_4 + 2Cr^{3+} + 6H_2O \rightarrow 6NO_3^- + 2Cr + 12H^+$ E° = - 1.54 v

b) Is the forward rx spontaneous? no The reverse rx? yes

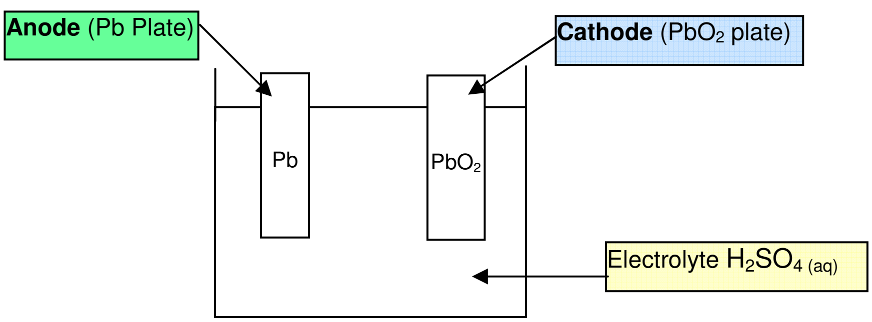
Read SW. p. 215-224

Do Ex. 35 p. 217 and Ex. 36 a-d & 37-45 on p. 224-226 of SW

Practical Applications of Electrochemical Cells

-See SW. p. 230 - 233

The Lead-Acid Storage Battery (Automobile battery)



-This cell is **rechargeable** (Reactions can be reversed)

Anode ½ reaction (**Discharging** or operating)

$\mathbf{Pb}_{(s)} + HSO_4^-{}_{(aq)} \rightarrow \mathbf{Pb}SO_{4\,(s)} + H^+{}_{(aq)} + 2e^-$

Ox # = 0 → Ox # = +2

You can tell this is **oxidation** because ox # of Pb ___creases and electrons are _____. (**LEOA**)

Cathode ½ reaction (**Discharging** or operating)

$\mathbf{Pb}O_{2\,(s)} + HSO_4^-{}_{(aq)} + 3H^+{}_{(aq)} + 2e^- \rightarrow \mathbf{Pb}SO_{4\,(s)} + 2H_2O_{(l)}$

Ox # of Pb = ______

Ox # of Pb = ______

GERC

Write the balanced equation for the **overall redox reaction** (discharging)