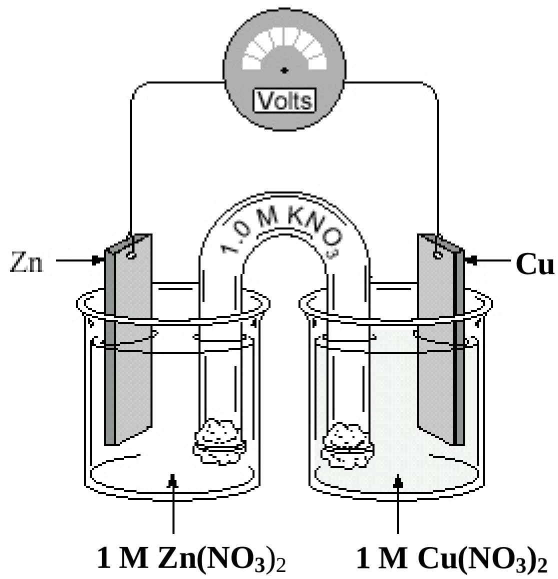
Electrochemical Cells

Demonstration (Cu/Zn Cell)



Definitions

Electrochemical cell – A device which converts chemical energy into electrical energy
Electrode – A conductor (usually a metal) at which a half-cell reaction.
(oxidation or reduction) occurs
Anode - The electrode at which **oxidation** occurs. (A & O are both vowels) LEOA
(label the anode in the diagram above)
Cathode – The electrode at which **reduction** occurs. (R & C are both consonants) GERC
(Label the anode in the diagram above)

Half-cell reactions

Anode – Oxidation half-rx

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

Metal atoms are changed to **+ ions**. Metal dissolves and anode loses mass as the cell operates.

Cathode – Reduction half-rx

$Cu^{2+} + 2e^- \rightarrow Cu$

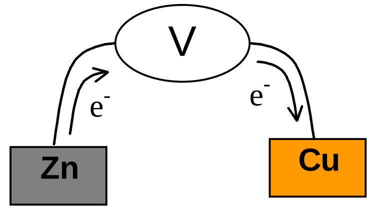
+ ions are changed to **metal atoms**. New metal is formed so the cathode gains mass.

Flow of electrons

-Since the anode loses e^-'s, (LEOA) and the cathode gains e^-'s (GERC)

-**Electrons** flow from the **anode toward the cathode** in the **wire** (conducting solid)

Anode – $Zn \rightarrow Zn^{2+} + 2e^-$

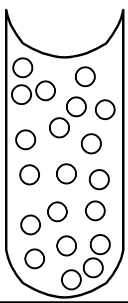


Cathode – $Cu^{2+} + 2e^- \rightarrow Cu$

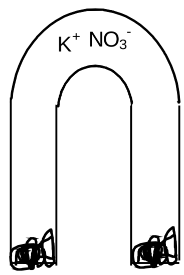
e^-'s flow from A → C in the wire

Flow of Ions in the salt bridge

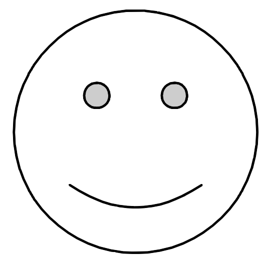
-**Salt bridge** contains any **electrolyte** (conducting solution)



Porous barrier which ions can pass through

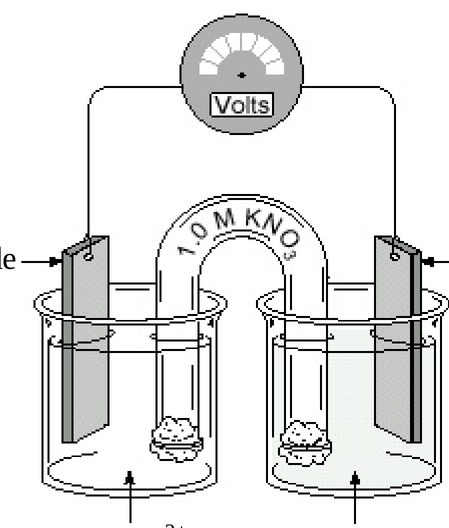


Most common – U-tube containing a salt such as KNO_3 or $NaNO_3$



Common things which contain electrolytes, e.g.) potatoes, apples, oranges, lemons, frogs, people

Anode



Cathode

$Zn \rightarrow Zn^{2+} + 2e^-$

If there was no SB + ions (cations) would build up at the anode

$Cu^{2+} + 2e^- \rightarrow Cu$

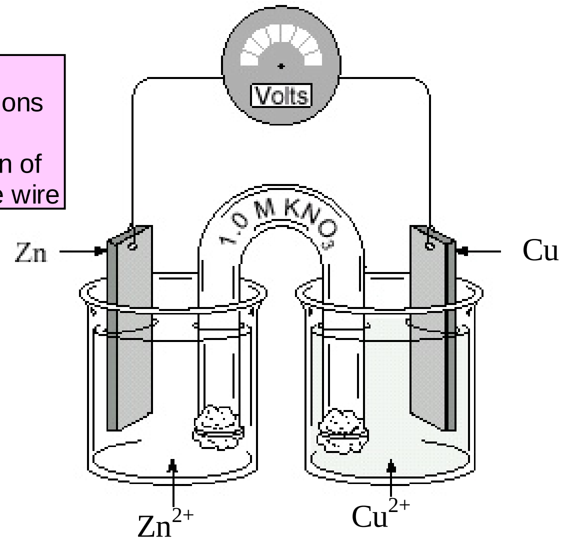
If there was no SB + ions are used up, so there would be an excess of – ions (anions) at the cathode

1 M Zn^{2+}

1 M Cu^{2+}

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+}				
Ni/Ni^{2+}	Al/Al^{3+}				
Au/Au^{3+}	Ag/Ag^+				
Mg/Mg^{2+}	H_2/H^+				
Co/Co^{2+}	Sn/Sn^{2+}				

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

1) Electrochemical cells convert __________ energy into ___________ energy.
2) ___________ is the electrode where oxidation occurs.
3) Electrons are ________ at the anode.
4) _________ is the electrode where reduction occurs.
5) In the half-rx at the cathode, e^-'s are on the ______ side of the equation.
6) Electrons flow from the ______ toward the ______ in the ___________.
7) Cations ((+) ions) flow from the ____ beaker toward the ______ beaker through the _______.
8) Anions ((-) ions flow from the _____ beaker through the __________.
9) The higher half-rx on the table is the one for the ________ and is not reversed.
10) The lower half-rx on the table is the one for the ________ and **is** reversed.
11) Electrons do not travel through the ______ _______, only through the _______.
12) Ions (cations & anions) do not travel through the wire but only through the _____________.
13) The salt bridge can contain any ______________.
14) The anode will ________(gains/loses) mass as it is __________(oxidized/reduced).
15) The cathode will ________ mass as it is _______(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

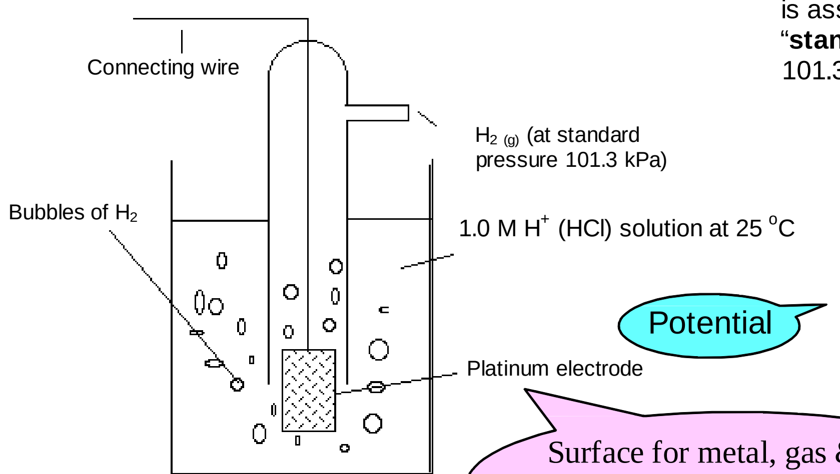
-Both people spent \$20 on the calculator.

-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).

- A “**standard**” half-cell was arbitrarily chosen to compare other half-cells with.
- It was assigned a “**reduction potential**” of **0.000 v**
-
- It is: $\mathbf{2H^+_{(aq)} + 2e^- \rightleftarrows H_{2(g)} \quad E^o = 0.000\ v}$

- Since potential depends on gas pressure, temp. and $[H^+]$ this half cell is assigned a value of 0.000 v at “**standard state**” which is 25^{o}C, 101.3 kPa and $[H^+]$ =1.0 M



Means standard state

Potential

$E^o = 0.000v$

Surface for metal, gas & solution to contact

-The standard half-cell acts as an anode (LEOA) or cathode (GERC) depending on what it is connected to: For example, when the standard half-cell is connected to the Ag/Ag^+ half-cell.

For this cell, the voltage is 0.80 volts with the electrons flowing toward the Ag.

Found by experiment

So the cathode is the Ag/Ag^+ half-cell
The anode is the H_2/H^+ half-cell

Draw the Diagram:

(GERC)	**Cathode** half-rx	$Ag^+ + e^- \rightarrow Ag \quad E^o = ?$
(LEOA)	**Anode** half-rx	$H_2 \rightarrow 2H^+ + 2e^- \quad E^o = 0.00$ volts
		Voltage of cell = 0.80 volts

-From this we can see that the E^o for the Ag/Ag^+ half-cell must be 0.80 V **different** than that of the standard half-cell. Since the Ag/Ag^+ is the one which is reduced, we say it has a higher reduction potential than the standard. Therefore the reduction potential of the of Ag/Ag^+ half-cell is +0.80 V.

Another example:

The standard (H_2/H^+) half-cell is connected to the Ni/Ni^{2+} half-cell.

-Electrons are found to flow away from the nickel toward the H_2/H^+ half-cell and the voltage (at 25 ^oC, 101.3 Kpa & 1.0 M solutions) is found to be 0.26 volts.

Give the: Cathode Half-rx: ___________________

Anode Half-rx: _____________________

Determine the E^o for the Ni/Ni^{2+} half cell: _________________

Now look at **Standard Reduction Table**.

Notice: -all half-rx's are written as **reductions**

-The $\mathbf{E^o}$ is the **standard reduction potential** for the species on the **left side**.

Eg) Of the following combinations, find the one which gives the highest voltage? ______

a) Ag^+/Ag with Cu^{2+}/Cu
b) Pb^{2+}/Pb with Ni^+/Ni
c) Ag^+/Ag with Pb^+/Pb
d) Au^{3+}/Au with Ni^{2+}/Ni

-Which combo gives the lowest voltage? _______

<u>Using the reduction table to find the initial voltage of ECC's at standard state</u>

1) Find the two metals on the reduction table. **Higher** one is the **cathode**. (**HIC**)

2) Write the cathode half-rx as is on the table (cathode - reduction) Include the reduction potential (E^o) beside it.

3) **Reverse** the **anode** reaction (**AIR**) (anode → oxidation) **Reverse the sign** on the E^o (If (+) → (-) | If (-) → (+))

4) **Multiply** half-rx's by factors that will make **e^-'s cancel**. **DON'T** multiply the E^o's by these factors.

5) **Add up half-rx's** to get **overall redox** reaction.

6) **Add up $\mathbf{E^o}$'s** (as you have written them) to get the **initial voltage** of the cell.

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)

______________________________ ______________________

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

______________________________ ______________________

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

______________________________ ______________________

d) What is the **initial cell voltage**? __________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.

Overall redox reaction ____

Initial cell voltage: ______________________________volts.

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: _________ Solution: ____________
Metal: _________ Solution: ____________

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^o)

_____________________________________ ________________________

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

____ _

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

____ _

f) The initial voltage of this cell is _________volts.
g) In this cell, e^-'s are flowing toward which metal?__________ In the ________
h) Positive ions are moving toward the _______ solution in the ______ ______.
i) Nitrate ions migrate toward the ____________ solution in the ______ _______.
j) __________ metal is gaining mass
__________ 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?

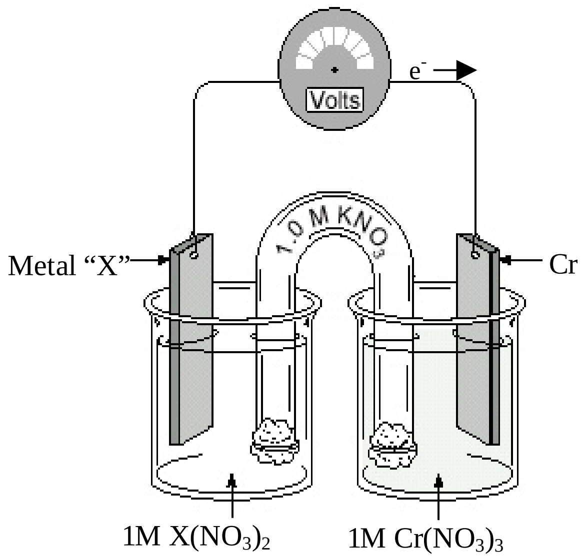
Metal ___________ Solution _____________
Metal ___________ Solution _____________

l) Find the **overall redox equation** for this cell.

_________________________________ _

m) Find the **initial cell voltage** of this cell __________volts.

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^o.

____ E^o: _________v

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

____ E^o: _________v

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

____E^o: __________

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

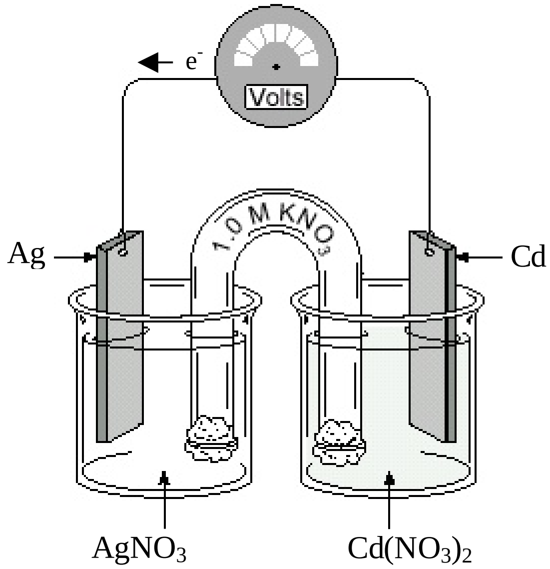
E^o: __________v

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

_______________________ _

f) Name the actual metal "X" ________________________________

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^o

____ E^o= ____ ___v

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

____ E^o= ____ ___v

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

____ E^o= ____ ___v

d) Find the oxidation potential for Cd: E^o= ____ ___v

e) Find the reduction potential for Cd^{2+}: E^o= ____ ___v

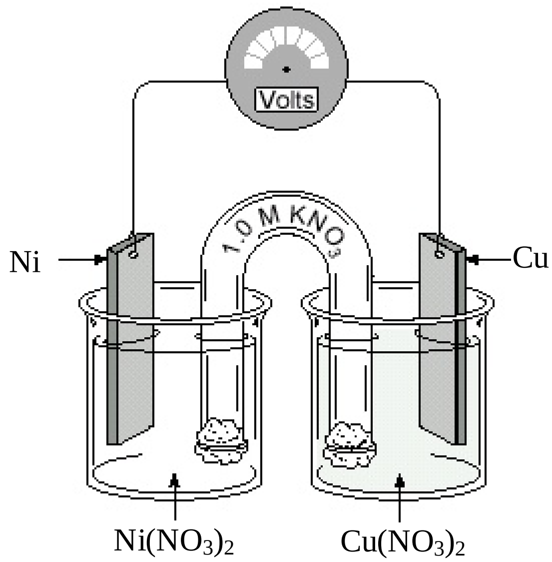
f) Which electrode gains mass as the cell operates? _______

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

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? __________Which metal now is the cathode? _________

Consider the following electrochemical cell:



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

____ E^o= ____ ___v

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

____ E^o= ____ ___v

c) Write the balanced equation for the redox reaction taking place.
____ E^o= ____ ___v

d) What is the initial cell voltage? _______________ _

e) Show the direction of electron flow on the diagram above with an arrow with an "e$^-$" written above it.

f) 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 $\longrightarrow$

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 ^oC.

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

Answer: _____________v

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

Answer: _____________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.

____

d) 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: ______________creases

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

Cell voltage ______________creases

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

The $[Fe^{2+}]$ will _____crease & cell voltage will ______crease

iv) Cr^{3+} ions are removed by precipitation. Voltage: ______creases

v) The surface area of the Fe electrode is increased (see "conclusion near middle of page 223 SW) Voltage: ______________________________________

vi) The salt bridge is removed. Voltage______________________________

Predicting spontaneity from E^o of a redox reaction

If E^o for any redox (overall) reaction is > 0 (positive) the reaction is **Spontaneous**.
If E^o is < 0 (negative) the reaction is **Non-spontaneous**
When a reaction is **reversed** the **sign** of E^o changes

Example:

a) Find the standard potential (E^o) 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^o = _____

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.

$$\boxed{MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^- \quad E^o = +0.60}$$

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^o. Since Sn^{2+} must stay on the left side, the half-rx on the table must be reversed as well as its E^o.

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

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

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

$$2MnO_4^- + 4H_2O + 3Sn^{2+} \rightarrow 2MnO_2 + 8OH^- + 3Sn^{4+} \qquad E^o = +0.45\ V$$

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

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

c) The E^o for the reverse reaction would be **– 0.45 v** so the **reverse reaction** is **non-spontaneous**.

Question

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

b) Is the forward rx spontaneous? _________ The reverse rx? ___________

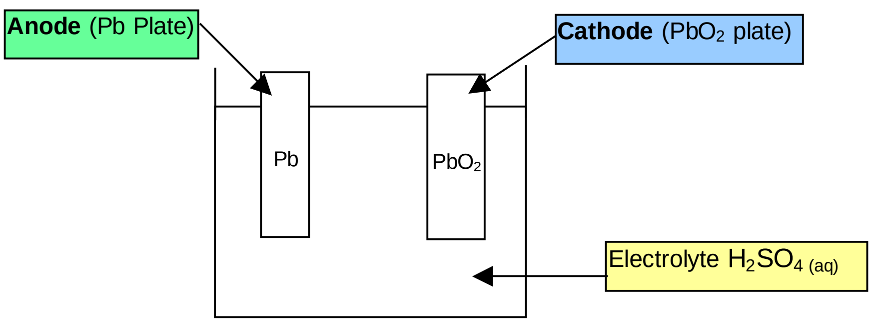
Read SW. p. 215-224

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)

The **overall redox reaction**: (discharging or operating)

$$\underset{\text{Anode}}{Pb_{(s)}} + \underset{\text{Cathode}}{PbO_{2(s)}} + \underbrace{2H^+_{(aq)} + 2HSO_4^-{}_{(aq)}}_{\text{From \_\_\_\_\_ in the electrolyte}} \rightarrow \underbrace{2PbSO_{4\,(s)}}_{\text{White solid forms on plates as battery discharges}} + 2H_2O_{(l)} + \text{electrical energy}$$

Notes: As cell discharges the anode (Pb) and cathode (PbO_2) disintegrate and the white solid ($PbSO_4$) forms on both plates.
Originally, $[H^+]$ & $[HSO_4^-]$ is high. i.e.) $[H_2SO_4]$ is high. H_2SO_4 is denser than H_2O therefore the density (specific gravity) of the electrolyte is **high** to start with. As the cell discharges, H_2SO_4 (H^+ & HSO_4^-) is used up and H_2O is formed. Therefore, electrolyte gets less dense as the battery discharges. Condition of the battery can be determined using a "hydrometer" or battery tester. (Higher the float, the **denser** the electrolyte)

Adding electrical energy to this reaction will **reverse** it (**recharging**)

Charging Reaction:

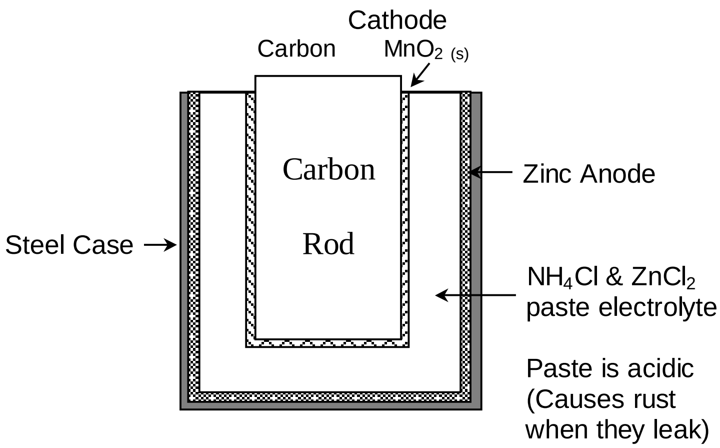
$$\text{Electrical energy} + 2PbSO_{4(s)} + H_2O_{(l)} \rightarrow Pb_{(s)} + PbO_{2(s)} + 2H^+_{(aq)} + 2HSO_4^-{}_{(aq)}$$

Supplied by **alternator** or generator

The E^o for the **discharging** rx, is +2.04 volts. A typical car battery has _____ of these in

(Series/parallel) ____________ to give a total voltage =__________V.

The Zinc-Carbon battery (LeClanche-Cell, Common Dry cell, or regular carbon battery. Often called “Heavy Duty”)



Cathode ½ reaction:

(GERC) $2MnO_{2\ (s)} + 2NH_4^+{}_{(aq)} + 2e^- \rightarrow 2MnO(OH)_{(s)} + 2NH_{3\ (aq)}$

Or simplified: $Mn^{4+} + e^- \rightarrow Mn^{3+}$

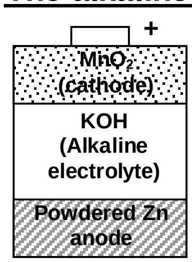
Anode ½ reaction:

(LEOA) $Zn_{(s)} + 4NH_{3\ (aq)} \rightarrow Zn(NH_3)_4^{2+} + 2e^-$

Or simplified: $Zn_{(s)} \rightarrow Zn^{2+} + 2e^-$

-**Not rechargeable**
-Doesn’t last too long – especially with large currents
-Fairly cheap

The alkaline dry cell

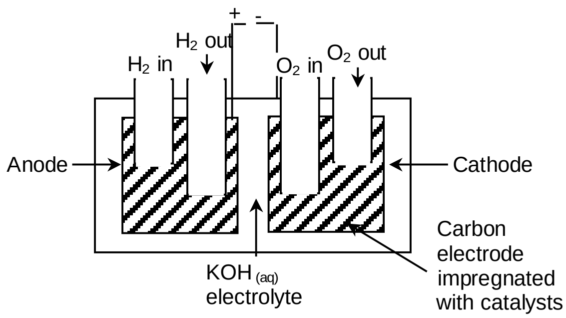


-Operates under **basic** conditions
- Delivers much **greater current**
- Voltage remains constant
- More **expensive**
- **Lasts longer**

Cathode ½ reaction (GERC) $2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^-$
Anode ½ reaction (LEOA) $\mathbf{Zn}_{(s)} + 2OH^- \rightarrow \mathbf{Zn}O + H_2O + H_2O + 2e^-$
Ox # = ___ Ox # = ___

Fuel cells

-Fuel cells are continuously fed fuel and they convert the **chemical** energy in fuel to **electrical** energy
-more **efficient** (70-80%) than burning gas or diesel to run generators (30-40%)
-no pollution – only produces **water**
can use $\mathbf{H_2}$ and $\mathbf{O_2}$ or **hydrogen rich fuels** (e.g. methane CH_4) and O_2.
-used in space capsules –H_2 & O_2 in tanks H_2O produced used for drinking



Anode ½ reaction:

$$2H_{2(g)} + 4OH^-_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^-$$

Cathode ½ reaction:

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

Overall reaction:

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

Applied electrochemistry—The Breathalyzer Test

After drinking, breath contains ethanol C_2H_5OH.
Acidified dichromate (at E^o = 1.23 on the reduction table) will **oxidize** alcohol. The unbalanced formula equation is:

$$\mathbf{C}_2H_5OH + K_2\mathbf{Cr}_2O_7 + H_2SO_4 \rightarrow \mathbf{C}H_3\mathbf{C}OOH + \mathbf{Cr}_2(SO_4)_3 + K_2SO_4 + H_2O$$

Ox # of C= ___ Ox # of Cr= ___ Ox # of C= ___ Ox # of Cr= ___

$K_2Cr_2O_7$ is yellow (orange at higher concentrations)

$Cr_2(SO_4)_3$ is green

-Exhaled air is mixed with standardized acidified dichromate
-Put in a spectrophotometer set at the wavelength of green light
-More alcohol produces more green $Cr_2(SO_4)_3$ (green)
-Machine is calibrated with known concentration samples of alcohol to ensure accuracy

Question: In the reaction above name

a) The oxidizing agent _________
b) The reducing agent _________
c) The product of oxidation ________
d) The product of reduction ________