



AP* Chemistry ELECTROCHEMISTRY

Terms to Know:

Electrochemistry—the study of the interchange of chemical and electrical energy

OIL RIG - oxidation is loss, reduction is gain (of electrons)

Oxidation - the loss of electrons, increase in charge

Reduction - the gain of electrons, reduction of charge

Oxidation number - the assigned charge on an atom

Leo Says Ger - Lose electrons Oxidize , Gain electrons Reduction

ELECTROCHEMISTRY INVOLVES TWO MAIN TYPES OF PROCESSES:

- Galvanic (voltaic) cells** - which are thermodynamically favored chemical reactions (**it's a battery**)
- Electrolytic cells** - which are not thermodynamically favored and require external *electricity*~ source
- BOTH of these fit into the category entitled **Electrochemical** cells

GALVANIC CELLS

Parts of the voltaic or galvanic cell:

- o **Anode**—the electrode where oxidation occurs. After a period of time, the anode become smaller as it falls into solution, o

Cathode— the anode where reduction occurs. After a period of time it gets larger, due to ions from solution plating onto it.

inert electrodes—used when a gas is involved OR ion to ion involved such as Fe^{3+} being reduced to Fe^{2+} rather than Fe^0 . Made of Pt or graphite, o

Salt bridge — a device used to maintain electrical neutrality in a galvanic cell. This may be filled with agar which contains a neutral salt or it may be replaced with a porous cup. o

Electron flow — always from anode to cathode, (through the wire)

Standard cell notation (line notation) – know this **order** anode/solution// cathode solution/ cathode
Ex. $Zn/Zn^{2+} // Cu^{2+}/Cu$

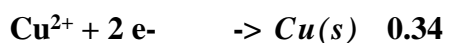
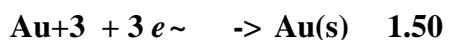
Voltmeter - measures the cell potential (emf) Usually is measured in volts

salt bridge—it's job is to balance the charge using an electrolyte [usually in a U-shaped tube filled with agar that has the salt dissolved into it before it gels]. It connects the two compartments, ions flow from it, AND it keeps each "cell" neutral. Use KNO_3 as the salt when constructing your own diagram so that no precipitation occurs! **porous disk or gel**—also allows both cells to remain neutral by allowing ions to flow.

cell potential— E_{cell} , Emf , or s_{cell} —it is a measure of the electromotive force or the "pull" of the electrons as they travel from the anode to the cathode [more on that later!]

- **volt** (V)—the unit of electrical potential; equal to 1 joule of work per coulomb of charge transferred
- **voltmeter**—measures electrical potential; some energy is lost as heat [resistance] which keeps the voltmeter reading a tad lower than the actual or calculated voltage. Digital voltmeters have less resistance. If you want to get picky and eliminate the error introduced by resistance, you attach a variable-external-power source called a **potentiometer**. Adjust it so that zero current flows—the accurate voltage is then equal in magnitude but opposite in sign to the reading on the potentiometer.

STANDARD REDUCTION POTENTIALS



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Each half-reaction has a cell potential

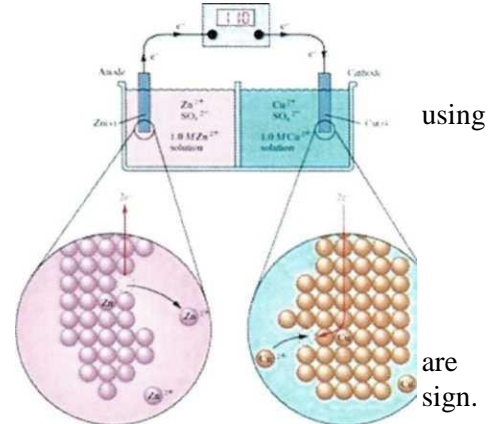
Each potential is measured against a standard which is the standard hydrogen electrode [consists of a piece of inert Platinum that is bathed by hydrogen gas at 1 atm].

The hydrogen electrode is assigned a value of ZERO volts. All other reduction potentials are based on hydrogen

standard conditions—1 atm for gases, 1.0M for solutions and 25°C for all (298 K) **naught,** e^- —we use the naught to symbolize standard conditions

The diagram to the right illustrates what really happens when a Galvanic cell is constructed from zinc sulfate and copper(II) sulfate the respective metals as electrodes.

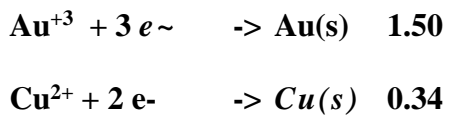
- Notice that 1.0M solutions of each salt are used
- Notice an overall voltage of 1.10 V for the process



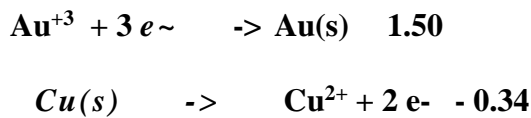
"*" elements that have the *most positive reduction potentials are easily reduced* *■ elements that have the least positive reduction potentials easily oxidized and the reaction must be flipped around including the **The overall reaction must have a positive E cell value to be a battery.**

Can also be used as an activity series. Metals having less positive reduction potentials are more active and will replace metals with more positive potentials.

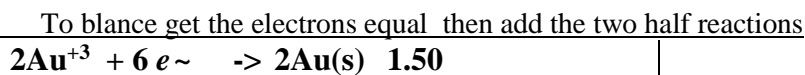
HOW CAN WE DETERMINE WHICH SUBSTANCE IS BEING REDUCED AND WHICH IS BEING OXIDIZED??



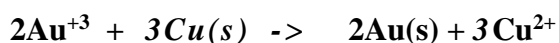
The MORE POSITIVE reduction potential gets to indeed be reduced IF you are trying to set up a cell that can act as a battery so flip the less positive reduction half reaction to make it oxidation (look below)



If you add the Ecell it would be a +1.16



Balanced equation



•
CELL POTENTIAL, ELECTRICAL WORK & FREE ENERGY

- > **faraday** (symbol F) the charge on one Mole of electrons = 96,485 coulombs
- > $n = \# \text{ moles of electrons} \times F$
- > $E = E_{\text{cell}}$

For a process carried out at constant temperature and pressure, w_{max} is equal to ΔG , therefore....

$$\Delta G^\circ = -nFE^\circ$$

G = Gibb's free energy - remember is G is negative it's a thermodynamically favored reaction

(good for a battery)

n = number of moles of electrons

F = Faraday constant $9.6485309 \times 10^4 \text{ J/V} \cdot \text{mol}$

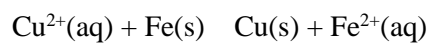
So it follows that:

$-E^\circ$ implies nonspontaneous.

$+E^\circ$ implies spontaneous (would be a good battery!)

Exercise 3

Using the table of standard reduction potentials, calculate ΔG° for the reaction



Is this reaction spontaneous?

Calculating Standard Cell Potential Symbolized by E°_{cell} OR Emf [I'll mix and match!]

1. Decide which element is oxidized or reduced using the table of reduction potentials. Remember:
2. **THE MORE POSITIVE REDUCTION POTENTIAL GETS TO BE REDUCED.**
3. Write both equations AS IS from the chart with their voltages.
4. Reverse the equation that will be oxidized **and change the sign of the voltage** [this is now $E^\circ_{\text{oxidation}}$]
4. Balance the two half reactions ****do not multiply voltage values****
5. Add the two half reactions and the voltages together.
6. $-E^\circ_{\text{cell}} = E^\circ_{\text{oxidation}} + E^\circ_{\text{reduction}}$ $^\circ$ means standard conditions: 1 atm, 1M, 25°C

Neumonic Devices that come in handy when constructing spontaneous cell—one that can act as a battery:

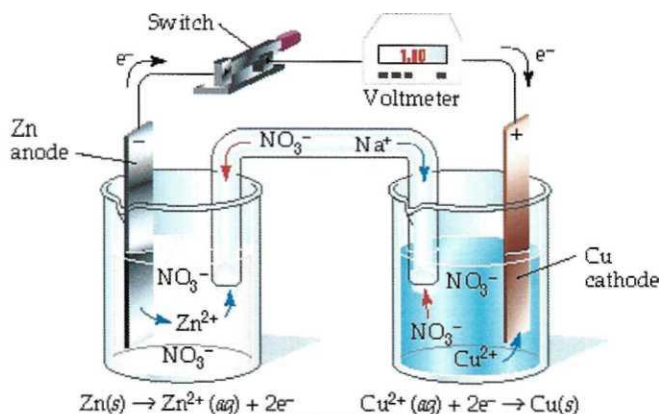
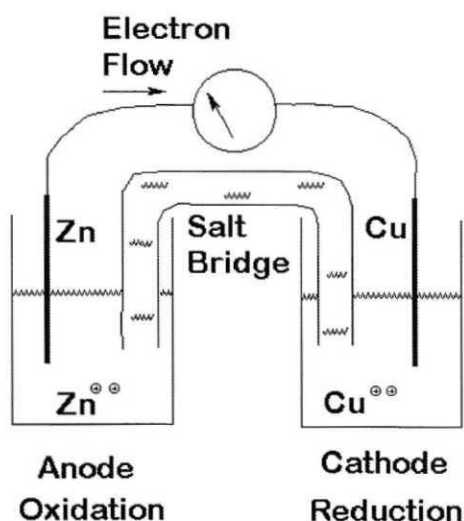
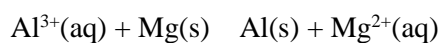
AN **OX** - oxidation occurs at the anode (may show mass decrease) **RED CAT** - reduction occurs at the cathode (may show mass increase) **FAT CAT** - The electrons in a voltaic or galvanic cell **ALWAYS** flow From the Anode To the **CATHode**

Ca+hode - the cathode is + in galvanic (voltaic) cells

Salt Bridge - bridge between cells whose purpose is **to provide ions to balance the charge.**

Usually made of a salt filled agar (KNO_3) or a porous cup.

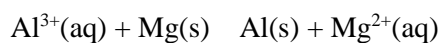
EPA - in an electrolytic cell, there is a positive anode.



ANIONS from the salt move to the anode while CATIONS from the salt move to the cathode!

Exercise 1

a. Consider a galvanic cell based on the reaction



Give the balanced cell reaction and calculate E° for the cell.

LINE NOTATION

Standard cell notation (line notation) - "Ion sandwich" in alphabetical order

Anode metal/anode ion//cathode ion//Cathode metal For Reaction: $M + N^+ \rightarrow N + M^+$

Anode || Cathode (alphabetical order!)
M(electrode)|M⁺ (solution)|| N⁺ (solution)|N(electrode)

| - indicates phase boundary || -
indicates salt bridge

EX: $Zn / Zn^{2+} (1.0 M) || Cu^{2+} (1.0 M) | Cu$

Sample Problem: Calculate the cell voltage for the following reaction. Draw a diagram of the galvanic cell for the reaction and label completely.

