ELECTROCHEMISTRY

Electron Transfer Reactions

- Electron transfer reactions are oxidation-reduction or redox reactions.
- Results in the generation of an electric current (electricity) or be caused by imposing an electric current.
- Therefore, this field of chemistry is often called ELECTROCHEMISTRY.

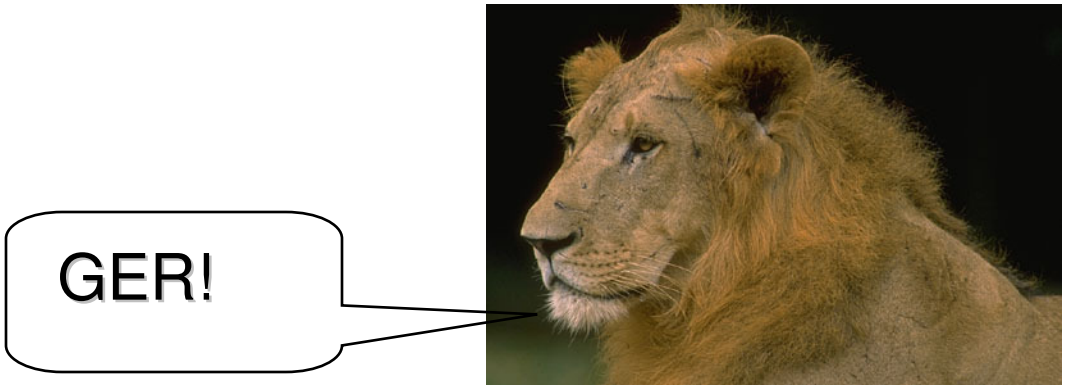
Terminology for Redox Reactions

- **OXIDATION**—loss of electron(s) by a species; increase in oxidation number; increase in oxygen.
- **REDUCTION**—gain of electron(s); decrease in oxidation number; decrease in oxygen; increase in hydrogen.
- **OXIDIZING AGENT**—electron acceptor; species is reduced.
- **REDUCING AGENT**—electron donor; species is oxidized.

You can't have one… without the other!

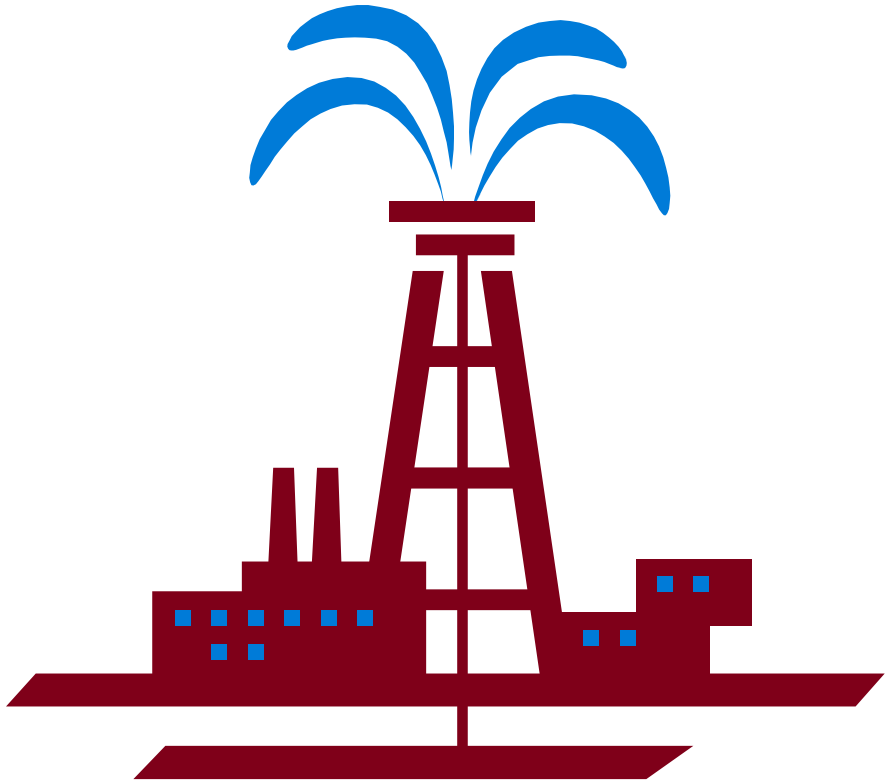
- **Reduction (gaining electrons) can't happen without an oxidation to provide the electrons.**
- **You can't have 2 oxidations or 2 reductions in the same equation. Reduction has to occur at the cost of oxidation**

LEO the lion says GER!



Another way to remember

- **OIL RIG**



OXIDATION-REDUCTION REACTIONS

Direct Redox Reaction

Oxidizing and reducing agents in direct contact.

$Cu(s) + 2\ Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2\ Ag(s)$

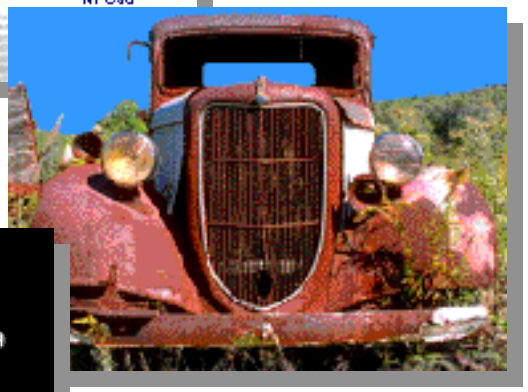
OXIDATION-REDUCTION REACTIONS

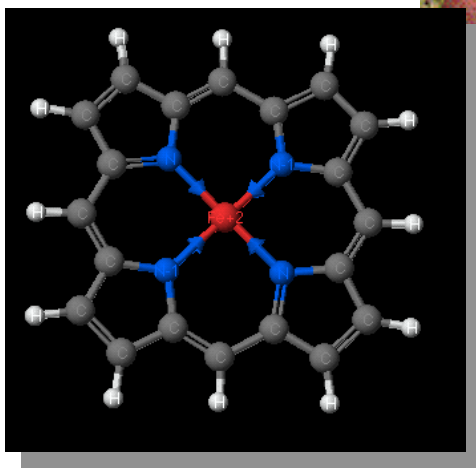
Indirect Redox Reaction

A battery functions by transferring electrons through an external wire from the reducing agent to the oxidizing agent.

Why Study Electrochemistry?

- Batteries
- Corrosion
- Industrial production of chemicals such as Cl_2, NaOH, F_2 and Al
- Biological redox reactions





The heme group

Electrochemical Cells

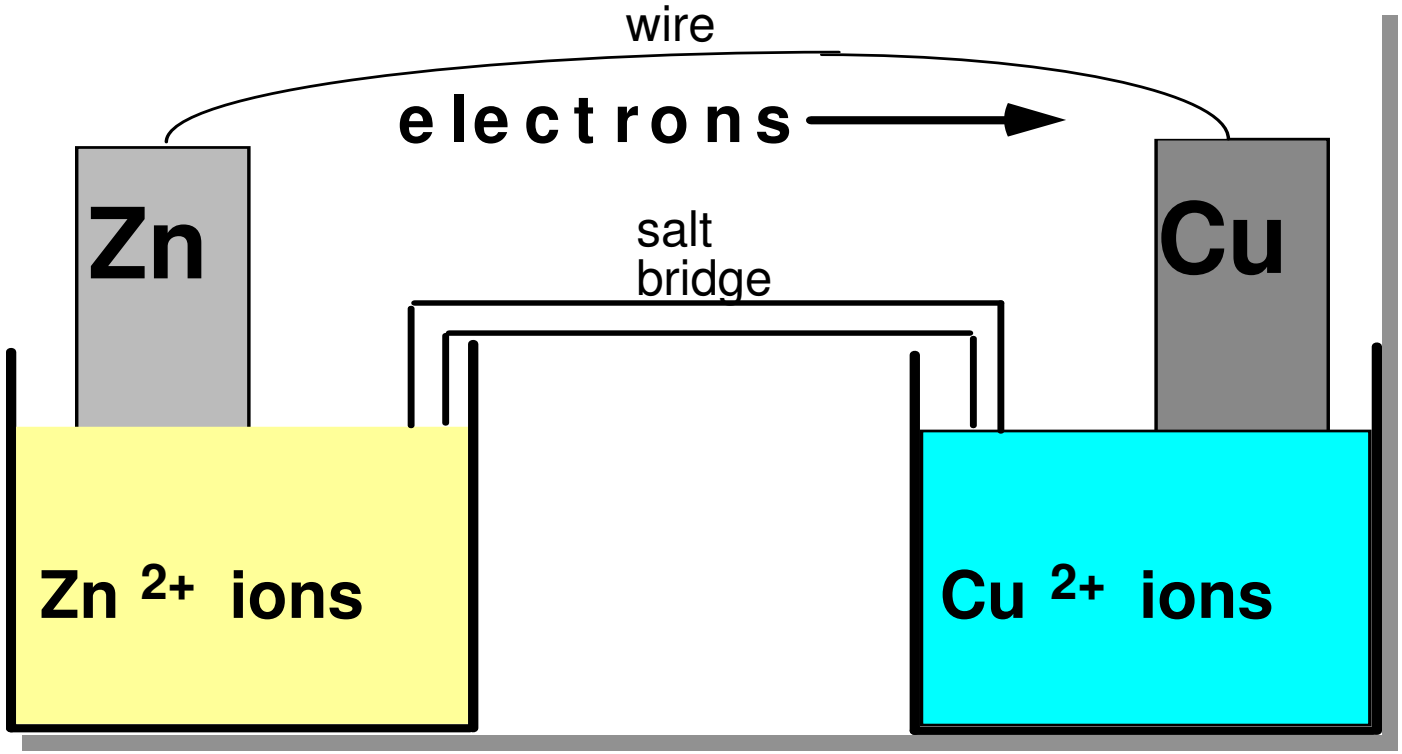
- An apparatus that allows a redox reaction to occur by transferring electrons through an external connector.
- voltaic or galvanic cell: it is a product favored reaction, where chemical reaction occurs spontaneously and produce electric current
- Examples: Le Clanche cell Zn/MnO_2 used in watches and Hydrogen fuel cell H_2/O_2 used in space crafts and cars.
- Electrolytic cell: it is a reactant favored reaction, where chemical reaction occurs non- spontaneously by using electric current
- Examples: The cell used in production of chlorine

Batteries are voltaic cells

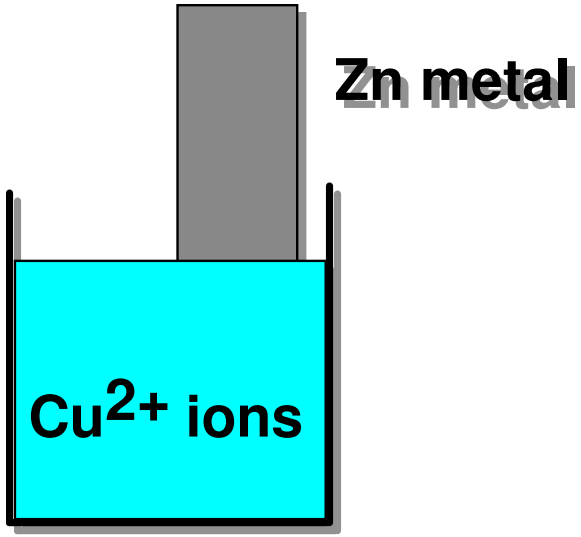
Lead storage battery

- It is Pb-PbO_2-H_2SO_4 cell.
- It is working as galvanic cell when it is being used as a battery in your car (Discharging and produce electricity).
- It is working as an electrolytic cell when it is being charged.

Basic Concepts of Electrochemical Cells



CHEMICAL CHANGE ---> ELECTRIC CURRENT



With time, Cu plates out onto Zn metal strip, and Zn strip "disappears."

- **Zn is oxidized** and is the reducing agent

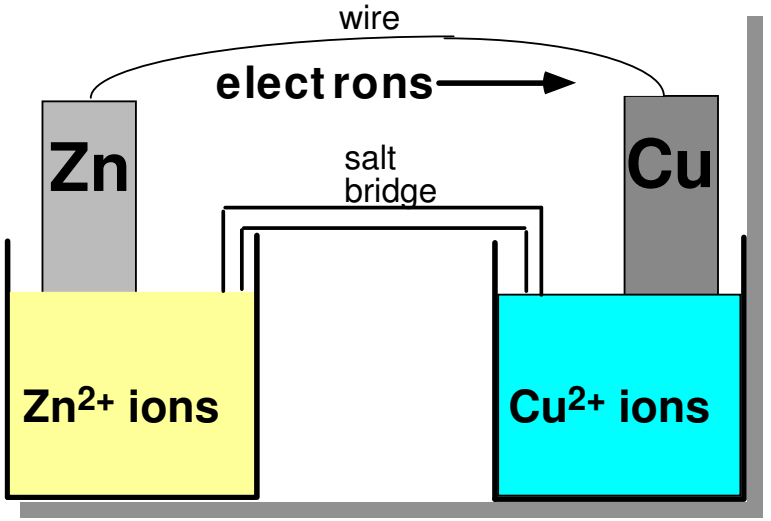
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

- **Cu^{2+} is reduced** and is the oxidizing agent

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

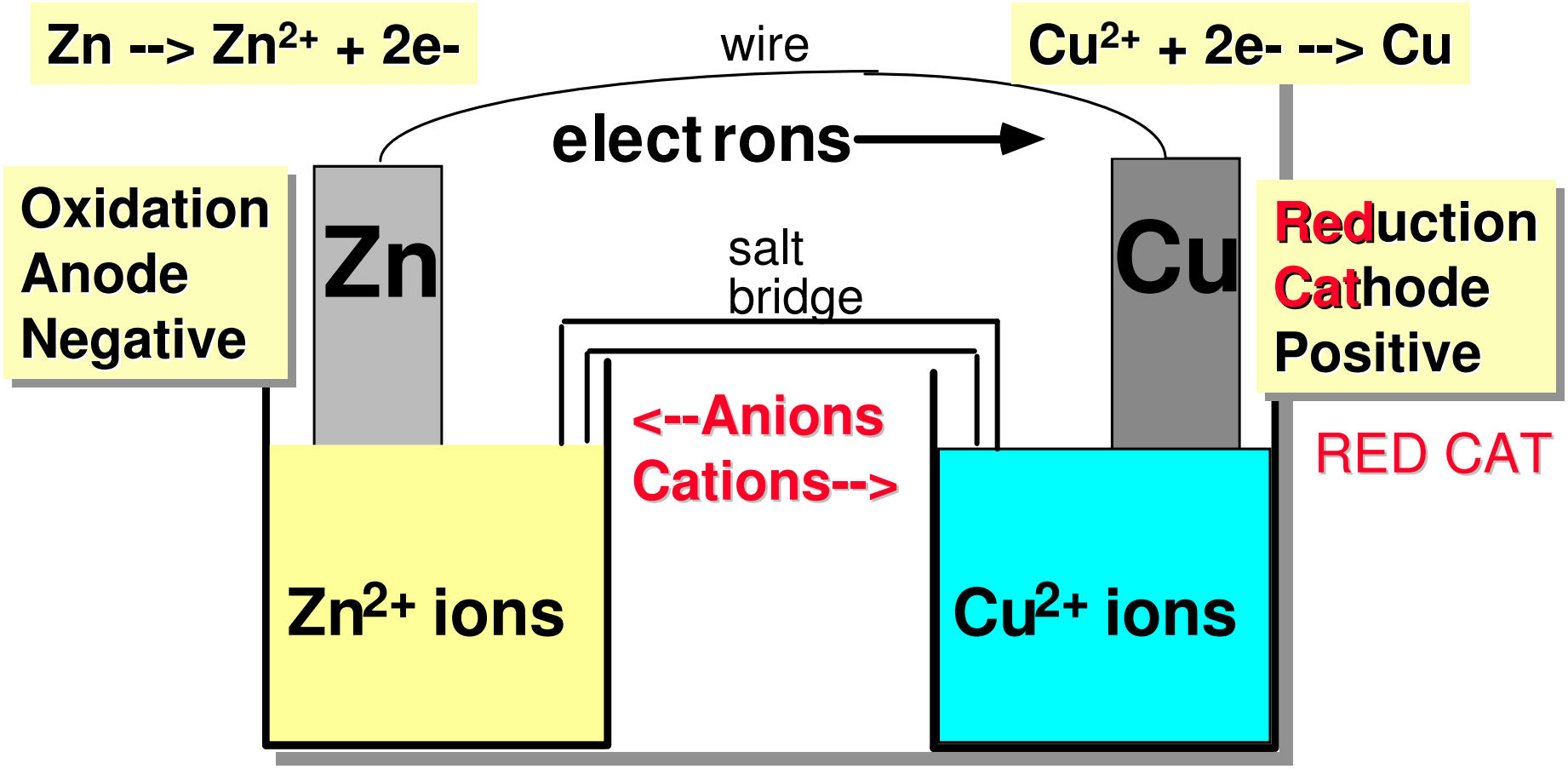
CHEMICAL CHANGE ---> ELECTRIC CURRENT

- To obtain a useful current, we separate the oxidizing and reducing agents so that electron transfer occurs thru an external wire.



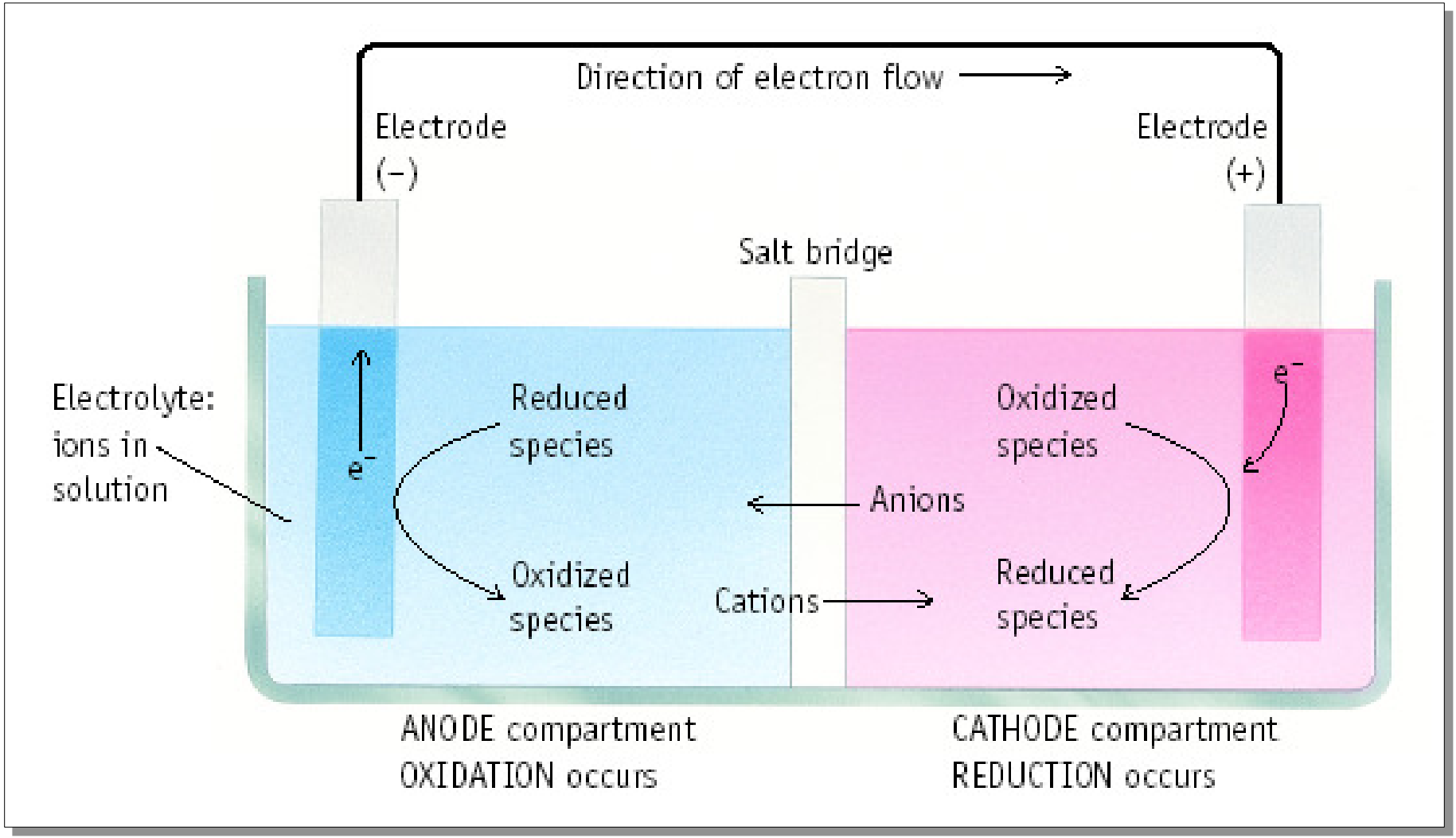
This is accomplished in a **GALVANIC** or **VOLTAIC** cell. http://www.mhhe.com/physsci/chemistry/essentialchemistry/flash/galvan5.swf

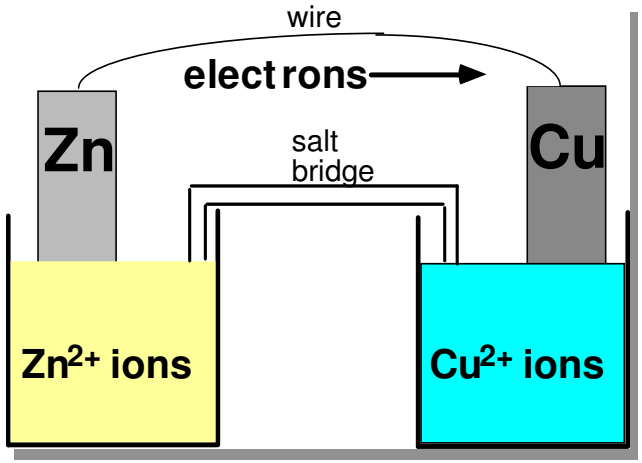
A group of such cells is called a **battery**.



- Electrons travel thru external wire.
- **Salt bridge** allows anions and cations to move between electrode compartments.

Terms Used for Voltaic Cells





CELL POTENTIAL, E

- For Zn/Cu cell, potential is +1.10 V at 25 ˚C and when $[Zn^{2+}]$ and $[Cu^{2+}]$ = 1.0 M.
- This is the STANDARD CELL POTENTIAL, E^{o}
- —a quantitative measure of the tendency of reactants to proceed to products when all are in their standard states at 25 ˚C.

Calculating Cell Voltage

- **Balanced half-reactions can be added together to get overall, balanced equation.**

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$
$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$
$$\text{----------}$$
$$Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s)$$

If we know E^o for each half-reaction, we could get E^o for net reaction.

TABLE OF STANDARD REDUCTION POTENTIALS

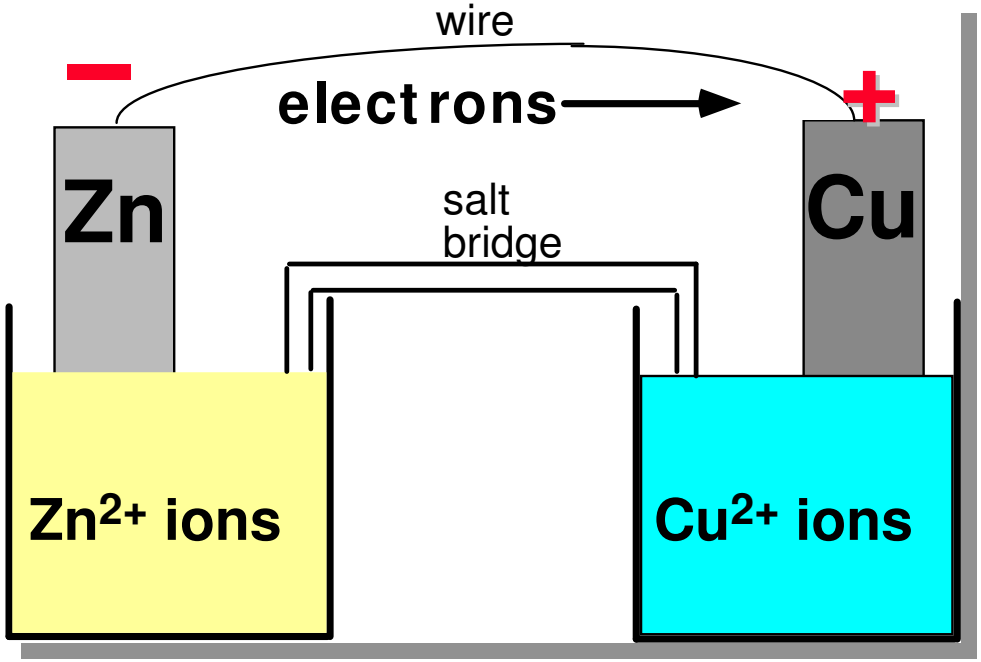
oxidizing ability of ion

	E^o (V)
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$2\,H^+ + 2e^- \rightarrow H_2$	0.00
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76

reducing ability of element

To determine an oxidation from a reduction table, just take the opposite sign of the reduction!

Zn/Cu Electrochemical Cell



Anode, negative, source of electrons

Cathode, positive, sink for electrons

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $E^o = +0.76$ V

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E^o = +0.34$ V

$Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s)$

$E^o = +1.10$ V

Table 20.1 • Standard Reduction Potentials in Aqueous Solution at 25 °C*

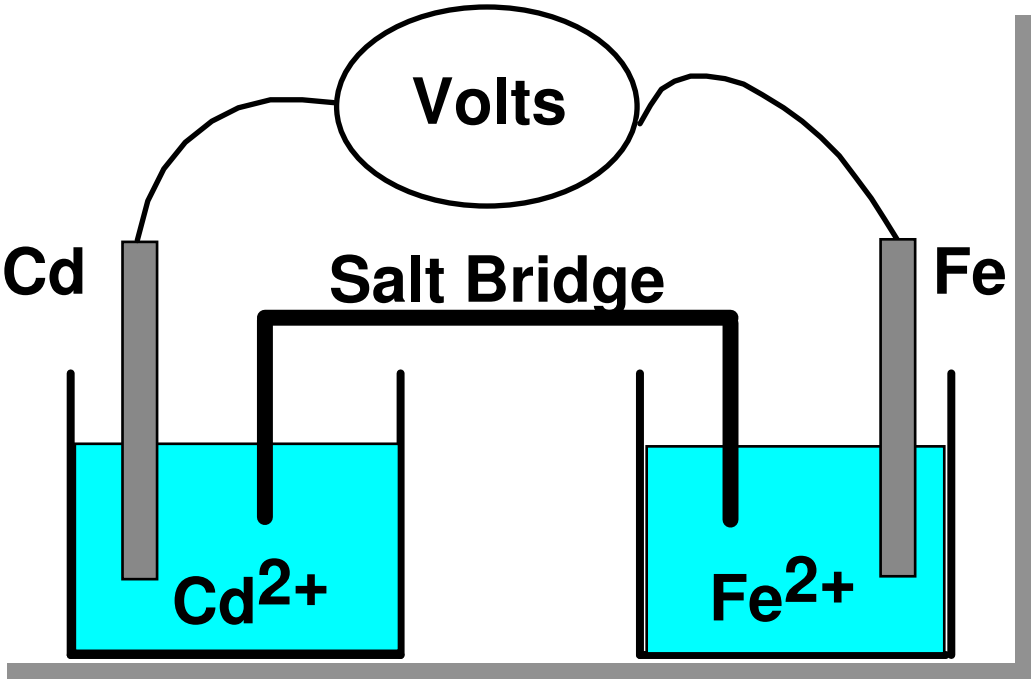
Reduction Half-Reaction		$E°$ (V)
$F_2(g) + 2\ e^-$	$\longrightarrow 2\ F^-(aq)$	+2.87
$H_2O_2(aq) + 2\ H^+(aq) + 2\ e^-$	$\longrightarrow 2\ H_2O(\ell)$	+1.77
$PbO_2(s) + SO_4^{2-}(aq) + 4\ H^+(aq) + 2\ e^-$	$\longrightarrow PbSO_4(s) + 2\ H_2O(\ell)$	+1.685
$MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^-$	$\longrightarrow Mn^{2+}(aq) + 4\ H_2O(\ell)$	+1.52
$Au^{3+}(aq) + 3\ e^-$	$\longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2\ e^-$	$\longrightarrow 2\ Cl^-(aq)$	+1.360
$Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^-$	$\longrightarrow 2\ Cr^{3+}(aq) + 7\ H_2O\ (\ell)$	+1.33
$O_2(g) + 4\ H^+(aq) + 4\ e^-$	$\longrightarrow 2\ H_2O(\ell)$	+1.229
$Br_2(\ell) + 2\ e^-$	$\longrightarrow 2\ Br^-(aq)$	+1.08
$NO_3^-(aq) + 4\ H^+(aq) + 3\ e^-$	$\longrightarrow NO(g) + 2\ H_2O(\ell)$	+0.96
$OCl^-(aq) + H_2O(\ell) + 2\ e^-$	$\longrightarrow Cl^-(aq) + 2\ OH^-(aq)$	+0.89
$Hg^{2+}(aq) + 2\ e^-$	$\longrightarrow Hg(\ell)$	+0.855
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	+0.80
$Hg_2^{2+}(aq) + 2\ e^-$	$\longrightarrow 2\ Hg(\ell)$	+0.789
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	+0.771
$I_2(s) + 2\ e^-$	$\longrightarrow 2\ I^-(aq)$	+0.535
$O_2(g) + 2\ H_2O(\ell) + 4\ e^-$	$\longrightarrow 4\ OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2\ e^-$	$\longrightarrow Cu(s)$	+0.337
$Sn^{4+}(aq) + 2\ e^-$	$\longrightarrow Sn^{2+}(aq)$	+0.15
$2\ H^+(aq) + 2\ e^-$	$\longrightarrow H_2(g)$	0.00
$Sn^{2+}(aq) + 2\ e^-$	$\longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2\ e^-$	$\longrightarrow Ni(s)$	−0.25
$V^{3+}(aq) + e^-$	$\longrightarrow V^{2+}(aq)$	−0.255
$PbSO_4(s) + 2\ e^-$	$\longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.356
$Cd^{2+}(aq) + 2\ e^-$	$\longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2\ e^-$	$\longrightarrow Fe(s)$	−0.44
$Zn^{2+}(aq) + 2\ e^-$	$\longrightarrow Zn(s)$	−0.763
$2\ H_2O(\ell) + 2\ e^-$	$\longrightarrow H_2(g) + 2\ OH^-(aq)$	−0.8277
$Al^{3+}(aq) + 3\ e^-$	$\longrightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2\ e^-$	$\longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.714
$K^+(aq) + e^-$	$\longrightarrow K(s)$	−2.925
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.045

Increasing strength of oxidizing agents ↑

Increasing strength of reducing agents ↓

*In volts (V) versus the standard hydrogen electrode.

E^o for a Voltaic Cell



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Increasing strength of oxidizing agents →

← Increasing strength of reducing agents

*In volts (V) versus the standard hydrogen electrode.

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

or

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

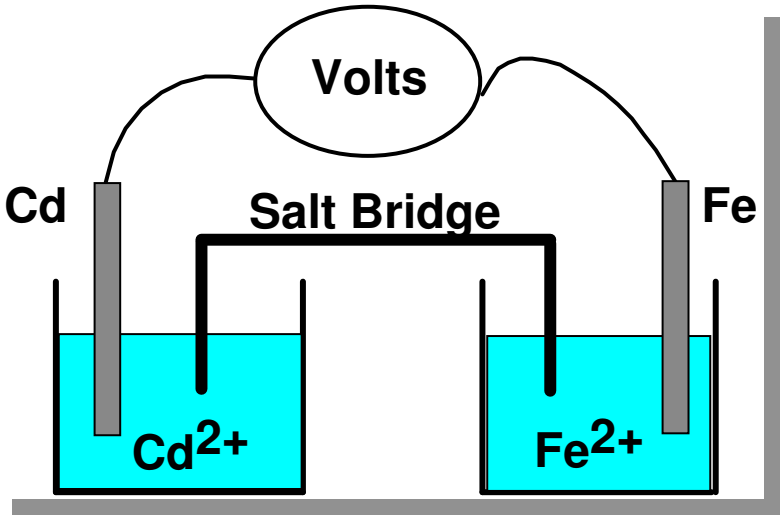
$Fe \rightarrow Fe^{2+} + 2e^-$

or

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

All ingredients are present. Which way does reaction proceed?

E^o for a Voltaic Cell



From the table, you see

- Fe is a better reducing agent than Cd
- Cd^{2+} is a better oxidizing agent than Fe^{2+}

More About Calculating Cell Voltage

Assume I^- ion can reduce water.

$2\ H_2O + 2e^- \rightarrow H_2 + 2\ OH^-$ Cathode

$2\ I^- \rightarrow I_2 + 2e^-$ Anode

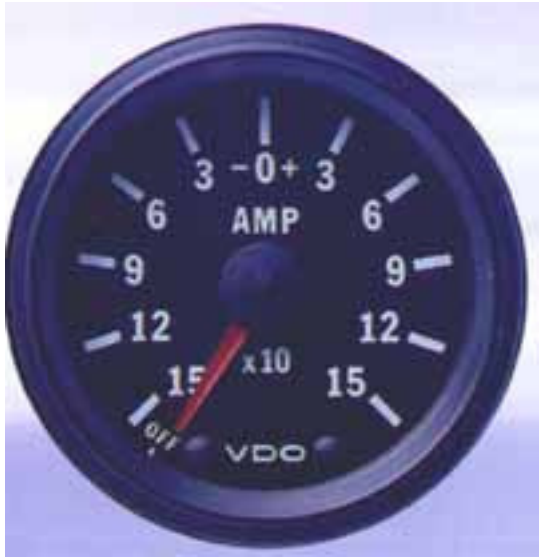
$2\ I^- + 2\ H_2O \rightarrow I_2 + 2\ OH^- + H_2$

Assuming reaction occurs as written,

$E^\circ = E^\circ_{cat} + E^\circ_{an} = (-0.828\ V) - (-+0.535\ V) =$ **-1.363 V**

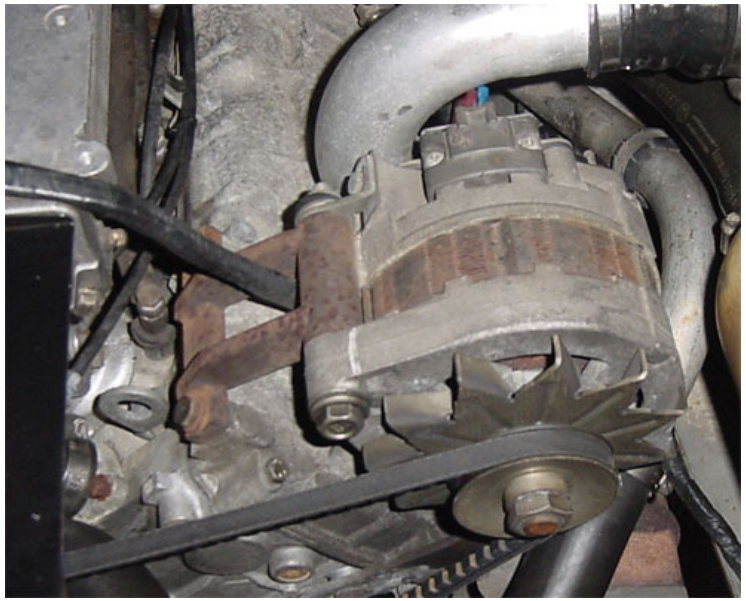
Minus E° means rxn. occurs in opposite direction (the connection is backwards or you are recharging the battery)

Charging a Battery

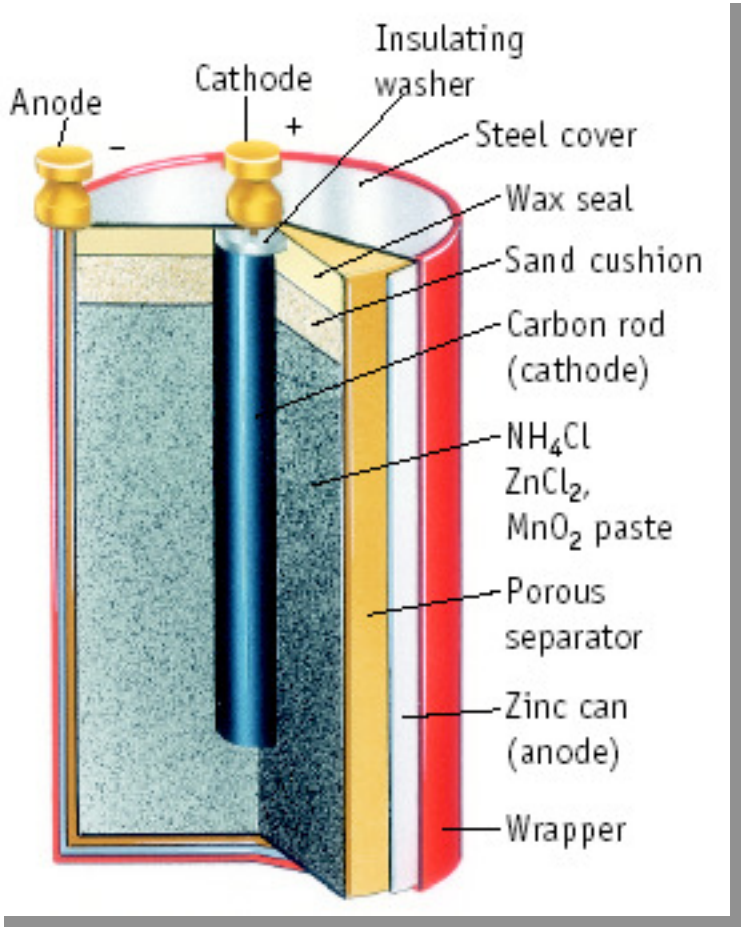


When you charge a battery, you are forcing the electrons backwards (from the + to the -). To do this, you will need a higher voltage backwards than forwards. This is why the ammeter in your car often goes slightly higher while your battery is charging, and then returns to normal.

In your car, the battery charger is called an alternator. If you have a dead battery, it could be the battery needs to be replaced OR the alternator is not charging the battery properly.



Dry Cell Battery



Anode (-)

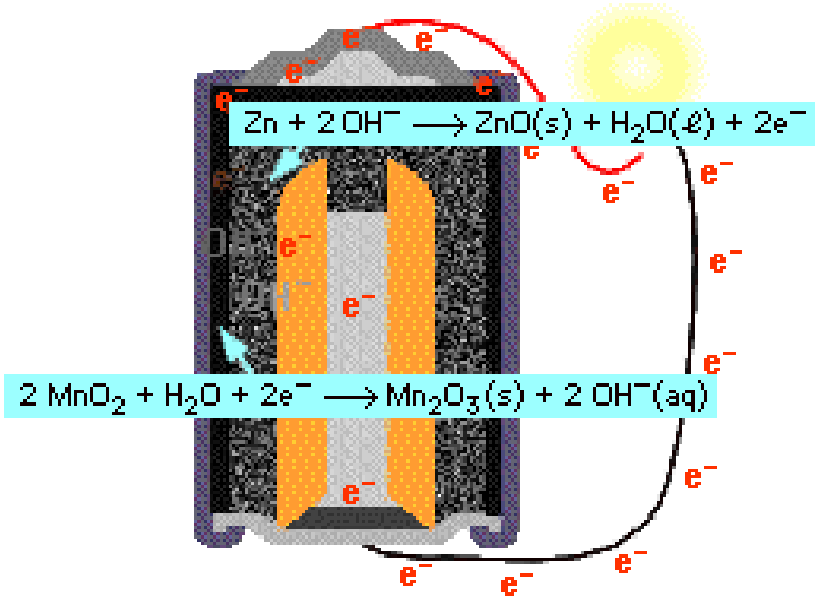
$Zn \rightarrow Zn^{2+} + 2e^-$

Cathode (+)

$2\ NH_4^+ + 2e^- \rightarrow 2\ NH_3 + H_2$

Alkaline Battery

Nearly same reactions as in common dry cell, but under basic conditions.



Anode (-): $Zn + 2\ OH^- \rightarrow ZnO + H_2O + 2e^-$

Cathode (+): $2\ MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2\ OH^-$

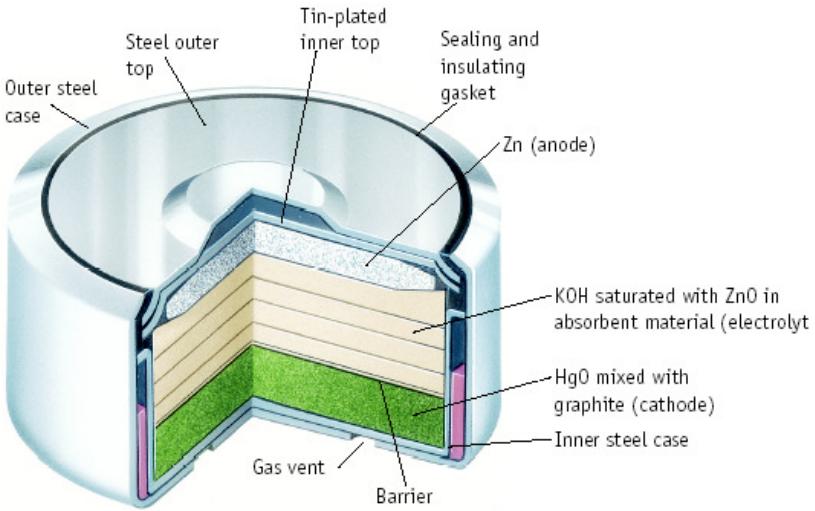
Mercury Battery

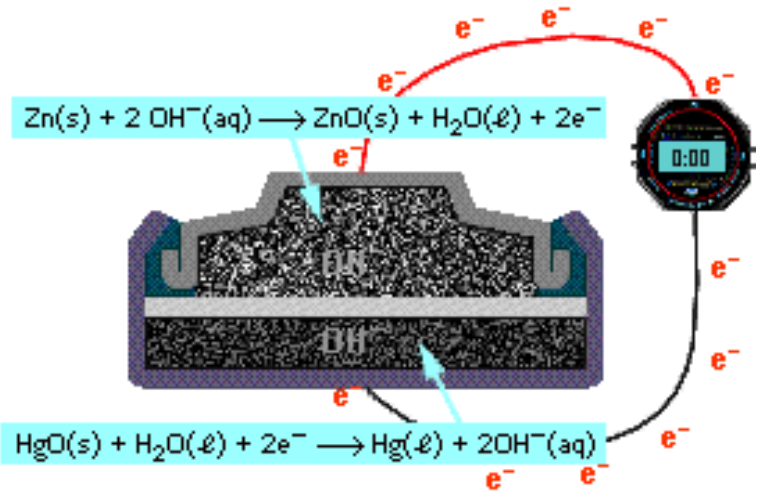
Anode:

Zn is reducing agent under basic conditions

Cathode:

$HgO + H_2O + 2e^- \dashrightarrow Hg + 2\ OH^-$





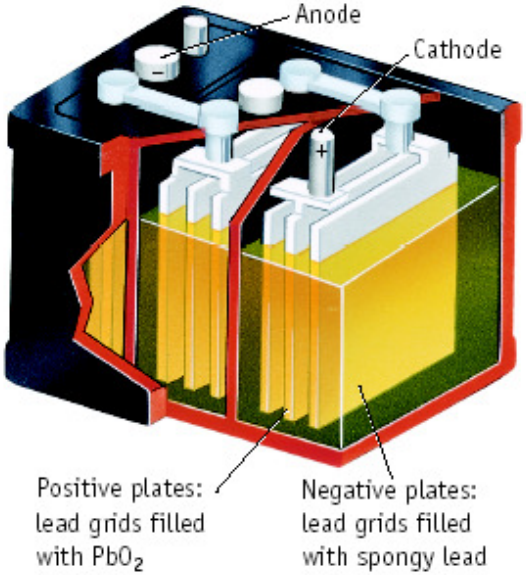
Lead Storage Battery

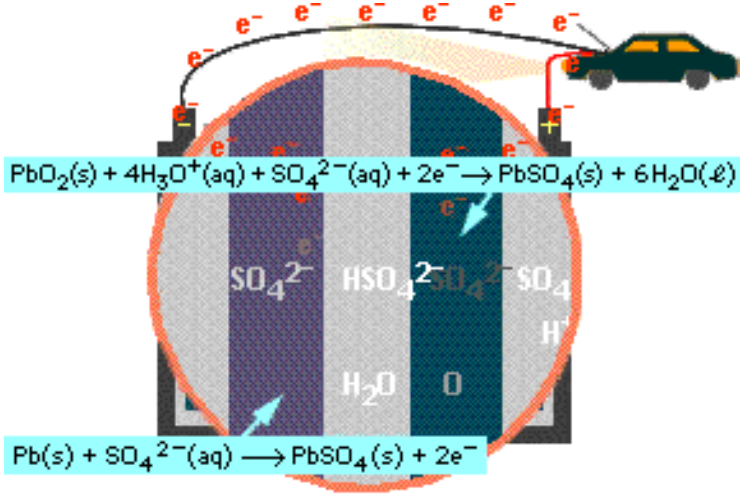
Anode (-) $E^o = +0.36$ V

$Pb + HSO_4^- \rightarrow PbSO_4 + H^+ + 2e^-$

Cathode (+) $E^o = +1.68$ V

$PbO_2 + HSO_4^- + 3\,H^+ + 2e^- \rightarrow PbSO_4 + 2\,H_2O$





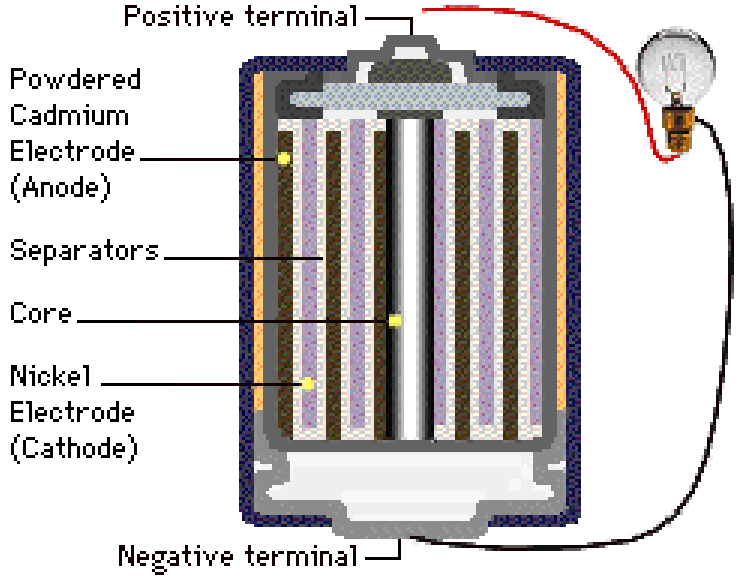
Ni-Cad Battery

Anode (-)

$$Cd + 2\,OH^- \rightarrow Cd(OH)_2 + 2e^-$$

Cathode (+)

$$NiO(OH) + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$$



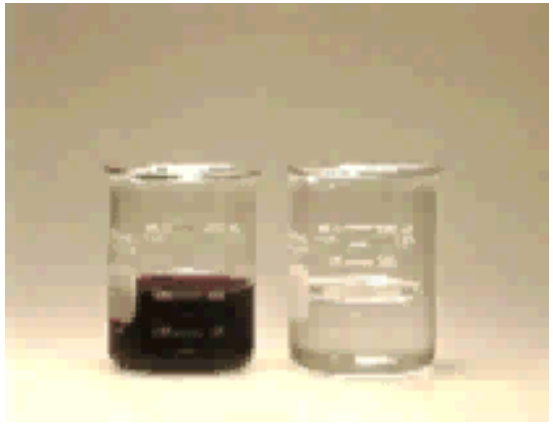
H_2 as a Fuel

(b) A prototype of a hydrogen-powered BMW.

Cars can use electricity generated by H_2/O_2 fuel cells.
H_2 carried in tanks or generated from hydrocarbons

Balancing Equations for Redox Reactions

Some redox reactions have equations that must be balanced by special techniques.



MnO_4^- + 5 Fe^{2+} + 8 H^+
---> Mn^{2+} + 5 Fe^{3+} + 4 H_2O

Mn = +7 Fe = +2

Mn = +2 Fe = +3

Balancing Equations

Consider the reduction of Ag^+ ions with copper metal.

$Cu + Ag^+ \text{ --give--> } Cu^{2+} + Ag$

Balancing Equations

Step 1: Divide the reaction into half-reactions, one for oxidation and the other for reduction.

Ox $Cu \rightarrow Cu^{2+}$

Red $Ag^{+} \rightarrow Ag$

Step 2: Balance each element for mass. Already done in this case.

Step 3: Balance each half-reaction for charge by adding electrons.

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

Red $Ag^{+} + e^- \rightarrow Ag$

Balancing Equations

Step 4: Multiply each half-reaction by a factor so that the reducing agent supplies as many electrons as the oxidizing agent requires.

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

Oxidizing agent $2\,Ag^+ + 2\,e^- \rightarrow 2\,Ag$

Step 5: Add half-reactions to give the overall equation.

$Cu + 2\,Ag^+ \rightarrow Cu^{2+} + 2Ag$

The equation is now balanced for both charge and mass.

Balancing Equations

Balance the following in acid solution—

$$VO_2^+ + Zn \rightarrow VO^{2+} + Zn^{2+}$$

Step 1: **Write the half-reactions**

Ox $Zn \rightarrow Zn^{2+}$

Red $VO_2^+ \rightarrow VO^{2+}$

Step 2: **Balance each half-reaction for mass.**

Ox $Zn \rightarrow Zn^{2+}$

Red $2\,H^+ + VO_2^+ \rightarrow VO^{2+} + H_2O$

Add H_2O on O-deficient side and add H^+ on other side for H-balance.

Balancing Equations

Step 3: Balance half-reactions for charge.

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

Red $e^- + 2\,H^+ + VO_2^+ \rightarrow VO^{2+} + H_2O$

Step 4: Multiply by an appropriate factor.

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

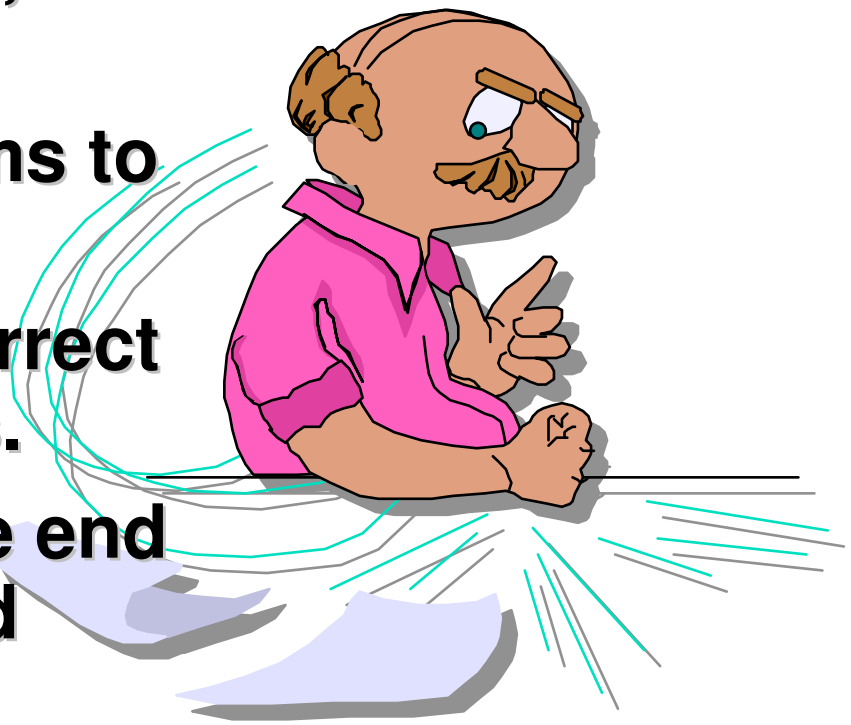
Red $2e^- + 4\,H^+ + 2\,VO_2^+ \rightarrow 2\,VO^{2+} + 2\,H_2O$

Step 5: Add *balanced* half-reactions

$$Zn + 4\,H^+ + 2\,VO_2^+ \rightarrow Zn^{2+} + 2\,VO^{2+} + 2\,H_2O$$

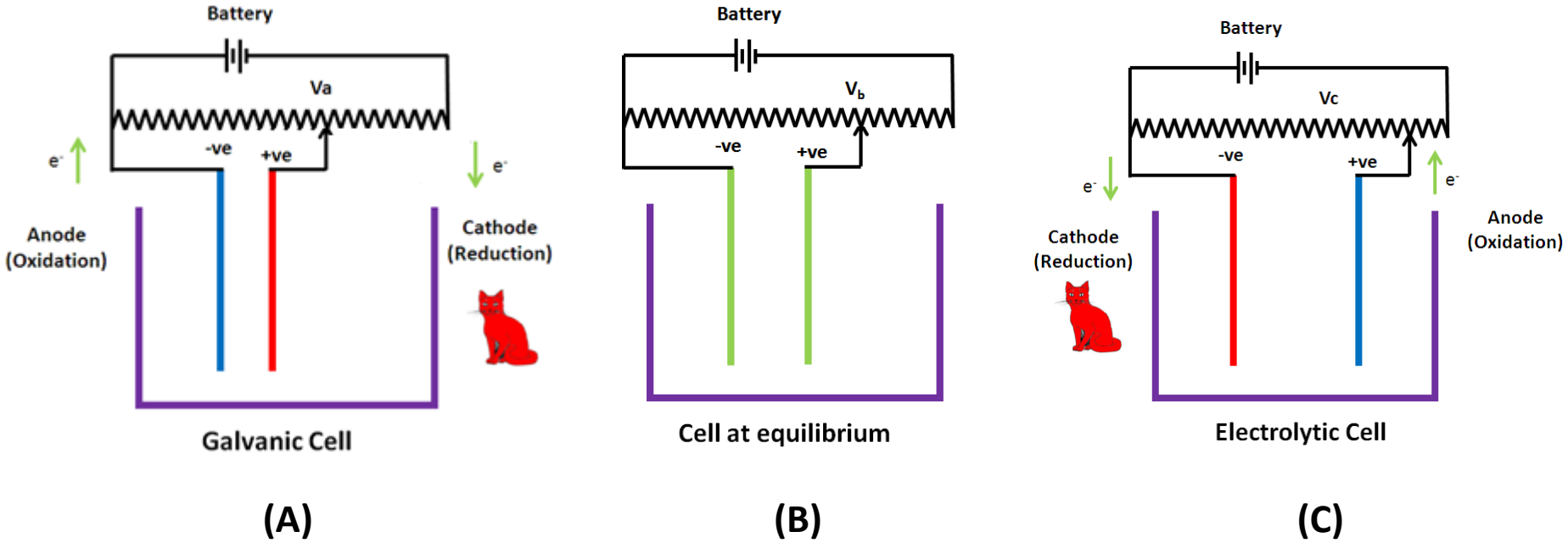
Tips on Balancing Equations

- Never add O_2, O atoms, or O^{2-} to balance oxygen.
- Never add H_2 or H atoms to balance hydrogen.
- Be sure to write the correct charges on all the ions.
- Check your work at the end to make sure mass and charge are balanced.
- PRACTICE!



Measurement of Cell potential

The difference in potential between the cathode and anode of a cell can be measured using a potentiostate.



(A) **(B)** **(C)**

The battery and resistor with a sliding contact is used to apply fraction of potential difference across the slide wire to an electrochemical cell.

(A)If the applied potential difference (Va) is less than EMF of the cell, the cell work as galvanic cell (discharge spontaneously).

(B)If the applied potential difference (Vb) is equal to EMF of the cell, the current is zero and the cell will be at equilibrium.

(C)If the applied potential difference (Vc) is larger than EMF of the cell, it derives the cell reaction in the reverse direction. The cell now is working as electrolytic cell.

Note:

1) The anode in case (A) on left but it is on the right in case (C).

2) The definition of anode and cathode in terms of oxidation and reduction are independent of whether a cell is a galvanic cell or an electrolytic cell.

3) The terms anode and cathode should not used for the electrodes in an electrochemical cell at equilibrium.

Cell without liquid junction

- **Example:**

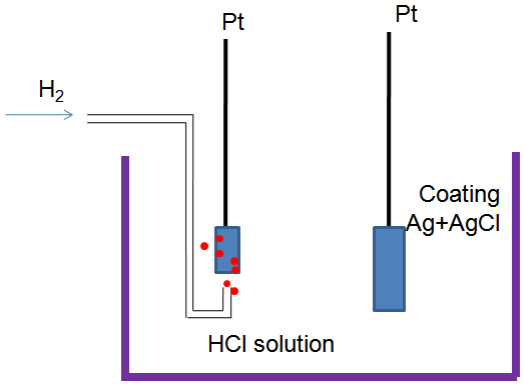
$Pt(s) \mid H_{2(g)} \mid HCl_{(m)} \mid AgCl_{(s)} \mid Ag_{(s)}$

$Pt(s) \mid H_{2(g)} \mid HCl_{(m)} \mid Cl_{2(g)} \mid Pt_{(s)}$

$Hg\text{-}Na\ (x_{Na}) \mid NaOH_{(m)} \mid Hg\text{-}Na\ (x_{Na})$

The vertical lines represent phase boundaries.

Cells of this type can be held equilibrium, and they can give exact thermodynamic treatment.

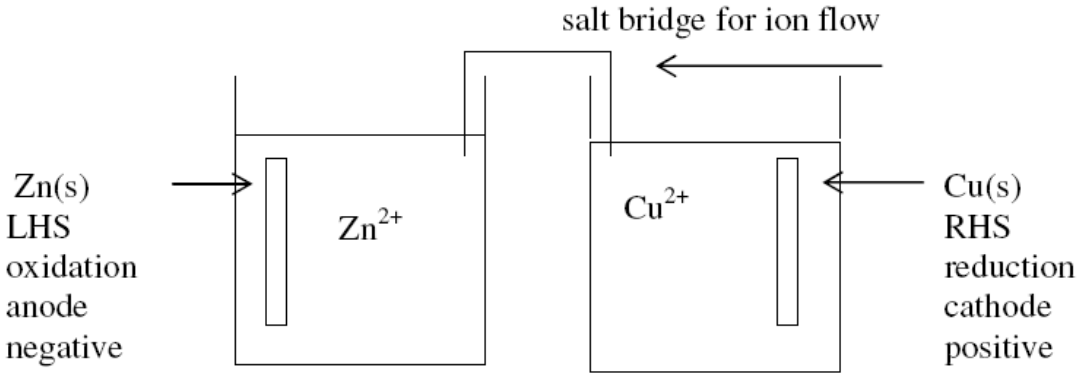


Cell with liquid junction

- **Example:**

$Zn(s) \mid Zn^{2+}(m_1) \,\vdots\, Cu^{2+}(m_1) \mid Cu(s)$

$Ag(s) \mid AgCl(s) \mid Cl^{-2} \,\|\, Ag^{+}(m) \mid Ag(s)$



$\vdots$ It represent a junction between two liquids $\|$ It represent a salt bridge (conc. KCl)

- **Is necessary to know that when solution in contact can react with each other.**
- **Cells with liquid junctions are never completely at equilibrium because diffusion occurs at the liquid junction and contributes with an unknown potential.**

- The Nernst Equation. **Cell reactions must be spontaneous, otherwise there would be no reaction and hence no electron transfer when the circuit is completed. For the general redox reaction**
- $aA + bB \longrightarrow cC + dD$

  where n electrons are transferred recall that the reaction Gibbs energy is:

$$\Delta_r G = \Delta_r G^{\theta} + RT \ln\left(\frac{a_C^c a_D^d}{a_A^a a_B^b}\right) = \Delta_r G^{\theta} + RT \ln Q$$

We can show that :

$\Delta_r G$ = chemical driving force = - nFE = electrical driving force.

For electrons to be transferred there must be a difference in the electric potential between the two parts of the cell. This is similar to the flow of heat which only occurs due to a temperature difference between two points. This potential difference is designated E, the emf of the cell or the electromotive force or the electric potential.

Recall that the maximum non pV work = $\Delta_r G = w_{e,max}$.

Consider the work done when one mole of a cell reaction occurs [the reaction as written occurs N_A times] and nN_A electrons are transferred across the cell where a potential difference E exits. Since each electron carries a charge e =1.602 x 10^{-19} Coulombs, the total charge transferred across E is nN_Ae

From basic electricity theory:

Electrical work = charge x potential across which charge moves

= $-nN_Ae$ E

Thus: $\Delta_r G = w_{e,max.} = -nN_Ae$ E

eN_A ≡ Faraday constant = 1.602 x 10^{-19} Coulombs x 6.023 x 10^{23} mol^{-1} = 96490 C mol^{-1}

Thus $\Delta_r G = -nF$ E and also $\Delta_r G^q = -nF$ E^q

- **where E^q ; the standard emf, is the electrical driving force when the reaction mixture is composed of reactants and products present in their standard states.** It must be > 0.
- **Substituting into the equation for the reaction Gibbs energy gives the Nernst equation.**

$$E = E^{\theta} - \frac{RT}{\nu F}\ln Q$$

- **When the Nernst equation is applied to a balanced reaction where the number of electrons transferred is known there are only three things that are unknown: the cell potential E, the standard cell potential E^q and Q which contains concentrations and activity coefficients of the species. If the standard potential is known and the cell potential is measured for a particular concentration then it is possible to get the mean activity coefficient.**