

# Electrochemistry

# Vocabulary

**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

**Oxidizing agent (OA)** – the species that is reduced and thus *causes oxidation*

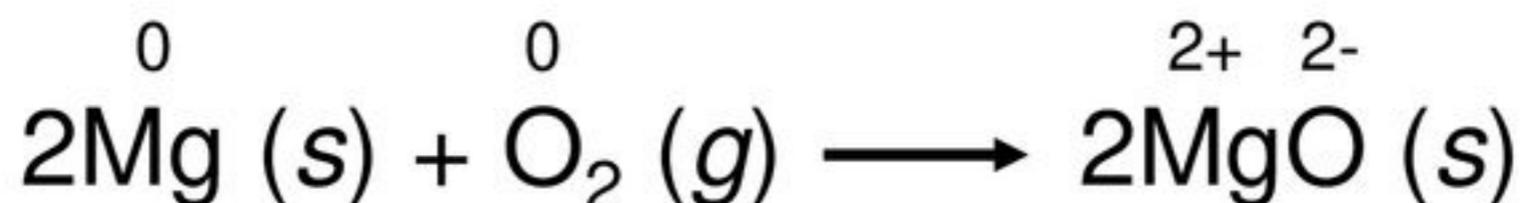
**Reducing agent (RA)** – the species that is oxidized and thus *causes reduction*

# **ELECTROCHEMISTRY INVOLVES TWO MAIN TYPES OF PROCESSES:**

- A. Galvanic (voltaic) cells – which are spontaneous chemical reactions (battery)**
- B. Electrolytic cells – which are non-spontaneous and require external e- source (*DC power source*)**
- C. BOTH of these fit into the category entitled  
**Electrochemical cells****

**Electrochemical** processes are oxidation-reduction reactions in which:

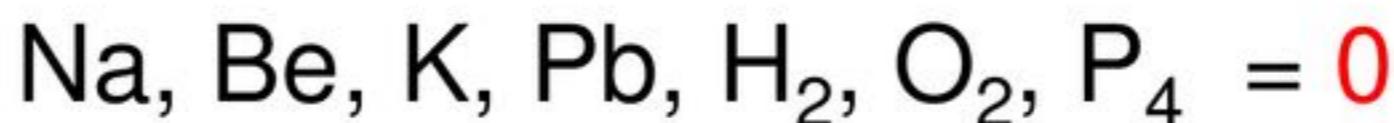
- the energy released by a spontaneous reaction is converted to electricity or
- electrical energy is used to cause a nonspontaneous reaction to occur



# Oxidation number

The charge the atom would have in a molecule (or an ionic compound) if electrons were completely transferred.

1. Free elements (uncombined state) have an oxidation number of zero.



2. In monatomic ions, the oxidation number is equal to the charge on the ion.



3. The oxidation number of oxygen *is usually -2*. In  $\text{H}_2\text{O}_2$  and  $\text{O}_2^{2-}$  it is **-1**.

- The oxidation number of hydrogen is **+1** except when it is bonded to metals in binary compounds. In these cases, its oxidation number is **-1**.
- Group IA metals are **+1**, IIA metals are **+2** and fluorine is always **-1**.
- The sum of the oxidation numbers of all the atoms in a molecule or ion is equal to the charge on the molecule or ion.



Oxidation numbers of all the atoms in  $\text{HCO}_3^-$  ?



$$\text{O} = \textcolor{red}{-2} \quad \text{H} = \textcolor{red}{+1}$$

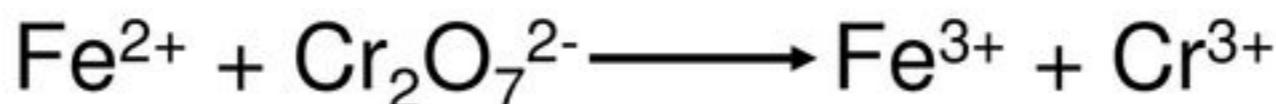
$$3 \times (\textcolor{red}{-2}) + 1 + ? = -1$$

$$\text{C} = \textcolor{red}{+4}$$

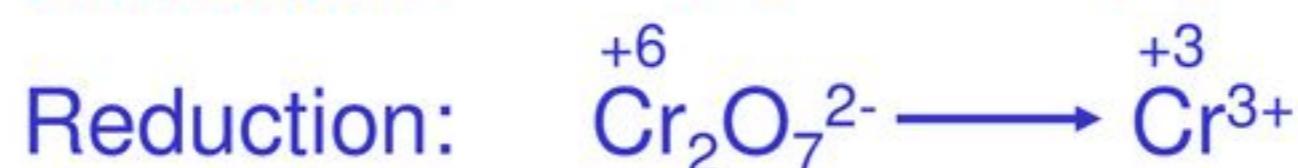
# Balancing Redox Equations

The oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  by  $\text{Cr}_2\text{O}_7^{2-}$  in acid solution?

1. Write the unbalanced equation for the reaction ion ionic form.



2. Separate the equation into two half-reactions.



3. Balance the atoms other than O and H in each half-reaction.

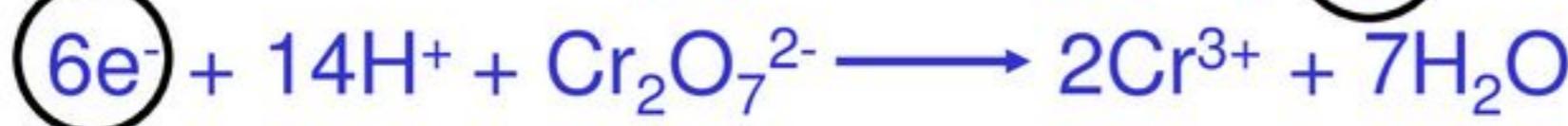


## Balancing Redox Equations

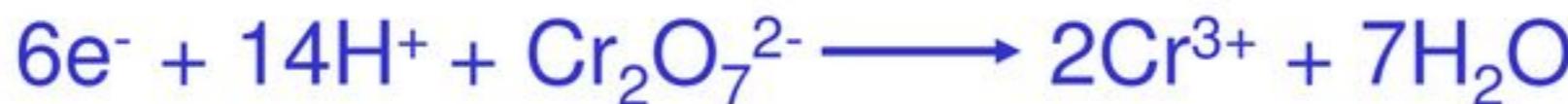
4. For reactions in acid, add H<sub>2</sub>O to balance O atoms and H<sup>+</sup> to balance H atoms.



5. Add electrons to one side of each half-reaction to balance the charges on the half-reaction.



6. If necessary, equalize the number of electrons in the two half-reactions by multiplying the half-reactions by appropriate coefficients.



## Balancing Redox Equations

7. Add the two half-reactions together and balance the final equation by inspection. **The number of electrons on both sides must cancel.**

Oxidation:



8. Verify that the number of atoms and the charges are balanced.

$$14 \times 1 - 2 + 6 \times 2 = 24 = 6 \times 3 + 2 \times 3$$

9. For reactions in basic solutions, add  $\text{OH}^-$  to **both sides** of the equation for every  $\text{H}^+$  that appears in the final equation.

# GALVANIC CELLS

*Parts of the voltaic or galvanic cell:*

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

**Cathode**-- the anode where reduction occurs. After a period of time it may appear larger, due to ions from solution plating onto it.

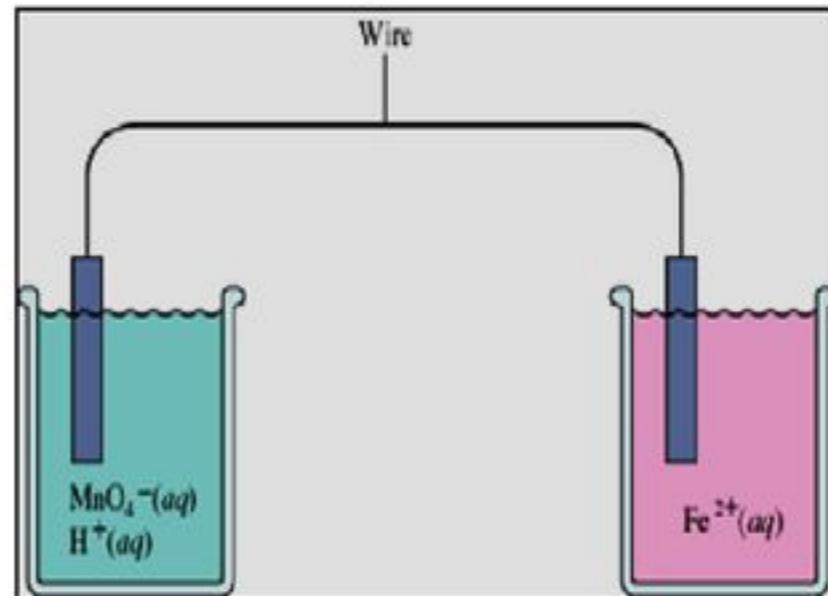
**Inert electrodes** -- used when a gas is involved OR ion to ion involved such as  $\text{Fe}^{3+}$  being reduced to  $\text{Fe}^{2+}$  rather than  $\text{Fe}^0$ . Made of Pt or graphite.

**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.

**Electron flow** -- always from anode to cathode. (through the wire)

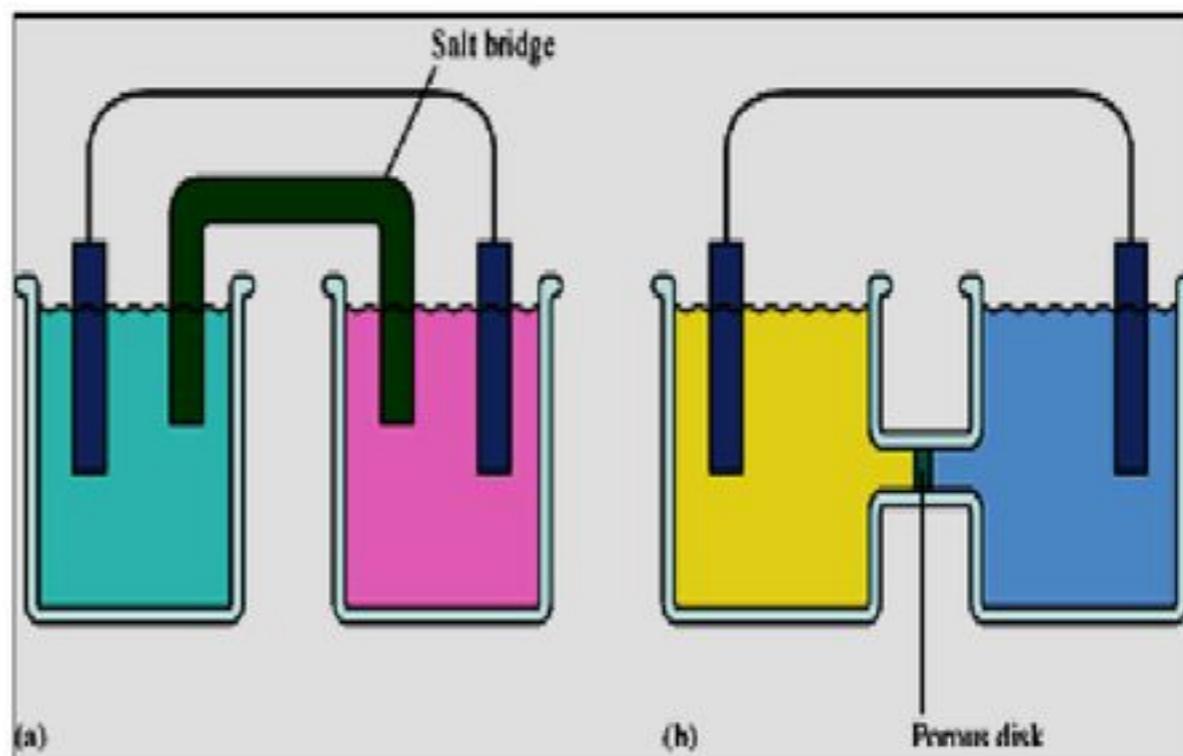
**Standard cell notation** (line notation) - anode/solution// cathode solution/cathode  
Ex.  $\text{Zn}/\text{Zn}^{2+} \text{ (1.0 M)} // \text{Cu}^{2+} \text{ (1.0 M)} / \text{Cu}$

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



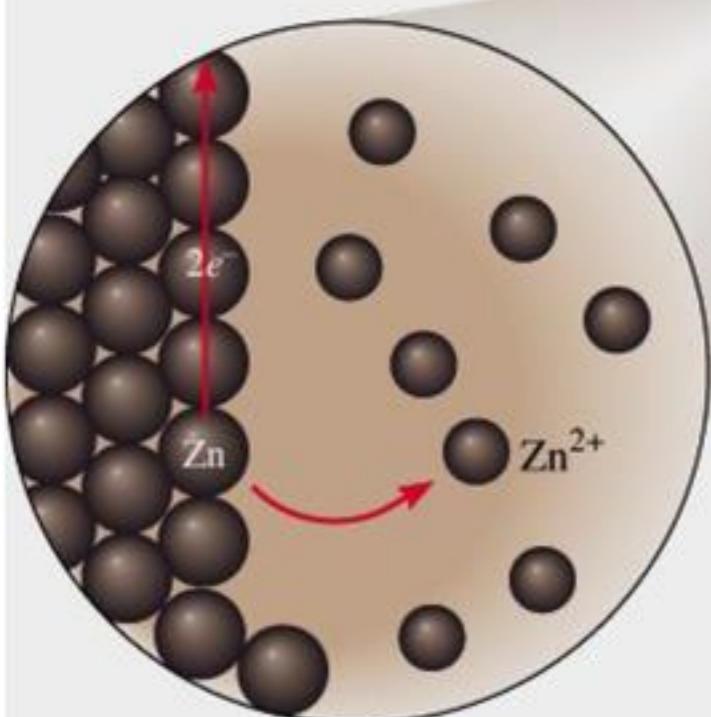
Why separate beakers?  
Why connected by wire?  
What do we need?

- Salt Bridge
- Cell potential -Volts (V) J/Coulomb)
- Volt meter

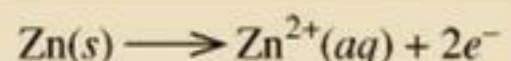


# Galvanic Cells

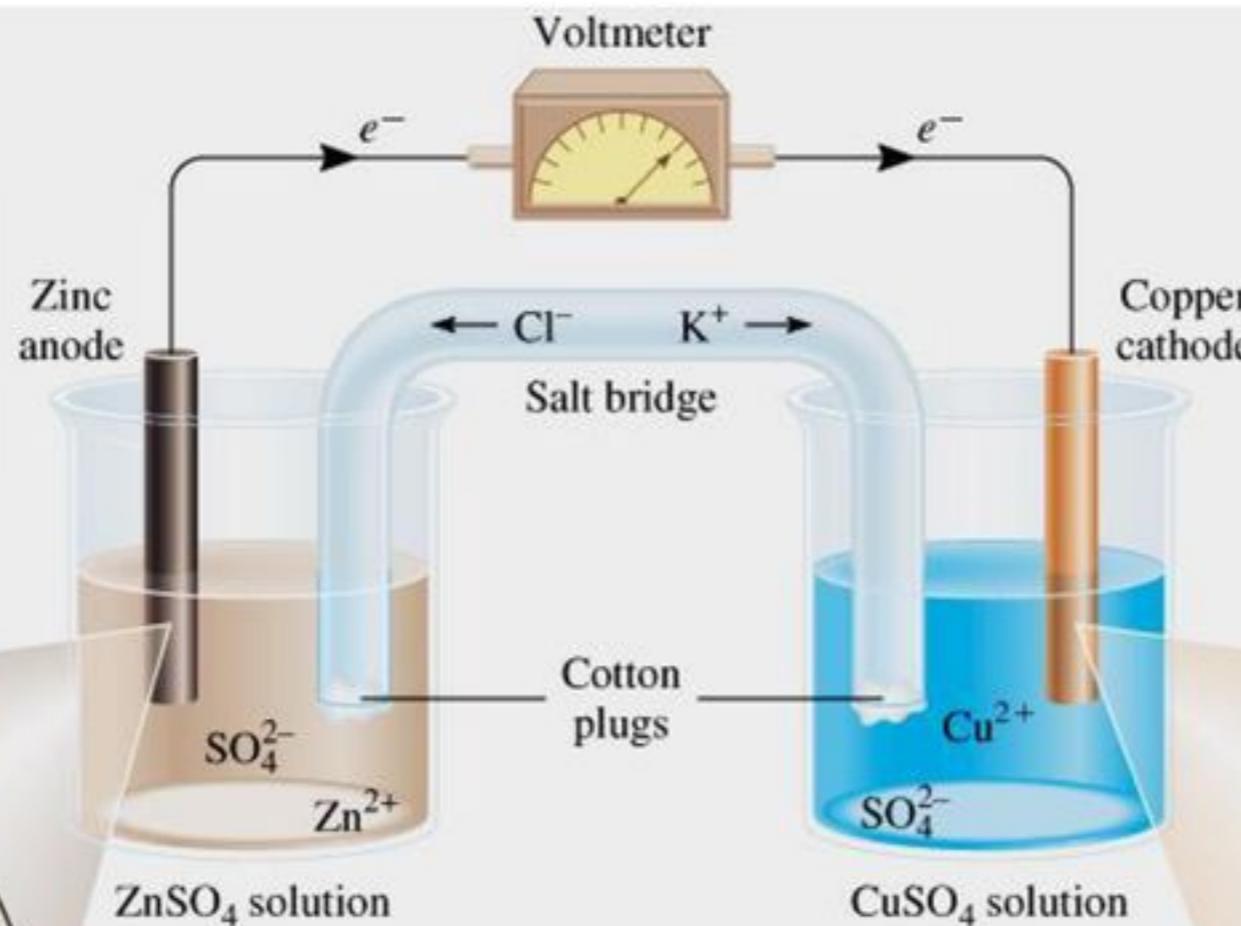
anode oxidation



$Zn$  is oxidized to  $Zn^{2+}$  at anode.

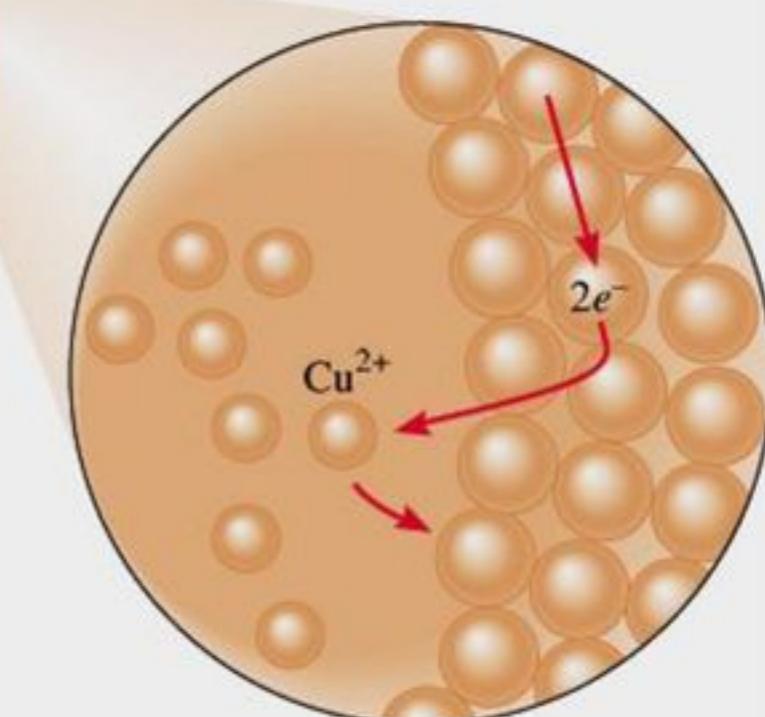
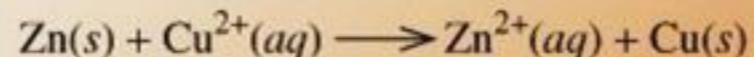


cathode reduction

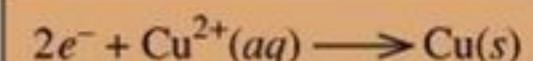


spontaneous redox reaction

Net reaction



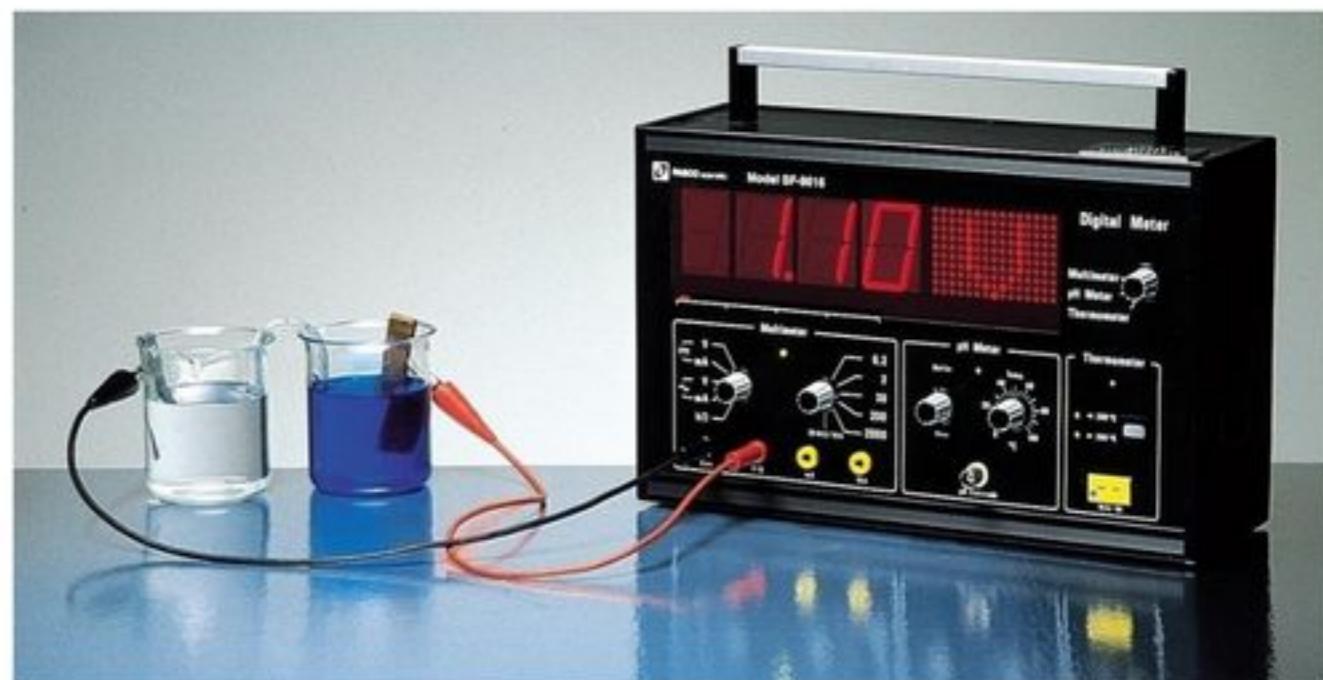
$Cu^{2+}$  is reduced to  $Cu$  at cathode.



# Galvanic Cells

The difference in electrical potential between the anode and cathode is called:

- ***cell voltage***
- ***electromotive force (emf)***
- ***cell potential***



## Cell Diagram



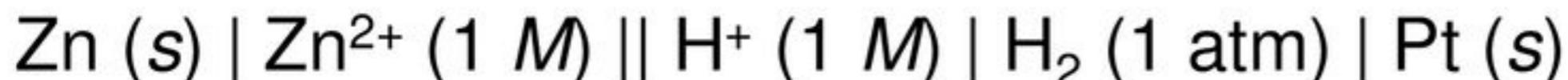
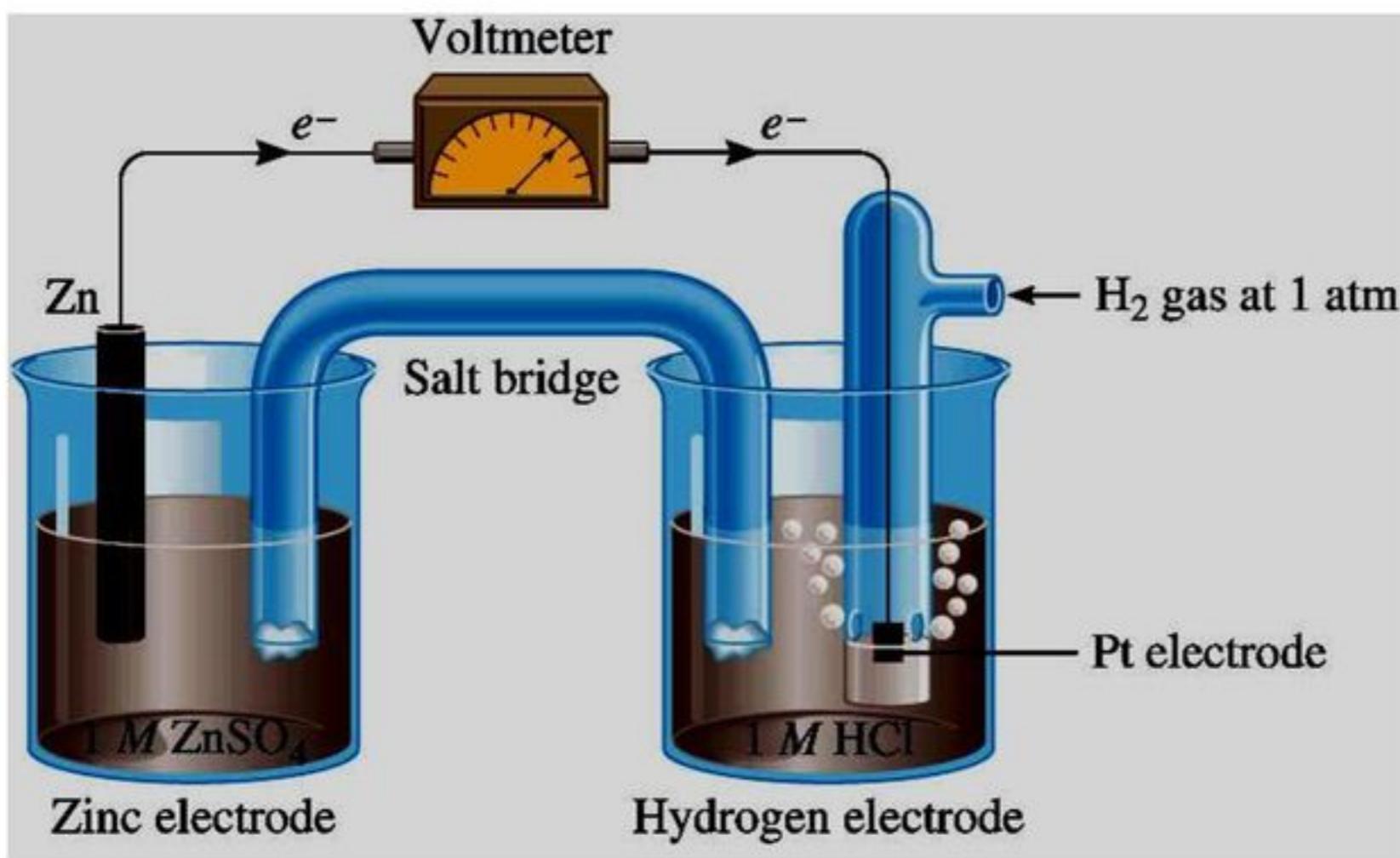
$$[\text{Cu}^{2+}] = 1 \text{ M} \text{ & } [\text{Zn}^{2+}] = 1 \text{ M}$$



anode

cathode

# Standard Reduction Potentials



Anode (oxidation):

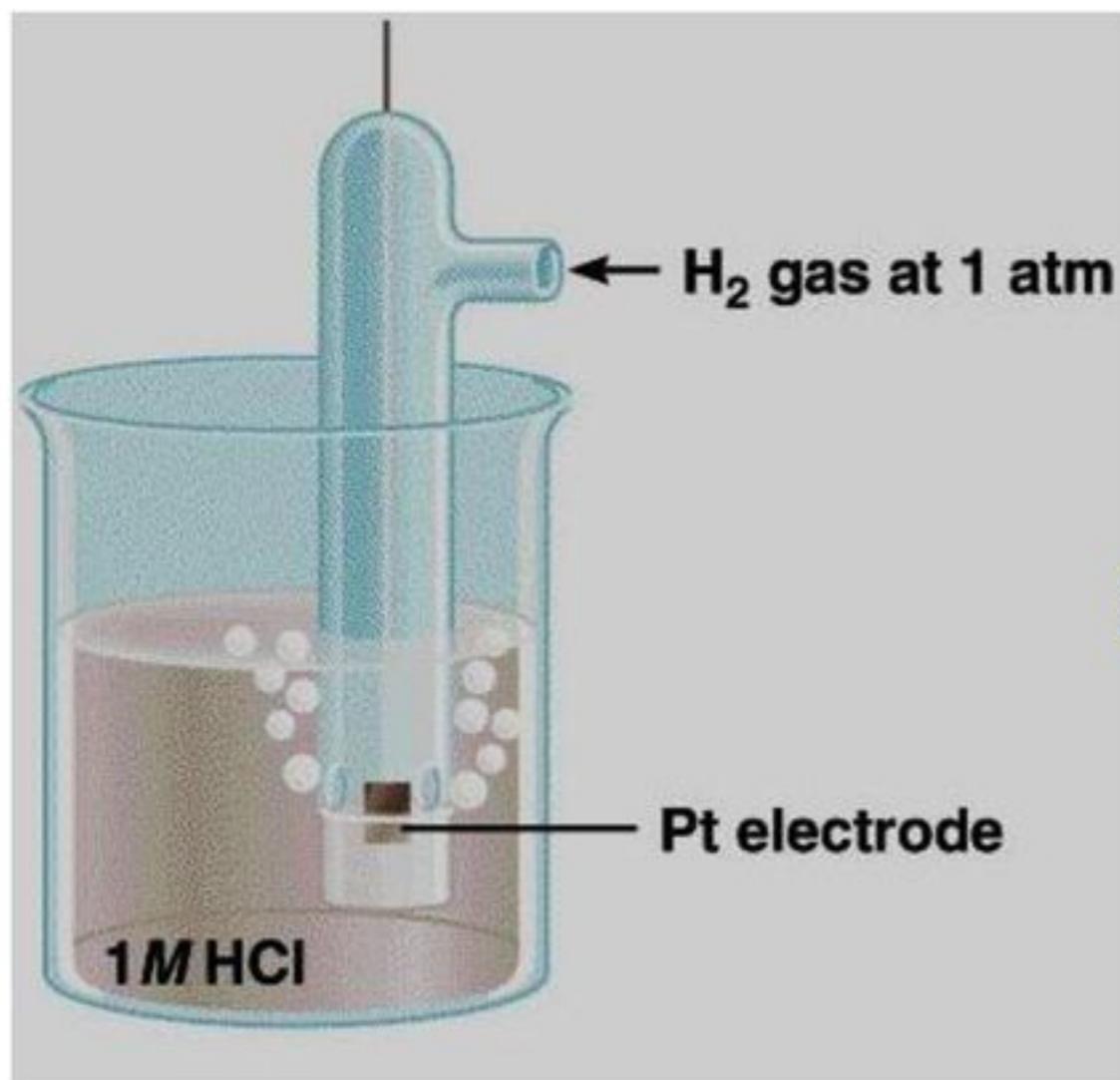


Cathode (reduction):  $2\text{e}^- + 2\text{H}^+ (1 \text{ M}) \longrightarrow \text{H}_2 (1 \text{ atm})$

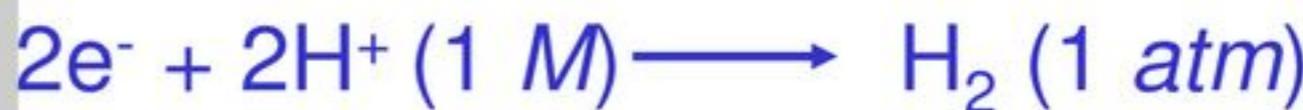


# Standard Reduction Potentials

**Standard reduction potential ( $E^0$ )** is the voltage associated with a **reduction reaction** at an electrode when all solutes are 1 M and all gases are at 1 atm.



Reduction Reaction

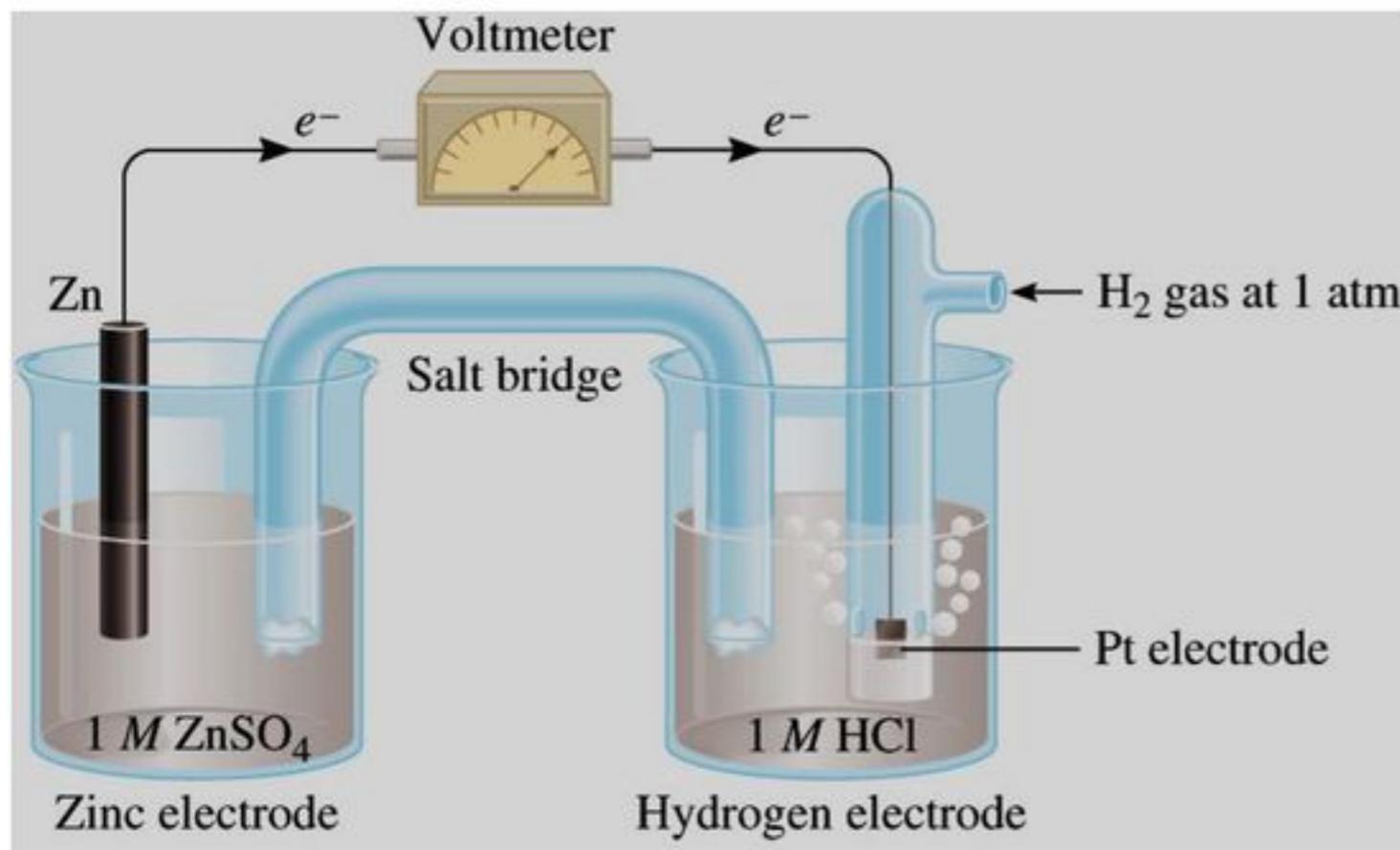


$$E^0 = 0 \text{ V}$$

Standard hydrogen electrode (SHE)

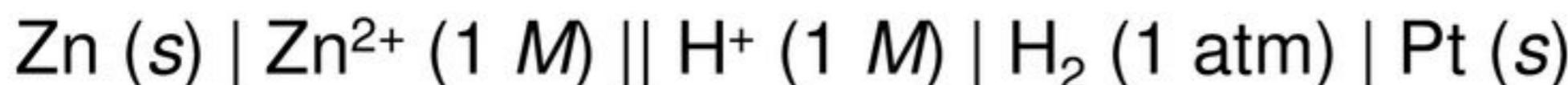
# Standard Reduction Potentials

$$E_{cell}^0 = 0.76 \text{ V}$$



**Standard emf ( $E_{cell}^0$ )**

$$E_{cell}^0 = E_{cathode}^0 - E_{anode}^0$$



$$E_{cell}^0 = E_{\text{H}^+/\text{H}_2}^0 - E_{\text{Zn}^{2+}/\text{Zn}}^0$$

$$0.76 \text{ V} = 0 - E_{\text{Zn}^{2+}/\text{Zn}}^0$$

$$E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.76 \text{ V}$$

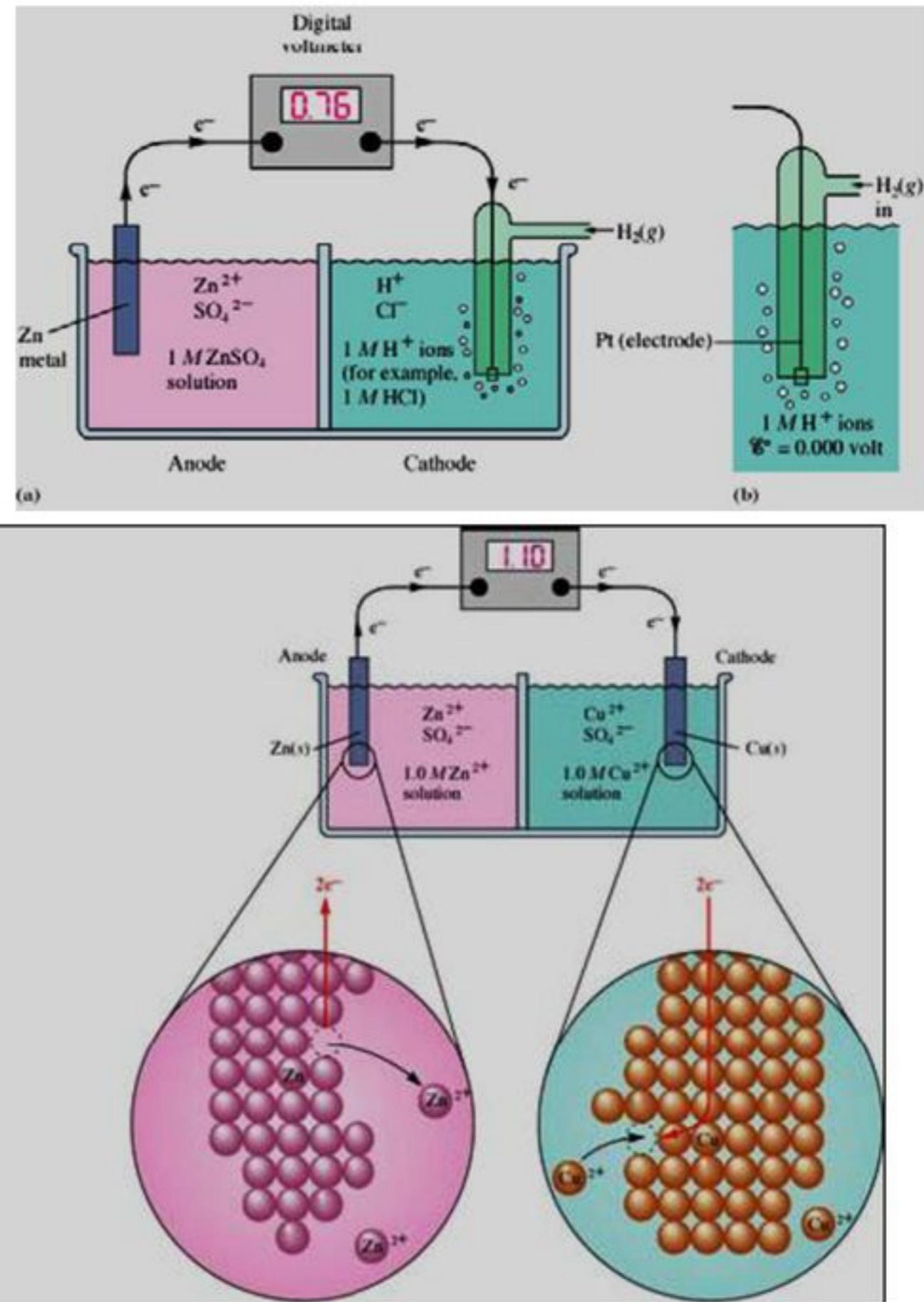


## STANDARD REDUCTION POTENTIALS

- 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.**
- Standard conditions—1 atm for gases, **1.0M for solutions and 25°C for all (298 K)**
- naught, ° -- we use the naught to symbolize standard Conditions. That means  $E_{cell}$ ,  $E_{mf}$ , or  $\varepsilon_{cell}$  become  $E_{cell}^{\circ}$ ,  $E_{mf}^{\circ}$ , or  $\varepsilon_{cell}^{\circ}$  when measurements are taken at standard conditions.

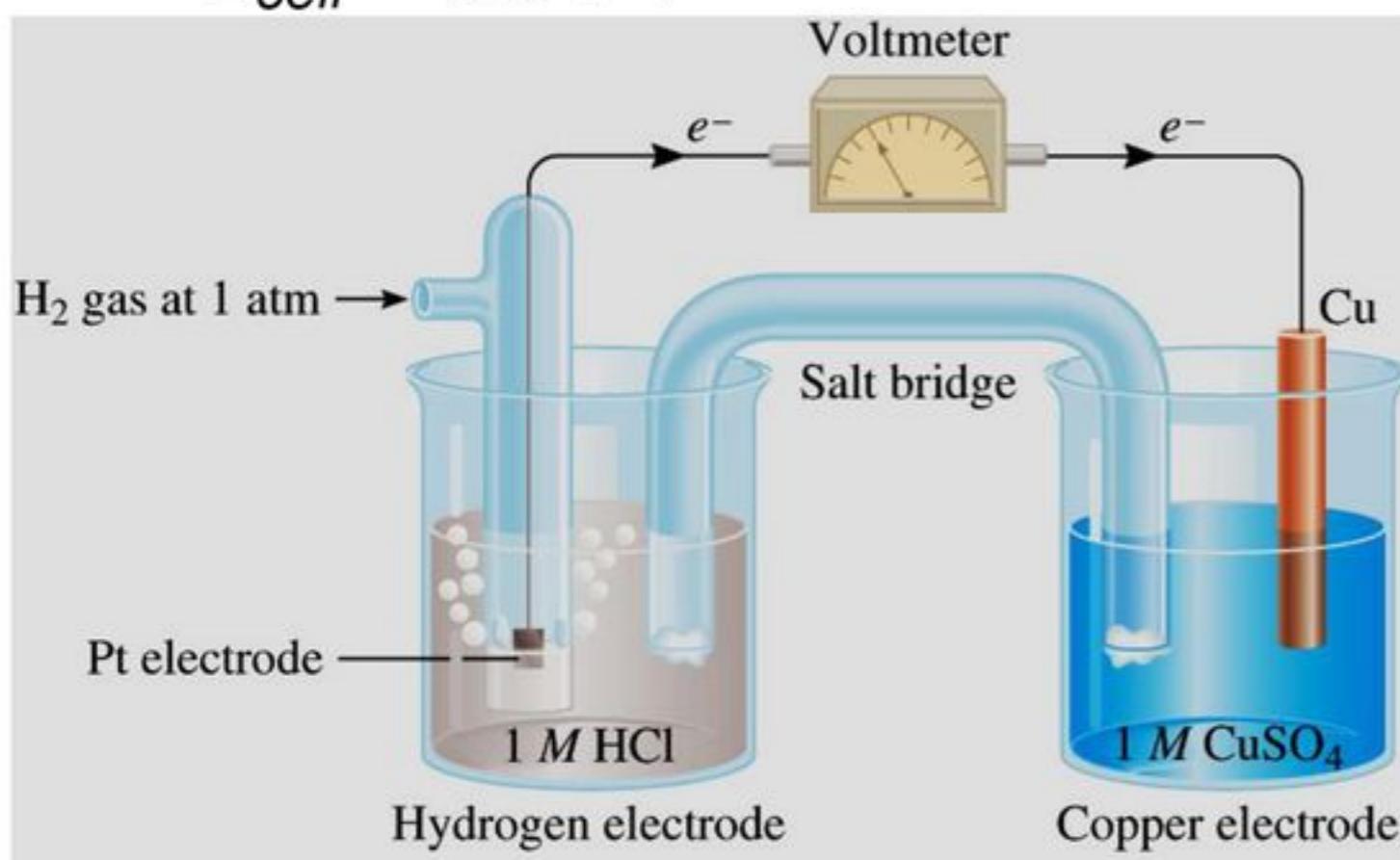
The diagram to the right illustrates what really happens when a Galvanic cell is constructed from zinc sulfate and copper(II) sulfate using the respective metals as electrodes.

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



# Standard Reduction Potentials

$$E_{cell}^0 = 0.34 \text{ V}$$

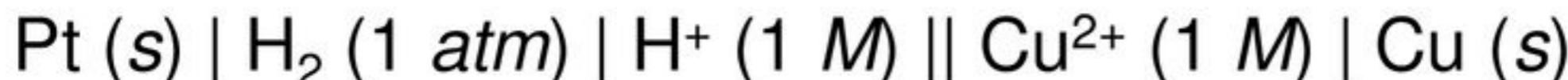


$$E_{cell}^0 = E_{cathode}^0 - E_{anode}^0$$

$$E_{cell}^0 = E_{Cu^{2+}/Cu}^0 - E_{H^+/H_2}^0$$

$$0.34 = E_{Cu^{2+}/Cu}^0 - 0$$

$$E_{Cu^{2+}/Cu}^0 = 0.34 \text{ V}$$



Anode (oxidation):



Cathode (reduction):  $2\text{e}^- + \text{Cu}^{2+} (1 \text{ M}) \longrightarrow \text{Cu (s)}$

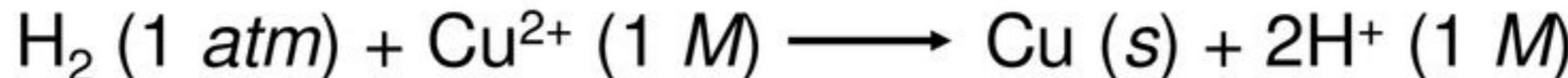


TABLE 19.1 Standard Reduction Potentials at 25°C\*

Half-Reaction	$E^\circ(V)$
$\text{F}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{F}^-(\text{aq})$	+2.87
$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{O}_2(\text{g}) + \text{H}_2\text{O}$	+2.07
$\text{Co}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Co}^{2+}(\text{aq})$	+1.82
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$	+1.77
$\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2\text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}$	+1.70
$\text{Ce}^{4+}(\text{aq}) + \text{e}^- \rightarrow \text{Ce}^{3+}(\text{aq})$	+1.61
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}$	+1.51
$\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Au}(\text{s})$	+1.50
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$	+1.36
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}$	+1.33
$\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}$	+1.23
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	+1.23
$\text{Br}_2(\text{l}) + 2\text{e}^- \rightarrow 2\text{Br}^-(\text{aq})$	+1.07
$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \rightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}$	+0.96
$2\text{Hg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Hg}_2^{2+}(\text{aq})$	+0.92
$\text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Hg}(\text{l})$	+0.85
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	+0.80
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2(\text{aq})$	+0.68
$\text{MnO}_4^-(\text{aq}) + 2\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{MnO}_2(\text{s}) + 4\text{OH}^-(\text{aq})$	+0.59
$\text{I}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{I}^-(\text{aq})$	+0.53
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$	+0.40
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.34
$\text{AgCl}(\text{s}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) + \text{Cl}^-(\text{aq})$	+0.22
$\text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}$	+0.20
$\text{Cu}^{2+}(\text{aq}) + \text{e}^- \rightarrow \text{Cu}^+(\text{aq})$	+0.15
$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}^{2+}(\text{aq})$	+0.13
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0.00
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$	-0.13
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}(\text{s})$	-0.14
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.25
$\text{Co}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Co}(\text{s})$	-0.28
$\text{PbSO}_4(\text{s}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq})$	-0.31
$\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cd}(\text{s})$	-0.40
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.44
$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Cr}(\text{s})$	-0.74
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Mn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mn}(\text{s})$	-1.18
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Al}(\text{s})$	-1.66
$\text{Be}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Be}(\text{s})$	-1.85
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mg}(\text{s})$	-2.37
$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.71
$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ca}(\text{s})$	-2.87
$\text{Sr}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sr}(\text{s})$	-2.89
$\text{Ba}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ba}(\text{s})$	-2.90
$\text{K}^+(\text{aq}) + \text{e}^- \rightarrow \text{K}(\text{s})$	-2.93
$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.05

Increasing strength as reducing agent

- $E^\circ$  is for the reaction as written
- The more positive  $E^\circ$  the greater the tendency for the substance to be reduced
- The half-cell reactions are reversible
- The sign of  $E^\circ$  changes when the reaction is reversed
- Changing the stoichiometric coefficients of a half-cell reaction **does not** change the value of  $E^\circ$

- Elements that have the most positive reduction potentials are easily reduced (*in general, non-metals*)
- Elements that have the least positive reduction potentials are easily oxidized (*in general, metals*)
- The table can also be used to tell the **strength** of various oxidizing and reducing agents.
- 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 be reduced - IF you are trying to set up a cell that can act as a battery.

## How to Calculate “Standard Cell Potential”, Symbolized by $E^\circ_{cell}$ OR $Emf^\circ$ OR $\varepsilon_{cell}^\circ$ (*terms are interchangeable*)

1. Decide which element is oxidized or reduced using the table of reduction potentials.

Remember: **THE MORE POSITIVE REDUCTION POTENTIAL GETS TO BE REDUCED.**

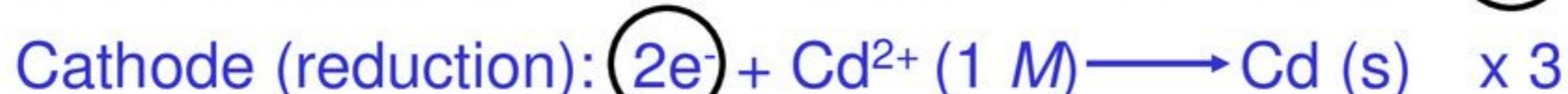
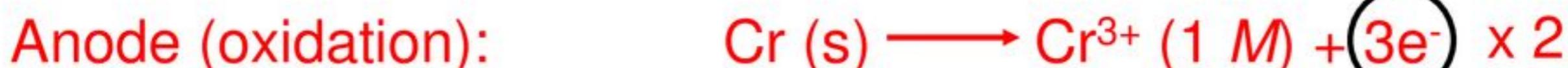
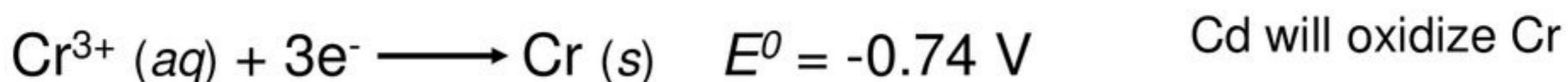
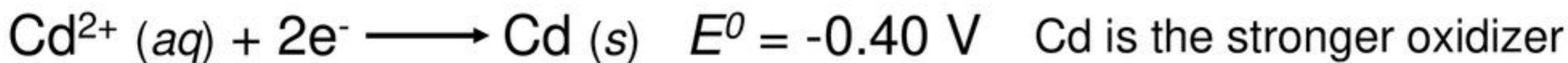
2. Write both equations AS IS from the chart with their voltages.
3. Reverse the equation that will be oxidized **and change the sign** of the voltage - This is now:  $E^\circ_{oxidation}$
4. Balance the two half reactions **\*\*do not multiply voltage values\*\***
5. Add the two half reactions and the voltages together.
6.  $E^\circ_{cell} = E^\circ_{oxidation} + E^\circ_{reduction}$  (where  $^\circ$  means standard conditions: 1atm, 1M, 25°C)

## **Neumonic Devices - Handy when constructing a “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**
- EPA--in an electrolytic cell, there is a positive (+) anode.**
- Salt Bridge – bridge between cells whose purpose is to provide ions to balance the charge.** Usually made of a salt filled agar (KNO<sub>3</sub>) or a porous cup.



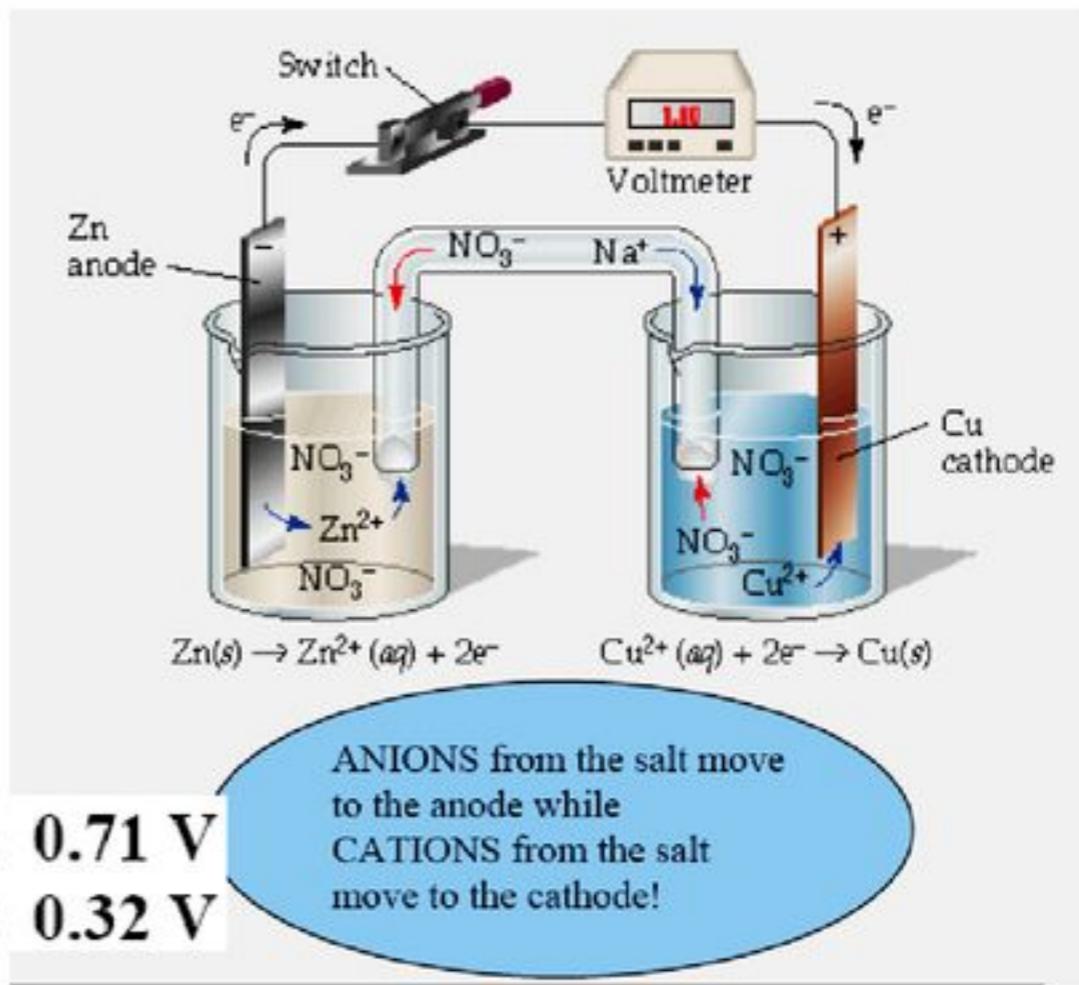
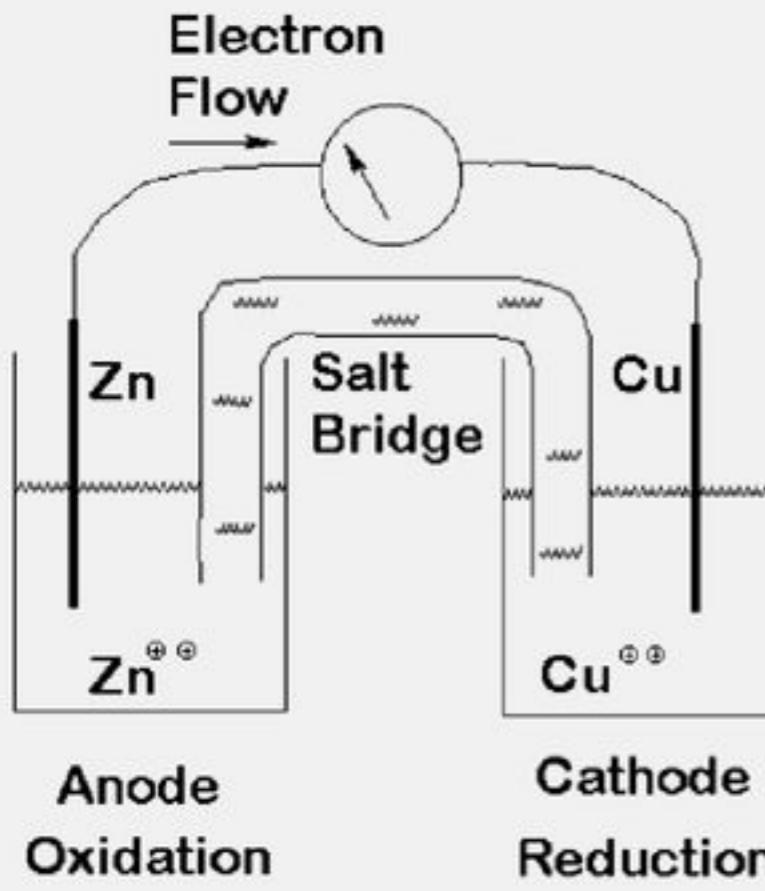
What is the standard emf of an electrochemical cell made of a Cd electrode in a 1.0 M Cd(NO<sub>3</sub>)<sub>2</sub> solution and a Cr electrode in a 1.0 M Cr(NO<sub>3</sub>)<sub>3</sub> solution?



$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

$$E_{\text{cell}}^{\circ} = -0.40 - (-0.74)$$

$$E_{\text{cell}}^{\circ} = 0.34 \text{ V}$$



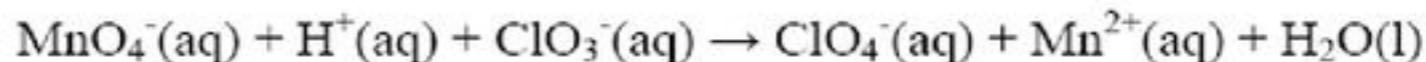
### Exercise 1

a. Consider a galvanic cell based on the reaction



Give the balanced cell reaction and calculate  $E^\circ$  for the cell.

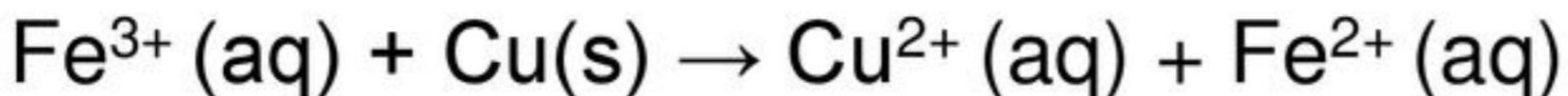
b. A galvanic cell is based on the reaction [you'll need a more complete table of reduction potentials!]



Give the balanced cell reaction and calculate  $E^\circ$  for the cell.

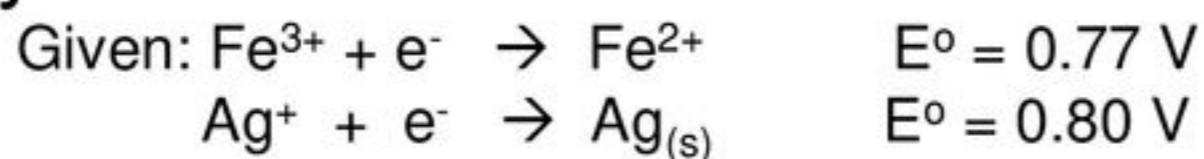
*Sample Problem:*

- a) Calculate the cell voltage for the following reaction.
- b) Draw a diagram of the galvanic cell for the reaction and label completely.



## Exercise 2

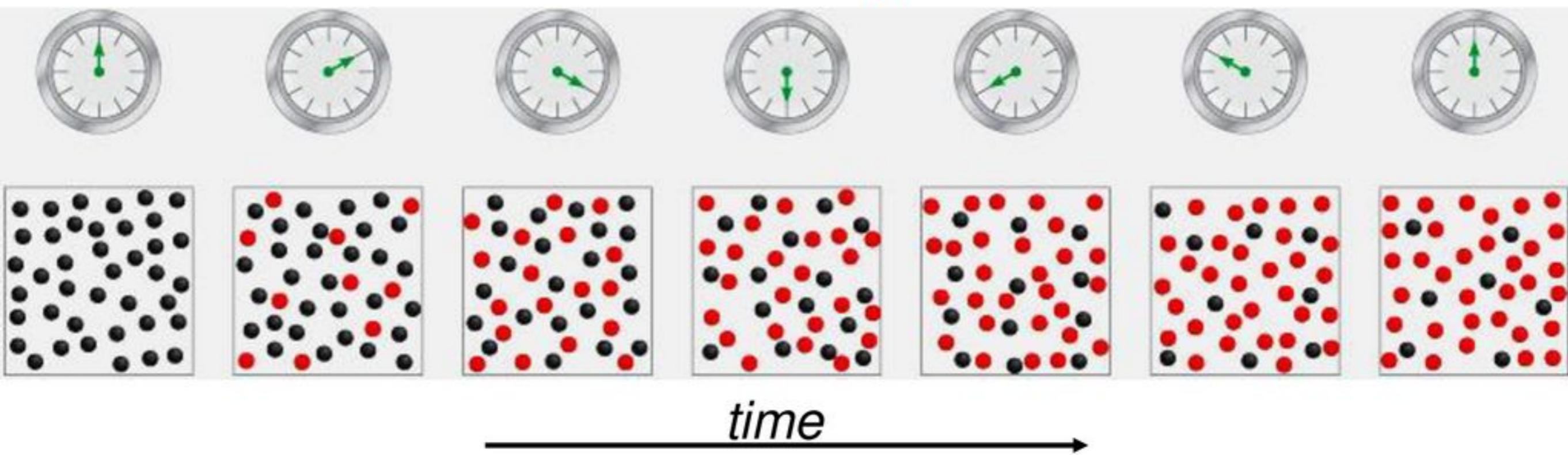
- a) Calculate the cell voltage for the galvanic cell that would utilize silver metal and involve iron(II) ion and iron(III) ion.
- b) Draw a diagram of the galvanic cell for the reaction and label completely.



$$E^\circ_{\text{cell}} = 0.03 \text{ V}$$

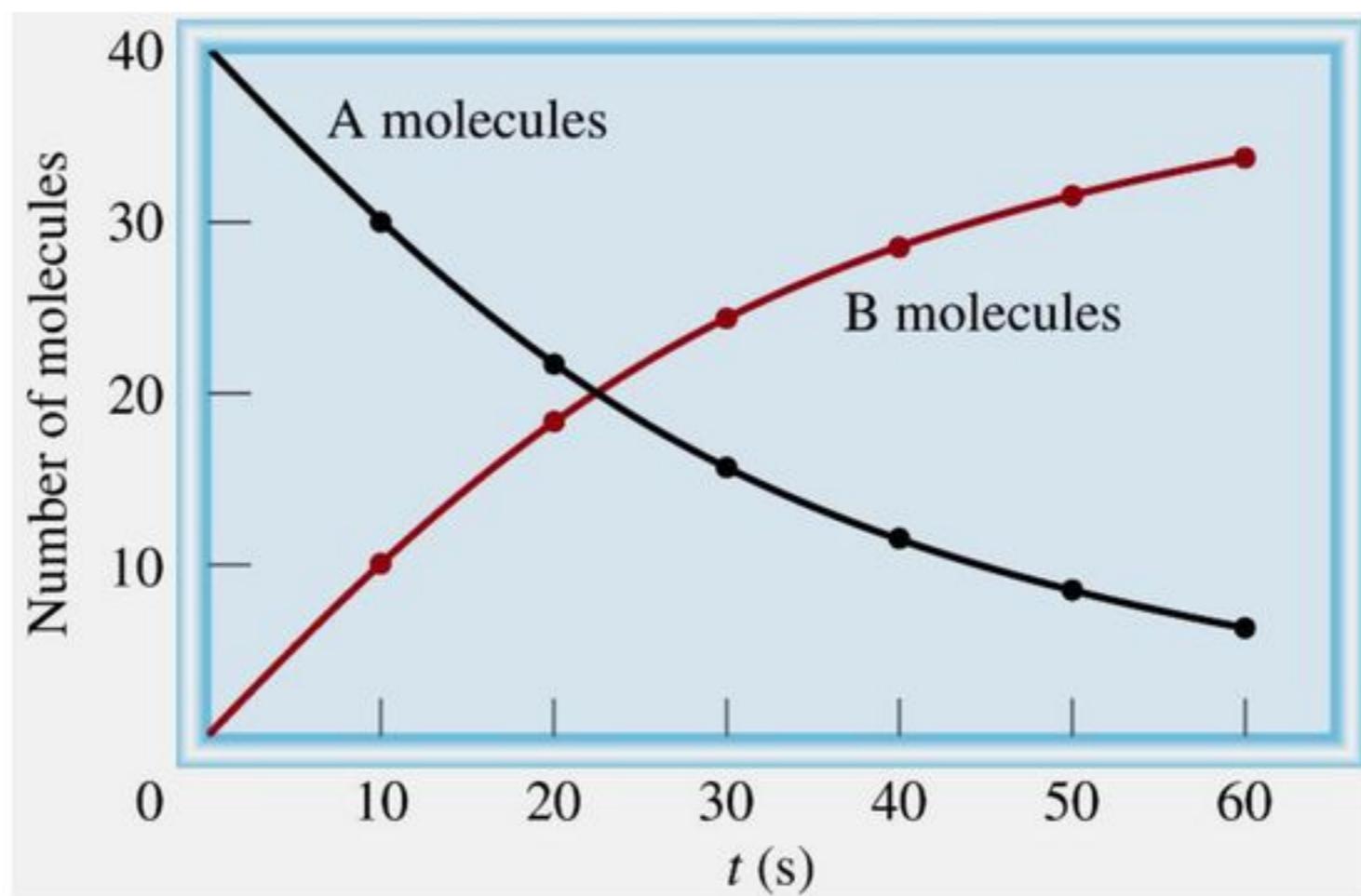
# Reaction Quotient

- Q: equal to equilibrium expression but does not have to be at equilibrium
- used to tell if a reaction is at equilibrium or not
- relationship between Q and K tells which way the reaction will shift
  - $Q = K$ : at equilibrium, no shift
  - $Q > K$ : too large, forms reactants, shift to left
  - $Q < K$ : too small, forms products, shift to right



$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$



# Law of Mass Action

- created in 1864 by Guldberg and Waage (Norweigen)
- For a reaction:  $jA + kB \rightleftharpoons lC + mD$ 
  - equilibrium constant: K

# Law of Mass Action

- because
  - $\text{Rate}_f = k_f[A]^j[B]^k$
  - $\text{Rate}_r = k_r[C]^l[D]^m$
  - so if  $\text{Rate}_f = \text{Rate}_r$
  - $k_f[A]^j[B]^k = k_r[C]^l[D]^m$

$$\frac{k_f}{k_r} = K = \frac{[C]^l [D]^m}{[A]^j [B]^k}$$

# Spontaneity of Redox Reactions

$$\Delta G = -nFE_{\text{cell}} \quad n = \text{number of moles of electrons in reaction}$$

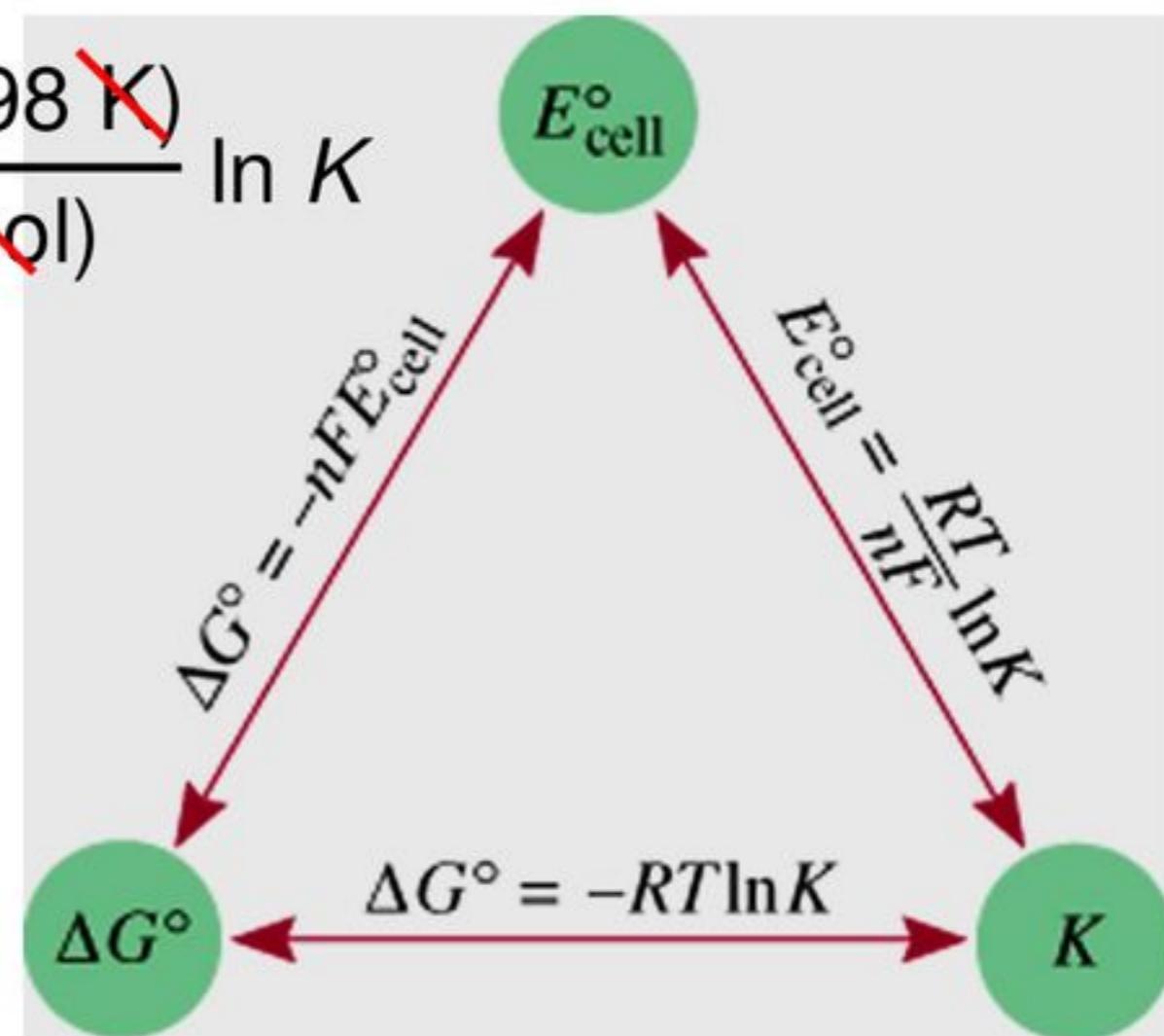
$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ} \quad F = 96,500 \frac{\text{J}}{\text{V} \cdot \text{mol}} = 96,500 \text{ C/mol}$$

$$\Delta G^{\circ} = -RT \ln K = -nFE_{\text{cell}}^{\circ}$$

$$E_{\text{cell}}^{\circ} = \frac{RT}{nF} \ln K = \frac{(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K})}{n (96,500 \text{ J/V}\cdot\text{mol})} \ln K$$

$$E_{\text{cell}}^{\circ} = \frac{0.0257 \text{ V}}{n} \ln K$$

$$E_{\text{cell}}^{\circ} = \frac{0.0592 \text{ V}}{n} \log K$$



# Spontaneity of Redox Reactions

**TABLE 19.2** Relationships Among  $\Delta G^\circ$ ,  $K$ , and  $E_{\text{cell}}^\circ$

$\Delta G^\circ$	$K$	$E_{\text{cell}}^\circ$	Reaction Under Standard-State Conditions
Negative	$>1$	Positive	Favors formation of products.
0	$=1$	0	Reactants and products are equally favored.
Positive	$<1$	Negative	Favors formation of reactants.

$$\Delta G^\circ = -RT \ln K = -nFE_{\text{cell}}^\circ$$



What is the equilibrium constant for the following reaction at 25°C?  $\text{Fe}^{2+}(\text{aq}) + 2\text{Ag}(\text{s}) \rightleftharpoons \text{Fe}(\text{s}) + 2\text{Ag}^+(\text{aq})$

$$E_{\text{cell}}^0 = \frac{0.0257 \text{ V}}{n} \ln K$$

Oxidation:



$$n = 2$$



$$E^0 = E_{\text{Fe}^{2+}/\text{Fe}}^0 - E_{\text{Ag}^+/\text{Ag}}^0$$

$$E^0 = -0.44 - (0.80)$$

$$E^0 = -1.24 \text{ V}$$

$$K = \exp \left[ \frac{E_{\text{cell}}^0 \times n}{0.0257 \text{ V}} \right] = \exp \left[ \frac{-1.24 \text{ V} \times 2}{0.0257 \text{ V}} \right]$$

$$K = 1.23 \times 10^{-42}$$

## The Effect of Concentration on Cell Emf

$$\Delta G = \Delta G^0 + RT \ln Q \quad \Delta G = -nFE \quad \Delta G^0 = -nFE^0$$

$$-nFE = -nFE^0 + RT \ln Q$$

**Nernst equation**

$$E = E^0 - \frac{RT}{nF} \ln Q$$

At 298

$$E = E^0 - \frac{0.0257 \text{ V}}{n} \ln Q$$

$$E = E^0 - \frac{0.0592 \text{ V}}{n} \log Q$$

# CELL POTENTIAL, ELECTRICAL WORK & FREE ENERGY

Combining thermodynamics and electrochemistry, and a bit of physics:

- The work that can be accomplished when electrons are transferred through a wire depends on the “push” or *emf* which is defined in terms of a potential difference [in volts] between two points in the circuit.

$$(V = J/C)$$

$$emf(V) = \varepsilon = \frac{work(J)}{charge(C)}$$

Thus “one joule of work” is produced [or required] when one coulomb of charge is transferred between two points in the circuit that differ by a potential of one volt

- IF work flows OUT it is assigned a MINUS sign

When a cell produces a current, the cell potential is positive and the current can be used to do work THEREFORE “ $\varepsilon$ ” and “work” have opposite signs!

$$\varepsilon = -\frac{\text{work(J)}}{\text{charge(C)}} = \frac{-w}{q} \therefore -w = \varepsilon q$$

A “faraday” ( $F$ ) - *the charge on one MOLE of electrons = 96,485 coulombs (AP Exam uses 96,500) And:  $q = \# \text{ moles of electrons} \times F$*

For a process carried out at constant temperature and pressure,  $w_{\max}$  [*neglecting the very small amount of energy that is lost as friction or heat*] is equal to  $\Delta G$ , therefore....

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

$G$  = *Gibb's free energy*

$n$  = *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!*)



Will the following reaction occur spontaneously at 25°C if  $[Fe^{2+}] = 0.60\text{ M}$  and  $[Cd^{2+}] = 0.010\text{ M}$ ?



Oxidation:



$$n = 2$$

Reduction:  $2e^- + Fe^{2+} \longrightarrow Fe$

$$E^0 = E_{Fe^{2+}/Fe}^0 - E_{Cd^{2+}/Cd}^0$$

$$E^0 = -0.44 - (-0.40)$$

$$E^0 = -0.04\text{ V}$$

$$E = E^0 - \frac{0.0257\text{ V}}{n} \ln Q$$

$$E = -0.04\text{ V} - \frac{0.0257\text{ V}}{2} \ln \frac{0.010}{0.60}$$

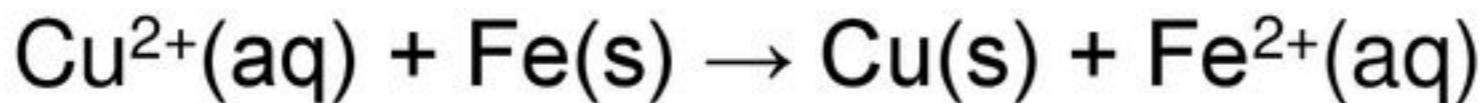
$$E = 0.013$$

$$E > 0$$

Spontaneous

## Bell Work - 9-27-2013 (Exercise 3)

Using the table of standard reduction potentials, calculate  $\Delta G^\circ$  for the reaction



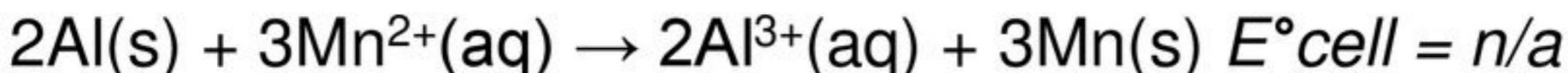
## **Exercise 4**

Using the table of standard reduction potentials, predict whether 1 M HNO<sub>3</sub> will dissolve gold metal to form a 1 M Au<sup>3+</sup> solution.

## DEPENDENCE OF CELL POTENTIAL ON CONCENTRATION

**Voltaic cells at NON-standard conditions: LeChatlier's principle can be applied.** An increase in the concentration of a reactant will favor the forward reaction and the cell potential will increase. (The converse is also true!)

**Exercise 5** - For the cell reaction:



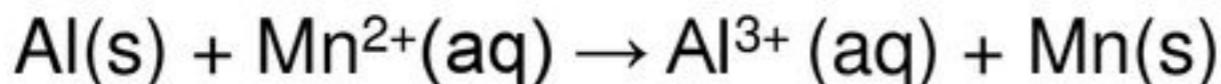
predict whether  $E_{\text{cell}}$  is larger or smaller than  $E^\circ_{\text{cell}}$  for the following cases.

a.  $[\text{Al}^{3+}] = 2.0 \text{ M}$ ,  $[\text{Mn}^{2+}] = 1.0 \text{ M}$

b.  $[\text{Al}^{3+}] = 1.0 \text{ M}$ ,  $[\text{Mn}^{2+}] = 3.0 \text{ M}$

# Bell Work Oct 19, 2013

For the cell reaction:



1) Balance the equation

2) Calc  $E^\circ_{cell}$

3) Predict whether  $E_{cell}$  is larger or smaller than  $E^\circ_{cell}$  for the following cases.

a.  $[\text{Al}^{3+}] = 2.0 \text{ M}$ ,  $[\text{Mn}^{2+}] = 1.0 \text{ M}$

b.  $[\text{Al}^{3+}] = 1.0 \text{ M}$ ,  $[\text{Mn}^{2+}] = 3.0 \text{ M}$

4) Calc. the  $E_{cell}$  for each of the above solutions.

5) Calc  $\Delta G^\circ$  for the “std conditions rxn” (#2) and  $\Delta G$  for each of the different concentrations from #3

For a more quantitative approach..... When cell is not at standard conditions, use **Nernst Equation:**

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

$$E = E^\circ - \frac{0.0592}{n} \log Q \text{ @ } 25^\circ\text{C (298K)}$$

*R = Gas constant 8.315 J/K• mol*

*F = Faraday constant*

*Q = reaction quotient [products]<sup>coefficient</sup>/[reactants]<sup>coefficient</sup>*

*E = Energy produced by reaction*

*T = Temperature in Kelvins*

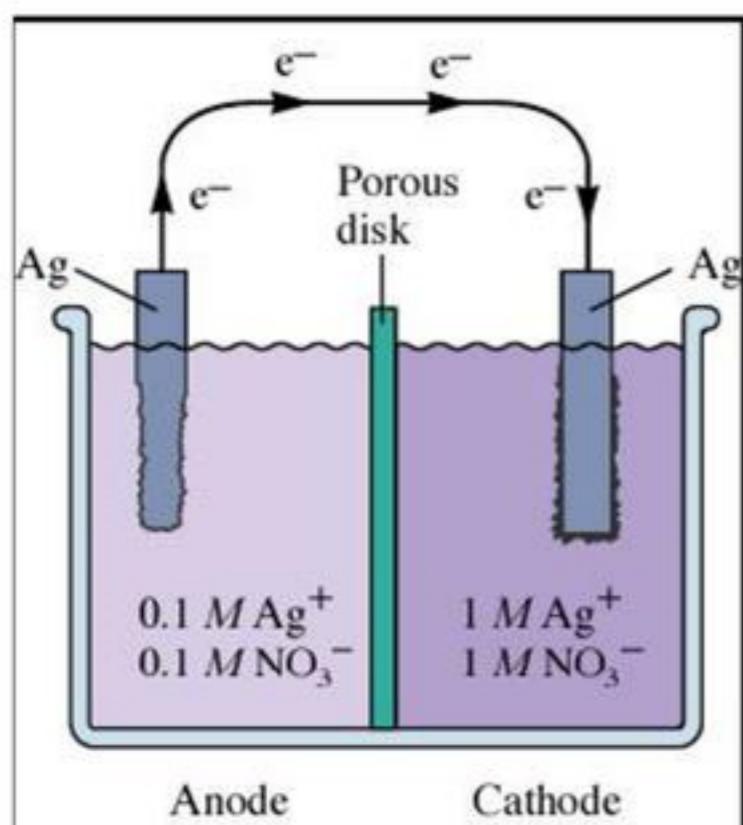
*n = # of electrons exchanged in BALANCED redox equation*

As  $E$  declines with reactants converting to products,  $E$  eventually reaches zero.

**Zero potential means reaction is at equilibrium [dead battery]. Also,  $Q = K$  AND  $\Delta G = 0$  as well.**

## CONCENTRATION CELLS

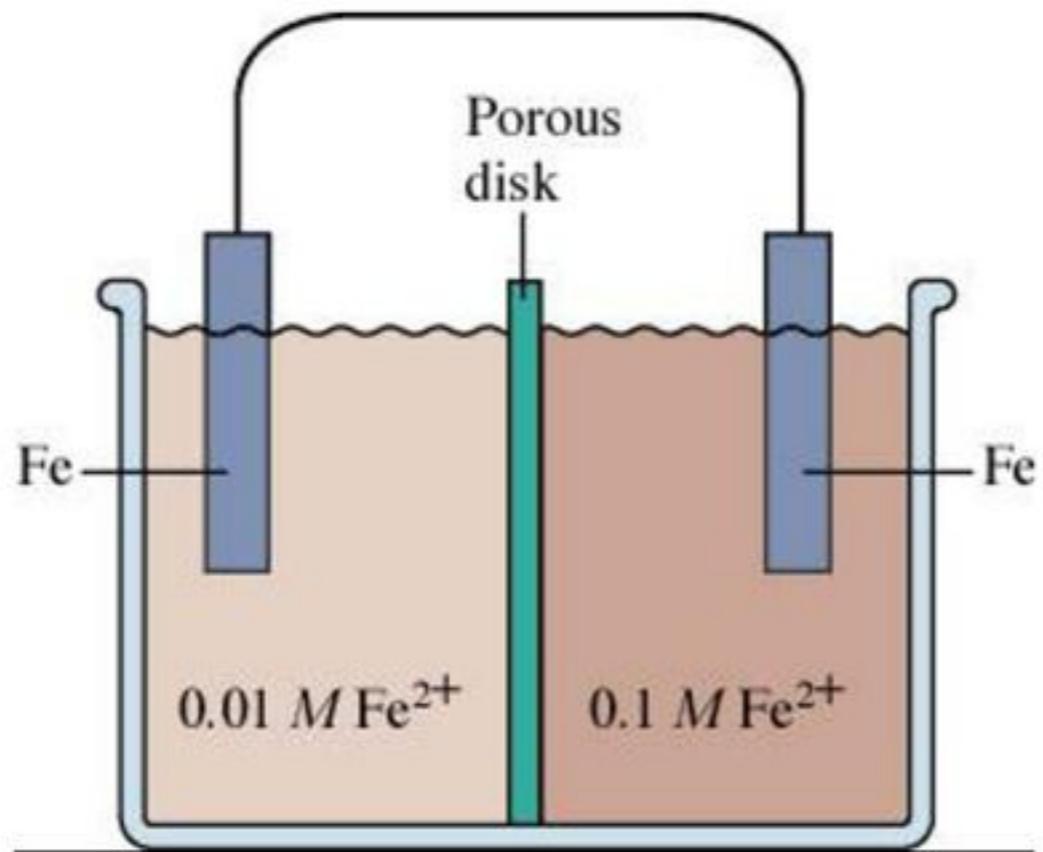
We can construct a cell where both compartments contain the **same** components BUT at **different** concentrations.



Notice the difference in the concentrations pictured at left. Because the right compartment contains  $1.0 \text{ M } \text{Ag}^+$  and the left compartment contains  $0.10 \text{ M } \text{Ag}^+$ , there will be a driving force to transfer electrons from left to right. Silver will be deposited on the right electrode, thus lowering the concentration of  $\text{Ag}^+$  in the right compartment. In the left compartment the silver electrode dissolves [producing  $\text{Ag}^+$  ions] to raise the concentration of  $\text{Ag}^+$  in solution.

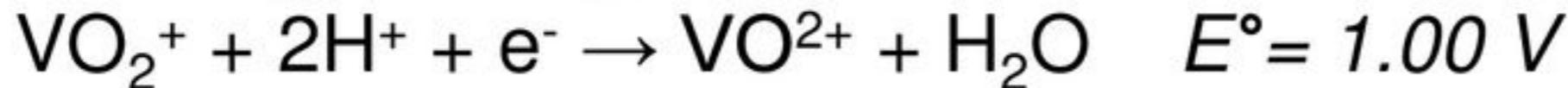
## Exercise 6

Determine the direction of electron flow and designate the anode and cathode for the cell represented here.



## Exercise 7

Determine  $E_{\text{cell}}^{\circ}$  and  $E_{\text{cell}}$  based on the following half-reactions:



Where:

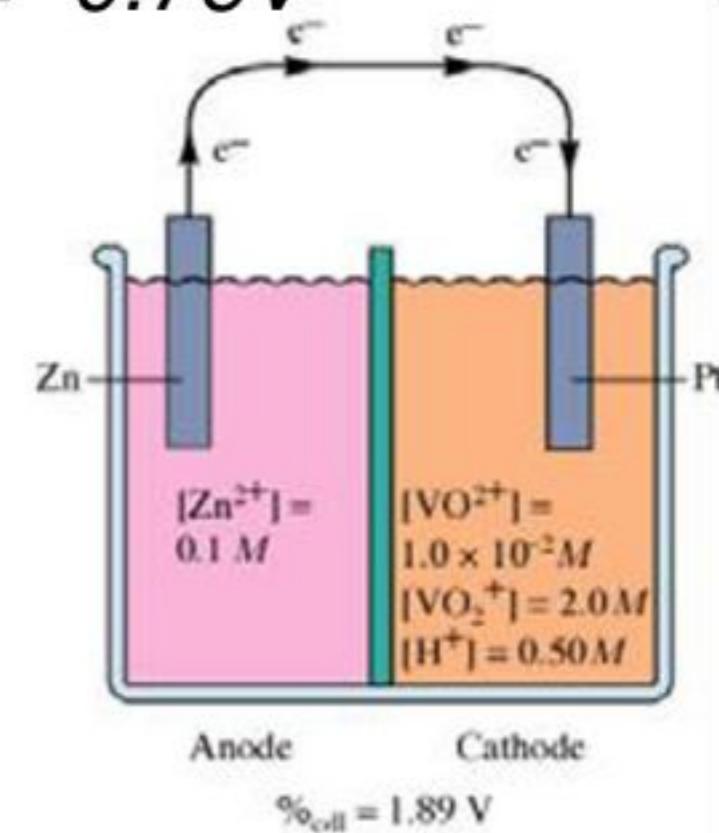
$$T = 25^{\circ}\text{C}$$

$$[\text{VO}_2^+] = 2.0 \text{ M}$$

$$[\text{H}^+] = 0.50 \text{ M}$$

$$[\text{VO}^{2+}] = 1.0 \times 10^{-2} \text{ M}$$

$$[\text{Zn}^{2+}] = 1.0 \times 10^{-1} \text{ M}$$



$$\%_{\text{cell}} = 1.89 \text{ V}$$

$$E_{\text{cell}}^{\circ} = 1.76 \text{ V}$$

$$E_{\text{cell}} = 1.89 \text{ V}$$

# SUMMARY OF GIBB'S FREE ENERGY AND CELLS

$-E^\circ$  implies NON-spontaneous.

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

$E = 0$ , equilibrium reached (dead battery)

The larger the voltage, the more spontaneous the reaction

$\Delta G$  will be negative in spontaneous reactions

$K > 1$  are favored (product favored)

Two important equations:

$$\Delta G = -nFE^\circ \text{ -- ["minus nunfe"]}$$

$$\Delta G = -RT\ln K \text{ -- ["ratlink"]}$$

$G$  = Gibbs free energy [Reaction is spontaneous if  $\Delta G$  is negative]

$n$  = number of moles of electrons.

$F$  = Faraday const.  $9.6485309 \times 10^4 \text{ J/V}$  ( $1 \text{ mol of electrons carries } 96,500 \text{ C}$ )

$E$  = cell potential

$R = 8.31 \text{ J/mol}\cdot\text{K}$

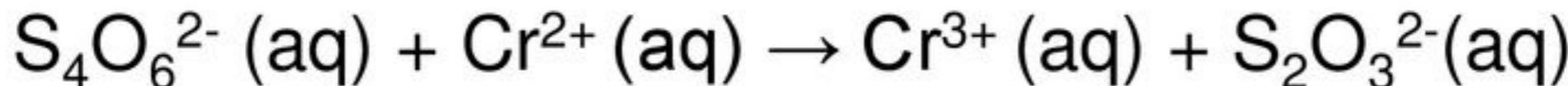
$T$  = Kelvin temperature

$K$  = equilibrium constant --  $[\text{products}]^{\text{coeff}} / [\text{reactants}]^{\text{coeff}}$

\*\*Favored conditions:  $E_{\text{cell}} > 0 \Delta G < 0 K > 1$ \*\*

## Exercise 8

For the oxidation-reduction reaction:



The appropriate half-reactions are:



Balance the redox reaction, and calculate  $E^\circ$  and  $K$  (at 25°C).

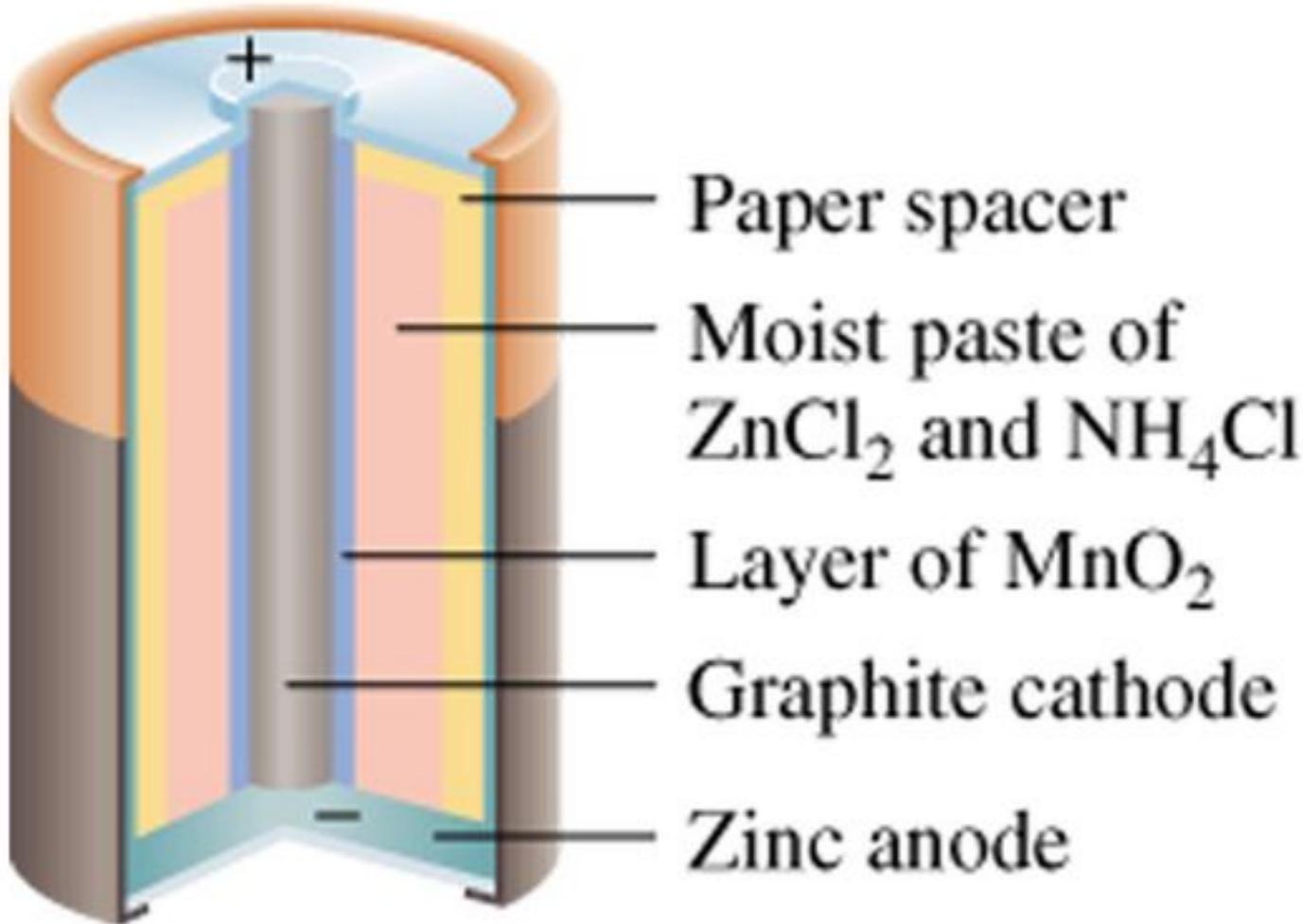
$$E^\circ = 0.67 \text{ V}$$

$$K = 10^{22.6} = 4 \times 10^{22}$$

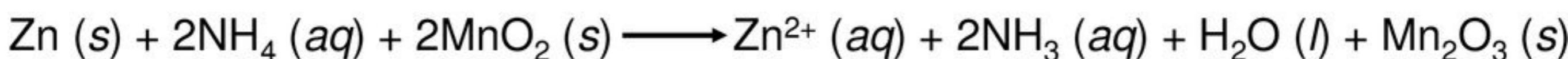
# Batteries

Dry cell

***Leclanché cell***

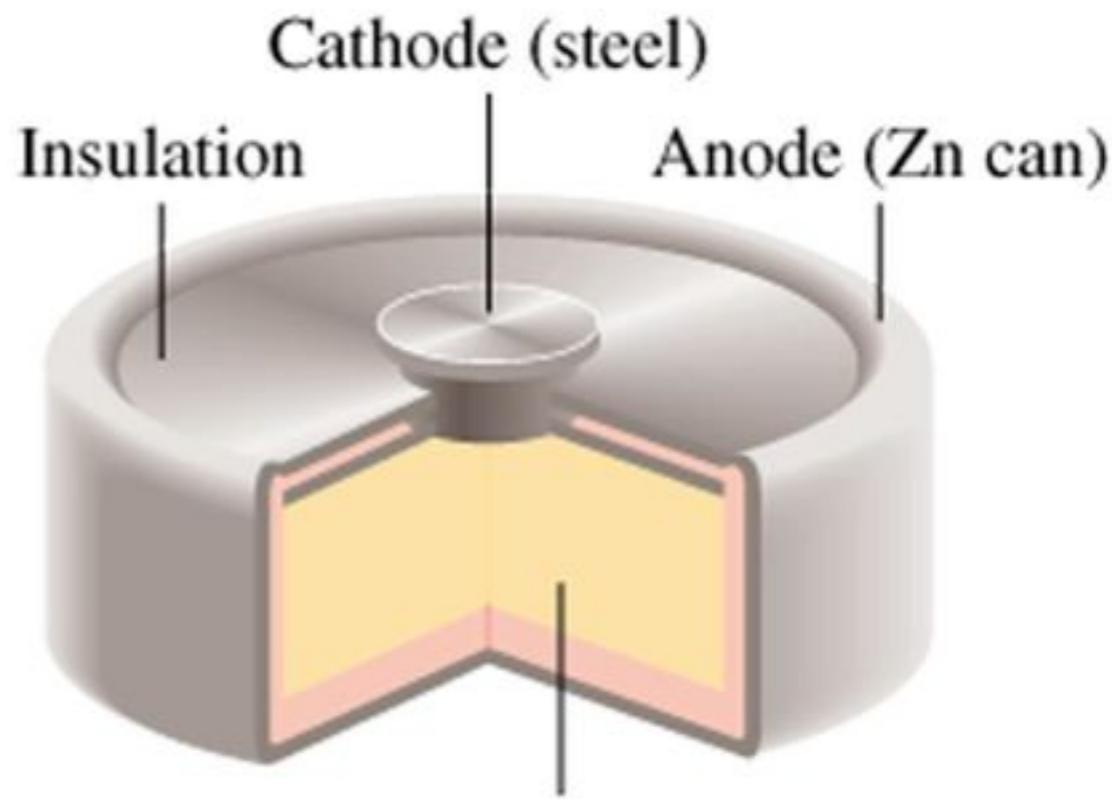


Anode:



# Batteries

## Mercury Battery

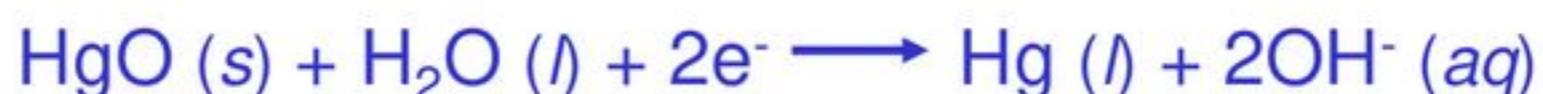


Electrolyte solution containing KOH  
and paste of Zn(OH)<sub>2</sub> and HgO

Anode:

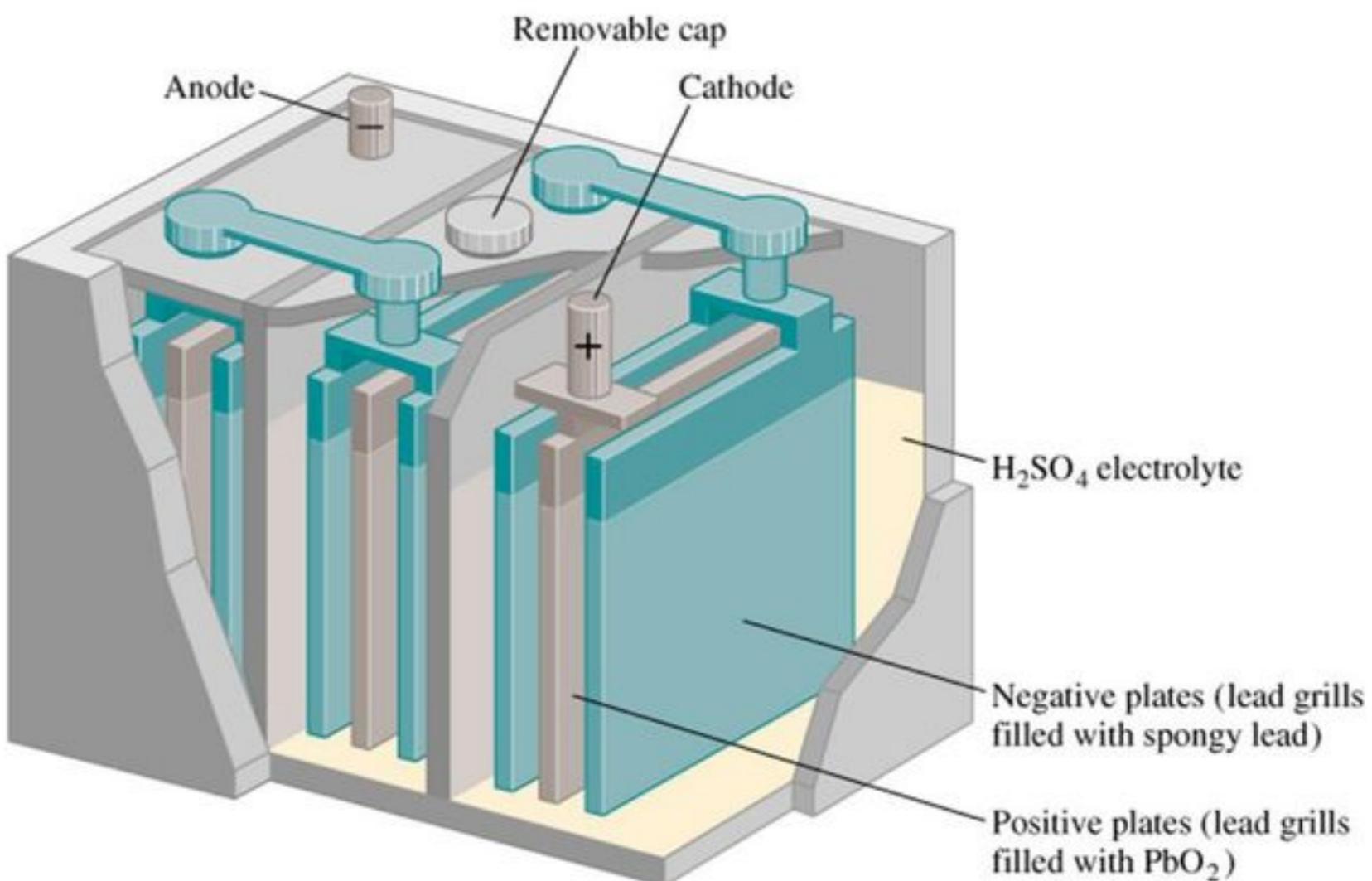


Cathode:



# Batteries

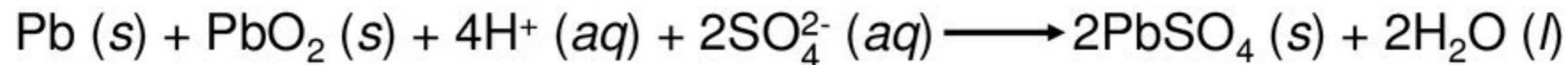
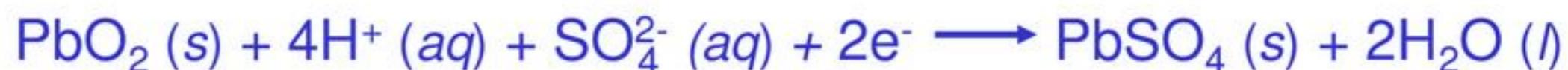
Lead storage battery



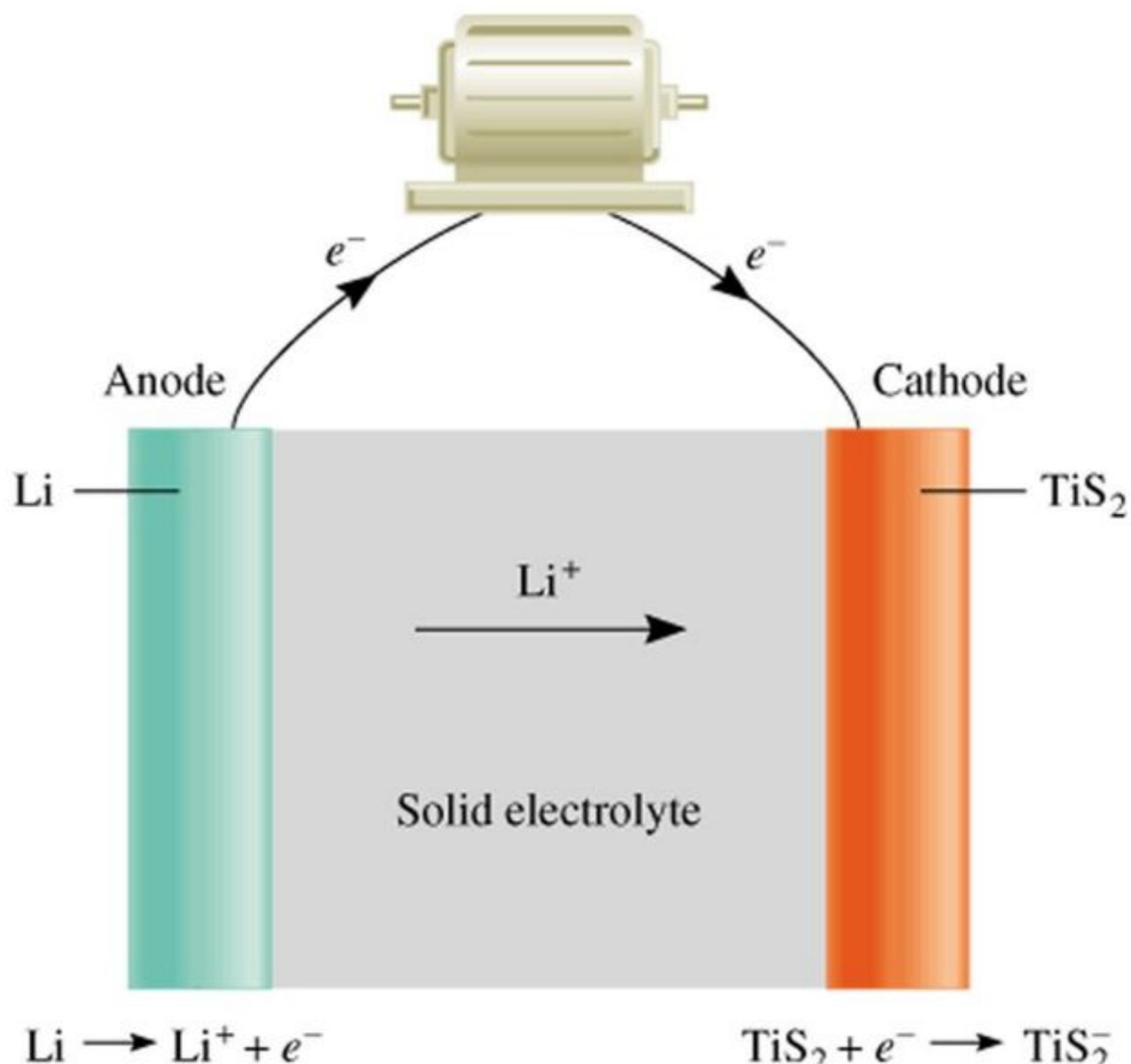
Anode:



Cathode:

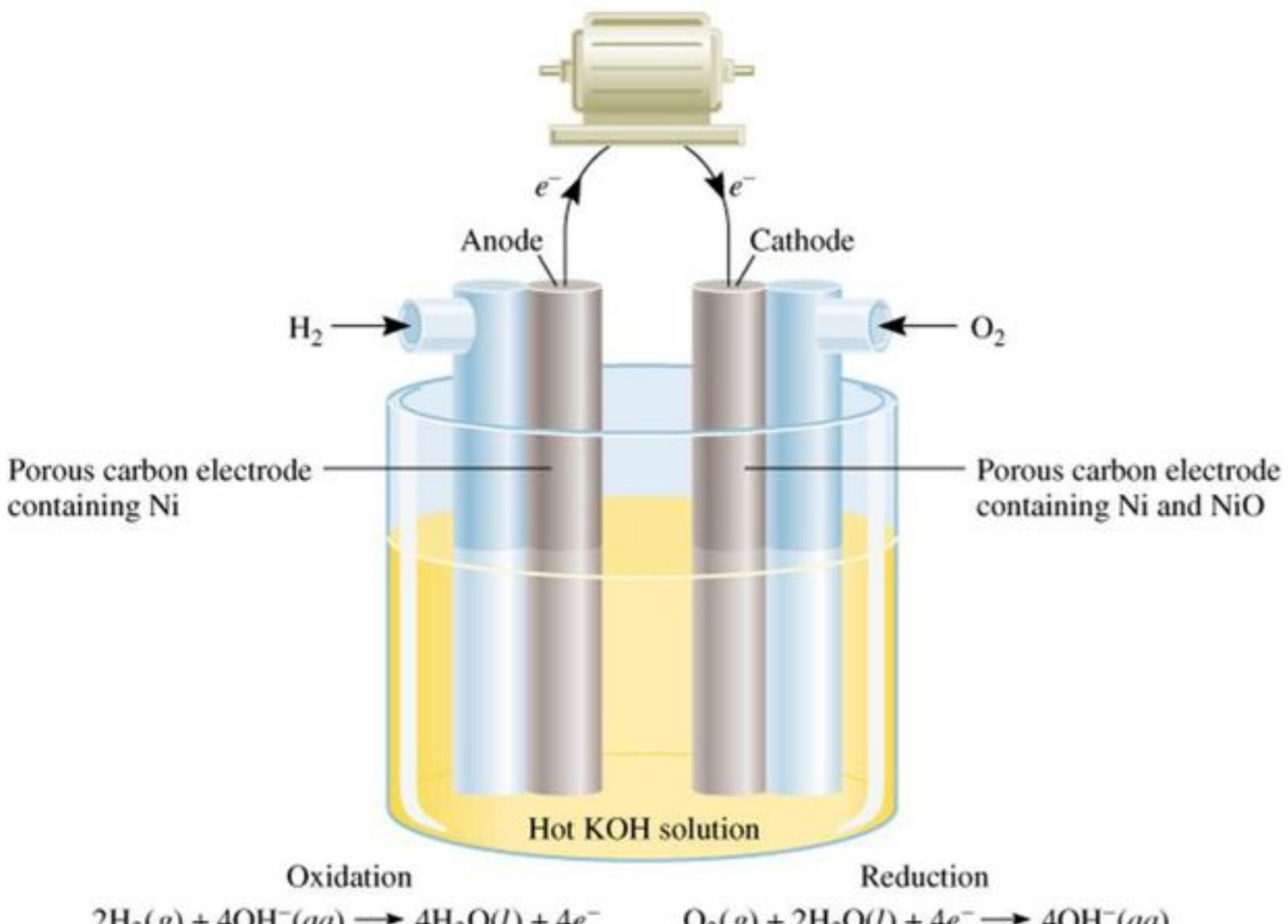


# Batteries



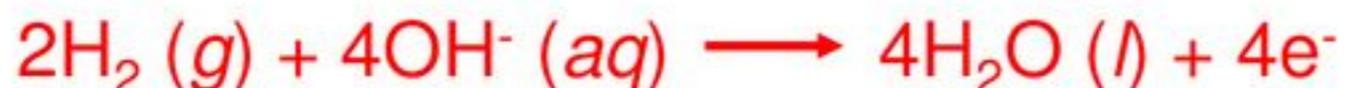
Solid State Lithium Battery

# Batteries

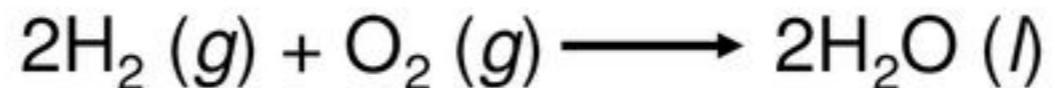


A **fuel cell** is an electrochemical cell that requires a continuous supply of reactants to keep functioning

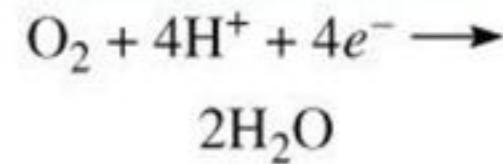
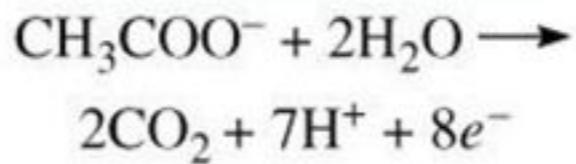
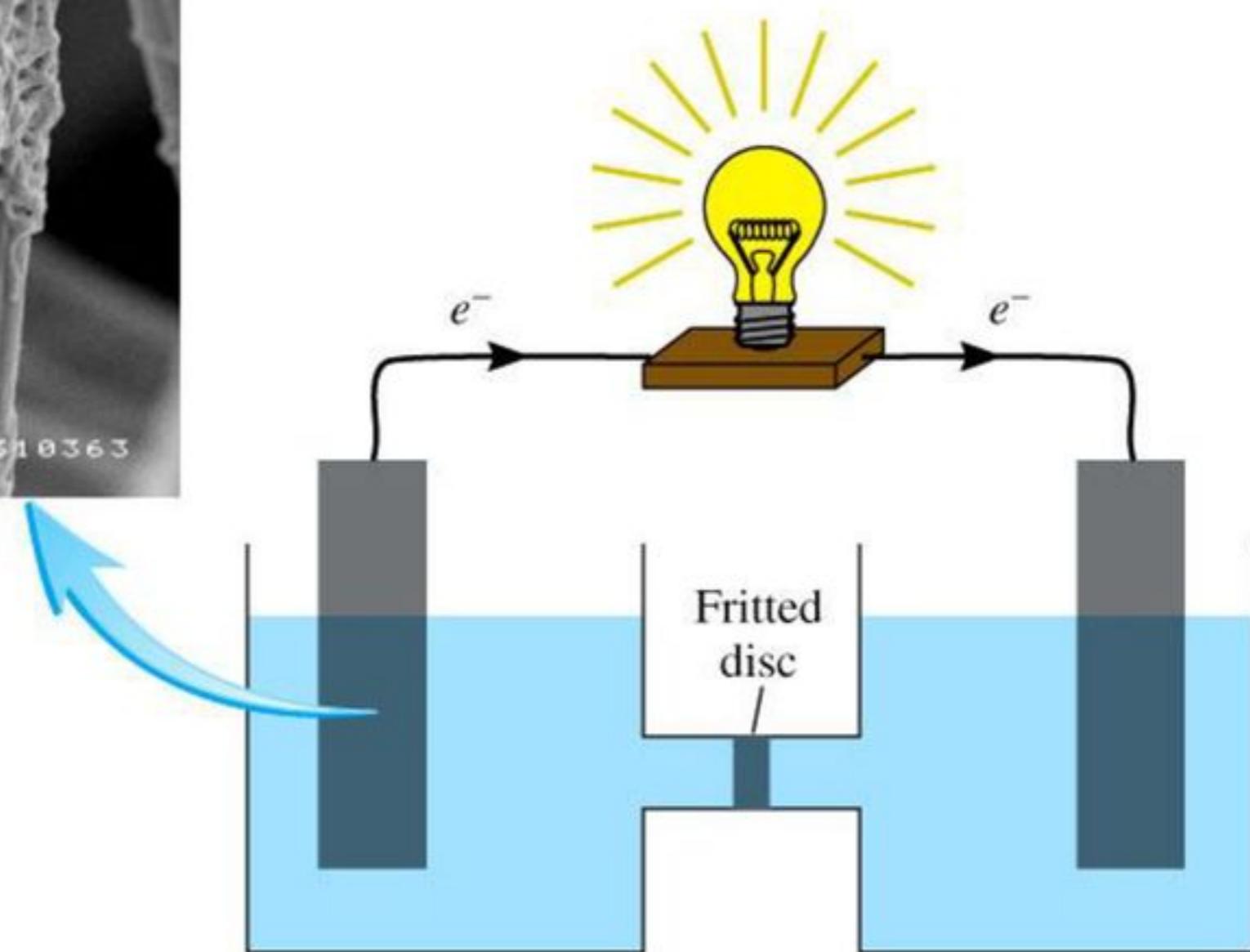
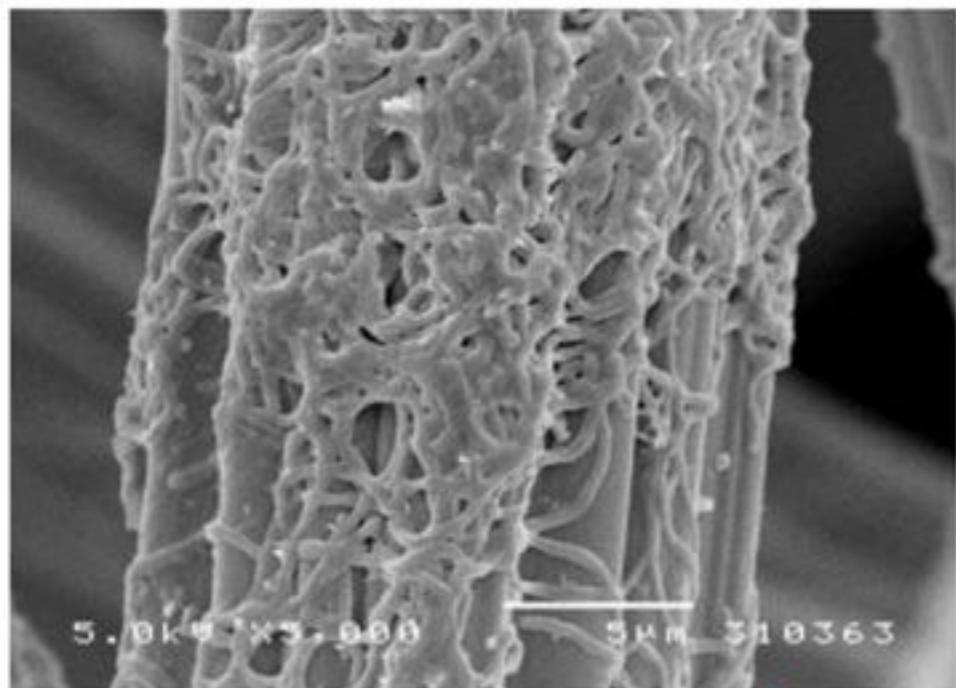
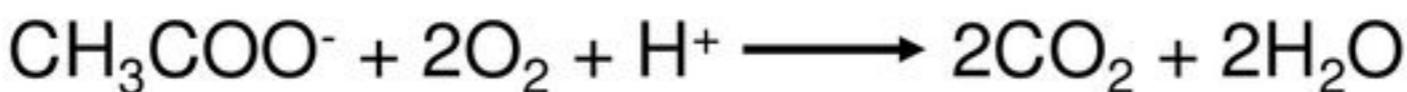
Anode:



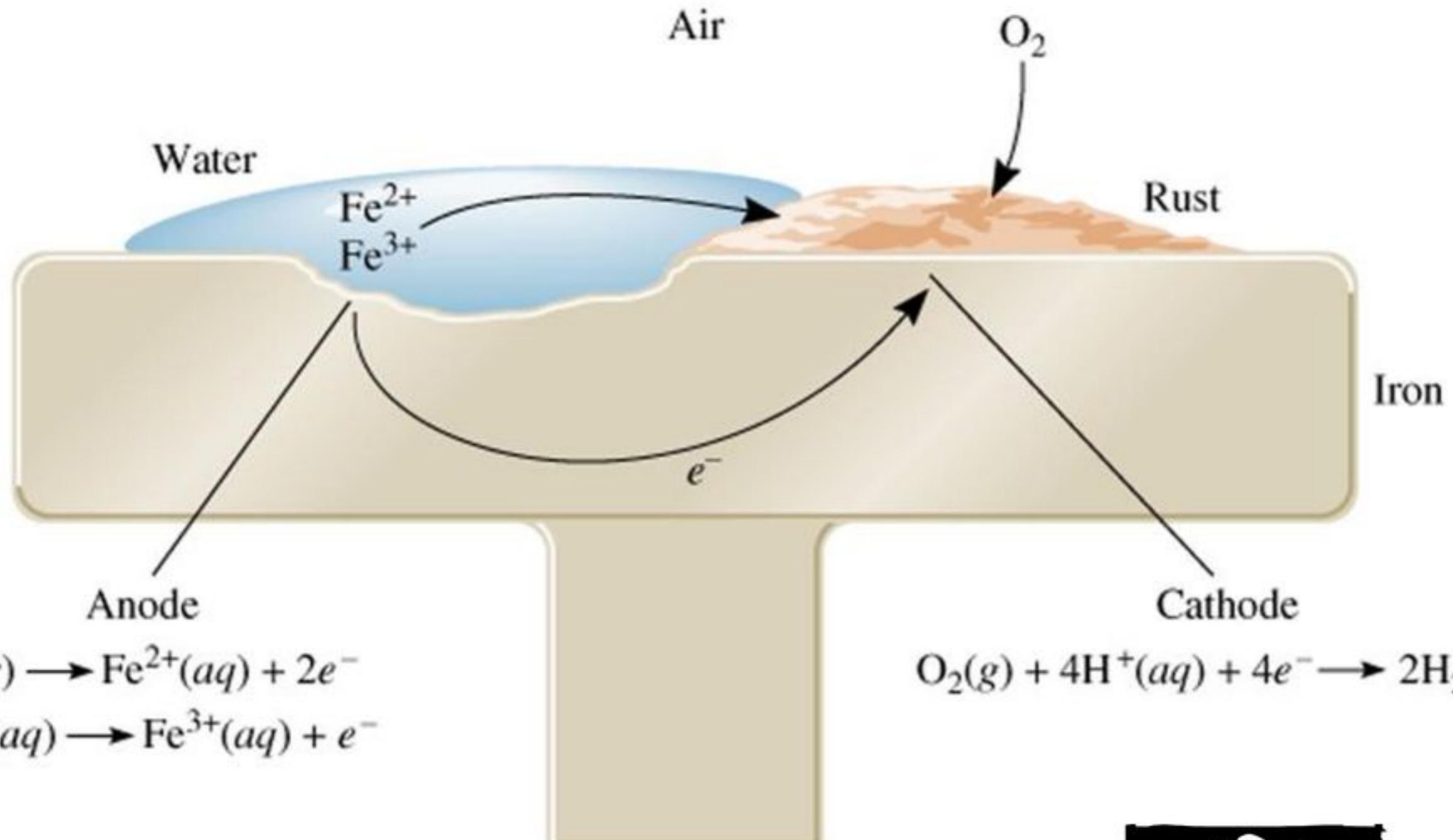
Cathode:



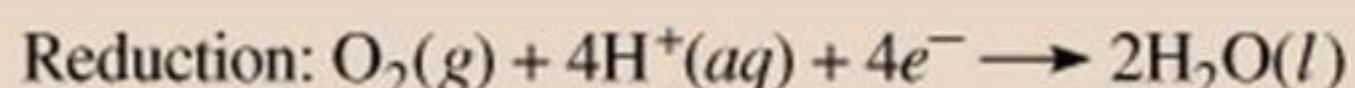
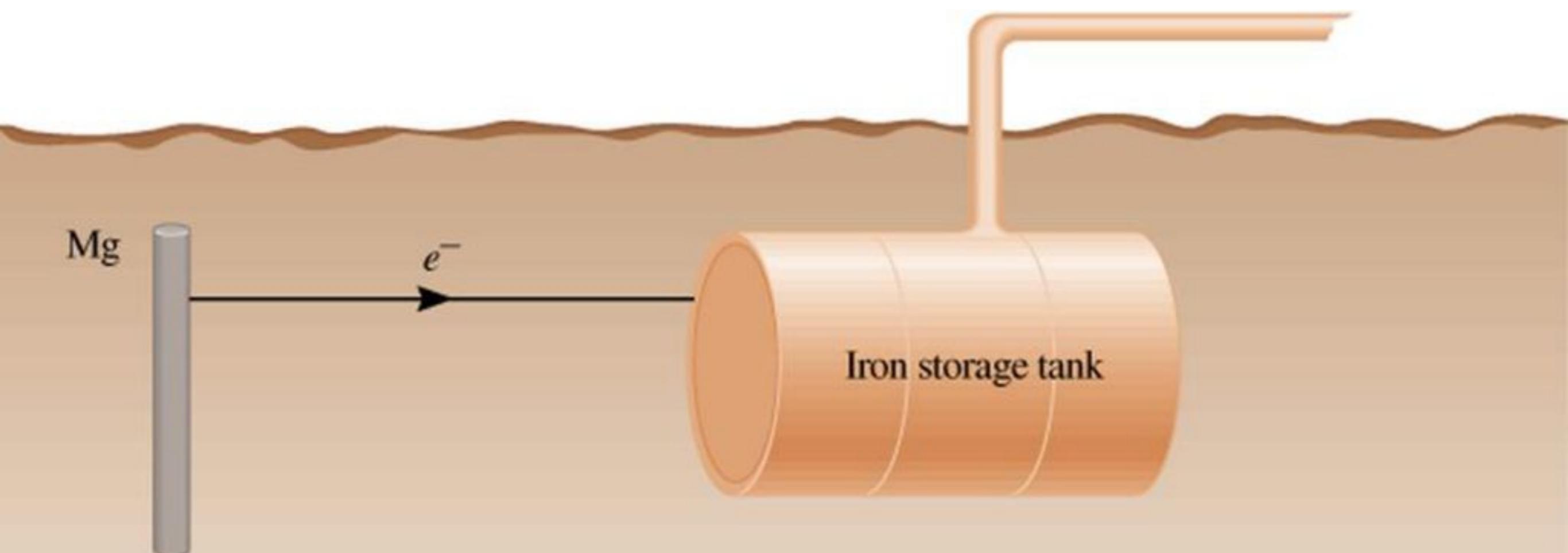
# Chemistry In Action: Bacteria Power



# Corrosion

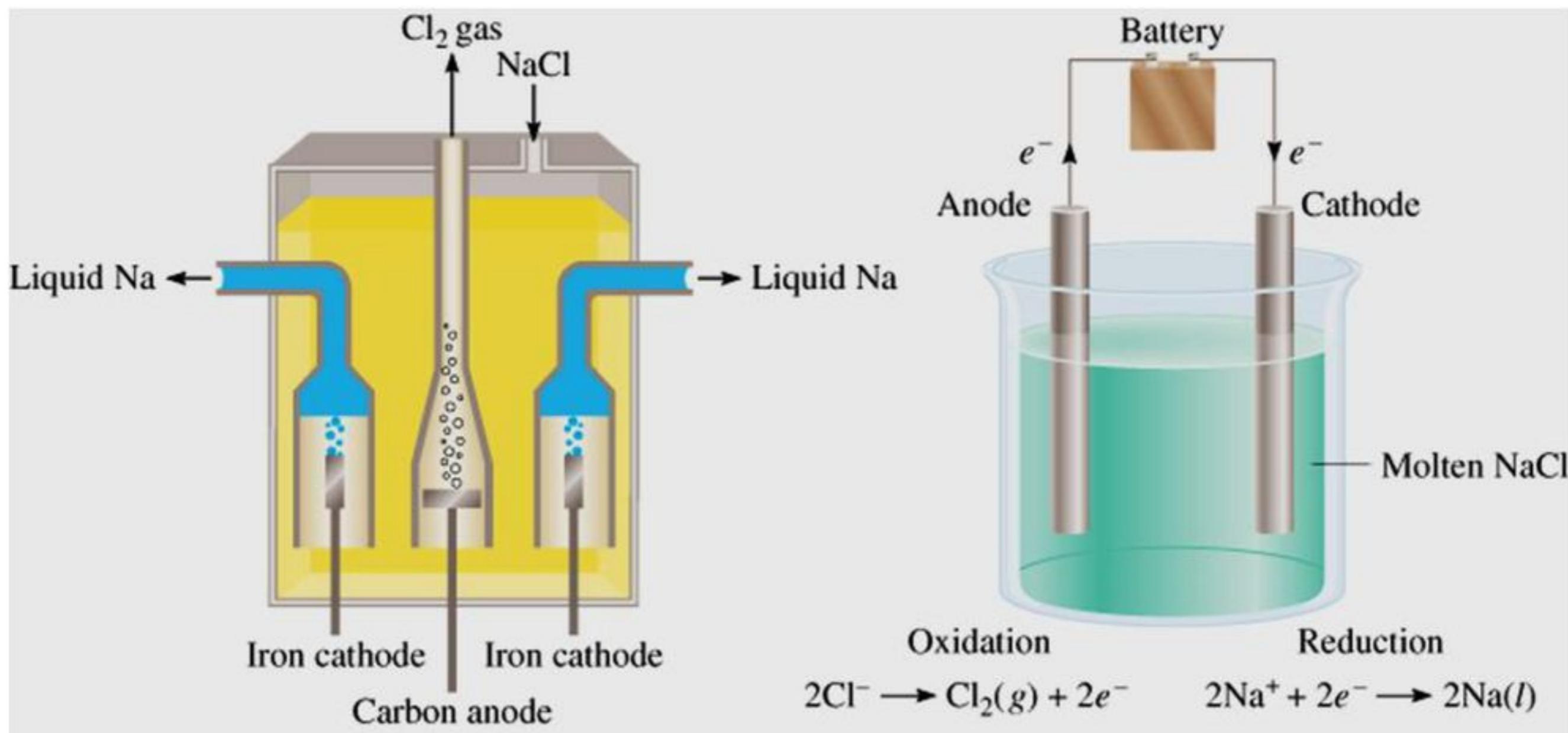


# Cathodic Protection of an Iron Storage Tank



# **Electrolysis**

**Electrolysis** is the process in which electrical energy is used to cause a **nonspontaneous** chemical reaction to occur.



# ELECTROLYSIS AND ELECTROLYTIC CELLS

**Electrolysis- the use of electricity to bring about chemical change. Literal translation “split with electricity”**

**Electrolytic cells [NON spontaneous cells]:**

Used to separate ores or plate out metals.

Important differences between a voltaic/galvanic cell and an electrolytic cell:

- 1) Voltaic cells are spontaneous and electrolytic cells are forced to occur by using an electron pump or battery or any DC source.
- 2) A voltaic cell is separated into two half cells to generate electricity; an electrolytic cell occurs in a single container.
- 3) A voltaic [or galvanic] cell IS a battery, an electrolytic cell NEEDS a battery
- 4) AN OX and RED CAT still apply BUT the polarity of the electrodes is reversed. The cathode is Negative and the anode is Positive (remember **E.P.A – electrolytic positive anode). Electrons** still flow FATCAT.
- 5) Usually use inert electrodes

## **Predicting the Products of Electrolysis:**

**If NO water is present and you have a pure molten ionic compound, then:**

the cation will be reduced (gain electrons/go down in charge)

the anion will be oxidized (lose electrons/go up in charge)

**If water IS present and you have an aqueous solution of the ionic compound, then:**

you'll need to figure out if the ions are reacting or the water is reacting. You can look at a reduction potential table to figure it out but, OR as a rule of thumb:

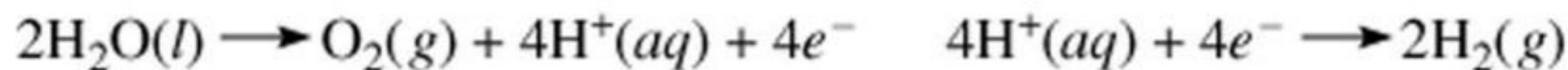
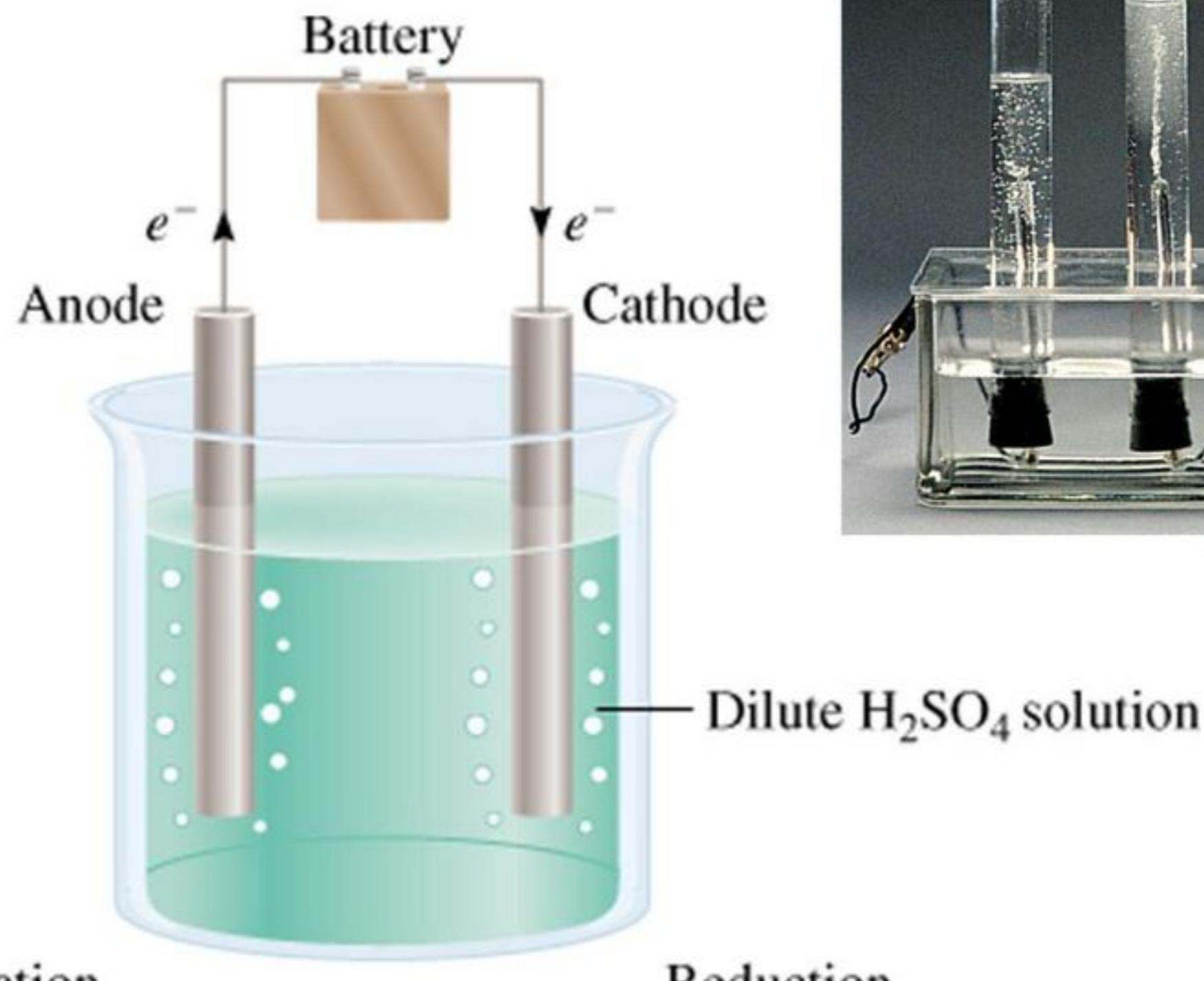
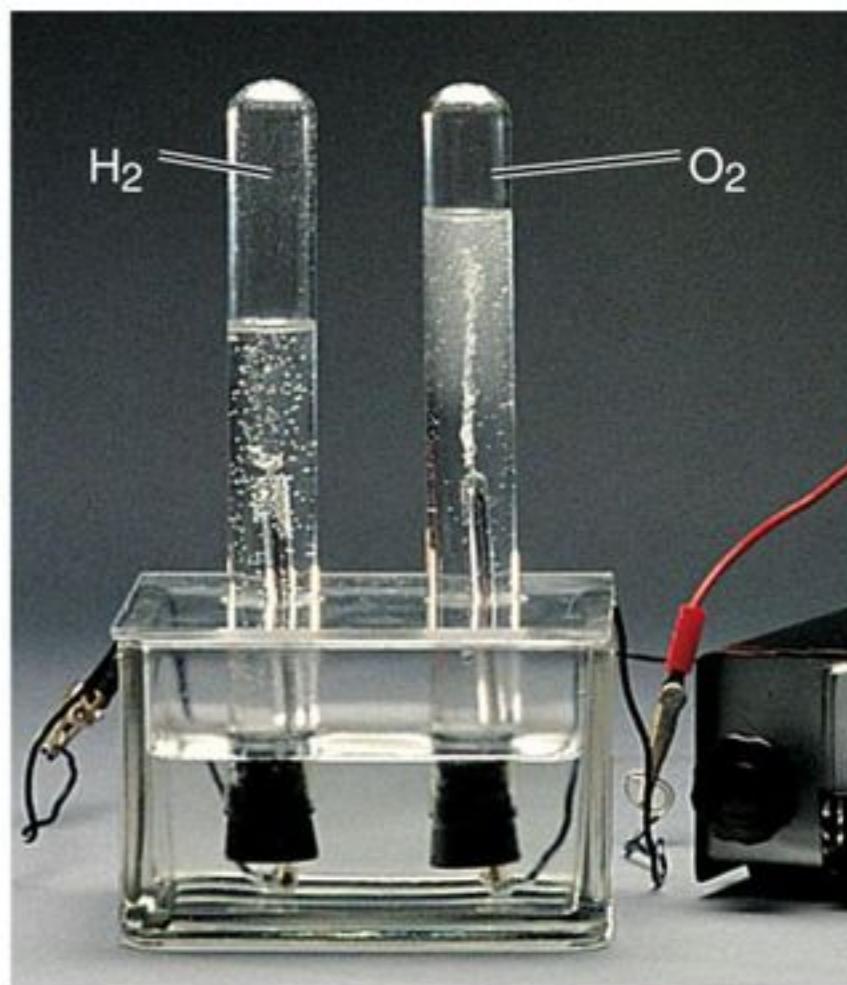
- No group IA or IIA metal will be reduced in an aqueous solution**

- Water will be reduced instead.**

- No polyatomic will be oxidized in an aqueous solution**

- Water will be oxidized instead.**

# Electrolysis of Water



# Calculating the Electrical Energy of Electrolysis

*How much metal could be plated out?*

*How long would it take to plate out?*

**Faraday's Law:** The amount of a substance being oxidized or reduced at each electrode during electrolysis is directly proportional to the amount of electricity that passes through the cell.

Use dimensional analysis (unit factor, T-chart) for these calculations, remembering: **# coulombs =  $It$**  where:

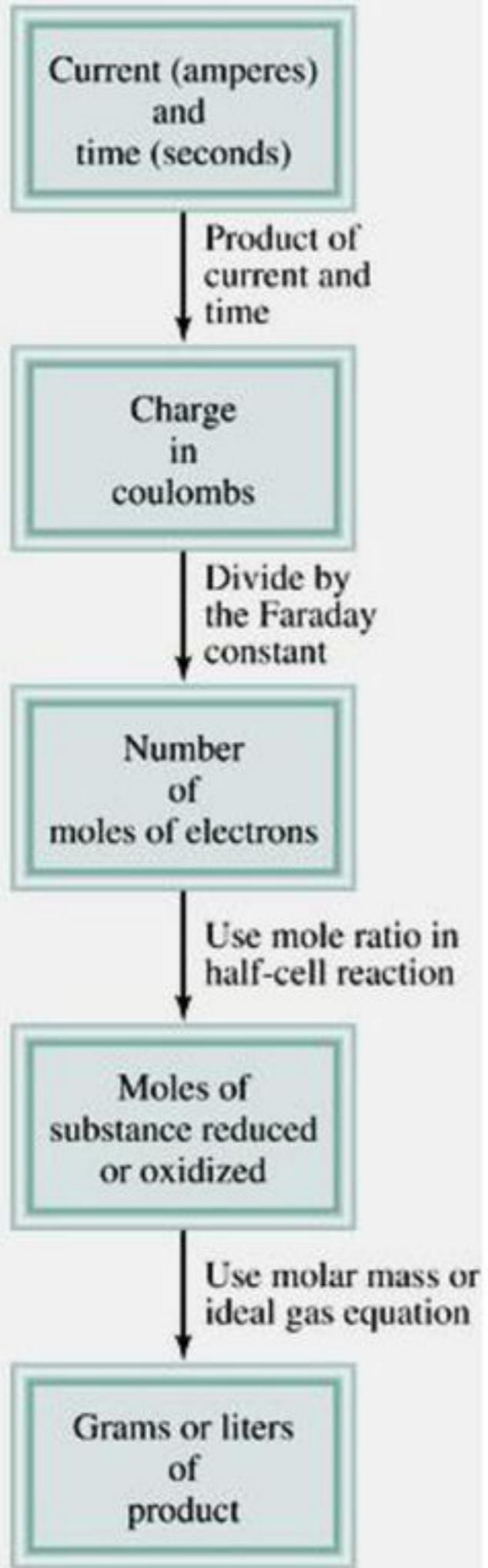
**1 Volt = 1 Joule/Coulomb**

**1 Amp = 1 Coulomb/second** (current is measured in amp, but symbolized by  $I$ )

**Faraday = 96,500 Coulombs/mole of electrons**

Balanced redox equation gives #moles of  $e^-$ /mole of substance

Formula weight gives grams/mole



## Electrolysis and Mass Changes

$$\text{charge (C)} = \text{current (A)} \times \text{time (s)}$$

$$1 \text{ mole } e^- = 96,500 \text{ C}$$



How much Ca will be produced in an electrolytic cell of molten  $\text{CaCl}_2$  if a current of 0.452 A is passed through the cell for 1.5 hours?

Anode:



Cathode:



$$2 \text{ mole e}^- = 1 \text{ mole Ca}$$

$$\text{mol Ca} = 0.452 \cancel{\frac{\text{C}}{\text{s}}} \times 1.5 \cancel{\text{hr}} \times 3600 \cancel{\frac{\text{s}}{\text{hr}}} \times \frac{1 \text{ mole e}^-}{96,500 \cancel{\text{C}}} \times \frac{1 \text{ mol Ca}}{2 \cancel{\text{mole e}^-}}$$

$$= 0.0126 \text{ mol Ca}$$

$$= 0.50 \text{ g Ca}$$

## **Exercise 9**

How long must a current of 5.00 A be applied to a solution of  $\text{Ag}^+$  to produce 10.5 g silver metal?

$$= 31.3 \text{ min}$$

## Exercise 10

An acidic solution contains the ions  $\text{Ce}^{4+}$ ,  $\text{VO}_2^+$ , and  $\text{Fe}^{3+}$ . Using the  $E^\circ$  values [listed in Table 17.1, Zumdahl] give the order of oxidizing ability of these species and predict which one will be reduced at the cathode of an electrolytic cell at the lowest voltage.



## **Applications of electrolytic cells:**

- Production of pure forms of elements from mined ores  
Aluminum from Hall-Heroult process
- Separation of sodium and chlorine (Down's cell)
- Purify copper for wiring
- Electroplating—applying a thin layer of an expensive metal to a less expensive one Jewelry --- 14 K gold plated
- Bumpers on cars --- Chromium plated
- Charging a battery --- i.e. your car battery when the alternator functions

## **Corrosion – The process of returning metals to their natural state, the ores.**

- Involves oxidation of the metal which causes it to lose its structural integrity and attractiveness.
- The main component of steel is iron.
- 20% of the iron and steel produced annually is used to replace rusted metal!
- most metals develop a thin oxide coating to protect them, patina's, tarnish, rust, etc.