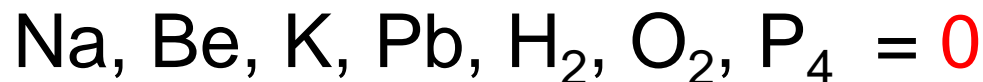


# Oxidation number

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.

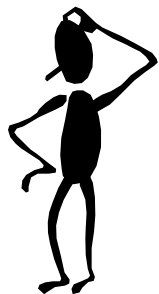


2. In monatomic ions, the oxidation number is equal to the charge on the ion.



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  $\text{HCO}_3^-$  ?



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

$$3x(-2) + 1 + ? = -1$$

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

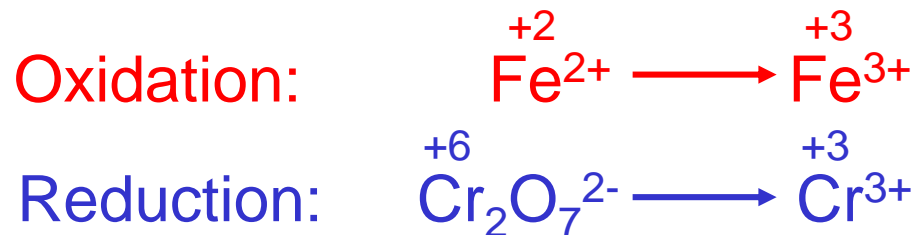
# Balancing Redox Equations

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 in ionic form.



2. Separate the equation into two half-reactions.



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

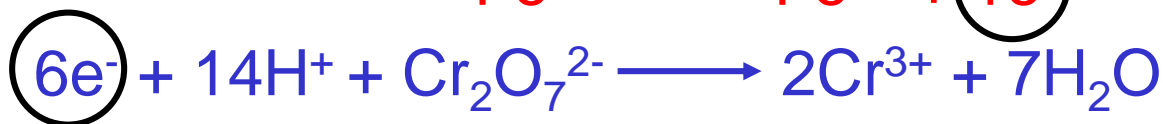
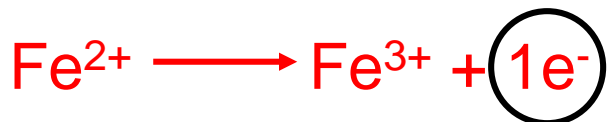


# Balancing Redox Equations

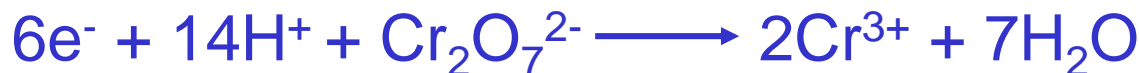
4. For reactions in **acid**, add  $\text{H}_2\text{O}$  to balance O atoms and  $\text{H}^+$  to balance H atoms.



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

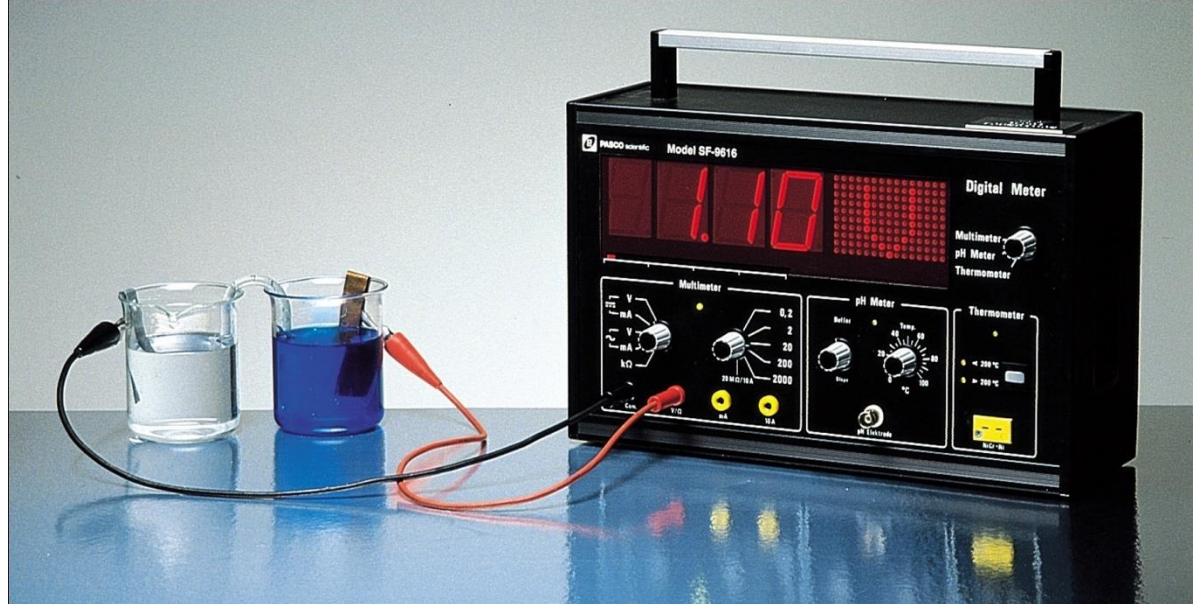
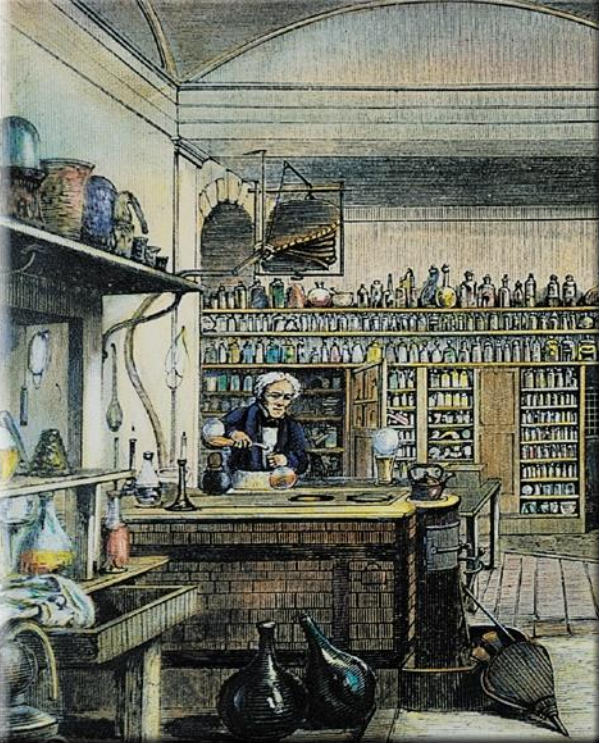
7. Add the two half-reactions together and balance the final equation by inspection. **The number of electrons on both sides must cancel.**



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

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

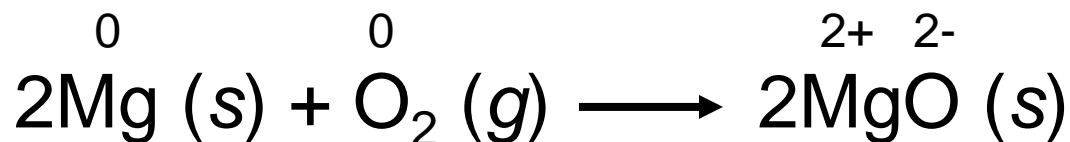
9. Note: For reactions in basic solutions, add  $\text{H}_2\text{O}$  to the side having every an excess of O atom and add  $2\text{OH}^-$  to **other side** of the equation to balance both H and O atoms, and so forth.



# Electrochemistry

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

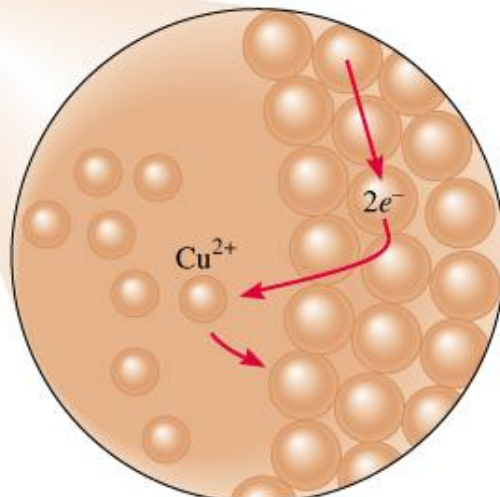
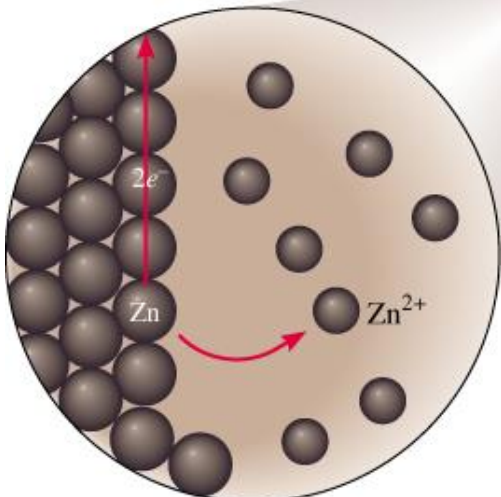
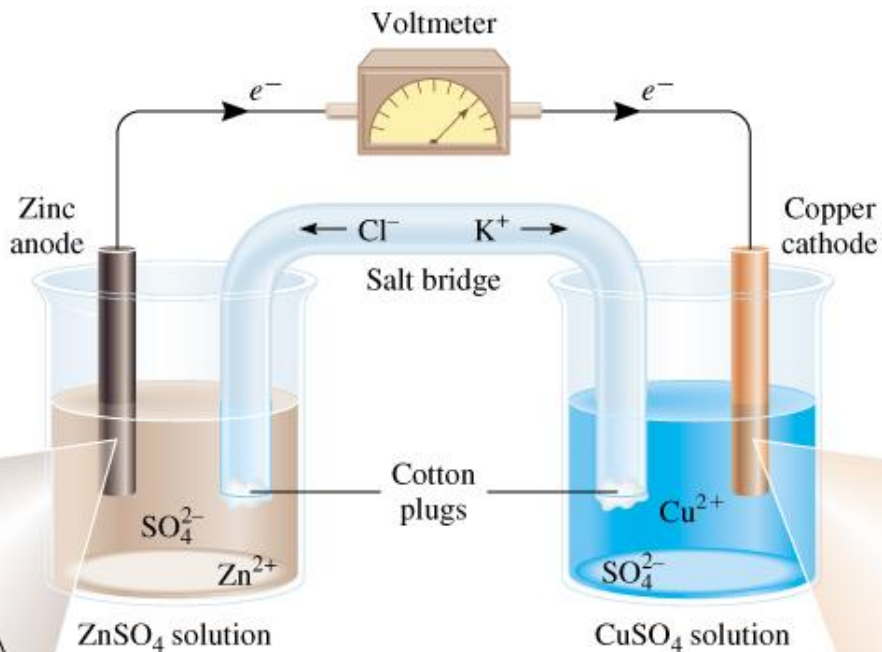
- the energy released by a spontaneous reaction is converted to electricity or
- electrical energy is used to cause a nonspontaneous reaction to occur



# Galvanic Cells

anode  
oxidation

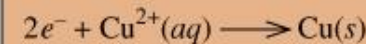
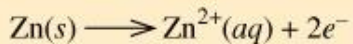
cathode  
reduction



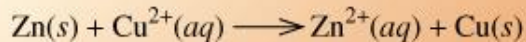
spontaneous  
redox reaction

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

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



Net reaction

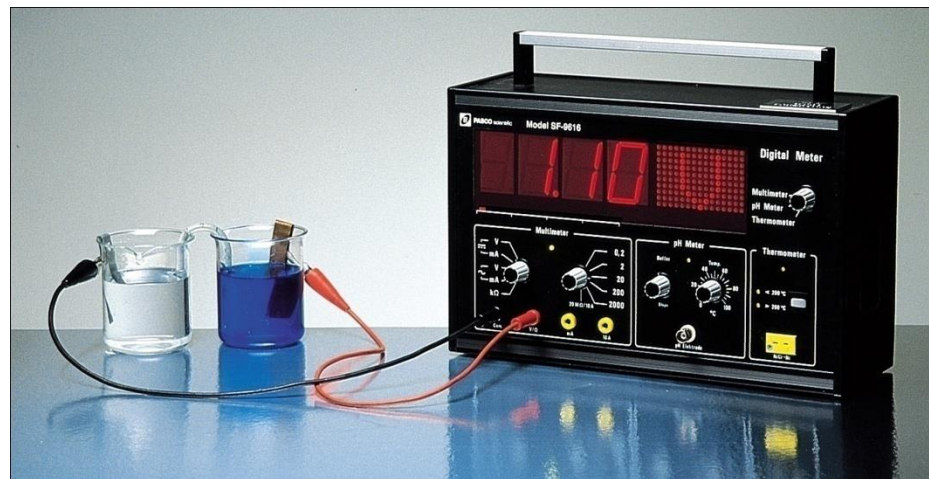




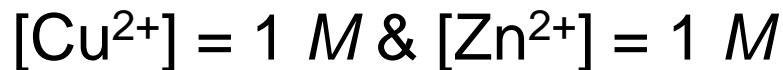
# Galvanic Cells

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

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



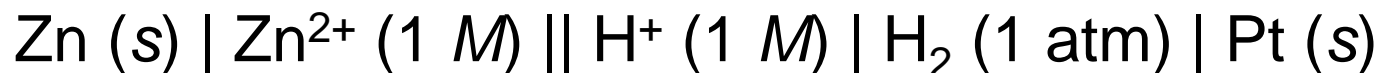
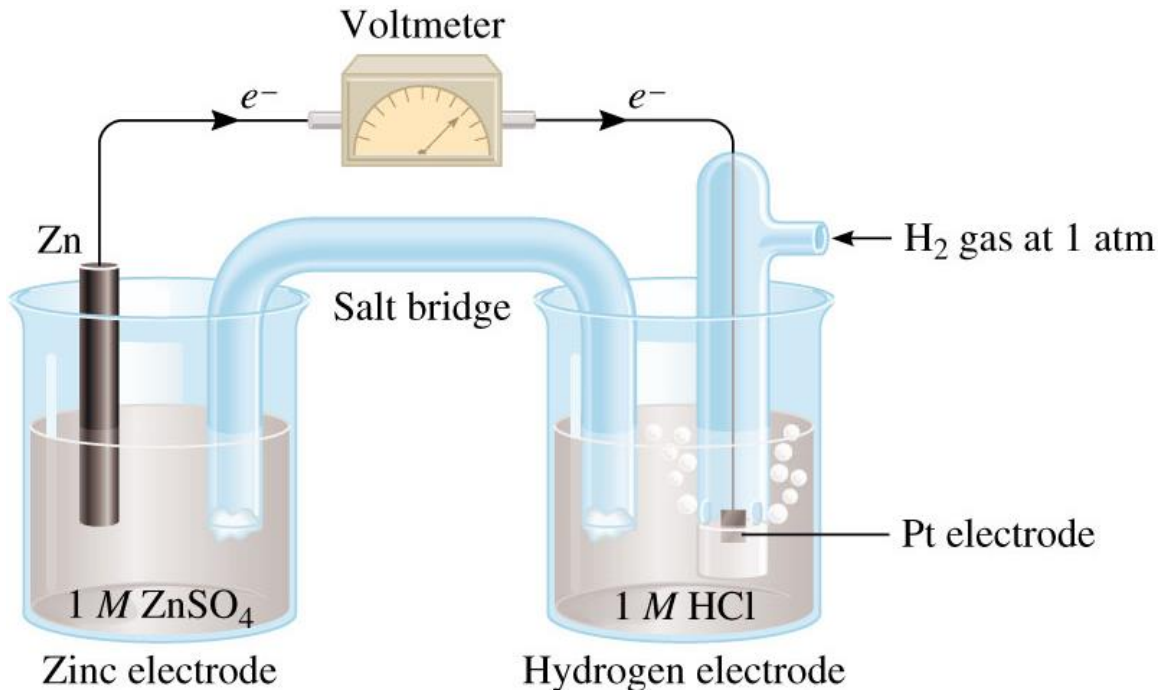
## Cell Diagram



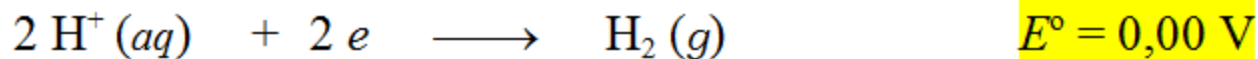
**anode**

**cathode**

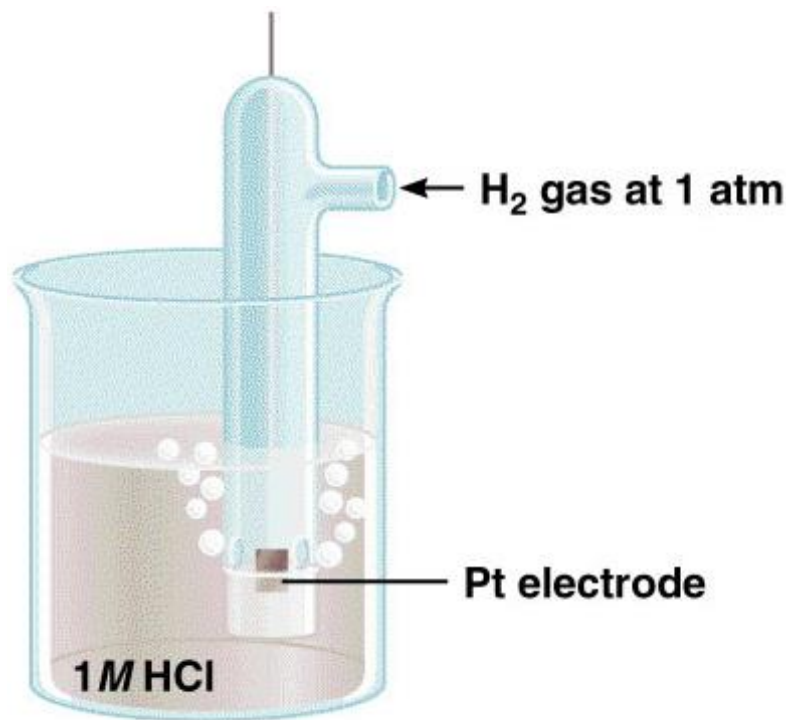
# Standard Reduction Potentials



# Standard Reduction Potentials



**Standard reduction potential ( $E^\circ$ )** 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

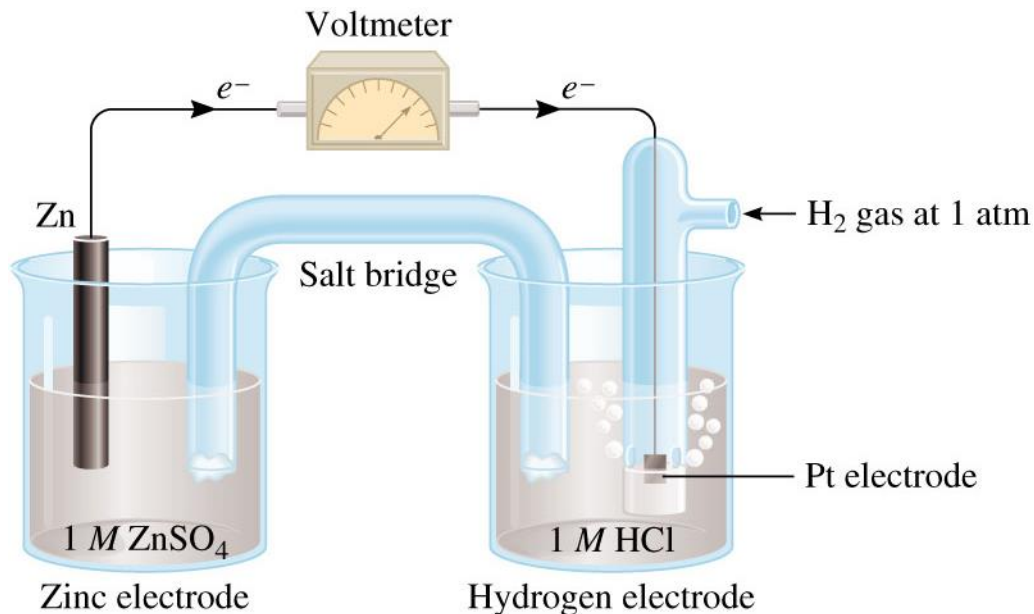


$$E^\circ = 0 \text{ V}$$

Standard hydrogen electrode (SHE)

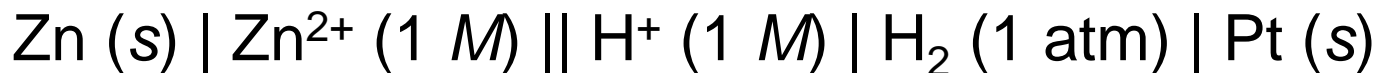
# Standard Reduction Potentials

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



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

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



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

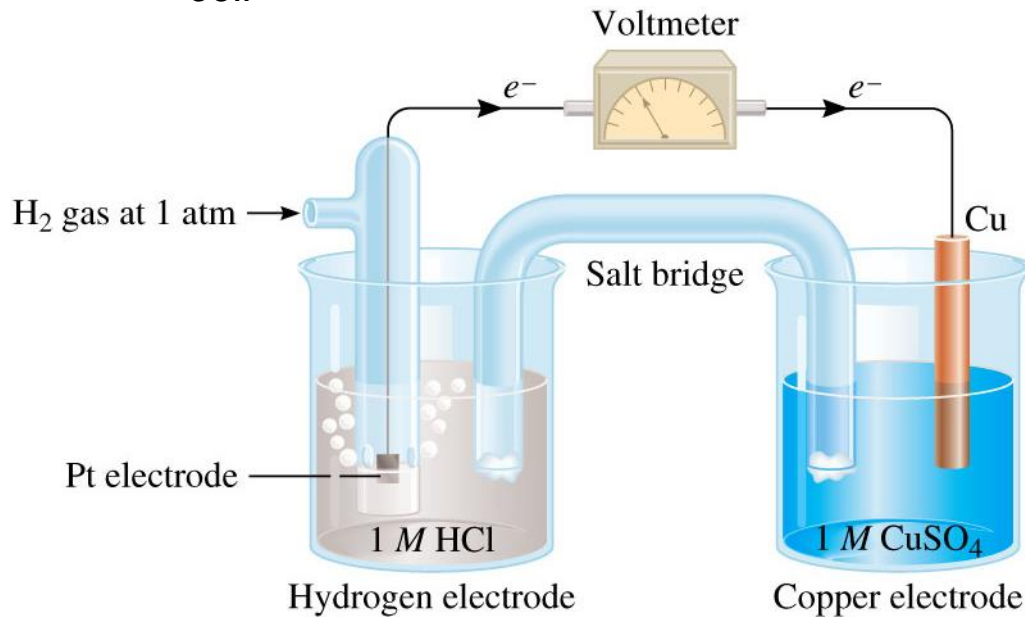
$$0.76 \text{ V} = 0 - E_{\text{Zn}^{2+}/\text{Zn}}^0$$

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



# Standard Reduction Potentials

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

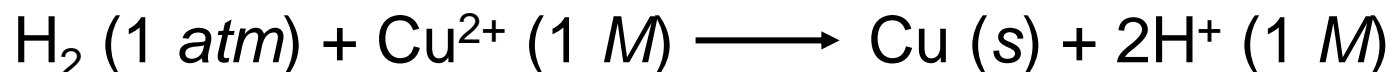
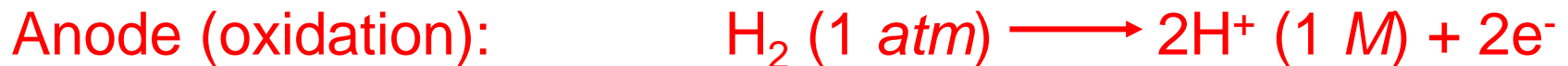
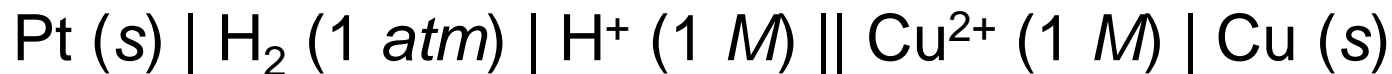


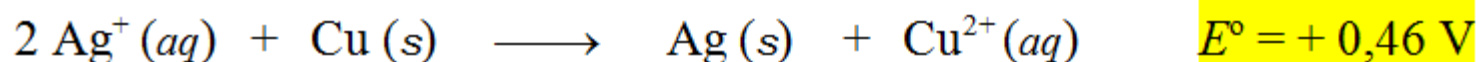
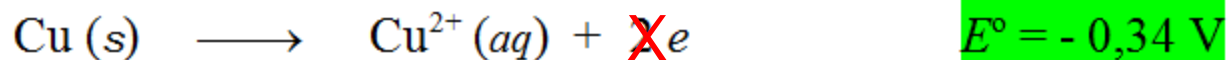
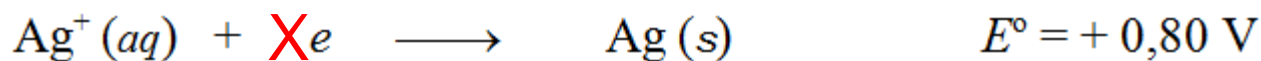
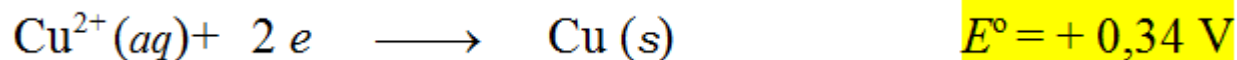
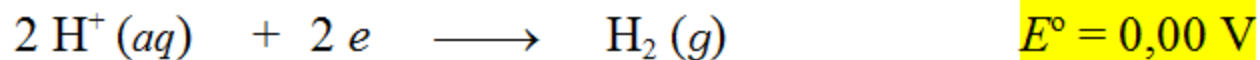
$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$$

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

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

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



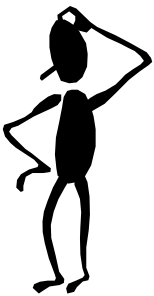


$$E^\circ_{\text{cell}} = +0,46 \text{ V}$$

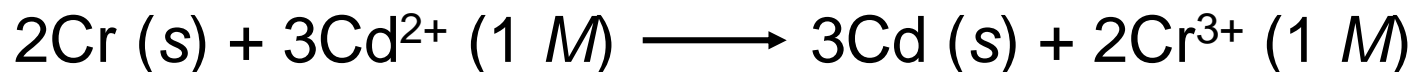
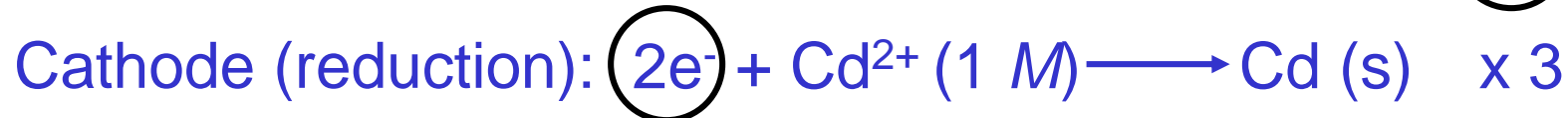
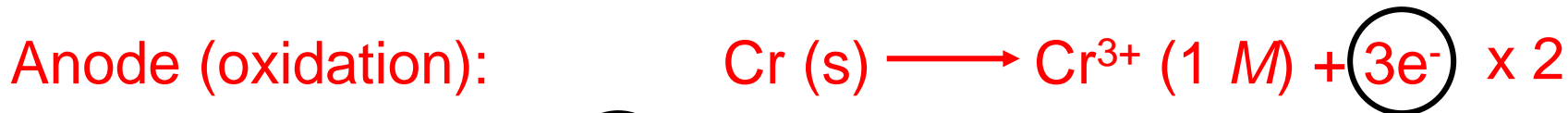
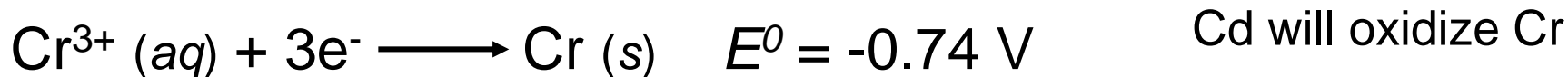
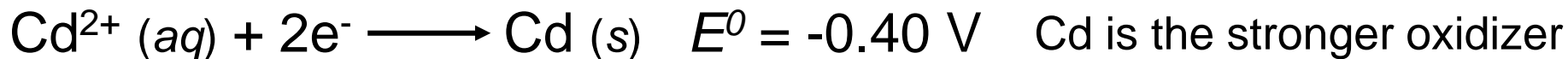
**TABLE 19.1 Standard Reduction Potentials at 25°C\***

Half-Reaction	$E^{\circ}$ (V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O$	+2.07
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$	+1.70
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.96
$2Hg_2^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	-0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	-0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	-0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	-0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	-0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	-0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	-0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	-0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	-0.76
$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	-0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	-1.18
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	-1.66
$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	-1.85
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	-2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	-2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	-2.87
$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	-2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	-2.90
$K^+(aq) + e^- \longrightarrow K(s)$	-2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	-3.05

- $E^{\circ}$  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  $E^{\circ}$



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?



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

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

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



# Spontaneity of Redox Reactions

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

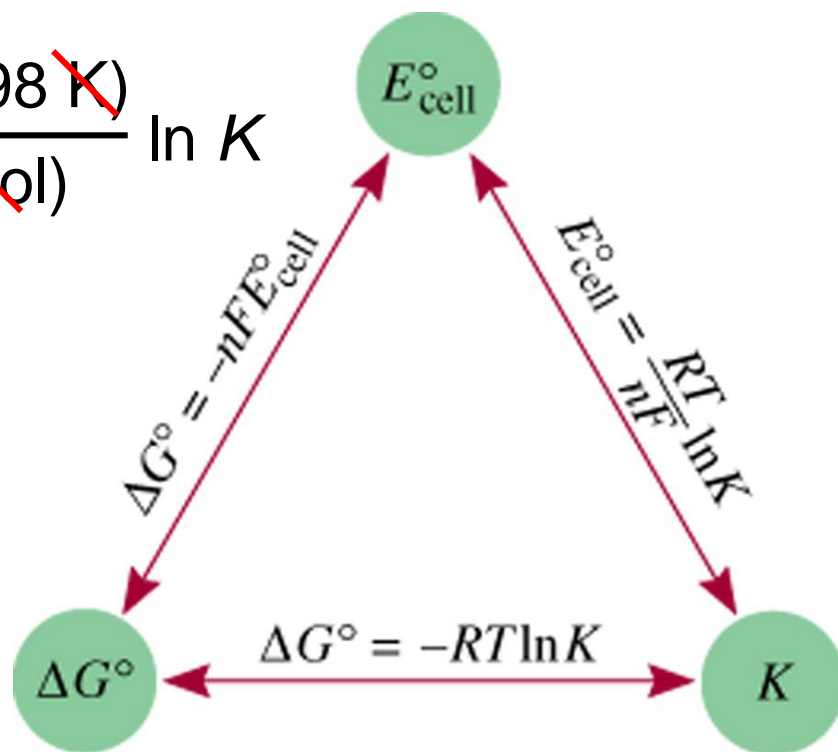
$$\Delta G^0 = -nFE_{\text{cell}}^0 \quad F = 96,500 \frac{\text{J}}{\text{V} \cdot \text{mol}} = 96,500 \text{ C/mol}$$

$$\Delta G^0 = -RT \ln K = -nFE_{\text{cell}}^0$$

$$E_{\text{cell}}^0 = \frac{RT}{nF} \ln K = \frac{(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})}{n (96,500 \text{ J/V} \cdot \text{mol})} \ln K$$

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

$$E_{\text{cell}}^0 = \frac{0.0592 \text{ V}}{n} \log K$$



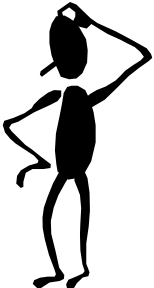
# Spontaneity of Redox Reactions

**TABLE 19.2**

**Relationships Among  $\Delta G^\circ$ ,  $K$ , and  $E^\circ_{\text{cell}}$**

$\Delta G^\circ$	$K$	$E^\circ_{\text{cell}}$	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.

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



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

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



$$n = 2$$

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

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

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

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

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

# The Effect of Concentration on Cell Emf

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

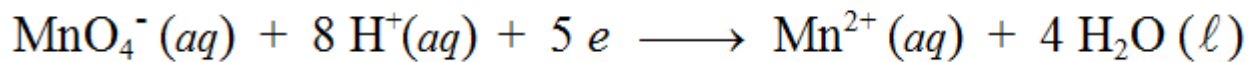
$$-nFE = -nFE^0 + RT \ln Q$$

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

At 298  $R = 8,31 \text{ V C mol}^{-1} \text{ K}^{-1}; F = 9,65 \times 10^4 \text{ C mol}^{-1}$

$$E = E^0 - \frac{0.0257 \text{ V}}{n} \ln Q \quad E = E^0 - \frac{0.0592 \text{ V}}{n} \log Q$$

$$E = E^0 - \frac{RT}{nF} \ln \frac{[\text{product}]}{[\text{reactant}]} \quad E = E^0 - \frac{0,0591 \text{ V}}{n} \log \frac{[\text{product}]}{[\text{reactant}]}$$



$$E^\circ = +1,70 \text{ V}$$

This means at 298 K,  $\text{MnO}_4^-$  ion ( $[\text{MnO}_4^-] = 1 \text{ mol.L}^{-1}$ )

is a strong oxydising agent (+ 1,70 V) in acidic condition  $[\text{H}^+] = 1 \text{ mol L}^{-1}$

If the pH is increased to 4,00 ( $[\text{H}^+]$  decreasing to  $10^{-4} \text{ mol L}^{-1}$ ),

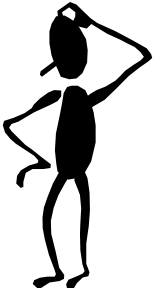
while  $\text{MnO}_4^-$  remains  $1 \text{ mol L}^{-1}$ , hence according to Nernst:

$$E = +1,70 \text{ V} - \frac{8,31 \text{ V C mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{5 \times 9,65 \times 10^4 \text{ C mol}^{-1}} \ln \frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-][\text{H}^+]^8}$$

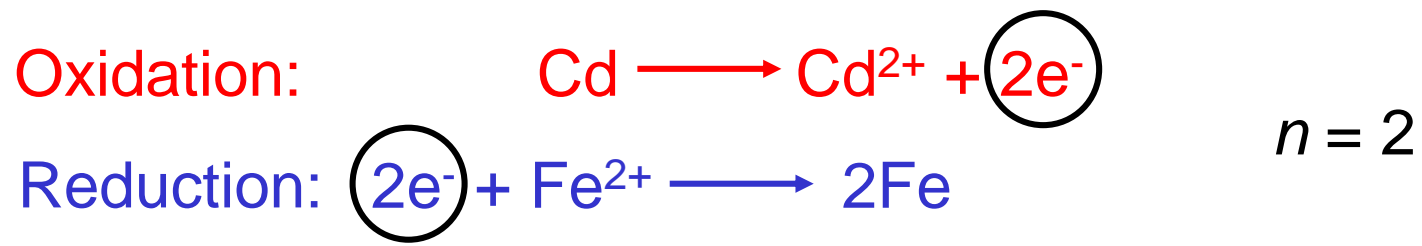
$$= +1,70 \text{ V} - 5,13 \times 10^{-3} \text{ V} \ln \frac{[1,00]}{[1,0][1,0 \times 10^{-4}]^8}$$

$$= +1,70 \text{ V} - 5,13 \times 10^{-3} \text{ V} \ln (1,0 \times 10^{32})$$

$$= + 1,32 \text{ V} \quad (\text{becoming weaker})$$



Will the following reaction occur spontaneously at 25°C if [Fe<sup>2+</sup>] = 0.60 M and [Cd<sup>2+</sup>] = 0.010 M?



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

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

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

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

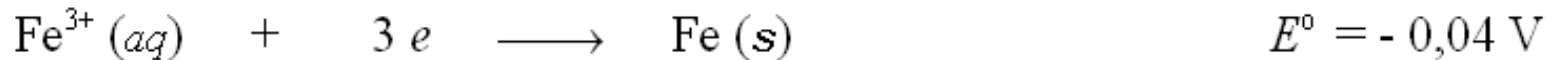
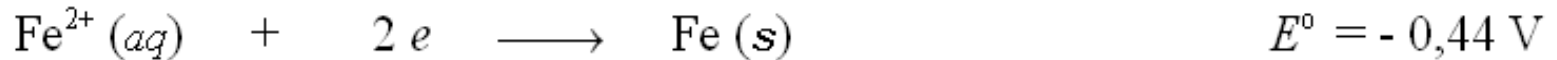
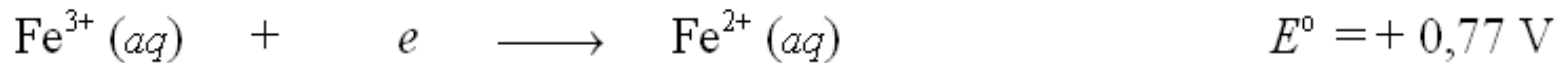
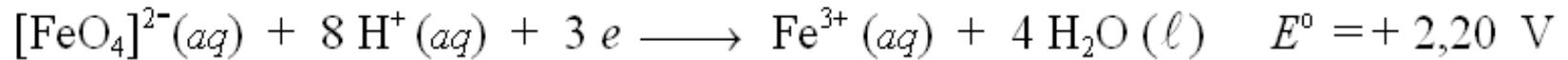
$$E = -0.04 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{0.010}{0.60}$$

$$E = 0.013$$

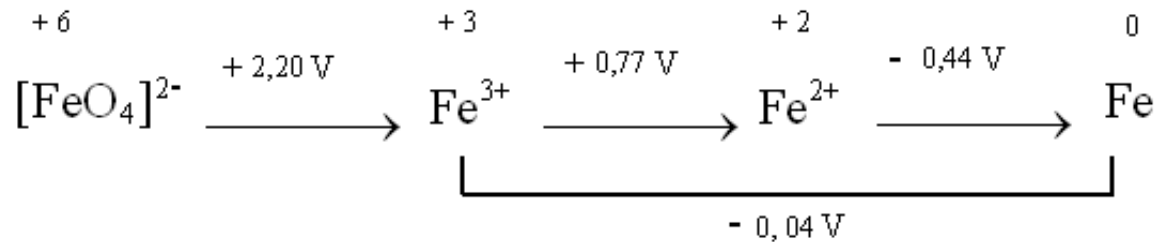
$E > 0$       Spontaneous

# LATIMER DIAGRAM

Potential Reduction for each reduction:

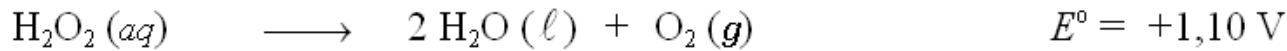


Latimer puts them in a diagram to be more informative as follows:

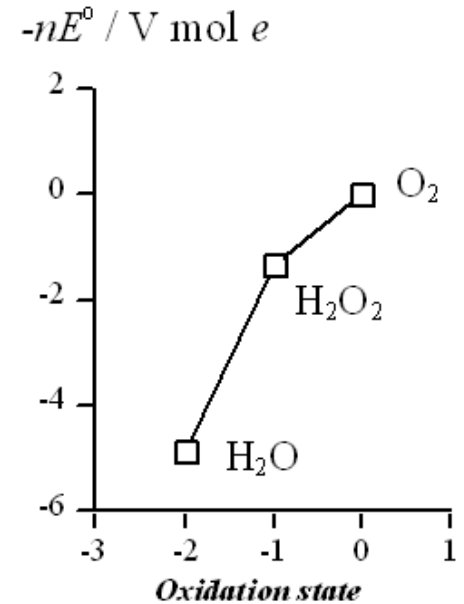
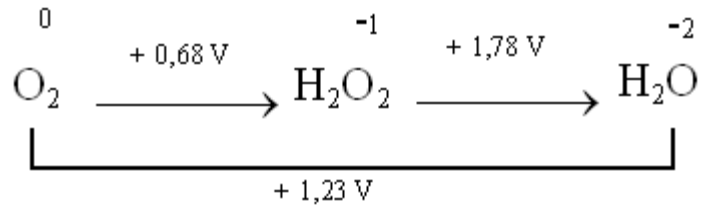


# FROST DIAGRAM

Frost depicted a plot of oxidation number vs DG ( $-nE^0$ )



+



Frost diagram of O<sub>2</sub> in acidic solution



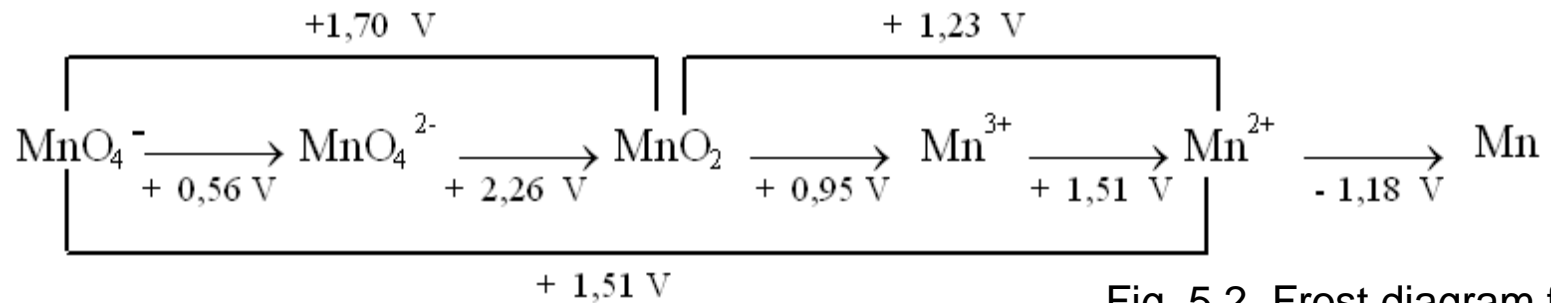
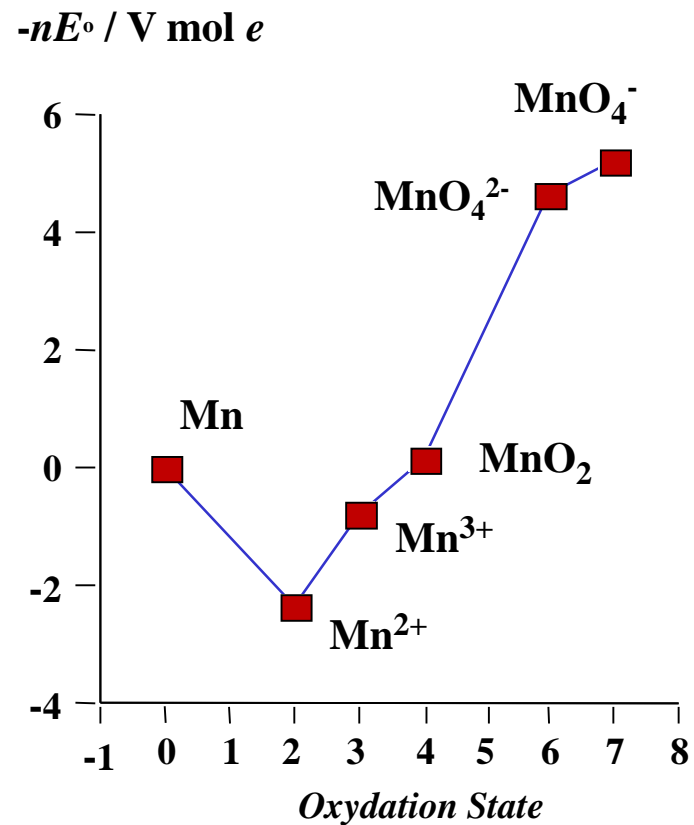
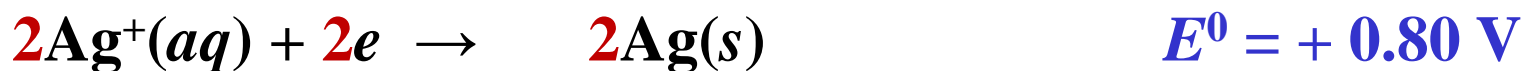
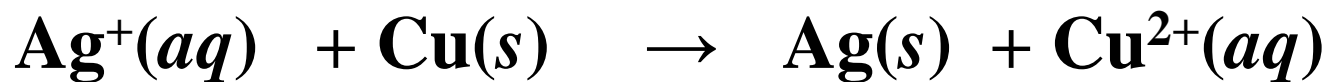


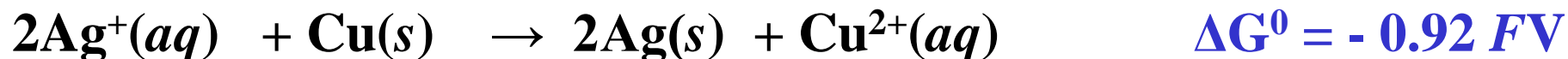
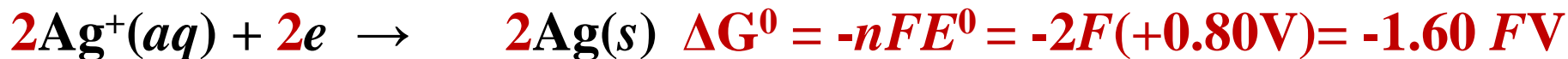
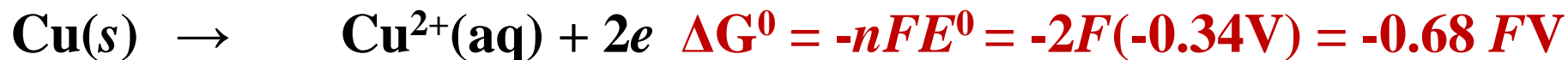
Fig. 5.2 Frost diagram for Mn in acid solution



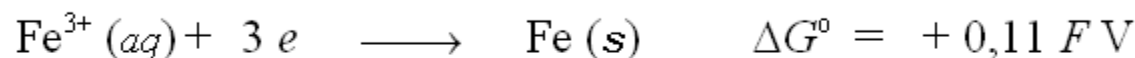
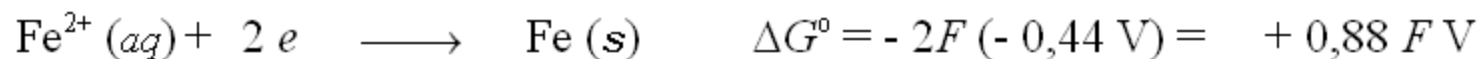
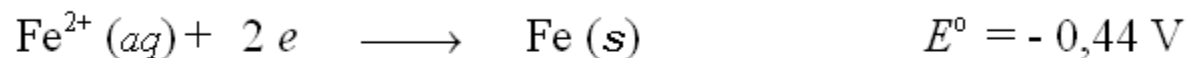
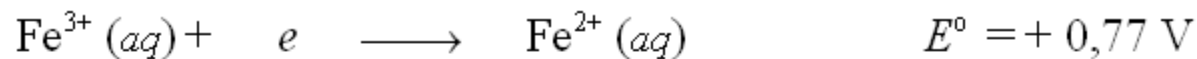
What is the  $E^0_{\text{cell}}$  of this redox:



By calculating of  $\Delta G$  of each half-reaction



$$E^0 = -\Delta G^0 / nF = -(-0.92 \text{ FV}) / 2F = +0.46 \text{ V}$$

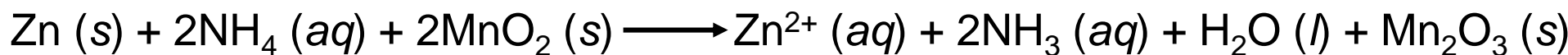
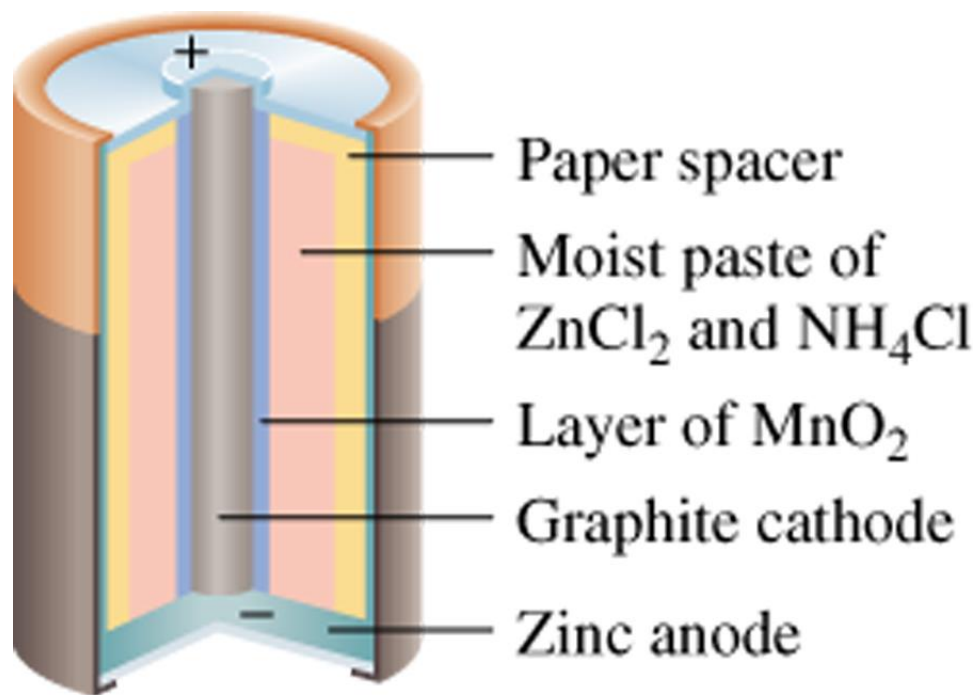


+

$$E^{\circ} = -\Delta G^{\circ} / nF = -0,11 F \text{ V} / 3F = -0,04 \text{ V}$$

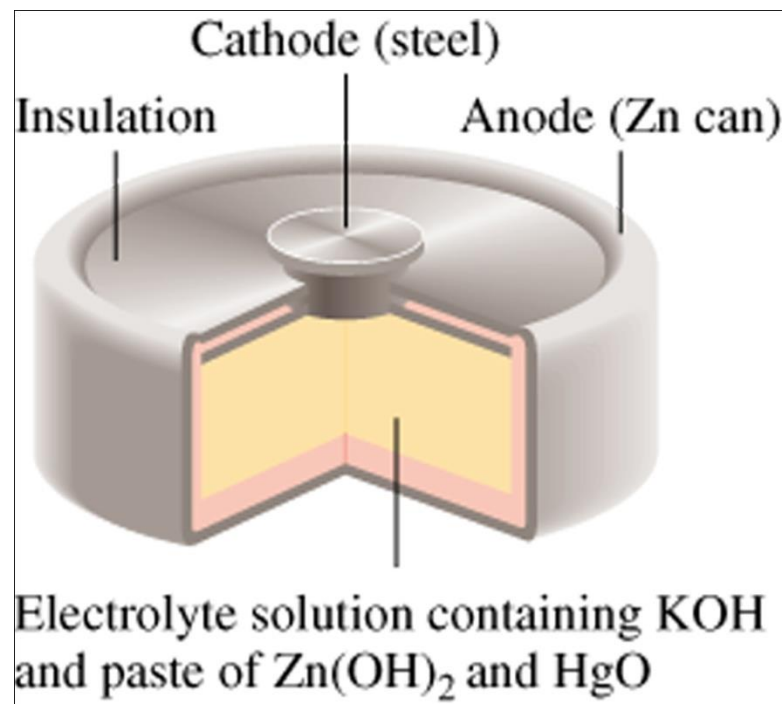
# Batteries

Dry cell  
***Leclanché cell***



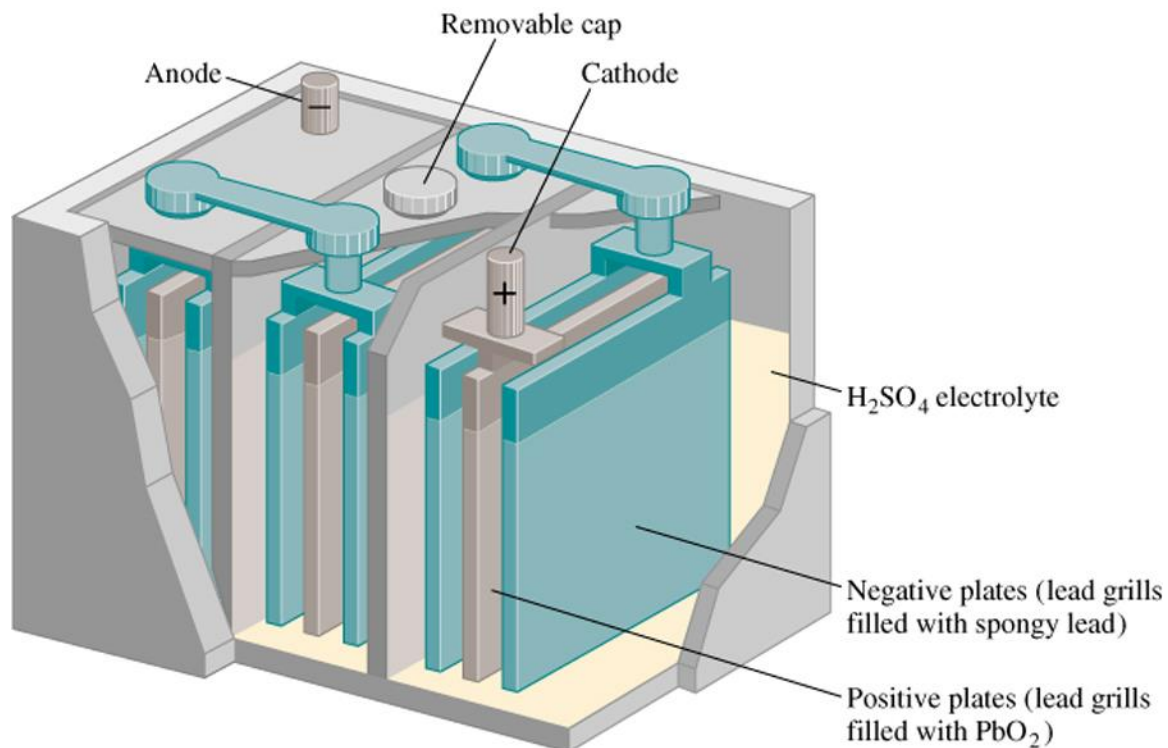
# Batteries

## Mercury Battery

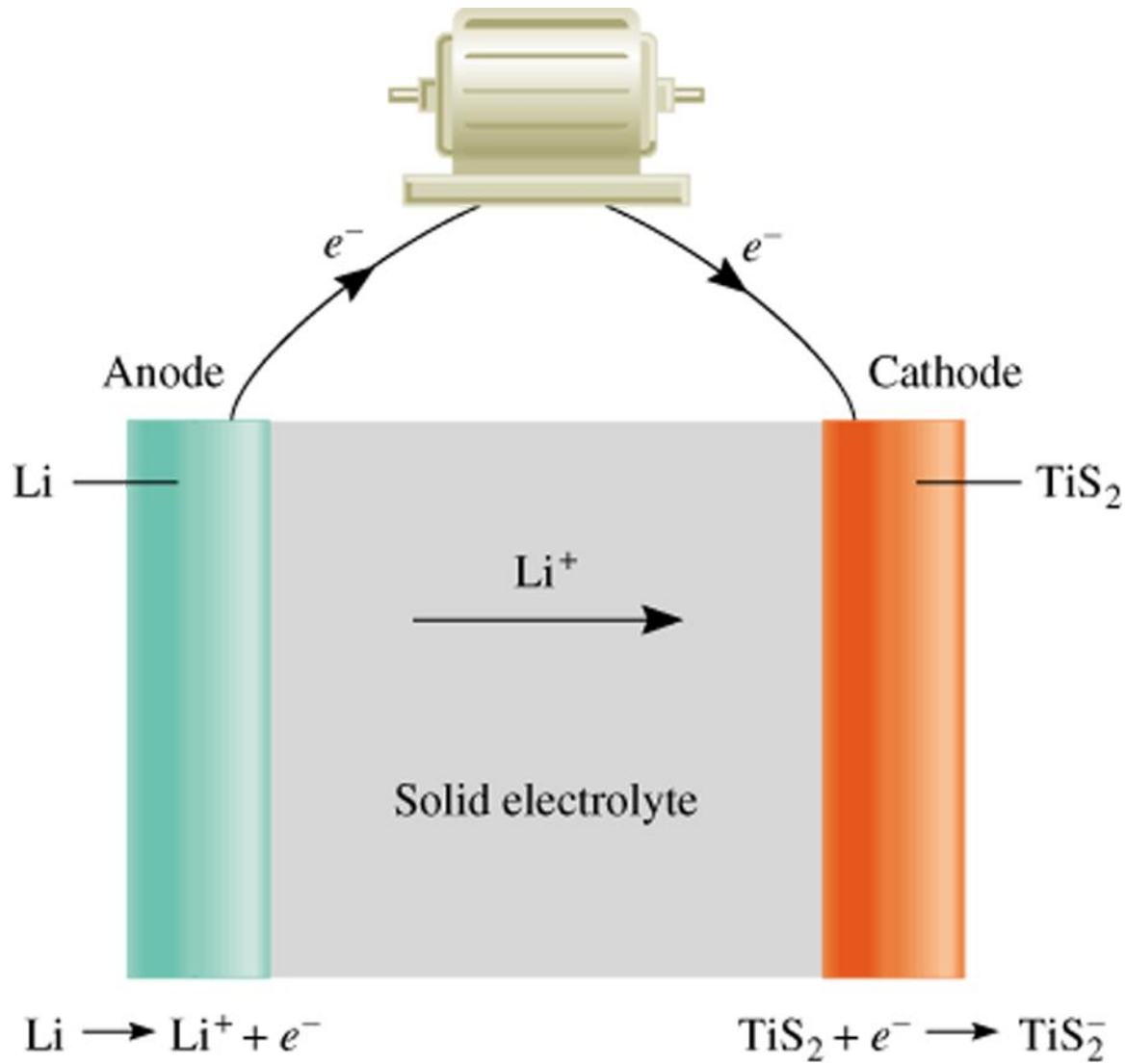


# Batteries

## Lead storage battery

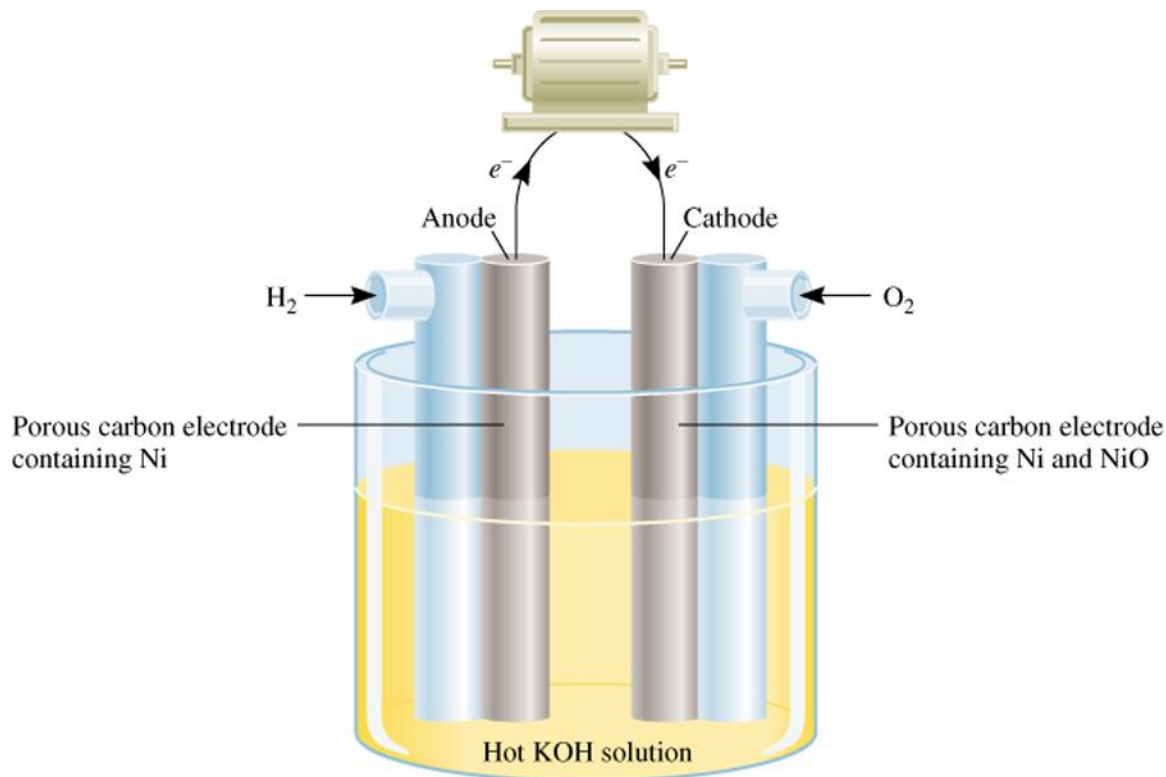


# Batteries



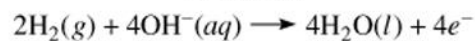
Solid State Lithium Battery

# Batteries

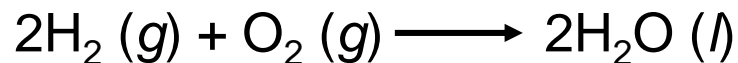
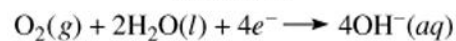


A ***fuel cell*** is an electrochemical cell that requires a continuous supply of reactants to keep functioning

Oxidation

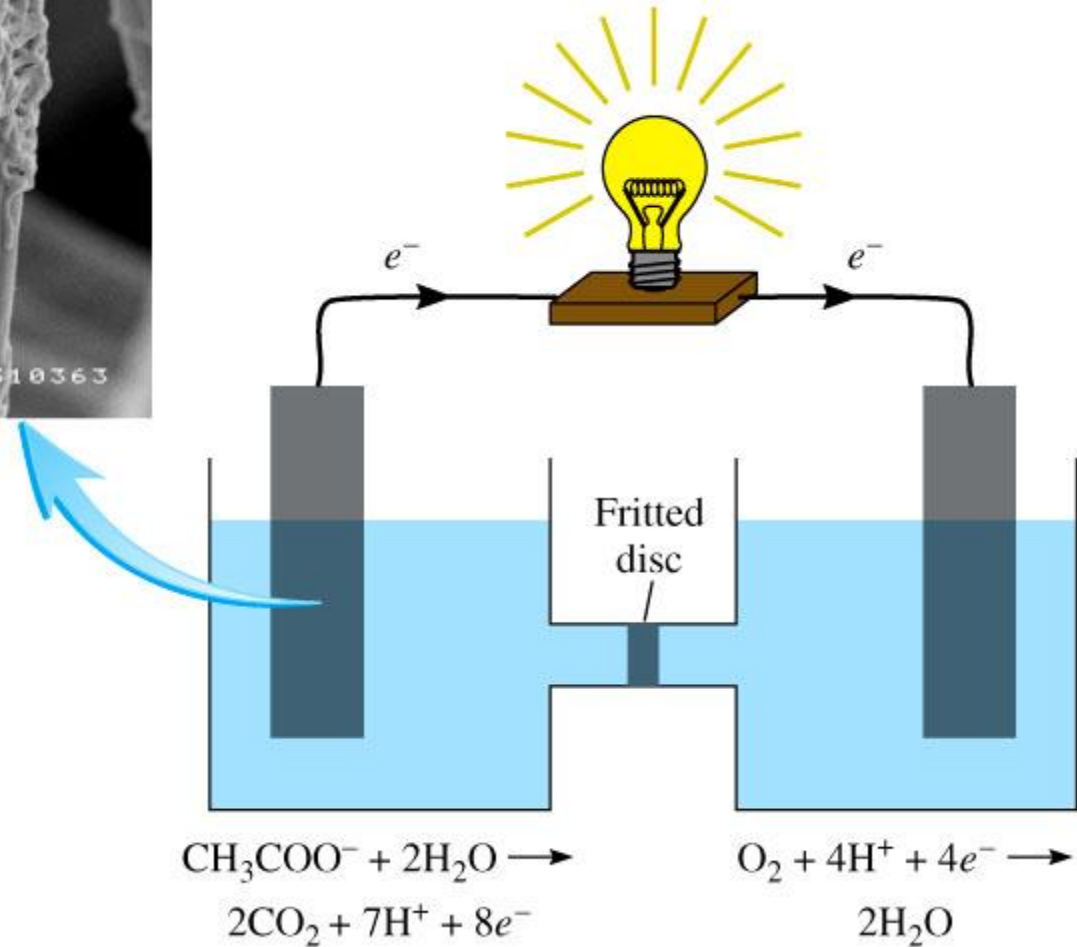
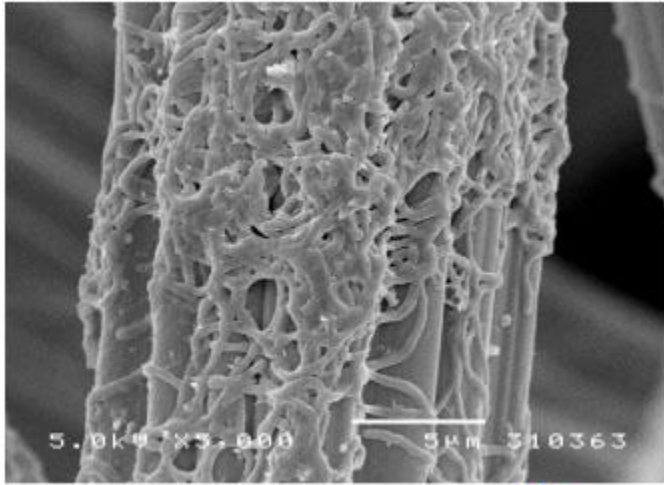
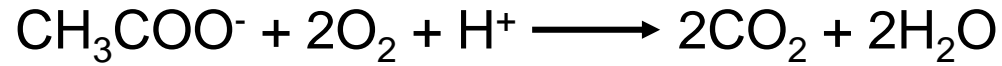


Reduction

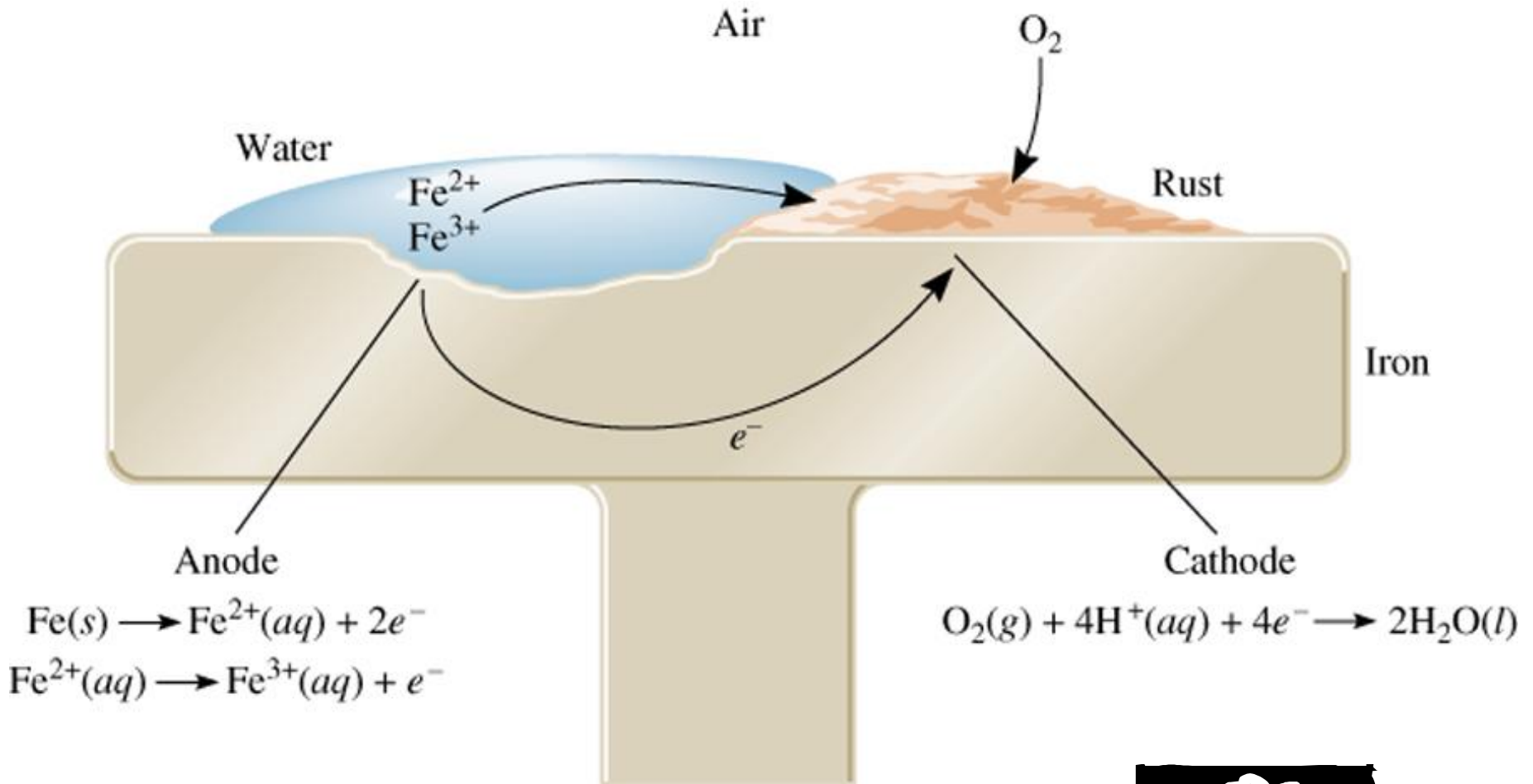




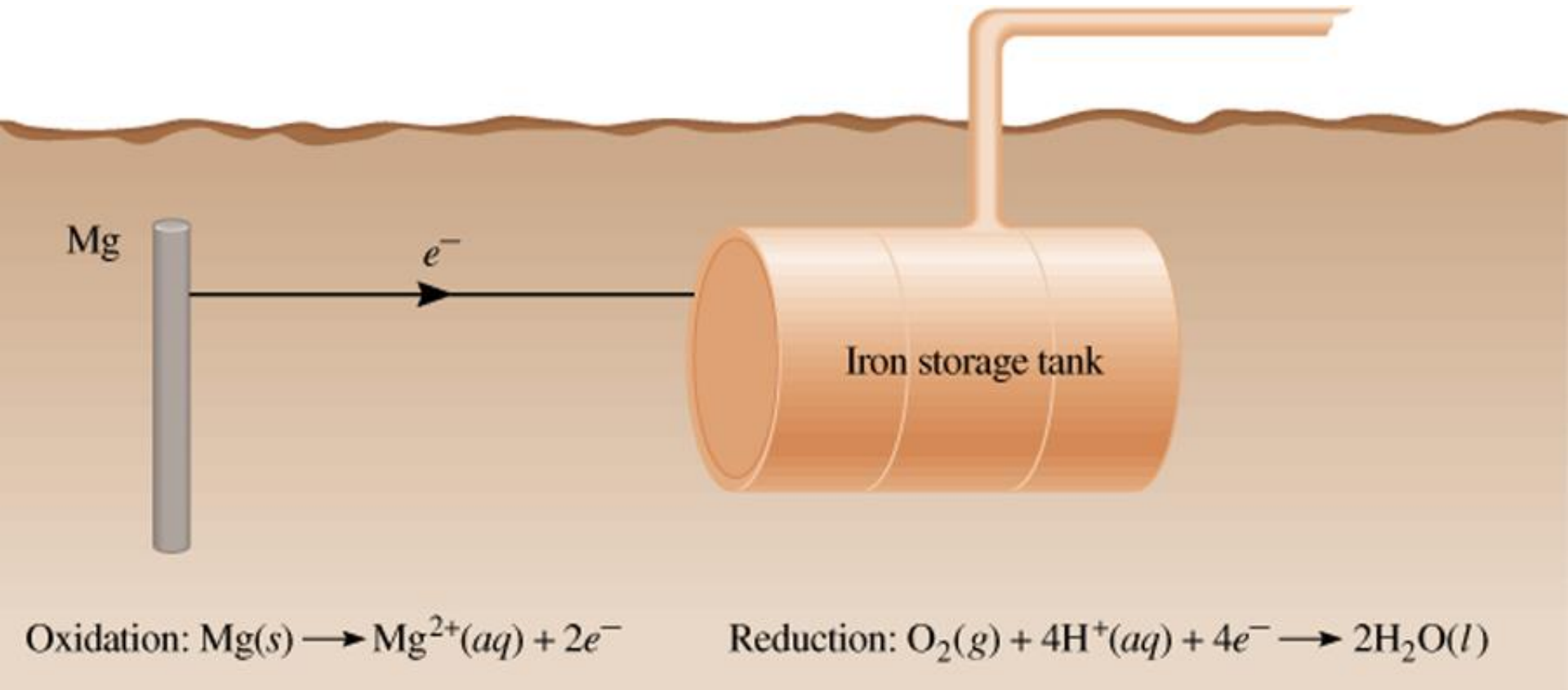
# Chemistry In Action: Bacteria Power



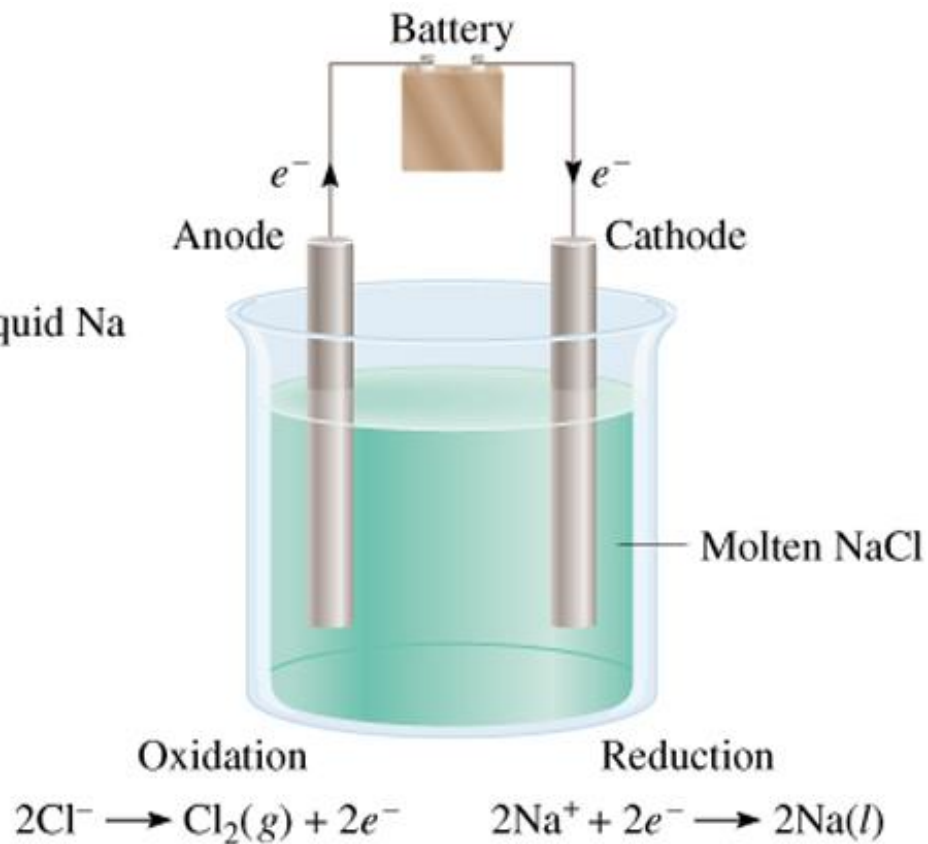
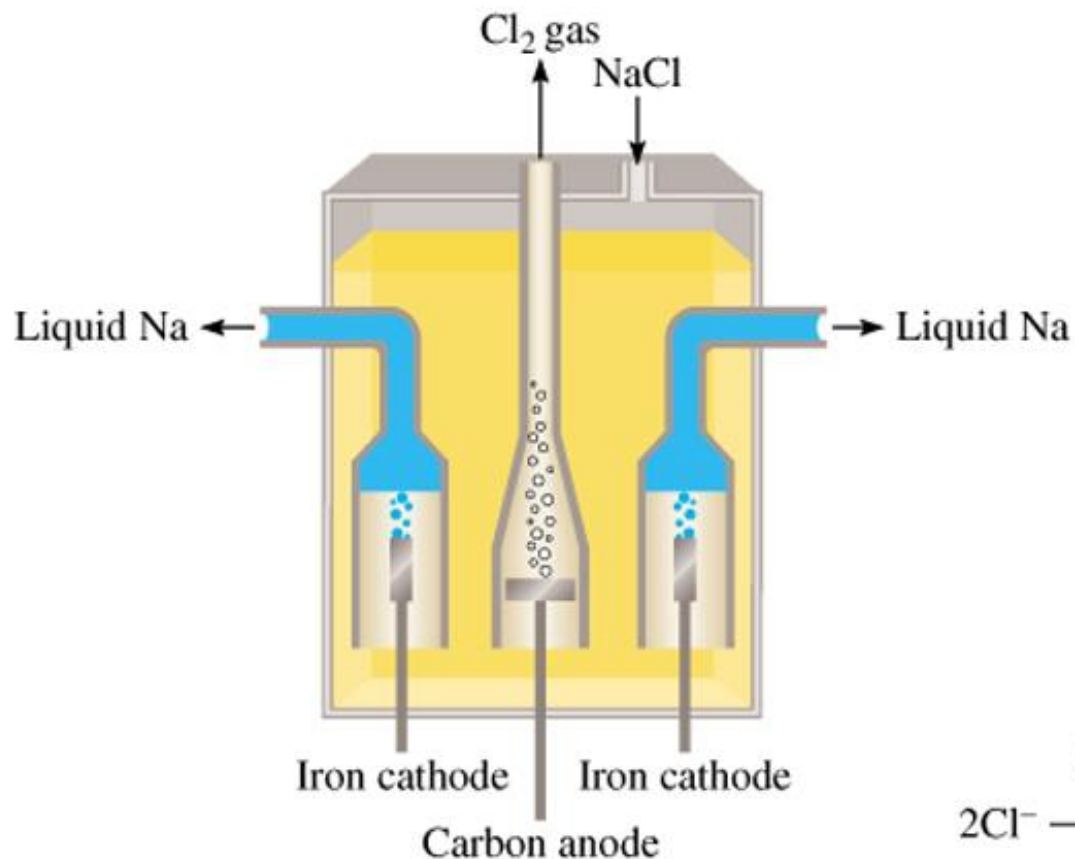
# Corrosion



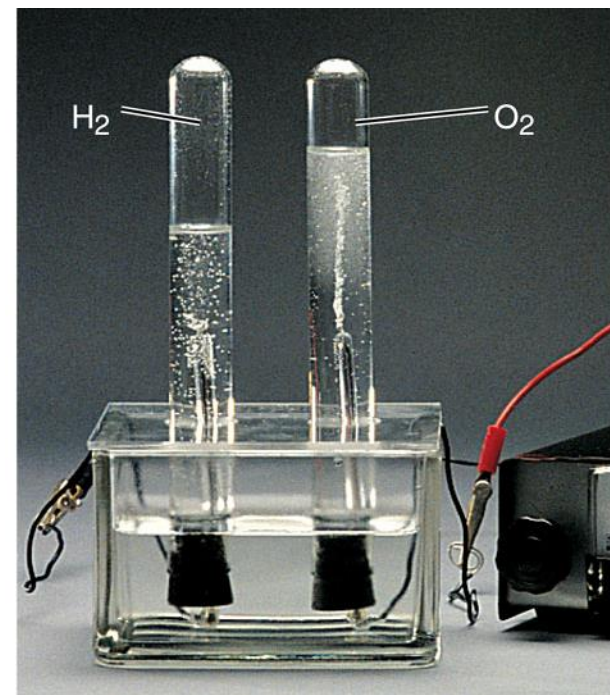
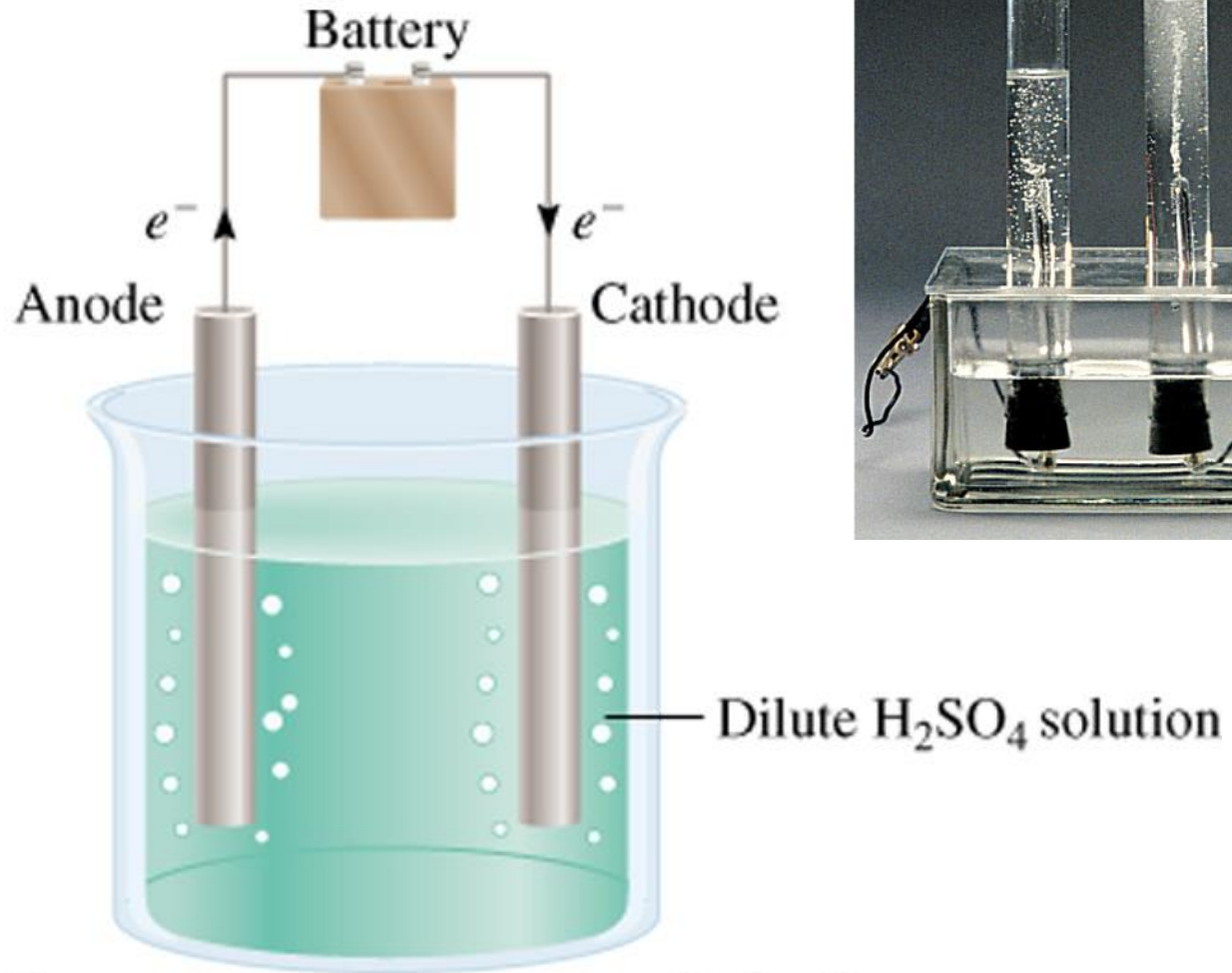
# Cathodic Protection of an Iron Storage Tank



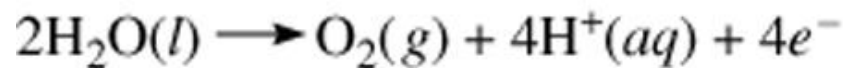
**Electrolysis** is the process in which electrical energy is used to cause a **nonspontaneous** chemical reaction to occur.



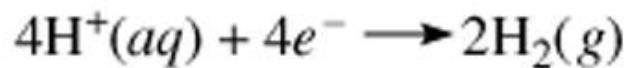
# Electrolysis of Water

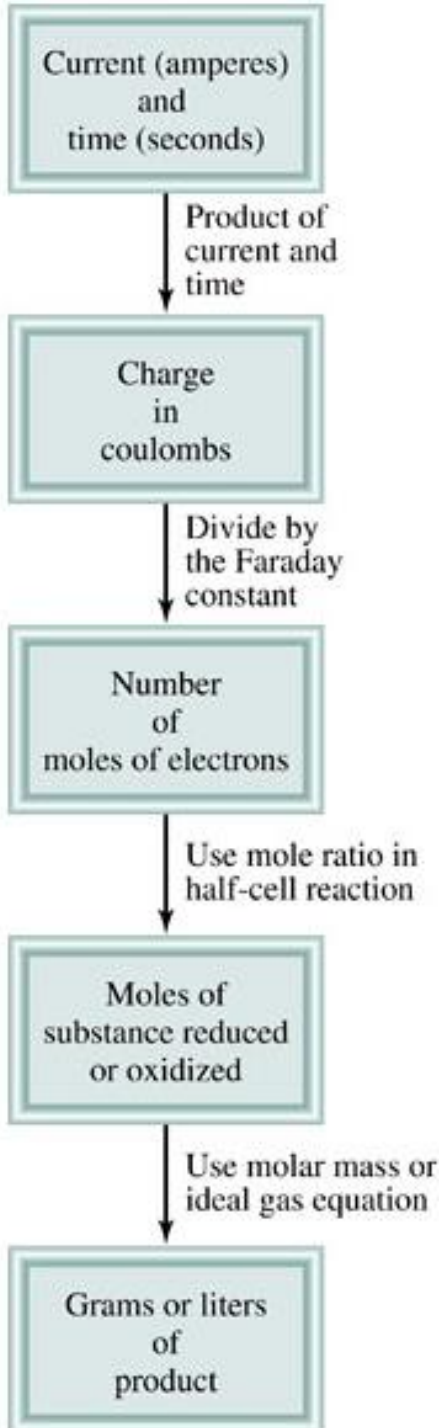


Oxidation



Reduction





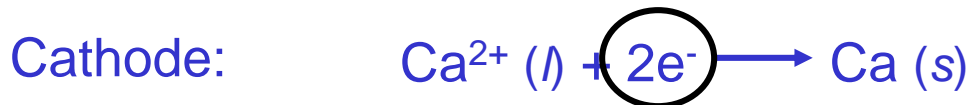
## Electrolysis and Mass Changes

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

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



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?



2 mole  $e^-$  = 1 mole Ca

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

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

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

# Chemistry In Action: Dental Filling Discomfort

## Corrosion of a Dental Filling

