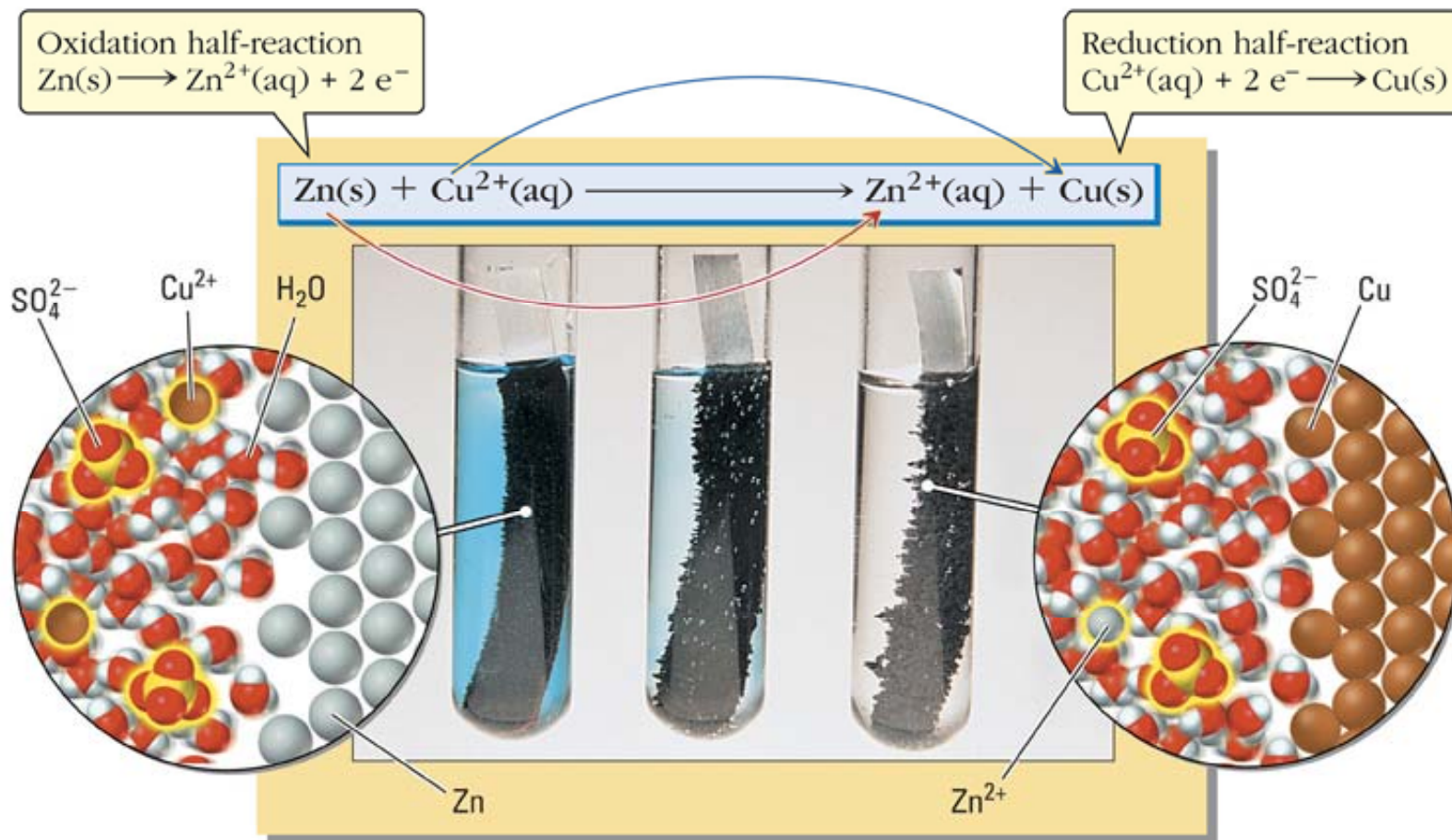


Chapter 19

Electrochemistry and Its Applications

Redox Reactions



Electrochemistry

- the study of chemical reactions that produce electrical currents or voltages and of the chemical reactions that are caused by the action of currents or voltages.

Basic Definitions

reduction - gain of electrons

oxidation - loss of electrons

oxidation-reduction reaction (redox reaction) - reaction in which one substance loses electrons to another substance

half-reaction - half of a redox reaction;
either the half of the reaction where oxidation occurs;
or, the half reaction where reduction occurs

More Definitions

oxidizing agent - substance that causes oxidation while undergoing reduction; attracts electrons away from a substance

reducing agent - substance that causes reduction while undergoing oxidation; loses electrons to another a substance

Balancing Oxidation-Reduction Equations

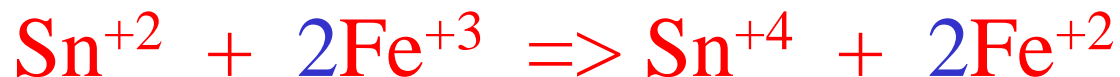
half-reaction technique



oxidation half reaction:



reduction half reaction:



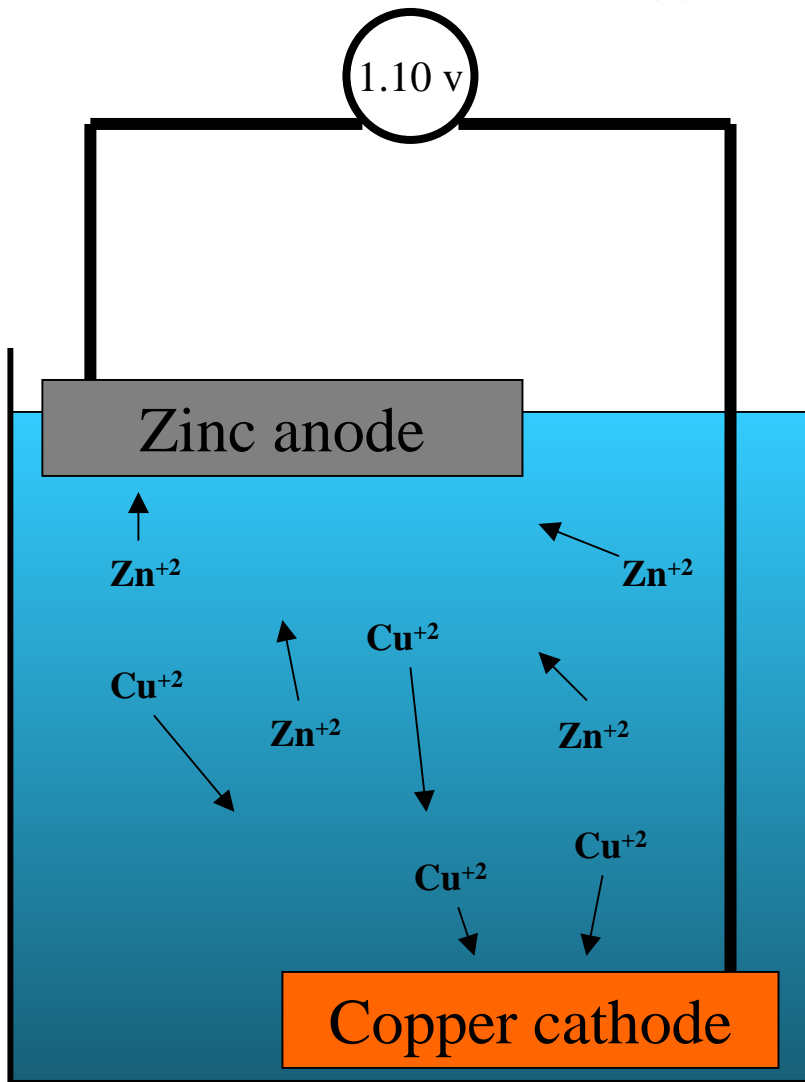
Rules for Assigning Oxidation States

1. zero for uncombined element
2. charge on monatomic ion
3. F is always -1; other halogens -1 except when combined with more electronegative halogen or oxygen ion or molecule
4. H is +1 except in metal hydrides, where H is -1
5. O is -2 except when combined with F (then +1 or +2) or in peroxides, -1.
6. sum of oxidation states equals charge on ion or molecule

Electrochemical Cells

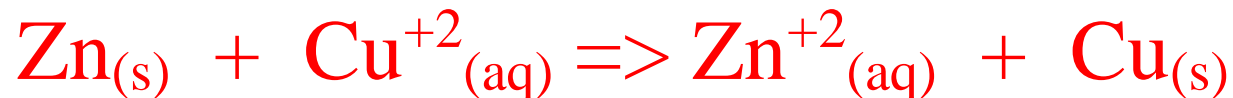
- harnessed chemical reaction which produces an electric current
- called *Voltaic Cells* or *Batteries*
- anode - electrode where oxidation occurs
- cathode - electrode where reduction occurs
- **Cell Potential** - the potential difference, in volts, between the electrodes of an electrochemical cell

Daniel's Cell

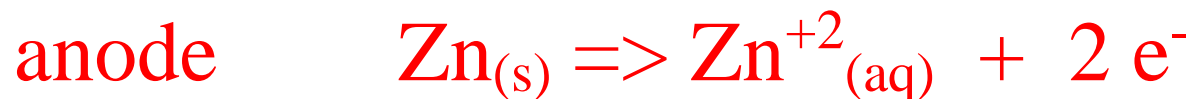


- battery for telegraph
- copper electrode dipped into a solution of copper(II) sulfate
- zinc electrode dipped into a solution of zinc sulfate

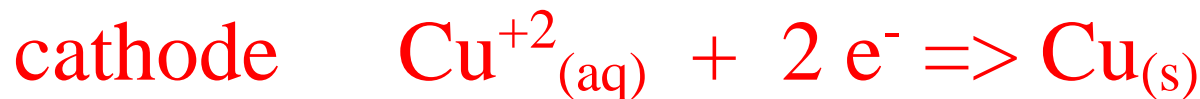
Daniel's Cell



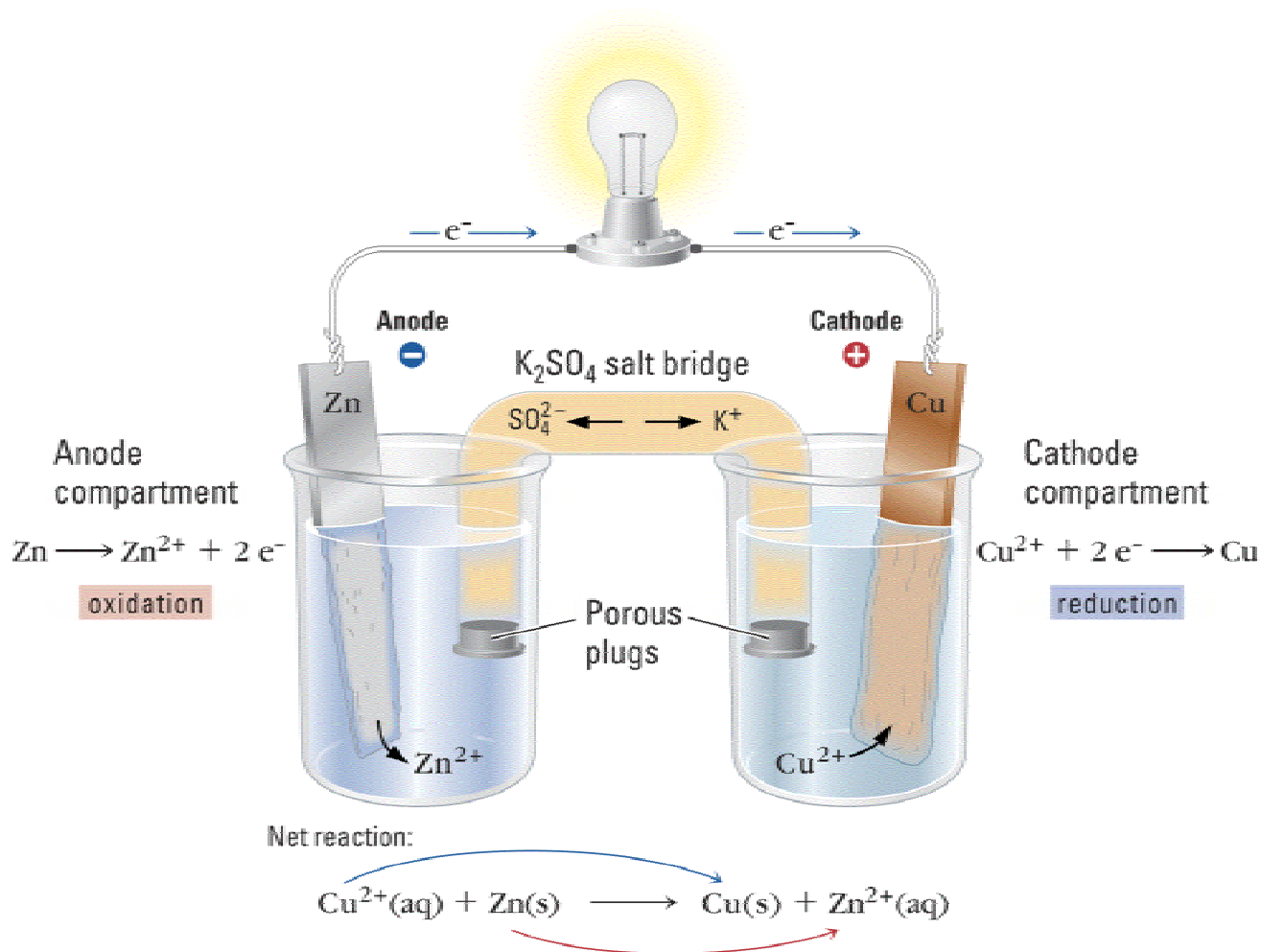
oxidation half reaction



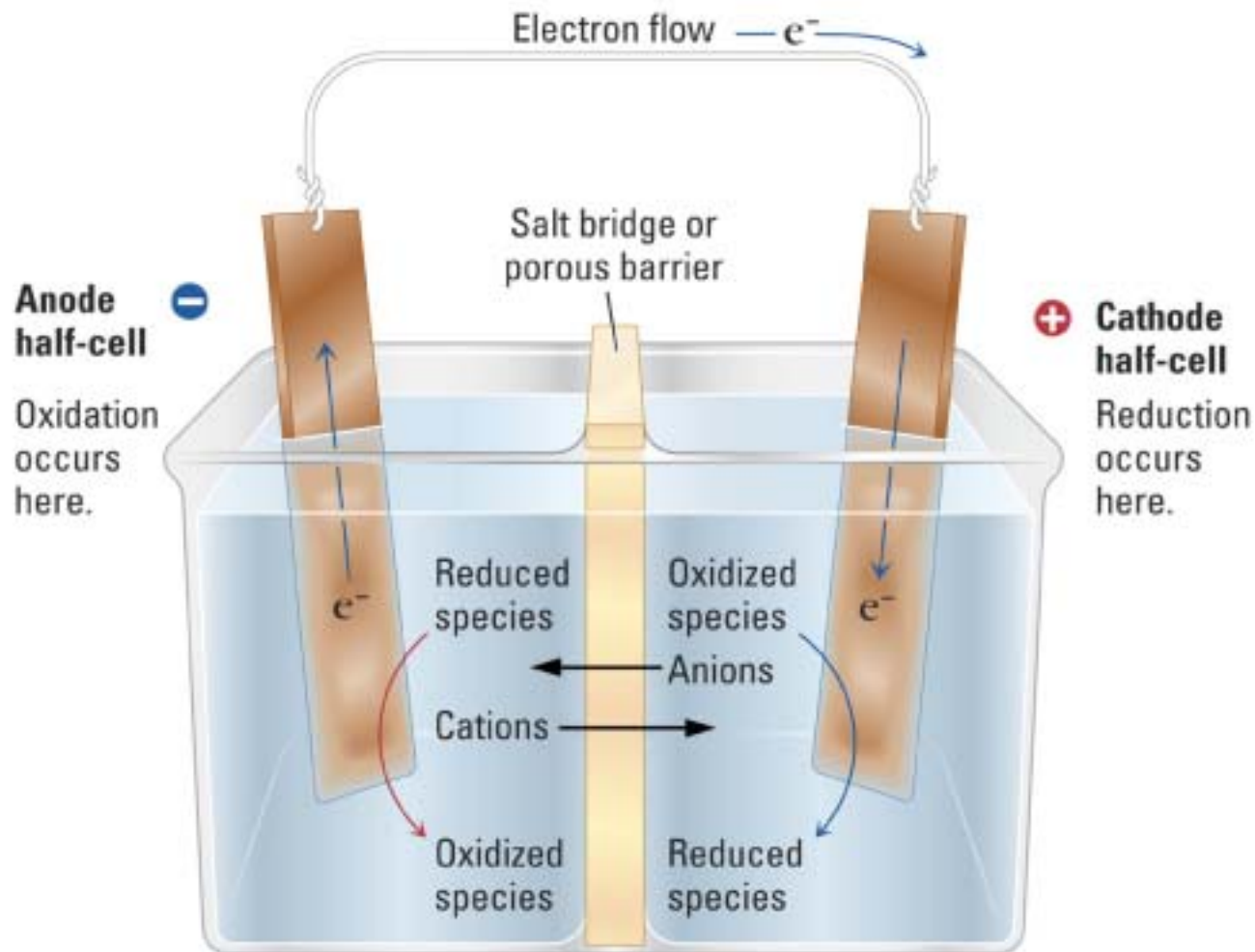
reduction half reaction



Simple Electrochemical Cell



Electrochemical Terminology



Electrical Work

electrical work = charge \times potential energy difference

Coulombs(C) = amperes(A) \times seconds(t)

1 volt = 1 joule/coulomb

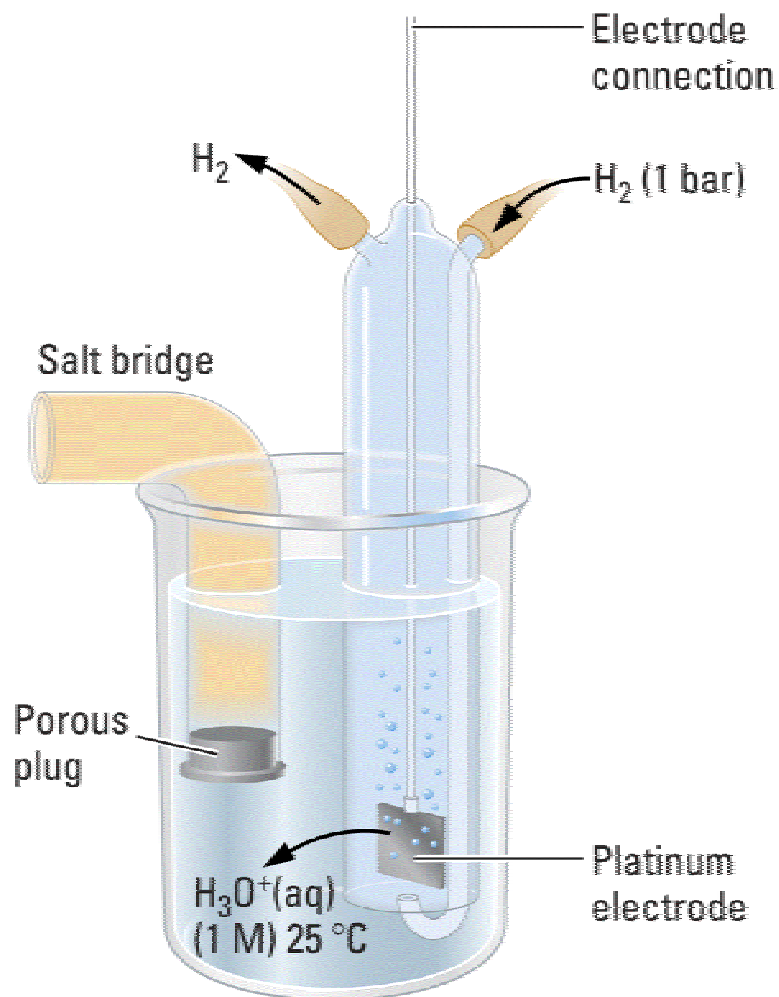
thus

1 joule = 1 volt \times 1 coulomb

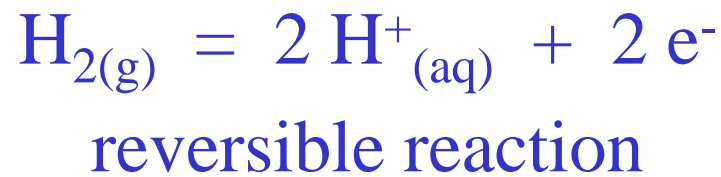
Standard Cell Potential

- the potential difference (in volts) between the electrodes of an electrochemical cell, when the all concentrations of all solutes is 1 molar, all the partial pressures of any gases are 1 atm, and the temperature at 25°C
- direction of Oxidation-Reduction Reactions
- positive value indicates a spontaneous reaction

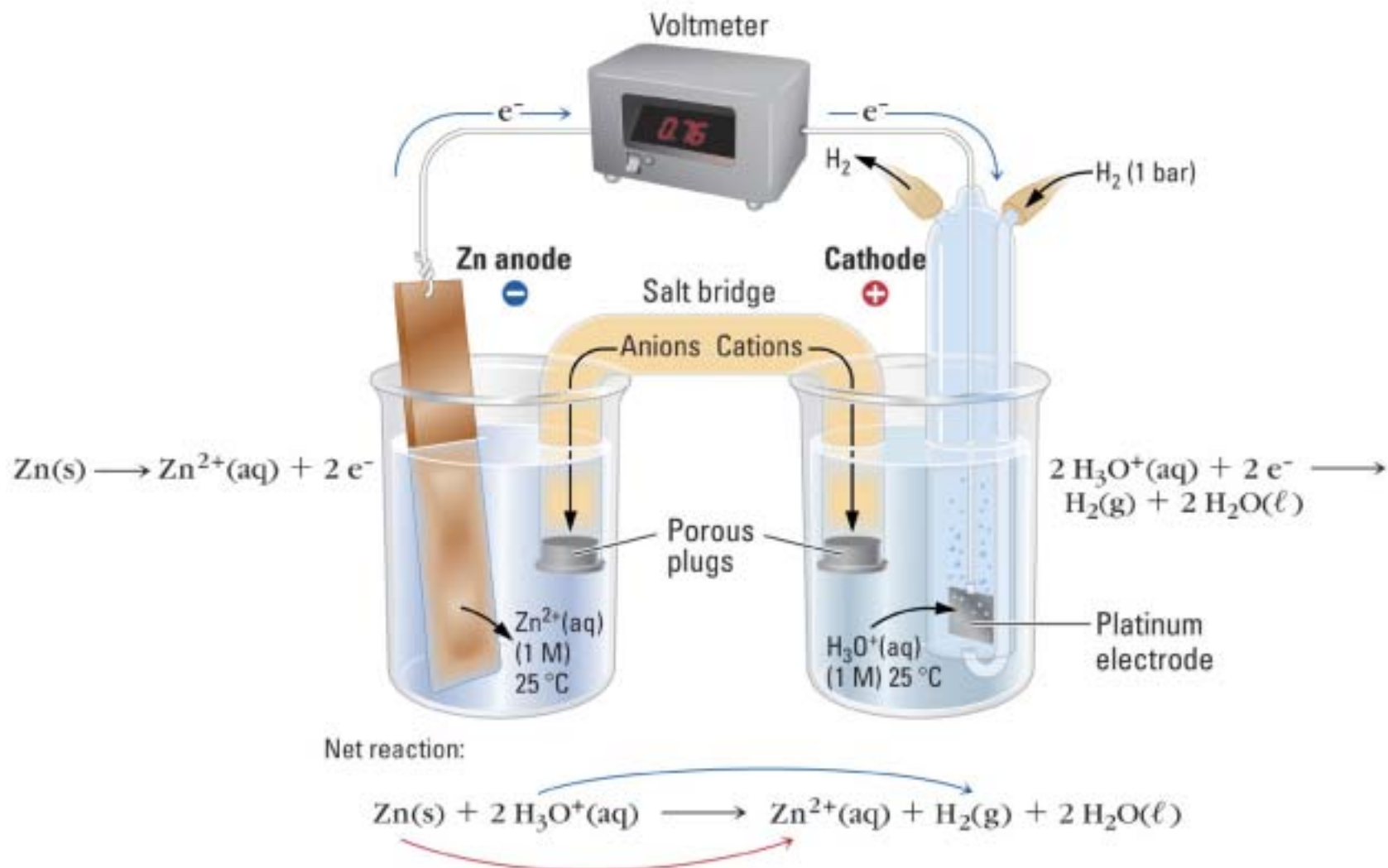
Standard Hydrogen Electrode



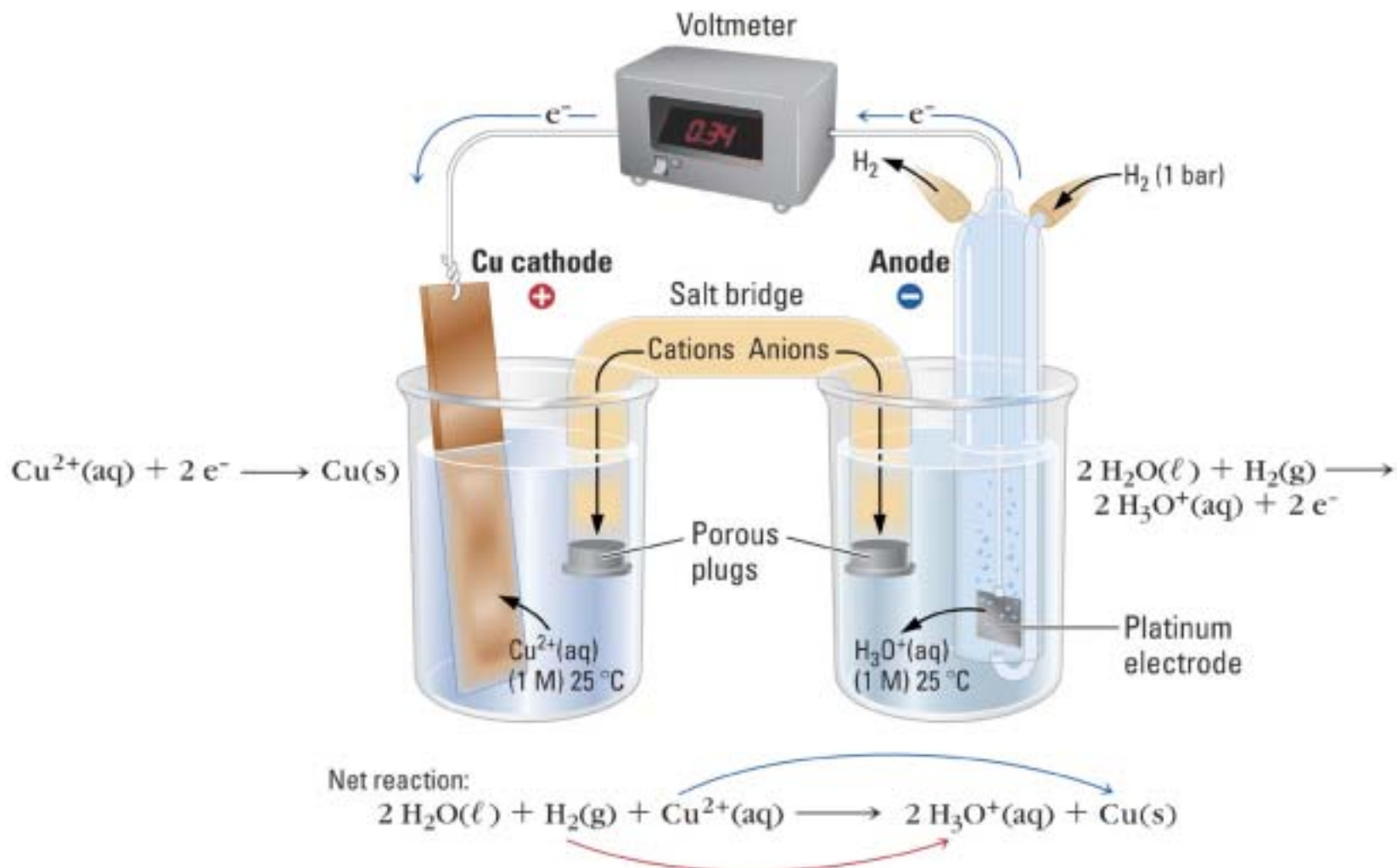
- consists of a platinum electrode covered with a fine powder of platinum around which $H_{2(g)}$ is bubbled. Its potential is defined as zero volts.



Zn vs. Hydrogen Electrode



Cu vs. Hydrogen Electrode



Standard Reduction Potentials

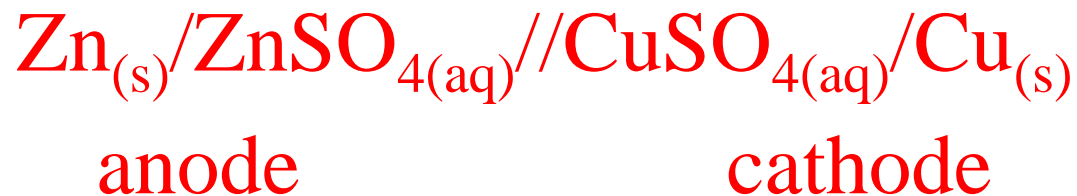
TABLE 19.1 Standard Reduction Potentials in Aqueous Solution at 25 °C*

Reduction half-reaction	E° (V)
$\text{F}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{F}^-(\text{aq})$	+2.87
$\text{H}_2\text{O}_2(\text{aq}) + 2 \text{H}_3\text{O}^+(\text{aq}) + 2 \text{e}^- \rightarrow 4 \text{H}_2\text{O}(\ell)$	+1.77
$\text{PbO}_2(\text{s}) + \text{SO}_4^{2-}(\text{aq}) + 4 \text{H}_3\text{O}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 6 \text{H}_2\text{O}(\ell)$	+1.685
$\text{MnO}_4^-(\text{aq}) + 8 \text{H}_3\text{O}^+(\text{aq}) + 5 \text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 12 \text{H}_2\text{O}(\ell)$	+1.52
$\text{Au}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Au}(\text{s})$	+1.50
$\text{Cl}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{Cl}^-(\text{aq})$	+1.360
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}_3\text{O}^+(\text{aq}) + 6 \text{e}^- \rightarrow 2 \text{Cr}^{3+}(\text{aq}) + 21 \text{H}_2\text{O}(\ell)$	+1.33
$\text{O}_2(\text{g}) + 4 \text{H}_3\text{O}^+(\text{aq}) + 4 \text{e}^- \rightarrow 6 \text{H}_2\text{O}(\ell)$	+1.229
$\text{Br}_2(\ell) + 2 \text{e}^- \rightarrow 2 \text{Br}^-(\text{aq})$	+1.08
$\text{NO}_3^-(\text{aq}) + 4 \text{H}_3\text{O}^+ + 3 \text{e}^- \rightarrow \text{NO}(\text{g}) + 6 \text{H}_2\text{O}(\ell)$	+0.96
$\text{OCl}^-(\text{aq}) + \text{H}_2\text{O}(\ell) + 2 \text{e}^- \rightarrow \text{Cl}^-(\text{aq}) + 2 \text{OH}^-(\text{aq})$	+0.89
$\text{Hg}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Hg}(\ell)$	+0.855
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	+0.80
$\text{Hg}_2^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow 2 \text{Hg}(\ell)$	+0.789
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	+0.771
$\text{I}_2(\text{s}) + 2 \text{e}^- \rightarrow 2 \text{I}^-(\text{aq})$	+0.535
$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\ell) + 4 \text{e}^- \rightarrow 4 \text{OH}^-(\text{aq})$	+0.40
$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.337
$\text{Sn}^{4+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Sn}^{2+}(\text{aq})$	+0.15
$2 \text{H}_3\text{O}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g}) + 2 \text{H}_2\text{O}(\ell)$	0.00
$\text{Sn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Sn}(\text{s})$	-0.14
$\text{Ni}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.25
$\text{PbSO}_4(\text{s}) + 2 \text{e}^- \rightarrow \text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq})$	-0.356
$\text{Cd}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cd}(\text{s})$	-0.40
$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.44
$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.763
$2 \text{H}_2\text{O}(\ell) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$	-0.8277
$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Al}(\text{s})$	-1.66
$\text{Mg}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Mg}(\text{s})$	-2.37
$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.714
$\text{K}^+(\text{aq}) + \text{e}^- \rightarrow \text{K}(\text{s})$	-2.925
$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.045

* In volts (V) versus the standard hydrogen electrode

Cell Diagram

- the shorthand representation of an electrochemical cell showing the two half-cells connected by a salt bridge or porous barrier, such as:



Redox Reaction

- the reduction half reaction is the half reaction with the more positive reduction potential
- the half reaction with the lower reduction potential is reverse and the sign of the potential is changed
- the cell potential is the sum of the half reaction potentials

Cell Potentials & ΔG

$$\Delta G = -nFE \quad \text{or} \quad \Delta G^\circ = -nFE^\circ$$

where n ; number of electrons
involved in reaction

F ; Faraday's constant,
1 mole e^- = 96,500 coulombs

$$\Delta G = \Delta G^\circ + RT \ln Q$$

thus

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

or

$$E = E^\circ - (RT/nF) \ln Q$$

Cell Potentials, ΔG , and K

$$E = E^\circ - (RT/nF) \ln Q$$

at equilibrium

$$0 = E^\circ - (RT/nF) \ln K_{\text{eq}}$$

and

$$(nFE^\circ)/(RT) = \ln K_{\text{eq}}$$

thus

$$K_{\text{eq}} = e^{(nFE^\circ / RT)}$$

Effect of Concentration on Cell Voltage: The Nernst Equation

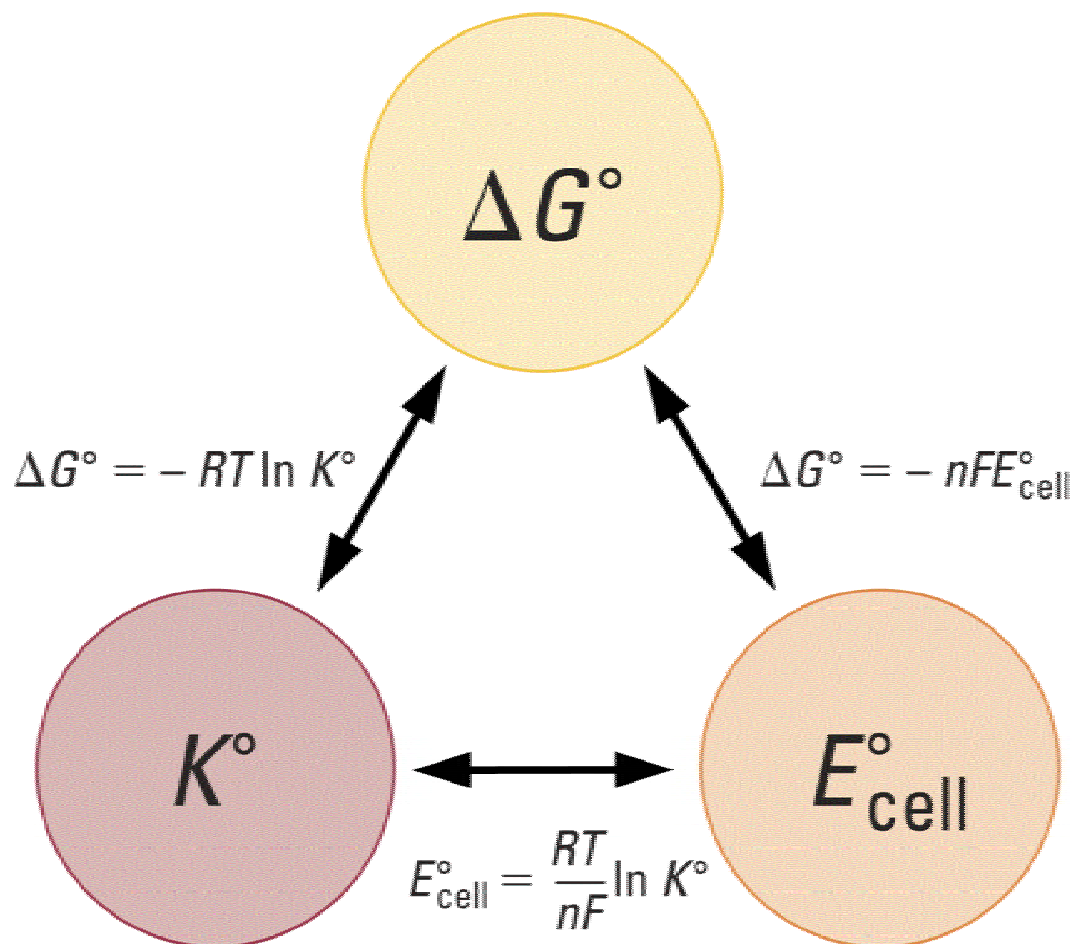
$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - (RT/nF)\ln Q$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.0592/n)\log Q$$

where Q is reaction quotient

$$Q = [\text{products}]/[\text{reactants}]$$

Relationships Linking: ΔG° , E_{cell}° , and K°



EXAMPLE: What is the cell potential for the Daniel's cell when the $[\text{Zn}^{+2}] = 10 [\text{Cu}^{+2}]$?

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.0592/n)\log Q$$

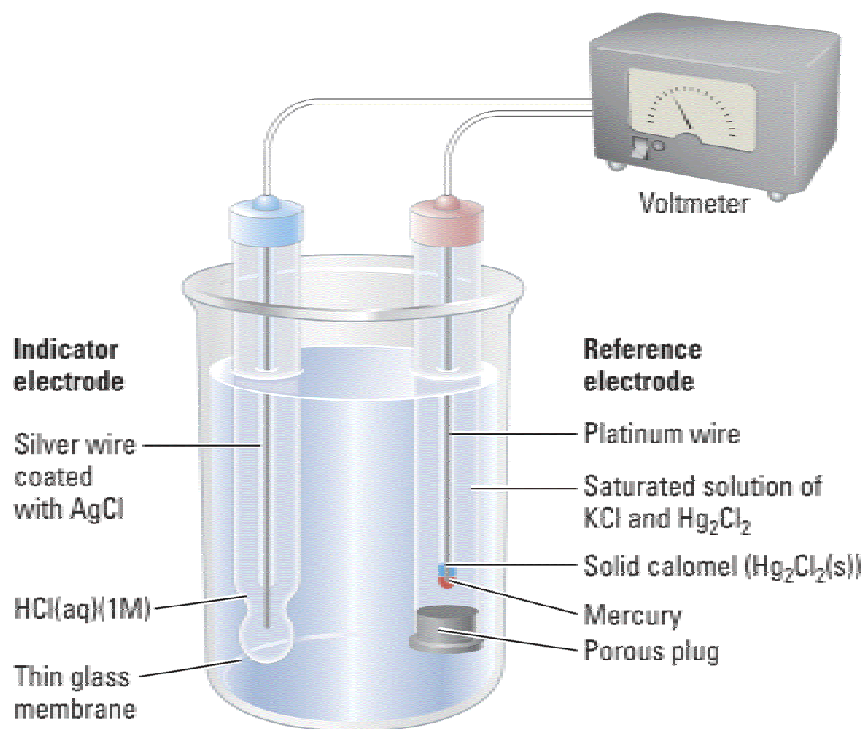
$$Q = ([\text{Zn}^{+2}]/[\text{Cu}^{+2}]) = (10 [\text{Cu}^{+2}])/[\text{Cu}^{+2}] = 10$$

$$E^{\circ} = (0.34 \text{ V})_{\text{Cu couple}} + (-(-0.76 \text{ V}))_{\text{Zn couple}}$$

$n = 2$, 2 electron change

$$\begin{aligned} E_{\text{cell}} &= (1.10 - (0.0592/2)\log 10) \text{ V} \\ &= 1.07 \text{ V} \end{aligned}$$

pH Meter



$$E_{\text{glass electrode}} = 0.0592\text{pH} + \text{constant}$$

Batteries

Primary Cells

non-reversible, non-rechargeable
electrochemical cell

"dry" cell & alkaline cell 1.5 v/cell

mercury cell 1.34 v/cell

fuel cell 1.23v/cell

Batteries

Secondary Cells

reversible, rechargeable electrochemical cell

lead-acid (automobile battery) 2 v/cell

NiCad 1.25 v/cell

Electrolysis

- **non-spontaneous reaction is caused by the passage of an electric current through a solution**

Quantitative Aspects of Electrolysis

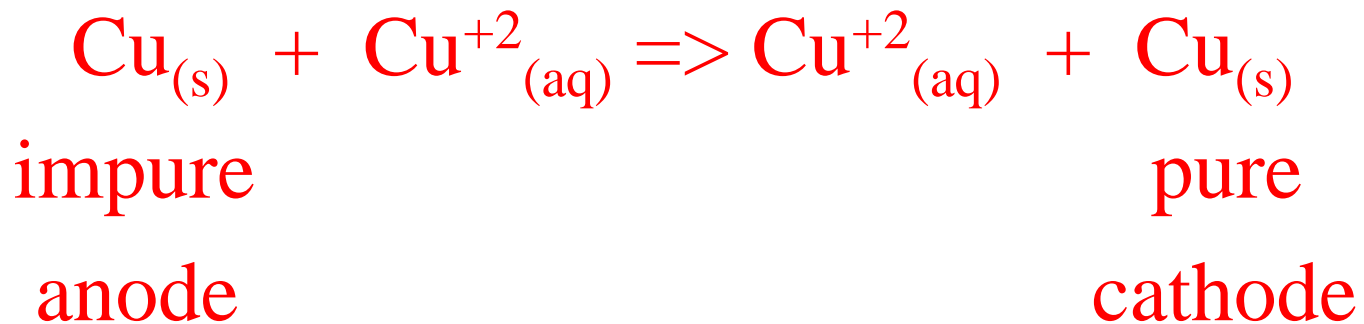
- $1 \text{ coulomb} = 1 \text{ amp sec}$
- $1 \text{ mole } e^- = 96,500 \text{ coulombs}$

Electrolysis of Sodium chloride

molten NaCl \Rightarrow liquid sodium and chlorine
gas

aqueous NaCl \Rightarrow caustic soda (sodium
hydroxide) and chlorine gas

Electrolytic Refining of Copper



impurities: anode mud; Ag, Au, Pb

EXAMPLE: How many grams of chromium can be electroplated from a Cr^{+6} solution in 45 minutes at a 25 amp current?

$$\begin{aligned} \#g \text{ Cr} &= (45 \text{ min}) \frac{(60 \text{ sec})}{(1 \text{ min})} (25 \text{ amp}) \frac{(1 \text{ C})}{(1 \text{ amp sec})} \\ &\quad \frac{(1 \text{ mol e}^-)}{(96,500 \text{ C})} \frac{(52 \text{ g Cr})}{(6 \text{ mole e}^-)} \\ &= 58 \text{ g Cr} \end{aligned}$$