Assigning Oxidation Numbers:

1. Oxidation number of a free element or diatomic molecule is zero.

Ex: Na(s), Cu(s), H_2(g), F_2(g)

2. In most cases the oxidation number of hydrogen is +1, oxygen is -2, and fluorine is -1 when combined with another element.

3. The sum of the oxidation numbers of each of the elements in a molecule or ion must equal the charge.

Reduction-Oxidation Reactions (REDOX):

Oxidation- **Process in which oxidation state of an element increases. Species loses electrons.**

Reduction- Process in which oxidation state of an element decreases. Species gains electrons.

Using Oxidation Numbers:

Ex:

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

$Zn(s)$: oxidized(lost electrons).

$Cu^{2+}(aq)$: reduced(gained electrons).

Ex:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

$H_2(g)$: oxidized(lost electrons).

$O_2(g)$: reduced(gained electrons).

REDOX cont…:

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

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

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

Zn(s): oxidized/reducing agent.

Cu^{2+}(aq): reduced/oxidizing agent.

Writing Balanced Redox Reactions:

Oxidation and reduction reactions occur together. Occur in acidic or basic medium.

Ex: (acidic)

$$SO_3^{2-} + MnO_4^{-} \rightarrow SO_4^{2-} + Mn^{2+}$$

STEP 1: Identify the oxidized and reduced species and write the corresponding half reactions.

Writing Balanced Redox Reactions cont…:

STEP 2: Balance each of the half reactions. First atoms other than H and O. Balance O atoms by adding H_2O molecules and then balance H atoms by adding H^+ ions.

STEP 3: Balance the number of electrons.

STEP 4: Add both half reactions and simplify.

Writing Balanced Redox Reactions cont…

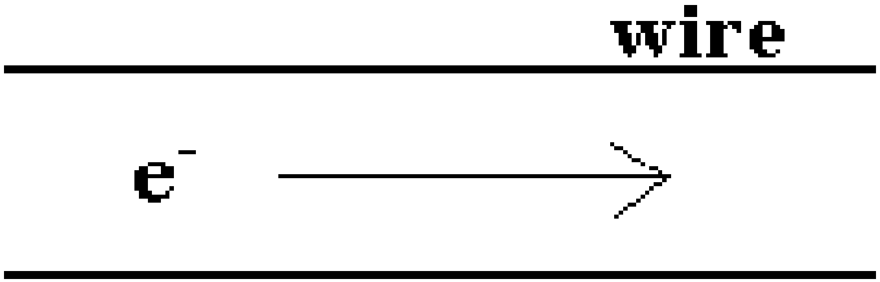
Balance the following redox reaction which occurs in a basic medium.

$$CrO_4^{2-} + S^{2-} \rightarrow Cr(OH)_3(s) + S(s)$$

NOTE: In basic medium add an equal number of OH^- ions to both sides to neutralize H^+ ions.

$$OH^- + H^+ \rightarrow H_2O$$

Electrochemical Cells:



I: current(flow)

V: voltage(pressure)

Consider,

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

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

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

Electrochemical Cells:

Electrode- Strip of metal.

Half cell-Strip of metal in contact with its ion.

Salt bridge- Allows passage of charge but not reactants.

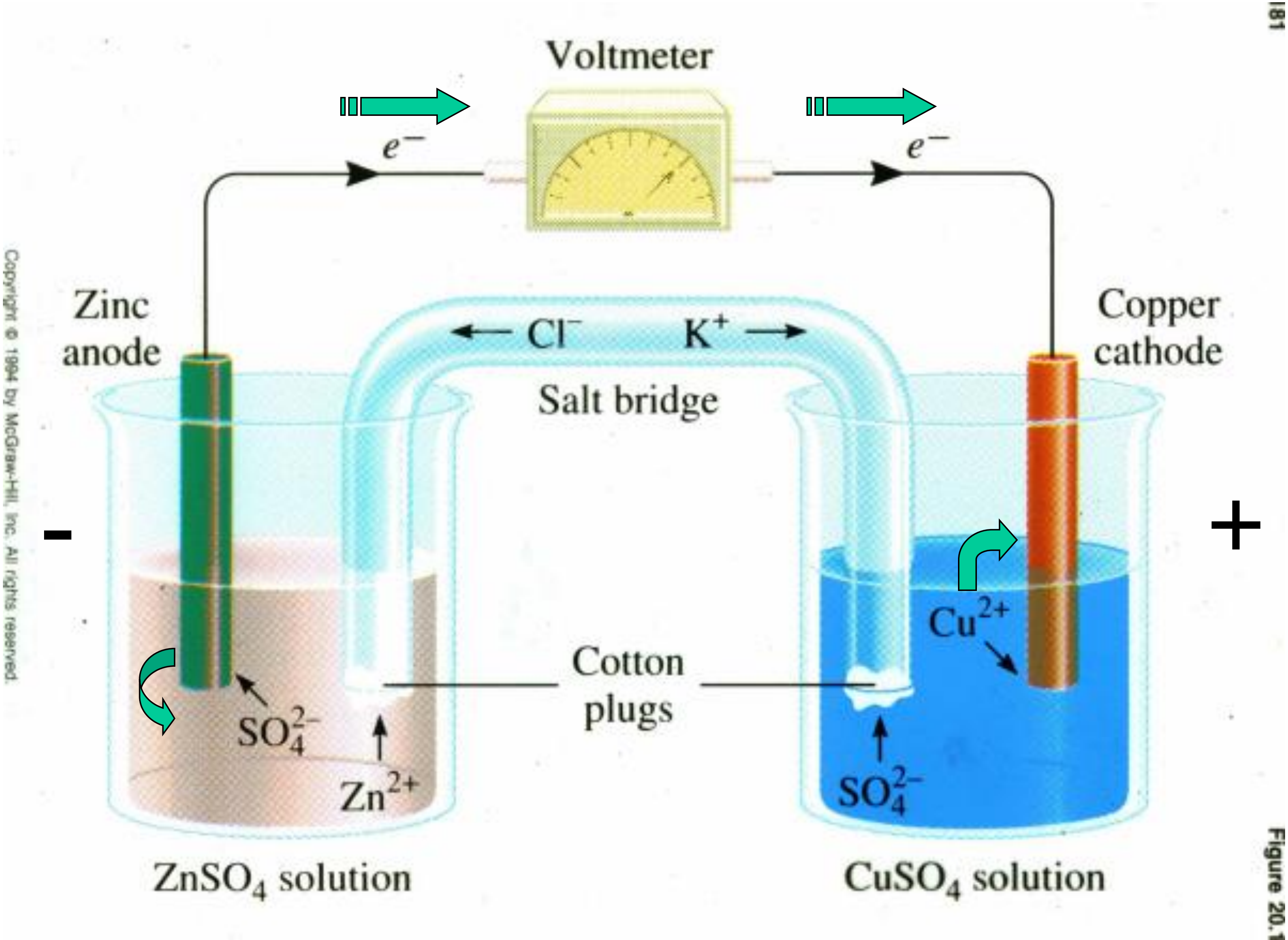
Anode:

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

Cathode:

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

Electrochemical Cells cont…:



Electrode Potentials:

The voltage recorded by an electrochemical cell is referred to as the electromotive force(emf) and given the following symbol.

$$E_{cell}$$

Describing Electrochemical Cells (Cell Diagram):

ANODE(OXIDATION) on left.
CATHODE(REDUCTION) on right.
| indicates phase change.
|| indicates salt bridge.

$$M(s)\,|\,M^{n+}(aq)\,||\,M^{n+}(aq)\,|\,M(s)$$

(anode) **(cathode)**

Standard Electrode Potentials:

Reaction occurs under standard conditions: 25°C and all substances are at unit concentration
(1 M for all ions and 1 atm for all gases).
Measured potential given the following symbol.

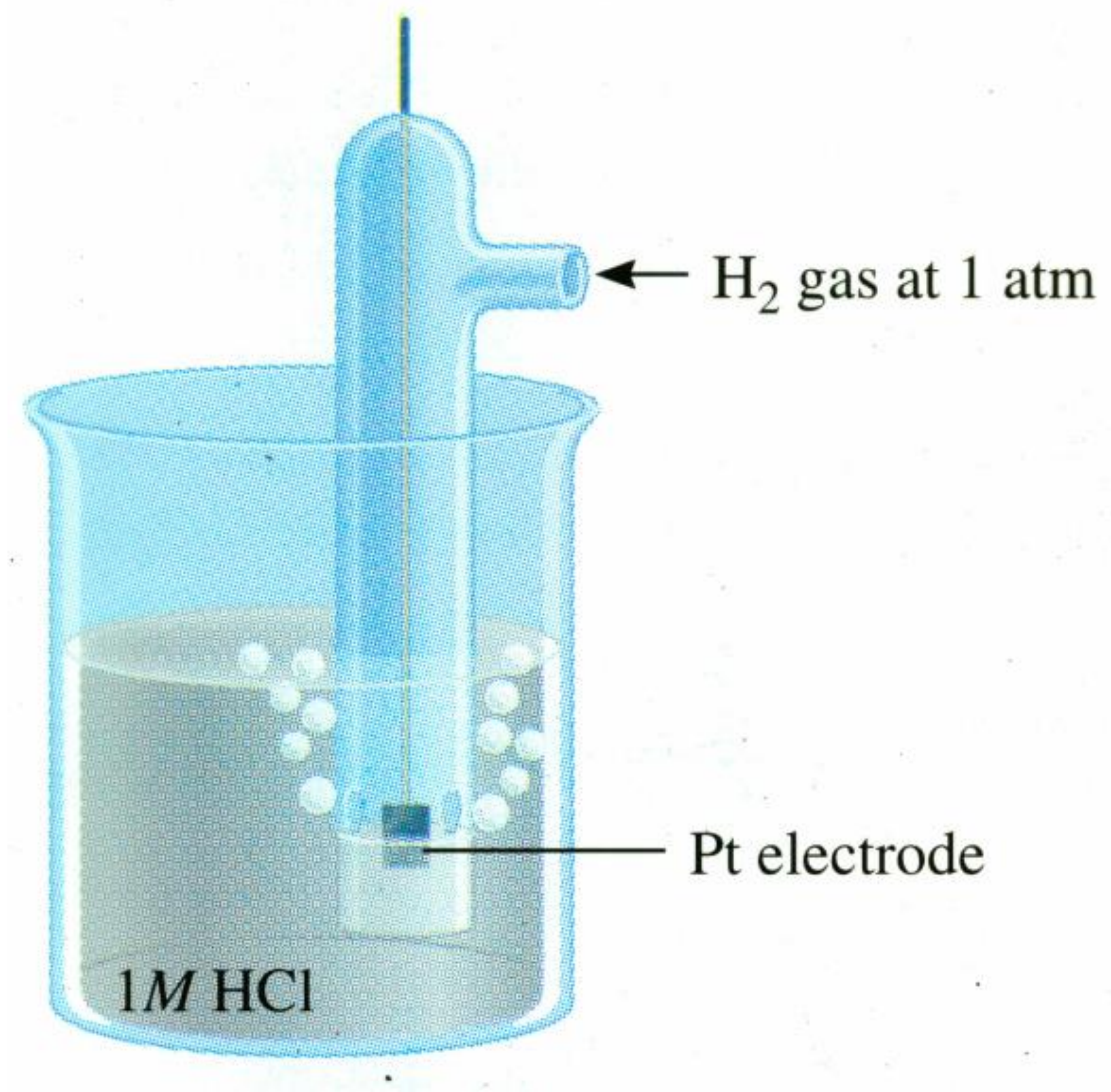
$$E^o_{cell}$$

The cell potential can be broken up into two components or half cells.

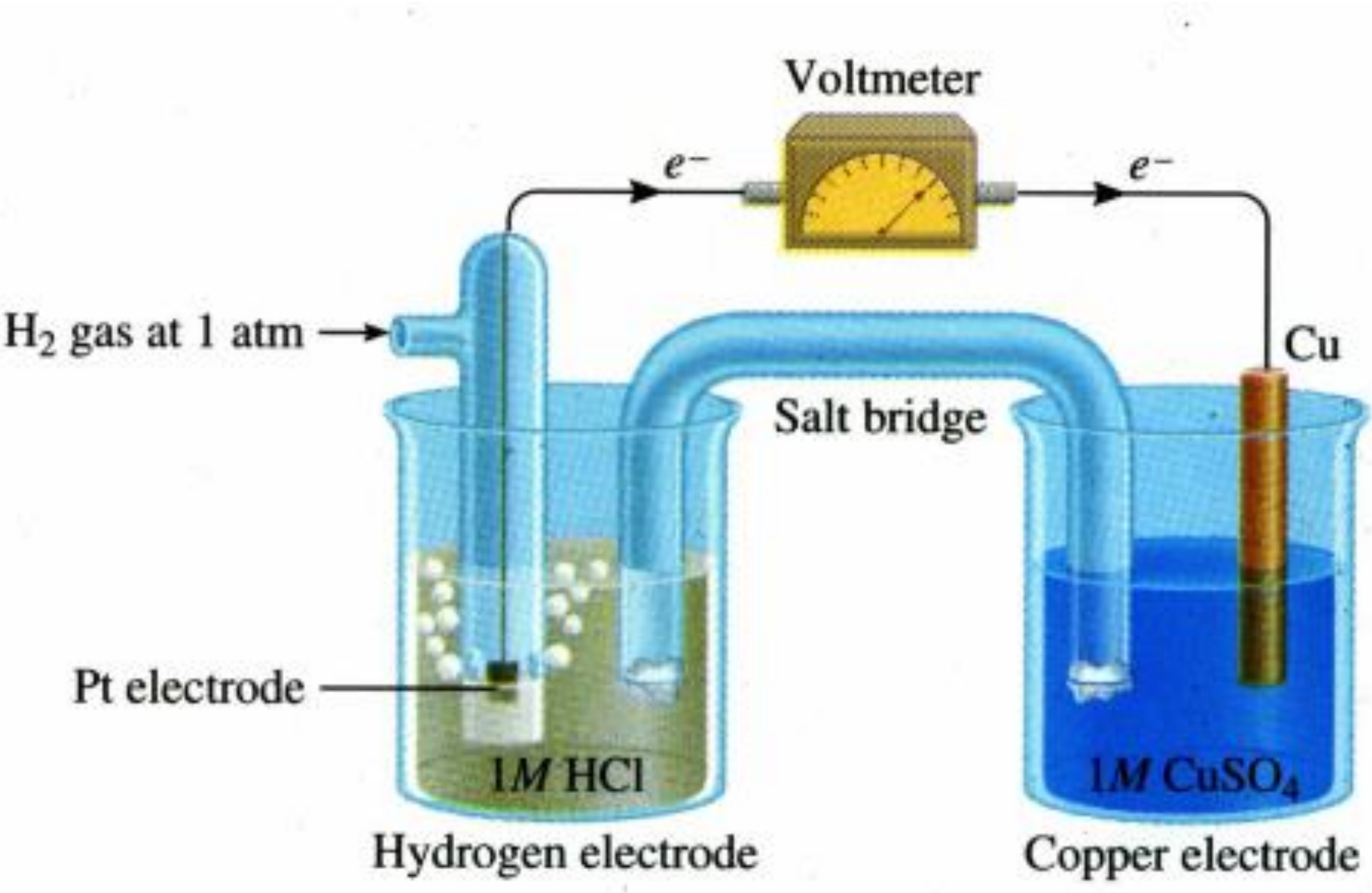
$$E^o_{cell} = E^o_{oxidation} + E^o_{reduction}$$

Standard Hydrogen Electrode(SHE):

$$2H^+(aq)(1\ M) + 2e^- \rightarrow H_2(g)(1\ atm) \quad E^o = 0\ V$$

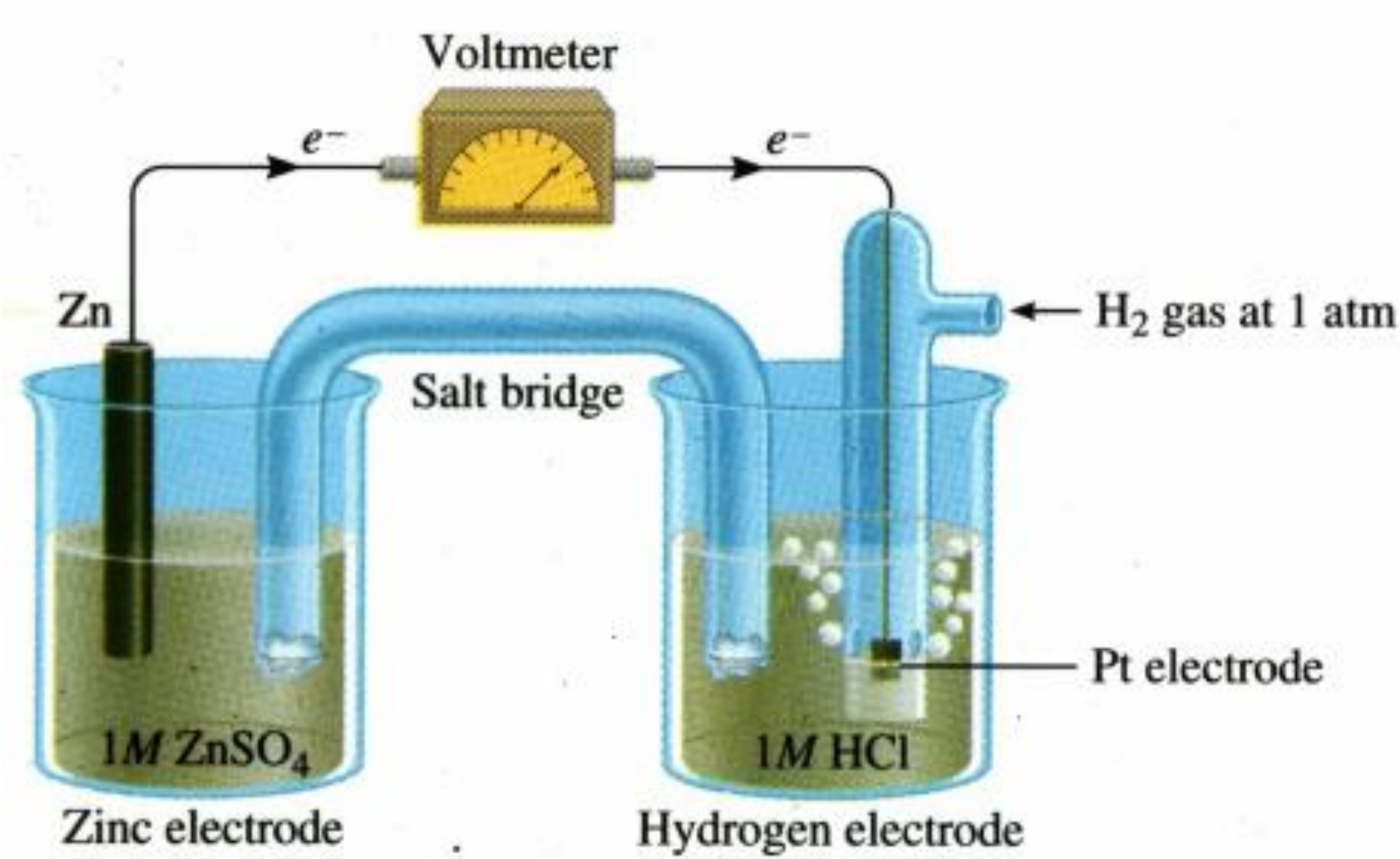


SHE/Cu



$$E^o_{cell} = +\,0.337\ \text{V}$$

Zn/SHE



$$E^o_{cell} = +0.763\,\mathrm{V}$$

Standard Reduction Potentials:

Can now determine the potential for each half cell. Tabulated and are referred to as standard reduction potentials.

Ex:Calculate the standard cell potential for the following:

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

Given: $E_{reduc}°(V)$

$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ $+0.337\ V$

$Cd^{2+}(aq) + 2e^{-} \rightarrow Cd(s)$ $-0.403\ V$

Standard Reduction Potentials cont…

Ex2: Calculate the standard cell potential for the following:

$$2Al(s) + 3Cu^{2+}(aq) \rightarrow 3Cu(s) + 2Al^{3+}$$

Given:	$E_{red}°$(V)
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.337 V
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	-1.66 V

Predicting Spontaneous Redox Reactions:

$w_{electrical} = nF\,E_{cell}$ $\Delta G = -nF E_{cell}$

$w_{electrical}$ = electrical work

n = # moles of electrons transferred

F = Faraday constant(96485 C/mole)

E_{cell} = Voltage of cell. NOTE: 1 J = 1 C·V

ΔG Gibbs Free Energy

$\Delta G < 0$ process is spontaneous

E_{cell} + # process is spontaneous

$\Delta G > 0$ process is not spontaneous

E_{cell} - # process is not spontaneous

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

$$E^{o}_{cell} = +1.10\ \text{V} \quad \text{spontaneous}$$

Reverse reaction

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

$$E^{o}_{cell} = -1.10\ \text{V} \quad \text{not spontaneous}$$

Consider:	$E_{red}°$(V)
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.337 V
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	-0.763 V

Cu^{2+} more likely to be reduced.

Cell Potential as a Function of Concentration:

Nernst Equation:

$$E_{cell} = E^{\circ}_{cell} + \frac{-0.0592V}{n} LogQ$$

Where if aA + bB → cC + dD

$$\mathbf{Q} = \frac{[\mathbf{C}]^{\mathbf{c}}[\mathbf{D}]^{\mathbf{d}}}{[\mathbf{A}]^{\mathbf{a}}[\mathbf{B}]^{\mathbf{b}}}$$

Cell Potential as a Function of Concentration cont…:

Ex: Calculate E_{cell} for the following voltaic cell.

$Zn(s)|Zn^{2+}(0.15\ M)||Cu^{2+}(0.20\ M)|Cu(s)$

Ex:2 Calculate E_{cell} for the following voltaic cell.

$Pt(s)|H_2(g)(0.5\ atm)|H^+(0.50\ M)||Ag^+(0.20\ M)|Ag(s)$

Electrolysis:

Electricity is used to cause a non-spontaneous redox reaction to occur.

Ex: Electrolysis of molten sodium chloride.

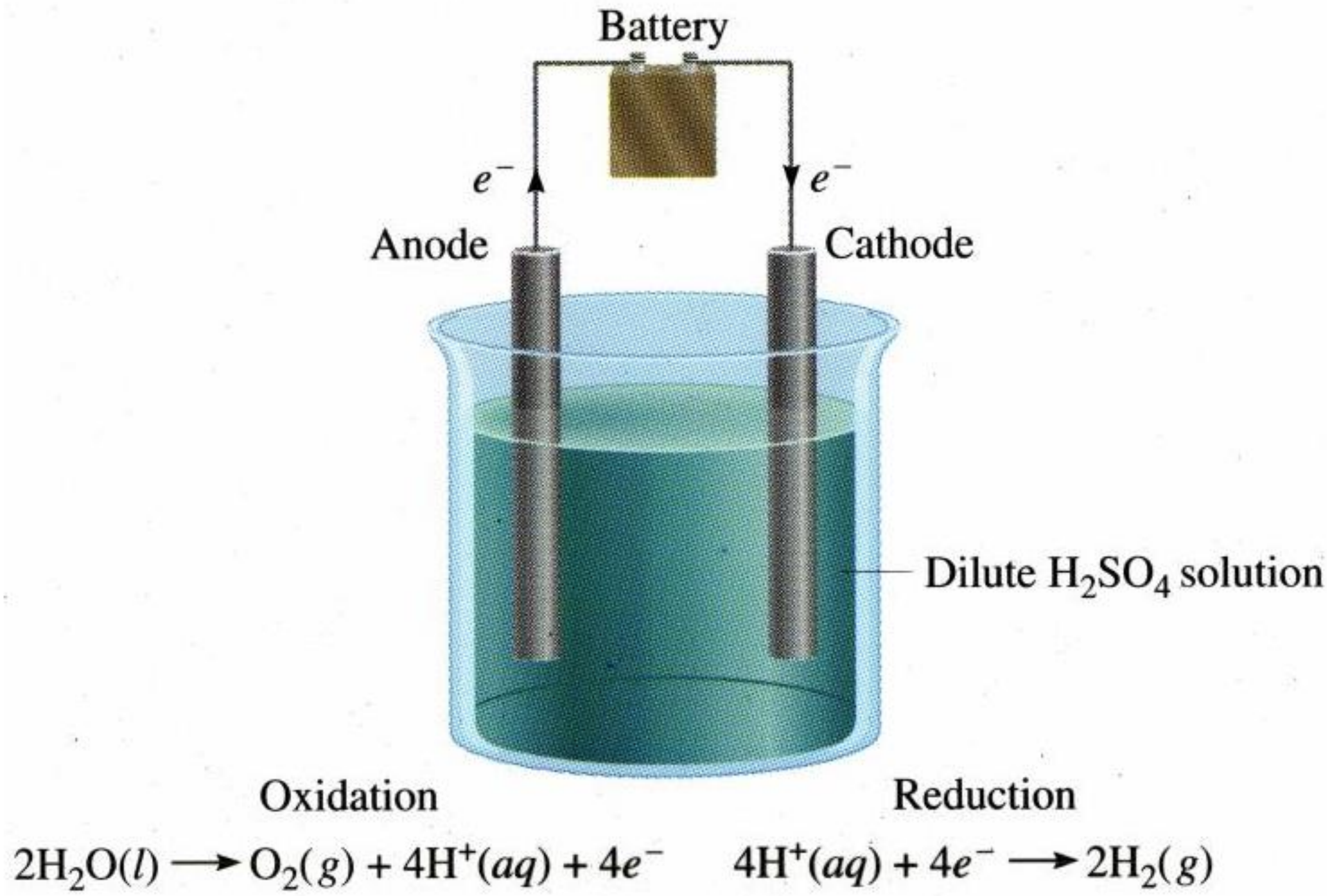
$$2Na^{+}(aq) + 2Cl^{-}(aq) \rightarrow 2Na(s) + Cl_2(g)$$

$E_{cell}° = -4.07\ V$ **NOT SPONTANEOUS!!!**

Electrolysis of Water:

Ex:

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g) \qquad E_{cell}° = -1.23V$$



Quantitative Electrolysis:

Direct relationship between the amount of electricity used and the amount of products obtained from an electrolysis.

$$E = IR$$

E = voltage   I: current(in amps)

R: resistance(in ohms)

1 mole of electrons = 1 F(faraday)

1 F = 96500 C

$1A = 1\ C{\cdot}s^{-1}$

Quantitative Electrolysis Examples:

Ex:

$$2Na^{+} \quad + \quad 2Cl^{-} \rightarrow \quad 2Na(s) \; + Cl_2(g)$$

In the electrolysis of NaCl, how much Na(s) and Cl_2(g) is produced by a current of 0.500 A in 10.0 minutes.

Quantitative Electrolysis Examples:

Ex: 2

$$Cu^{2+} + H_2O \rightarrow O_2(g) + Cu(s)$$

Balance the following redox reaction and calculate the mass of $O_2(g)$ and Cu(s) produced in 30 sec by a current of 1.50 A.

Ex: 3

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

If a current of 1.00 A is used, how many minutes does it take to electrolyze 0.0146 g of copper?

Corrosion:

Deteriation of metals.

Rust forms when Fe(s) is oxidized to Fe_2O_3 and $O_2(g)$ is reduced to H_2O.

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3$$

(brittle)

$E_{cell} = + \#$ **occurs spontaneously**

$Ag(s) \rightarrow Ag_2S$

$Cu(s) \rightarrow CuCO_3$ **(patina)**