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:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

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

$N_2(g)$: 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)

$$Br^- + MnO_4^- \rightarrow Br_2 + Mn^{2+}$$

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…

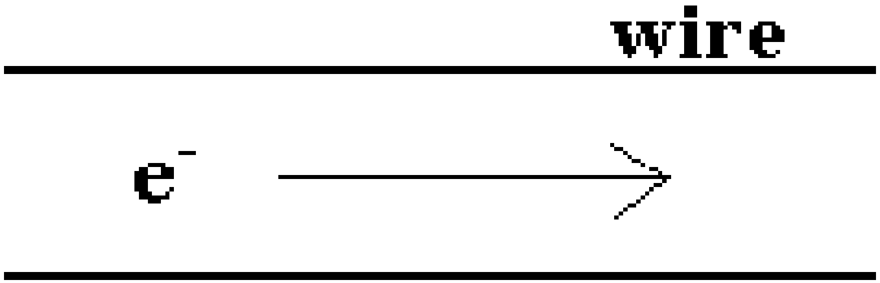
Balance the following redox reaction which occurs in a basic medium.

$$MnO_4^- + Br^- \rightarrow Br_2 + Mn^{2+}$$

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.

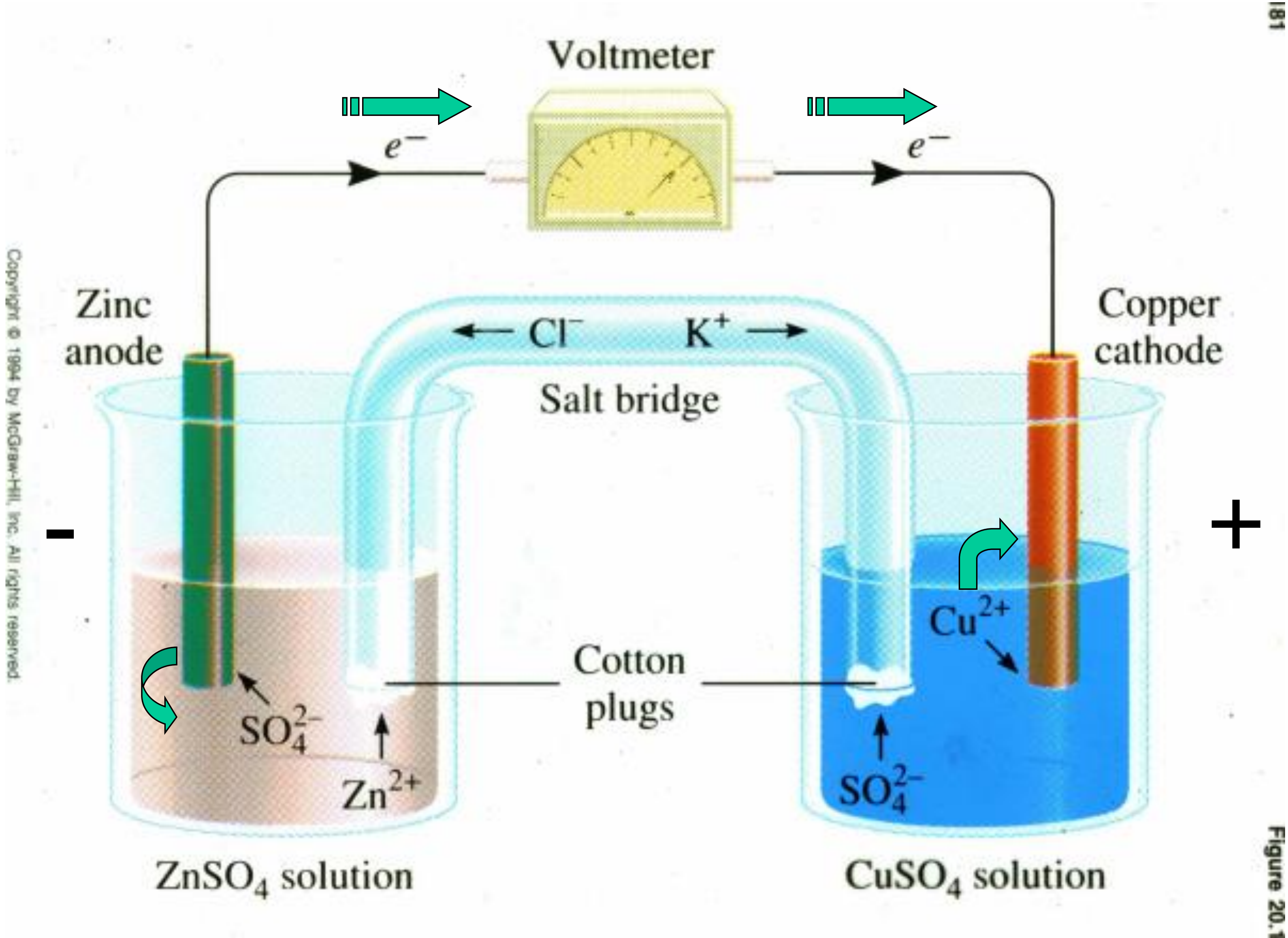
Anode:

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

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.

$$E_{cell}$$

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.

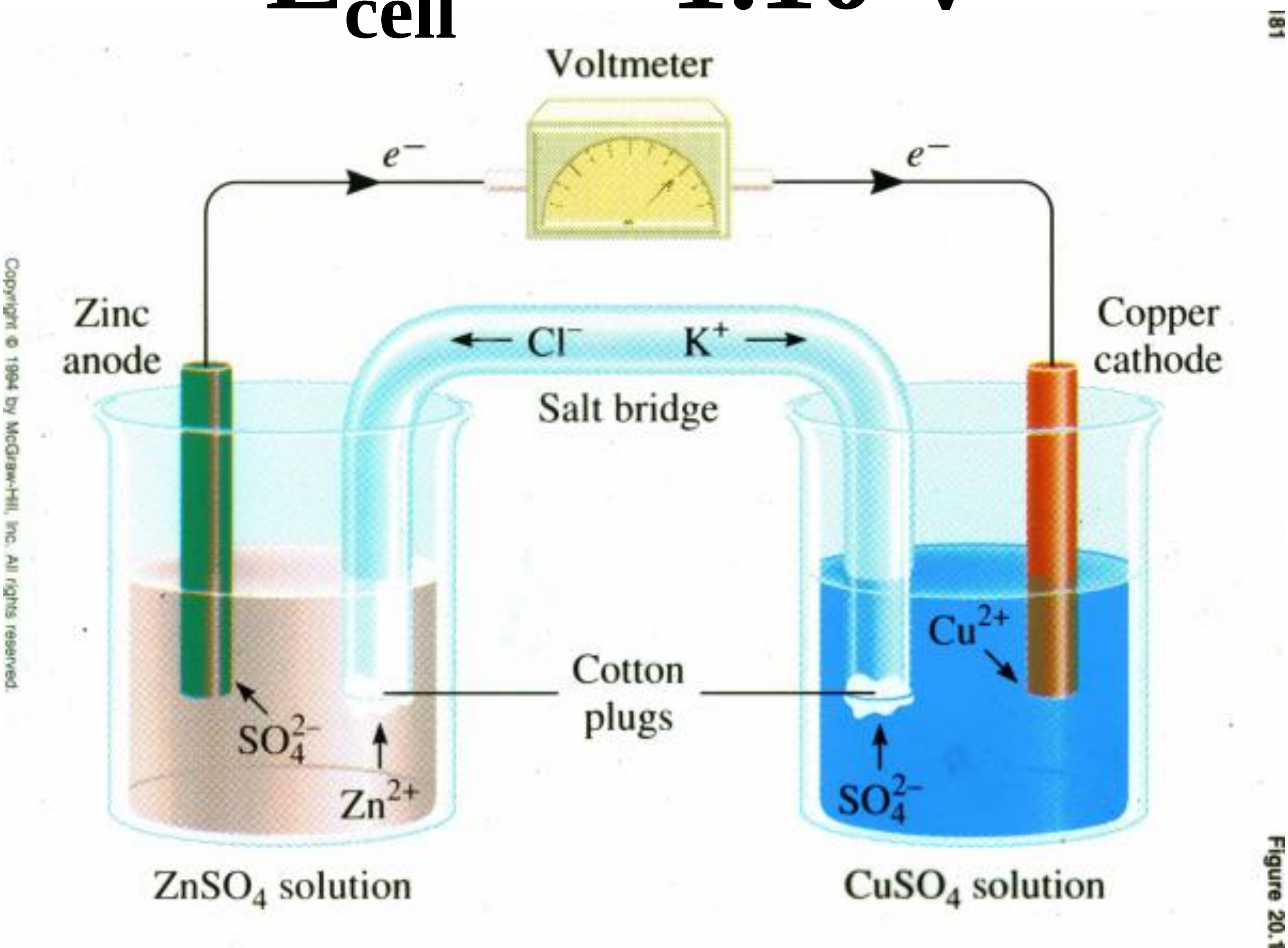
$$E^{o}_{cell}$$

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

$$E^{o}_{cell} = E^{o}_{oxidation} + E^{o}_{reduction}$$

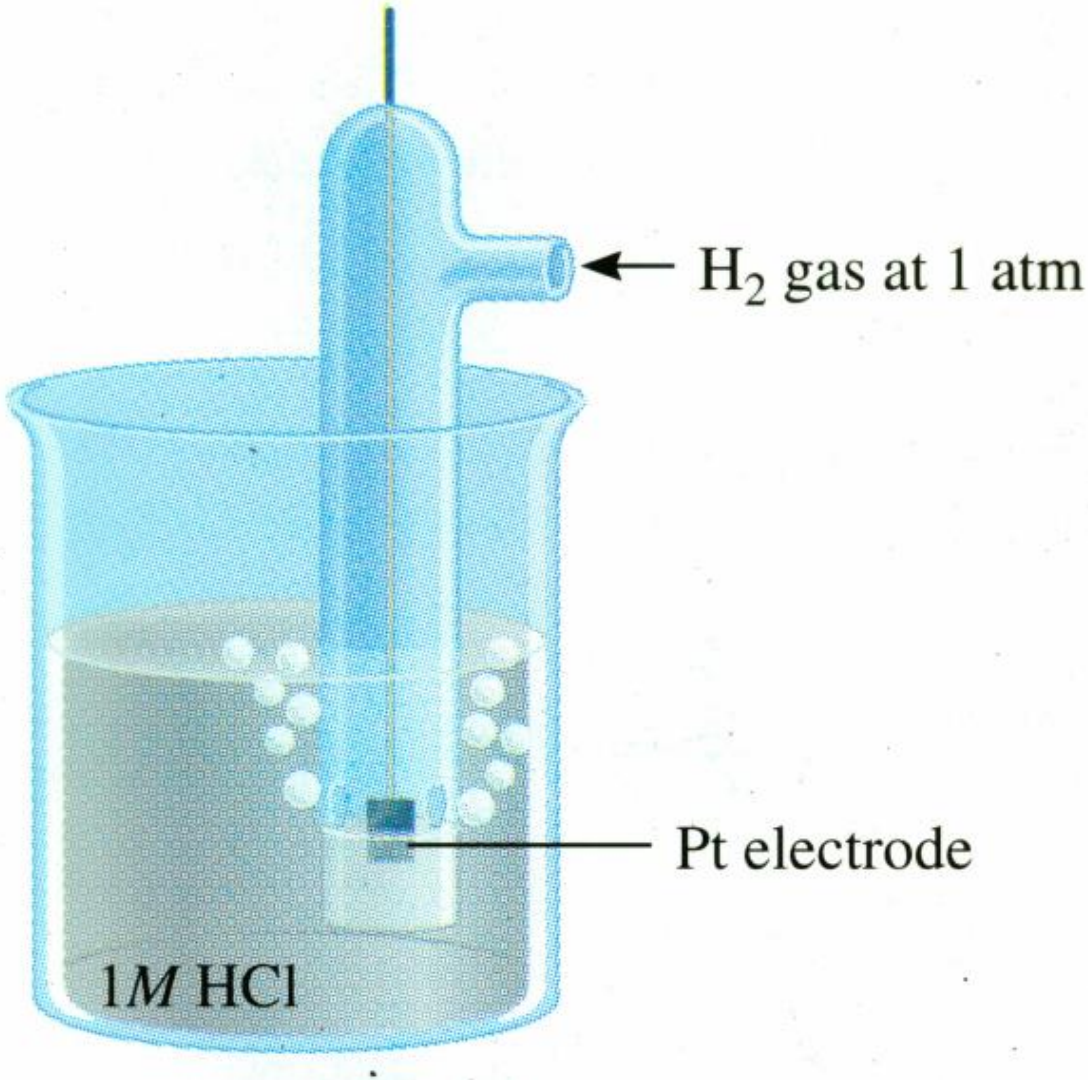
Electrochemical Cells cont…:

$$E_{cell} = +1.10\ V$$

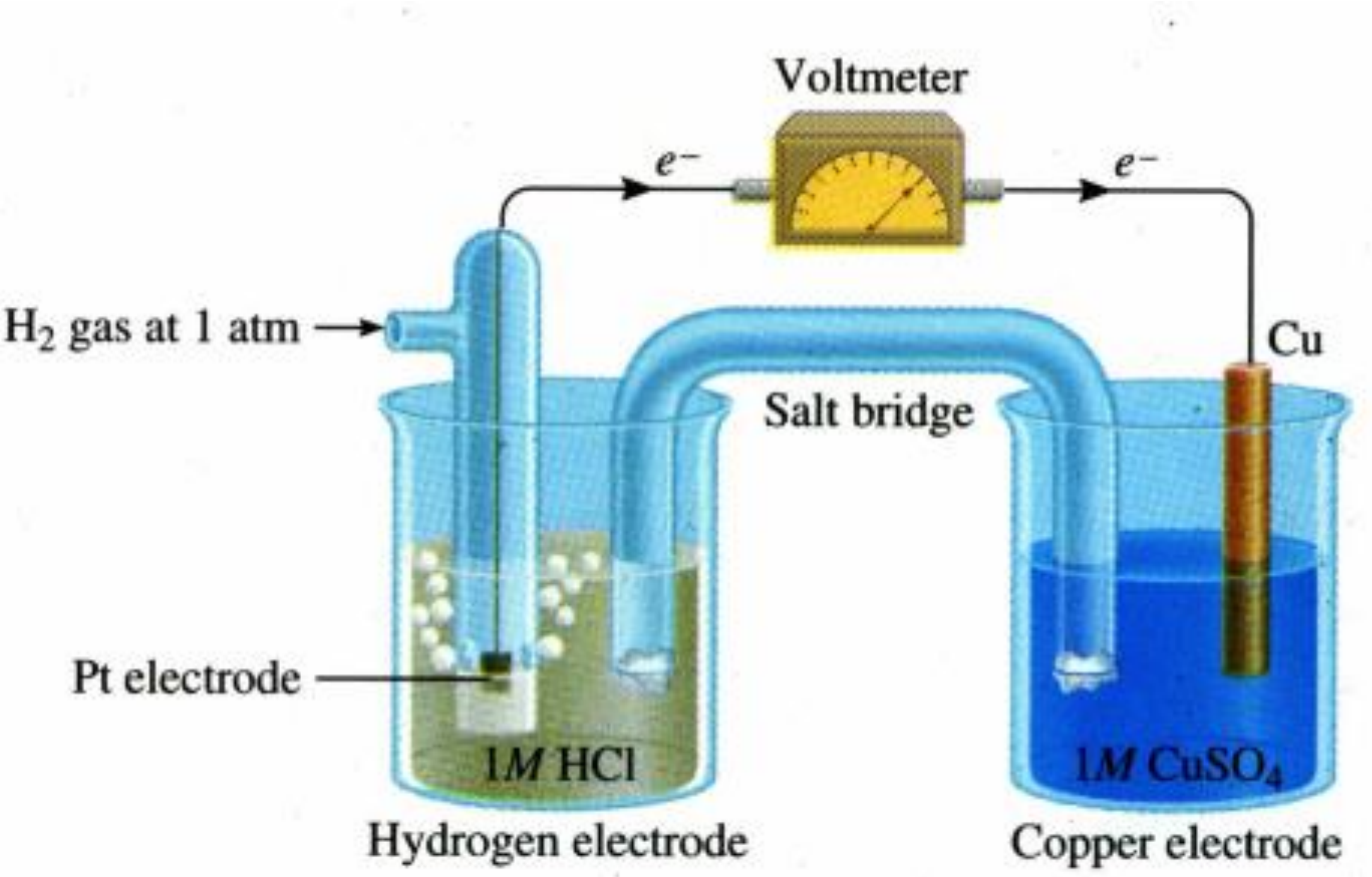


Standard Hydrogen Electrode(SHE):

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

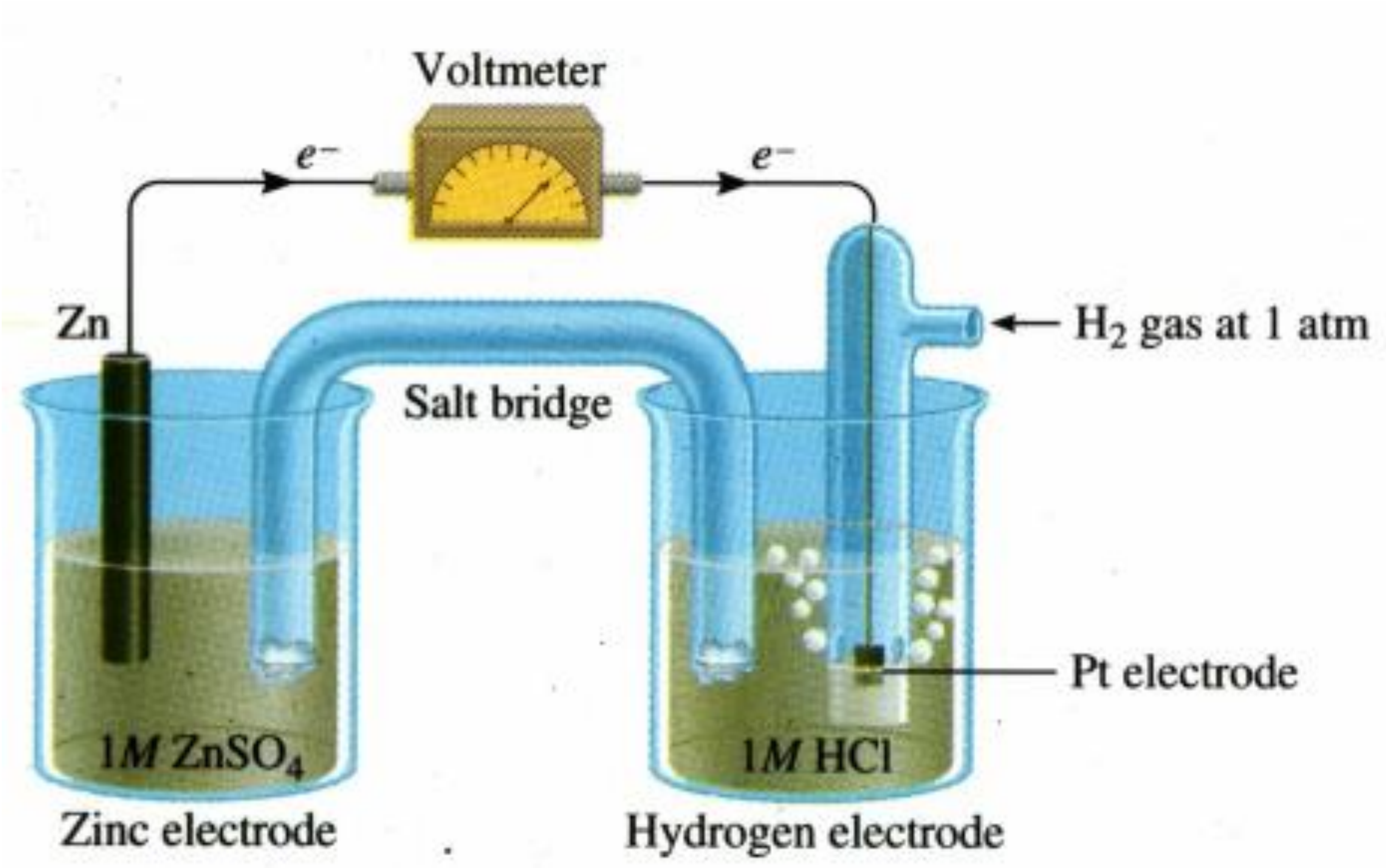


SHE/Cu



$$E^{o}_{cell} = +0.337\ \text{V}$$

Zn/SHE



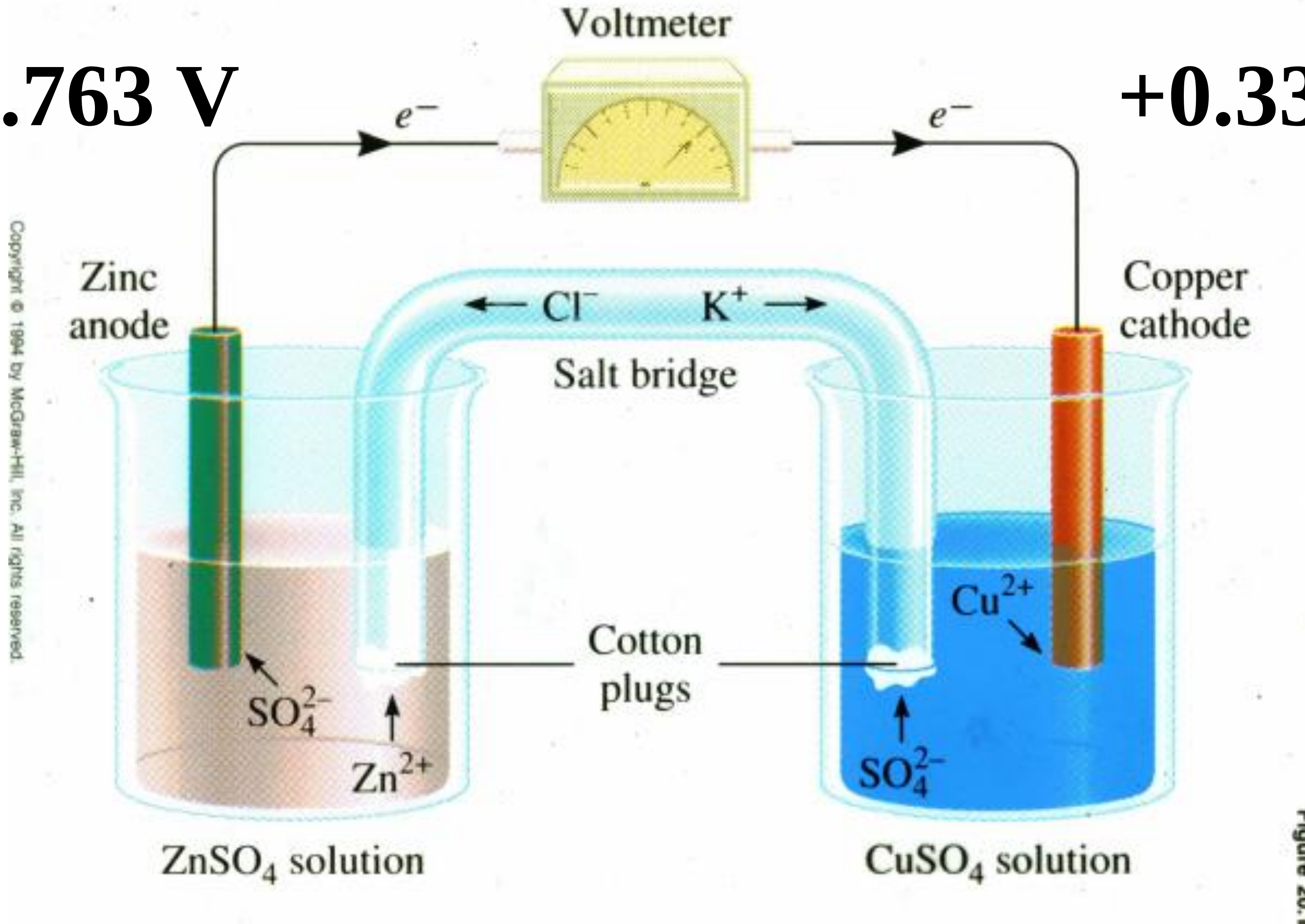
$$E^{o}_{cell} = +0.763\,\mathrm{V}$$

Electrochemical Cells cont…:

$$E_{cell} = +1.10\ V$$

+0.763 V

+0.337 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:

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

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:

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

$w_{electrical}$ = 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 <u>not</u> spontaneous

E_{cell} = - # process is <u>not</u> 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.