# **Reduction-Oxidation Reactions** (REDOX):

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

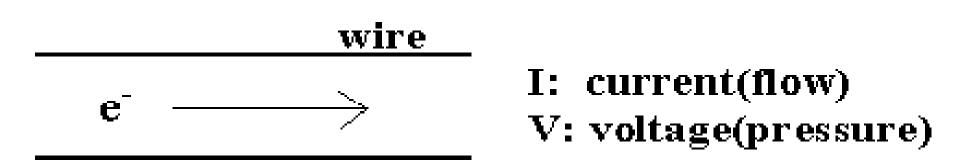
### <u>Reduction</u>- Process in which oxidation state of an element decreases. Species gains electrons.

### **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<sup>2+</sup>(aq): reduced/oxidizing agent.

#### **Electrochemical Cells:**



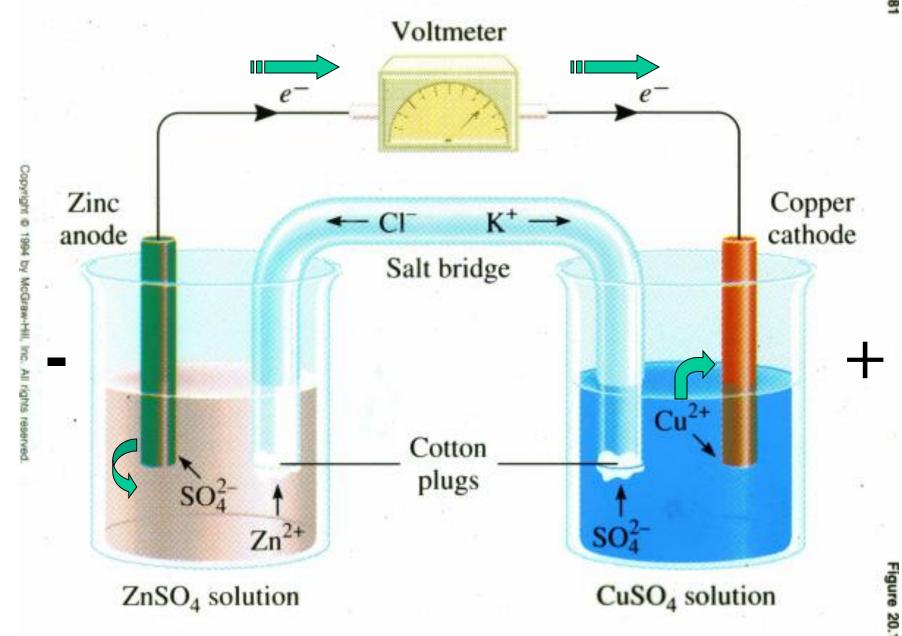
Consider,  $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ 

# **Electrochemical Cells:**

# **Electrode-** Strip of metal.

- <u>Half cell</u>-Strip of metal in contact with its ion. <u>Salt bridge-</u> 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...:**



# **Describing Electrochemical Cells** (Cell Diagram):

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

M(s) |M<sup>n+</sup>(aq) | |M<sup>n+</sup>(aq) |M(s) (anode) (cathode)

#### **Cell Diagram cont..:**

 $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ **Anode:**  $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ **Cathode:**  $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ Zn(s)  $Zn^{2+}(aq) | Cu^{2+}(aq) | Cu(s)$ (anode) (cathode)

# **Electrode Potentials:**

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

Ecoll

# **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.

$$E_{cell}^{o} = E_{oxidation}^{o} + E_{reduction}^{o}$$

#### **Electrochemical Cells cont...:** $\mathbf{E_{cell}} = +1.10 \ \mathbf{V}$ Voltmeter Copyright @ 1994 by McGra Zinc Copper $K^+$ CI cathode anode Salt bridge Inc. All rights reserved Cu<sup>2+</sup>

Cotton

plugs

ZnSO<sub>4</sub> solution

 $SO_4^2$ 

Zn<sup>2+</sup>

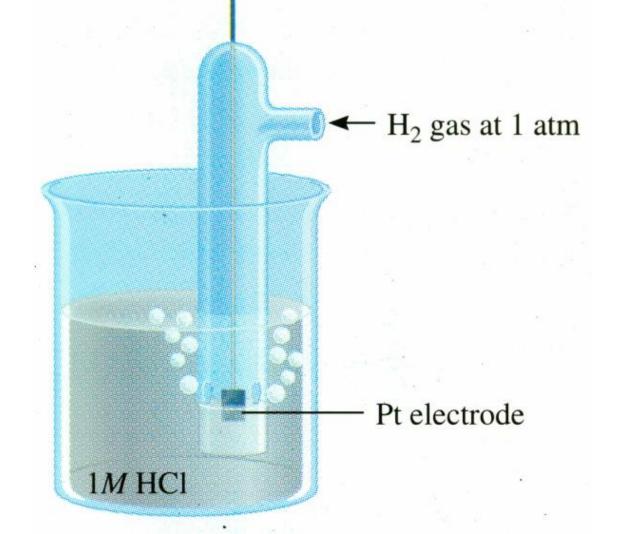
Figure 20.1

CuSO<sub>4</sub> solution

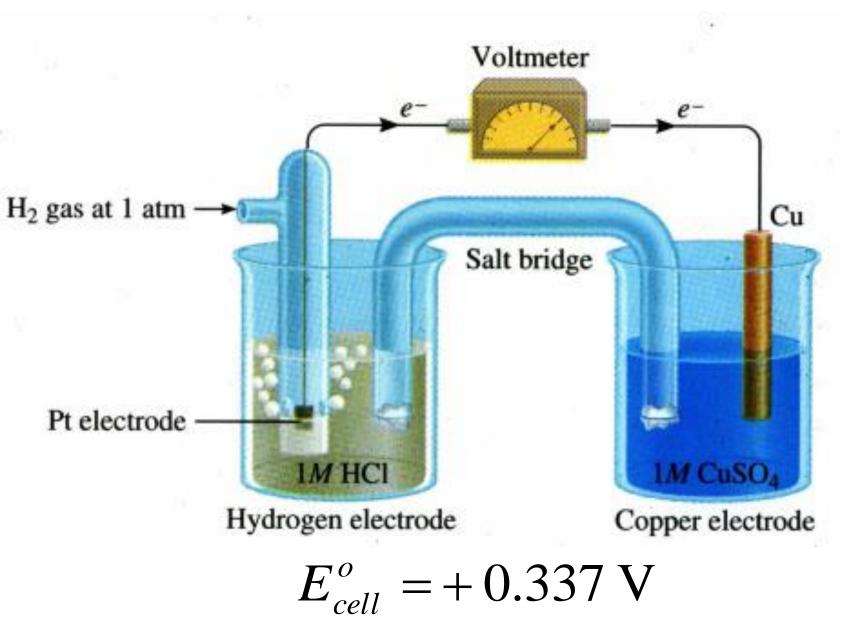
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# **Standard Hydrogen Electrode(SHE):**

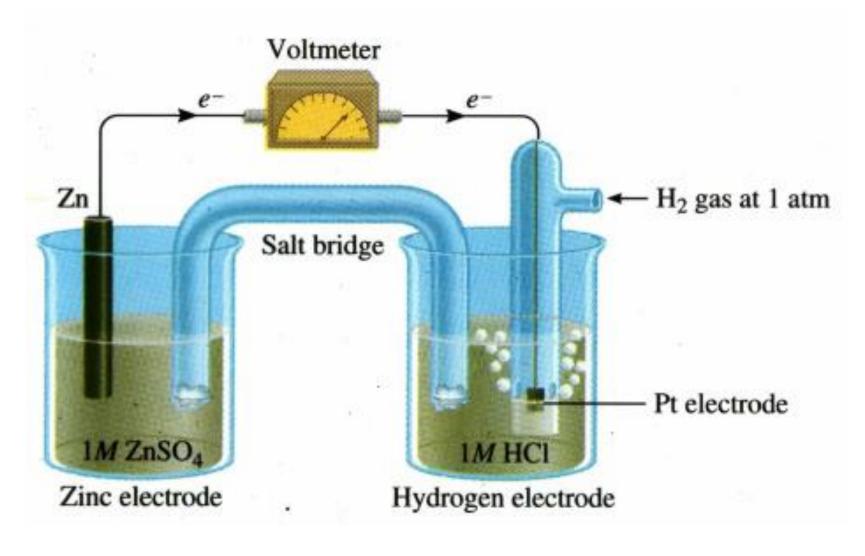
#### $2H^+(aq)(1 M) + 2e^- \rightarrow H_2(g)(1 atm)$ $E^o = 0 V$



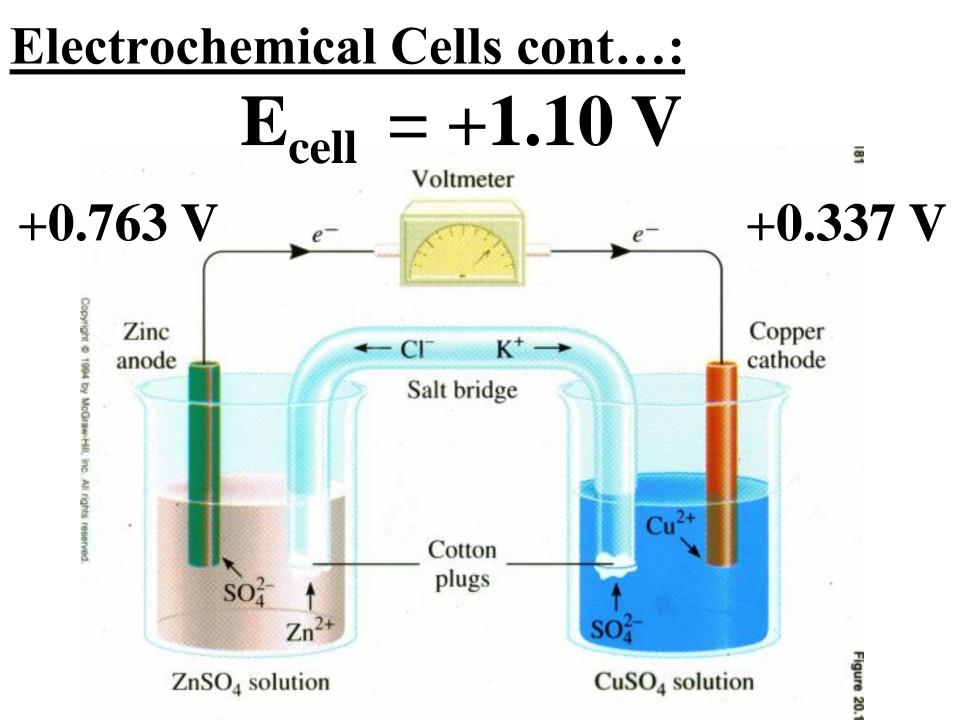
# SHE/Cu



### Zn/SHE



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



# **Predicting Spontaneous Redox Reactions:**

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

- **w**<sub>electrical</sub> = electrical work
- **n** = # moles of electrons transferred
- F = Faraday constant(96485 C/mole)
- $E_{\text{cell}} = \text{Voltage of cell.} \text{ NOTE: } 1 \text{ J} = 1 \text{ C} \cdot \text{V}$  $\Delta G$  Gibbs Free Energy

 $K_{G_{II}} = \# processoises point poet an eous$  $K_{G_{II}} = \# processoise not spont to the eous$ 

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

 $E_{cell}^{o} = +1.10 \text{ V}$  spontaneou s

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

 $E_{cell}^{o} = -1.10 \,\mathrm{V}$  not spontaneou s

Consider:  $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$  $Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$  *E*<sub>red</sub>°(V) +0.337 V -0.763 V

Cu<sup>2+</sup> more likely to be reduced.

# **Cell Potential as a Function of Concentration: Nernst Equation:** $E_{cell} = E_{cell}^{\circ} + \frac{-0.0592V}{LogQ}$ n Where if $aA + bB \rightarrow cC + dD$ $\mathbf{Q} = \frac{[\mathbf{C}]^{\mathbf{c}}[\mathbf{D}]^{\mathbf{d}}}{[\mathbf{A}]^{\mathbf{a}}[\mathbf{B}]^{\mathbf{b}}}$

#### **Nernst Equation cont:**

#### Consider

 $Zn(s) + Cu<sup>2+</sup>(aq) \rightarrow Zn<sup>2+</sup>(aq) + Cu(s)$   $E_{cell} = E_{cell}^{o} + \frac{-0.0592 V}{n} Log \frac{[Zn^{2+}]}{[Cu^{2+}]}$   $E_{cell} = +1.100V + \frac{-0.0592 V}{2} Log \frac{0.50 M}{0.50 M}$ 

### $E_{cell} = +1.100V$

 $Cu(s) + Cu^{2+}(0.10 \text{ M}) \rightarrow Cu^{2+}(dilute) + Cu(s)$ 

$$E_{cell} = 0V + \frac{-0.0592 V}{2} Log \frac{[Cu^{2+}](dilute)}{0.10 M}$$

Use  $E_{cell}$  to determine  $[Cu^{2+}]$  at equilibrium and thus  $K_f$  for Cu-NH<sub>3</sub> complex.

## **Electrolysis:**

# **Electricity is used to cause a nonspontaneous redox reaction to occur.**

- **Ex: Electrolysis of molten sodium chloride.**
- $2Na^{+}(aq) + 2Cl^{-}(aq) \rightarrow 2Na(s) + Cl_{2}(g)$

 $E_{cell}^{\circ} = -4.07 \text{ V NOT SPONTANEOUS!!!}$ 

# **Electrolysis of Aqueous KI:**

- Anode:
- $2I^{-}(aq) \rightarrow I_{2}(aq) + 2e^{-} E^{\circ} = -0.6195 V$ Cathode:
- $2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$   $E^\circ = -0.828 V$

## $2\mathbf{I}^{-}(\mathbf{aq}) + 2\mathbf{H}_{2}\mathbf{O}(\mathbf{l}) \rightarrow \mathbf{I}_{2}(\mathbf{aq}) + 2\mathbf{OH}^{-}(\mathbf{aq}) + \mathbf{H}_{2}(\mathbf{g})$

 $E_{cell}$ °= -1.448 V not spontaneous