These Notes are to <u>SUPPLIMENT</u> the Text, They do NOT Replace reading the Text Book Material. Additional material that is in the Text Book will be on your tests! To get the most information, <u>READ</u> <u>THE CHAPTER</u> prior to the Lecture, bring in <u>these lecture notes and make comments on these notes</u>. <u>These notes alone are NOT enough to pass any test!</u>

## NOTE THESE ARE DRAFT LECTURE NOTES!

**Electron Transfer or Redox** – Oxidation-Reduction involve a transfer of electrons How to spot a Redox reactions, see if there is a "Pure" Element on one side of the Reaction Equation

**Oxidation:** Loss of electrons – or increase in oxidation number **Reduction:** Gain of electrons – or decrease in oxidation number

**Oxidation Agent:** Accepts electrons, this species is reduced, oxidation number decreases **Reducing Agent:** Donates electrons, this species is oxidized, oxidation number increases

### **Oxidation Number**

- 1. A pure atom has an oxidation number of zero
- 2. Monatomic ions have an oxidation number equal to their ion charge
- 3. When combined with another element, Fluorine has an oxidation number of -1
- 4. Oxygen has an oxidation number of -2 in most compounds
  - a. Oxygen combined with Fluorine, oxygen has a positive oxidation number
  - b. Oxigen's oxidation number un peroxides, H2O2, is -1 and in superoxides, KO2 is -1/2

5. Cl and Br have oxidation number of -1 in compounds, except when combined with oxygen or fluorine.

6. The oxidation number for H is +1 in most compounds, in hydrides NaH, it is -1.

7. The sum of all of the oxidation numbers for the atoms in a neutral compound must be zero.

Copper in an aqueous solution of Silver Nitrate, Silver will plate out onto the Copper.

Cu oxidized, oxidation number increases;  
Cu is the reducing agent.  
Cu(s) + 2 Ag<sup>+</sup>(aq) 
$$\longrightarrow$$
 Cu<sup>2+</sup>(aq) + 2 Ag(s)  
Ag<sup>+</sup> reduced, oxidation number decreases;  
Ag<sup>+</sup> is the oxidizing agent.

## **Balancing of Redox Reactions using half reactions:**

Reduction  $\frac{1}{2}$  ReactionAg++ e^- $\rightarrow$  Ag  $\downarrow$ Oxidation  $\frac{1}{2}$  ReactionCu  $\downarrow$  $\rightarrow$  Cu2+ + 2 e<sup>-</sup>

Notice the Silver uses one electron and the copper generates 2 electrons. Therefore we need to multiply the Silver 1/2 reaction by 2:

Reduction <sup>1</sup> / <sub>2</sub> Reaction	2 Ag+ + 2 e-	$\rightarrow$ 2 Ag $\downarrow$	
Oxidation <sup>1</sup> /2 Reaction	Cu↓	$\rightarrow$ Cu <sup>2+</sup> + 2 e <sup>-</sup>	
Net Ionic Equation	$2 \text{ Ag}^+ + \text{Cu} \downarrow$	$\rightarrow$ 2 Ag $\downarrow$ + Cu <sup>2+</sup>	The 2 electrons cancel out
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IE 20.1 Balance Redox of Aluminum and Copper 2+

Reduction <sup>1</sup> /2 Reaction	Cu+2 + 2 e-	$\rightarrow$	Cu↓
Oxidation <sup>1</sup> /2 Reaction	Al↓	$\rightarrow$	Al <sup>3+</sup> + 3 e <sup>-</sup>

Copper uses 2 electrons, Aluminum generates 3 electrons, so cross multiply 3 Cu<sup>+2</sup> and 2 Al  $\downarrow$ 

Reduction <sup>1</sup> /2 Reaction	3 Cu <sup>+2</sup> + 6 e <sup>-</sup>	→ 3 Cu ↓	
Oxidation <sup>1</sup> /2 Reaction	2 <u>A</u> l↓	$\rightarrow$ 2 Al <sup>3+</sup> + 6 e <sup>-</sup>	
Net Ionic Equation	$3 \operatorname{Cu}^{+2} + 2 \operatorname{Al} \downarrow$	$\rightarrow$ 3 Cu $\downarrow$ + 2 Al <sup>3+</sup>	The 6 electrons cancel out

**Balancing Redox Equations in Acid Solutions**  $Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+}$ 

1. A	ssign an oxidat +2 Fe <sup>2+</sup> +	+7		+3		+2 Mn <sup>2+</sup>	I	n Acidic So	lutions	
2. S	plit the reactio	n to tw	o half r	eactior	ıs:					
	+2		+3			ation, Fe	goes fro	om +2 to +3	3,	
	Fe <sup>2+</sup>	$\rightarrow$				•	0	ates the elec		
						0 0				
	+7		+2		Redu	ction, Mr	n goes fi	rom +7 to +	-2	
	MnO <sub>4</sub> -	$\rightarrow$	$Mn^{2+}$		Oxida	ation Age	nt, acce	epts the elec	ctrons	
3. E	Balance the half a. Balance a b. Balance (	all aton	ns excep			one side	of the e	equation		
	+2		+3	0		+7		1	+2	
	Fe <sup>2+</sup>	$\rightarrow$	•			MnO <sub>4</sub> -		$\rightarrow$	$Mn^{2+}$	+ 4 H <sub>2</sub> O
	c. Balance H	I atom	s by ade	ding H	+ to on	e side of	the read	ction		-
	+2		+3			+7			+2	
	Fe <sup>2+</sup>	$\rightarrow$	Fe <sup>3+</sup>			MnO <sub>4</sub> -	+ 8 H <sup>-</sup>	$+ \rightarrow$	$Mn^{2+}$	+ 4 H <sub>2</sub> O
	d. Balance e	electric	charge	by add	ling ele	ectons, e-,	, to the	more positi	ive side	
	+2		+3			+7		+2		
	Fe <sup>2+</sup>	$\rightarrow$	Fe <sup>3+</sup>	+ e-		MnO <sub>4</sub> -	+ 8 H+	+ 5 e-→	$Mn^{2+}$	+ 4 H <sub>2</sub> O

4. Combine each half reaction. Multiply each half reaction by a factor such that when the half reactions are combined, the electrons cancel. Hint: multiply the  $1^{st}$  half reaction by the number of electrons in the  $2^{nd}$  and multiply the  $2^{nd}$  half reaction by the number of electrons in the first.

 $5^{*}(Fe^{2+} \rightarrow Fe^{3+} + e^{-})$   $1^{*}(MnO_{4^{-}} + 8 H^{+} + 5 e^{-} \rightarrow Mn^{2+} + 4 H_{2}O)$   $5 Fe^{2+} \rightarrow 5 Fe^{3+} + 5 e$   $\underline{MnO_{4^{-}} + 8 H^{+} + 5 e^{-}} \rightarrow Mn^{2+} + 4 H_{2}O$   $5 Fe^{2+} + MnO_{4^{-}} + 8 H^{+} \rightarrow 5 Fe^{3+} + Mn^{2+} + 4 H_{2}O$ 

**IE 20.2** Balance the following in Acidic solution:  $VO_{2^+} + Zn \rightarrow VO^{2+} + Zn^+$ 

### **Balancing Redox Equations in Basic Solutions**

$$\mathrm{SO}_3^{2-} + \mathrm{MnO}_4^- \rightarrow \mathrm{SO}_4^{2-} + \mathrm{MnO}_2\downarrow$$

1.	Assign a	n oxidation	number to	each atom
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+4	+7	+6	+4	
SO <sub>3</sub> <sup>2-</sup> +	$MnO_4 \rightarrow$	SO4 <sup>2-</sup> +	MnO₂↓	In Basic Solutions

2. Split the reaction to two half reactions:

+4	$\rightarrow$	+6	Oxidation, Sulfur goes from +4 to +6,
SO <sub>3</sub> <sup>2-</sup>		SO <sub>4</sub> <sup>2-</sup>	Reducing Agent, donates the electrons
+7	$\rightarrow$	+4	Reduction, Mn goes from +7 to +4
MnO <sub>4</sub> -		MnO₂↓	Oxidation Agent, accepts the electrons

### 3. Balance the half reactions

a. Balance all atoms except O and H

b. Balance O atoms by adding H2O's to one side of the equation +4 +6 +7 +2  $SO_3^{2-} + H_2O \rightarrow SO_4^{2-} MnO_4^{-} \rightarrow MnO_2\downarrow + 2 H_2O$ 

c. Balance H atoms by adding H+ to one side of the reaction

+4	+6	+7		+2
$\mathrm{SO}_{3^{2-}} + \mathrm{H}_2\mathrm{O} \rightarrow$	SO <sub>4</sub> <sup>2-</sup> + 2 H <sup>+</sup>	$MnO_4^- + 4 H^+$	$\rightarrow$	$MnO_2\downarrow + 2 H_2O$

d. Balance electric charge by adding electons, e<sup>-</sup>, to the more positive side +4 +6 +7 +2  $SO_3^{2^-} + H_2O \rightarrow SO_4^{2^-} + 2 H^+ + 2 e^- MnO_4^- + 4 H^+ + 4 e^- \rightarrow MnO_2\downarrow + 2 H_2O$ 

4. Combine each half reaction. Multiply each half reaction by a factor such that when the half reactions are combined, the electrons cancel. Hint: multiply the  $1^{st}$  half reaction by the number of electrons in the  $2^{nd}$  and multiply the  $2^{nd}$  half reaction by the number of electrons in the first.

$3 * (SO_3^{2-} + H_2O)$	$\rightarrow$ SO <sub>4</sub> <sup>2-</sup> + 2 H <sup>+</sup> + 2 e <sup>-</sup> )	6 e <sup>-</sup> cancel out
$2 * (MnO_4 + 4 H^+ +$	$3 e^{-} \rightarrow MnO_2 \downarrow + 2 H_2O)$	<u>6 e- cancel out</u>
$3 \text{ SO}_3^{2-} + 3 \text{ H}_2\text{O} + 2 \text{ M}_2$	$MnO_4^- + 8 H^+ \rightarrow 3 SO_4^{2-} + 6 H$	$H^+ + 2 \operatorname{MnO}_2 \downarrow + 4 \operatorname{H}_2 O$

Cancel some water and H<sup>+</sup>

 $3 \text{ SO}_3^{2-} + 2 \text{ MnO}_4^- + 2 \text{ H}^+ \rightarrow 3 \text{ SO}_4^{2-} + 2 \text{ MnO}_2 \downarrow + \text{H}_2\text{O}$ 

5. Add the number of OH<sup>-</sup> to each side as there are H+ on one side

 $3 \operatorname{SO}_3^{2^-} + 2 \operatorname{MnO}_4^- + 2 \operatorname{H}^+ + 2 \operatorname{OH}^- \rightarrow 3 \operatorname{SO}_4^{2^-} + 2 \operatorname{MnO}_2 \downarrow + \operatorname{H}_2 \operatorname{O} + 2 \operatorname{OH}^-$ 

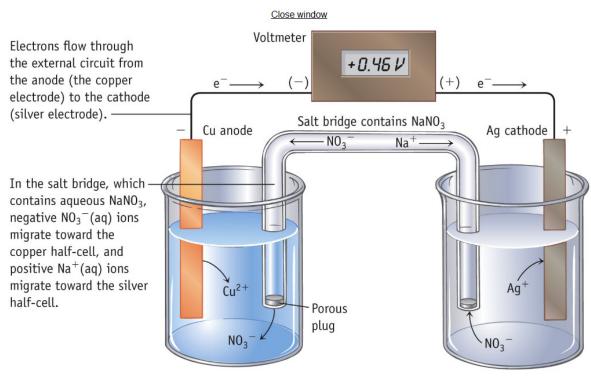
6. Combine 2 H<sup>+</sup> + OH<sup>-</sup>  $\rightarrow$  H<sub>2</sub>O and cancel waters

$$3 \operatorname{SO}_3^{2^-} + 2 \operatorname{MnO}_4^- + 2 \operatorname{H}_2 \operatorname{O}^- \rightarrow 3 \operatorname{SO}_4^{2^-} + 2 \operatorname{MnO}_2 \downarrow + \operatorname{H}_2 \operatorname{O}^+ + \operatorname{OH}^-$$

 $3 \operatorname{SO}_3^{2^-} + 2 \operatorname{MnO}_4^- + \operatorname{H}_2^{0^-} \rightarrow 3 \operatorname{SO}_4^{2^-} + 2 \operatorname{MnO}_2 \downarrow + OH^-$ 

## 20.2 Simple Voltaic Cells





Net reaction:  $Cu(s) + 2 Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2 Ag(s)$ 

On Left:Copper half cell is copper metal and Cu2+ solutionOn Right:Silver half cell is silver metal and Ag+ solution

**Salt Bridge:** cell connection that allows cations and anions to move between the two cells, but does not allow the solutions to mix

Anode (-): Electrode where oxidation occurs, increase in oxidation number, metal to ion The Copper electrode

**Cathode (+) :** Electrode where reduction occurs, decrease in oxidation number, ion to metal ( plates out) The Silver electrode

Electrons flow from the Anode to the Cathode via an external circuit

Anode Cathode:	$\begin{array}{ccc} \mathrm{Cu} \downarrow & \rightarrow & \mathrm{Cu}^{2+} + \\ 2 & \mathrm{Ag}^{+} + & 2 & \mathrm{e}^{-} \end{array} \xrightarrow{} & 2 & \mathrm{Ag} \downarrow \end{array}$	2 e-
Example 20.4	Students do this one	$Fe \downarrow + Cu^{2+} \rightarrow Cu \downarrow + Fe^{2+}$

**Voltaic Cells with Inert Electrodes** The **Hydrogen Electrode** – this is the standard reference Bubble H2 gas over a platinum electrode in a solution containing H+

 $2 H^+ + 2 e^- \rightarrow H_2 \downarrow - or - H_2 \downarrow \rightarrow 2 H^+ + 2 e^-$ 

An Iron / Hydrogen cell  $Fe^{3+} + e^- \rightarrow Fe^{2+}$  and  $H_2 \downarrow \rightarrow 2 H^+ + 2 e^-$ 

 $2 \operatorname{Fe}^{3+} + \operatorname{H}_2 \downarrow \rightarrow 2 \operatorname{Fe}^{2+} + 2 \operatorname{H}^+$ 

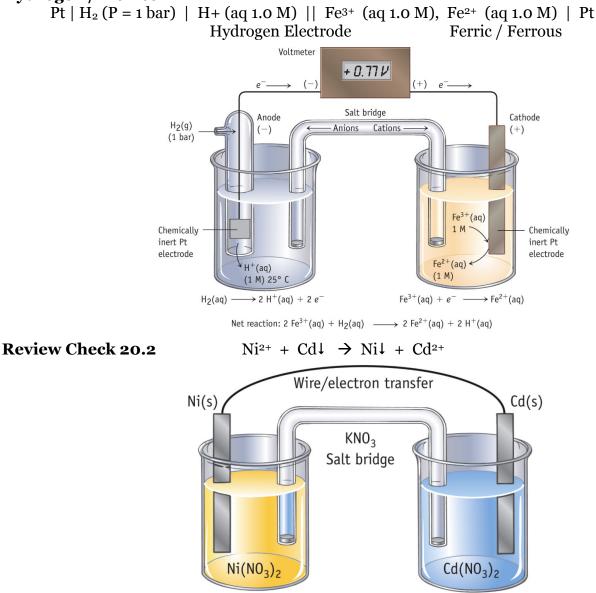
# $\begin{array}{c|c} \textbf{Electrochemical Cell Notations} & Cu \downarrow \mid Cu^{2+} (aq \ 1.0 \ M) \mid \mid Ag^{+} (aq \ 1.0 \ M) \mid Ag \downarrow \\ Anode on the left & Cathode on the right \end{array}$

| is a phase boundary such as between the metal and the ions

| | is the salt bridge

Note: The concentration of ionic solutions is give

# Hydrogen / Iron cell



Write out balanced half reactions and label Anode, Cathode, Electron Flow

# 20.3 Commercial Voltaic Cells

The previously discussed Voltaic Cells do not make good Commercial Cells

- 1. There not robust
- 2. Voltage varies with the concentration of the ions
- 3. Current flow is low
- A good Commercial Cell
- 1. Have a large mass of reactants to produce current over a long period
- 2. Would be nice to be Re-Chargeable

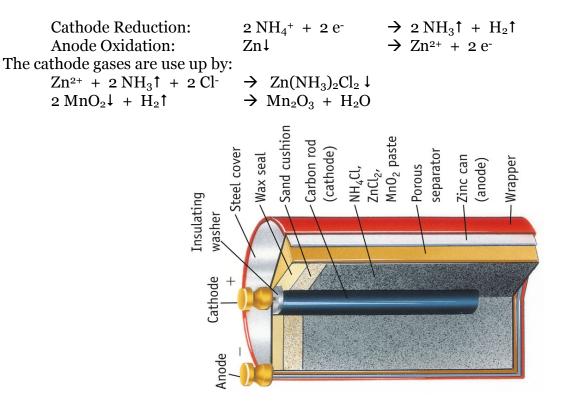
## Primary Battery: cannot be recharged

Secondary or Rechargeable: the reactions can be reversed to recharge the cell

# Common Dry Cell or Zinc / Graphite cell

Voltage:	1.5
Pros:	Inexpensive
Cons:	Can leak with use as Zn is used up, generates gas's, voltage drops,

Contains a moist paste of  $NH_4Cl$ ,  $ZnCl_2$  and  $MnO_2$ , Zinc metal can and graphite rod The Zinc outer can is used up and the battery can leak:



Alkaline Batteries – last 50% longer then dry cells,

Voltage:1.54 vPros:Voltage does not decline with use, can generate high currentCons:Voltage does not decline with use, can generate high current

Cathode Reduction: Anode Oxidation	$2 \operatorname{MnO}_2 \downarrow + \operatorname{H}_2 O + 2 \operatorname{e}^{-} Zn \downarrow + 2 \operatorname{OH}^{-}$	$  \begin{array}{l} \rightarrow  \mathrm{Mn_2O_3} \downarrow + 2 \ \mathrm{OH^-} \\ \rightarrow  \mathrm{ZnO} \downarrow + \ \mathrm{H^2O} + 2 \ \mathrm{e^-} \end{array} $
<b>Silver Oxide Battery</b> Voltage: 1.5 v Cathode Reduction: Anode Oxidation	$Ag_2O \downarrow + H_2O + 2e^{-}$ Zn \downarrow + 2OH <sup>-</sup>	→ 2 Ag ↓ + 2 OH <sup>-</sup> → ZnO ↓ + H <sub>2</sub> O + 2 e <sup>-</sup>
Zinc-Oxygen Battery Voltage: 1.15 – 1.35 v Cathode Reduction Anode Oxidation	$O2\uparrow + 2H_2O + 4e^{-2}$ Zn \downarrow + 2OH^-	→ $4 \text{ OH}^-$ → $2\text{nO}\downarrow + \text{H}_2\text{O} + 2 \text{ e}^-$

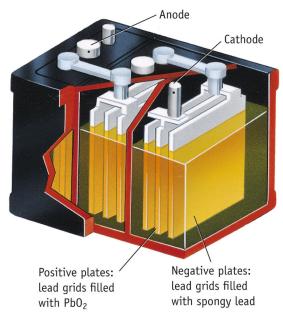
# **Rechargeable Batteries**

Lead Storage. Cathode is Lead metal / Lead (IV) Oxide, the anode is Lead metal.

<b>Cathode Reduction</b>	$PbO_2 \downarrow + 4 H^+ + SO_4^{2-} + 2 e^-$	$\rightarrow$ PbSO <sub>4</sub> ↓ + 2 H <sub>2</sub> O
Anode Oxidation	$Pb\downarrow + SO_4^{2-}$	$\rightarrow$ 2 PbSO <sub>4</sub> + 2 H <sub>2</sub> O
Net Ionic Equation	$Pb\downarrow + PbO_2\downarrow + 2 H2SO4$	$\rightarrow$ 2 PbSO <sub>4</sub> + 2 H <sub>2</sub> O

Students should be able to prove the Net Ionic Equation

This is the current generating equation, to charge the battery, reverse the reactions



## **Nickel-Cadmium Battery**

Pros: Produce a constant voltage, lightweight, rechargeable Cons: Cost is high, Cadmium is toxic

Cathode Reduction	$NiO(OH) \downarrow + H2O + e^{-1}$	$\rightarrow$ Ni(OH)2 $\downarrow$ + OH <sup>-</sup>
Anode Oxidation	Cd↓ + 2 OH-	$\rightarrow$ Cd(OH)2 $\downarrow$ + 2 e <sup>-</sup>

# Nickel-Metal Hydride

Cathode Reduction	$NiO(OH) \downarrow + H2O + e^{-1}$	$\rightarrow$ Ni(OH)2 $\downarrow$ + OH <sup>-</sup>
Anode Oxidation	Alloy-H + OH-	$\rightarrow$ Alloy + H <sub>2</sub> O + e <sup>-</sup>
Alloy contains Lanthanum	, Cerium or Neodymium	

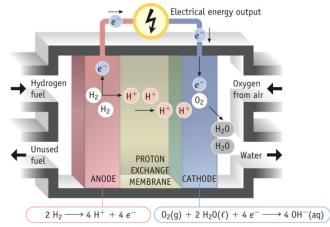
## **Lithium Battery**

Pros: Can be made into any shape, high current, many cycles, light weight

Cathode Reduction	$Li_{1-x}CoO_2 \downarrow + x Li^+ + x e^-$	$\rightarrow$ LiCoO2 $\downarrow$
Anode Oxidation	Li <sub>x</sub> C <sub>6</sub> ↓	$\rightarrow$ x Li <sup>+</sup> + x e <sup>-</sup> + 6 C $\downarrow$

## **Fuel Cell**

Pros:	Reactants can be supplied continuously 40-60% efficiency			
Cons:	Reactants are	e hard to distribute v	via a "Gas Station", operating temp	o 70-80 °C
Cathode Red	luction	$O_2 \uparrow + 2 H_2 O + 4 O$	.e- → 4 OH-	
Anode Oxida	tion	$H_2$ 1	→ 2 H <sup>+</sup> + 2 e <sup>-</sup>	
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# **20.4 Standard Electrochemical Potentials**

Electromotive Force or emf is measured in Volts.

One Volt is the potential difference needed to impart one joule of energy to an electric charge of one coulomb J = V C

One coulomb is the quantity of current when 1 ampere flows for 1 sec **C** = **A** Time

# **Standard Potentials**

- 1. Reactants and products are present in their standard states
- 2. Aqueous solutions are 1.0 M
- 3. Gases area at a pressure of 1.0 Bar

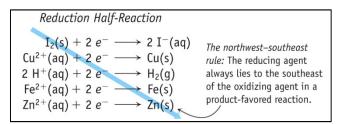
**Standard Cell Potential** E<sup>o</sup><sub>cell</sub> is at 25 °C Are referenced to the Standard Hydrogen Electrode Which way do the electrons flow? They always flow from the anode (-) to the cathode (+)

# Table 20.1 Standard Reduction Potentials in Aqueous Solutions at 25 °C

1. <sup>1</sup>/<sub>2</sub> Reactions are written as "Oxidized + e-  $\rightarrow$  Reduced", species on left is oxidizing agent, on right reducing agent. All potentials are for Reduction Reactions, decrease in Oxidation Number, potentials are in Volts vs the Standard Hydrogen Electrode (SHE) and are called Standard Reduction Potentials.

- 2. The more Positive value of E<sup>o</sup>, the better the oxidizing ability.
- 3. The more Negative value for  $E^{\circ}$ , the less likely the  $\frac{1}{2}$  reaction will occur.

4. The reaction of any substance on the left (an oxidizing agent) with a substance LOWER than it on the right (a reducing agent) is product favored at equilibrium (it will occur). Product favored reactions will always involve a reducing agent that is "Southeast" of the oxidizing agent

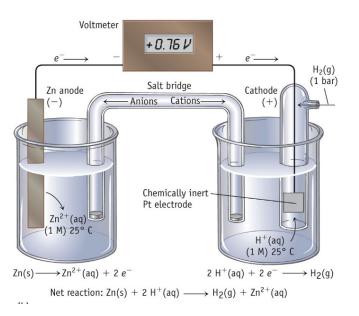


5. The algebraic sign of the  $\frac{1}{2}$  reaction reduction potential is compared to the SHE.

6. Electrochemical potentials depend on the nature of he reactants and products and their concentrations, not on the quantities of material used.

 $E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$ When  $E^{o}_{cell} = positive$ , the reaction as written is predicted to be**Product-Favored**, If **negative**, it is **Reactant Favored**.The further apart the Oxidizing and Reducing Agents, the greater is  $E^{o}_{cell}$ 22-July-2012Page 8 of 14

Reduction Half-Reaction		<i>E</i> ° (V)
F <sub>2</sub> (g) + 2 e <sup>-</sup>	$\rightarrow$ 2 F <sup>-</sup> (aq)	+2.87
$H_2O_2(aq) + 2 H^+(aq) + 2 e^-$	$\rightarrow$ 2 H <sub>2</sub> O( $\ell$ )	+1.77
$PbO_2(s) + SO_4^{2-}(aq) + 4 H^+(aq) + 2 e^{-1}$		+1.685
$MnO_4^{-}(aq) + 8 H^+(aq) + 5 e^-$	$\rightarrow Mn^{2+}(aq) + 4 H_2O(\ell)$	+1.51
$Au^{3+}(aq) + 3e^{-}$	→ Au(s)	+1.50
Cl <sub>2</sub> (g) + 2 e <sup>-</sup>	→ 2 Cl <sup>-</sup> (aq)	+1.36
$Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e^-$	$\rightarrow$ 2 Cr <sup>3+</sup> (aq) + 7 H <sub>2</sub> O( $\ell$ )	+1.33
$O_2(g) + 4 H^+(aq) + 4 e^-$	$\rightarrow$ 2 H <sub>2</sub> O( $\ell$ )	+1.229
$Br_2(\ell) + 2e^-$	→ 2 Br-(aq)	+1.08
$NO_3^{-}(aq) + 4 H^+(aq) + 3 e^-$	$\rightarrow NO(g) + 2 H_2O(\ell)$	+0.96
$OCl^{-}(aq) + H_2O(\ell) + 2e^{-}$	$\rightarrow$ Cl <sup>-</sup> (aq) + 2 OH <sup>-</sup> (aq)	+0.89
$Hg^{2+}(aq) + 2e^{-}$	$\rightarrow$ Hg( $\ell$ )	+0.855
$Ag^+(aq) + e^-$	$\rightarrow$ Ag(s)	+0.799
$Hg_2^{2+}(aq) + 2e^{-}$	$\rightarrow$ 2 Hg( $\ell$ )	-0.789
Fe <sup>1+</sup> (aq) + e <sup>-</sup>	$\rightarrow$ Fe <sup>2+</sup> (aq)	+0.771
I <sub>2</sub> (s) + 2 e <sup>-</sup>	→ 2 I <sup>_</sup> (aq)	5 +0.535
$0_2(g) + 2 H_20(\ell) + 4 e^-$	$\rightarrow$ 4 OH <sup>-</sup> (aq)	+0.40
$Cu^{2+}(aq) + 2e^{-}$	$\rightarrow$ Cu(s)	면 +0.337
Sn <sup>4+</sup> (aq) + 2 <i>e</i> <sup>-</sup>	$\rightarrow$ Sn <sup>2+</sup> (aq)	+0.15
2 H+(aq) + 2 e-	$\rightarrow H_2(g)$	.000
$Sn^{2+}(aq) + 2 e^{-}$	$\rightarrow$ Sn(s)	-0.14
Ni <sup>2+</sup> (aq) + 2 e <sup>-</sup>	→ Ni(s)	-0.25
$V^{3+}(aq) + e^{-}$	$\rightarrow V^{2+}(aq)$	-0.255
PbSO <sub>4</sub> (s) + 2 <i>e</i> <sup>-</sup>	$\rightarrow Pb(s) + SO_4^{2-}(aq)$	-0.356
Cd <sup>2+</sup> (aq) + 2 <i>e</i> <sup>-</sup>	$\rightarrow$ Cd(s)	-0.40
Fe <sup>2+</sup> (aq) + 2 <i>e</i> <sup>-</sup>	$\rightarrow$ Fe(s)	-0.44
Zn <sup>2+</sup> (aq) + 2 e <sup>-</sup>	$\rightarrow$ Zn(s)	-0.763
2 H₂0(ℓ) + 2 e <sup>-</sup>	$\rightarrow$ H <sub>2</sub> (g) + 2 OH <sup>-</sup> (aq)	-0.827
Al <sup>3+</sup> (aq) + 3 e <sup>-</sup>	$\rightarrow$ Al(s)	-1.66
Mg <sup>2+</sup> (aq) + 2 e <sup>-</sup>	$\rightarrow$ Mg(s)	-2.37
$Na^+(aq) + e^-$	→ Na(s)	-2.714
K+(aq) + e-	$\rightarrow$ K(s)	-2.925
Li+(aq) + e-	$\rightarrow$ Li(s)	-3.045



$Zn^{2+} + H_2 \uparrow \rightarrow Zn \downarrow + 2 H^+$	Zinc is oxidizing agent, it accepts electrons
	H <sub>2</sub> reducing agent, it donates electrons
$Zn^{2+} + 2e- \rightarrow Zn\downarrow$	$E^{o}$ = -0.763 v, is the Anode as it gives up e <sup>-</sup>
$H_2 \uparrow \rightarrow + 2e^- + 2 H^+$	$E^{o} = o$

 $E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = -0.763 - 0 = -0.763$  This reaction will not occur as written!

## **Calculating Standard Cell Potentials**

Net Ionic	2 Ag+ + Cu↓	$\rightarrow$ 2 Ag $\downarrow$ + Cu <sup>2+</sup>	
1/2 Reaction	Cu↓	$\rightarrow$ Cu <sup>2+</sup> + 2e <sup>-</sup>	Cu↓ gives up e-, so it is the Anode
1/2 Reaction	2 Ag+ + 2e-	$\rightarrow 2 \text{ Ag} \downarrow$	Ag <sup>+</sup> then is the Cathode

Silver is the Cathode, at the cathode there is a decrease in oxidation number, it is the Oxidation Agent

$$Ag^+$$
 (ON = 1)  $\rightarrow$   $Ag \downarrow$  (ON = 0)

Copper is then the Anode and is the Reducing Agent

 $E^{\circ} Ag^{+} = +0.799 v$   $E^{\circ} Cu \downarrow = -0.337 v$ 

 $E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = E^{o}_{Ag+} - E^{o}_{Cu_{1}} = (+0.799) - (-0.337) = +0.462 v$ 

The Positive value for E<sup>o</sup>cell says this is a Product-Favored Reaction – it will run as written

## **Relative Strengths of Oxidizing and Reducing Agents**

<i>E</i> °, V		Reduction Half-Reaction
+1.36 +0.80 +0.00 -0.25 -0.76	Increasing strength as oxidizing agents	$\begin{array}{l} \operatorname{Cl}_2(g) + 2 \ e^- \longrightarrow 2 \ \operatorname{Cl}^-(aq) \\ \operatorname{Ag}^+(aq) + e^- \longrightarrow \operatorname{Ag}(s) \\ 2 \ \operatorname{H}^+(aq) + 2 \ e^- \longrightarrow \operatorname{H}_2(g) \\ \operatorname{Ni}^{2+}(aq) + 2 \ e^- \longrightarrow \operatorname{Ni}(s) \\ \operatorname{Zn}^{2+}(aq) + 2 \ e^- \longrightarrow \operatorname{Zn}(s) \end{array}$

Upper left of this and Table 20.1 shows  $Cl_2$  the strongest oxidizing agents, these are easily reduced.

Bottom left shows Zn2+ which is a poor oxidizing agent or easily reduced.

Upper Right shows Cl-, a poor reducing agent

Lower Right shows  $Zn \downarrow$ , which is a good reducing agent.

<b>Oxidizing Agents:</b>	$Cl2 > Ag^+ > H^+ > Ni^{2+}$	$> Zn^{2+}$
<b>Reducing Agents:</b>	$Zn > Ni > H_2 > Ag$	> Cl-
	Strong	Weak

# 20.5 Electrochemical Cells under Nonstandard Conditions

The Nernst Equation:  $E = E^{o} - (RT/nF) \ln Q$ E is the cell voltage, E<sup>o</sup> the standard cell voltage R the gas constant 8.314472 J/K mol T is temperature in K n is the number of moles of electrons transferred F the Faraday Constant 9.6485338 x 104 C/mol C = couloub = 1 ampere for 1 second Q is the reaction quotient  $E = E^{0} - (0.0257/n) \ln Q$ The Nernst Equation Reduces to: at 25 °C The Math behind the pH Meter The following Voltaic Cell: 1.00 M Cu/Cu<sup>2+</sup> vs the SHE Cathode Reduction:  $Cu^{2+} + 2e^{-} \rightarrow Cu \downarrow$ <u>H<sub>2</sub></u>  $\rightarrow$  2 H<sup>+</sup> + 2 e<sup>-</sup> Anode Oxidation:  $H_2\uparrow$  gives up e-, so it is the Anode  $Cu^{2+} + H_2 \uparrow \rightarrow Cu \downarrow + 2 H^+$ Net Ionic Equation:  $E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = E^{o}_{Cu2+} - E^{o}_{H2}\uparrow = (+0.337 \text{ v}) - (0.00 \text{ v}) = +0.337 \text{ v}$  $Q = [H^+]^2 / [Cu^{2+}] P_{H_2}$  $E = 0.337v - (0.257/2) \ln ([H^+]^2 / [Cu^{2+}] P_{H_2})$ E is measured at 0.490 v  $0.490 \text{ v} = 0.337 \text{ v} - (0.257/2) \ln ([\text{H}^+]^2 / (1.00)(1.00))$  $-11.9 = \ln ([H^+]^2)$  $[H+] = 3 \times 10^{-3} M$ pH = 2.6

In practice a standard Ag/AgCl or Calomel Electrode is used in place of the Copper electrode

# Eº and the Equilibrium Constant

As a Voltaic cell produces electric current, the reactant concentration decreases and the cell voltage changes. When  $E_{cell} = 0$ , there is no further net reaction and the reaction is in equilibrium.

$$E = E^{o} - (0.0257/n) \ln Q = 0 = E^{o} - (0.0257/n) \ln K$$
 or

Ln K = n E<sup>o</sup> / 0.0257 at 25 °C

22-July-2012

<b>IE 20.9</b> Calculate K for:	Fe↓ + Cd <sup>2+</sup>	$\leftrightarrows \mathrm{Fe}^{_{2+}} + \mathrm{Cd} \!\downarrow$	
Cathode Reduction	Cd <sup>2+</sup> + 2e-	$\rightarrow$ Cd $\downarrow$	E <sup>o</sup> = -0.40 v
Anode Oxidation	Fe↓	$\rightarrow$ Fe <sup>2+</sup> + 2e-	E <sup>o</sup> =-0.44 v

Note: Even though the reaction is reversed, the sign of the voltage IS NOT reversed  $E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = E^{o}_{Cd2+} - E^{o}_{Fe_{\downarrow}} = (-0.40 \text{ v}) - (-0.44 \text{ v}) = +0.04 \text{ V}$ Ln K = n E<sup>o</sup> / 0.0257 = 2 \* 0.44 V / 0.0257 - 3.1

#### K = 20

**20.7** Electrolysis the use of electrical energy to bring about a chemical change

Electrolysis of molten Sodium Chloride to get Sodium metal and Chlorine gas

Cathode Reduction	2 Na+ + 2 e-	$\rightarrow$ 2 Na <sup>1</sup>	e- from electrode to chemical species
Anode Oxidation	2 Cl-	$\rightarrow$ Cl <sub>2</sub> † + 2 e <sup>-</sup>	e- from chemical species to electrode
Net Ionic Equation	2 Na+ + 2 C	$l \rightarrow 2 \text{ Na} \downarrow + Cl_2 \uparrow$	

# **Electrolysis of Aqueous Solutions**

Water is an Electro Active substance, it can electrolyze as well as molten NaCl Electrolysis of an aqueous solution of NaI yields the following ions: Na<sup>+</sup>, I<sup>-</sup>, and H<sup>2</sup>O.

Cathode Reduction	Na <sup>+</sup> + e <sup>-</sup> 2 H <sub>2</sub> O + 2 e-	-	Na↓ H <sub>2</sub> ↑ + 2 OH <sup>-</sup>
Anode Oxidation	$\begin{array}{ccc} 2 & I^{-} & \rightarrow & I_{2} + 2 & e^{-} \\ 2 & H_{2}O & \rightarrow & O_{2}\uparrow + & 4 \end{array}$	H+	+ 4 e-

Any Sodium Metal (Na<sup>↓</sup>) formed would immediately react with water to produce NaOH and H<sub>2</sub><sup>↑</sup>

Cathode Reduction	2 H <sub>2</sub> O + 2 e-	$\rightarrow$ H <sub>2</sub> ↑ + 2 OH <sup>-</sup>	$E^{o}_{a}$ = -0.8277 V	
Anode Oxidation	2 I-	$\rightarrow$ I <sub>2</sub> + 2 e <sup>-</sup>	$E_{a}^{o}$ = -0.535 V	
Note Text states _0.621 v, See table 20.1 and reverse the value!				
Net Ionic Equation	$2 H_2O + 2 I^2$	$\rightarrow$ H <sub>2</sub> ↑ + 2 OH <sup>-</sup> + I <sub>2</sub>		

 $E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = (-0.8277 \text{ V}) - (-0.535 \text{ V}) = -0.293 \text{ v}.$  The process is NOT spontaneous

# **20.8** Counting Electrons

Electrolysis of aqueous AgNO3 requires one mole of electrons to produce one mole of silver as only one electron is transferred  $Ag^+ + e^- \rightarrow Ag \downarrow$ 

Electrolysis of aqueous Tin +2 requires 2 moles of electrons as two electrons are transferred: Sn<sup>2+</sup> + 2 e<sup>-</sup>  $\rightarrow$  Sn  $\downarrow$ 

Electric Charge (Coulombs, C) = Current (amperes, A) \* Time (seconds)

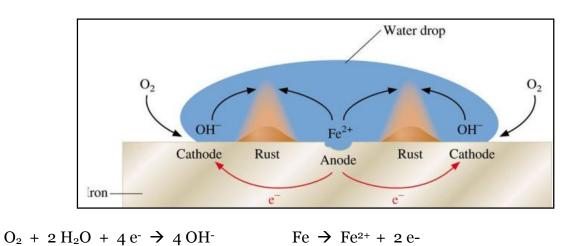
Moles of  $e^- = C/F = Coulombs / 9.648 \times 10^4 C/mol e^-$ 

**IE 20.11** 2.40 A is passed through a Cu<sup>2+</sup> aqueous solution for 30.0 min, how many grams of Cu is deposited?

$$C = A * t = 2.40 A * 30.0 min * 60 sec/min = 4.32 x 10^3 C$$

Moles of 
$$e^- = (4.32 \times 10^3 \text{ C}) / 96,485 \text{ C/mol} e^- = 4.48 \times 10^{-2} \text{ mol} e^-$$

g Cu = (4.48 x 10<sup>-2</sup> mol e<sup>-</sup>) \* (1 mol Cu/2 mol e<sup>-</sup>)(63.55 g Cu/1 mol Cu) = 1.42 g



# Rusting from a drop of water - the electrochemical process of rusting iron

$Fe^{+2} + 2 OH^{-} \rightarrow Fe(OH)_{2}$	$4 \operatorname{Fe}(OH)_2 + O_2 \rightarrow 2 \operatorname{Fe}_2O_3 + H_2O$

# **CHEAT SHEET**

**Oxidation:** Loss of electrons – or increase in oxidation number **Reduction:** Gain of electrons – or decrease in oxidation number

**Oxidation Agent:** Accepts electrons, this species is reduced, oxidation number decreases **Reducing Agent:** Donates electrons, this species is oxidized, oxidation number increases

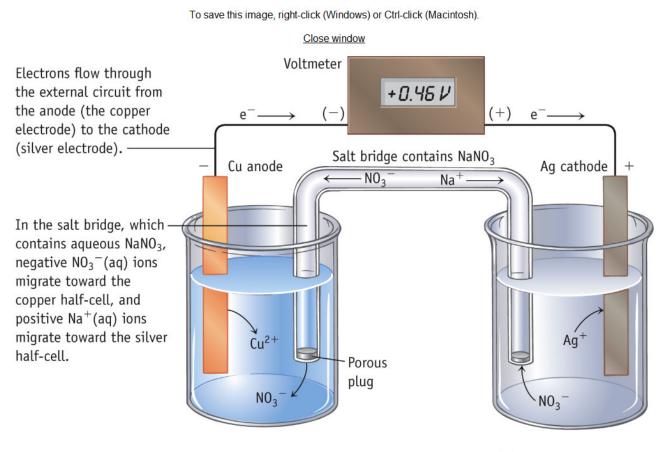
## **Oxidation Number**

**Salt Bridge:** cell connection that allows cations and anions to move between the two cells, but does not allow the solutions to mix

Anode (-): Electrode where <u>oxidation</u> occurs, increase in oxidation number, metal to ion

**Cathode (+) :** Electrode where <u>reduction</u> occurs, decrease in oxidation number, ion to metal ( plates out)

## Electrons flow from the Anode to the Cathode via an external circuit



Net reaction:  $Cu(s) + 2 Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2 Ag(s)$