Electrochemistry

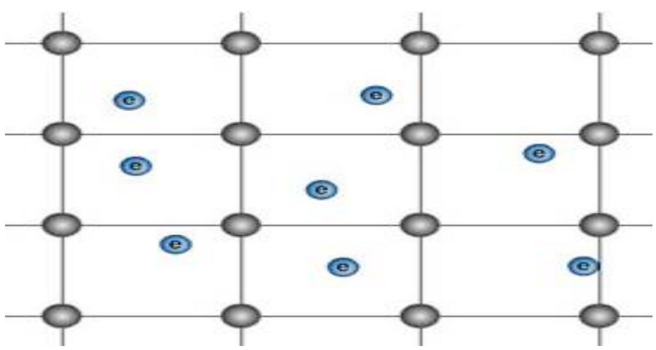
<u>Some Key Topics</u>
Conduction metallic electrolytic
Electrolysis effect and stoichiometry
Galvanic cell
Electrolytic cell
Electromotive Force (potential in volts)
Electrode Potentials
Gibbs Free Energy
Gibbs Free Energy and Equilibrium
Concentration Effects, Nernst Equation

<u>Types of Cells</u>
Chemical transformations to produce electricity- **Galvanic cell** or Voltaic cell (**battery**)

Electrical energy to cause chemical transformations- **Electrolytic cell**

<u>Conduction</u>

In **Metal**
Metallic conduction- charge carried by electrons



http://www.chemsoc.org/exemplarchem/entries/igrant/theory_noflash.html

Lattice of cations through which delocalised electrons flow.
Positive metal ions (cations) and mobile electron clouds
Free electrons can move through metal and carry charge

In **Ionic Solution** or **Salt Bridge**
Movement of positive and negative ions can carry charge

Useful Symbols and Units

A	ampere	measure of current I
C	coulomb	measure of electric charge q
V	volt	potential difference ε or EMF (electromotive force)

It is this difference that forces electrons to flow through wire

C = A s   where 1 coulomb is the charge equivalent to 6.24×10^{18} electrons together

Energy = (charge) (potential)
Joule = (coulomb) (volt)   J = C V

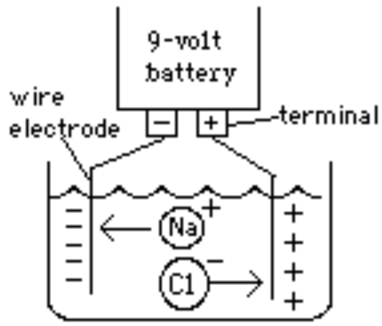
Energy available or Maximum work available flowing out of system

t	Time	(s)	
I	Current	(A)	ampere
q	Electric charge	(C)	Coulomb
ε	potential	(V)	ε = I*R
E	Energy	(J)	
R	Resistance	(Ω)	Ohm
F	Faraday	96,485 C	the charge of 1 mole of electrons

Unit Conversion
C = A s
J = C V

Ohms law   ε = I R   potential = current x resistance

Electolytic Cell examples



http://chemsrvr2.fullerton.edu/HES/cond_liquids/cond_liquids_tchr.htm

Cathode Reduction | Anode Oxidation

$$(2\,e^- + 2\,H_2O \rightarrow H_2 + 2\,OH^-)$$
$$\underline{2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^-}$$
$$2\,H_2O \rightarrow 2\,H_2 + O_2 + 4\,OH^- + H^+$$

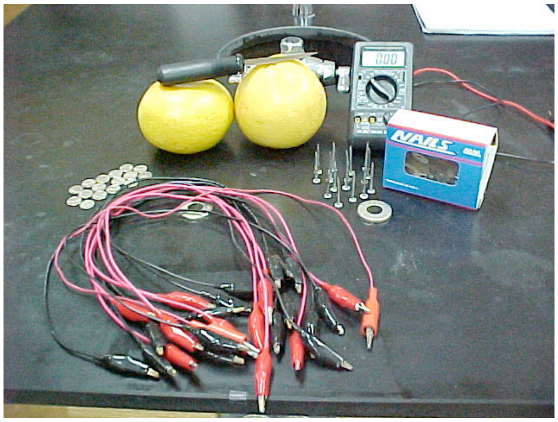
$$4\,OH^- \rightarrow O_2\,(g) + 2\,H_2O + 4\,e^-$$
$$2\,H_2O \rightarrow O_2\,(g) + 4\,H^+ + 4\,e^-$$

$$2\,e^- + 2\,H^+ \rightarrow H_2\,(g)$$
$$2\,e^- + 2\,H_2O \rightarrow H_2\,(g) + 2\,OH^-$$

Electrolytic Cell examples

				Potential (V)
Reduction	Cu^{2+}	$+\ 2\,e^- \rightarrow$	Cu	+.30
Oxidation		$Zn \rightarrow$	$Zn^{2+}\ +2\,e^-$	+.80
Reduction	$2\,H^+$	$+\ 2\,e^- \rightarrow$	H_2	0

Need acidic solution or even acidic fruit



http://www.unit5.org/christjs/Tim%20Paturi/materials.html

Volta – early 1800s, said use acidic solution and different metal pieces to generate electricity, burn oil to make it run and box on wheels to sit on (in other words – a car!)

We use lead storage cell (battery) in cars to generate electricity to start engine

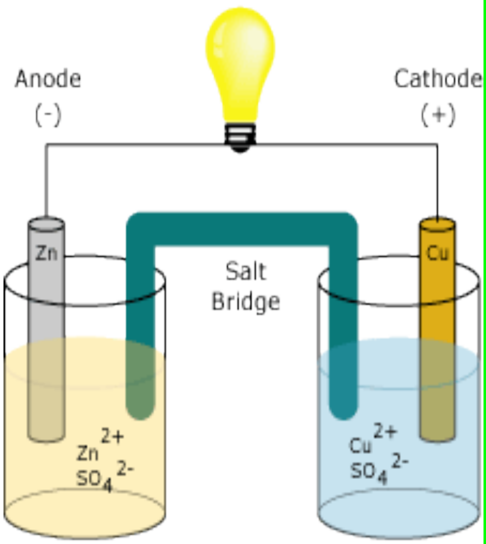
Anode $Pb\ (s) + SO_4^{2-} \rightarrow PbSO_4\ (s) + 2\ e^-$
Cathode $2\ e^- + PbO_2\ (s) + SO_4^{2-} + 4\ H^+ \rightarrow PbSO_4\ (s) + 2\ H_2O$

$Pb + PbO_2 + 2\ SO_4^{2-} + 4\ H^+ \rightarrow 2\ PbSO_4$

To start we use (galvanic cell)
When car running pass current through (battery now an electrolytic cell) to reverse reaction and recharge the same battery

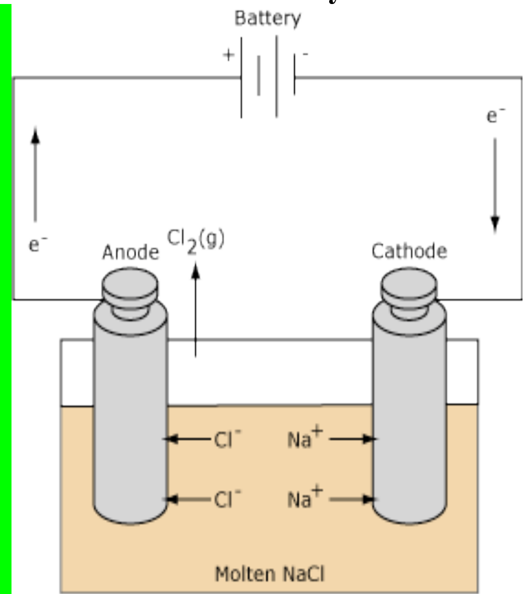
Types of Cells

Galvanic Cell (or Voltaic Cell)



Daniell Cell

Electrolytic Cell



Electrolytic Cell

http://chemistry.about.com/library/weekly/aa082003a.htm

First find Source of electrons and that helps identify negative electrode

Electrolytic – flow of electrons causes chemistry to occur
Galvanic – chemistry that occurs cause electron flow to occur (makes a battery)

Later will look at reduction potential tables and find that:
Minimum Voltage- reacts first in electrolytic cell
Highest (+) Voltage – occurs in galvanic cell

Electrolytic Conduction (Electrolytic Cell)

Charge carried by ions
Molten salts
Solutions of electrolytes

Ions move and chemical changes occur

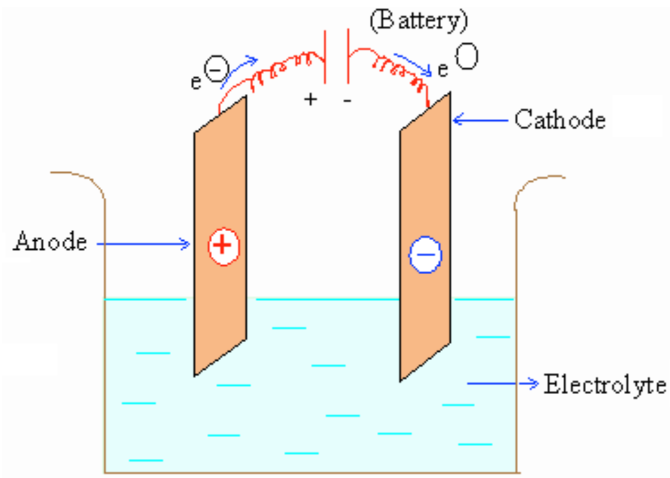


Figure 20 An electrolytic cell

http://www.pinkmonkey.com/studyguides/subjects/chem/chap9/c0909201.asp

Electrolysis cell in molten salt (Electrolytic Cell)

Cations attracted to cathode pick up electrons
Anions attracted to anode release electrodes

$2\,(Na^+ + e^- \rightarrow Na)$ gain e- reduction
$2\,Cl^- \rightarrow Cl_2 + 2\,e^-$ loss e- oxidation
$2\,Na^+ + 2\,Cl^- \rightarrow 2\,Na\,(l) + Cl_2\,(g)$ (2 NaCl)
$T \sim 600°C$

Molten salt
Increase temp. causes decrease in resistance
Movement of ions enhances charge that is carried through solution

Electrolysis Effect (Electrolytic Cell)

Pass charge through pure water form H_2 gas and O_2 gas

Recall water is a weak electrolyte $H_2O \Leftrightarrow H^+ + OH^-$

Cathode	2 (2 H^+	+	2 e^- $\rightarrow$	H_2 (g))					
	4 OH^-		$\rightarrow$	O_2 (g)	+	2 H_2O	+	4 e^-	
	4 H^+	+	4 OH^- $\rightarrow$	2 H_2	+	O_2	+	2 H_2O	

Ions come from water: electrolysis

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

What happens with other ions in solution?

Cation or H+ will be reduced at cathode
Anions or OH- will be oxidized at anode

Whichever will occur more easily will take place
There could be several ions in solution

Expect to predict that whatever reaction will occur in electrolytic cell will be a reaction with ε^o closer to zero but does not always work

Because of overvoltage- can make it more difficult larger ε^o than expected especially in the case of Cl_2 or O_2 gas

Electolytic Cell Examples

Later learn how to predict what will happen but for now look at possibilities

NaCl in solution

Cathode (reduction) $2e^- + 2\,H_2O \rightarrow H_2\,(g) + 2\,OH^-\,(g)$

Anode (oxidation) $2\,Cl^- \rightarrow Cl_2\,(g) + 2\,e^-$

$2\,H_2O + 2\,Cl^- \rightarrow H_2\,(g) + Cl_2\,(g) + 2\,OH^-$

Used in commercial production of H_2 and Cl_2 and NaOH after evaporation

$CuSO_4$ in solution

Cathode (red.) $2\,(2\,e^- + Cu^{2+} \rightarrow Cu)$

Anode (oxid.) $2\,H_2O \rightarrow O_2 + 4\,H^+ + 4e^-$

$2\,H_2O + 2\,Cu^{2+} \rightarrow Cu + O_2 + 4\,H^+$

Net Reaction: no electrons, balanced charge to give overall redox reaction

$CuCl_2$ in solution

Cathode (red) $2\,e^- + Cu^{2+} \rightarrow Cu$

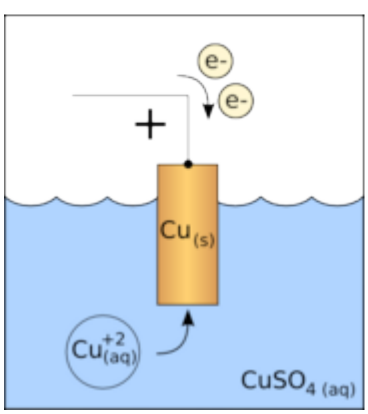
Anode (ox) $2\,Cl^- \rightarrow Cl_2\,(g) + 2\,e^-$

$Cu^{2+} + 2\,Cl^- \rightarrow Cu\,(s) + Cl_2\,(g)$

Copper metal plates out of solution

Other Solutions:
$CuSO_4$ with copper electrode
Reaction can involve electrodes!!!

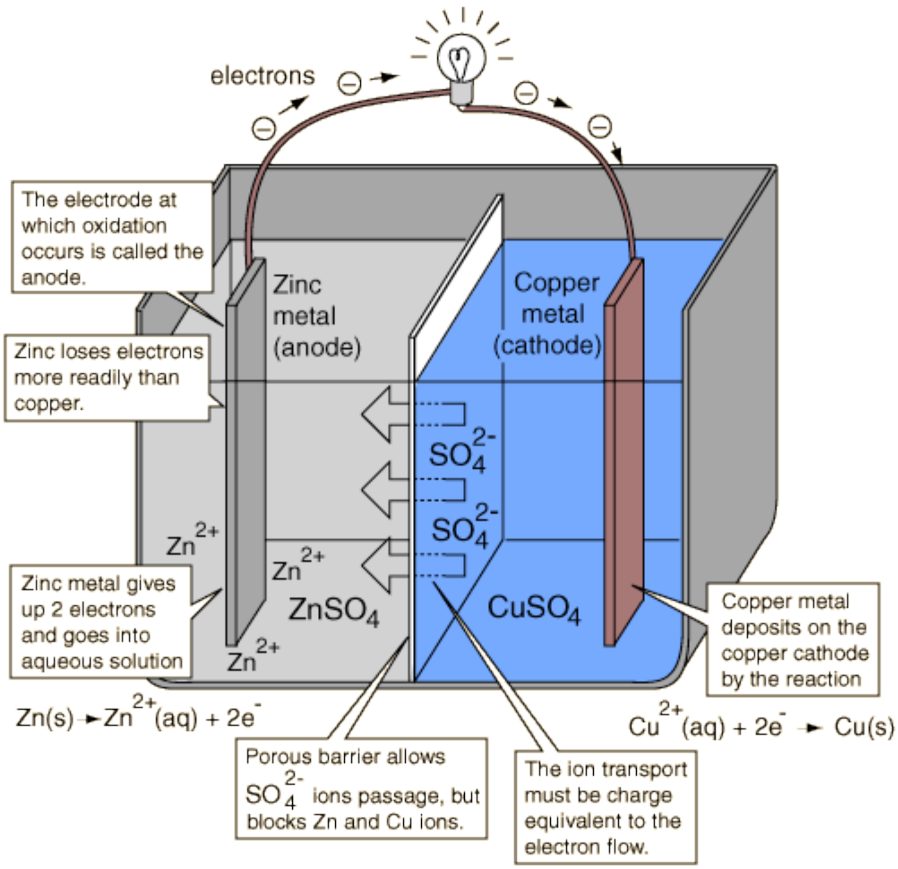
This occurs more readily



http://www.answers.com/main/ntquery?tname=cathode&print=true&nofollow=1

Galvanic Cell (Voltaic Cell)

Source of electricity
Chemical reaction → electron flow



http://hyperphysics.phy-astr.gsu.edu/hbase/chemical/electrochem.html

anode	cathode (think of a red cat)
oxidation	reduction
e- leave cell	e- enter cell

Note: - and + electorodes are opposite on electrolytic and voltaic cell
source of electrons gives the negative electrode

Positive or negative electrodes
Electrolytic:
(-) Reduction e- → (+) Oxidation

Galvanic:
(-) Oxidation e- → (+) Reduction

Oxidation			Zn (s) →		Zn^{2+} (aq)	+	2 e-
Reduction	2 e-	+	Cu2+ (aq) →		Cu (s)		
Overall Redox	Zn (s)	+	Cu^{2+} (aq) →		Zn^{2+} (aq)	+	Cu (s)

Will occur directly in solution of zinc metal placed in copper solution

Separate by porous wall in cell and connect by wire to create electron flow.
Ions move toward electrode of opposite charge

Find Voltage and Overall Reaction from given Half Reactions (Galvanic Cell)

Consider Zn^{2+} / Zn and Cu^{2+} / Cu and given half-reactions below from Table of reduction potentials

					ε°
Cu^{2+}	+	$2\ e^-$ →		Cu	+0.34
Zn^{2+}	+	$2\ e^-$ →		Zn	-0.76

Spontaneous direction is for maximum positive value of potential (+ ε°) so,
Reverse one reaction from red to ox to get maximum positive

Reduction	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
Oxidation	$Zn \rightarrow Zn^{2+} + 2e^-$	+0.76

Add two voltages (can change sign but never change value)

Red + ox = (+0.34V) + (+0.76V) = + 1.10 V

Add two half-reactions so all electrons cancel out.

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

Another Example:

Consider Ag^+ and Ag and Ni^{2+} and Ni

Ag^+	+	$e^- \rightarrow$	Ag	+0.80
Ni^{2+}	+	$2\ e^- \rightarrow$	Ni	-0.25

Reverse one reaction and change sign of voltage, add voltages and combine reactions

$2\ (Ag^+ + e^- \rightarrow Ag)$ +0.80

$Ni \rightarrow Ni^{2+} + 2\ e^-$ +0.25

$Ni + 2\ Ag^+ \rightarrow Ag + Ni^{2+}$ + 1.05 V

Abbreviated cell can be written as: $Ni \mid Ni^{2+} \parallel Ag^+ \mid Ag$

Or $Ag^+ \mid Ag \parallel Ni \mid Ni^{2+}$

In above note that

Multiply reaction by 2 to balance for electrons, but DO NOT multiply ε° by 2

ε° can change sign but numerical value always remains the same

Combination of half reactions giving largest positive $\varepsilon°_{cell}$ will occur with one oxidation and one reduction

$Li \rightarrow Li^+ + e^-$ oxidized

large negative ε° because it is strong reducing agent – wants to give electrons

$e^- + F \rightarrow F^-$ reduced

large positive ε° because it is strong oxidizing agent – wants to take electrons

so therefore the reaction

$2\ Li + F_2 \rightarrow 2\ LiF$ Will definitely occur gives maximum positive potential

see Reduction tables to find the potential volts for above

Gibbs Free Energy and Equilibrium

ΔG^o = change in Gibbs Free Energy with substances in standard state conditions

In general $\mathbf{\Delta G = \Delta G^o + RT \ln Q}$
Q is reaction quotient, like equilibrium constant, but not at equilibrium
$Q = \frac{\text{actual products}}{\text{Reactants}}$

Since Q = K at equilibrium, $\Delta G = 0$ at equilibrium so
At equilibrium $\mathbf{\Delta G^o = - RT \ln Q}$

ΔG^o (kJ)	K	
-100	3.3×10^{17}	products favored
-25	2.4×10^{4}	
0	1.0	
25	4.2×10^{-5}	reactants favored
100	3.0×10^{-18}	

$\mathbf{K = e^{-\Delta Go/RT}}$
R = 8.31 J/mol K
T = K

Electromotive Force

Shorthand notation to represent cell
In order going from anode to cathode

anode cathode
$Zn(s) | Zn^{2+}$ (1 M) | Cu^{2+} (1M) | Cu (s)

Є electromotive force (emf) maximum potential volts can be produced
$Є^o$ – standard emf at at 25^o C, species are in standard state
solution is 1 M concentration
gas is 1 atm pressure

Electrode Potentials (How to find ϵ^o cell)

Can divide the emf of a cell reaction ϵ^o cell into two half reactions
$\epsilon^o cell = \epsilon^o ox + \epsilon^o red$

Need reference to measer half reactions against starting point, because cannot run half reaction alone

Use standard hydrogen electrode (SHE)
$2\ H^+ + 2\ e^- \rightarrow H_2$ 0.00 V

Pt (s) | H_2(g) H^+ (aq) || Cu^{2+} (aq) | Cu (s) H_2 = hydrogen gas || = salt bridge

Anode: $H_2\ (g) \rightarrow 2H^+ + 2e$ $\epsilon^o ox = 0.00V$
Cathode: $2e^- + Cu^{2+} \rightarrow Cu$ $\epsilon^o red = 0.34V$

See Table for electrode potentials

Half reactions are written as reductions (gain e)
so reverse sign if half reaction is changed to oxidation (give up e)

Cell EMF (voltage potential) must be positive for reaction to occur

Gibbs free energy and potential

$\Delta G = -nF\varepsilon$

Units: ΔG = Gibbs free energy change (J)
n = moles of electrons transferred in reaction
F = 96485 C/mol Faraday constant
ε = potential or EMF (V)

ΔG measures whether or not spontaneous reaction will occur.

ϵ (+)	ΔG (-)	yes
ϵ (0)	ΔG (0)	at equilibrium
ϵ (-)	ΔG (+)	no reverse will happen

Only if ϵ is positive will ΔG be negative

For zinc copper cell for 2 mol of electrons transferred at voltage of 1.10 V:

ΔG = -(2 mol) (96485 C/mol) (1.10 V)
= -212000 C V
= -212000 J (kJ/ 1000 J)
= -212 kJ

Concentration Effects-Nernst Equation (derivation shown below)

Effect of Concentration on cell potential at other than standard state

$\Delta G^o = -2.303\ RT\ \log K$ same as $\Delta G^o = -\ RT\ \ln K$ because $2.303 \log X = \ln X$

$\Delta G^o = -nF\epsilon^o$

Combine above equations gives:

$$\epsilon^o = \frac{2.303\ RT}{nF} \log K$$ relates electrode potential to equilibrium

and if concentrations are not at equilibrium can write

$\Delta G = \Delta G^o + 2.303\ RT \log Q$

Q= reaction quotient, same form as equilibrium constant but not at equilibrium concentrations

Example below shows Q is like K = products/reactants

$aA + bB \rightarrow yY + zZ$

$$Q = \frac{[Y]^y [Z]^z}{[A]^a [B]^b}$$

Since $\log(X) = \ln(X)/ 2.303$ then

$\Delta G = \Delta G^o + 2.303\ RT \log Q$ can be written $\Delta G = \Delta G^o + RT \ln Q$

And sub in gives:

$-nF\epsilon = -nF\epsilon^o + 2.303 RT \log Q$ or

$\epsilon = \epsilon^o - 2.303\ RT/nF \log Q$

And since $RT/F = \frac{(8.31\ J/molK)(298\ K)}{96485\ C/mol} = 0.0592\ J/C$ or 0.0592 V

<u>so Result is Nernst Equation</u>

(do not have to know derivation given above but given if interested)

$\epsilon = \epsilon^o\ (-\ 0.0592/n) \log Q$ n = # of e^- transferred in reactions

Standard state: Q=1 1 M concentration 1atm pressure

So at standard state **$\epsilon = \epsilon^o - 0$** but at other than standard state **ϵ not equal ϵ^o**

Nernst Equation Applications

Given $2e^- + Zn^{2+} \rightarrow Zn$ if $[Zn^{2+}] = 0.1$ $Є^o = -0.76V$ Find Є

Є = -0.76 – (0.592/2) log (1/0.1)
log (10) = 1
Є = -0.76 – (+.030)
Є = -0.79 V

Note below -even when large change in concentration
only small change in emf (potential in volts)

$[Zn^{2+}]$	Є (V volt)
.01	-.82
.1	-.79
1	-.76
10	-.73
100	-.70

Nernst Equation agrees with Le Chatlier's principle

Reactants	**Products**	**Є**	**shift**
increase	decrease	increase	→
decrease	increase	decrease	←

Example problem using Nernst Equation

Given: Ni | Ni^{2+} (0.010M) || Cl^-(0.20M) | Cl_2 (0.5 atm) | Pt

	$Є^o$ (v)
$Ni^{2+} + 2e^- \rightarrow Ni$	-.25
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36

Find $Є^o$ and Є

	$Є^o$ (v)	
$Ni \rightarrow Ni^{2+} + 2e^-$	0.25	
$Ni + Cl_2 (g) \rightarrow Ni^{2+} + 2Cl^-$	1.61	(Potential Standard State)

$$Є = Є^o - (.092/n)\log\left(\frac{[Ni^{2+}][Cl^-]^2}{P_{Cl2}}\right) \qquad Q = [products]/[reactants]$$

$$= 1.61 - (.0592/2) \log\left(\frac{[.010][.20]^2}{(.5)}\right)$$

$$= 1.61 - (0.592/2)\log(8.00 \times 10^{-4})$$

$$= 1.61 - (.0592/2)(-3.10)$$
$$= 1.61 + 0.092$$

Є = 1.70V (Potential at actual concentrations different than standard state 1.61V)

Electrolysis Stoichiometry

F faraday charge of 1 mole of electrons
1 F = 96485C/mol e
charge of 1 single electron 1 $e^{-} = 1.60 \times 10^{-19}$ C coulomb
charge of 1 mol of electrons 1 mol e^{-} = 96485 C

Useful for calculations to know how much of a substance used up or produced for a certain current flow

Example:
$2Cl^{-} \rightarrow Cl_2(g) + 2e^{-}$
2 moles of e^{-} to produce 1 mole $Cl_2(g)$
2 Faraday of charge required (that is charge of 2 mol of electrons)

$4OH^{-} \rightarrow$	$O_2(g)$ +	$2H_2O$ +	$4e^{-}$
4 mole	1 mole	2mole	4 F of electricity

Example Calculation
1) determine number of mol of e
2) convert mol of e to mol and g

Electrolysis of $CuSO_4$, current 0.75 A for 10 minutes
How much Cu metal plated out?

A = C/s so C = A s or charge = (current)(time)

1) = 10.0 min (60s/1min)(.75C/s)(mol/96485 C)
= 0.00466 mol of e

$Cu^{2+} + 2e^{-} \rightarrow Cu(s)$
2 F for 1 mole of Cu 1 mole = 63.5g

2) Grams of Cu = (.00466 mol e) (1mol Cu/2mol e)(63.5g/1mol) = 0.148 g Cu

Conversions shown below and connections shown below each conversion
Mass ⇔ mol metal ⇔ mol e ⇔ charge(coloumb) ⇔ current time
(Molar mass) (Balance eq) (mol/96485 C) (C = A s)

EXTRA MATERIAL – NOT COVERED IN CLASS

<u>Ohm's Law</u>

ϵ = IR

ϵ	electric potential	(V) volts
I	current	(A) amperes
R	resistance	(Ω) ohms

The greater the electrical potential the greater the current flow
Current flow like water running downhill

Resistance increases with increasing temperature vibration of metal ions about lattice positions is increased and vibrations interfere with e^- flow