

Electrochemistry

The Last Chapter of Chemistry...
M-CATS

The Powerhouse of the Cell

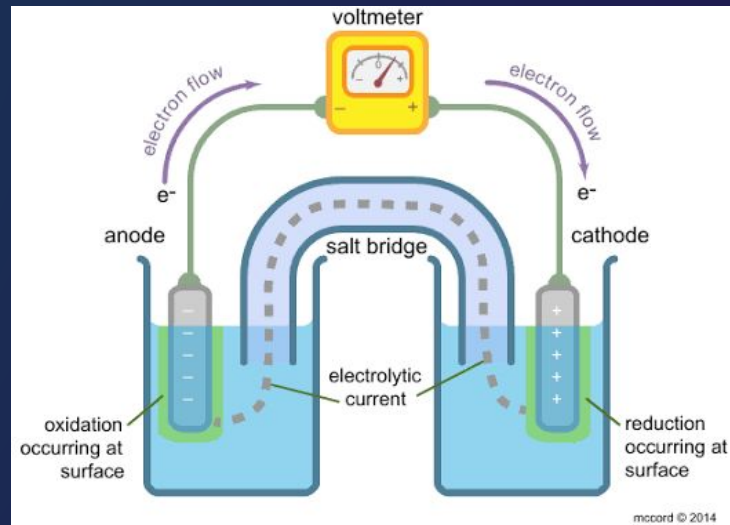
As you've learned already, mitochondria is the powerhouse of the cell... but how?

- Proton Gradient
- ATP synthase



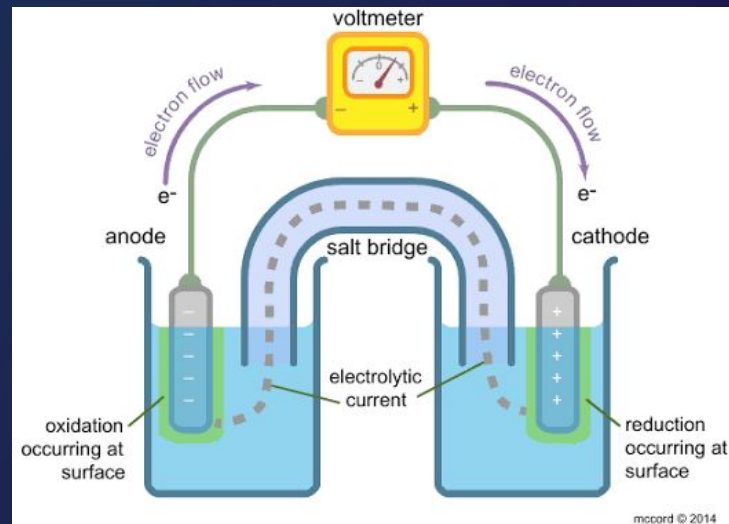
The (Electrochemical) Cell

- Anode & Cathode
 - An Ox & Red Cat
 - Does Oxidation or Reduction produce electrons?
 - Electron Flow is equal and opposite to current
 - Spontaneous vs Nonspontaneous (Gibbs Free Energy and Electromotive Force)
 - Is the sum of the potentials of the half reactions
 - Galvanic (Spontaneous) vs Electrolytic (Nonspontaneous)



Parts of an Electrochemical Surface

- Wire
- Half cells with Anode and Cathode
- Salt bridge (what might constant movement of electrons cause)
- **Galvanization/plating/precipitation



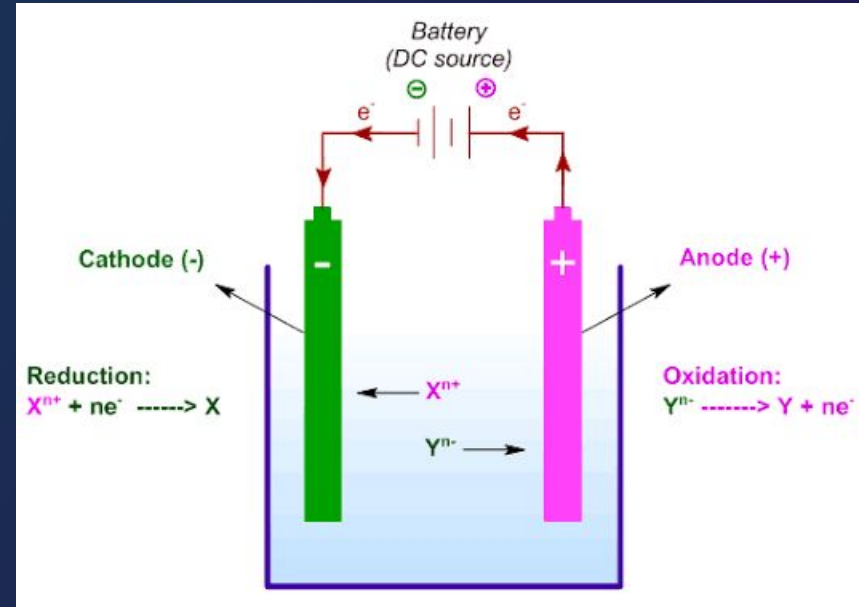
Cell Diagram notation



- Reactants $\Rightarrow$ Products
- Phase boundary is indicated by $\mid$; Half cells are separated by $\parallel$
- Listed in the direction of the flow of electrons Anode $\Rightarrow$ Cathode

The Electrolytic Cell

- Nonspontaneous
- Electro - Lysis
- Why not two cells?
- Flow of electrons from anode to power source and from power source to cathode
-



Faraday (the constant and the dude)

- The constant is the amount of charge in 1 mole of e^- : 96,485 C
 - Round to 100,000 to make calculations easier
- Because electrochemical reactions rely on electron flow, the reaction can be quantified in terms of the amount of electron flow, or vice versa
- $M = It/nF$



How might that equation show up?

An electrolytic cell is run with a solution of TiO_2 at 400 milliamps for 5 minutes. How much titanium metal plates onto the cathode?

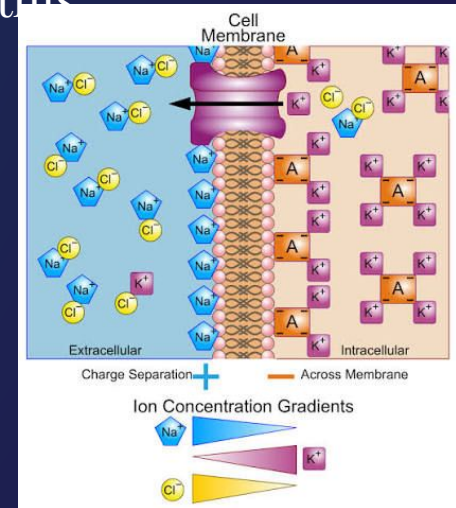
- What's the n ?
- What is the current and duration

The inverse: An electrolytic cell of lithium chloride is run for 3 minutes and deposits .27 moles of lithium onto the cathode. What current was the cell run at?

Concentration cells

Current is established via a difference in concentrations of solutes

- Electrons flow in the direction of equilibrium
- Nernst Equation
- Nerve cells and resting membrane potential are based on this
- More in chapter 8 of Biochemistry



Rechargeable batteries

- Must be able to act as both Galvanic and Electrolytic batteries
 - Lead-acid batteries
 - Charged-Pb anode and porous PbO_2 Cathode, filled with concentrated H_2SO_4
 - Discharged- PbSO_4 electrodes with dilute H_2SO_4
 - Anode is straightforward oxidation of Pb and HSO_4^-
 - Cathode is more complicated, but essentially uses reduction to produce PbSO_4 and H_2O
 - By supplying a voltage, both sides are reversed to charge the battery
 - Nickel-Cadmium Batteries
 - Cadmium + 2OH^- is oxidized into $\text{Cd}(\text{OH})_2$, while $\text{NiO}(\text{OH}) + \text{H}_2\text{O}$ becomes $\text{Ni}(\text{OH})_2$
 - Reversing potentials allows the reaction to run in reverse. What does this reaction produce?
 - Flipping the reactions requires also changing the direction that current runs, why?

Reduction Potential

Standard reduction potential = E° =

- This is at 298k, at 1 M concentrations, and 1 atm
- These are based on how likely a molecule is to gain electrons (Related to Electronegativity)
- Standard Gibbs Free Energy is based on the E°
 - If a cell has a positive E, the reaction will occur (galvanic) and Delta G is negative (spontaneous)
 - Electrolytic cells are the exact inverse

Half Reaction	Potential E°
$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.05
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mg}(\text{s})$	-2.36
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Al}(\text{s})$	-1.67
$\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.44
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.23
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$	-0.13
$\text{Fe}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.036
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	0.34
$\text{Cu}^+(\text{aq}) + \text{e}^- \rightarrow \text{Cu}(\text{s})$	0.52
$\text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Hg}(\text{l})$	0.8
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	0.8
$\text{Pt}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pt}(\text{s})$	1.2
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.23
$\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Au}(\text{s})$	1.5
$\text{F}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{F}^-(\text{aq})$	2.87

Calculating the Electromotive force of a cell

Reduction potential of cathode rxn + Oxidation potential of anode rxn

- Oxidation potential is the negative of the reduction potential

These standard potentials are intrinsic properties, so do not multiply them with stoichiometry

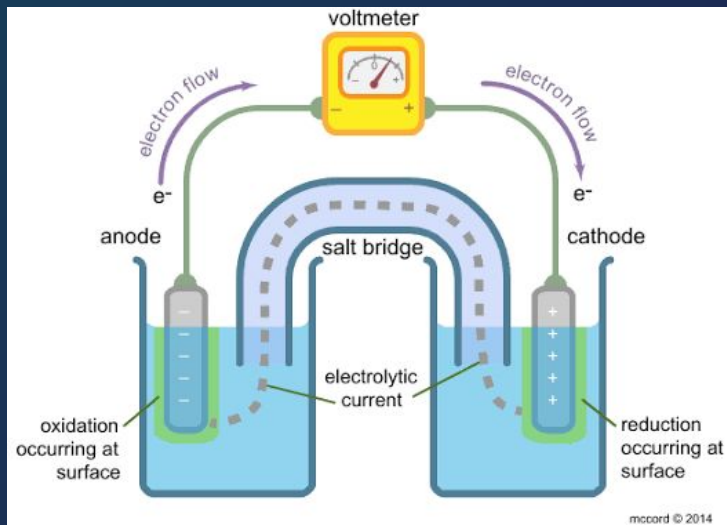
Simply add them together to calculate the emf (or voltage) of the cell

If the emf is negative, the cell is electrolytic

If positive, the cell is galvanic

What type of cell would be formed by these pairings?

- $3\text{Li} + \text{Au}^{3+} \gg 3\text{Li}^+ + \text{Au}$
- $3\text{Li}^+ + \text{Au} \gg 3\text{Li} + \text{Au}^{3+}$
- $6\text{H}^+ + 2\text{Fe} \gg 2\text{Fe}^{3+} + 3\text{H}_2$



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Thermodynamics (Yayy)

$$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$$

Here is where you account for e^{-} stoichiometry

Also, note that this is essentially the emf multiplied by the amount of charge that moves in 1 mole of the reaction

Nonstandard Conditions and Nernst Eq.

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln Q$$

Under nonstandard conditions, this is the equation that you'll be using to determine the nonstandard emf

Q is the concentration of the aqueous ions (Anode product/cathode reactant)

Note that there are quite a few constants, and if the temperature is kept standard, the equation simplifies to:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{n} \log Q$$

Example problem

Calculate the potential of a galvanic cell at 298K. The half cell has an a platinum electrode and has a concentration of 1M Pt^{2+} . The other electrode is made of magnesium, and the half cell has a concentration of 0.01M Mg^{2+} .

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Emf can be used to determine equilibrium concentrations

$$RT \ln(K) = \Delta G^\circ = -nFE^\circ_{\text{cell}}$$

From this, given the standard electromotive force and the n of a reaction, the equilibrium ratio of ions can be calculated

Conceptually:

- What does a large equilibrium constant imply about the emf? Small?
- What kind of cell would each situation produce? Galvanic or Electrolytic?

Given this relation, this follows:

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

Congrats!! You are officially done with Chemistry!!

Lolll... just kidding. Now for the hard part. Make sure you go back and review this content to internalize it. You've studied it now, but it's very easy to forget everything you've learned.

We're still working on integrating a Q-bank into the website, but once we do, please use it. The best way to make sure you remember something is to test yourself consistently. With that said, best of luck!!