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Lecture #3 of 20

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Looking forward... our review of Chapter "0"

- Cool applications
- Redox half-reactions
- Balancing electrochemical equations
- History of electrochemistry and Batteries (halfway complete)
- IUPAC terminology and $E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$
- Thermodynamics and the Nernst equation
- Common reference electrodes
- Standard and Absolute potentials
- Latimer and Pourbaix diagrams
- Calculating E_{cell} under non-standard-state conditions
- Conventions

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RECALL: Voltaic pile

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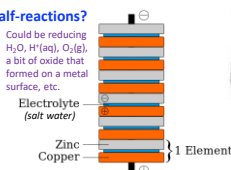
Invented by Alessandro Volta (1800) but the elements of the pile (galvanic cells) were named after Galvani.

What are the combined half-reactions?

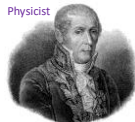


At the Tempio Voltiano (the Volta Temple)
near Volta's home in Como, Italy.

http://en.wikipedia.org/wiki/Voltaic_pile



Physicist



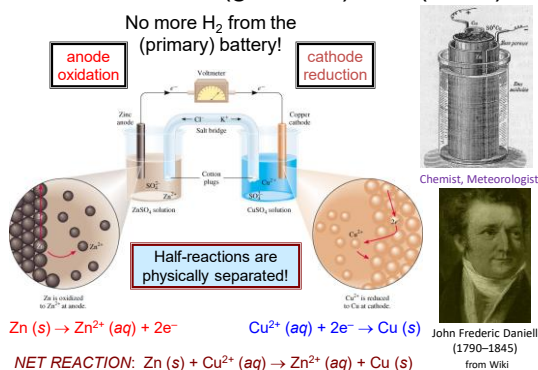
Alessandro Volta
(1745–1827)
from Wiki

Volta presenting his "Voltaic Pile" to Napoleon and his court... and now he is a Count!



http://en.wikipedia.org/wiki/Alessandro_Volta

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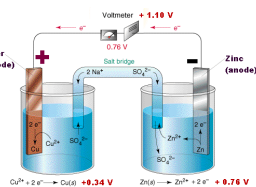
RECALL: Daniell (galvanic) Cell (1836) ⁶⁸

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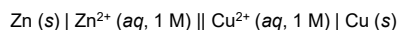
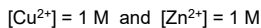
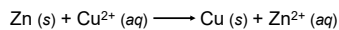
Voltage Produced by Galvanic Cells ⁶⁹

The difference in electric potential between the anode and the cathode is called:

- ✓ **Cell potential**
- ✓ **Cell voltage**
- ✓ **emf (electromotive force)**

**Cell Diagram**

This should be -0.76 V!
(we will discuss this soon)

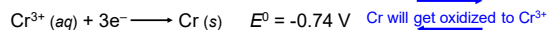
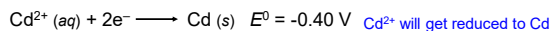


anode salt bridge cathode

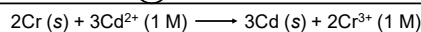
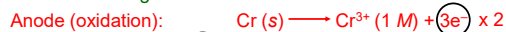
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EXAMPLE: What is the (standard) potential of a galvanic cell consisting of a Cd electrode immersed in aqueous 1.0 M Cd(NO₃)₂ and a Cr electrode immersed in aq. 1.0 M Cr(NO₃)₃?

Which half-reaction is reducing?



More negative of the two ... thus, it is reducing



$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}}^0 = -0.40 \text{ V} - (-0.74 \text{ V})$$

$$E_{\text{cell}}^0 = +0.34 \text{ V} \text{ (positive = spontaneous, since } \Delta G = -nFE)$$

... if your answer is negative then you switched the anode/cathode in the galvanic cell

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Electrochemistry:

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conventions... oh, conventions!

Cathode – electrode where catholyte species are reduced

Anode – electrode where anolyte species are oxidized

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Electrochemistry:

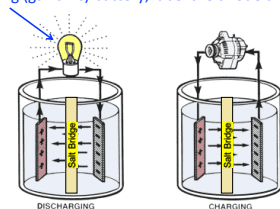
(UPDATED) 72**conventions... oh, conventions!**

Cathode – electrode where catholyte species are reduced

Anode – electrode where anolyte species are oxidized

Does a Negative/Positive Electrode = Cathode or Anode?... It depends!

For the discharging (galvanic) battery, label the anode and the cathode.

<http://autoshop101.com/>

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Electrochemistry:

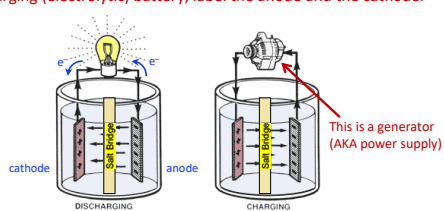
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Electrochemistry:

(UPDATED) 74

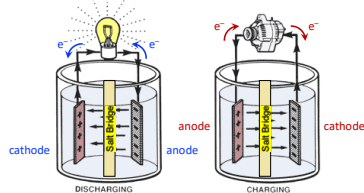
conventions... oh, conventions!

Positive electrode – positively charged; immersed in the **posolyte**
Negative electrode – negatively charged; immersed in the **negolyte**

... I'm not kidding!

... Sheesh!...

... **Take-home message: For batteries, don't call electrodes anodes and cathodes** (but naming convention used by most is for discharge)


<http://autoshop101.com/>

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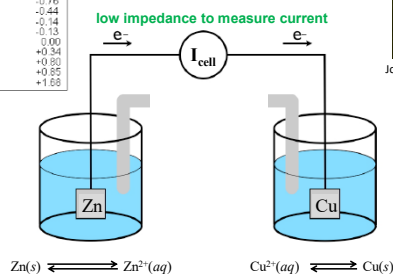
electro-chemical series	
Potassium	-2.92
Calcium	-2.87
Sodium	-2.71
Magnesium	-2.37
Aluminium	-1.66
Zinc	-0.76
Iron	-0.44
Tin	-0.14
Lead	-0.13
Hydrogen	0.00
Copper	+0.34
Silver	+0.80
Mercury	+0.85
Gold	+1.68

The Daniell Cell (1836)

Chemist, Meteorologist



John Frederic Daniell
(1790–1845)
from Wiki



As drawn,
current flows
for << 1 sec
and then
stops due to
lack of charge
neutrality...
... capacitive
charging

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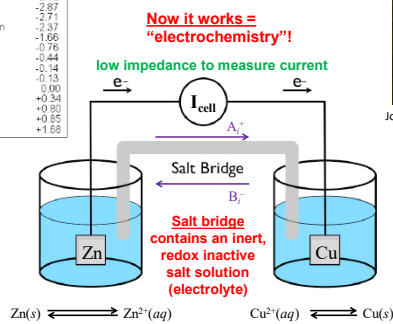
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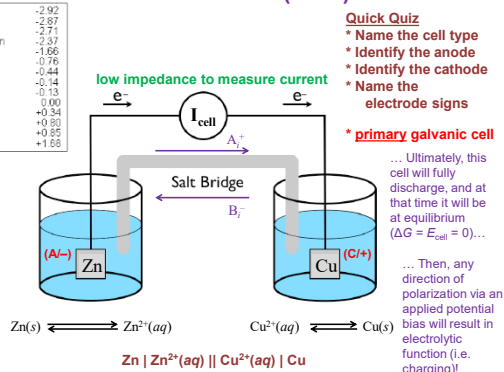


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The Daniell Cell (1836)



Quick Quiz

- * Name the cell type
- * Identify the anode
- * Identify the cathode
- * Name the electrode signs

* primary galvanic cell

... Ultimately, this cell will fully discharge, and at that time it will be at equilibrium ($\Delta G = E_{\text{cell}} = 0$)...

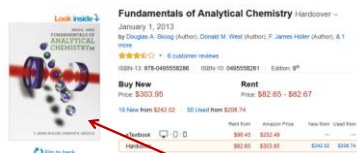
... Then, any direction of polarization via an applied potential bias will result in electrolytic function (i.e. charging)!

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International Union of Pure and Applied Chemistry (IUPAC)

(Accepted) Nomenclature and Terminology that you've learned, but may have forgotten

- Coulomb (in units of $C = A \cdot s$) is the unit of charge (96,485 C are in a mole of singly charged species = Faraday constant, $F = 96,500 \text{ C/mol} \approx 10^5 \text{ C/mol}$)
- Electricity is the flow of current (I ; in units of $A = C/s$) and is negative (cathodic) or positive (anodic) depending on the direction and sign of the current-carrying species (e.g. e^- , H^+)



(Sources: B&F, M3LC course textbook, and <http://goldbook.iupac.org/>)

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- (Electrode) (electric) potential (V or E ; in units of $V = J/C$) is written as a reduction

Based on our **current sign convention**, it is best to only write reduction potentials; however, if we lived in an oxidation-potential-centric world, we could write them all (i.e. everything) as oxidation potentials; **simply put, it is best to not mix the conventions and so stick with reduction potentials**

$E^\circ(Cu^{2+}/Cu) = +0.34 \text{ V vs. SHE}$ ✓
 $E^\circ(Cu^{0}/Cu^{2+}) = -0.34 \text{ V vs. SHE}$ ✗
 ... is incorrect!

You can subtract reduction potentials but do not change the sign of the potential and then call it an oxidation potential!

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 - (Electrode) (electric) potential (V or E ; in units of V = J/C) is written as a reduction. This relates to Gibbs free energy as $\Delta G = -nFE_{\text{cell}}$ (electrical work per mole), and...
 - ... partial molar Gibbs free energy is the **electrochemical potential** (μ , in units of J/mol)
 - Chemical potential (μ , in units of J/mol)
 - Galvani/inner (electric) potential (ϕ , in units of V)
- ... and in summary, $\mu = \mu + zF\phi$
- Cannot be measured independently!**

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 - Galvani/inner (electric) potential (ϕ , in units of V)
- Also, standard state is a solvent, a solid, and a species at unit activity (~1 M solutes, ~1 bar gases). Also, $E = IR$ (Ohm's law) when resistance is constant
- Galvanic cells produce power (P ; in units of W = A x V = C/s x J/C = J/s) by spontaneous redox reactions
 - Electrolytic cells require a power input to drive redox reactions; thus, the reactions are thermodynamically unfavorable
 - A battery has an **anode/anolyte** and a **cathode/catholyte**, but these descriptors change depending on whether the battery is being discharged (galvanic) or charged (electrolytic); **negative electrode/negolyte** and **positive electrode/posolyte** are better
- opposites**

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For "clarity," a brief (more rigorous) "review" of thermodynamics... **[BRIEFLY]** 82

Electrochemical potential of species i in phase β is an energy (J/mol),

$$\bar{\mu}_i^\beta = \left(\frac{\partial G}{\partial n_i^\beta} \right)_{T,p,n_{j \neq i}} = \mu_i^\beta + z_i F \phi^\beta, \text{ where}$$

G (Gibbs free energy (J))

n_i (amount of species i (mol))

$\mu_i = \mu_i^0 + RT \ln a_i$ (chemical potential (J/mol))

z_i (valency of species i)

$F \approx 10^5$ (Faraday constant (C/mol))

ϕ^β (Galvani/inner electric potential (V))

a_i (activity of species i)

For an uncharged species $\bar{\mu}_i^\beta = \mu_i^\beta$.

... more on this later...

Parsons, *Pure & Appl. Chem.*, 1973, 37, 501
IUPAC Gold (<http://goldbook.iupac.org>)

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