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Lecture #3 of 17

(UPDATED) 64

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 $E_{cell} = E_{red} - E_{ox}$**
- **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

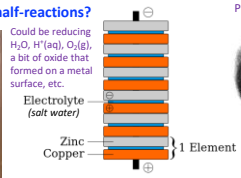
Invented by Alessandro Volta (1800) but the elements of the pile (galvanic cells) were named after Galvani.

What are the combined half-reactions?

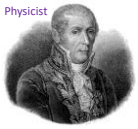
At the Tempio Voltiano (the Volta Temple) near Volta's home in Como, Italy.

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

Could be reducing H_2O, $H^+(aq)$, $O_2(g)$, a bit of oxide that formed on a metal surface, etc.



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

RECALL: Galvanic Cells

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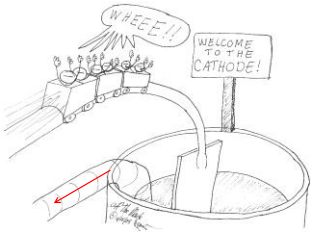
Every non-equilibrium cell is a galvanic cell (in one direction, i.e. the spontaneous direction)

Physically separating the half-reactions allows the electrons to go over a long distance, from the anode to the cathode via a (solid) conductor: basis for conversion of chemical energy into electricity = "Electrochemistry"!



Salt bridge is an ionic conduit to prevent buildup of charge in both compartments and also to prevent bulk mixing of the two solutions

Electrolysis of water

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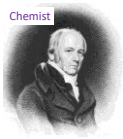


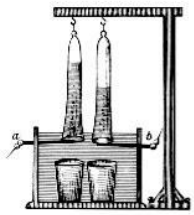
William Nicholson (1753–1815)

Sir Anthony Carlisle (1768–1840)

Johann Wilhelm Ritter (1776–1810)

William Cruickshank (17??–1810(1))

Volta's results were shared with the scientific community and then, **boom**, many people demonstrated electrolysis the same year, and later electroplating!



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

Daniell (galvanic) Cell (1836)

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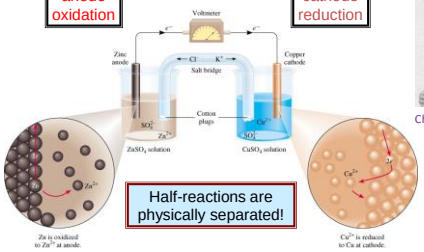
No more H_2 from the (primary) battery!

anode oxidation

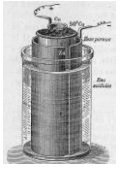
cathode reduction



$Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2e^-$

$Cu^{2+}\ (aq) + 2e^- \rightarrow Cu\ (s)$

NET REACTION: $Zn\ (s) + Cu^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + Cu\ (s)$



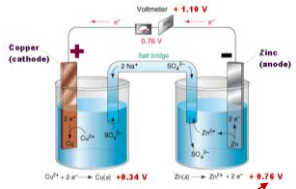
Chemist, Meteorologist

John Frederic Daniell (1790–1845) from Wiki

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)*

$Zn\ (s) + Cu^{2+}\ (aq) \longrightarrow Cu\ (s) + Zn^{2+}\ (aq)$

$[Cu^{2+}] = 1\ M$ and $[Zn^{2+}] = 1\ M$

$Zn\ (s)\ |\ Zn^{2+}\ (aq, 1\ M)\ ||\ Cu^{2+}\ (aq, 1\ M)\ |\ Cu\ (s)$

anode salt bridge cathode

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EXAMPLE: What is the (standard) potential of a galvanic cell consisting of a Cd electrode in a 1.0 M $Cd(NO_3)_2$ solution and a Cr electrode in a 1.0 M $Cr(NO_3)_3$ solution? 70

Which half-reaction is reducing?

$Cd^{2+}\ (aq) + 2e^- \longrightarrow Cd\ (s)$ $E^0 = -0.40$ V — Cd^{2+} will get reduced to Cd

$Cr^{3+}\ (aq) + 3e^- \longrightarrow Cr\ (s)$ $E^0 = -0.74$ V — Cr will get oxidized to Cr^{3+}

… thus, it is reducing

More negative of the two

Anode (oxidation): $Cr\ (s) \longrightarrow Cr^{3+}\ (1\ M) + 3e^-$ x 2

Cathode (reduction): $2e^- + Cd^{2+}\ (1\ M) \longrightarrow Cd\ (s)$ x 3

$2Cr\ (s) + 3Cd^{2+}\ (1\ M) \longrightarrow 3Cd\ (s) + 2Cr^{3+}\ (1\ M)$

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

$E^0_{cell} = -0.40\ V - (-0.74\ V)$

$E^0_{cell} = +0.34$ V (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: 71

conventions… oh, conventions!

Cathode – electrode where catholyte species are reduced

Anode – electrode where anolyte species are oxidized

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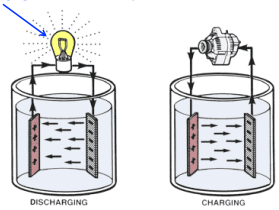
Electrochemistry: 72

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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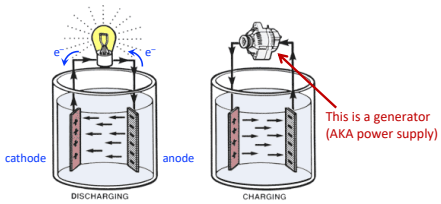
Electrochemistry: 73

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 charging (electrolytic) battery, label the anode and the cathode.



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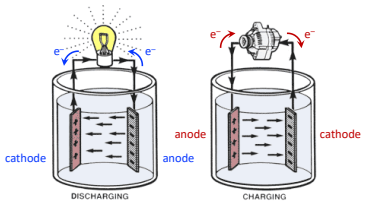
Electrochemistry: 74

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)*



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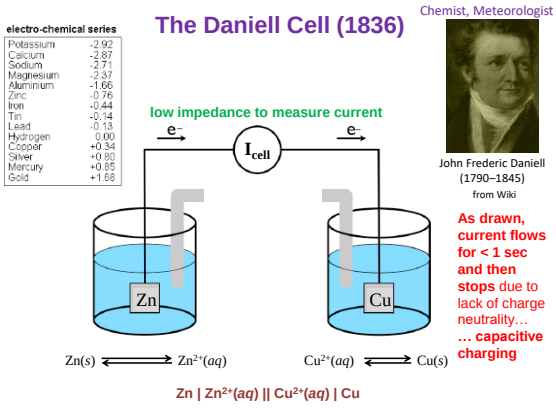
electro-chemical series
Potassium -2.92
Calcium -2.87
Sodium -2.71
Magnesium -2.37
Aluminium -1.66
Zinc -0.76
Iron -0.44
Tin -0.14
Lead -0.13
Hydrogen 0.00
Copper +0.34
Silver +0.80
Mercury +0.85
Gold +1.68
The Daniell Cell (1836)
Chemist, Meteorologist
low impedance to measure current
e⁻
e⁻
I cell
Zn
Cu
Zn(s) ⇌ Zn²⁺(aq)
Cu²⁺(aq) ⇌ Cu(s)
Zn | Zn²⁺(aq) || Cu²⁺(aq) | Cu
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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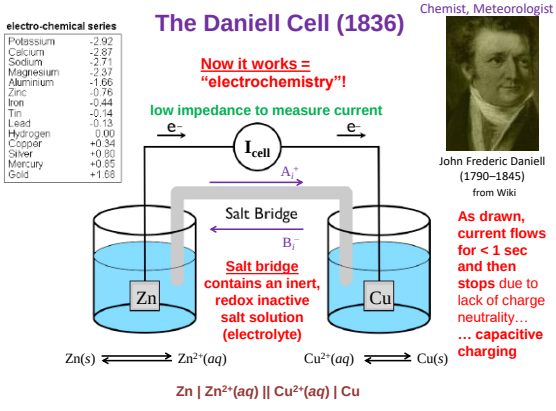
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The Daniell Cell (1836)
Chemist, Meteorologist
Now it works =
"electrochemistry"!
low impedance to measure current
e⁻
e⁻
I cell
A_i⁺
Salt Bridge
B_i⁻
Salt bridge contains an inert, redox inactive salt solution (electrolyte)
Zn
Cu
Zn(s) ⇌ Zn²⁺(aq)
Cu²⁺(aq) ⇌ Cu(s)
Zn | Zn²⁺(aq) || Cu²⁺(aq) | Cu
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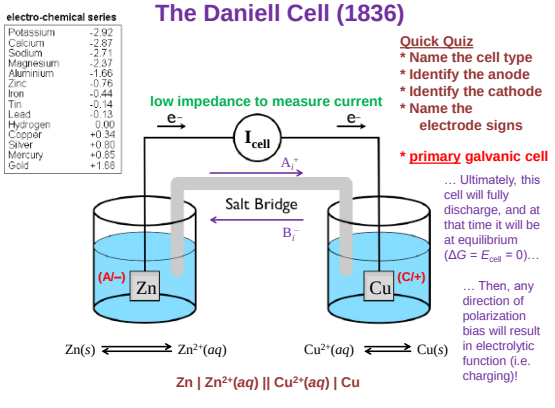
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Copper +0.34
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Gold +1.68
The Daniell Cell (1836)
Quick Quiz
* Name the cell type
* Identify the anode
* Identify the cathode
* Name the electrode signs
* primary galvanic cell
low impedance to measure current
e⁻
e⁻
I cell
A_i⁺
Salt Bridge
B_i⁻
(A/–)
Zn
Cu
(C/+)
Zn(s) ⇌ Zn²⁺(aq)
Cu²⁺(aq) ⇌ Cu(s)
Zn | Zn²⁺(aq) || Cu²⁺(aq) | Cu
… Ultimately, this cell will fully discharge, and at that time it will be at equilibrium (ΔG = E_cell = 0)…
… Then, any direction of polarization bias will result in electrolytic function (i.e. charging)!

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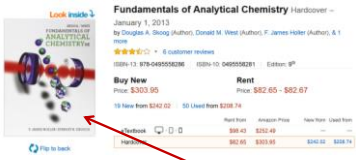
International Union of Pure and Applied Chemistry (IUPAC)

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

- Coulomb (in units of C = A·s) is the unit of charge (96,485 C are in a mole of singly charged species = Faraday constant, $F \approx 96{,}500$ C/mol $\approx 10^5$ C/mol)
  - **differentiate**, with respect to time
  - **integrate**, over time
- 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**

$E^0(Cu^{2+/0})$ = +0.34 V vs. SHE ✓

$E^0(Cu^{0/2+})$ = –0.34 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 $\Delta G = -RT \ln K = -nFE_{cell}$ (electrical work per mole), and…

… partial molar Gibbs free energy is the electrochemical potential ($\tilde{\mu}$, 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, $\tilde{\mu} = \mu + zF\phi$

Cannot be measured independently!

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International Union of Pure and Applied Chemistry (IUPAC)

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  differentiate, with respect to time — **integrate**, over time
- 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^+)
- (Electrode) (electric) potential (V or E; in units of V = J/C) is written as a reduction
  - This relates to Gibbs free energy as $\Delta G = -RT \ln K = -nFE_{cell}$ (electrical work per mole), and…
  - … partial molar Gibbs free energy is the electrochemical potential ($\bar{\mu}$, 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, $\bar{\mu} = \mu + zF\phi$
  - 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

opposites

- 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

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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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