Lecture #3 of 17

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*

RECALL: Voltaic pile

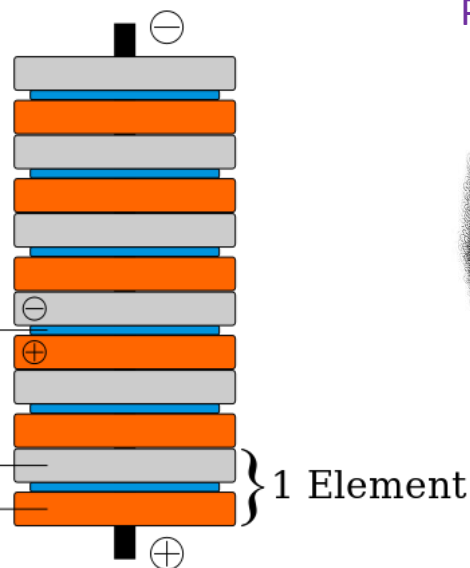Invented by Alessandro Volta (1800) but the elements of the pile (galvanic cells) were named after Galvani.

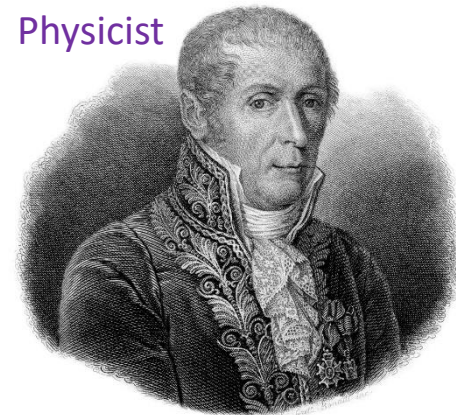**What are the combined half-reactions?**

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

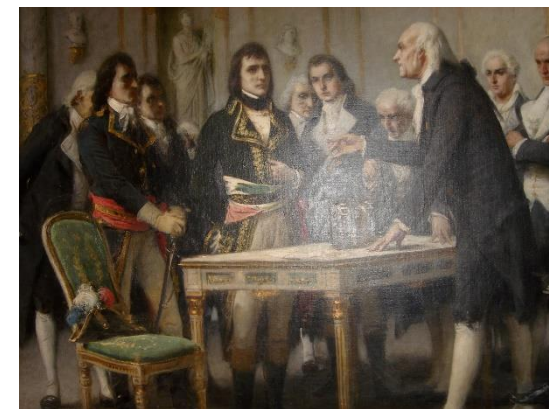Electrolyte — *(salt water)*

Zinc —
Copper — } 1 Element

Physicist

Alessandro Volta
(1745–1827)
from Wiki

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

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

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

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

RECALL: Galvanic Cells

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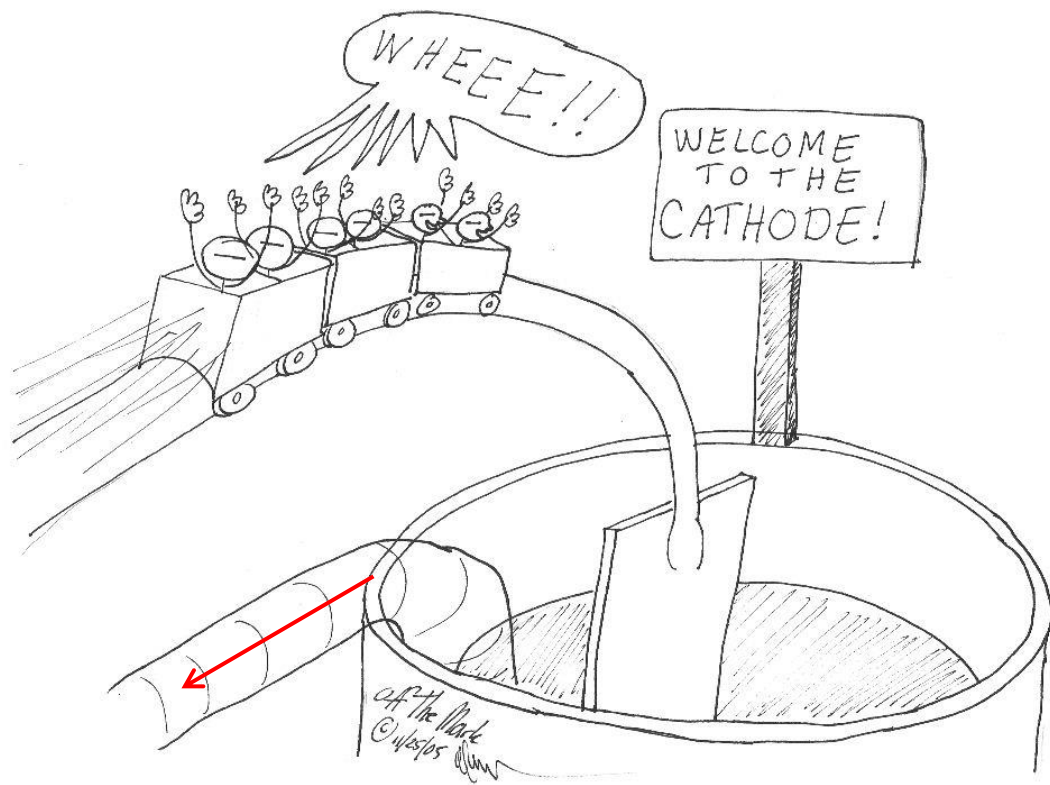
Salt bridge is an ionic conduit to prevent buildup of charge in both compartments and also to prevent bulk mixing of the two solutions

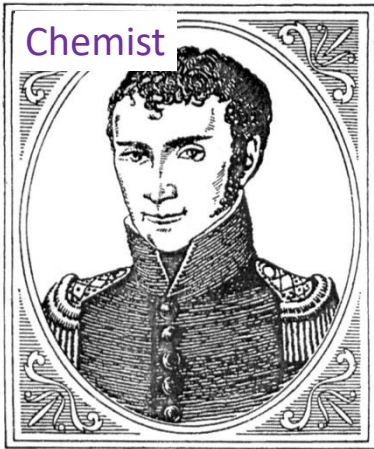# Electrolysis of water

Chemist
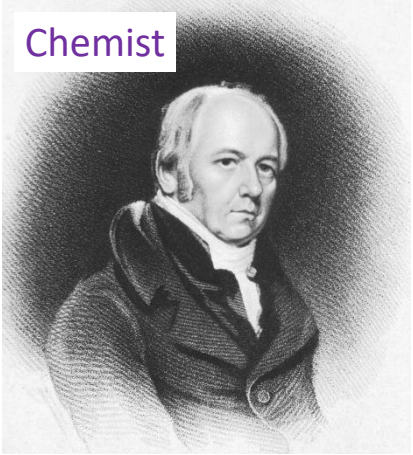
William Nicholson
(1753–1815)

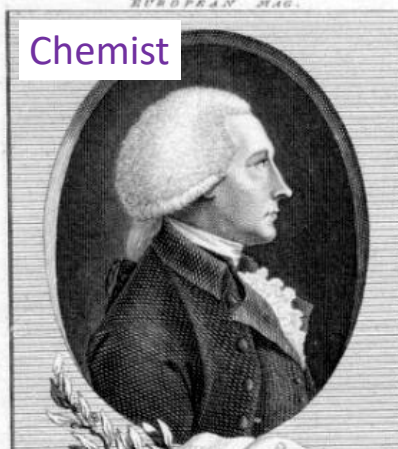Surgeon

Sir Anthony Carlisle
(1768–1840)

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

Chemist

Johann Wilhelm Ritter
(1776–1810)

Chemist

William Cruickshank
(17??–1810(1))
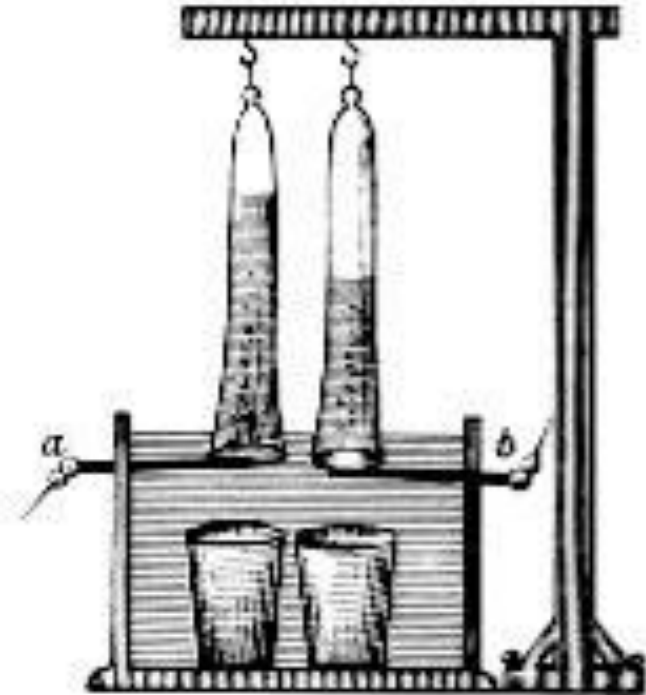
http://en.wikipedia.org/wiki/Johann_Wilhelm_Ritter

Daniell (galvanic) Cell (1836)

No more H_2 from the (primary) battery!

anode oxidation

cathode reduction

Voltmeter

e^-

e^-

Zinc anode

$\leftarrow Cl^-$ $K^+ \rightarrow$

Salt bridge

Copper cathode

SO_4^{2-}

Zn^{2+}

Cotton plugs

Cu^{2+}

SO_4^{2-}

ZnSO$_4$ solution

CuSO$_4$ solution

$2e^-$

Zn

Zn^{2+}

Cu^{2+}

$2e^-$

Half-reactions are physically separated!

Zn is oxidized to Zn^{2+} at anode.

Cu^{2+} is reduced to Cu at cathode.

Chemist, Meteorologist

Cu SO^{4}Cu
Vase poreux
Zn
Eau acidulée

John Frederic Daniell (1790–1845)
from Wiki

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

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

NET REACTION: $Zn\ (s) + Cu^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + Cu\ (s)$
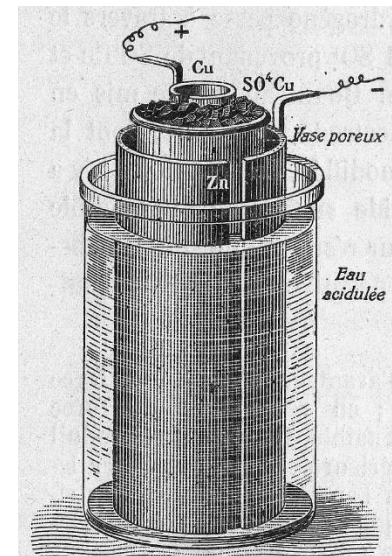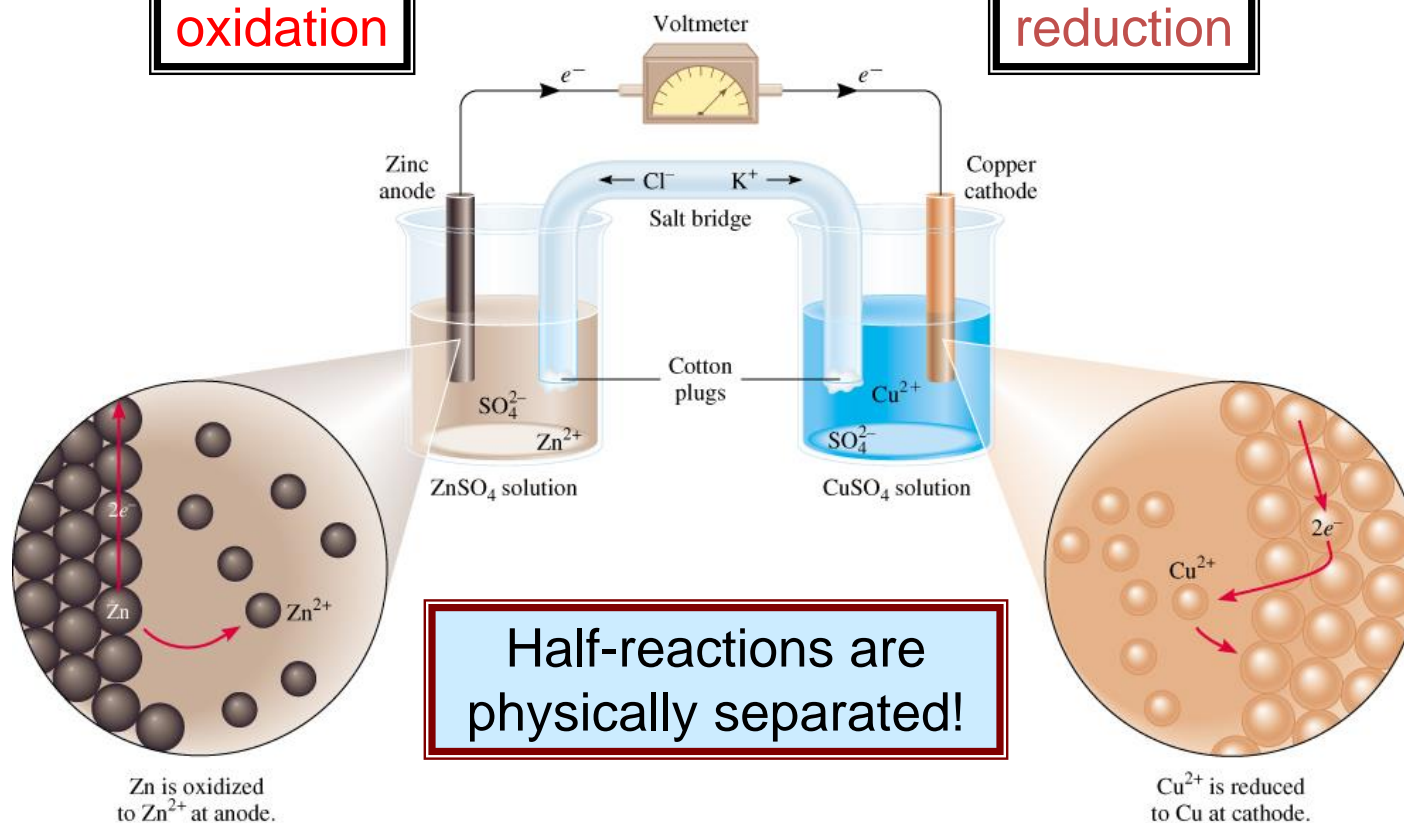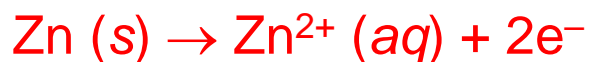
Voltage Produced by Galvanic Cells

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

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

Voltmeter **+ 1.10 V**

0.76 V

Copper (cathode)

Salt bridge

Zinc (anode)

$2 Na^+$ SO_4^{2-}

$2 e^-$ Cu^{2+} SO_4^{2-} Zn^{2+} $2 e^-$

Cu   Zn SO_4^{2-}

$Cu^{2+} + 2 e^- \longrightarrow Cu(s)$ **+0.34 V**

$Zn(s) \longrightarrow Zn^{2+} + 2 e^-$ **+ 0.76 V**
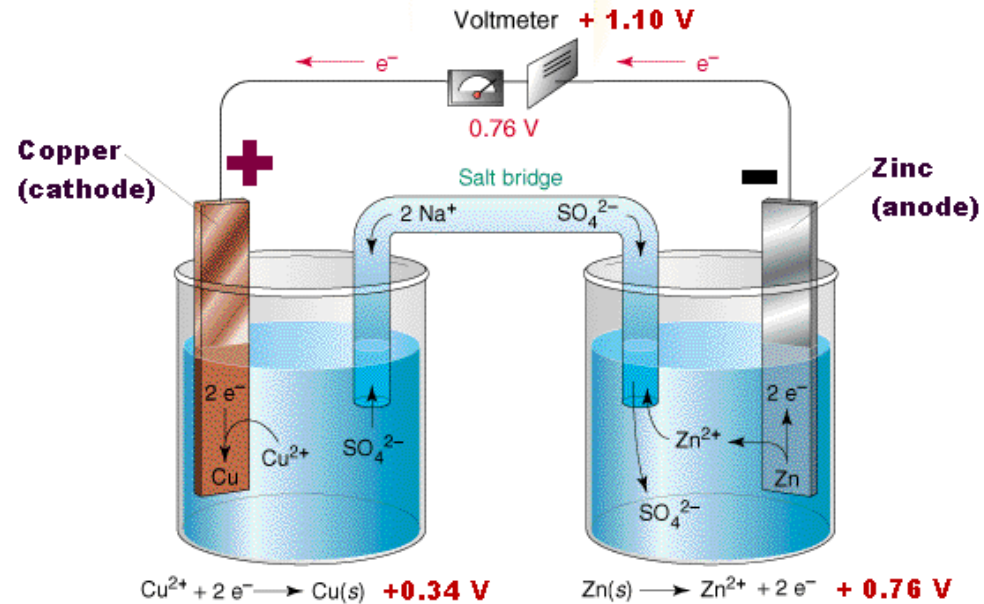
This should be −0.76 V!
(we will discuss this soon)

Cell Diagram

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

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

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

anode   salt bridge   cathode

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?

Which half-reaction is reducing?

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

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

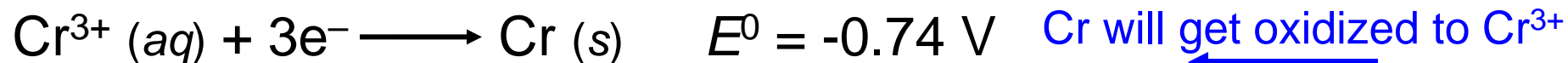More negative of the two   … thus, it is reducing

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

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

2Cr (*s*) + 3Cd^{2+} (1 M) ⟶ 3Cd (*s*) + 2Cr^{3+} (1 M)
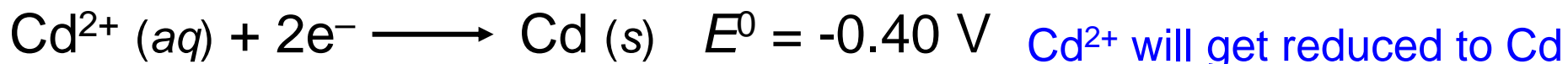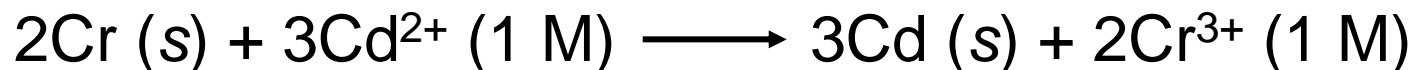
E_{cell} = $E_{cathode}$ – E_{anode}

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

Electrochemistry:
conventions… oh, conventions!

Cathode – electrode where catholyte species are reduced
Anode – electrode where anolyte species are oxidized

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.

DISCHARGING   CHARGING

Electrochemistry:

conventions… oh, conventions!
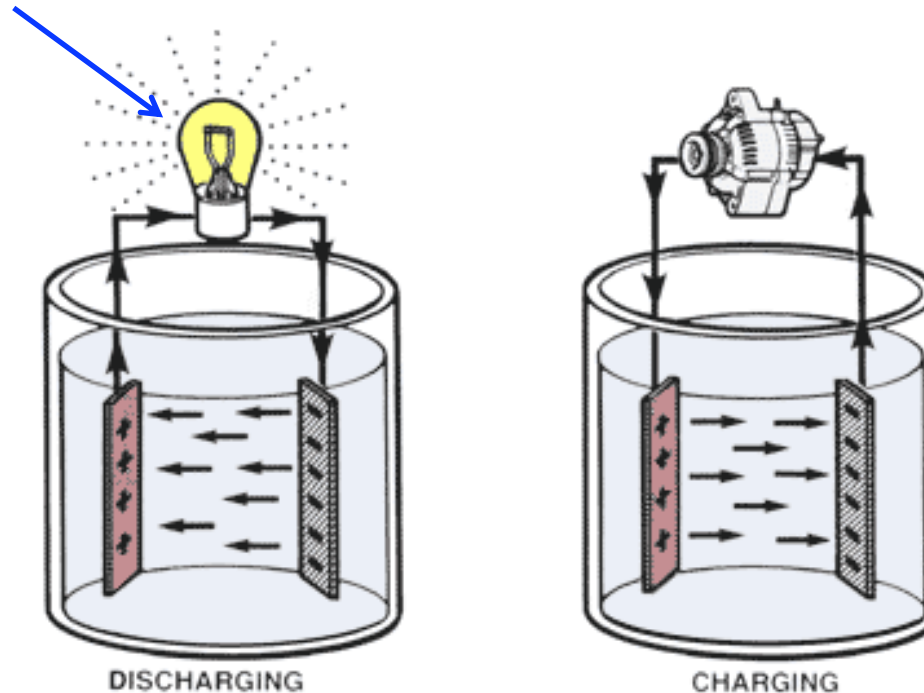
Cathode – electrode where catholyte species are reduced
Anode – electrode where anolyte species are oxidized

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

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

e⁻   e⁻

cathode   anode

This is a generator
(AKA power supply)

DISCHARGING   CHARGING

http://autoshop101.com/
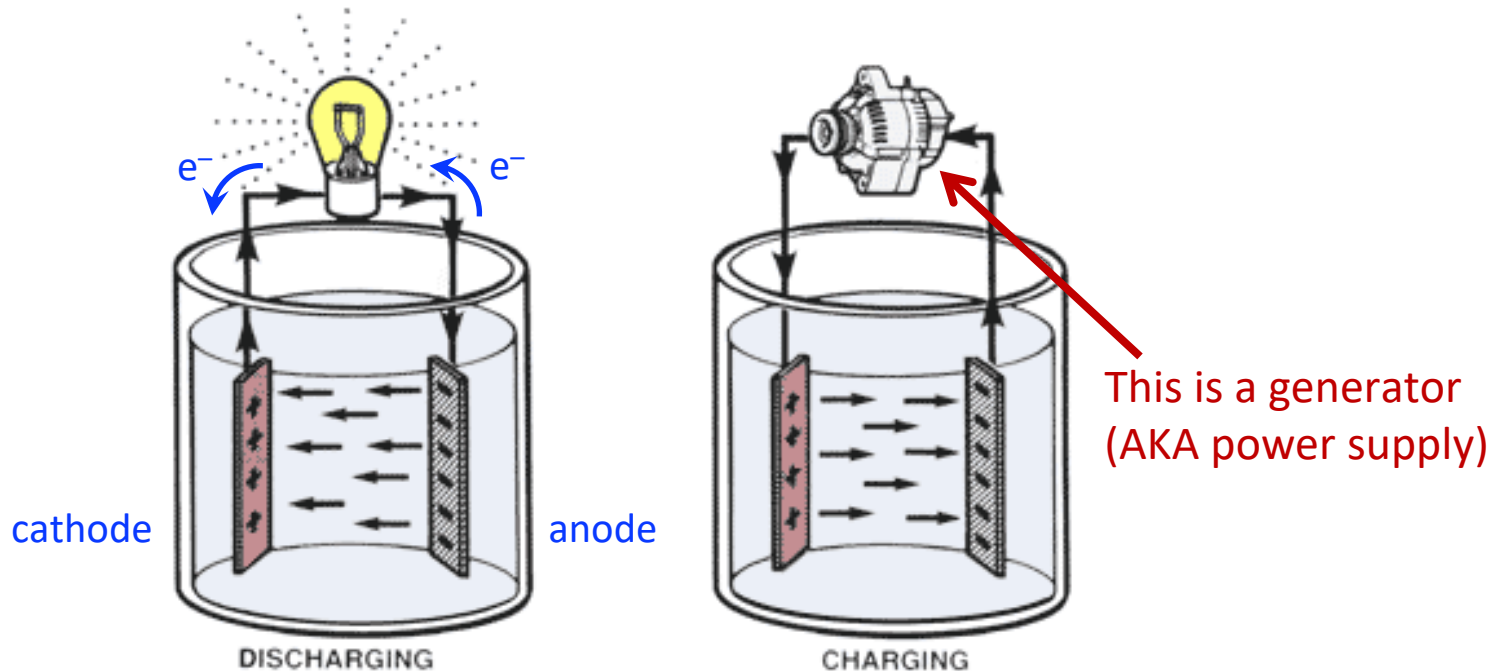
conventions… oh, conventions!

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/

The Daniell Cell (1836)

Chemist, Meteorologist

John Frederic Daniell
(1790–1845)
from Wiki

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

low impedance to measure current

e^- e^-

I_{cell}

Zn   Cu

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

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

Zn | Zn^{2+}(*aq*) || Cu^{2+}(*aq*) | Cu

The Daniell Cell (1836)

Chemist, Meteorologist
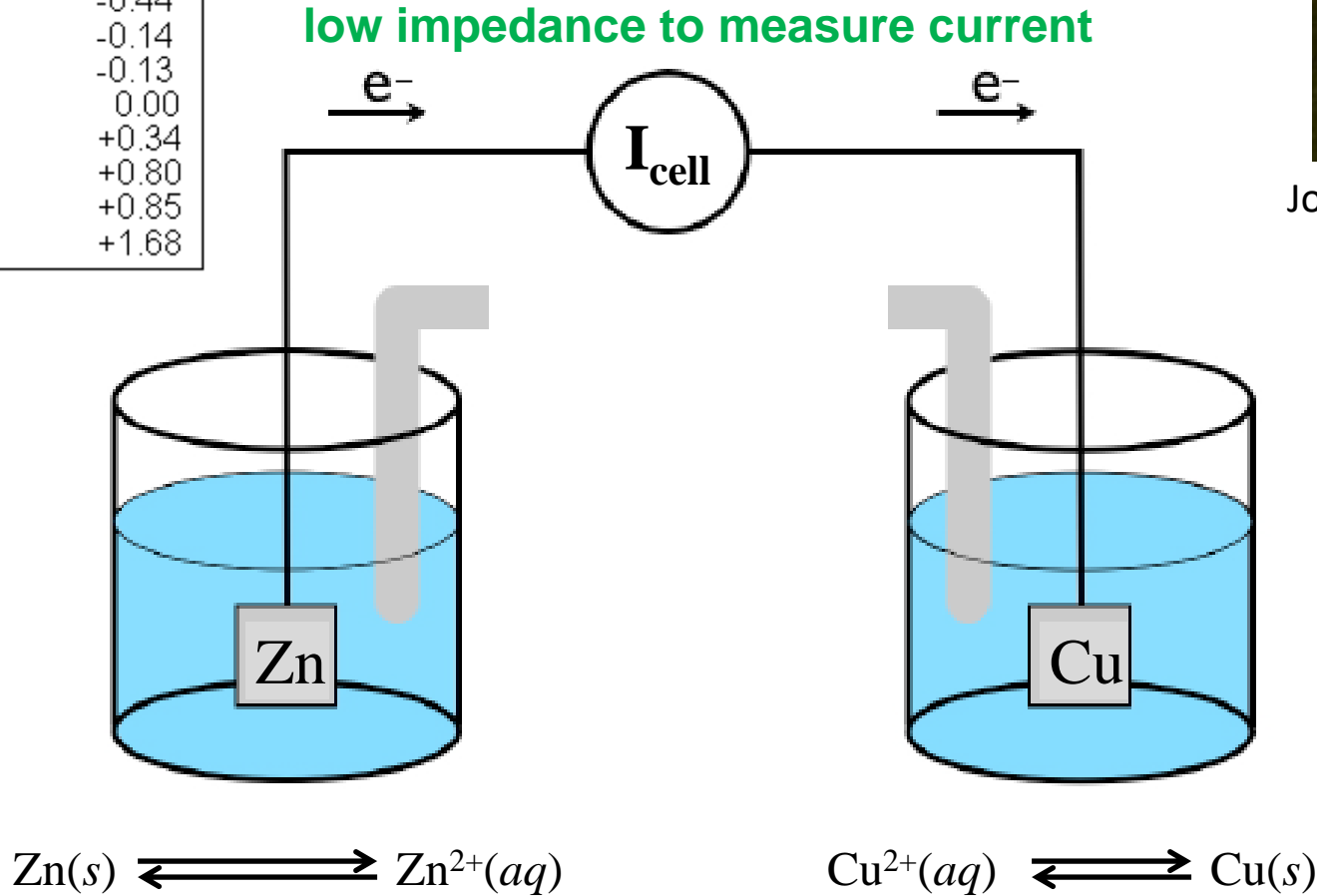
John Frederic Daniell
(1790–1845)
from Wiki

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

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

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

… capacitive charging

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

Zn | Zn²⁺(aq) || Cu²⁺(aq) | Cu
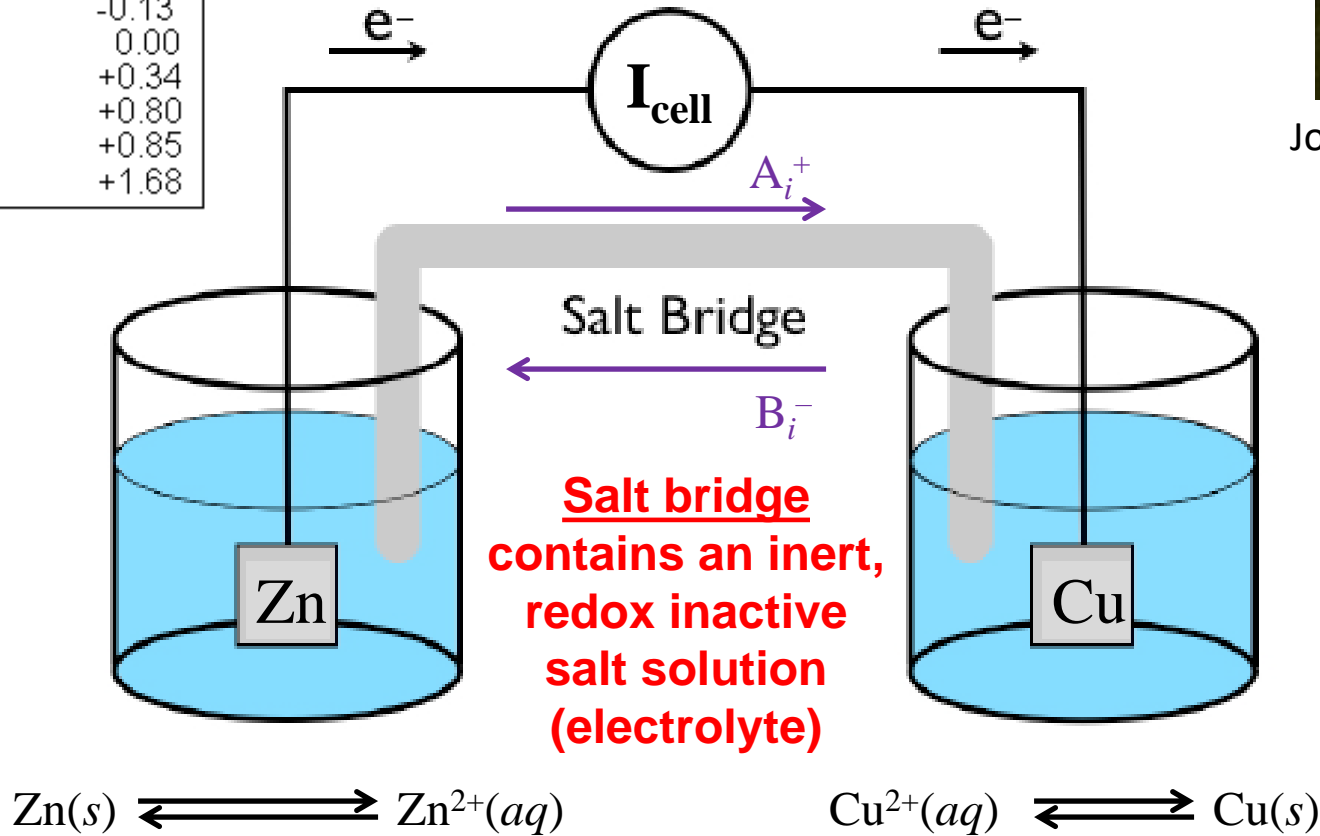
The Daniell Cell (1836)

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

Quick Quiz
* Name the cell type
* Identify the anode
* Identify the cathode
* Name the
   electrode signs

* <u>primary</u> galvanic cell
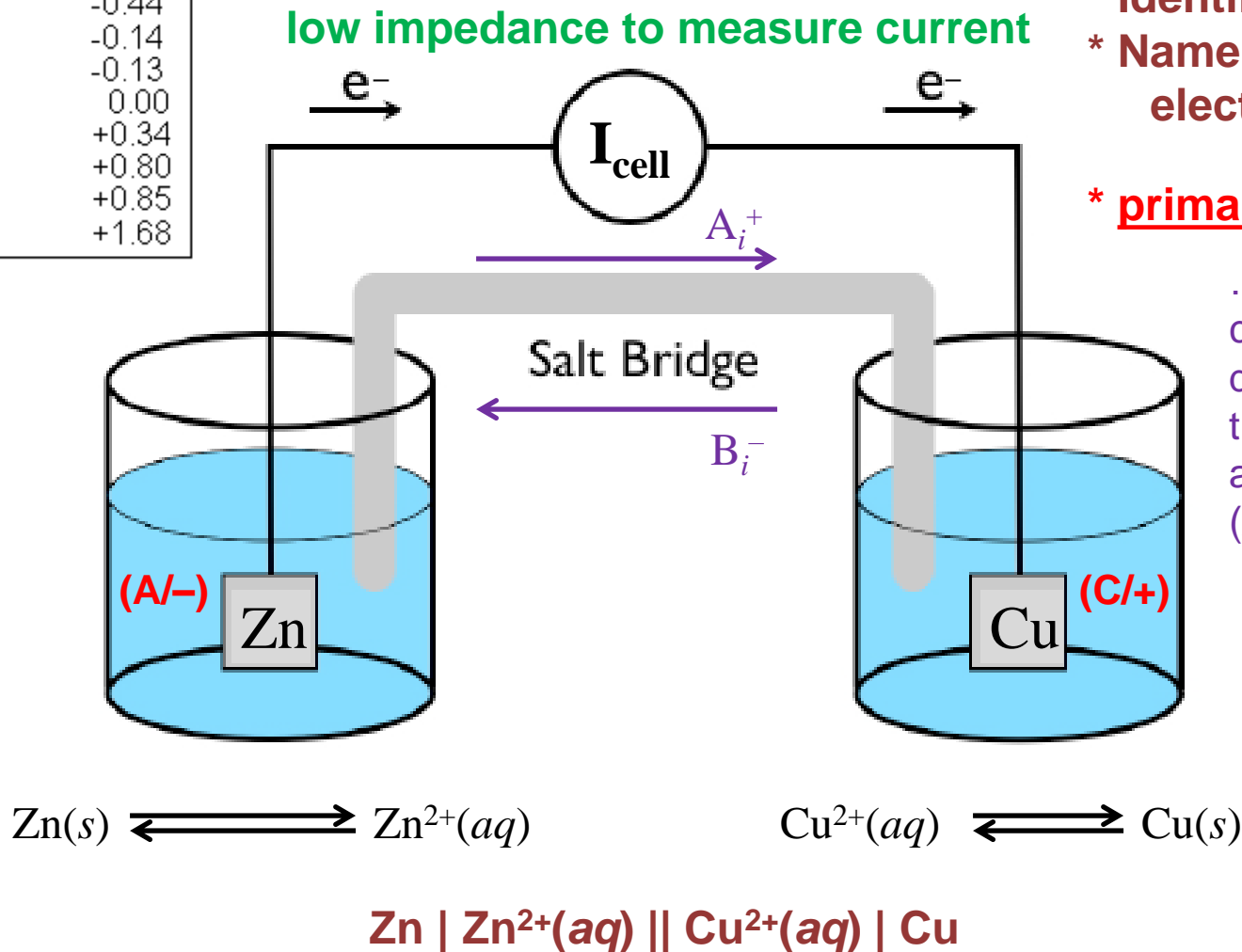
… Ultimately, this cell will fully discharge, and at that time it will be at equilibrium ($\Delta G = E_{cell} = 0$)…

… Then, any direction of polarization bias will result in electrolytic function (i.e. charging)!

low impedance to measure current

e^- e^-

I_{cell}

A_i^+

Salt Bridge

B_i^-

(A/–) Zn   Cu **(C/+)**

$Zn(s) \rightleftharpoons Zn^{2+}(aq)$ $Cu^{2+}(aq) \rightleftharpoons Cu(s)$
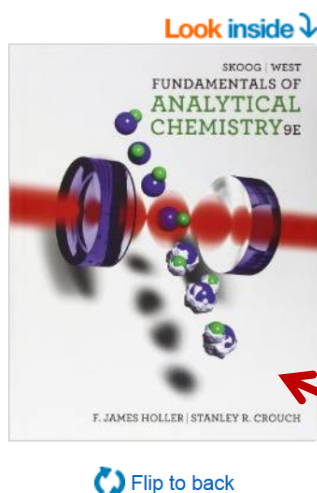
Zn | Zn²⁺(aq) || Cu²⁺(aq) | Cu

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^+)

Look inside ↓

SKOOG | WEST
FUNDAMENTALS OF
ANALYTICAL
CHEMISTRY 9E

F. JAMES HOLLER | STANLEY R. CROUCH

↻ Flip to back

Fundamentals of Analytical Chemistry Hardcover –
January 1, 2013
by Douglas A. Skoog (Author), Donald M. West (Author), F. James Holler (Author), & 1 more
★★★☆☆ ▼ 6 customer reviews
ISBN-13: 978-0495558286 | ISBN-10: 0495558281 | Edition: 9th

Buy New	**Rent**
Price: $303.95	Price: $82.65 - $82.67

19 New from $242.02 | 50 Used from $208.74

	Rent from	Amazon Price	New from	Used from
eTextbook 🖥+▢+▯	$98.43	$252.49	—	—
Hardcover	$82.65	$303.95	$242.02	$208.74

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

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^+)

- (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!

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^+)

- (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, $\bar{\mu} = \mu + zF\phi$

Cannot be measured independently!

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^+)

- (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

opposites

- 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

For "clarity," a brief (*more rigorous*) "review" of thermodynamics.**(BRIEFLY)** **Electrochemical __potential__** of species *i* in phase β <u>is an energy</u> (J/mol),

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

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 $\overline{\mu}_i^{\beta} = \mu_i^{\beta}$.

… more on this later…

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