Looking forward… our review of Chapter "0"

- Cool applications
- Redox half-reactions
- Balancing electrochemical equations
- History of electrochemistry and Batteries
- IUPAC terminology and $E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$
- Thermodynamics and the Nernst equation
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**RECALL:** Daniell (galvanic) Cell (1836)

No more H₂ from the (primary) battery!

Zn (s) → Zn²⁺ (aq) + 2e⁻

Cu²⁺ (aq) + 2e⁻ → Cu (s)

NET REACTION: Zn (s) + Cu²⁺ (aq) → Zn²⁺ (aq) + Cu (s)

John Frederic Daniell (1790–1845)

from Wiki
 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)

Cell Diagram

\[ \text{Zn (s)} + \text{Cu}^{2+} (\text{aq}) \rightarrow \text{Cu (s)} + \text{Zn}^{2+} (\text{aq}) \]

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

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

Anode salt bridge Cathode

This should be \(-0.76 \text{ V}\) (we will discuss this later)

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?

\[ \text{Cd}^{2+} (\text{aq}) + 2e^- \rightarrow \text{Cd (s)} \quad E^{\circ} = -0.40 \text{ V} \quad \text{Cd}^{2+} \text{ will get reduced to Cd} \]

\[ \text{Cr}^{3+} (\text{aq}) + 3e^- \rightarrow \text{Cr (s)} \quad E^{\circ} = -0.74 \text{ V} \quad \text{Cr will get oxidized to Cr}^{3+} \]

More negative of the two

Anode (oxidation): \[ \text{Cr (s)} \rightarrow \text{Cr}^{3+} (1 \text{ M}) + 3e^- \times 2 \]

Cathode (reduction): \[ \text{2Cd (s)} + 2\text{Cd}^{2+} (1 \text{ M}) \rightarrow \text{3Cd (s)} + 2\text{Cr}^{3+} (1 \text{ M}) \]

\[ E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \]

\[ E_{\text{cell}} = -0.40 \text{ V} - (-0.74 \text{ V}) \]

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

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

Electrochemistry:

conventions... oh, conventions!

Cathode – electrode where catholyte species are reduced
Anode – electrode where anolyte species are oxidized
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 discharging (galvanic) battery, label the anode and the cathode.

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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.

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Electrochemistry: 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/
John Frederic Daniell (1790–1845)

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

The Daniell Cell (1836)

low impedance to measure current

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

Now it works = "electrochemistry"!

Salt bridge contains an inert, redox inactive salt solution (electrolyte)

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

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

Ultimately, this cell will have fully discharged, and at which point it will be at equilibrium ($\Delta G = E_{\text{cell}} = 0$)
...Then, any direction of polarization bias will result in electrolytic function (i.e. charging)!
Quick Check on Your Understanding

You try!

(a) What is the standard $E_{\text{cell}}$ for a galvanic cell based on zinc and silver?

$b_{\text{cell}} = +0.80 \text{ V} - (-0.76 \text{ V}) = 1.56 \text{ V}$

(b) If one wanted to electrolytically charge the cell from part a (before any reactions took place), what potential would one have to provide?

$b_{\text{cell}} < -1.56 \text{ V}$ such that $b_{\text{cell}} + b_{\text{cell}} < 0$ (this is the observed value)

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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 = As) is the unit of change (96,485 C are in a mole of singly charged species, $F = 96,500 \text{ C/mole} \times 10 \text{ C/mol}$)

Electromotive force (EMF) 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-, $H^+$)

Integrate, over time

Differentiate, with respect to time

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

$E^\circ(\text{Cu}^{2+}/\text{Cu}) = +0.34 \text{ V vs. SHE}$

$E^\circ(\text{Cu}^{2+}/\text{Cu}) = +0.34 \text{ V vs. SHE}$

... is incorrect! You can subtract redox potentials but do not change the sign of the potential and then call it an oxidation potential!
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(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, F = 96,500 C/mol) 
- Electricity is the flow of current (I) in units of A = C/s and is a 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 \( \Delta G = -RT \ln \frac{N_{a}}{P_{a}} \) (electrical work per mole), and... partial molar Gibbs free energy is the electrochemical potential (\( \mu \), in units of J/mol)
  - Chemical potential (\( \mu \), in units of J/mol)
  - Reduced/electrochemical potential (\( \bar{\mu} \) in units of J/C)
  - and in summary, \( \Delta G = \bar{\mu} + RT \phi \)
  - Cannot be measured independently!

Galvanic cells produce power (P) in units of W = A x V = C/s x J/C = J/s) by spontaneous redox reactions

Galvanic 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 electrolyte/negolyte and positive electrolyte/posolyte are better

For "clarity," a brief (more rigorous) "review" of thermodynamics...

For an uncharged species \( \mu_i^\beta = \mu_i \).

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

\[
\bar{\mu}_i^\beta = \left( \frac{\partial G}{\partial n_i^\beta} \right)_{T,P,n_{\text{all}}} = \mu_i + z_i F \phi^\beta ,
\]

where

- \( G \) (Gibbs free energy (J))
- \( n_i \) (amount of species \( i \) (mol))
- \( \mu_i = \mu_i^\beta + RT \ln a_i \) (chemical potential (J/mol))
- \( z_i \) (valency of species \( i \))
- \( F = 10^5 \) (Faraday constant (C/mol))
- \( \phi^\beta \) (Galvani/inner electric potential (V))
- \( a_i \) (activity of species \( i \))

For an uncharged species \( \mu_i^\beta = \mu_i \).

... more on this later... Parsons, Pure & Appl. Chem., 1973, 57, 901
IUPAC Gold (http://goldbook.iupac.org)
Half reactions, at non-unity activity, obey the Nernst equation...

Take $\Delta G = \Delta G^0 + RT \ln Q$ and use the relation $\Delta G = -nFE$.

But first... what is $Q$, again? ... the reaction quotient!

$$Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Half reactions, at non-unity activity, obey the Nernst equation...

Take $\Delta G = \Delta G^0 + RT \ln Q$ and use the relation $\Delta G = -nFE$.

But first... what is $Q$, again? ... the reaction quotient!

$$Q = \frac{\prod_p a_p^{v_p}}{\prod_r a_r^{v_r}} = \frac{\prod_i (\gamma_i c_i)^{v_i}}{\prod_j (\gamma_j c_j)^{v_j}}$$

$Q = \frac{\prod_p a_p^{v_p}}{\prod_r a_r^{v_r}}$, for dilute solutions... which we never have!

- $a_p$ is the activity of product $p$
- $a_r$ is the activity of reactant $r$
- $v_i$ is the stoichiometric number of $i$
- $\gamma_i$ is the activity coefficient of $i$
- $c_i$ is the concentration of $i$
- $c_i^0$ is the standard state concentration of $i$

Half reactions, at non-unity activity, obey the Nernst equation...

Take $\Delta G = \Delta G^0 + RT \ln Q$ and use the relation $\Delta G = -nFE$.

And at 298.15 K, $E = E^0 - 0.05916 \frac{RT}{n} \ln Q$

Memorize ~60 mV per order in log, but do not forget $n$ and that this is at 25 °C!
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Half reactions must be referenced to something…

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

Since the method of half-reactions ultimately results in us taking their difference, we can add an arbitrary constant to all half reactions... By one (somewhat arbitrary) convention, it is often assumed that $E^0$ for the standard hydrogen electrode (SHE) is equal to zero.

**Half-Reaction for Hydrogen gas (H$_2$):**

$$H^+ + e^- \rightarrow \frac{1}{2} H_2 (g)$$

$$E_{H_2} = E_{H_2}^0 + \frac{RT}{F} \ln \frac{\sqrt{P_{H_2}}}{[H^+]}$$

$$E_{H_2}^0 = 0$$

Thus, the potentials for half-cell reactions are actually full-cell potential (difference(s)) versus SHE, or other!