Electroanalytical Chemistry: Fundamentals

Investigations based on electron-transfer reactions (redox)
Oxidation:
Reduction:

We describe the tendency for a reaction to occur as "Potential"
- Thermodynamics
- Related to Free Energy (ΔG or ΔG^o) (easier to measure!!)

Classes of electroanalytical techniques:
- Controlled Current:
- Controlled Potential:

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Let's Look at a Reaction

What happened?

From a thermodynamics standpoint, what can we say?

What does this say about the oxidizing ability of Cu^{2+} compared to Zn^o?

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Cu/Zn Reaction

Let's write the oxidation and reduction reactions:

Oxidation:

Reduction:

What if we split the ½ reactions?

What happens when we close the switch?

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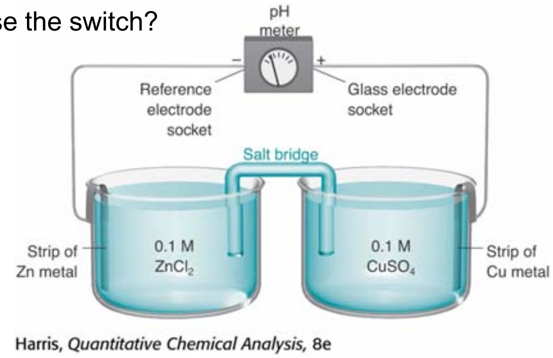
Cu/Zn Reaction

What happens when we close the switch?



Harris, *Quantitative Chemical Analysis*, 8e
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Galvanic vs. Electrolytic Cells

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Quantifying Potential Difference: Standard Reduction Potential

- Tabulated for unit activity
- Convention is to write things as a reduction
- Oxidizing/Reducing Agents
- Remember: $\Delta G^o = -nFE^o$

How do we determine free energy changes for a reaction?

Reaction	E^o (V)
$F_2(g) + 2e^- = 2 F^-$	+2.890
$O_3(g) + 2H^+ + 2e^- = O_2(g) + H_2O$	+2.075
$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$	+1.507
$Ag^+ + e^- = Ag(s)$	+0.799
$Cu^{2+} + 2e^- = Cu(s)$	+0.339
$AgCl + e^- = Ag(s) + Cl^-$	+0.222
$2H^+ + 2e^- = H_2(g)$	0.000
$Cd^{2+} + 2e^- = Cd(s)$	-0.402
$Zn^{2+} + 2e^- = Zn(s)$	-0.762
$K^+ + e^- = K(s)$	-2.936
$Li^+ + e^- = Li(s)$	-3.040

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Quantifying Potential Difference

Rxn 1 (Cathode)	$Cu^{2+} + 2e^- = Cu(s)$	$E^o = +0.339$
Rxn 2 (Anode)	$Zn^{2+} + 2e^- = Zn(s)$	$E^o = -0.762$ V
Net Rxn		E^o = ??

General Expression: E^o_{cell} =

Cell shorthand notation:

| =

‖ =

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Quantifying Potential Difference

Unfortunately, ΔG^o and E^o are for standard conditions, kinda rare! How do we deal with nonstandard conditions?

$$\Delta G = \Delta G^o + RT\ln Q$$

But, $\Delta G^o = -nFE^o$

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Nernst Equation

$$E = E^0 - \frac{0.05916V}{n}\log Q$$

This relationship (Nernst Eqn.) applies to cell reactions and to half reactions!

So, what if $[Zn^{2+}]$ = 0.100 M and $[Cu^{2+}]$ = 0.050 M?

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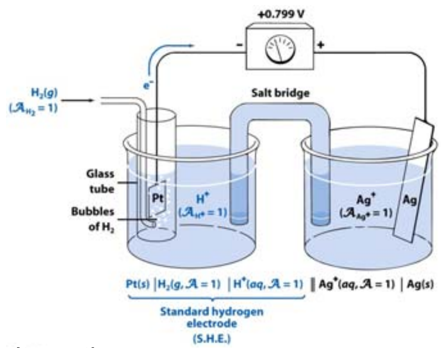
Measuring Potentials

All potentials are determined or tabulated relative to some reference state. For standard reduction potentials, reference state is the "Standard Hydrogen Electrode"

- E^o defined as 0.000 V
- $H^+ (aq) + e^- = ½ H_2(g)$
- S.H.E. is the anode
- Pt│ H_2, H^+ ‖ *cathode*
- Sometimes called "Normal Hydrogen Electrode" (NHE)



S.H.E. isn't very practical, so we use alternatives:

- *Silver/Silver Chloride*:
  Ag│ AgCl│ Cl^- ‖*cathode* E^o = +0.197V (sat'd KCl)
- *Saturated Calomel (SCE):*
  Pt│ Hg│Hg_2Cl_2│ Cl^- ‖*cathode* E^o = +0.241V (sat'd KCl)

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