

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°) (easier to measure!!)

Classes of electroanalytical techniques:

- Controlled Current:

- Controlled Potential:

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° ?

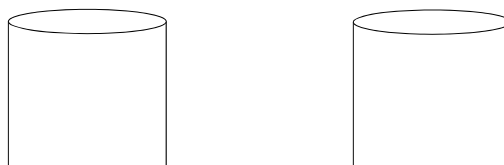
Cu/Zn Reaction

Let's write the oxidation and reduction reactions:

Oxidation:

Reduction:

What if we split the $\frac{1}{2}$ reactions?

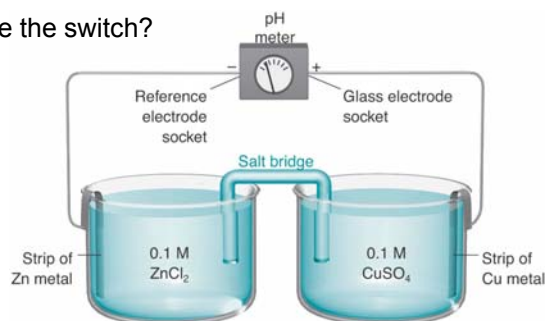


What happens when we close the switch?

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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: $\Delta G^\circ = -nFE^\circ$

How do we determine free energy changes for a reaction?

Reaction	E° (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)	$Cu^{2+} + 2e^- = Cu(s)$	$E^\circ = +0.339$
Rxn 2 (Anode)	$Zn^{2+} + 2e^- = Zn(s)$	$E^\circ = -0.762 V$
Net Rxn		$E^\circ = ??$

General Expression: $E^\circ_{cell} =$

Cell shorthand notation:



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Quantifying Potential Difference

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

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

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

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Nernst Equation

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

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

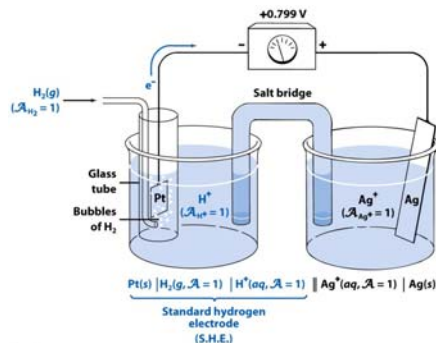
So, what if $[Zn^{2+}] = 0.100 \text{ M}$ and $[Cu^{2+}] = 0.050 \text{ M}$?

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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° defined as 0.000 V
- $\text{H}^+(\text{aq}) + \text{e}^- = \frac{1}{2} \text{H}_2(\text{g})$
- S.H.E. is the anode
- $\text{Pt} | \text{H}_2, \text{H}^+ || \text{cathode}$
- Sometimes called "Normal Hydrogen Electrode" (NHE)



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

- Silver/Silver Chloride:
 $\text{Ag} | \text{AgCl} | \text{Cl}^- || \text{cathode} \quad E^\circ = +0.197\text{V (sat'd KCl)}$
- Saturated Calomel (SCE):
 $\text{Pt} | \text{Hg} | \text{Hg}_2\text{Cl}_2 | \text{Cl}^- || \text{cathode} \quad E^\circ = +0.241\text{V (sat'd KCl)}$