

February 4, 2005

- **Reminder:** Exam #1, Feb. 16th at 7pm!
 - Info page will be posted early next week
 - Email me next week if you have a conflict with the time
- **Error! Error! Error!**
 - Did you find the error in the EChem assigned reading?
(one of your classmates did - thanks!)

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Electroanalytical Chemistry

Chem 221
Instrumental Analysis
Spring 2005

Overview/Background

- Based on electrochemical basics that were covered in *Intro Chem*
- How can we *apply* those principles to **chemical analysis**?
- Recall the general area: *Redox Chemistry*
 - electron transfer reactions
- Measure either:
 - *Potential* for a reaction to occur
 - *Extent or Progress* of a reaction that has been induced

How are these related to **analyte concentration**?

Electrochemical Cells

■ Galvanic Cells

- no external source
- measure *potential* for analyte to react
- no current flows** (reaction is not allowed to occur)
- Voltage** is measured (*Potentiometry*)

How is *cell potential* related to **analyte concentration**?

The Nernst Equation

For this reversible process: $Ox + ne^- \rightarrow Red$

$$E = E^{\circ} - \frac{2.303RT}{nF} \text{Log} (a_{red}/a_{ox})$$

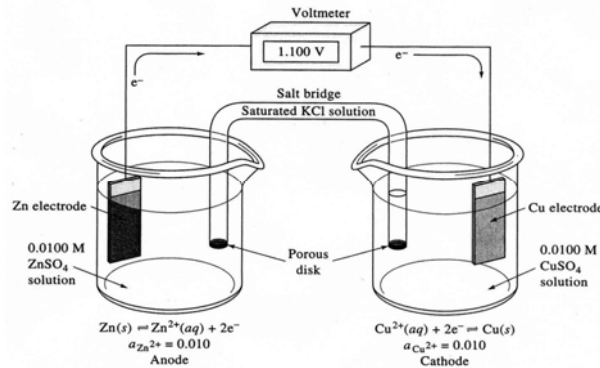
Cell Potential and Concentration

Recall:

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

If:

- Anode is a reference cell (constant potential)
- Temp is 298 K
- Assume activities and concentrations are same



Then: $E_{\text{cell}} = E^{\circ}_{\text{cathode}} + (0.0592/n)\text{Log}[\text{Ox}] - E_{\text{ref}}$

So, $E_{\text{cell}} \propto \text{Log}[\text{Ox}]$ - Potentiometry (ISE)

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Electrolytic Cells

- Use an *external potential source* to **drive** reaction
- Magnitude of *applied potential* = e^- energy
- **Recall:** As E° gets more negative, need *more energetic electrons* in order to cause **reduction**
 - So, if E_{applied} is *more negative* than E° , **reduction will occur**
 - And, if E_{applied} is *more positive* than E° , **oxidation will occur**

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Current Happens

- Current Flows in electrolytic cells
 - Reaction occurs
 - Current flows
 - Measure current (indicative of reaction rate)
- Where does the reaction take place?
 - On electrode *surface*
 - NOT in bulk solution

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Analytical Implications?

■ Coulometry

- ✓ Set E_{applied} so that desired reaction occurs
- ✓ Stir solution
- ✓ *Measure Current*

■ Voltammetry

- ✓ *DON'T stir solution*
- ✓ Vary ("scan") E_{applied}
- ✓ *Measure Current*
 - Indicates reaction rate
 - Reaction at electrode surface produces concentration gradient with bulk solution
 - Diffusion brings fresh, unreacted species to electrode surface

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Voltammetry . . . in Detail

■ How does the system respond temporally?

Current (reaction rate) depends on mechanisms of *mass transport*:

➤ Electrostatic Migration

-coulombic attraction/repulsion of charged species

➤ Mechanical/Convective Forces

-*macro* mass movement

➤ Diffusion

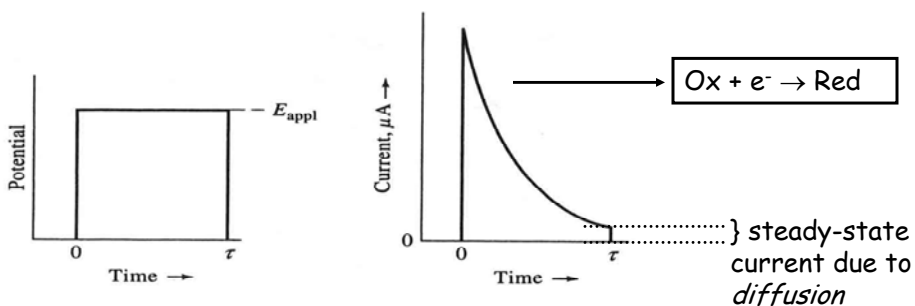
-due to *concentration gradient*

If: solution buffered with *electrolyte* (~0.1 - 1 M KNO₃, KCl, HNO₃, etc.) and *not stirred*

THEN: mass transport will be controlled by *diffusion*

Time-Dependent Diffusion Controlled Current

■ What happens if $E_{\text{appl}} \ll E^0$?



Cottrell Equation

- From Fick's Diffusion Law and Faraday's Law:

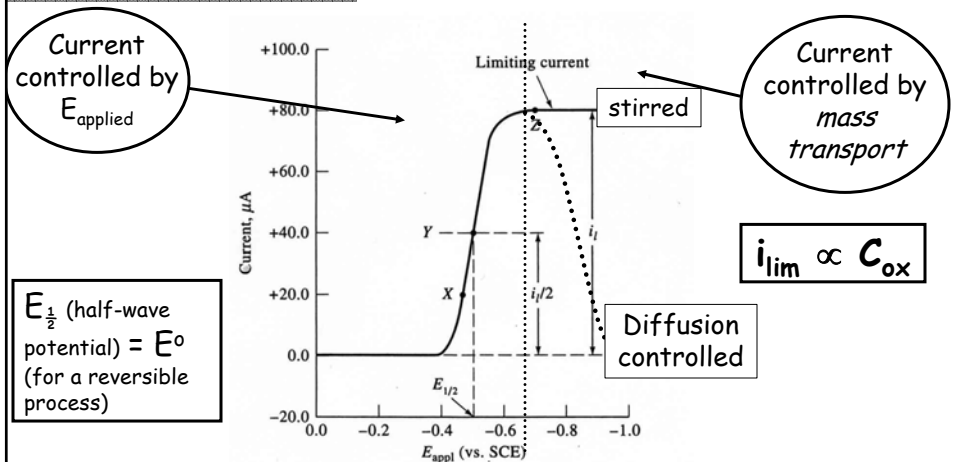
$$i = nFAD_{\text{ox}}(dC_{\text{ox}}/dX)$$

Concentration gradient will vary with time, giving us:

$$i = \frac{nFA(D_{\text{ox}})^{\frac{1}{2}}C_{\text{ox}}}{(\pi t)^{\frac{1}{2}}}$$

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How does current vary with changing E_{applied} ?



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Problems

■ Temporal dependence of current (Cottrell Equation)

- current *decreases* with time at fixed E_{applied}

■ Build-up of reduced species on electrode

- Reduces electrode surface area
- Results in a decrease in current as reaction rate decreases

Solution: *Voltammetry with a dropping Hg electrode (DME)*

- Polarography (*Heyrovsky, 1920's; 1959 Nobel Prize*)