

## January 30, 2012

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➤ EChem: Readings and Problem Set posted

➤ Coming Soon: Exam #1 Info Page™

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# Electroanalytical Chemistry

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Chem 221  
**Instrumental Analysis**  
Spring 2012

## 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:  $\text{Ox} + n\text{e}^- \rightarrow \text{Red}$

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

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# Cell Potential and Concentration

## Recall:

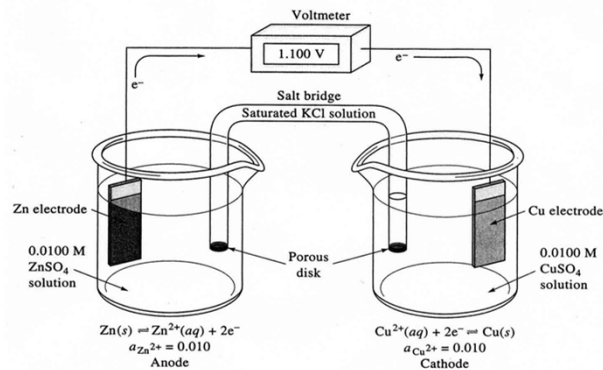
$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

## If:

• Anode is a reference cell (constant potential)

• Temp is 298 K

• Assume activities and concentrations are same



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

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

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# Electrolytic Cells

■ Use an *external potential source* to **drive** reaction

■ Magnitude of *applied potential* =  $e^-$  energy

■ **Recall:** As  $E^{\circ}$  gets more negative, need *more energetic electrons* in order to cause **reduction**

➤ So, if  $E_{\text{applied}}$  is *more negative* than  $E^{\circ}$ , **reduction will occur**

➤ And, if  $E_{\text{applied}}$  is *more positive* than  $E^{\circ}$ , **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  $E_{\text{applied}}$  so that desired reaction occurs
  - ✓ Stir solution
  - ✓ *Measure Current*
- Voltammetry
  - ✓ *DON'T stir solution\**
  - ✓ Vary ("scan")  $E_{\text{applied}}$
  - ✓ *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

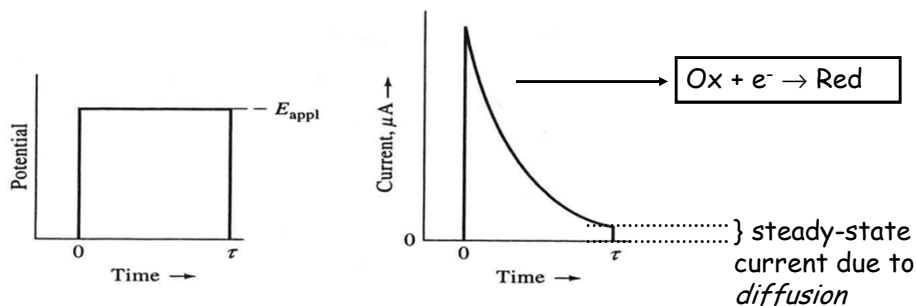
-due to *concentration gradient*

If: solution buffered with *electrolyte* ( $\sim 0.1 - 1 \text{ M KNO}_3$ , KCl,  $\text{HNO}_3$ , 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:

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