

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!)

1

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: $Ox + ne^- \rightarrow Red$

$$E = E^{\circ} - \frac{2.303RT}{nF} \log \left(\frac{a_{red}}{a_{ox}} \right)$$

4

Cell Potential and Concentration

Recall:

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

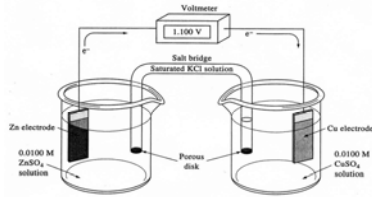
If:

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

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

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

5



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**

6

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

7

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

8

Voltammetry . . . in Detail

- How does the system respond temporally?

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

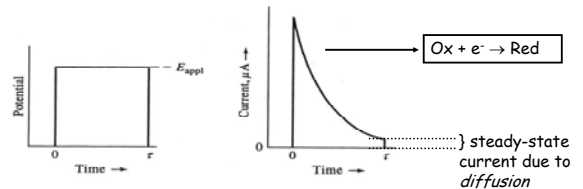
 - Electrostatic Migration
 - coulombic attraction/repulsion of charged species
 - Mechanical/Convective Forces
 - *macro* mass movement
 - Diffusion
 - due to *concentration gradient*

If: solution buffered with *electrolyte* (~0.1 - 1 M KNO_3 , KCl , HNO_3 , etc.) and *not stirred*

THEN: mass transport will be controlled by *diffusion*

Time-Dependent Diffusion Controlled Current

- What happens if $E_{\text{appl}} \ll E^\circ$?



10

Cottrell Equation

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

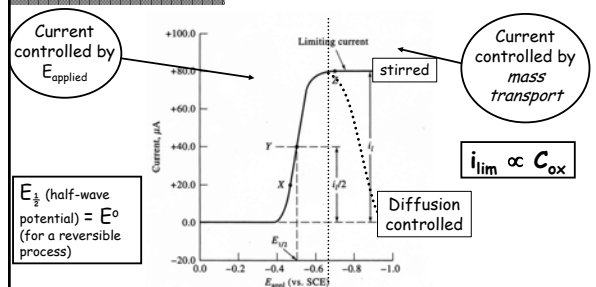
$$i = nFA D_{\text{Ox}} \left(\frac{dC_{\text{Ox}}}{dx} \right)$$

Concentration gradient will vary with time, giving us:

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

11

How does current vary with changing E_{applied} ?



12

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*)