

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: $Ox + ne^- \rightarrow Red$

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

3

Cell Potential and Concentration

Recall:

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

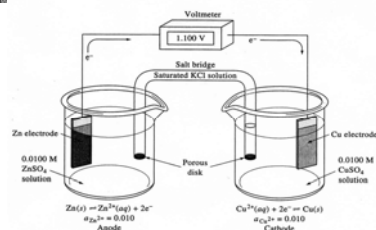
If:

• **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)



4

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**

5

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

6

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

7

Voltammetry . . . in Detail

■ How does the system respond *temporally*?

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

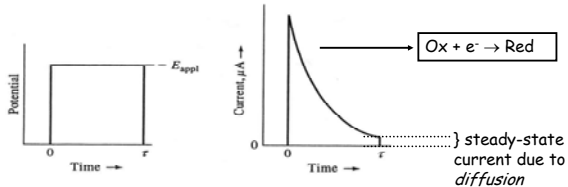
- **Electrostatic Migration**
- coulombic attraction/repulsion of charged species
- **Mechanical/Convective Forces**
- *macro* mass movement
- **Diffusion**
- due to *concentration gradient*

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 $E_{\text{appl}} \ll E^0$?



9

Cottrell Equation

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

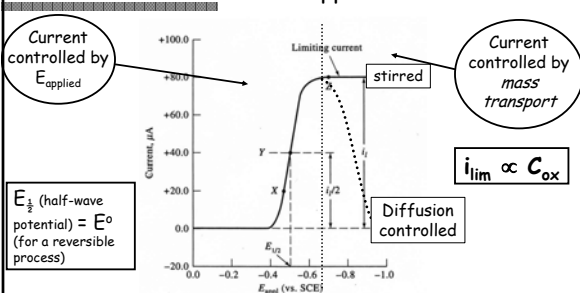
$$i = nFAD_{\text{ox}}(dC_{\text{ox}}/dx)$$

Concentration gradient will vary with time, giving us:

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

10

How does current vary with changing E_{applied} ?



11

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)

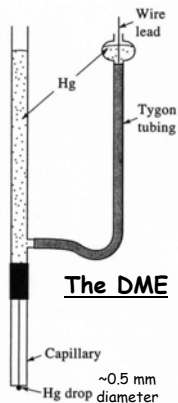
- Polarography (Heyrovsky, 1920's; 1959 Nobel Prize)

12

Polarography

DME provides:

- Fresh electrode surface with each drop
- Increasing surface area as drop expands



The DME

The Ilkovic Equation

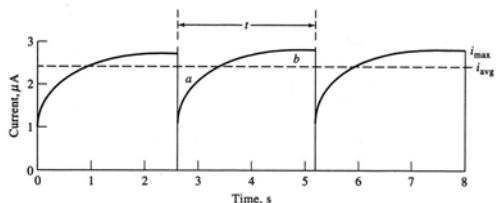
- If we take the Cottrell Equation and assume:
 - Spherical Hg drop
 - Diffusion-controlled mass transport

$$(i_d)_{\max} = 706 n D_{\text{ox}}^{1/2} m^{2/3} t^{1/6} C_{\text{ox}}$$

Diffusion current, μA Misc constants (607 for $(i_d)_{\text{avg}}$) # e⁻/mol Hg mass flow, mg/sec Diffusion Coefficient, cm^2/sec Drop time, sec Bulk solution concentration, mmol/L

Current during Drop Lifetime

At a constant E_{applied} :



Increasing drop surface area compensates for decreasing diffusion-controlled current (Cottrell Equation).

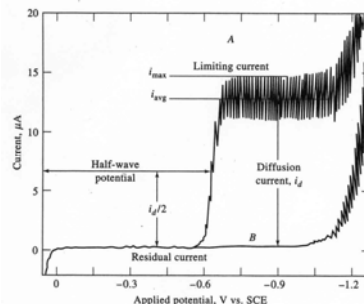
Polarogram

For Cd^{2+} :

For a reversible system:

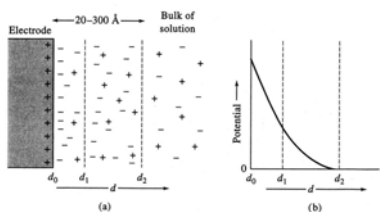
$$E_{\text{appl}} = E^{\circ} - (0.0592/n) \log(i/(i_d - i))$$

So, at $i = \frac{1}{2} i_d$:
 $E_{\text{appl}} (= E_{1/2}) = E^{\circ}$



Background Current

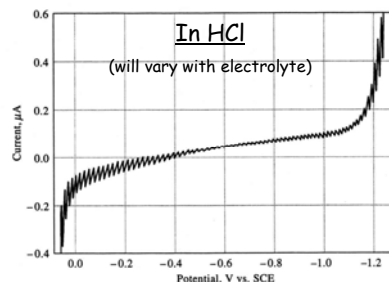
Let's look more closely at the electrode/solution interface:



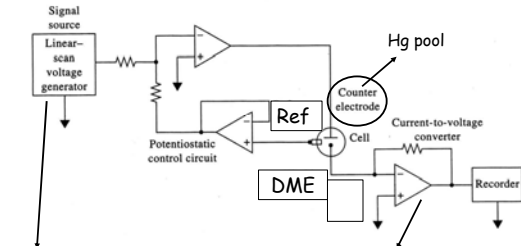
Charge separation → capacitance → charging current (i_{cc})

Charging Current

Our ability to distinguish i_f from i_{cc} will determine detectability



Instrumentation for Polarography



Generates a linear voltage ramp between the DME and Reference electrodes

Measures current flow between DME and Counter electrodes

19

E_{applied} Ramp Function

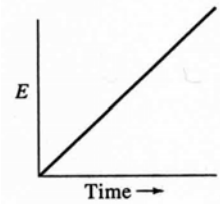
• E_{applied} usually limited to:

-2 volts
(solvent/electrolyte reduction)

0 volts
(oxidation of Hg)

• Slope of ramp:

2 - 5 mV/sec



dc Polarography

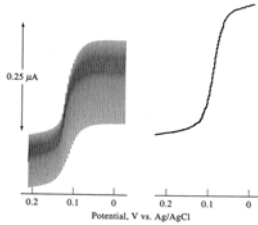
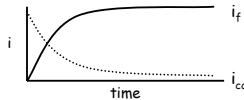
20

Current Measurement

■ Since current is relatively *constant* late in the drop lifetime, measure current only near the end of the drop lifetime:

• Sampled-dc Polarography:

- Use drop knocker with DME
- Current measured only during final 5 - 10 ms of drop
- Simpler polarogram with slight improvement in DL



21

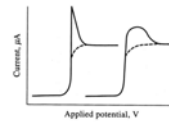
Applications

First, some practical considerations:

■ Purge system of O_2

- > O_2 reducible at ~ 0 volts
- > Bubble N_2 before analysis to remove O_2
- > Keep gentle flow of N_2 over electrode during analysis

■ Add surfactant to solution



e.g., Triton x-100, gelatin
-eliminates current maxima that occur due to surface adsorption effects

22

Qualitative Analysis

■ Analyte must be reducible in solution

■ Recall: $E_{\frac{1}{2}} = E^{\circ}$

- IF: -system is *electrochemically reversible*
-no competing reactions
(e.g., complex formation)

How do we know if a system is reversible?

Electron transfer is *fast* relative to the E_{applied} scan rate

23

Confirming Reversibility

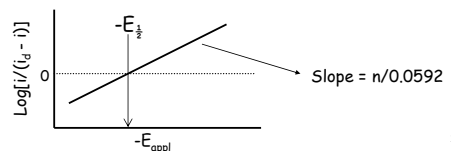
Recall:

$$E_{\text{appl}} = E^{\circ} - (0.0592/n) \log[i/(i_d - i)]$$

Rearranging:

$$\log[i/(i_d - i)] = (n/0.0592)(E^{\circ} - E_{\text{appl}})$$

So, a plot of $\log[i/(i_d - i)]$ versus $-E_{\text{appl}}$ should be linear:



24

Quantitative Analysis

- From Ilkovic equation:

$$i_d = kC$$

usually use method of Standard Additions
(with μL additions, no volume correction needed)

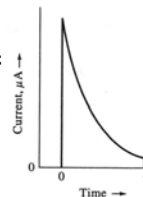
- Detection Limits:** $\sim 10^{-5} - 10^{-6} \text{ M}$ (low ppm)
- Resolution:** $\Delta E_{\frac{1}{2}} \approx 0.2 \text{ V}$ (not very good)

How can DL and resolution be improved?

25

Pulse Polarography

Recall *initial* shape of current after application of E_{appl} more negative than E^0 :



Faradaic Current (i_f) Enhancement

-high concentration of analyte species at electrode surface

Charging Current (i_{cc}) Attenuation

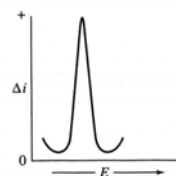
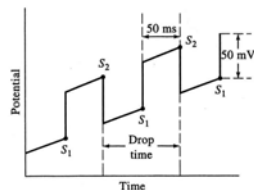
-decays more rapidly than does i_f

- So:**
- Apply short pulse ($\sim 50 \text{ ms}$) at E_{appl} near end of drop lifetime
 - Measure current near the end of the pulse
 - enhanced i_f and attenuated i_{cc} gives S/B enhancement

26

Differential Pulse Polarography: Peaks!

- Make a *differential* current measurement to change the shape of the polarogram:



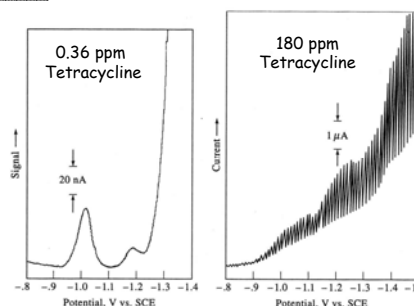
- $\Delta i = S_2 - S_1$
- Plot Δi versus E_{appl}

27

Benefits of DPP

- Resolution:**
 $\Delta E \approx 50 \text{ mV}$

- Det. Limits:**
 $\sim 10^{-8} \text{ M}$



Other EChem Methods

ac Polarography

- superimpose $\pm 5 \text{ mV}$ ac ($10 - 50 \text{ Hz}$) potential onto linear sweep
- only measure *ac component* of current
- get a peak for any *reversible* analyte reaction

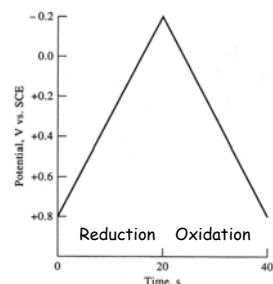
Square-Wave Polarography

- apply an *increasing square wave* potential ramp
- use on a *single Hg drop*
- rapid sweep* (scan 1 volt in < 1 second)
- differential current measurement (get a *peak*)

29

Cyclic Voltammetry

- On a single Hg drop (HMDE), apply both an *anodic* and a *cathodic* sweep:



30

A Cyclic Voltammogram

System is *reversible* if:

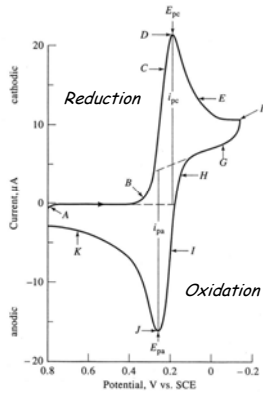
$$\Delta E = 0.0592/n$$

and

$$i_{pc} = i_{pa}$$

Note: $E_{pc} \neq E^{\circ}$

$$E_{pc} = E^{\circ} - 1.1[RT/nF]$$



Stripping Methods: The Ultimate in Detectability

■ Concept:

- Pre-concentrate analyte species onto electrode (electrolysis)
- Strip reduced species off of electrode and measure current (voltammetry)

■ Requirement:

Reduced analyte must form an *amalgam* with Hg electrode

32

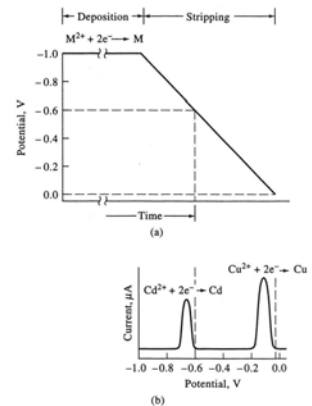
Anodic Stripping Voltammetry (ASV)

- Use a HMDE
- Stir solution and apply potential ~200 mV more negative than E° of analyte
 - Allow reduction to proceed for 5 - 60 minutes
 - Stop electrolysis and stop stirring solution
- ➡ Apply a *slow ANODIC* potential ramp (or DPP)
- ➡ Measure current due to *oxidation of reduced analyte species*

33

ASV: Example

Can you find the mistake?



DPP-ASV: Multi-Component Ultra-Trace Analysis

-all components must be able to form an *amalgam* with Hg
(about 15 - 20 elements can)

-Detection limits can be as low as $10^{-9} M$

