

February 9, 2005

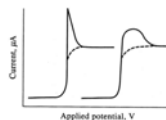
- **Reminder:** Exam #1, Feb. 16<sup>th</sup> at 7pm
- Info page posted!
- Email me by Friday if you have a conflict with the time
- Review session? Sunday? Tuesday?

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## Applications

First, some practical considerations:

- **Purge system of O<sub>2</sub>**
  - O<sub>2</sub> reducible at ~ 0 volts
  - Bubble N<sub>2</sub> before analysis to remove O<sub>2</sub>
  - Keep gentle flow of N<sub>2</sub> over electrode during analysis
- **Add surfactant to solution**



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

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## 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  $E_{\text{applied}}$  scan rate

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## Confirming Reversibility

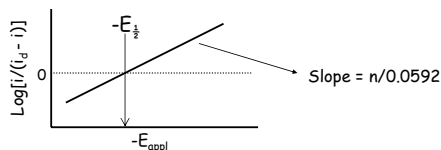
Recall:

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

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*:



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## Quantitative Analysis

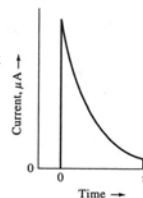
- From Ilkovic equation:  
 $i_d = kC$   
usually use method of Standard Additions (with  $\mu\text{L}$  additions, no volume correction needed)
- **Detection Limits:**  $\sim 10^{-5} - 10^{-6} \text{ M}$  (low ppm)
- **Resolution:**  $\Delta E_{\frac{1}{2}} \approx 0.2 \text{ V}$  (not very good)

How can DL and resolution be improved?

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## Pulse Polarography

Recall *initial* shape of current after application of  $E_{\text{appl}}$  more negative than  $E^{\circ}$ :



Faradaic Current ( $i_f$ ) Enhancement

-high concentration of analyte species at electrode surface

Charging Current ( $i_{cc}$ ) Attenuation

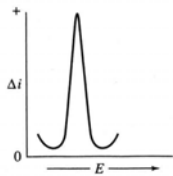
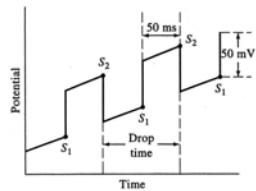
-decays more rapidly than does  $i_f$

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

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## Differential/Pulse Polarography: Peaks!

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



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