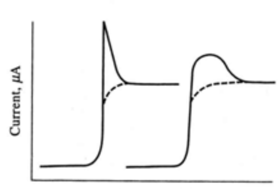
February 9, 2005

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

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

Qualitative Analysis

- Analyte must be reducible in solution
- **<u>Recall:</u>** $E_{\frac{1}{2}} = E^o$
  - **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

Confirming Reversibilty

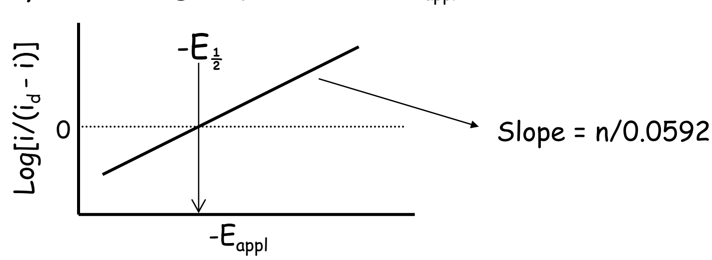
<u>Recall:</u>

$$E_{appl} = E^o - (0.0592/n)\,\mathrm{Log}[i/(i_d - i)]$$

<u>Rearranging:</u>

$$\mathrm{Log}[i/(i_d - i)] = (n/0.0592)(E^o - E_{appl})$$

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



Quantitative Analysis

- From Ilkovic equation:

$$i_d = kC$$

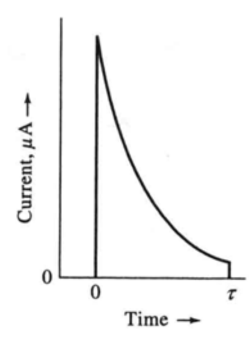
usually use method of Standard Additions
(with μL additions, no volume correction needed)

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

How can DL and resolution be improved?

Pulse Polarography

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



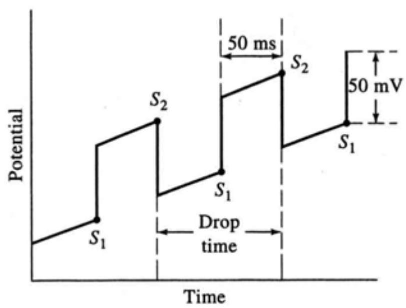
Faradaic Current (i_f) Enhancement
-high concentration of analyte species at electrode surface

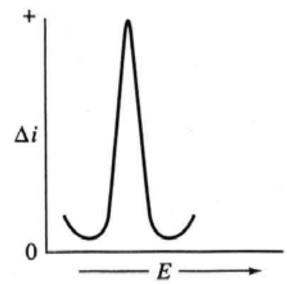
Charging Current (i_{cc}) Attenuation
-decays more rapidly than does i_f

So: -Apply short pulse (~50 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

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}