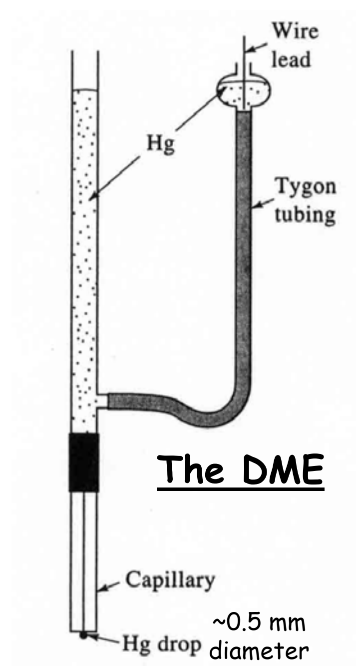
February 7, 2005

- **Reminder:** Exam #1, Feb. 16th at 7pm!
  - Info page will be posted later today
  - Email me next week if you have a conflict with the time
- **Office "Hour":** Today! 1:10 – 1:45 A223 Cook
- Physics Seminar: Today!
  - ***Holography: How it Works*** – Prof John Perry (Holographics North)

  "There is myth and confusion surrounding the 3-D image-making process of holography. The technologies used today will be described in some detail, and many of the myths will be put to rest. The powers and limitations of the medium will be demonstrated with holograms and a laser. Some of the recent projects at Holographics North, a Burlington based company, will also be discussed."
  - **7 pm TODAY B106 Angell**

Polarography

- **DME provides:**
  - *Fresh electrode surface* with each drop
  - *Increasing surface area* as drop expands



The Ilkovic Equation

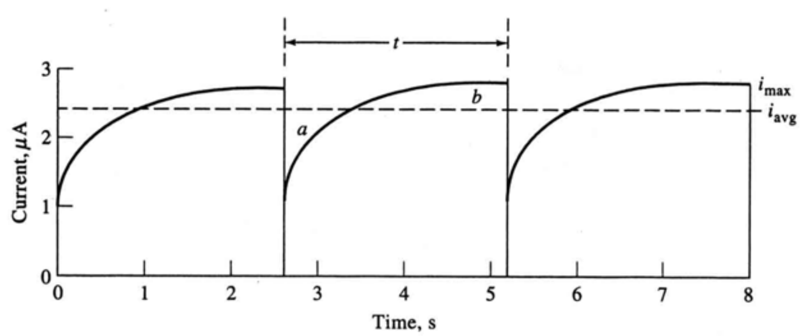
- If we take the Cottrell Equation and assume:
  - Spherical Hg drop
  - Diffusion-controlled mass transport

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

- $(i_d)_{max}$: Diffusion current, μA
- 706: Misc constants *(607 for $(i_d)_{avg}$)*
- n: # e^-/mol
- D_{ox}: Diffusion Coefficient, cm^2/sec
- m: Hg mass flow, mg/sec
- t: Drop time, sec
- C_{ox}: 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

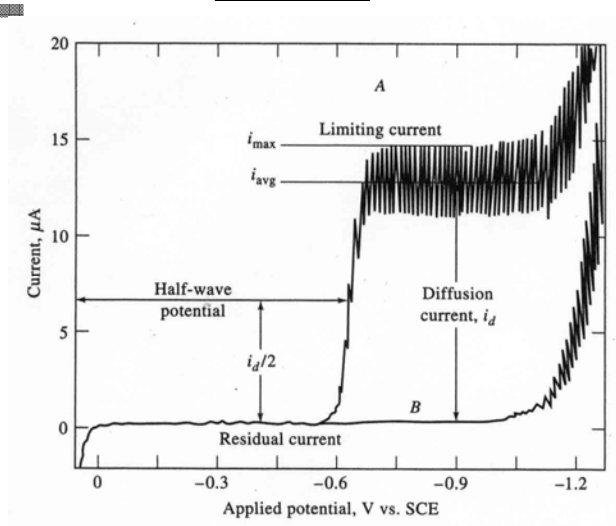
For Cd^{2+}:

For a *reversible* system:

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

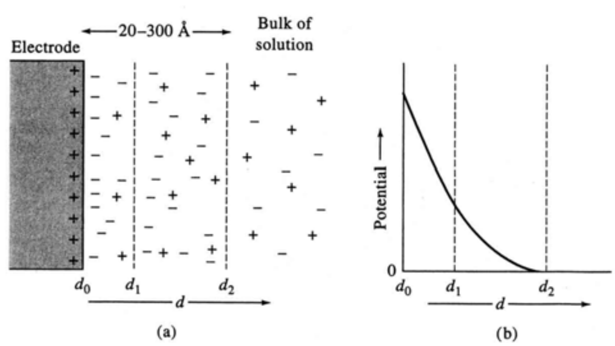
So, at $i = \frac{1}{2} i_d$:

$\mathbf{E_{appl}}$ ($= E_{\frac{1}{2}}$) = $\mathbf{E^o}$



Background Current

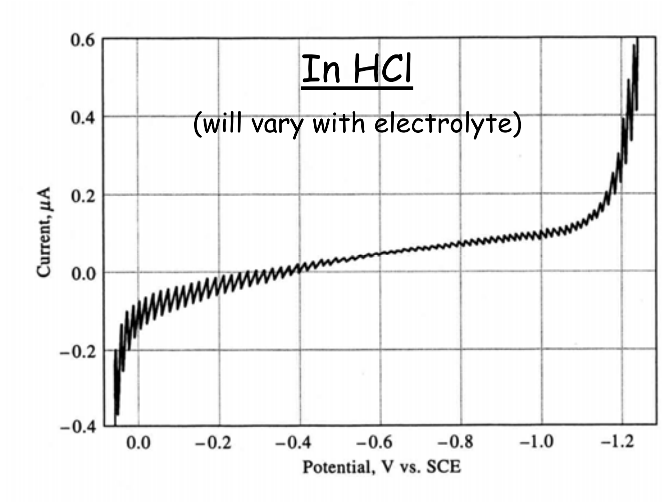
Let's look more closely at the electrode/solution interface:



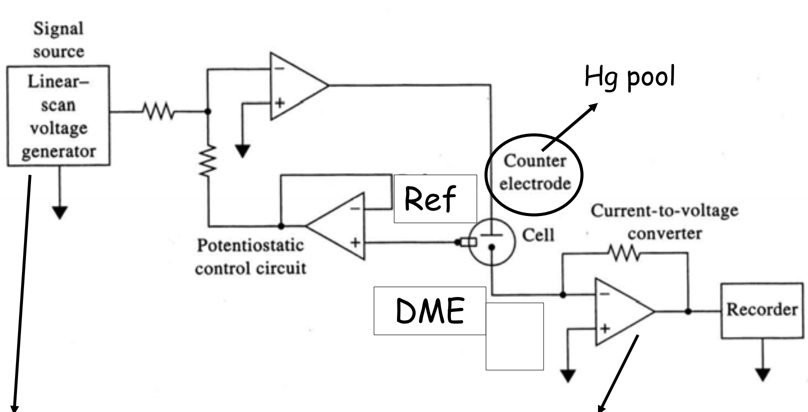
Charge separation → capacitance → charging current (i_{cc})

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

$E_{applied}$ Ramp Function

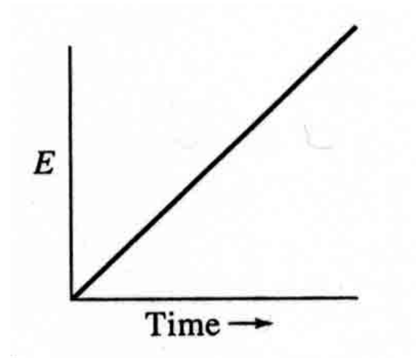
•$E_{applied}$ usually limited to:

-2 volts
(solvent/electrolyte reduction)

0 volts
(oxidation of Hg)

•Slope of ramp:

2 - 5 mV/sec



dc Polarography

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