Electroanalytical Chemistry

techniques covered to date

- Potentiometry – based on galvanic cell
- Controlled Potential Electrolysis – electrolytic
- Chronoamperometry – electrolytic cell
- Chronopotentiometry– electrolytic cell
- Coulometry (potential or current) - electrolytic
- Voltammetry (stirred & unstirred) - electrolytic
- DC Polarography – electrolytic cell

Polarography (DC or direct current)

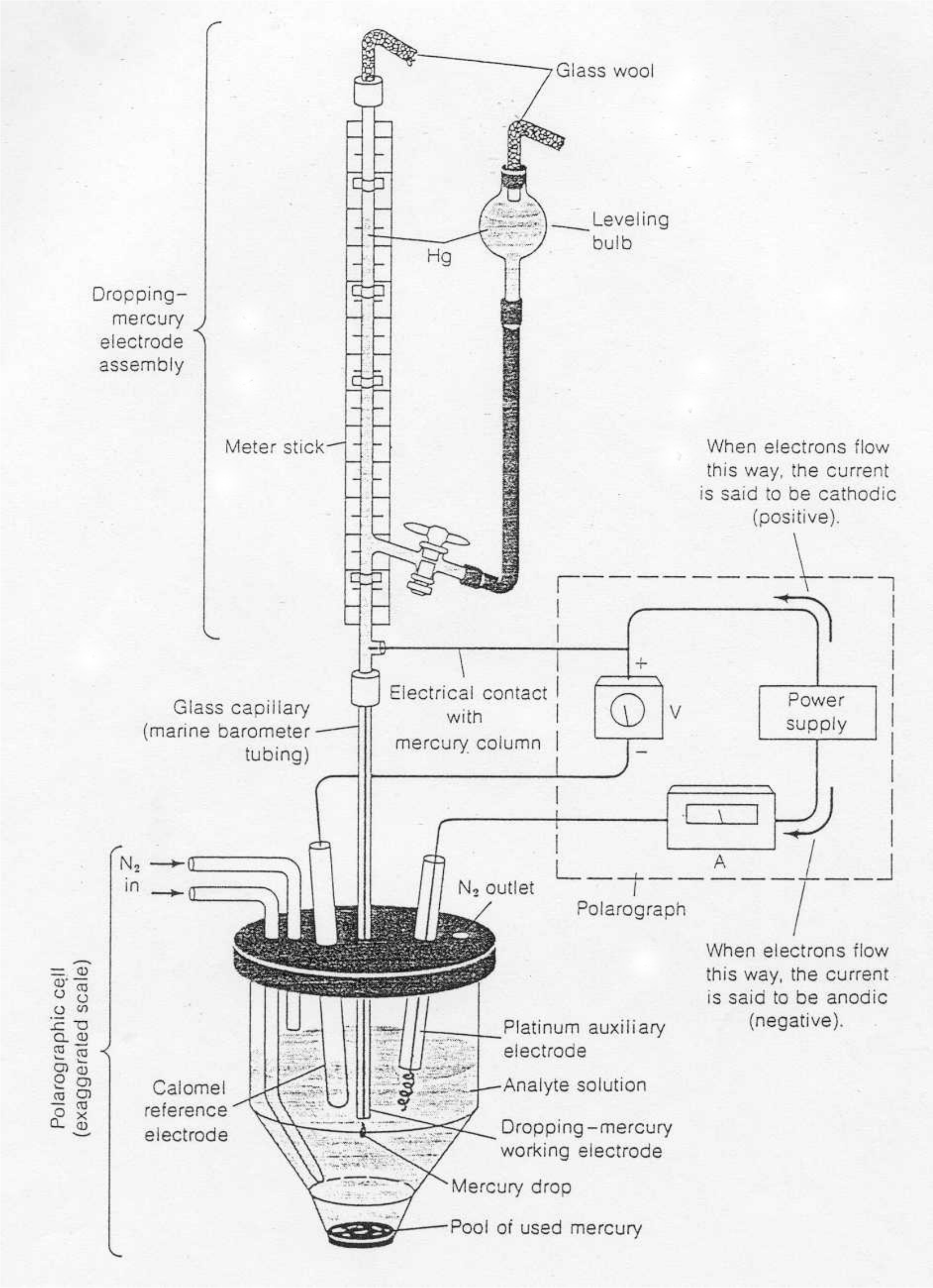
- Same as voltammetry in unstirred solution except, use Dropping Mercury Electrode (DME)
- Vary potential linearly with time
- Measure current vs time

Theory

assume Ox + n e^- ←→ Red

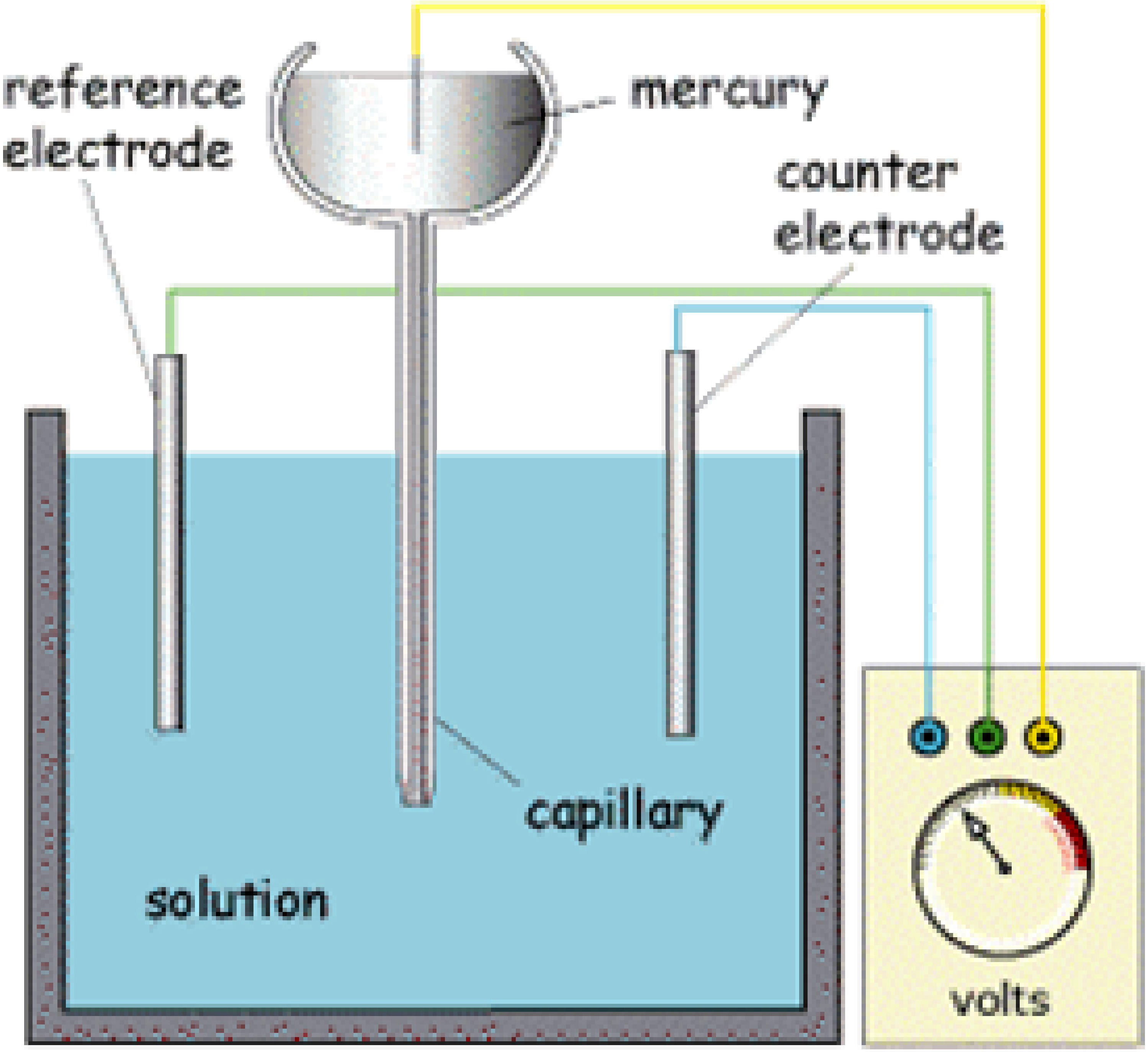
- both Ox & Red are soluble or Ox soluble & Red dissolves in mercury electrode

- reversible reaction (electrochemically)



Realistic diagram of a DME for polarography

Slow flow of Hg through tubing → drop forms, expands and falls off → new drop forms


reference electrode
mercury
counter electrode
capillary
solution
volts

Advantages of DME

1) A new electrode surface forms every few seconds preventing buildup of impurities or reaction products → clean surface
2) Metallic products dissolve or amalgamate with Hg leaving surface clean also
3) High hydrogen overvoltage allows more negative potentials than other electrodes
4) Expansion of drop area and decrease in diffusion limited current counteract each other

Disadvantages of DME

1) Hg is easily oxidized which prevents the use of more positive (oxidizing) potentials
2) DME is cumbersome to set up and use
3) DME is fragile, not rugged
4) Hg is highly toxic & has measurable vapor pressure
5) Continual Hg dropping becomes costly
6) Hg must be highly pure
7) Hg can air oxidize and the oxide can clog the capillary tube where the drop forms

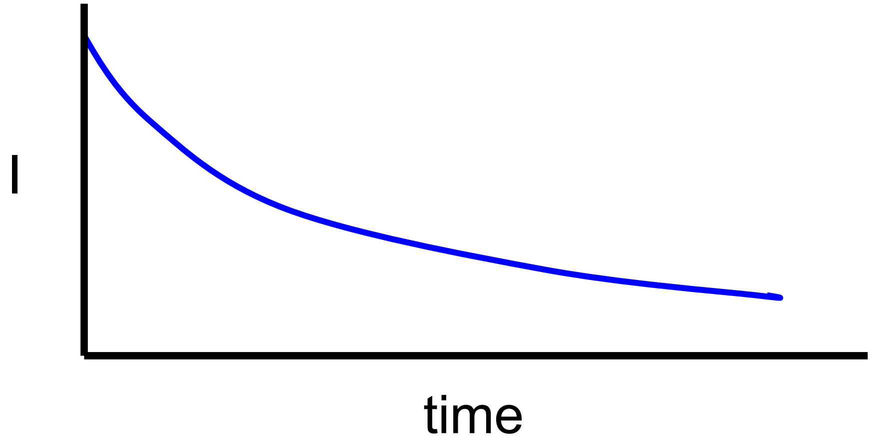
Static Mercury Drop Electrode & Controlled Growth Electrode

As drop forms:

1) Concentration polarization occurs at the electrode surface as described by Cottrell Eq.

$$I = nFAc_o\sqrt{\frac{D}{\pi t}}$$

The Cottrell equation



2) Size of drop increases → area increases

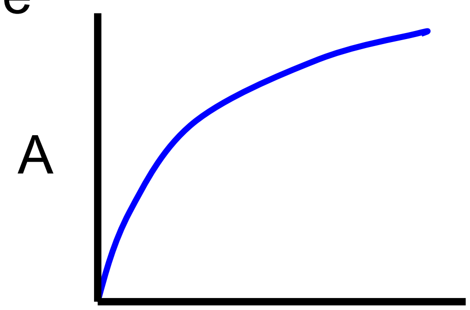
drop time

$$A = (4\pi)^{1/2}\left(\frac{3 \times 10^{-3}}{\rho_{Hg}}\right)^{2/3}(m\ t)^{2/3}$$

area

density of Hg

mass flow rate (mg/sec)



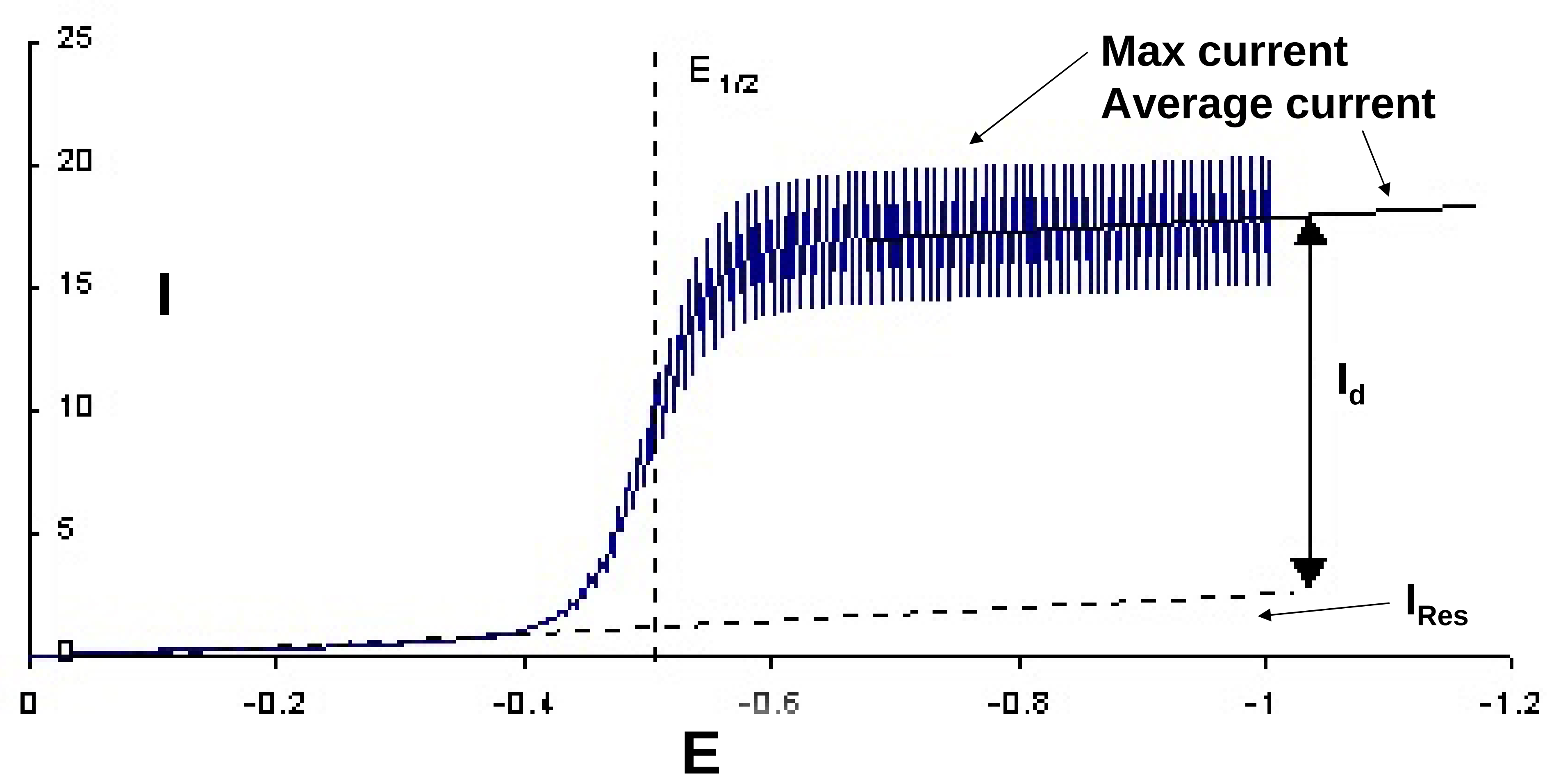
drop time = time for 1 drop

- The two effects, concentration polarization which decreases current, and the area increase which increases current, tend to cancel each other out
- Combining equations gives the Ilkovic Eq.

$I = 708\ n\ D^{1/2}\ m^{2/3}\ t^{2/3}\ C$ max current

$I = 607\ n\ D^{1/2}\ m^{2/3}\ t^{2/3}\ C$ average current

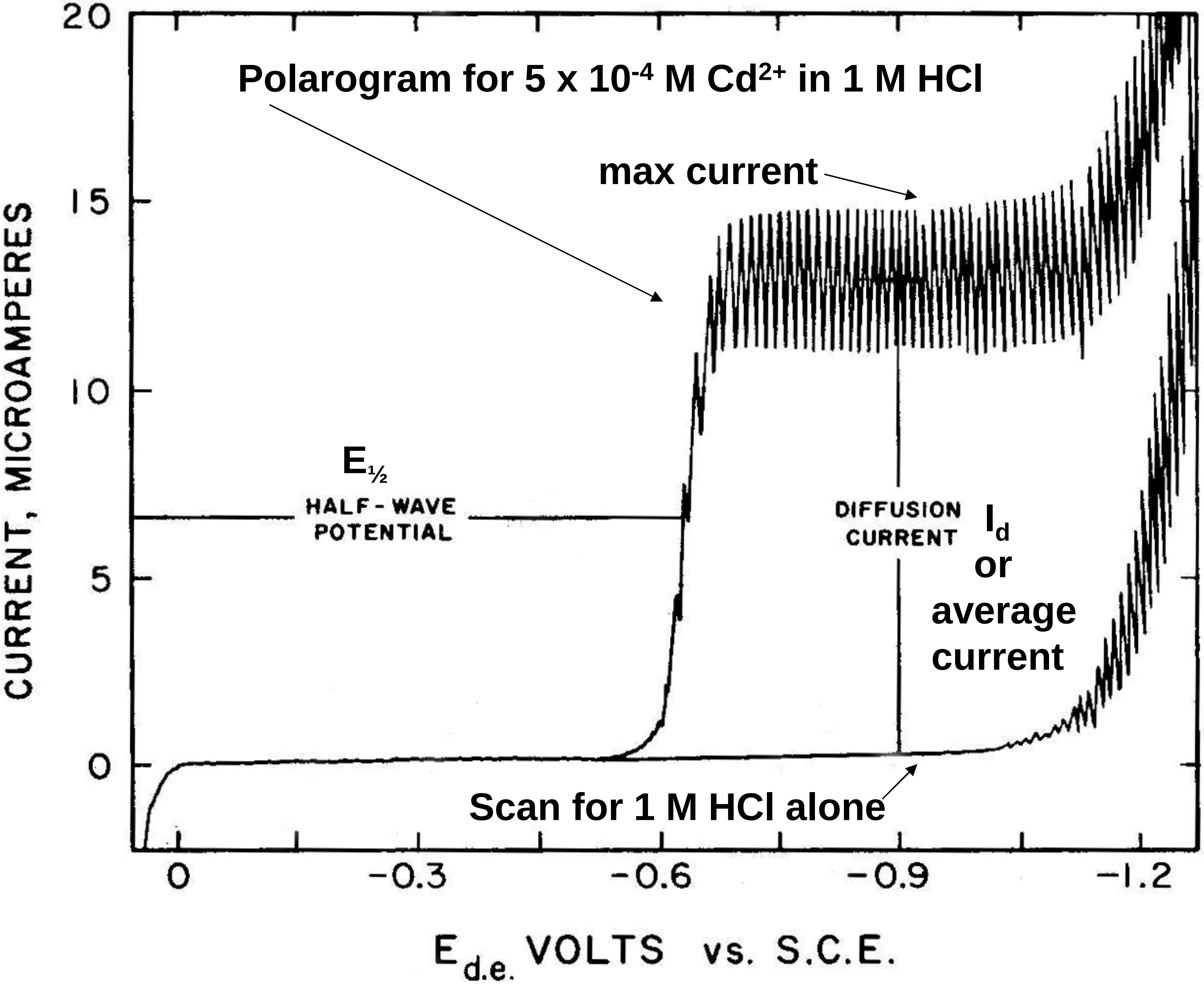
Polarogram



Two name changes occur in polarography

I_L the limiting current becomes I_d the diffusion current

I_{Cap} the capacitive current is I_{Res} the residual current



Polarogram for 5 x 10^{-4} M Cd^{2+} in 1 M HCl

max current

$E_{½}$

I_d or average current

Scan for 1 M HCl alone

Remember for LSV

$$E_{DME} = E_{½} - \frac{RT}{nF} \ln \frac{(I_d - I)}{I}$$

A plot of log $\frac{(I_d - I)}{I}$ vs. E yields a straight line

With slope of 0.059/n if process is reversible

- This plot is used to establish reversibility & to determine “n”
- $E_{½}$ is characteristic of species reduced
- I_d is used for quantitative analysis

Effect of complexation on $E_{1/2}$ for metal ion reduction

- Electrochemical methods measure free ion
- Metals bound in complexes are not measured

$$\underset{\substack{\uparrow \\ \text{measured}}}{M^{n+}} + x\,L \rightleftharpoons \underset{\substack{\uparrow \\ \text{not measured}}}{ML_x} \qquad K_f = \frac{[ML_x^{n+}]}{[M]\,[L]^x}$$

- However, voltammetric methods, like polarography, actually remove metal ion from solution at the electrode surface

$$M^{n+} + n\,e^- \rightleftharpoons M(Hg)$$

- Two effects 1) it takes more energy to do this

2) it shifts equilibrium to left, releasing metal ion

1) Extra energy required to reduce metal from a complex results in an $E_{1/2}$ that is more negative than $E_{1/2}$ for metal ion alone

$$\Delta E_{1/2} = E_{1/2ML} - E_{1/2M}$$

Plot $\Delta E_{1/2}$ vs. ln C_L to get K & x for complex

2) Equilibrium shift caused by release of metal ion from complex can cause errors in analysis depending on complex kinetics

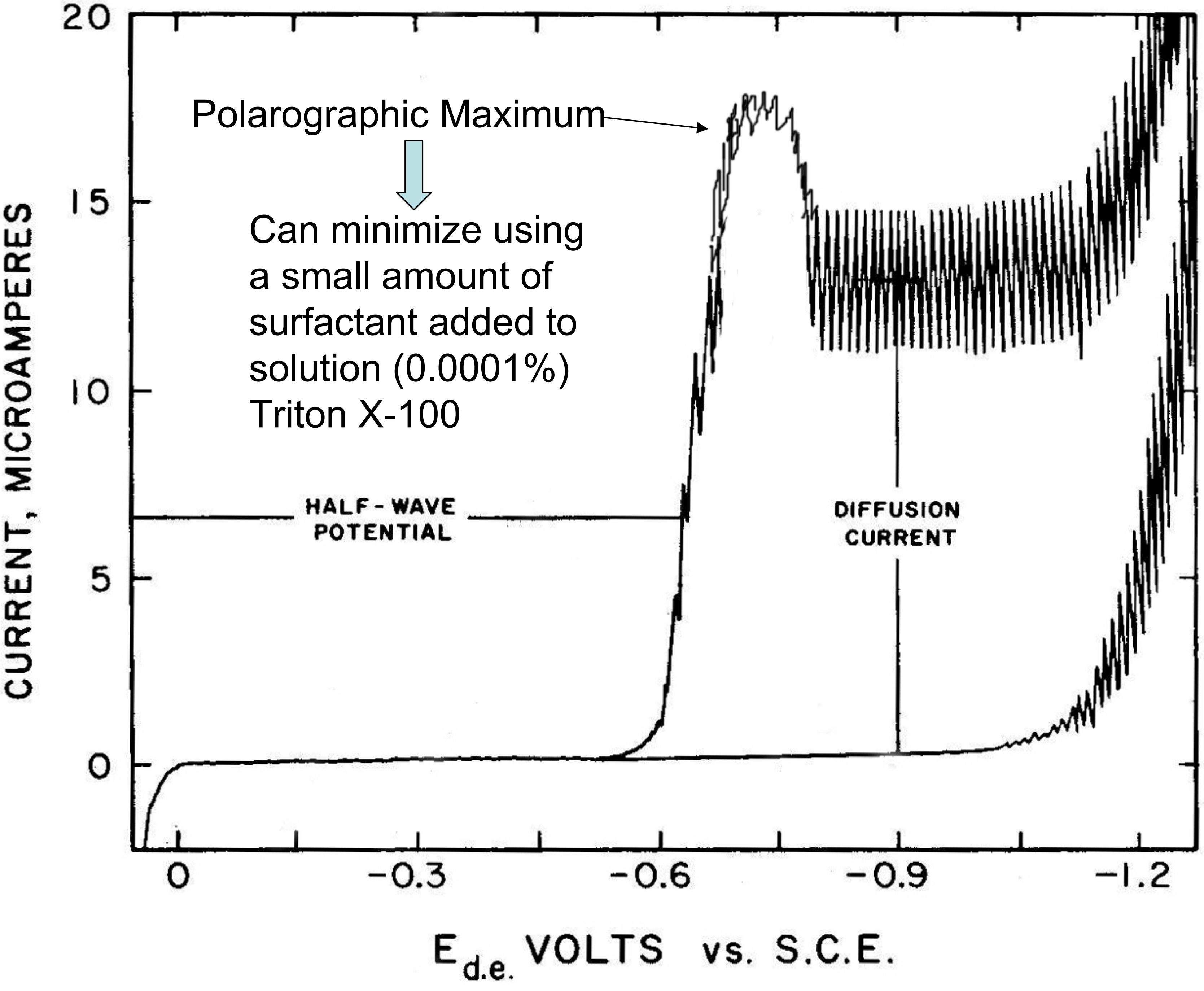
Operational Aspects of Polarography

1) Oxygen dissolved in solutions can be reduced and cause an oxygen wave

$$O_2 + 2\ H^+ + 2\ e^- \rightarrow H_2O_2$$

Routinely bubble an inert gas through solution to displace O_2, usually N_2, He, Ar

2) Polarographic maxima (= interfering peaks) sometimes form in polarogram due to convection currents resulting from drop expansion and dislodging



Polarographic Maximum

Can minimize using a small amount of surfactant added to solution (0.0001%) Triton X-100

Summary of DC Polarography

- Polarography is good for many metals
- Works well even at high salt concentrations
- Applicable to many organic functional groups
- Can be used to study metal complexation
- In practice DC Polarography has been replaced by other polarographic variations
- Particularly variations that handle capacitive current better
- Working range 10^{-3} M to 10^{-5} M
- Precision 1 – 2 %

Summary of DC Polarography (cont.)

- Can do 3 or 4 metals simultaneously if concentrations are compatible
- Still difficult to measure one species in the presence of a large excess of a second species because waves don’t stack well
- Can have problems with complex matricies like wastewater, sludge, biological samples that foul the electrode
- DC polarography is a fundamental technique which has many variations and improvements

Calibration Methods for Electrochemistry

1) Absolute Calibration – use theoretical relationship for current to calculate conc.

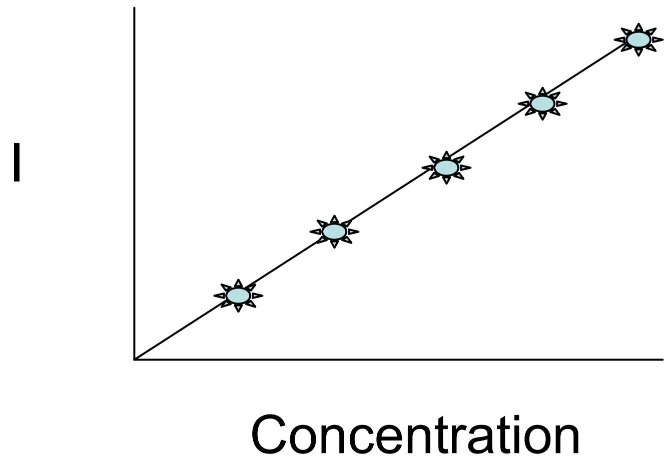
   e.g., $I = 708\ n\ D^{1/2}\ m^{2/3}\ t^{2/3}\ C$

   Measure m and t and look up n and D

   Solve Ilkovic equation for C

This is not the most reliable method because it requires very accurately measured values of m & t as well as reliable info on D which varies with solution composition, also I_{cap} is problem

2) Calibration curve – construct plot of current vs. concentration for several standard solutions



Each point represents a separate solution introduced into the electrochemical cell and analyzed

Calibration curves are sometimes used in electrochemistry for calibration, but they are not the most common method

3) Internal Standard (Pilot Ion) – add a more easily reduced species to both the unknown sample & the standard solution

$$\frac{I_{unk}}{I_{pilot}} = \frac{\cancel{708}\ \cancel{n}\ \cancel{D^{1/2}}\ \cancel{(m^{2/3}\ t^{2/3})}}{\cancel{708}\ \cancel{n}\ \cancel{D^{1/2}}\ \cancel{(m^{2/3}\ t^{2/3})}}\ \frac{C_{unk}}{C_{pilot}}$$

Response ratio of ion in unknown sample to pilot ion is equal to ratio of concentrations

Compensates for variations in solution matrix

4) Standard Additions – spike a small volume (V_s) of standard solution of known concentration (C_s) into original volume of sample (V_o) measuring first the current for the current for the original sample (I_o), then the current for the spiked sample (I_s)

$$C_u = \frac{I_o V_s C_s}{(I_s V_s) + (I_s - I_o) V_o}$$

where C_u is concentration of the unknown