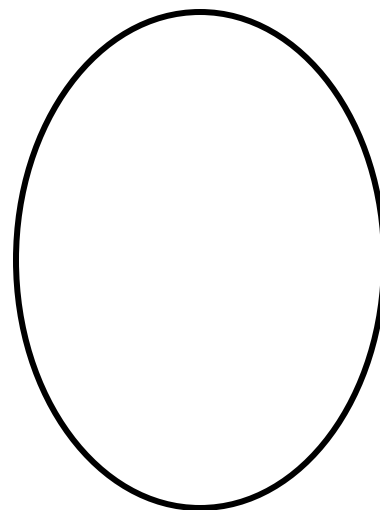


BASIC ELECTROCHEMISTRY



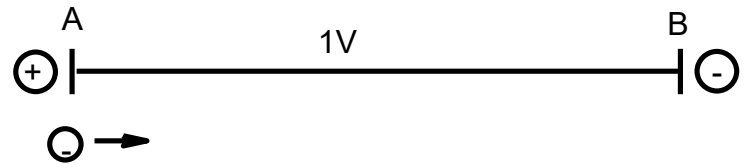
THE CHARGE AND CURRENT

- Electrochemistry studies the processes which involve charge
- The charge is a source of electric field

Element of charge: $1.602 \cdot 10^{-19} \text{ C}$

The energy change is $\pm 1.602 \cdot 10^{-19} \text{ J}$ if we move the charge across the potential drop of 1V

If we do the same with 1 mol of charges, we obtain...



The current is the change of charge per time

$$I = \frac{dQ}{dt}$$

FARADAY'S LAWS (1834)

“The chemical power of a current of electricity is in direct proportion to the absolute quantity of electricity which passes”

“Electrochemical Equivalents coincide, and are the same, with ordinary chemical equivalents”



$$m = \frac{MI t}{zF}$$

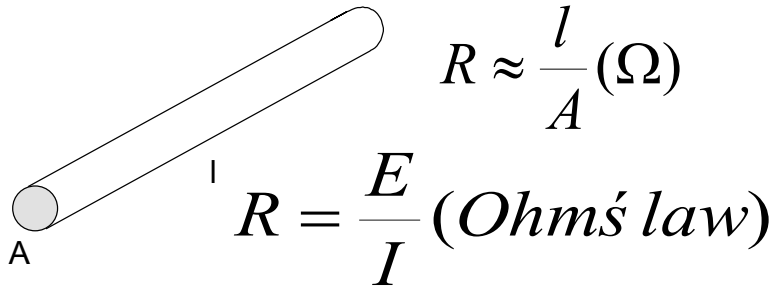
$$\frac{m}{M} = \frac{Q}{zF}$$

$$m = \frac{M \int_{t=0}^t I dt}{zF}$$

Area under current-time curve (and frequently the current-potential curve also) is the charge!! This way can be deduced how much material was transformed.

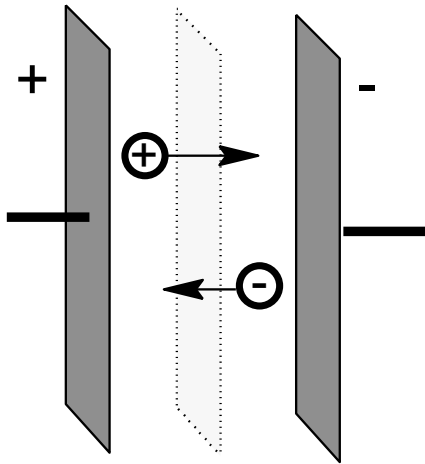
CONDUCTIVITY

Electrolytes: same principle, but conductivity is preferred



$$G = \chi \frac{A}{l}$$

The unit for conductivity is Siemens, what is the unit of specific conductivity?



For species $K_X A_Y$:

Migration velocities can be different

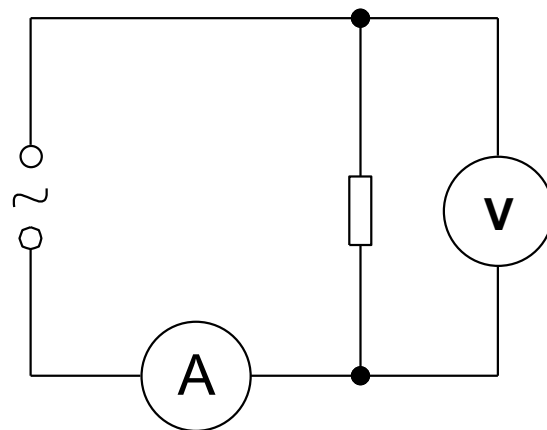
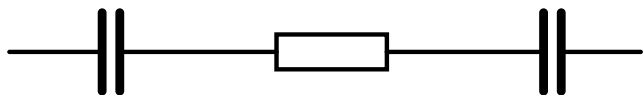
Stokes force is balanced by force induced by electric field

Only the cations distant from the plane by v_A or nearer will cross the plane. In unit field (1V) and unit area will cross the boundary

$\chi c \alpha F z_{cat} u_{cat}$ cations

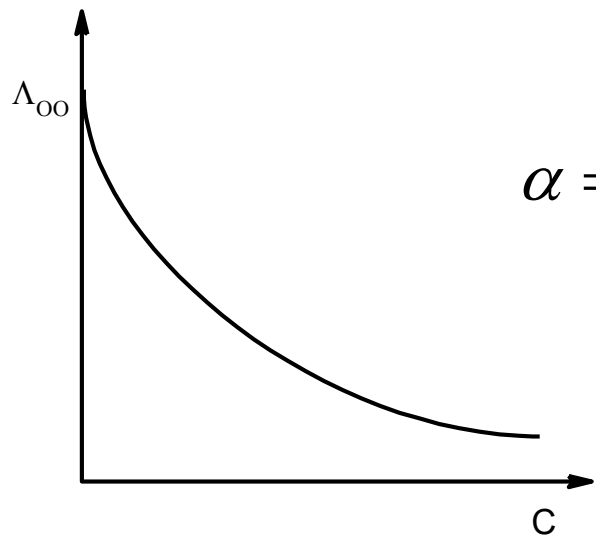
$$\chi = x c \alpha F z_{cat} u_{cat} + y c \alpha F z_{an} u_{an}$$

CONDUCTIVITY



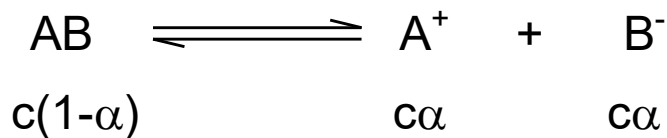
Solutions can have different concentrations:

$$\Lambda = \frac{\chi}{c} \left[\frac{S \ m^3}{m \ mol} = Sm^2 mol^{-1} \right]$$



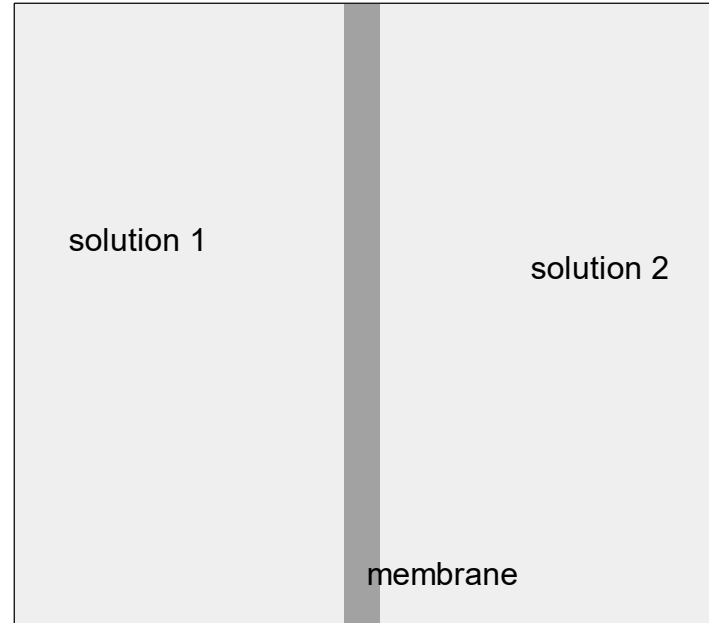
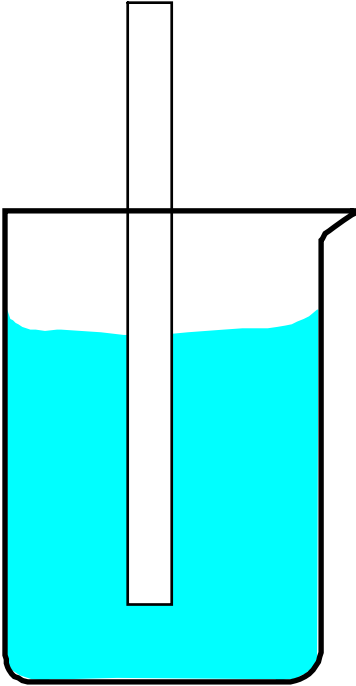
$$\alpha = \frac{\Lambda}{\Lambda_{\infty}}$$

This is used for measurements of dissociation constants:



$$K_D = \frac{c^2 \alpha^2}{c(1-\alpha)} = \frac{c \left(\frac{\Lambda}{\Lambda_{\infty}} \right)^2}{1 - \frac{\Lambda}{\Lambda_{\infty}}}$$

HOW AND WHERE THE POTENTIAL DIFFERENCE DEVELOPS



Junction potential
(Henderson)

Donnan potential

Potential difference develops where a charge separation in space occurs

THE NERNST EQUATION

The combination of two basic physical chemistry equations:

$$-\Delta G = zFE$$

and

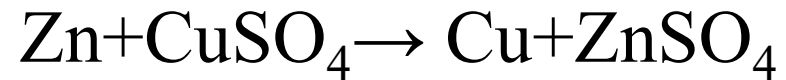
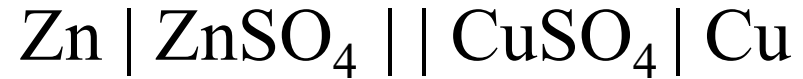
$$-\Delta G = RT \ln K$$

All processes in which charge separation occurs go to equilibrium

...but what is K?

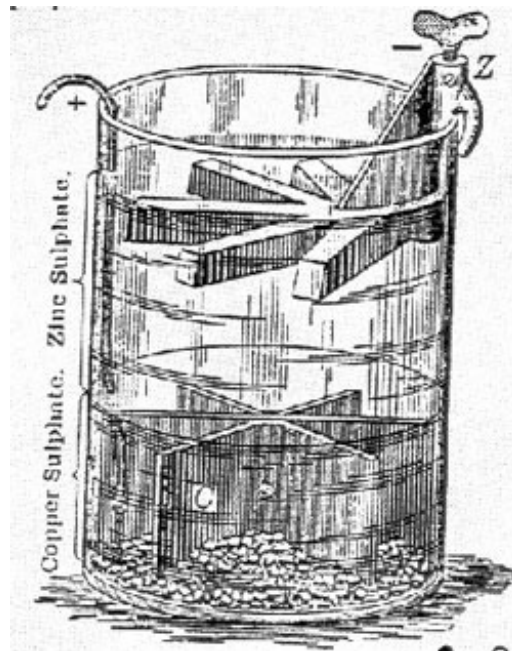


DANIEL CELL



$$zFE_{MN} = RT \ln \frac{[\text{Cu}][\text{ZnSO}_4]}{[\text{Zn}][\text{CuSO}_4]}$$

...is it OK?



BACK TO NERNST EQUATION

$$E = E^0 + \frac{RT}{zF} \ln \frac{a_{ox}}{a_{red}}$$

$$E = E^0 - \frac{RT}{zF} \ln \frac{a_{red}}{a_{ox}}$$

$$E = E^0 + \frac{2.303RT}{zF} \log \frac{a_{ox}}{a_{red}}$$

$$\frac{2.303RT}{F} = 0.059V$$

(at 25°C)

ELECTRODES OF THE FIRST KIND

The term electrode is here used in a sense of a half-cell.

Metal immersed into the solution of its own soluble salt. The potential is controlled by the concentration of the salt.

$$E = E_{Me/Me^+}^0 + \frac{RT}{zF} \ln a_{Me^+}$$

Zn in ZnCl₂, Ag in AgNO₃, Cu in CuSO₄ etc.

Non-metallic electrodes – gas electrodes (hydrogen and chlorine electrode)

THE HYDROGEN ELECTRODE

Fig. 1 From: *Introductory quantitative analysis*, L.E. Wilson, Merrill, Columbus, 1974, p. 218 (Fig. 9-1)

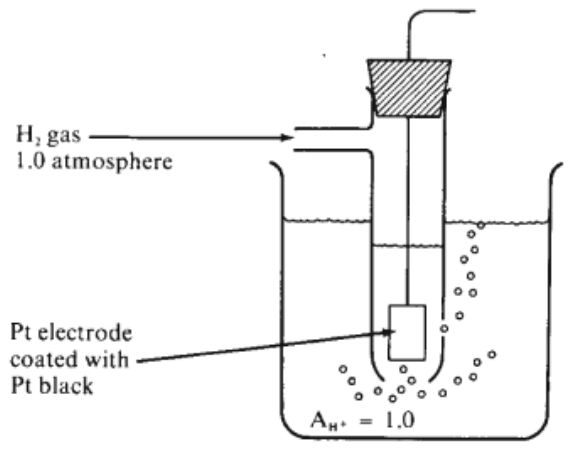


Fig. 2 From: *Quantitative analysis*, 6th edn., R.A. Day Jr. and A.L. Underwood, Prentice-Hall, Englewood Cliffs, 1991 p. 262 (Fig. 10.4)

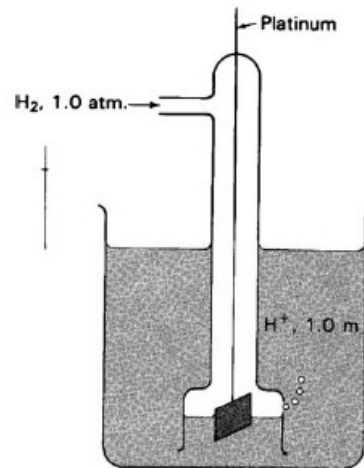
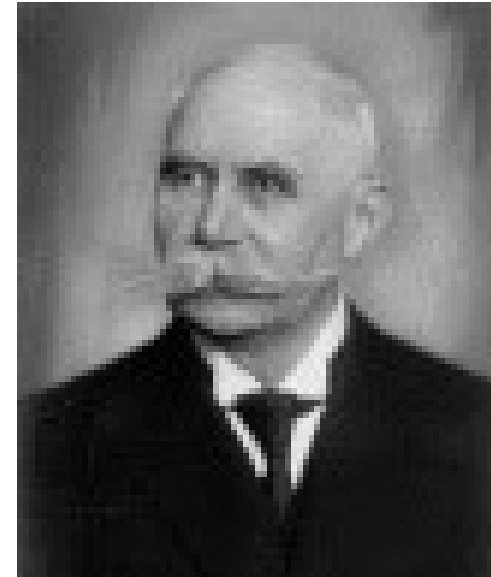
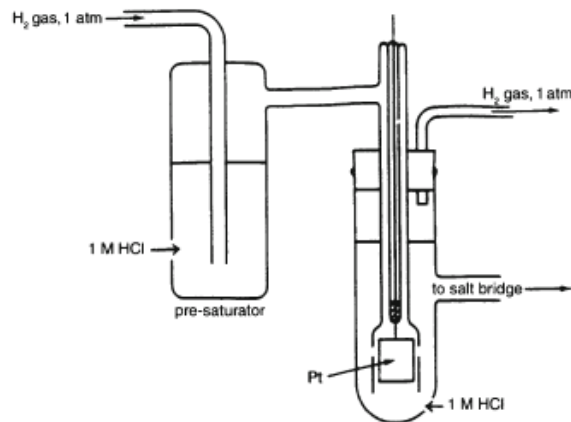


Fig. 3 From *Undergraduate instrumental analysis*, 6th edn., J.W. Robinson, E.M. Skelly Frame, and G.M. Frame II, Dekker, New York, 2005, p. 925 (Fig. 15.4)

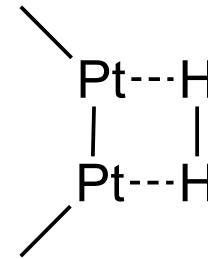
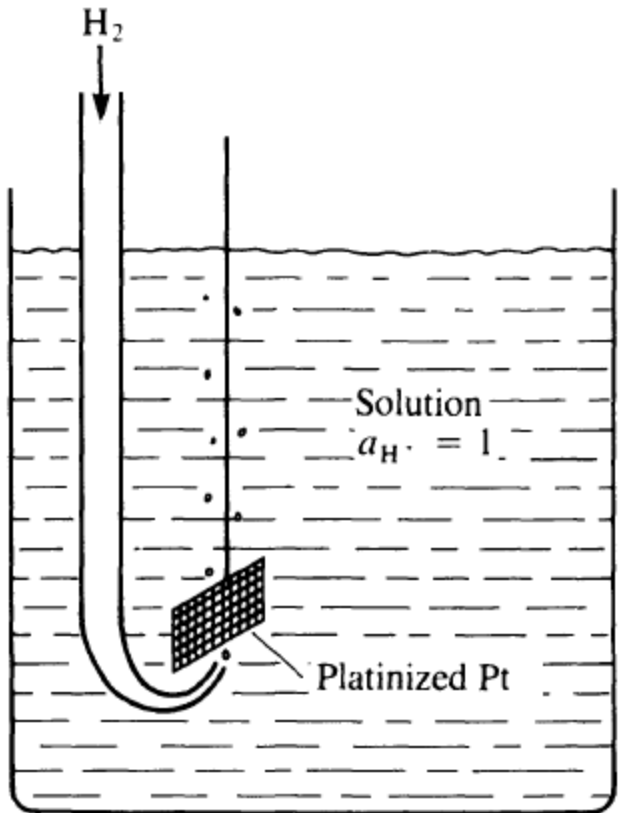


Anal Bioanal Chem (2008) 392:9–10
DOI 10.1007/s00216-008-2227-1

ANALYTICAL CHALLENGE



THE HYDROGEN ELECTRODE



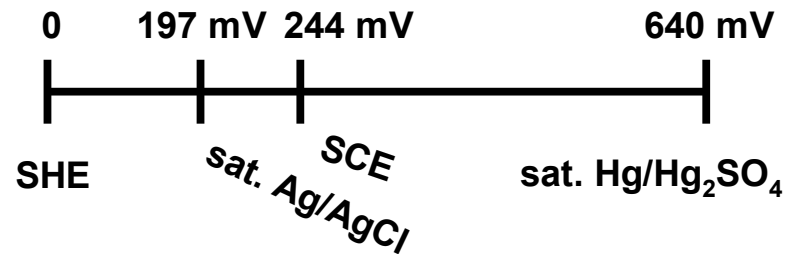
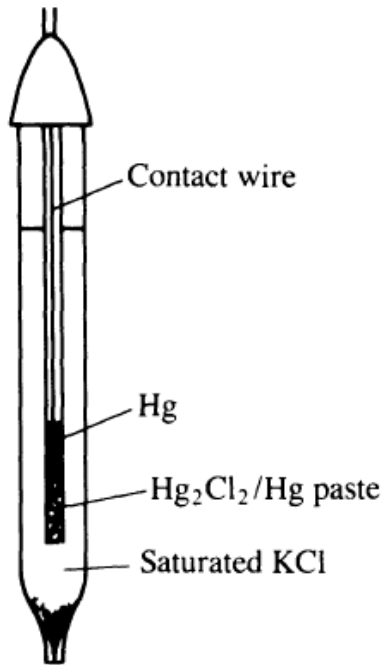
$$E = E_{H_{at}/H^+}^0 - \frac{RT}{F} \ln \sqrt{KK_H p_{H_2}} + \frac{RT}{F} \ln [H^+]$$

ELECTRODES OF THE SECOND KIND

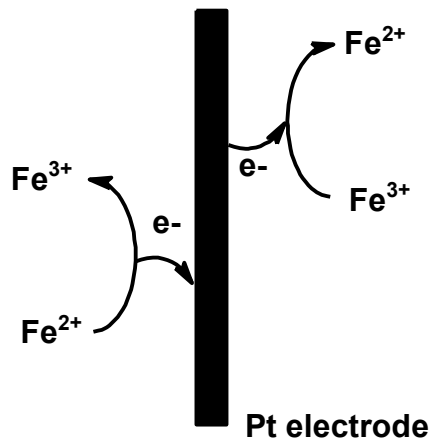
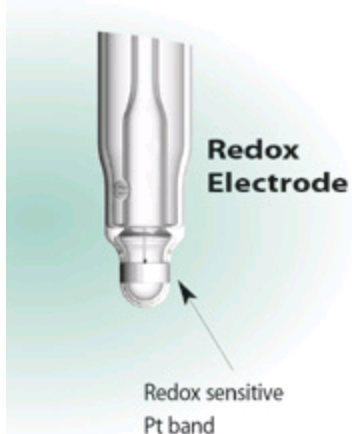
Argentochloride $\text{Ag} | \text{AgCl} | \text{KCl} ||$

Calomel $\text{Hg} | \text{Hg}_2\text{Cl}_2 | \text{KCl} ||$

Mercurysulphate $\text{Hg} | \text{Hg}_2\text{SO}_4 | \text{K}_2\text{SO}_4 ||$



REDOX ELECTRODES



The electrode serves as an electron sink

Redox combo

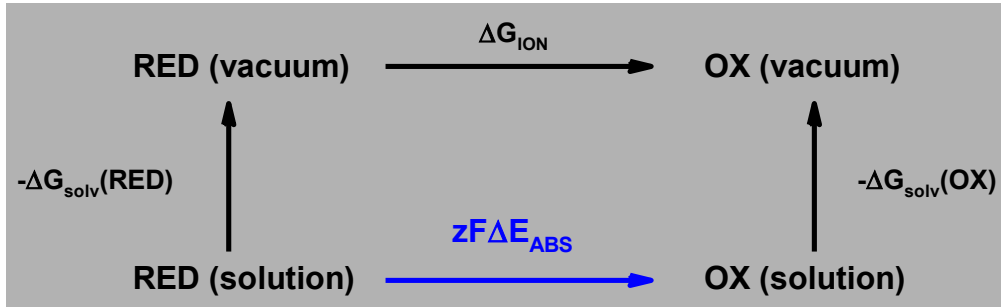
ELECTRODES OF THE THIRD KIND

..just a curiosity



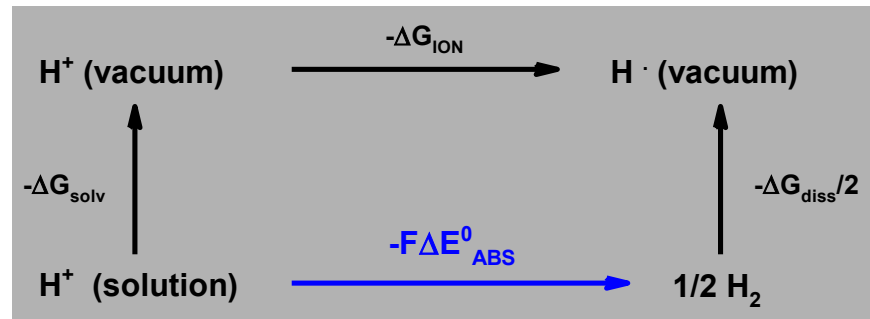
We can measure the concentration of Ca^{2+} , but there's a better device to do this...

THE ABSOLUTE SCALE OF POTENTIALS

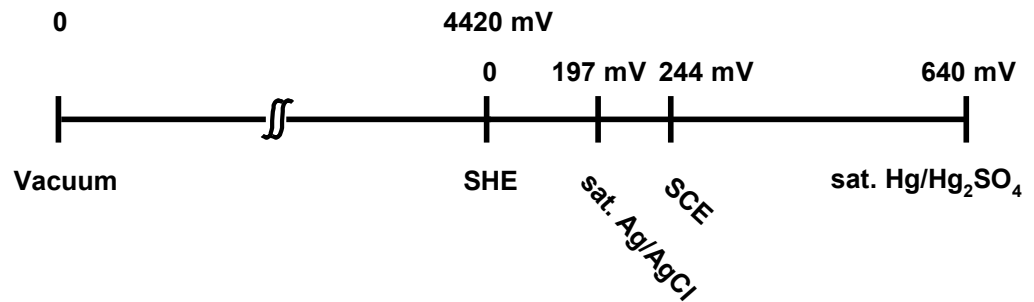


Reference to vacuum
(instead of hydrogen electrode)

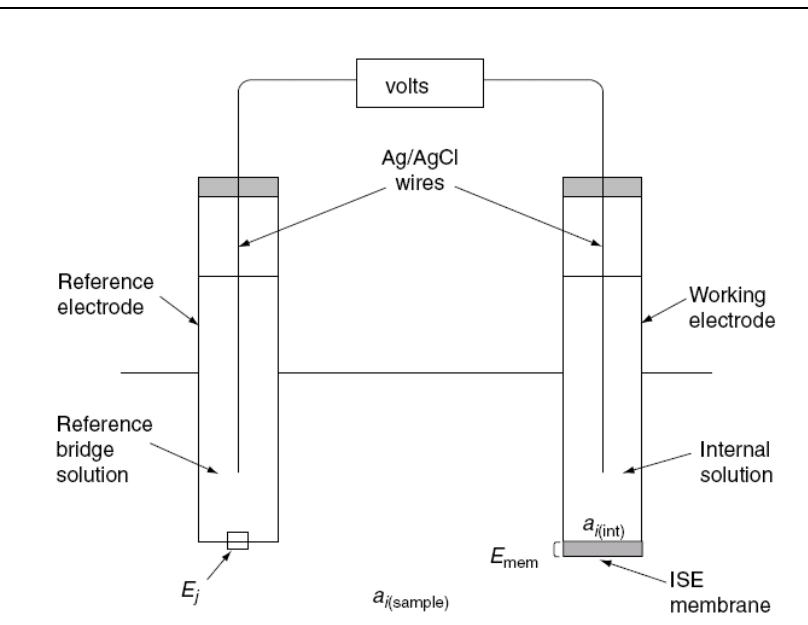
Thermodynamic cycle for hydrogen



The most commonly accepted value is 4.42V, but values around 4.8V are also reported

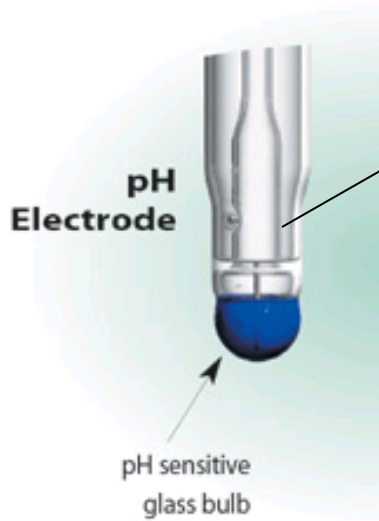


ION SELECTIVE ELECTRODES

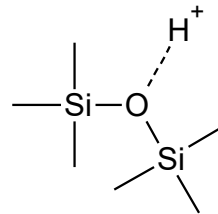


Membrane potential reflects the gradient of activity of the analyte ion in the inner and outer (sample) solutions.

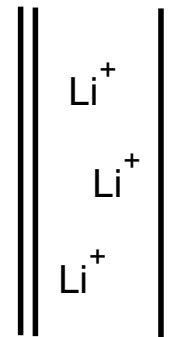
- The trick is to find a membrane material, to which an analyte is selectively bound. The membrane must be conductive (a little bit, at least), but it should not leak



Liquid junction for reference electrode (sometimes is high)



Nikolski eq.



hydrated Haugaard layers

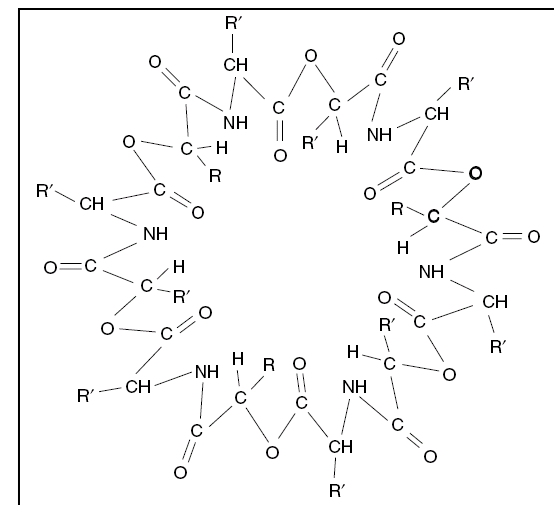
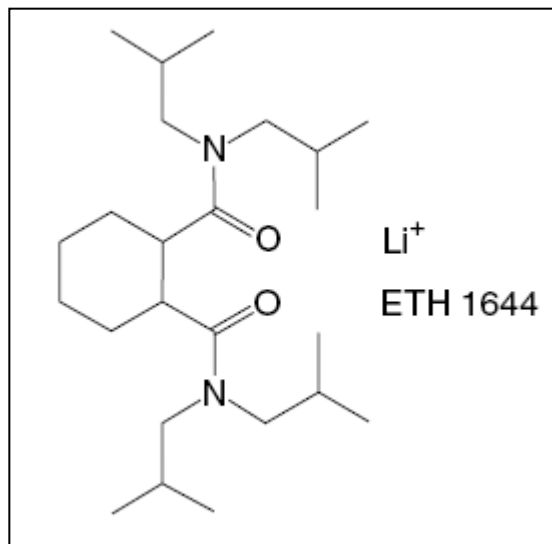
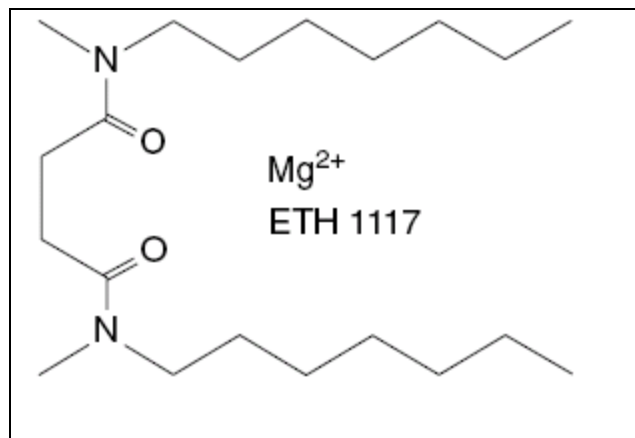
Li ions partially free

400 MΩ

$$E = E_{\text{assym}} + \frac{RT}{F} \ln a_{\text{H}_3\text{O}^+} + X \cdot \frac{RT}{F} \ln a_{\text{Na}^+}$$

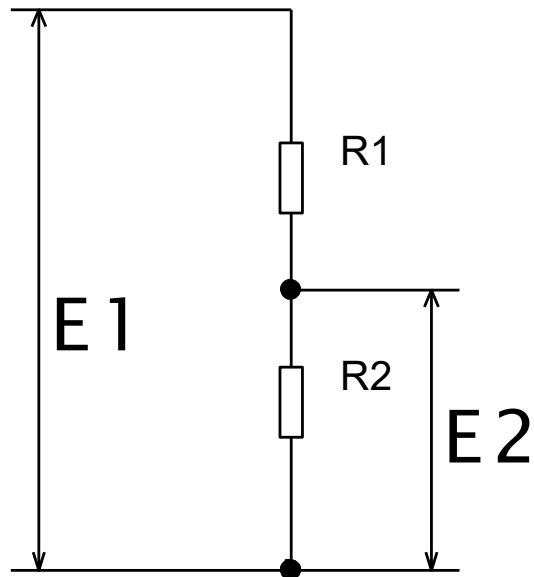
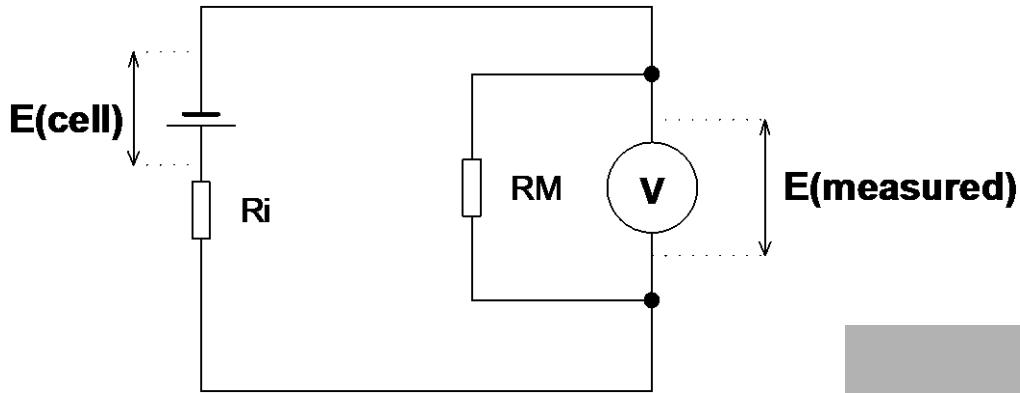
MEMBRANES FOR ISEs

- **Glass membranes** (H^+ , for other cations change in the composition of glass membrane (Al_2O_3 or B_2O_3 in glass to enhance binding for ions other than H^+ (Na^+ , Li^+ , NH_4^+ , K^+ , Rb^+ , Cs^+ and Ag^+))
- **Crystalline Membranes** (single crystal of or homogeneous mixture of ionic compounds cast under high P, $d \sim 10$ mm, thickness: 1-2 mm. Conductivity: doping or nonstoichiometry, Ag^+ in $AgCl$ or Ag_2S , Cu^+ in Cu_2S . Fluoride electrode: determines F^- , LaF_3 crystal doped with EuF_2).
- **Liquid membranes** (organic, immiscible liquid held by porous (PVC) membrane with ion exchange properties or neutral macrocyclic compounds selectively binding the analyte in their cavities)



POTENTIOMETRY

Cell and voltmeter behaves as a voltage divider circuit



$$E_2 = E_1 \frac{R_2}{R_1 + R_2}$$

$$E_{\text{measured}} = E_{\text{cell}} \frac{R_M}{R_M + R_i}$$

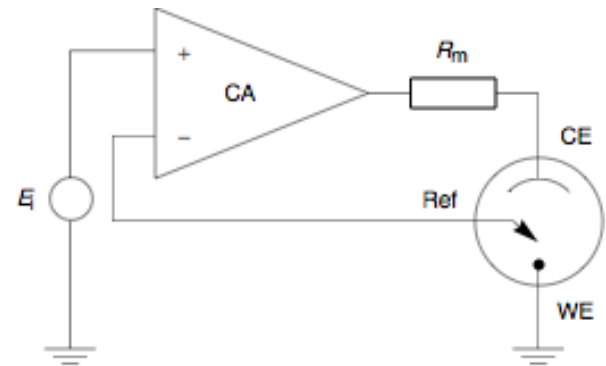
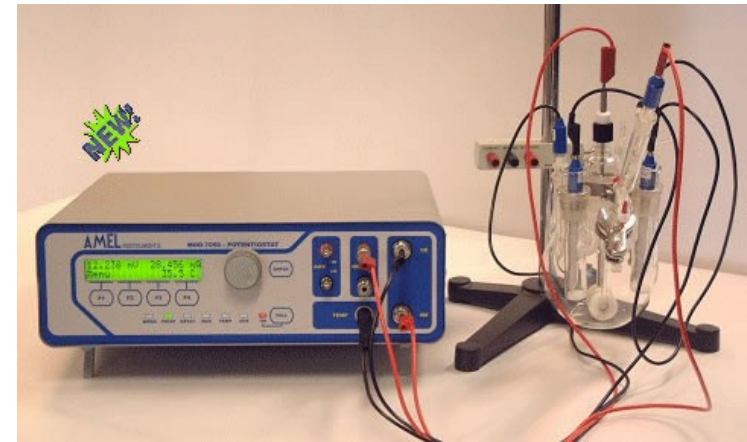
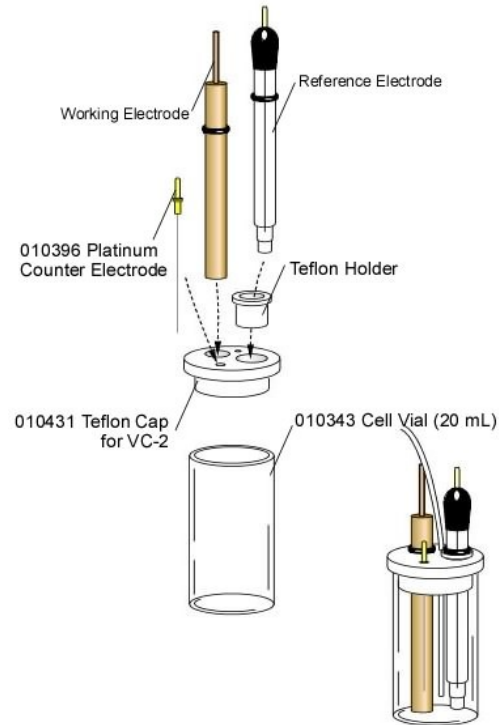
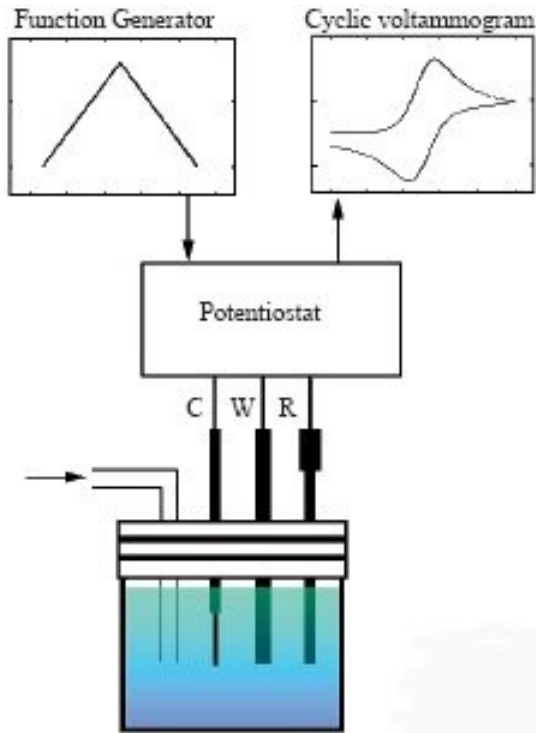
POTENTIOMETRY AND PHYSICAL CHEMISTRY

1. Activity coefficients determination
2. Solubility products determination
3. Ion product of water determination



Ionic product of water: $1.008 \cdot 10^{-14}$ (25°C) – good agreement with conductivity measurement

3-ELECTRODE CELLS AND POTENTIOSTATS



Polarizable and nonpolarizable

ELECTRODE MATERIALS

Inert metals (Hg, Pt, Au)

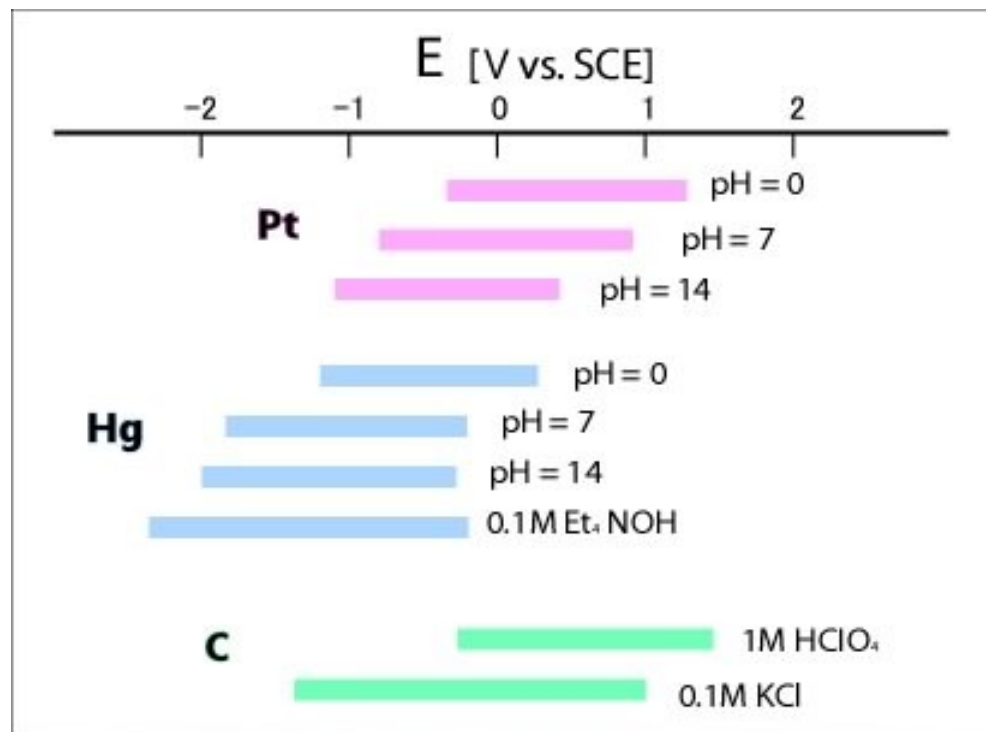
- Polycrystalline
- Monocrystals

Carbon electrodes

- Glassy carbon
 - reticulated
- Pyrrolytic graphite
 - Highly oriented (edge plane,)
 - Wax impregnated
- Carbon paste
- Carbon fiber
- Diamond (boron doped)

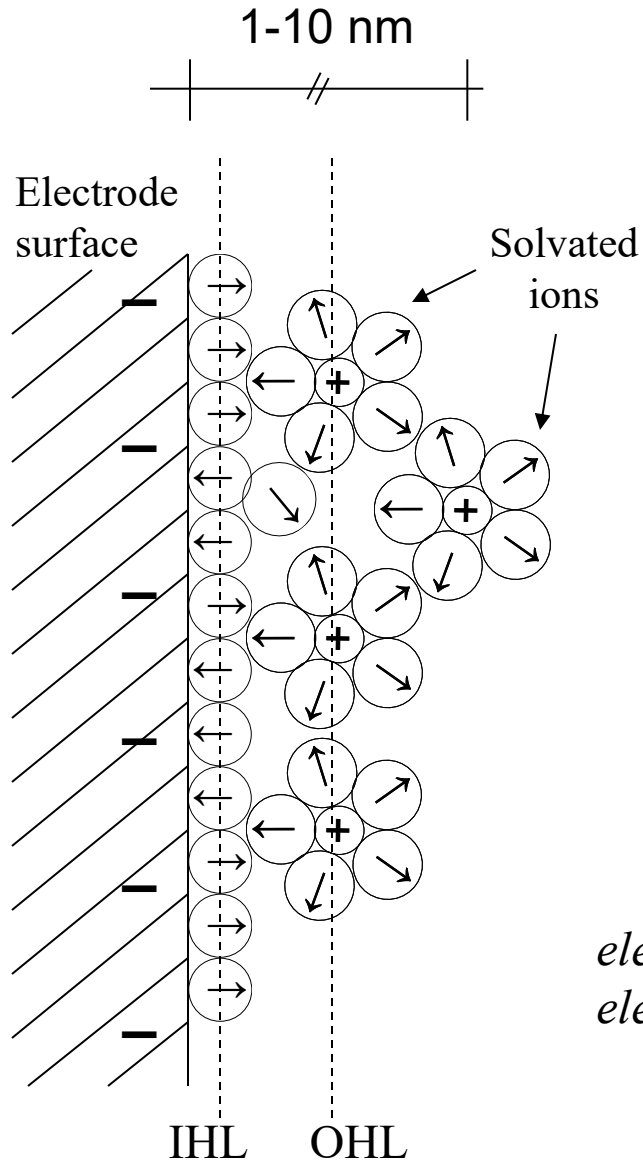
Semiconductor electrodes (ITO)

Modified electrodes



Potential window available for experiments is determined by destruction of electrode material or by decomposition of solvent (or dissolved electrolyte)

ELECTRON TRANSFER PHENOMENON



The double-layer region is:

Where the truncation of the metal's Electronic structure is compensated for in the electrolyte.

1-10 nm in thickness

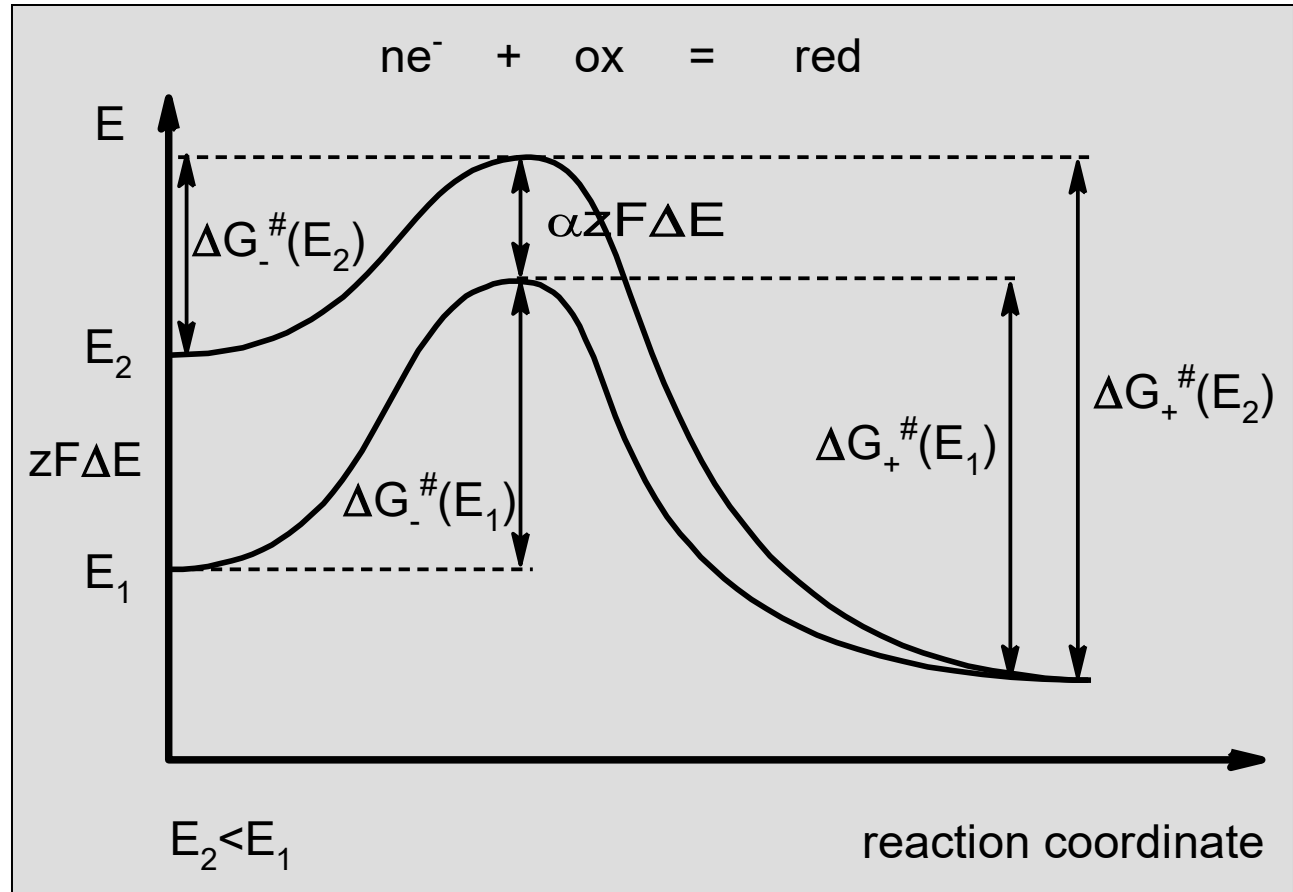
~1 volt is dropped across this region...

Which means fields of order 10^{7-8} V/m

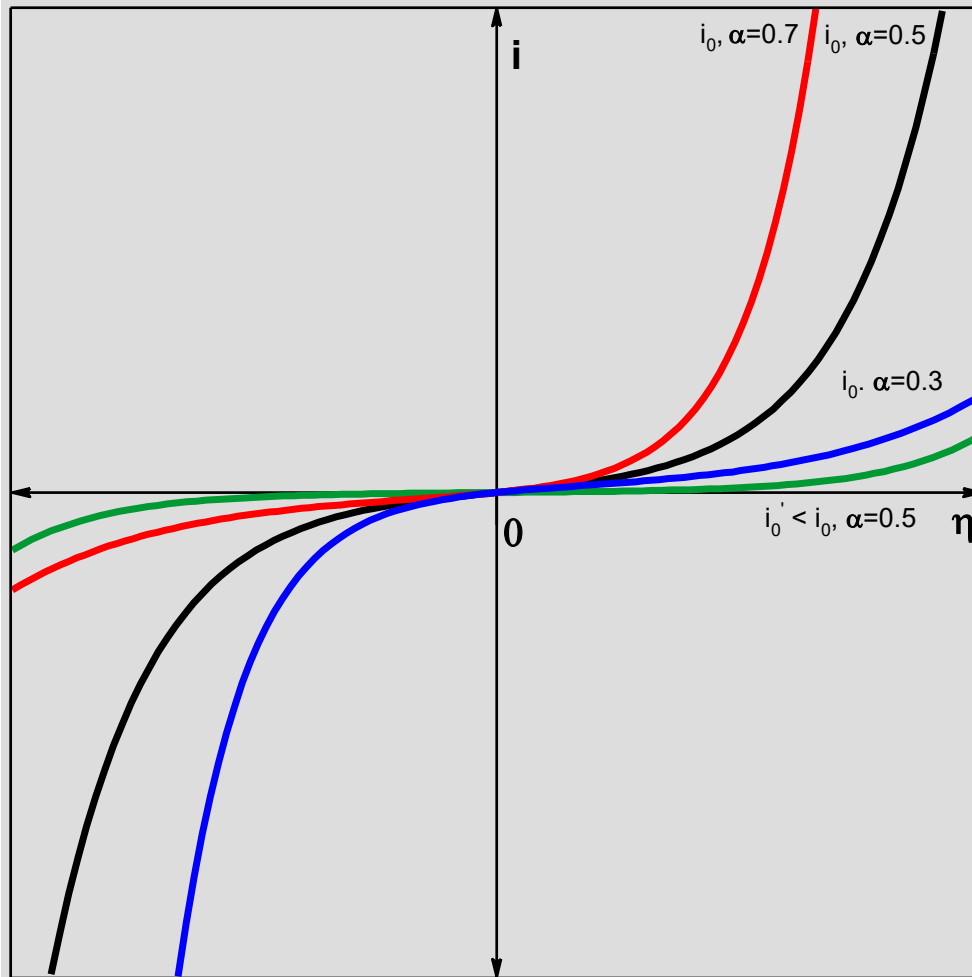
"The effect of this enormous field at the electrode-electrolyte interface is, in a sense, the essence of electrochemistry." [1]

[1] Bockris, Fundamentals of Electrochemistry, 2000

BUTLER-VOLMER AND TAFEL EQUATIONS



BUTLER-VOLMER AND TAFEL EQUATIONS



Exchange current density

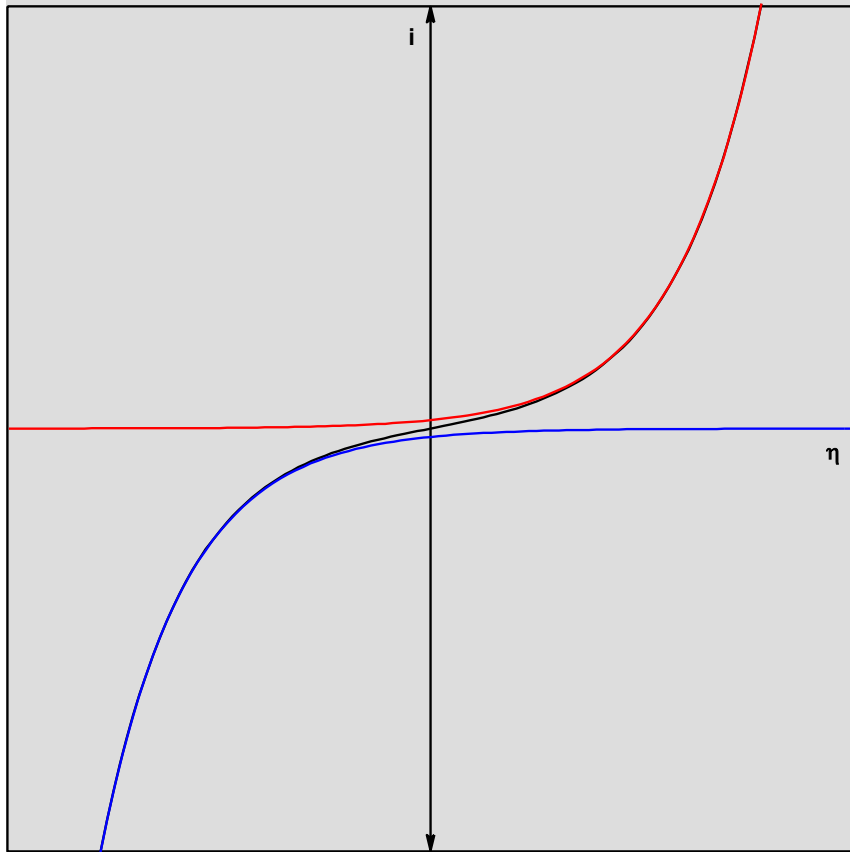
Depends on the species undergoing redox transformation and on the electrode material

In fact, large overpotential for hydrogen evolution on Hg surfaces enables us to observe reductions in aqueous solutions

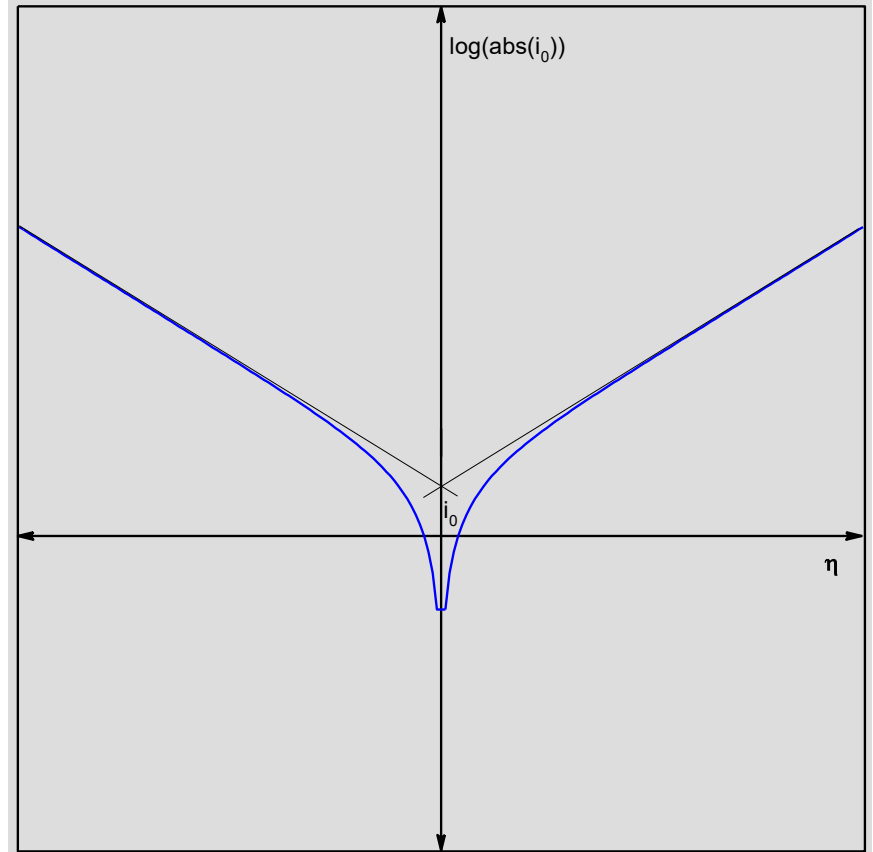
Also, the development of modern modified electrodes is based on finding the modifying layer which increase the exchange current density on the electrode surface

$$i = i_0 \left(\exp\left(\frac{(1-\alpha)nF}{RT}(E-E^\circ)\right) - \exp\left(\frac{\alpha nF}{RT}(E-E^\circ)\right) \right)$$

BUTLER-VOLMER AND TAFEL EQUATIONS



$$i = i_0 \left(\exp\left(\frac{(1-\alpha)zF}{RT}(E-E^\circ)\right) - \exp\left(\frac{\alpha zF}{RT}(E-E^\circ)\right) \right)$$



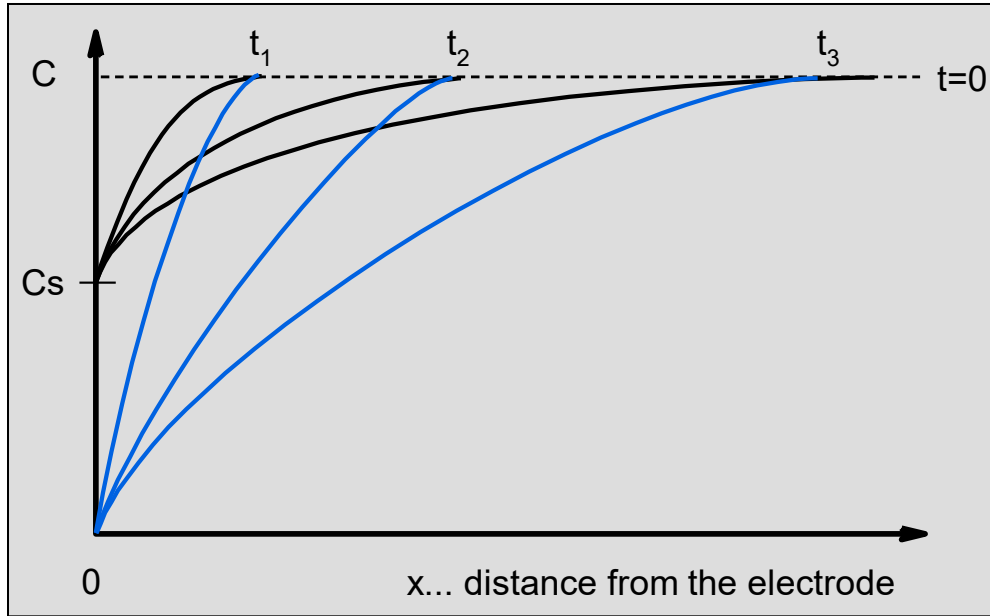
$$\log(i) = \log(i_0) - \left(\frac{2.303\alpha zF}{RT}(E - E^\circ) \right)$$

MASS TRANSFER

- Migration
- Convection
- Diffusion

We try to avoid migration by the addition excess supporting electrolyte

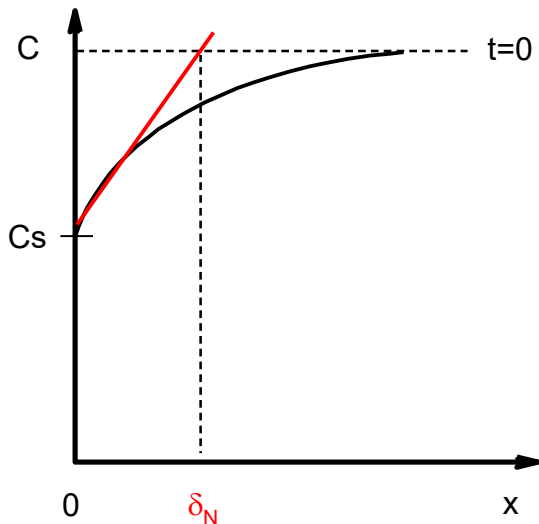
TRANSPORT BY DIFFUSION



1st Fick Law

$$j = -D \frac{\partial C}{\partial x}$$

$$i = zFD \left(\frac{\partial c}{\partial x} \right)_{x=0}$$



Nernst diffusion layer

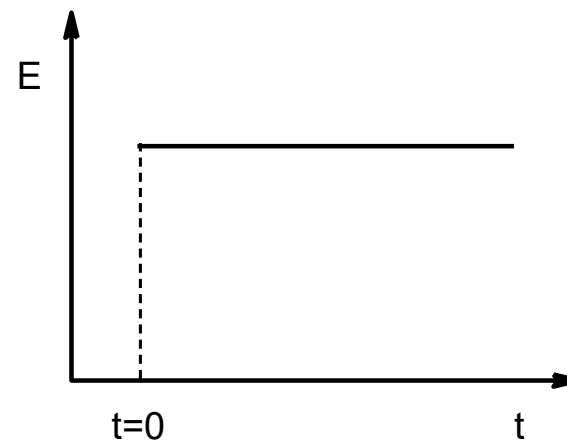
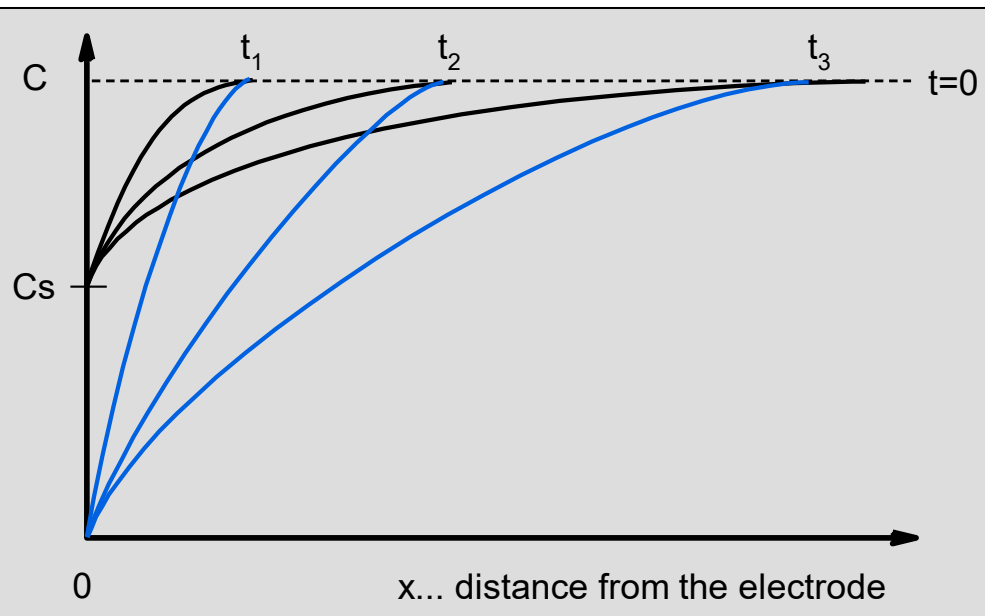
$$i = zFD \frac{C_0 - C_s}{\delta_N}$$

$$i_{\text{lim}} = zFD \frac{C_0}{\delta_N}$$

$$\eta_D = E - E' = \frac{RT}{zF} \ln \frac{C_s}{C_0}$$

$$\eta_D = E - E' = \frac{RT}{zF} \ln \left(1 - \frac{i}{i_{\text{lim}}} \right)$$

THE COTTRELL EQUATION



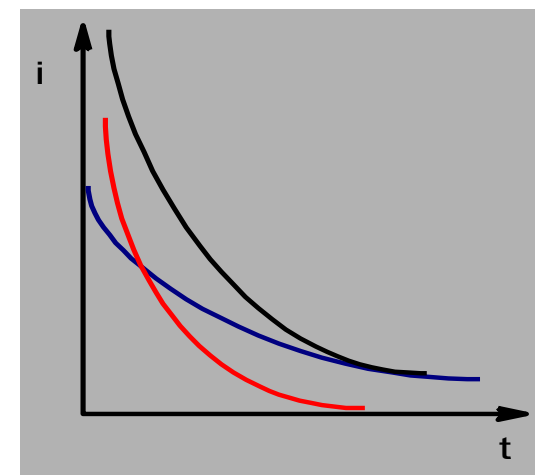
$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad \text{Second Fick's law}$$

Mathematical solution for boundary conditions of CA experiment is very complicated, but the result is simple:

$$i = zFD \frac{c_0 - c_s}{\sqrt{\pi Dt}}$$

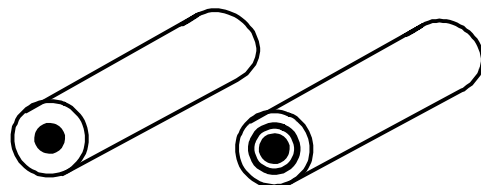
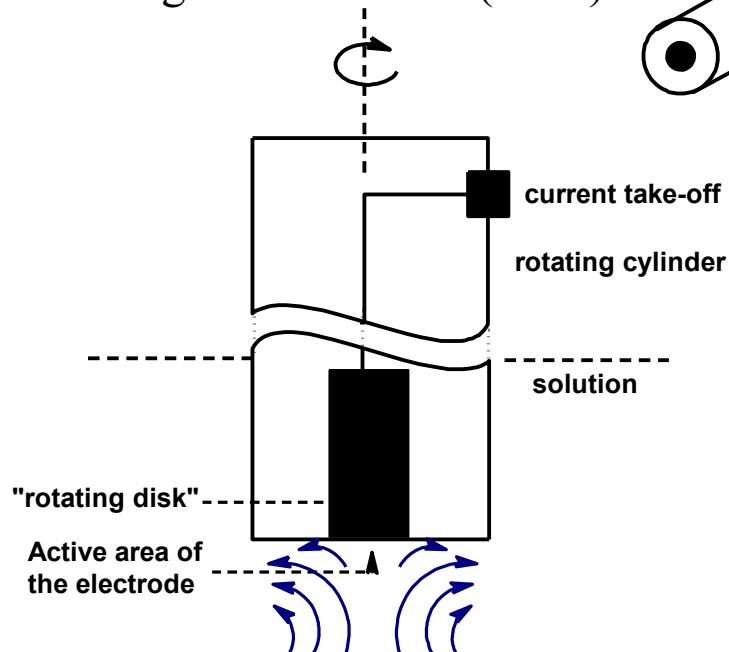


This is how Nernst layer thickness changes over time

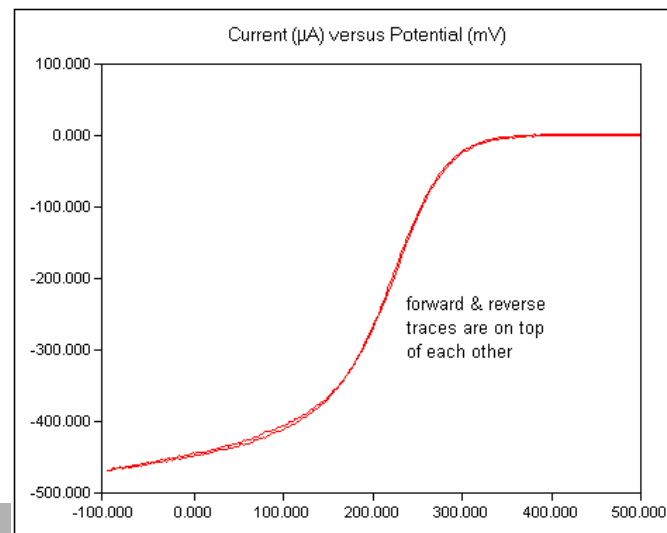
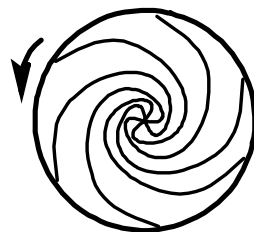


TRANSPORT BY CONVECTION

Rotating disk electrode (RDE)



Rotating ring disk electrode (RRDE)



$$I_L = (0,620) \cdot z \cdot F \cdot A \cdot D^{2/3} \cdot \omega^{1/2} \cdot \nu^{-1/6} \cdot c \quad \text{Levich Equation}$$

ω speed of rotation ($\text{rad} \cdot \text{s}^{-1}$),

ν kinematic viscosity of the solution ($\text{cm}^2 \cdot \text{s}^{-1}$),

kinematic viscosity is the ratio between solution viscosity and its specific weight.

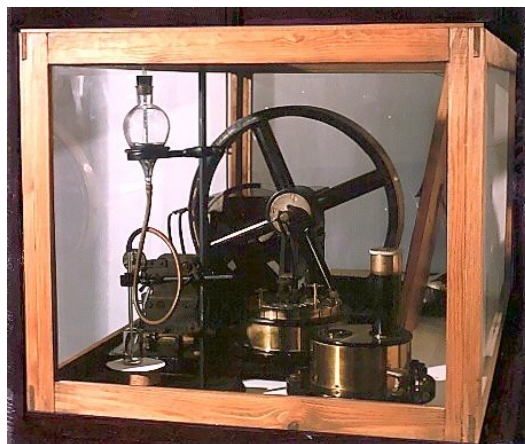
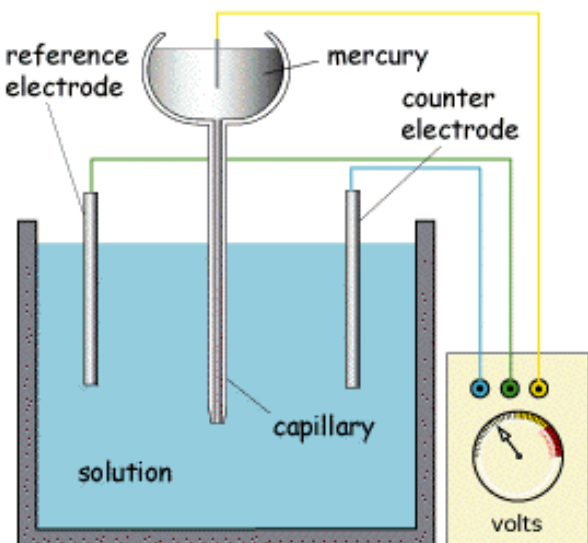
For pure water: $\nu = 0,0100 \text{ cm}^2 \cdot \text{s}^{-1}$, For $1.0 \text{ mol} \cdot \text{dm}^{-3} \text{ KNO}_3$ is $\nu = 0,00916 \text{ cm}^2 \cdot \text{s}^{-1}$

(at 20°C).

c concentration of electroactive species (in $\text{mol} \cdot \text{cm}^{-3}$, note unusual unit)

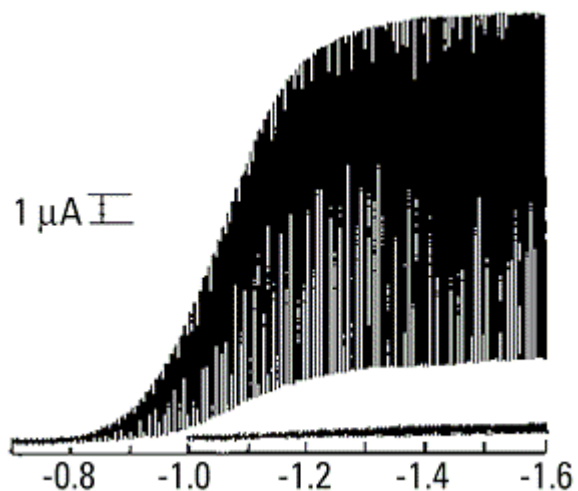
D diffusion coefficient ($\text{cm}^2 \cdot \text{s}^{-1}$), A electrode area in cm^2

POLAROGRAPHY



Halfwave potential

Limiting diffusion current (Ilkovic equation)

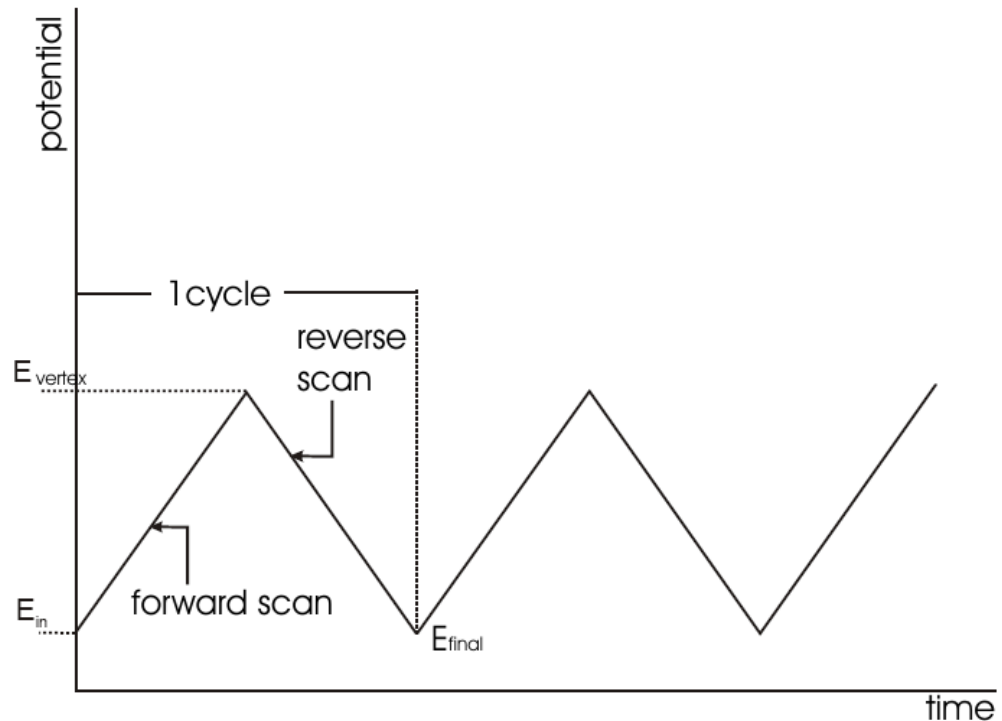
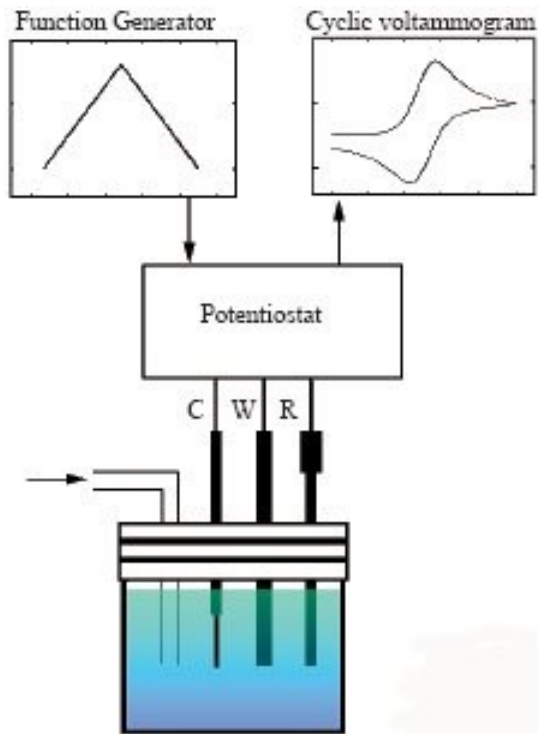


$$I_d = ckFnD^{1/2}m^{2/3}t^{1/6}$$

(I_d is diffusion current (A), (c) concentration of the depolarizer (mol/cm^3), k is a constant which includes π and the density of mercury, and with the Faraday constant (F) has been evaluated at 708 for max current and 607 for average current, D is the diffusion coefficient of the depolarizer in the medium (cm^2/s), n is the number of electrons exchanged in the electrode reaction, m is the mass flow rate of Hg through the capillary (mg/sec), and t is the drop lifetime in seconds, and c is depolarizer concentration in mol/cm^3).

CYCLIC VOLTAMMETRY

CV – the most important electrochemical method



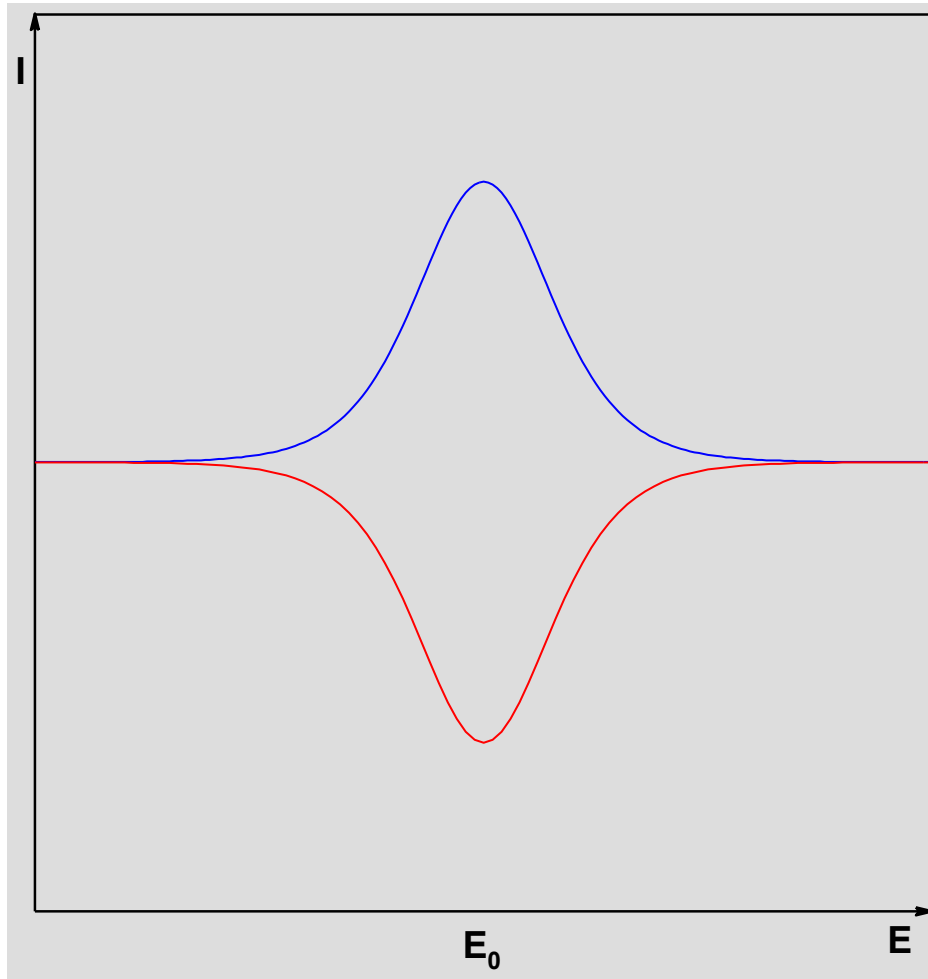
One or more cycles ... CV
Half cycle ... LSV

$$0 \leq t \leq t_r : E = E_i + vt$$

$$t_r \leq t \leq 2t_r : E = E_i + v(t - t_r)$$

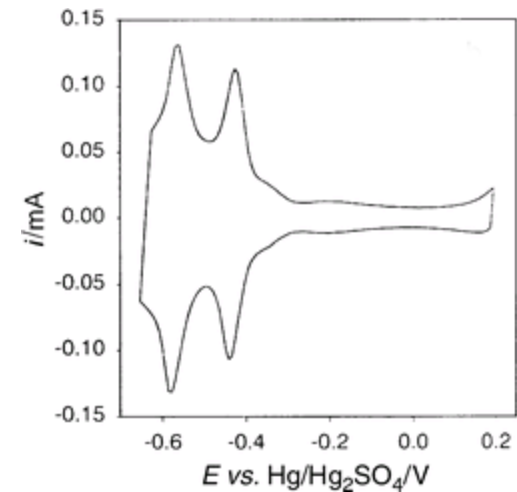
v... the scan rate

REVERSIBLE CYCLIC VOLTAMMOGRAM

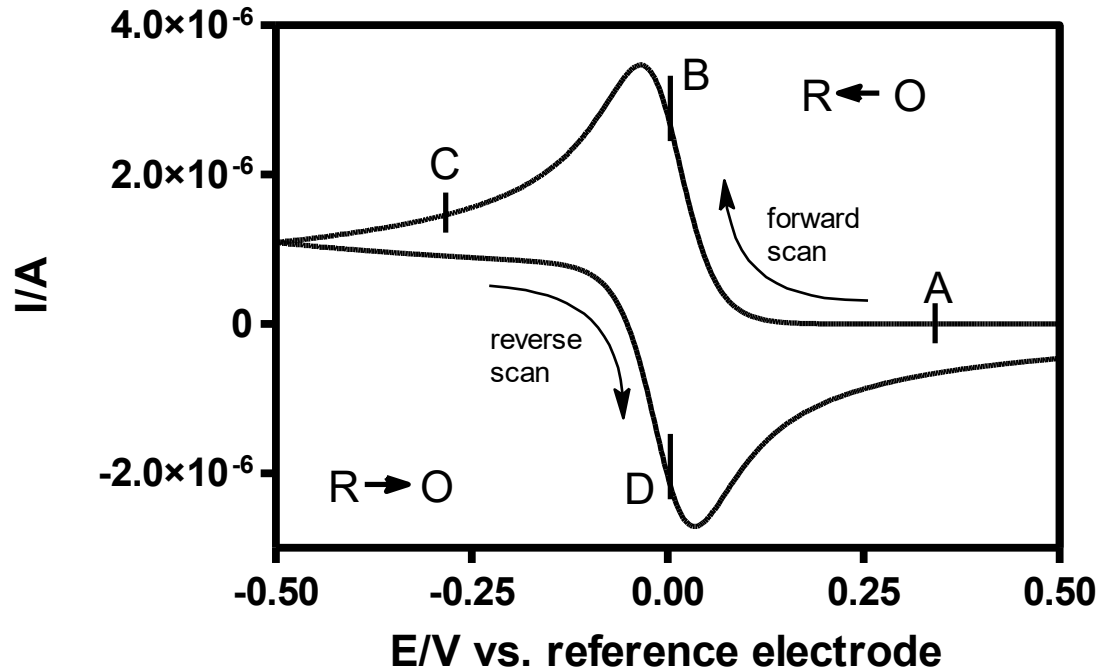


Electroactive species attached to the electrode, both redox forms stable

$$I = FA\Gamma_0\nu \frac{F}{RT} \frac{\exp\left[\frac{F}{RT}(E - E^0)\right]}{\left\{1 + \left[\exp\frac{F}{RT}(E - E^0)\right]\right\}^2}$$



REVERSIBLE CYCLIC VOLTAMMOGRAM



Electroactive species in solution, both stable

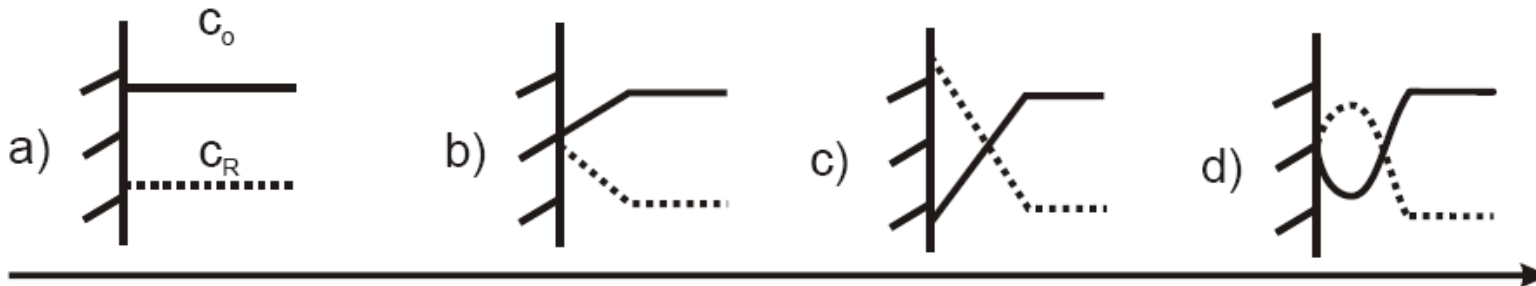
IUPAC convention

Peak separation is $59/z$ mV

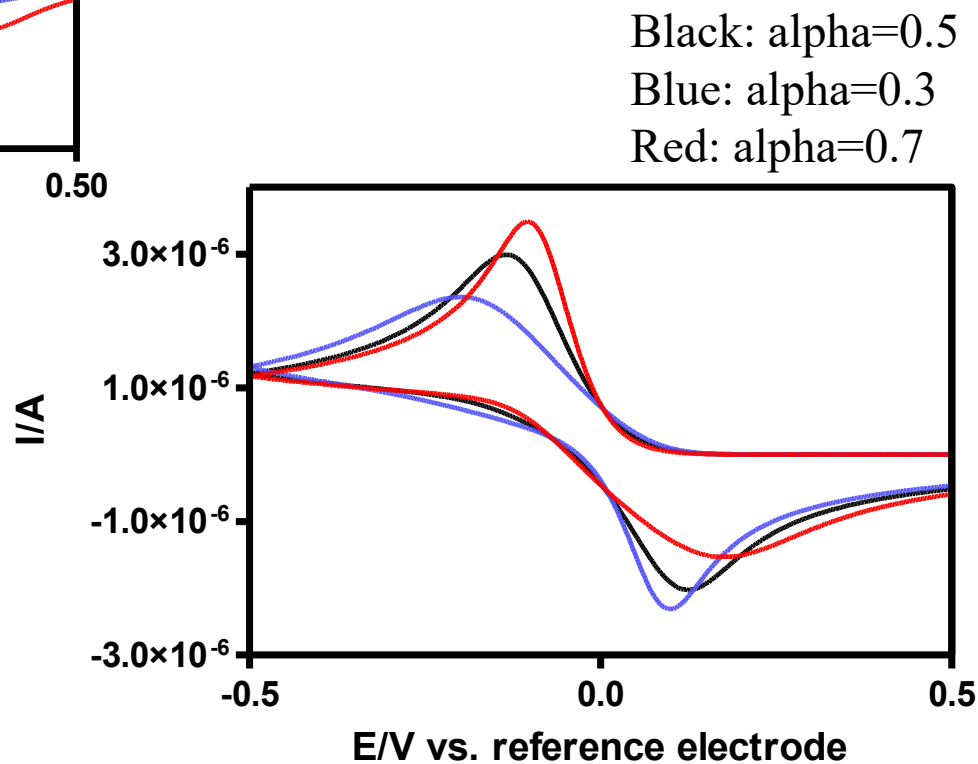
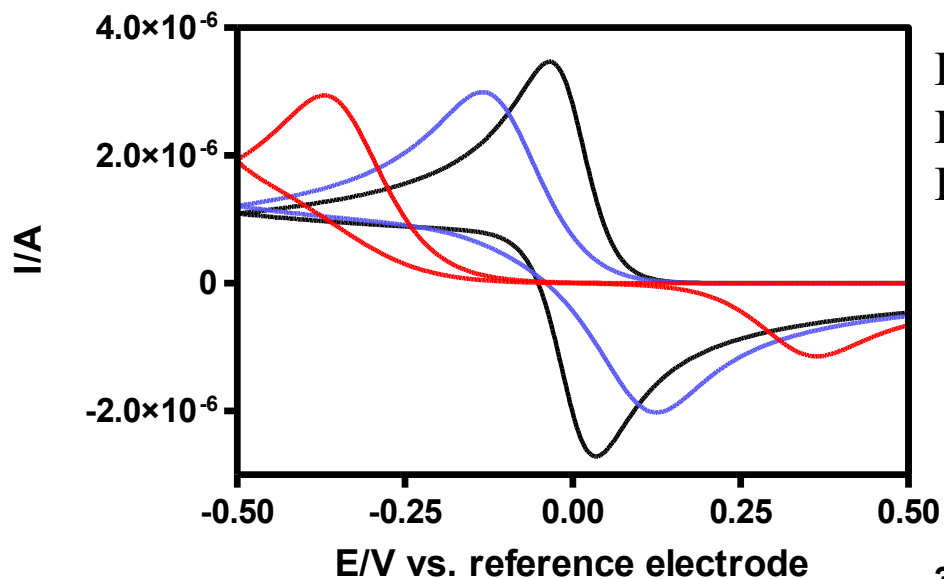
Randles-Sevcik equation:

$$I_{pc} = I_{pa} = 2,69 \cdot 10^5 \cdot A \cdot z^{3/2} \cdot D^{1/2} \cdot c \cdot v^{1/2}$$

A in cm^2 , D in $\text{cm}^2\text{s}^{-1/2}$, c in molcm^{-3} , v in V/s



QUASI AND IRREVERSIBLE VOLTAMMOGRAMS

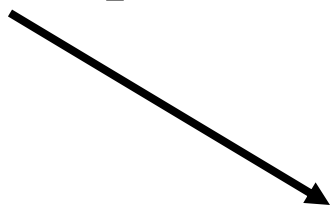


BASIC MECHANISMS IN CV

E, C notation

(E... electron transfer,

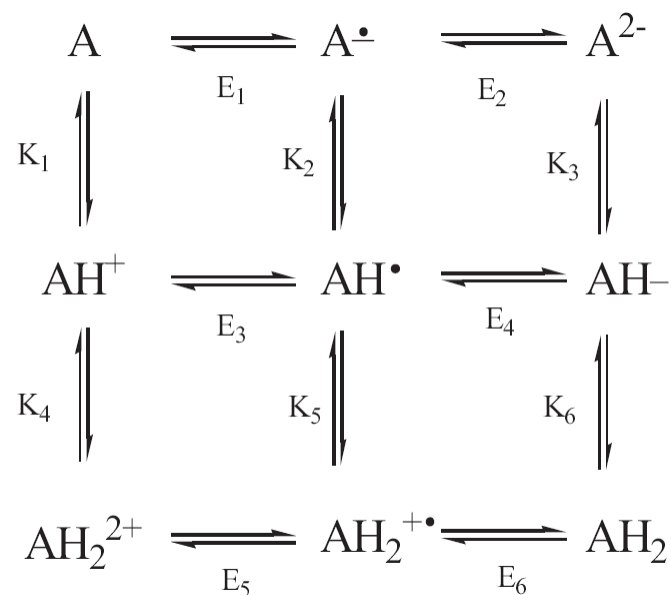
C... coupled chemical reaction)



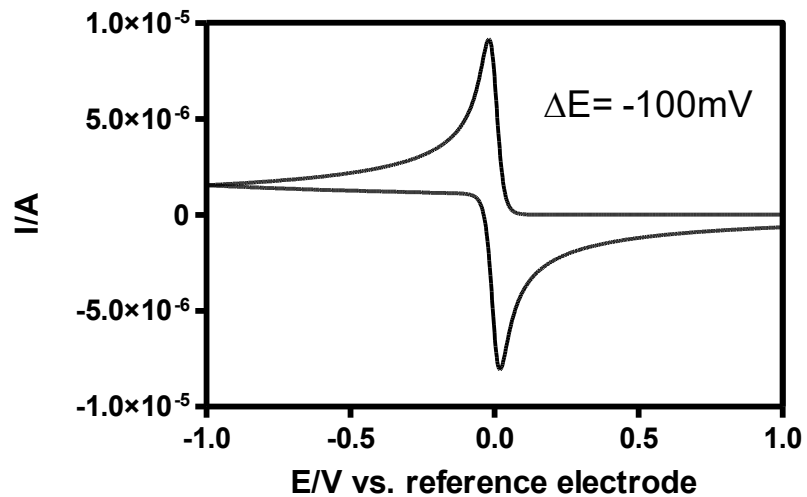
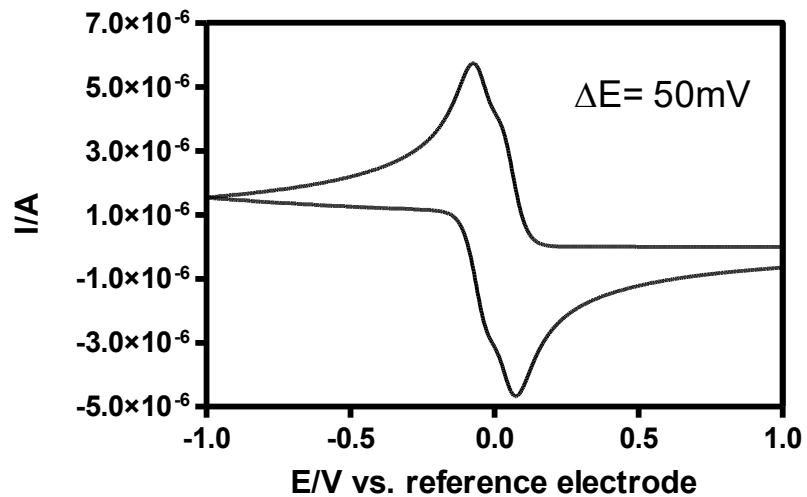
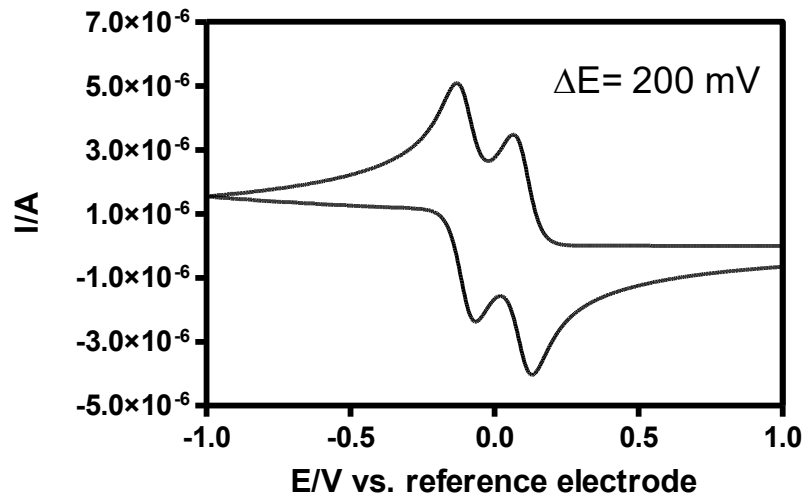
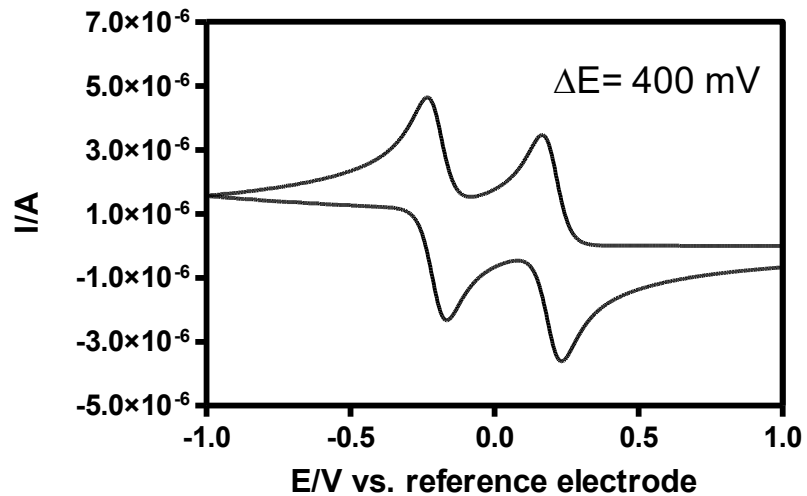
E, EE, CE, EC, ECcat etc.

Mechanisms can be very complex
even for simple systems

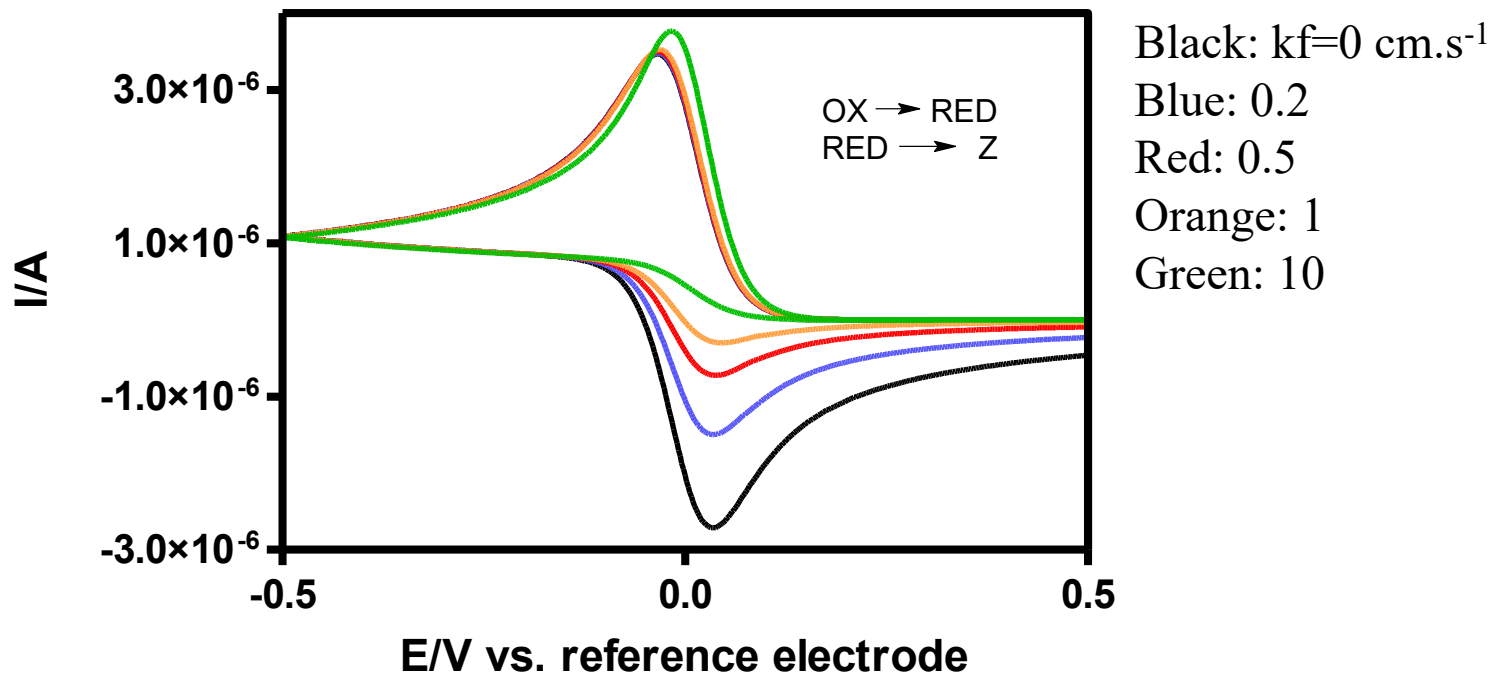
Two electron-two proton system =
„square scheme“



THE EE MECHANISM



THE EC MECHANISM



There are many variations of this mechanism:

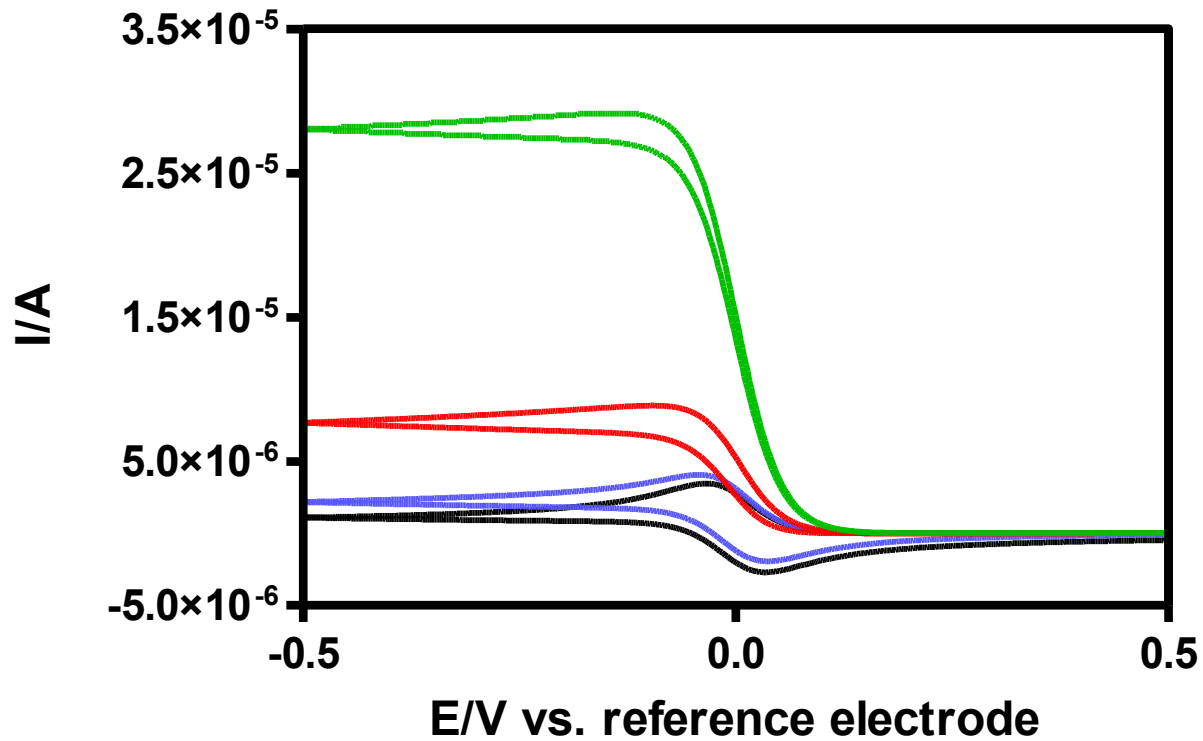
Reaction with solvent

Dimerization

Radical substrate reaction

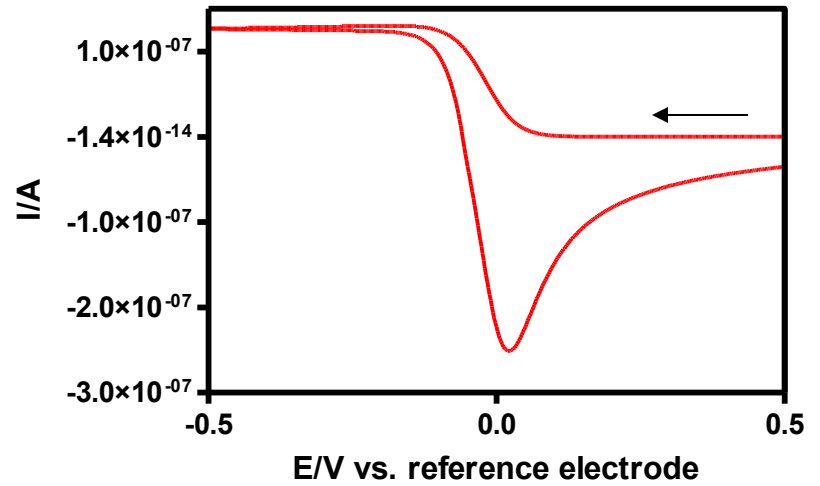
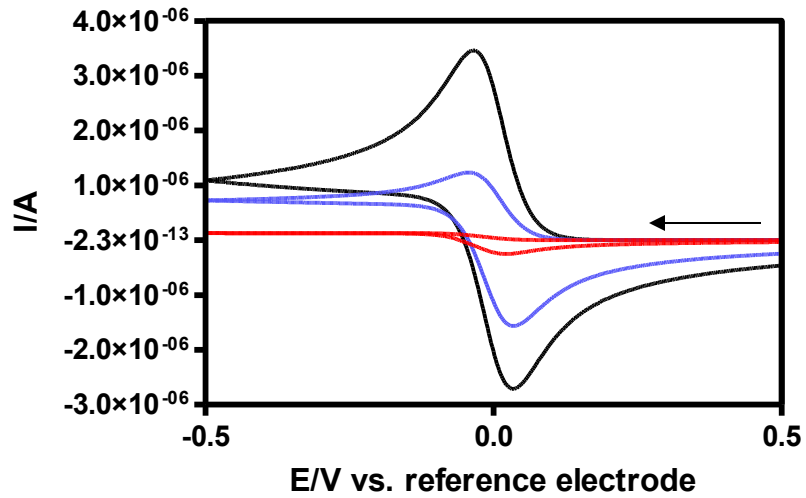
EC catalytic ... etc.

EC catalytic



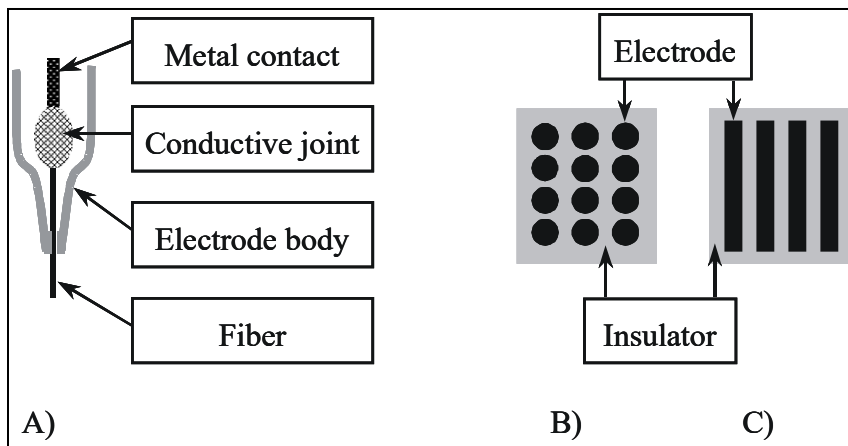
Black : no A
Blue: A ($c=1$)
Red: A ($c=10$)
Green: A ($c=100$)

THE CE MECHANISM

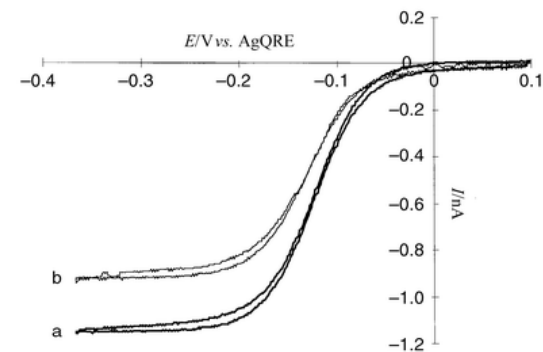
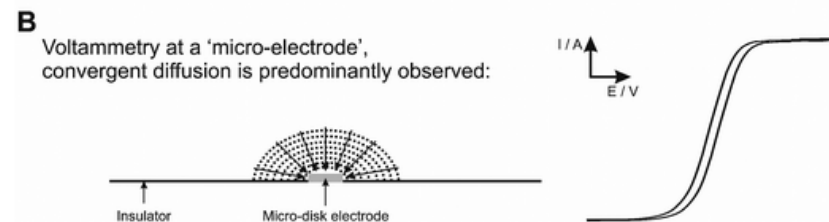
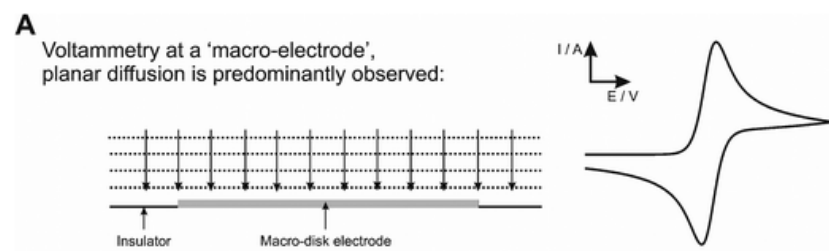


MICROELECTRODES

Microelectrode: at least one dimension must be comparable to diffusion layer thickness (sub μm upto ca. $25 \mu\text{m}$). Produce steady state voltammograms.



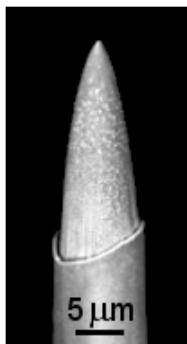
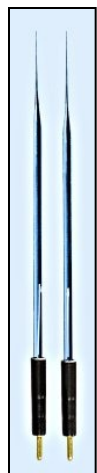
Converging diffusional flux



$$I = nFADc_0 \left(\frac{1}{\delta} + \frac{1}{r} \right) \quad \delta = \sqrt{2\pi Dt}$$

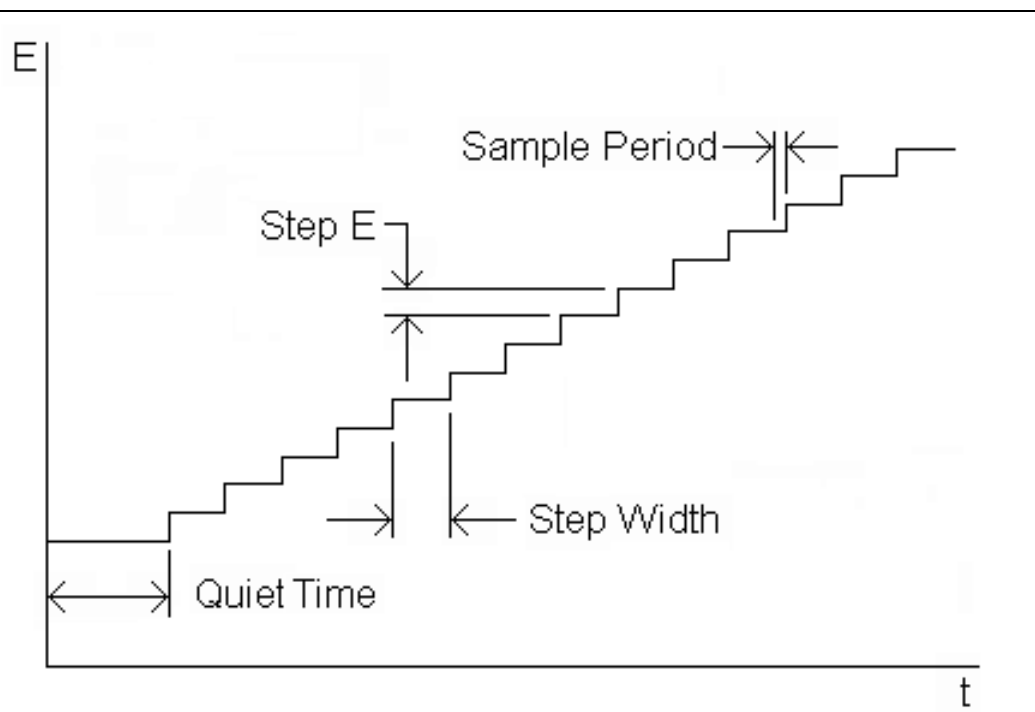
Advantages of microelectrodes:

- fast mass flux - short response time (e.g. faster CV)
- significantly enhanced S/N (I_F / I_C) ratio
- high temporal and spatial resolution
- measurements in extremely small environments
- measurements in highly resistive media

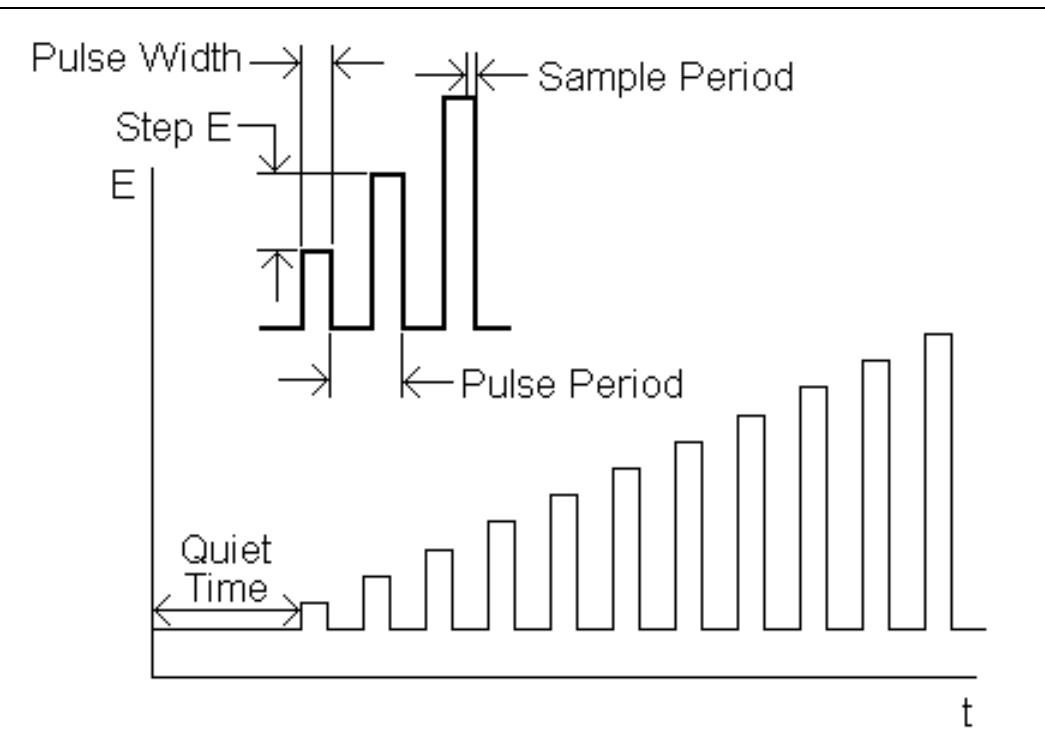


PULSED TECHNIQUES

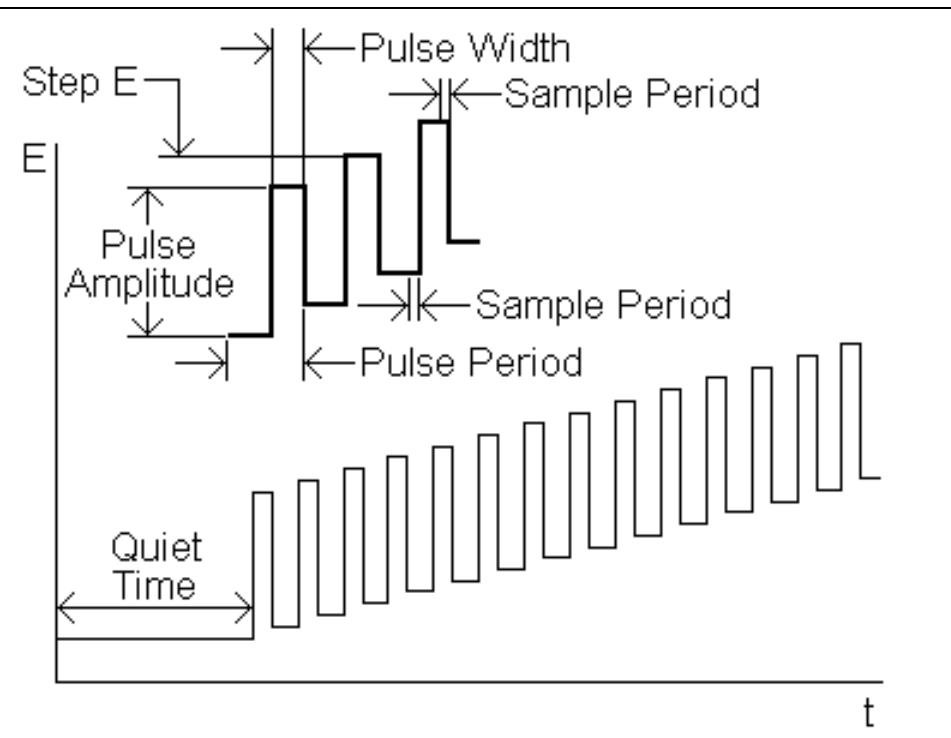
TAST POLAROGRAPHY SAMPLED DC POLAROGRAPHY



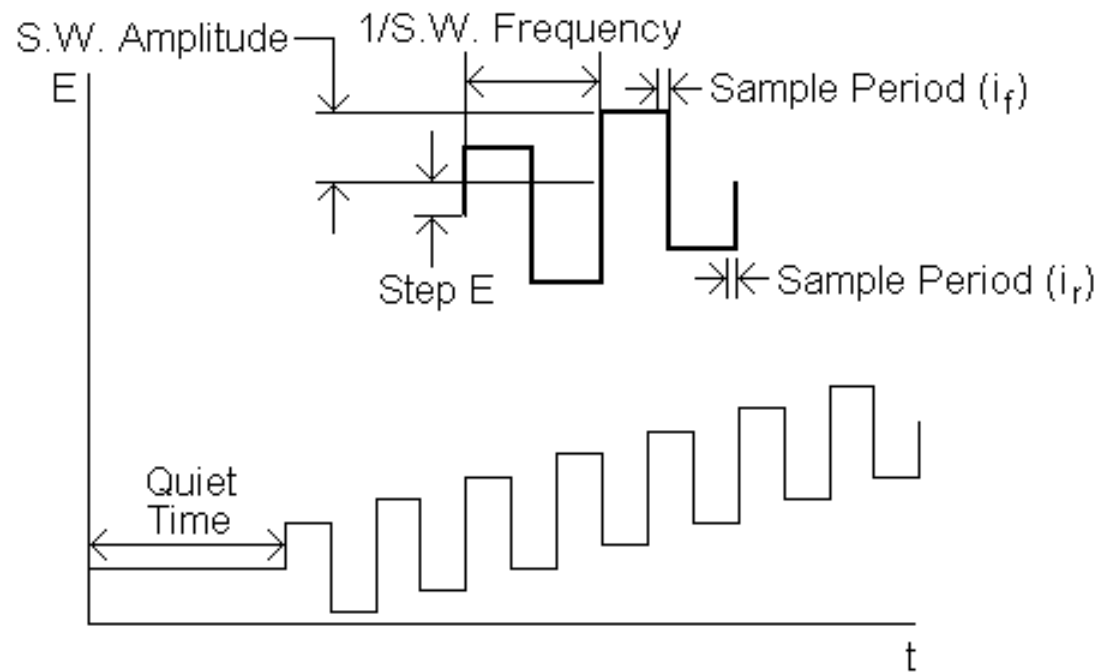
NORMAL PULSE VOLTAMMETRY



DIFFERENTIAL PULSE VOLTAMMETRY



SQUARE WAVE VOLTAMMETRY



AC voltammetry

