BASIC ELECTROCHEMISTRY

$$= E^\circ - \frac{RT}{nF} \ln \frac{C_B}{C_O}$$

THE CHARGE AND CURRENT

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

Element of charge: $1.602 \cdot 10^{-19}$ C
The energy change is $\pm 1.602 \cdot 10^{-19}$ J if we move the charge across the potential drop of 1V
If we do the same with 1 mol of charges, we obtain…
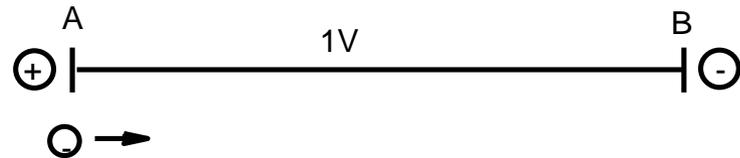
The current is the change of charge per time

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

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"

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

$$m = \frac{MIt}{zF}$$

$$m = \frac{M \int\limits_{t=0}^{t} Idt}{zF}$$

Area under current-time curve (and freqently 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

$$R \approx \frac{l}{A} \, (\Omega)$$

$$R = \frac{E}{I} \, (Ohm\acute{s} \, law)$$
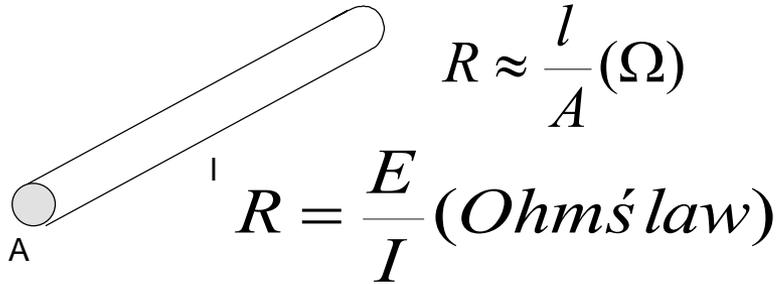
$$G = \chi \frac{A}{l}$$

The unit for conductivity is Siemens, what is the unit of specific conductivity?
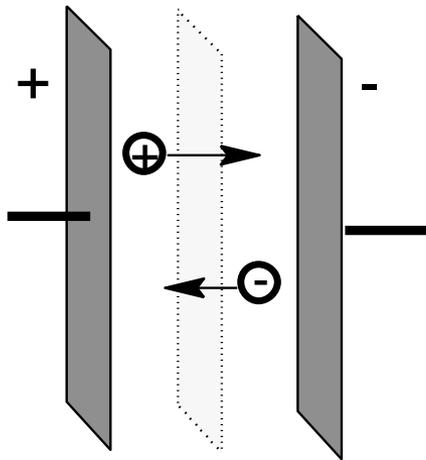
For species $K_X A_Y$:
Migration velocities can be different
Stokes force is balanced by force induced by electric field
Only the cations distant from the plane by v_A or nearer will cross the plane. In unit field (1V) and unit area will cross the boundary $xc\alpha F z_{cat} u_{cat}$ cations

$$\chi = xc\alpha F z_{cat} u_{cat} + yc\alpha F z_{an} u_{an}$$

CONDUCTIVITY
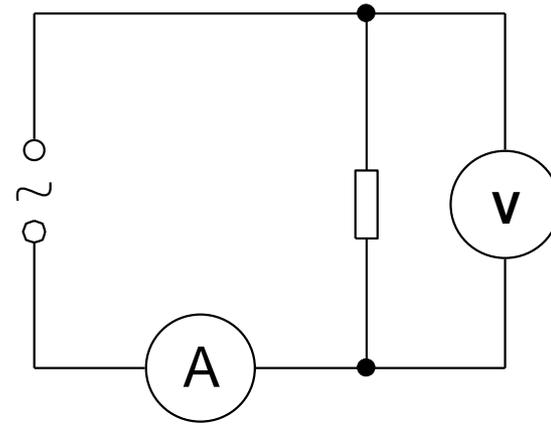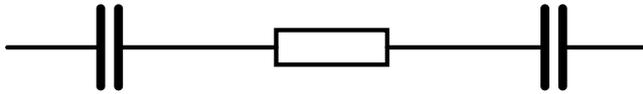
Solutions can have different concentrations:

$$\Lambda = \frac{\chi}{c} \left[\frac{S}{m} \frac{m^3}{mol} = Sm^2 mol^{-1} \right]$$
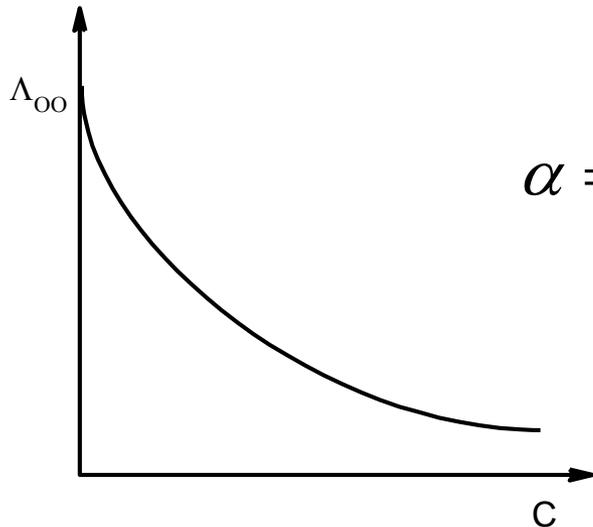
This is used for measurements of dissociation constants:

$$AB \rightleftharpoons A^+ + B^-$$

$$c(1-\alpha) \qquad c\alpha \qquad c\alpha$$

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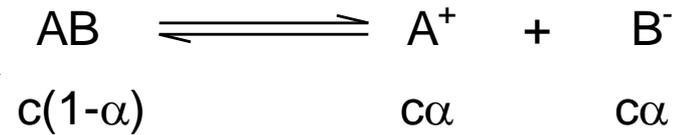
$$K_D = \frac{c^2 \alpha^2}{c(1-\alpha)} = \frac{c\left(\dfrac{\Lambda}{\Lambda_\infty}\right)^2}{1 - \dfrac{\Lambda}{\Lambda_\infty}}$$

HOW AND WHERE THE POTENTIAL DIFFERENCE DEVELOPS

solution 1

solution 2

membrane
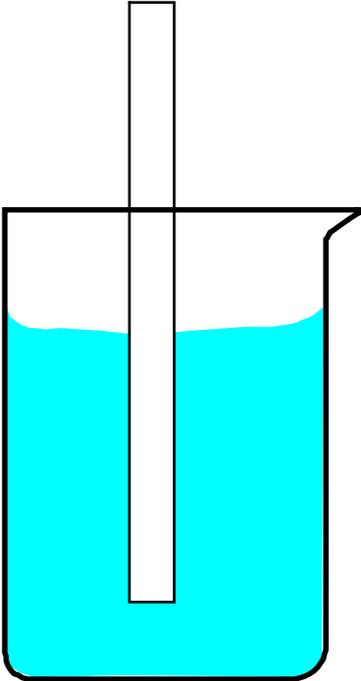
Junction potential (Henderson)

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

$$Zn \mid ZnSO_4 \mid\mid CuSO_4 \mid Cu$$
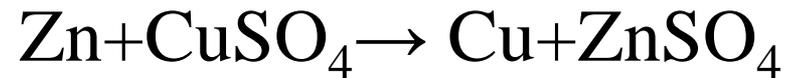
$$Zn + CuSO_4 \rightarrow Cu + ZnSO_4$$

$$zFE_{MN} = RT \ln \frac{[Cu][ZnSO_4]}{[Zn][CuSO_4]}$$

…is it OK?
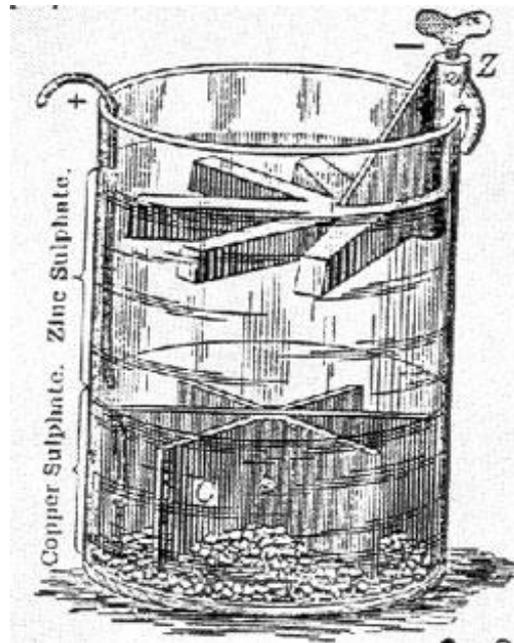
BACK TO NERNST EQUATION

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

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

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

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

$$(at\ 25°C)$$

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.

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

Zn in $ZnCl_2$, Ag in $AgNO_3$, Cu in $CuSO_4$ 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)

H₂ gas 1.0 atmosphere

Pt electrode coated with Pt black

$A_{H^+} = 1.0$
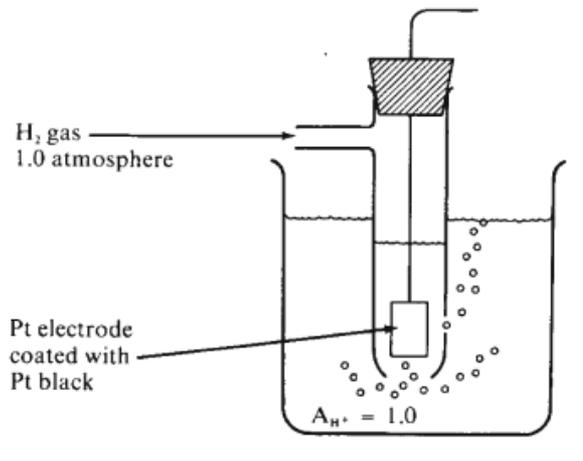
Fig. 2 From: *Quantitative analysis*, 6th edn., R.A. Day Jr. and A.L. Underwood, Prentice-Hall, Englewood Cliffs, 1991 p. 262 (Fig. 10.4)

Platinum

H₂, 1.0 atm.

H⁺, 1.0 m
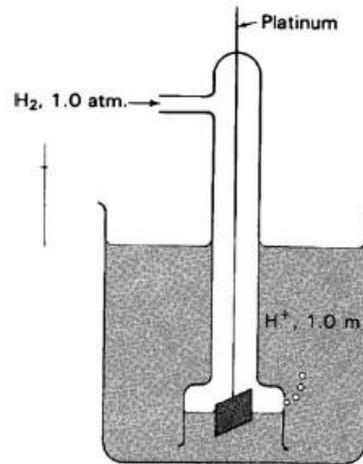
Fig. 3 From *Undergraduate instrumental analysis*, 6th edn., J.W. Robinson, E.M. Skelly Frame, and G.M. Frame II, Dekker, New York, 2005, p. 925 (Fig. 15.4)

H₂ gas, 1 atm

H₂ gas, 1 atm

1 M HCl

pre-saturator

to salt bridge

Pt

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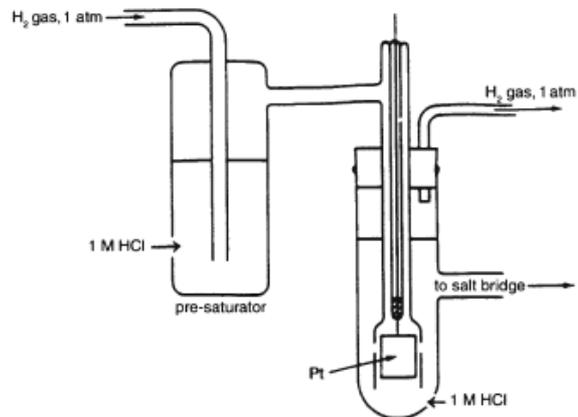
Anal Bioanal Chem (2008) 392:9–10
DOI 10.1007/s00216-008-2227-1

ANALYTICAL CHALLENGE

THE HYDROGEN ELECTRODE

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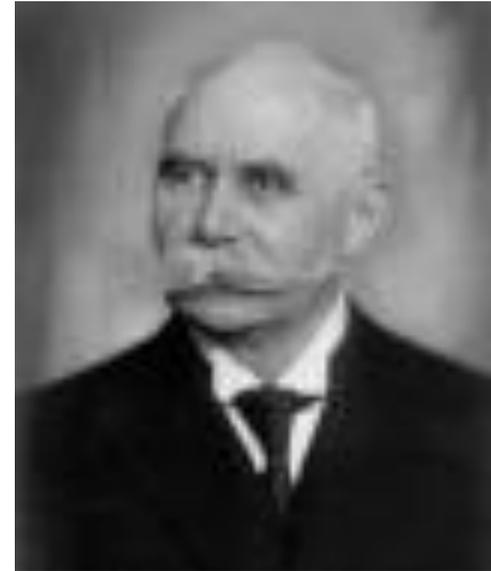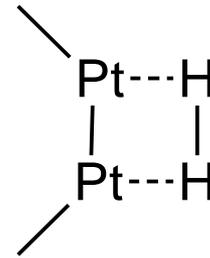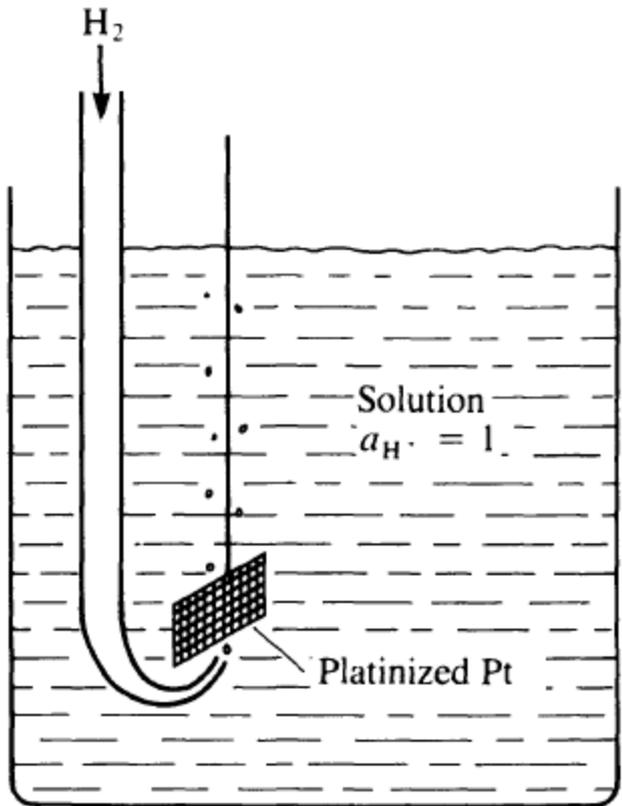
$$E = E^0_{H_{at}/H^+} - \frac{RT}{F} \ln \sqrt{KK_H p_{H_2}} + \frac{RT}{F} \ln[H^+]$$

ELECTRODES OF THE SECOND KIND

Argentochloride Ag | AgCl | KCl | |
Calomel Hg | Hg_2Cl_2 | KCl | |
Mercurysulphate Hg | Hg_2SO_4 | K_2SO_4 | |

0   197 mV   244 mV   640 mV

SHE   sat. Ag/AgCl   SCE   sat. Hg/Hg_2SO_4

Contact wire

Hg

Hg_2Cl_2/Hg paste

Saturated KCl

REDOX ELECTRODES

Redox
Electrode

Redox sensitive
Pt band

Fe^{2+}

Fe^{3+} e- Fe^{3+}

e-

Fe^{3+}

Fe^{2+}
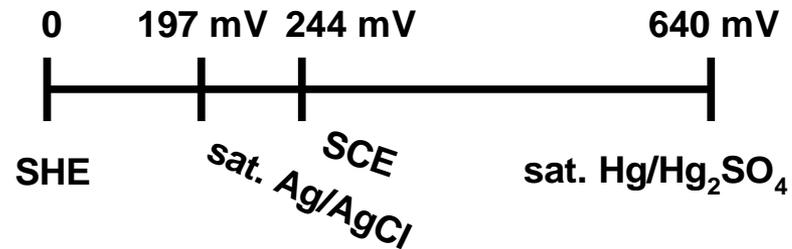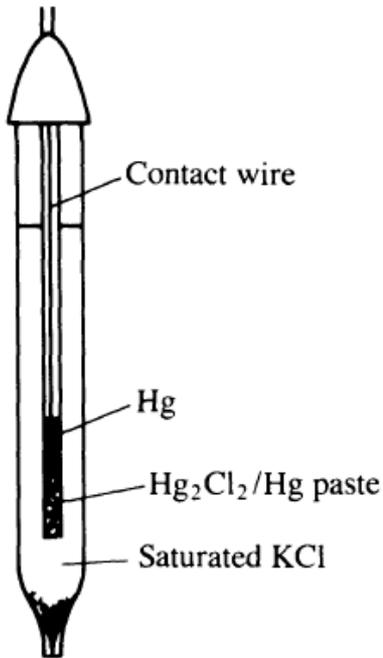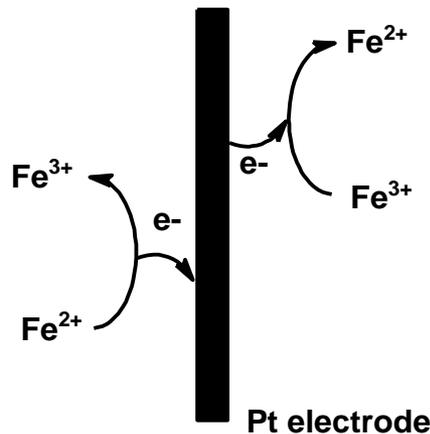
Pt electrode

The electrode serves as an electron sink

Redox combo

..just a curiosity

$$Zn \mid Zn_2C_2O_4 \mid CaC_2O_4 \mid CaCl_2 \mid\mid$$

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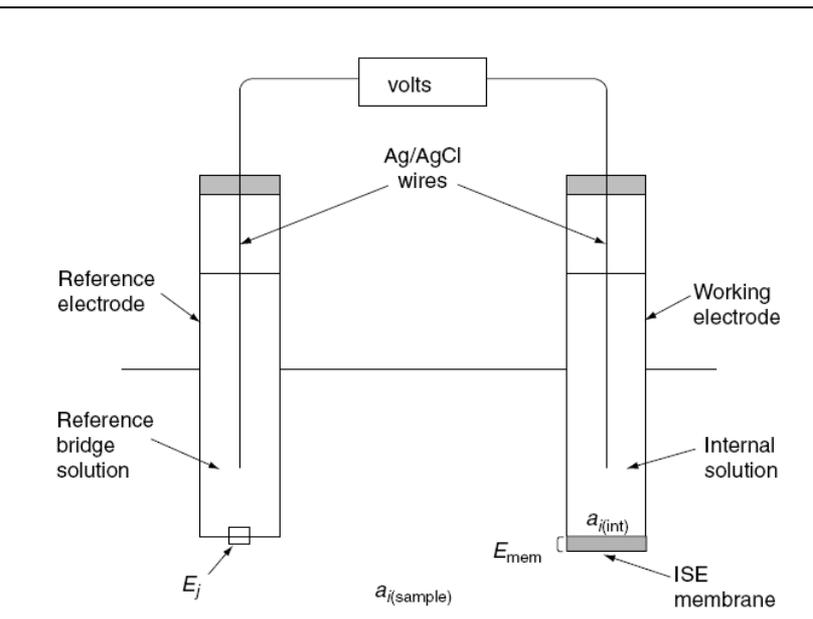
Membrane potential reflects the gradient of activity of the analyte ion in the inner and outer (sample) solutions.

• 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
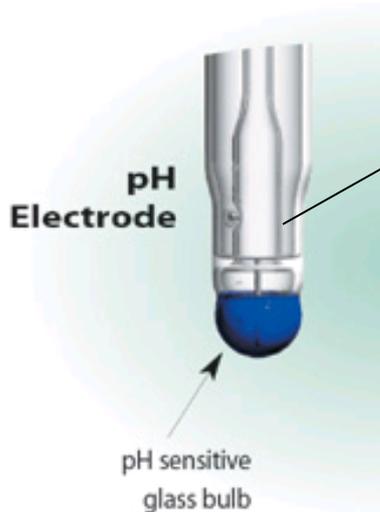
Liquid junction for reference electrode (sometimes is high)
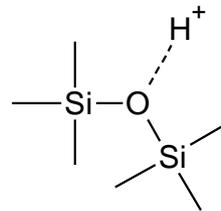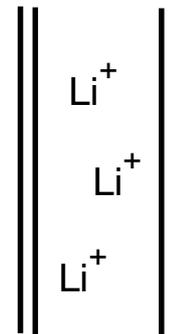
hydrated Haugaard layers

Li ions partially free

400 MΩ

Nikolski eq.

$$E = E_{assym} + \frac{RT}{F} \ln a_{H_3O^+} + X \cdot \frac{RT}{F} \ln a_{Na^+}$$

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~10 mm, thickness: 1-2 mm. Conductivity: doping or nonstechiometry, 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 compouds selectively binding the analyte in their cavities)
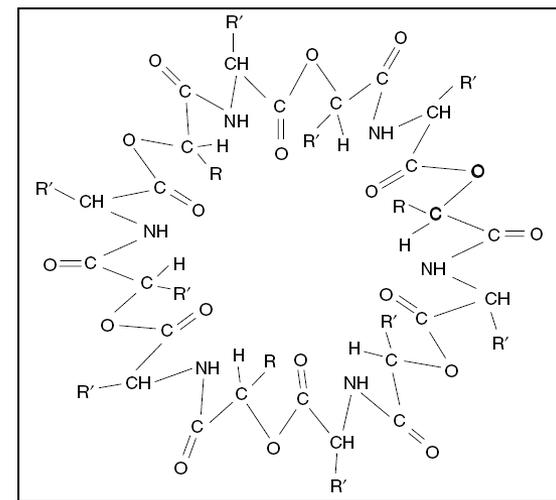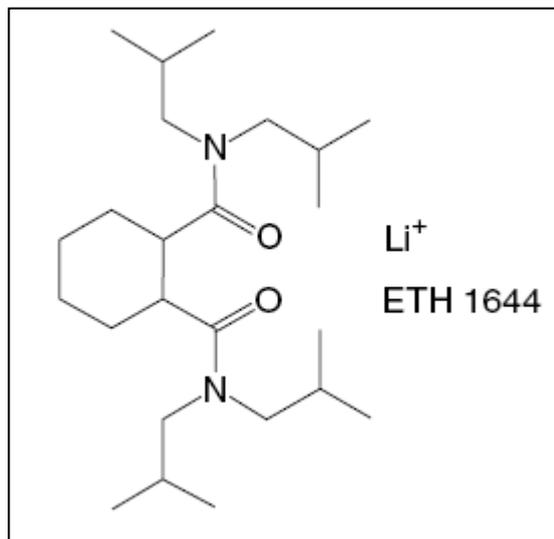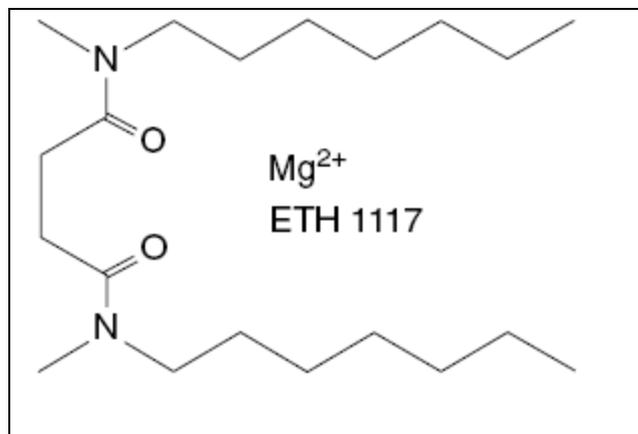
POTENTIOMETRY

Cell and voltmeter behaves as a voltage divider circuit

E(cell)

Ri

RM   **V**

E(measured)

E 1

R1

R2

E 2
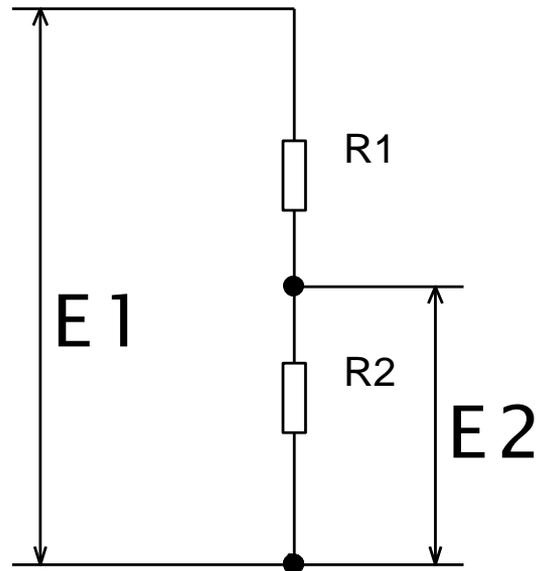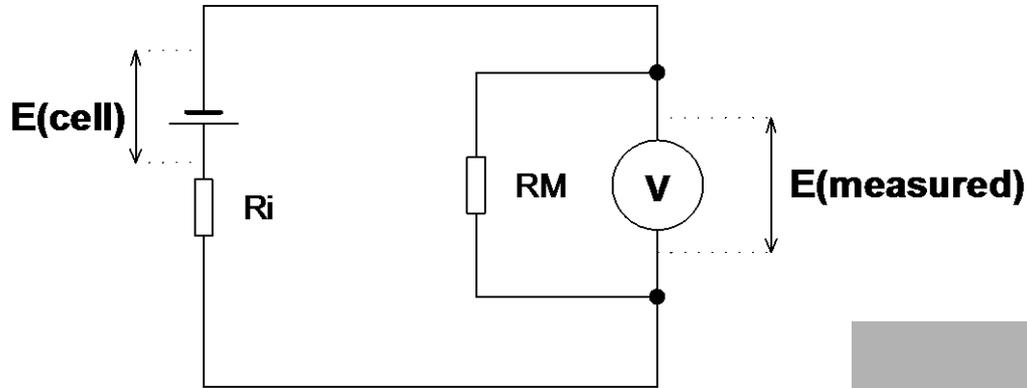
$$E_2 = E_1 \frac{R_2}{R_1 + R_2}$$

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

POTENTIOMETRY AND PHYSICAL CHEMISTRY

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

$$\text{Pt} \mid H_2 \mid HCl \mid AgCl \mid Ag$$

$$\text{Ag} \mid AgNO_3 \mid \mid KNO_3 \mid \mid KX, AgX \mid Ag$$

$$\text{Pt} \mid H_2 \mid KOH \mid \mid KCl \mid AgCl \mid Ag$$

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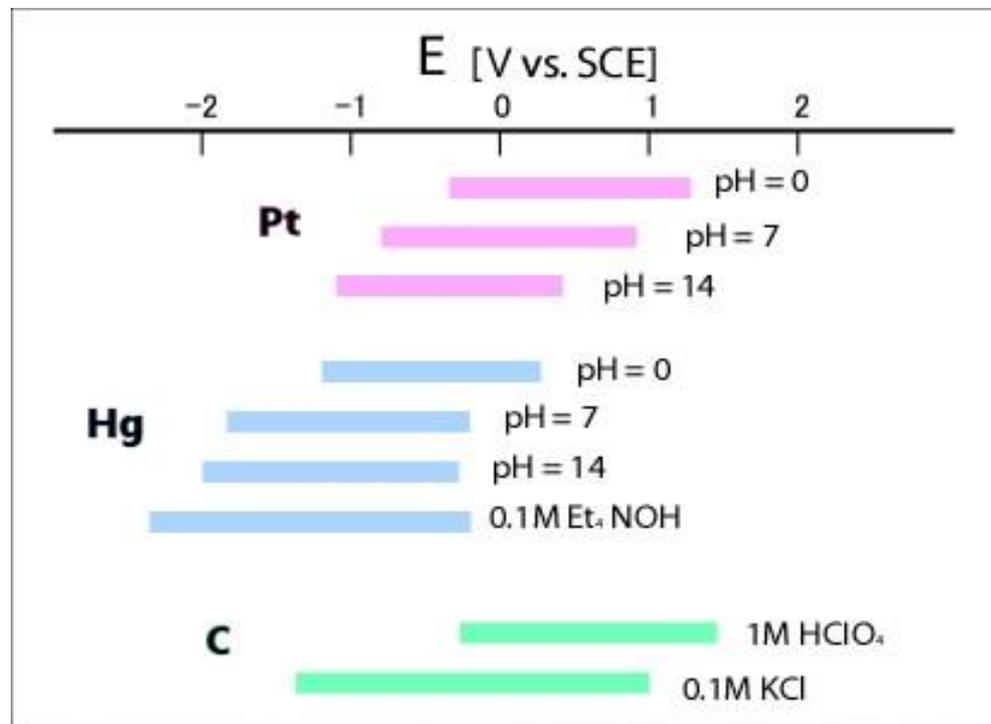
Potential window available for experiments is determined by destruction of electrode material or by decomposition of solvent (or dissolved electrolyte)

ELECTRON TRANSFER PHENOMENON

1-10 nm

Electrode surface

Solvated ions

IHL   OHL
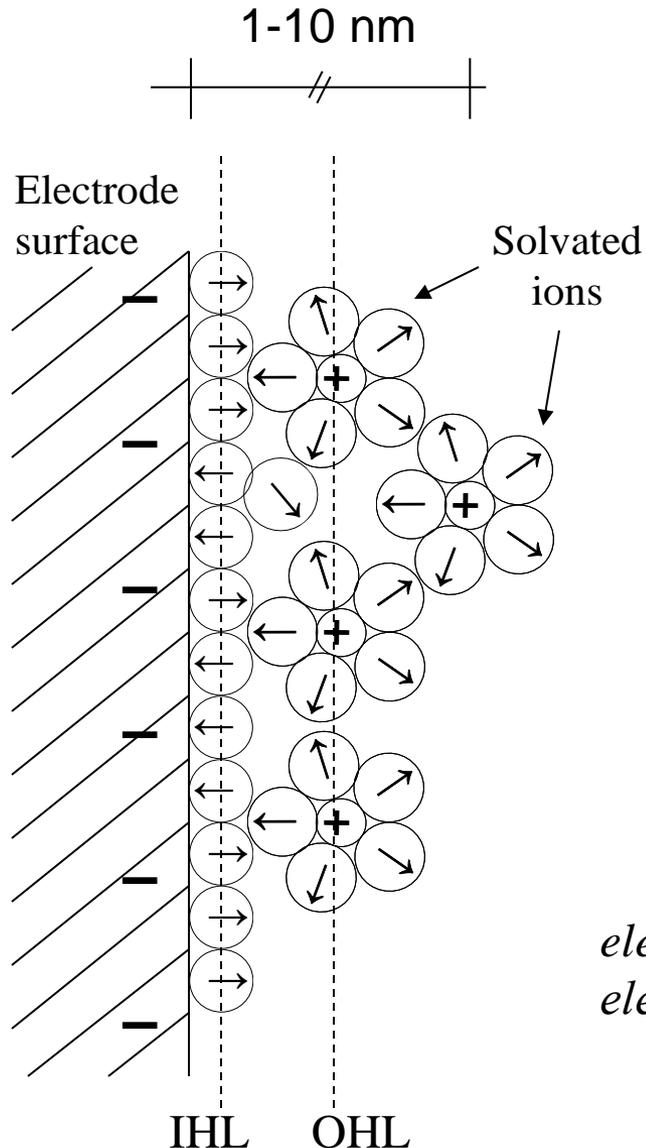
The double-layer region is:

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 $10^{7\text{-}8}$ 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 Electrodics, 2000
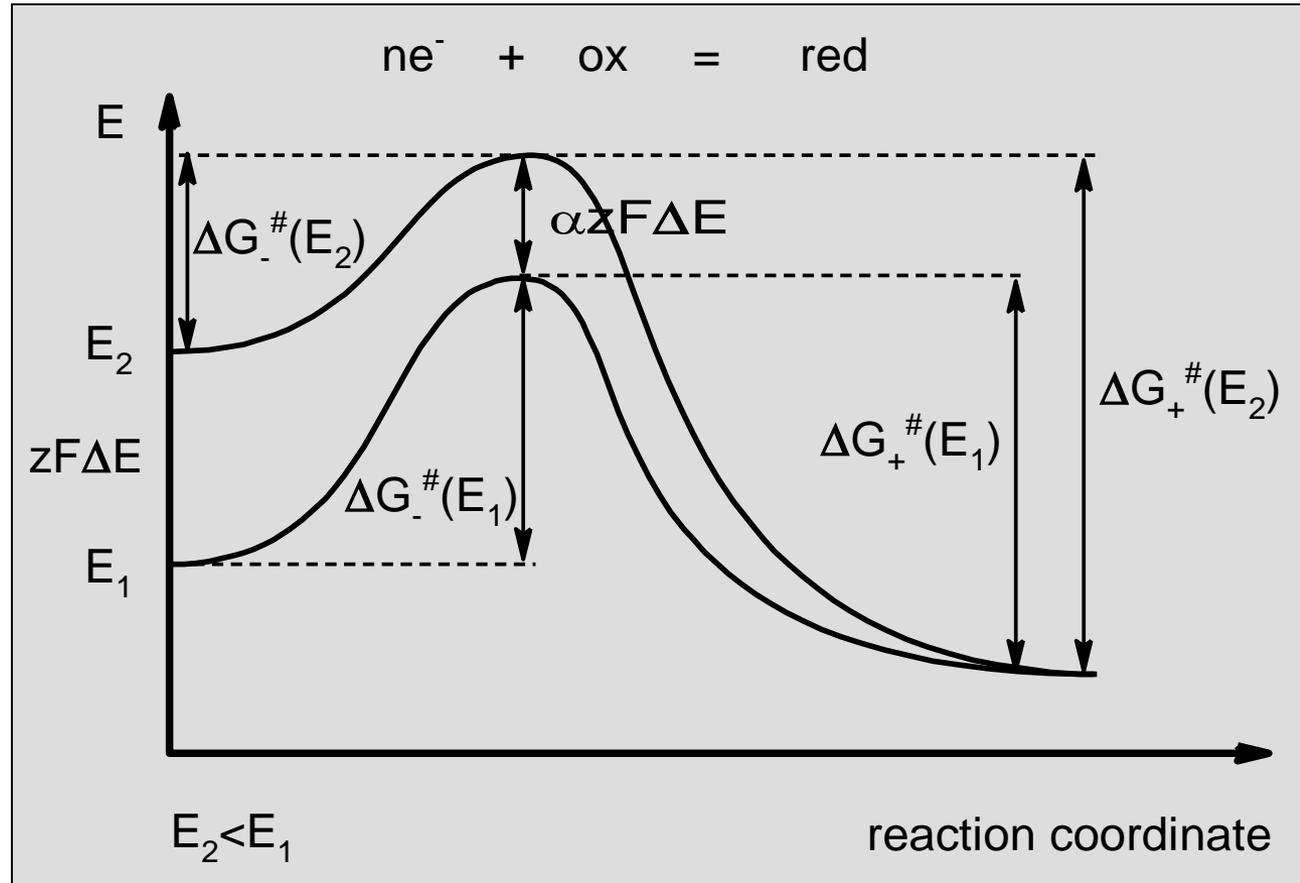
BUTLER-VOLMER AND TAFEL EQUATIONS
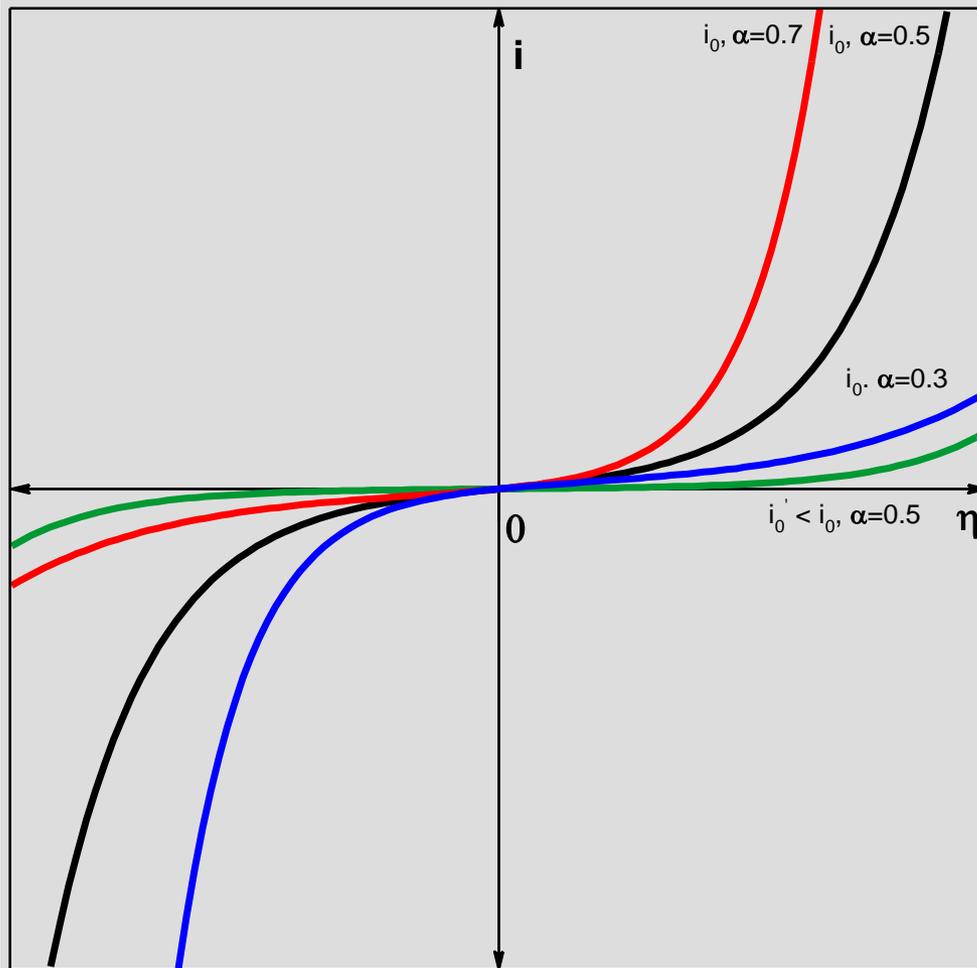
Exchange current density

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
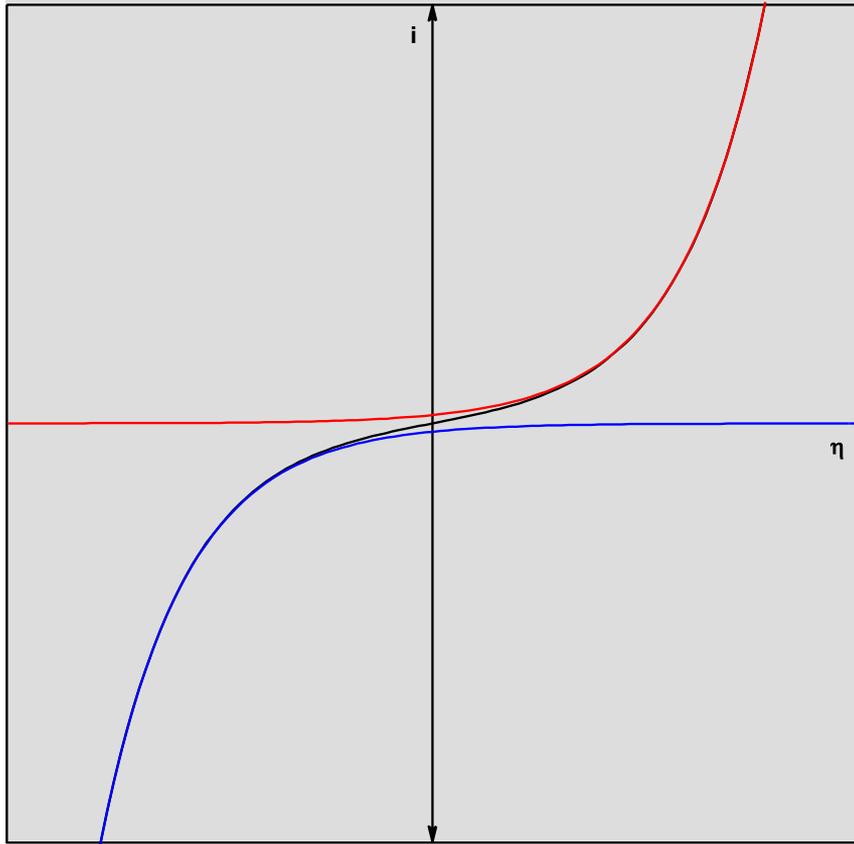
$$i = i_0 \left(\exp\left(\frac{(1-\alpha)zF}{RT}(E-E^\circ) \right) - \exp\left(\frac{\alpha zF}{RT}(E-E^\circ) \right) \right)$$
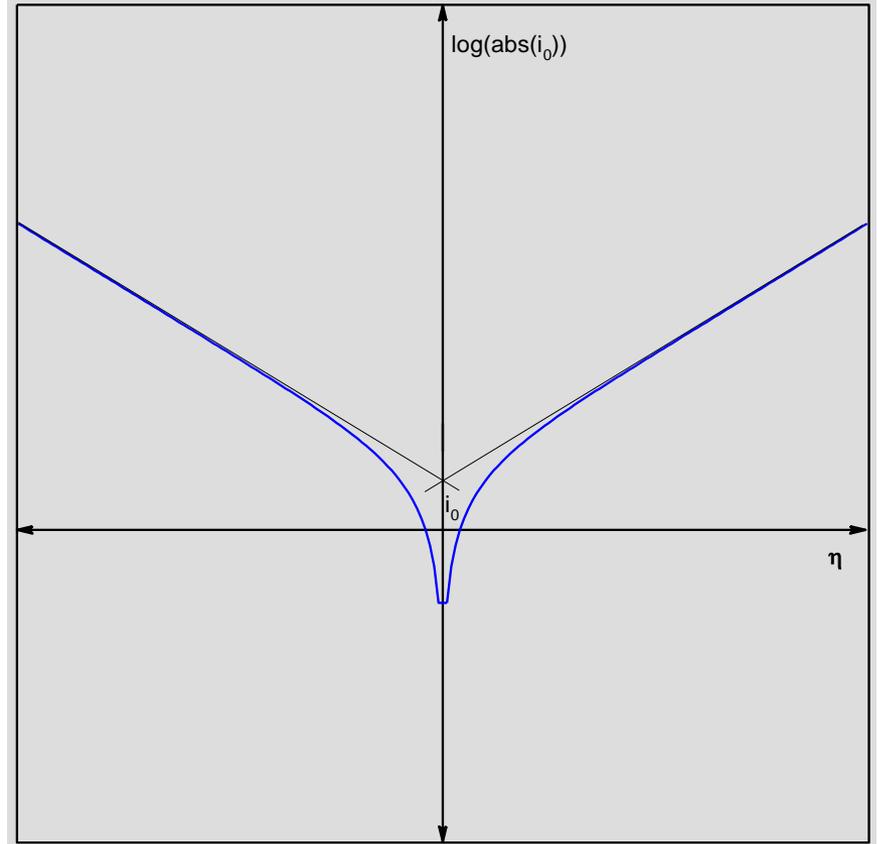
$$\log(i) = \log(i_0) - \left(\frac{2.303\alpha zF}{RT}(E-E^\circ) \right)$$

MASS TRANSFER

- Migration
- Convection
- Diffusion

We try to avoid migration by the addition excess supporting electrolyte

TRANSPORT BY DIFFUSION
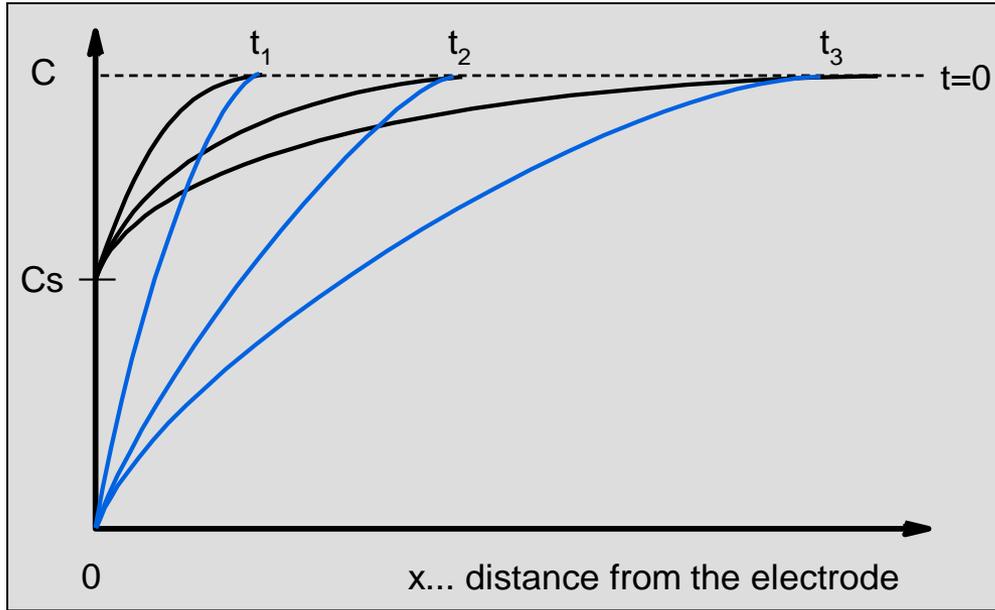
1st Fick Law

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

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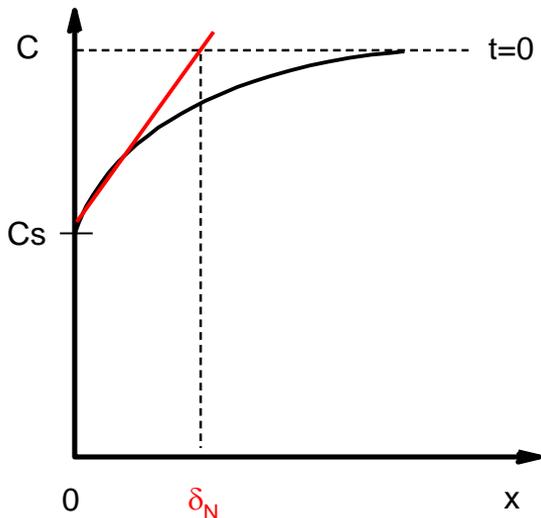
Nernst diffusion layer

$$i = zFD\,\frac{c_0 - c_s}{\delta_N}$$

$$\eta_D = E - E' = \frac{RT}{zF}\ln\frac{c_S}{c_0}$$

$$i_{\text{lim}} = zFD\,\frac{c_0}{\delta_N}$$

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

THE COTTRELL EQUATION
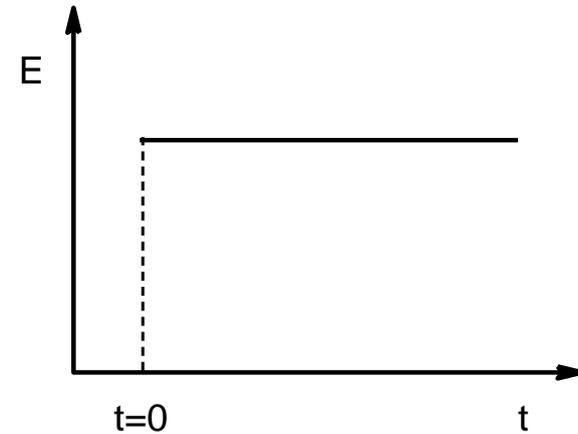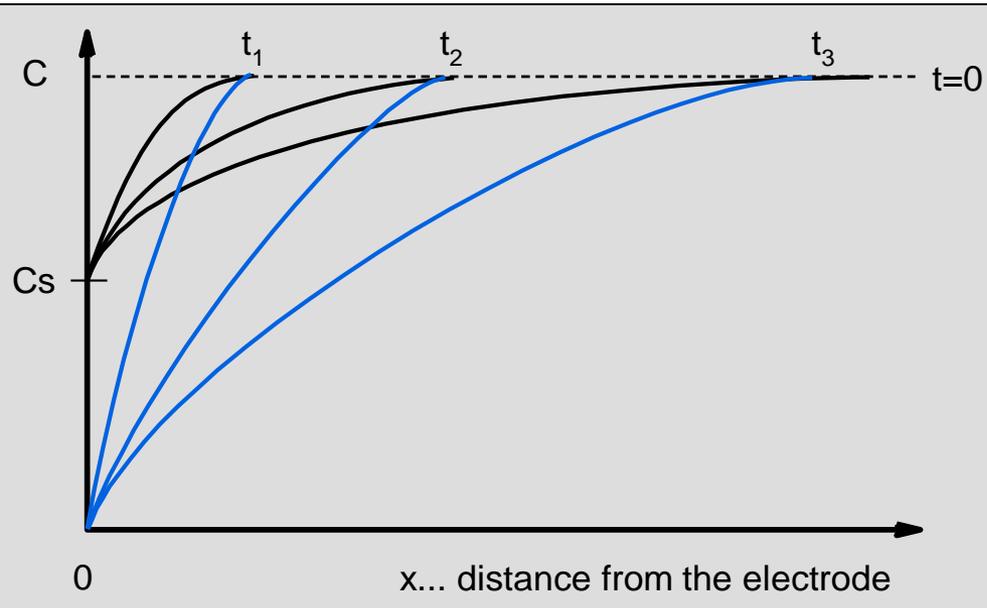
$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$ Second Fick's law

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

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

This is how Nernst layer thickness changes over time
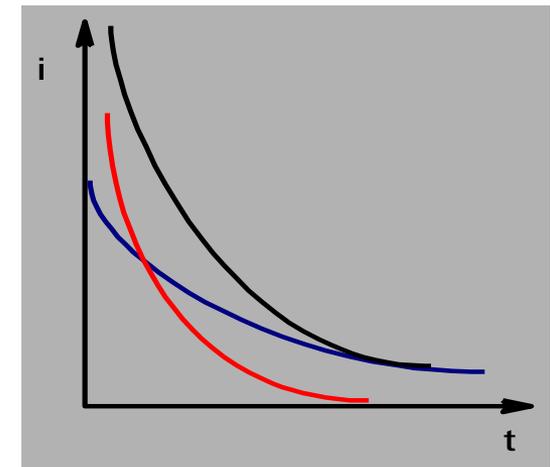
TRANSPORT BY CONVECTION

Rotating disk electrode (RDE)
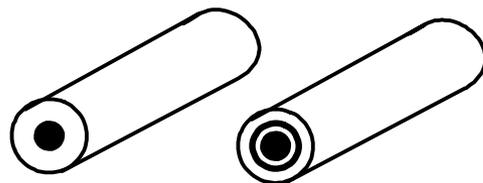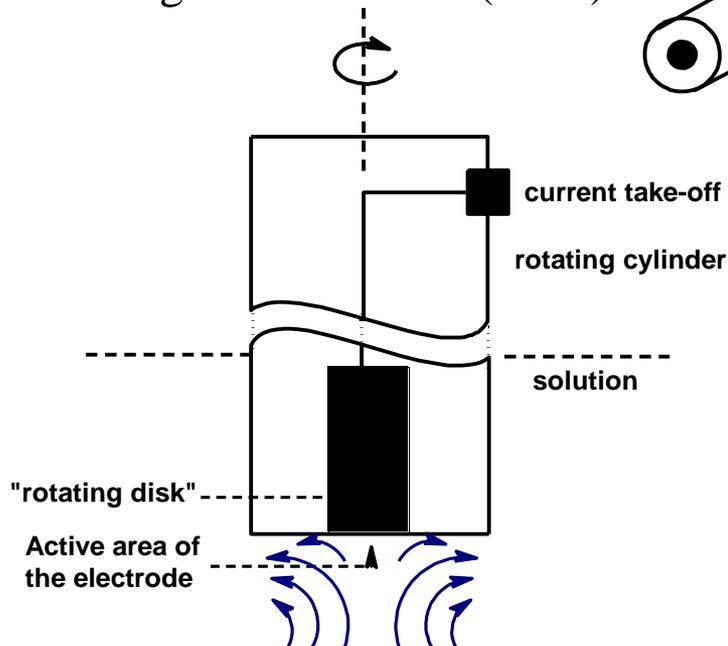
Rotating ring disk electrode (RRDE)

current take-off

rotating cylinder

solution

"rotating disk"

Active area of
the electrode

Current (μA) versus Potential (mV)

forward & reverse
traces are on top
of each other
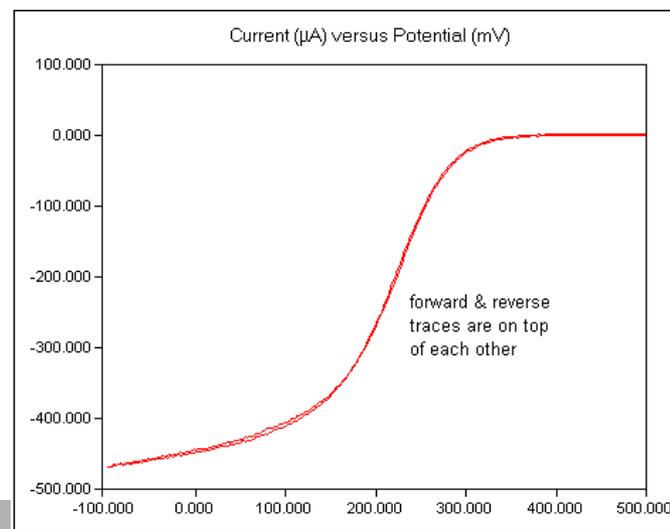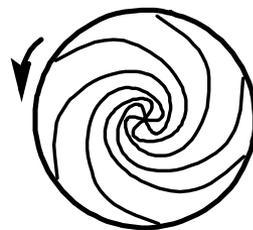
$$I_L = (0,620) \cdot z \cdot F \cdot A \cdot D^{2/3} \cdot \omega^{1/2} \cdot \nu^{-1/6} \cdot c \quad \text{Levich Equation}$$

ω **speed of rotation (rad·s^{-1}),**

ν **kinematic viscosity of the solution (cm^2·s^{-1}),**

> **kinematic viscosity is the ratio between solution viscosity and its specific weight.**
> **For pure water: $\nu = 0,0100$ cm^2·s^{-1}, For 1.0 mol·dm^{-3} KNO$_3$ is $\nu = 0,00916$ cm^2·s^{-1}**
> **(at 20°C).**

c concentration of electroactive species (in mol.cm^{-3}, note unusual unit)

D diffúsion coefficient (cm^2·s^{-1}), A electrode area in cm^2

POLAROGRAPHY
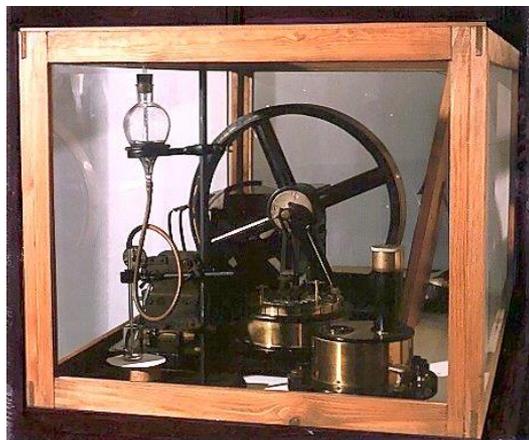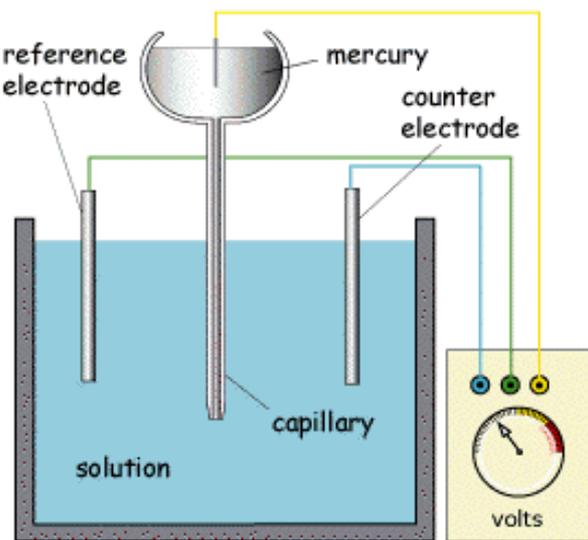
Halfwave potential
Limiting diffusion current (Ilkovic equation)
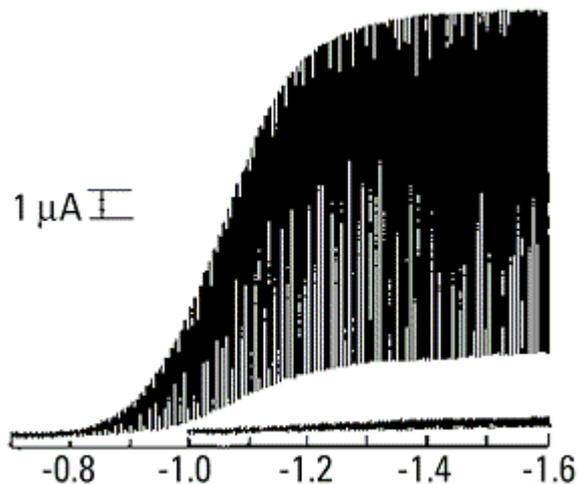
$$I_d = ckFnD^{1/2}m^{2/3}t^{1/6}$$

(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
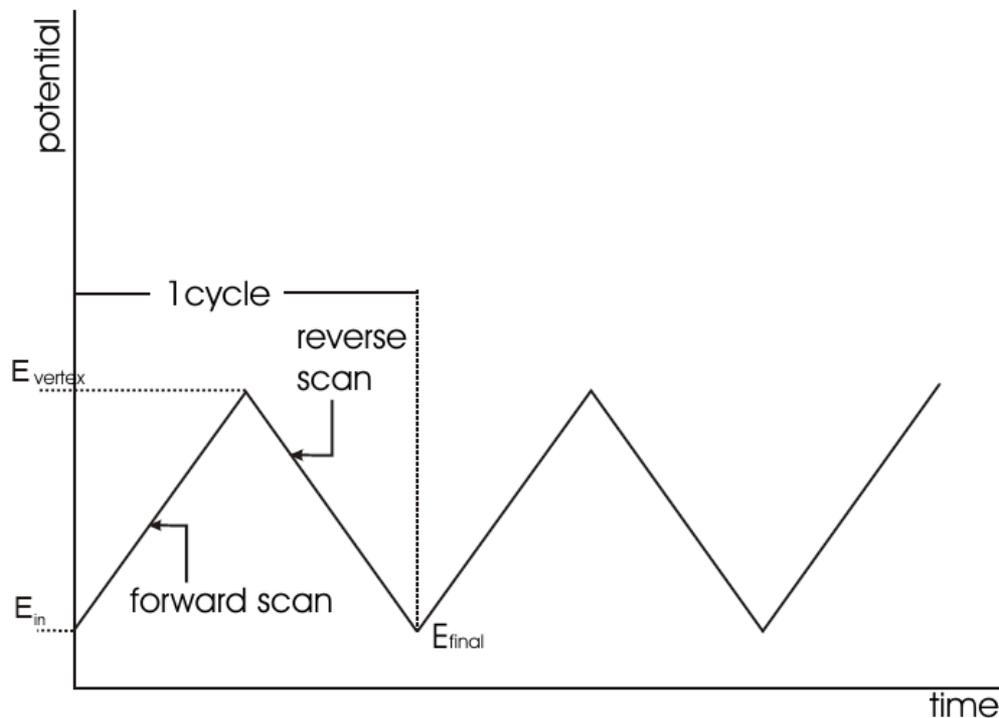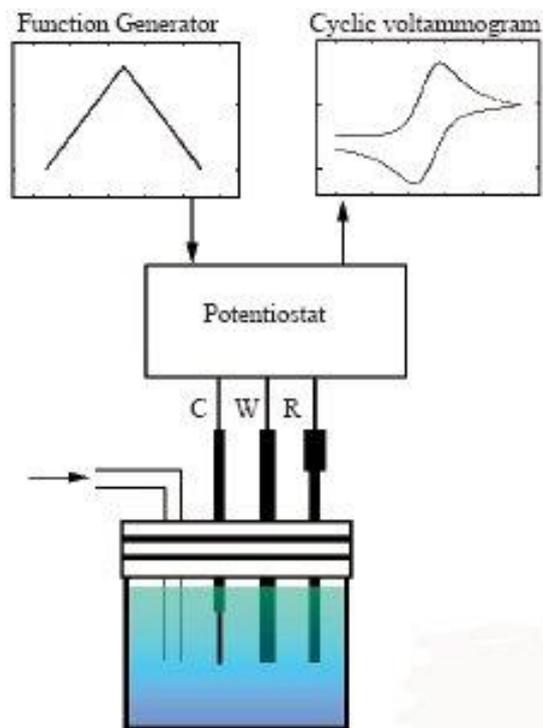
One or more cycles …CV
Half cycle … LSV

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

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

v… the scan rate

Electroactive species attached to the electrode, both redox forms stable

$$I = FA\Gamma_0 v \frac{F}{RT} \frac{\exp\left[\frac{F}{RT}\left(E - E^0\right)\right]}{\left\{1 + \left[\exp\frac{F}{RT}\left(E - E^0\right)\right]\right\}^2}$$
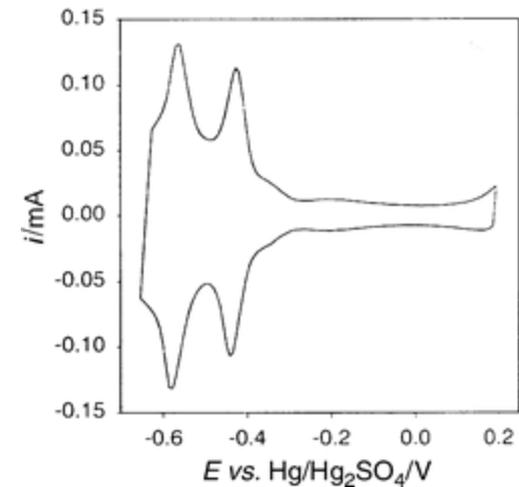
REVERSIBLE CYCLIC VOLTAMMOGRAM
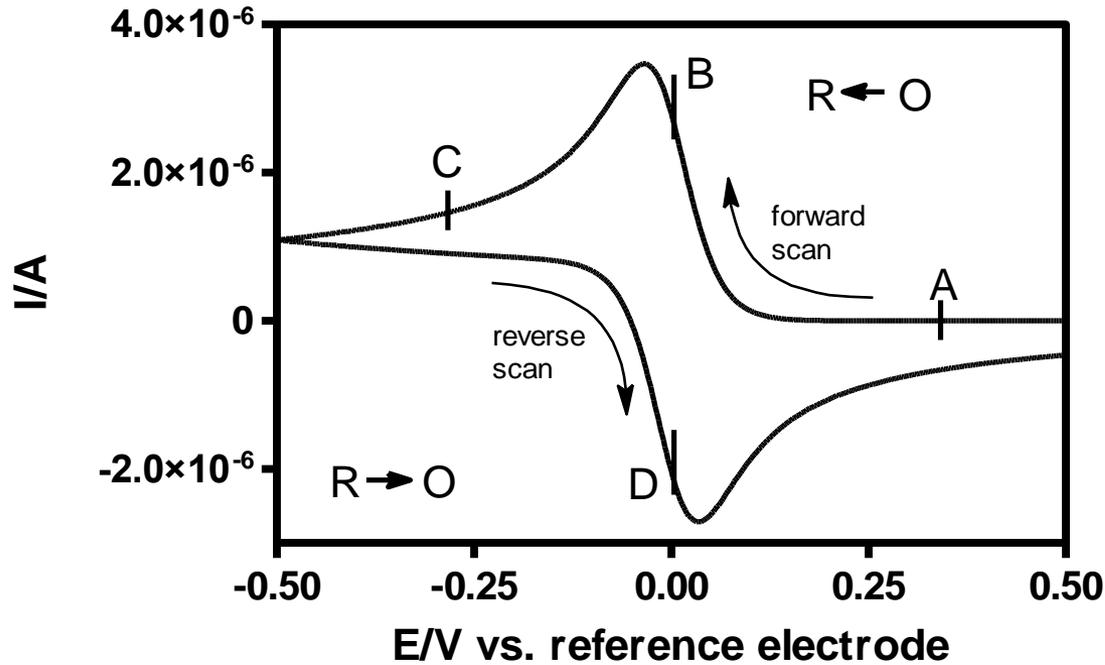
Electroactive species in solution, both stable

IUPAC convention

Peak separation is 59 /z mV

Randles-Sevcik equation:

$$I_{pc} = I_{pa} = 2{,}69.10^5 \cdot A \cdot z^{3/2} \cdot D^{1/2} \cdot c \cdot v^{1/2}$$

A in cm^2, D in cm^{2}s$^{-1/2}$, c in molcm^{-3}, v in V/s
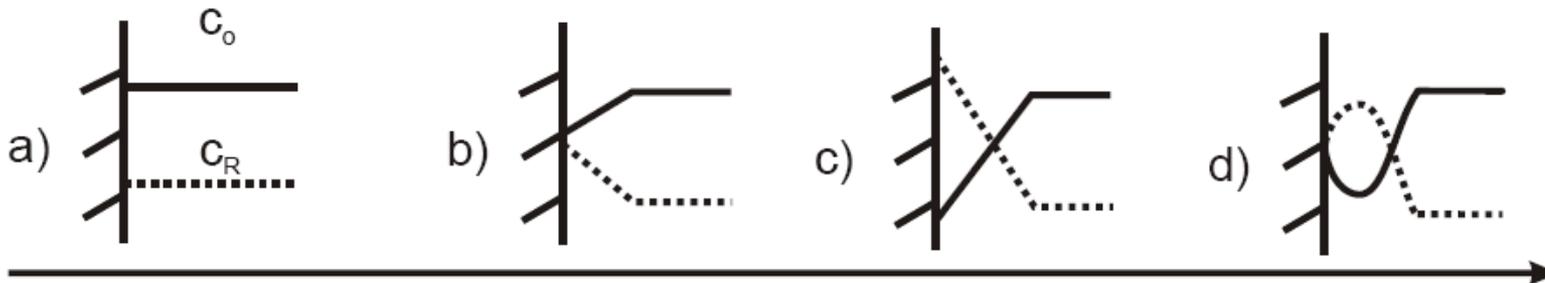
QUASI AND IRREVERSIBLE VOLTAMMOGRAMS

Black: k=1cmsec^{-1}
Blue: k=0.001
Red: k=0.00001

Black: alpha=0.5
Blue: alpha=0.3
Red: alpha=0.7
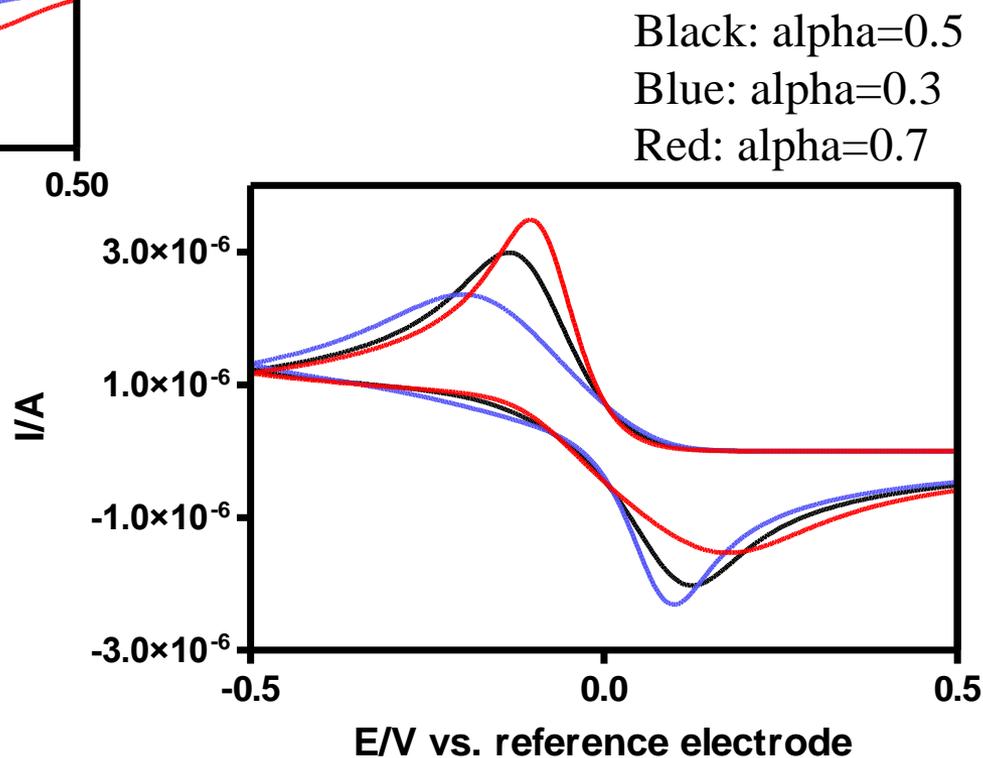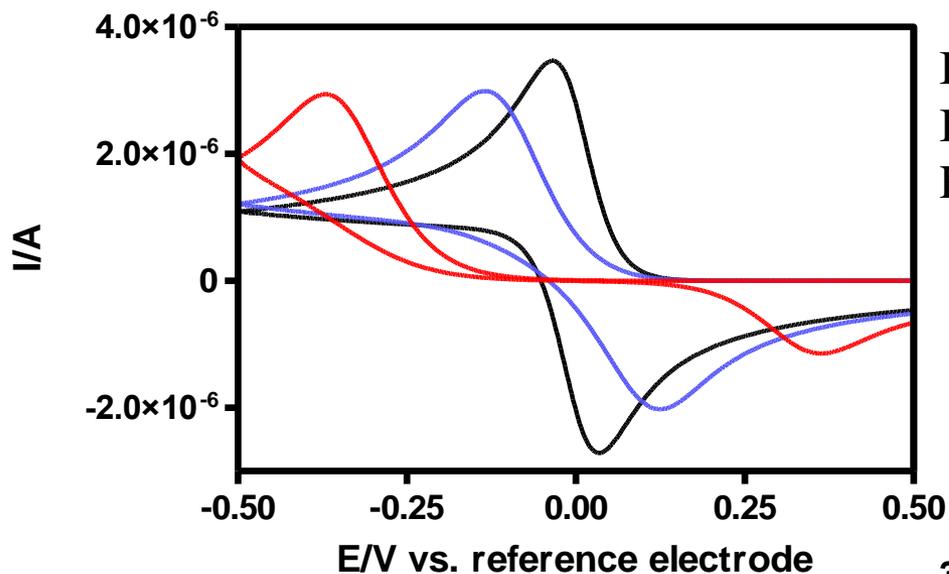
E, C notation
(E… electron transfer,
 C… coupled chemical reaction)
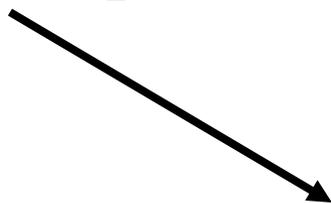
E, EE, CE, EC, ECcat etc.

Mechanisms can be very complex
even for simple systems

Two electron-two proton system =
„square scheme"

$$
\begin{array}{ccccc}
A & \underset{E_1}{\rightleftharpoons} & A^{-\bullet} & \underset{E_2}{\rightleftharpoons} & A^{2-} \\
K_1 \updownarrow & & K_2 \updownarrow & & K_3 \updownarrow \\
AH^+ & \underset{E_3}{\rightleftharpoons} & AH^{\bullet} & \underset{E_4}{\rightleftharpoons} & AH^- \\
K_4 \updownarrow & & K_5 \updownarrow & & K_6 \updownarrow \\
AH_2^{2+} & \underset{E_5}{\rightleftharpoons} & AH_2^{+\bullet} & \underset{E_6}{\rightleftharpoons} & AH_2
\end{array}
$$

THE EC MECHANISM

Black: kf=0 cm.s^{-1}
Blue: 0.2
Red: 0.5
Orange: 1
Green: 10
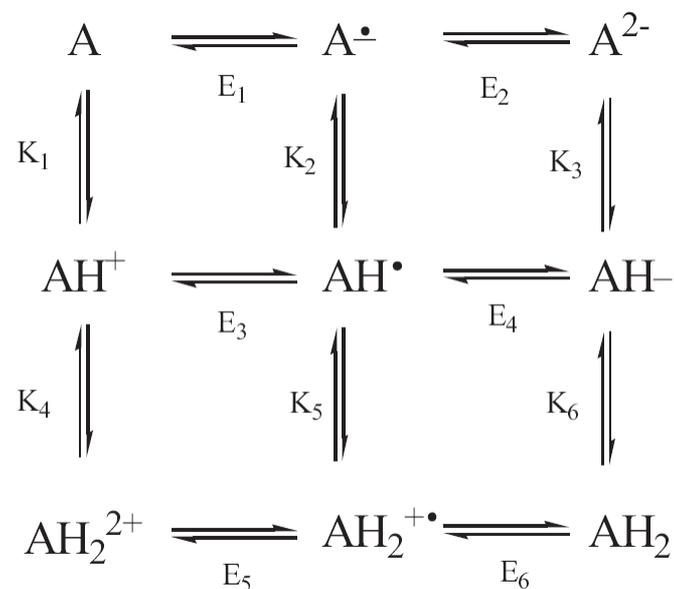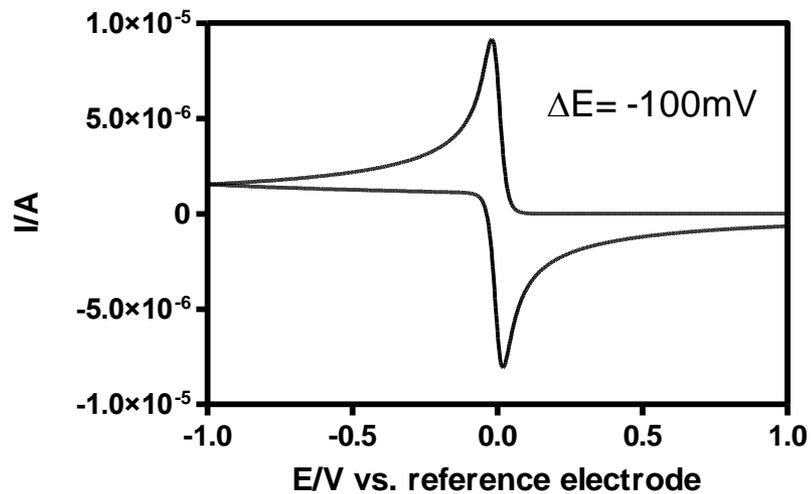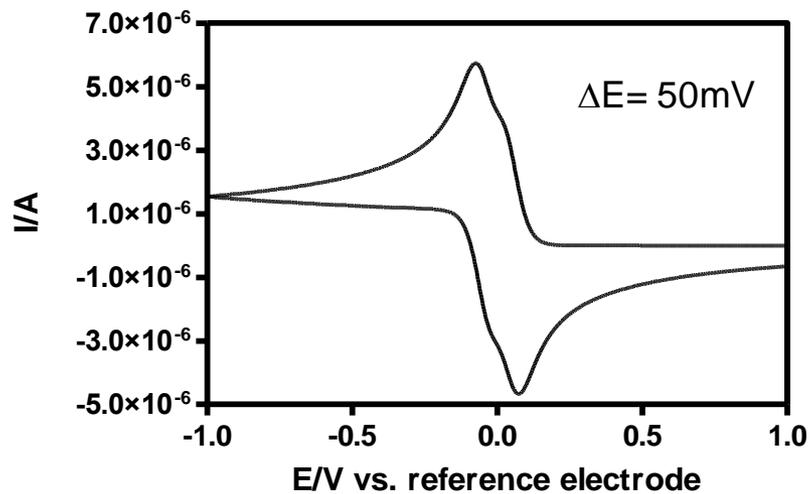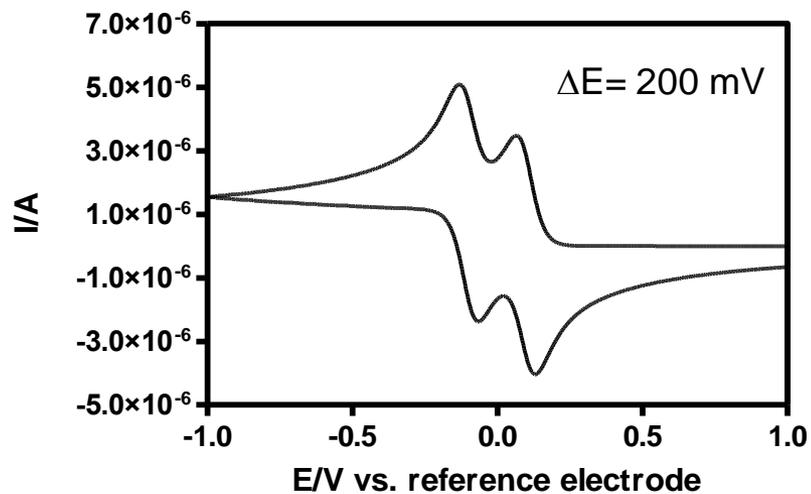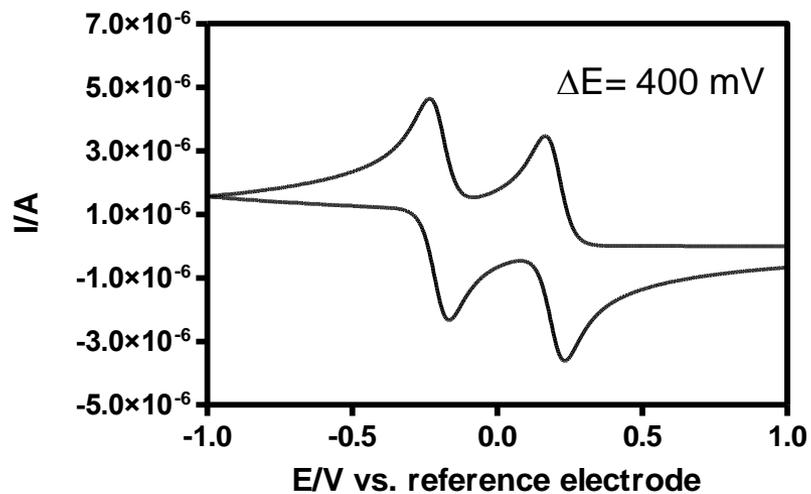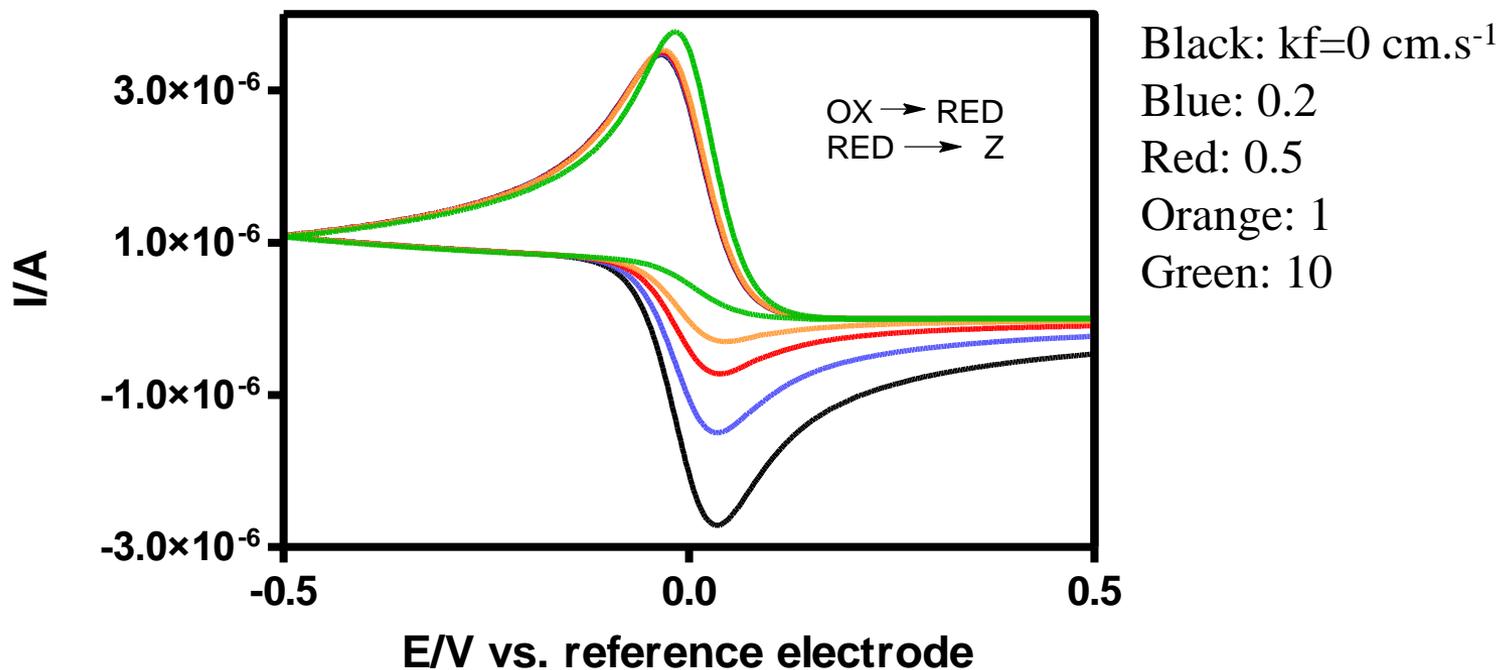
There are many variations of this mechanism:
Reaction with solvent
Dimerization
Radical substrate reaction
EC catalytic … etc.

EC catalytic

OX → RED
RED + A → OX + Z
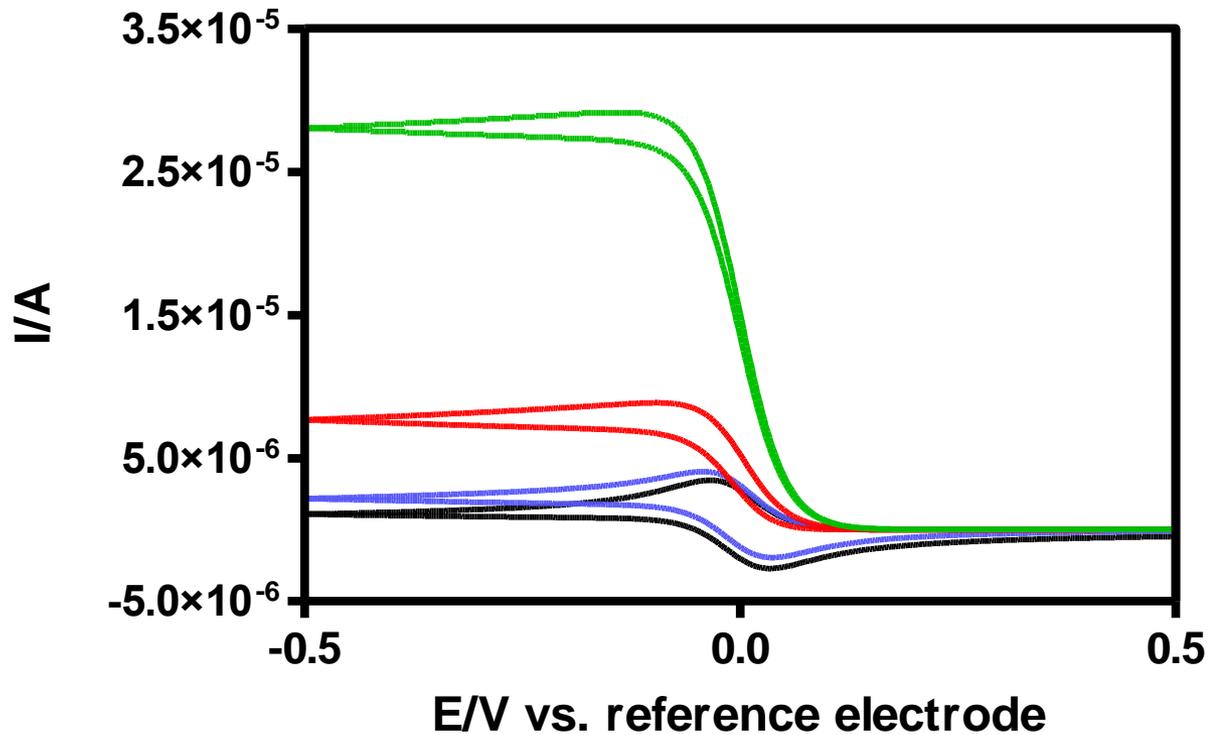
Black : no A
Blue: A (c=1)
Red: A (c=10)
Green: A (c=100)

THE CE MECHANISM
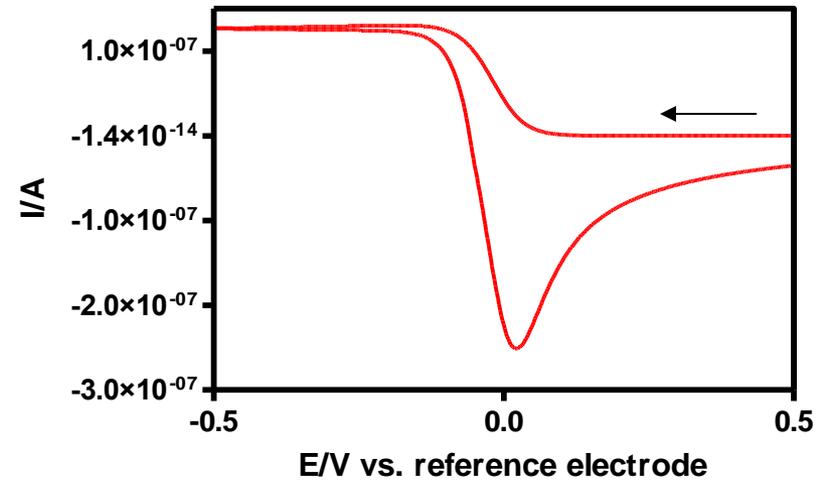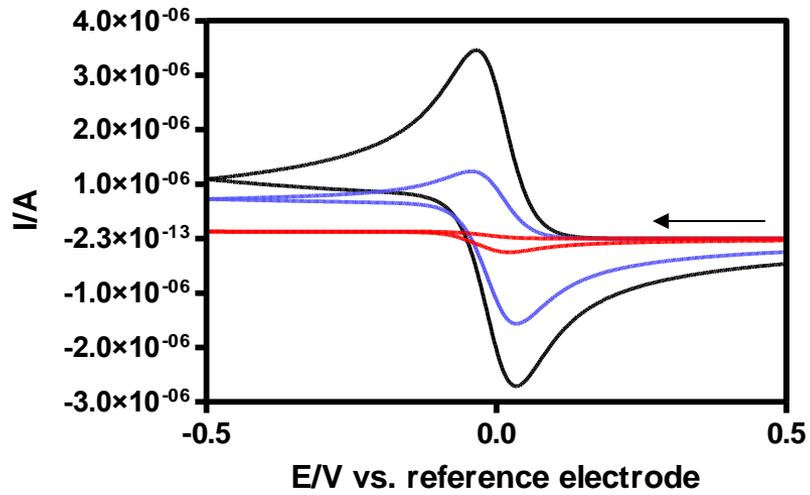
MICROELECTRODES

Microelectrode: at least one dimension must be comparable to diffusion layer thickness (sub µm upto ca. 25 µm). Produce steady state voltammograms.

A) B) C)
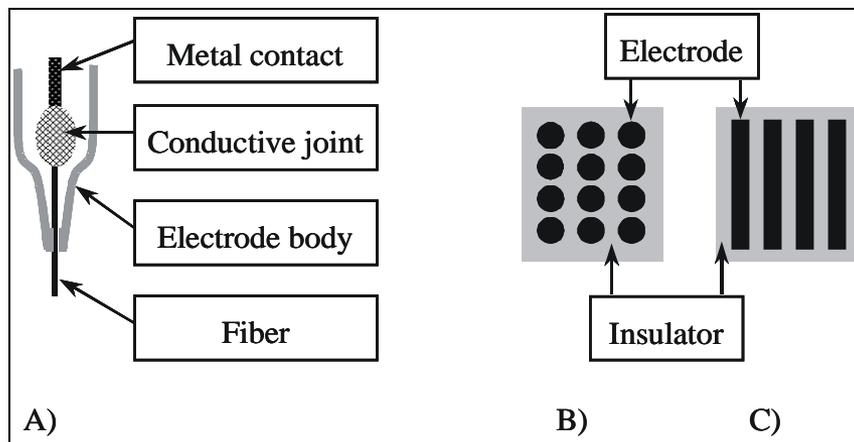
Converging diffusional flux

$$I = nFADc_0 \left(\frac{1}{\delta} + \frac{1}{r} \right)$$

$$\delta = \sqrt{2\pi Dt}$$

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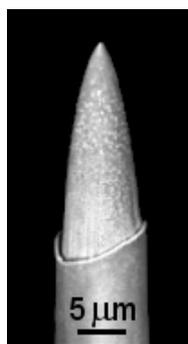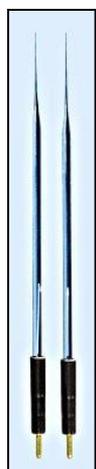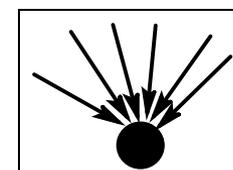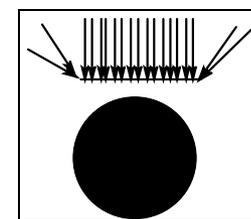
Advantages of microelectrodes:
- fast mass flux - short response time (e.g. faster CV)
- significantly enhanced S/N (I_F / I_C) ratio
- high temporal and spatial resolution
- measurements in extremely small environments
- measurements in highly resistive media
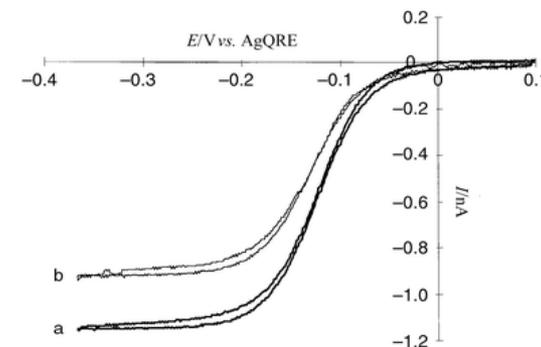
PULSED TECHNIQUES

TAST POLAROGRAPHY
SAMPLED DC POLAROGRAPHY
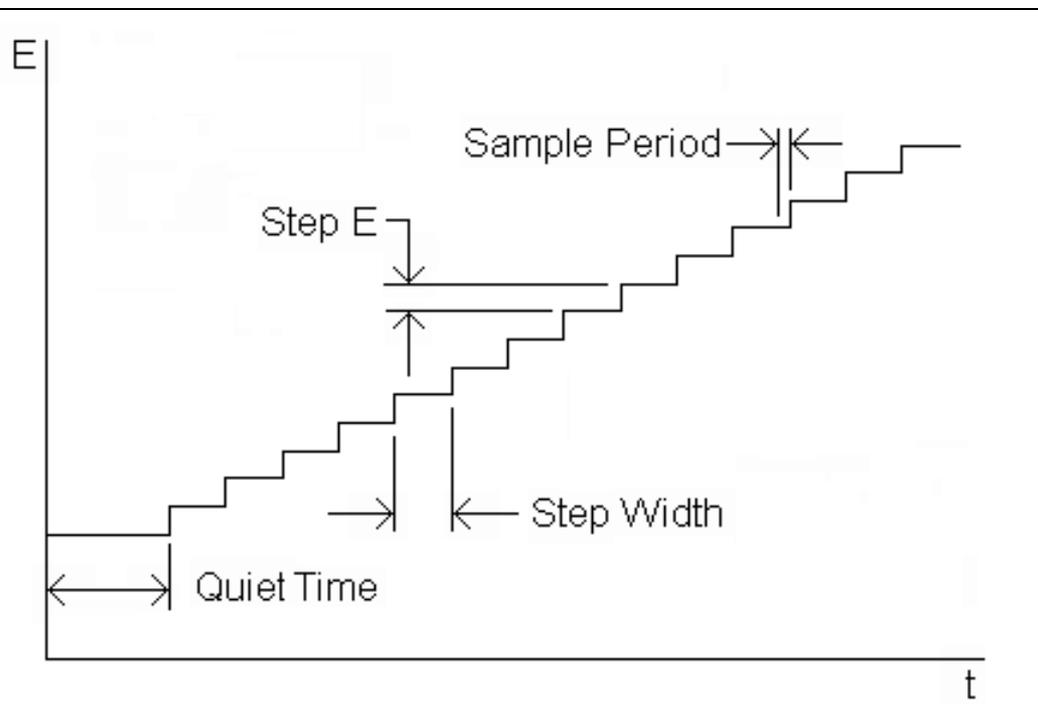
NORMAL PULSE VOLTAMMETRY
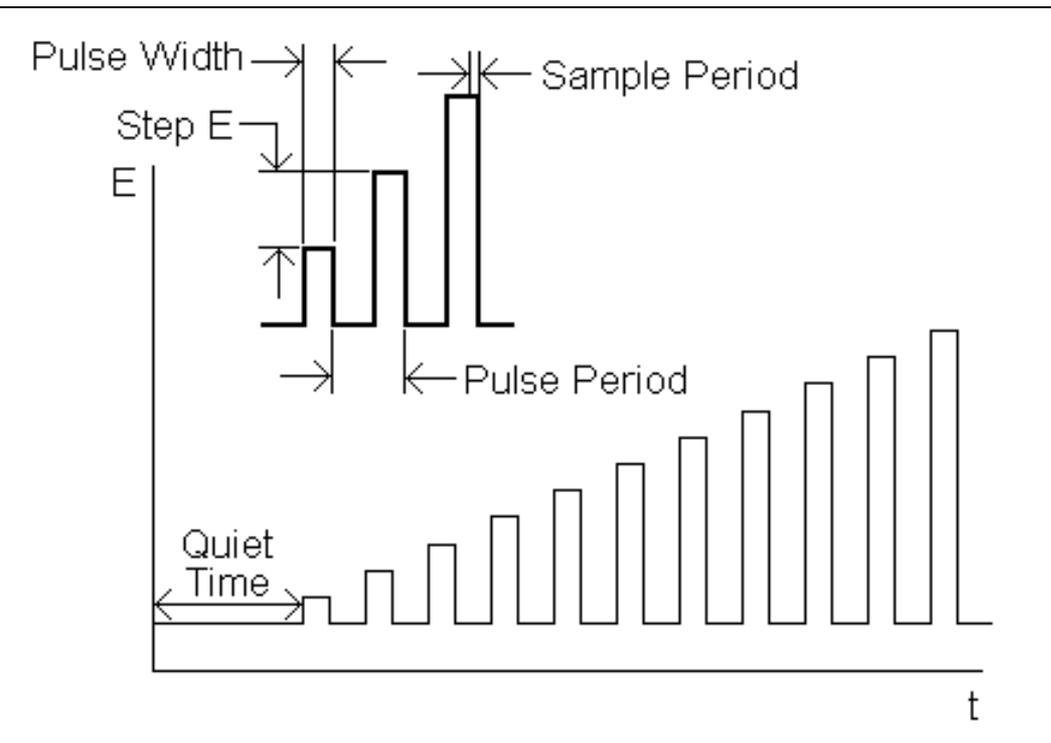
DIFFERENTIAL PULSE VOLTAMMETRY
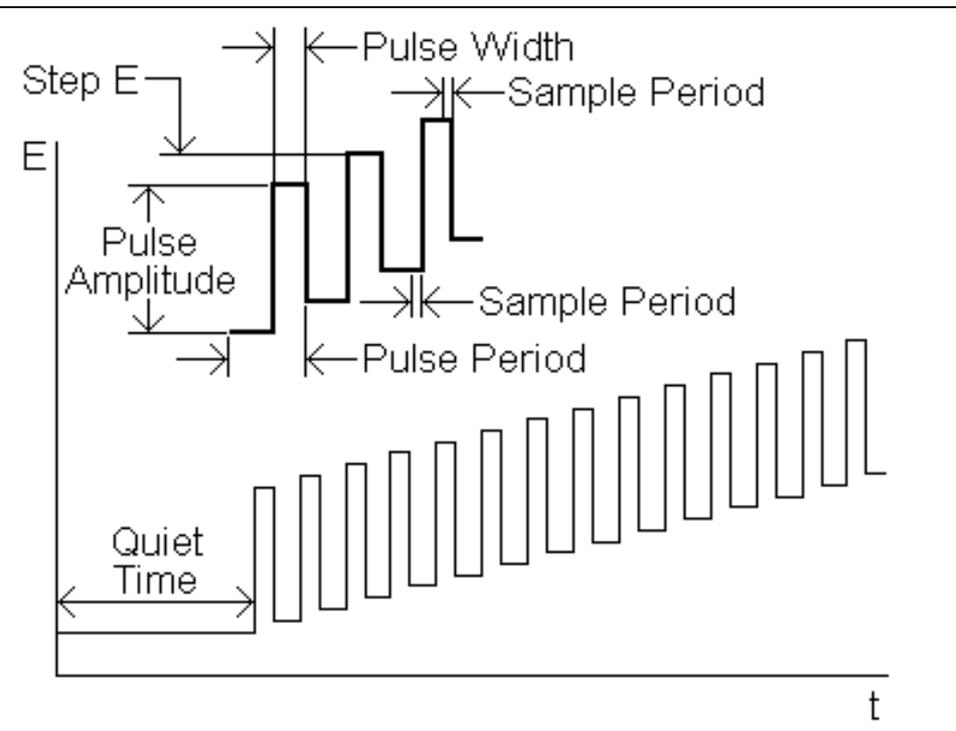
SQUARE WAVE VOLTAMMETRY

AC voltammetry