1.1 Electrochemical cell as a tool of chemical analysis

Electroanalytical Chemistry

A science on applications of physicochemical processes taking place in an electrochemical cell for chemical analysis of matter.

Electrochemical Cell

Two electronic conductors in contact with an electrolyte solution.

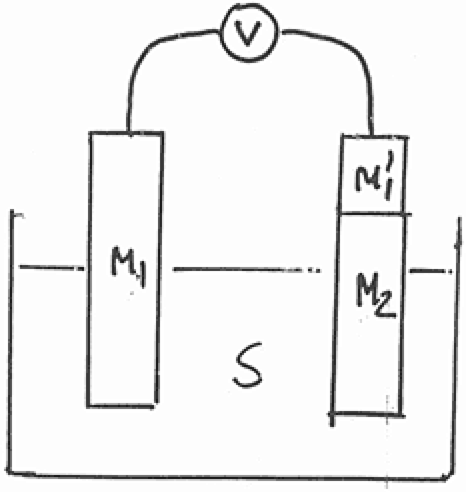
Electrode

The system electronic conductor in contact with ionic conductor.

Interface

The boundry between ionic and electronic conductor

Potential Difference between two metals in a cell without liquid junction

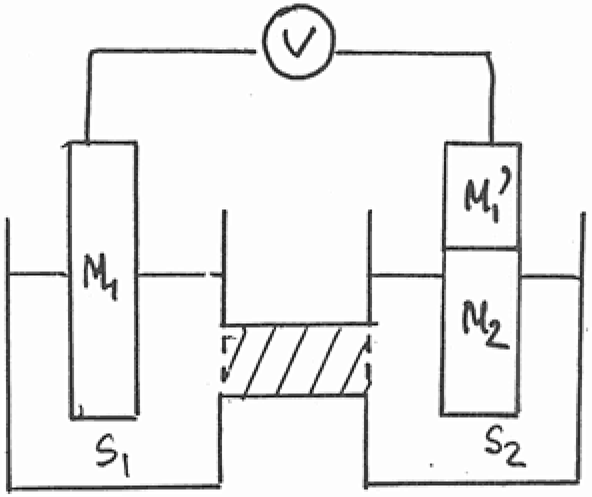


V = potential M'_1 - potential M_1
(right electrode) (left electrode)

$$\boxed{V = PD_{M'_1/M_2} + PD_{M_2/S} + PD_{S/M_1}}$$

In the most simple case the potential difference of the cell is equal to a sum of potential differences across three interfaces.

Potential difference between two metals in a cell with liquid junction



$$\boxed{V = PD_{M'_1/M_2} + PD_{M_2/S_2} + PD_{S_2/S_1} + PD_{S_1/M_1}}$$

The potential difference of the above cell is equal to the sum of potential differences of four phase bounderies.

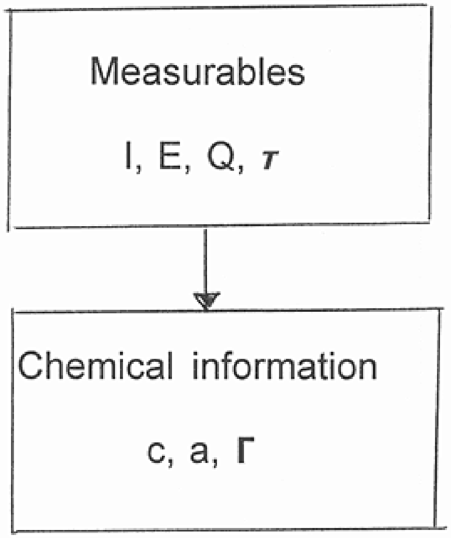
In this bioelectroanalytical experiment the two electrodes are separated by large number of interfaces

FIG. 5. The arrangement of electrodes for cyclic voltammetry in kidney cortex of a rat.

The principle of electroanalytical experiment consists of keeping the potential difference at all but one interface constant

Electrode with variable PD - indicator electrode

Electrode with constant PD - reference electrode



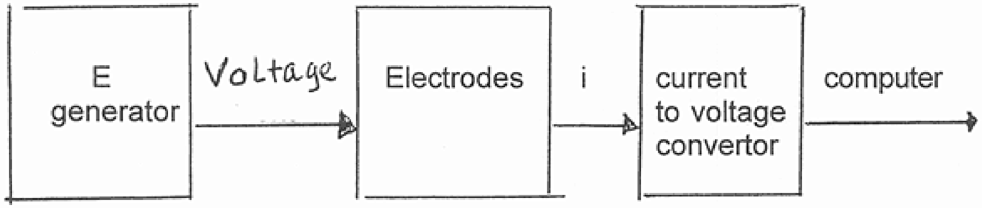
Measurables

I, E, Q, τ

Chemical information

c, a, Γ

Polarography



E generator

Voltage

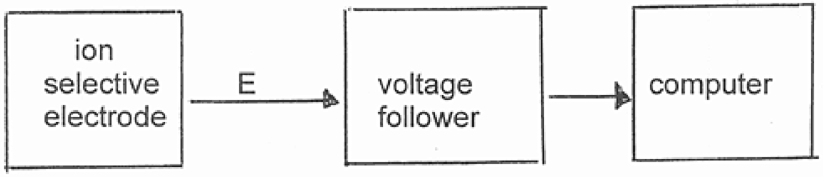
Electrodes

i

current to voltage convertor

computer

Potentiometry



ion selective electrode

E

voltage follower

computer

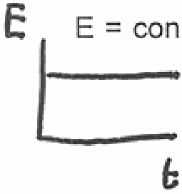
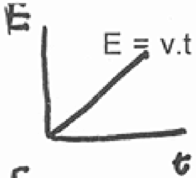
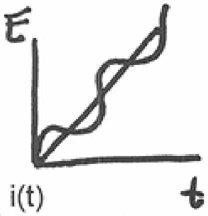
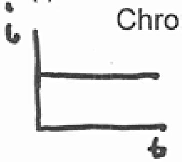
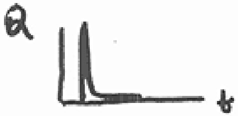
1.2 Classification of Electroanalytical techniques

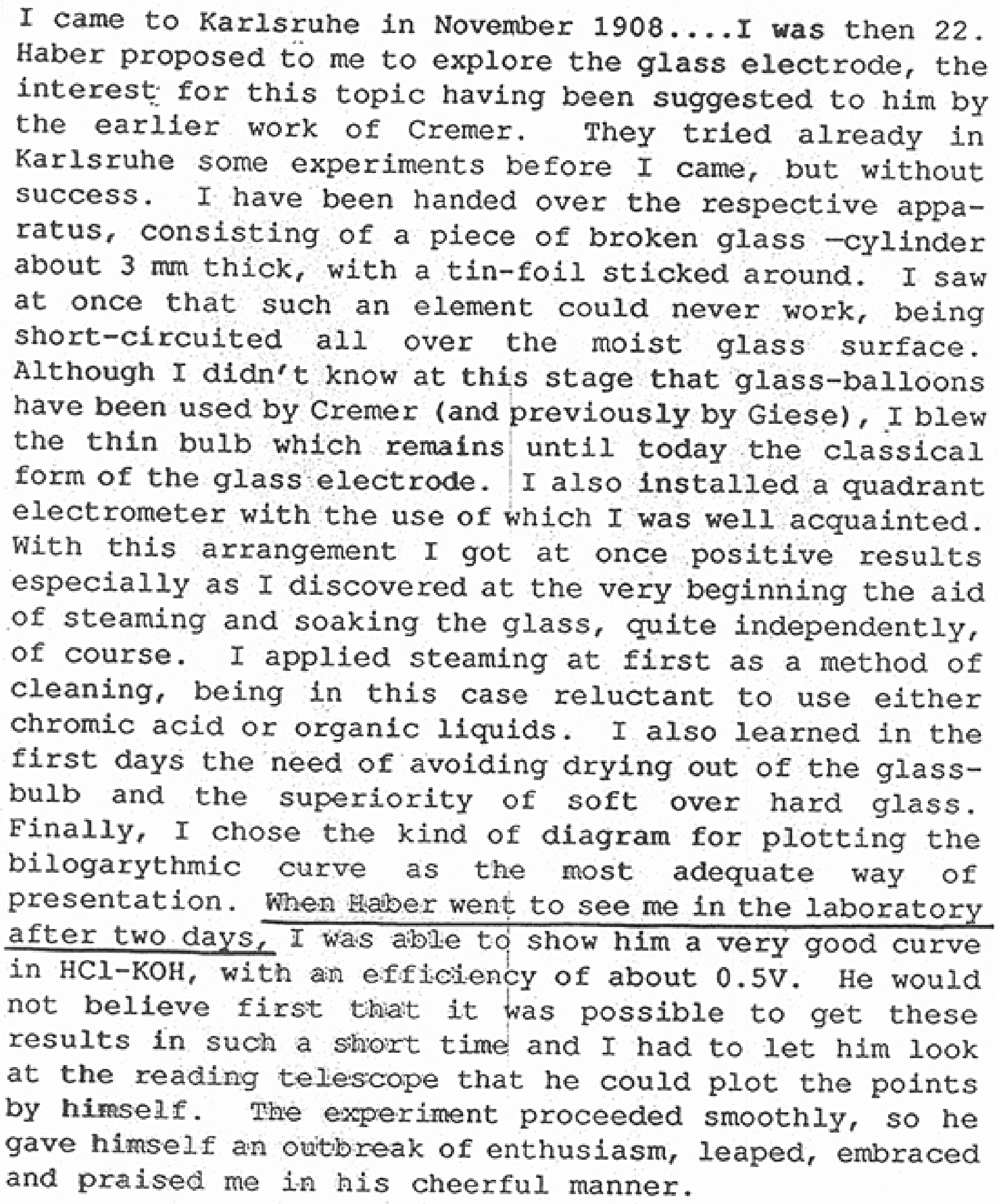
1. Potentiometry - consists of measuring the potential difference of the electrochemical cell at zero current flow. Potentiometry includes analytical applications of the ion selective electrodes

2. Voltammetric techniques - consist of introducing a controlled perturbation and following the response of the cell to this perturbation

Perturbation	Response	Technique
$E(t)$	$i(t)$	voltammetry
$i = \text{const}$	$Q = i \cdot t$	coulometry

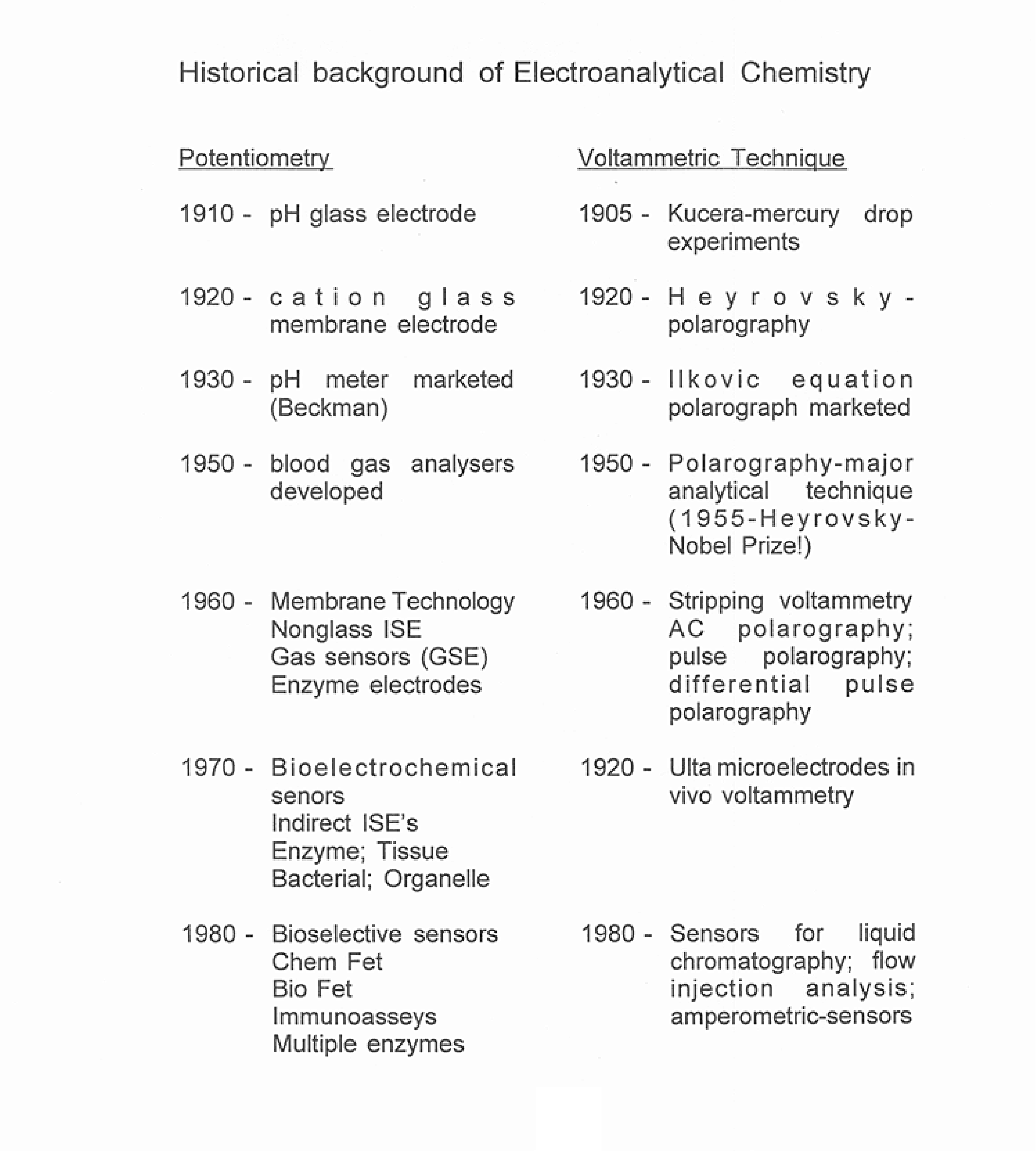
Voltammetric techniques

		perturbation	response	detection limit
I)		E(t)	I(t), Q(t)	mole dm^{-3}
		Amperometric		
	1.	 E = const	polarography	10^{-2}-10^{-5}
	2.	 E = v.t	cyclic voltummetry	10^{-2}-10^{-5}
	3.		pulse polarography	10^{-2}-10^{-7}
	4.		a.c. polarography	10^{-2}-10^{-7}
II	5.	i(t)	E(t)	
		Chronopotentiometry 	chronopotentiometry	10^{-2}-10^{-5}
III	6.	Q(t) 	E(t) coulostatic	10^{-4}-10^{-7}



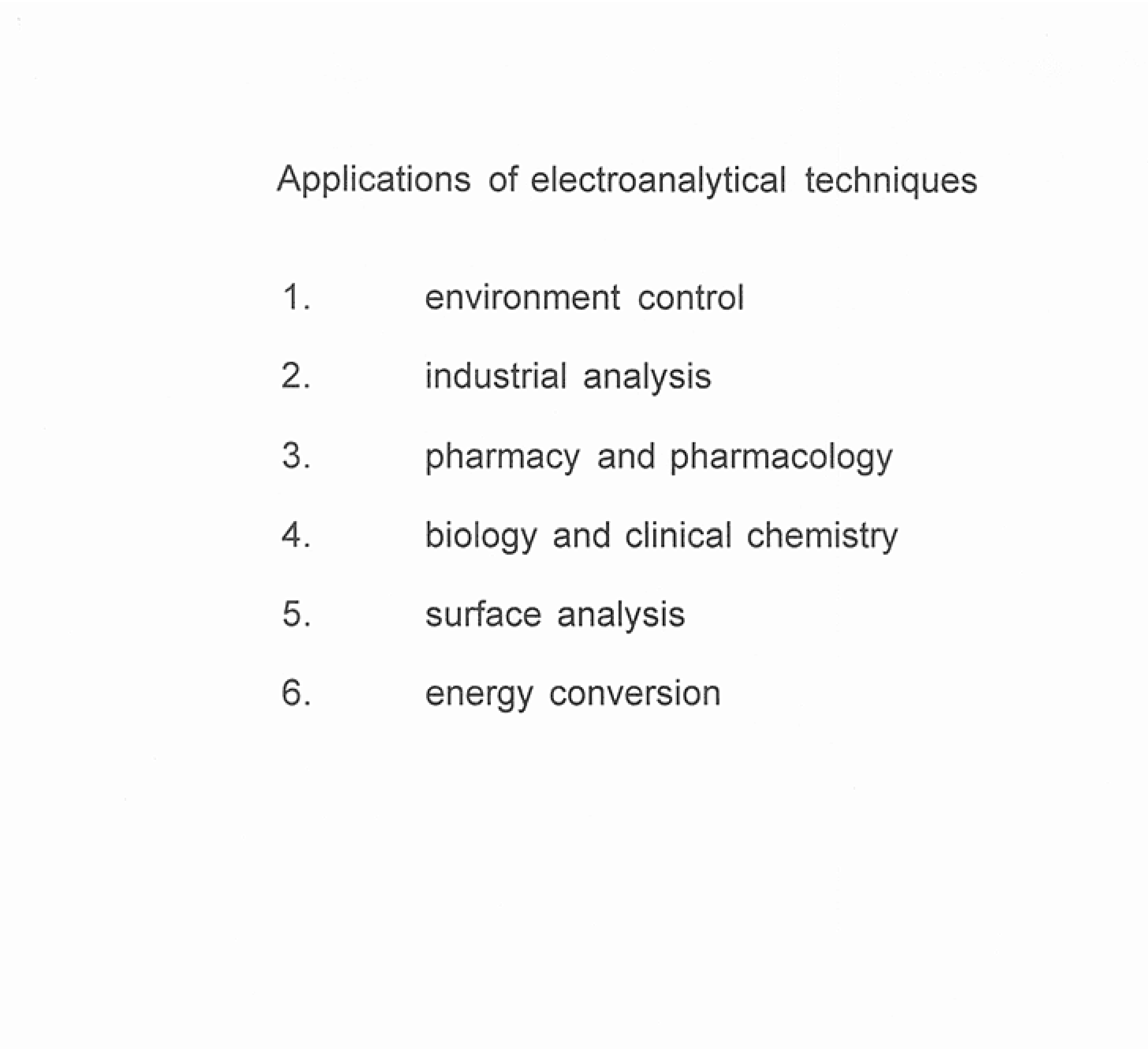
I came to Karlsruhe in November 1908....I was then 22. Haber proposed to me to explore the glass electrode, the interest for this topic having been suggested to him by the earlier work of Cremer. They tried already in Karlsruhe some experiments before I came, but without success. I have been handed over the respective apparatus, consisting of a piece of broken glass –cylinder about 3 mm thick, with a tin-foil sticked around. I saw at once that such an element could never work, being short-circuited all over the moist glass surface. Although I didn't know at this stage that glass-balloons have been used by Cremer (and previously by Giese), I blew the thin bulb which remains until today the classical form of the glass electrode. I also installed a quadrant electrometer with the use of which I was well acquainted. With this arrangement I got at once positive results especially as I discovered at the very beginning the aid of steaming and soaking the glass, quite independently, of course. I applied steaming at first as a method of cleaning, being in this case reluctant to use either chromic acid or organic liquids. I also learned in the first days the need of avoiding drying out of the glass-bulb and the superiority of soft over hard glass. Finally, I chose the kind of diagram for plotting the bilogarythmic curve as the most adequate way of presentation. When Haber went to see me in the laboratory after two days, I was able to show him a very good curve in HCl-KOH, with an efficiency of about 0.5V. He would not believe first that it was possible to get these results in such a short time and I had to let him look at the reading telescope that he could plot the points by himself. The experiment proceeded smoothly, so he gave himself an outbreak of enthusiasm, leaped, embraced and praised me in his cheerful manner.

A letter from Klemensiewicz to Malcolm Dole



Historical background of Electroanalytical Chemistry

Potentiometry		Voltammetric Technique	
1910 -	pH glass electrode	1905 -	Kucera-mercury drop experiments
1920 -	cation glass membrane electrode	1920 -	Heyrovsky-polarography
1930 -	pH meter marketed (Beckman)	1930 -	Ilkovic equation polarograph marketed
1950 -	blood gas analysers developed	1950 -	Polarography-major analytical technique (1955-Heyrovsky-Nobel Prize!)
1960 -	Membrane Technology Nonglass ISE Gas sensors (GSE) Enzyme electrodes	1960 -	Stripping voltammetry AC polarography; pulse polarography; differential pulse polarography
1970 -	Bioelectrochemical senors Indirect ISE's Enzyme; Tissue Bacterial; Organelle	1920 -	Ulta microelectrodes in vivo voltammetry
1980 -	Bioselective sensors Chem Fet Bio Fet Immunoasseys Multiple enzymes	1980 -	Sensors for liquid chromatography; flow injection analysis; amperometric-sensors



Applications of electroanalytical techniques

1. environment control
2. industrial analysis
3. pharmacy and pharmacology
4. biology and clinical chemistry
5. surface analysis
6. energy conversion

2.Introduction to potentiomentry

2.1. Galvani potential and electrochemical potential

Zero energy – charged particle in vacuum at infinite separation from a charged phase

Basic concepts

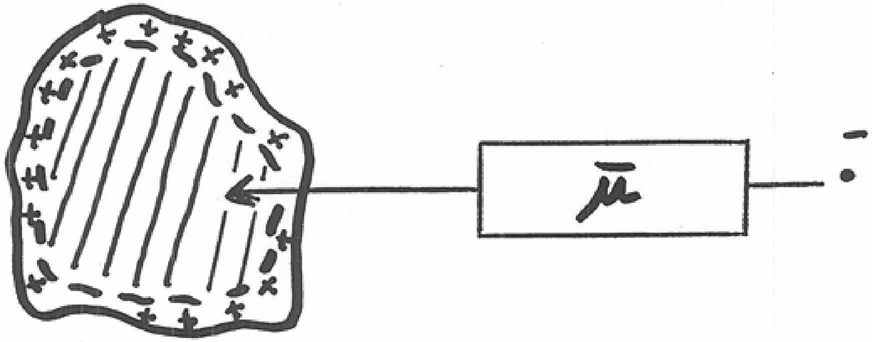
1. **Electrochemical potential - $\bar{\mu}$**

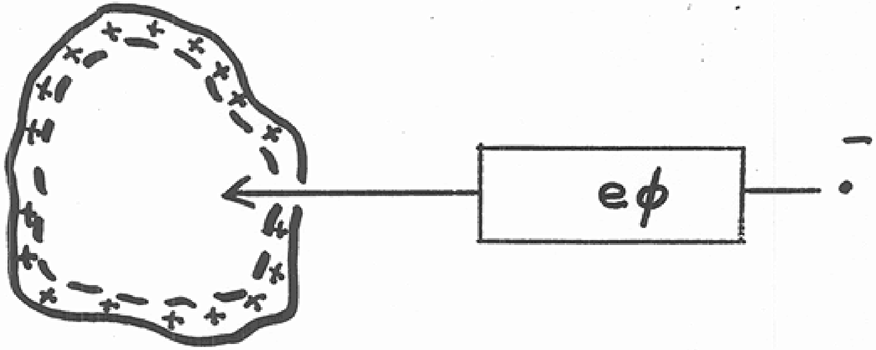
   work done when a charged particle is transferred from infinite separation in vacuum to the interior of a charged phase

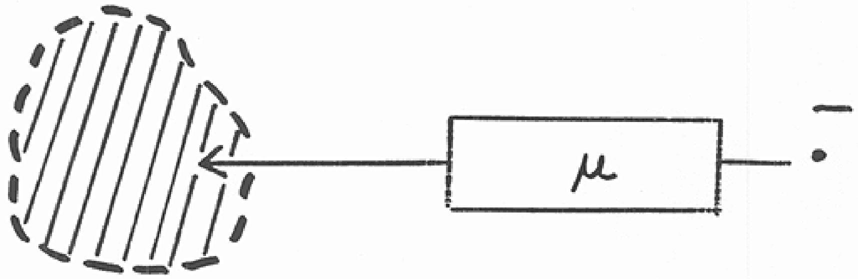
2. **Chemical potential - μ**

   work done when a charged particle is transferred from infinite separation in vacuum to the interior of a phase stripped from the charged surface layer

3. **Inner potential (Galvani potential) - ϕ work done when a charged particle is transferred from infinite separation in vacuum across a surface shell which contains an excess charge and oriented dipoles**







$$\bar{\mu} = \mu + e\phi$$

The inner potential may be regarded as a sum of:

1) Potential created by the excess charge, the so called outer potential or Volta potential, denoted as *Ψ.* For a charge *q* on a sphere of radius *a*:

$$\psi = \frac{q}{a}$$

2. Potential created by oriented dipoles with dipole moment *p* referred to as surface potential, denoted as χ *and equal to :*

$$\chi = 4\pi Np / \varepsilon$$

Therefore the inner potential is equal to:

$$\phi = \psi + \chi$$

Thermodynamic relationships

In a charged system the inner potential ϕ is an additional independent variable of the total Gibbs free energy:

$$G = f\,(p, T, n_j, \phi)$$

Basic thermodynamic definitions:

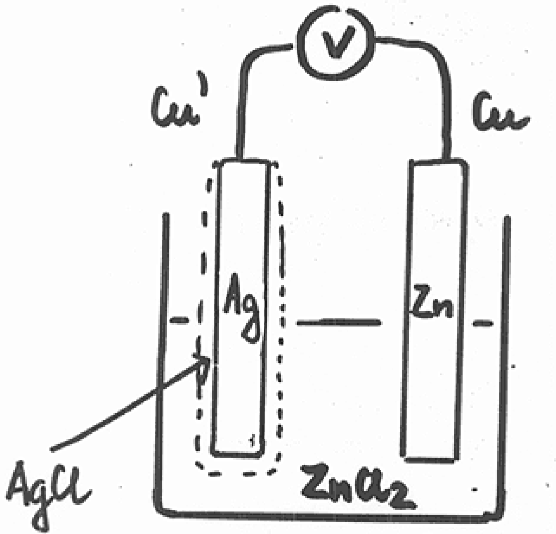
1. $\bar{\mu}_i = (dG/dn_i)_{p,T,n_j \neq n_i,\phi}$

2. $\mu_i = (dG/dn_i)_{p,T,n_j \neq n_i,\phi=0}$

Equilibrium condition: two phases α and β are in thermodynamic equilibrium when:

$$\bar{\mu}_i^{\alpha} = \bar{\mu}_i^{\beta}$$

2.2 Electrochemical equilibria and electromotive force (emf) of a cell without liquid junction



$\mathrm{Cu'|Ag|AgCl|Cl^-,Zn^{2+}|Zn|Cu}$

Reactions

$2Ag + 2Cl^- \rightarrow 2\,AgCl + 2e\,(Cu')$

$Zn^{2+} + 2e \rightarrow Zn$

$Zn^{2+} + 2Ag + 2Cl^- + 2e(Cu) = Zn + 2AgCl + 2e(Cu')$

Note that vertical bars in the scheme of the cell denote a phase boundary

The cell at equilibrium

$$\bar{\mu}_{Zn^{2+}} + 2\bar{\mu}_e(Cu) + 2\bar{\mu}_{Cl^-} + 2\mu_{Ag} = \mu_{Zn} + 2\mu_{AgCl} + 2\bar{\mu}_e(Cu')$$

After rearrangement

$$\left(\mu_{Zn^{2+}} - \mu_{Zn}\right) - \left(2\mu_{AgCl} - 2\mu_{Ag} - 2\mu_{Cl^-}\right) = -2\left(\bar{\mu}_e(Cu) - \bar{\mu}_e(Cu')\right)$$

Electromotive force of the cell

recall

$$\bar{\mu}_e = \mu_e - F\phi$$

$$-2\left(\bar{\mu}_e(Cu) - \bar{\mu}_e(Cu')\right) = 2F\left(\phi(Cu) - \phi(Cu')\right) = 2FE$$

Electromotive force of a cell

$$E = \phi(Cu) - \phi(Cu')$$

or

$$\underbrace{\frac{\left(\mu_{Zn^{2+}} - \mu_{Zn}\right)}{2F}}_{} - \underbrace{\frac{\left(2\mu_{AgCl} - 2\mu_{Ag} - 2\mu_{Cl^-}\right)}{2F}}_{} = E$$

$$E_1 = \frac{\left(\mu_{Zn^{2+}} - \mu_{Zn}\right)}{2F} \qquad E_2 = \frac{\left(2\mu_{AgCl} - 2\mu_{Ag} - 2\mu_{Cl^-}\right)}{2F}$$

However this separation is formal or conventional in reality:

$$\mu_{ZnCl_2} - \mu_{Zn} + 2\mu_{Ag} - 2\mu_{AgCl} = -\Delta G = 2FE$$

Examples of electrochemical cells and their emf

1. Cu’│Ag│AgCl│Cl^-, Zn^{2+}│Zn│Cu

$$E = \frac{\left(\mu_{Zn^{2+}} - \mu_{Zn}\right)}{2F} - \frac{\left(2\mu_{AgCl} - 2\mu_{Ag} - 2\mu_{Cl^-}\right)}{2F}$$

2. Cu’│Ag│AgCl│Cl-, Mn2+│Mn│Cu

$$E = \frac{\left(\mu_{Mn^{2+}} - \mu_{Mn}\right)}{2F} - \frac{\left(2\mu_{AgCl} - 2\mu_{Ag} - 2\mu_{Cl^-}\right)}{2F}$$

3. Cu’│Ag│AgCl│Cl-, Sn^{4+},Sn^{2+} │Pt│Cu

$$E = \frac{\left(\mu_{Sn^{4+}} - \mu_{Sn^{2+}}\right)}{2F} - \frac{\left(2\mu_{AgCl} - 2\mu_{Ag} - 2\mu_{Cl^-}\right)}{2F}$$

The second term in all three equations is the same hence we can write

$$E = E_{test} - const$$

Reference electrode convention

$$\frac{\left(2\mu_{AgCl}-2\mu_{Ag}-2\mu_{Cl^-}\right)}{2F}=0$$

1. Cu’│Ag│AgCl│Cl$^-$, Zn^{2+}│Zn│Cu

$$E=\frac{\left(\mu_{Zn^{2+}}-\mu_{Zn}\right)}{2F}$$

2. Cu’│Ag│AgCl│Cl-, Mn2+│Mn│Cu

$$E=\frac{\left(\mu_{Mn^{2+}}-\mu_{Mn}\right)}{2F}$$

3. Cu’│Ag│AgCl│Cl-, Sn^{4+},Sn│Pt│Cu

$$E=\frac{\left(\mu_{Sn^{4+}}-\mu_{Sn^{2+}}\right)}{2F}$$

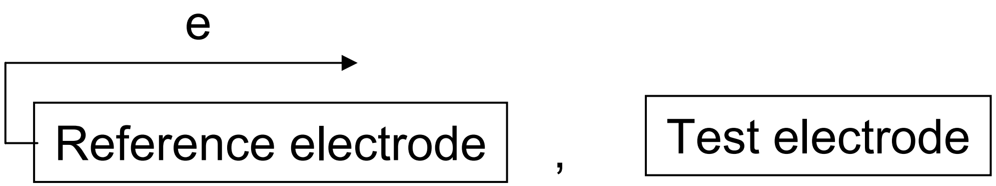
Electrode potential – emf of a cell built up from a given test electrode and a reference electrode

Reference electrodes

$H_3O^+ \vert H_2 \vert Pt$	Hydrogen electrode
$Cl^- \vert Hg_2Cl_2 \vert Hg$	Calomel electrode
$Cl\text{-} \vert AgCl \vert Ag$	Siver chloride electrode

Electrode sign convention

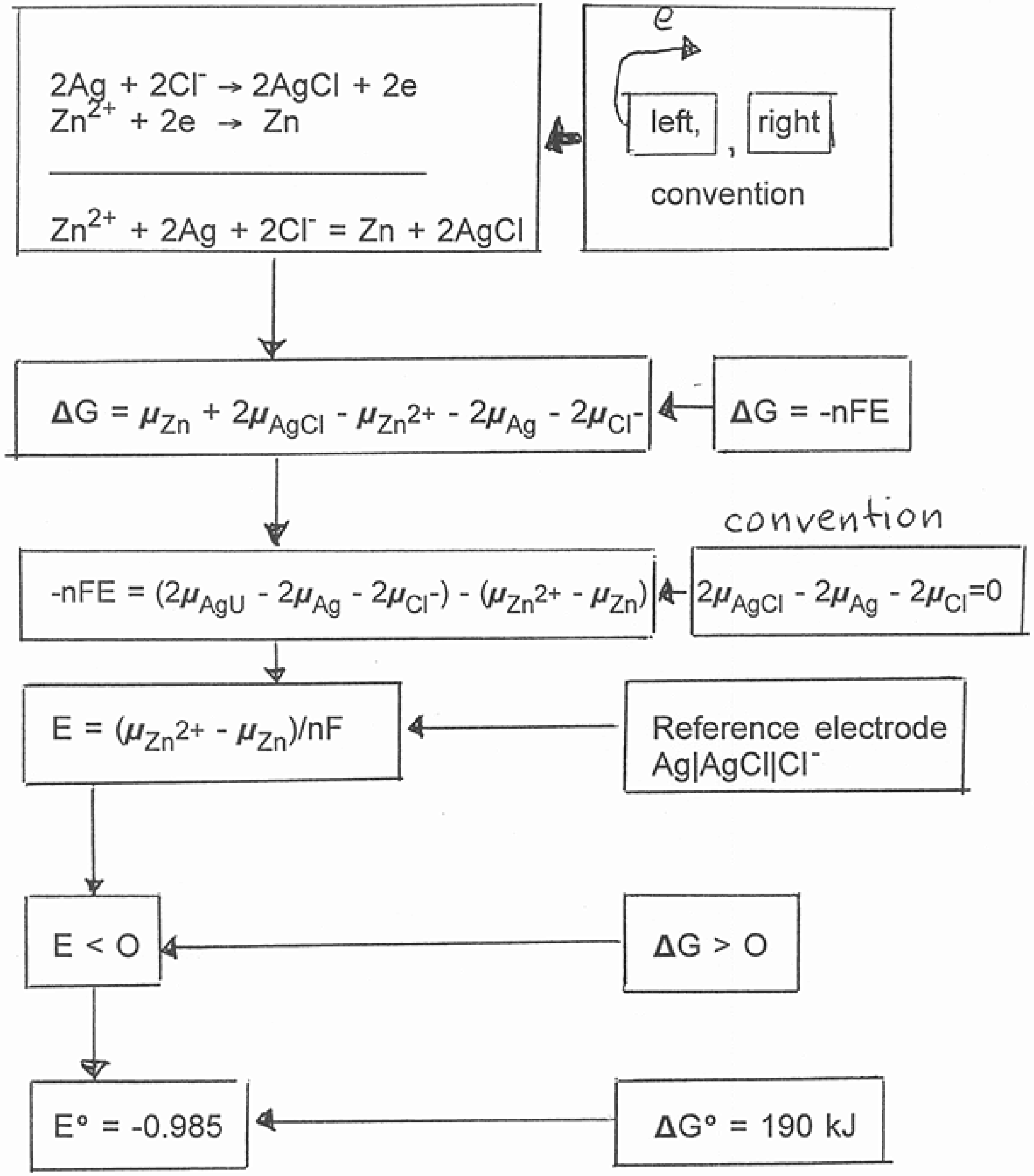
Write electrode reactions such that electrons flow through an external circuit from the reference to the test electrode



$\Delta G>0$ $E<0$

$\Delta G<0$ $E>0$

$Ag|AgCl|Cl^-$, $Zn^{2+}|Zn$



$2Ag + 2Cl^- \rightarrow 2AgCl + 2e$

$Zn^{2+} + 2e \rightarrow Zn$

$Zn^{2+} + 2Ag + 2Cl^- = Zn + 2AgCl$

left, , right

convention

$\Delta G = \mu_{Zn} + 2\mu_{AgCl} - \mu_{Zn^{2+}} - 2\mu_{Ag} - 2\mu_{Cl^-}$

$\Delta G = -nFE$

convention

$-nFE = (2\mu_{AgU} - 2\mu_{Ag} - 2\mu_{Cl^-}) - (\mu_{Zn^{2+}} - \mu_{Zn})$

$2\mu_{AgCl} - 2\mu_{Ag} - 2\mu_{Cl} = 0$

$E = (\mu_{Zn^{2+}} - \mu_{Zn})/nF$

Reference electrode
$Ag|AgCl|Cl^-$

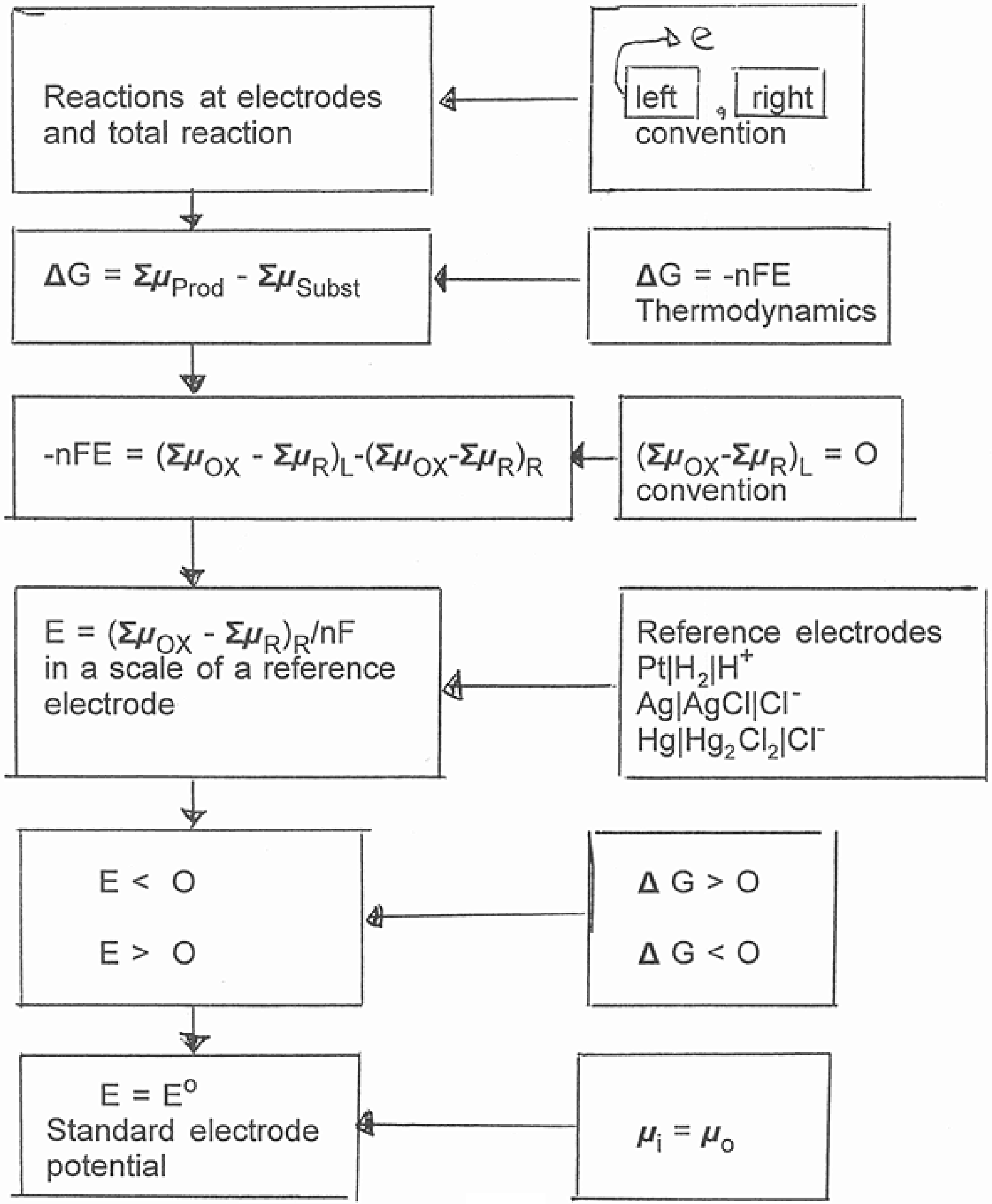
$E < 0$

$\Delta G > 0$

$E^\circ = -0.985$

$\Delta G^\circ = 190$ kJ

Electrochemical cell



Reactions at electrodes and total reaction

e

left , right

convention

$\Delta G = \Sigma\mu_{Prod} - \Sigma\mu_{Subst}$

$\Delta G = -nFE$

Thermodynamics

$-nFE = (\Sigma\mu_{OX} - \Sigma\mu_{R})_L - (\Sigma\mu_{OX} - \Sigma\mu_{R})_R$

$(\Sigma\mu_{OX} - \Sigma\mu_{R})_L = 0$

convention

$E = (\Sigma\mu_{OX} - \Sigma\mu_{R})_R / nF$

in a scale of a reference electrode

Reference electrodes

$Pt|H_2|H^+$

$Ag|AgCl|Cl^-$

$Hg|Hg_2Cl_2|Cl^-$

$E < 0$

$E > 0$

$\Delta G > 0$

$\Delta G < 0$

$E = E^o$

Standard electrode potential

$\mu_i = \mu_o$

Nernst equation

$$2FE = \mu_{Zn^{2+}} - \mu_{Zn}$$

$$2FE = \mu^o_{Zn^{2+}} - \mu^o_{Zn} + RT\ln(a_{Zn^{2+}}/a_{Zn})$$

$$E = E^o + (RT/2F)\ \ln\ (a_{Zn^{2+}}/a_{Zn})$$

$$E = E^o + (RT/nF)\ \ln\ (a_{OX}/a_{Rod})$$

electrode - transducer ↑

$$E^o = \frac{\left(\mu^o_{Zn^{2+}} - \mu_{Zn}\right)}{2F}$$

or

$$E^o = \frac{\left(\mu^o_{Ox} - \mu_{\mathrm{Re}d}\right)}{nF}$$

Type of electrodes

1. Electrodes of the first order

   $Zn^{2+}|Zn$, $Cd^{2+}|Cd(Hg)$

   metal in contact with its own ions:

   $$E = (\mu_{M^{n+}} - \mu_M)/nF = E^o + RT/F \ln a_{M^{n+}}$$

2. Electrodes of the second order, metal covered by insoluble salt of this metal in contact with solution of the anion of the insoluble salt

   $Ag|AgCl|Cl^-$

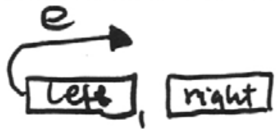
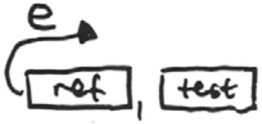
   $$E = (\mu_{AgCl} - \mu_{Ag} - \mu_{Cl^-})/ F = E^o - RT/F \ln a_{Cl^-}$$

3. Electrodes of the third order Metal covered by two films of two insoluble salts

   $M_1|M_1X_1|M_2X_1|M_2^{2+}$

   electrodes sensitive to the metal of the second insoluble salt.

Summary of concepts and conventions

quantity	Assumptions	Conceptual non-measurable quantity	Convention
Electrochemical potential $\bar{\mu}$	separation: $\bar{\mu}_i = \mu_i + z_i F\phi$	ϕ - inner potential μ_i - chemical potential of an ionic species	
Electromotive force E	 $E = E_{Test} - E_{ref}$	electrode potential	$E_{ref} = 0$ chemical potentials of all species of the reference electrode equal to zero
Electromotive force		sign of the electrode potential	 $E < 0$; $\Delta G > 0$ $E > 0$; $\Delta G < 0$

2.3 Conductance, transference numbers, mobility, flux and current

Transference number

When current flows through a cell a fraction t_+ is carried by cations and a fraction t_- by anions such that:

$$t_+ + t_- = 1$$

or in general

$$\sum_i t_i = 1$$

t_i is the transference or transport number

Conductance

Conductance of an electrolyte equal to the reciprocal or resistance is given by:

$$L = \frac{1}{R} = \frac{\kappa A}{l}$$

Where κ is the conductivity, A is the area and l is the length of a segment of electrolyte conducting current

Ionic mobility

Ionic mobility u_i is a limiting velocity of an ion in an electric field of unit field strength. Ionic mobility is measured in $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ or (cm/s per V/m). It is related to the ionic conductivity κ by the formula:

$$\kappa = F\sum_i |z_i| u_i C_i$$

The transference number of ion i is the contribution to conductivity made by that Ion divided by the total conductivity:

$$t_i = \frac{\kappa_i}{\kappa} = \frac{|z_i| u_i C_i}{\sum_j |z_j| u_j C_j}$$

Ionic mobilities in aqueous solution at 25 °C, $u/10^{-4}\ \mathrm{cm^2\ s^{-1}\ V^{-1}}$

Cations		Anions	
H^+	36.23	OH^-	20.64
Li^+	4.01	F^-	5.70
Na^+	5.19	Cl^-	7.91
K^+	7.62	Br^-	8.09
Rb^+	7.92	I^-	7.96
Ag^+	6.42	NO_3^-	7.40
NH_4^+	7.63	CO_3^{2-}	7.46
Ca^{2+}	6.17	SO_4^{2-}	8.29
Cu^{2+}	5.56	$CH_3CO_2^-$	4.24
La^{3+}	7.21		

Equivalent conductivity

Defined by:

$$\Lambda = \frac{\kappa}{C\left|z\right|}$$

since $\kappa = F\sum_i \left|z_i\right| u_i C_i$ and $\kappa_i = F\left|z_i\right| u_i C_i$

$$\Lambda = F(u_+ + u_-)$$

or

$$\Lambda = (\lambda_+ + \lambda_-)$$

where

$$\lambda_i = F u_i$$

is the equivalent conductivity of individual ion

In the case of a single electrolyte :

$$t_i = \frac{\lambda_i}{\Lambda}$$

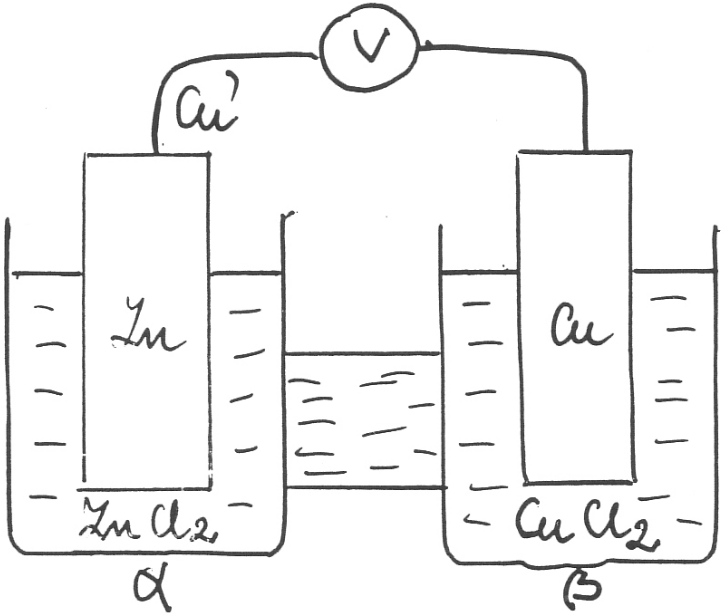
or

$$t_i = \frac{u_i}{u_+ + u_-}$$

or

$$t_i = \frac{|z_i| C_i \lambda_i}{\sum_j |z_j| C_j \lambda_j}$$

2.4 Electrochemical cell with a liquid junction potential

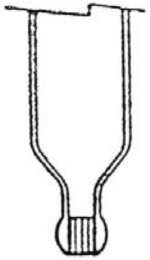


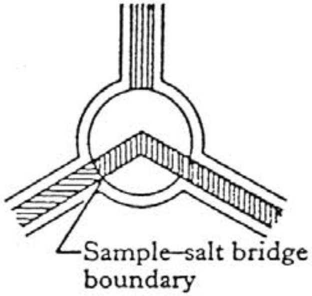
$$Cu' \,|\, Zn \,|\, ZnCl_2 \,\vdots\, CuCl_2 \,|\, Cu$$

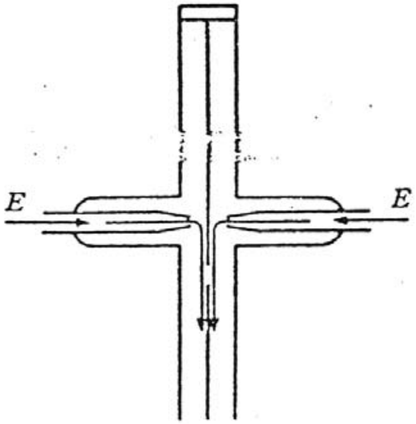
$$E = \phi(Cu) - \phi(Cu') = \left\{\phi(Zn) - \phi(Cu')\right\} + \left\{\phi(\alpha) - \phi(Zn)\right\} + \left\{\phi(\beta) - \phi(\alpha)\right\} + \left\{\phi(Cu) - \phi(\beta)\right\}$$

$$\left\{\phi(\beta) - \phi(\alpha)\right\} = E_{LJ}$$

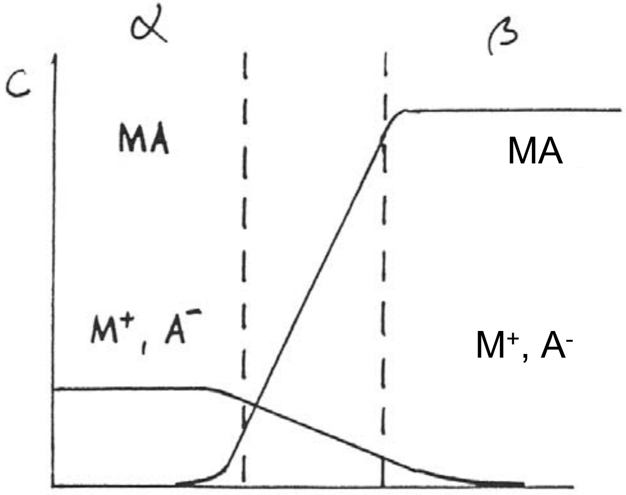
Different ways to make the liquid junction potential





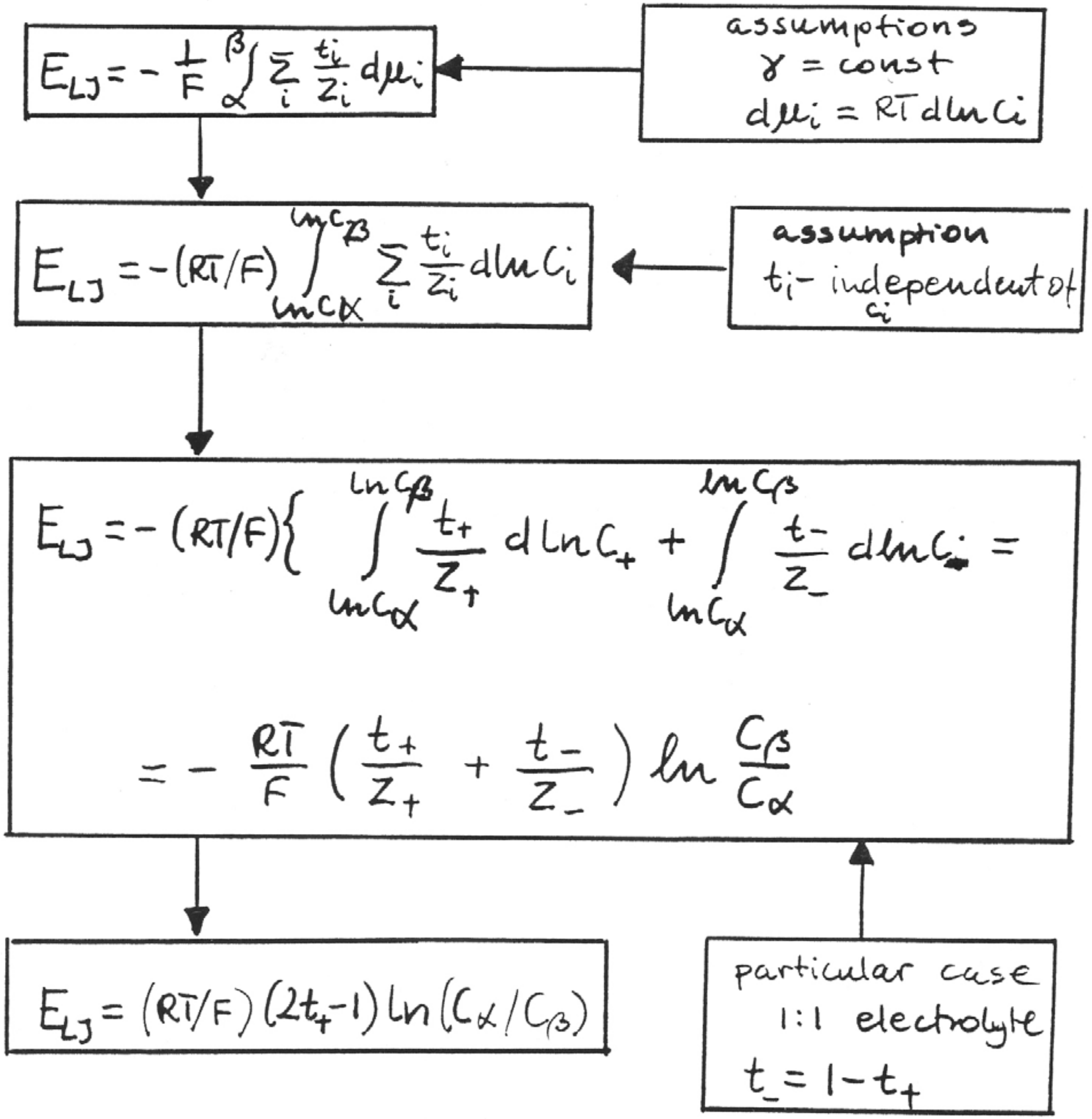


Boundary between two electrolyte solutions



$$\boxed{E_{LJ} = \phi_\beta - \phi_\alpha = -\frac{1}{F}\int_\alpha^\beta \sum_i \frac{t_i}{z_i}\, d\mu_i}$$

Liquid junction potential between two different solutions of the same electrolyte



$$E_{LJ} = -\frac{1}{F}\int_{\alpha}^{\beta}\sum_i \frac{t_i}{z_i}\, d\mu_i$$

assumptions
$\gamma = const$
$d\mu_i = RT\, d\ln c_i$

$$E_{LJ} = -(RT/F)\int_{\ln c_\alpha}^{\ln c_\beta}\sum_i \frac{t_i}{z_i}\, d\ln c_i$$

assumption
t_i - independent of c_i

$$E_{LJ} = -(RT/F)\left\{\int_{\ln c_\alpha}^{\ln c_\beta}\frac{t_+}{z_+}\, d\ln c_+ + \int_{\ln c_\alpha}^{\ln c_\beta}\frac{t_-}{z_-}\, d\ln c_i = \right.$$

$$= -\frac{RT}{F}\left(\frac{t_+}{z_+} + \frac{t_-}{z_-}\right)\ln\frac{c_\beta}{c_\alpha}$$

$$E_{LJ} = (RT/F)(2t_+ - 1)\ln(c_\alpha/c_\beta)$$

particular case
1:1 electrolyte
$t_- = 1 - t_+$

Example: concentration cell

$$Ag \,|\, AgCl \,|\, \underset{\alpha}{MCl\,(C_1)} \;\vdots\; \underset{\beta}{MCl\,(C_2)} \,|\, AgCl \,|\, Ag$$

$$E_1 = -\left(\frac{RT}{F}\right) \ln C_{Cl^-}^{(1)} + const$$

$$E_2 = -\left(\frac{RT}{F}\right) \ln C_{Cl^-}^{(2)} + const$$

$$E_{LJ} = \left(\frac{RT}{F}\right)(2t_+ - 1) \ln C_1/C_2$$

$$E = E_2 - E_1 + E_{LJ}$$

$$E = (RT/F)\{\ln C_1/C_2 + (2t_+ - 1) \ln C_1/C_2 =$$

$$= (RT/F)\, 2t_+ \ln C_1/C_2$$

$$E_{LJ} = E\,\frac{(2t_+ - 1)}{2t_+}$$

Computed Potentials of the Liquid Junction in Cells of the Type

$$Ag'|AgCl|MCl(C_1) \,\vdots\, MCl(C_2)|AgCl|Ag$$

$C_1 = 0.04M \,\vdots\, C_2 = 0.005M$

Electrolyte	t_M	Measured E/mV	E_{LJ}	calculated $E_2 - E_1$ mV
NaCl	0.391	39.6	−11.1	50.7
KCl	0.490	49.6	−1.0	50.6
HCl	0.826	84.2	+33.2	50.9

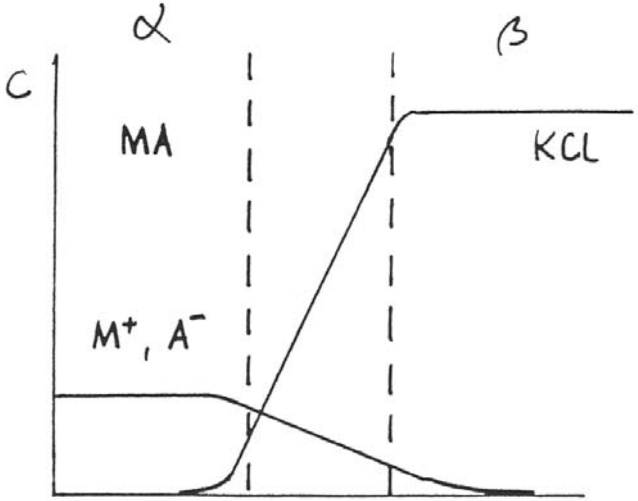
Henderson equation

Activity coefficients independent of concentration and the liquid junction a continuous mixture of the two electrolytes

$$\boxed{E_{LJ} = \frac{RT}{F} \frac{\sum_{n} u_i z_i (c_i'' - c_i')}{\sum z^2 u_i (c_i'' - c_i')} \ln \frac{\sum z^2 c_i' u_i}{\sum z^2 c_i'' u_i}}$$

How to eliminate liquid junction potential?

Consider the following interface



$$t_{A^-} = \frac{u_{A^-}C_{A^-}}{u_{A^-}C_{A^-} + u_{Cl^-}C_{Cl^-} + u_{K^+}C_{K^+} + u_{M^+}C_{M^+}} \qquad t_{A^-} = \frac{u_{A^-}C_{A^-}}{u_{A^-}C_{A^-} + u_{Cl^-}C_{Cl^-} + u_{K^+}C_{K^+} + u_{M^+}C_{M^+}}$$

assume that $C_{KCl} >> C_{MA}$ then $u_{Cl^-}C_{Cl^-} + u_{K^+}C_{K^+} >> u_{A^-}C_{A^-} + u_{M^+}C_{M^+}$

in predominant fraction of the liquid – junction region:

$$t_{A^-} = \frac{u_{A^-}}{u_{Cl^-} + u_{K^+}}\left(\frac{C_{MA}}{C_{KCl}}\right) \approx 0 \qquad \text{and} \qquad t_{M^+} = \frac{u_{M^+}}{u_{Cl^-} + u_{K^+}}\left(\frac{C_{MA}}{C_{KCl}}\right) \approx 0$$

Consequently:

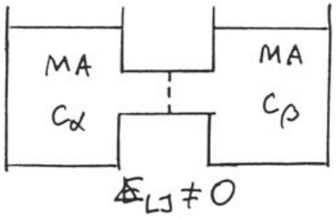
$$E_{LJ} = -\frac{1}{F}\int_{\alpha}^{\beta}\sum_{i}\frac{t_i}{z_i}d\mu_i = -\frac{1}{F}\int_{\alpha}^{\beta}\left(t_{K^+}d\mu_{K^+} - t_{Cl^-}d\mu_{Cl^-}\right)$$

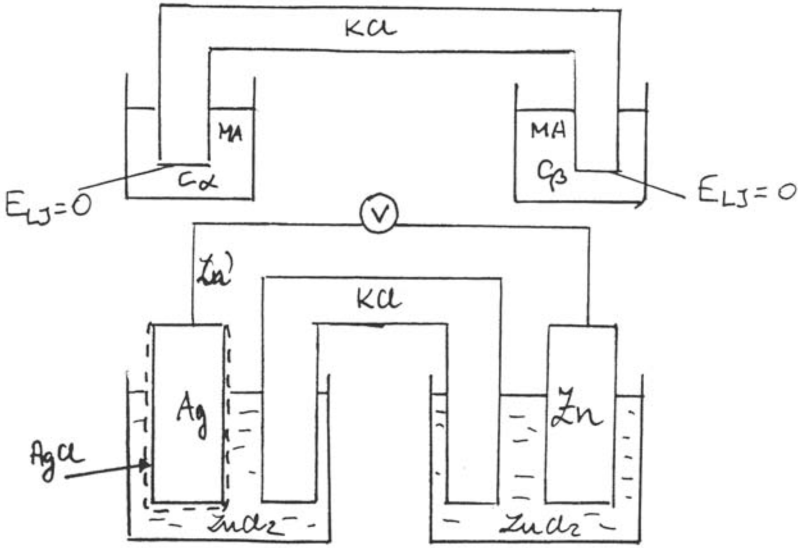
To a good approximation $d\mu_{K^+} = d\mu_{Cl^-} = \frac{1}{2}d\mu_{KCl}$ and since

$$t_{K^+} \approx t_{Cl^-}$$

$$E_{LJ} = -\frac{1}{F}\int_{\alpha}^{\beta}\left(t_{K^+}d\mu_{K^+} - t_{Cl^-}d\mu_{Cl^-}\right) = -\frac{1}{F}\int_{\alpha}^{\beta}\frac{1}{2}\left(t_{K^+} - t_{Cl^-}\right)d\mu_{KCl} \approx 0$$

Elimination of the liquid junction potential by a salt bridge





$$E = \frac{RT}{2F} \ln a_{Zn} + \text{const}$$

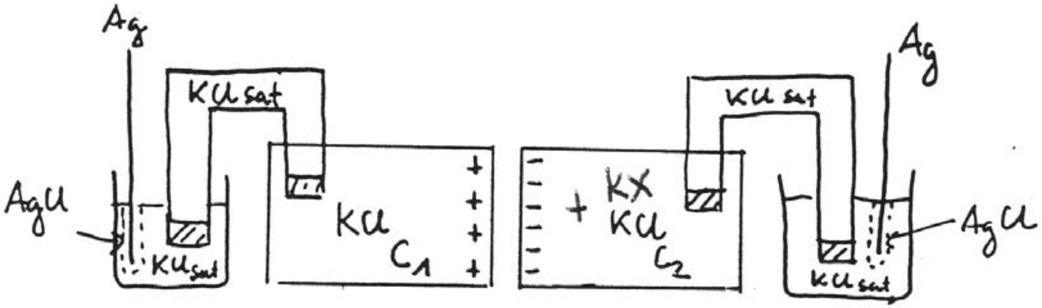
2.5 Donnan equilibrium and Donnan potential(IUPAC definitions)

Donnan equilibrium

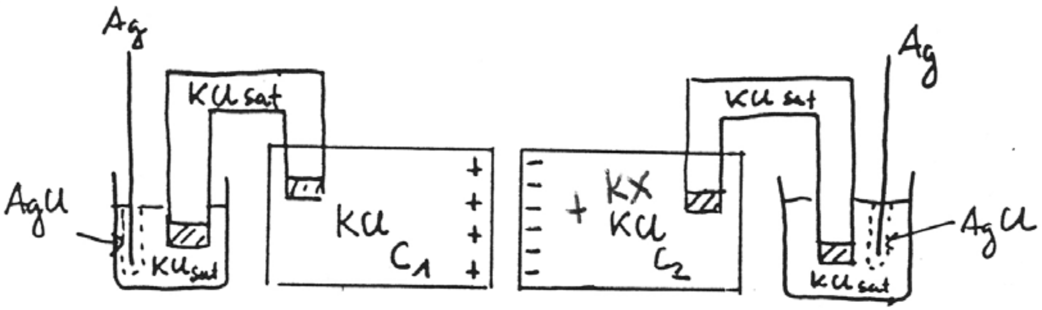
The equilibrium characterized by an unequal distribution of diffusible ions between two ionic solutions (one or both of the solutions may be gelled) separated by a membrane which is impermeable to at least one of the ionic species present, e.g. because they are too large to pass through the pores of the membrane. The membrane may be replaced by other kinds of restraint, such as gelation, the field of gravity, etc., which prevent some ionic components from moving from one phase to the other, but allow other components to do so.

Donnan emf (Donnan potential)

The potential difference E_{D} at zero electric current between two identical salt bridges, usually saturated KCl bridges (conveniently measured by linking them to two identical electrodes) inserted into two solutions in



Donnan equilibrium and Donnan potential



$$\bar{\mu}_K(1) = \bar{\mu}_K(2)$$

$$\bar{\mu}_{Cl}(1) = \bar{\mu}_{Cl}(2)$$

$$\bar{\mu}_i = \mu_i^0 + RT \ln a_i + z_i F \phi$$

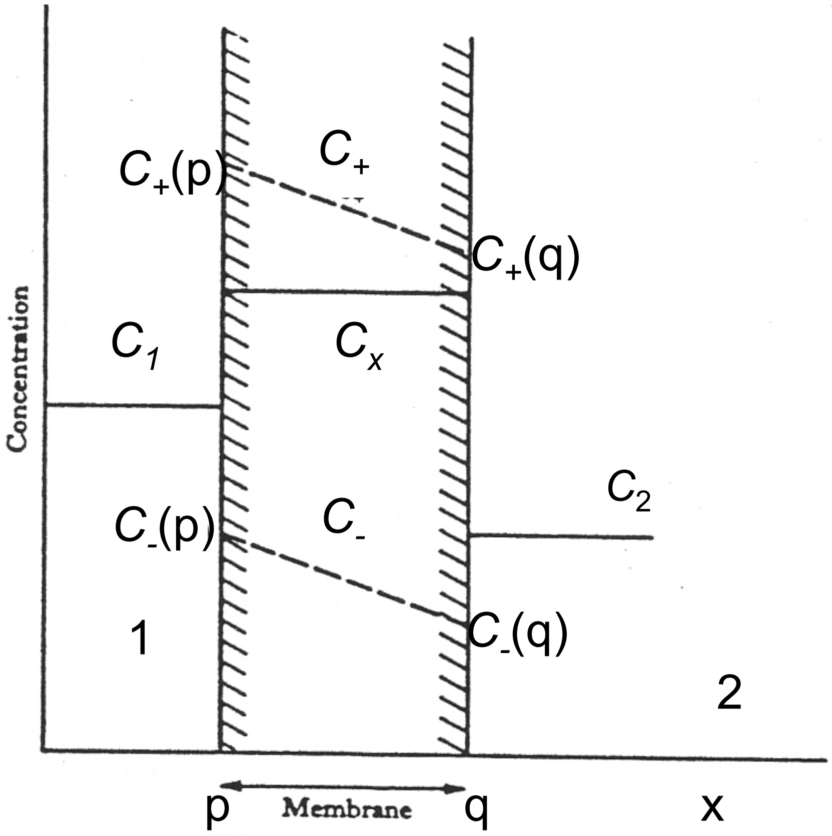
$$\mu_K^0 + RT \ln a_K(1) + F\phi_1 = \mu_K^0 + RT \ln a_K(2) + F\phi_2$$

$$\mu_{Cl}^0 + RT \ln a_{Cl}(1) - F\phi_1 = \mu_{Cl}^0 + RT \ln a_{Cl}(2) - F\phi_2$$

$$\boxed{\begin{aligned} \Delta\phi_D = \phi_2 - \phi_1 &= \frac{RT}{F} \ln \frac{a_K(1)}{a_K(2)} \approx \frac{RT}{F} \ln \frac{c_K(1)}{c_K(2)} = \\ &= \frac{RT}{F} \ln \frac{c_{Cl}(2)}{c_{Cl}(1)} \end{aligned}}$$

Donnan Potential

2.6 Selectively permeable membranes



$$\Delta\phi = \phi(2) - \phi(1) = \left\{\phi(2) - \phi(q)\right\} + \left\{\phi(q) - \phi(p)\right\} + \left\{\phi(p) - \phi(1)\right\}$$

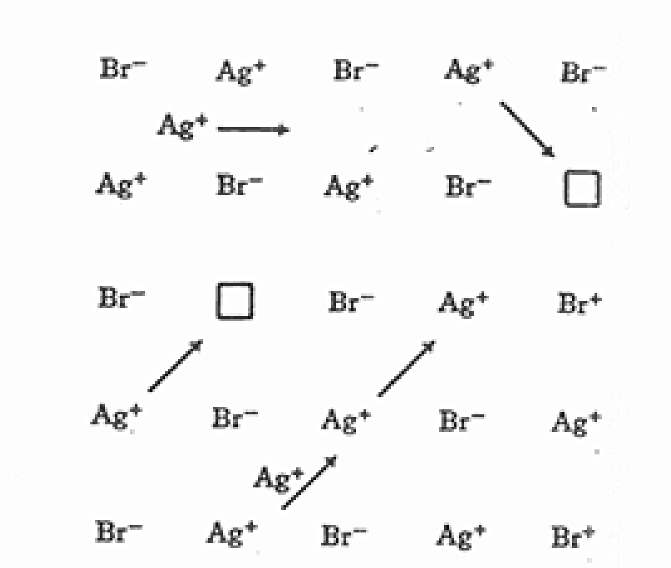
$$\Delta\phi = \Delta\phi_D(2) + \Delta\phi_{LJ} + \Delta\phi_D(1)$$

Classification of ion-selective eletcrodes

Primary ion-selective electrodes

1. Crystalline Electrodes contain mobile ions of one sign and fixed sites of opposite sign. They may be homogeneous or heterogeneous.

   a. *Homogeneous membrane electrodes* are ion-selective electrodes in which the membrane is a crystalline material prepared from either a single compound or a homogeneous mixture of compounds (e.g., Ag_2S, AgI/Ag_2S). **or AgBr**



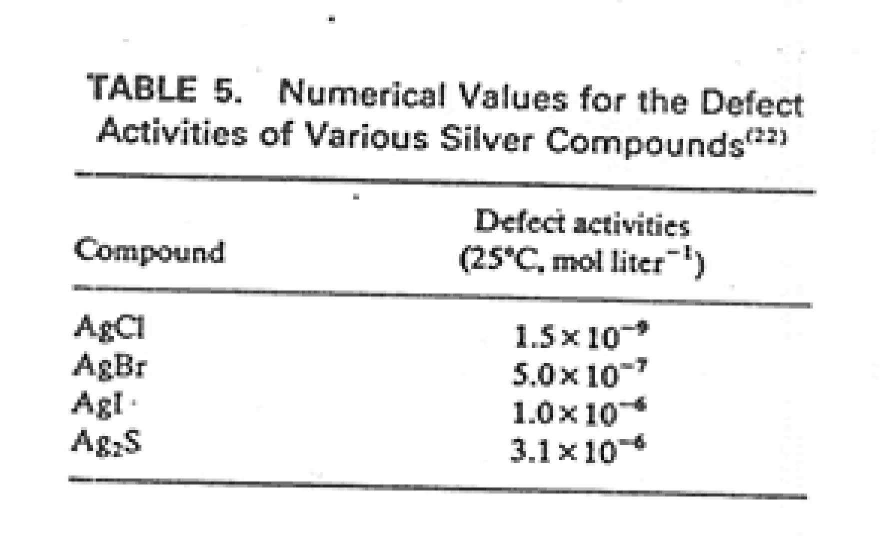


TABLE 5. Numerical Values for the Defect Activities of Various Silver Compounds[22]

Compound	Defect activities (25°C, mol liter^{-1})
AgCl	1.5×10^{-9}
AgBr	5.0×10^{-7}
AgI	1.0×10^{-6}
Ag_2S	3.1×10^{-6}

Frenkel's scheme for the transport of silver ions in the AgBr crystal lattice. The silver cations are in interstitial positions in the crystal lattice and the same number of unoccupied lattice positions are in the cation part of the lattice

2. Non-crystalline Electrodes. In these electrodes, a support matrix, containing an ion exchanger (either cationic or anionic), a plasticizer solvent, and possibly an uncharged, selectivity-enhancing species, form the ion-selective membrane which is usually interposed between two aqueous solutions. The matrix can be either macroporous (e.g., poly(propylene carbonate) filter, glass frit, etc.) or microporous (e.g., "thirsty" glass or polymeric material such as PVC) yielding with the ion-exchanger and the solvent a "solidified" homogeneous mixture. These electrodes exhibit a response due to the presence of the *selectivity-enhancing species* (which exhibit an ion-exchange property) in the membrane. The *solvent-polymeric-membrane* is an example.

   a. *Rigid, self-supporting, matrix electrodes* (e.g., synthetic cross-linked polymer or glass electrodes) are ion-selective electrodes in which the sensing membrane is a thin polymer with fixed sites or a thin piece of glass. The chemical composition of the polymer (e.g. polystyrenesulfonate, sulfonated poly(tetrafluoroethylene), poly(vinyl chloride) aminated) or the glass determines the membrane selectivity. *pH glass electrode* see in section 3.4.12.

General purpose glass electrode

Glass composition

22% Na_2O
6% CaO
72% SiO_2

SiO_4^{4-} - charged silicate groups - charge is balanced by cations

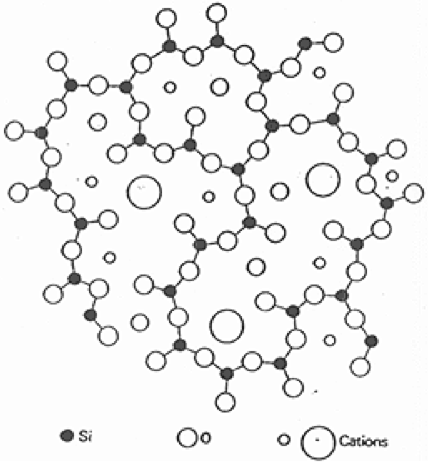
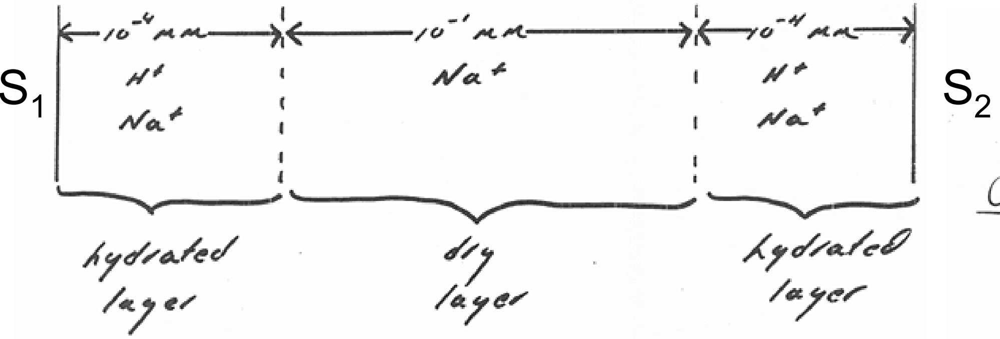


FIGURE 20–4 Cross-sectional view of a silicate glass structure. In addition to the three Si—O bonds shown, each silicon is bonded to an additional oxygen atom, either above or below the plane of the paper. (Adapted with permission

GLASS ELECTRODE



Conduction across the membrane occurs by the following reactions:

$$H^+(s_1) + Na^+(p) = H^+(p) + Na^+(s_1)$$
$$H^+(s_2) + Na^+(q) = H^+(q) + Na^+(s_2)$$

In the dry layer mobile Na^+ ions are responsible for conduction

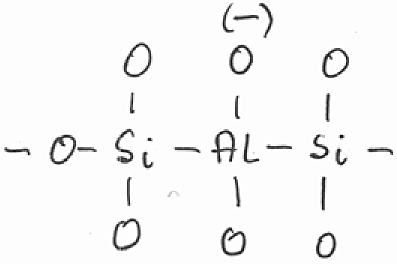
The above equilibria are determined by the H^+ activities in the solutions on the two sides of the membrane

Diffusion coefficients of Na^+	
Hydrated layer	5×10^{-11} cm²s⁻¹
Dry layer	5×10^{-14} cm²s⁻¹
Aqueous solution	5×10^{-6} cm²s⁻¹

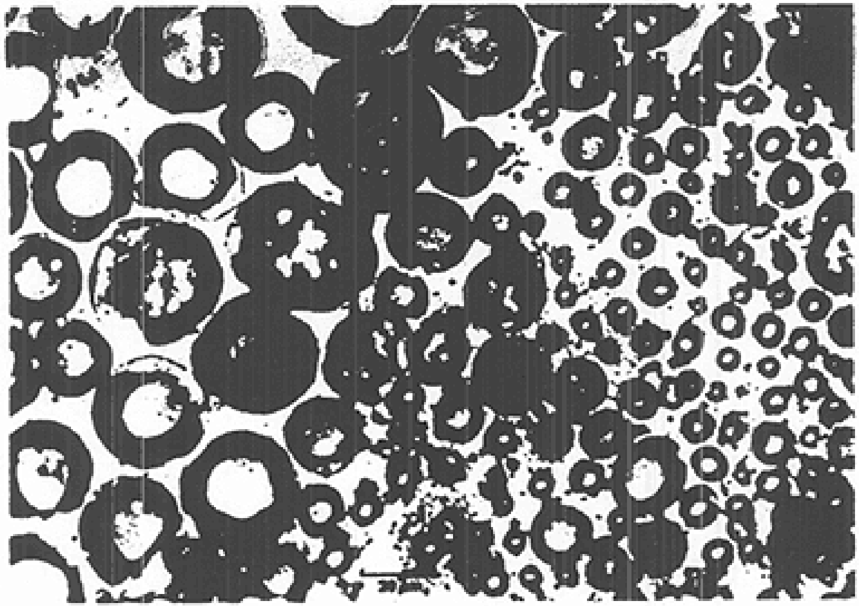
Glass electrodes suitable for determining Li^+, Na^+, K^+

Cation	Glass composition
Li^+	15% Li_2O - 25% Al_2O_3 - 60% SiO_2
Na^+	11% Na_2O - 18% Al_2O_3 - 71% SiO_2
K^+	27% K_2O - 5% Al_2O_3 - 68% SiO_2

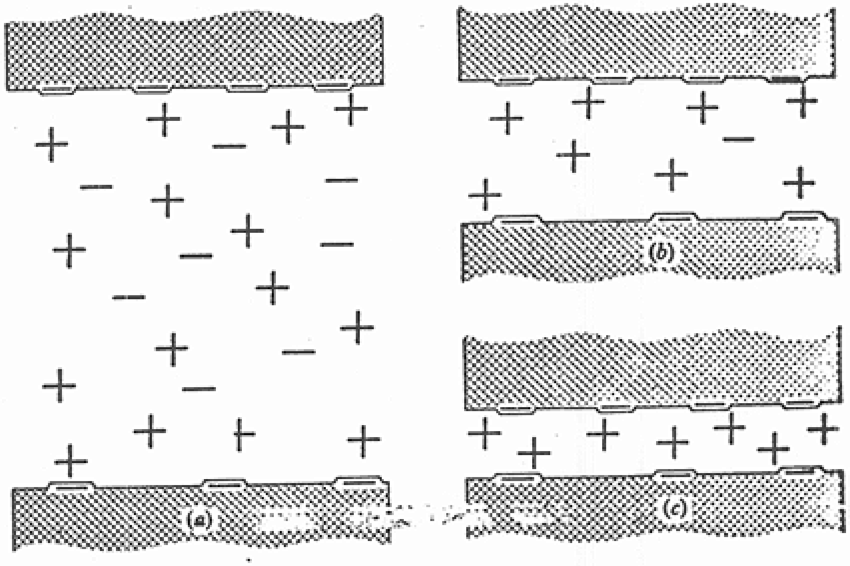
Glass electrodes sensitive to alkali metal ions - contain trivalent metal ions such as Al^{3+} which create the ion exchange centers



A

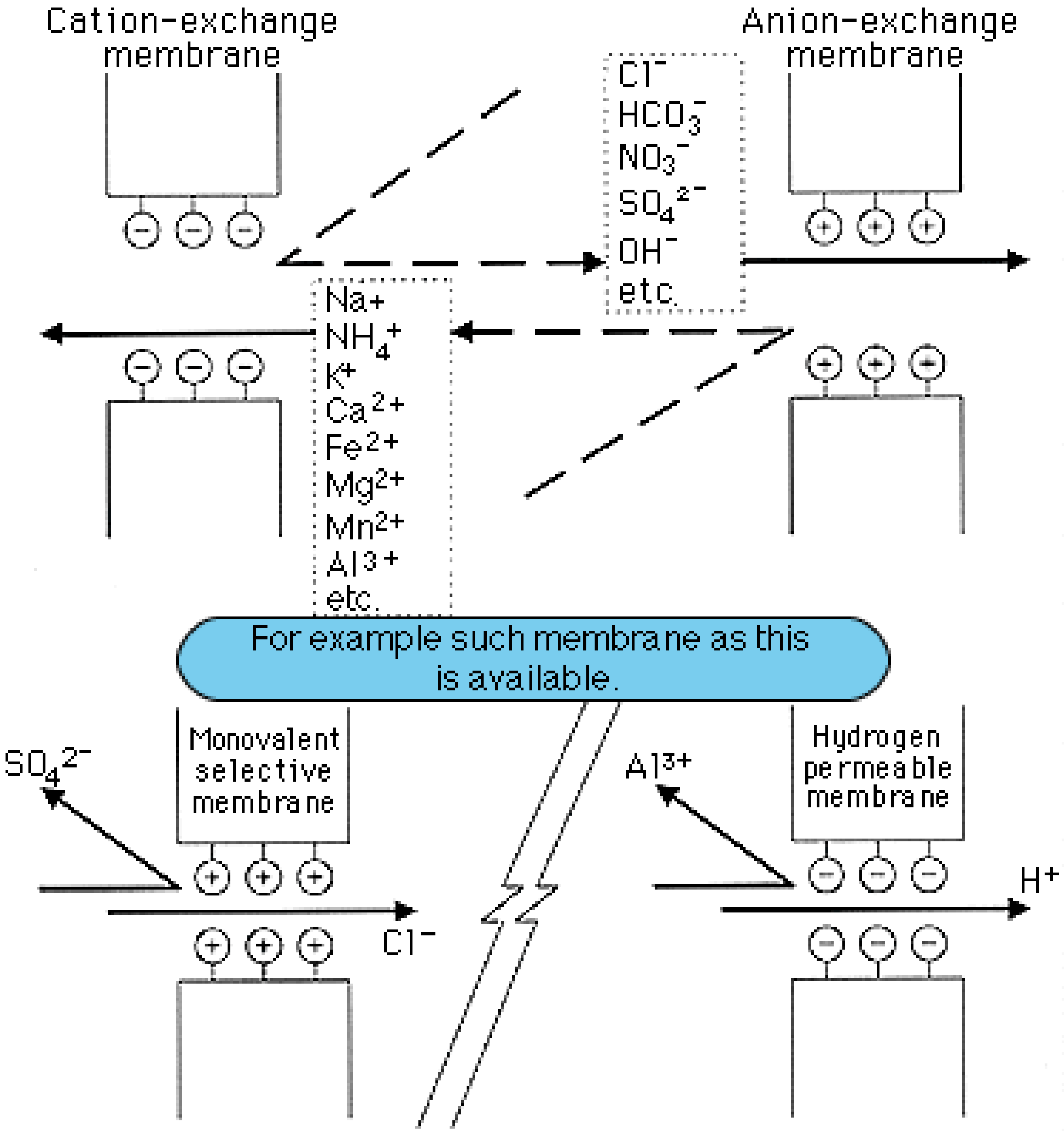


B



A Visible-light microscope photomicrograph showing pores (dark circles) in polyvinyl chloride matrix membrane incorporating didecylphosphoric acid–dioctylphenylphosphonate shaken with a molar solution of calcium chloride [358]. By permission of the Society for Analytical Chemistry, London.

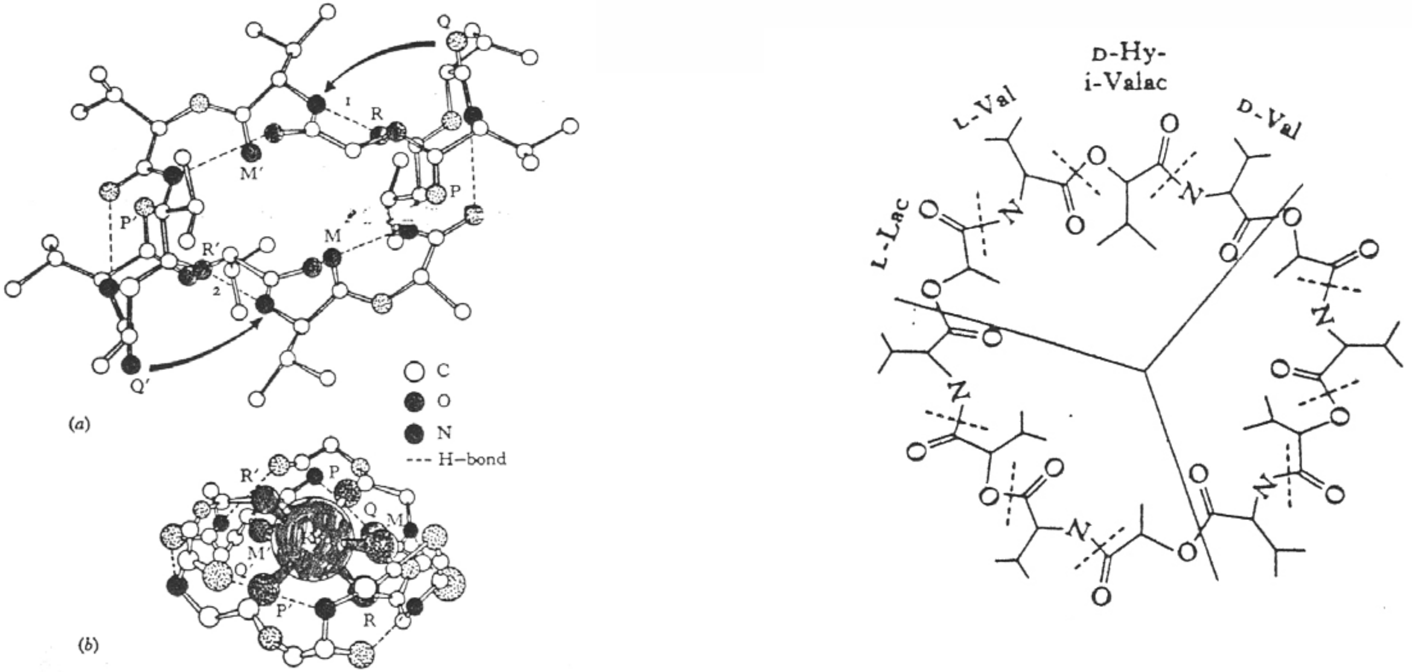
B Ion distribution in a porous membrane with fixed negative ions: (*a*) pore diameter is large so that the electric double layer and the pore walls do not affect the passage of anions; (*b*) pore diameter is smaller so that the electric double layer decreases the permeability for anions; (*c*) the pore diameter is very small so that the electric double layer completely suppresses the permeability for anions. After Sollner [1025].



For example such membrane as this is available.

b. *Electrodes with mobile charged sites*:

1. Positively charged, hydrophobic cations (e.g., quaternary ammonium cations or cations of substitutionally inert, transition metal complexes of such ligands as derivatives of 1,10-phenanthroline) of which, when dissolved in a suitable organic solvent and held in an inert support (e.g., poly(propylene



valinomicine

Liquid Membranes with Dissolved Ion – Exchanger

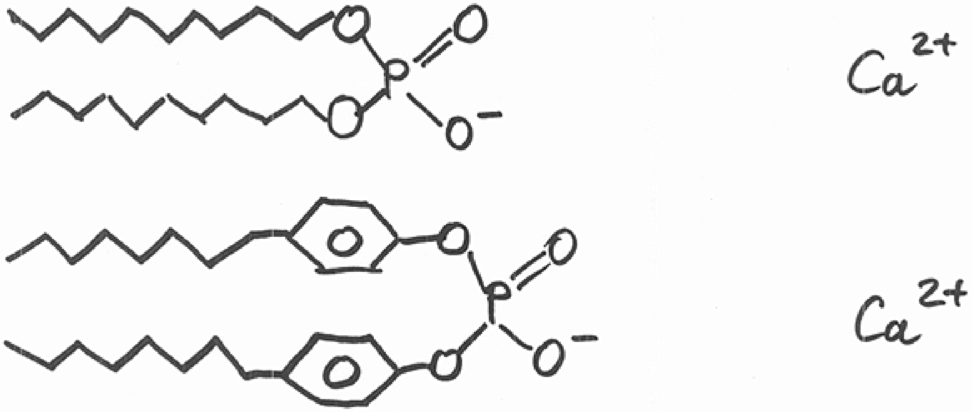
Liquid membranes are formed from immiscible liquids that contain exchangers selectively binding certain ions.

Early liquid membranes were prepared from immiscible liquid and ion exchangers that were retained in the immiscible liquid.

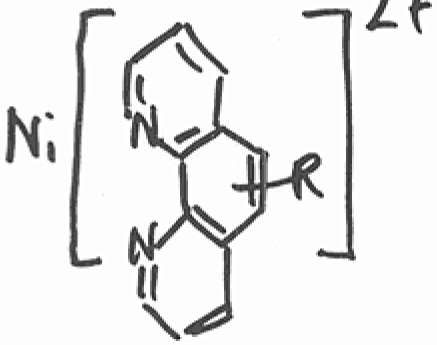
Recently ion – exchangers are dissolved in a PVC membrane. The liquid ion- exchanger and PVC are dissolved in a solvent such a s tetrahydrofuran. Evaporation of the solvent leaves a flexible membrane, which can be cut and cemented to the end of a glass or plastic tube.

There are three kinds of active substances in liquid membranes:

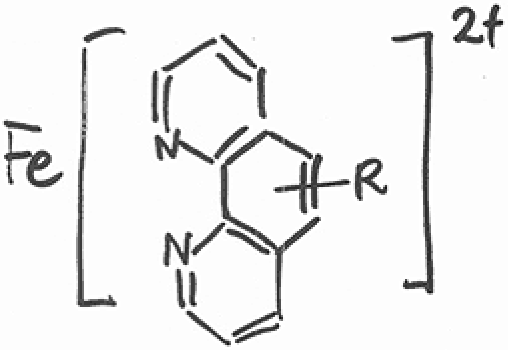
cation exchangers



anion exchangers

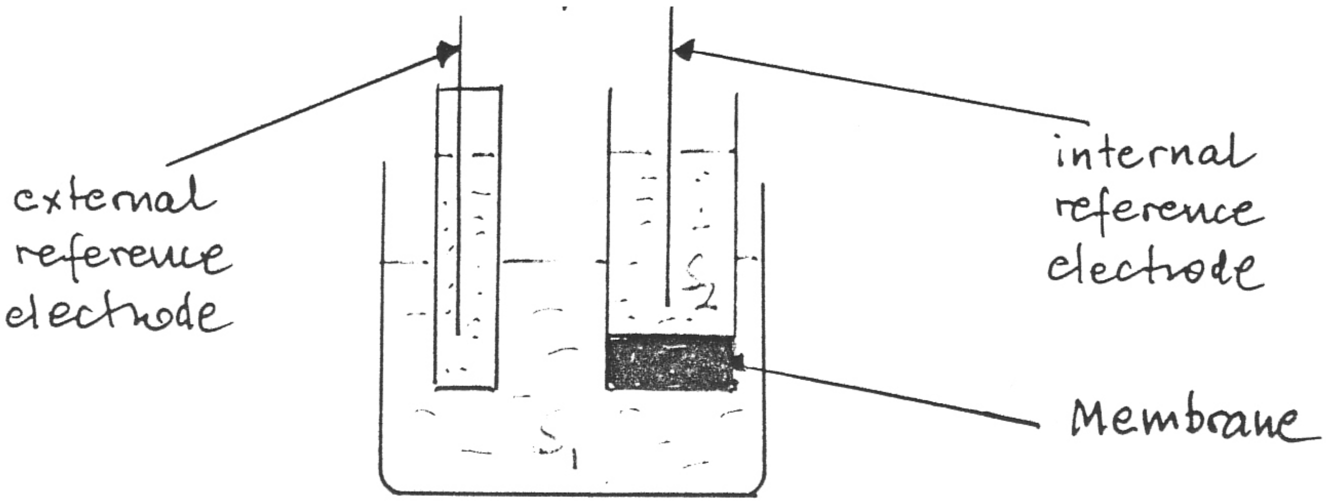


NO_3^-



Cl^-

2.8. Membrane potential – overview



$$E_{cell} = E_{ref,int} - E_{ref,ext} + \sum E_{LJ} + E_M$$

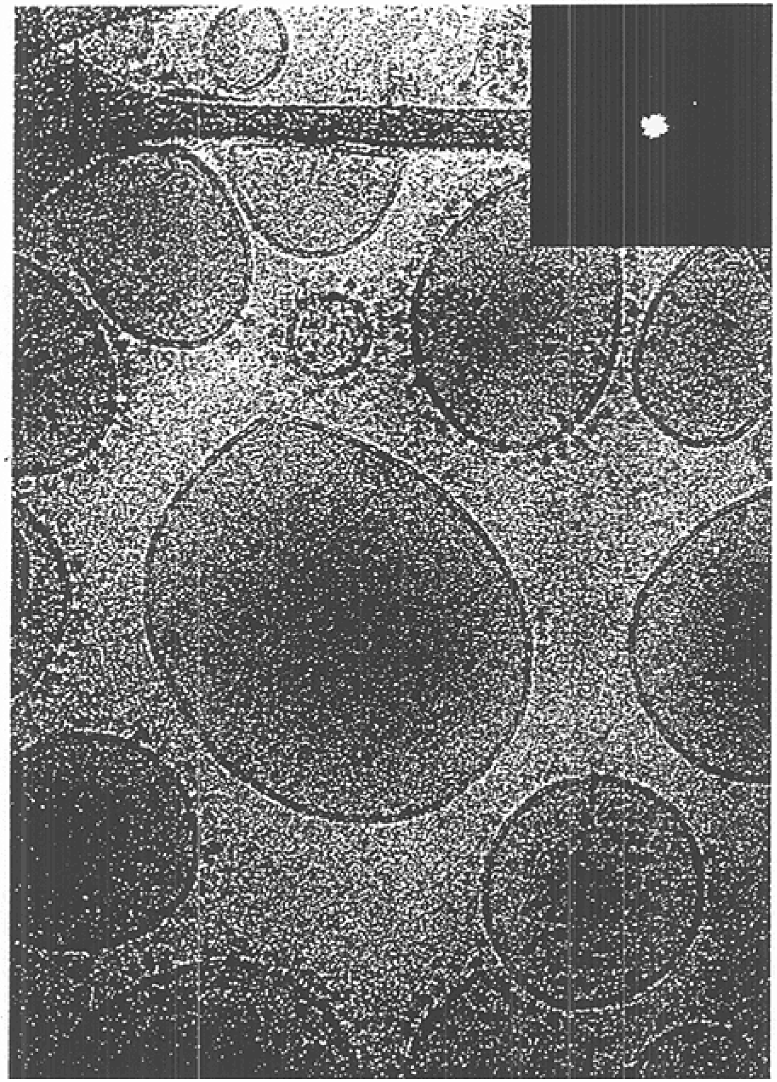
$$\text{if } E_{ref,int} = E_{ref,ext} \text{ and } \sum E_{LJ} \simeq 0$$

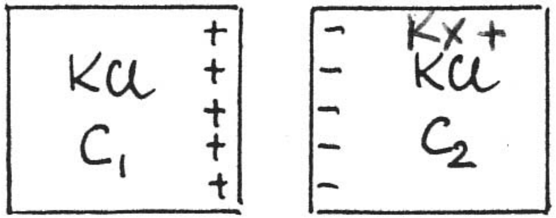
$$E_{cell} = E_M = \phi(2) - \phi(1)$$

1. Ultrathin membranes (phospholipid bilayer)

1. Biological membranes

TEM image with nm resolution shows phospholipid bilayer with protein channels that provide selective transport of K^+ and Na^+ across the membrane



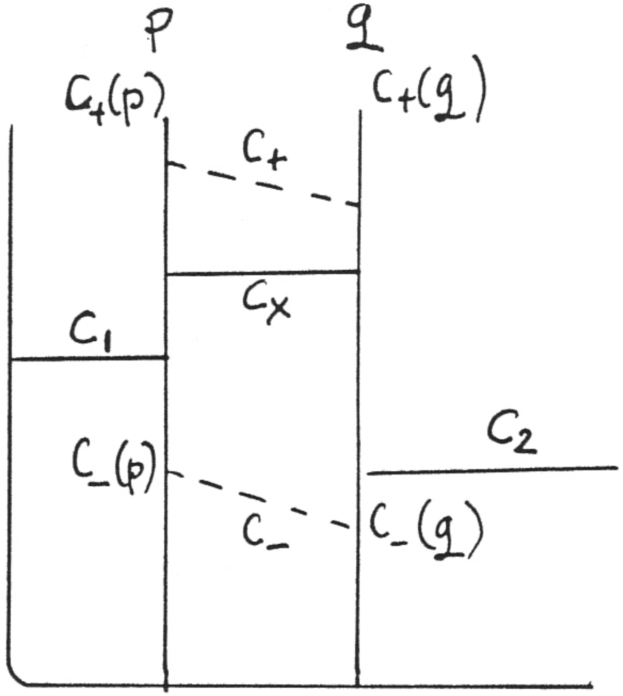


Donnan equilibrium

$$\Delta\phi_D = \phi(2) - \phi(1) = \frac{RT}{F}\ln\frac{c_{K^+}(1)}{c_{K^+}(2)} =$$

$$= -\frac{RT}{F}\ln\frac{c_{Cl^-}(1)}{c_{Cl^-}(2)}$$

2. Macroscopic membranes



$$E_M = \phi_2 - \phi_1 = \underbrace{\{\phi(2) - \phi(q)\}}_{} + \underbrace{\{\phi(q) - \phi(p)\}}_{} + \underbrace{\{\phi(p) - \phi(1)\}}_{}$$

$$E_M = \Delta\phi_D(2) + \Delta\phi_{LJ} + \Delta\phi_D(1)$$

General expression for the membrane potential

$$E_M = \frac{RT}{z_K F} \ln \{ a_K(1) + K_{KJ}^{pot} a_J(1) \} + \text{const}$$

2.8 Selectivity of the membrane electrode

No electrode is entirely selective towards the ion specified. The presence of other ions can seriously impair electrode performance.

If the analyte contains inerferent J with activity a_j , the ISE potential is given by :

$$E_M = E_o + \frac{RT}{z_i F} \ln\left\{a_i + K_{ij} a_j^{z_i/z_j}\right\}$$

where K_{ij} is called the selectivity coefficient of the ISE for ion I with respect to ion J. K_{ij} is a measure of the effect of interfering ions on the determination of the test ion I . For example , for Na^+ being the interfering ion for the calcium ion selective electrode, $K_{CaNa} = 10^{-3}$. This means that the electrode is 1000 times more responsive to Ca^{2+} than to Na^+

$$E_M = \Delta\phi_M = \frac{RT}{z_k F} \ln\left\{ a_k + \sum K_{kj}^{pot} a_j^{\frac{z_k}{z_j}} \right\} + const$$

Limiting solutions

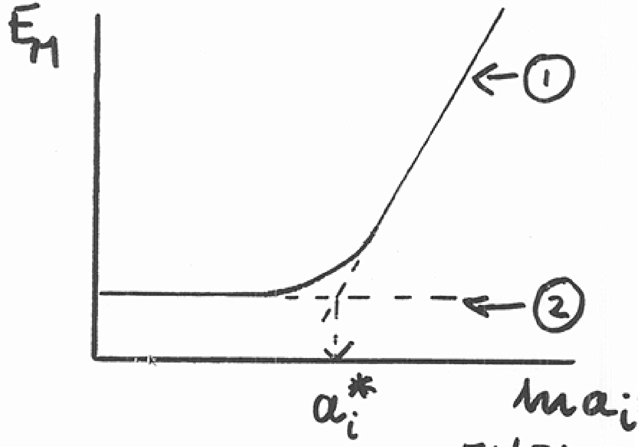
① $a_i \gg K_{ij} a_j^{z_i/z_j}$

$$\boxed{E_M = E_0 + \frac{RT}{z_i F} \ln a_i}$$ (Nernstian behaviour)

② $a_i \ll K_{ij} a_j^{z_i/z_j}$

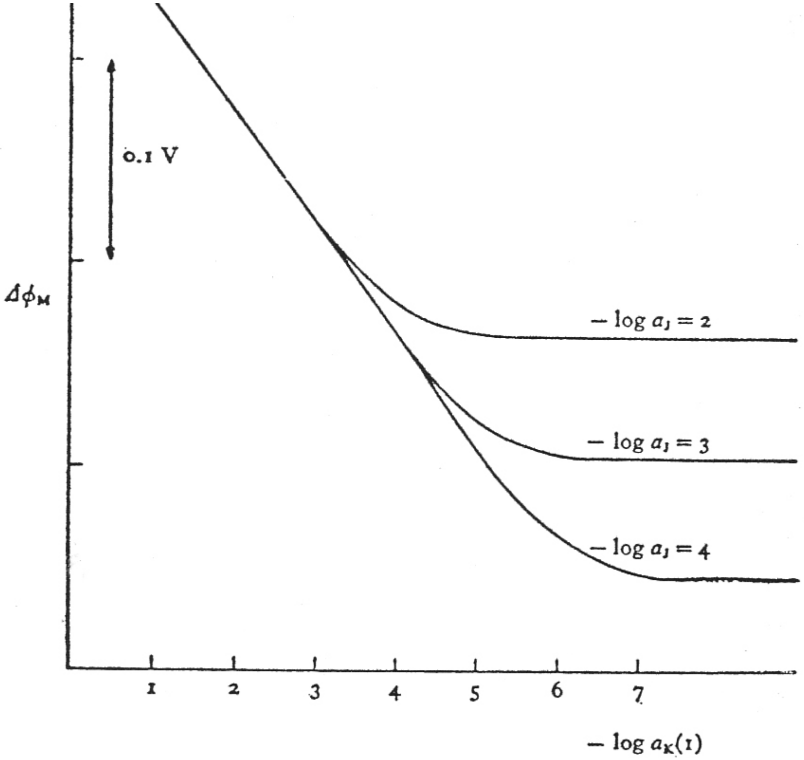
$$E_M = E_0 + \frac{RT}{z_i F} \ln K_{ij} a_j^{z_i/z_j} =$$

$$\boxed{= E_0 + \frac{RT}{z_i F} \ln K_{ij} + \frac{RT}{z_j F} \ln a_j}$$

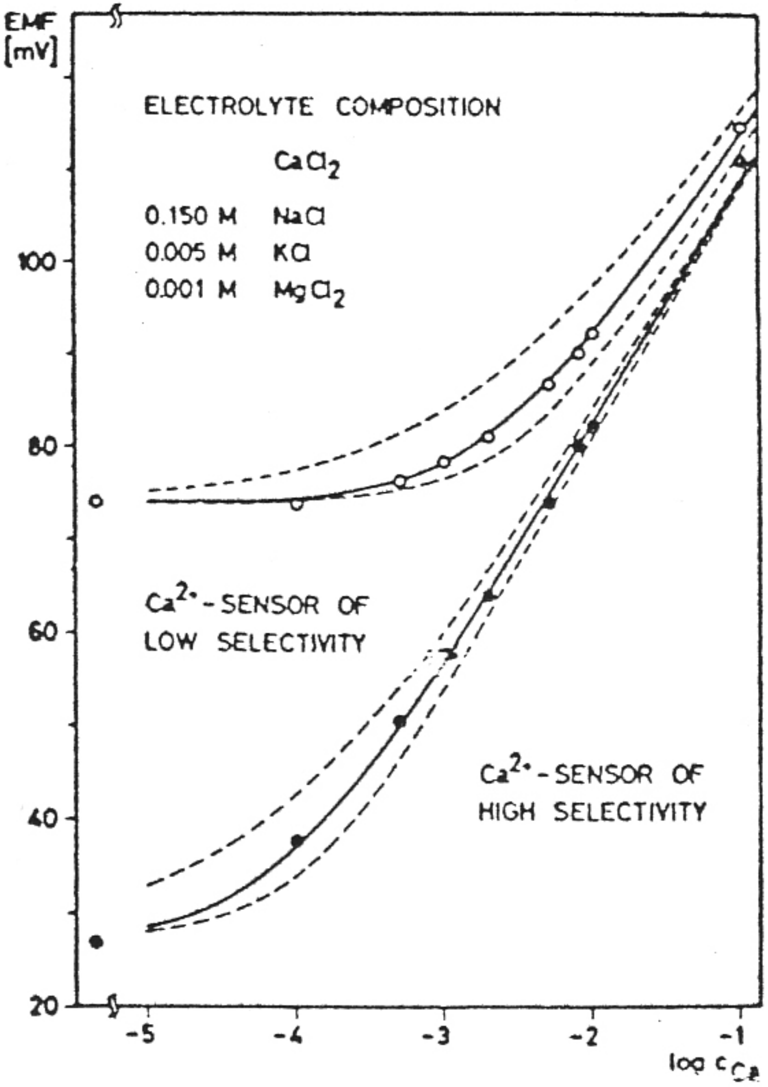


$a_i^* = K_{ij} \, a_j^{z_i/z_j}$; $\boxed{K_{ij} = \dfrac{a_i^*}{a_j^{z_i/z_j}}}$

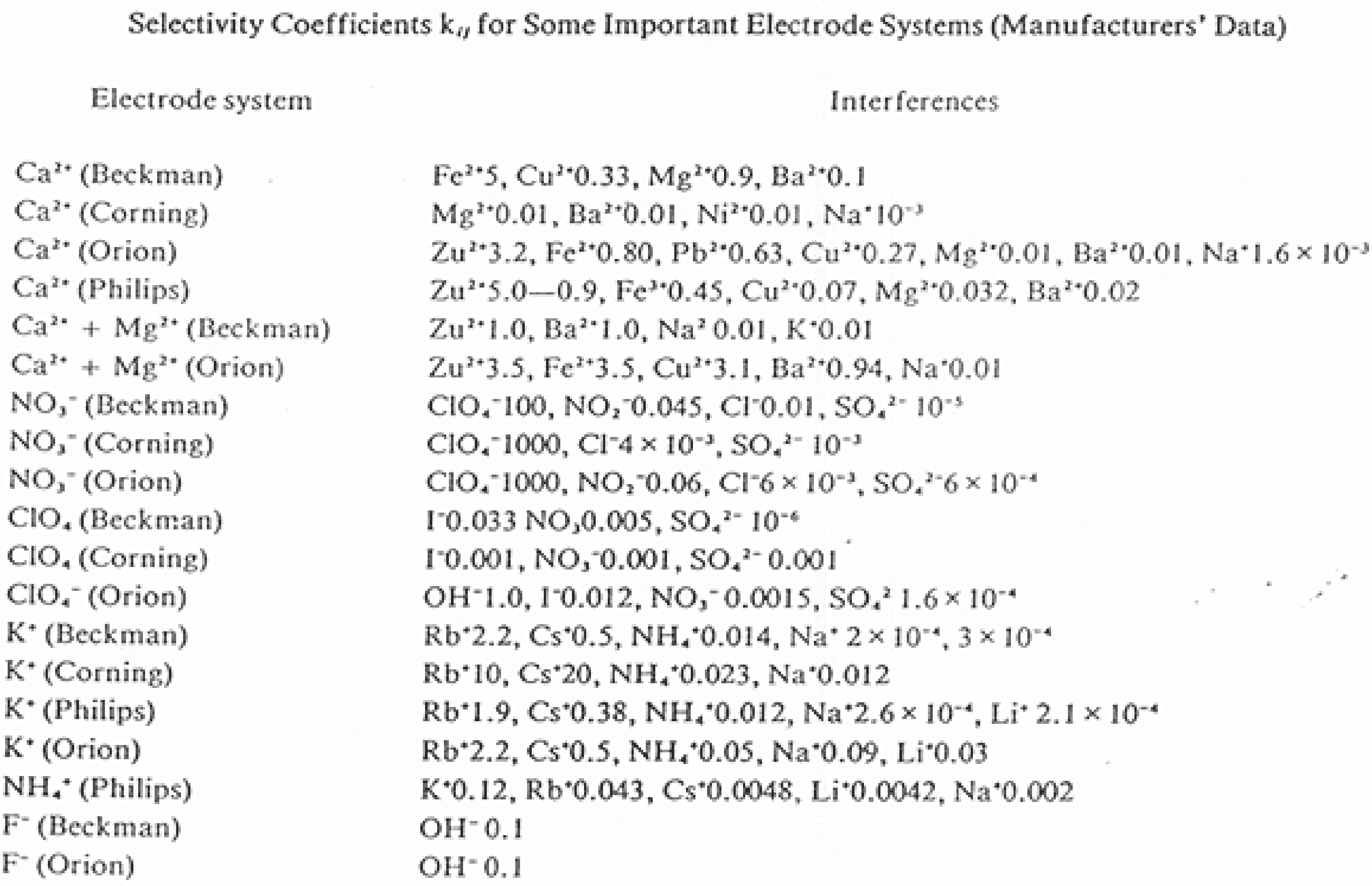
$$E = E_0 + \frac{RT}{z_k F} \ln\{a_k + K_{kj}\, a_j^{(z_k/z_j)}\}$$



Dependence of $\Delta\phi_M$ on the activity of ion K^+ at various activities of ion J^+ when there is a diffusion potential across the membrane.



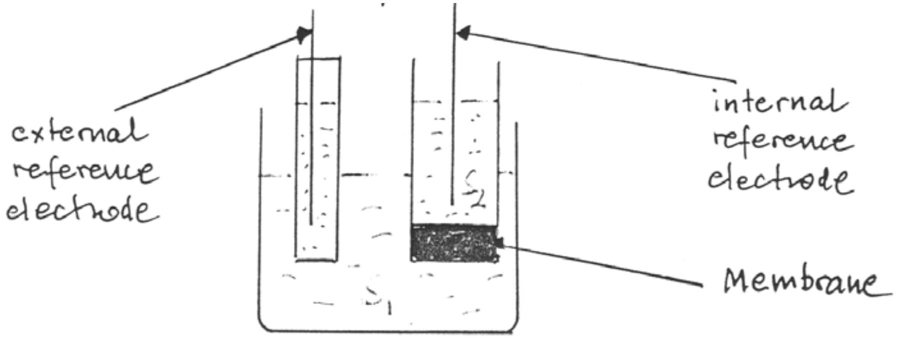
Comparison between calculated and measured EMF-response curves for different Ca^{2+}-sensitive carrier-based PVC membrane electrodes



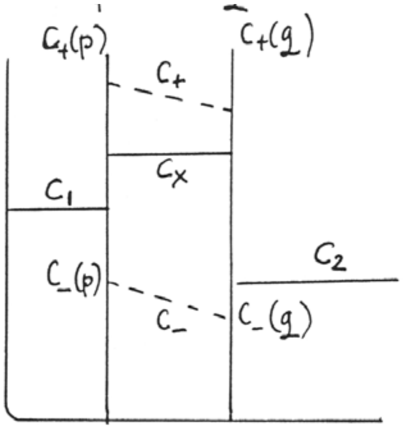
Selectivity Coefficients k_{ij} for Some Important Electrode Systems (Manufacturers' Data)

Electrode system	Interferences
Ca^{2+} (Beckman)	$Fe^{2+}5$, $Cu^{2+}0.33$, $Mg^{2+}0.9$, $Ba^{2+}0.1$
Ca^{2+} (Corning)	$Mg^{2+}0.01$, $Ba^{2+}0.01$, $Ni^{2+}0.01$, $Na^{+}10^{-3}$
Ca^{2+} (Orion)	$Zu^{2+}3.2$, $Fe^{2+}0.80$, $Pb^{2+}0.63$, $Cu^{2+}0.27$, $Mg^{2+}0.01$, $Ba^{2+}0.01$, $Na^{+}1.6 \times 10^{-3}$
Ca^{2+} (Philips)	$Zu^{2+}5.0$—0.9, $Fe^{3+}0.45$, $Cu^{2+}0.07$, $Mg^{2+}0.032$, $Ba^{2+}0.02$
Ca^{2+} + Mg^{2+} (Beckman)	$Zu^{2+}1.0$, $Ba^{2+}1.0$, Na^{2} 0.01, $K^{+}0.01$
Ca^{2+} + Mg^{2+} (Orion)	$Zu^{2+}3.5$, $Fe^{2+}3.5$, $Cu^{2+}3.1$, $Ba^{2+}0.94$, $Na^{+}0.01$
NO_3^- (Beckman)	ClO_4^-100, $NO_2^-0.045$, $Cl^-0.01$, SO_4^{2-} 10^{-5}
NO_3^- (Corning)	ClO_4^-1000, $Cl^-4 \times 10^{-3}$, SO_4^{2-} 10^{-3}
NO_3^- (Orion)	ClO_4^-1000, $NO_2^-0.06$, $Cl^-6 \times 10^{-3}$, $SO_4^{2-}6 \times 10^{-4}$
ClO_4 (Beckman)	$I^-0.033$ $NO_3 0.005$, SO_4^{2-} 10^{-6}
ClO_4 (Corning)	$I^-0.001$, $NO_3^-0.001$, SO_4^{2-} 0.001
ClO_4^- (Orion)	$OH^-1.0$, $I^-0.012$, NO_3^- 0.0015, SO_4^{2} 1.6×10^{-4}
K^+ (Beckman)	$Rb^+2.2$, $Cs^+0.5$, $NH_4^+0.014$, Na^+ 2×10^{-4}, 3×10^{-4}
K^+ (Corning)	Rb^+10, Cs^+20, $NH_4^+0.023$, $Na^+0.012$
K^+ (Philips)	$Rb^+1.9$, $Cs^+0.38$, $NH_4^+0.012$, $Na^+2.6 \times 10^{-4}$, Li^+ 2.1×10^{-4}
K^+ (Orion)	$Rb^+2.2$, $Cs^+0.5$, $NH_4^+0.05$, $Na^+0.09$, $Li^+0.03$
NH_4^+ (Philips)	$K^+0.12$, $Rb^+0.043$, $Cs^+0.0048$, $Li^+0.0042$, $Na^+0.002$
F^- (Beckman)	OH^- 0.1
F^- (Orion)	OH^- 0.1

Review



$$E_{cell} = E_M = \phi(2) - \phi(1)$$



$$E_M = \phi_2 - \phi_1 = \underbrace{\{\phi(2) - \phi(q)\}} + \underbrace{\{\phi(q) - \phi(p)\}} + \underbrace{\{\phi(p) - \phi(1)\}}$$

$$E_M = \Delta\phi_D(2) + \Delta\phi_{LJ} + \Delta\phi_D(1)$$

1. Solid state membrane (AgCl pelet)

$$\Delta\phi_{LJ} = 0$$

2. Membrane with dissolved ion exchanger

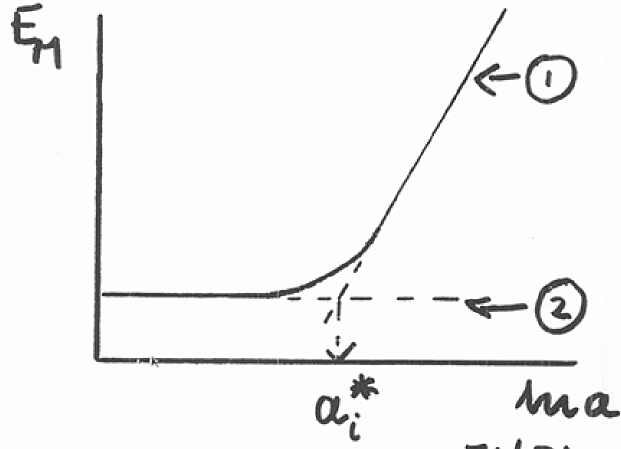
$$\Delta\phi_{LJ} = 0$$

3. Membrane with a fixed ion exchanger

$$\Delta\phi_{LJ} \neq 0$$

General expression for the membrane potential

$$E_M = \Delta\phi_M = \frac{RT}{Fz_i}\ln\left\{a_i + K_{ij}^{pot} a_j^{\frac{z_i}{z_j}}\right\}$$



$a_i^* = K_{ij}\, a_j^{z_i/z_j}$; $\boxed{K_{ij} = \frac{a_i^*}{a_j^{z_i/z_j}}}$

Membrane	K_{KJ}^{pot}
1. Fixed ion exchanger $\Delta\phi_{LJ} \neq 0$	$\frac{u_K}{u_J} K_{KJ}$
2. Solid state membrane $\Delta\phi_{LJ} = 0$	$\frac{K_{so,AgCl}}{K_{so,AgI}}$
3. Liquid membrane with dissolved ion exchanger $\Delta\phi_{LJ} = 0$	K_{KJ}

Activity versus Concentration

- **Electrodes respond to Activity not Concentration**

- **Activity and Concentration related by activity Coefficient**

$$a_x = [\,X\,]\,\gamma_x$$

- **γ_x is activity coefficient – it depends on the ionic strength of the solution**

At low ionic strength, $\gamma_x \rightarrow 1$

Ionic strength

$$I = 0.5\sum_i C_i z_i^2$$

C_i – **concentration,** z_i – **ionic charge, sum extends over all ions in solution**

Debye- Hueckel provided expression for the activity coefficient:

$$\log \gamma = -0.51\, z_i^2 \sqrt{I} \quad \text{at} \quad 25^{\circ}\,\mathrm{C}$$

In general electrode response is related to activity rather than analyte concentration

However, we are interested primarily to know concentration. In principle, the determination of this quantity from a potentiometric measurements requires activity coefficient data.

More often than not activity coefficients will be unavailable because the ionic strength of the solution is either unknown or so high that the Deby – Hueckel equation is not applicable.

In order to circumvent the problem of the activity coefficient an excess of an inert electrolyte (ionic strength buffer) and the standard addition methods are used.

2.9 Quantitative analysis – Standard addition method

Standard addition method:

1) Use an excess of an "inert electrolyte" (0.15M NaCl in Ca^{2+} analysis) to keep the ionic strength constant (γ = constant).

2) Take the measurement of the unknown:

$$E_1 = E_0 + \frac{RT}{Fz_A}\ln C_A\gamma$$

3) Spike unknown with a standard solution (volume $V_{s,}$, concentration C_s)

$$E_2 = E_1 + \Delta E = E_0 + \frac{RT}{Fz_A}\ln\left(\gamma\frac{C_AV_A + C_sV_s}{V_A + V_s}\right)$$

4) Calculate the difference $E_2 - E_1 = \Delta E$

$$\Delta E = \frac{RT}{Fz_A}\ln\left(\frac{C_AV_A + C_sV_s}{C_A(V_A + V_s)}\right)$$

or

$$10^{\frac{z_AF\Delta E}{2.3RT}} = \frac{C_AV_A + C_sV_s}{C_A(V_A + V_s)}$$

and after rearrangement

$$C_A = \frac{C_s}{10^{\frac{z_AF\Delta E}{2.3RT}}\left(1 + \frac{V_A}{V_s}\right) - \frac{V_A}{V_s}}$$

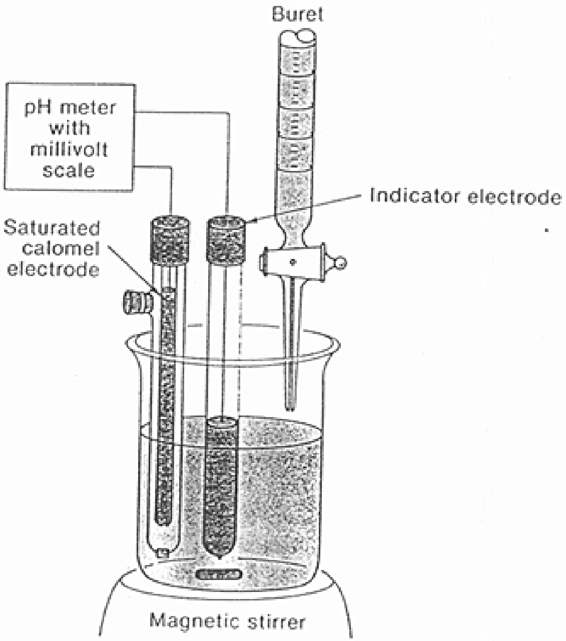
Potentiometric titrations

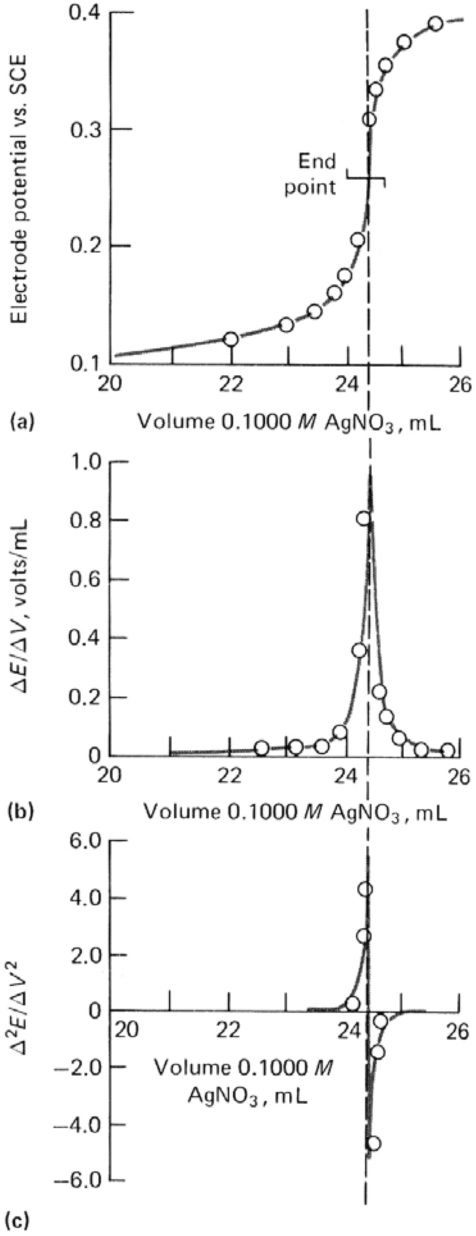
The measurement of the potential of a suitable indicator electrode permits the establishment of the equilibrium point for a titration.

The potentiometric endpoint provides inherently more accurate data than the corresponding method that makes use of indicators. It is particularly useful for titration of colored solutions.

Potentiometric titration is readily applied with automatic titration devices.

Apparatus for potentiometric titrations





(**a**) Potentiometric titration curve for 2.433 meq of Cl^- with 0.1000 *M* $AgNO_3$. (**b**) First-derivative curve. (**c**) Second-derivative curve.

Potentiometric titration – Gran method

$$A + T = AT$$

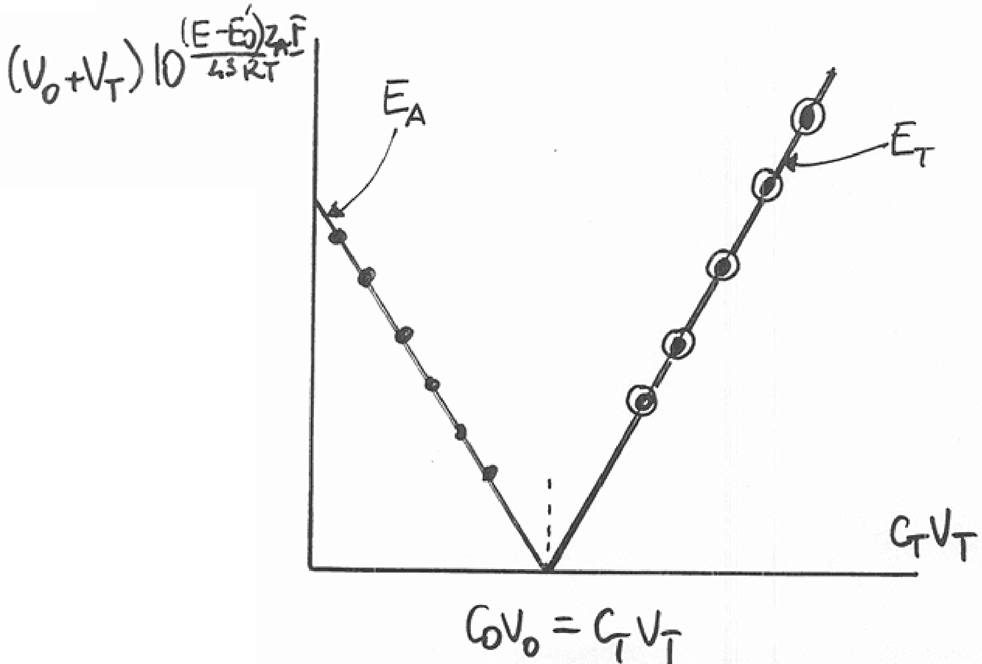
$$C_A = (V_0 C_0 - V_T C_T)/(V_0 + V_T)$$

$$E = \text{const} + \frac{RT}{Z_A F} \ln \gamma_A C_A \qquad (\text{const} = E_0)$$

$$E = E_0' + \frac{RT}{Z_A F} \ln\left\{\gamma_A \frac{V_0 C_0 - V_T C_T}{V_0 + V_T}\right\}$$

assume $\gamma_A = \text{const}$

$$C_0 V_0 - V_T C_T = (V_0 + V_T)\, 10^{(E - E_0')Z_A F/2{,}3RT}$$



ISE – sources of errors

1. **Liquid junction potentials**
2. **Drift**
3. **Changes in the activity coefficient**
4. **Storage**
5. **Interferences**

ISE – Figures of Merit

- detection limit	**0.1 ppm**
- accuracy	**1 to 5 %**
- precision	**better than accuracy**
- Selectivity	**high**
- cost	**very low**

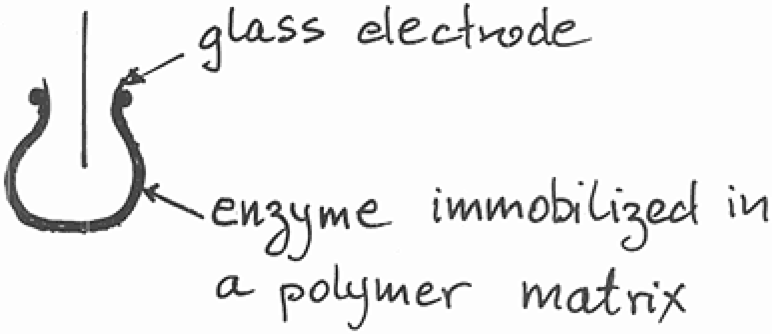
Activity errors resulting From errors in the measured potential

ΔE/mV	% error
0.1	0.4
1.0	4.0
2.0	8.1
5.0	21.5

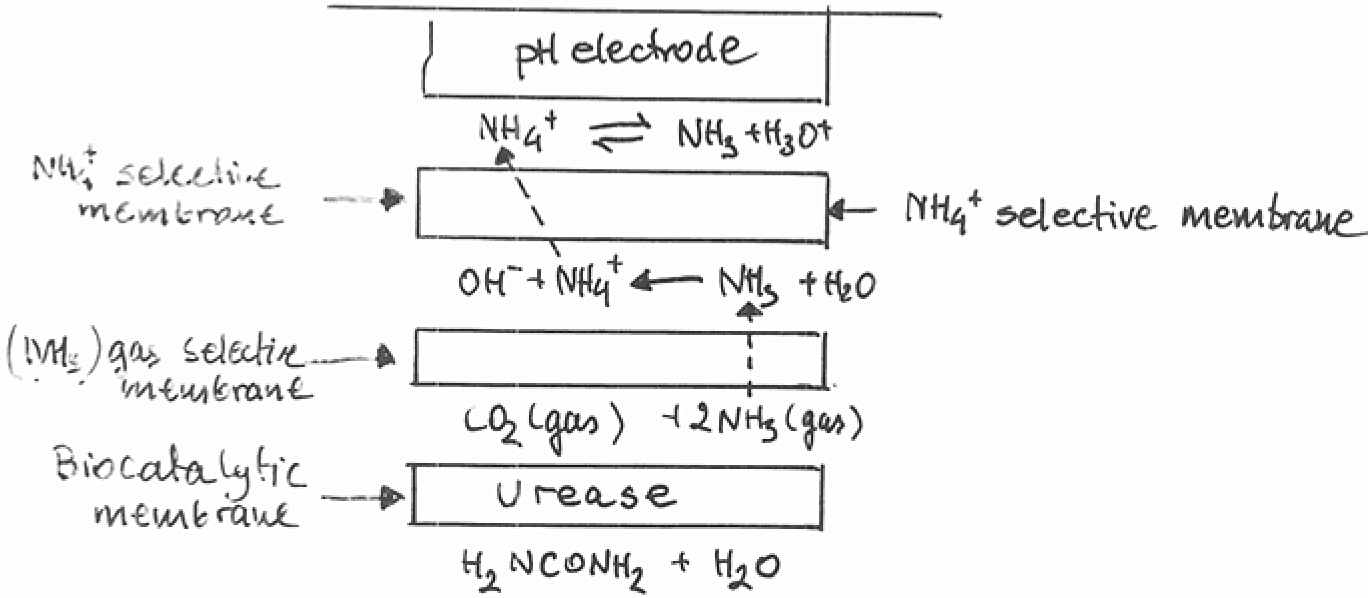
2.11 Biosensors

e. Enzyme electrode

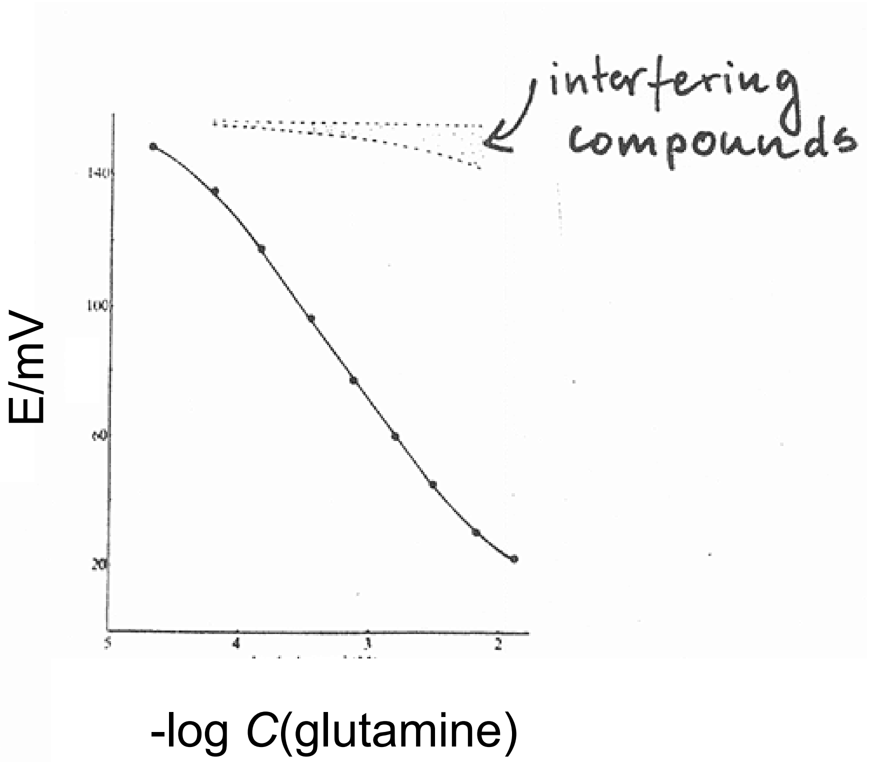
$$\text{Urea} + 3H_2O \xrightarrow{\text{Urease}} 2\,NH_4^+ + HCO_3^- + OH^-$$

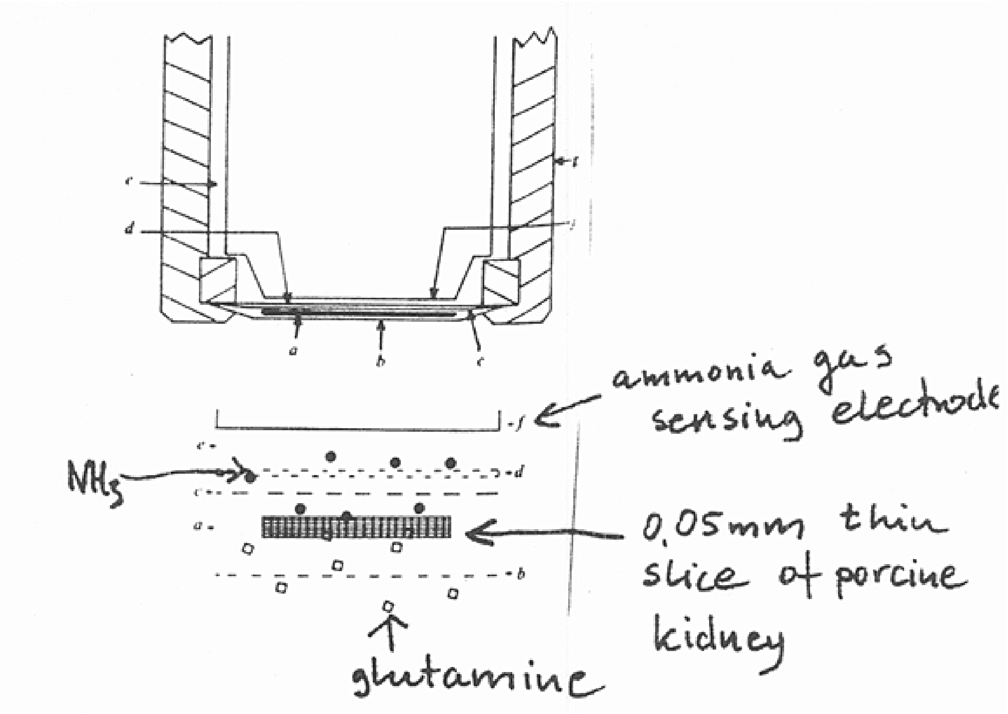


Structure of a biosensor



b) Tissue electrode





kidney tissue contains glutaminase

c) Bacterial electrode

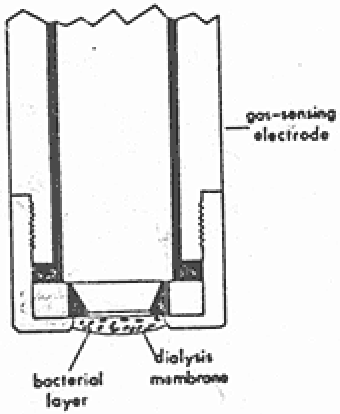
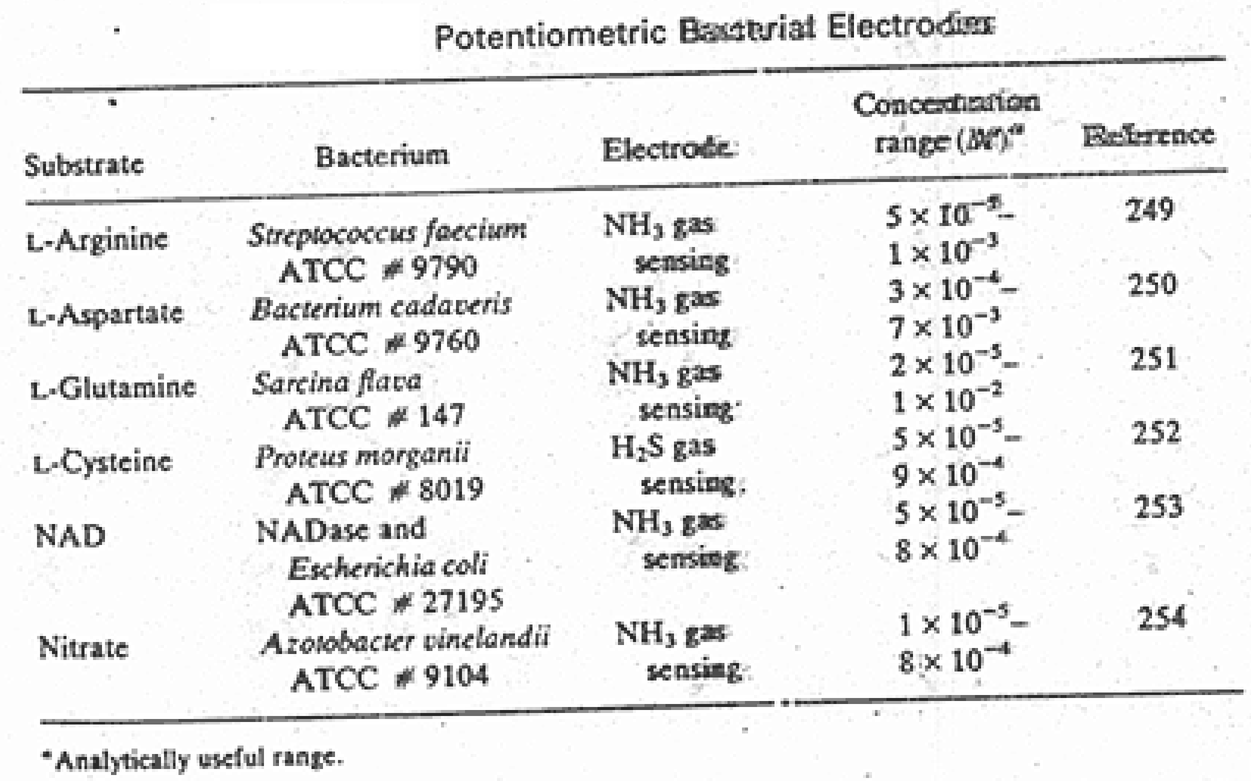


Fig. 14. Bacterial electrode.

ethanol + O_2 $\rightarrow$ acetic acid + H_2O



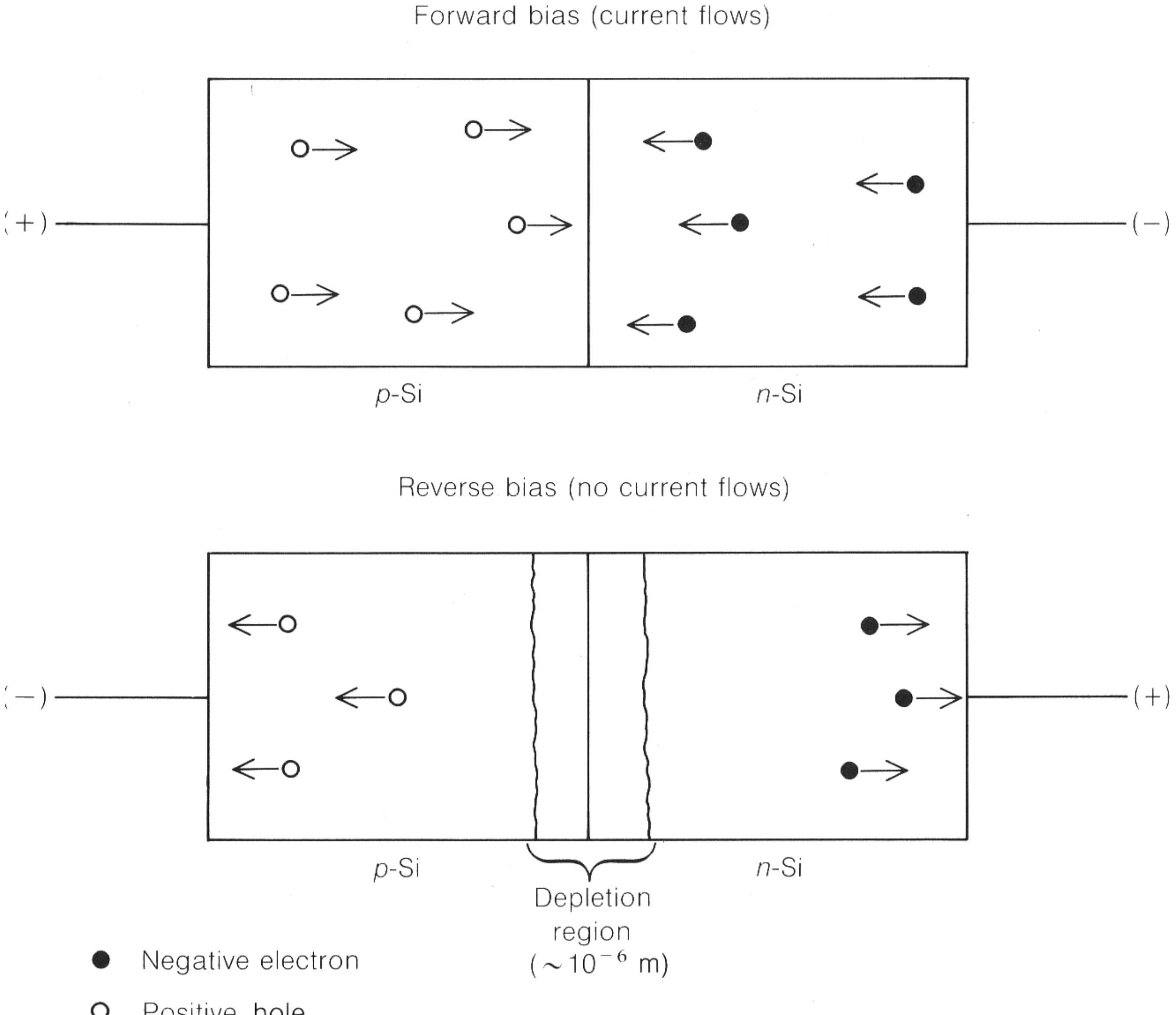
Potentiometric Bacterial Electrodes

Substrate	Bacterium	Electrode	Concentration range (M)[a]	Reference
L-Arginine	*Streptococcus faecium* ATCC # 9790	NH_3 gas sensing	5×10^{-5}–1×10^{-3}	249
L-Aspartate	*Bacterium cadaveris* ATCC # 9760	NH_3 gas sensing	3×10^{-4}–7×10^{-3}	250
L-Glutamine	*Sarcina flava* ATCC # 147	NH_3 gas sensing	2×10^{-5}–1×10^{-2}	251
L-Cysteine	*Proteus morganii* ATCC # 8019	H_2S gas sensing	5×10^{-5}–9×10^{-4}	252
NAD	NADase and *Escherichia coli* ATCC # 27195	NH_3 gas sensing	5×10^{-5}–8×10^{-4}	253
Nitrate	*Azotobacter vinelandii* ATCC # 9104	NH_3 gas sensing	1×10^{-5}–8×10^{-4}	254

[a] Analytically useful range.

d) Chemically modified field effect transistor

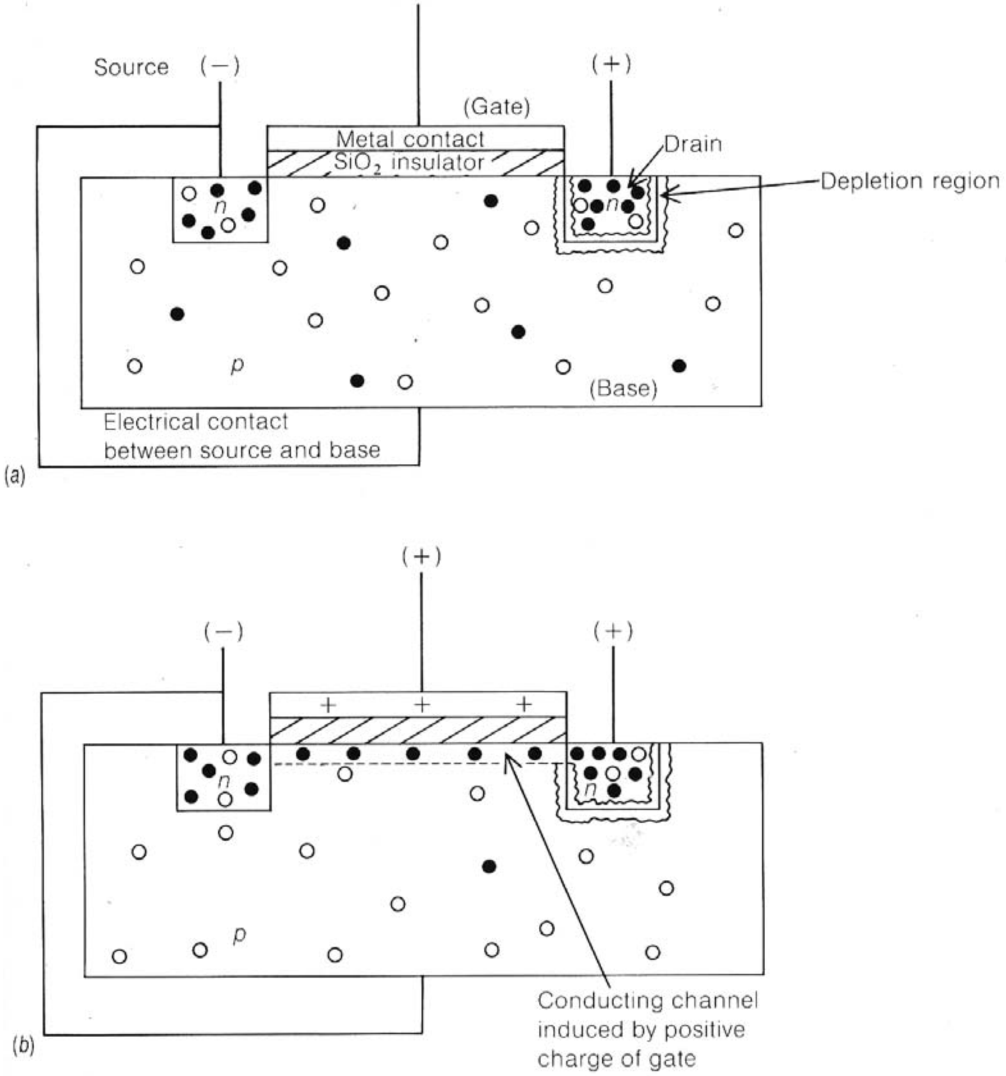
pn-junction



Forward bias (current flows)

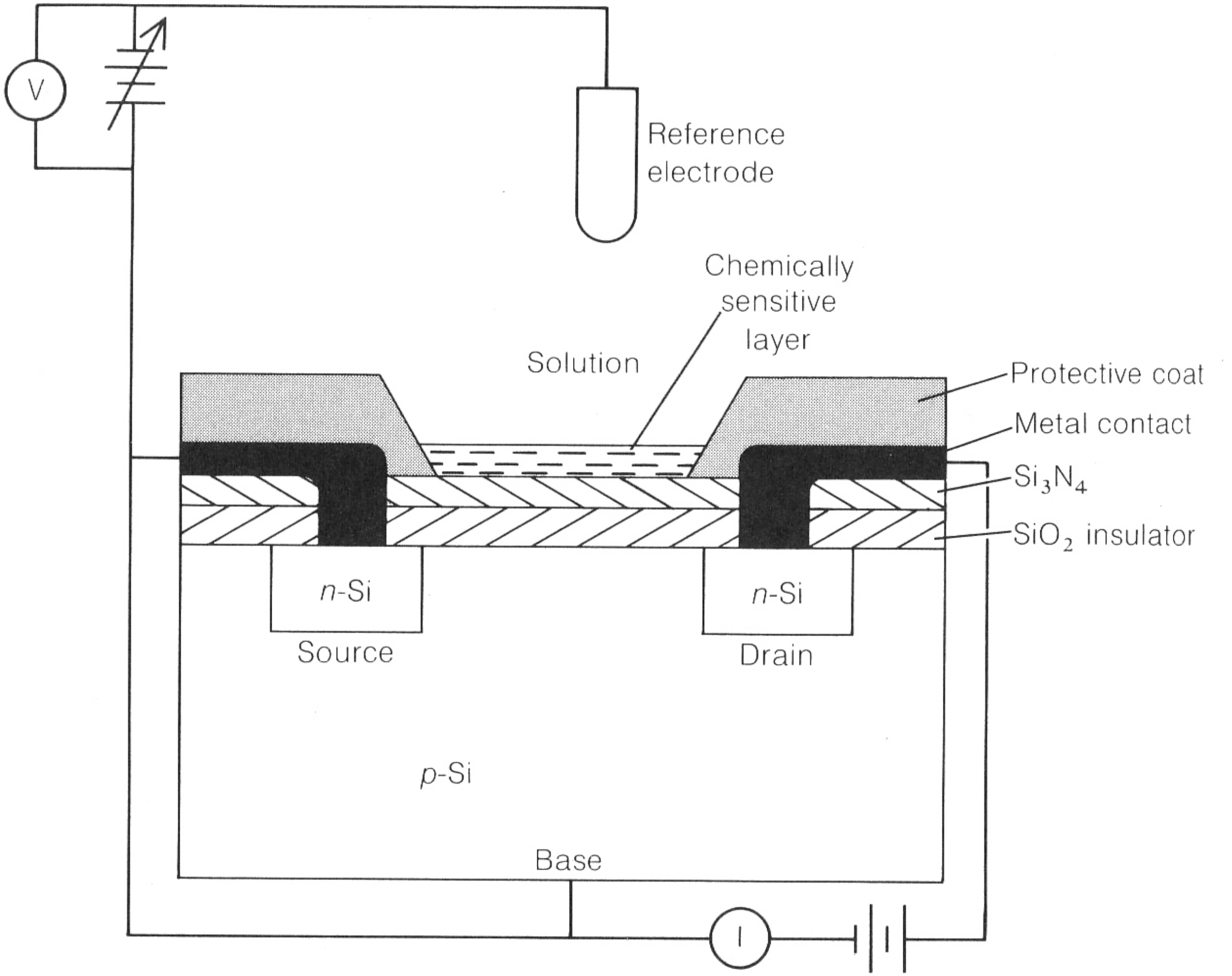
Reverse bias (no current flows)

Field effect transistor



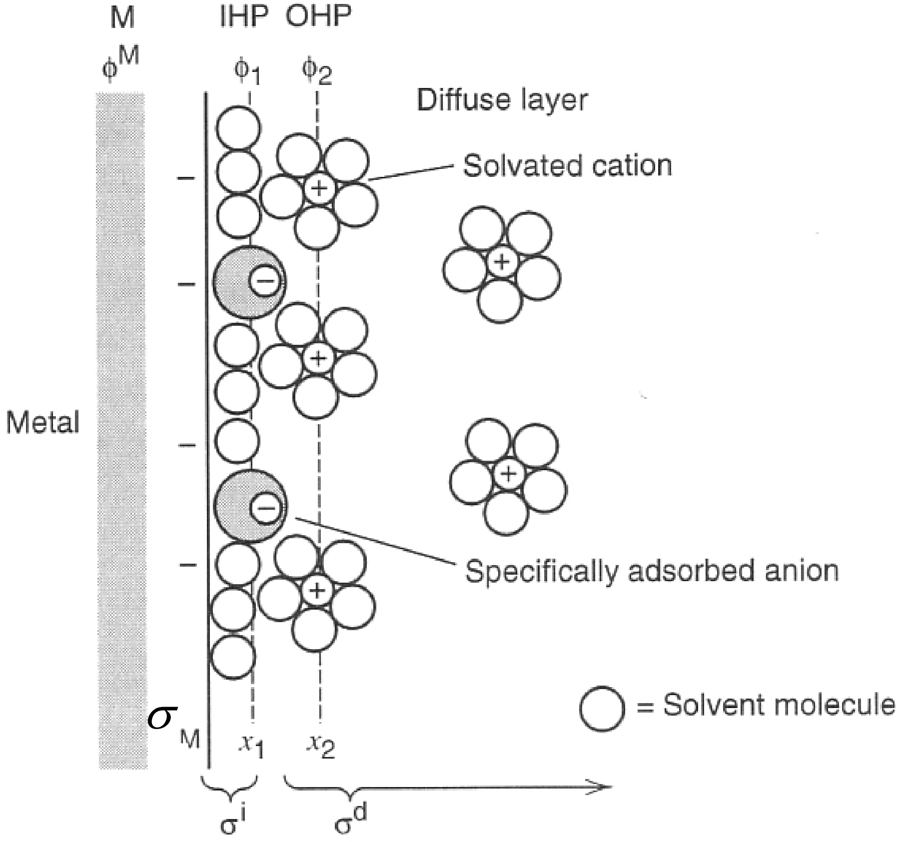
Operation of a field effect transistor. (a) Nearly random distribution of holes and electrons in the base in the absence of gate potential. (b) Positive potential at the gate causes electrons to accumulate in a channel beneath the gate. Current can flow through this channel between the source and drain.

Chemically modified field effect transistor



3. Introduction to electrometric methods

3.1 Structure of the metal interface



neutrality condition

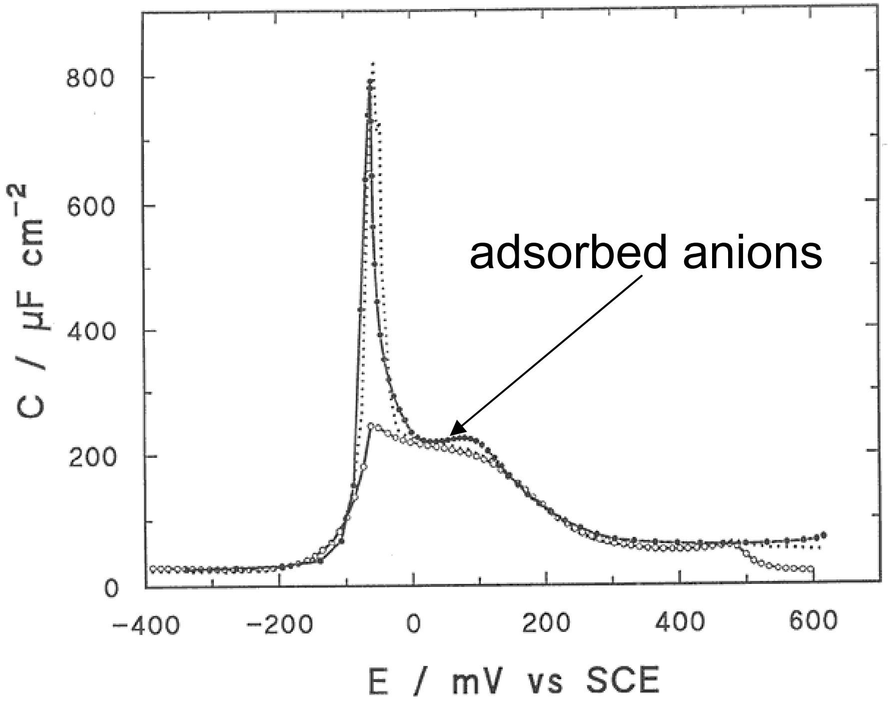
$$\sigma_M = -\left(\sigma_i + \sigma_d\right)$$

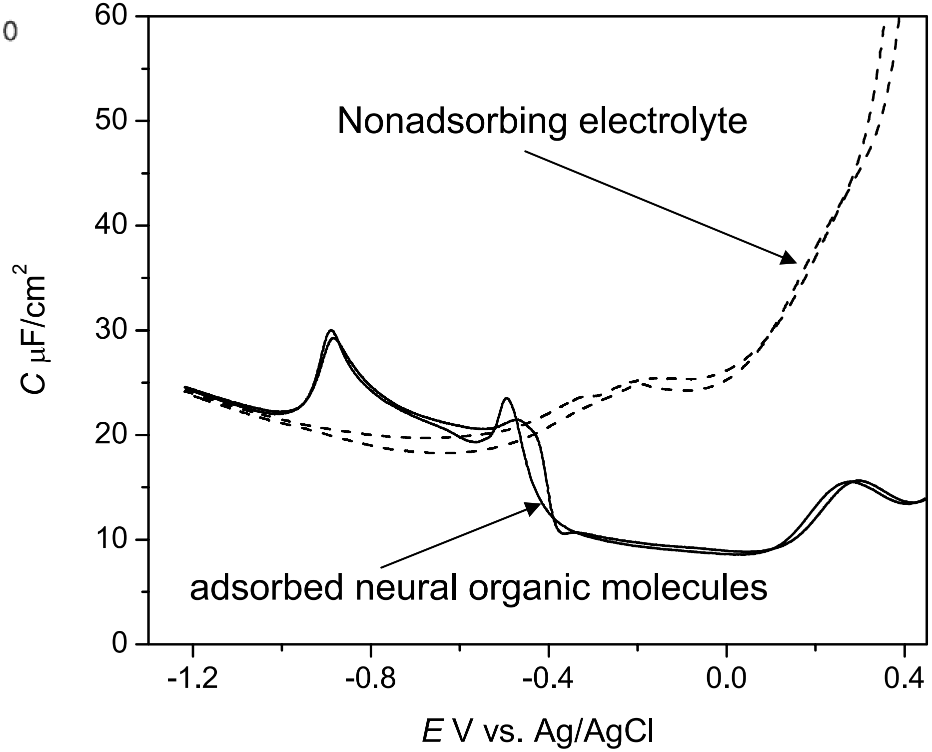
interface – two capacitors in series

$$\frac{1}{C} = \frac{1}{C_i} + \frac{1}{C_d}$$

OHP- outer Helmholtz plane; distance of the closest approach of solvated ions
IHP – inner Helmholtz plane; plane in which specifically adsorbed ions are located
Diffuse layer – layer within which ionic cloud screening the charge on the metal is located

Capacity of an Au electrode





Capacity of an electrode changes with potential – the changes reflect changes in the Coverage by specifically adsorbed ions or molecules

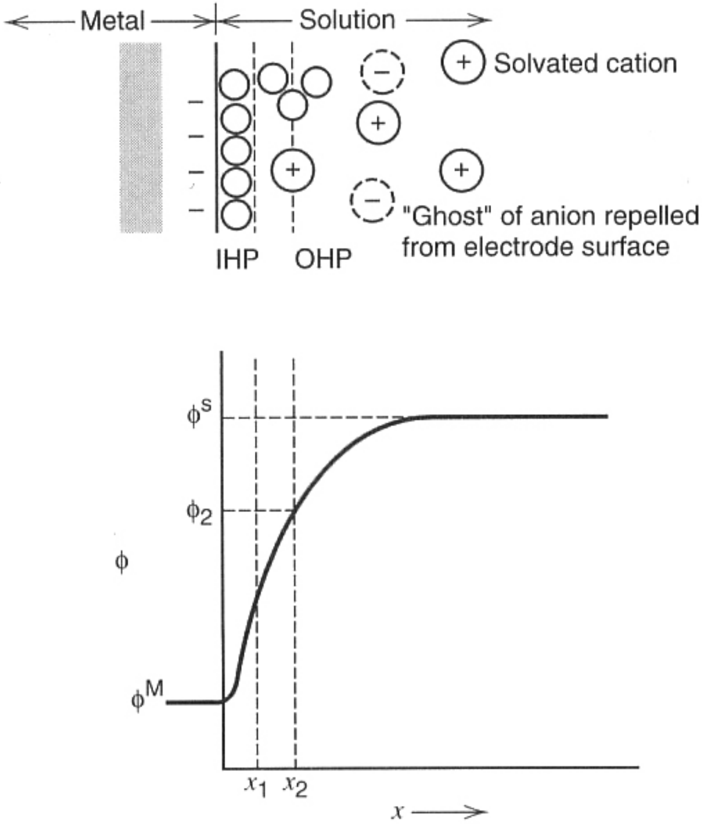
$$\sigma_M = f(E,\Gamma)$$

$$d\sigma_M = \left(\frac{\partial\sigma_M}{\partial E}\right)_\Gamma dE + \left(\frac{\partial\sigma_M}{\partial\Gamma}\right)_E d\Gamma$$

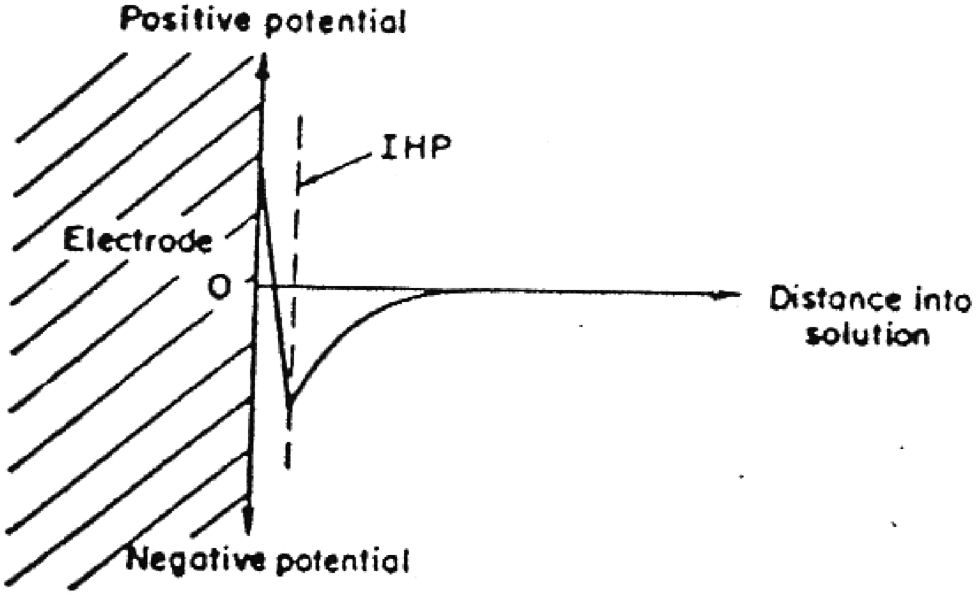
$$C = \frac{d\sigma_M}{dE} = \underbrace{\left(\frac{\partial\sigma_M}{\partial E}\right)_\Gamma}_{\text{true capacity}} + \underbrace{\left(\frac{\partial\sigma_M}{\partial\Gamma}\right)_E}_{\text{pseudo capacity}} \frac{d\Gamma}{dE}$$

Potential drop across the metal solution interface

no specific adsorption

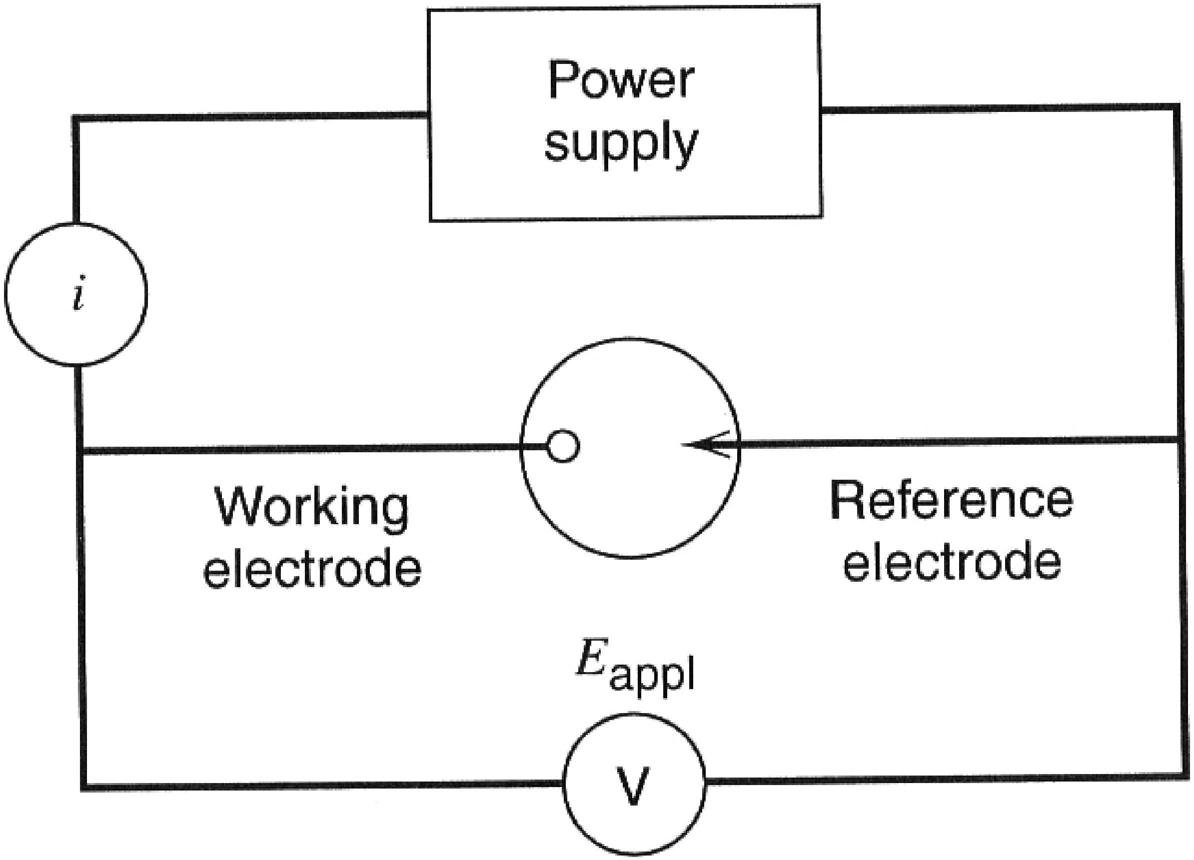


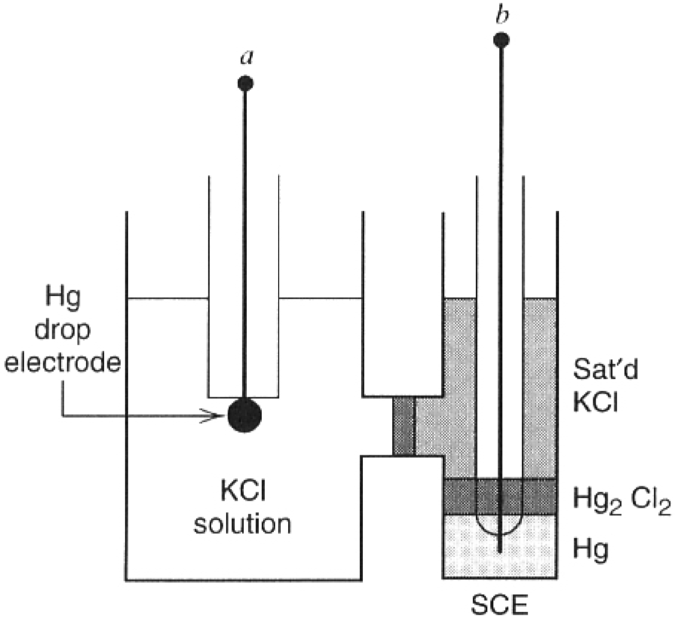
specific adsorption of anions



3.2 Electrochemical cell in the presence of a current flowing through the cell

Two electrode cell





when potential E is applied from an external source current flows through the cell

From Ohm's Law:

$$i = \frac{E}{Z}$$

$$Z = Z_i + Z_e + Z_{\mathrm{Re}f} + Z_{ext}$$

Z_i – *impedance of the indicator electrode*
Z_e – *impedance of the electrolyte*
Z_{Ref} – *impedance of the reference electrode*
Z_{ext} – *impedance of the external circuits*

In an electrochemical experiment Z_e, Z_{Ref}, Z_{ext} *must be eliminated*

a. Elimination of $Z_R ef$

$$Z = f(R, C)$$

$$Z_{\mathrm{Re}\,f} = R = \rho \frac{l}{A}$$

ρ - specific resistivity;

l - length;

A - area

$$Z_C = \frac{1}{\omega C}$$

C - capacity

$\omega = 2\pi\nu$ -angular frequency

$C \propto A$ hence $Z \propto A^{-1}$

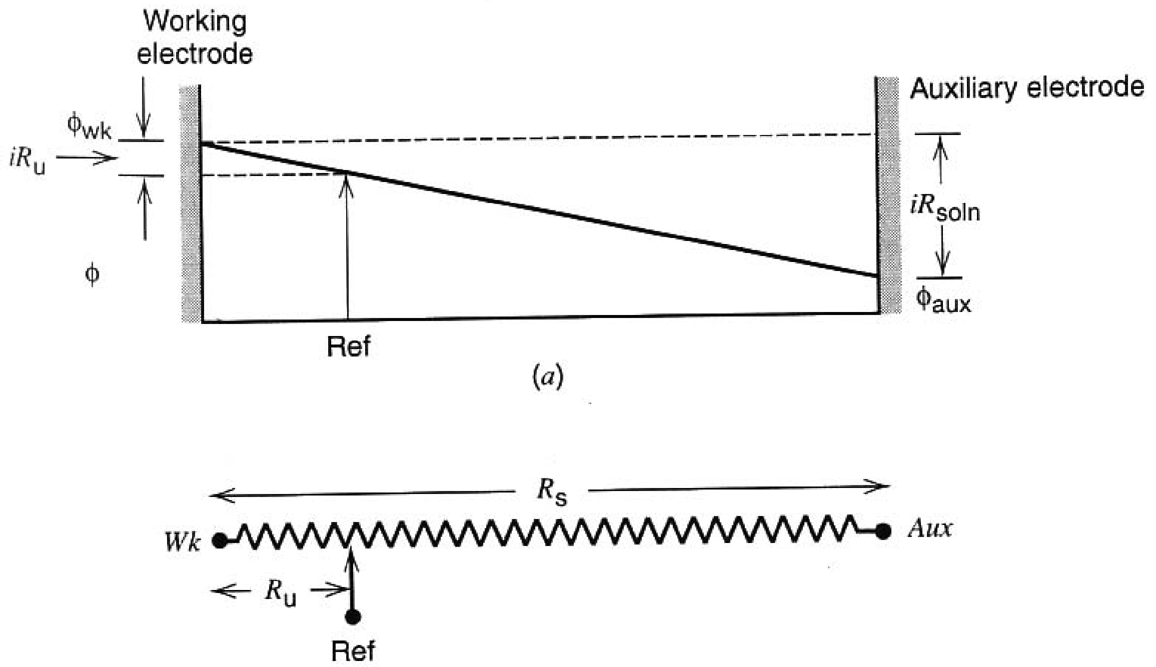
Consequently if : $A_i << A_{Ref}$ then $Z_i >> Z_{Ref}$

The surface area of an indicator electrode should be much smaller than the surface area of the reference or auxiliary electrodes

b) Elimination of Z_e

$$Z_e = R_e$$

Use 3-electrode system and Luggin capillary

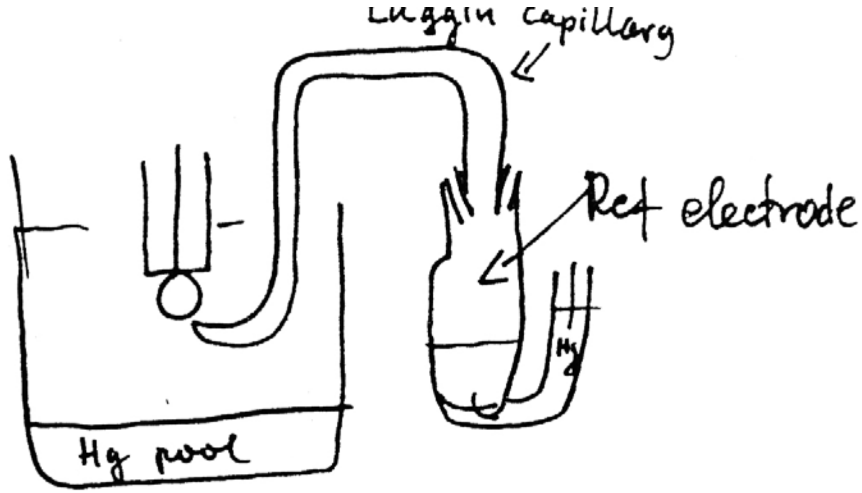


Luggin capillary and uncompensated resistance R_u

For a planar electrode : $$R_u = \rho \frac{x}{A}$$

For a spherical electrode: $$R_u = \rho \frac{1}{4\pi r_0}\left(\frac{x}{r_0 + x}\right)$$

r_0 - radius of the spherical electrode; x - distance from the electrode surface



Change of potential across the capacitor as a function of time

$$E = iR + \frac{q}{C_d}$$

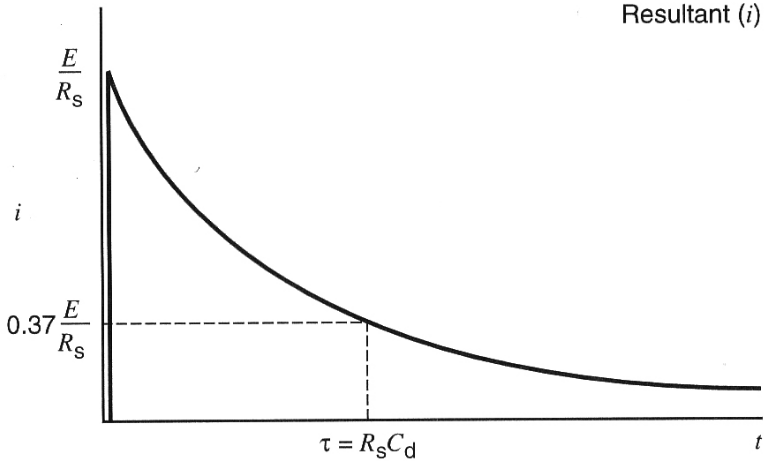
$$E_c = \frac{q}{C_d} = \frac{\int_0^t i\,dt}{C_d}$$

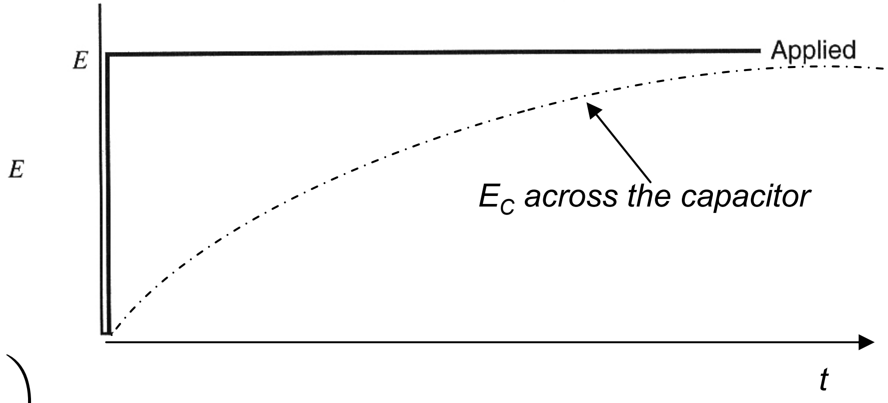
since:

$$i = \frac{E}{R_s} e^{-\frac{t}{R_s C_d}}$$

one obtains:

$$E_c = \frac{E}{R_s C_d} \int_0^t e^{-\frac{t}{R_s C_d}} dt = E\left(1 - e^{-\frac{t}{R_s C_d}}\right)$$





Linear potential sweep or voltage ramp

$$E = vt$$

where v is the sweep rate in V s^{-1}

$$E = iR + \frac{q}{C_d}$$

or

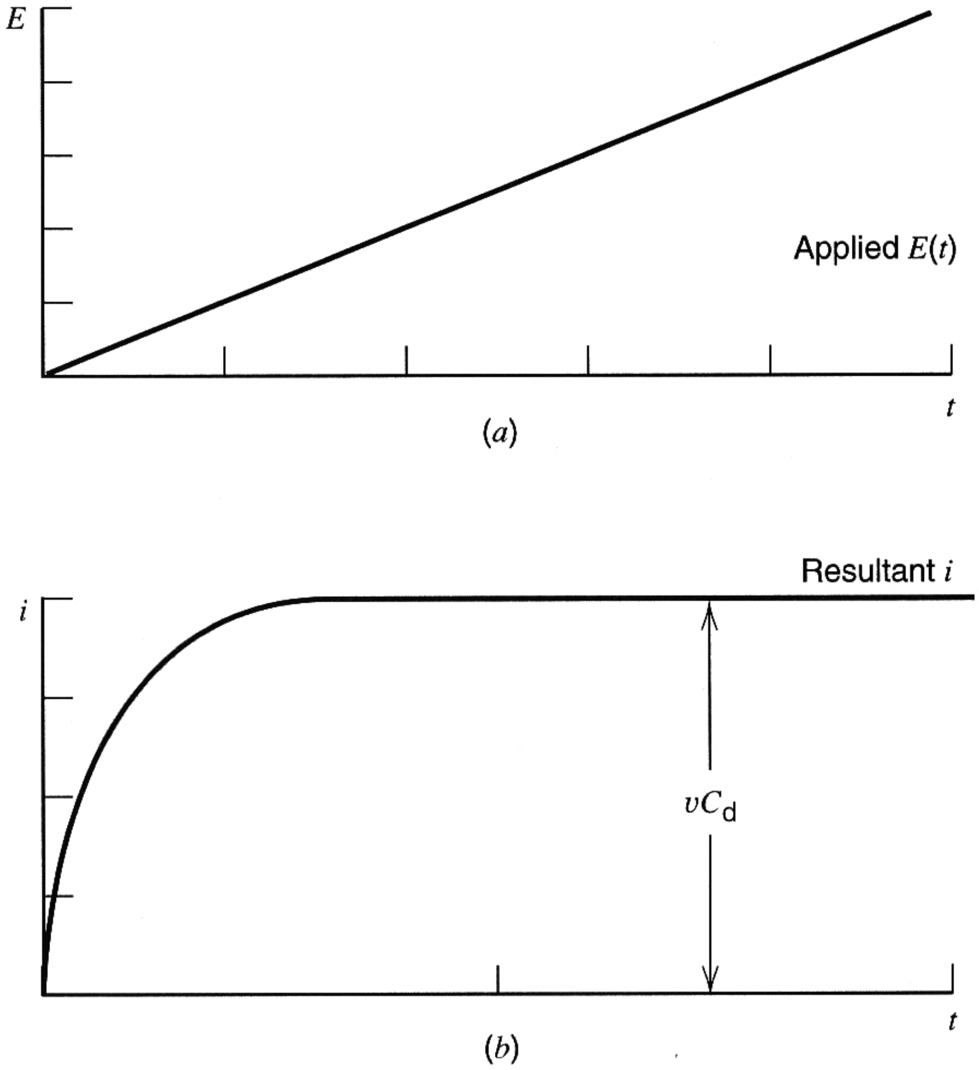
$$vt = R_s \frac{dq}{dt} + \frac{q}{C_d}$$

if $q=0$ at $t=0$

$$i = vC_d\left(1 - e^{-\frac{t}{R_s C_d}}\right)$$

if $t \gg R_s C_d$

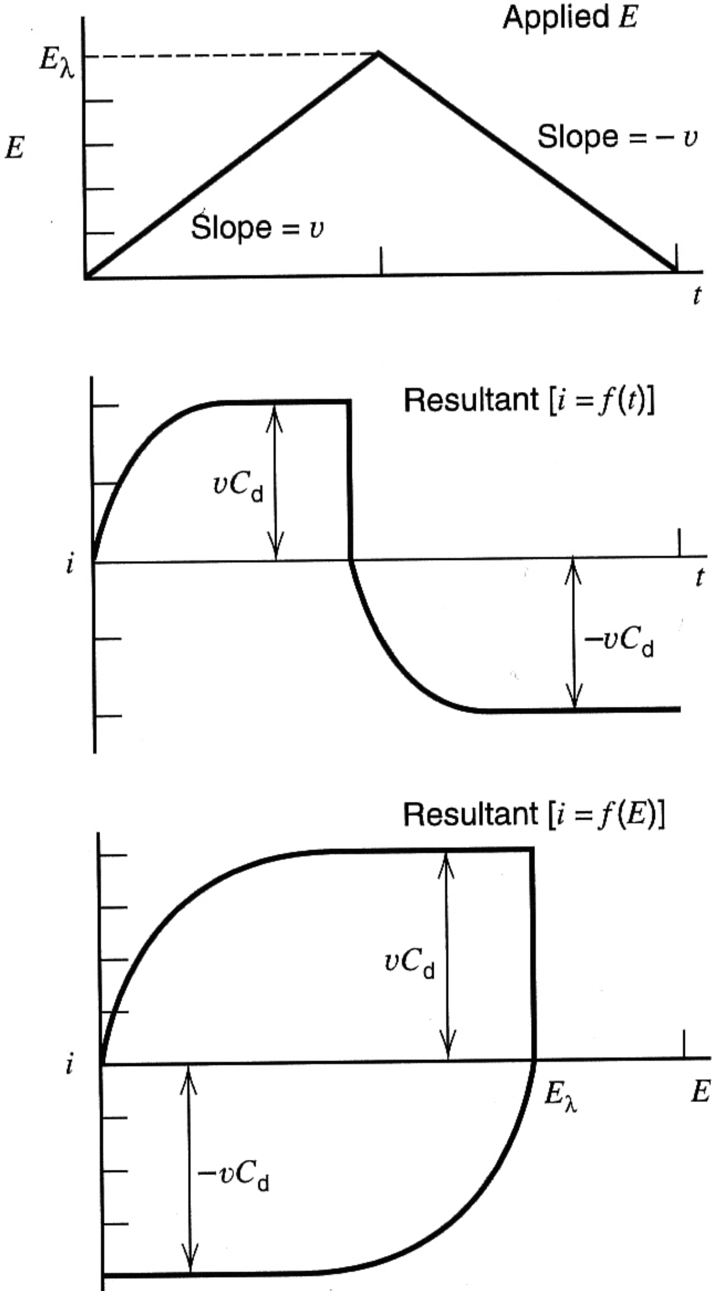
$$i = vC_d$$



Cyclic-linear potential sweep

$$E = vt$$

$$i = vC_d\left(1 - e^{-\frac{t}{R_s C_d}}\right)$$



4.1 Electrode reaction as a series of multiple consecutive steps

A charge transfer reaction provides an additional channel for current to flow through the interface. The amount of electricity that flows through this channel depends on the amount of species being oxidized or reduced according to the Faraday law:

$$m = \frac{M_A}{nF} it$$

Faraday law links electrical quantity such as current to the chemical quantity such as concentration or mass of the analyte:

$$m = CVM_A$$

This expression may be rearranged to give expression for current:

$$i = nF \frac{m}{M_A t} = nF \frac{N}{t}$$

n- number of electrons in a redox reaction, *N*-number of moles, M_A- molecular weight, *F*- Faraday constant, *C*-concentration, *V*-volume

Currents which are described by the Faraday law are called faradaic currents

$$i = nF\frac{m}{M_A t} = nF\frac{N}{t}$$

This equation described average current flowing through the electrode During time – t. During infinitesimal period dt the number of electrolyzed moles is dN and the expression for the instantaneous current is:

$$i = nF dN / dt$$

The rate of a chemical reaction is :

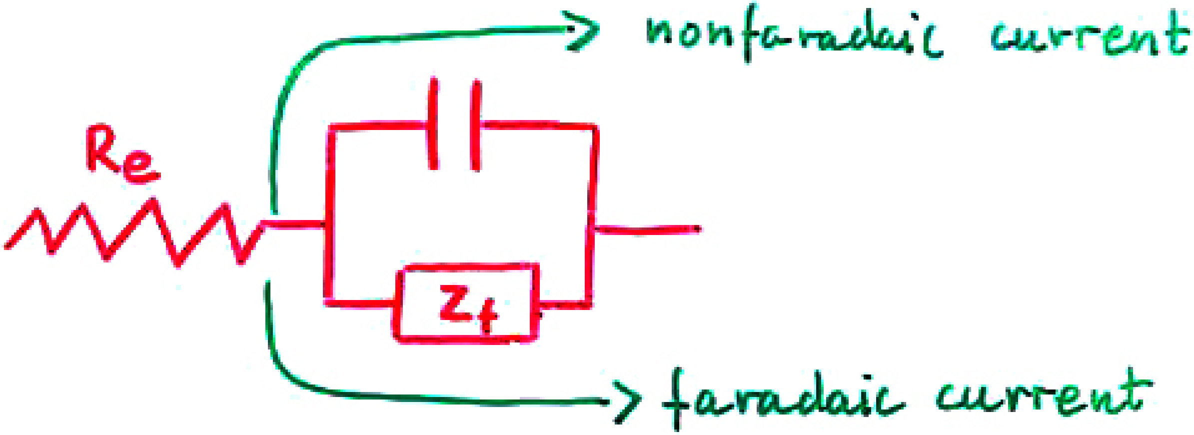
$$v = dN / dt$$

Hence faradaic current is a measure of a reaction rate

$$i = nF\frac{dN}{dt} = nFv$$

Current flowing in the absence of a redox reaction – nonfaradaic current

In the presence of a redox reaction – faradaic impedance is connected in parallel to the double layer capacitance. The scheme of the cell is:



The overall current flowing through the cell is :

$$i = i_f + i_{nf}$$

Only the faradaic current $-i_f$ contains analytical or kinetic information

Non-faradaic (capacitive) current constitutes a limitation to the detection limit of electrometric techniques

Experimental conditions for electroanalytical measurements:

1. $i_f >> i_{non}$ (large concentration of electroactive species, long times of experiment)

2. $i_f = i - i_{non}$ (correction for non-faradaic current)

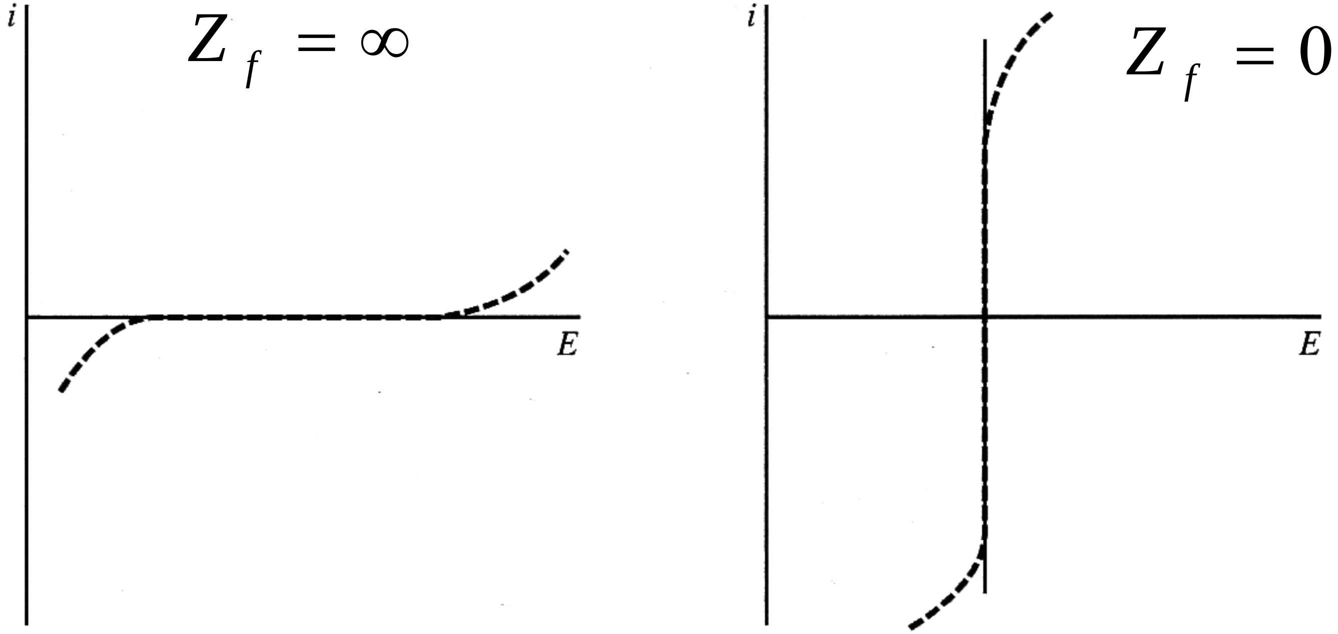
i_f and i_{non} are different functions of time

Under a steady state condition:

$i_f \neq 0$ but $i_{non} = 0$

Current – voltage characteristics of an ideal polarizable and ideal non-polarizable electrode

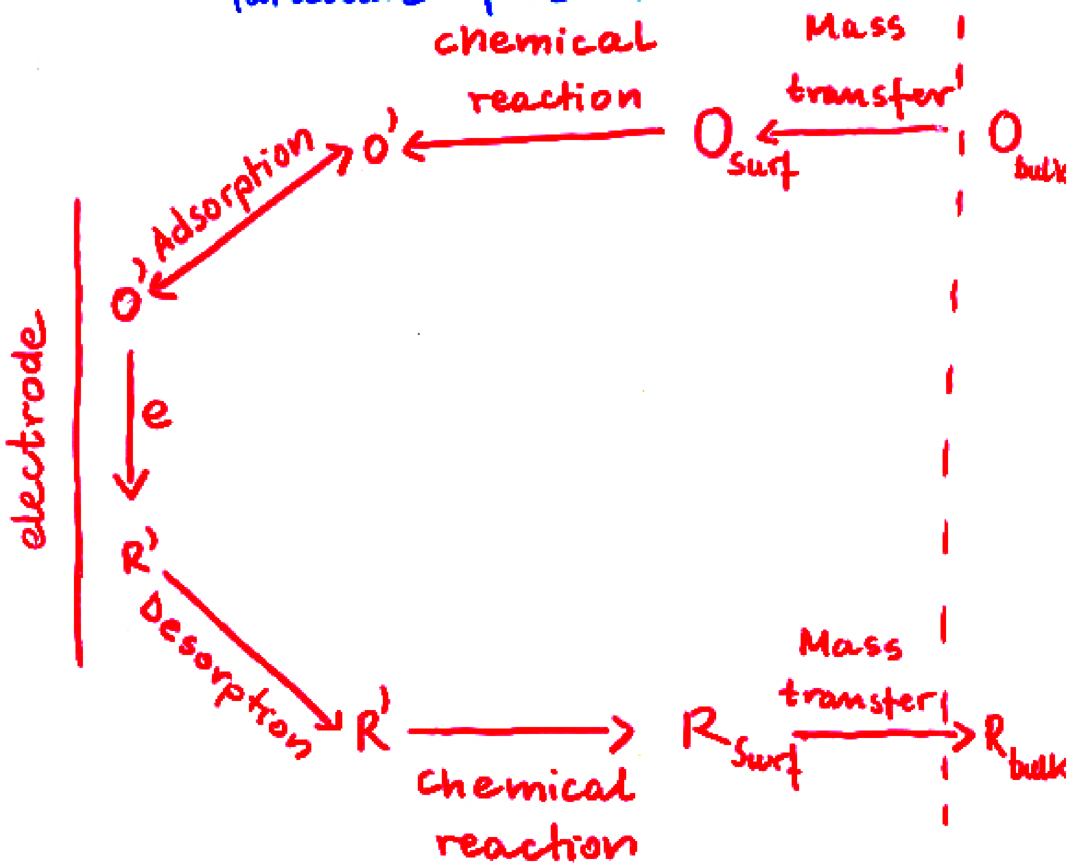
$$i = \frac{E}{Z}$$



(*a*) Ideal polarizable electrode (*b*) Ideal nonpolarizable electrode

Current-potential curves for ideal (*a*) polarizable and (*b*) nonpolarizable electrodes. Dashed lines show behavior of actual electrodes that approach the ideal behavior over limited ranges of current or potential.

General Scheme of a faradaic process



Electrode reaction – multistep reaction

Mechanism of el. reaction – consecutive multistep mechanism

$$\frac{1}{v} = \sum_i \frac{1}{v_i}$$

For a multistep reaction

$\frac{1}{v} = \Sigma \frac{1}{v_i}$ $\frac{1}{i} = \Sigma \frac{1}{i_i}$

The current flowing through the cell is limited by the current corresponding to the slowest reaction step

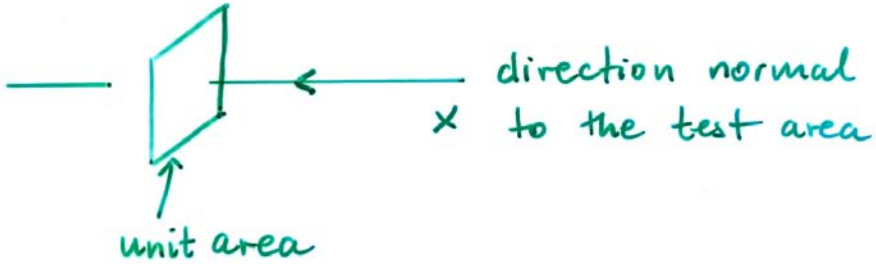
Types of faradaic currents

1) Charge transfer currents
2) adsorption currents
3) kinetic currents
4) mass transfer currents
    a) diffusion currents
    b) migration currents
    c) convection currents

5. Currents controlled by mass transfer

5.1. General introduction

J_i - flux of species i is the number of moles of i which pass through a unit area in a unit of time



Species i can be transported across the tested area if:

1) there is a gradient of electrochemical potential
2) the solution moves in the direction normal to the surface

Hence the flux is given by:

$$J_i = -\left(\frac{c_i D_i}{RT}\right)\frac{\partial \bar{\mu}_i}{\partial x} + c_i v \Big/ \text{mol s}^{-1}\text{cm}^{-2}$$

where v - is the solution velocity in the direction normal to the surface

$$\frac{\partial \bar{\mu}_i}{\partial x} = \frac{\partial \mu_i}{\partial x} + z_i F \frac{\partial \phi}{\partial x} = \frac{RT}{c_i}\frac{\partial c_i}{\partial x} + z_i F \frac{\partial \phi}{\partial x}$$

$$|z_i| F D_i / RT = u_i \quad / (m/s)/(V/m)$$

u_i - electrical mobility

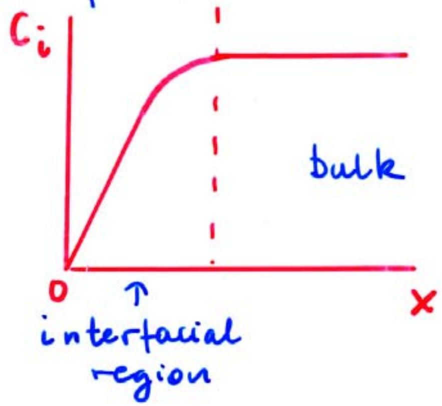
$$J_i = \underset{\underset{\text{diffusion}}{\uparrow}}{-D_i \frac{\partial c_i}{\partial x}} \underset{\underset{\text{migration}}{\uparrow}}{- u_i c_i \frac{\partial \phi}{\partial x}} \underset{\underset{\text{convection}}{\uparrow}}{+ c_i V}$$

$$\boxed{i_i = -nFAJ_i}$$

n – number of electrons per one mol of i

5.2. migration currents

assumption - convection negligible



in the interfacial region for i-electroactive

$$i = nFAD\frac{\partial c_i}{\partial x} + nFAu_i c_i \frac{\partial \phi}{\partial x} = i_d + i_m$$

in the bulk $\frac{\partial c_i}{\partial x} = 0$ current depends on migration of all the ions

$$i = \sum_j z_j F A u_j c_j \frac{d\phi}{dx}$$

$$\frac{i_m}{i} = \frac{nFAu_i c_i \frac{\partial \phi}{dx}}{\sum_j z_j FAu_j c_j \frac{d\phi}{dx}} = \frac{n}{z_i} t_i$$

$$t_i = \frac{z_i u_i c_i}{\sum_j z_j u_j c_j}$$

$$i_d = i - i_m = i\left(1 - \frac{n}{z_i} t_i\right)$$

to minimize i_m - use an excess of a supporting electrolyte.

5.3. Diffusion currents

a) Fick's first low of diffusion

In the absence of migration and convection the flux of species i at a location x and a given time t is equal to:

$$\boxed{J_i = -D_i \frac{\partial C_i(x,t)}{\partial x}}$$

If diffusion take place to an electrode, the electrode is placed at the distance $x=0$. Hence the current controlled by diffusion is equal to:

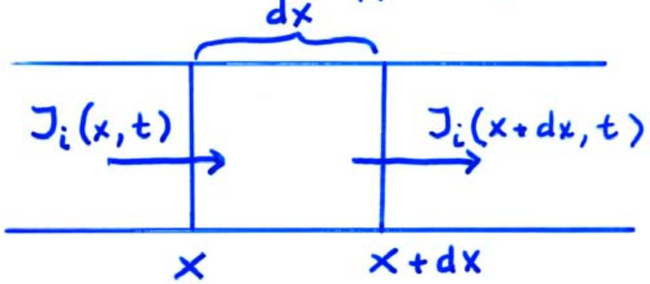
$$i = -nFAJ_i = nFAD_i \left(\frac{\partial C_i(x,t)}{\partial x} \right)_{x=0}$$

To find exact value of $\left(\frac{\partial C_i(x,t)}{\partial x} \right)_{x=0}$ exact dependence of C_i on x and t has to be known.

b) Fick's second low of diffusion

If species i diffuses in solution its concentration at location x varies with time. The variation of c_i with time depends on the geometry of diffusing space.

b. 1. linear diffusion



$$\frac{\partial c_i(x,t)}{\partial t} = \frac{J_i(x,t) - J_i(x+dx,t)}{dx}$$

$$J_i(x+dx,t) = J_i(x,t) + \frac{\partial J_i(x,t)}{\partial x} dx$$

$$\frac{\partial c_i(x,t)}{\partial t} = - \frac{\partial J_i(x,t)}{\partial x}$$

$$J_i = -D_i \frac{\partial c_i(x,t)}{\partial x}$$

$$\boxed{\frac{\partial c_i(x,t)}{\partial t} = D_i \frac{\partial^2 c_i(x,t)}{\partial x^2}}$$

5.4. Linear diffusion to a planar electrode – exact solution

What we want to find?

$$i = nFAD_i \underbrace{\left(\frac{\partial C_i(x,t)}{\partial x} \right)_{x=0}}_{\text{This is to be found}}$$

What we have to solve?

$$\frac{\partial C_i(x,t)}{\partial t} = D_i \frac{\partial^2 C_i(x,t)}{\partial x^2}$$

This is a partial differential equation

Solution of this equation involves three integrations. Hence, we need three extra relationships to determine the three integration constants. This is provided by one initial and two boundary conditions.

<u>initial condition</u>

at $t=0$ $\quad C_i(x,t) = C^*$

<u>boundary conditions</u>

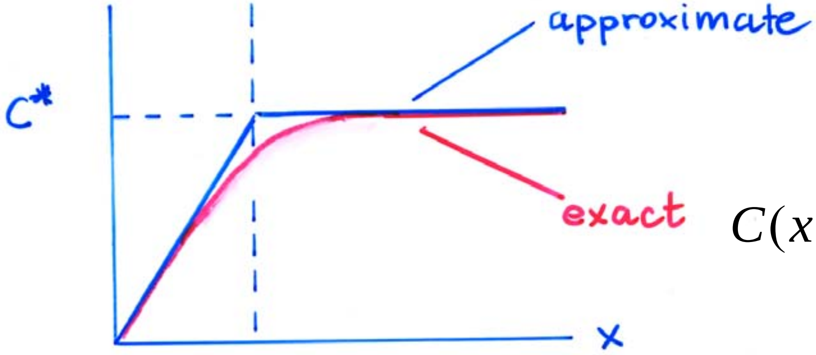
1. $\lim_{x \to \infty} C_i(x,t) = C^*$

2. at $t>0$ $\quad C_i(0,t) = 0$ (limiting current)

$$\boxed{i = nFAD_i \frac{C_i^*}{\sqrt{\pi D t}}}$$

Cotrell Equation

5.5. Comparison of the approximate and the exact solutions for the diffusion current flowing through a planar electrode



$$C(x,t) = C^* erf\left[\frac{x}{2(Dt)^{1/2}}\right]$$

$$\delta = \sqrt{\pi D t}$$

approximate

$$i = nFAD_i \frac{C_i^*}{\delta}$$

exact

$$i = nFAD_i \frac{C_i^*}{\sqrt{\pi D t}}$$

δ – thickness of the diffuse layer

for $D \approx 5\,10^{-6}\ \mathrm{cm^2 s^{-1}}$ and $t = 1\ \mathrm{s}$

$$\delta = 4 \times 10^{-3}\ \mathrm{cm}$$

5. 7. Diffusion to a spherical electrode

Differential equation

$$\frac{\partial C_i(r,t)}{\partial t} = D_i \left\{ \frac{\partial^2 C_i(r,t)}{\partial r^2} + \frac{2}{r}\,\frac{\partial C_i(r,t)}{\partial r} \right\}$$

initial condition

$$C_i(r,0) = C_i^* \qquad (r > r_0)$$

r_0 - radius of the electrode

boundary condition

1. $$\lim_{r \to \infty} C_i(r,t) = C_i^*$$

2. $$C_i(r_0,t) = 0 \qquad (t > 0)$$

(limiting current)

Solution

$$i(t) = nFAD_i C_i^* \left[\underbrace{\frac{1}{\sqrt{\pi D_i t}}}_{\text{Linear diffusion term}} + \underbrace{\frac{1}{r_0}}_{\text{Correction for sphericity}} \right]$$

5.8. Comparison of the expressions for diffusion currents to a planar and a spherical electrode

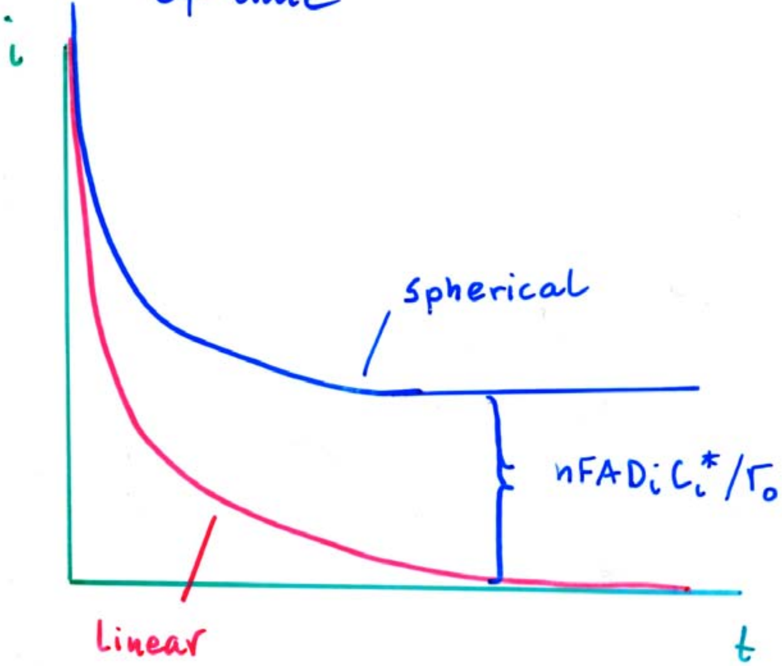
$$i(t) = nFAD_i C_i^* \left[\frac{1}{\sqrt{\pi D_i t}} + \frac{1}{r_0} \right]$$

if $\sqrt{\pi D_i t} \ll r_0$

$i_{sph} = i_{Lin}$

if $\sqrt{\pi D_i t} \gg r_0$

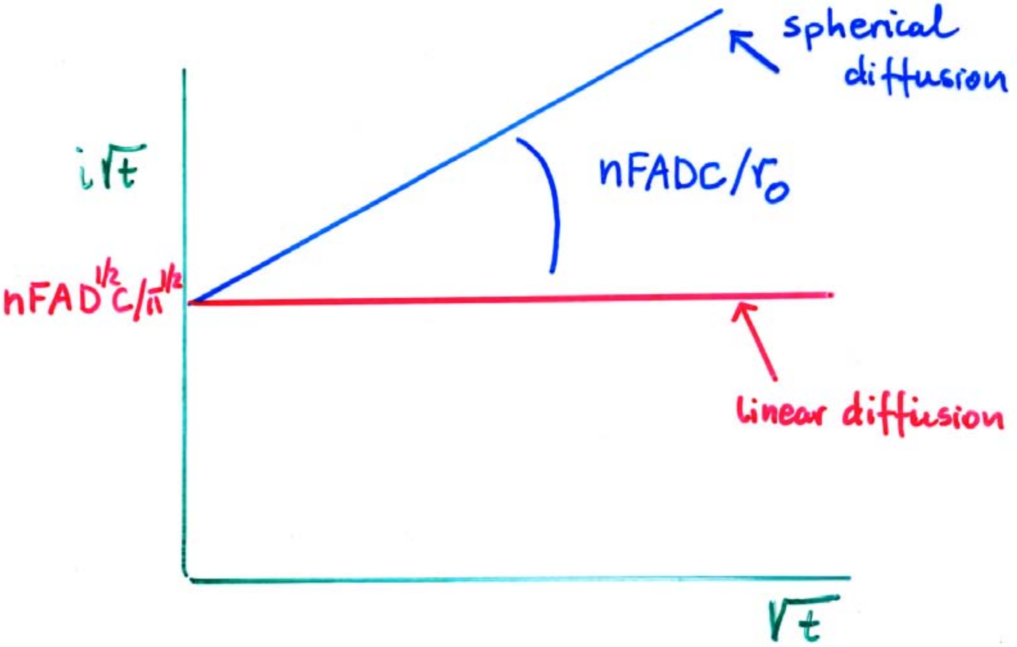
$i_{sph} = nFAD_i C_i^*/r_0$ – independent of time



Determination of diffusion coefficients

$$i = nFADC^* \left(\frac{1}{\sqrt{\pi D t}} + \frac{1}{r_0} \right)$$

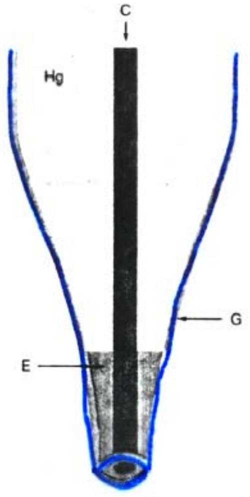
$$i\sqrt{t} = nFAD^{1/2}C^*/\pi^{1/2} + (nFADC^*/r_0)\, t^{1/2}$$



$$\frac{\text{slope}}{\text{intercept}} = \frac{D^{1/2}}{\pi^{1/2} r_0}$$

$$\boxed{D = \left(\frac{\text{slope}}{\text{intercept}} \right)^2 \pi^{-1} r_0^{\,2}}$$

ultramicroelectrodes



for $r = 10\mu m$ $i = nFADC/r$ at $t > 50ms$

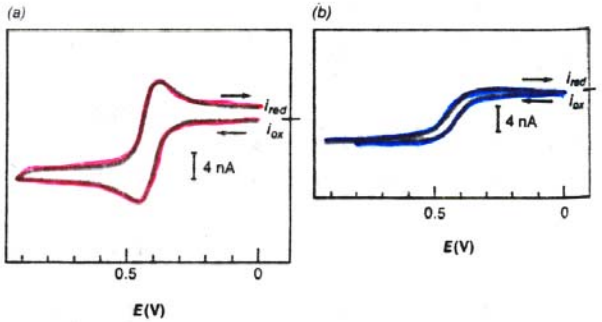
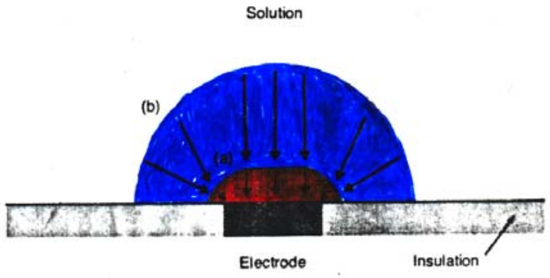


Figure 1. Cyclic voltammogram of ferrocene (1.0 mM) in acetonitrile with 0.1 M tetra-*n*-butylammonium perchlorate at a gold microdisk electrode ($r = 6.5\ \mu m$). (a) 10 V s^{-1} scan rate. (b) 0.1 V s^{-1} scan rate



Examples of Instrumental Analysis

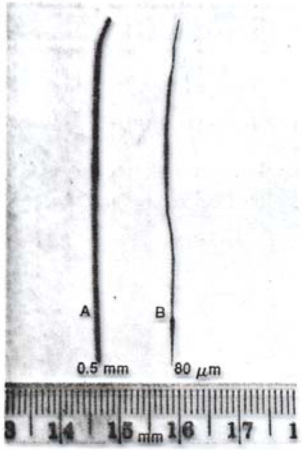


Figure 5. Micro graphite electrodes for in vivo brain voltammetry

A: teflon-sleeved (ventricle type) electrode, ca. 0.5 mm exposed graphite paste surface; B: micro glass capillary filled with graphite-epoxy resin, tip diameter ca. 80 μm

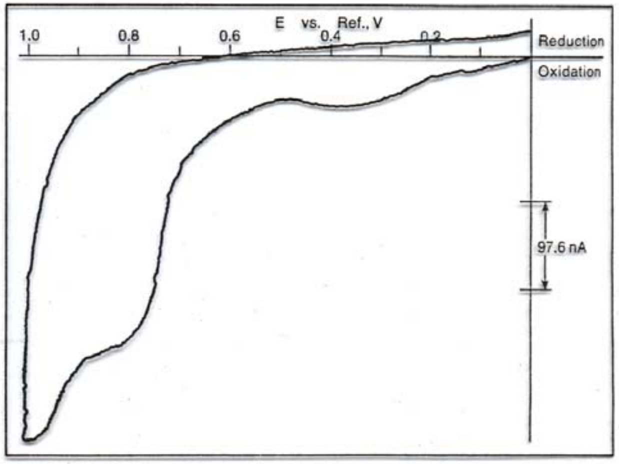


Figure 6. Typical tissue voltammograms in rat caudate nucleus

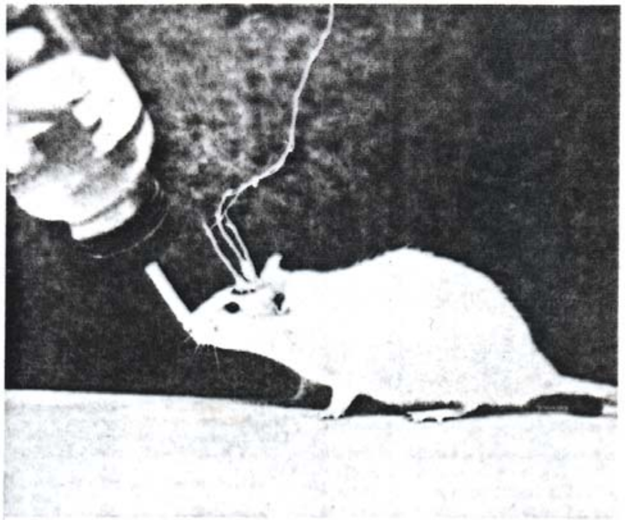


Figure 7. Unrestrained rat with chronically implanted voltammetric electrodes

Implanted electrodes consist of micro graphite electrode of Figure 5B, miniature enclosed SCE, and platinum auxiliary. Shrinkable Teflon shields extend up to protect thin connecting leads from breakage. Entire electrode "package" is conventionally sealed to skull with dental acrylic. During typical water drinking period shown in photograph, a cyclic voltammogram and chronoamperometric ($it^{1/2}$) measurement were being recorded via minicomputer-controlled potentiostat

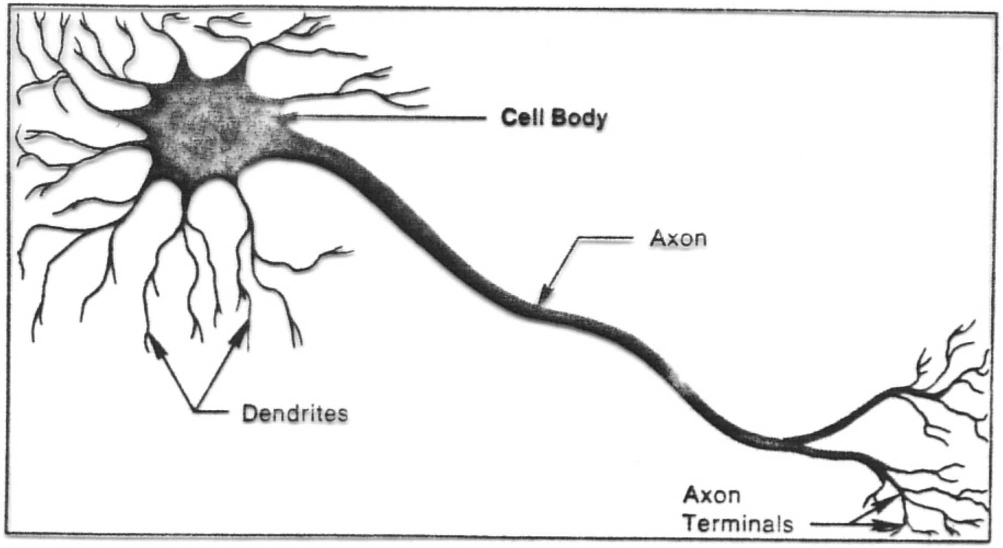
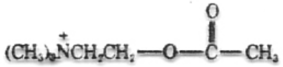
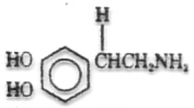
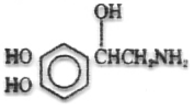
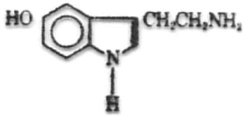
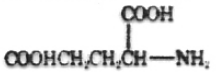
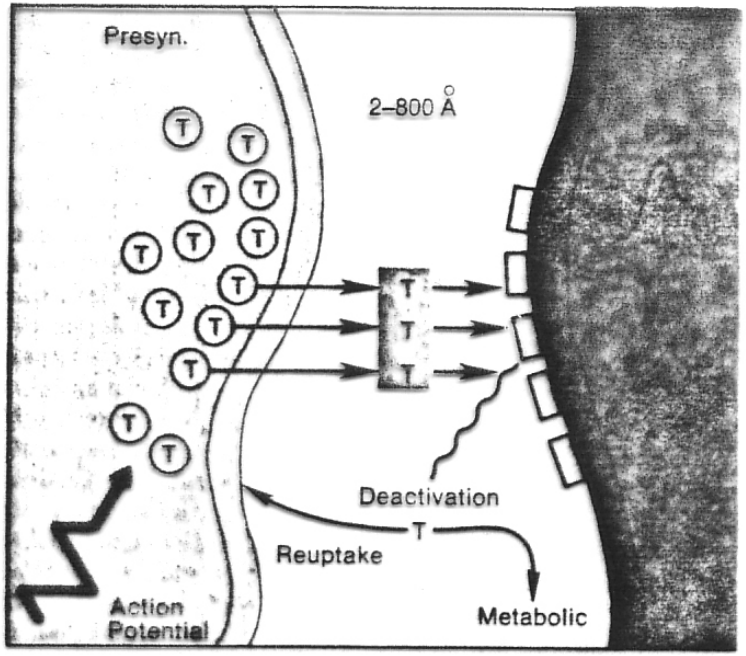


Figure 1. "Typical" neuron in mammalian brain

Table I. Chemical Neurotransmitter Systems

CHOLINERGIC		
Acetylcholine	ACh	 $(CH_3)_3\overset{+}{N}CH_2CH_2-O-\overset{O}{\overset{\vert}{C}}-CH_3$
ADRENERGIC		
Dopamine	DA	
Norepinephrine	NE	
SEROTONINERGIC		
5-Hydroxytryptamine **(Serotonin)**	5-HT	
AMINO ACIDS		
Glycine		$COOHCH_2NH_2$
γ-Aminobutyric acid	GABA	$COOHCH_2CH_2CH_2NH_2$
Glutamic acid		 $COOHCH_2CH_2\overset{COOH}{\overset{\vert}{CH}}-NH_2$



Review

Currents controlled by mass transport

$$i = nFAD \left(\frac{\partial C(x,t)}{\partial x}\right)_{x=0}$$

Cell a processor solving partial differential equations

$$\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2}$$ planar electrode

$$\frac{\partial C(r,t)}{\partial t} = D \left\{ \frac{\partial^2 C(r,t)}{\partial r^2} + \frac{2}{r} \frac{\partial C(r,t)}{\partial r} \right\}$$ spherical electrode

1. Initial condition ; $t=0$

   $C(x,0) = C^*$; $C(r,0) = C^*$

2. Boundary conditions

(i) $X = 0$ or $r = r_0$ $\quad C(0,t) = 0$

(ii) $x \to \infty$ or $r \to \infty$ $\quad C(\infty,t) = C^*$

Solutions

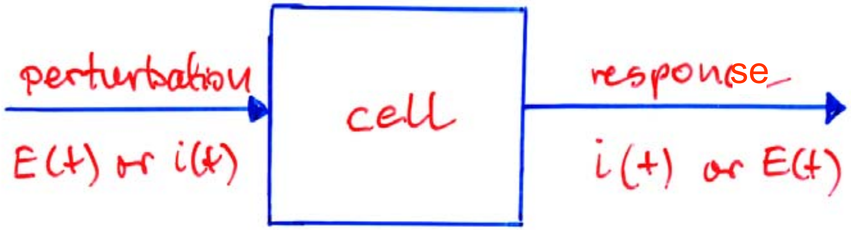
$i = nFADC^* / \sqrt{\pi D t}$ – planar electrode

$i = nFADC^* \left\{ \frac{1}{\sqrt{\pi D t}} + \frac{1}{r_0} \right\}$ – spherical electrode

if $\sqrt{\pi D t} \ll r_0$ $i_{sph} = i_{plan}$

if $\sqrt{\pi D t} \gg r_0$ ultramicroelectrodes

6. Electroanalytical Techniques



1. Chronoamperometry
2. Polarography
3. Tast Polarography
4. Normal Pulse Polarography
5. Differential Pulse Polarography
6. Cyclic Voltammetry

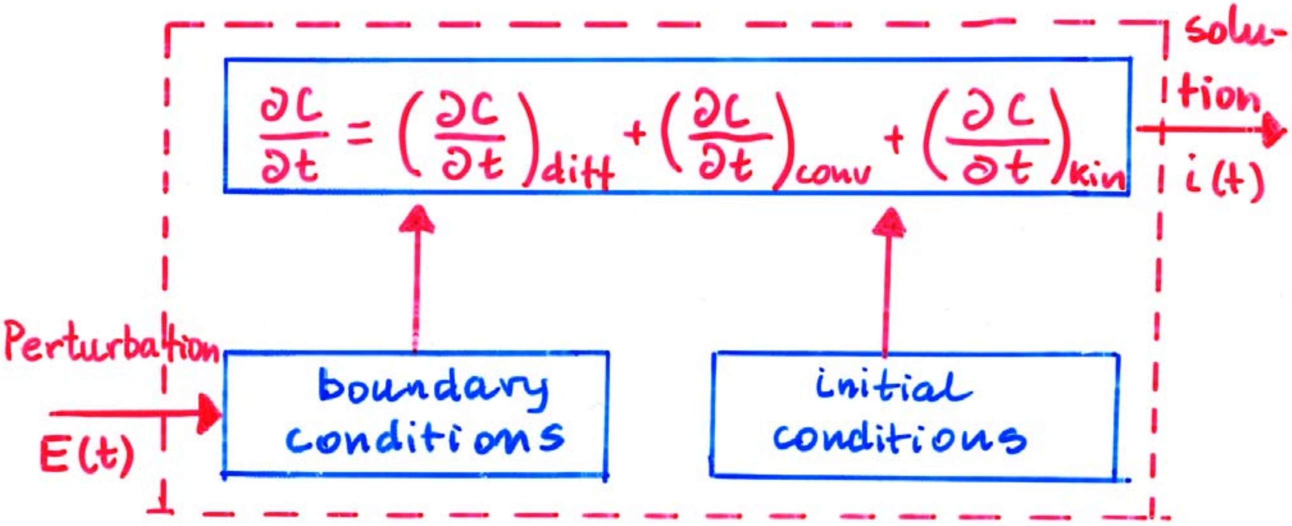
Response Depends on:

(i) Perturbation
(ii) Transport (diffusion or convection)
(iii) Electrode Geometry
(iv) Signal processing

6.1 Electroanalytical techniques based on electrolysis at the constant electrode potential

1. Introduction

The Cell can be visualized as a processor solving the partial differential equation for the boundary conditions set up by the type of electroanalytical technique used.

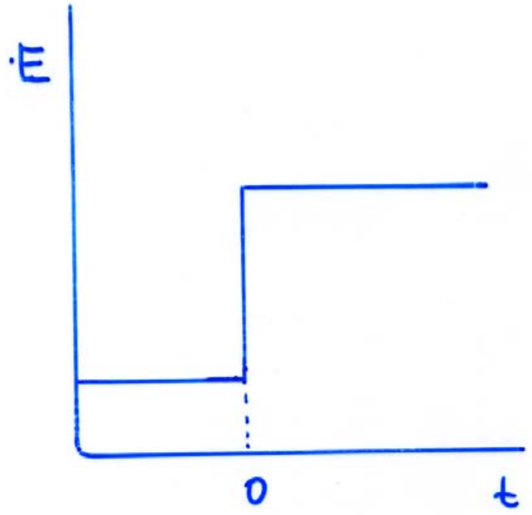


$$\frac{\partial c}{\partial t} = \left(\frac{\partial c}{\partial t}\right)_{diff} + \left(\frac{\partial c}{\partial t}\right)_{conv} + \left(\frac{\partial c}{\partial t}\right)_{kin}$$

6.2. Chronoamperometry

1. perturbation

E= const



2. no convection

3. all type of electrode geometries possible but in analytical practice only planar and spherical electrodes are used

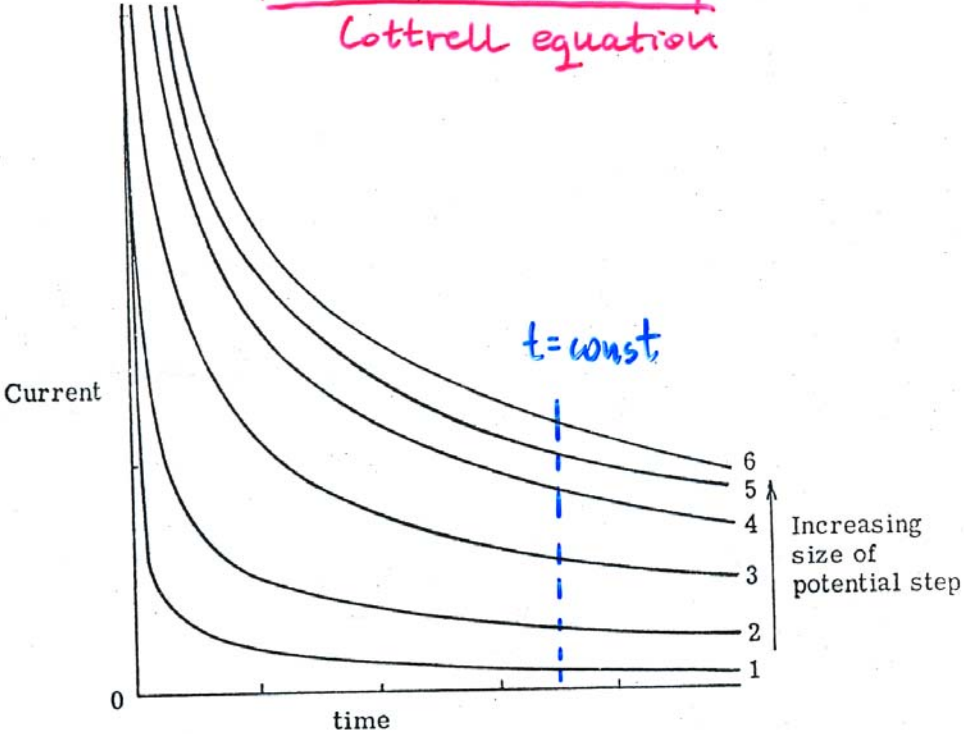
4. no signal processing

Potential-dependence of the Chronoamperometric Response

Limiting current $C_i(0,t) = 0$

$$\boxed{i(t) = \frac{nFAD^{1/2}C_i^*}{\pi^{1/2}t^{1/2}}}$$

Cottrell equation



at $C_i(0,t) \neq 0$

$$i(t) = nFAD^{1/2}\frac{C_i^* - C_i(0,t)}{\pi^{1/2}t^{1/2}}$$

diffusion control - reversible current

$$E = E_0 + \frac{RT}{nF}\ln\frac{C_{ox}(0,t)}{C_R(0,t)}$$

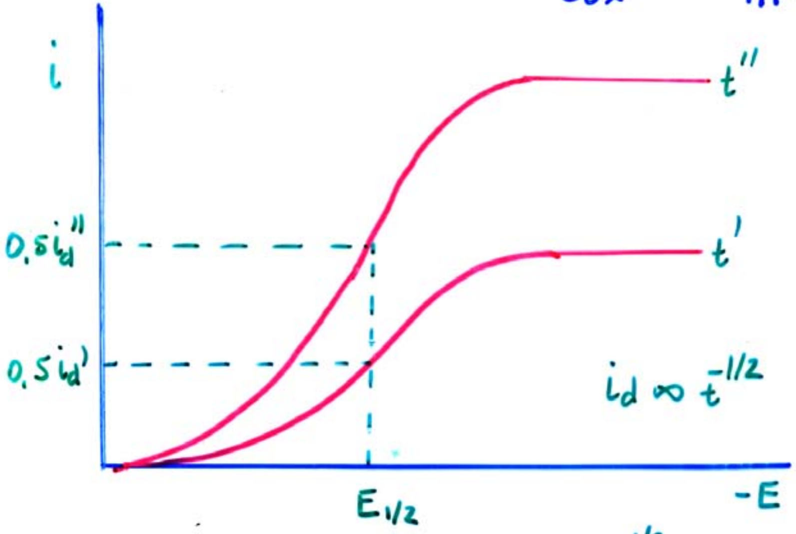
Reversible reactions

How $i(t)$ depends on E ?

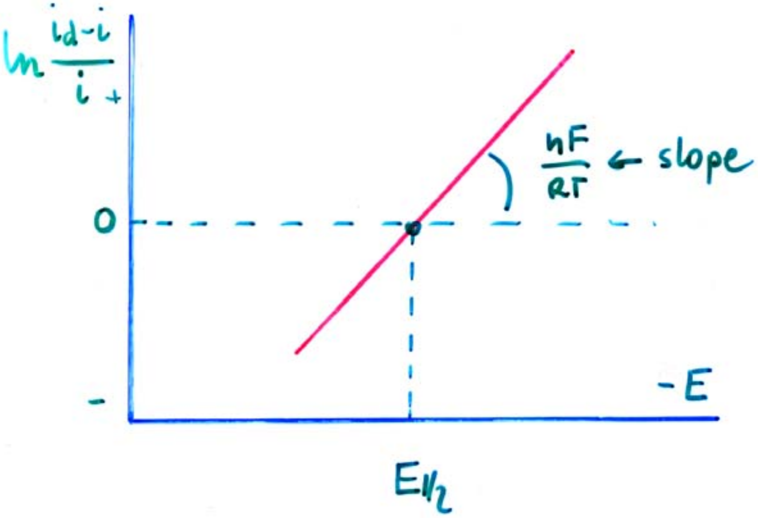
at t = const

$$\boxed{E = E_0 + \frac{RT}{nF}\ln\left(\frac{D_R}{D_{Ox}}\right)^{1/2} + \frac{RT}{nF}\ln\frac{i_d - i}{i}}$$

$$E = E_0 + \frac{RT}{nF} \ln \left(\frac{D_R}{D_{ox}} \right)^{1/2} + \frac{RT}{nF} \ln \frac{i_d - i}{i}$$

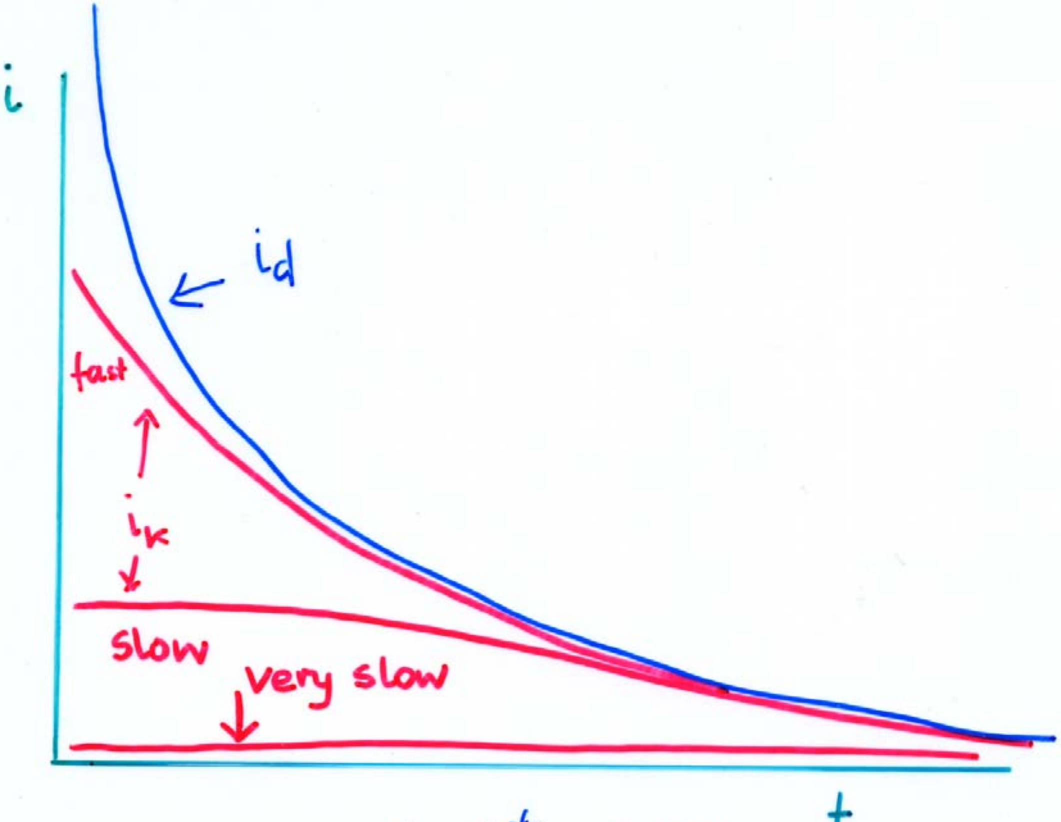


$$E_{1/2} = E^0 + \frac{RT}{nF} \ln \left(\frac{D_R}{D_{ox}} \right)^{1/2}$$



6.3 chronoamperometry - current controled by slow charge transfer kinetics (irreversible process)

a) experimental transients



$$i_d = nFA\,D^{1/2}\,\frac{C_i^* - C_i(0,t)}{\pi^{1/2}t^{1/2}}$$

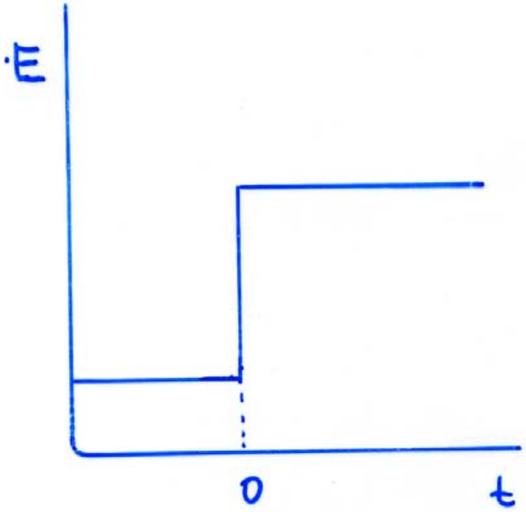
$$i_k = nFA\,k_{f,h}\,C_i(0,t)$$

Review

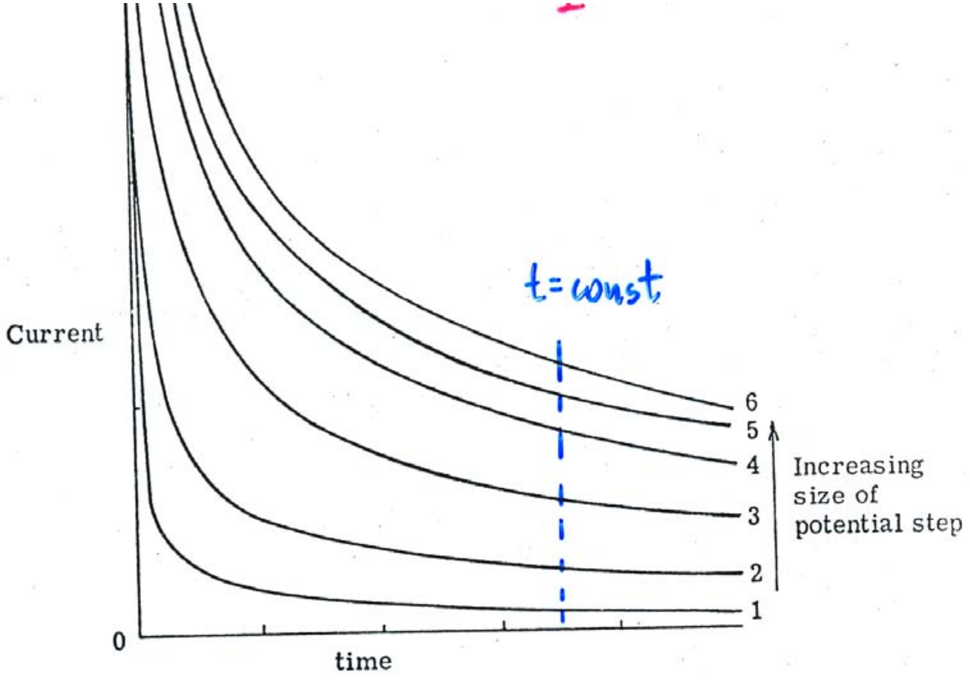
Chronoamperometry

perturbation

E= const



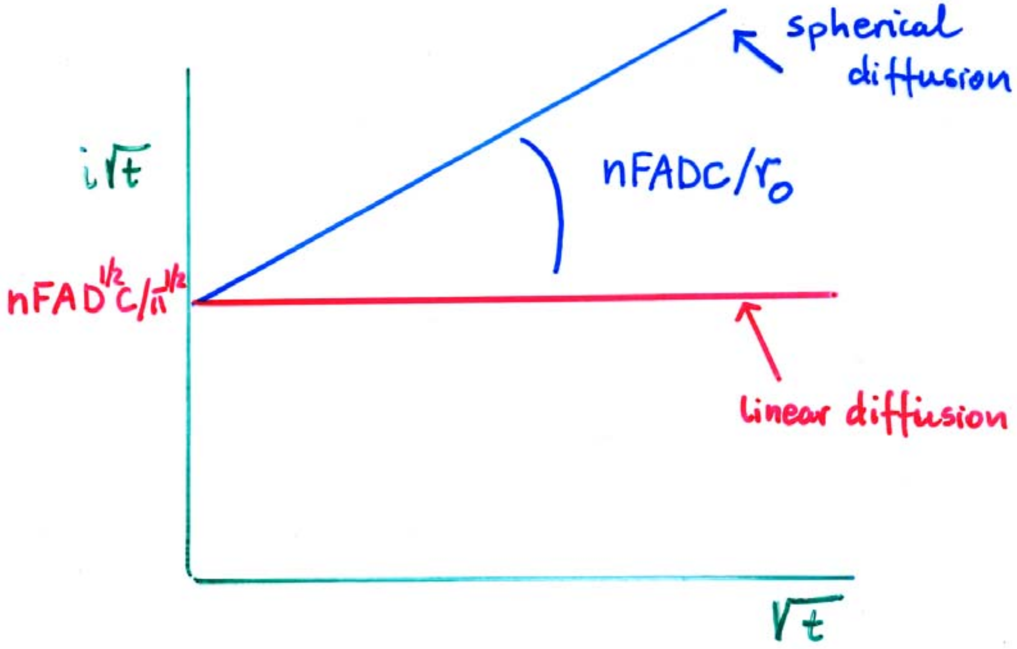
response



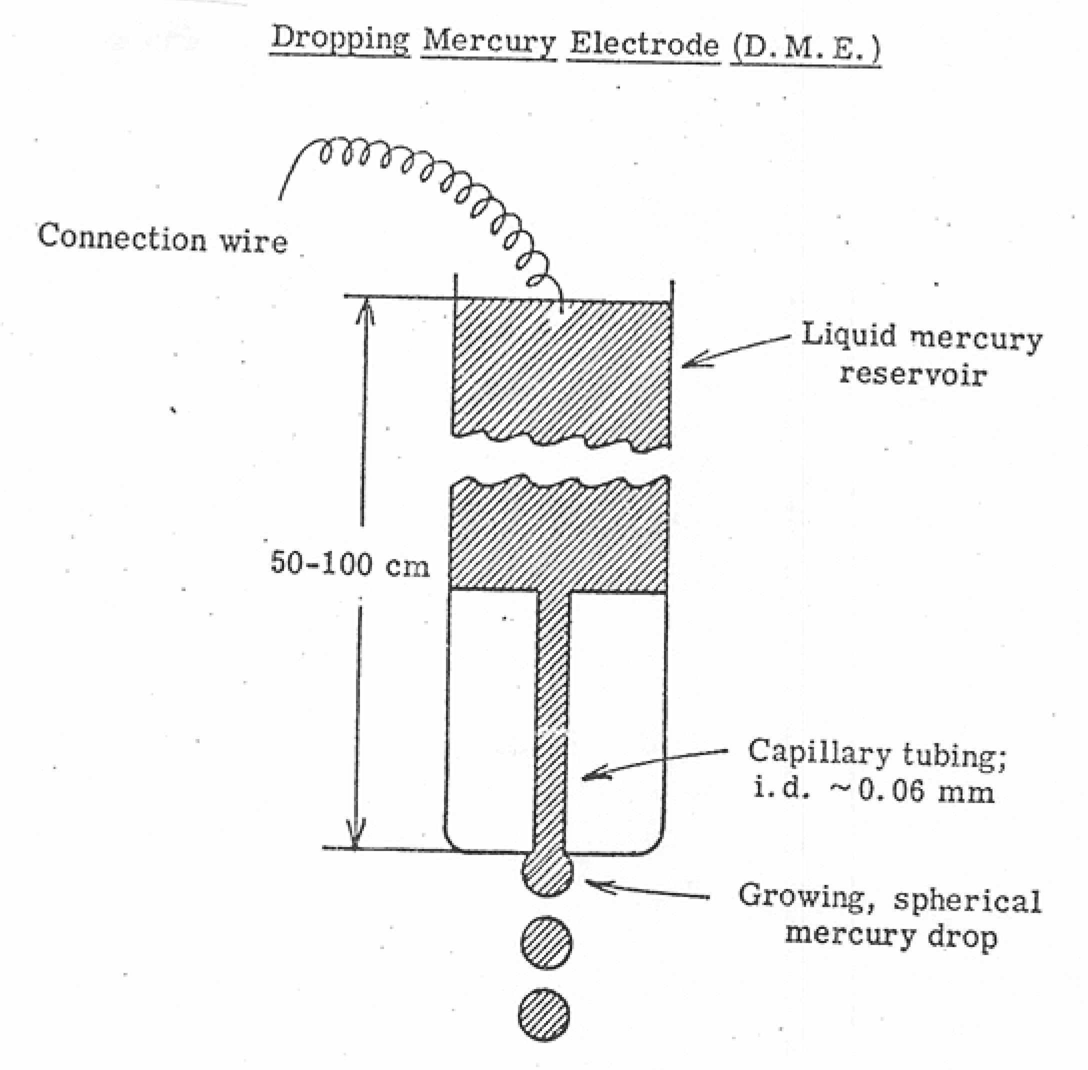
From limiting chronoamperometric curves – analytical information

$$i = nFADC^*\left(\frac{1}{\sqrt{\pi D t}} + \frac{1}{r_0}\right)$$

$$i\sqrt{t} = nFAD^{1/2}C^*/\pi^{1/2} + \left(nFADC^*/r_0\right)t^{1/2}$$

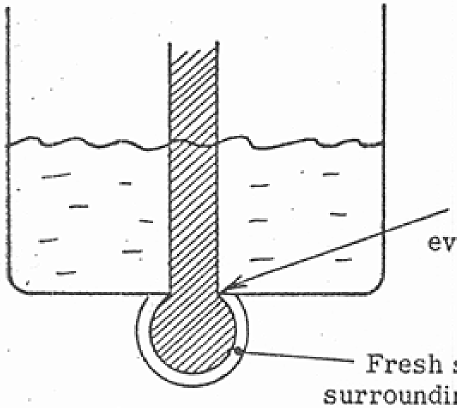


7.1 Polarography



Virtues of the Dropping Mercury Electrode

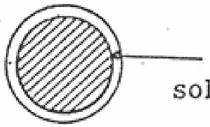
1. Reproducibility:



Fresh drop
every 4-6 seconds

Fresh solution layer
surrounding each new drop
provides reproducible behavior

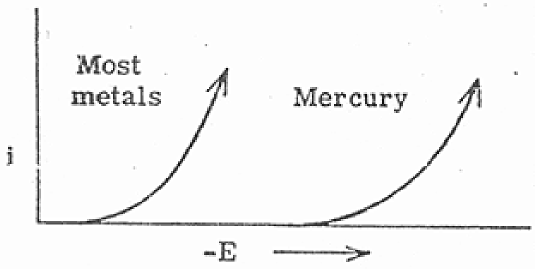
2. Self-cleansing:



Old, partially depleted
solution layer, carried away
with each falling drop

Adsorbed organic
impurities carried away
with each falling drop

3. High "hydrogen overvoltage": $H_2O + e^- \rightarrow \frac{1}{2}H_2 + OH^-$



polarography exact solution

1. perturbation E= const
2. diffusion and convection
3. spherical electrodes

Ilkovič equation - solution of the partial differential equation

$$\frac{\partial C_{ox}(x,t)}{\partial t} = D_{ox}\frac{\partial^2 C_{ox}}{\partial x^2} + \frac{2x\,\partial C_{ox}(x,t)}{3t\,\partial x}$$

$$i = \sqrt{\frac{7}{3}}\,\frac{nF D_{ox}^{1/2} A C}{(\pi t)^{1/2}} = 708\, n D^{1/2} C^{b} m^{2/3} t^{1/6}$$

Polarography:

1. Electrolysis at constant electrode potential at DME

2. Mass transport – convection + diffusion

$$i = \underset{\substack{\uparrow \\ \text{correction for} \\ \text{convection}}}{\left(\frac{7}{3}\right)^{1/2}} \underbrace{nFAD^{1/2}(C_b - C_{x=0})/\sqrt{\pi t}}_{\substack{\uparrow \\ \text{diffusion} \\ \text{toward electrode}}}$$

$$A = 0.85\, m^{2/3} t^{2/3}$$

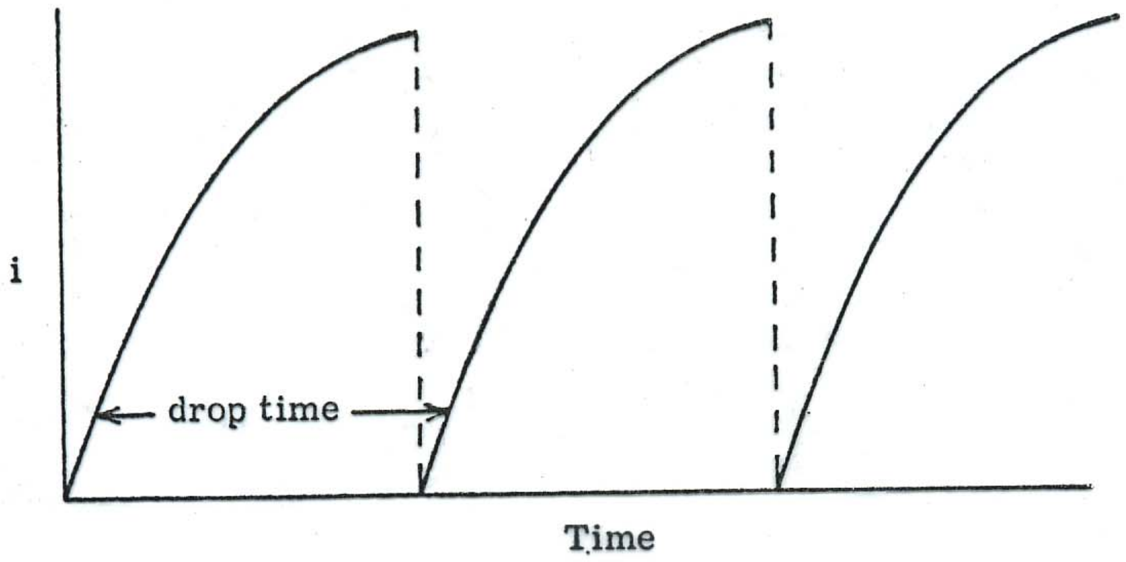
$$i = 708\, n D^{1/2} m^{2/3} t^{1/6} (C_b - C_{x=0})$$

limiting current

$$\boxed{i = 708\, n D^{1/2} m^{2/3} t^{1/6}\, C_b}$$

Ilkovič equation

Instantaneous Current-time Curves for a Dropping Mercury Electrode



The Ilkovič Equation:

$$i_d(\mu\,\text{amp}) = 708\, n D^{1/2} C^b m^{2/3} t^{1/6}$$

i_d = instantaneous current
m = mercury flow rate, milligrams/sec
t = drop age, sec
C^b = bulk concentration, millimolar
D = diffusion coefficient, $cm^2\,sec^{-1}$

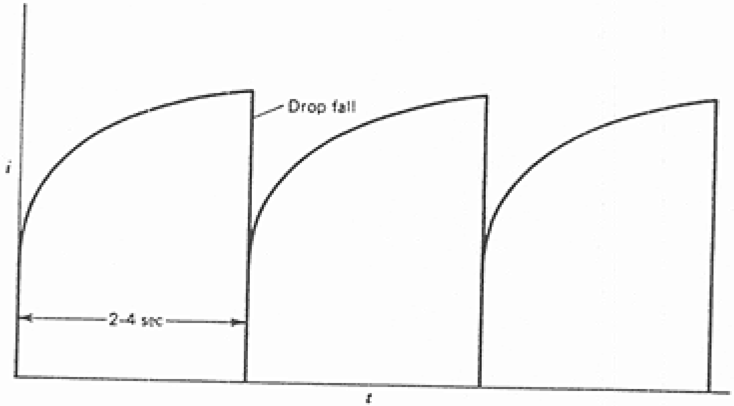
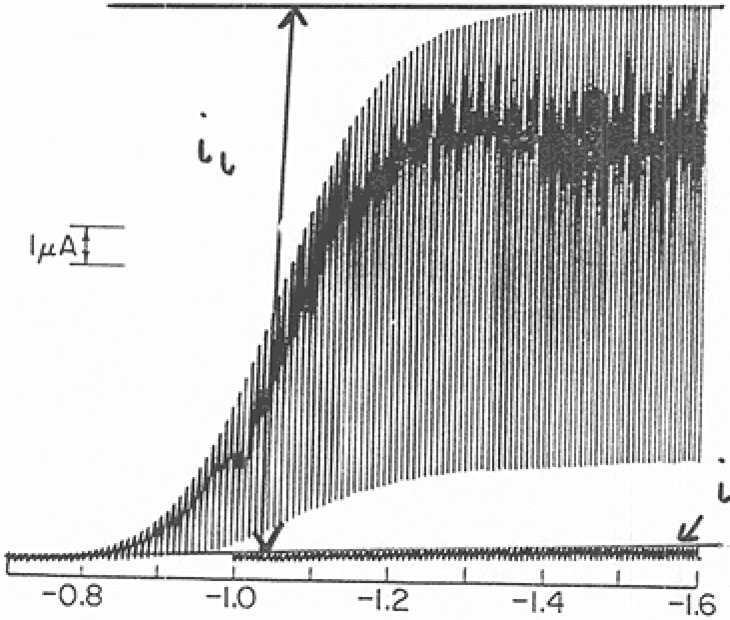


Figure 2
Current growth during three successive drops of a DME.

$i \propto t^{1/6}$



i_r - residual current

$i_r = i_c + i_p$

Figure 2
Polarogram for 1 mM CrO_4^{2-} in deaerated 0.1 M NaOH. The lower curve is the residual current observed in the absence of CrO_4^{2-}.

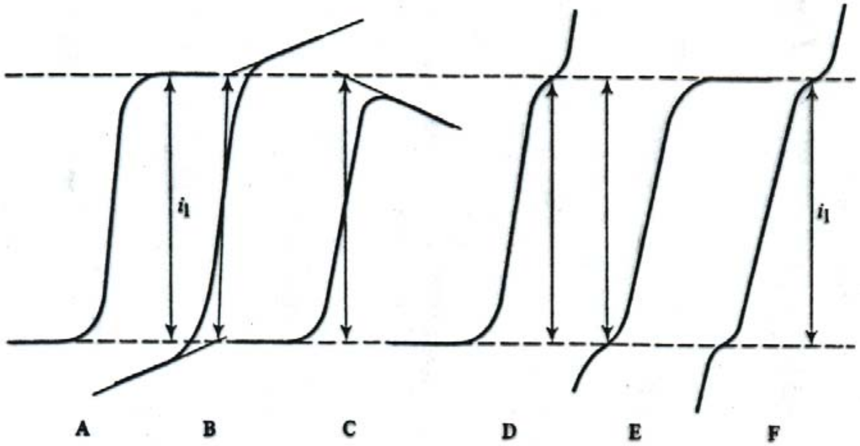


FIGURE 3.12. *Illustration of several methods for measuring the wave height of variously shaped polarographic waves. Curves A–C illustrate the technique of extrapolating the linear portions of the waves before and after the current rise. Curves D–F illustrate the technique of estimating current magnitudes for ill shaped waves.*

average current

$$\bar{i} = \frac{\int_0^{t_d} i\,dt}{t_d}$$

$$\bar{i} = 708\,n\,D^{1/2}\,C^b\,m^{2/3}\,\frac{\int_0^{t_d} t^{1/6}\,dt}{t_d}$$

$$\bar{i} = \left(\frac{6}{7}\right) 708\,n\,D^{1/2}\,C^b\,m^{2/3}\,t^{1/6}$$

$$\bar{i} = 607\,n\,D^{1/2}\,m^{2/3}\,t_d^{1/6}\,C^b$$

charging current

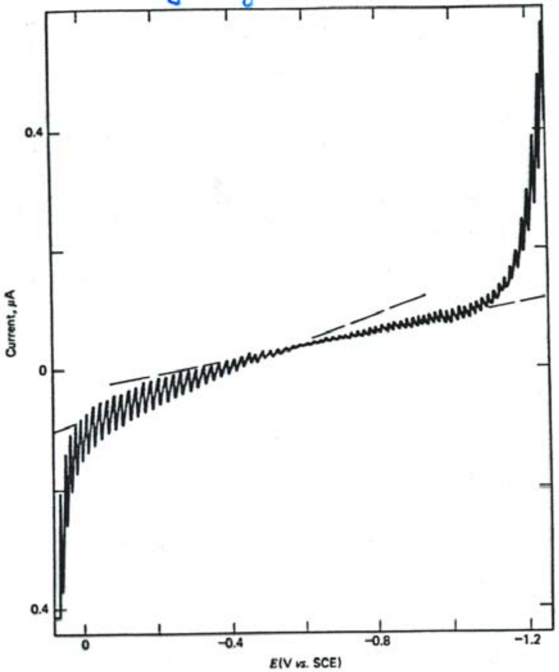


Figure 5.3.5

Residual current curve for 0.1 *M* HCl. (From L. Meites, "Polarographic Techniques," 2nd ed., Wiley-Interscience, New York, 1965, p. 101, with permission of John Wiley and Sons, Inc.)

instantaneous charging current

$$q = C_i A (E - E_2)$$

$$i_c = \frac{dq}{dt} = C_i (E - E_2) \frac{dA}{dt}$$

$$A = 4\pi \left(\frac{3mt}{4\pi d_{Hg}} \right)^{2/3}$$

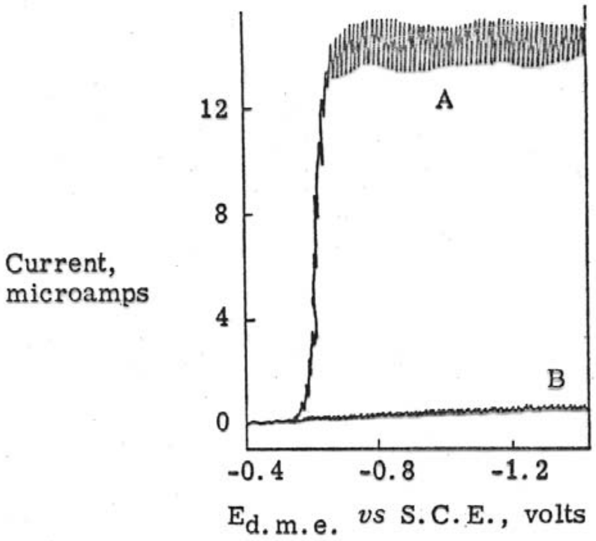
$$i_c = 0.00567\, C_i (E - E_2)\, m^{2/3} t^{-1/3}$$

average charging current

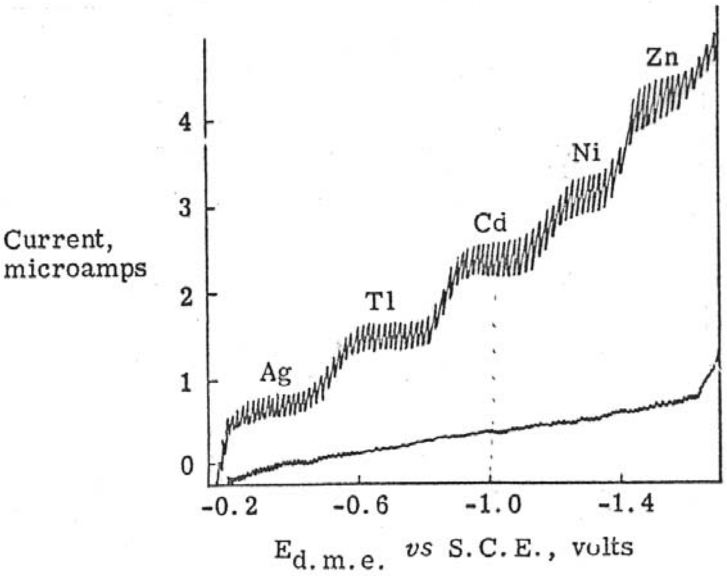
$$\bar{i}_c = \frac{\int_0^{t_d} i_c\, dt}{t_d}$$

$$\bar{i}_c = 0.0085\, C_i (E - E_2)\, m^{2/3} t_d^{-1/3}$$

Typical Polarogram



Polarogram of a Mixture of Ions



[Adapted from L. Meites, "Polarographic Techniques," Interscience Publishers, New York, 1965]

polarography - detection limit

$$\bar{I}_d = 607\, n\, D^{1/2}\, C^b\, m^{2/3}\, t_d^{1/6}$$

$$\bar{I}_c = 0.0085\, C_1\, (E - E_z)\, m^{2/3}\, t_d^{-1/3}$$

detection limit $\bar{I}_d = 2\bar{I}_c$

$$607\, n\, D^{1/2}\, C^b\, m^{2/3}\, t^{1/6} = 2\; 0.0085\, C_1\, (E - E_2)\, m^{2/3}\, t_d^{-1/3}$$

suppose

$E - E_2 = 0{,}1\ V$

$C_1 = 20\ \mu F/cm^2$

$n = 2$

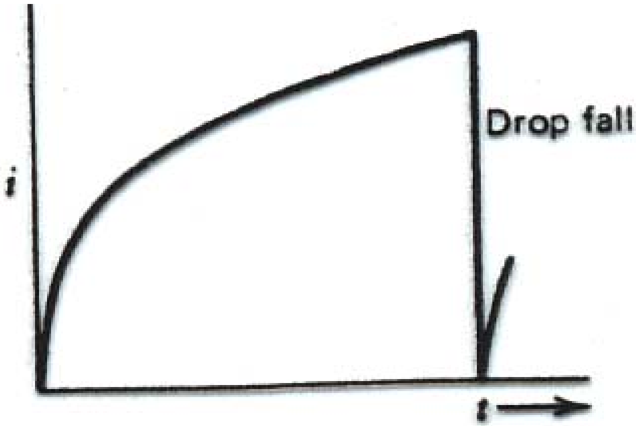
$t_d = 4\ s$

$D = 10^{-6}\ cm^2 s^{-1}$

$$C^b = \frac{2 \times 0.0085\, C_1\, (E - E_2)\, t^{-1/2}}{607\, n\, D^{1/2}}$$

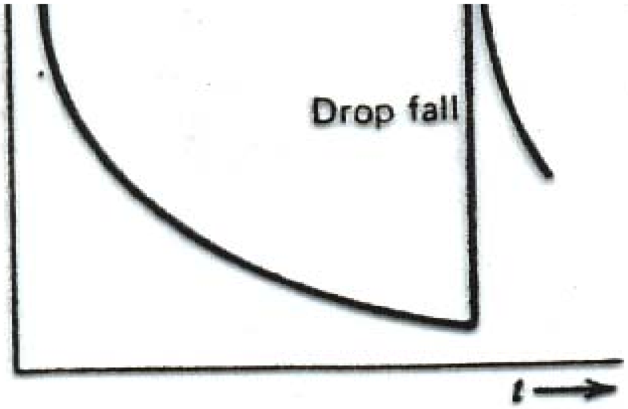
$$\underline{C^b \approx 10^{-5}\ M}$$

7.2 Tast Polarography



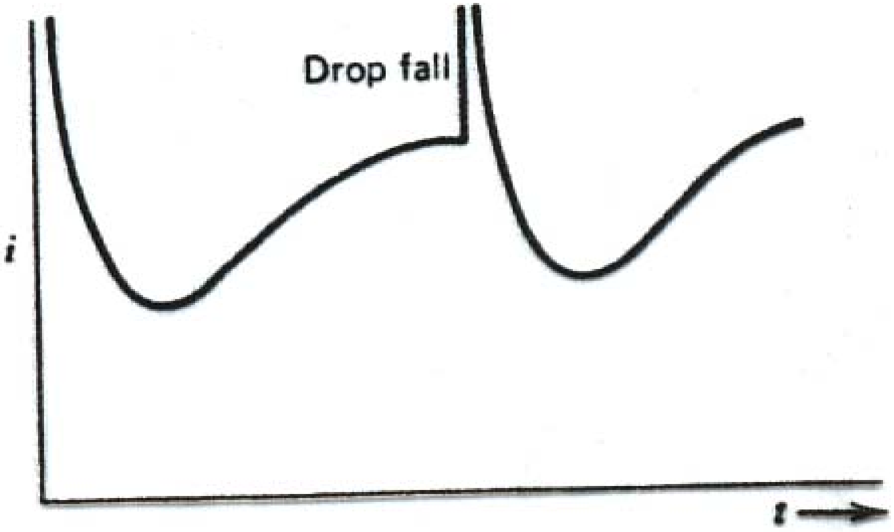
Faradaic current

$$i_d \propto t^{\frac{1}{6}}$$

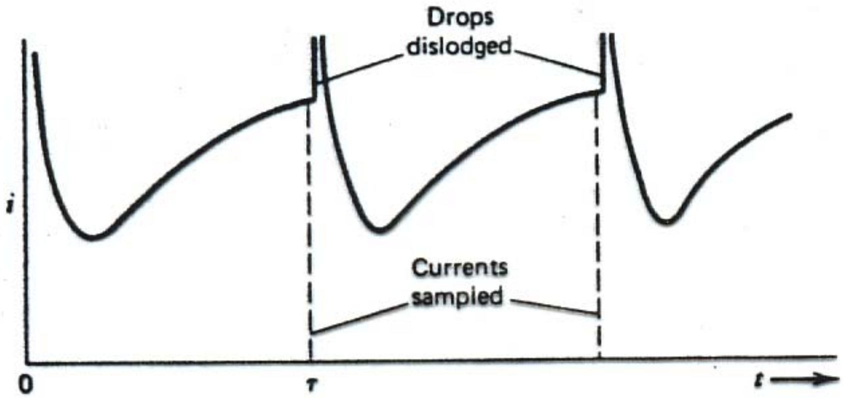


Charging current

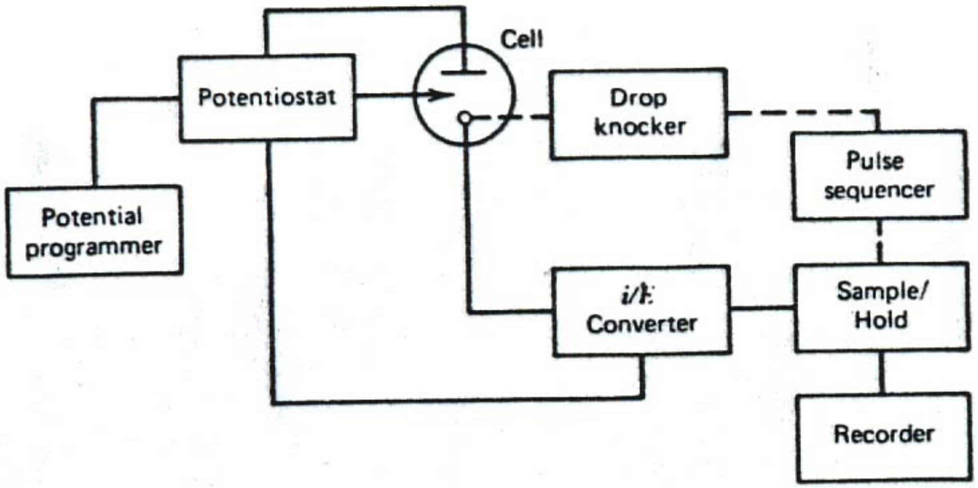
$$i_c \propto t^{-\frac{1}{3}}$$



Total current



Sampling scheme for tast polarography.



Schematic experimental arrangement for tast polarography.

Tast polarography

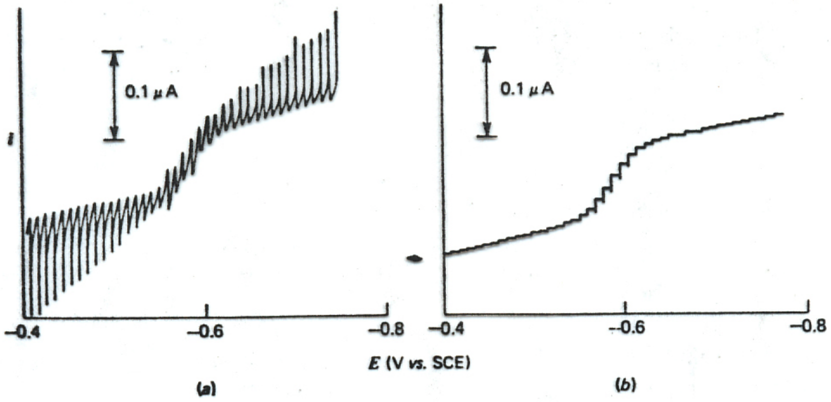


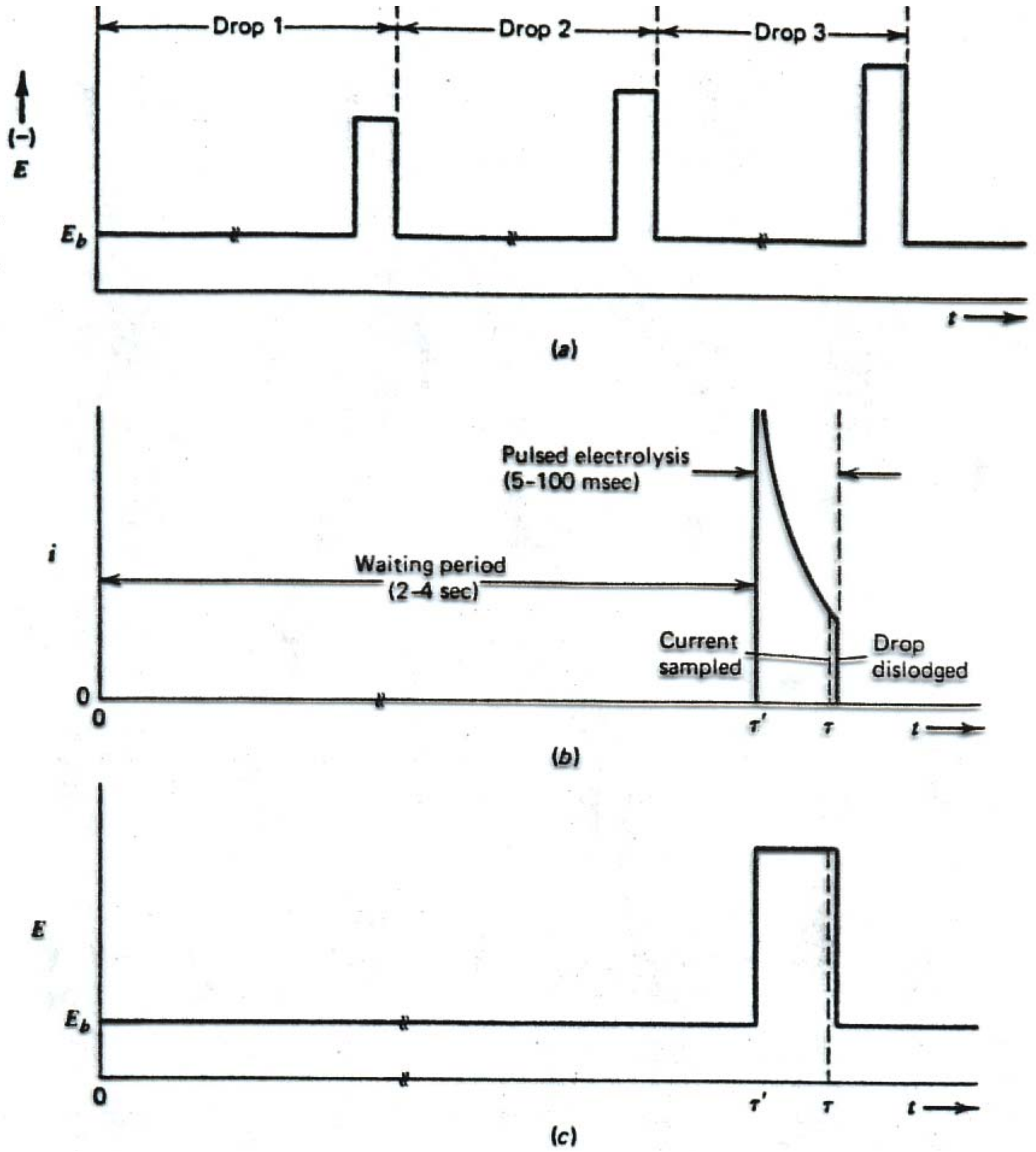
Figure 5.8.3
Polarograms for 10^{-5} *M* Cd^{2+} in 0.01 *M* HCl. (*a*) Conventional dc mode. (*b*) Tast mode.

$$\frac{i_d}{i_c} = \text{const}'' \, \tau^{1/2}$$

τ – sampling time

Detection limit 10^{-6} M

7.3 Pulse Polarography



$$i = \left(\frac{7}{3}\right)^{\frac{1}{2}} nFD^{\frac{1}{2}}C^{*}A/\sqrt{\pi t}$$

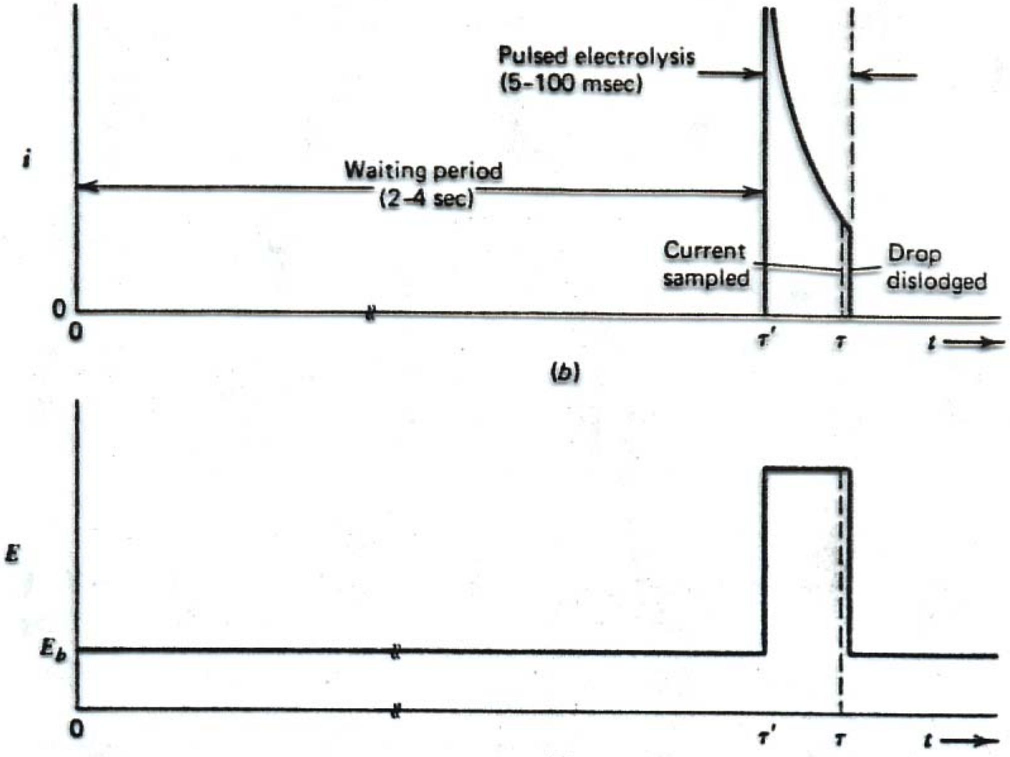
$$A = 0.85m^{\frac{2}{3}}t^{\frac{2}{3}}$$

Polarography

$$i = \left(\frac{7}{3}\right)^{\frac{1}{2}} nFD^{\frac{1}{2}}C^{*}0.85m^{\frac{2}{3}}t^{\frac{2}{3}}/\sqrt{\pi t}$$

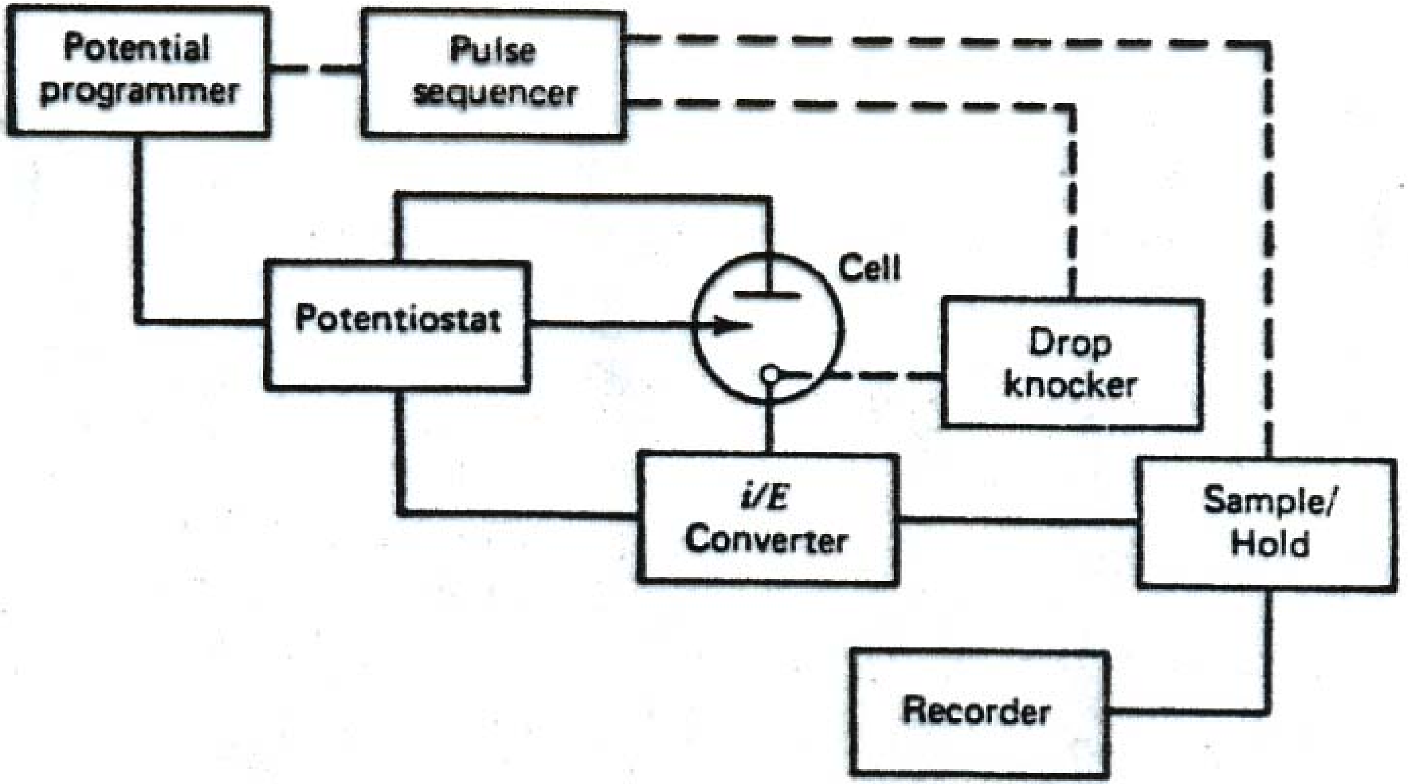
Pulse Polarography

$$i = \left(\frac{7}{3}\right)^{\frac{1}{2}} nFD^{\frac{1}{2}}C^{*}0.85m^{\frac{2}{3}}t^{\frac{2}{3}}/\sqrt{\pi(t-t^{'})}$$



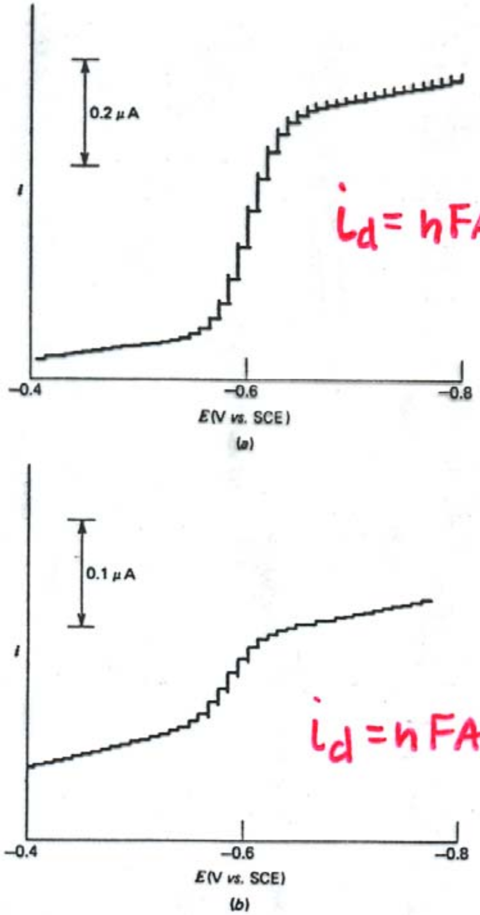
(b)

(c)



Schematics of a set up for pulse polarography

Detection limit 10^{-7}M



$$i_d = nFAD^{1/2}\pi^{-1/2}C^b/(\tau-\tau')^{1/2}$$

$$i_d = nFAD^{1/2}\pi^{-1/2}C^b/(\tau')^{1/2}$$

Figure 5.8.6

Polarograms for 10^{-5} M Cd^{2+} in 0.01 M HCl. (*a*) Normal pulse mode. (*b*) Tast mode.

$$(i_d)_p/(i_d)_t = (\tau'/\tau-\tau')^{1/2} = 10$$

suppose $\tau' — 4s$

$\tau-\tau' = 40ms$

$$(i_c)_p \approx (i_c)_t = 0.00567\, C_i\, (E-E_z)\, m^{2/3} t^{-1/3}$$

7.4 Differential pulse polarography

Current is sampled twice a time *t* and *t'*. Quantity measured is a difference ∂i :

$$\delta i = i(t) - i(t')$$

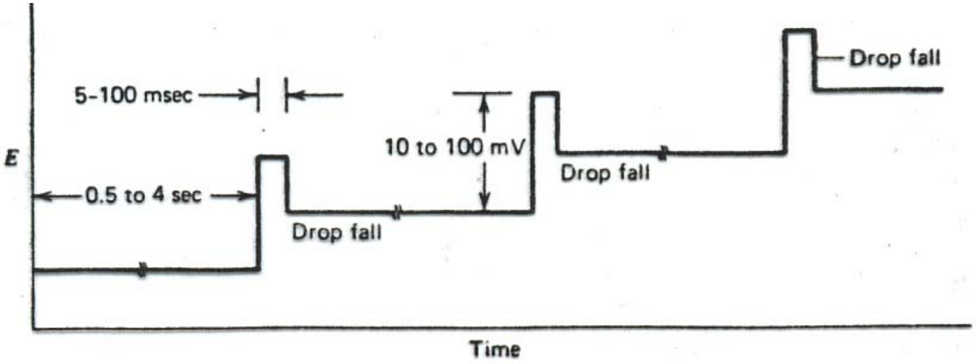
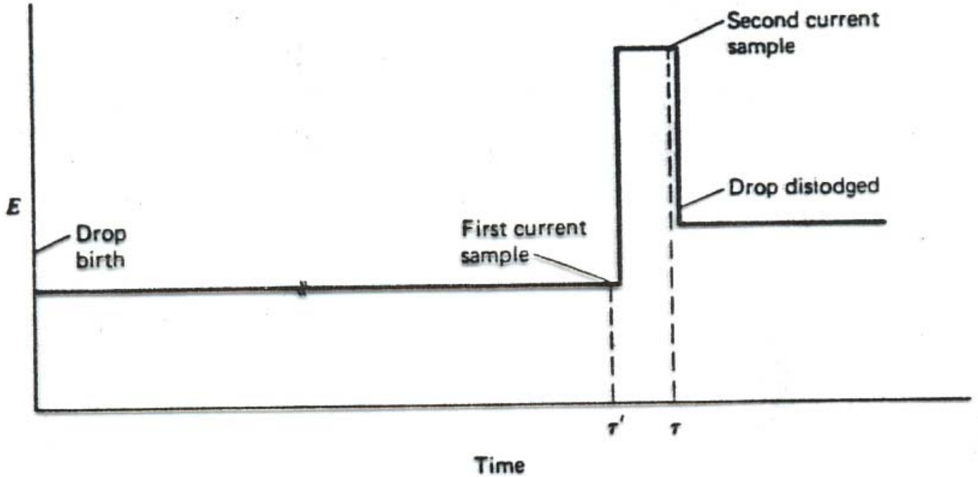


Figure 5.8.8
Potential program for several drops in a differential pulse polarographic experiment.



Differential pulse

$$\delta i = \delta i_d + \delta i_c$$

$$\delta i_c = i_c(t) - i_c(t')$$

Normal pulse

$$i = i_d(t - t') + i_c(t)$$

at peak potential

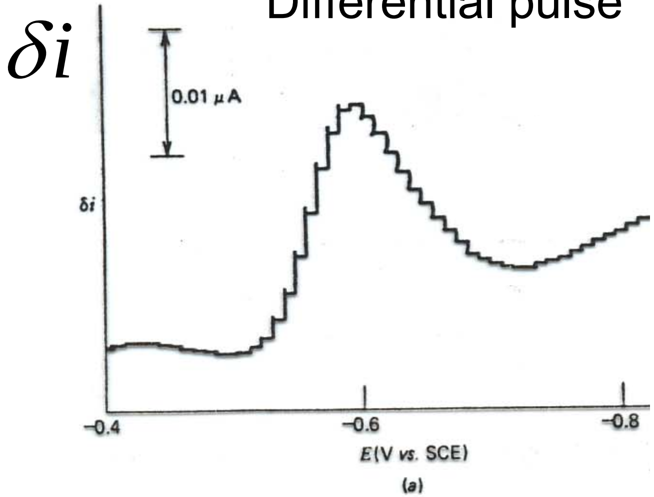
$$\delta i_d \approx i_d(t - t')$$

but

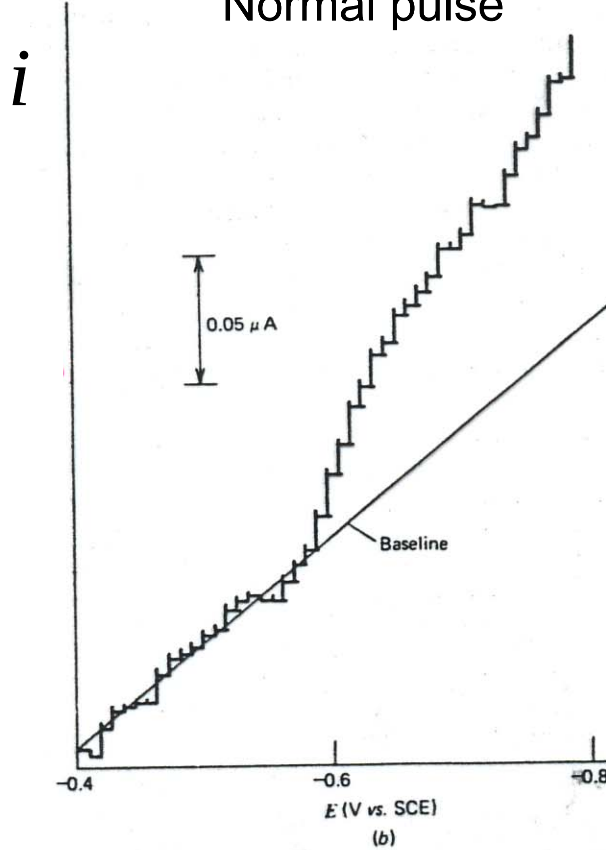
$$\delta i_c << i_c(t)$$

Detection limit of differential pulse polarography ~10^{-8}M

Differential pulse



Normal pulse



Examples of Pulse Polarographic Analysis:

Arsenic:

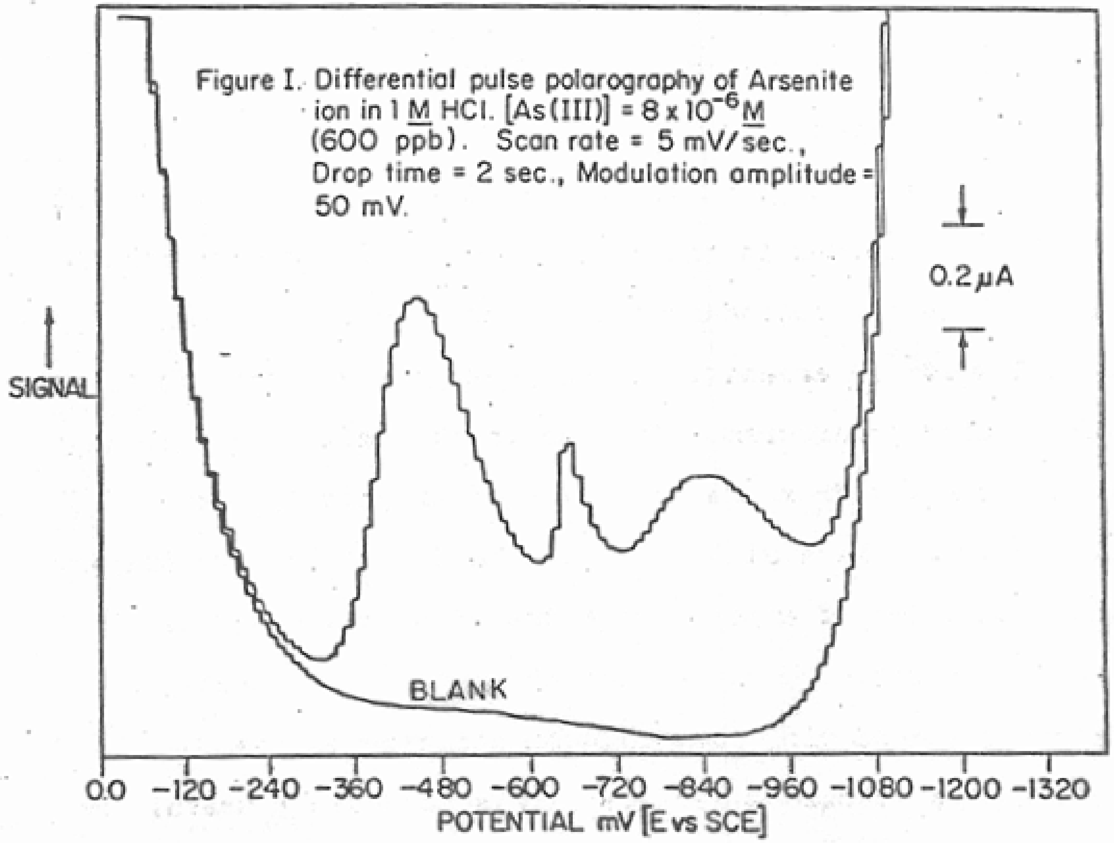
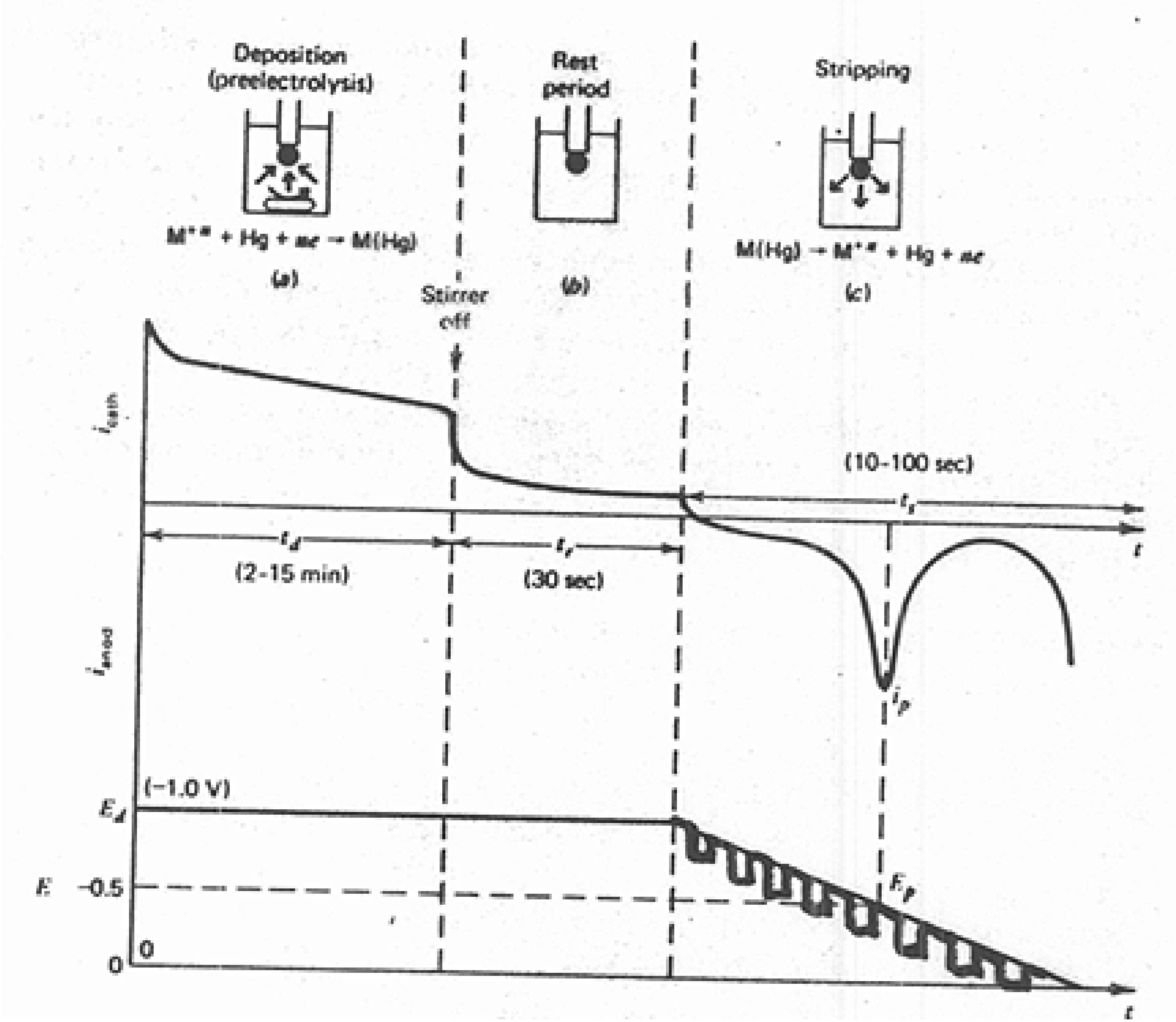
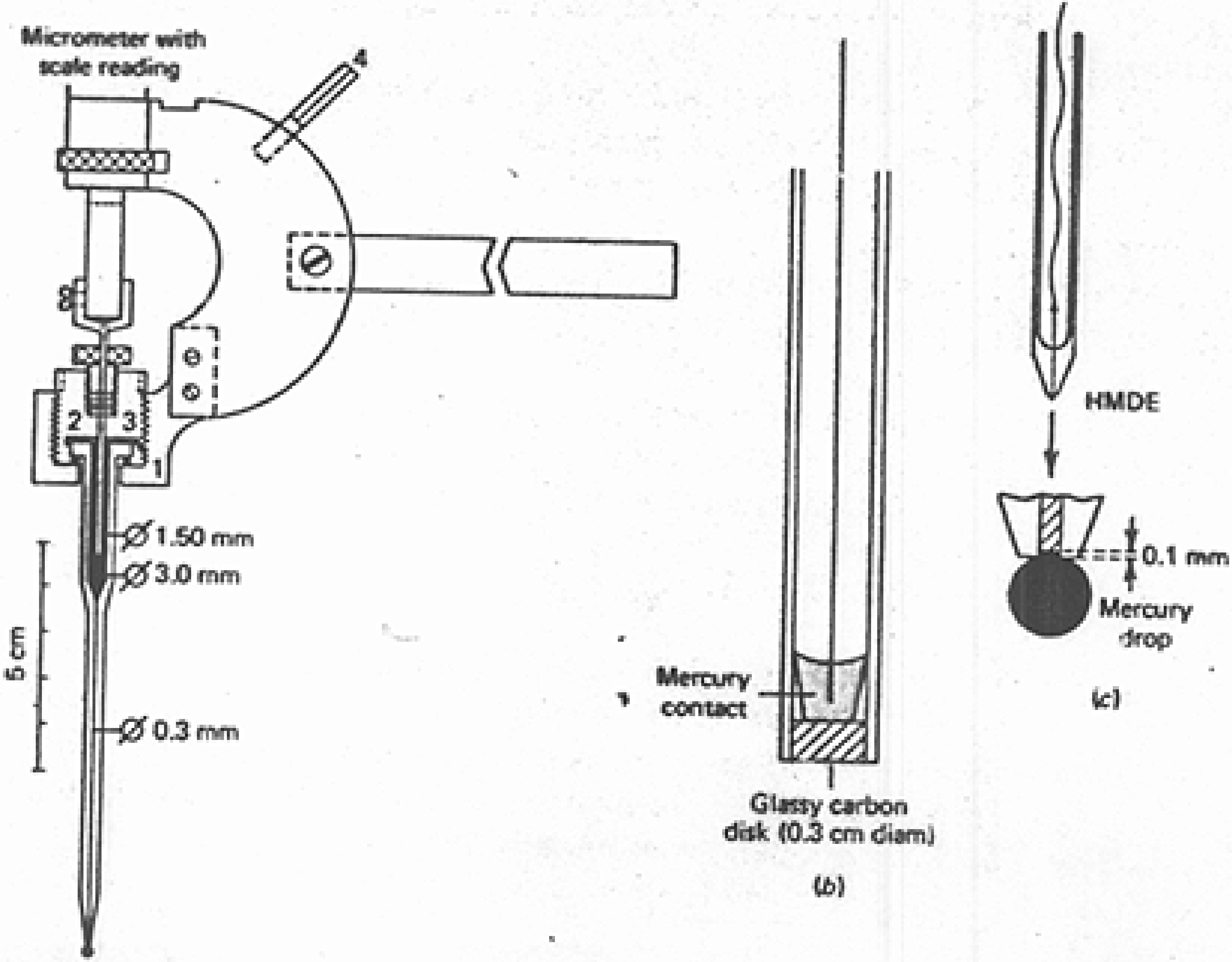
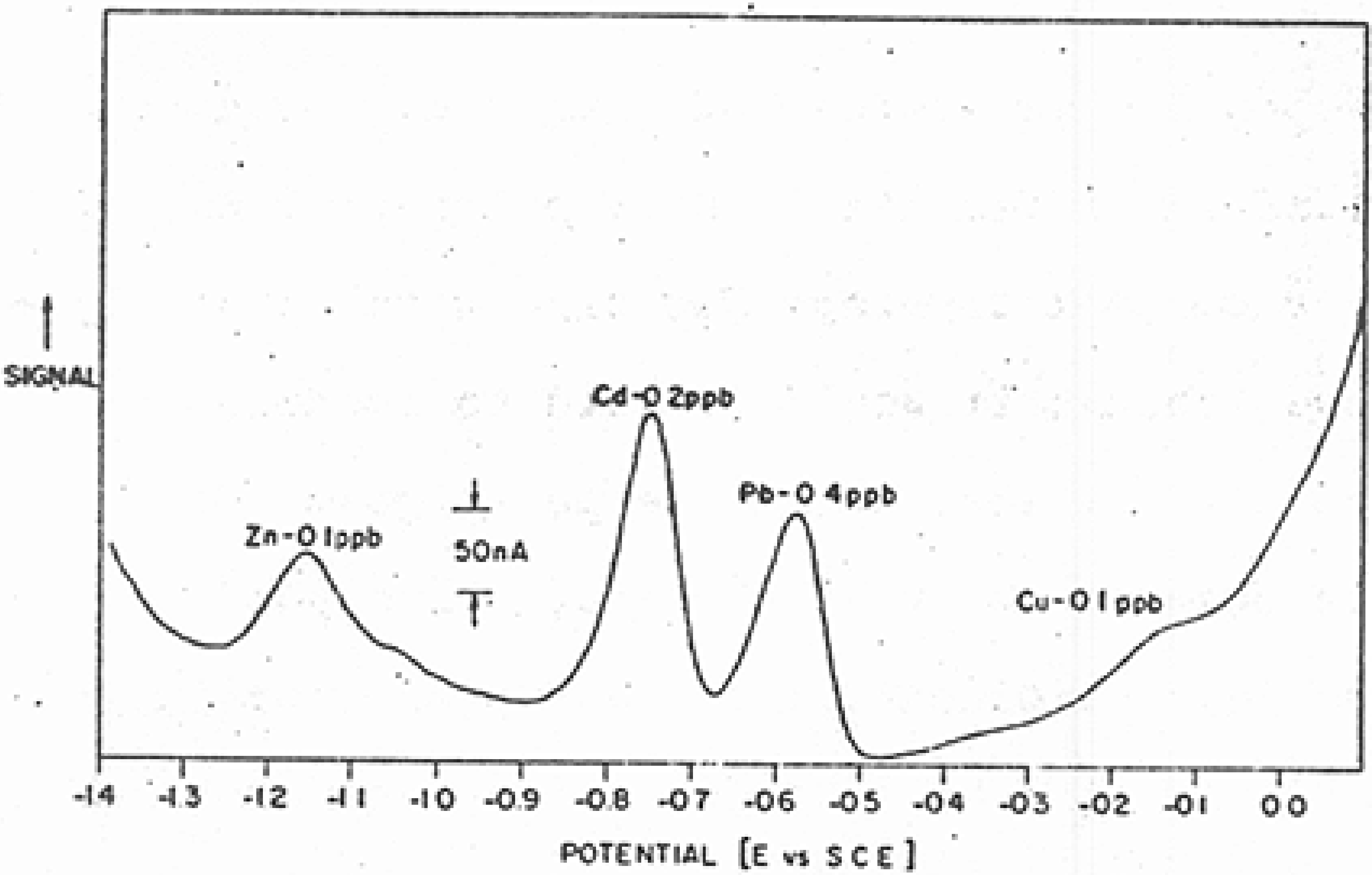


Figure I. Differential pulse polarography of Arsenite ion in 1 M HCl. [As(III)] = 8×10^{-6} M (600 ppb). Scan rate = 5 mV/sec., Drop time = 2 sec., Modulation amplitude = 50 mV.

7.5 Striping voltammetry

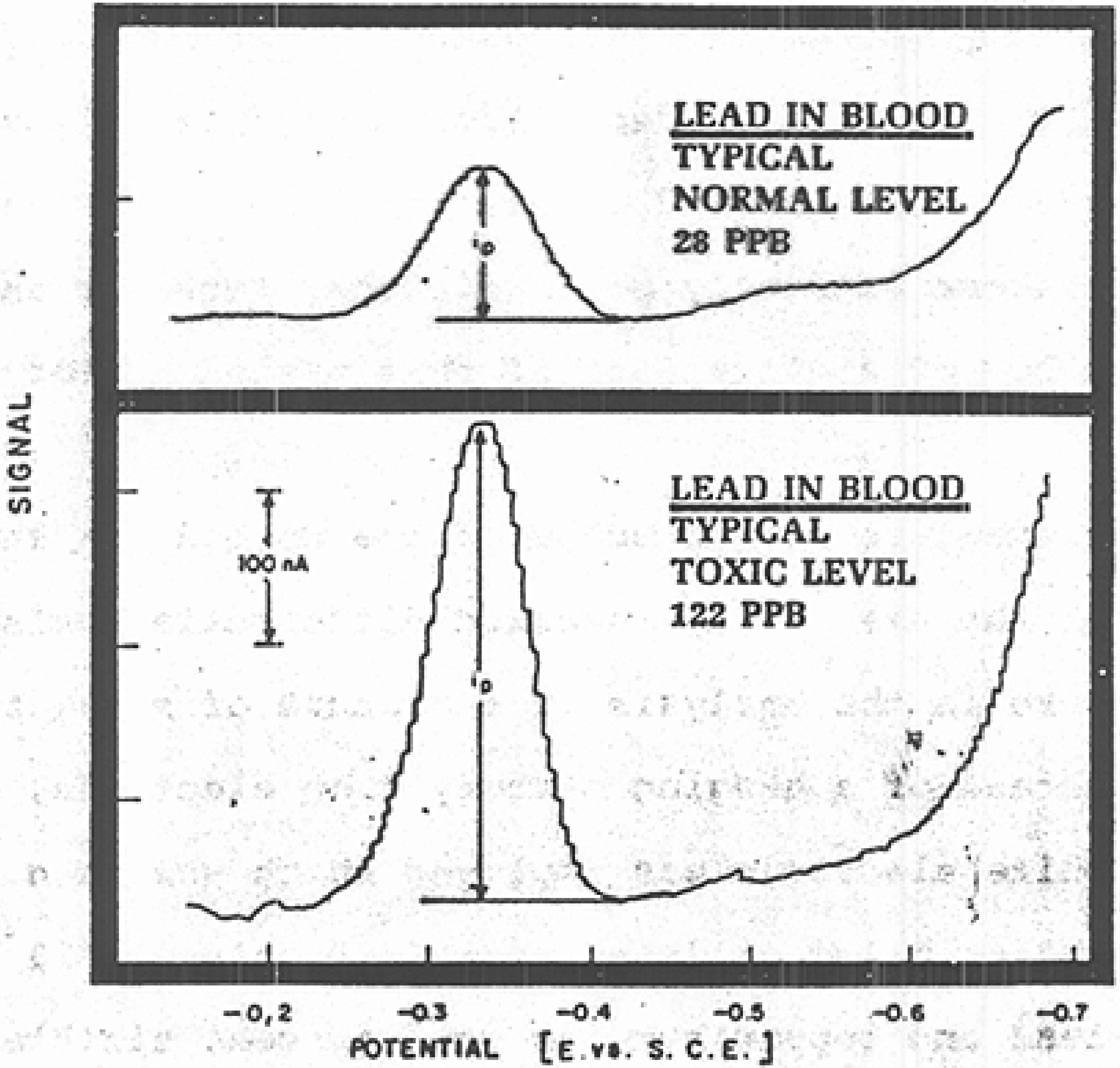



Micrometer with scale reading
4
2
3
1
Ø1.50 mm
Ø3.0 mm
5 cm
Ø0.3 mm
Mercury contact
Glassy carbon disk (0.3 cm diam)
(b)
HMDE
0.1 mm
Mercury drop
(c)

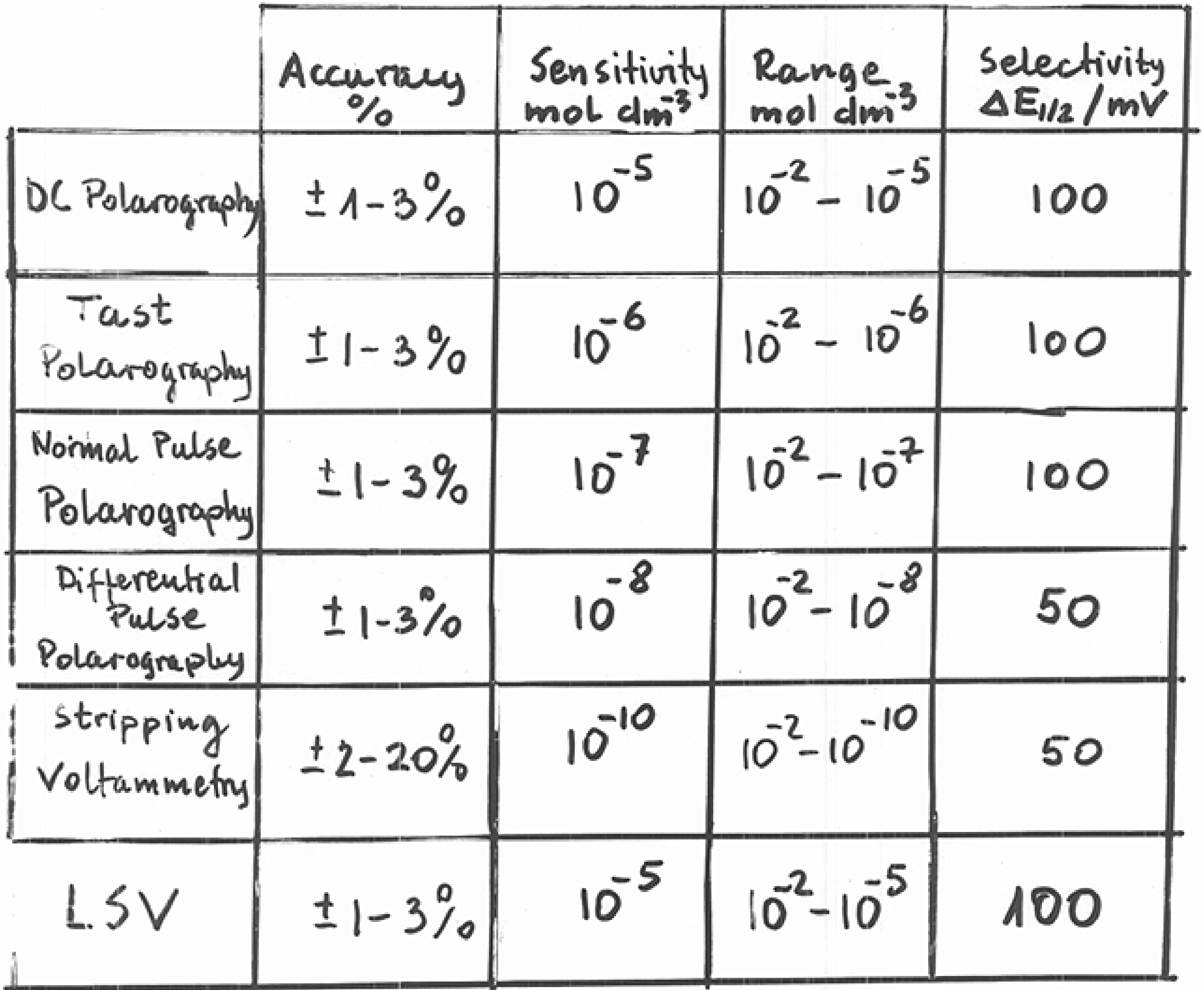


Differential pulse anodic stripping voltammetry. PAR Model 174 polarographic analyzer, Model 9319 wax-impregnated graphite electrode (mercury-plated). 2 × 10^{-9} *M* Zn, Cd, Pb, and Cu

Determination of lead in blood in the 10-100 parts per billion range:



Electroanalytical techniques – Figures of merits



	Accuracy %	Sensitivity mol dm^{-3}	Range mol dm^{-3}	Selectivity $\Delta E_{1/2}$ / mV
DC Polarography	± 1-3%	10^{-5}	$10^{-2} - 10^{-5}$	100
Tast Polarography	± 1-3%	10^{-6}	$10^{-2} - 10^{-6}$	100
Normal Pulse Polarography	± 1-3%	10^{-7}	$10^{-2} - 10^{-7}$	100
Differential Pulse Polarography	± 1-3%	10^{-8}	$10^{-2} - 10^{-8}$	50
Stripping Voltammetry	± 2-20%	10^{-10}	$10^{-2} - 10^{-10}$	50
LSV	± 1-3%	10^{-5}	$10^{-2} - 10^{-5}$	100

1. **Analyses of metals**

about 30 metals at levels $\geqslant$ 10 ppb

about 12 metals at levels less than a 1 ppb

2. **Analyses of non-metallic ions**

at ultra-trace quantities by stripping techniques

(Cl^-, Br^-, I^-, CN^-, N_3^-, S^{2-}, $S_2O_3^{2-}$ etc)

or

(ClO_2^-, NO_3^-, IO_3^-, IO_4^-.)

3. **Analysis of organics**

reducible functional groups

Imines, Oximes, Nitro, Nitrozo, Aldehyd

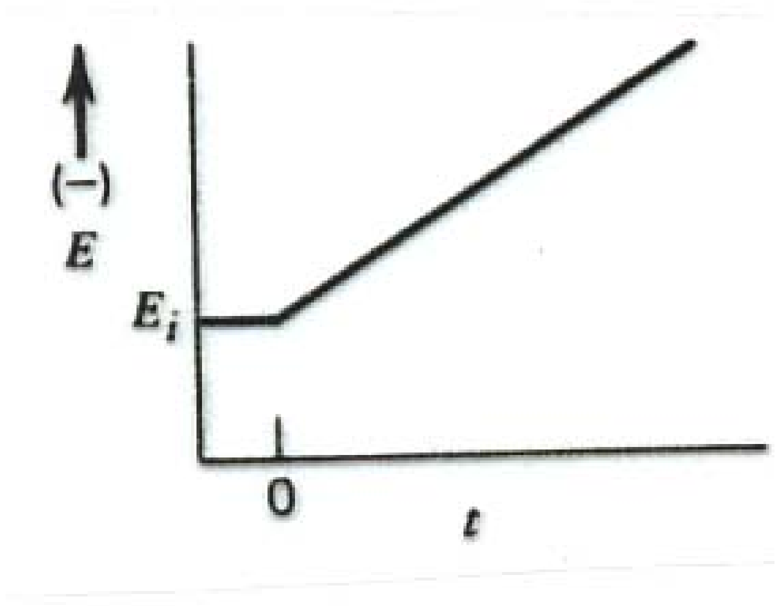
Halides, Organo-metallics etc.

8. Linear sweep voltammetry

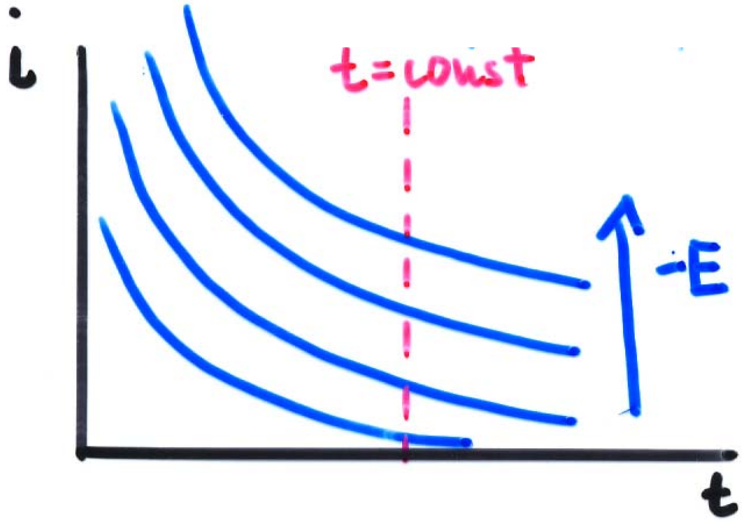
Perturbation – linear voltage sweep (voltage ramp)

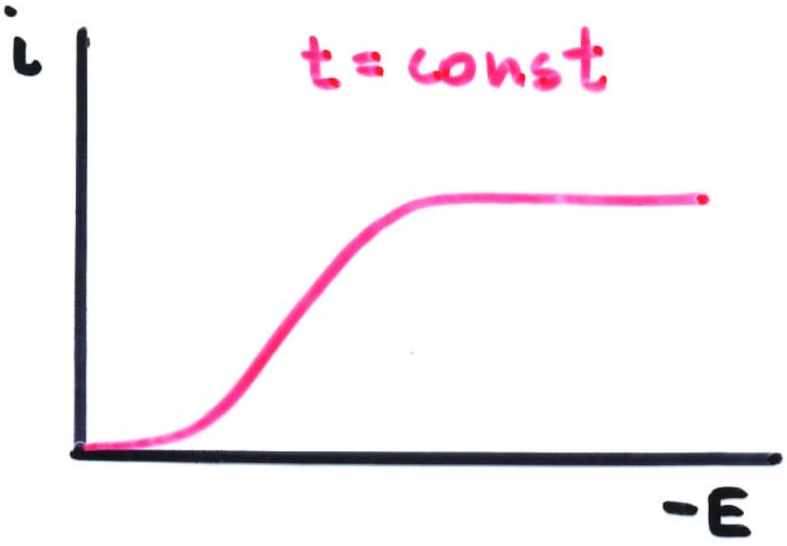
$$E = E_i - vt$$

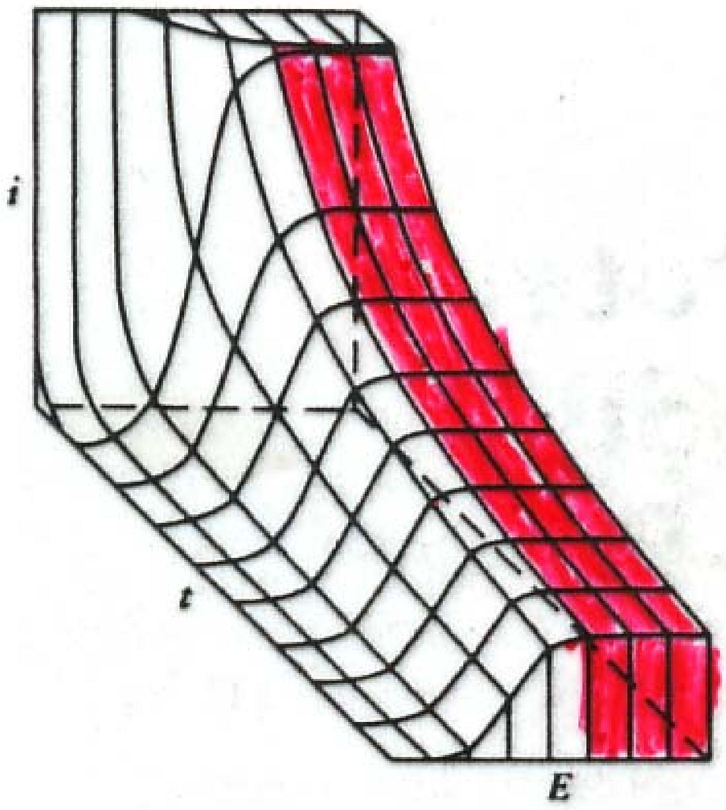
v sweep rate in V/s

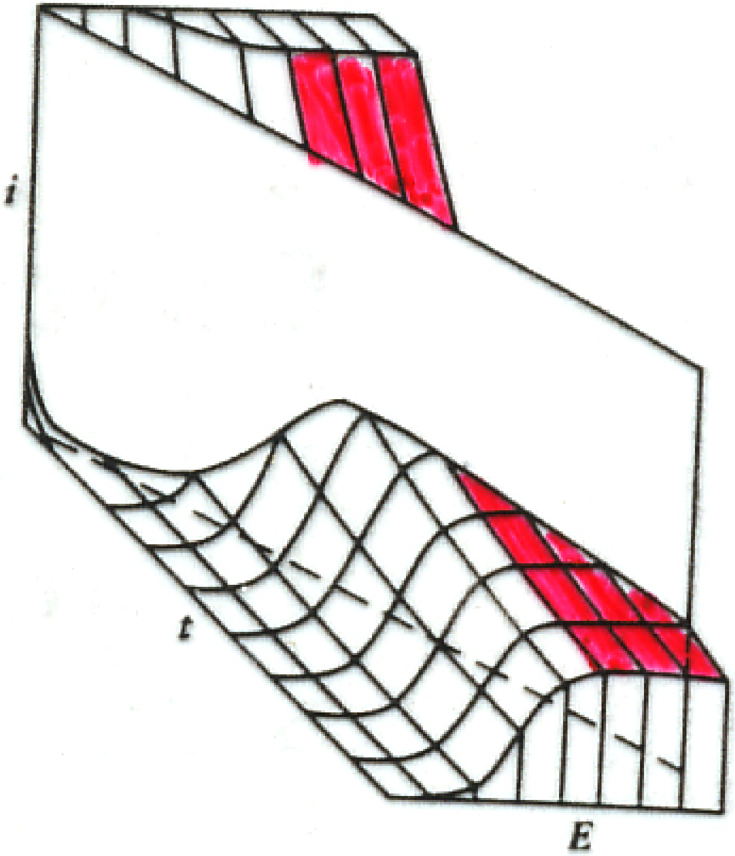


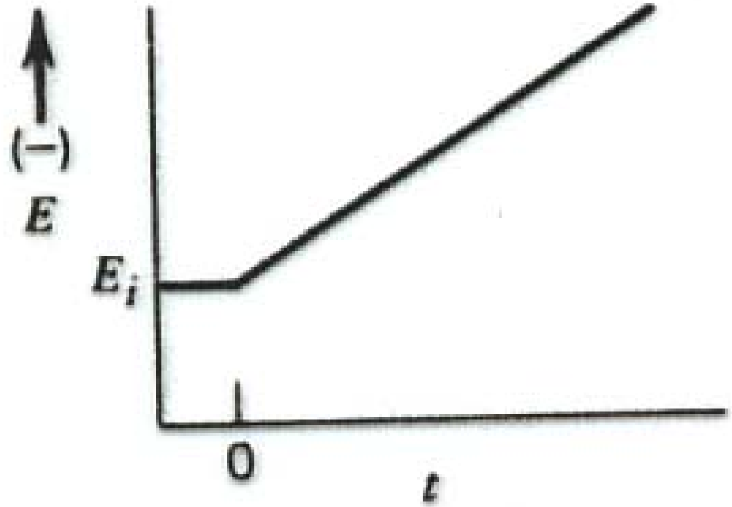
Qualitative prediction of the shape of a CV curve – chronoamperometric experiments

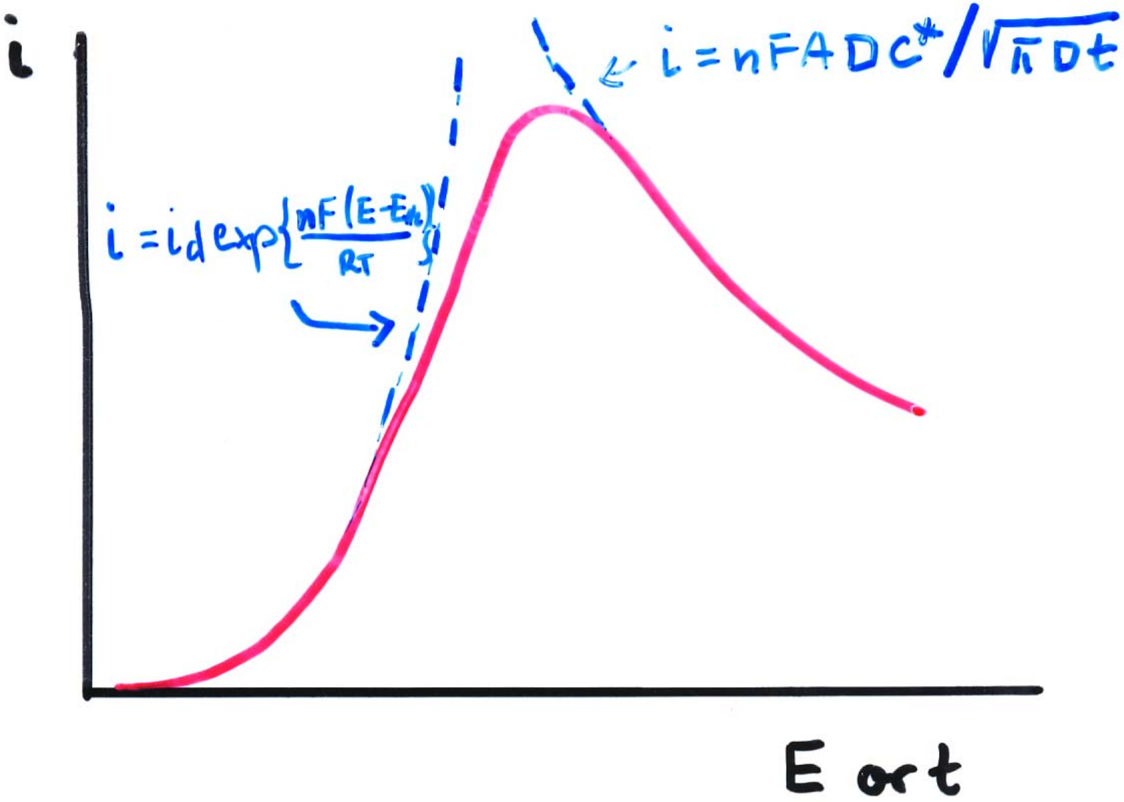







i
t
E


(−)
E
E_i
0
t


i
$i = nFADC^* / \sqrt{\pi D t}$
$i = i_d \exp\left\{\frac{nF(E-E_n)}{RT}\right\}$
E or t

There is no analytical solution to this problem – the equation has been solved numerically

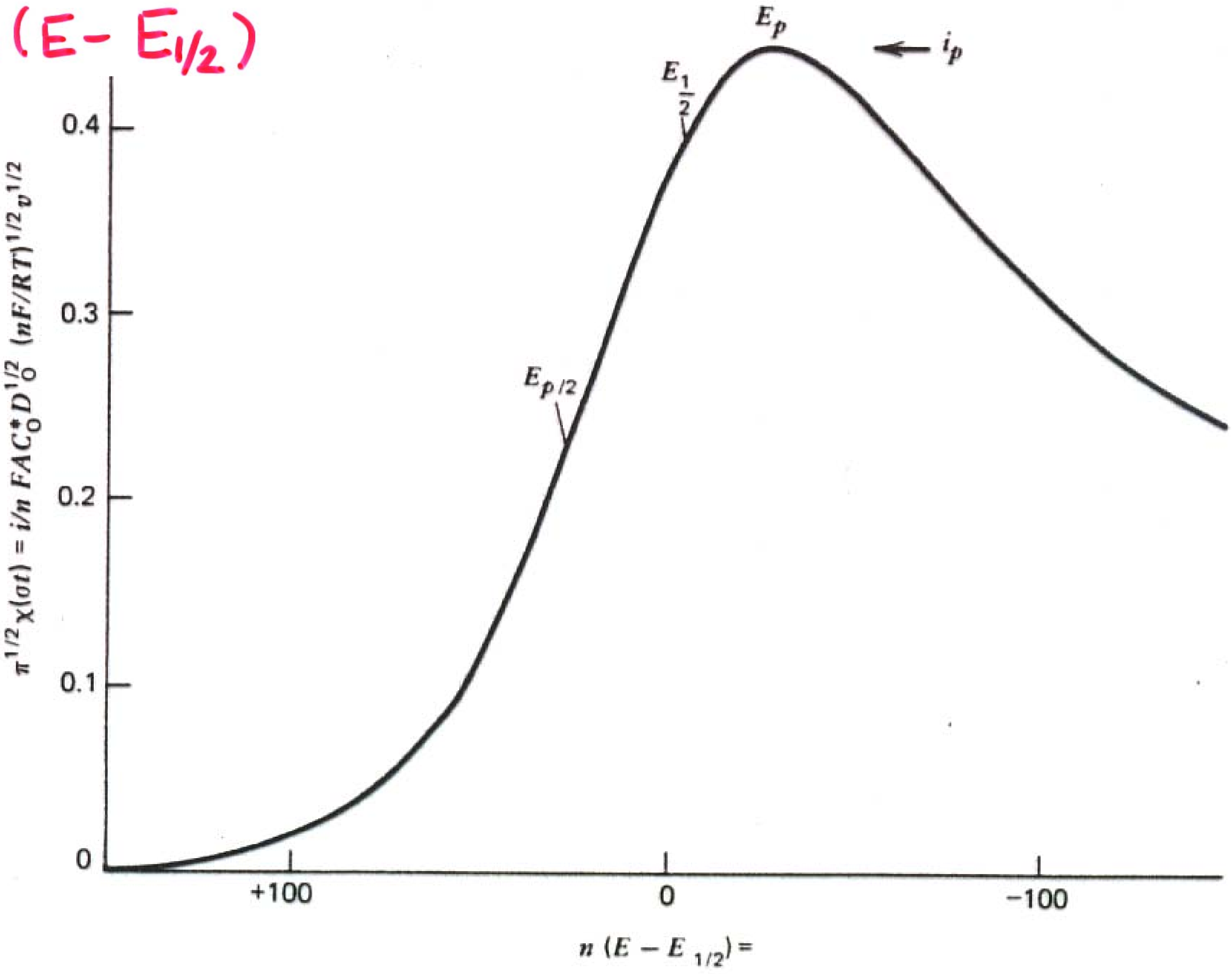
$$i = nFAC_o^* \left(\pi D_o \frac{nF\upsilon}{RT}\right)^{1/2} \chi(E - E_{1/2})$$

where $\chi(E - E_{1/2})$ at any given point is a pure number

The shape of the CV curve is determined by the shape of numerical function:

$$\chi(E - E_{1/2})$$

$\chi(E - E_{1/2})$


E_p
i_p
$E_{\frac{1}{2}}$
$E_{p/2}$
0.4
0.3
0.2
0.1
0
+100
0
−100
$\pi^{1/2}\chi(\sigma t) = i/nFAC_O^* D_O^{1/2}(nF/RT)^{1/2}v^{1/2}$
$n(E - E_{1/2}) =$

$$i_p = 0.4463\, nFA\, C_O^* \left(\frac{nF}{RT}\right)^{1/2} v^{1/2} D_O^{1/2}$$

$$E_p - E_{1/2} = -28.5\ \text{mV}/n$$

at 25°C

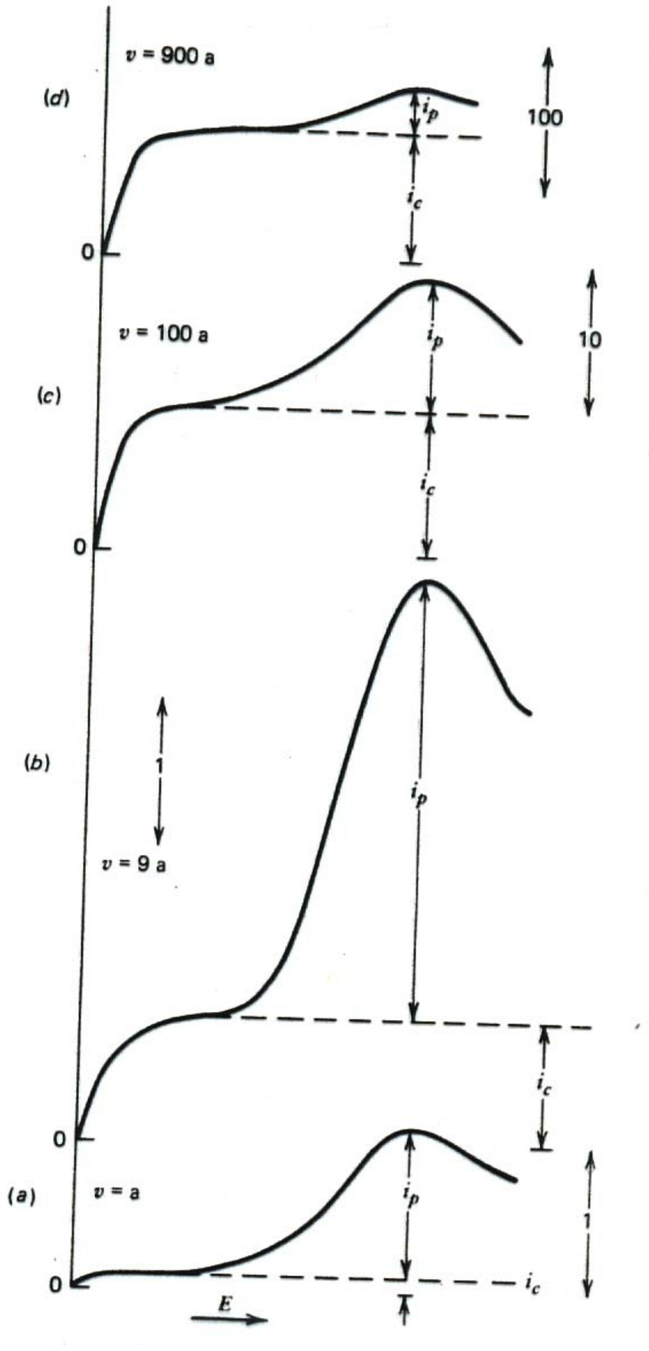
$$E_{p/2} = E_{1/2} + 28.0/n\ \text{mV}$$

$$|E_p - E_{p/2}| = 56.5/n\ \text{mV}$$

$$i = i_c + i_F$$

$$i_c = A\frac{dq}{dt} = A\frac{dq}{dE}\cdot\frac{dE}{dt} = ACd\cdot v$$

$$i = k_c v + k'_F v^{1/2}$$



LSV - detection limit

$$i_p \geqslant 2 i_c$$

$$0.446\, nFA \left(\frac{nF}{RT}v\right)^{1/2} D^{1/2} C^* = 2 A C_d v$$

$$C^* \geqslant \frac{2\, C_d \left(\frac{nF}{RT}v\right)^{1/2}}{D^{1/2}\, 0.45\, nF}$$

for

$D = 4 \times 10^{-6}\ \mathrm{cm^2\ s^{-1}}$

$C_d = 20\ \mu\mathrm{F\ cm^{-2}}$

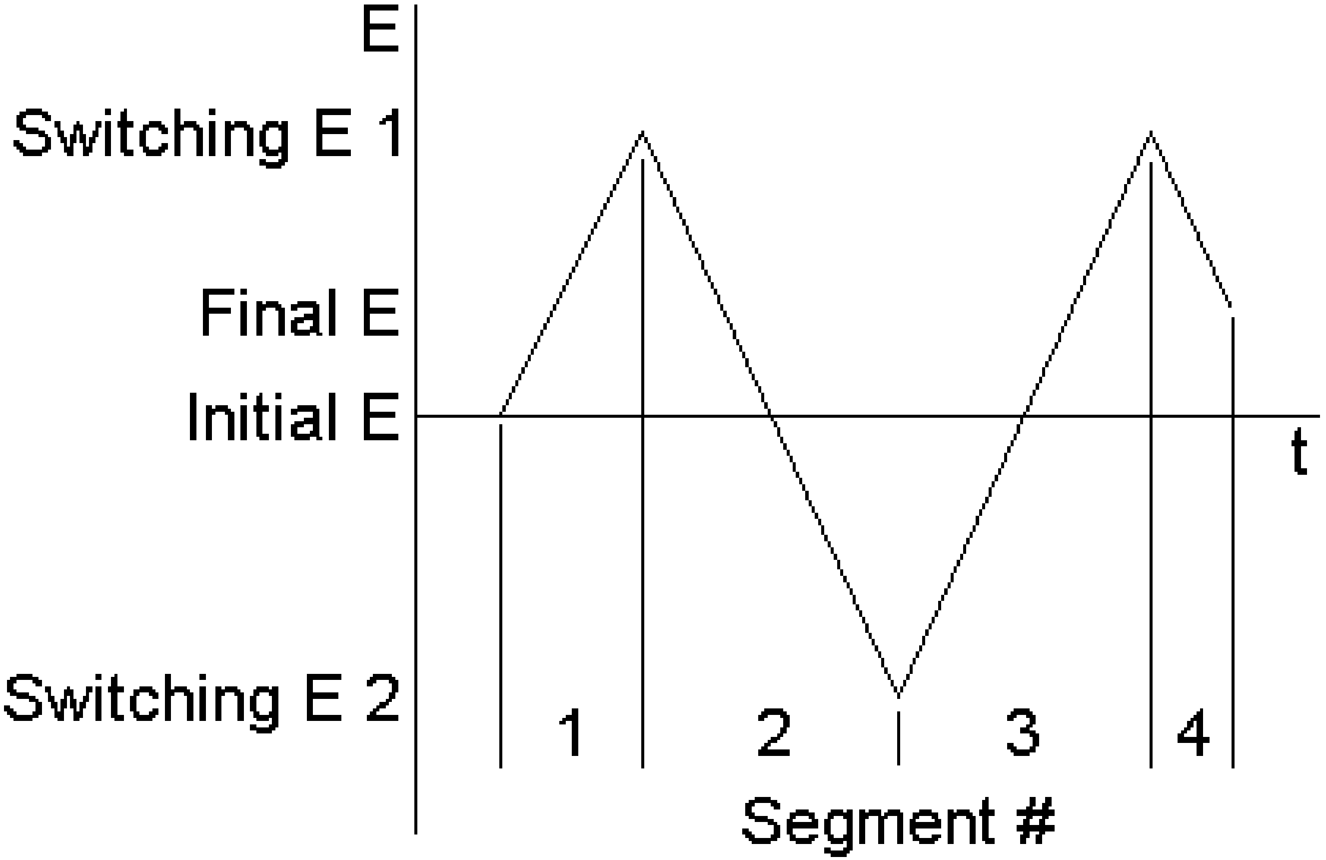
$n = 2$

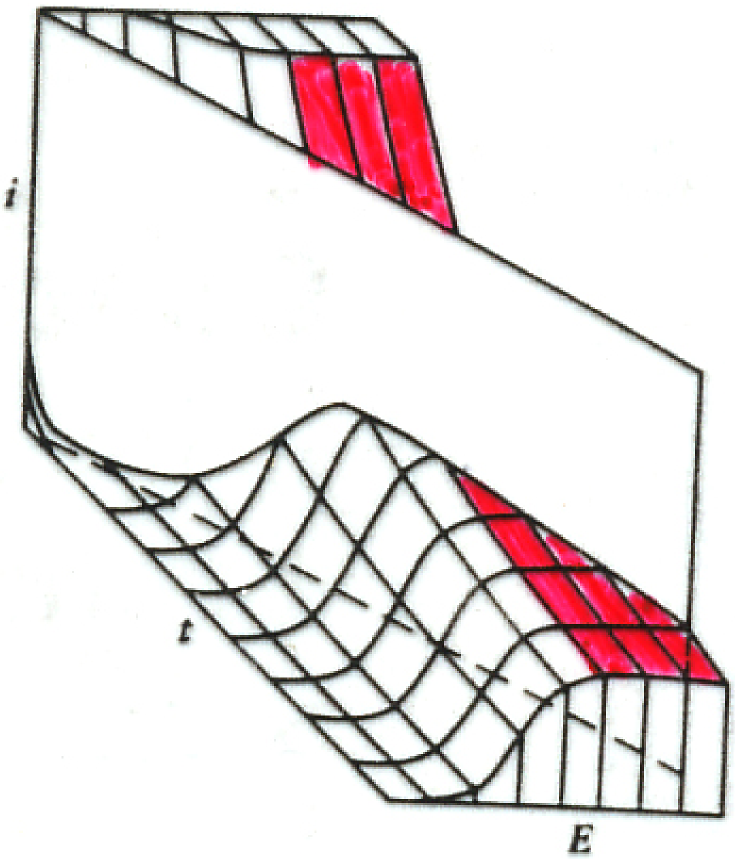
$\left(\frac{nF}{RT}v\right)^{1/2} = 1\ \mathrm{s^{1/2}}$ $\quad v \simeq 25\ \mathrm{mV\,s^{-1}}$

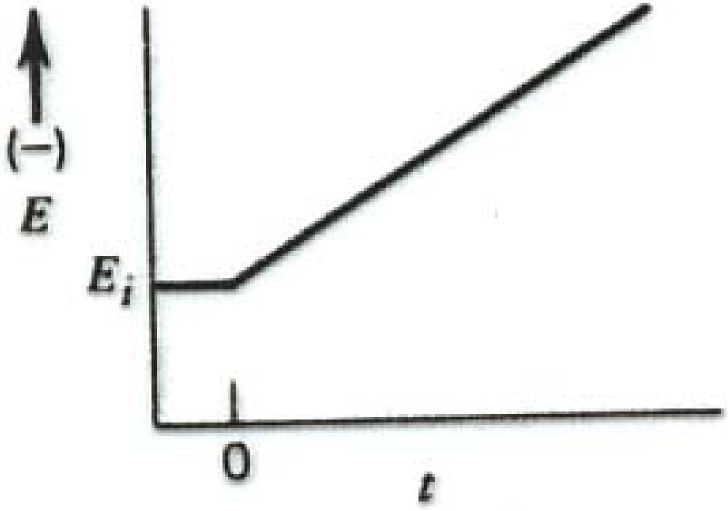
$$C^* \geqslant 10^{-5}\ \mathrm{mol\ dm^{-3}}$$

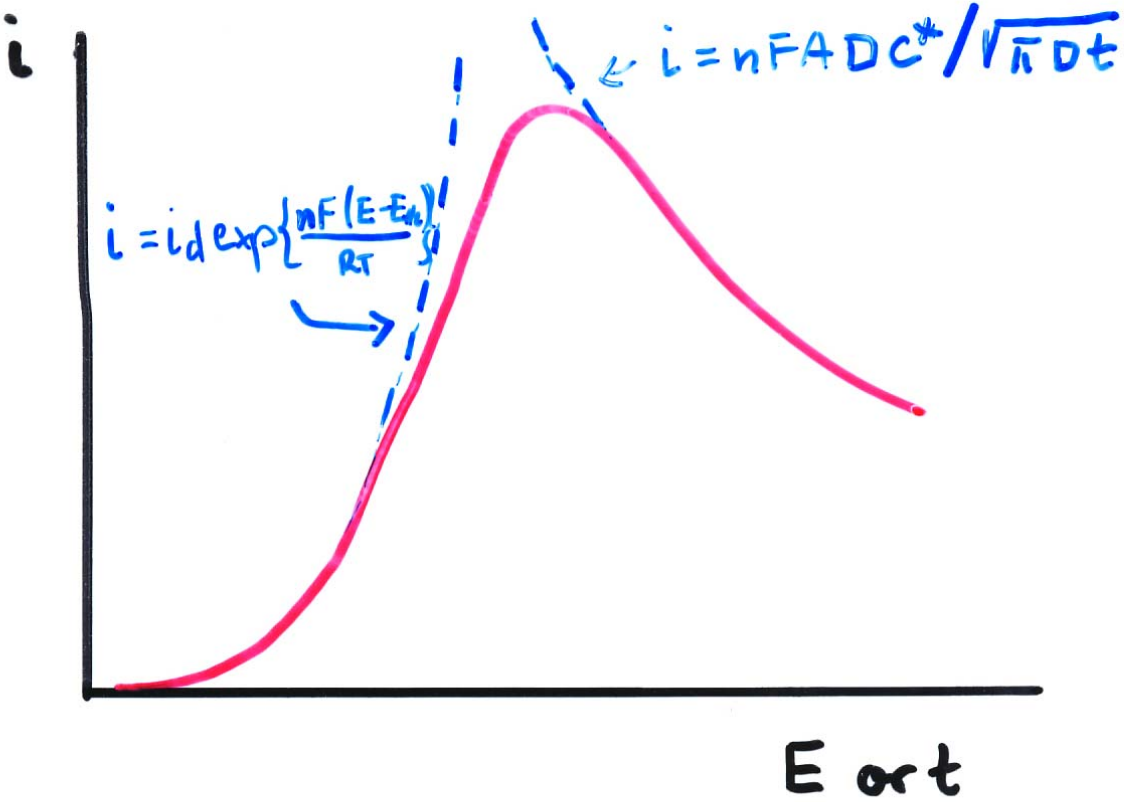
	time parameter	time window/s	reversibility lower limit of k_0/cm s^{-1}
DC Polarography	t_d	$1 - 10$	$10^{-3} - 3\,10^{-4}$
Tast Polarography	τ'	$1 - 10$	$10^{-3} - 3\,10^{-4}$
Normal Pulse polarography	$\tau - \tau'$	$10^{-2} - 10^{-1}$	$10^{-2} - 3\,10^{-3}$
Differential Pulse Polarography	$\tau - \tau'$	$10^{-2} - 10^{-1}$	$10^{-2} - 3\,10^{-3}$
LSV	$\frac{RT}{Fv}$	$1\,Vs^{-1} - 1\,mVs^{-1}$	$10^{-2} - 10^{-3}$

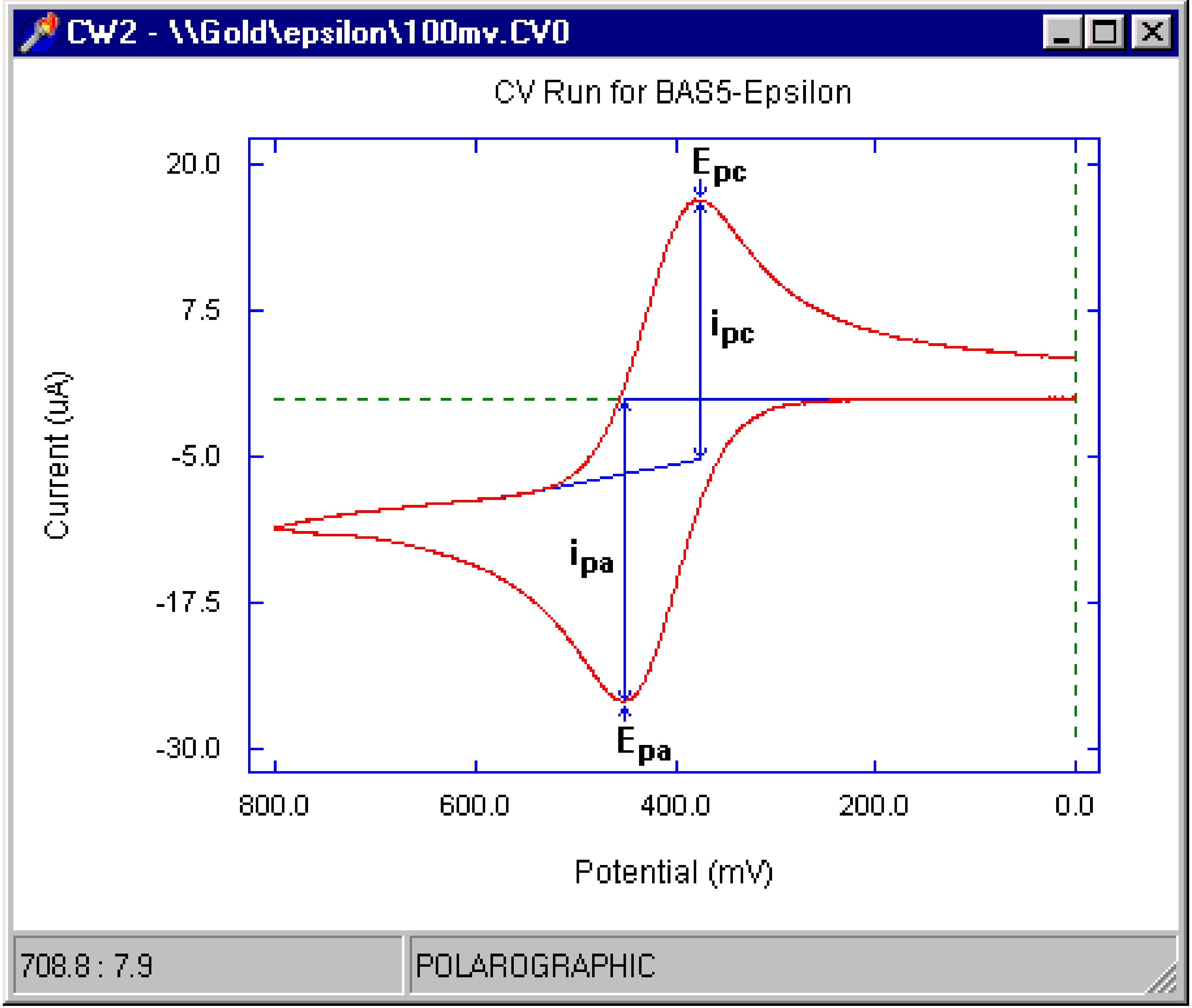
Cyclic voltammetry

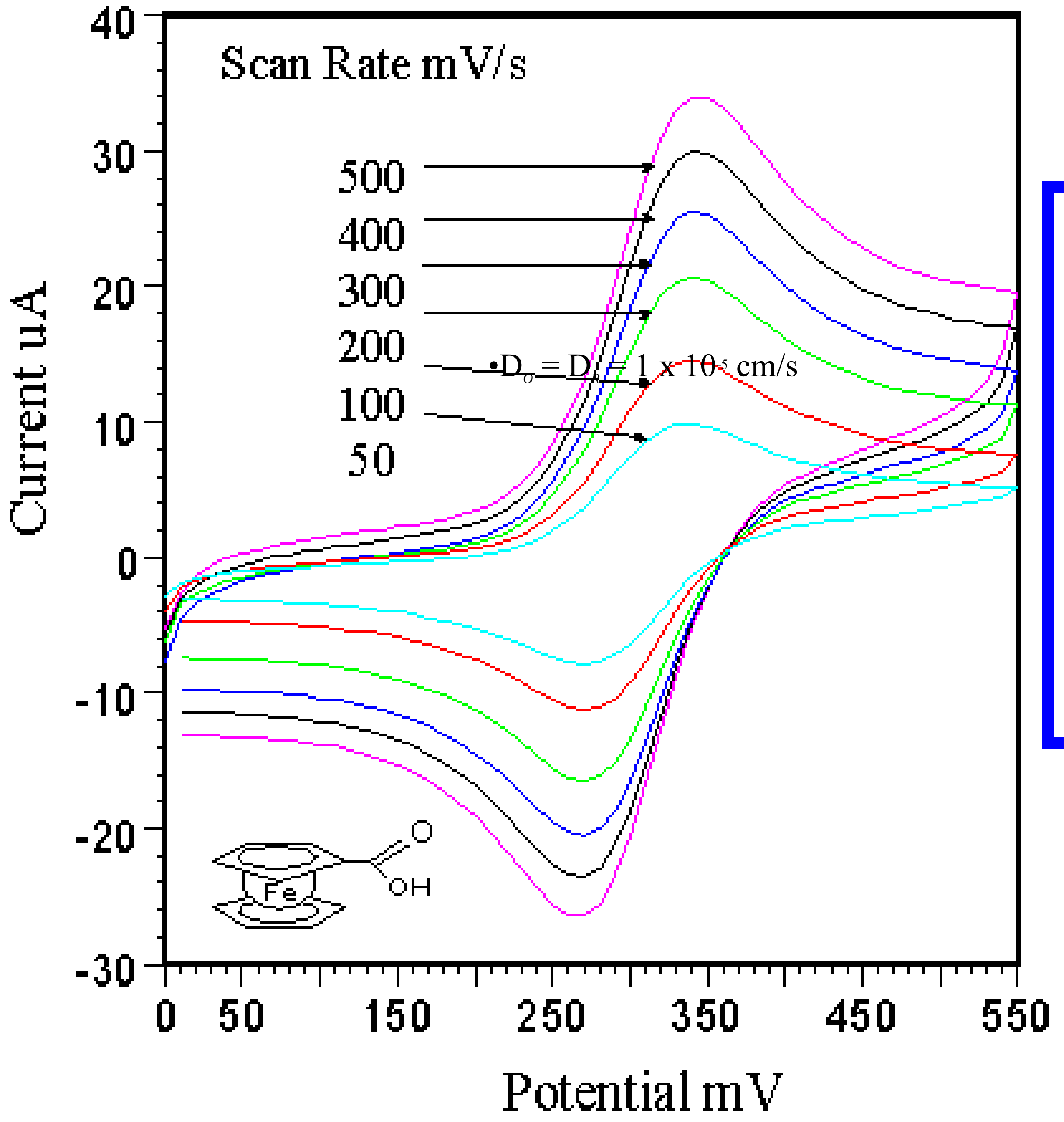



i
t
E


(−)
E
E_i
0
t


i
$i = nFADC^* / \sqrt{\pi D t}$
$i = i_d \exp\left\{\frac{nF(E-E_{1/2})}{RT}\right\}$
E ort


CW2 - \\Gold\epsilon\100mv.CV0
CV Run for BAS5-Epsilon
Current (uA)
20.0
7.5
-5.0
-17.5
-30.0
800.0
600.0
400.0
200.0
0.0
Potential (mV)
E_{pc}
i_{pc}
i_{pa}
E_{pa}
708.8 : 7.9
POLAROGRAPHIC



• $D_o = D_R = 1 \times 10^{-5}$ cm/s