

Electroquímica analítica

Principios:

Condiciones operatorias I y II

Modelo difusional

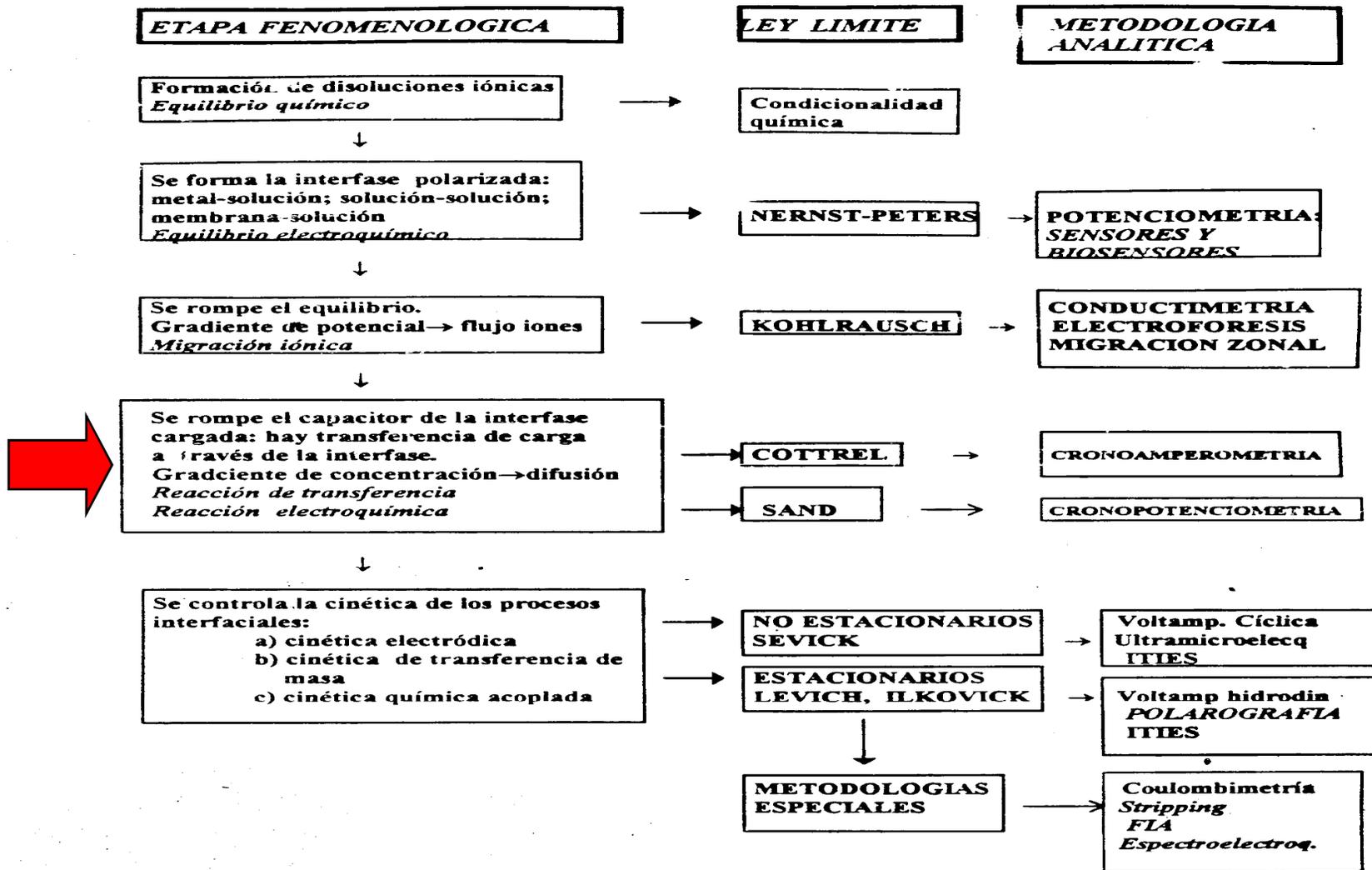
Cinética electródica

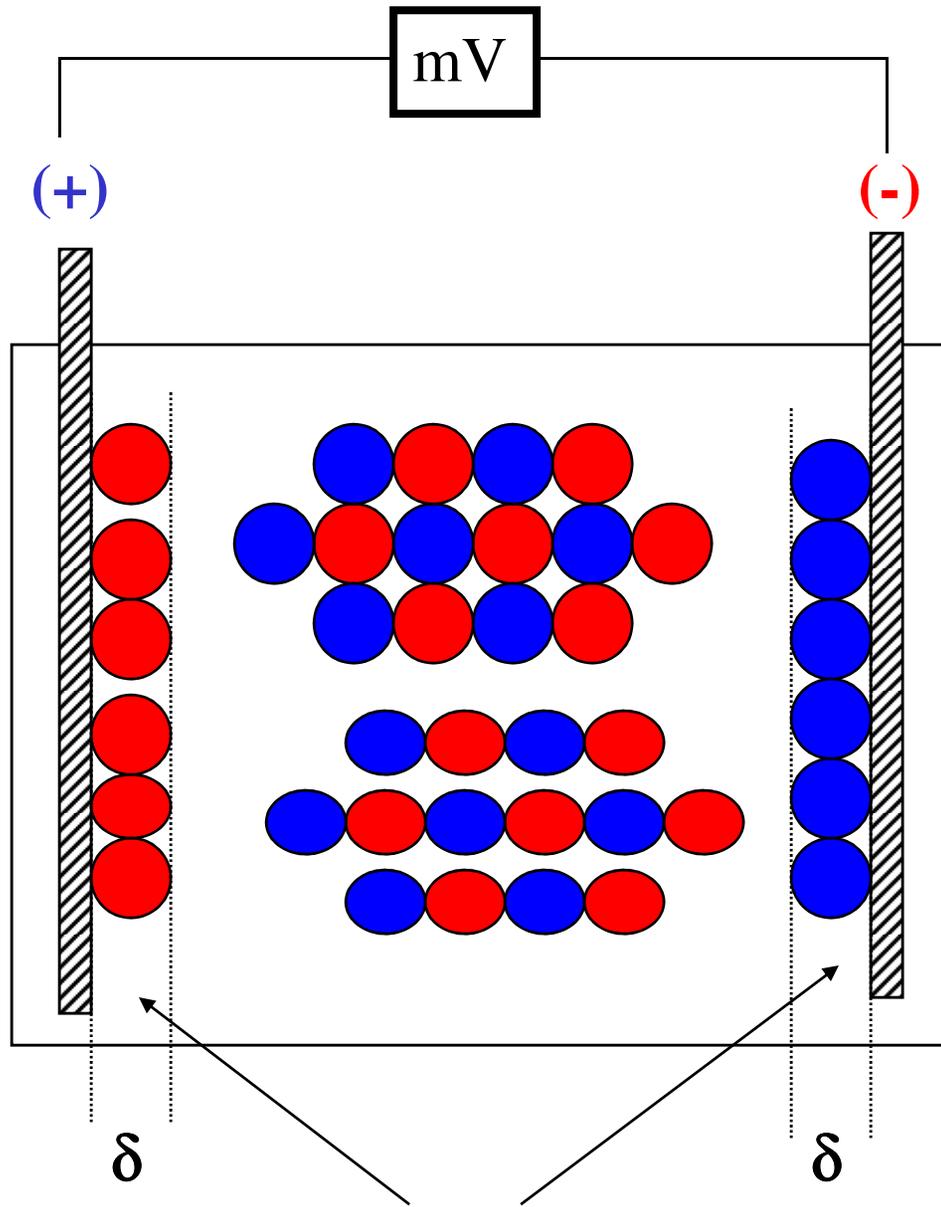
Cinética de transferencia de masa

Cinética química acoplada

Alejandro Baeza
FQ UNAM

ESQUEMA FENOMENOLOGICO PARA LA ENSEÑANZA DE LA ELECTROQUÍMICA ANALÍTICA
 Candidato a Doctor Alejandro Baeza

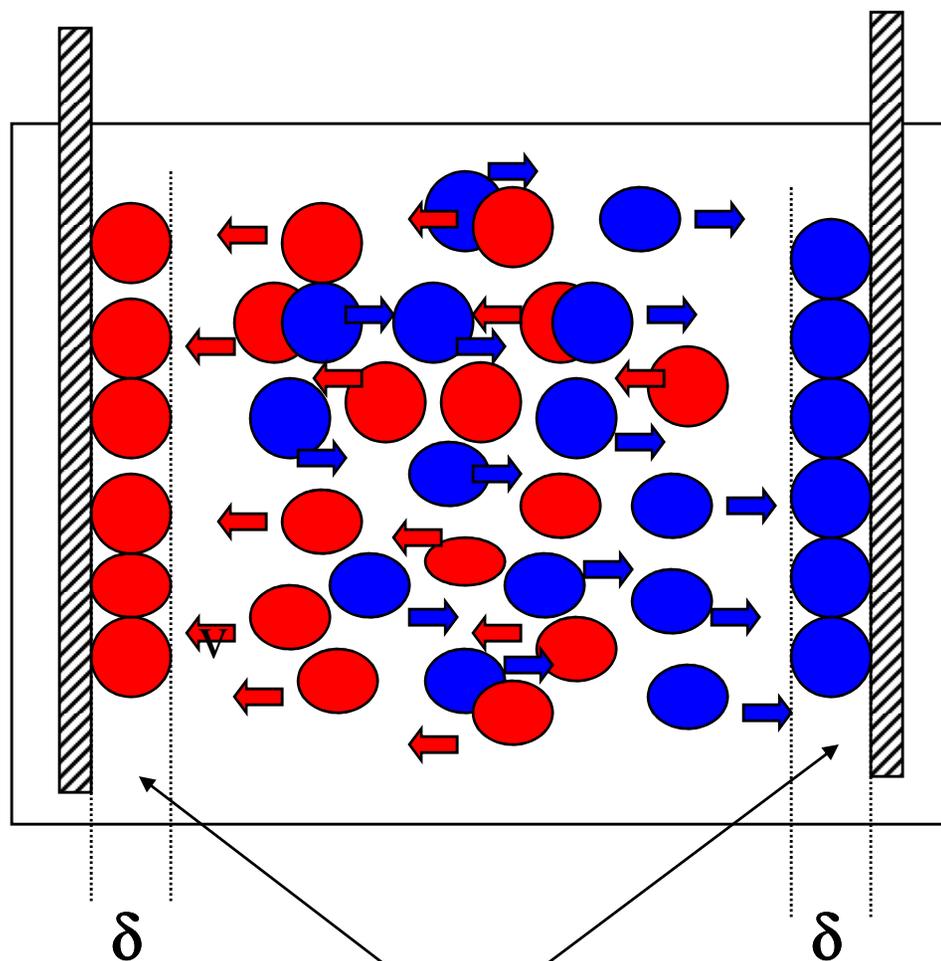
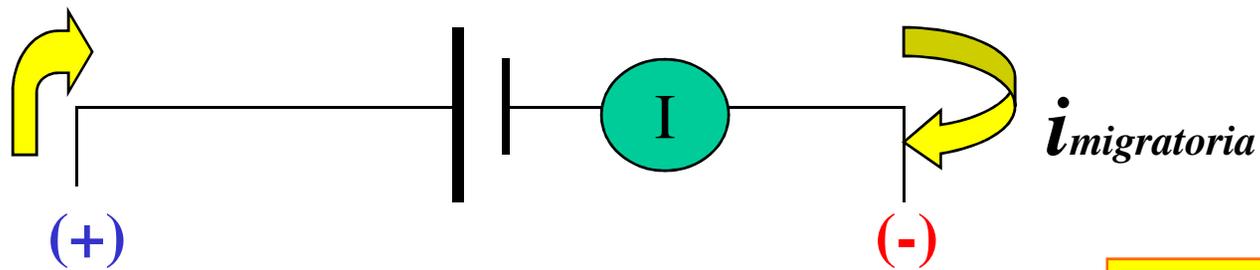




Equilibrio electroquímico

Se forma
La doble capa
electrica

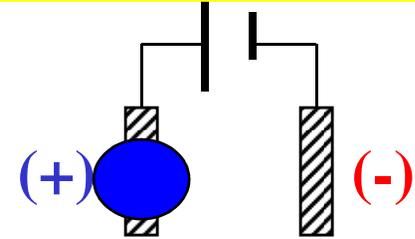
Interfases cargadas = electrodos



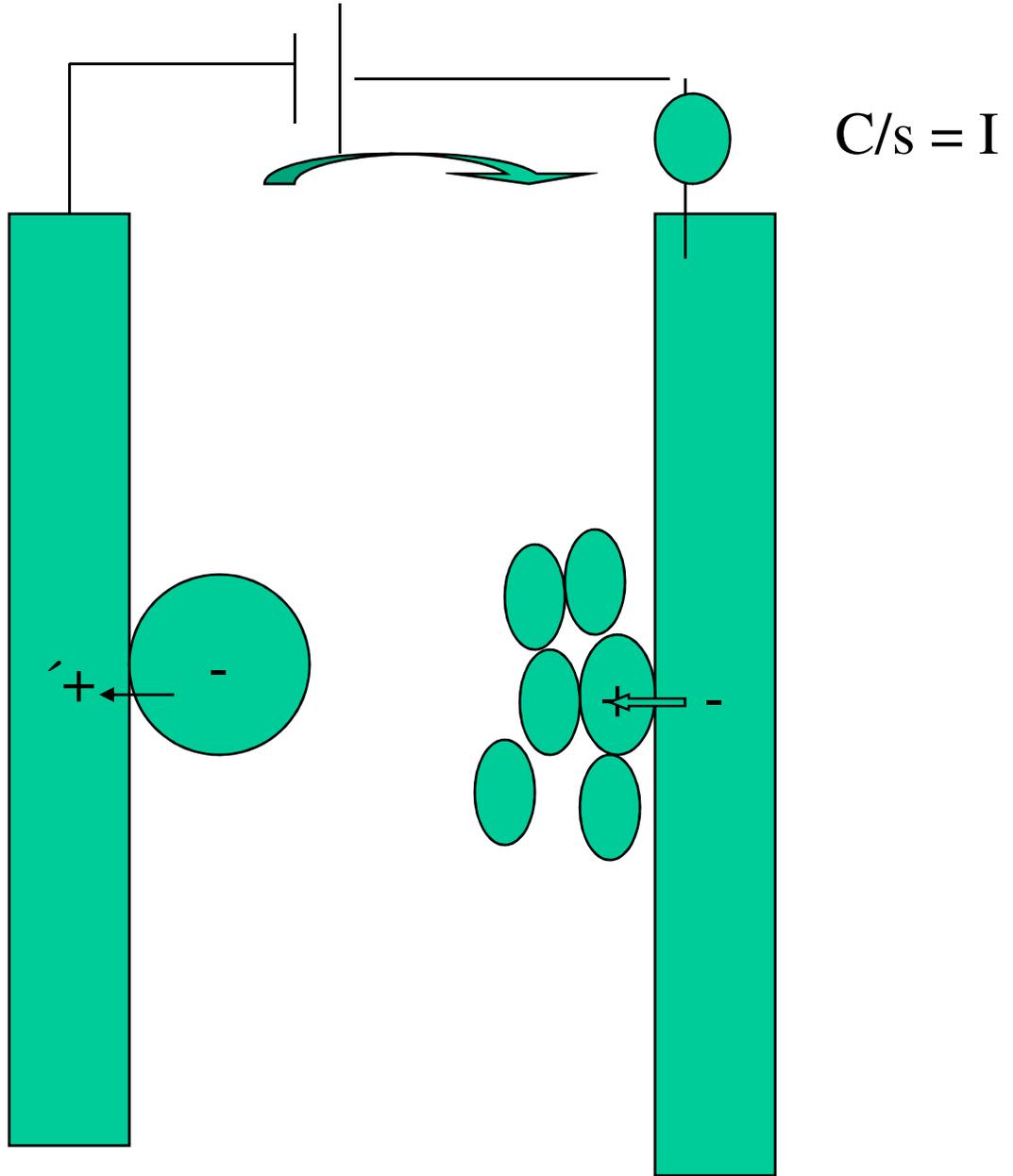
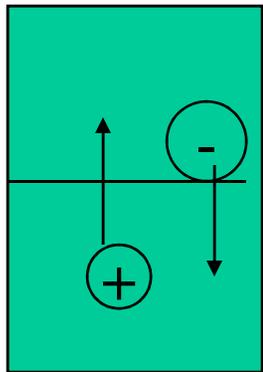
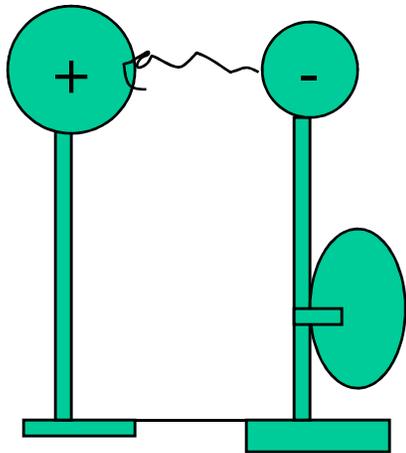
Se rompe el Equilibrio Electroquímico: *Migración iónica.*

Se enriquece la doble capa Eléctrica.

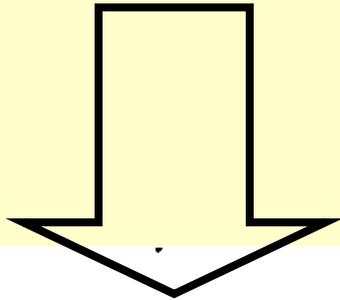
$$i_{migratoria} = i_{capacitiva}$$



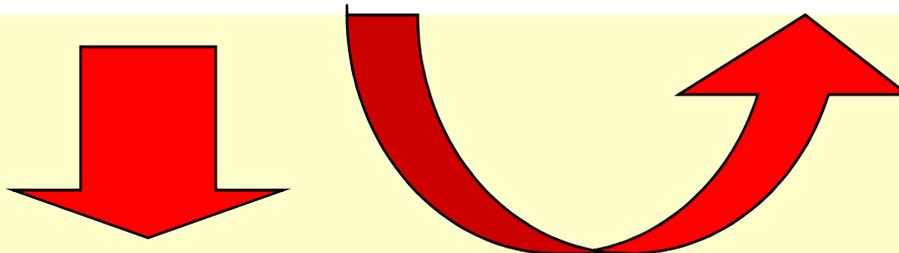
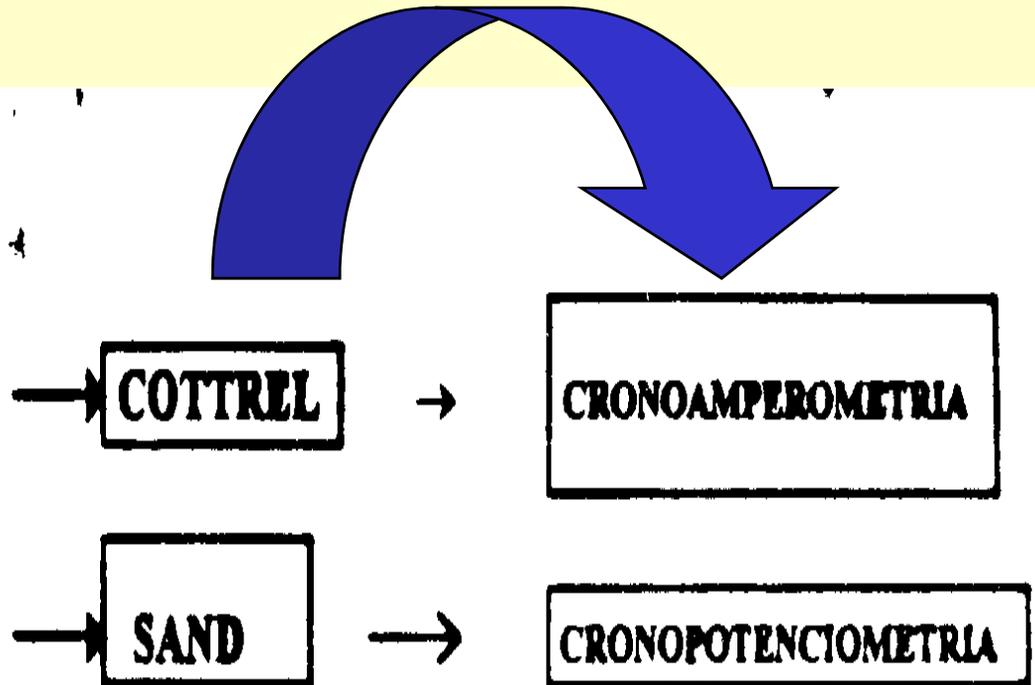
Interfases cargadas = electrodos



Esfera interna
Esfera externa

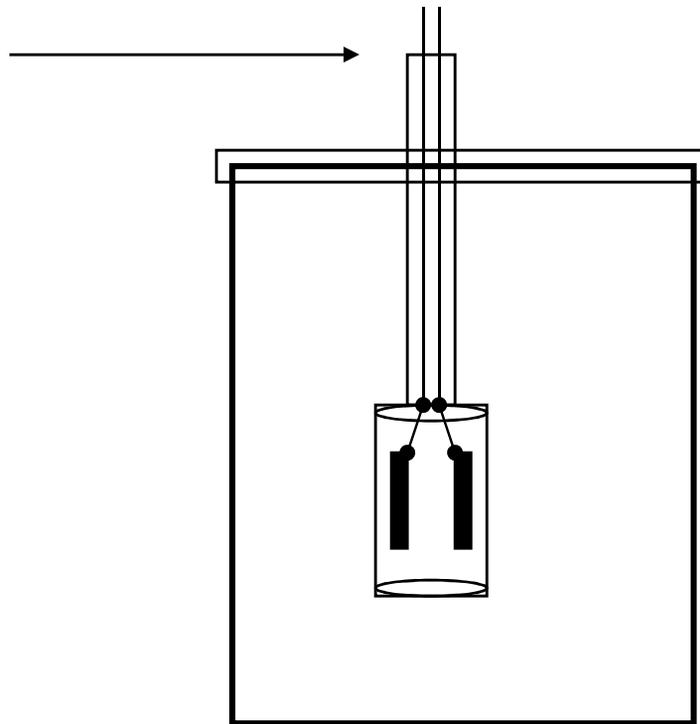


Se rompe el capacitor de la interfase
cargada: hay transferencia de carga
a través de la interfase.
Gradiente de concentración → difusión
Reacción de transferencia
Reacción electroquímica



CONDICIONES OPERATORIAS

¿cuál es la relación entre corriente, resistencia y el potencial impuesto externamente
Para una disolución iónica?



*Los iones se mueven
Lentamente.*

*Los electrodos
Se polarizan:*

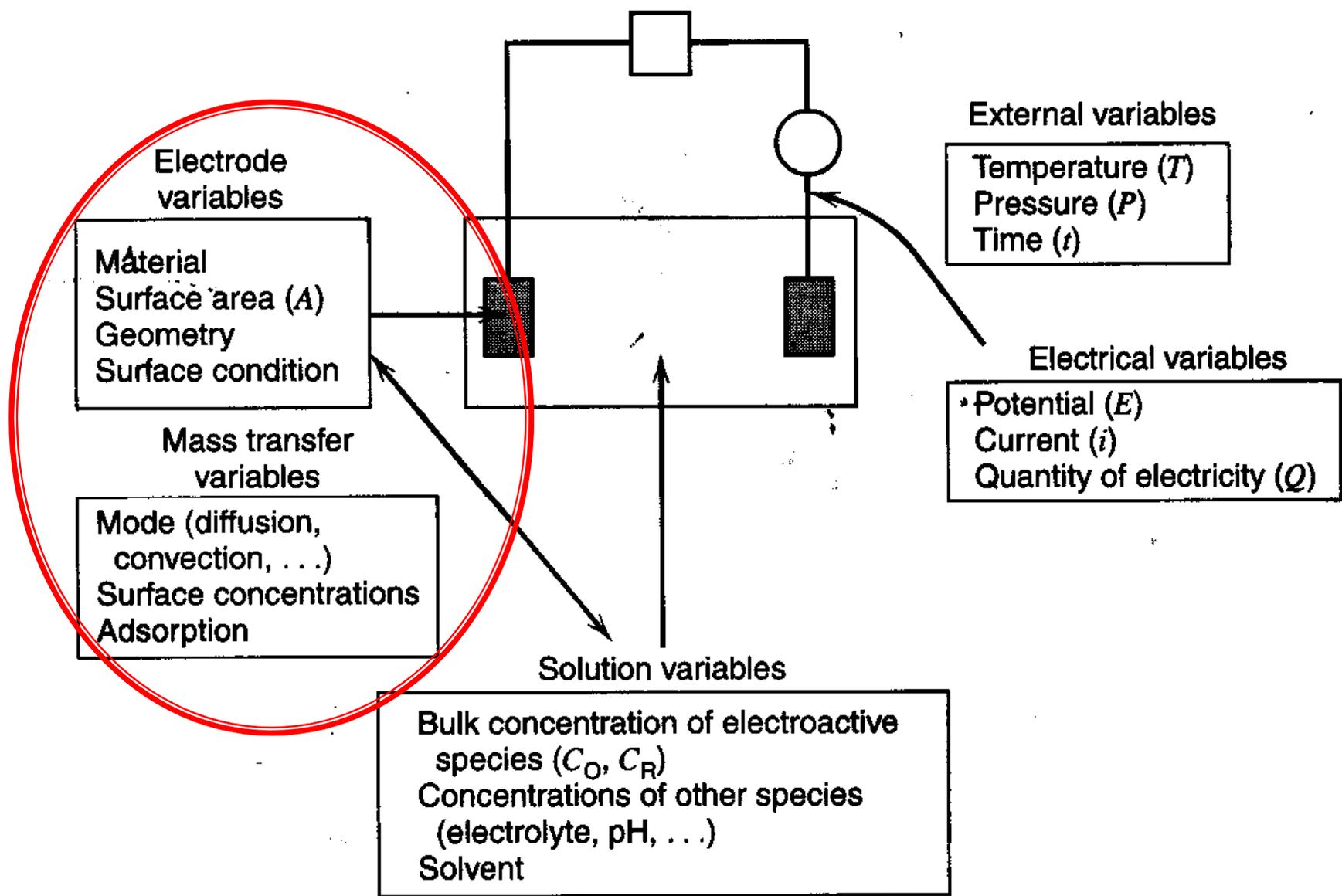
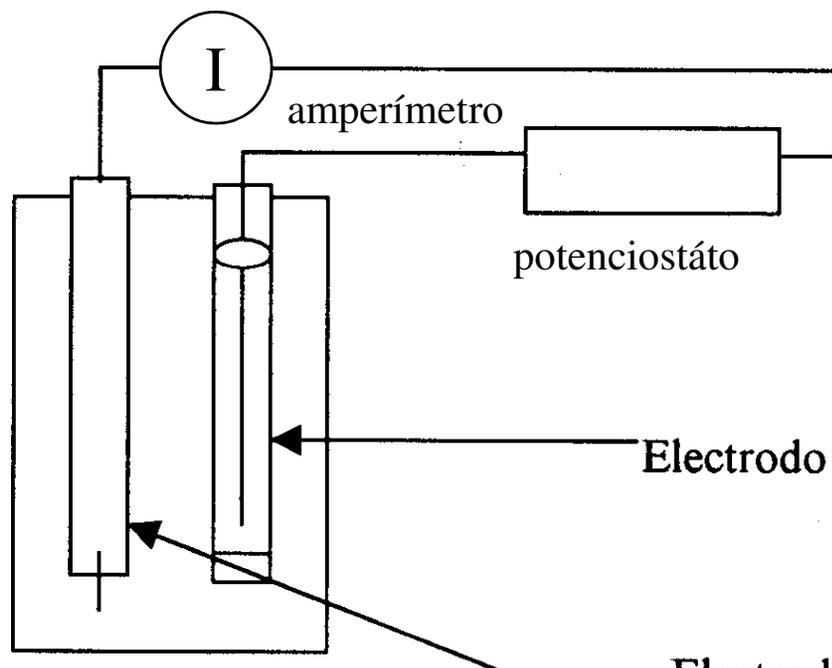


Figure 1.3.2 Variables affecting the rate of an electrode reaction.

LOS ELECTRODOS Y LAS CELDAS

Sistema de 2 electrodos:

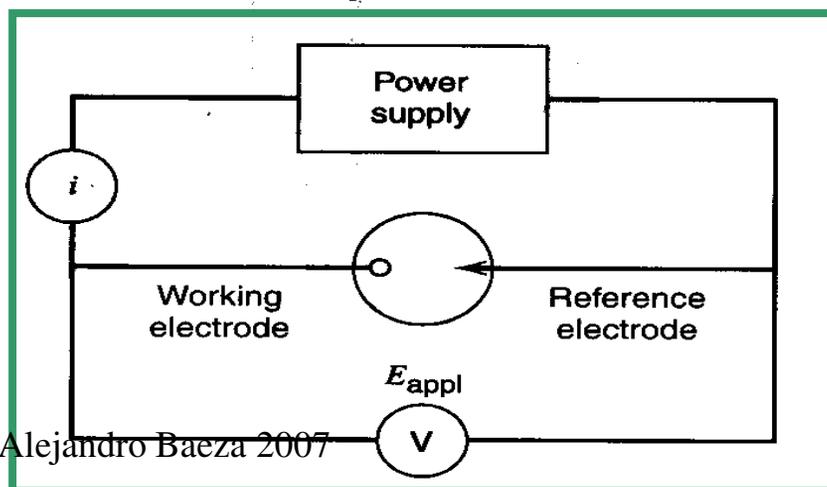
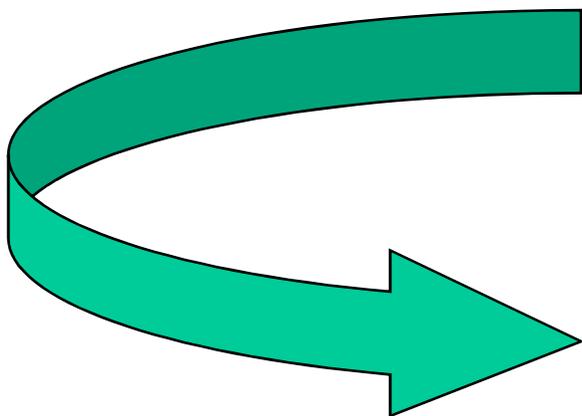


ANALITICA
3E 8 JUL 21

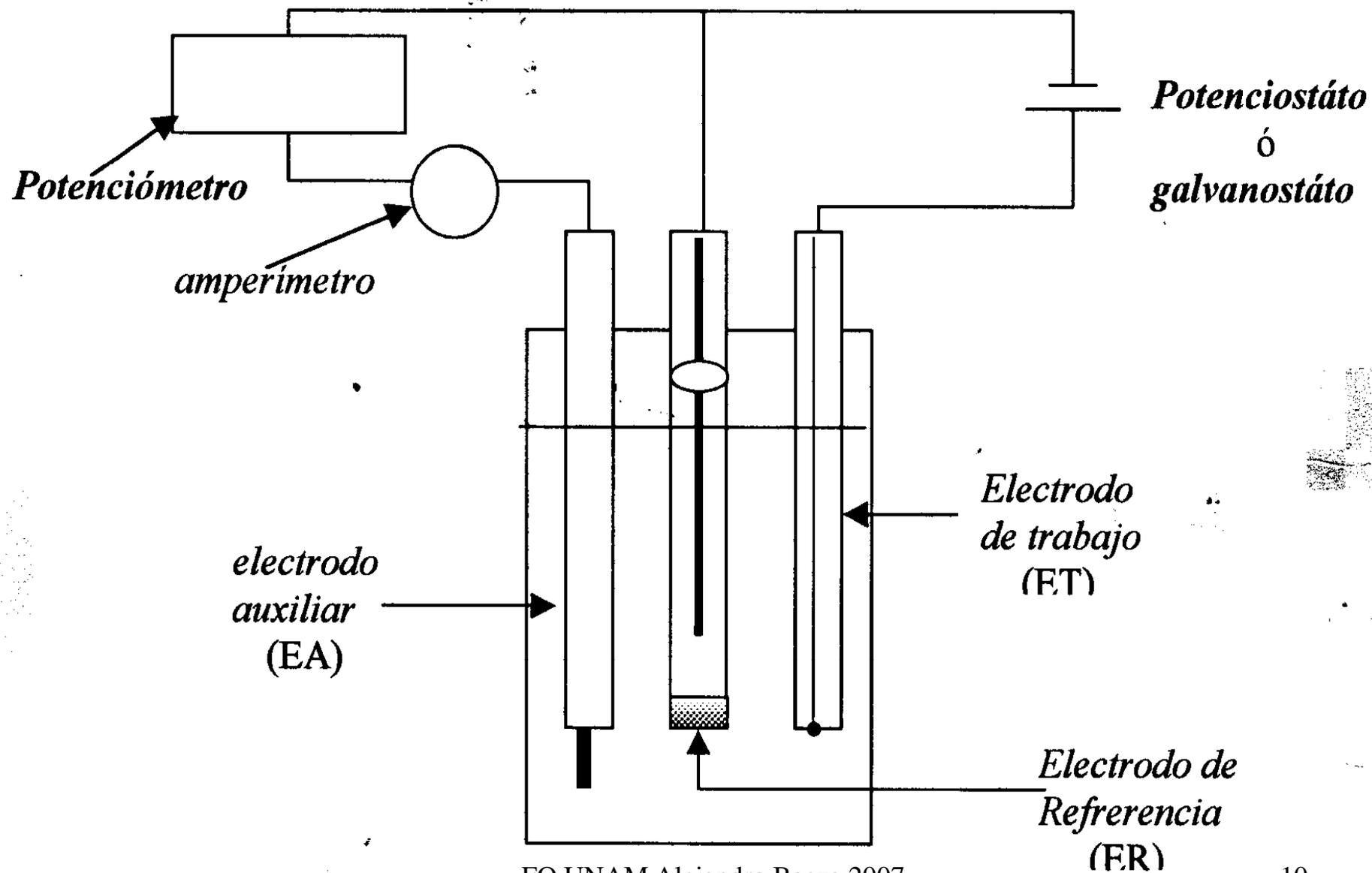
ALEJANDRO

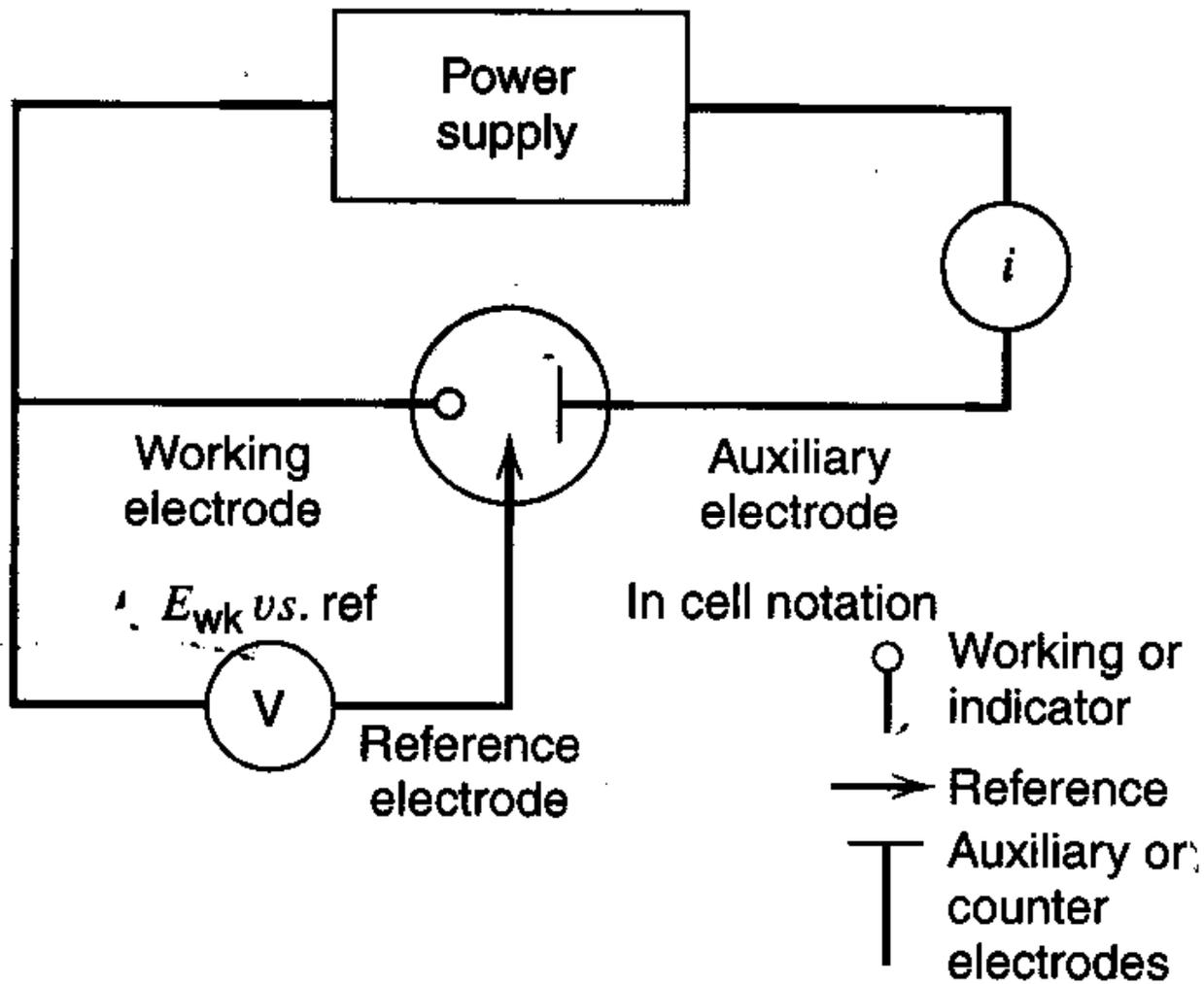
Electrodo de referencia: ER

Electrodo de trabajo o indicador: ET

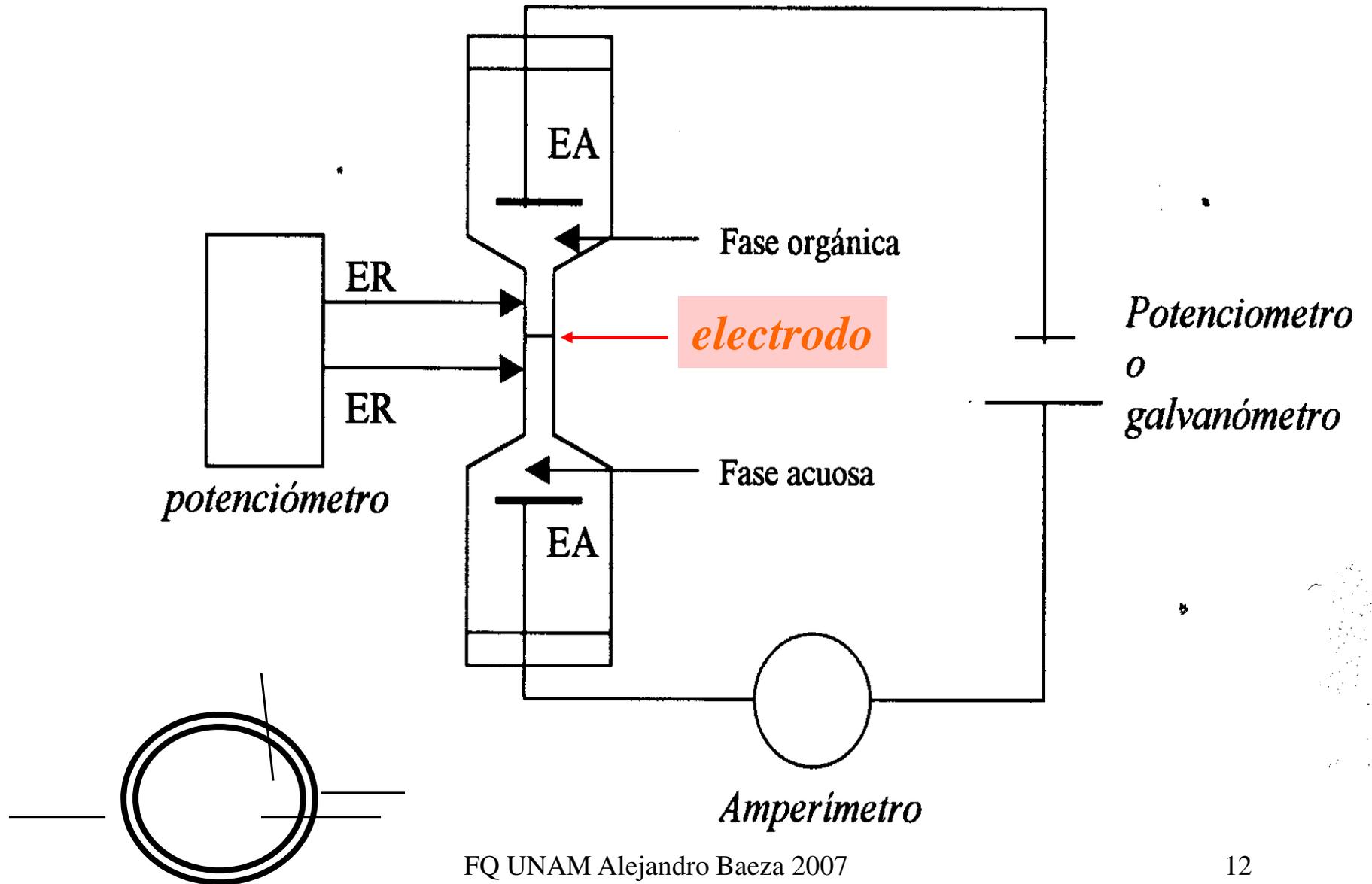


B) Sistema de tres electrodos:





C) Sistemas de 4 electrodos:



Condiciones operatorias (I)

1) Los electrodos: 3

EA: Gran superficie

ET: MICROELECTRODO

ER: $(dE/dI) \rightarrow 0$

1) Electrolito soporte inerte

2) Régimen hidrodinámico controlado

Régimen hidrodinámico controlado:

I/

Régimen convectivo laminar

II/

Sin agitar

ultramicroelectrodos

III/

Flujo continuo

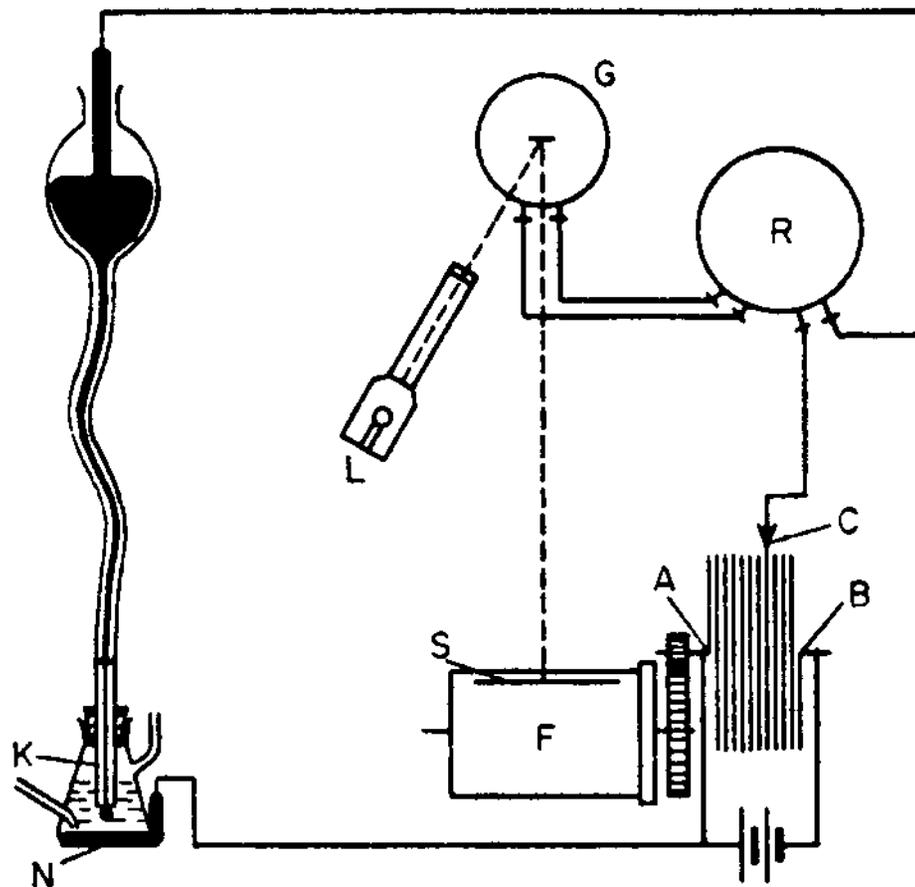
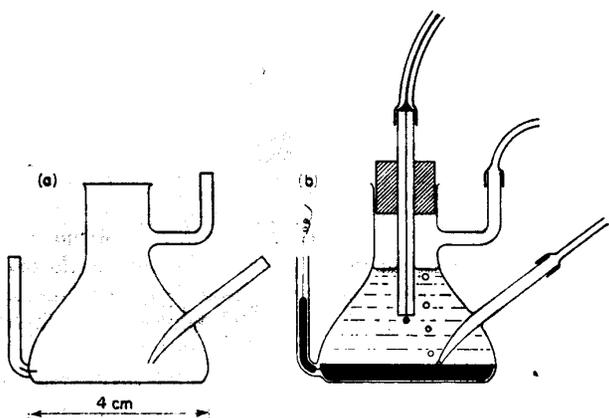
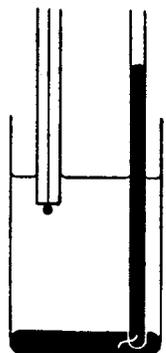
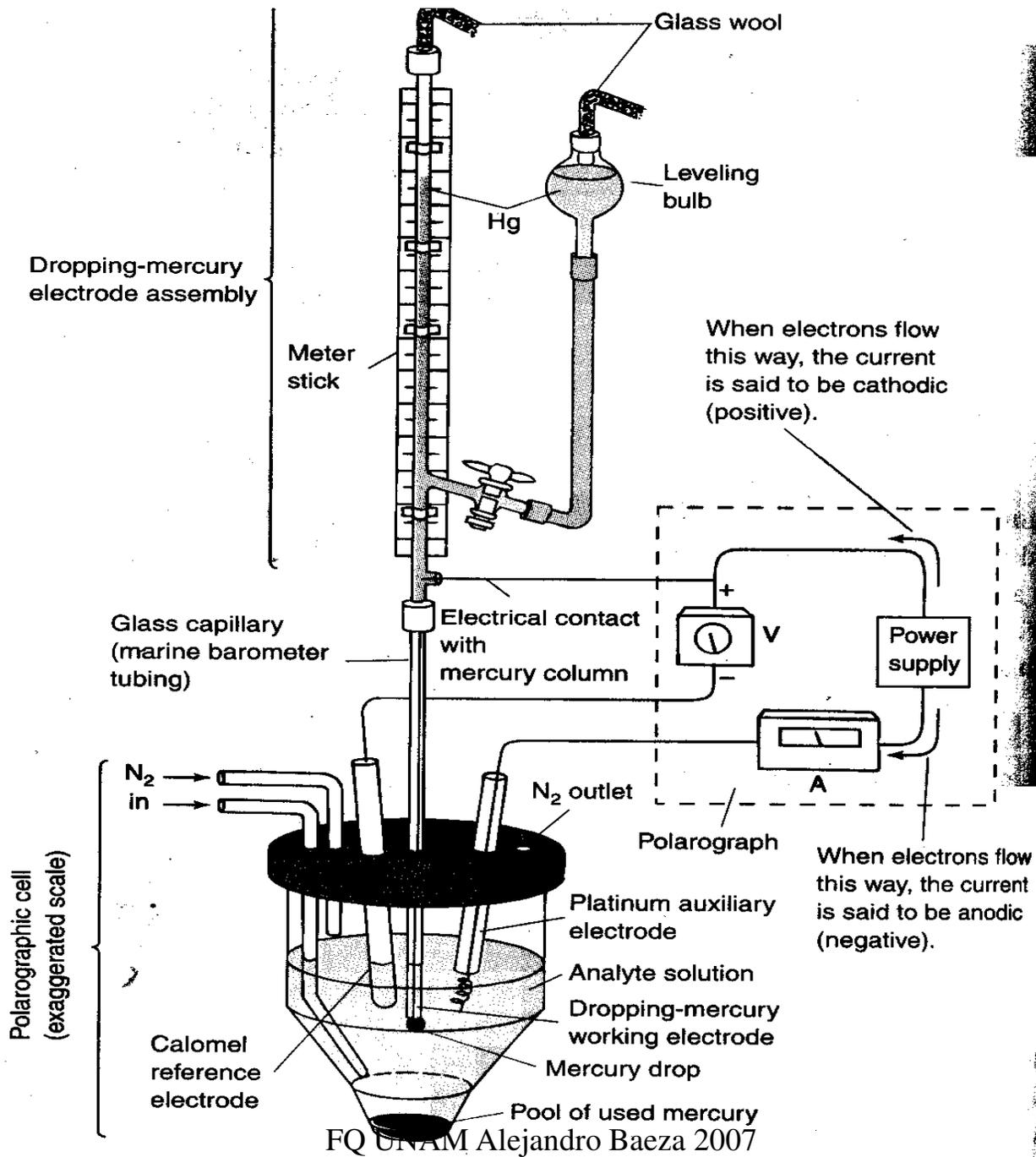
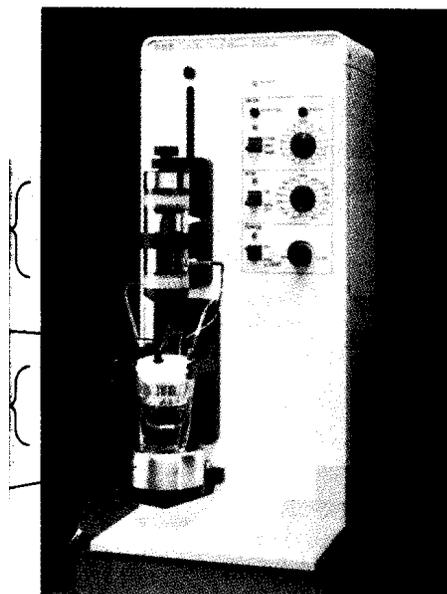


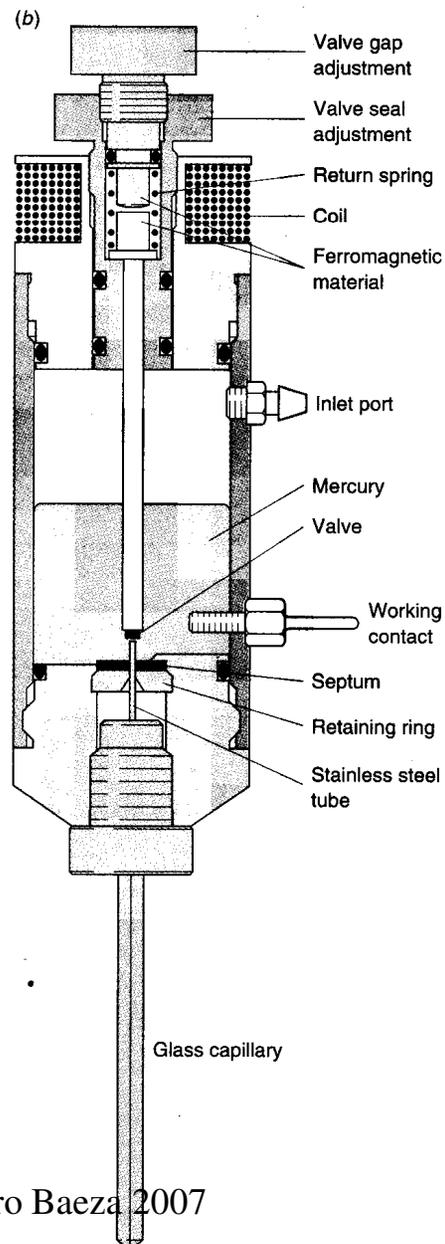
FIG. 19. Scheme of polarograph. (A)–(B) Potentiometric wire; (C) sliding contact; (F) photographic cassette; (G) mirror galvanometer; (K) dropping electrode; (N) reference electrode; (R) galvanometer sensitivity reductor; (S) slit through which the beam enters the photographic cassette.



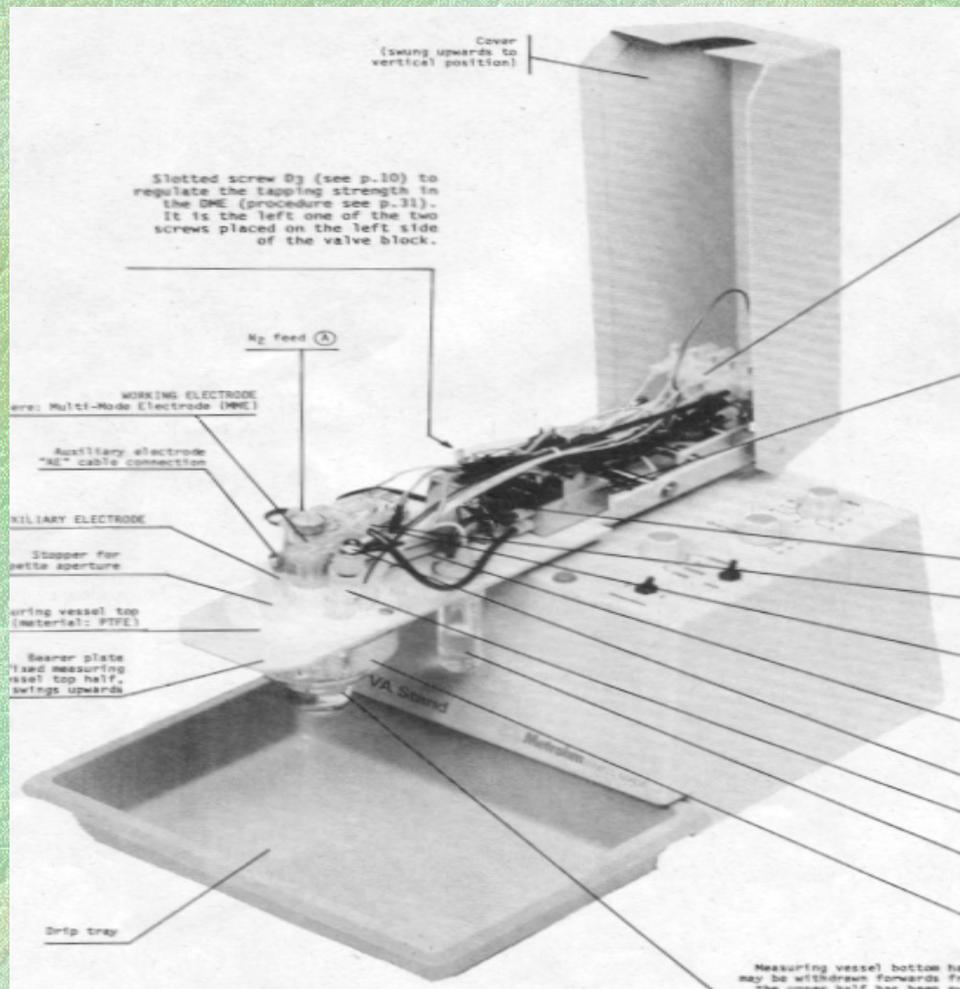


18-2 (a) Modern polarographic equipment showing mercury electrode, sample cell, and controls. (The instrument can also be controlled entirely from software on a computer unit that is not shown.) (b) Schematic of the dropping mercury electrode. Mercury from the internal reservoir flows through the glass capillary through the stainless steel tube. The valve is held in the closed position by the return spring at the top of the assembly. Electrical current is applied to the coil at the top of the assembly to open the valve for a precisely determined time to allow a mercury drop of the desired size to form before the valve closes. The drop is then measuring current and voltage with the static electrode. Upon the drop is dislodged by a mechanical drop (not shown) and a new drop of exactly the same size is formed. Continuous electrical contact is made to the dropping mercury column via the stainless steel tube even when the valve is closed. [Courtesy Bioanalytical Systems, West Lafayette, IN.]

18-2 Shape



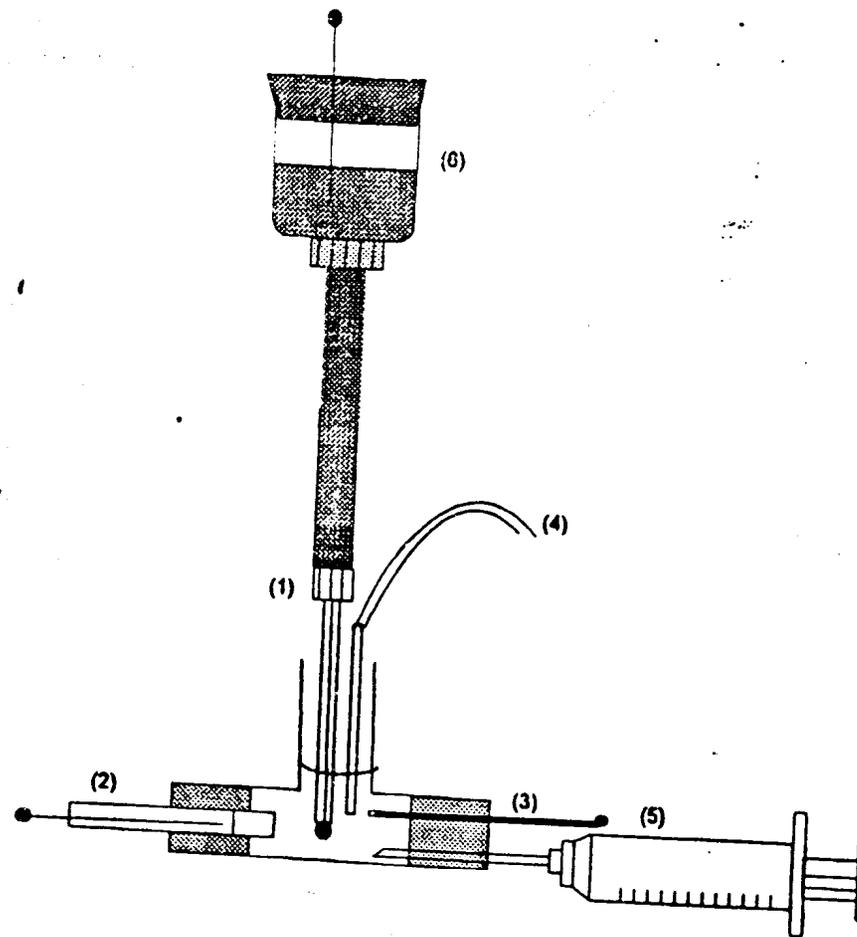
Antecedentes: celda convencional



HMDE

“hanging mercury dropping electrode

Volumen: 30 mL



F2

Micropolarographic cell, $V=500 \mu\text{L}$. 1) DME; 2) Reference electrode $\text{Ag}^\circ|\text{AgCl}_2|\text{KCl}$ 0.1M ; 3) C° auxiliary electrode; 4) nitrogen inlet; 5) Hg° purge; 6) Hg° pool.

H.Prado, P. Diaz. J.L. Ortiz and Alejandro Baeza

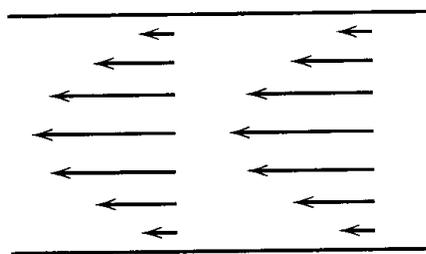
Polarographic determination of K_m' and of glutathione reductase

Current Separations 20-4(2004)117-122

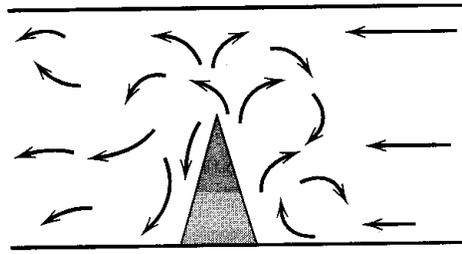
© ONAMI Alejandro Baeza 2007



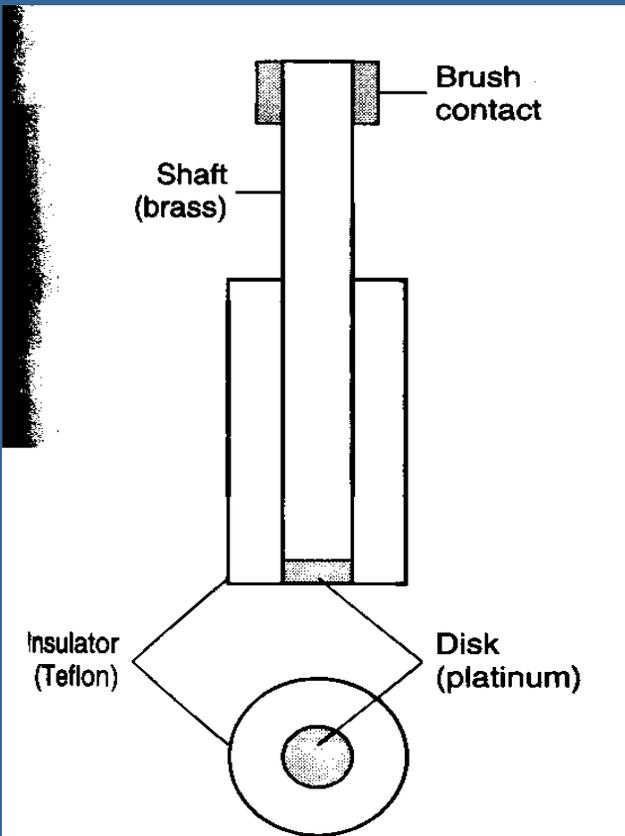
Electrodos giratorios de disco: EGD
Régimen hidrodinámico (convectivo laminar)



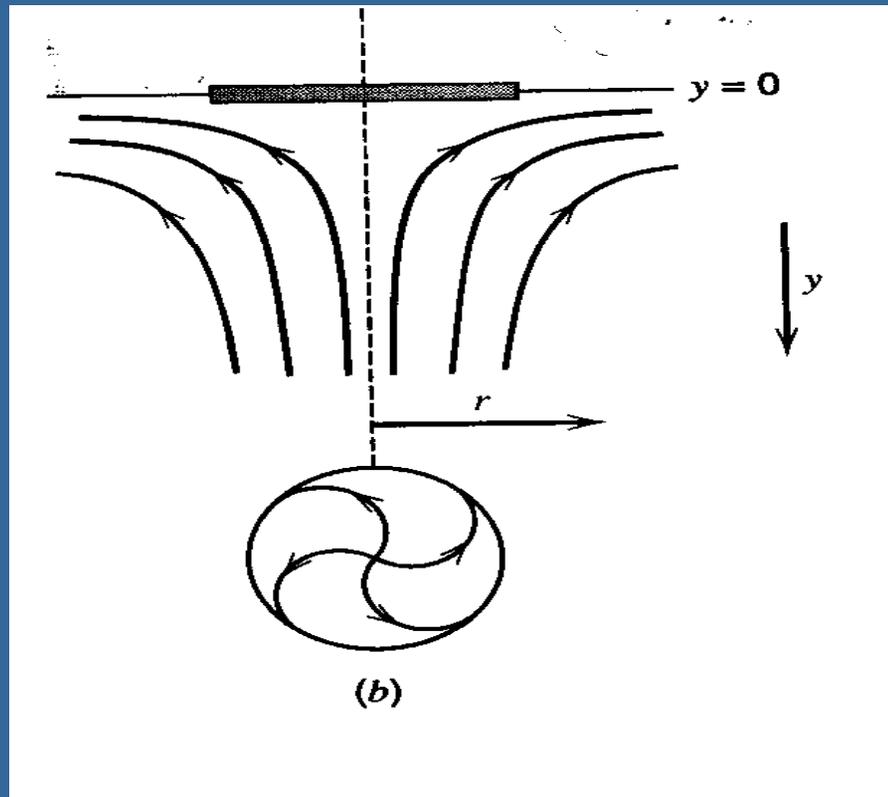
Laminar flow

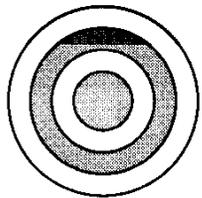
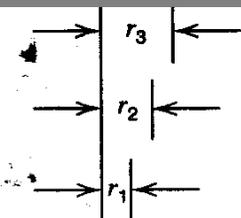


Turbulent flow

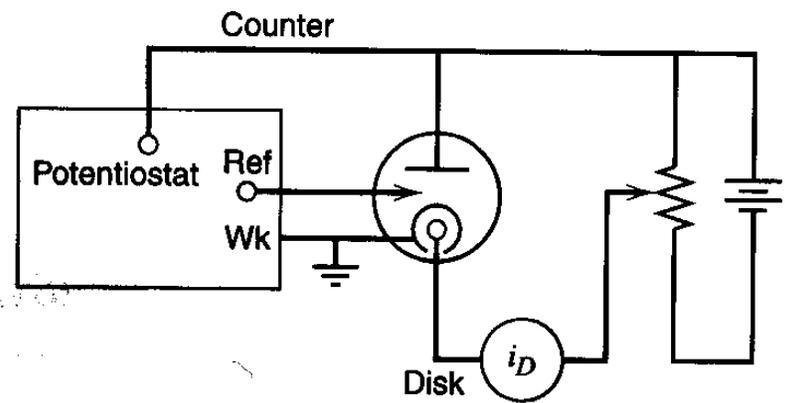
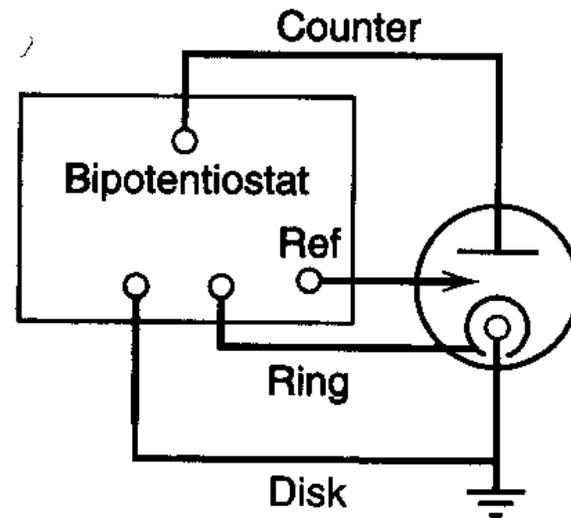
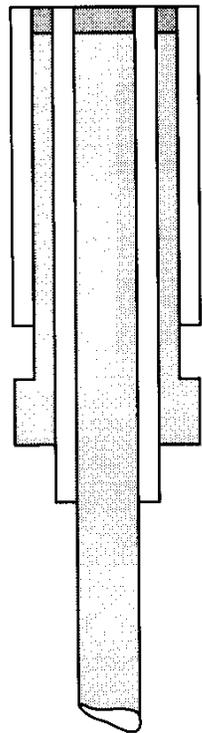


Bottom view

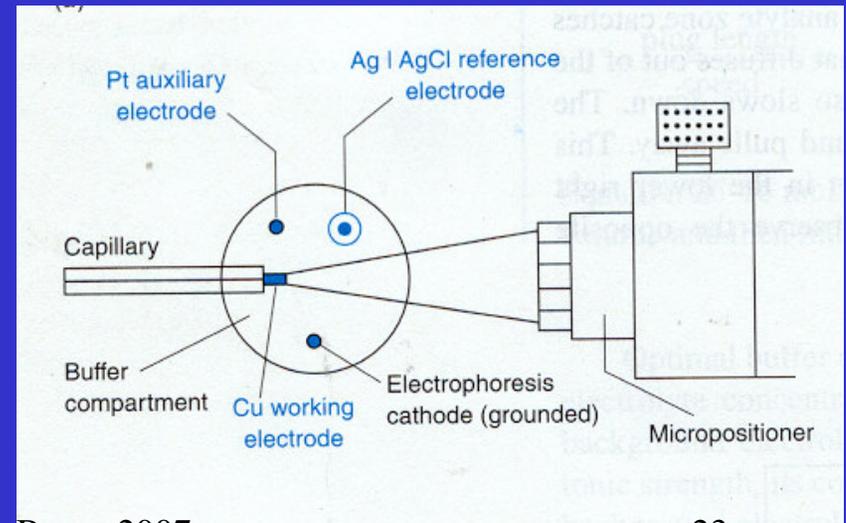
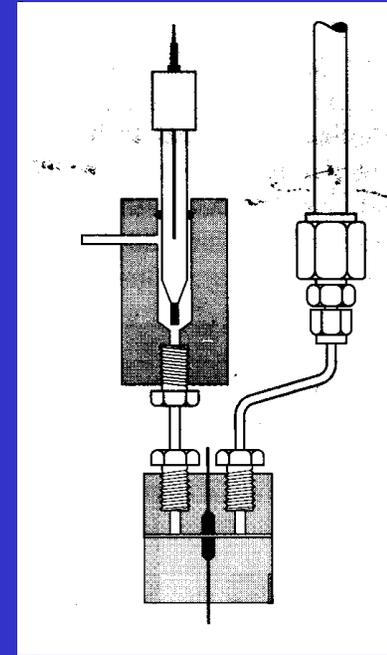
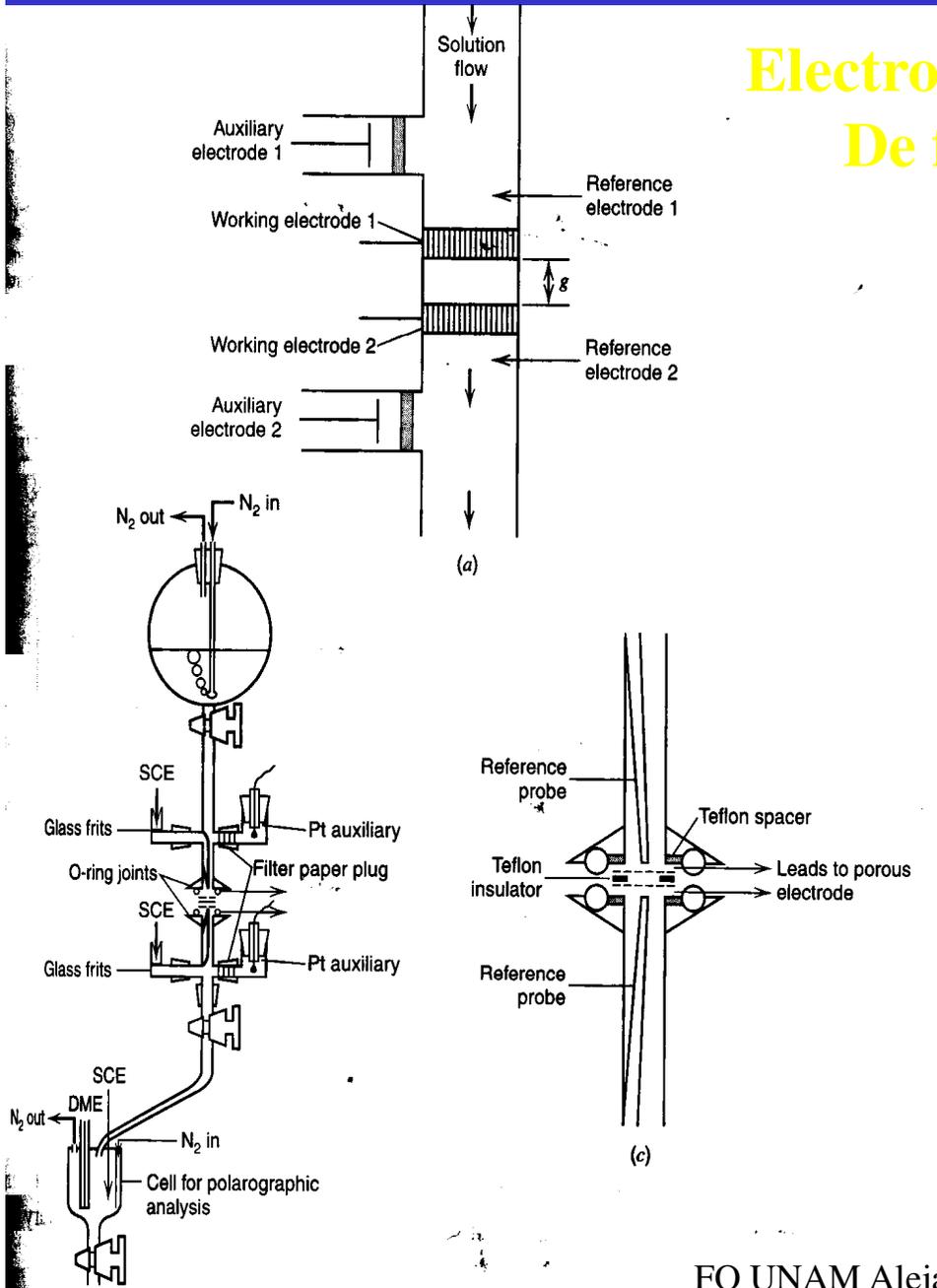




-  Electrode material (e.g., platinum)
-  Insulator (e.g., Teflon)
-  Shaft and ring material (e.g., brass)



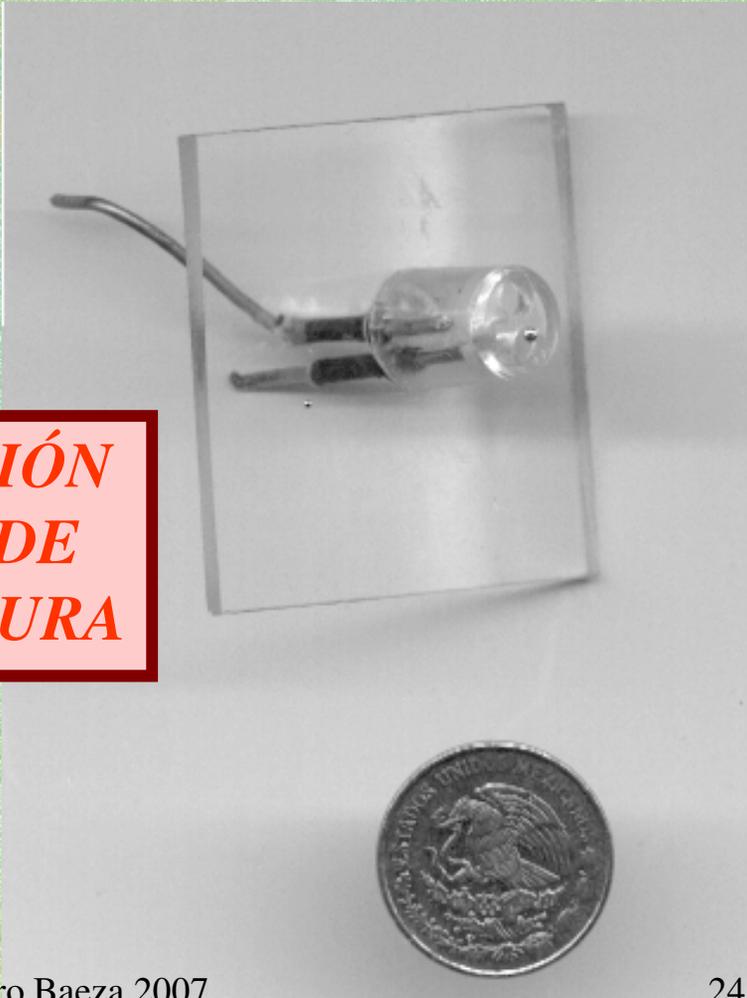
Electroquímica De flujo



Microcelda para ASV



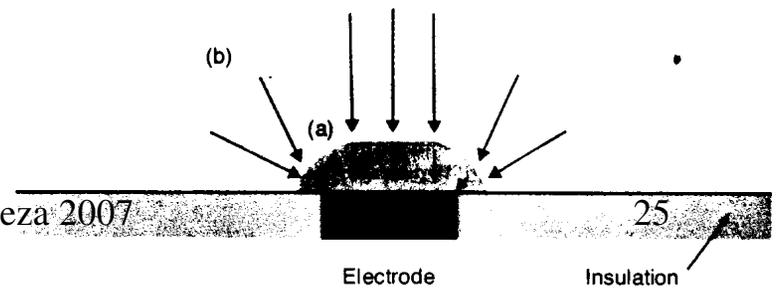
**SIN AGITACIÓN
REGIMEN DE
DIFUSIÓN PURA**



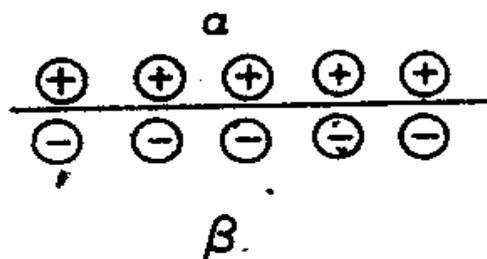
UME

SIN
AGITACIÓN
¡REGIMEN
CONVECTIVO!

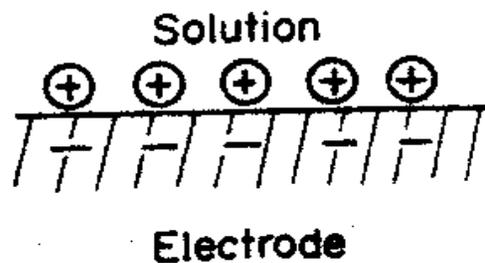
FQ UNAM Alejandro Baeza 2007



Liquid-liquid



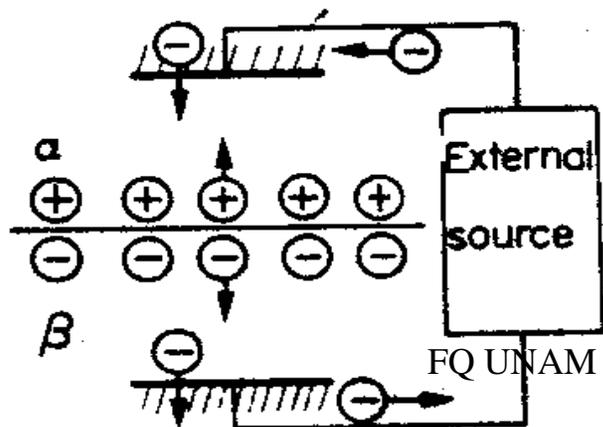
Electrode-liquid



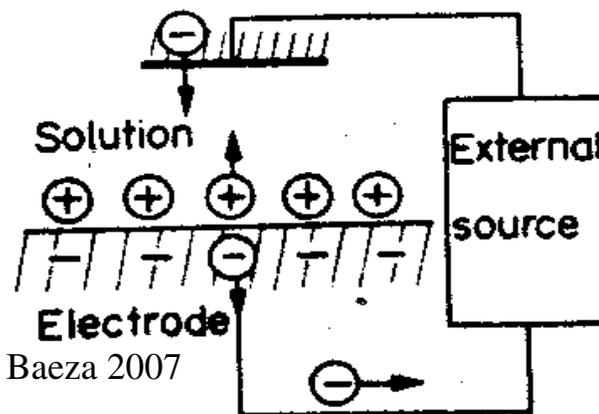
ITIES

Charging of interfaces

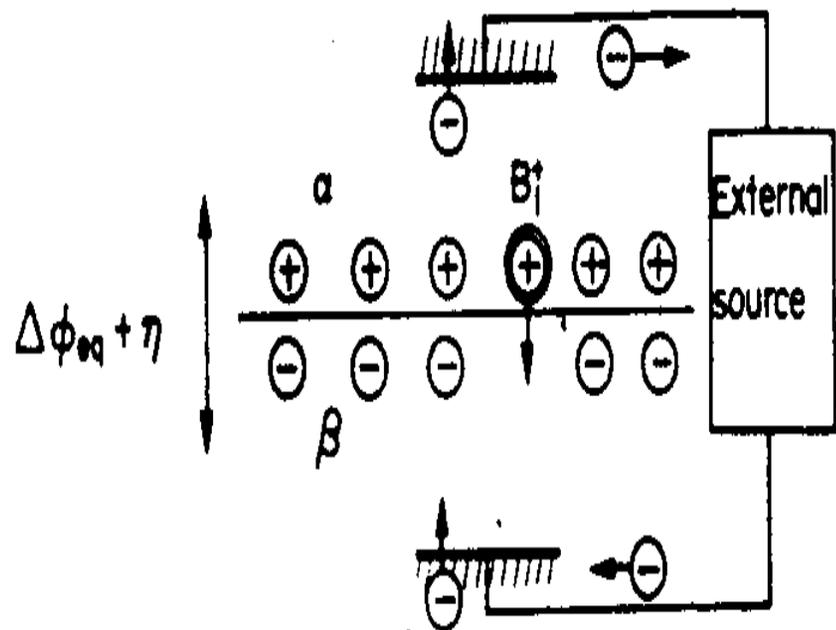
Liquid-liquid



Electrode-liquid

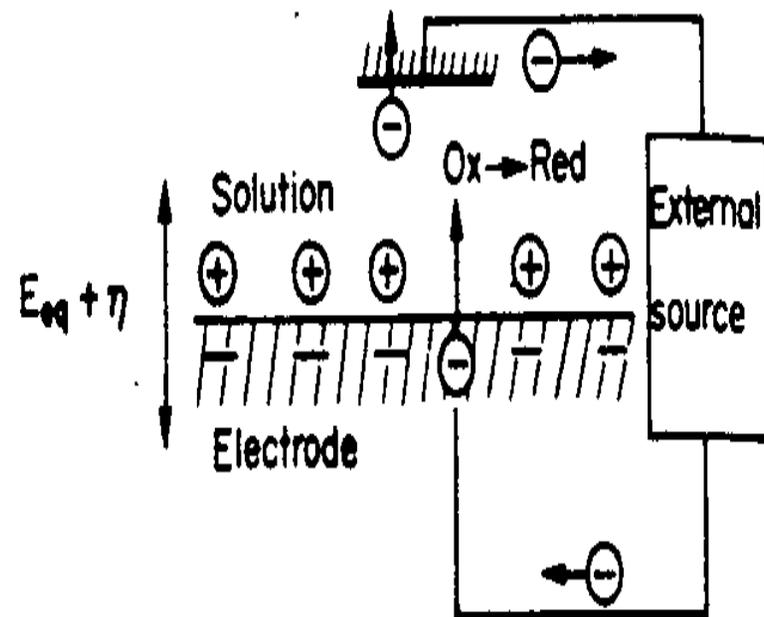


FQ UNAM Alejandro Baeza 2007



$$\Delta\phi_{eq} = \Delta_a^\beta \phi_{B_1^+}^0 + \frac{RT}{F} \ln \frac{a_{B_1^+}(\alpha)}{a_{B_1^+}(\beta)} =$$

$$= - \frac{\Delta G_{B_1^+, \alpha \rightarrow \beta}^0}{F} + \frac{RT}{F} \ln \frac{a_{B_1^+}(\alpha)}{a_{B_1^+}(\beta)}$$



$$E_{eq} = E_{Ox, Red}^0 + \frac{RT}{F} \ln \frac{a_{Ox}}{a_{Red}} =$$

$$= - \frac{\Delta G_{Ox, Red}^0}{F} + \frac{RT}{F} \ln \frac{a_{Ox}}{a_{Red}}$$

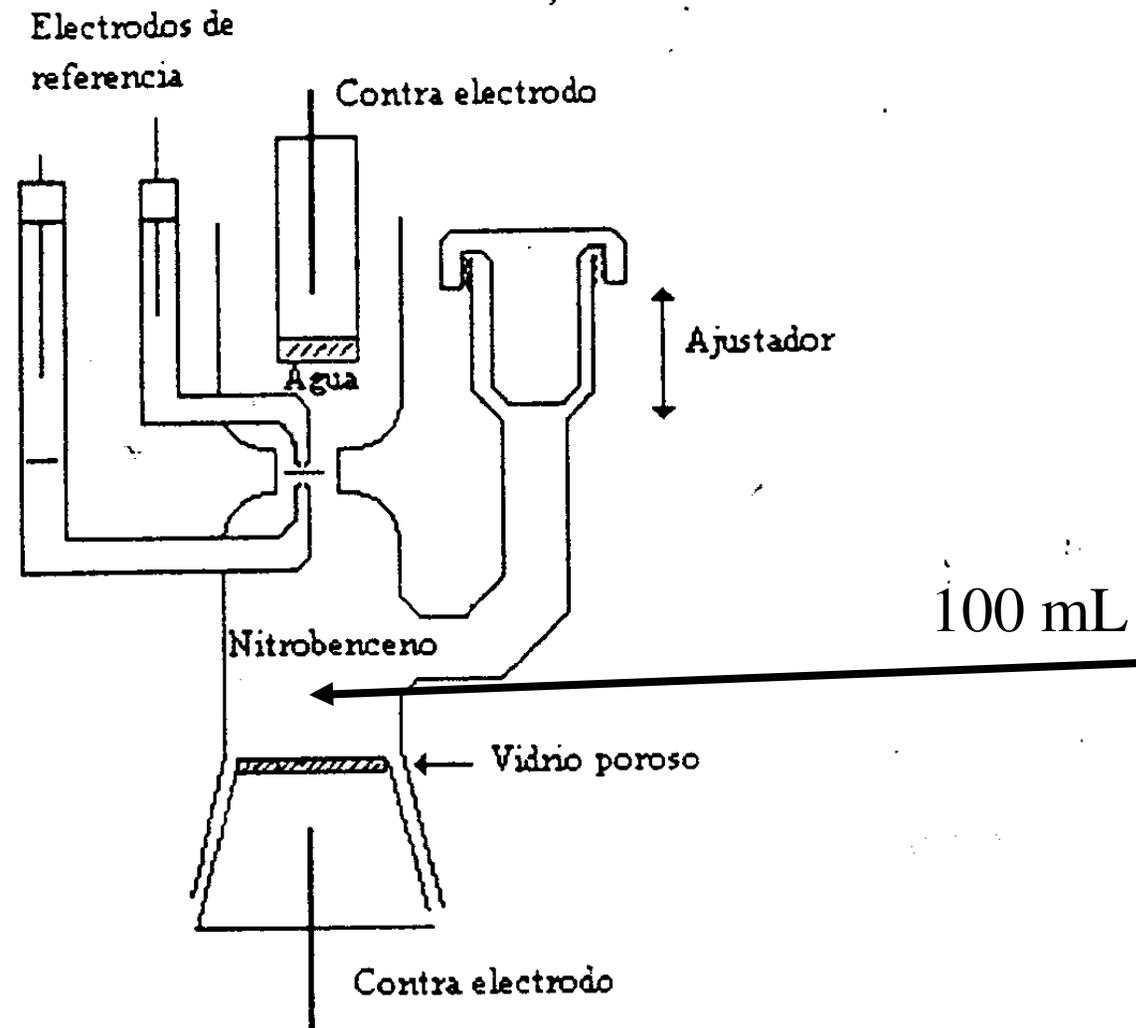


FIGURA 3. Modelo de celda para estudios de IDSEI utilizada por Vanýsek, 28

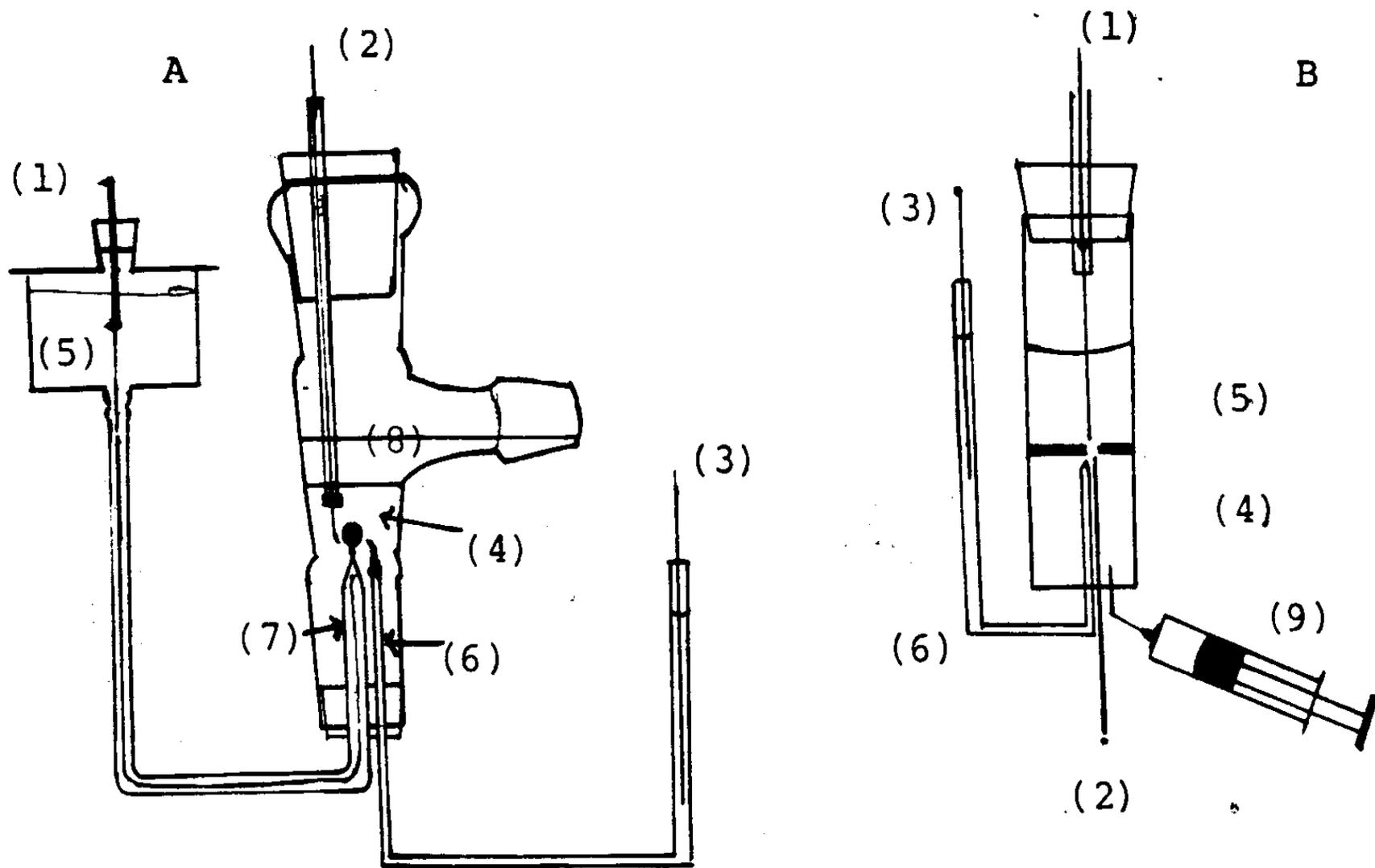
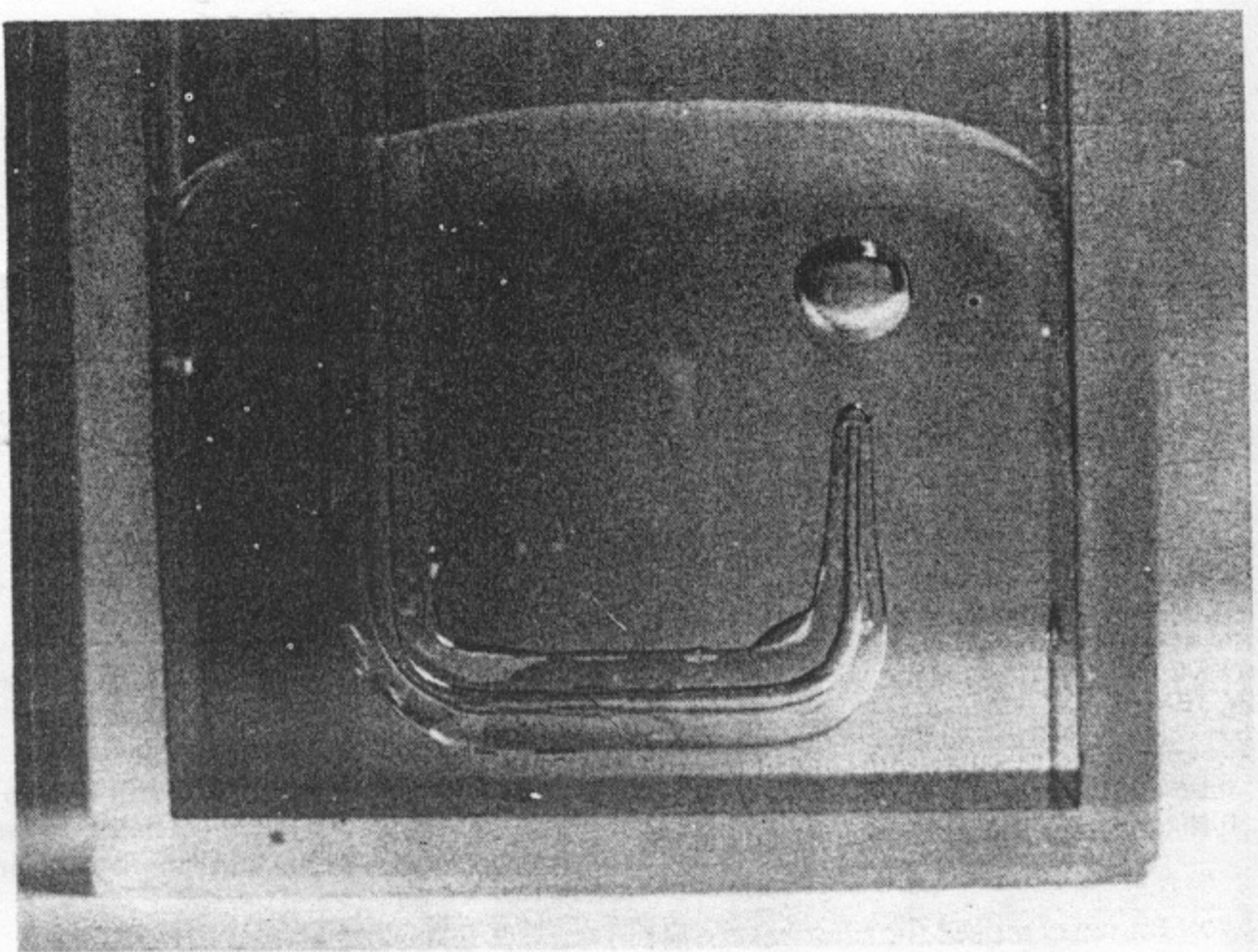


Figura 1 a) celda polarográfica , b) celda voltamperográfica; donde 1: EC1 & ER1, 2: EC2, 3: ER2, 4: Fase orgánica, 5: Fase acuosa, 6: Capilar de Lugin, 7: Capilar de goteo, 8: Fase acuosa remanente, 9: Jeringa para controlar en nivel de la fase orgánica, 10: Septum.

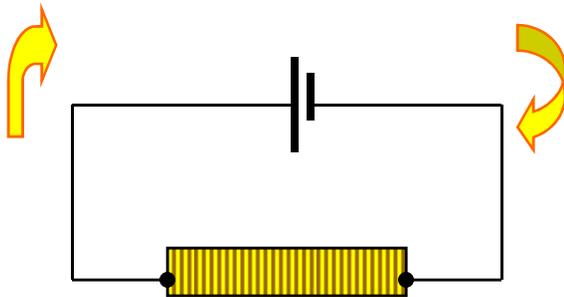


FQ UNAM Alejandro Baeza 2007

Fig. 8. The electrolyte dropping electrode.

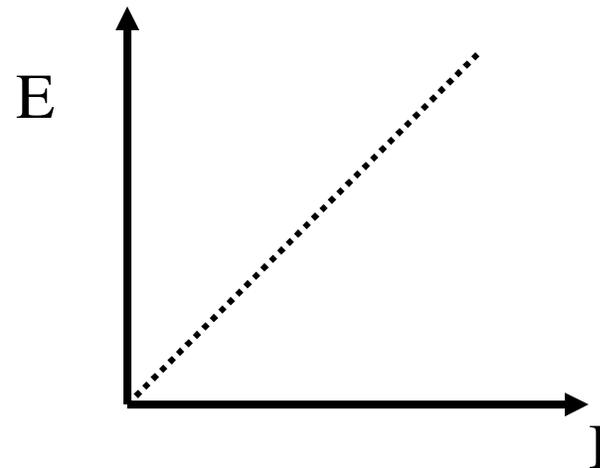
¿cuál es la relación entre corriente, resistencia y el potencial impuesto externamente?

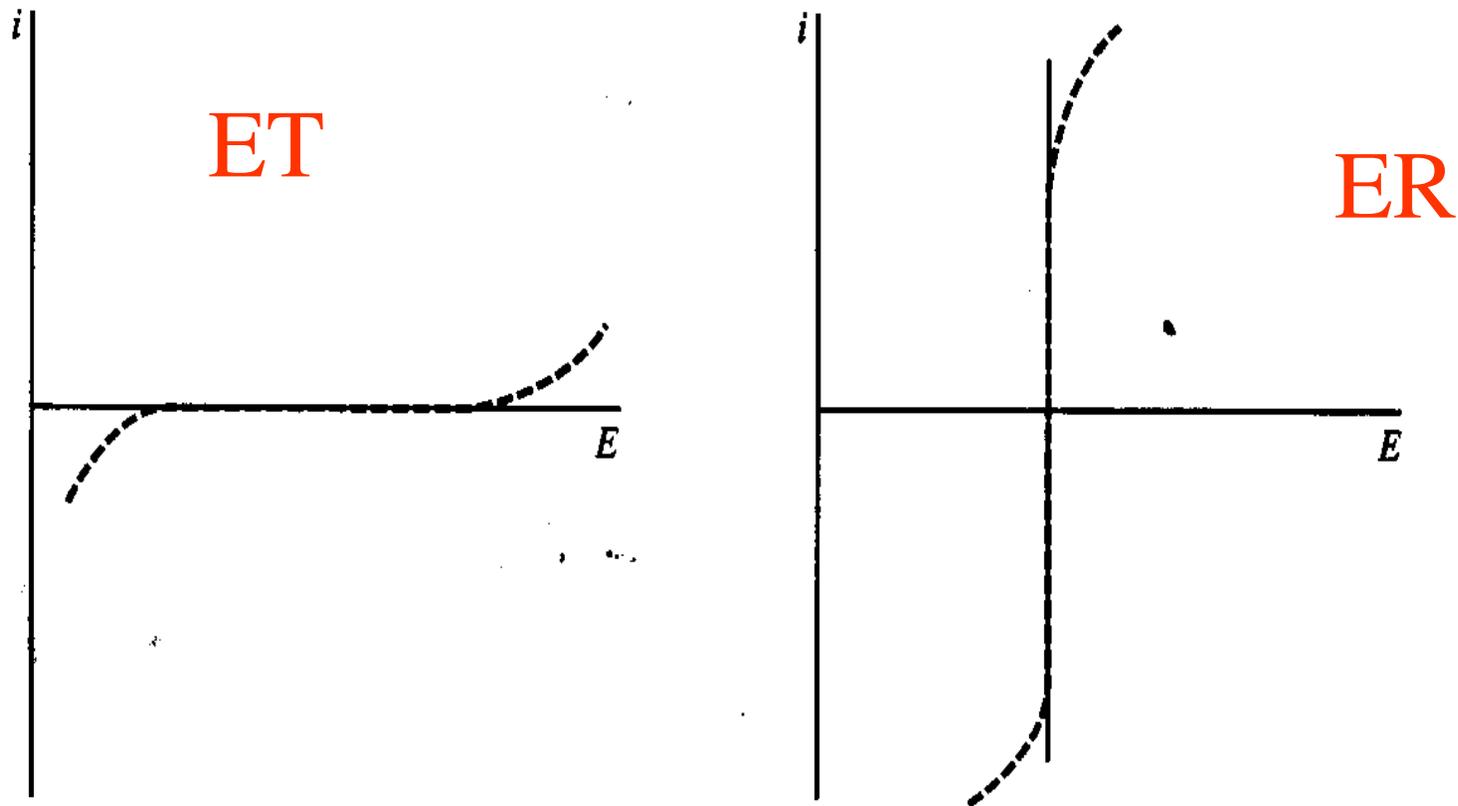
Resistencia ideal:



¡Ley de Ohm!

$$E=IR$$





(a) Ideal polarizable electrode

(b) Ideal nonpolarizable electrode

Figure 1.3.5 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.

Química Analítica



Determinación Analítica



Metodología Analítica



Análisis Químico

(medición, monitoreo, caracterización)



Metodos químicos

(reacción químico)

Metodos Fisicoquímicos

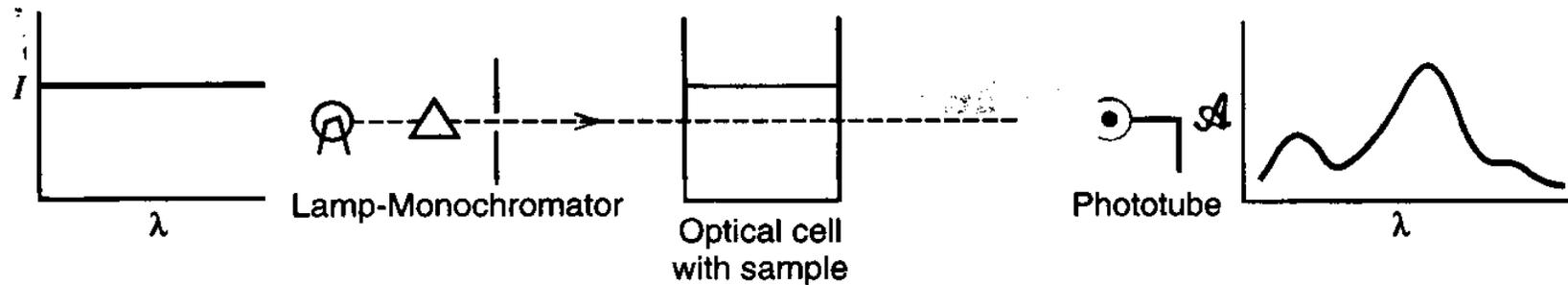
(interacción energía-materia)

CONDICIONES OPERATORIAS (II)

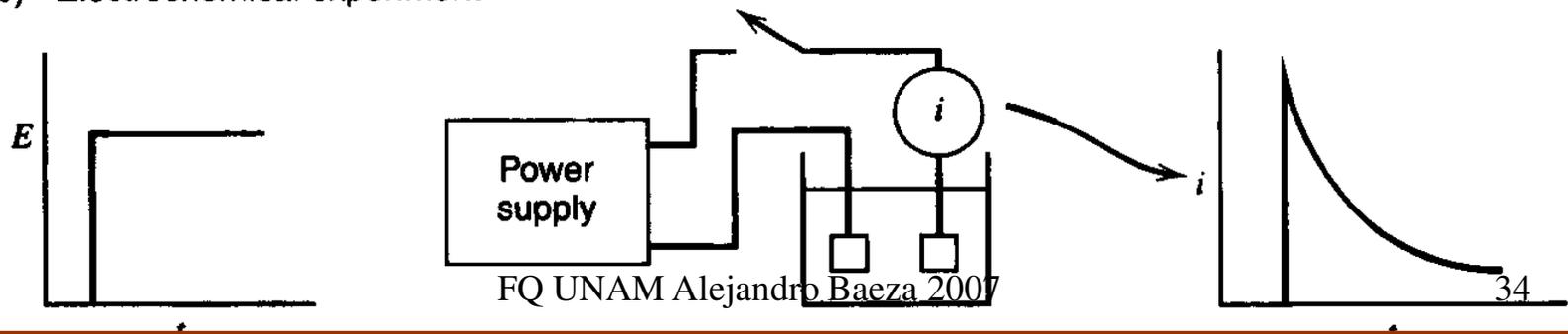
METODOLOGIA ELECTROANALÍTICA

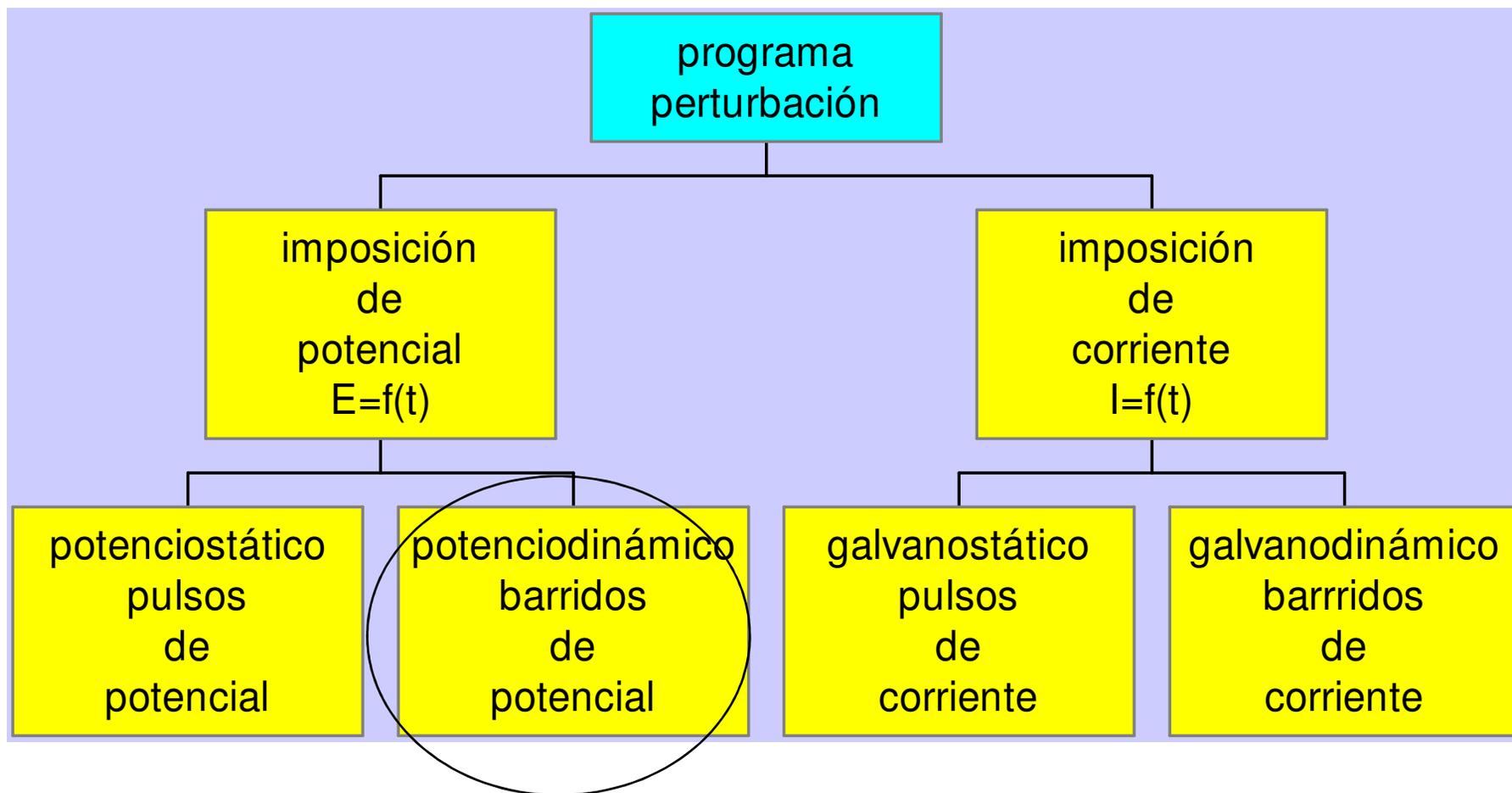
PERTURBACIÓN → SISTEMA → RESPUESTA

(b) Spectrophotometric experiment



(c) Electrochemical experiment





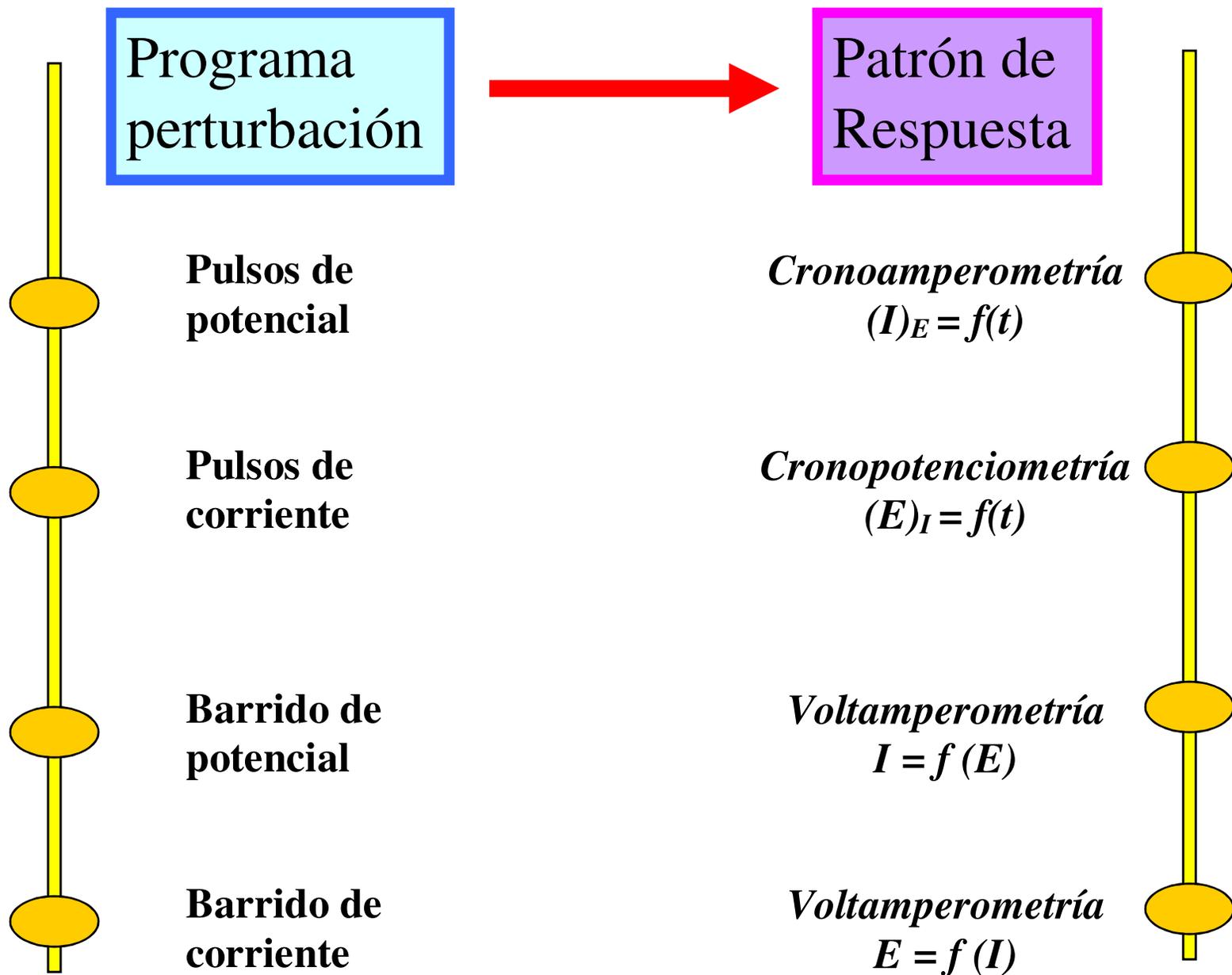


Table 4-1 / Controlled Potential Methods

Name of Technique	Potential Excitation Signal	Mass Transfer	Measurement	Analytical Relation to Bulk Concentration	Typical Display
Polarography (cathodic or normal)	Slow linear scan (or constant E)	Diffusion	i vs. E	$i_d \propto C$	
CV polarography	Slow linear scan + low amplitude sine wave	Diffusion	i_{ac} vs. E	$i_p \propto C$	
Pulse polarography	Square voltage pulses of increasing amplitude	Diffusion	i vs. E	$i_d \propto C$	
Differential pulse polarography	Square voltage pulses of constant amplitude + linear ramp	Diffusion	Δi vs. E	$i_p \propto C$	
Single sweep voltammetry	Linear scan E	Diffusion	i vs. E	$i_p \propto C$	
Cyclic voltammetry	Triangular scan E	Diffusion	i vs. E	$i_p \propto C$	
Chronoamperometry	Step E	Diffusion	i vs. t	$i_t \propto C$	
Chronocoulometry	Step E	Diffusion	Q vs. t	$Q \propto C$	
Hydrodynamic voltammetry	Linear scan E (or constant E)	Convection/diffusion	i vs. E	$i_p \propto C$	
Controlled potential coulometry	Constant E	Convection/diffusion	Q vs. t	$Q = \int_0^t i dt = nFVC$	
Controlled potential electrogravimetry	Constant E	Convection/diffusion	Weight of deposit	Weight $\propto VC$	None
Amperometric titration (one or two polarized electrodes)	Constant E + titrant addition	Convection/diffusion	i vs. volume	Volume of titrant $\propto VC$	
Stripping voltammetry	Constant E followed by linear scan or differential pulse scan	Convection/diffusion	i vs. E	$i_p \propto C$	

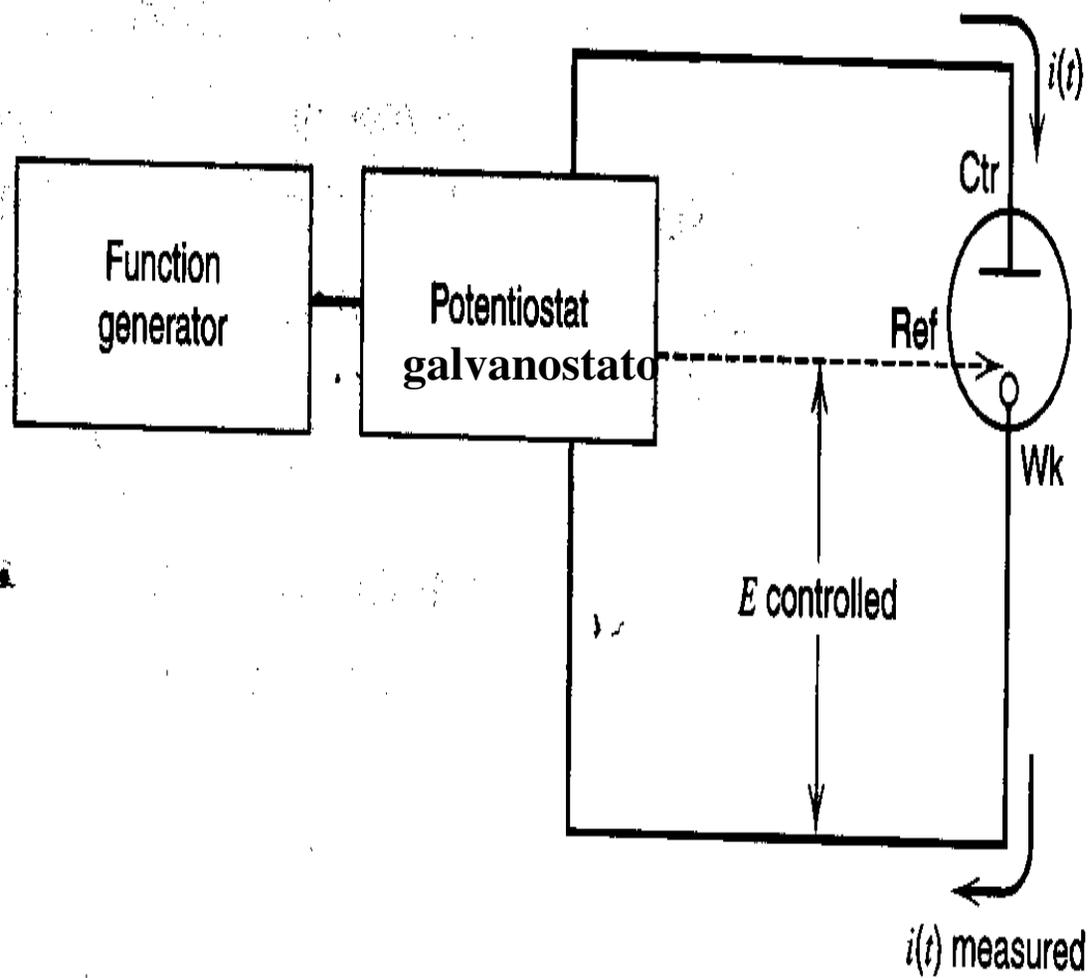


Figure 5.1.1
Experimental arrangement for controlled-potential experiments.

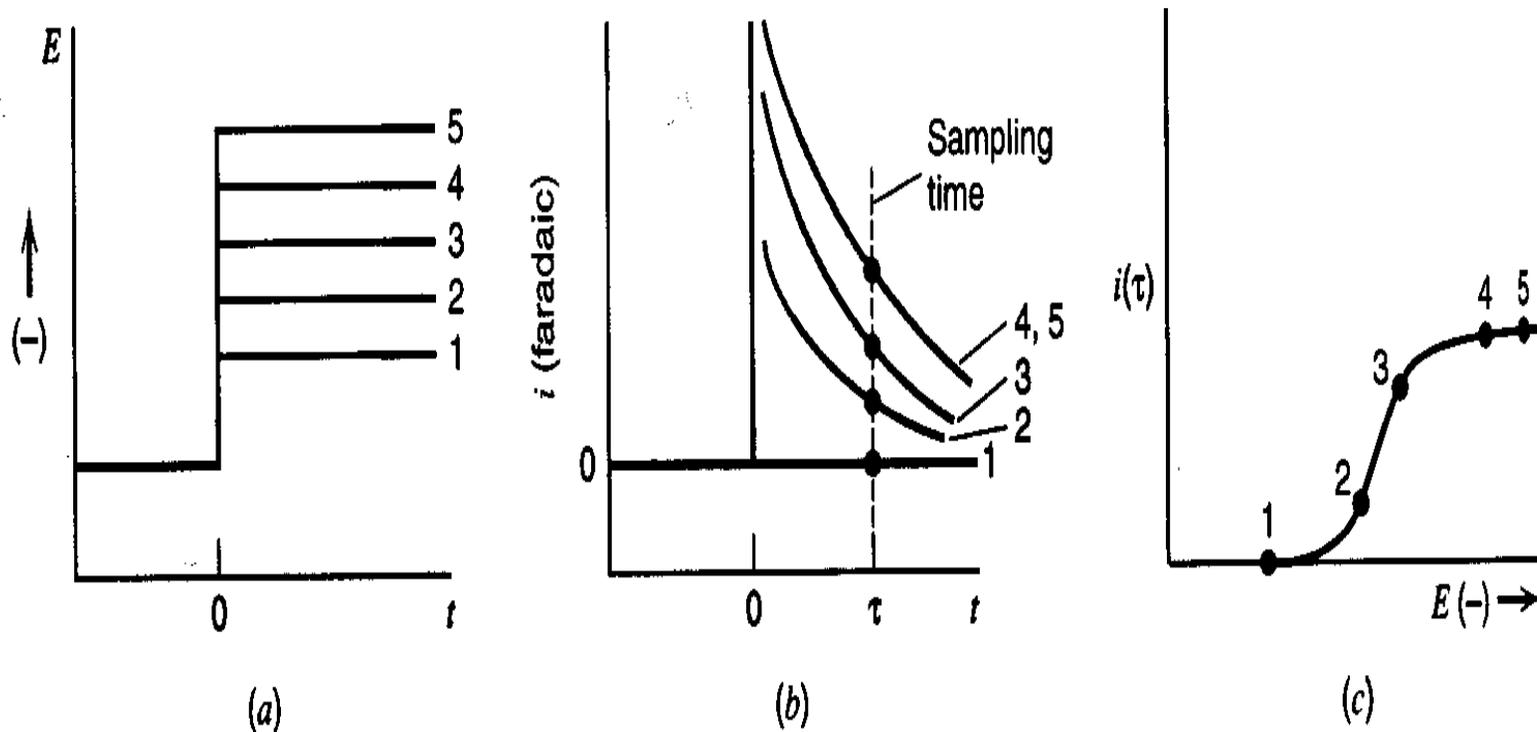


Figure 5.1.3 Sampled-current voltammetry. (a) Step waveforms applied in a series of experiments. (b) Current-time curves observed in response to the steps. (c) Sampled-current voltammogram.