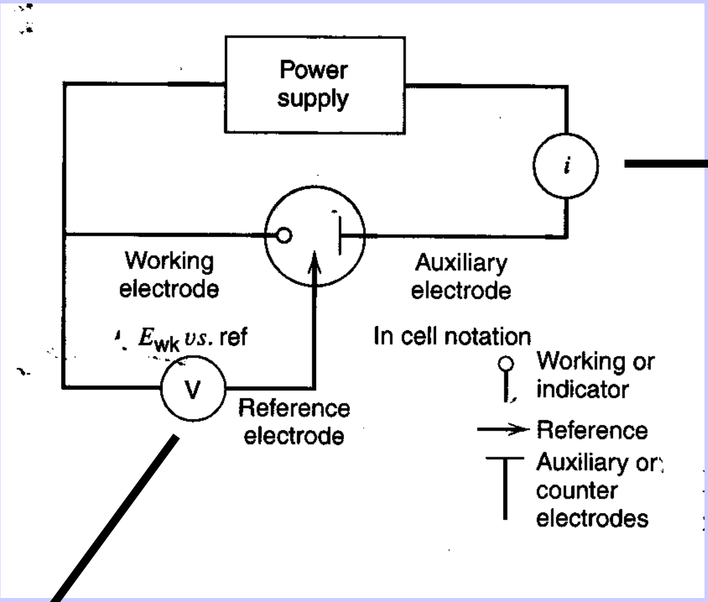
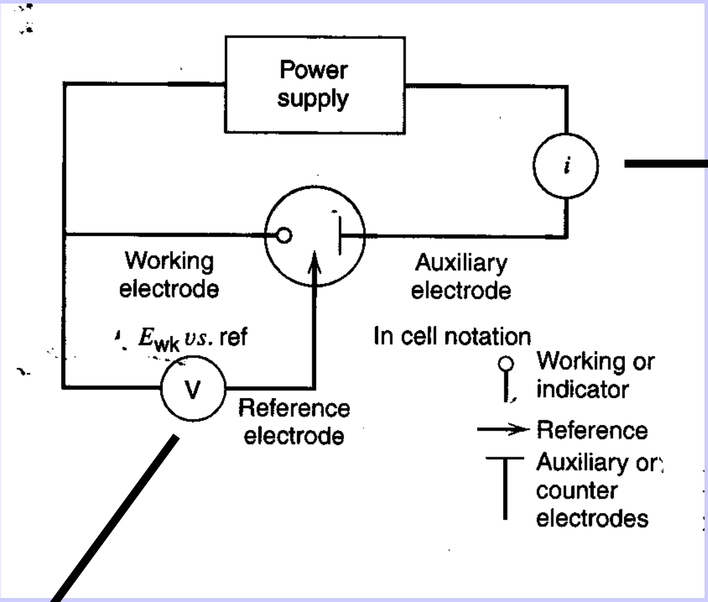
Condiciones operatorias II:

Hipótesis de Nernst y leyes de Faraday



$$I_{leía} = I_{capacitiva} + I_{faradaica} = I_{cap} + (I_{migr} + I_{convec} + I_{dif})$$

$$E_{imp.} = E_{ohm} + E_{despol} + \eta$$



microelectrodo

EGD

EGM

Sin agit

$$I_{leida} = \cancel{I_{capacitiva}} + I_{faradaica} = I_{cap} + (I_{migr} + I_{convec} + \boxed{I_{dif}})$$

EBS

$$E_{imp} = \cancel{E_{ohm}} + E_{despol} + \eta$$

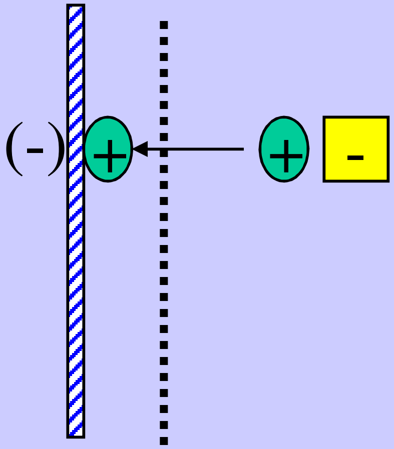
EBS:

"minimiza" la caída óhmica:

KNO_3 0.1 mol/L $\Rightarrow R_s \downarrow$

$IR_s \downarrow = E_{\text{caida óhmica}}$

"Minimiza" el número de Transporte del despolarizante: $I_m = t_+ I_m + t_- I_m$



a) Sin **KNO_3** :

$$t_+ = \frac{\lambda_+ C_+}{\lambda_+ C_+ + \lambda_- C_-} \approx 0.5$$

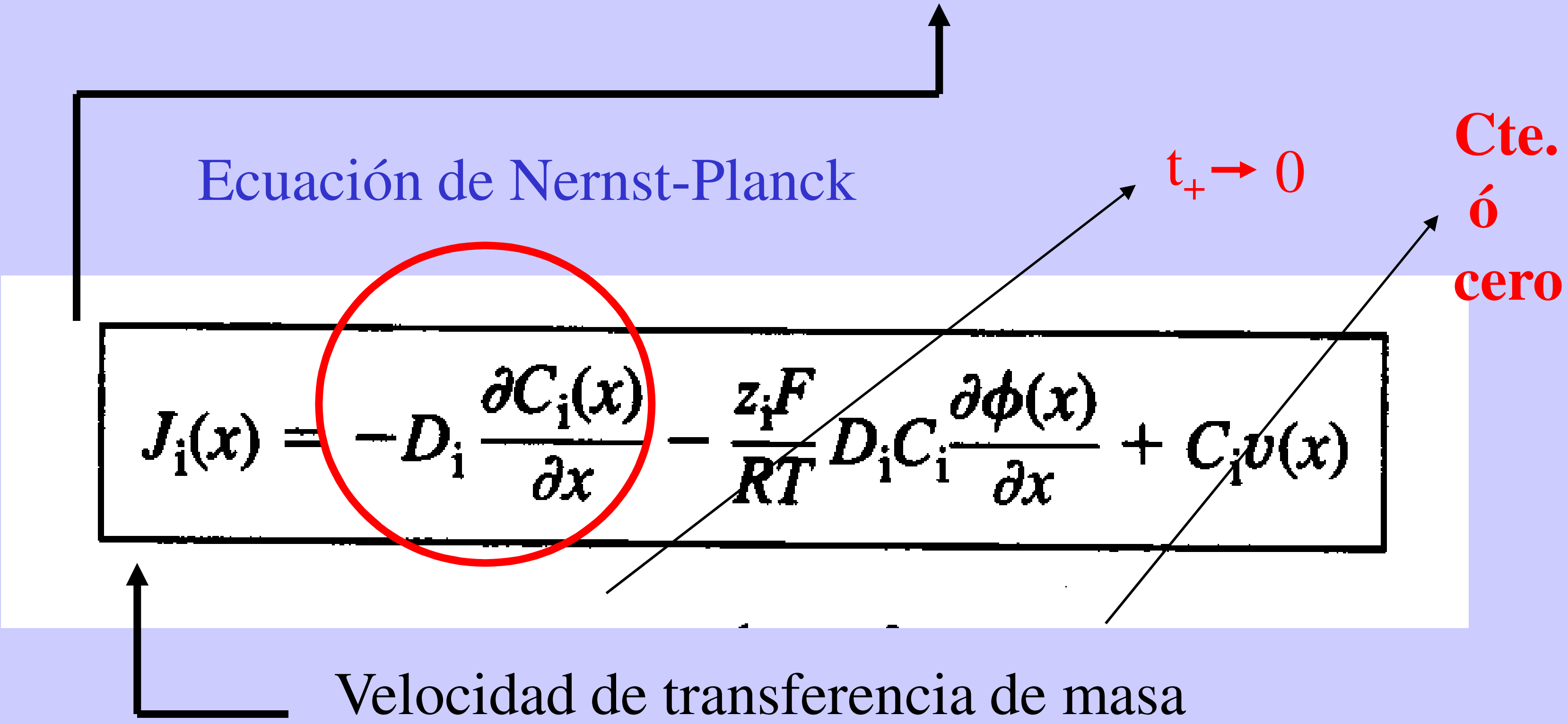
b) Con **KNO_3 $100C_+$**

$$t_+ = \frac{\lambda_+ C_+}{\lambda_+ C_+ + \lambda_- C_- + \Lambda_{KNO_3} 100C} < 0.001$$

Leyes de Faraday

$Q = nF\,m$ $\qquad$ $F = 96500$ C/mole

$(dQ/dt) = i = nF(dm/dt) = nF\,v_{elec}$



Ecuación de Nernst-Planck

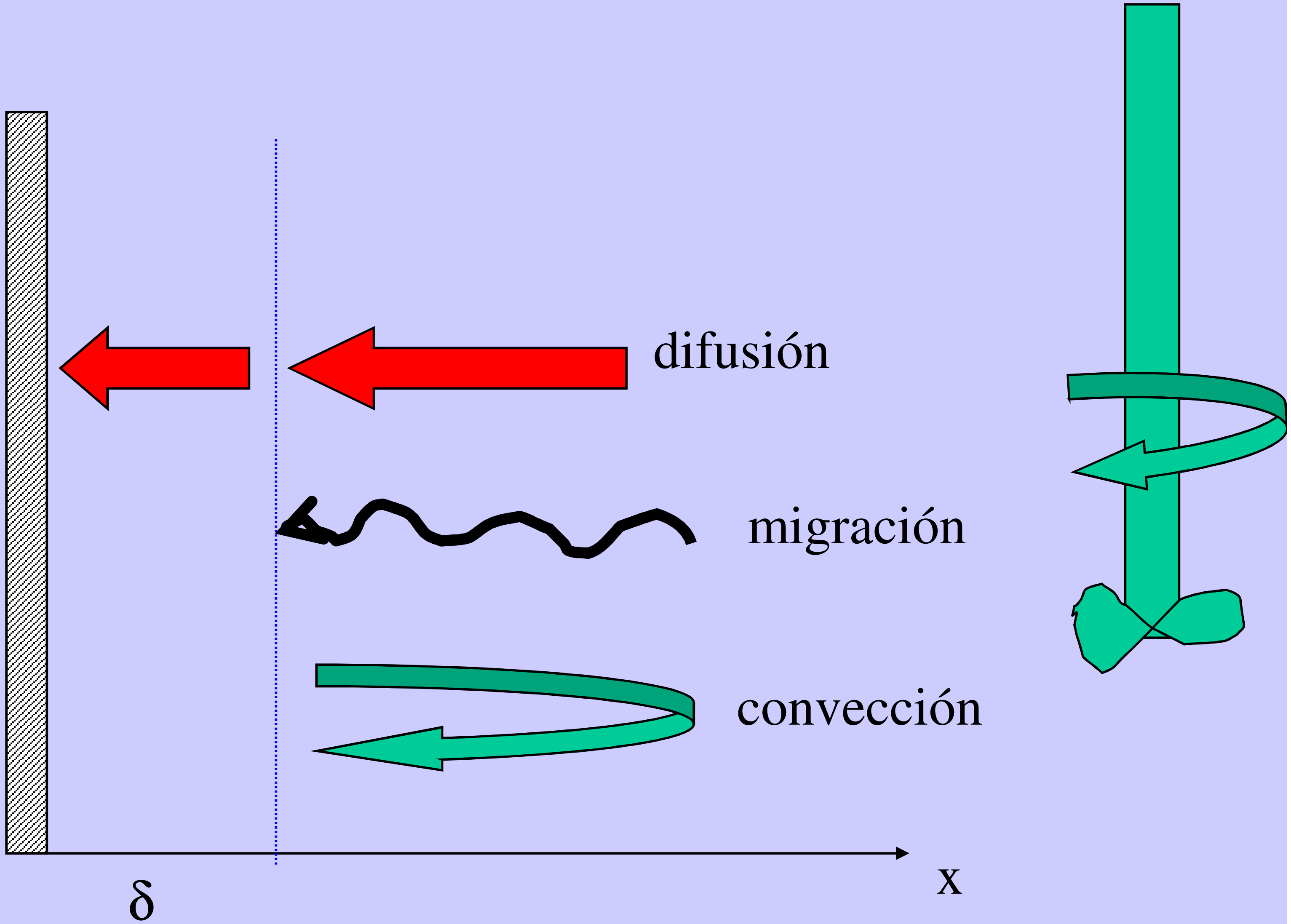
$t_+ \rightarrow 0$

Cte.
ó
cero

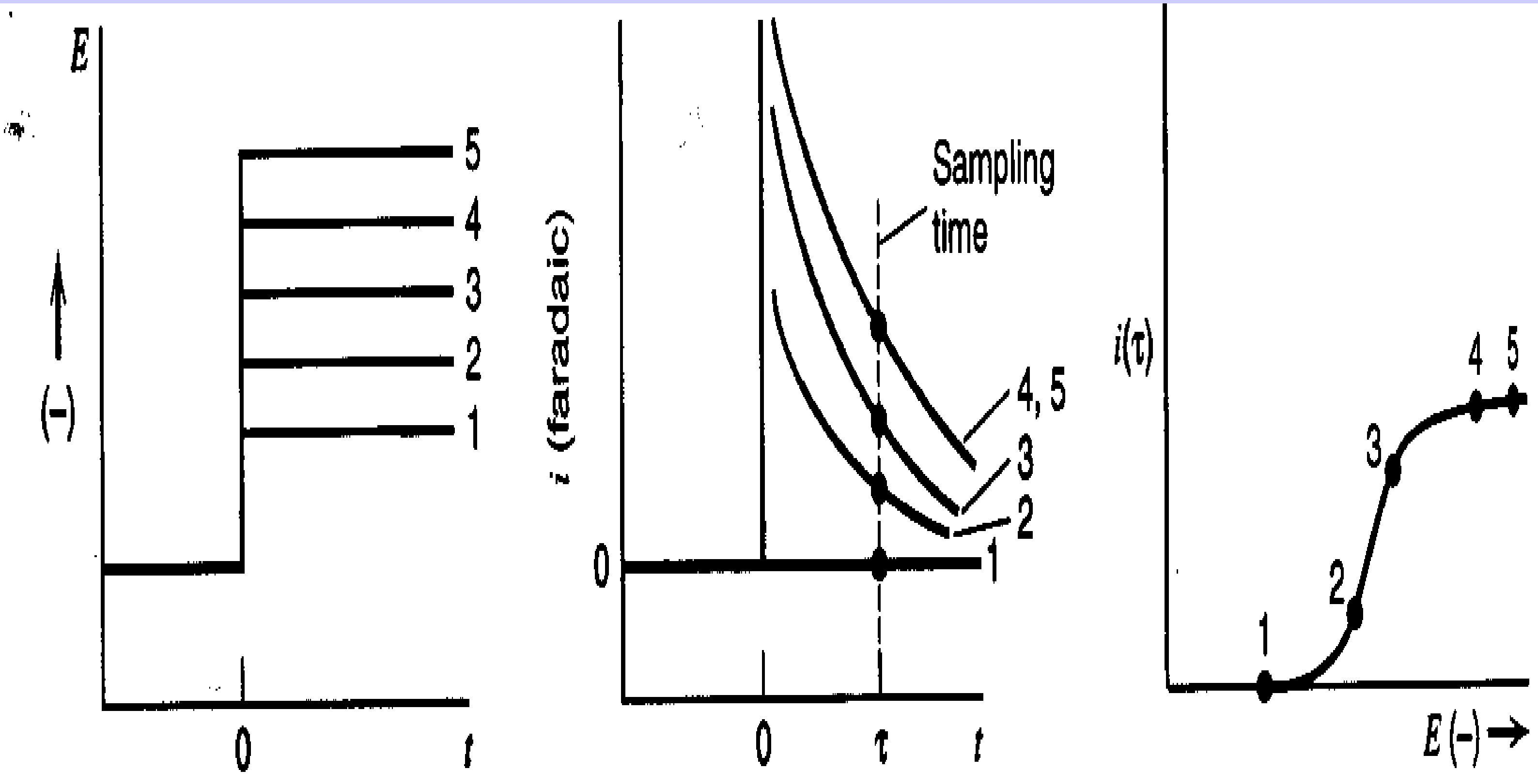
$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x)$$

Velocidad de transferencia de masa

Hipótesis de Nernst:



Capa de difusión de Nernst



(*a*) (*b*) (*c*)

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.

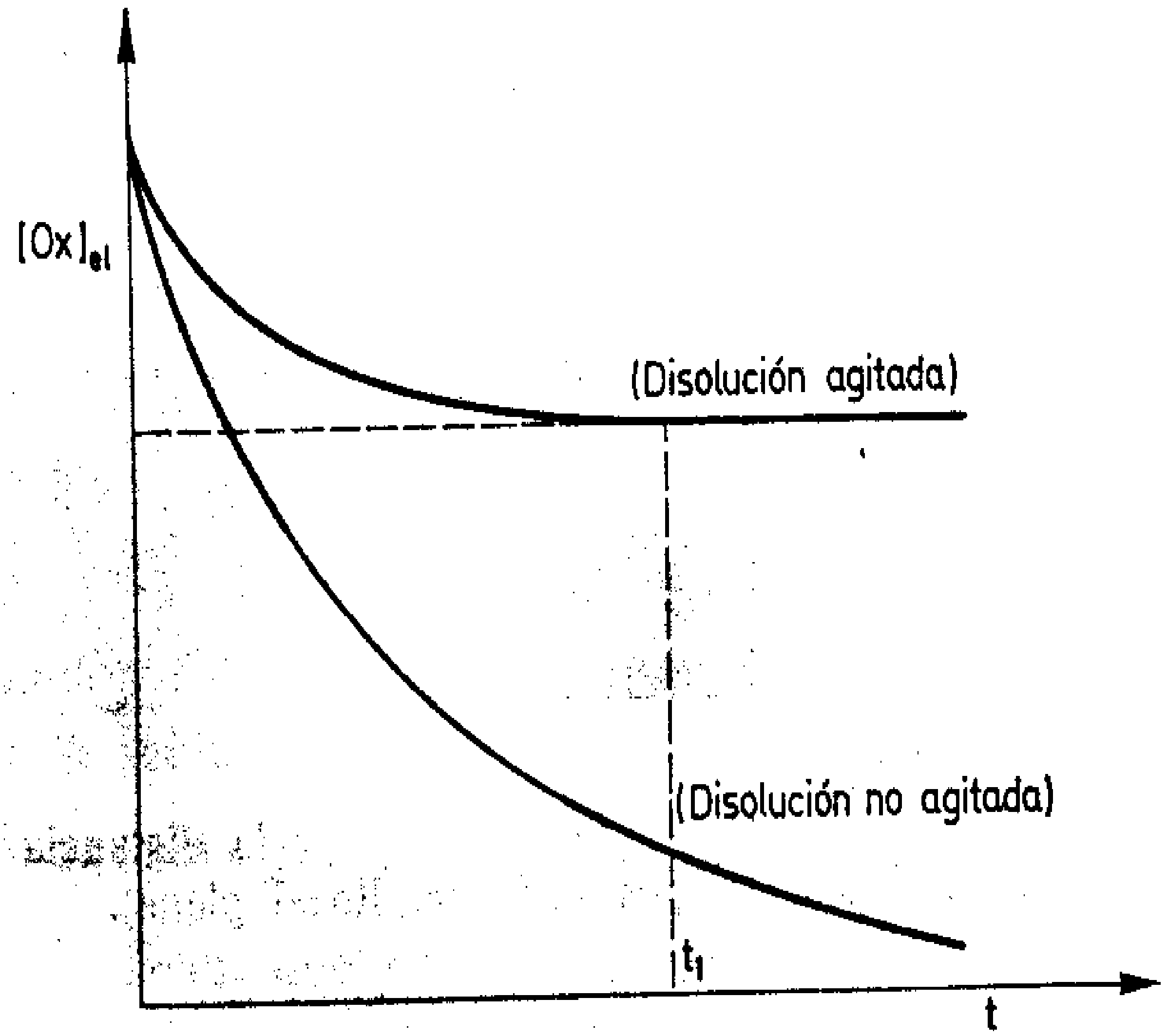


FIG. 2.10. Variación de la concentración de la sustancia electroactiva en la superficie del electrodo en función del tiempo.

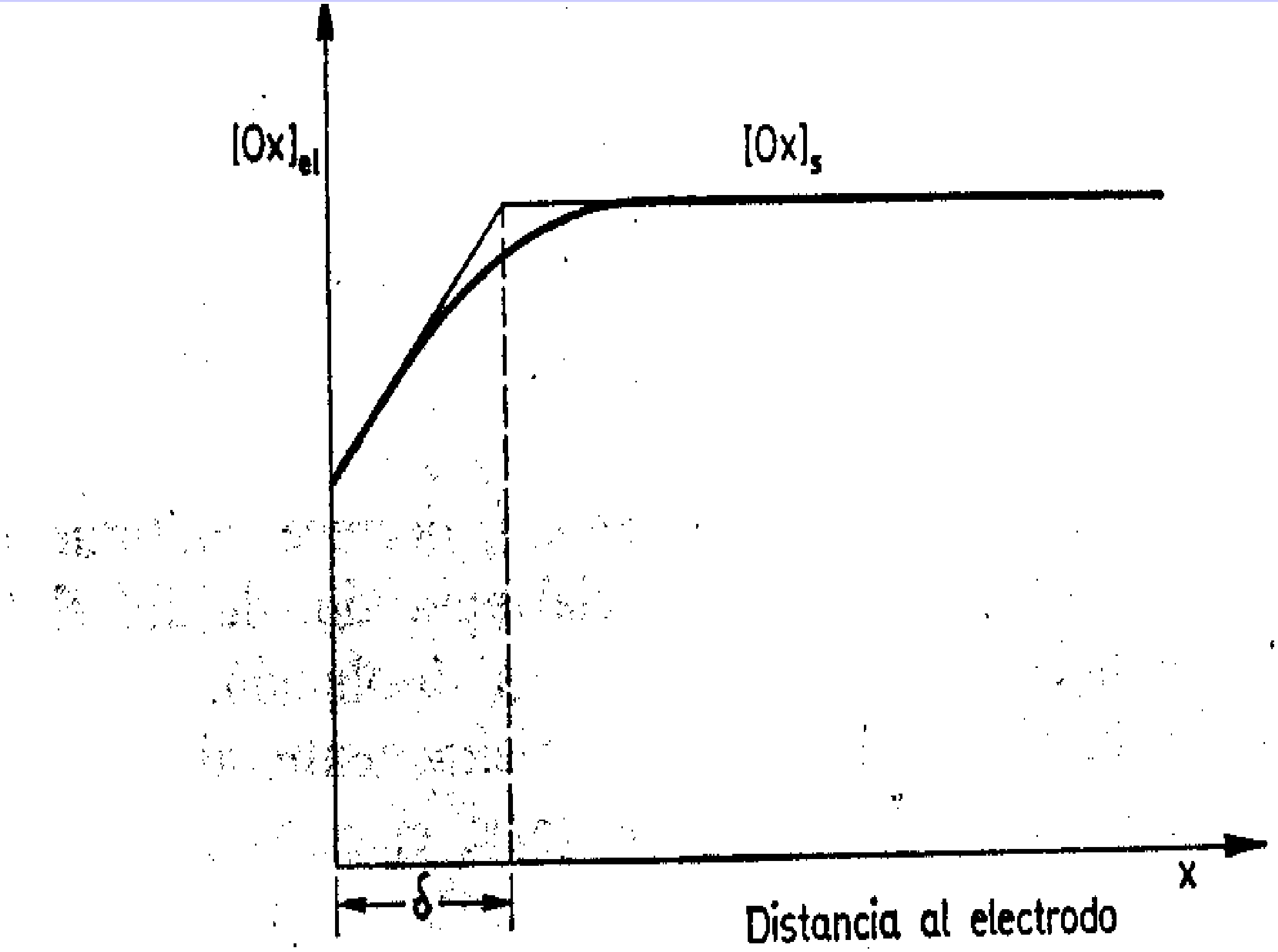


FIG. 2.11. Variación de la concentración de la especie electroactiva en función de la distancia al electrodo para un potencial determinado aplicado al mismo y en disolución agitada.

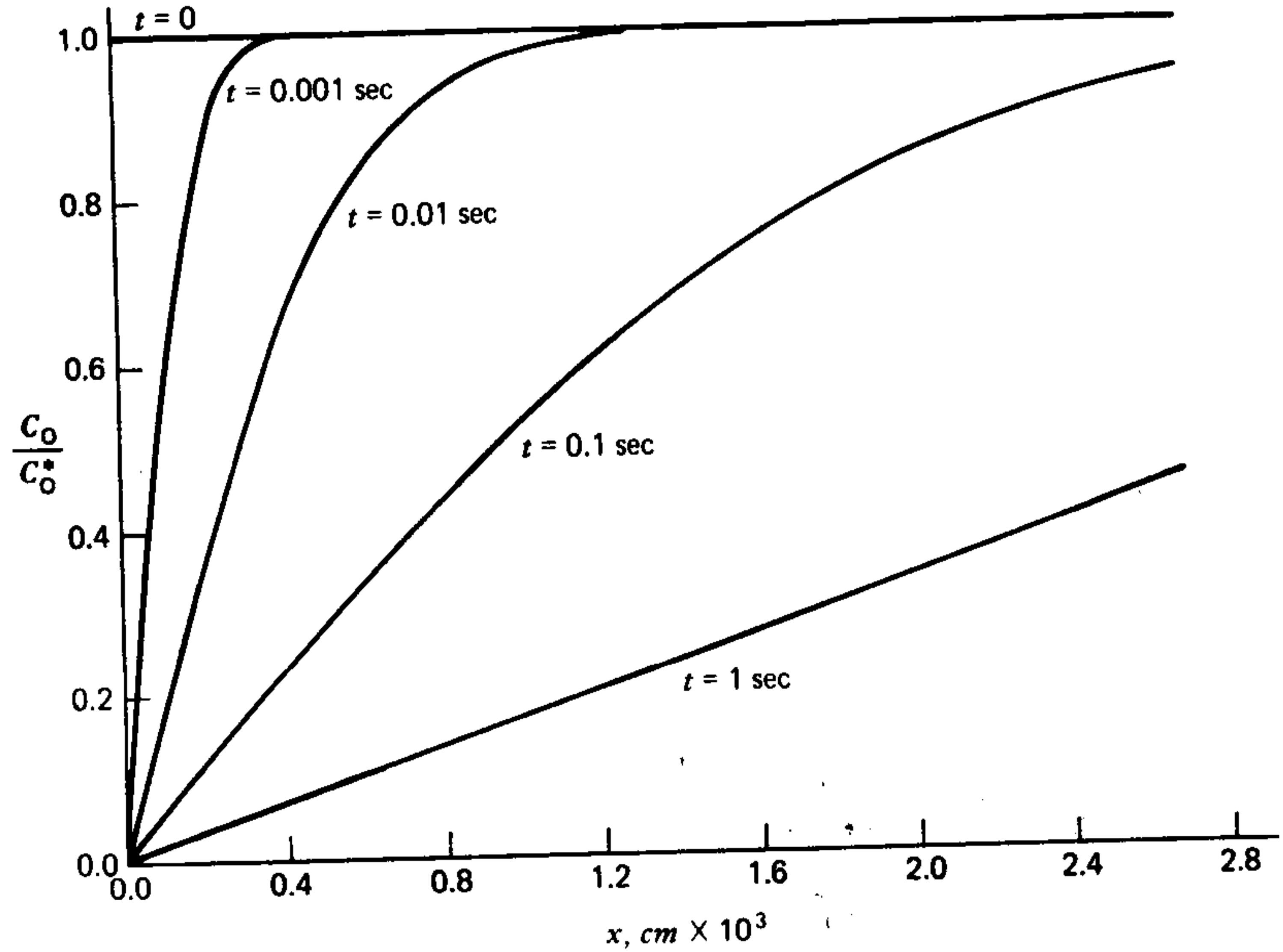


Figure 5.2.1

Concentration profiles for several times after the start of a Cottrell experiment. $D_O = 1 \times 10^{-5}$ cm²/sec.

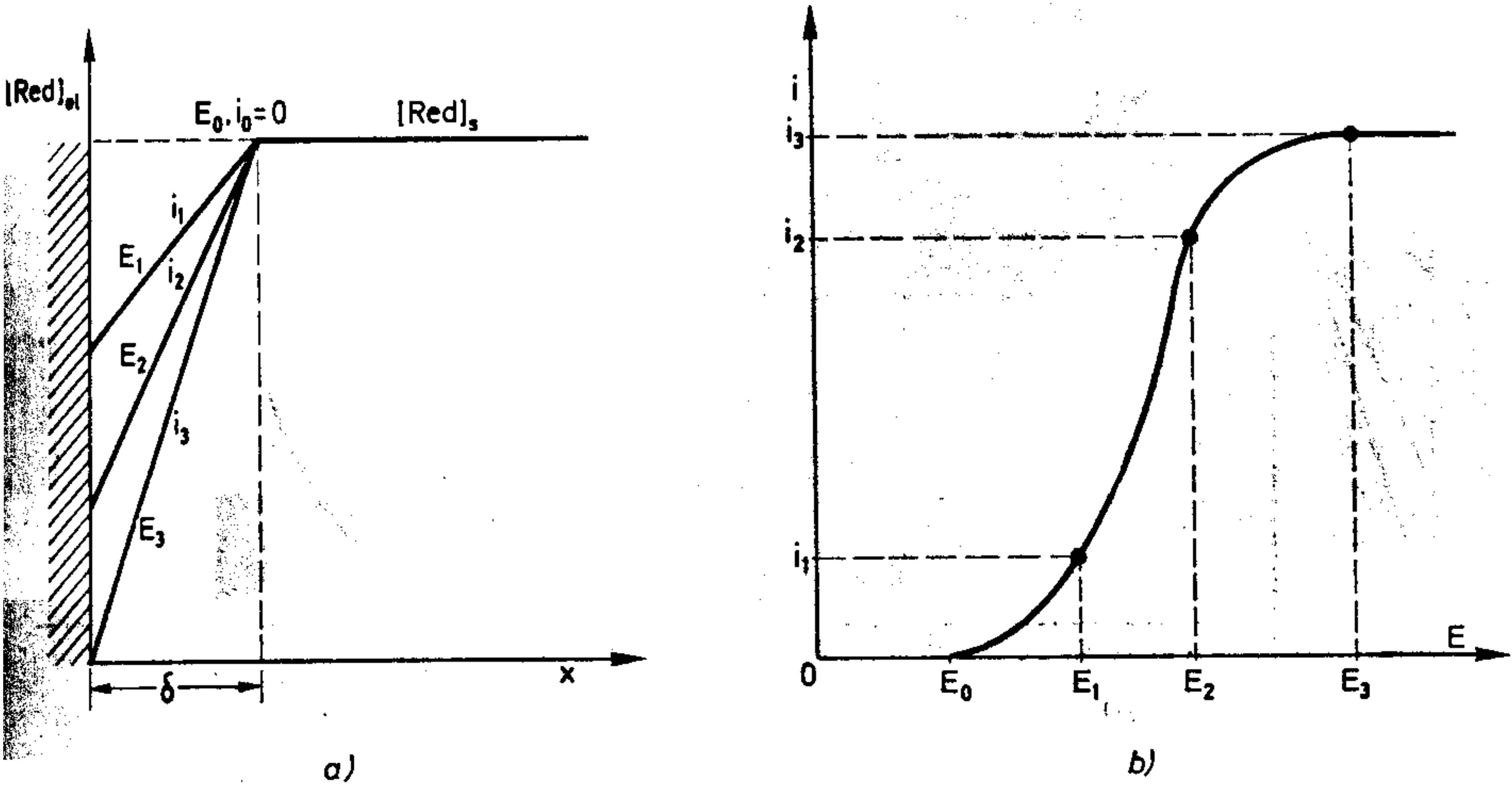
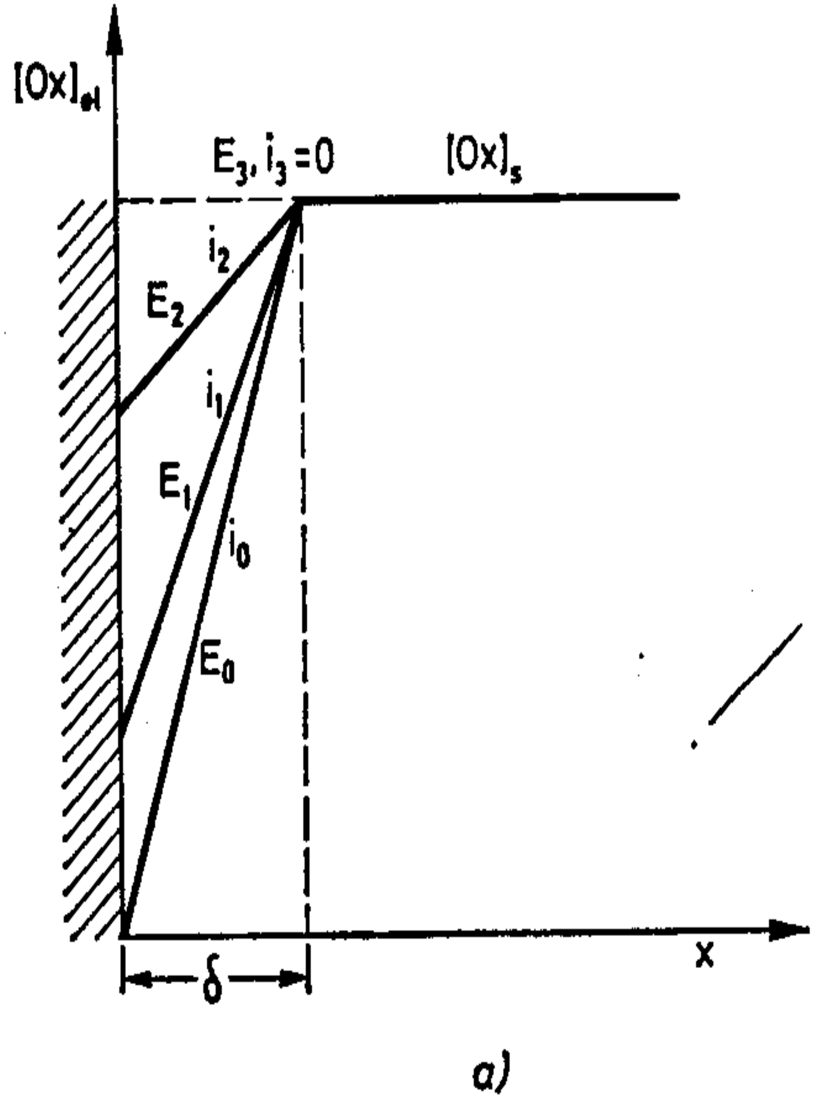


FIG. 2.12. ***a)*** **Variación del perfil de la concentración de Red en función de la distancia al electrodo del potencial del mismo; *b)* variación de *i* frente al potencial aplicado al electrodo.**



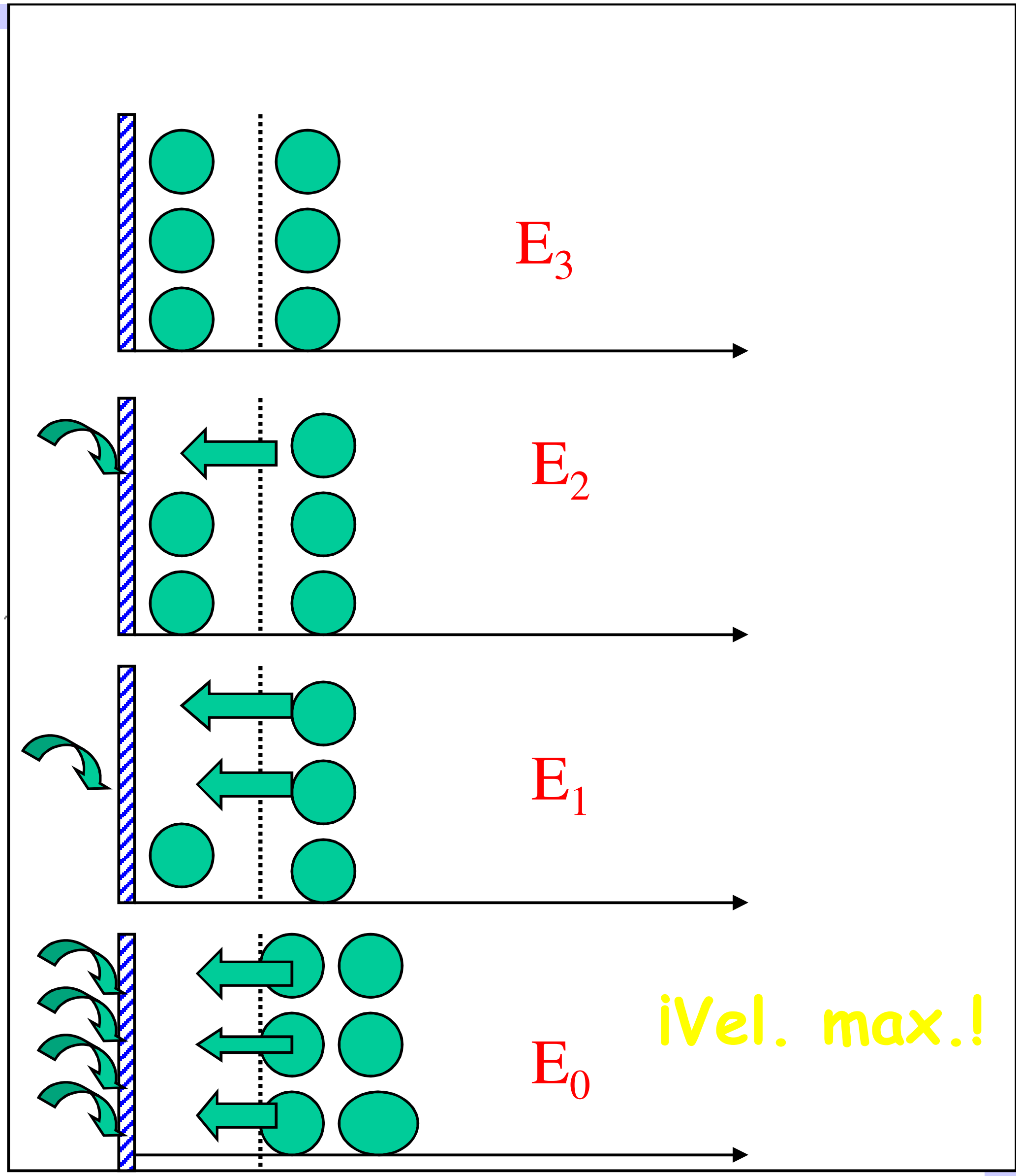
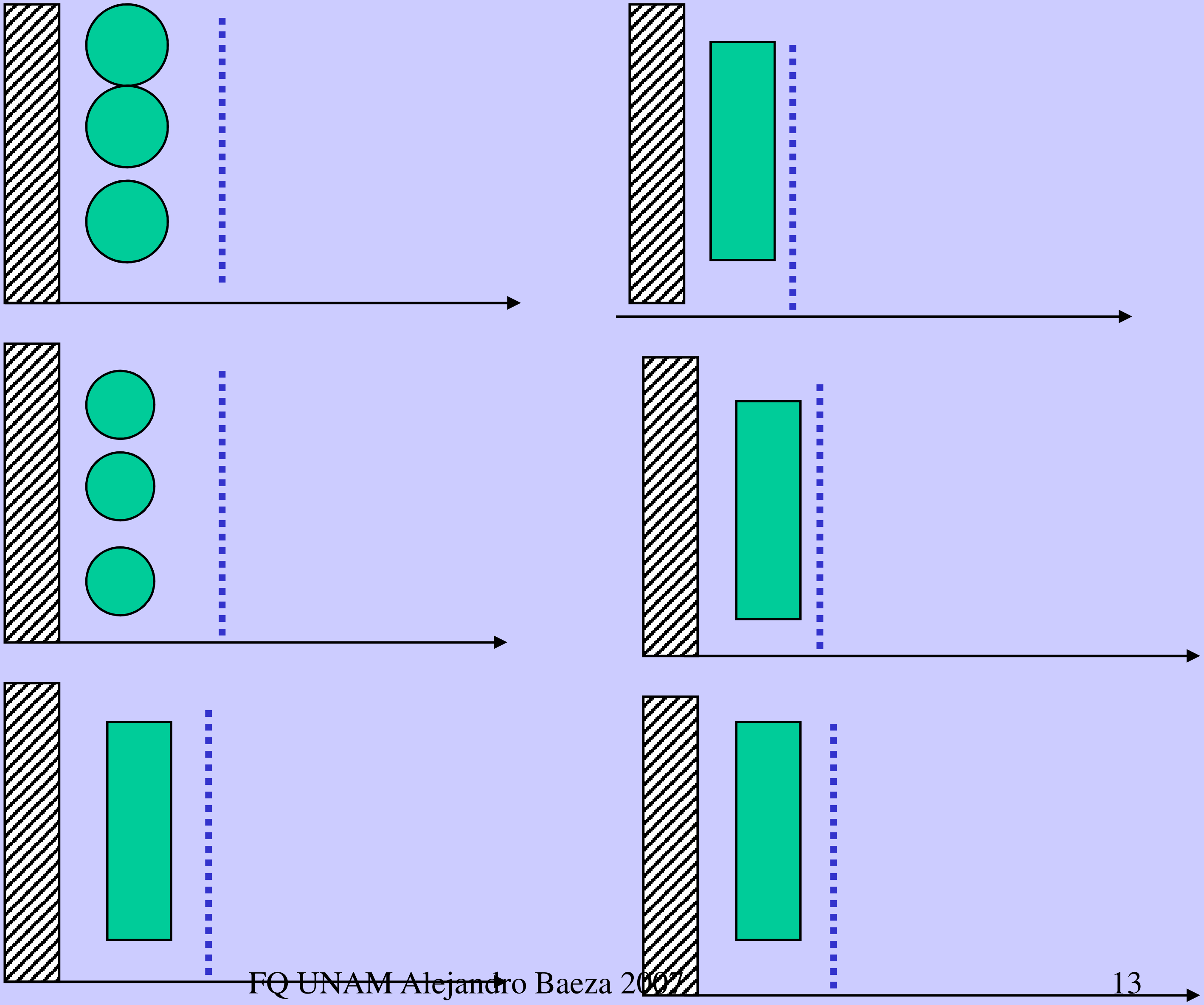
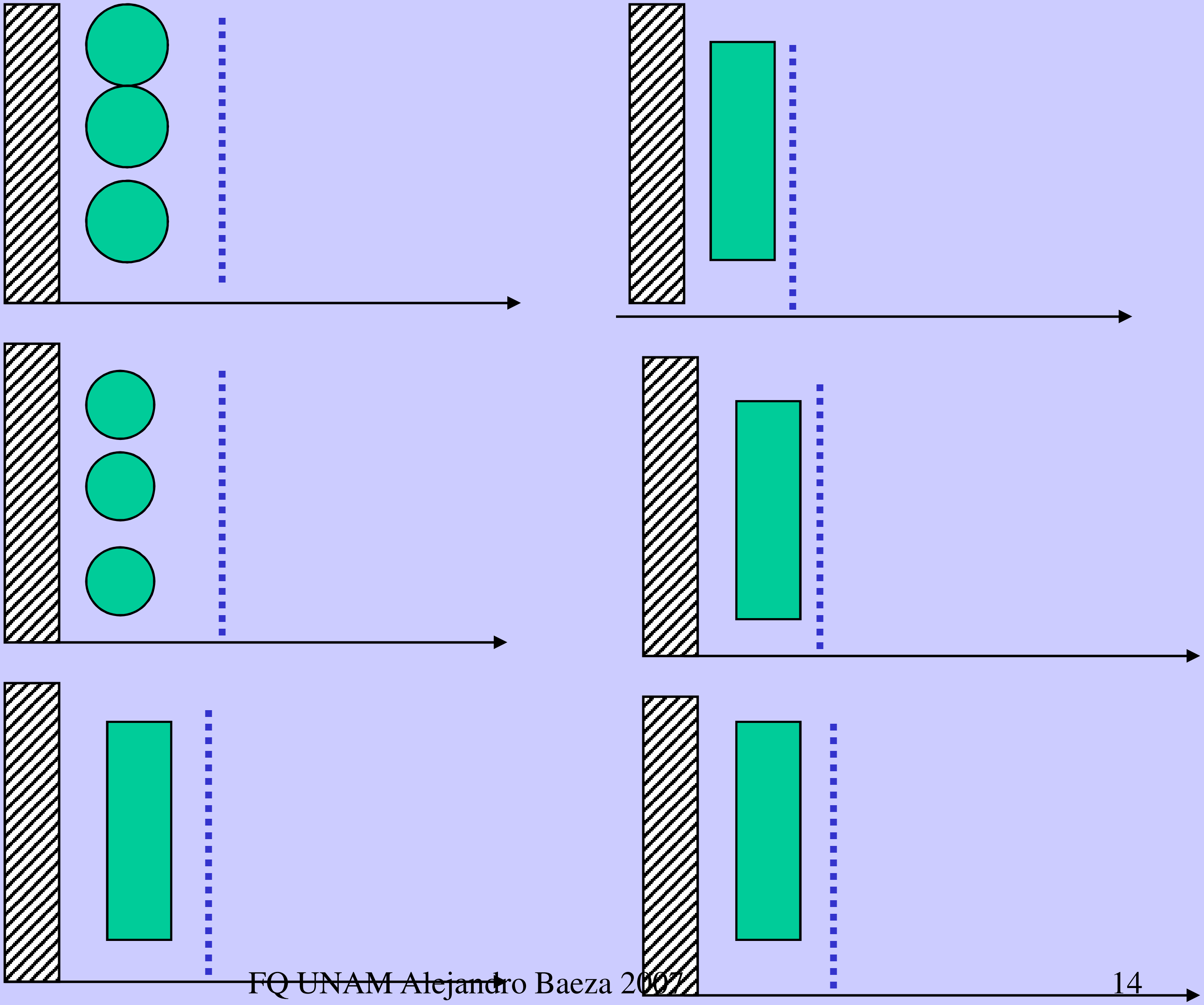
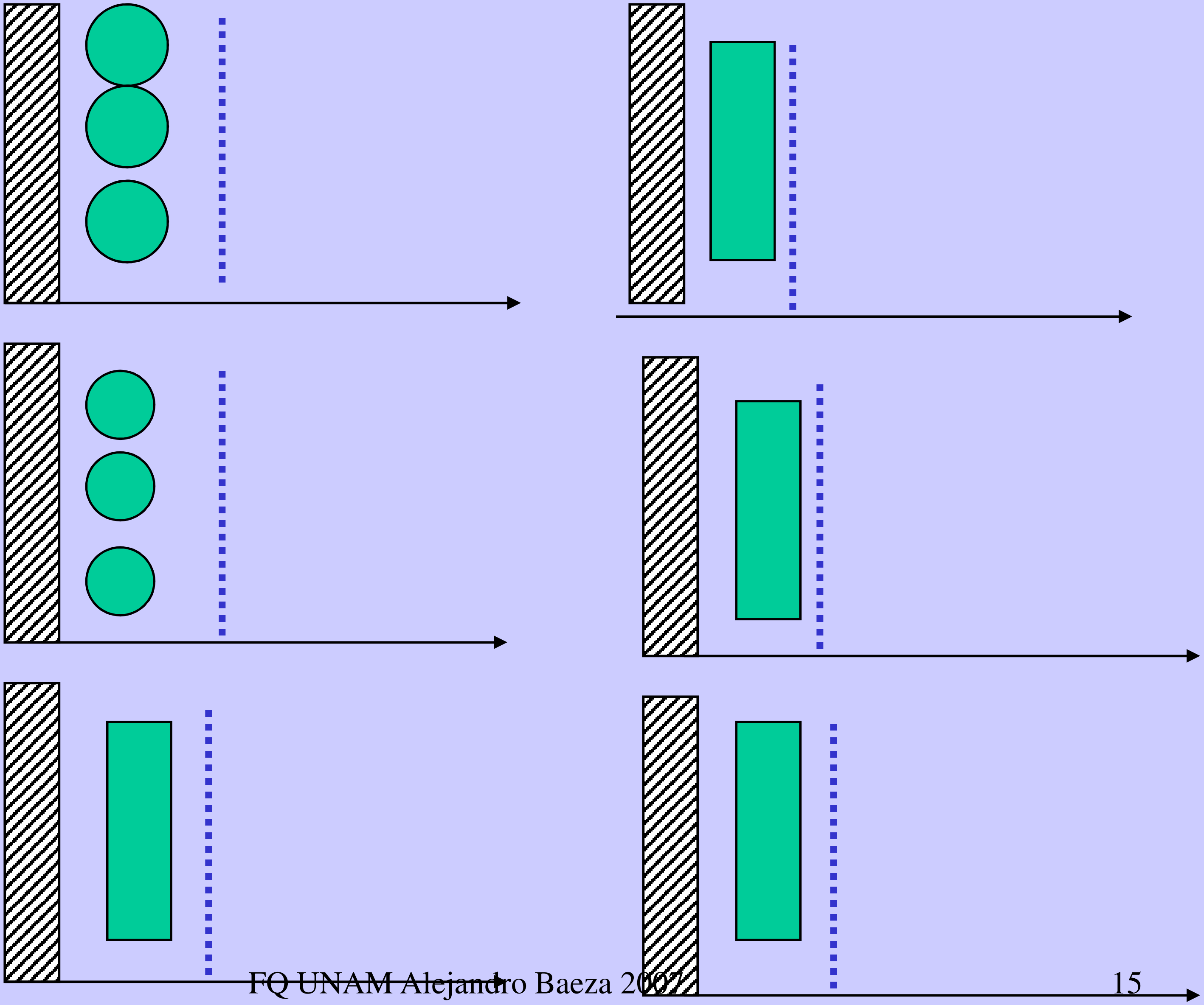
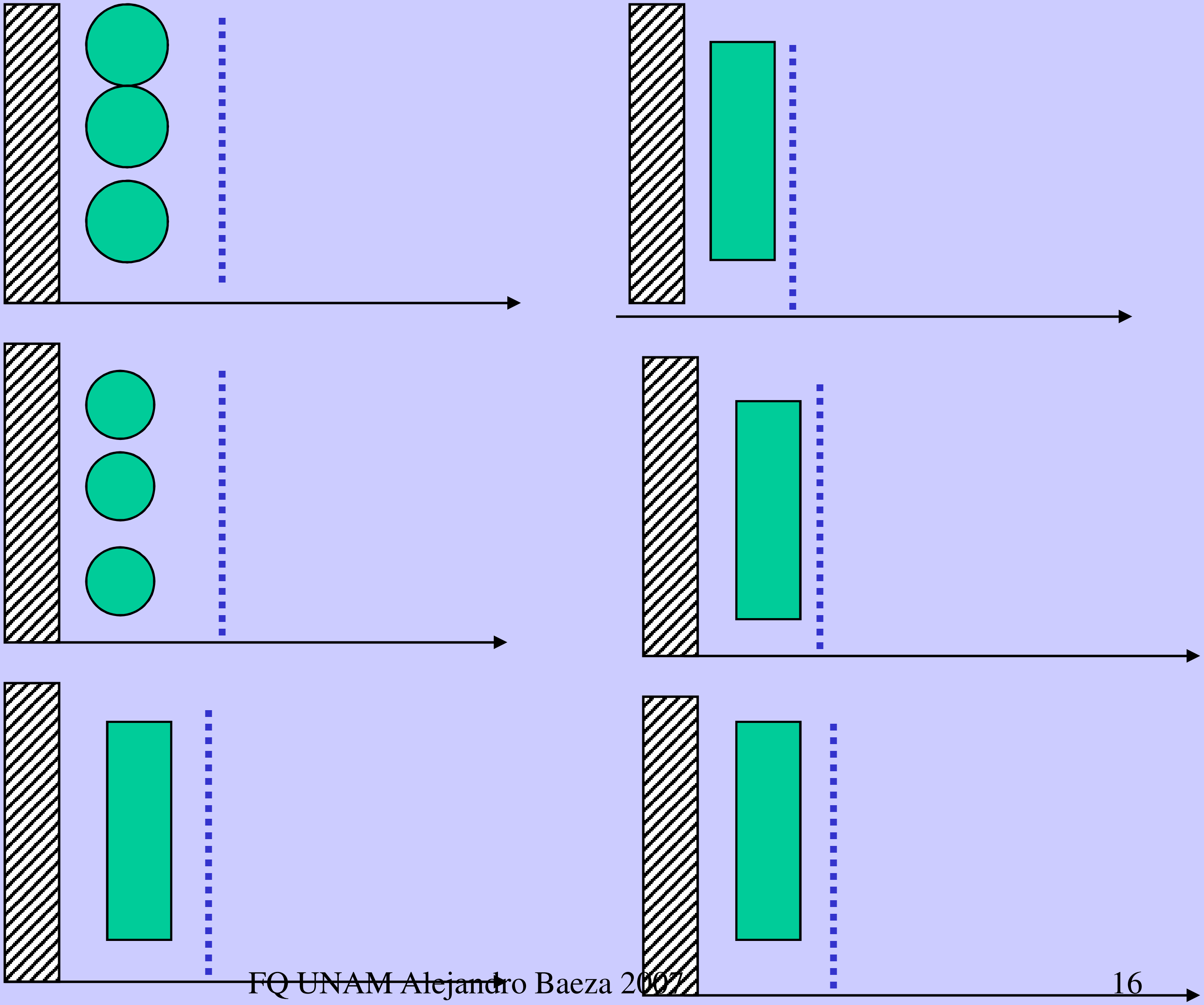


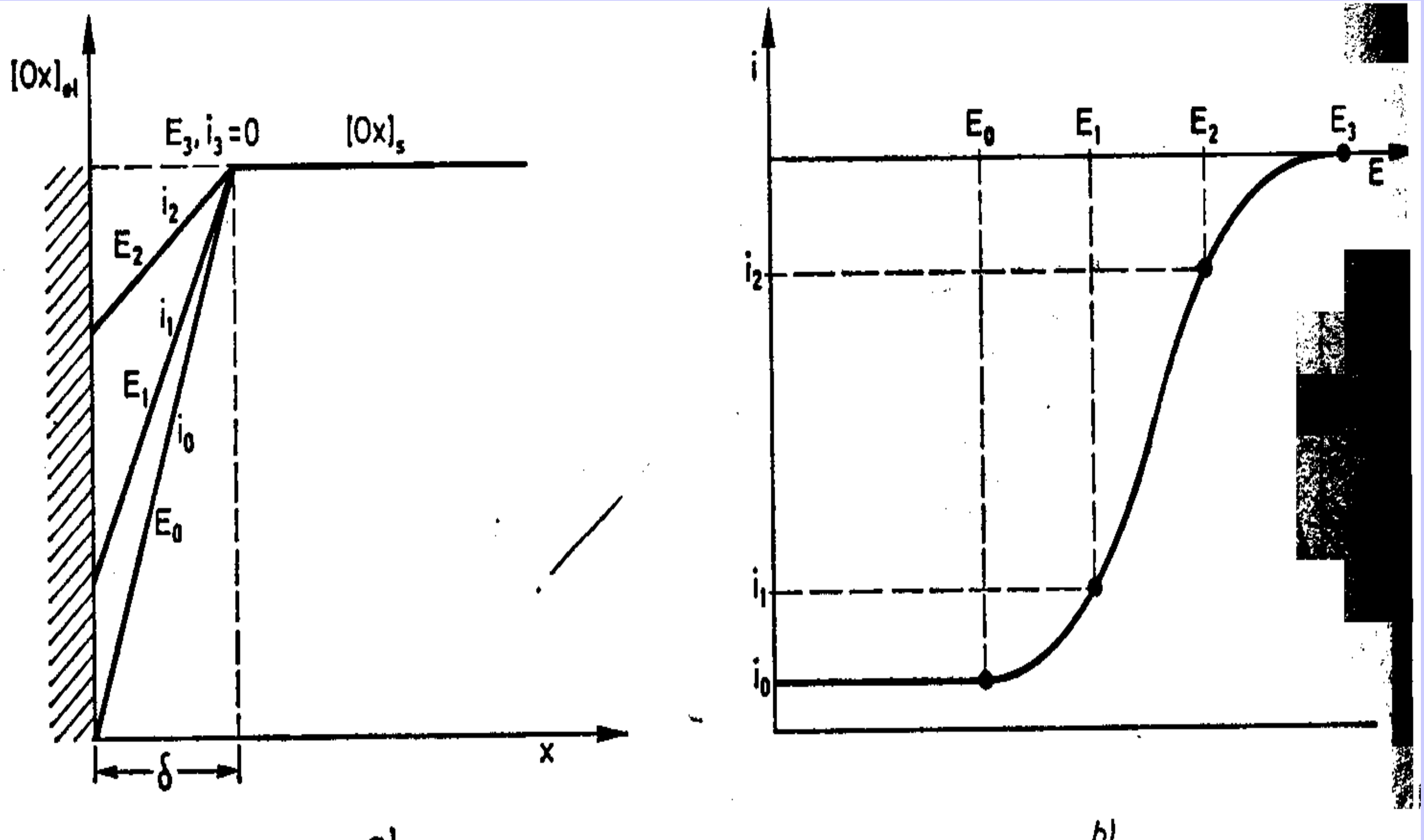
FIG. 2.13. *a)* Variación del perfil de la concentración de Ox en función del potencial aplicado al electrodo y de la distancia al mismo; *b)* variación de la corriente [illegible] en función del potencial.











a)

b)

Fig. 2.13. *a)* Variación del perfil de la concentración de Ox en función del potencial aplicado al electrodo y de la distancia al mismo; *b)* variación de la corriente de reducción en función del potencial.

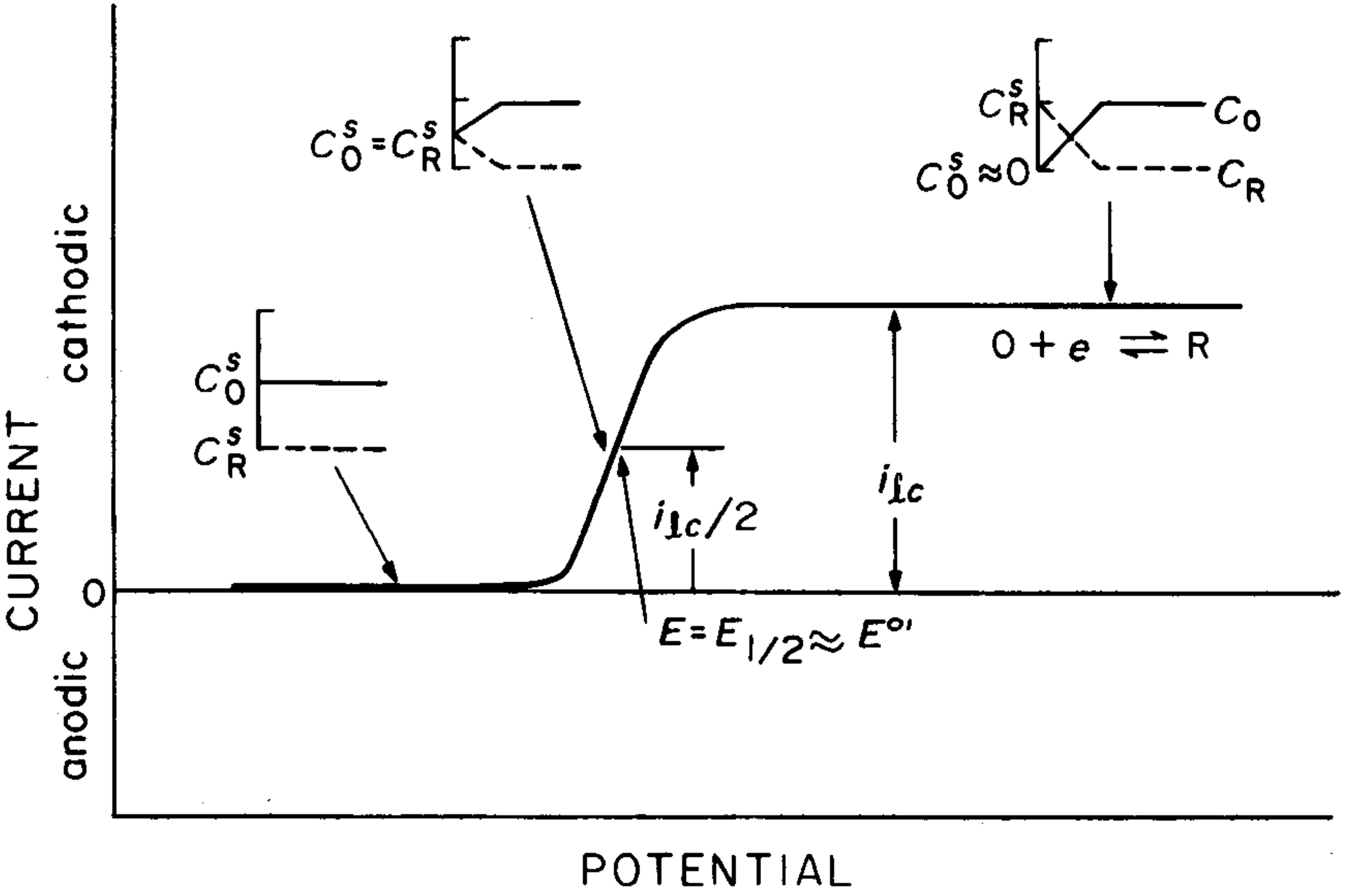
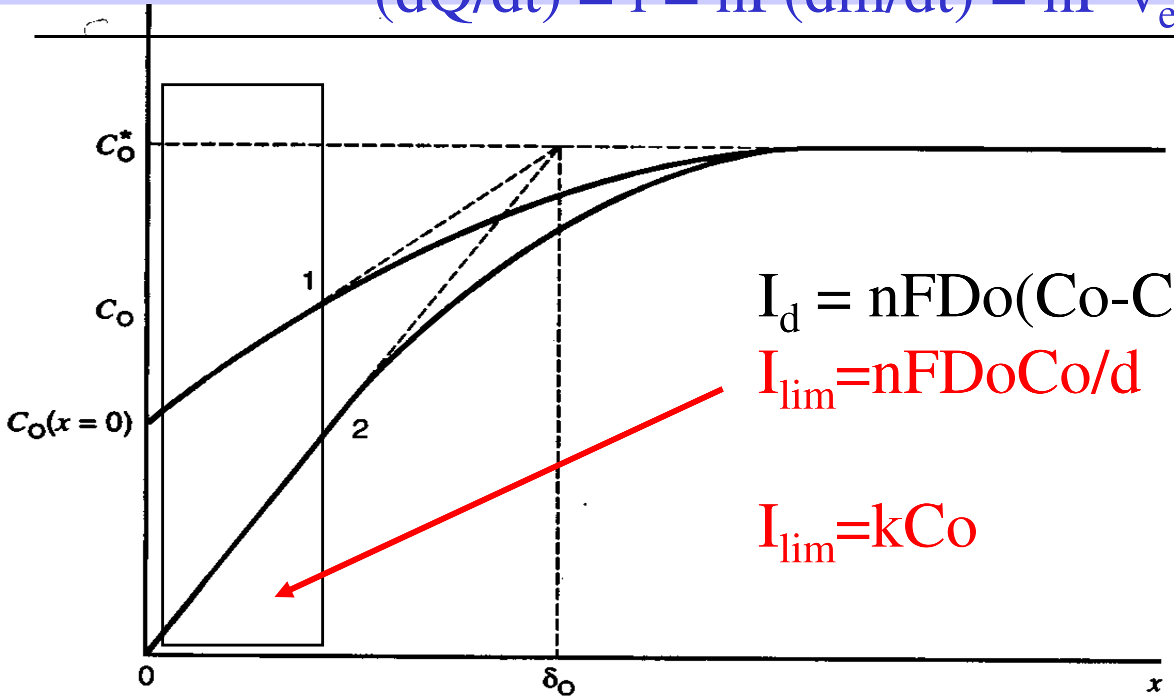


Figure 4-2 / Hydrodynamic voltammogram with representative concentration-distance profiles for a solution containing 1 m*M* of O and no R.

$$(dQ/dt) = i = nF(dm/dt) = nF\ v_{elec}$$



$$I_d = nFDo(Co-C_{el})/\delta$$

$$I_{lim}=nFDoCo/d$$

$$I_{lim}=kCo$$

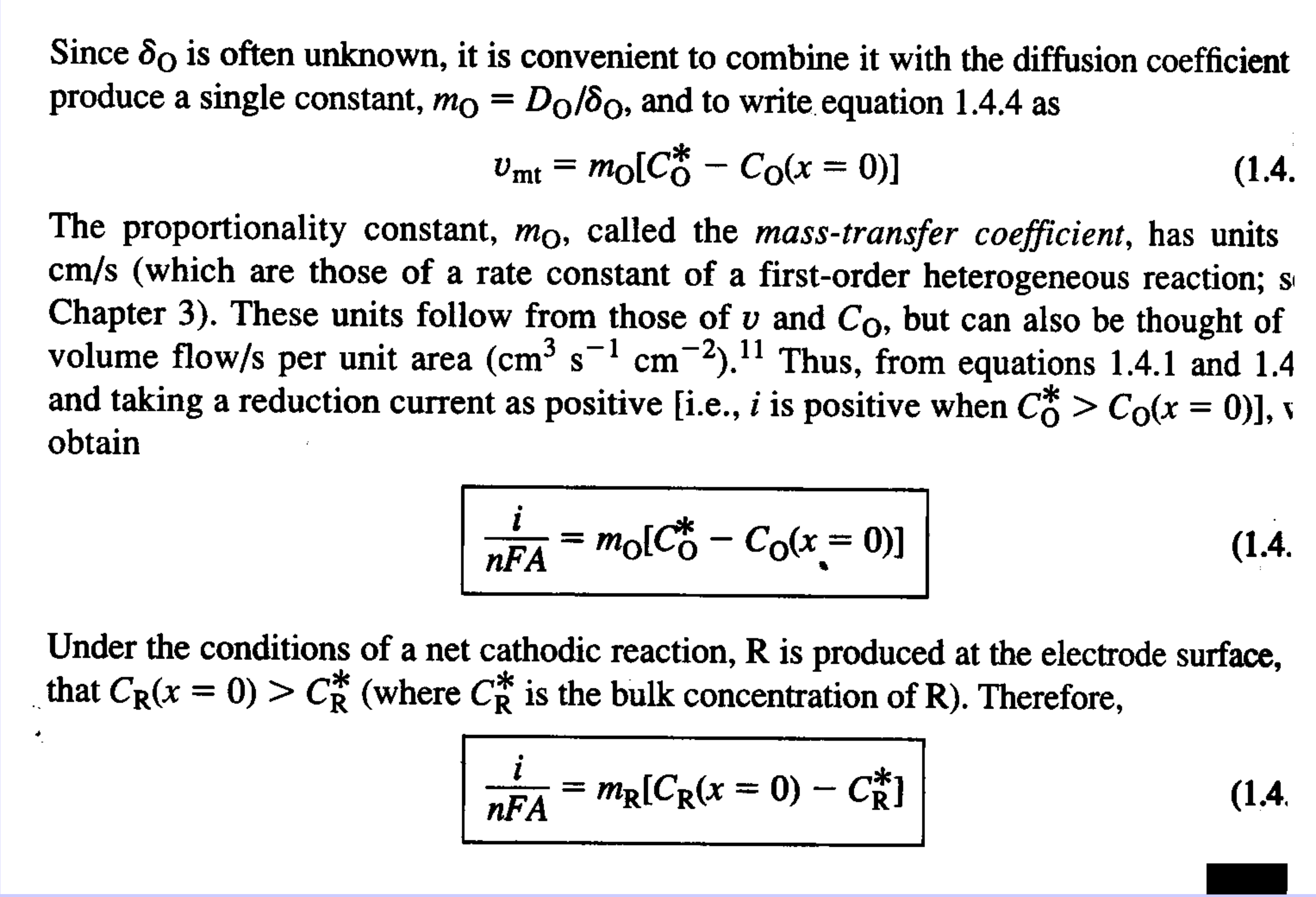
Figure 1.4.1 Concentration profiles (solid lines) and diffusion layer approximation (dashed lines). $x = 0$ corresponds to the electrode surface and δ_O is the diffusion layer thickness. Concentration profiles are shown at two different electrode potentials: (*1*) where $C_O(x = 0)$ is about $C^*_O/2$, (*2*) where $C_O(x = 0) \approx 0$ and $i = i_l$.

the electrode surface, as given by the first (diffusive) term in equation 1.4.2.

$$v_{\mathrm{mt}} \propto (dC_{\mathrm{O}}/dx)_{x=0} = D_{\mathrm{O}}(dC_{\mathrm{O}}/dx)_{x=0} \tag{1.4.3}$$

If one further assumes a linear concentration gradient within the diffusion layer, then, from equation 1.4.3

$$v_{\mathrm{mt}} = D_{\mathrm{O}}[C_{\mathrm{O}}^{*} - C_{\mathrm{O}}(x = 0)]/\delta_{\mathrm{O}} \tag{1.4.4}$$



Since δ_O is often unknown, it is convenient to combine it with the diffusion coefficient produce a single constant, $m_O = D_O/\delta_O$, and to write equation 1.4.4 as

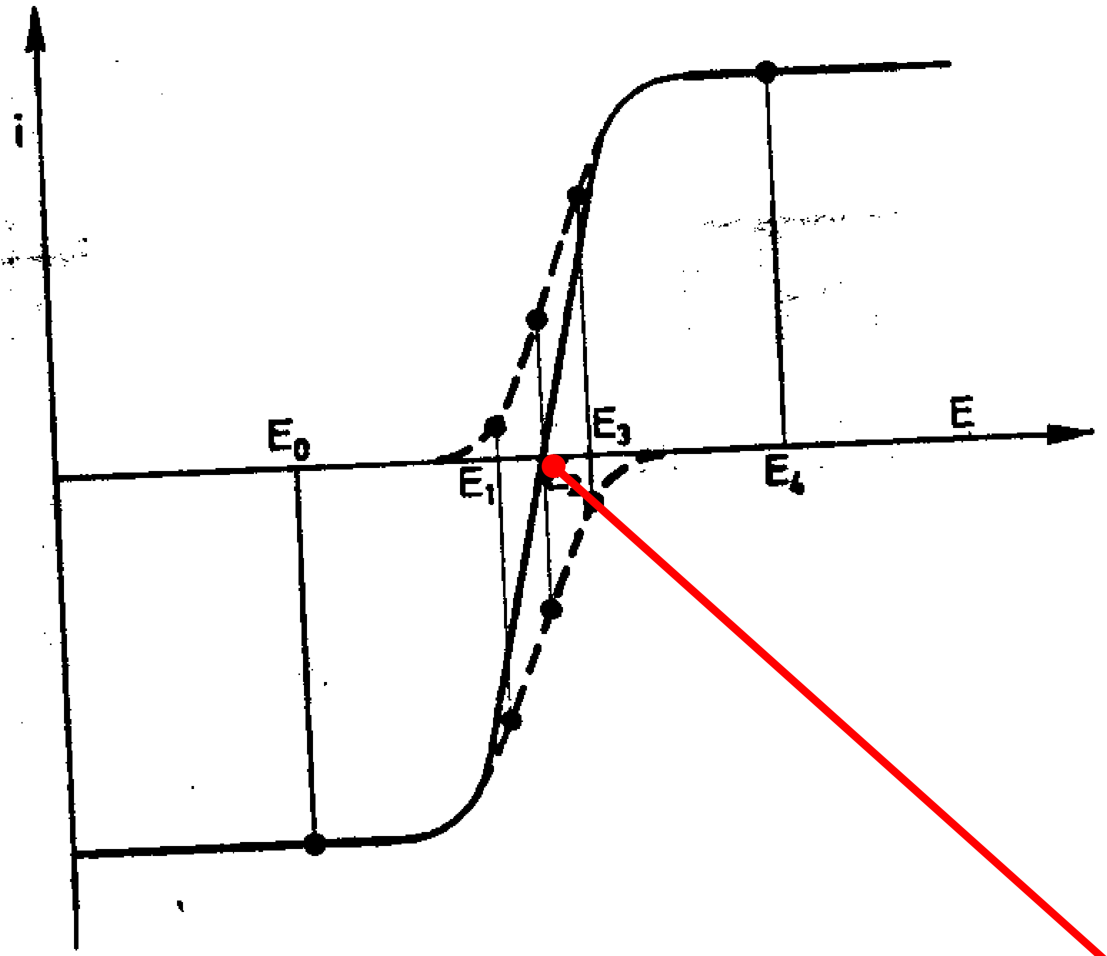
$$v_{mt} = m_O[C_O^* - C_O(x = 0)] \qquad (1.4.$$

The proportionality constant, m_O, called the *mass-transfer coefficient*, has units cm/s (which are those of a rate constant of a first-order heterogeneous reaction; s Chapter 3). These units follow from those of v and C_O, but can also be thought of volume flow/s per unit area ($cm^3\ s^{-1}\ cm^{-2}$).[11] Thus, from equations 1.4.1 and 1.4 and taking a reduction current as positive [i.e., i is positive when $C_O^* > C_O(x = 0)$], obtain

$$\boxed{\frac{i}{nFA} = m_O[C_O^* - C_O(x = 0)]} \qquad (1.4.$$

Under the conditions of a net cathodic reaction, R is produced at the electrode surface, that $C_R(x = 0) > C_R^*$ (where C_R^* is the bulk concentration of R). Therefore,

$$\boxed{\frac{i}{nFA} = m_R[C_R(x = 0) - C_R^*]} \qquad (1.4.$$



Curva intensidad-potencial global, correspondiente a la reacción electroquímica $\mathrm{Ox} + ne \rightleftharpoons \mathrm{Red}$.

$$I_{total} = i_{oxidación} - i_{reducción} \ : \quad \text{EQUILIBRIO} \quad i_{oxidac} = i_{reducc;} \ I_T = 0$$

Controlled potential:

(Cottrell equation)

$$i(t) = \boxed{\frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}}}$$ ✓

(Ilkovic equation)

$$i_d = \boxed{\underbrace{708nD_O^{1/2}}}\,C_O^*\,\boxed{\underbrace{m^{2/3}t^{1/6}}}$$ ✓

Controlled current:

(Sand equation)

$$\tau^{1/2} = \boxed{\frac{nFAD_O^{1/2}\pi^{1/2}}{2\,i}}\,\mathrm{Co}^*$$

Rotating disk electrode:

(Levich equation)

$$i_l = \boxed{0.620nFAD_O^{2/3}\omega^{1/2}\nu^{-1/6}}\,C_O^*$$

[Linear potential sweep (peak current, reversible wave)]

$$i_p = \boxed{(2.69 \times 10^5)n^{3/2}AD_O^{1/2}v^{1/2}}\,C_O^*$$

I_{lim}=mCo

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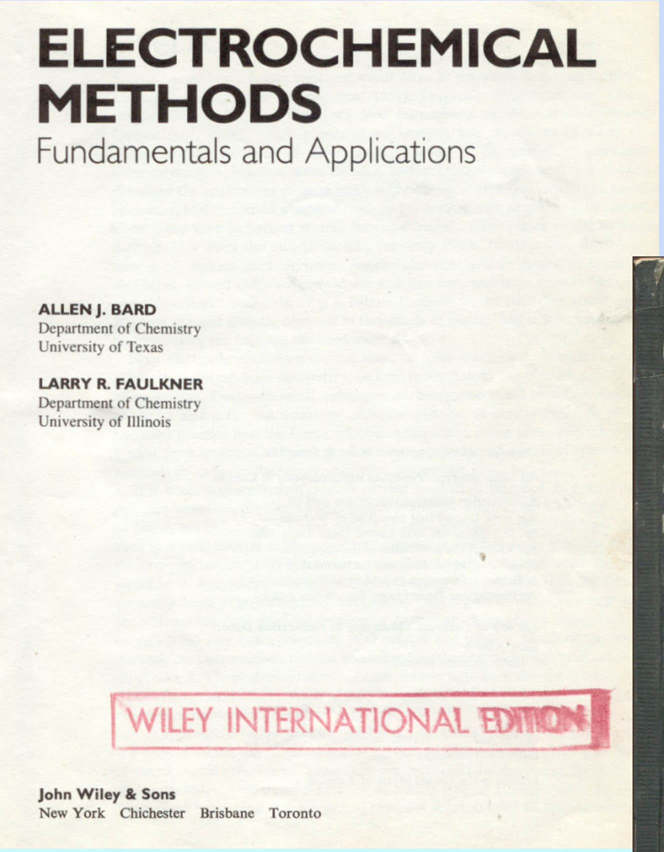

ELECTROCHEMICAL METHODS
Fundamentals and Applications

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fundamentos y aplicaciones
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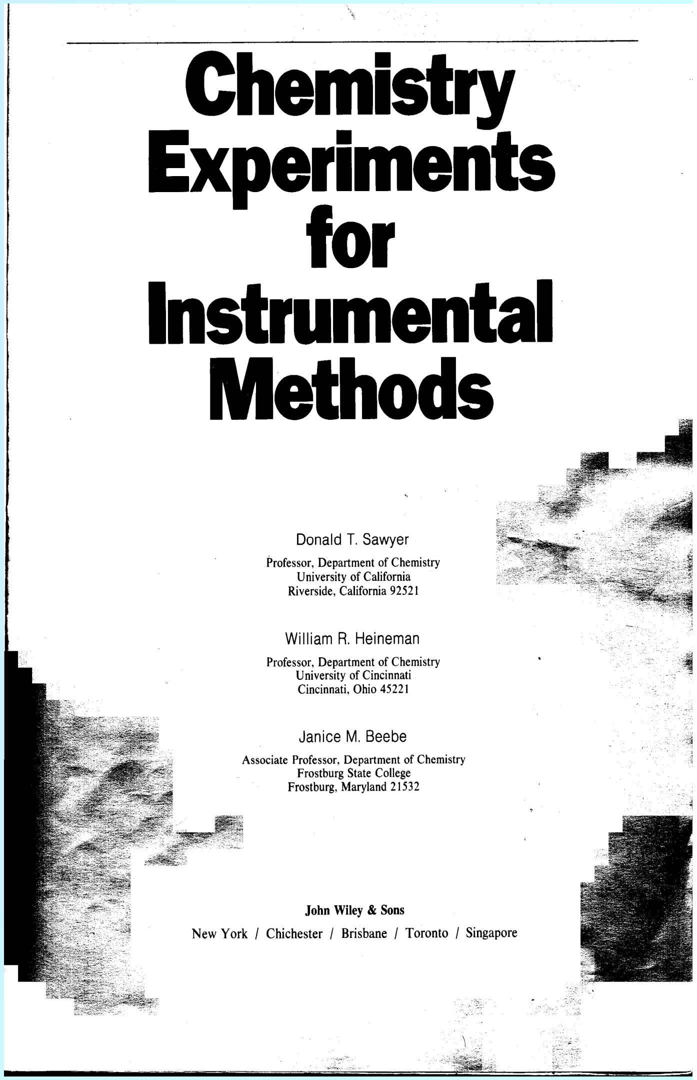

Chemistry Experiments for Instrumental Methods

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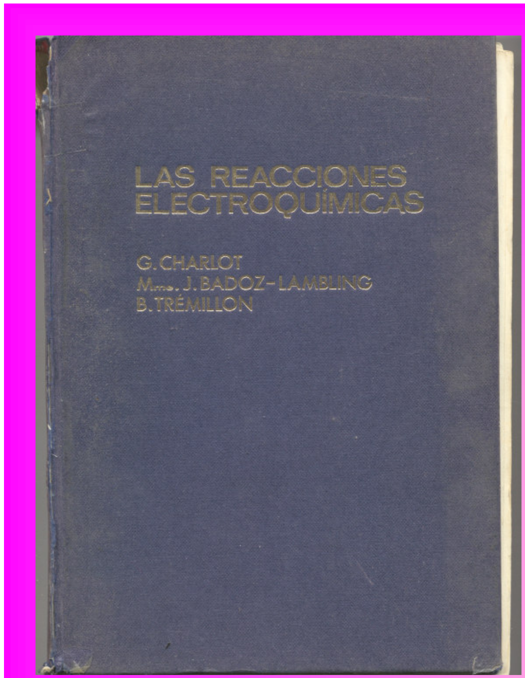

LAS REACCIONES ELECTROQUIMICAS

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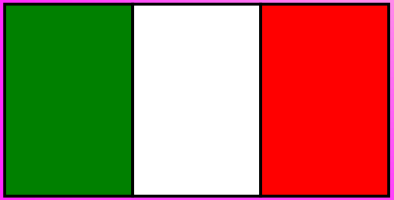

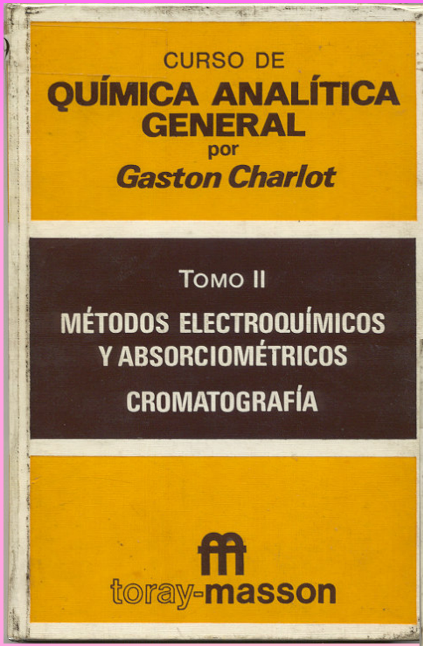

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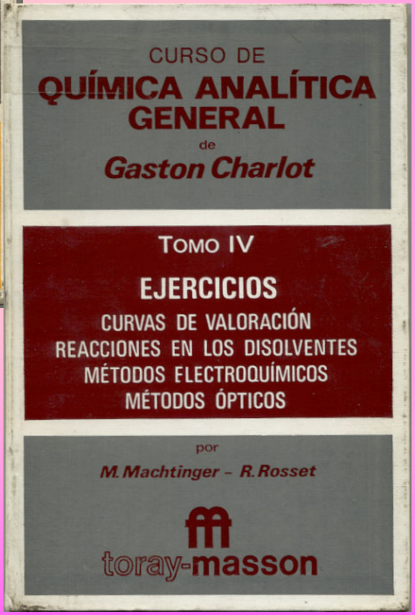

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MÉTODOS ÓPTICOS

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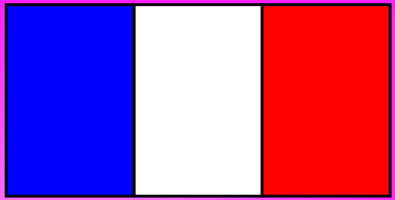

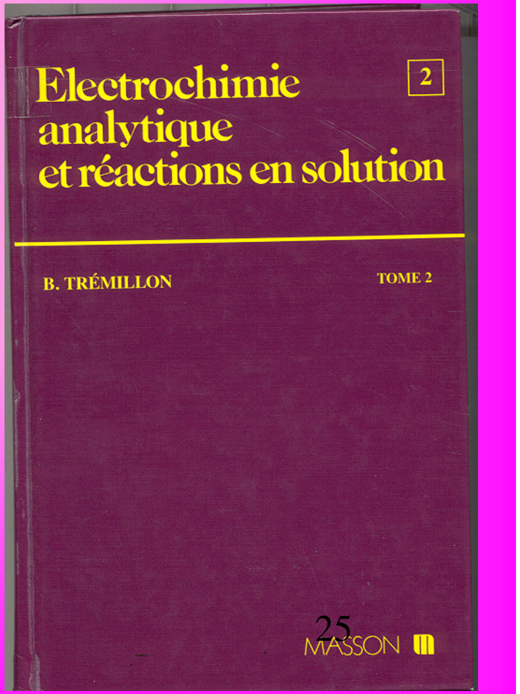

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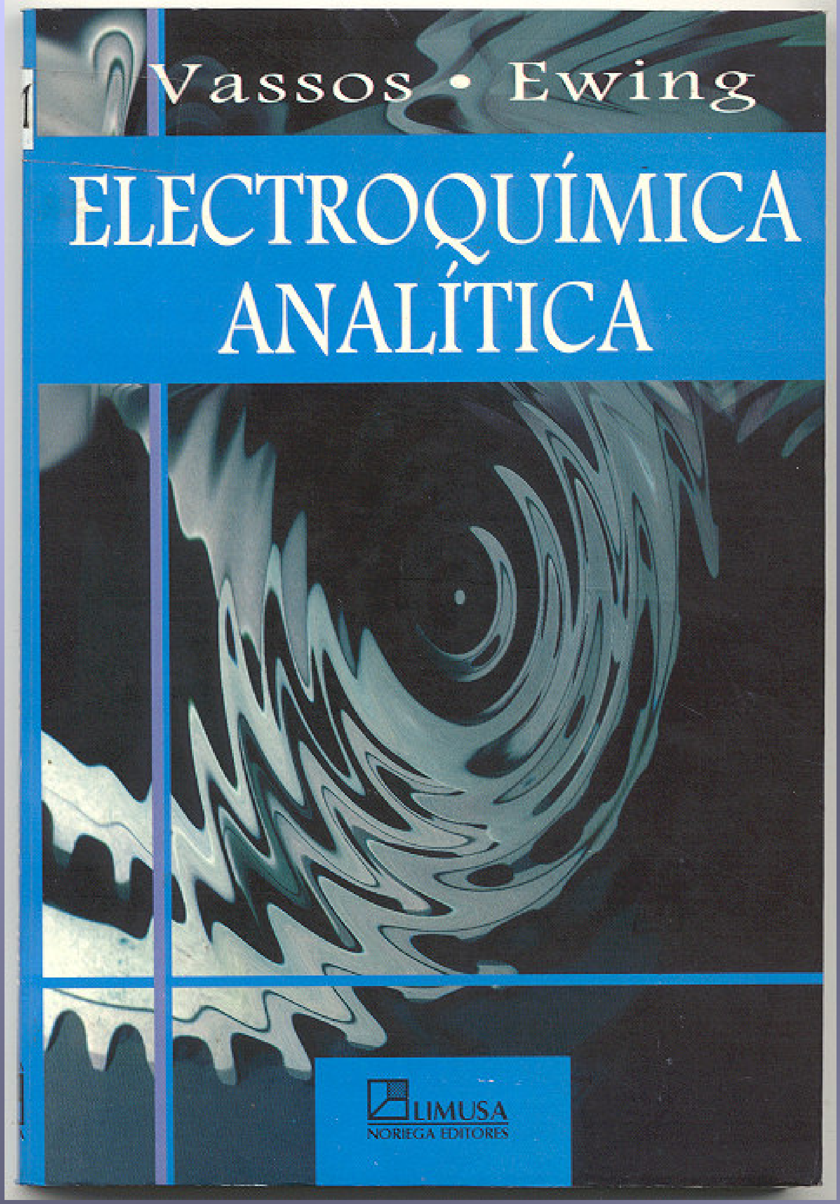

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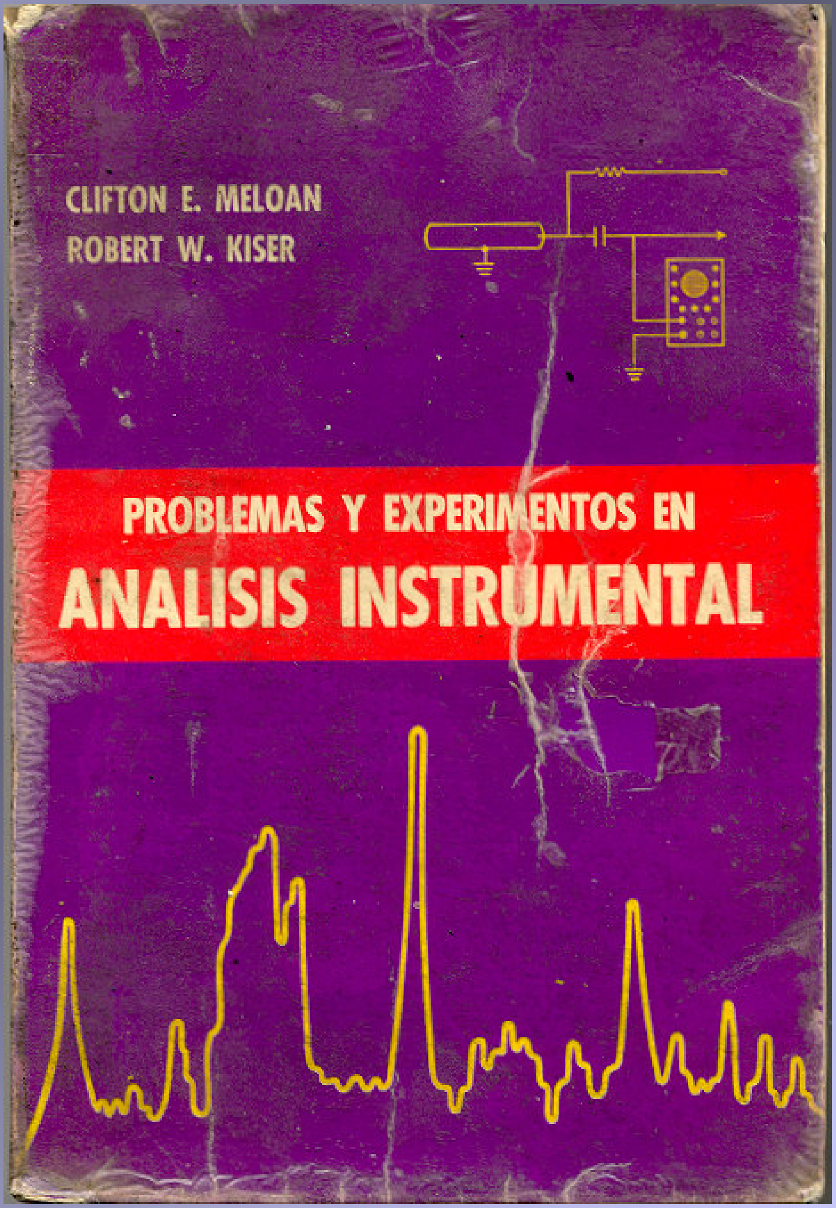

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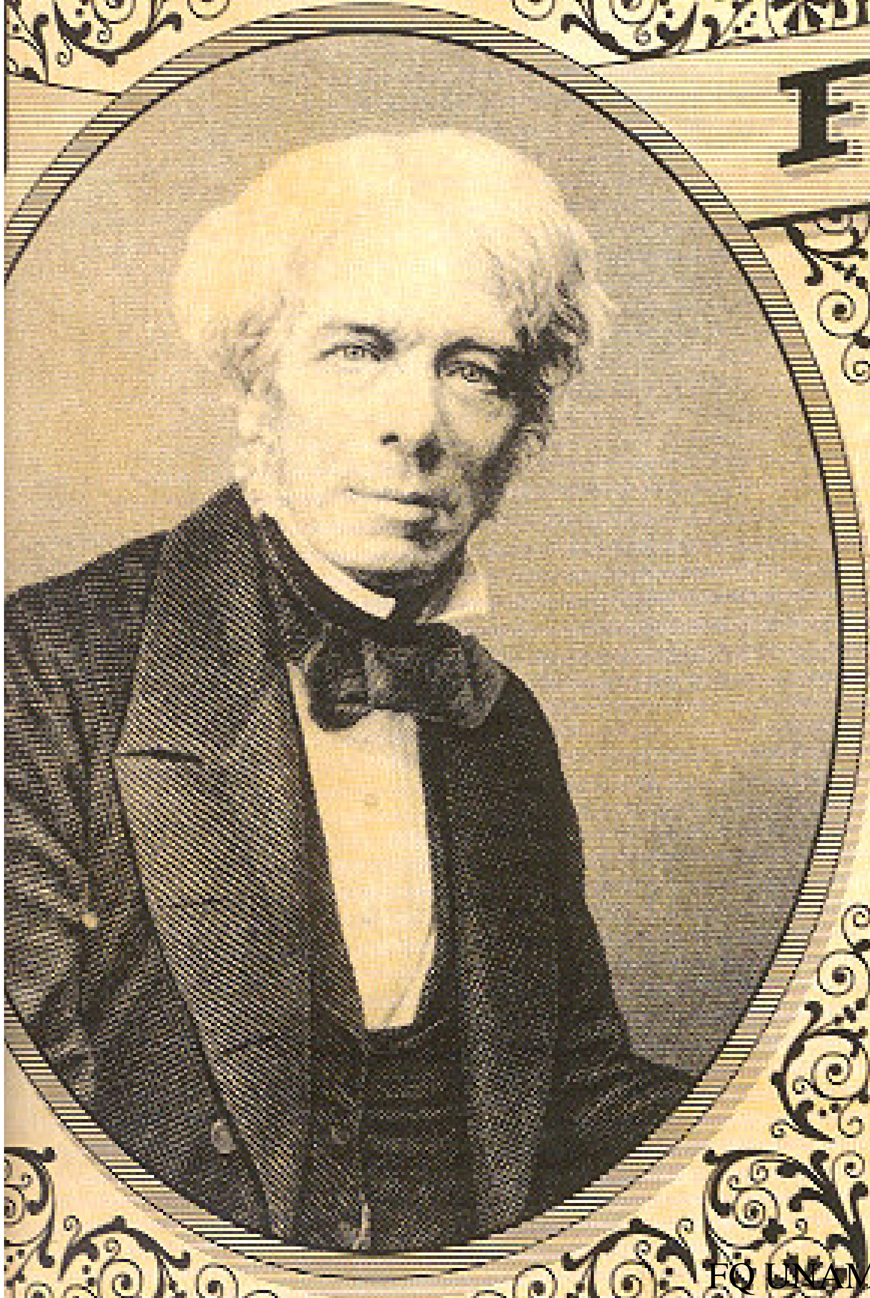

Faraday

To omit the mention of Humphry Davy from any discussion of Michael Faraday's (1791-1867) contribution to electrochemistry would be to omit an essential element of a key equation.

Davy was Faraday's mentor in his early years of physics and electrochemistry research. For a time, in fact, Faraday extended and developed the research begun by Davy at the Royal Institution in London, where Faraday began his career in 1813 as Davy's Laboratory Assistant. Most of Faraday's early experiments — and published papers — bore the stamp of Davy's involvement.

Faraday achieved scientific prominence of his own for the First Law of Electrochemistry, developed in 1834: "The chemical power of a current of electricity is in direct proportion to the absolute quantity of electricity which passes."

The Second Law of Electrochemistry, also defined by Faraday, states: "Electrochemical equivalents coincide, and are the same, with ordinary chemical equivalents."

The work that led to these two laws also resulted in many of the modern electrochemical terms — electrode, electrolyte, and ion, to name a few — all coined by Faraday.

But Faraday didn't consider himself an electrochemist; he preferred the title of "natural philosopher" and devoted his life to proving the interconnection of natural forces. His electrochemical research was one outcome of this effort, exploring the connection between the chemical and electrical forces of the voltaic battery. Among Faraday's greatest accomplishments are:

- His discovery of electromagnetic induction and the related development of the first transformer, electric generator, and the electric motor.
- Development of fundamental laws of electromagnetism.
- Discovery of the "Faraday Effect", the rotation of the plane of polarization of light by a magnetic field (which later served as the foundation for the field of magneto-optics).
- Discovery of paramagnetism and diamagnetism

Faraday was also a superb lecturer and initiated two lecture series, the "Friday Evening Discourses" and the "Christmas Lectures" at the Royal Institution. Both series continue to this day. Though he arose from very humble beginnings, left school at the age of 12 and was essentially self-taught, Faraday came to be respected as one of the greatest of all scientists.