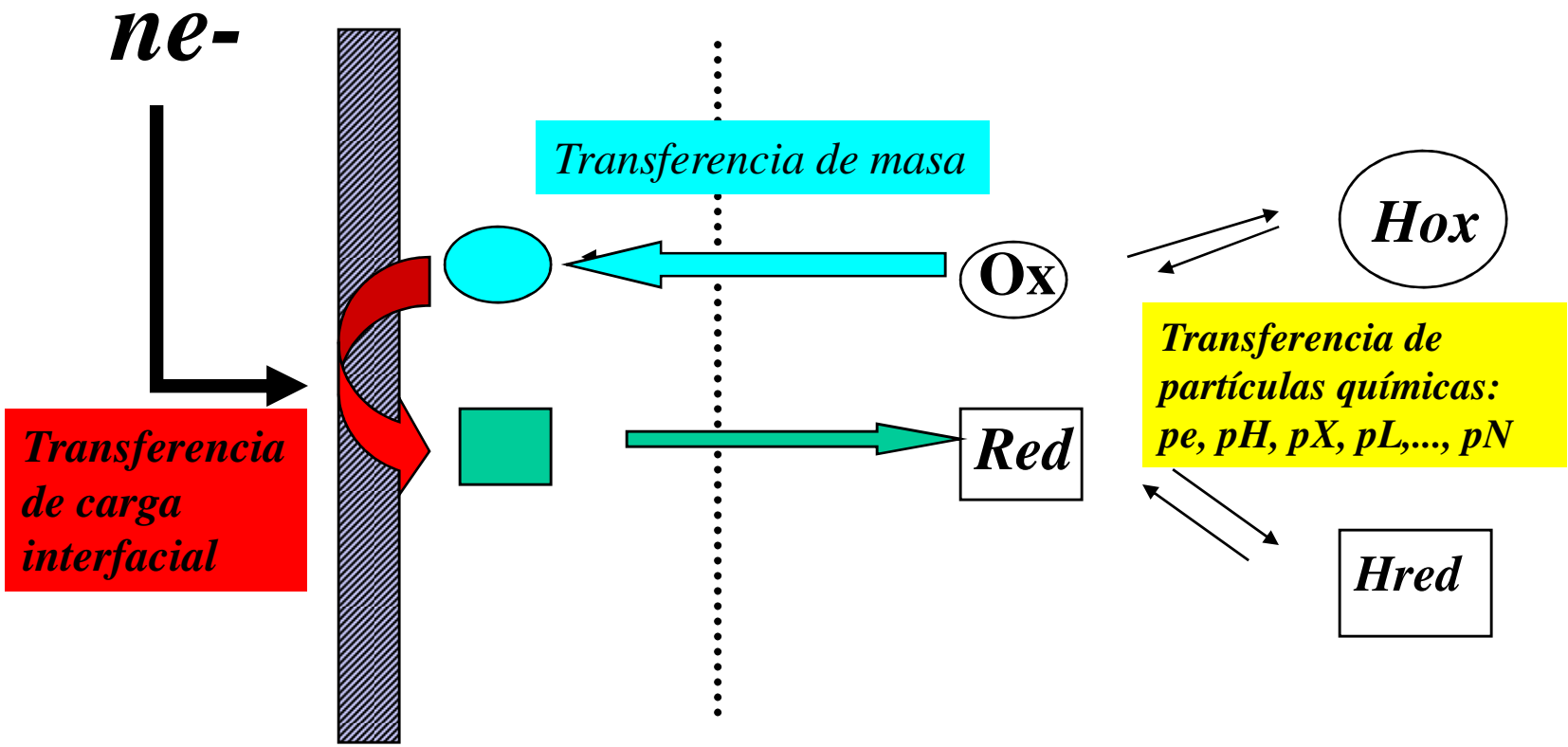
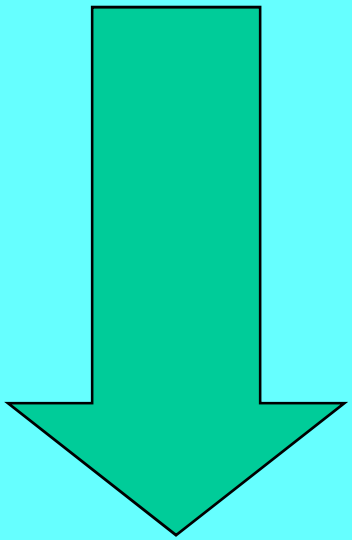
# Cinética electródica

# *Procesos cinéticos al electrodo*



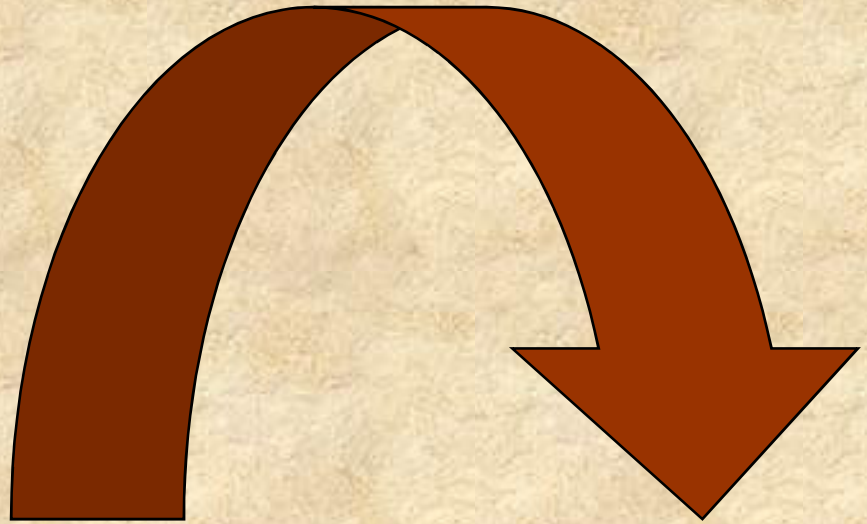
# *Transferencia de masa*



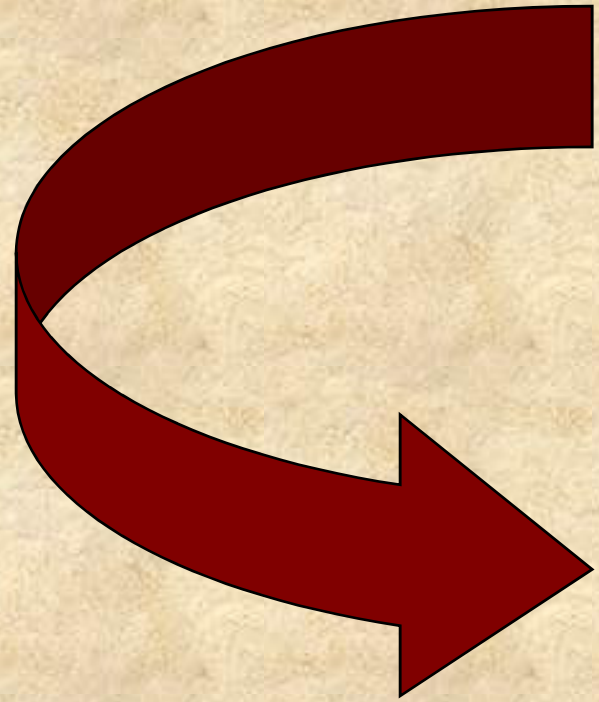
***Régimen hidrodinámico Controlado:***

- ***EGD***
- ***EGM***
- ***Difusión pura***
- ***Microelectrodos***
- ***Electrolito soporte***

***Transferencia de partículas químicas***

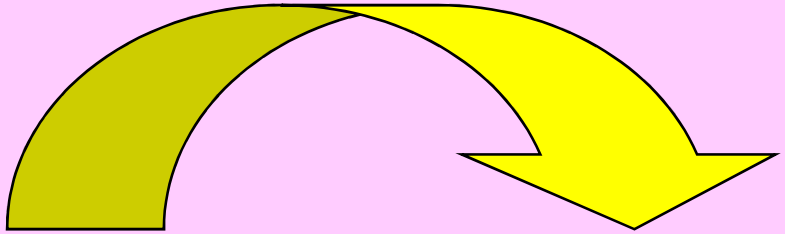


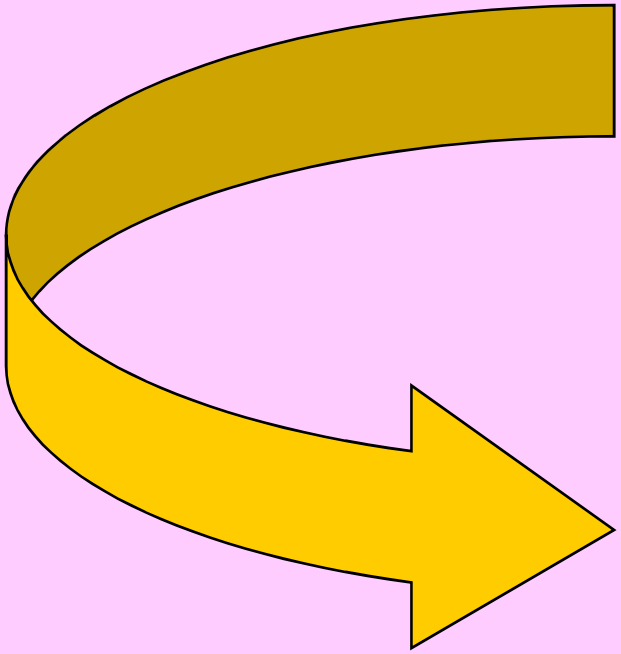
***Amortiguamiento Múltiple, pe=f(pH,pL,pM)***



***Disolvente***
***Temperatura, Fuerza iónica***
***Estructura***
***Catalizadores,***

# *Cinetica De transferencia de carga interfacial*





***Naturaleza del electrodo: Pt, Ru, Pd, Hg, C, etc.***

***Electrodos modificados***

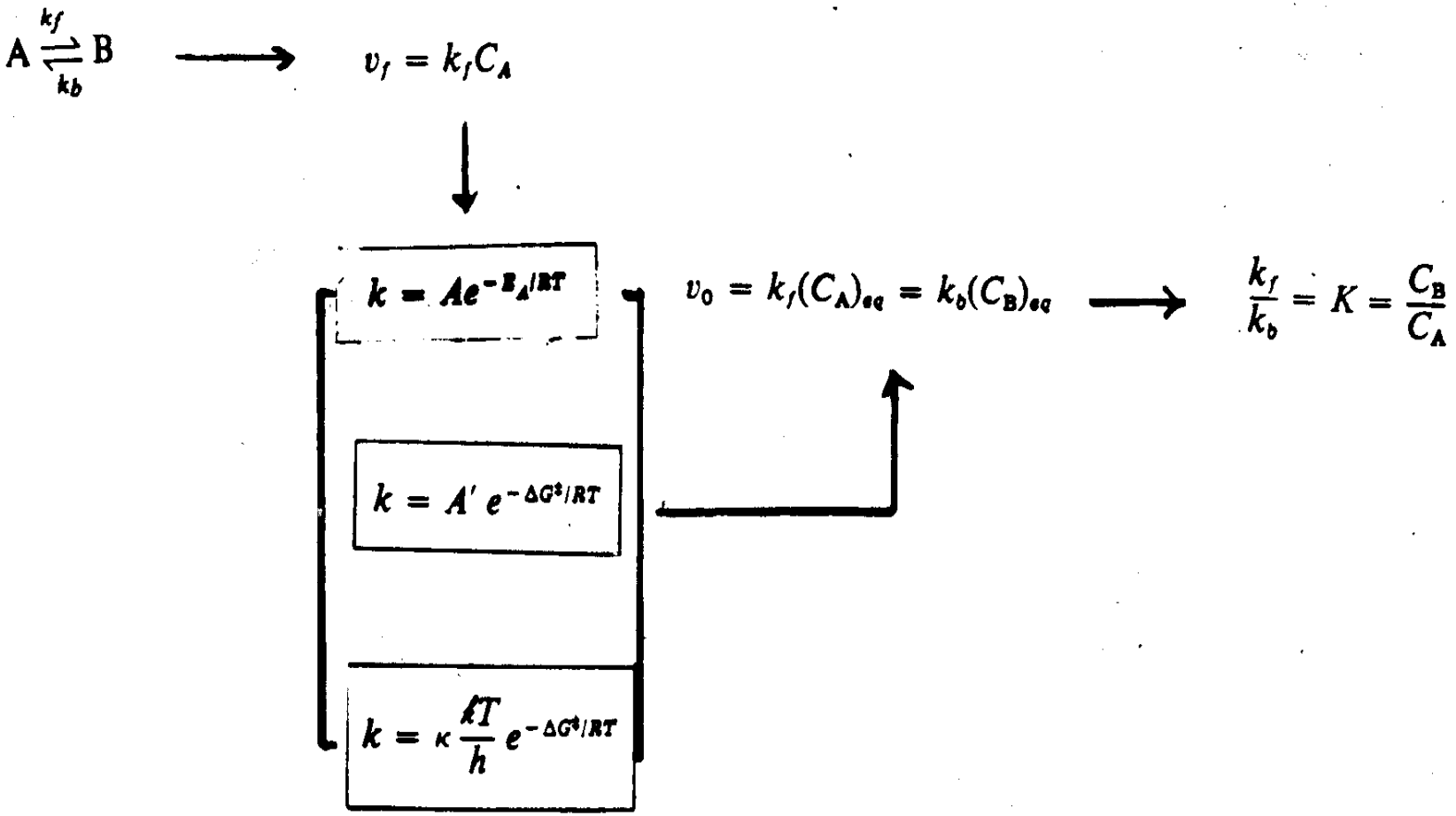
***Catalizadores***

***Disolvente***

***Temperatura***

# ¿cómo afecta a las curvas I/E la cinética electródica?

## HOMOGENEOUS KINETICS



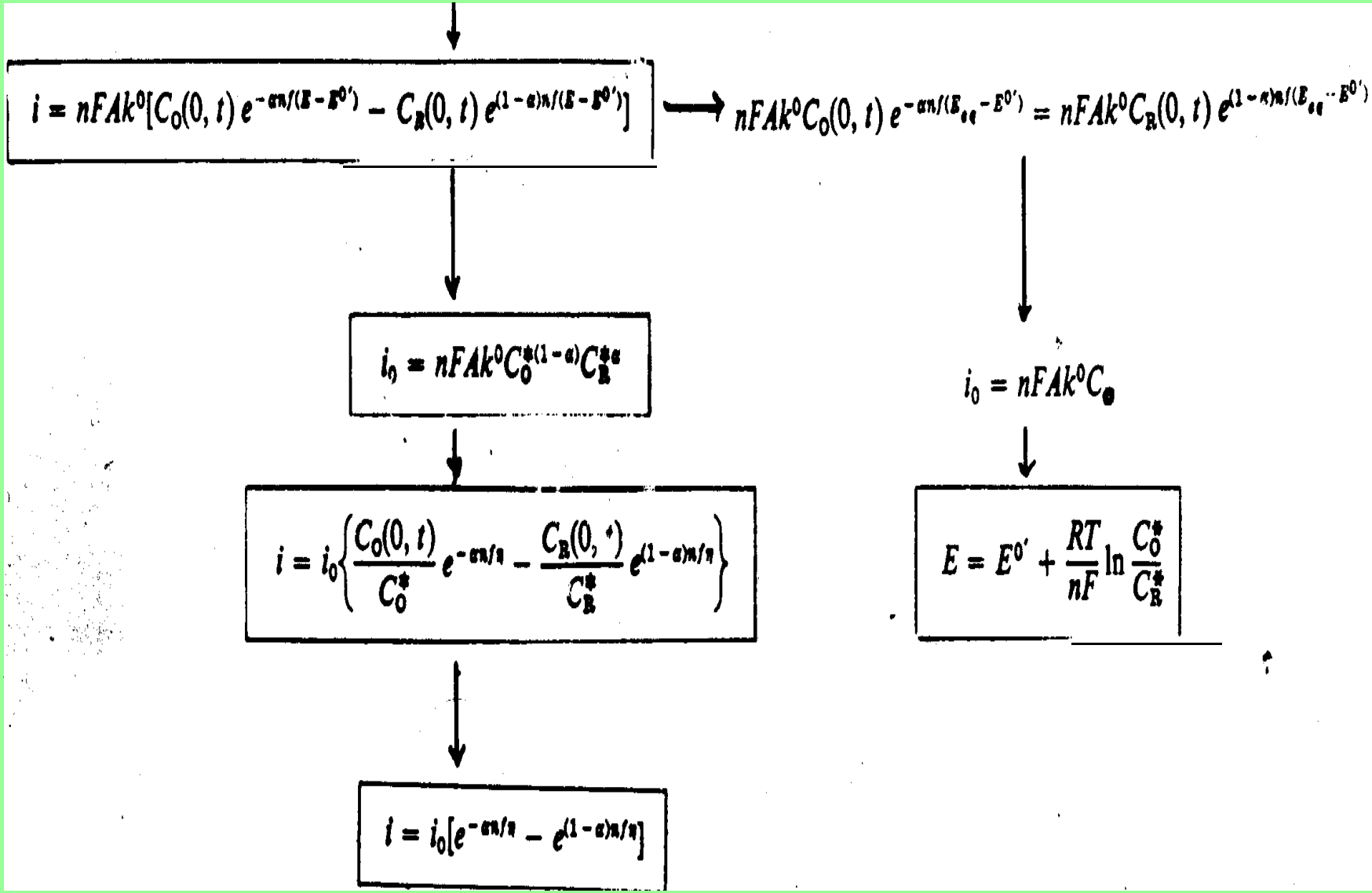
# ELECTRODE REACTIONS

$$O + ne \underset{k_b}{\overset{k_f}{\rightleftharpoons}} R \longrightarrow v_f = k_f C_O(0, t) = \frac{i_c}{nFA}$$

$$\eta = a + b \log i$$

$$k_f = k^0 e^{-\alpha n f (E - E^{0'})}$$

$$k_b = k^0 e^{(1-\alpha) n f (E - E^{0'})}$$


$i = nFAk^0[C_O(0,t)\,e^{-\alpha n/(E-E^{0'})} - C_R(0,t)\,e^{(1-\alpha)n/(E-E^{0'})}]$
$nFAk^0C_O(0,t)\,e^{-\alpha n/(E_{eq}-E^{0'})} = nFAk^0C_R(0,t)\,e^{(1-\alpha)n/(E_{eq}-E^{0'})}$
$i_0 = nFAk^0C_O^{*(1-\alpha)}C_R^{*\alpha}$
$i_0 = nFAk^0C_\bullet$
$i = i_0\left\{\frac{C_O(0,t)}{C_O^*}e^{-\alpha n/\eta} - \frac{C_R(0,t)}{C_R^*}e^{(1-\alpha)n/\eta}\right\}$
$E = E^{0'} + \frac{RT}{nF}\ln\frac{C_O^*}{C_R^*}$
$i = i_0[e^{-\alpha n/\eta} - e^{(1-\alpha)n/\eta}]$

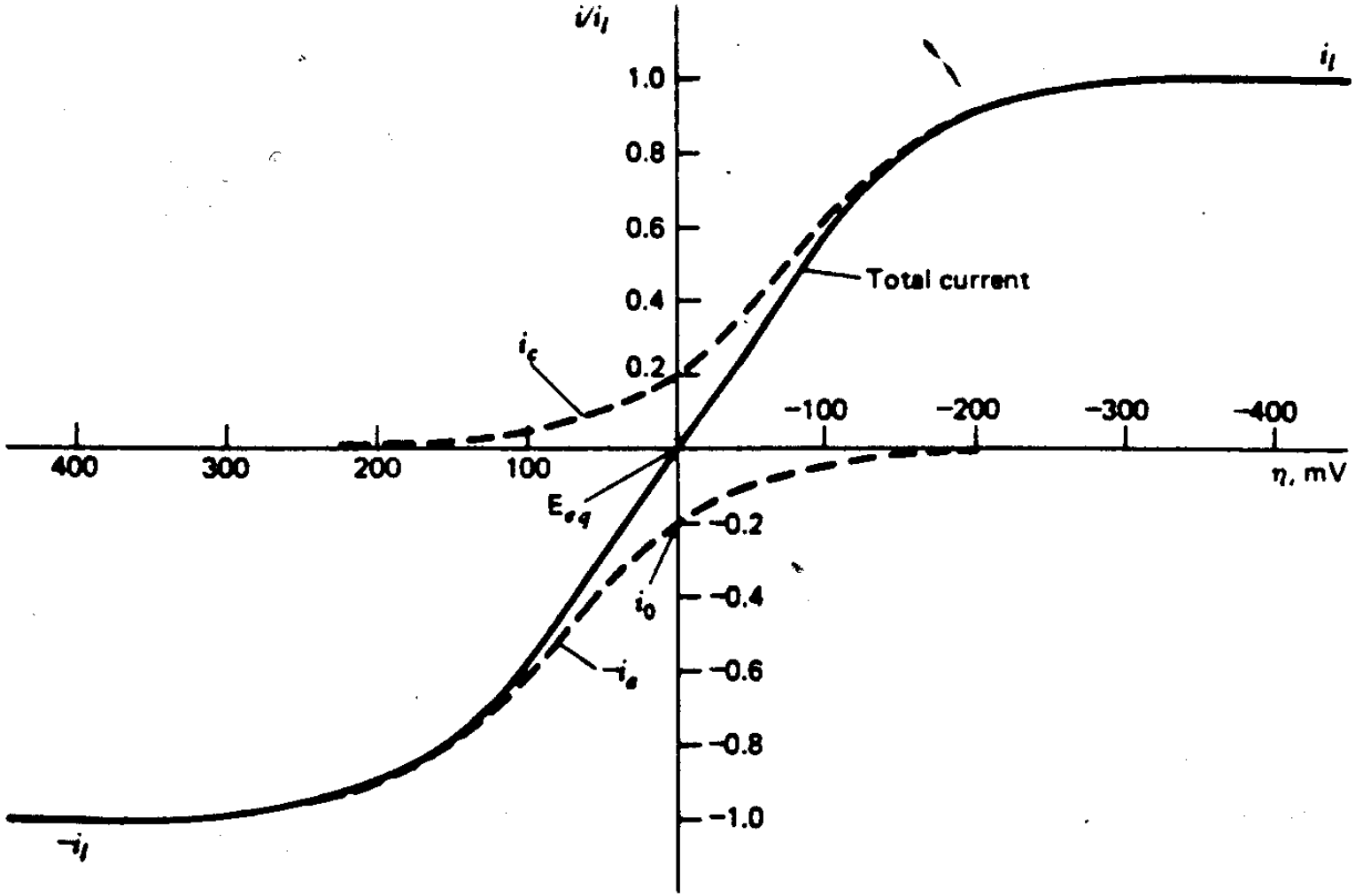



**Figure 3.5.1**

Current-overpotential curves for the system O + $ne \rightleftharpoons$ R with $\alpha = 0.5$, $n = 1$, $T = 298$ K, $i_{l,c} = -i_{l,a} = i_l$, and $i_0/i_l = 0.2$. The dotted lines show the component currents $i_c$ and $i_a$.

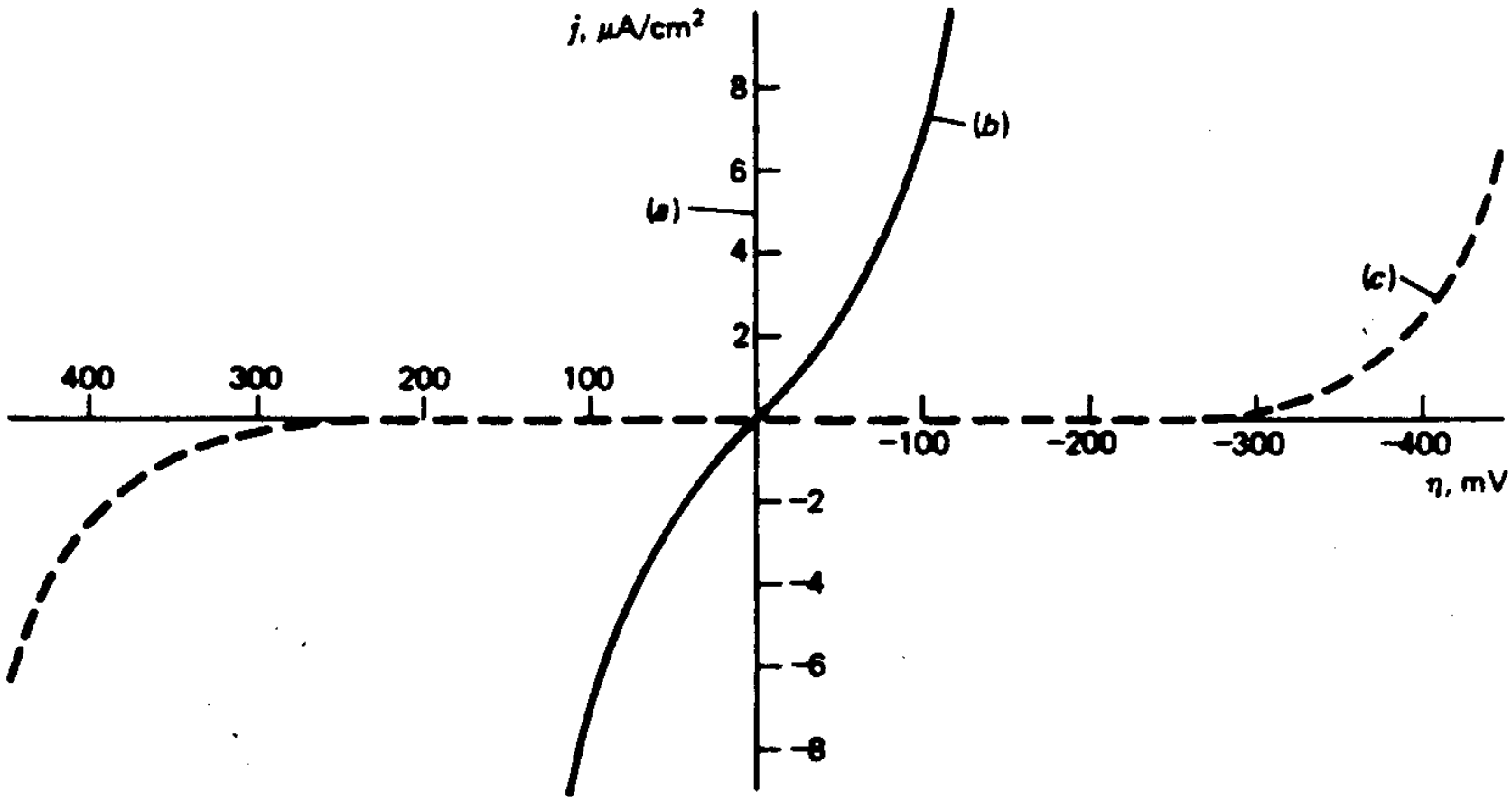



**Figure 3.5.2**

Effect of exchange current density on the activation overpotential required to deliver net current densities. (*a*) $j_0 = 10^{-3}$ A/cm², (*b*) $j_0 = 10^{-6}$ A/cm², (*c*) $j_0 = 10^{-9}$ A/cm². For all cases the reaction is O + $ne \rightleftharpoons$ R with $\alpha = 0.5$, $n = 1$, and $T = 298$ K.

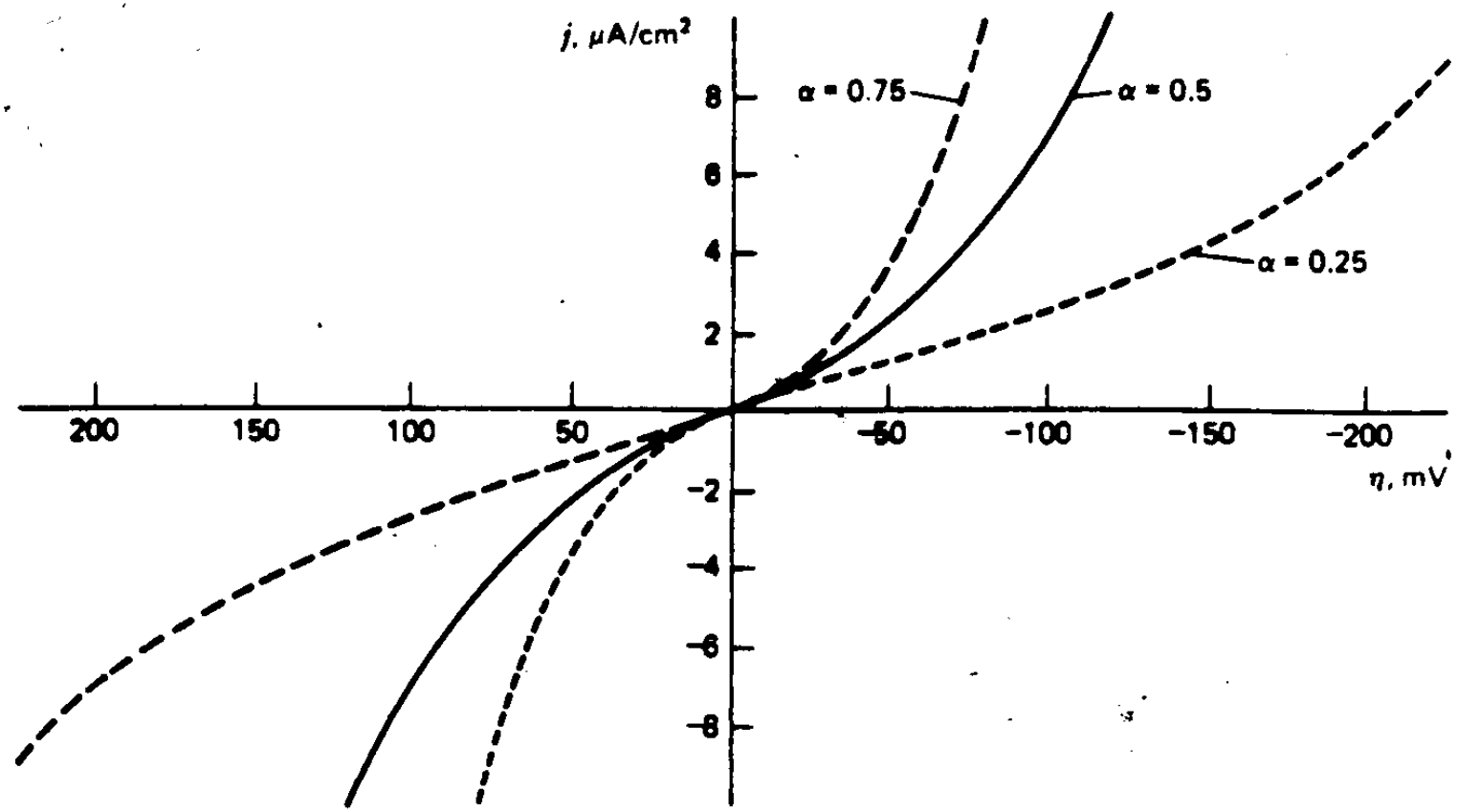



**Figure 3.5.3**

Effect of the transfer coefficient on the symmetry of the current-overpotential curves for $O + ne \rightleftharpoons R$ with $n = 1$, $T = 298$ K, and $j_0 = 10^{-6}$ A/cm².

$$i = i_0 e^{-\alpha n f \eta}(1 - e^{n f \eta}) \tag{3.5.20}$$

or

$$\log \frac{i}{1 - e^{n f \eta}} = \log i_0 - \frac{\alpha n F \eta}{2.3RT} \tag{3.5.21}$$

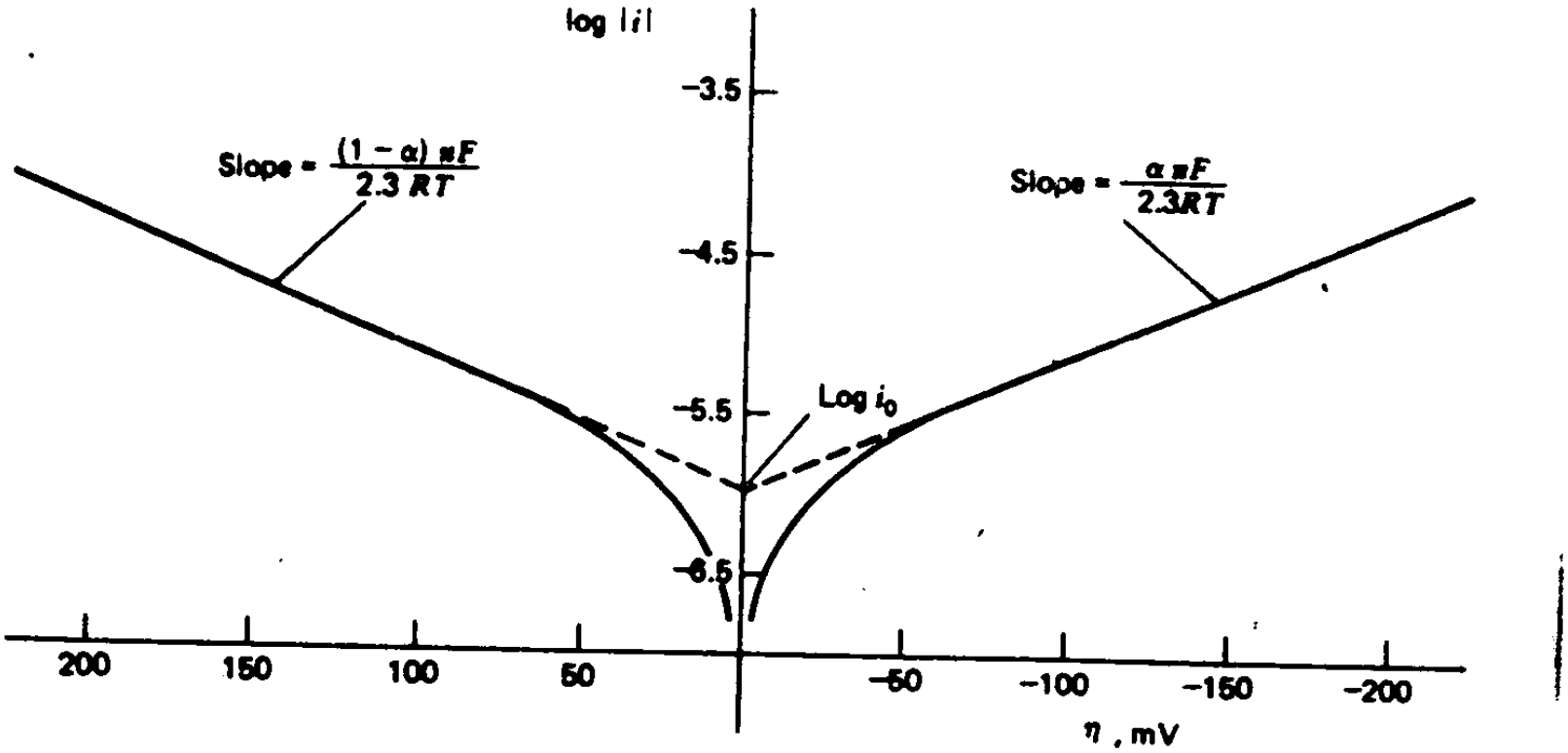



**Figure 3.5.4**

Tafel plots for anodic and cathodic branches of the current-overpotential curve for $O + ne \rightleftharpoons R$ with $n = 1$, $\alpha = 0.5$, $T = 298$ K, and $j_0 = 10^{-6}$ A/cm².

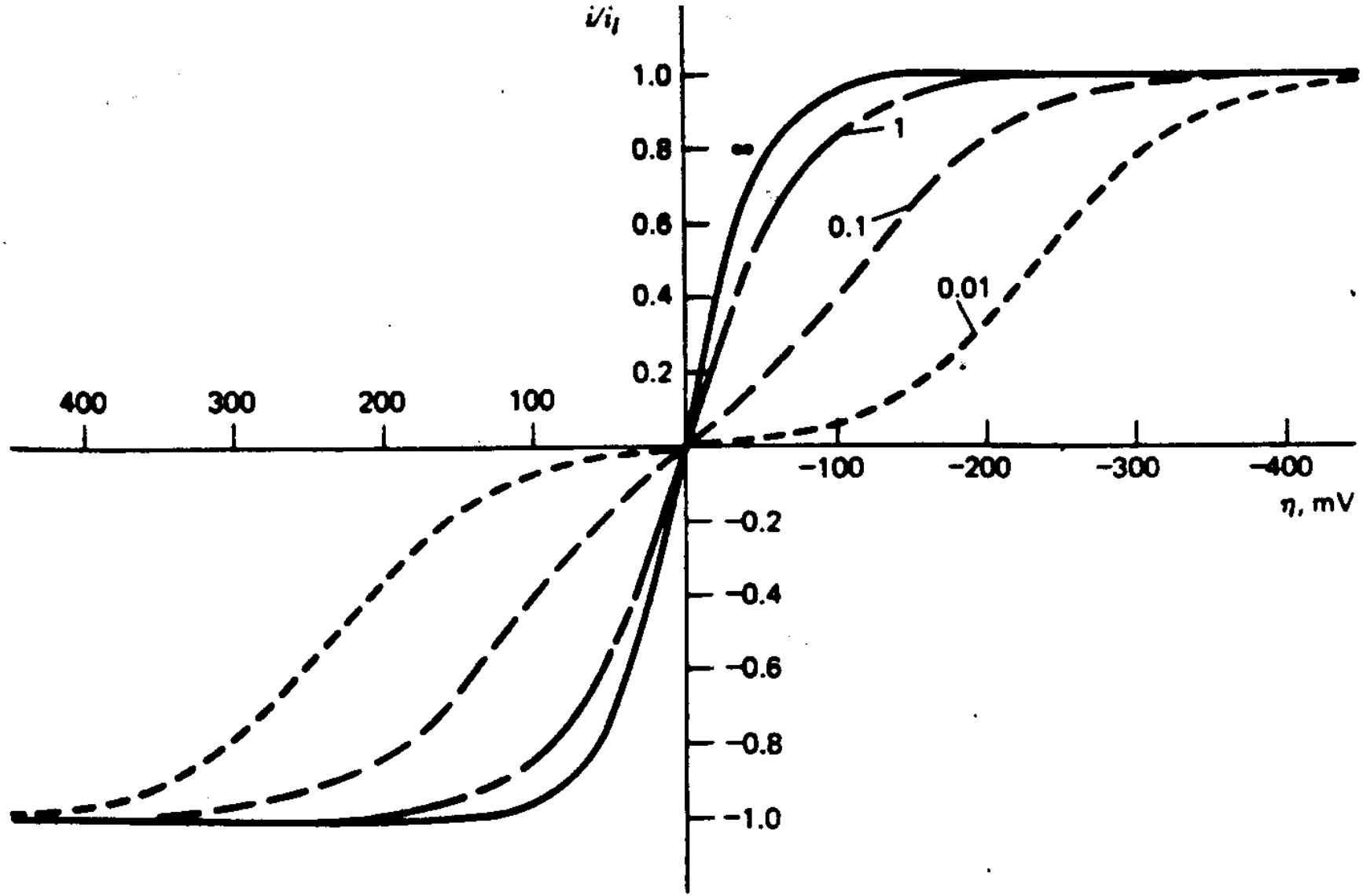



**Figure 3.5.6**

Relationship between the manifestation of an activation overpotential and net current demands relative to the exchange current. The reaction is O + $ne \rightleftharpoons$ R with $\alpha = 0.5$, $n = 1$, $T = 298$ K, and $i_{l,c} = -i_{l,a} = i_l$. Numbers by curves show $i_0/i_l$.

La rapidez de un intercambio electrodico solo se define por k° o i°

1 - 10 cm/s hasta $10^{-9}$ cm/sec

el coeficiente alfa solo es una medida de la "fracción" electrotrans-
formada a un estado energético dado

La ecu ación de Butler-Volmer es muy particular

ıique :

$$j_{global} = j_a + j_c$$

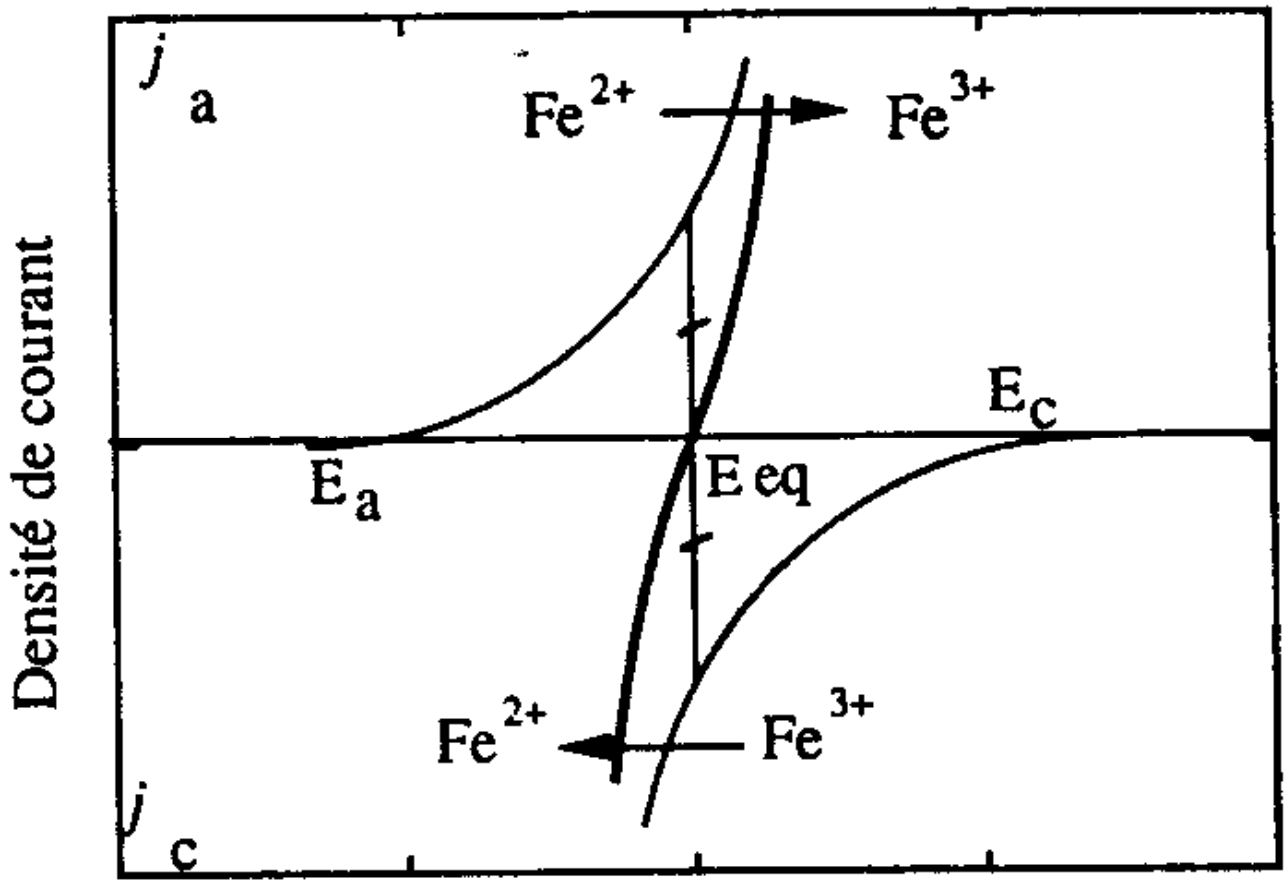
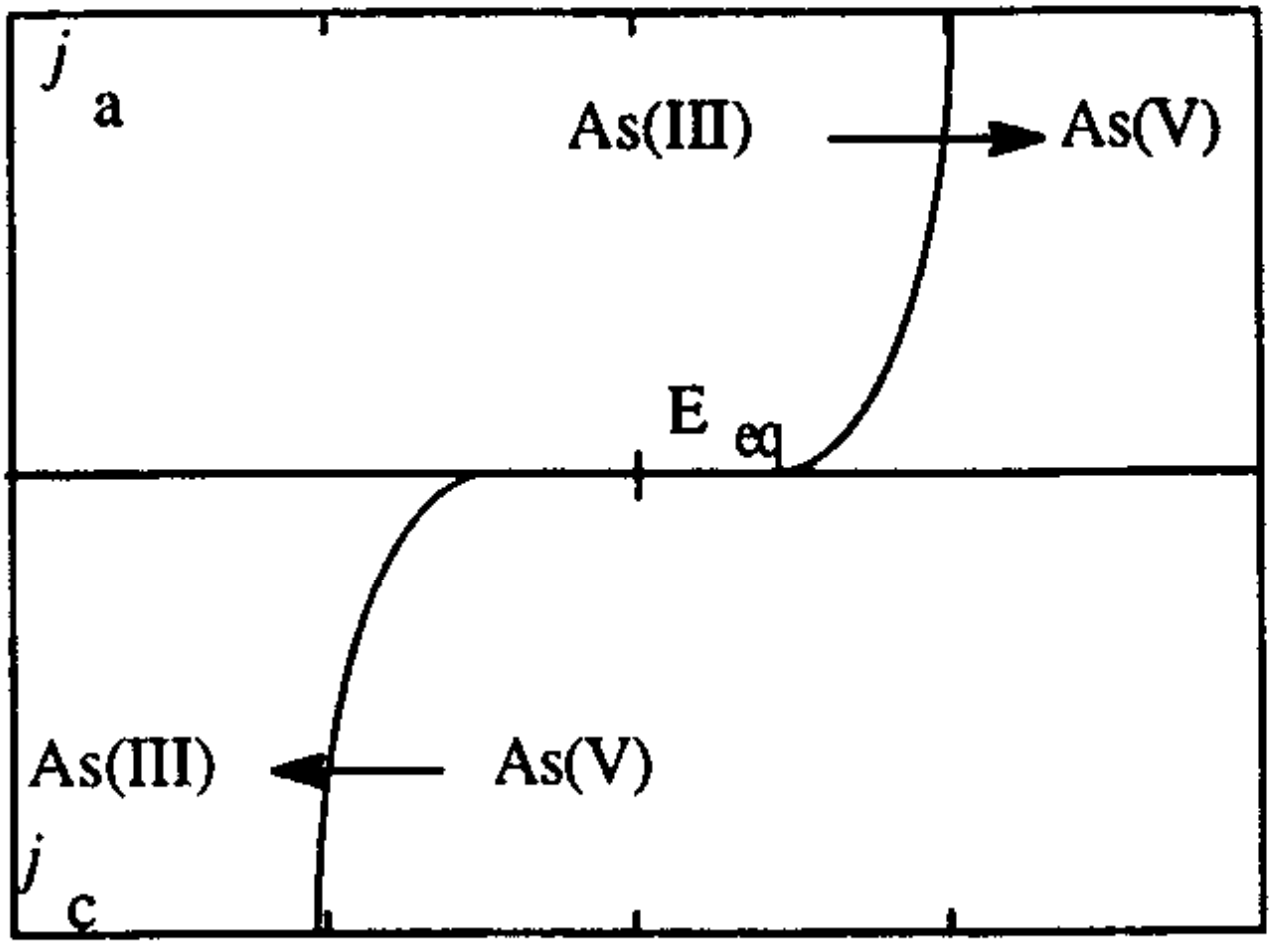



Figure 4.2




Différence de potentiel E-E eq

Figure 4.3

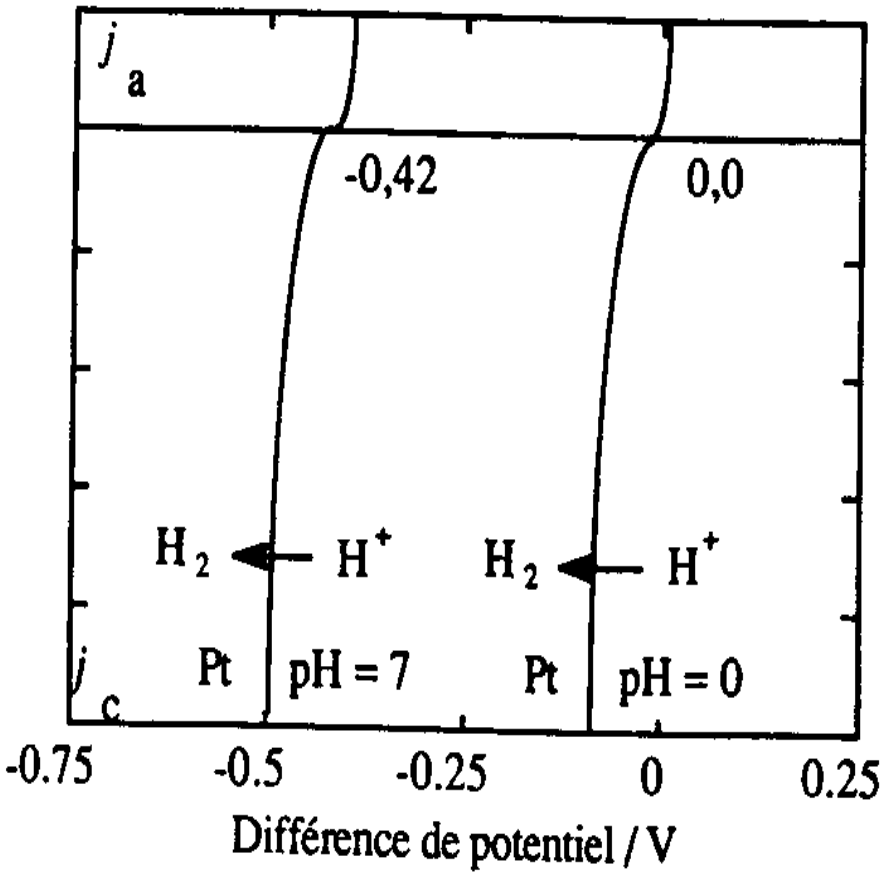



Figure 4.5

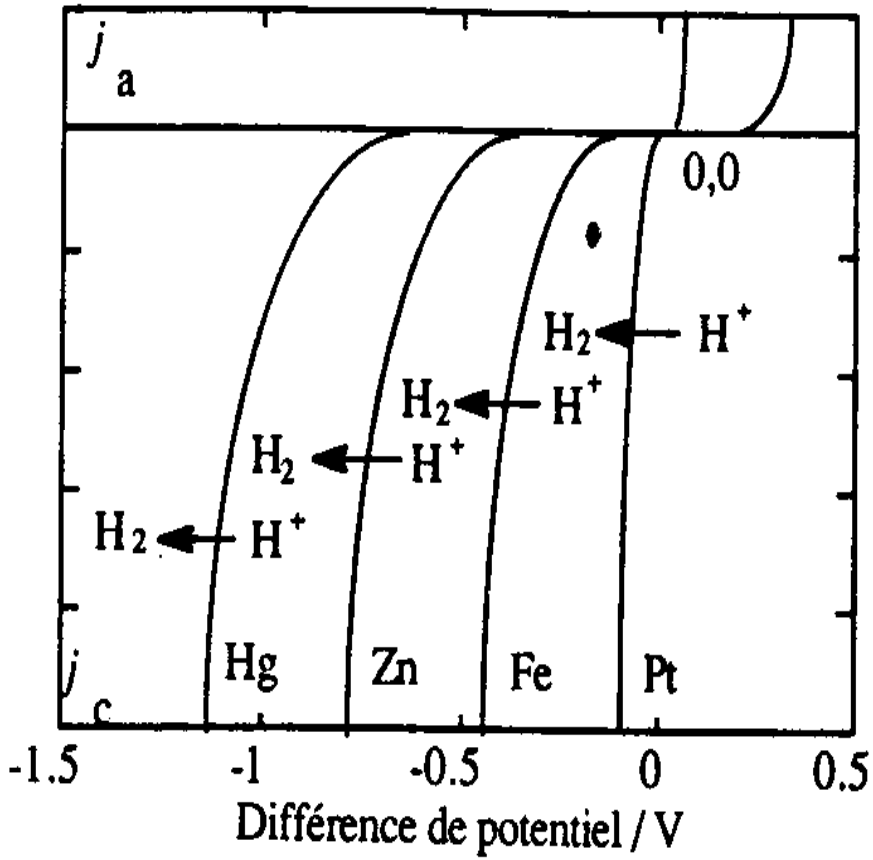
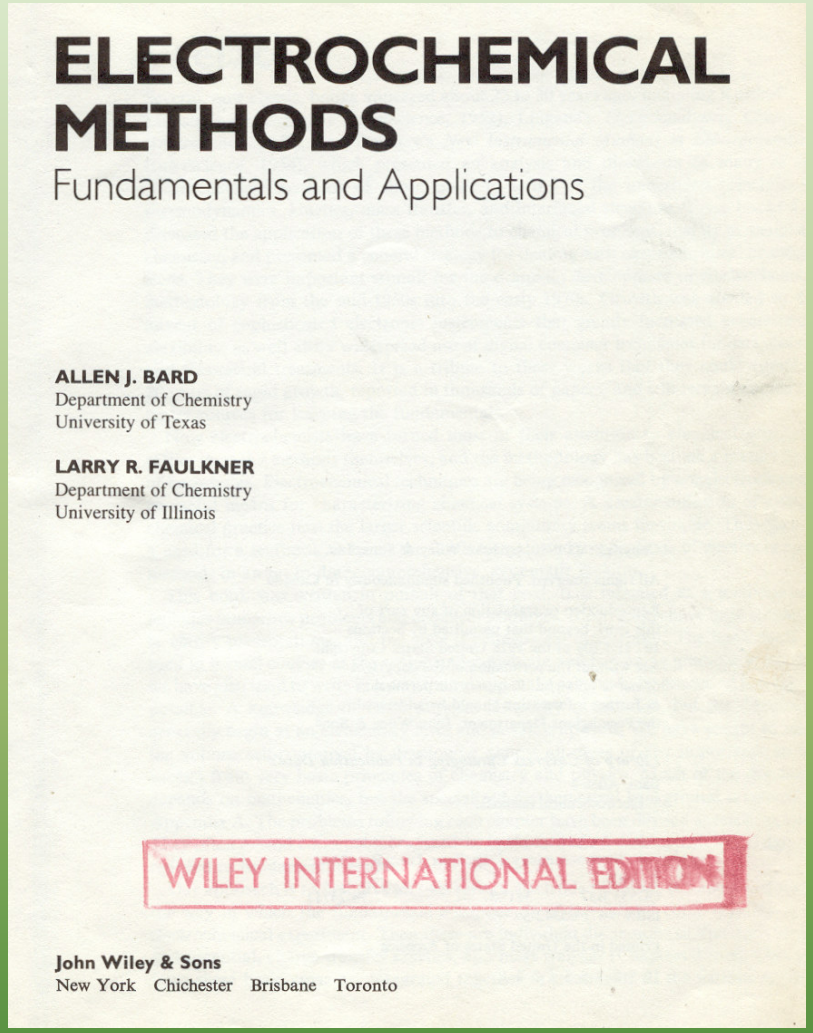



Figure 4.6

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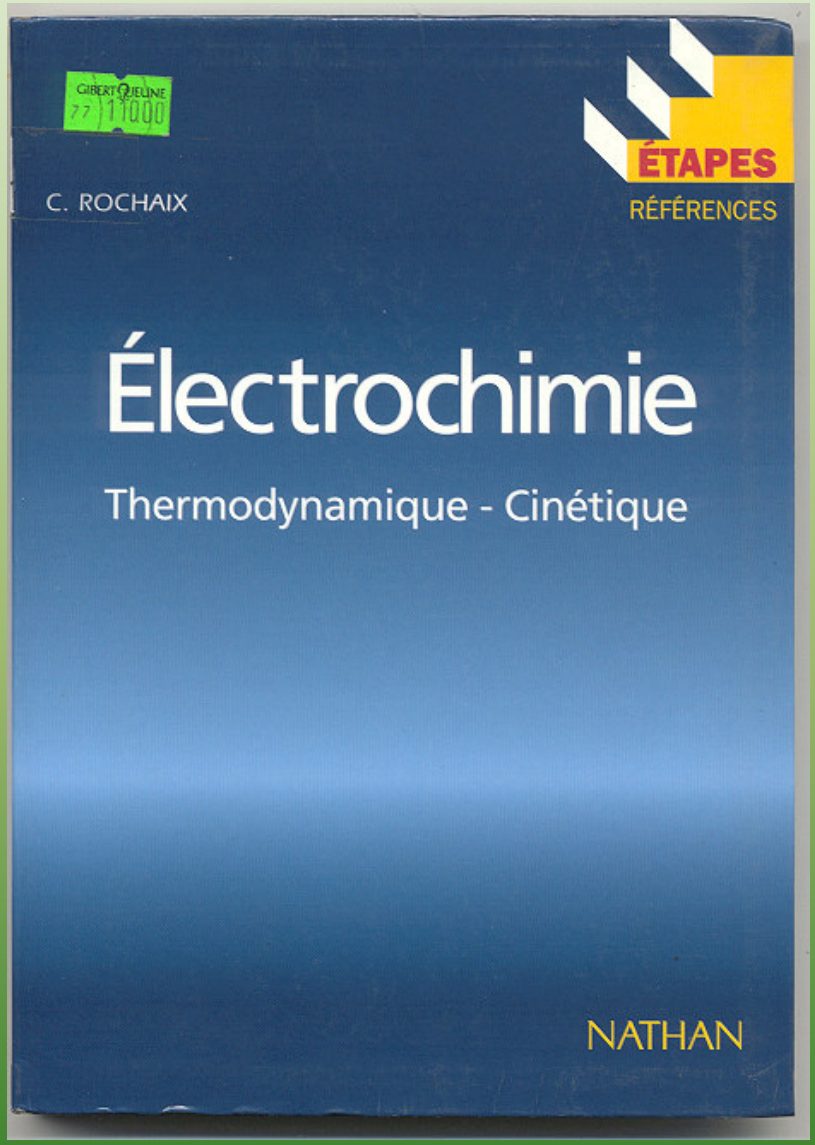


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bibliografía