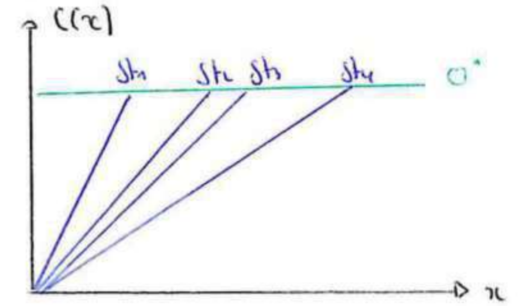
Cours

Electrochimie

Semiempirical treatment of the transient response

Potential step under diffusion control

We have to take into account that the thickness of the diffusion layer is a time-dependent quantity: $\delta(t)$
for instance in an unstirred solution.



semiempirical treatment

Hypotheses and approximations:
- the concentration gradients are still linear in $\delta(t)$
- Nernstian E process (fast kinetics)

$$\Longrightarrow i = -nFA\frac{D_o}{\delta(t)}\left[O^* - O(0)\right]$$

xperimental conditions: a potential step of magnitude E is applied to an lectrode.

t any time, the volume of the diffusion layer is $A\delta(t)$
The number of moles (Ox for instance) in the diffusion layer is given by:

$$\int_0^\delta \underbrace{A\,dx}_{\text{volume }(x)} . \underbrace{C(x)}_{\text{concentration }x} = A\int_0^\delta C(x)\,dx$$

If concentration gradients are linear:

$$\Longrightarrow \left(\frac{dO(x)}{dx}\right) = cst = a = \frac{O^* - O(0)}{\delta} \text{ and } O(x) = O(0) + x\left(\frac{O^* - O(0)}{\delta}\right)$$

$$A\int_0^\delta O(x)\,dx = A\int_0^\delta \left(O(0) + x\left(\frac{O^* - O(0)}{\delta}\right)\right)dx = A\left(O(0)\delta + (O^* - O(0))\frac{\delta}{2}\right) = \frac{A\delta}{2}\left(O^* + O(0)\right)$$

The number of moles (Ox for instance) in the diffusion layer at a given ime is thus given by: $O(t)|_\delta = \frac{A\delta(t)}{2}\left(O^* + O(0)\right)$

The number of moles (Ox for instance) electrolyzed is then given by:

$$\underbrace{A\delta(t)O^*}_{\text{if nothing has been consumed}} - \underbrace{\frac{A\delta(t)}{2}\left(O^* + O(0)\right)}_{\text{moles in the diff. layer at } t.} = \frac{A\delta(t)}{2}\left(O^* - O(0)\right) = -\underbrace{\int_0^t \frac{i\,dt}{nF}}_{I:\text{ reduction current}} \text{ since } n_e = \frac{Q}{nF} = \int_0^t \frac{i\,dt}{nF}$$

with: $O(x) = O(0) + x\left(\frac{O^* - O(0)}{\delta(t)}\right)$

y differentiation: $-\frac{A}{2}\left(O^* - O(0)\right)\frac{d\delta(t)}{dt} = \frac{i}{nF}$

nd we know that: $\frac{i}{nFA} = -D_o\left(\frac{dO(x)}{dx}\right)_{x=0} = -D_o\left(\frac{O^* - O(0)}{\delta(t)}\right)$ 1st Fick eq

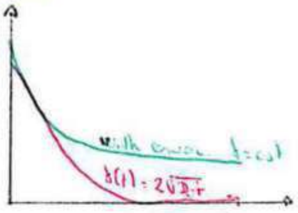
$$\Longrightarrow -\frac{1}{2}\left(O^* - O(0)\right)\frac{d\delta(t)}{dt} = -D_o\left(\frac{O^* - O(0)}{\delta(t)}\right)$$

$$\Longrightarrow \frac{1}{2}\frac{d\delta(t)}{dt} = \frac{D_o}{\delta(t)} \text{ or } \frac{1}{2}\delta(t)\,d\delta(t) = D_o\,dt$$

which can be integrated in $\frac{1}{4}\delta^2(t) = D_o t$ or $\delta^2(t) = 4D_o t$

nowing how the diffusion layer varies with time, the current then becomes

$$\frac{i}{nFA} = -D_O\left(\frac{O^* - O(0)}{\delta(t)}\right) = -D_O\left(\frac{O^* - O(0)}{2\sqrt{D_O t}}\right) = \frac{-D_O^{1/2}}{2t^{1/2}}\left(O^* - O(0)\right)$$



This approximate treatment in transient regime predicts:
- The diffusion layer grows with $t^{1/2}$
- The current decays with $t^{-1/2}$

It differs only by a factor of $2/\pi^{1/2}$ from the rigorous description of current calculated for a Nernstian system during a potential step.

COTTREL EQUATION : $i(t) = \frac{-nFAD_O^{1/2}O^*}{\pi^{1/2}t^{1/2}}$

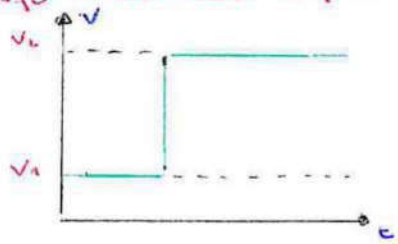
Rigorous treatment of transient electrochemical response

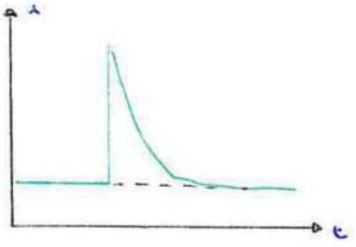
Potential step under diffusion control

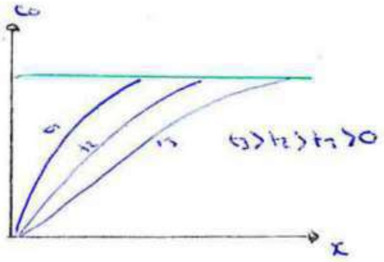
Description of the step experiment:

lana-electrode (unidirectional semi-infinite diffusion regime), no stirring, instantaneous change in potential from a value where no electrolysis occurs to a instantaneous change in potential from a value where no electrolysis occurs to a value in the mass transfer-controlled region:

$Ox + ne^- \rightleftarrows red$





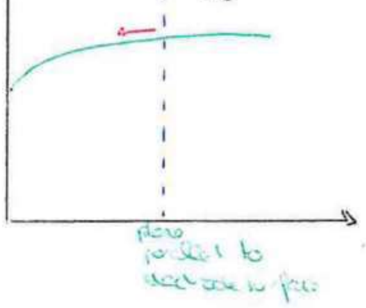


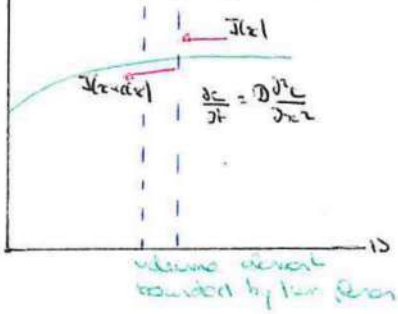
- The concentration is readily = 0 at the electrode surface
- Current gets under diffusion control
- Current is independent of E
- Applies to fast and slow kinetics (activation will of course require a suitable overpotential o reach the mass transfer controlled domain).

Introduction to the second Fick equation

Linear diffusion to a flat, planar electrode

$D = \frac{cm^2}{s}$ $(1.10^{-5}\,cm^2.s^{-1})$ Rate = Flux = $-D\left(\frac{\partial C}{\partial x}\right)_{x=0}$ $mol.s^{-1}.cm^{-2}$





$$\frac{\partial C_O(x,t)}{\partial t} = \left(\frac{\partial}{\partial x}\right)\left(D_O\left(\frac{\partial C_O(x,t)}{\partial x}\right)\right)$$

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

From 1st to 2d Fick equations

Decrease in concentration over dx.

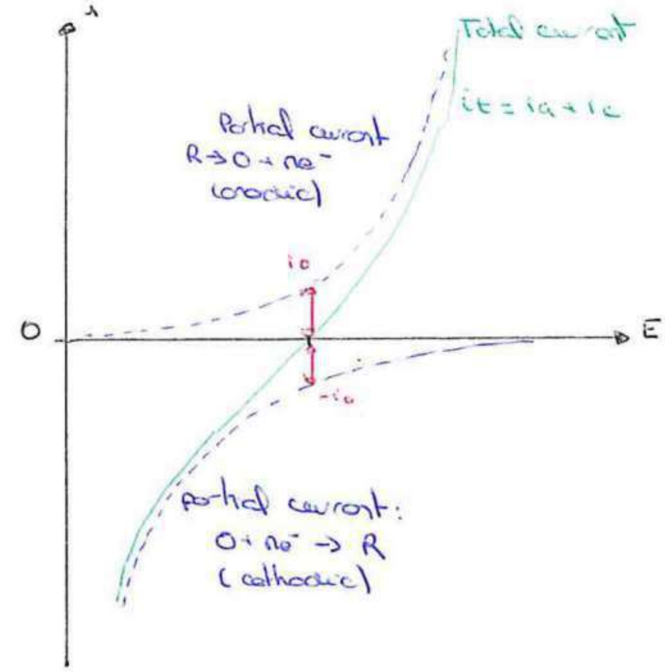
$dC(x) = \left(\frac{J(x) - J(x+dx)}{Adx}\right)Adt$

with: $dJ = J(x+dx) - J(x)$

$\rightarrow \frac{dC(x)}{dt} = -\frac{dJ}{dx} \Rightarrow \frac{\partial C(x,t)}{\partial t} = D\left(\frac{\partial^2 C(x,t)}{\partial x^2}\right)$

At : $E = E_{eq}$

$(i_a)_{eq} = (|i_c|)_{eq} = i_0$



Approximate form of the BV relation

$$i_t = i_0 \left(\underbrace{\exp\left(\frac{\alpha_o n F \eta}{RT}\right)}_{i_o} - \underbrace{\exp\left(-\frac{\alpha_r n F \eta}{RT}\right)}_{i_r} \right)$$

Even though the net current is zero at equilibrium, the exchange current provides information on the balanced Faradic activity.

---

i_0 and $k°$ caracterise the electron transfer kinetic of a given redox couple.

- Fast electron transfer
  large values of i_0 and $k°$
- slow electron transfer
  small values of i_0 and $k°$

The heterogeneous e-transfert is considered as being fast when $k° > 0.1$ $cm^2.s^{-1}$ and slow when $k° < 10^{-5}$ $cm^2.s^{-1}$

TAFEL equations: Limit cases

When η is highly positive $(+\eta \to -\infty)$: oxydation $E > E^{th}$

$$i = i_t = i_0 \left(\exp(\alpha_o n f \eta) - \underset{\longrightarrow 0}{\exp(-\alpha_r n f \eta)} \right)$$

$$i \simeq i_{to} = i_0 \exp(\alpha_o n f \eta)$$

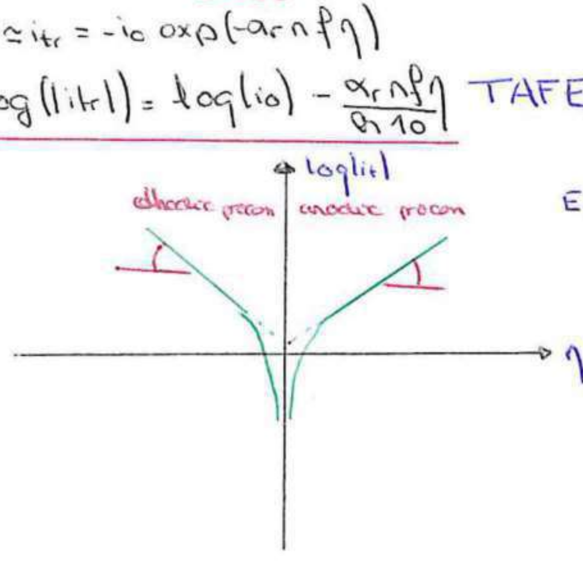
$$\log(i_{to}) = \log(i_0) + \frac{\alpha_o n f \eta}{\ln 10}$$ TAFEL EQUATION (anodic)

When η is highly negative $(\eta \to -\infty)$: reduction $E < E^{th}$

$$i = i_t = i_0 \left(\underset{\longrightarrow 0}{\exp(\alpha_o n f \eta)} - \exp(-\alpha_r n f \eta) \right)$$

$$i \simeq i_{tr} = -i_0 \exp(-\alpha_r n f \eta)$$

$$\log(|i_{tr}|) = \log(i_0) - \frac{\alpha_r n f \eta}{\ln 10}$$ TAFEL EQUATION (cathodic)



Experimental determination of kinetic parameters:
i_0, α_o et α_r

Electrochimie

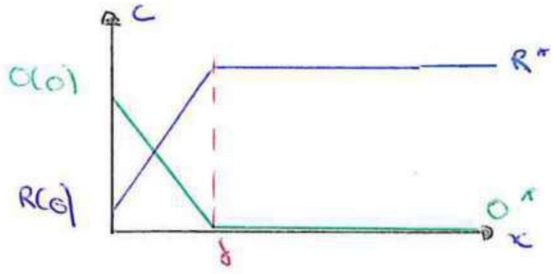
Semi-Empirical treatment of steady-state mass transfer for a Nernstian E process

Mass transfer by diffusion is the only limiting process, the flow is determined by the 1st Fick equation:

$$J_o(x,t) = -D_o \frac{\partial O(x,t)}{\partial x}$$

The steady state regime implies that:

$$\left(\frac{\partial C}{\partial t}\right)_x = 0$$



convection is large enough to ensure a continuous replacement at the electrode interface

$$Ox + ne^- \rightleftharpoons Red$$

$$i = nFAJ_o(0) = -nFAD_o\left(\frac{\partial O(x)}{\partial x}\right)_{x=0} = -nFAm_o\left(O^* - O(0)\right)$$

$$i = -nFAJ_R(0) = nFAD_r\left(\frac{\partial R(x)}{\partial x}\right)_{x=0} = nFAm_r\left(R^* - R(0)\right)$$

For RDE: $m_o = 0{,}62\, D_o^{2/3}\omega^{1/2}\nu^{-1/6}$

At a disk microelectrode: $m_o = 4D_o/(\pi r_o)$.

$$\left.\begin{aligned} i_{d,c} &= -nFAm_o O^* \\ i_{d,a} &= nFAm_r R^* \end{aligned}\right\} \Rightarrow E = E^{0'}_{O/R} + \frac{RT}{nF}\ln\left(\frac{O(0)}{R(0)}\right) = E^{0'}_{O/R} + \frac{RT}{nF}\ln\left(\frac{m_r}{m_o}\right) + \frac{RT}{nF}\ln\left(\frac{i-i_{dc}}{i_{da}-i}\right)$$

Half-wave potential: $E_{1/2} = E \quad i = \frac{i_{dc}+i_{da}}{2}$

$$\Rightarrow E_{1/2} = E^{0'}_{O/R} + \frac{RT}{nF}\ln\left(\frac{m_r}{m_o}\right)$$

The Levich equation:

$$\boxed{\underset{A}{i_{d,c}} = 0{,}620\, nF\underset{cm^2}{A}\underset{cm^2.s^{-1}}{D_o^{2/3}}\underset{rad.s^{-1}}{\omega^{1/2}}\overset{cm^2.s^{-1}}{\nu^{-1/6}}\overset{mol.cm^{-3}}{O^*}}$$

Kinetics of the electrochemical reaction: The Butler-Volmer model

$$Ox + ne^- \underset{k_o}{\overset{k_r}{\rightleftharpoons}} Red$$

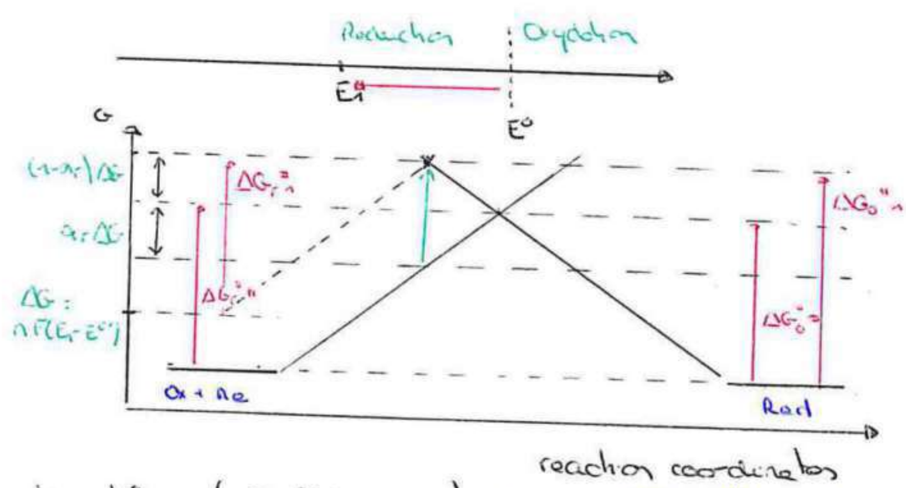
k_o et k_r: kinetic constants associated to the heterogeneous electron transfer (cm.s⁻¹).

$$(V_{O\to R})_s = (v_r)_s - (v_o)_s = \frac{-i}{nFA} = k_r O(0) - k_o R(0)$$

$$(V_{R\to O})_s = (v_o)_s - (v_R)_s = \frac{i}{nFA} = k_o R(0) - k_r O(0)$$

k_o and k_R depend on the reaction activation barrier and T.

Arrhenius law $k = A\exp\left(\frac{-\Delta G^{0\neq}}{RT}\right)$



$$\Delta G_r^{\neq}{}_1 = \Delta G_r^{0\neq} + \alpha_r nF(E_1-E^{0'})$$
$$\Delta G_o^{\neq}{}_1 = \Delta G_o^{0\neq} - nF(\underbrace{1-\alpha_r}_{\alpha_o = 1-\alpha_r})(E_1-E^{0'})$$

$\alpha_r + \alpha_o = 1$ transport coeff.

$$k_r = k^0 \exp\left(\frac{-\alpha_r nF}{RT}(E_1-E^{0'})\right)$$ k^0 is called the standard rate constant
$$k_o = k^0 \exp\left(\frac{\alpha_o nF}{RT}(E_1-E^{0'})\right)$$

Let's consider the special case in which the interface is at equilibrium with a solution in which $O^* = R^*$. In those conditions $E_1 = E^{0'}$ and $k_r = k_o = k^0$ the net current is zero. E_0' is thus the potential where the forward and reverse ate constants have the same value.

k^0 is called the standard rate constant

→ system with a large k^0 will achieve equilibrium on a short time scale

→ system with a low k^0 will achieve equilibrium on long time scales.

but: k_R and k_o can still be very large even when k^0 is low.

$$v = v_o - v_r = \frac{i}{nFA} = k_o R(0) - k_r O(0)$$
$$= \underbrace{R(0)k^0 \exp\left(\frac{\alpha_o nF(E-E^{0'})}{RT}\right)}_{\substack{i_a \geq 0 \\ \text{Oxydation}}} - \underbrace{O(0)k^0 \exp\left(\frac{-\alpha_r nF(E-E^{0'})}{RT}\right)}_{\substack{i_c \leq 0 \\ \text{Reduction}}}$$

When $i = 0$, the reduction and oxydation processes proceed at the same speed

$$(i_a)_{eq} = (|i_c|)_{eq} = i_0 \qquad E = E_{eq};\ R(0) = R^* \text{ and } O(0) = O^*$$

$$i = 0 = nFAk^0\left(R^* \exp\left(\frac{\alpha_o nF(E_{eq}-E^{0'})}{RT}\right) - O^* \exp\left(\frac{-\alpha_r nF(E_{eq}-E^{0'})}{RT}\right)\right)$$
$$\frac{i_0}{nFA} = \underline{O^* k^0 \exp\left(\frac{-\alpha_r nF(E_{eq}-E^{0'})}{RT}\right)} = \underline{R^* k^0 \exp\left(\frac{\alpha_o nF(E_{eq}-E^{0'})}{RT}\right)}$$

$$\frac{i}{nFA} = R(0)k^0 \exp\left(\frac{\alpha_o nF(E-E_{eq}) + \alpha_o nF(E_{eq}-E^{0'})}{RT}\right) - O(0)k^0 \exp\left(\frac{-\alpha_R nF(E-E_{eq}) - \alpha_R nF(E_{eq}-E^{0'})}{RT}\right)$$
$$= R(0)k^0 \exp\left(\frac{\alpha_o nF(E_{eq}-E^{0'})}{RT}\right)\exp\left(\frac{\alpha_o nF\eta}{RT}\right) - O(0)k^0 \exp\left(\frac{-\alpha_R nF(E_{eq}-E^{0'})}{RT}\right)\exp\left(\frac{-\alpha_r nF\eta}{RT}\right)$$
$$i = \frac{R(0)}{R^*} i_0 \exp\left(\frac{\alpha_o nF\eta}{RT}\right) - \frac{O(0)}{O^*} i_0 \exp\left(\frac{-\alpha_R nF\eta}{RT}\right)$$
$$= \underline{i_0\left(\overset{=1}{\cancel{\frac{R(0)}{R^*}}} \exp\left(\frac{\alpha_o nF\eta}{RT}\right) - \overset{=1}{\cancel{\frac{O(0)}{O^*}}} \exp\left(-\frac{\alpha_R nF\eta}{RT}\right)\right)}$$

The electron transfer controls the kinetics

→ CT current.

if $O(0) = O^*$ and $R(0) = R^*$ (upon neglecting the mass-transfer effects). If the solution is well stirred, or currents are kept so low that the surface concentrations do not differ appreciably from the bulk values. Reasonable approximation when i is lower than about 10 % of limit diff.

The $C(x,t)$ function can be used to solve the first Fick equation. $J_o(0,t) = -D_o\left(\frac{\partial C_o(x,t)}{\partial x}\right)_{x=0}$

Using $C_o(x,t) = C_o^* \,\mathrm{erf}\left(\frac{x}{2(Dt)^{1/2}}\right)$ and $i(t) = nFAJ_o(0,t) = -nFAD_o\left(\frac{\partial C_o(x,t)}{\partial x}\right)_{x=0} > 0$

The derivation can be made easily using the transformed functions.

$\bar{C}_o(x,s) = \frac{C_o^*}{s} - \frac{C_o^*}{s}\exp\left(-\sqrt{\frac{s}{D}}\,x\right)$ and $\bar{i}(s) = nFA\bar{J}_o(0,s) = -nFAD_o\left(\frac{\partial \bar{C}_o(x,s)}{\partial x}\right)_{x=0}$

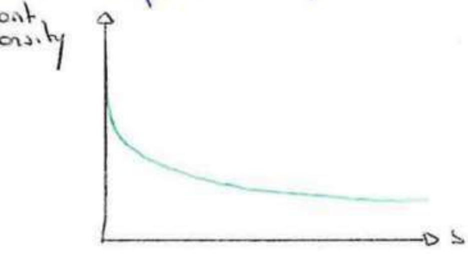
$\bar{i}(s) = -nFAD_o\left(\frac{\partial \bar{C}_o(x,s)}{\partial x}\right)_{x=0} = -\frac{nFAD_oC_o^*}{s}\sqrt{\frac{s}{D}}\exp\left(-\sqrt{\frac{s}{D}}\,x\right)_{x=0} = \frac{-nFAD_o^{1/2}C_o^*}{s^{1/2}}$

$\overset{TL^{-1}}{\Longrightarrow} i(t) = \frac{-nFAD_o^{1/2}C_o^*}{\pi^{1/2}t^{1/2}}$ COTTREL EQUATION

The $1/(t)^{1/2}$ dependence is a mark of diffusive control over the rate of electrolysis.

Limitation in Cottrel experiments

- Ohmic drop/capacitive effects (R_u, C_d): Non faradaic current may also flow during potential step experiments. This current decays exponentially with a cell time constant, R_uC_d where R_u is the uncompensated resistance and C_d is the double-layer capacitance). This contribution might interfere



For reduction
$[i(t)]_r = \frac{-nFAD_o^{1/2}C_o^*}{\pi^{1/2}t^{1/2}}$

For oxidation
$[i(t)]_o = \frac{nFAD_R^{1/2}C_R^*}{\pi^{1/2}t^{1/2}}$

$\Rightarrow$ Determination of diffusion coefficients

Case of a spherical electrode

Experimental conditions: a potential step of magnitude E is applied to a spherical electrode. This potential is large enough to ensure $O(0)=0$ for $t>0$.

The Fick equation in spherical coordinates becomes: $\frac{\partial C(r,t)}{\partial t} = D\left(\frac{\partial^2 C(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial C(r,t)}{\partial r}\right)$

Changing the variable from $C(r,t)$ to $u(r,t)$ using $u(r,t) = rC(r,t)$ with $r = cst$ allows to simplify the eq:

$\frac{\partial C(r,t)}{\partial t} = \frac{1}{r}\frac{\partial u(r,t)}{\partial t}$

$\frac{\partial^2 C(r,t)}{\partial r^2} = \frac{\partial^2}{\partial r^2}\left(\frac{u(r,t)}{r}\right) = (r^{-1}u)''$

$\frac{2}{r}\frac{\partial C(r,t)}{\partial r} = \frac{2}{r}\frac{\partial}{\partial r}\left(\frac{u(r,t)}{r}\right) = 2r^{-1}(r^{-1}u)'$

$\left(\frac{f}{g}\right)' = \frac{f'g - fg'}{g^2}$ $(fg)'' = f''g + 2f'g' + fg''$

$(r^{-1}u)'' = r^{-1}u'' + 2u'(r^{-1})' + u(r^{-1})'' = r^{-1}u'' - 2r^{-2}u' + 2r^{-3}u$

$(ur^{-1}) = \left(\frac{u}{r}\right)' = \frac{u'r - ur'}{r^2} = \frac{u'r - u}{r^2} = u'r^{-1} - ur^{-2}$

$\Rightarrow D(r^{-1}u'' - 2r^{-2}u' + 2r^{-3}u + 2r^{-1}(u'r^{-1} - ur^{-2})) = D(r^{-1}u'' - 2r^{-2}u' + 2r^{-3}u + 2r^{-2}u' - 2r^{-3}u) = D(r^{-1}u'')$.

$$\frac{\partial C(r,t)}{\partial t} = D\left(\frac{\partial^2 C(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial C(r,t)}{\partial r}\right) \overset{u(r,t)=rC(r,t)}{\Longrightarrow} \frac{\partial u(r,t)}{\partial t} = D\left(\frac{\partial^2 u(r,t)}{\partial r^2}\right)$$

$L\left\{\frac{\partial u(r,t)}{\partial t}\right\} = L\left\{D\frac{\partial^2 u(r,t)}{\partial r^2}\right\}$

$\int_0^\infty e^{-st}\frac{\partial u(r,t)}{\partial t}dt = D\int_0^\infty e^{-st}\frac{\partial^2 u(r,t)}{\partial r^2}dt = D\frac{\partial^2}{\partial r^2}\int_0^\infty e^{-st}u(r,t)dt = D\frac{d^2\bar{u}(r,s)}{dr^2}$

$s\bar{u}(r,s) - u(r,0) = D\frac{d^2\bar{u}(r,s)}{\partial r^2}$ and with the boundary condition $C(r,0) = C^* \overset{u(r,t)=rC(r,t)}{\Longrightarrow} u(r,0) = rC$
$\Rightarrow \bar{u}(r^0,0) = 0$

$s\bar{u}(r,s) - rC^* = \frac{Dd^2\bar{u}(r,s)}{dr^2}$

$\frac{d^2\bar{u}(r,s)}{dr^2} - \frac{s}{D}\bar{u}(r,s) + \frac{rC^*}{D} = 0 \Rightarrow \bar{u}(r,s) = \frac{rC^*}{s} + A'\exp\left(-\sqrt{\frac{s}{D}}\,r\right) + B'\exp\left(\sqrt{\frac{s}{D}}\,r\right)$

Experimental conditions: a potential step of magnitude E is applied to an electrode. Calculation of the diffusion-limited current and of the concentration profile, C(x,t) involves the solution of the linear diffusion equation (unidirectional diffusion regime

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2} \quad \text{eq } 1$$

Boundary conditions are needed (only Ox present at

$C(x,0) = C^* \quad \lim_{x \to \infty} C(x,t) = C^* \quad C(0,t) = 0$ for t>

Transforming eq 1 using Laplace Transformation leads to: $L\left(\frac{\partial C(x,t)}{\partial t}\right) = L\left(D\frac{\partial^2 C(x,t)}{\partial x^2}\right)$

$$\int_0^\infty e^{-st}\frac{\partial C(x,t)}{\partial t}dt = D\int_0^\infty e^{-st}\frac{\partial^2 C(x,t)}{\partial x^2}dt = D\frac{\partial^2}{\partial x^2}\underbrace{\int_0^\infty e^{-st}C(x,t)\,dt}_{\overline{C}(x,s)} = D\frac{d^2\overline{C}(x,t)}{dx^2}$$

integral /t and derivative /x

$$L\left(\frac{\partial C(x,t)}{\partial t}\right) = s\overline{C}(x,s) - C(x,0) = D\frac{d^2\overline{C}(x,s)}{\partial x^2}$$

and with the boundary condition $C(x,0) = C^*$

$$\Rightarrow s\overline{C}(x,s) - C^* = D\frac{d^2\overline{C}(x,s)}{dx^2}$$

$$\Rightarrow \frac{d^2\overline{C}(x,s)}{dx^2} - \frac{s}{D}\overline{C}(x,s) = -\frac{C^*}{D}$$

How to solve such equation? LT makes it possible.

Let's set: $\overline{C}(x,s) = u(x)$ which can be submitted to a second transformation

$$L\left\{\frac{d^2u(x)}{dx^2}\right\} = s'^2\overline{u}(s') - s'u(0) - u'(0)$$

$$L\left\{\frac{s}{D}u(x)\right\} = \frac{s}{D}\overline{u}(s') \quad L\{1\} = \frac{1}{s'}$$

$$\frac{d^2u(x)}{dx^2} - \frac{s}{D}u(x) + \frac{C^*}{D} = 0$$

$$\xrightarrow{LT} s'^2\overline{u}(s') - s'u(0) - u'(0) - \frac{s}{D}\overline{u}(s') + \frac{C^*}{Ds'} = 0$$

$$\overline{u}(s')\left(s'^2 - \frac{s}{D}\right) = s'u(0) + u'(0) - \frac{C^*}{Ds'}$$

$$\overline{u}(s')\left(s'^3 - \frac{ss'}{D}\right) = s'^2u(0) + u'(0)s' - \frac{C^*}{D}$$

$$\overline{u}(s') = \frac{s'^2u(0) + s'u'(0) - \frac{C^*}{D}}{s'\left(s'^2 - \frac{s}{D}\right)} = \frac{s'^2u(0) + s'u'(0) - C^*/D}{s'\left(s' - \sqrt{\frac{s}{D}}\right)\left(s' + \sqrt{\frac{s}{D}}\right)}$$

$$\overline{u}(s') = \frac{B'}{s' - \sqrt{\frac{s}{D}}} + \frac{A'}{s' + \sqrt{\frac{s}{D}}} + \frac{E'}{s'}$$

$$\overline{u}(s') = \frac{s'^2(B' + A' + E') + s'\sqrt{\frac{s}{D}}(B' - A') + \frac{E's}{D}}{\left(s' - \sqrt{\frac{s}{D}}\right)\left(s' + \sqrt{\frac{s}{D}}\right)s'} \Rightarrow \frac{E's}{D} = \frac{C^*}{D} \Rightarrow E' = \frac{C^*}{s}$$

$$\xrightarrow{LT^{-1}} L^{-1}\{\overline{u}(s')\} = L^{-1}\left\{\frac{B'}{s' - \sqrt{\frac{s}{D}}}\right\} + L^{-1}\left\{\frac{A'}{s' + \sqrt{\frac{s}{D}}}\right\} + L^{-1}\left\{\frac{E'}{s'}\right\}$$

$$u(x) = \overline{C}(x,s) = E' + A'\exp\left(-\sqrt{\frac{s}{D}}x\right) + B'\exp\left(\sqrt{\frac{s}{D}}x\right) \text{ with } E' = \frac{C^*}{s}$$

$$\frac{d^2\overline{C}(x,s)}{dx^2} - \frac{s}{D}\overline{C}(x,s) + \frac{C^*}{D} = 0 \xRightarrow{TL} \overline{C}(x,s) = \frac{C^*}{s} + A'\exp\left(-\sqrt{\frac{s}{D}}x\right) + B'\exp\left(\sqrt{\frac{s}{D}}x\right)$$

C(x,t) tends towards a finite value when $x \to \infty$ and so does $\overline{C}(x,s) \Rightarrow B' = 0$

Determination of A' using known boundary conditions

$C(x,0) = C^* \qquad C(0,t) = 0$ for t>0

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

$$\overline{C}(x,s) = \frac{C^*}{s} + A^*\exp\left(-\sqrt{\frac{s}{D}}x\right)$$

$\overline{C}(0,s) = 0$ leads to $\frac{C^*}{s} + A' = 0$ and $A' = -\frac{C^*}{s} \Rightarrow \underline{\overline{C}(x,s) = \frac{C^*}{s} - \frac{C^*}{s}\exp\left(-\sqrt{\frac{s}{D}}x\right)}$

from the table of Laplace transformation we know that L^{-1}: $L^{-1}\left\{s^{-1}\exp\left(-\sqrt{\frac{s}{D}}x\right)\right\} = \operatorname{erfc}\left(\frac{x}{2(Dt)^{1/2}}\right)$

$$\overline{C}(x,s) = \frac{C^*}{s} - \frac{C^*}{s}\exp\left(-\sqrt{\frac{s}{D}}x\right) \xRightarrow{TL^{-1}} \underline{C(x,t) = C^* - C^*\operatorname{erfc}\left(\frac{x}{2(Dt)^{1/2}}\right) = C^*\operatorname{erf}\left(\frac{x}{2(Dt)^{1/2}}\right)}$$

Sigmoid shaped function occurring in probability, statistics, and partial differential equations describing diffusion.

Error function: $\operatorname{erf}(x) = \frac{2}{\pi}\int_0^x \exp(-t^2)\,dt$

Complementary error function: erfc(x)=

$C(r,t)$ tends towards a finit value when $x \to \infty$ and so does $\bar{u}(r,s) \Rightarrow B' = 0$

Determination of A' using known boundary conditions

$C(r^\circ,t) = 0$ for $t > 0$

$\Rightarrow u(r^\circ,t) = 0 \Rightarrow \bar{U}(r^\circ,s) = 0$

$$\bar{u}(r,s) = \frac{rC^*}{s} + A' \exp\left(-\sqrt{\frac{s}{D}}\, r\right)$$

$\bar{u}(r^\circ,s) = 0$ Leads to $\frac{r^\circ C^*}{s} + A' \exp\left(-\sqrt{\frac{s}{D}}\, r^\circ\right) = 0$ and $A' = -\frac{r^\circ C^*}{s} \exp\left(\sqrt{\frac{s}{D}}\, r^\circ\right)$

$$\Rightarrow \bar{u}(r,s) = r\bar{C}(r,s) = \frac{rC^{*s}}{s} - \frac{r^\circ C^*}{s} \exp\left(-\sqrt{\frac{s}{D}}(r-r^\circ)\right) \Rightarrow \bar{C}(r,s) = \frac{C^*}{s} - \frac{r^\circ C^*}{rs} \exp\left(-\sqrt{\frac{s}{D}}(r-r^\circ)\right)$$

The $C(r,t)$ function can be used to solve the first Fick equation

$$J_O(r^\circ,t) = -D_O \left(\frac{\partial C_O(r^\circ,t)}{\partial r}\right)_{r=r^\circ}$$

using $i(t) = nFAJ_O(r^\circ,t) = -nFAD_O \left(\frac{\partial C_O(r,t)}{\partial r}\right)_{r=r_0}$

This derivation can be made easily using the transformed functions.

$\bar{C}(r,s) = \frac{C^*}{s} - \frac{r^\circ C^*}{rs} \exp\left(-\sqrt{\frac{s}{D}}(r-r^\circ)\right)$ and $\bar{i}(s) = nFA\bar{J}_O(r^\circ,s) = -nFAD_O \left(\frac{\partial \bar{C}_O(r,s)}{\partial r}\right)_{r=r^\circ}$

$$\left(\frac{\partial \bar{C}_O(r,s)}{\partial r}\right)_{r=r_0} = -\frac{r^\circ C^*}{s}\left(-\frac{1}{r^2}\exp\left(-\sqrt{\frac{s}{D}}(r-r^\circ)\right) + \frac{1}{r}\left(-\sqrt{\frac{s}{D}}\right)\exp\left(-\sqrt{\frac{s}{D}}(r-r^\circ)\right)\right)$$

$$= -\frac{r^\circ C^*}{s}\left(-\frac{1}{r^{\circ 2}} - \frac{1}{r^\circ}\sqrt{\frac{s}{D}}\right) = \frac{r^\circ C^*}{r^{\circ 2} s} + \frac{r^\circ C^*}{s r^\circ}\sqrt{\frac{s}{D}} = \frac{C^*}{r^\circ s} + \frac{C^*}{\sqrt{sD}}$$

$$\bar{i}(s) = -nFAD_O C_O^* \left(\frac{1}{r^\circ s} + \frac{1}{(sD_O)^{1/2}}\right) \xRightarrow{TL^{-1}} i(t) = -nFAD_O C_O^* \left(\frac{1}{r^\circ} + \frac{1}{(D_O \pi t)^{1/2}}\right)$$

$$id(\text{spherical}) = id(\text{linear}) - \frac{nFAD_O C_O^*}{r^\circ} \qquad \lim_{t \to \infty} id(\text{spherical}) = \frac{-nFAD_O C_O^*}{r^\circ}$$

Linear sweep voltametry for a simple Nernstian E process

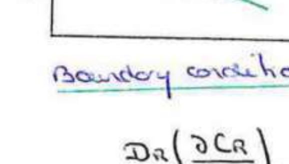
$$Ox + ne^- \rightleftharpoons Red$$

Description of the sweep experiment:

Planar electrode (unidirectionnal semi-infinite diffusion regime), no stirring. The potential is initially set to a value where no reaction occur (open circuit potential). The potential is step linearly at a given scan rate v (V/s).

Case of a reduction: Ox is the only species present in solution $E_i \gg E^\circ$

$$E = E_i - v \times t$$



$$\frac{\partial C_O(x,t)}{\partial t} = D_O \frac{\partial^2 C_O(x,t)}{\partial x^2}$$

$$\frac{\partial C_R(x,t)}{\partial t} = D_R \frac{\partial^2 C_R(x,t)}{\partial x^2}$$

Boundary conditions: $C_O(x,0) = C_O^*$ $\lim_{x \to \infty} C_O(x,t) = C_O^*$

$C_R(x,0) = 0$ $\lim_{x \to \infty} C_R(x,t) = 0$

$$D_R\left(\frac{\partial C_R}{\partial x}\right)_{x=0} + D_O\left(\frac{\partial C_O(x,t)}{\partial x}\right)_{x=0} = 0$$

The system is Nernstian (fast ET rate):

- The concentration of Ox and Red adjust at the electrode surface according the Nernst equation

$$\frac{C_O(0,t)}{C_R(0,t)} = \exp\left(\frac{nF}{RT}(E - E^{\circ\prime})\right) \xRightarrow{E = E_i - vt} \frac{C_O(0,t)}{C_R(0,t)} = \exp\left(\frac{nF}{RT}(E_i - vt - E^{\circ\prime})\right)$$

The concentration ratio now depends on time. This is the main difference with constant potential experiments.

Changing notations:

$$\frac{C_O(0,t)}{} = \exp\left(\frac{nF}{RT}(E_i - E^{\circ\prime})\right)\exp\left(-\frac{nF}{RT}vt\right) = \theta_0 \exp(-\sigma t) = \theta_0 S(t)$$ with

$\theta_0 = \exp\left(\frac{nF}{RT}(E_i - E^{\circ\prime})\right)$ Fixed value

$\sigma = \frac{nF}{RT} v$ possibly variable value

Solving the Fick equations with TL gives the L{concentrations}

$$\frac{\partial C_o(x,t)}{\partial t} = D_o \frac{\partial^2 C_o(x,t)}{\partial x^2} \overset{TL}{\Longrightarrow} \bar{C}_o(x,s) = \frac{C_o^*}{s} + A_o(s)\exp\left(-\sqrt{s/D}\,x\right)$$

since $C_R^* = 0$

$$\frac{\partial C_r(x,t)}{\partial t} = D_R \frac{\partial^2 C_R(x,t)}{\partial x^2} \overset{TL}{\Longrightarrow} \bar{C}_R(x,s) = \frac{C_R^*}{s} + A_r(s)\exp\left(-\sqrt{\frac{s}{D}}\,x\right) = A_R(s)\exp\left(-\sqrt{\frac{s}{D}}\,x\right)$$

L{Current} then becomes

$$\bar{i}(s) = nFA\bar{J}_o(0,s) = -nFAD_o\left(\frac{\partial \bar{C}_o(x,s)}{\partial x}\right)_{x=0} \quad \text{with} \quad \left(\frac{\partial \bar{C}_o(x,s)}{\partial x}\right)_x = -\sqrt{\frac{s}{D}}\,A_o(s)\exp\left(-\sqrt{\frac{s}{D}}\,x\right)$$

$$\Rightarrow \bar{i}(s) = -nFAD_o\left(\frac{\partial \bar{C}_o(x,s)}{\partial x}\right)_{x=0} = nFAD_o\sqrt{\frac{s}{D_o}}\,A_o(s) = nFA\sqrt{D_o s}\,A_o(s) \Rightarrow A_o(s) = \frac{\bar{i}(s)}{nFA(D_o s)^{1/2}}$$

$$\Rightarrow \bar{C}_o(x,s) = \frac{C_o^*}{s} + \frac{\bar{i}(s)}{nFA(D_o s)^{1/2}}\exp\left(-\sqrt{\frac{s}{D}}\,x\right) \quad \text{and} \quad \bar{C}_o(0,s) = \frac{C_o^*}{s} + \frac{\bar{i}(s)}{nFA(D_o s)^{1/2}}$$

$\bar{C}_o(0,s) = \frac{C_o^*}{s} + \frac{\bar{i}(s)}{nFA(D_o s)^{1/2}}$ Inversion of the transform cannot be carried out from tabulated functions.

$L^{-1}\{h(s) \times g(s)\} = H(t) \times G(t)$ The star represent $= \int_0^t H(t-\tau)\,G(\tau)\,d\tau$ the convolution integral

τ = auxiliary variable.

One can obtain it from the convolution integral:

$$\xrightarrow[h(s) = 1/s^{1/2}]{\text{Upon setting } g(s) = \bar{i}(s)} \quad \bar{C}_o(0,s) = \frac{C_o^*}{s} + \frac{1}{nFA(D_o)^{1/2}}\left(h(s) \times g(s)\right)$$

Then knowing that $L\{i(t)\} = \bar{i}(s)$ and $L\left\{\frac{1}{(\pi t)^{1/2}}\right\} = \frac{1}{s^{1/2}}$

$$\Rightarrow L^{-1}\{\bar{C}_o(0,s)\} = C_o(0,t) = C_o^* + \frac{1}{nFA(\pi D_o)^{1/2}}\int_0^t (t-\tau)^{-1/2}\,i(\tau)\,d\tau.$$

$$C_o(0,t) = C_o^* - \frac{1}{(\pi D_o)^{1/2}}\int_0^t (t-\tau)^{-1/2} f(\tau)\,d\tau \quad \text{with} \quad f(\tau) = \frac{-i(\tau)}{nFA}$$

NB: $\int_0^t (t-\tau)^{-1/2} f(\tau)\,d\tau$
Is also called the convoluted current noted $\hat{I}(t)$
$\Rightarrow C_o(0,t) = C_o^* - \frac{\hat{I}(t)}{(\pi D_o)^{1/2}}$

And one can similarly demonstrate that, knowing that:

$$\frac{C_o(0,t)}{C_R(0,t)} = \exp\left(\frac{nF}{RT}(E_i - E^{o\prime})\right)\exp\left(-\frac{nF}{RT}vt\right) = \theta_o\exp(-\sigma t) = \theta_o S(t)$$

(which means that the ET is Nernstian and that E varies linearly with t)

$$\Rightarrow \quad = \frac{C_o^* - \frac{1}{(\pi D_o)^{1/2}}\int_0^t (t-\tau)^{-1/2} f(\tau)\,d\tau}{\frac{1}{(\pi D_R)^{1/2}}\int_0^t (t-\tau)^{-1/2} f(\tau)\,d\tau} \quad \Rightarrow \quad \frac{C_o(0,t)}{C_R(0,t)} = \frac{C_o^* - \frac{\hat{I}(t)}{(\pi D_o)^{1/2}}}{\frac{\hat{I}(t)}{(\pi D_R)^{1/2}}}$$

$$C_o^* - \frac{1}{(\pi D_o)^{1/2}}\int_0^t (t-\tau)^{-1/2} f(\tau)\,d\tau = \theta_o S(t)\frac{1}{(\pi D_R)^{1/2}}\int_0^t (t-\tau)^{-1/2} f(\tau)\,d\tau.$$

$$C_o^* = \left(\theta_o S(t)\frac{1}{(\pi D_R)^{1/2}} + \frac{1}{(\pi D_o)^{1/2}}\right)\int_0^t (t-\tau)^{-1/2} f(\tau)\,d\tau \Rightarrow \frac{C_o^*}{\theta_o S(t)\frac{1}{(\pi D_R)^{1/2}} + \frac{1}{(\pi D_o)^{1/2}}} = \int_0^t (t-\tau)^{-1/2} f(\tau)\,d\tau$$

$$\frac{nFA(\pi D_o)^{1/2}C_o^*}{\theta_o S(t)\left(\frac{D_o}{D_R}\right)^{1/2} + 1} = -\int_0^t (t-\tau)^{-1/2}\,i(\tau)\,d\tau$$

$$\frac{nFA(\pi D_o)^{1/2}C_o^*}{\theta_o S(t)\xi + 1} = -\int_0^t (t-\tau)^{-1/2}\,i(\tau)\,d\tau$$

No exact solution to this equation, requires a numerical treatment.

Since the goal is to calculate current-potential curves rather than current-time curves it is more convenient to change from $i(t)$ to $i(E)$. To go from $i(t)$ to $i(E)$ we use the following change in variable $\tau \to \boxed{\sigma\tau}$ < dimensionless and proportional to potential

$$\text{Let} \begin{cases} f(t) = g(\sigma t) \\ \text{and we note } z = \sigma\tau = \frac{nF}{RT}v\tau \Rightarrow dz = \sigma\,d\tau. \end{cases} \quad \text{with:} \begin{cases} \sigma t = \frac{nF}{RT}vt \text{ and } \begin{matrix} E = E_1 - vt \\ vt = E_1 - E. \end{matrix} \\ f(t) = \frac{-i(t)}{nFA} \end{cases}$$

$$\frac{(\pi D_o)^{1/2}C_o^*}{\theta_o S(t)\xi - 1} = \int_0^t (t-\tau)^{-1/2} f(\tau)\,d\tau.$$

$$\int_0^t (t-\tau)^{-1/2} f(\tau)\,d\tau = \int_0^t (t-\tau)^{-1/2} g(\sigma\tau)\,d\tau = \int_0^{\sigma t}\left(t - \frac{z}{\sigma}\right)^{-1/2} g(z)\frac{dz}{\sigma}$$

since $z = 0$ for $\tau = 0$ and $z = \sigma t$ for $\tau = t$

$$\frac{1}{\sigma}\int_0^{\sigma t}\left(\frac{\sigma t - z}{\sigma}\right)^{-1/2} g(z)\,dz = \frac{1}{\sigma}\left(\frac{1}{\sigma}\right)^{-1/2}\int_0^{\sigma t}(\sigma t - z)^{-1/2} g(z)\,dz = \left(\frac{1}{\sigma}\right)^{1/2}\int_0^{\sigma t}(\sigma t - z)^{-1/2} g(z)\,dz$$

$$= \sigma^{-1/2}\int_0^{\sigma t}(\sigma t - z)^{-1/2} g(z)\,dz.$$

$$(\pi D_o)^{1/2}C_o^* \quad \sigma^{-1/2}\int^{\sigma t}(\sigma t - z)^{-1/2} g(z)\,dz \Rightarrow 1 \quad = \frac{\sigma^{-1/2}}{} \int^{\sigma t}(\sigma t - z)^{-1/2} g(z)\,dz$$

his integral can be made dimensionless using $\chi(z) = \frac{g(z)}{(\pi D_o \sigma)^{1/2} C_o^*}$

$$\frac{1}{\theta_o S(\sigma t)\xi + 1} = \int_0^{\sigma t} (\sigma t - z)^{-1/2} \chi(z)\, dz = \int_0^{\sigma t} \frac{\chi(z)}{(\sigma t - z)^{1/2}}\, dz \Rightarrow \frac{1}{\theta_o S(\sigma t)\xi + 1} = \int_0^{\sigma t} \frac{\chi(z)}{(\sigma t - z)^{1/2}}\, dz$$

And Since : $\begin{cases} f(t) = -\frac{i(t)}{nFA} \\ f(\tau) = g(\sigma\tau) = g(z) \\ z = \sigma t \end{cases} \Rightarrow \begin{matrix} g(z) = (\pi D_o \sigma)^{1/2} C_o^* \chi(z) \\ g(z) = g(\sigma t) = (\pi D_o \sigma)^{1/2} C_o^* \chi(\sigma t) \end{matrix}$ This integral provides values of $\chi(\sigma t)$ as a function of σt.

$\Rightarrow i = -nFA(\pi D_o \sigma)^{1/2} C_o^* \chi(\sigma t)$ $\qquad \frac{1}{\theta_o S(\sigma t)\xi + 1} = \int_0^{\sigma t} \frac{\chi(z)}{(\sigma t - z)^{1/2}}\, dz$

or a given value of E at t, $S(\sigma t)$ can be calculated which leads to $\chi(\sigma t)$ and then to the urrent $i(t)$

$$\underset{\text{can be calculated}}{S(t)} = \exp\left(-\frac{nF}{RT} v t\right) = \exp(-\overset{\text{cste}}{\sigma} t) \Rightarrow \frac{\overset{\text{cste}}{1}}{\theta_o S(\sigma t)\overset{\text{cste}}{\xi} + 1} = \int_0^{\sigma t} \frac{\chi(z)}{(\sigma t - z)^{1/2}}\, dz \Rightarrow i(t) = -nFA(\pi D_o \sigma)^{1/2} C_o^* \chi(\sigma t)$$

$\pi^{1/2}\chi(\sigma t)$ reaches a maximum where $\pi^{1/2}\chi(\sigma t) = 0{,}4463$ at $E = E_{peak}$

$$i_{peak,cathodic} = -0{,}4463 \times nFA \left(\frac{D_o nF v}{RT}\right)^{1/2} C_o^* = -0{,}4463 \times nFA \left(\frac{nF}{RT}\right)^{1/2} D_o^{1/2} v^{1/2} C_o^*$$

andles - Sevcik equation : $\underset{A}{i_{p,c}} = -(2{,}69 \cdot 10^5)\, n^{3/2} \overset{cm^2}{A} \underset{cm^2 s^{-1}}{D_o^{1/2}} \underset{V s^{-1}}{v^{1/2}} C_o^*$ mol.cm⁻³

The potential value Epeak corresponding to $I_{p,c}$ can be calculated

$$E_{p,c} = E^{0'} - \frac{RT}{nF}\ln\xi - 1{.}109\frac{RT}{nF} \qquad \xi = \left(\frac{D_o}{D_R}\right)^{1/2}$$

$$E_{p,c} = E_{1/2} - 1{.}109\frac{RT}{nF} = E_{1/2} - \frac{0{,}0285\ V}{n}$$ at 25°C found from numerical treatments

⇒ Epeak is invariant with concentration and scan rate

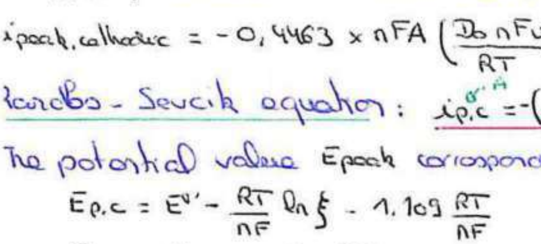
⇒ Ipeak varies with $v^{1/2}$ which indicates a diffusion control

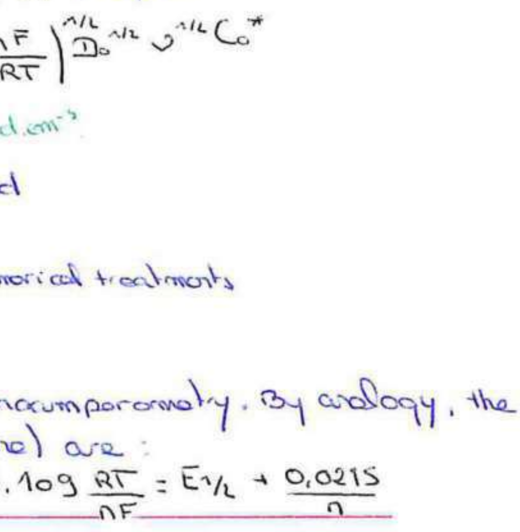
his is analogous to the variation of ip with $t^{-1/2}$ in chronoamperometry. By analogy, the eak current and peak potential for an oxidation (Red alone) are :

$$i_{p,a} = (2{,}69 \cdot 10^5)\, n^{3/2} A D_R^{1/2} v^{1/2} C_R^* \qquad E_{p,a} = E_{1/2} + 1{.}109\frac{RT}{nF} = E_{1/2} + \frac{0{,}0285}{n}$$

$$\Rightarrow |\Delta E_p| = E_{p,c} - E_{p,a} = \frac{0{,}056\ V}{n}$$

lethods for determining the proper baseline for Ip measurements :





Nicholson semiempirical formula

$$\frac{i_{pc}}{i_{pa}} = \left(\frac{i_{pc}^0}{i_{pa}}\right) + \frac{0{,}485\, i_\lambda}{i_{pa}} + 0{,}086$$

Linear sweep voltametry for a slow electrochemical reaction

Case of a reduction : Ox is the only species present in solution

Fully irreversible : with $\eta > 0{,}12n$, the inverse reaction (oxidation of red) can be neglected

We have established that $C_o(0,t) = C_o^* - \frac{1}{(\pi D_o)^{1/2}} \int_0^t (t-\tau)^{-1/2} f(\tau)\, d\tau$

$$\frac{i}{nFA} = -k_r C_o(0,t) = -k_r^0 C_o(0,t) \exp\left(-\frac{\alpha_r nFE}{RT}\right)$$

$$= -k_r C_o(0,t) \underbrace{\exp\left(-\frac{\alpha_r nFE_i}{RT}\right)}_{k_r'} \underbrace{\exp\left(\frac{\alpha_r nF v}{RT} t\right)}_{\exp \beta t} = k_r' C_o(0,t) \exp \beta t$$

hen let: $\begin{cases} f(t) = g(\beta t) \\ z = \beta\tau = \frac{\alpha_r nF v}{RT}\tau \end{cases} \Rightarrow \int_0^t (t-\tau)^{-1/2} f(\tau)\, d\tau \Rightarrow \int_0^{\beta t} \left(t - \frac{z}{\beta}\right)^{-1/2} g(z) \frac{dz}{\beta} = \beta^{-1/2} \int_0^{\beta t} (\beta t - z)^{-1/2} g(z)\, dz$

$$C_o(0,t) = C_o^* - \frac{1}{(\pi D_o)^{1/2}} \int_0^t (t-\tau)^{-1/2} f(\tau)\, d\tau \Rightarrow C_o(0,t) = C_o^* - \frac{1}{(\beta\pi D_o)^{1/2}} \int_0^{\beta t} (\beta t - z)^{-1/2} g(z)\, dz$$

$$\frac{C_O(0,t)}{C_O^*} = 1 - \frac{1}{C_O^*(\beta\pi D_O)^{1/2}}\int_0^{\beta t}(\beta t - z)^{-1/2} g(z)\,dz \xrightarrow[\chi(z)=\frac{g(z)}{C_O^*(\beta\pi D_O)^{1/2}}]{} \frac{C_O(0,t)}{C_O^*} = 1 - \int_0^{\beta t}\frac{\chi(z)}{(\beta t - z)^{1/2}}\,dz$$

$$\chi(z) = \frac{g(z)}{C_O^*(\beta\pi D_O)^{1/2}} = -\frac{i(\beta t)}{nFAC_O^*(\beta\pi D_O)^{1/2}}$$

$$i(\beta t) = -nFAC_O^*(\beta\pi D_O)^{1/2}\chi(\beta t) = -nFAC_O^*\left(\frac{\alpha_r n F v \pi D_O}{RT}\right)^{1/2}\chi(\beta t) = -nFA\pi^{1/2} D_O^{1/2} v^{1/2} C_O^*\left(\frac{\alpha_r n F}{RT}\right)^{1/2}\chi($$

$\Rightarrow$ The current is still proportional to C and to $v^{1/2}$

$\pi^{1/2}\chi(\beta t)$ goes through a maximum of 0,4953

$i_{p,c} = -(2{,}99 \times 10^5) \times n(\alpha_r n)^{1/2} A D_O^{1/2} v^{1/2} C_O^*$ → Calcul of an from ip.

$$E_{p,c} = -\frac{RT}{\alpha_r n F}\left(0{,}780 - \ln\frac{k_r^0}{D_O^{1/2}} + \ln\left(\frac{\alpha_r n F v}{RT}\right)^{1/2}\right)$$

$$= E^{0'} - \frac{RT}{\alpha_r n F}\left(0{,}780 - \ln\frac{k^0}{D_O^{1/2}} + \ln\left(\frac{\alpha_r n F v}{RT}\right)^{1/2}\right) \text{ with } k^0 = k_r^0 \exp\left(\frac{-\alpha_r n F E^{0'}}{RT}\right)$$

↳ Calcul of k^0 if an is known.

One can define $E_{p,c/2}$ as the potential where the current is at half the peak value. ($i_{p/2}$).

$\Rightarrow E_{p,c} - E_{p/2} = \frac{1{,}857 RT}{\alpha_r n F} = \frac{0{,}048}{\alpha_r n}$

$i_{pc} = -0{,}227\, nFAC_O^* k^0 \exp\left(\frac{-\alpha_r n F}{RT}\right)(E_{pc} - E^{0'})$ $\Rightarrow$ calcul of an from $\ln i_p = f(E_p - E^{0'})$ a slope of $-\alpha_r nF/RT$ and an intercept proportional to k^0.

This expression of $i_{p,c}$ is obtained upon combining: $i = -nFA\pi^{1/2} D_O^{1/2} v^{1/2} C_O^*\left(\frac{\alpha_r n F}{RT}\right)^{1/2}\chi(\beta t)$ and $E_{pc} = E^{0'} - \frac{RT}{\alpha_r n F}\left(0{,}780 - \ln\frac{k^0}{D_O^{1/2}} + \ln\left(\frac{\alpha_r n F v}{RT}\right)^{1/2}\right)$

Case of an oxidation: Red is the only species present in solution

$$i_{p,a} = (2{,}99 \times 10^5)\, n(1-\alpha_r)^{1/2} n^{1/2} A D_R^{1/2} v^{1/2} C_R^*$$

$$i_{p,a} = 0{,}227\, nFAC_R^* k^0 \exp\frac{\alpha_o n F}{RT}(E_{pa} - E^{0'})$$

Coupled chemical process

EC$_i$ mechanism in stationnary regime

$$\begin{array}{l} Ox + ne \rightleftharpoons Red \\ Red \xrightarrow{k} P \end{array} \quad \begin{cases} \frac{\partial C_O(x,t)}{\partial t} = 0 = D_O \frac{\partial^2 C_O(x,t)}{\partial x^2} \\ \frac{\partial C_R(x,t)}{\partial t} = 0 = D_R \frac{\partial^2 C_R(x,t)}{\partial x^2} - kC_R(x,t). \\ D_O = D_R \end{cases}$$

Case of a reduction

$$\begin{cases} C_R(x,0) = 0 & \lim_{x\to\infty} C_R(x,t) = 0 \\ C_O(x,0) = C_O^* & \lim_{x\to\infty} C_O(x,t) = C_O^* \\ C_P(x,0) = 0 & \lim_{x\to\infty} C_P(x,t) = 0 \end{cases}$$

Calculation of $C_O(x)$

$D\frac{\partial^2 C_O(x,t)}{\partial x^2} = 0 \Rightarrow$ The concentration profil $C_O(x)$ will be linear one can use the diffusion layer model where $\Rightarrow C_O(x) = C_O(0) - \frac{x}{\delta}(C_O(0) - C_O^*)$

$$i = -nFAD\left(\frac{\partial C_O(x)}{\partial x}\right)_{x=0} = -\frac{nFAD}{\delta}(C_O^* - C_O(0))$$

The flux conservation at the electrode gives $-D\left(\frac{\partial C_O(x)}{\partial x}\right)_{x=0} = D\left(\frac{\partial C_R(x)}{\partial x}\right)_{x=0} = \frac{i}{nFA}$

Calculation of $C_R(x)$ requires to solve $0 = D\frac{\partial^2 C_R(x,t)}{\partial x^2} - kC_R(x,t) \Rightarrow \frac{\partial^2 C_R(x,t)}{\partial x^2} = \frac{k}{D}C_R(x,t)$

$\Rightarrow C_R(x) = X\exp\left(-\sqrt{\frac{k}{D}}\,x\right) + Y\exp\left(\sqrt{\frac{k}{D}}\,x\right)$ with X, Y constants.

Flow conservation at the electrode: $D\left(\frac{\partial C_O(x)}{\partial x}\right)_{x=0} = -D\left(\frac{\partial C_R(x)}{\partial x}\right)_{x=0}$

leads to: $\frac{(C_O^* - C_O(0))}{\delta} = X\sqrt{\frac{k}{D}} - Y\sqrt{\frac{k}{D}}$

Also $\lim_{x\to\infty} C_R(x) = 0 \Rightarrow C_R(\delta) = 0 \Rightarrow C_R(\delta) = X\exp\left(-\sqrt{\frac{k}{D}}\,\delta\right) + Y\exp\left(\sqrt{\frac{k}{D}}\,\delta\right) = 0$

$\frac{[C_O^* - C_O(0)]}{\delta} = X\sqrt{\frac{k}{D}} - Y\sqrt{\frac{k}{D}}$

$Y\exp\left(\sqrt{k}\ \delta\right) = 0$

Further calculation requires to introduce the dimensionless parameter: $\lambda = \frac{k\delta^2}{D}$

$$\frac{[C_O^* - C_O(0)]}{\delta} = X\sqrt{\frac{k}{D}} - Y\sqrt{\frac{k}{D}}$$

$$C_R(\delta) = X\exp\left(-\sqrt{\frac{k}{D}}\delta\right) + Y\exp\left(\sqrt{\frac{k}{D}}\delta\right) = 0$$

$$\lambda = \frac{k\delta^2}{D} \Longrightarrow \boxed{\begin{array}{l} \frac{[C_O^* - C_O(0)]}{\sqrt{\lambda}} = X - Y \\ X\exp(-\sqrt{\lambda}) + Y\exp(\sqrt{\lambda}) = 0 \end{array}}$$

$$Y = \frac{[C_O(0) - C_O^*]}{\sqrt{\lambda}(1 + \exp(2\sqrt{\lambda}))}$$

$$X = \frac{[C_O^* - C_O(0)]\exp(2\sqrt{\lambda})}{\sqrt{\lambda}(1 + \exp(2\sqrt{\lambda}))}$$

$$C_R(0) = X + Y = \frac{[C_O(0) - C_O^*]}{\sqrt{\lambda}}\left(\frac{1 - \exp(2\sqrt{\lambda})}{1 + \exp(2\sqrt{\lambda})}\right) \Longleftarrow \tanh(z) = \frac{1 - \exp(-2z)}{1 + \exp(-2z)}$$

$$C_R(0) = X + Y = [C_O^* - C_O(0)]\frac{\tanh\sqrt{\lambda}}{\sqrt{\lambda}}$$

ernst $\longrightarrow \exp\left(\frac{nF(E - E^0)}{RT}\right) = \exp(\xi) = \frac{C_O(0)}{C_R(0)} \longrightarrow \exp(\xi) = \frac{C_O(0)}{[C_O^* - C_O(0)]\frac{\tanh\sqrt{\lambda}}{\sqrt{\lambda}}} = \frac{C_O(0)\sqrt{\lambda}}{[C_O^* - C_O(0)]\tanh\sqrt{\lambda}}$

$$E = E^0 + \frac{RT}{nF}\ln\left(\frac{C_O(0)}{C_O^* - C_O(0)}\right) + \frac{RT}{nF}\ln\left(\frac{\sqrt{\lambda}}{\tanh\sqrt{\lambda}}\right)$$

$\Rightarrow E = E^0 + \frac{RT}{nF}\ln\left(\frac{\sqrt{\lambda}}{\tanh\sqrt{\lambda}}\right) + \frac{RT}{nF}\ln\left(\frac{i_l - i}{i}\right)$ with: $i = nFAD\left(\frac{\partial C_O(x)}{\partial x}\right)_{x=0} = \frac{nFAD}{\delta}\left(C_O^* - C_O(0)\right)$

$i_l = \frac{nFA}{\delta}C_O^*$

he equation is similar to that obtained in the absence of chemical step but with E values shifted by: $\Delta E = \frac{RT}{nF}\ln\left(\frac{\sqrt{\lambda}}{\tanh\sqrt{\lambda}}\right)$ $\lambda = \frac{k\delta^2}{D}$

he apparent formal potential is then: $E_{app}^{0'} = E^{0'} + \frac{RT}{nF}\ln\left(\frac{\sqrt{\lambda}}{\tanh\sqrt{\lambda}}\right)$

λ is the dimensionless kinetic parameter which determines the amplitude of the otential shift $\lambda = \frac{k\delta^2}{D}$.

$\lambda \to \infty$ $\tanh(x) \to 1$ $\Delta E \to \frac{RT}{2nF}\ln\lambda = 2,3\frac{RT}{2nF}\log\lambda$ with $\ln\sqrt{\lambda} = \frac{1}{2}\ln\lambda$

t 25°C for $n = 1$ $\Delta E \to 0{,}03\log\lambda$

$\lambda = \frac{k\delta^2}{D}$ for RDE $\begin{cases} i_{l,c} = 0{,}0620\, nFAD_0^{2/3}\omega^{1/2}\nu^{-1/6}\, O^* \\ \delta_0 = 1{,}61\, D_0^{1/3}\omega^{-1/2}\nu^{1/6} \\ \Rightarrow \lambda \text{ varies with } 1/\omega \end{cases}$

λ varies with δ^2

$E_{app}^{0'} = f(\log\omega)$ gives a straight line with a slope

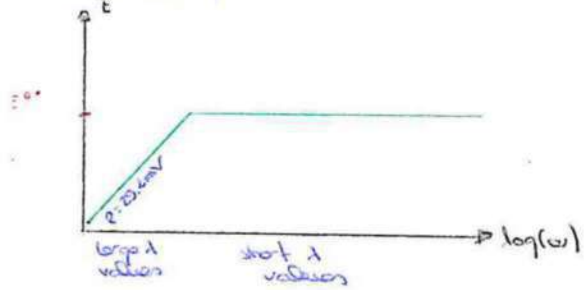
$p = \frac{-2{,}3\,RT}{2F} = -\frac{1{,}15\,RT}{F} = -29{,}2$ mV/decade

$\Longrightarrow$ Diagnostic of an EC_i process.

$Ox + ne \overset{E^0}{\rightleftarrows} Red$ $Red \xrightarrow{k} P$ key parameter imposed by the pb $\to k, E^0, C^*, D, \nu, n$
key exp. parameter to be adjusted $\to \omega$.

$\lambda \to 0$ $\frac{\sqrt{\lambda}}{\tanh\sqrt{\lambda}} \to 1$ $E_{app}^{0'} \to E^{0'}$ as if there is no reaction.

his happens for instance with RDE when the rotation rate gets very large, the diffusion layer s fed so well that the chemical step has no effects. Mass transport is much faster than e kinetics of the chemical reaction.



Allows to reveal the existence of an EC_i mechanism and eventually to estimate the E° value if λ is short enough.