Mass transfert or Mass transport

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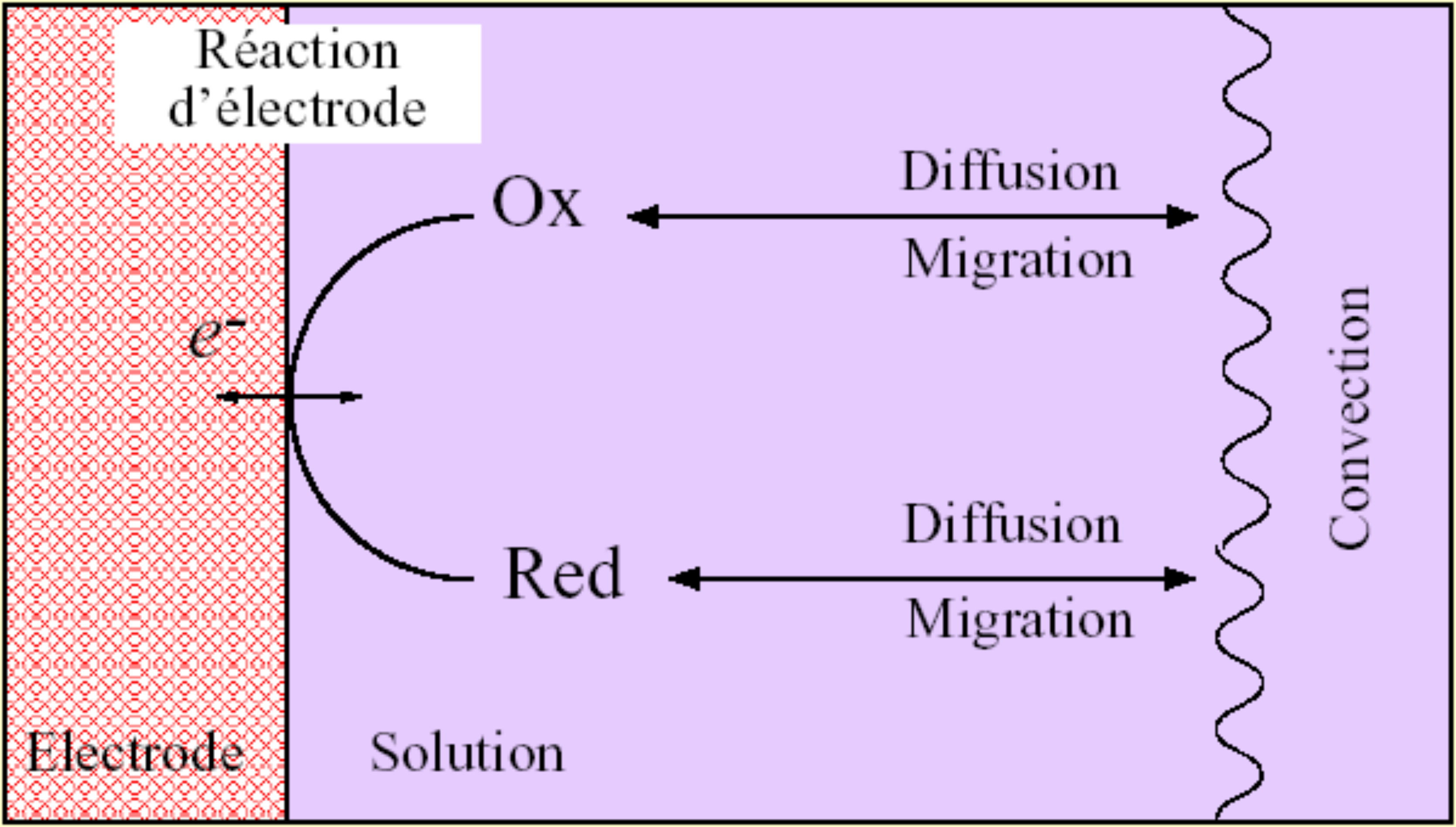
Mass transfert or Mass transport

- Migration or conduction

- Difussion

- Convection
  - natural
  - forced

Why mass transfer is important in electrochemistry?



Outline

- Introduction to mass transfer.
- Steady state voltammetry on a rotating disc (RDE).
- The microdisc electrode.
- A comparison of the RDE with microdisc electrodes.
- Migration – movement of charges due to an electric field.
- Summary.

Migration

eletric field : $\varepsilon = \dfrac{\Delta\phi}{l}$

charge of the ion : ze

Electric force : $F_e = z\,e\,\varepsilon = z\,e\,\dfrac{\Delta\phi}{l}$

Force against the movement? → Viscous force

Viscous coefficient

$$F_{at} = f\,s \qquad f = 6\,\pi\,\eta\,a$$

rate

Solvo-dynamic radii

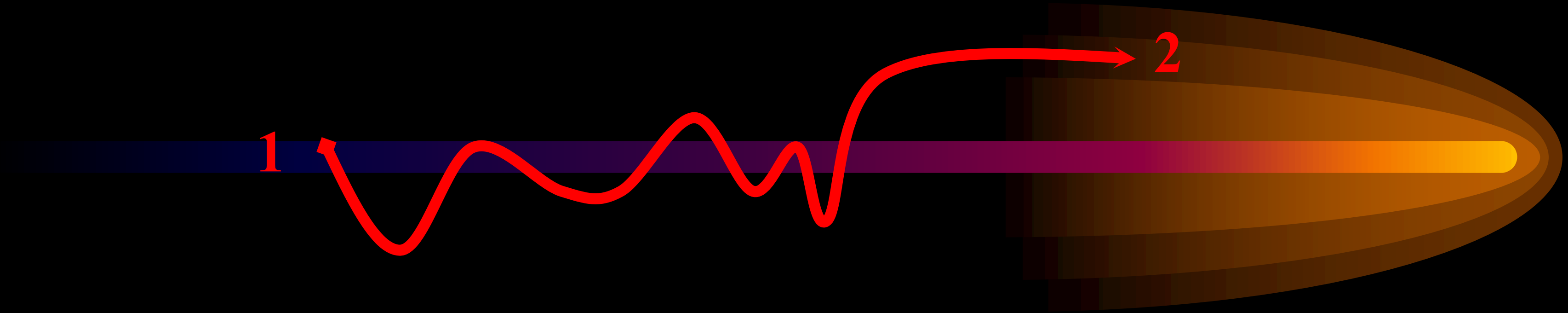
Migration: Steady State

$$F_e = F_{at} \mapsto z\,e\,\varepsilon = f\,s \mapsto s = \frac{z\,e\,\varepsilon}{f}$$

$$\boxed{\text{mobility}: u = \frac{s}{\varepsilon} = \frac{z\,e}{f} = \frac{z\,e}{6\,\pi\,\eta\,a}}$$

$$j = -\kappa \left(\frac{\partial V}{\partial x} \right) \text{(Ohmic Law)}$$

Diffusion



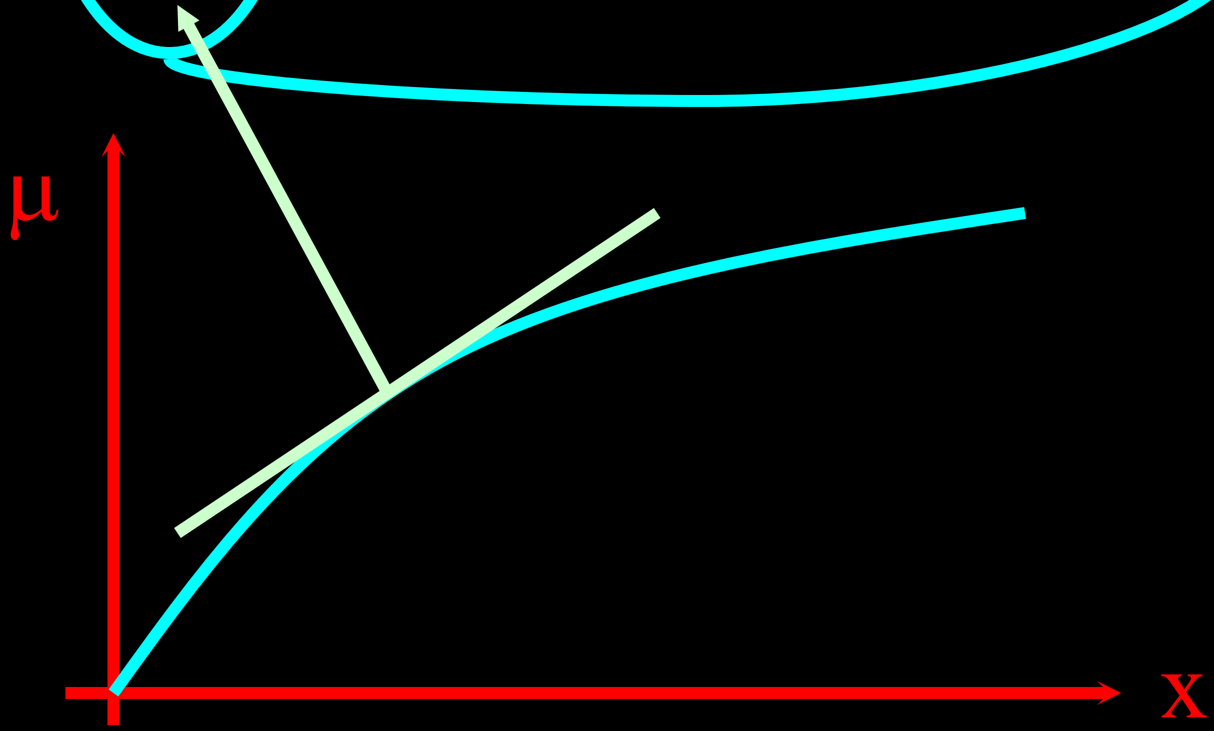
At constant T and P, which is the direction of the spontaneous transformation?

$$\boxed{w = \mu_2 - \mu_1 \rightarrow \text{if spontaneous} \rightarrow w < 0}$$

$$\boxed{dw = \mu(x + dx) - \mu(x) \qquad dw = \cancel{\mu(x)} + \left(\frac{\partial \mu}{\partial x}\right) dx - \cancel{\mu(x)}}$$

Diffusion

$$dw = \left(\frac{\partial \mu}{\partial x}\right) dx \qquad dw = - F\, dx$$



Diffusion

Chemical potential gradient $\left(\frac{d\mu}{dx}\right)$: $\qquad \xrightarrow{+}$

Driving force $\left(F_D = -\frac{d\mu}{dx}\right)$: $\qquad \longleftarrow$

Diffusional flux (J): $\qquad \longleftarrow$

Diffusion

Steady State: $J(t)$ = constant e $F_D(t)$ = constant

Which is the relationship between the flux and the concentration gradient?

$$J = A + BF_D + CF_D^2 + \ldots\ldots \qquad \text{with } A, B, C, \ldots \text{ constants}$$

$$\text{as } F_D \text{ must be small}: J = \cancel{A +} BF_D + \cancel{CF_D^2} + \ldots\ldots \Rightarrow J = BF_D$$

$$F_D = -\frac{d\mu}{dx}$$

e

$$\mu = \mu^o + RT\ln(f\,C)$$

$$F_D = -R\,T\frac{dC}{dx}\left[1 + \frac{d\ln f}{d\ln C}\right]$$

Diffusion

$$J = - B\,R\,T\left[1 + \frac{d\ln f}{d\ln C}\right]\left(\frac{dC}{dx}\right)$$

$$J = - D\left(\frac{dC}{dx}\right)$$

1st Fick Law

$$J = - D\left(\frac{dC}{dx}\right)\begin{cases} C = \mathrm{mol\,cm^{-3}} \\ J = \mathrm{mol\,cm^{-2}\,s^{-1}} \\ D = \mathrm{cm^{2}\,s^{-1}} \end{cases}$$

Diffusion

$$D = BRT\left[1 + \frac{d\ln f}{d\ln C}\right] = \text{Diffusion coefficient}$$

electrolyte	**D/10-5 cm2 s-1**	**(p/C molalidade)**		
	0,05	**0,1**	**0,2**	**0,5**
HCl	3,07	3,05	3,06	3,18
LiCl	1,28	1,28	1,27	1,28
NaCl	1,51	1,48	1,48	1,47

$$D(C,T) \approx D(T)$$

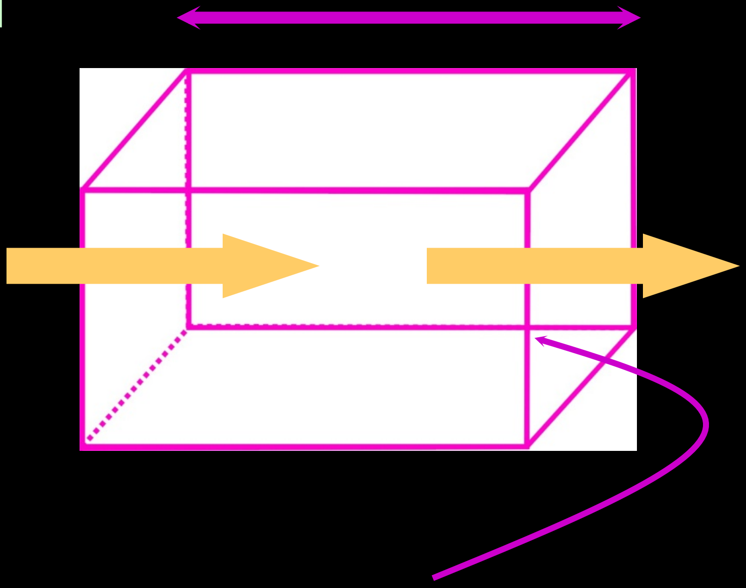
Diffusion out steady state

Steady State: J(t) = cte e C(x,t) = cte, c/t
Out of ss regime?

In

$$C_{eq} = C$$

$$J_{eq} = -D\frac{dC}{dx}$$



dx

Out

$$C_s = C + \frac{dC}{dx}dx$$

$$J_s = -D\frac{d}{dx}\left[C + \frac{dC}{dx}dx\right]$$

Transversal area = unity

Diffusion out steady state

$$J_s = -D\frac{d}{dx}\left[C + \frac{dC}{dx}dx\right] \Longrightarrow J_s = \underbrace{-D\frac{dC}{dx}}_{J_{eq}} - D\frac{d^2C}{dx^2}dx$$

$$J_{eq} - Js = D\frac{d^2C}{dx^2} \Longrightarrow \frac{dC(x,t)}{dt} = D\frac{d^2C}{dx^2}$$

Second Fick Law – C(x,t)

$$e^- + O_{(sol)} \rightarrow R_{(sol)} \quad t = 0 \quad C_o = C_o^o$$

If the O suppy is not effective : $C_o^{sup} < C_o^o$

If the R dispersion is not effective : $C_R^{sup} > C_R^o$

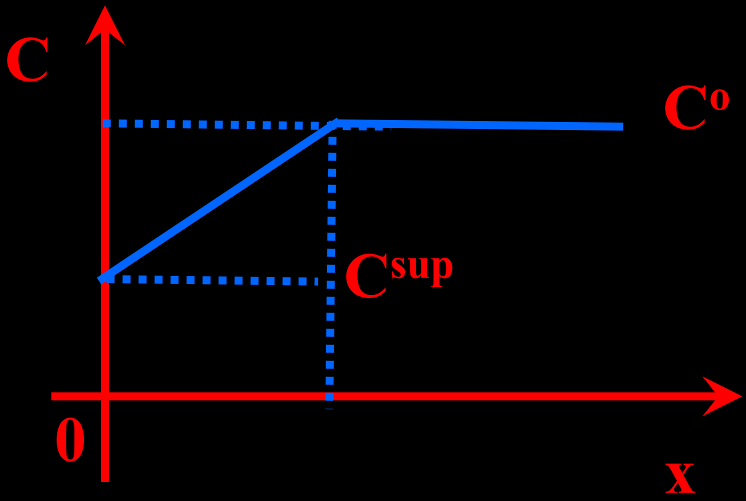
For t > 0 – Polarization for mass tranport

Diffusional flux given by the First Fick Law:

$$J_i^{dif} = -D_i\left(\frac{dC_i}{dx}\right)$$

Diffusion coefficient

Nernst approximation



$$\frac{dC_i}{dx} \approx \frac{C_i^o - C_i^{sup}}{\delta}$$

$$J_i^{dif} = -D_i\left(\frac{C_i^o - C_i^{sup}}{\delta}\right) = m_i\left(C_i^{sup} - C_i^o\right)$$

Mass transfer coefficient

Fast charge transfer, that is to say, not polarization by activation, so for t > 0

$$E = E^{o} - \frac{RT}{nF} \ln \frac{C_R^{sup}}{C_O^{sup}}$$

In a equilibrium:

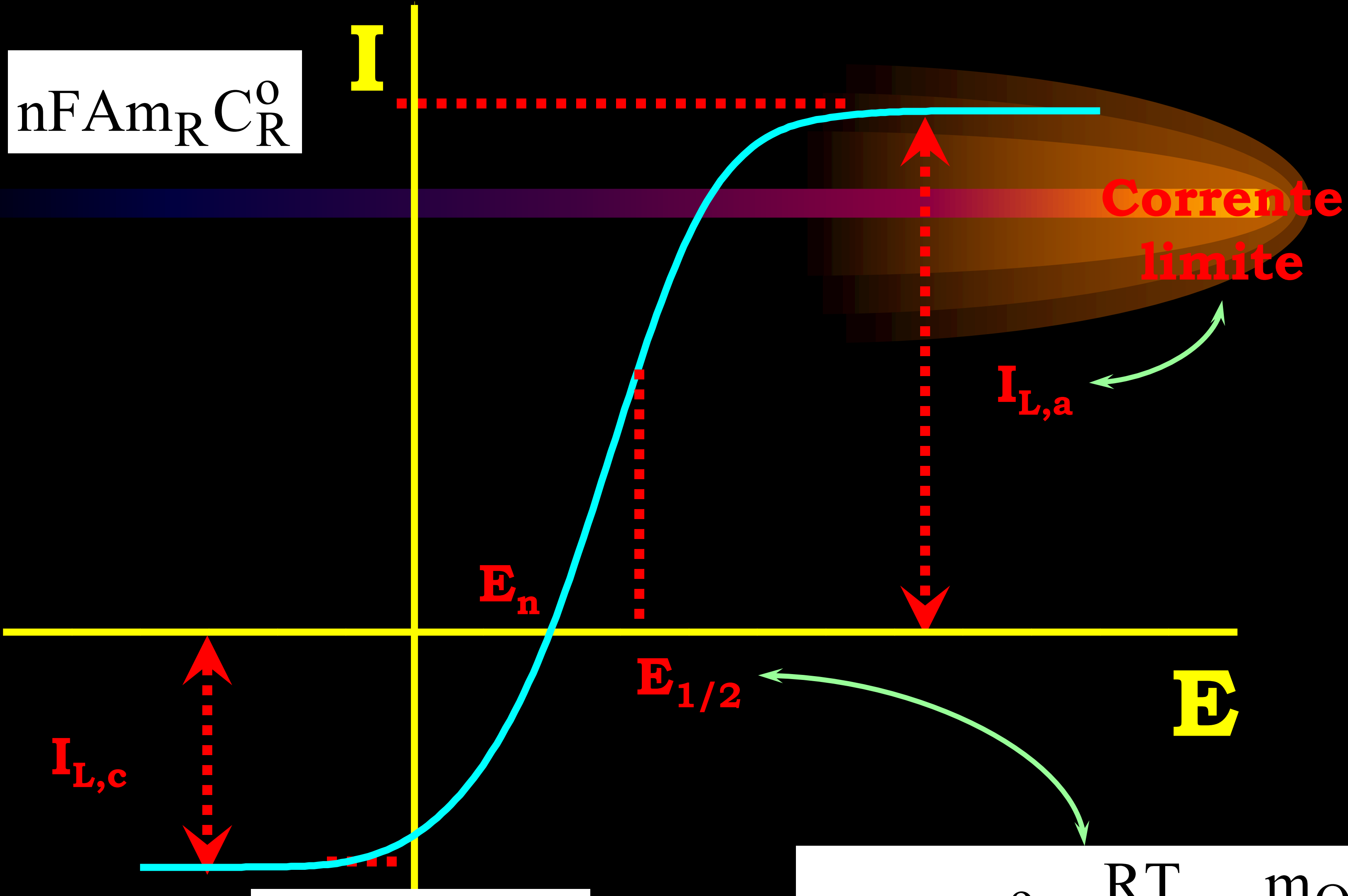
$$E_n = E^{o'} - \frac{RT}{nF} \ln \frac{C_R^{o}}{C_O^{o}}$$

$$\boxed{\eta_{conc} = E - E_n = \frac{RT}{nF} \ln \frac{C_R^{o}\, C_O^{sup}}{C_O^{o}\, C_R^{sup}}}$$

$$\text{As } j = nFv = nF\left(v_{ox} - v_{red}\right) \rightarrow v = J = m\left(C^{sup} - C^{o}\right)$$

$$\eta_{conc} = \frac{RT}{nF}\ln\left[\frac{C_R^o\, m_R}{C_O^o\, m_O}\right] + \frac{RT}{nF}\ln\left[\frac{I + nFAC_O^o\, m_O}{nFAC_R^o\, m_R - I}\right]$$

$$I = \frac{\left(e^{\frac{\eta_{conc}\, nF}{RT}}\, C_O^o\, m_O\, nFA\right)}{\left(nFAC_O^o\, m_O\right) + \left(e^{\frac{\eta_{conc}\, nF}{RT}}\, \frac{C_O^o\, m_O}{C_R^o\, m_R}\right)}$$



Corrente limite

$$nFAm_R C_R^o$$

$$-nFAm_O C_O^o$$

$$E_{1/2} = E^o - \frac{RT}{nF} \ln \frac{m_O}{m_R}$$

POTENTIAL STEP EXPERIMENTS

chronoamperometry and chronocoulometry

Time and distance are linked by diffusion. For example the flux, J specifies how many moles cross unit area in unit time.

Basic principle

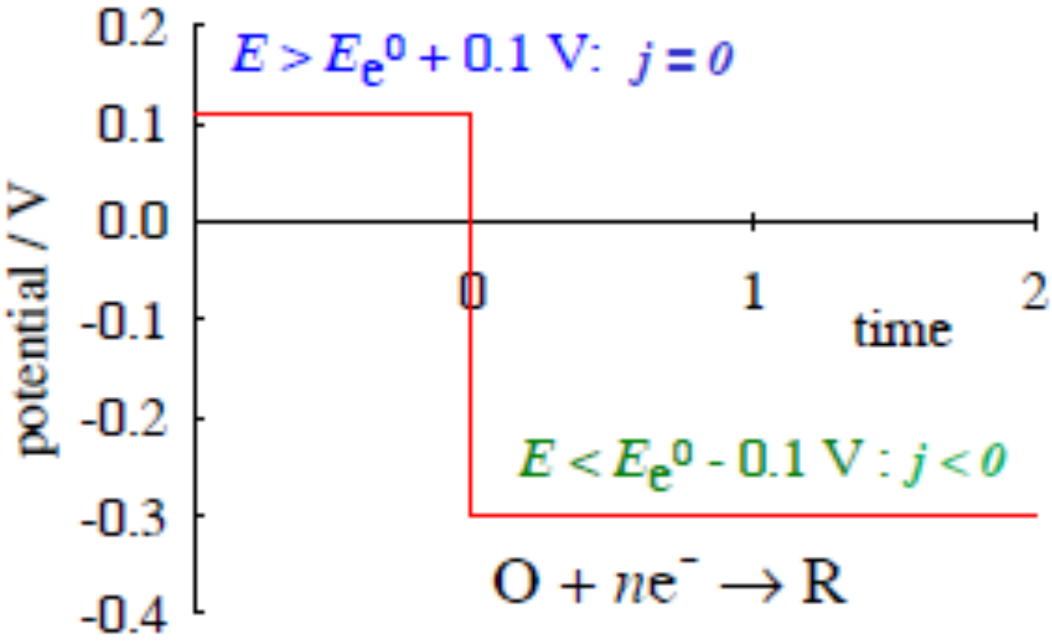
Take a solution containing only one component of the redox couple e.g O

Make a step change in the electrode potential (hence the boundary condition at the electrode surface) from a potential at which there is no reaction of O to give R to one at which electrochemical reaction occurs at the electrode consuming O and making R

$$\mathrm{O} + n\mathrm{e}^{-} \rightarrow \mathrm{R}$$

A Potential step Experiment

Apply a step change in potential and measure the current



Choose conditions such that mass transport is dominated by diffusion. Carry out the experiment at a macroscopic stationary electrode in a quiescent solution containing an excess of background electrolyte, hence

- no convection
- no migration
- only one-dimensional diffusion

What happens?

Before the potential step, $t < 0$

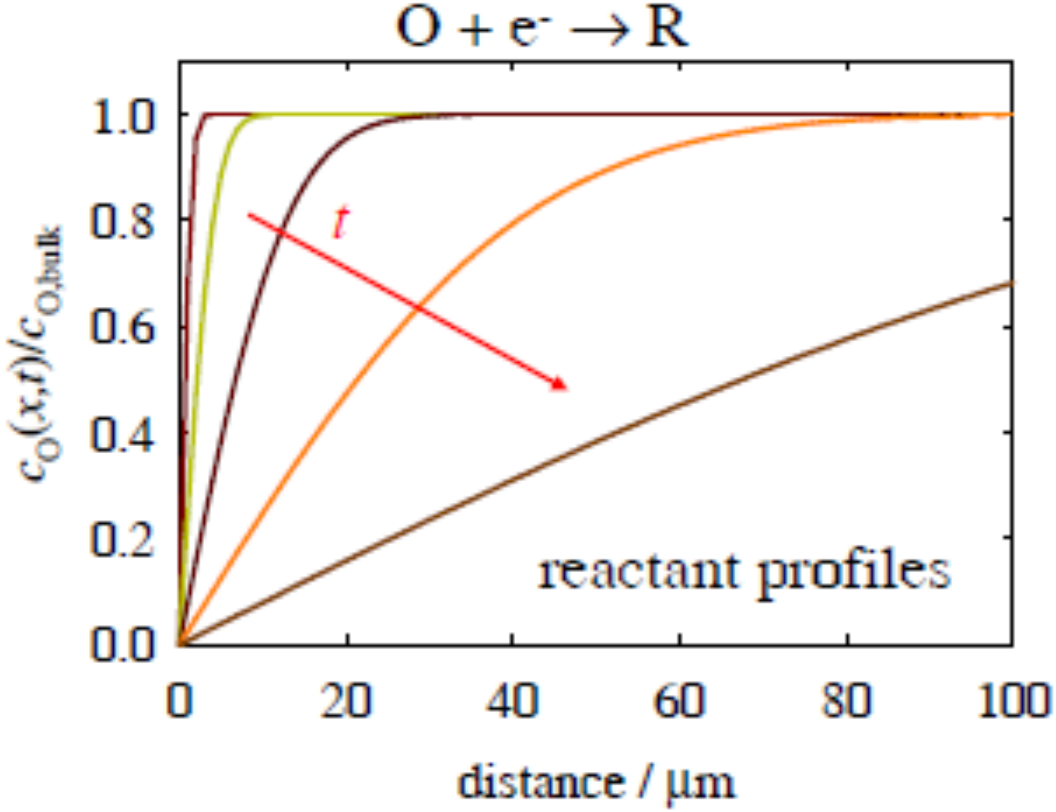
- the concentration profiles are flat, $\mathrm{d}c_O/\mathrm{d}x = 0$
- there is no current flowing, $I = 0$

After the potential step, $t > 0$

- O is consumed and R made at the electrode surface
- current flows
- concentration gradients are set up for O and R
- the concentration gradients change with time
- the current decreases with time as O near the electrode is consumed

Concentration profiles

Calculated for $D = 5 \times 10^{-6}$ cm^2 s^{-1}; t / s = 0.001, 0.01, 0.1, 1, 10



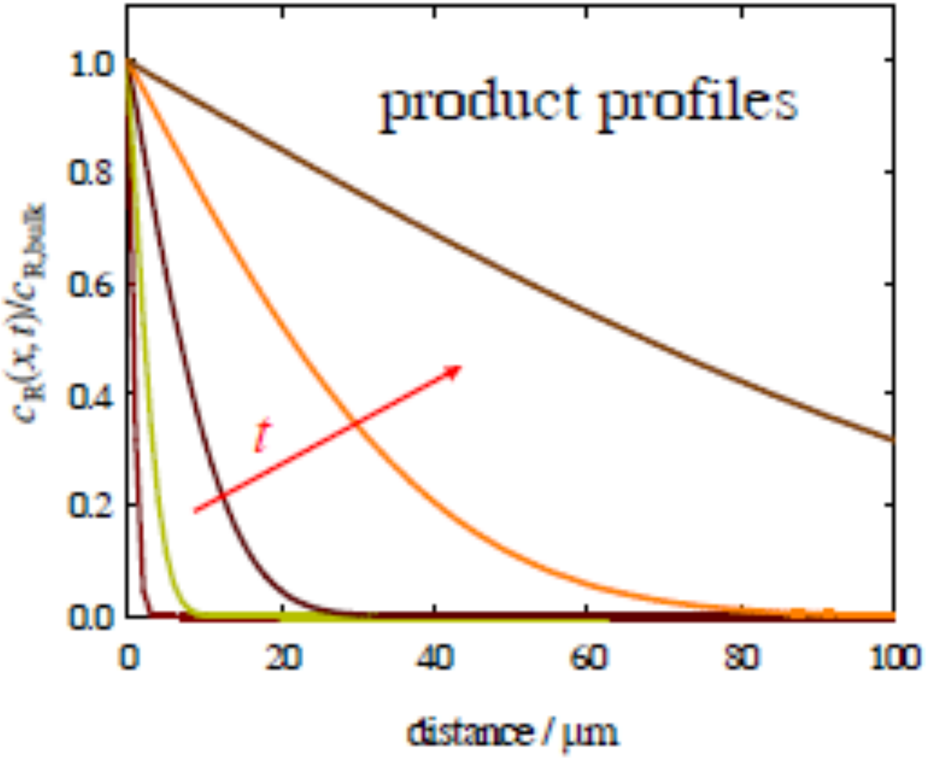
Fick's 1st law:

the steeper the concentration profile at the electrode surface the bigger the current

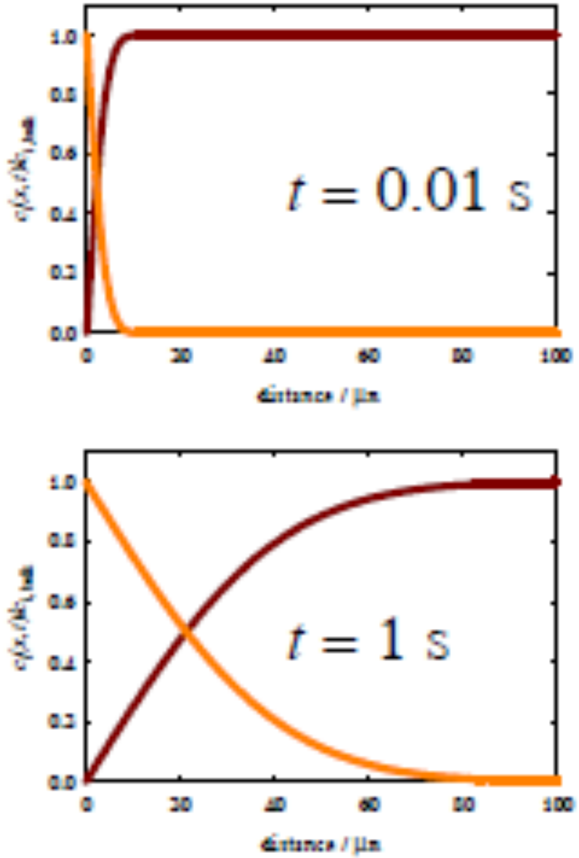
$$I = -nFAD\left(\frac{dc}{dx}\right)_{x=0}$$

If D_O and D_R are the same, the concentration profiles for the product are the mirror image of those for the reactant.

$O + e^- \rightarrow R$



reactant and product



At any point and at any time $c_O(x,t) + c_R(x,t) = c^\infty$

The Cottrell equation

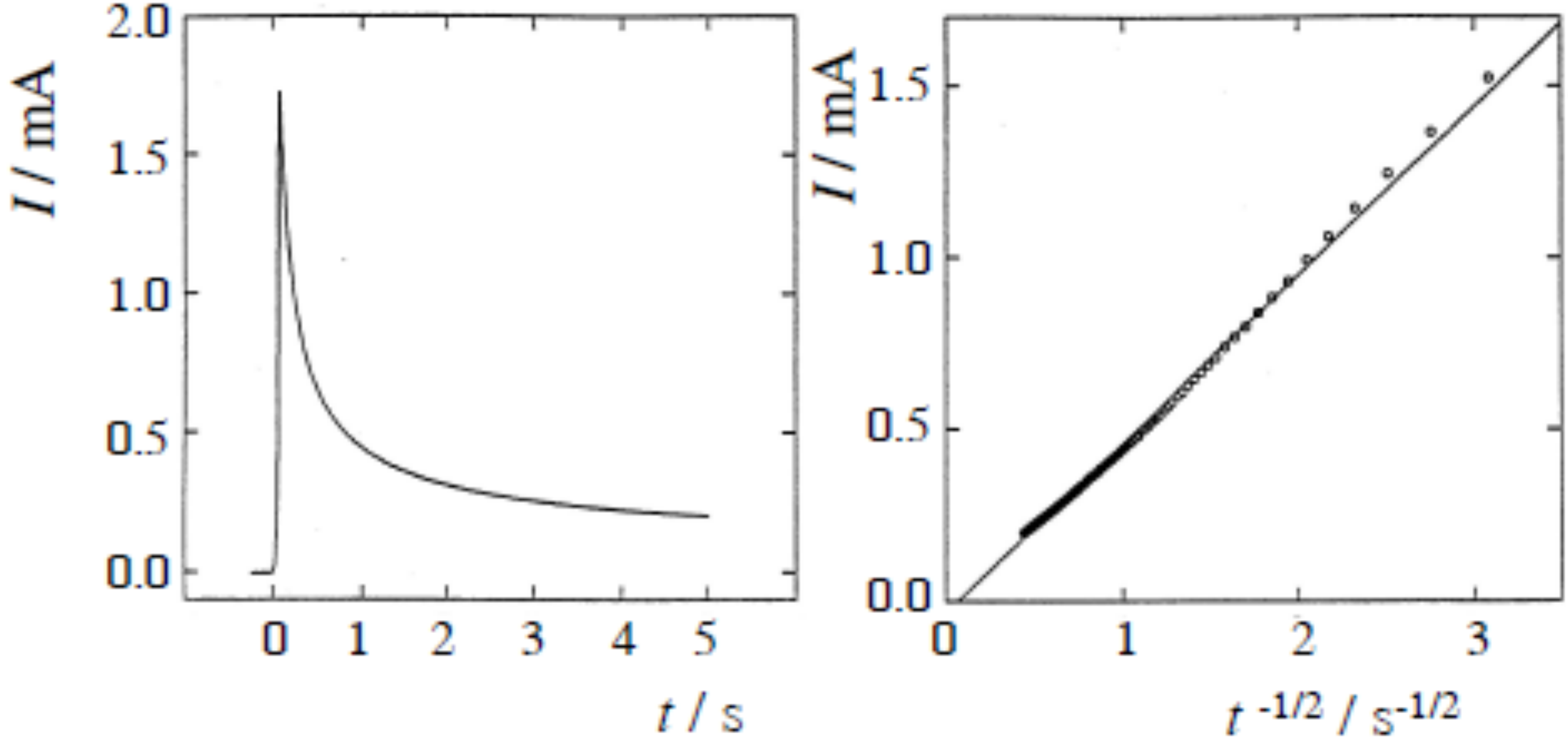
Solution of the 1-D diffusion problem

Fick's 2nd law $$D\frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t}$$

Boundary conditions $$t \leq 0;\ c(x,t) = c^{\infty}$$

$$t > 0;\ c(0,t) = 0$$

Solution $$\boxed{|j| = \frac{nFD^{1/2}c^{\infty}}{\pi^{1/2}t^{1/2}}}$$



Potential step 0.0 to +0.4 v vs SCE at a Pt electrode (area = 0.387 cm^2) in pH 6 phosphate buffer containing 8.25 mM ferrocene monocarboxylic acid

At short times:

in principle the current tends to infinity,

in practice the electrolyte resistance, R_u limits the current and useful timescale is limited to > 5 ms by:

- instrumental limitations (potentiostat)
- double layer charging ($R_u C_{dl}$ time)

At long times:

in principle the current tends to zero,

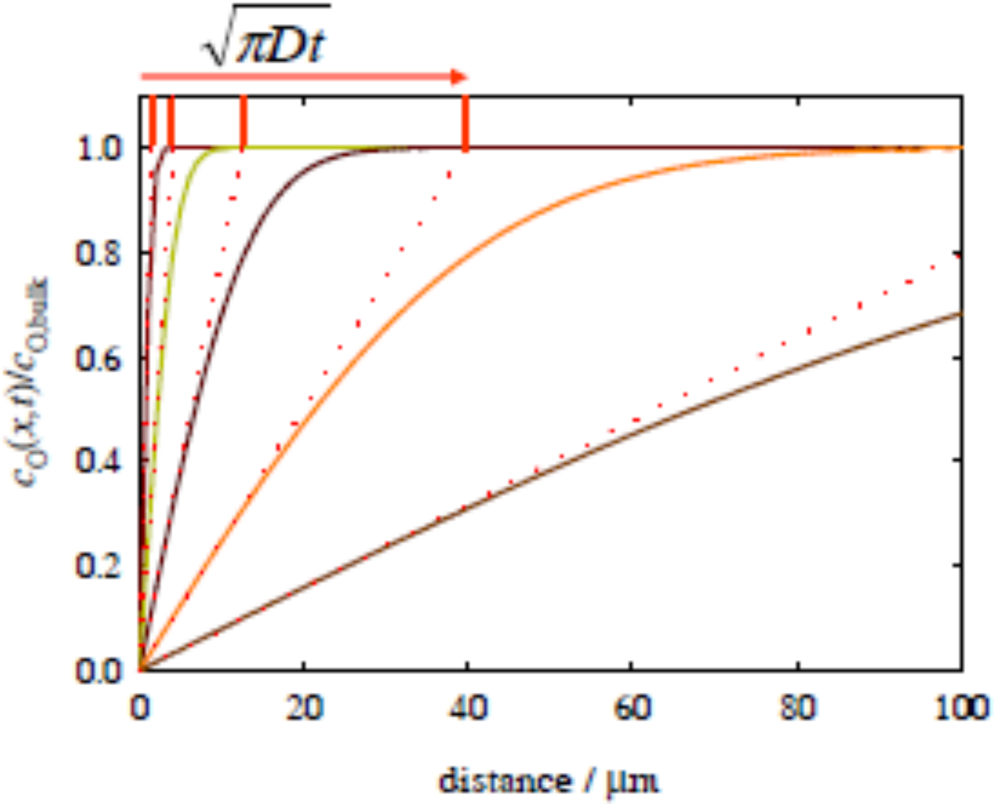
in practice the useful timescale is limited to < 10 s due to random convection:

- vibration
- thermal gradients
- density gradients

Need special precautions to work outside this range

The concentration profile spreads out with time

Characteristic distance is given by diffusion layer thickness



$$X_D(t) = \sqrt{\pi D t}$$

- The time to diffuse a distance l is of the order of $l^2/\pi D$
- This is non-steady state behaviour

Conditions leading to a steady state

- Current $\neq f(t)$ ☞ flux of species to electrode $\neq f(t)$
  - diffusion layer grows with time
  - the final thickness and flux to electrode are constant
- Mass transport control
  - diffusion control, e.g. microdisc electrode
  - convection control, e.g. RDE

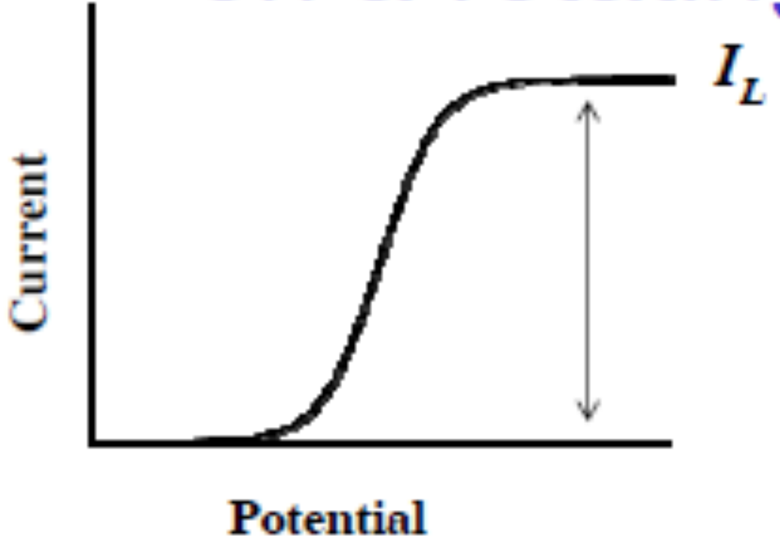
Controlled mass transport

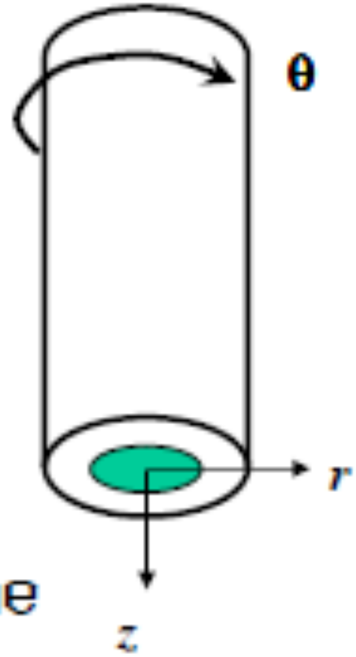
- techniques based on hydrodynamic control
  - rotating disc electrode, RDE
  - rotating ring disc electrode, RRDE
  - channel flow cell, etc…
- techniques based on diffusion control
  - microdisc electrode
  - thin layer cells
  - scanning electrochemical microscope, SECM

All the above techniques control or measure the mass transport coefficient:

$$\boxed{k_m = \frac{J}{c}} \qquad \boxed{J = k_m c}$$

Steady state voltammetry on a rotating disc

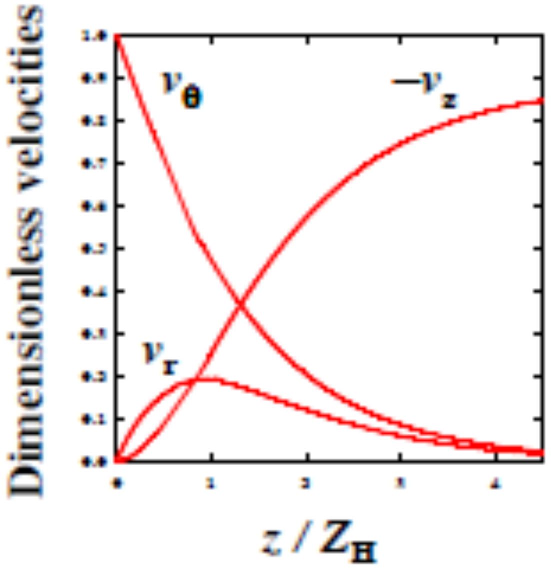




- amperometric current independent of time
- unique current – potential relationship
- current reaches a limit, I_L
- forward & back scans are identical

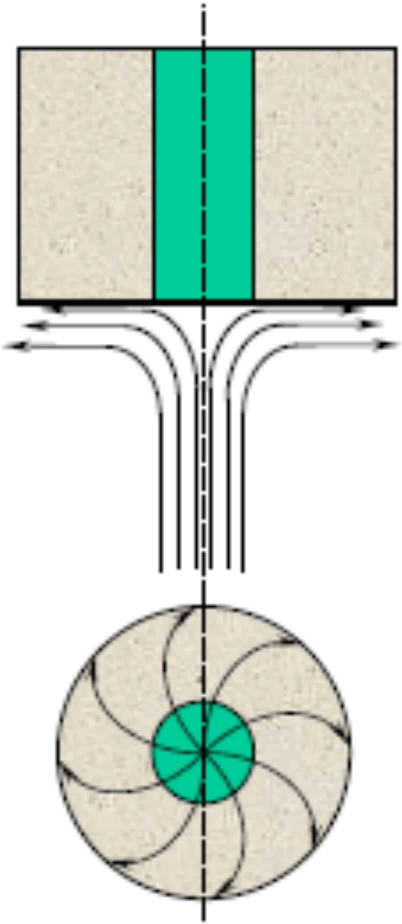
☞ voltammogram simpler to analyse

Well defined hydrodynamics (forced convection)

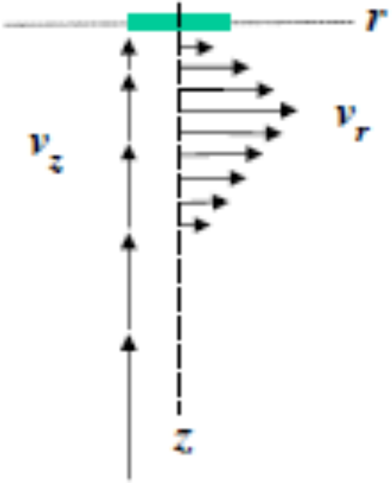


Flow velocities, v_z, v_r and v_θ, at the RDE. The distance is normalised with the hydrodynamic length, Z_H, where $Z_H = (\nu/\omega)^{1/2}$.

electrode is uniformly accessible



Streamlines for flow at the RDE



Vector representation of fluid velocities near disc.

Convective – diffusion theory

In cylindrical polar coordinates, the system is described as

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial z^2} + \frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial \theta^2}\right) - \left(v_r \frac{\partial c}{\partial r} + \frac{v_\theta}{r}\frac{\partial c}{\partial \theta} + v_z \frac{\partial c}{\partial z}\right)$$

diffusion **convection**

This simplifies to $D\frac{\partial^2 c}{\partial z^2} - v_z \frac{\partial c}{\partial z} = 0$ because

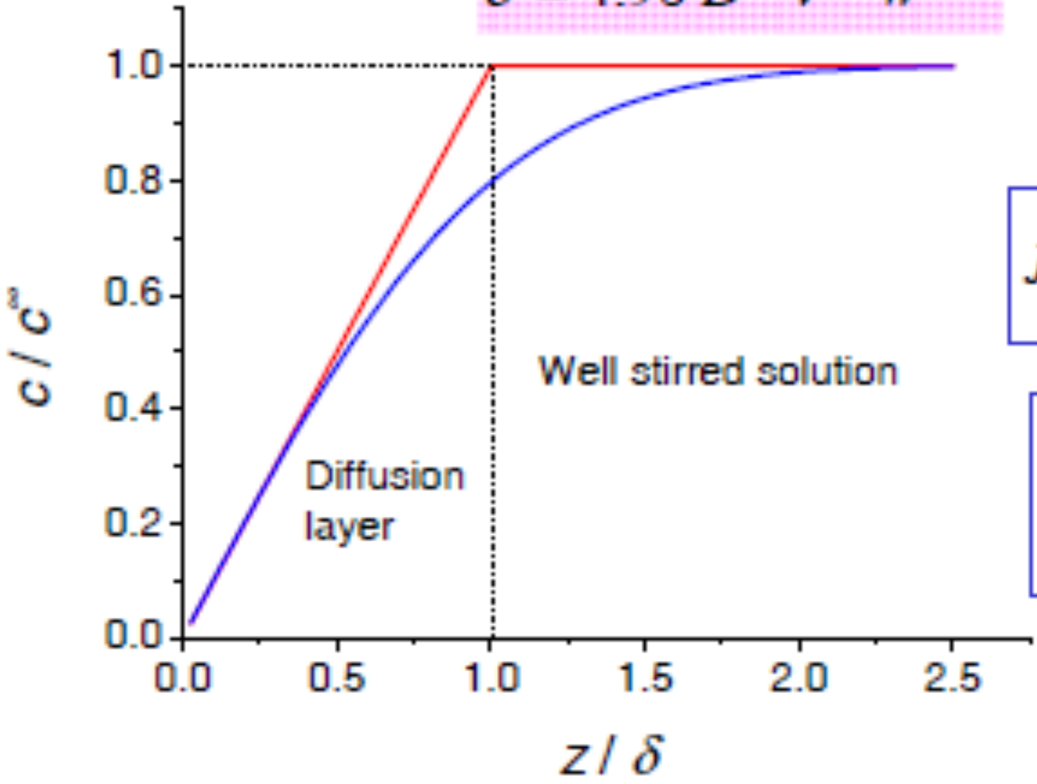
- disc symmetric w.r.t. θ so terms in $\partial c/\partial \theta$ equal zero
- conditions on entire disc are uniform so $\partial c/\partial r = 0$ and $\partial^2 c/\partial r^2 = 0$
- for small disc v_z independent of r
- for steady state experiments $\partial c/\partial t = 0$
- moreover near electrode, i.e. z small

Solving this equation with boundary conditions appropriate to electrochemical experiments yields concentration profile

The Nernst diffusion layer

$$\delta = 4.98\, D^{1/3} \nu^{1/6} w^{-1/2}$$

w in rpm

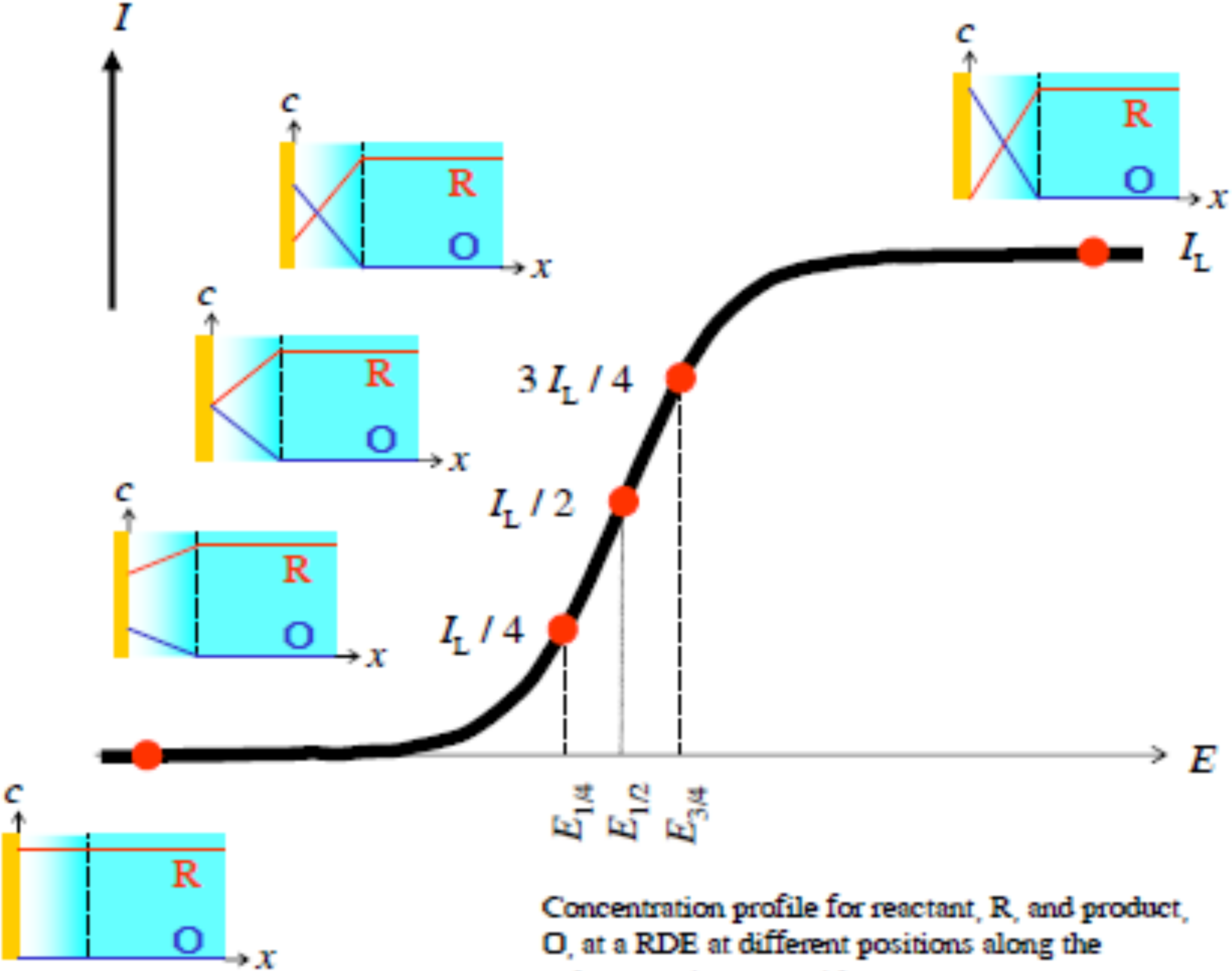


$$J = -D\,\frac{\partial c}{\partial x} = -D\,\frac{c_{\infty}}{\delta}$$

$$k_m = \frac{|J|}{c_{\infty}} = \frac{D}{\delta}$$

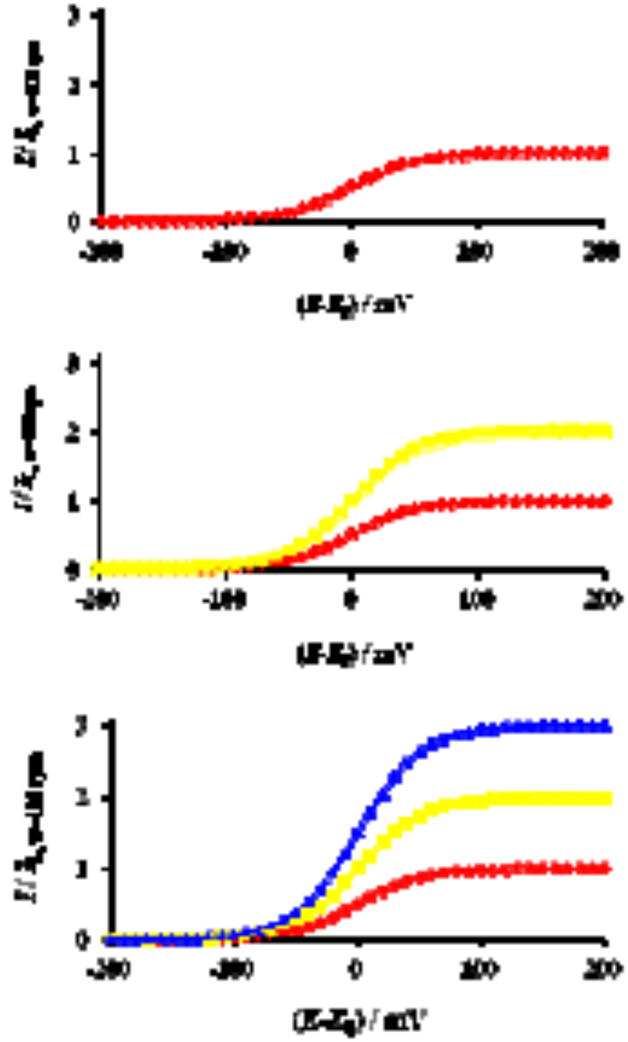
Equivalent and real concentration profiles at the RDE, showing the well stirred bulk where convection dominates and the thin stagnant layer at the electrode surface where diffusion dominates.

Voltammogram: reversible reaction

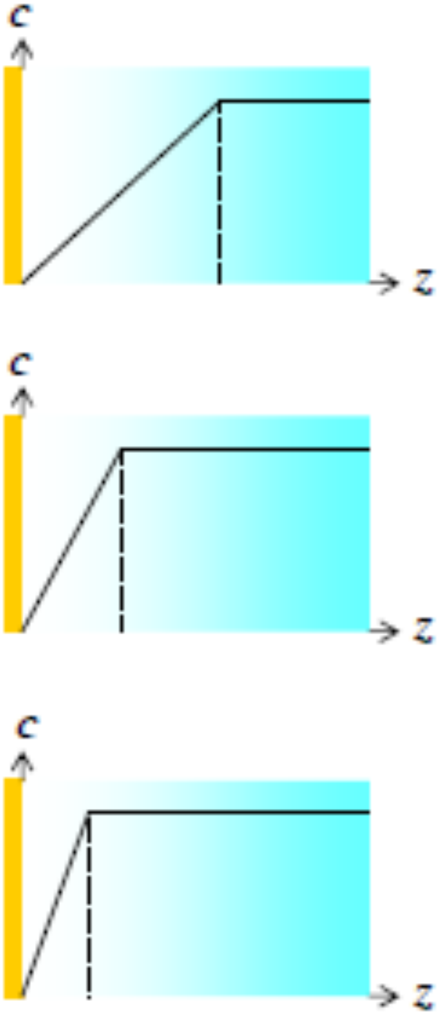


Concentration profile for reactant, R, and product, O, at a RDE at different positions along the voltammetric wave with w = const.

Influence of rotation rate



S.s. voltammograms for three different rotation speeds.



corresponding concentration profiles.

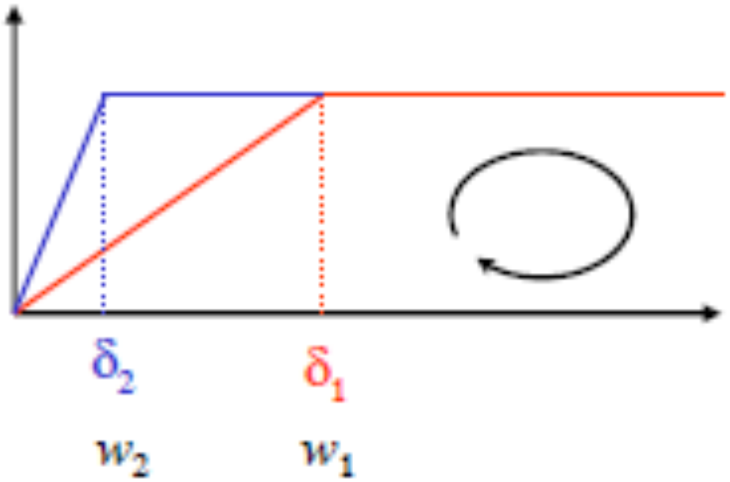
w = 100 rpm

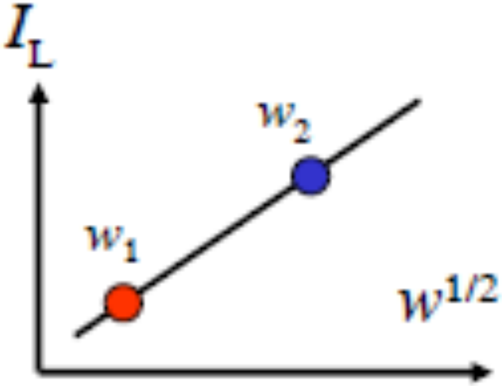
w = 400 rpm

w = 900 rpm

Mass transfer coeff. at the RDE

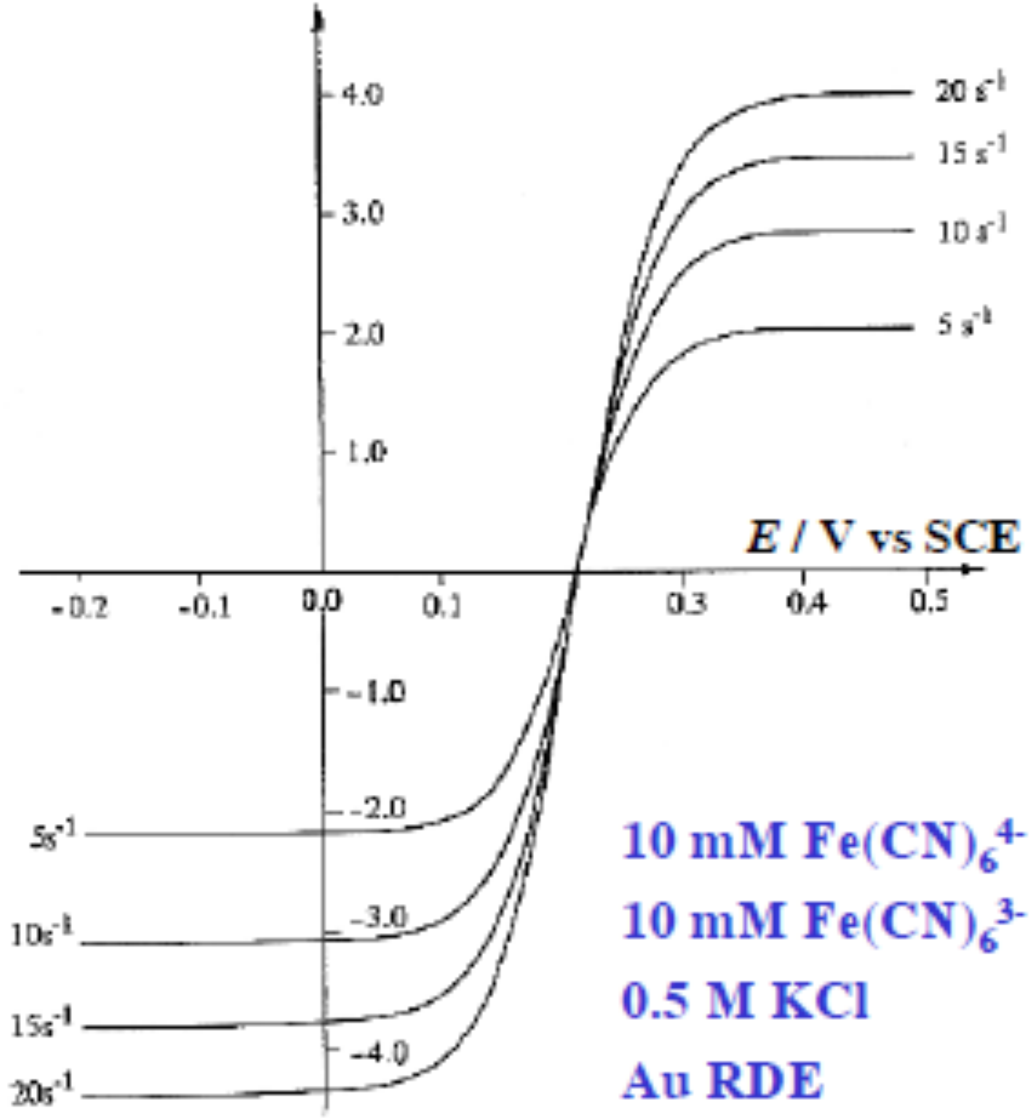
$$k_{\mathrm{m}} = \frac{D}{\delta} = \frac{D}{4.98\, D^{1/3} \nu^{1/6} w^{-1/2}} = 0.201\, D^{2/3} \nu^{-1/6} w^{1/2}$$





$w_1 < w_2$, the higher the rotation rate, the thinner the Nernst diffusion layer, the greater the rate of mass transport and the greater the limiting current.

Example



10 mM $Fe(CN)_6^{4-}$

10 mM $Fe(CN)_6^{3-}$

0.5 M KCl

Au RDE

Levich eq. for the limiting current

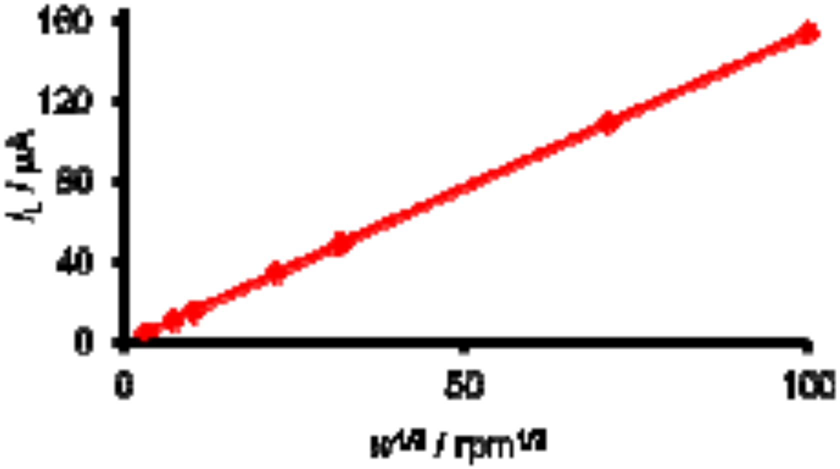
Derive limiting current from concentration profile

$$I_L = 0.201\, nFAD^{2/3}\nu^{-1/6}c^{\infty}w^{1/2}$$ w in rpm

$$I_L = 0.621\, nFAD^{2/3}\nu^{-1/6}c^{\infty}\omega^{1/2}$$ ω in rad s^{-1}

$$I_L = 1.554\, nFAD^{2/3}\nu^{-1/6}c^{\infty}W^{1/2}$$ W in Hz

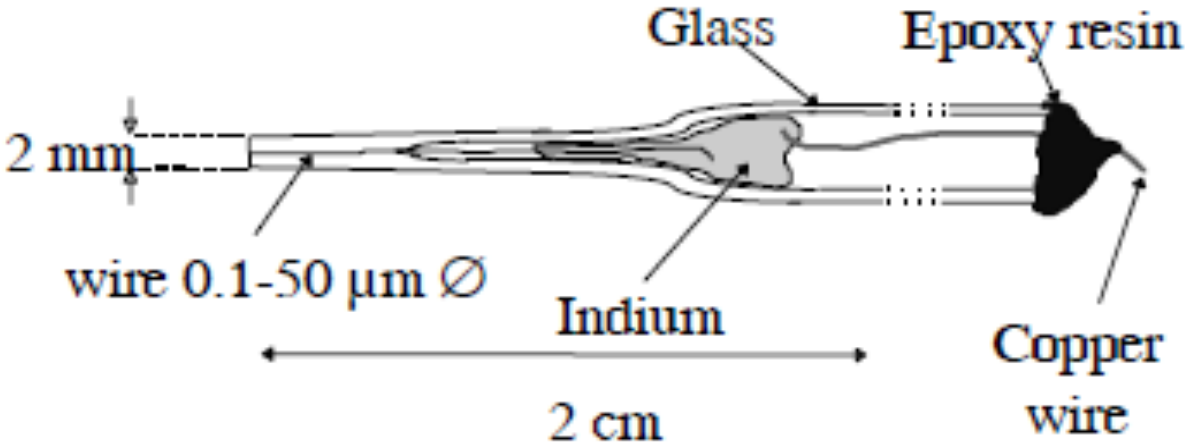
Levich eq.



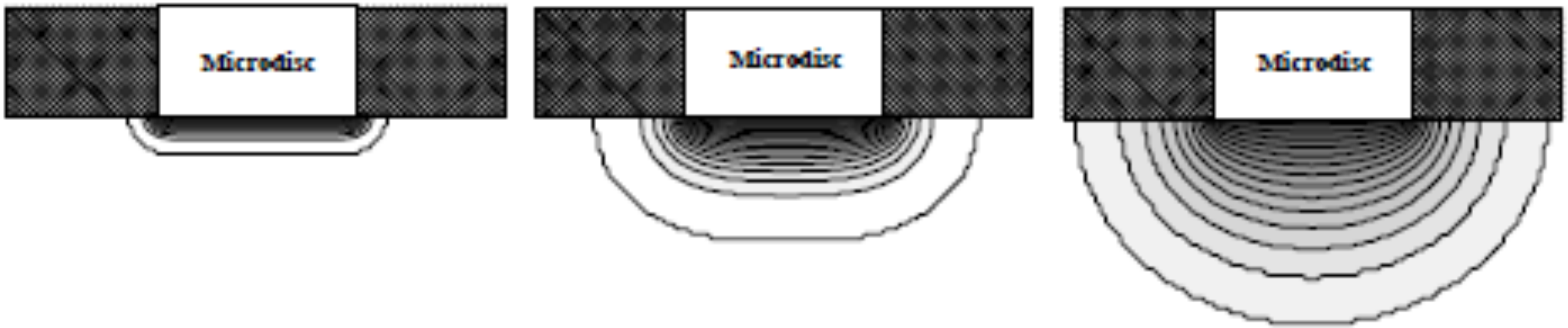
Levich plot for 1e oxidation of a typical 1 mM redox couple in aqueous solution.

The Microdisc electrode

- Properties affected by the size
  - Mass transport regime
  - Discrimination against charging current
  - Decreased distortion from iR_u drop
- Electrode: Pt, Au, C, Ag, Ni, Cu, Hg on C, Pd, W
- Insulator: Glass, epoxy resin, wax



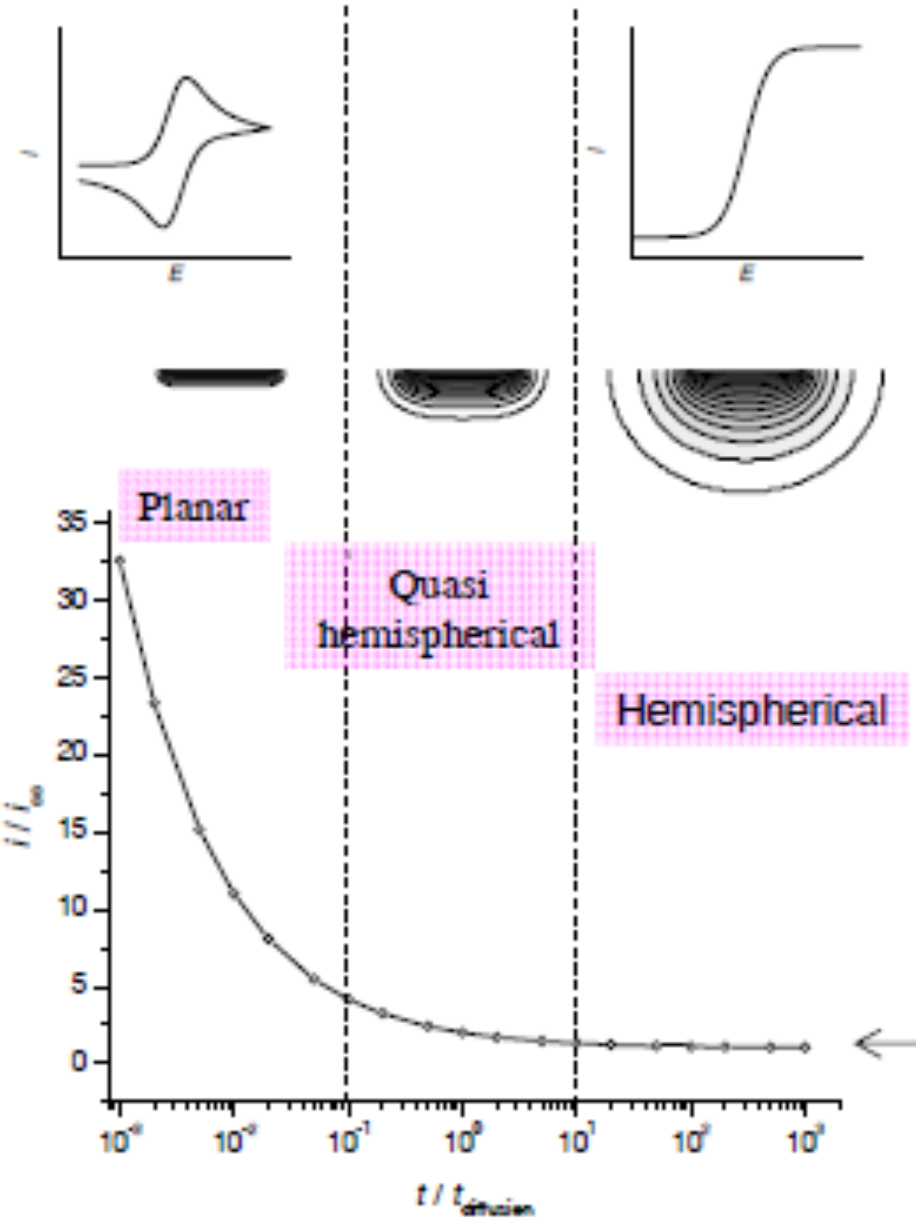
Disc: diffusion regime (I)



Diffusion regimes following a potential step to a microdisc

- planar diffusion at short times
- transition from planar to quasi-hemispherical
- hemi-spherical diffusion at long times = steady state

Disc: diffusion regimes (II)



$$I_L = 4\,n\,F\,D\,c^{\infty}\,a$$

Mass transfer coeff. at microdiscs

$$k_{\mathrm{m}} = \frac{D}{r_{\mathrm{s}}}$$ in cm s^{-1}

- r_s very small so k_m very high
- much greater than that of other steady state techniques
- possible to investigate fast processes in the steady state
  - rate of fast e$^-$ transfer
  - rate of fast homogeneous reactions
- conventional electrodes need transient techniques to achieve same rate of mass transport

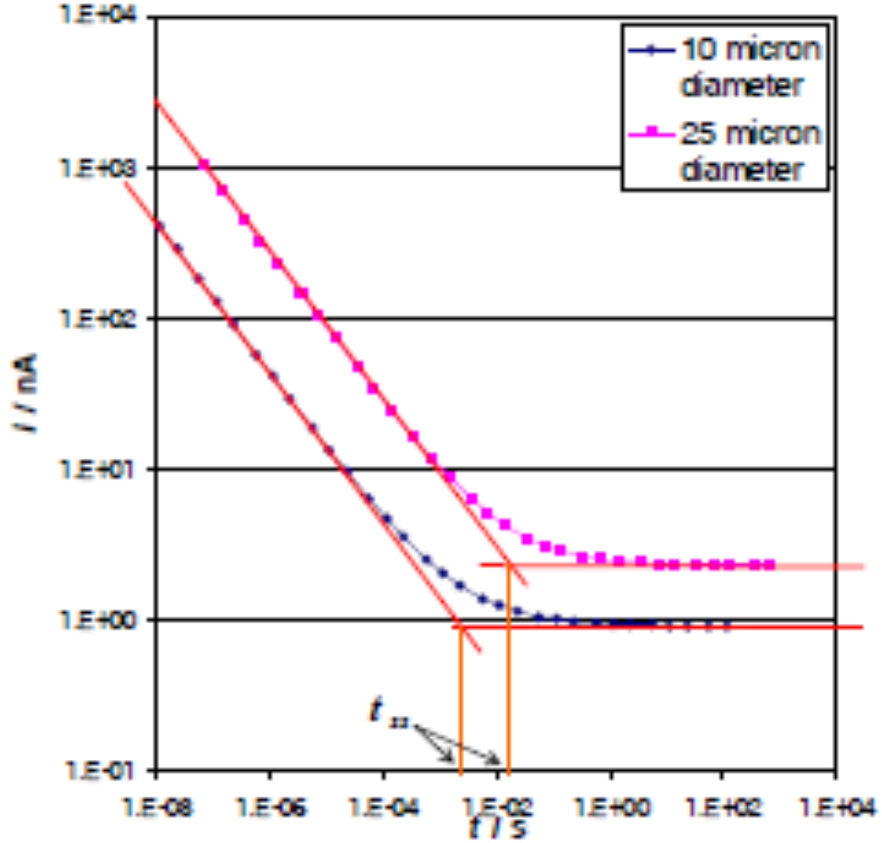
Smaller microdiscs ☞sooner steady state

Time when steady state is reached

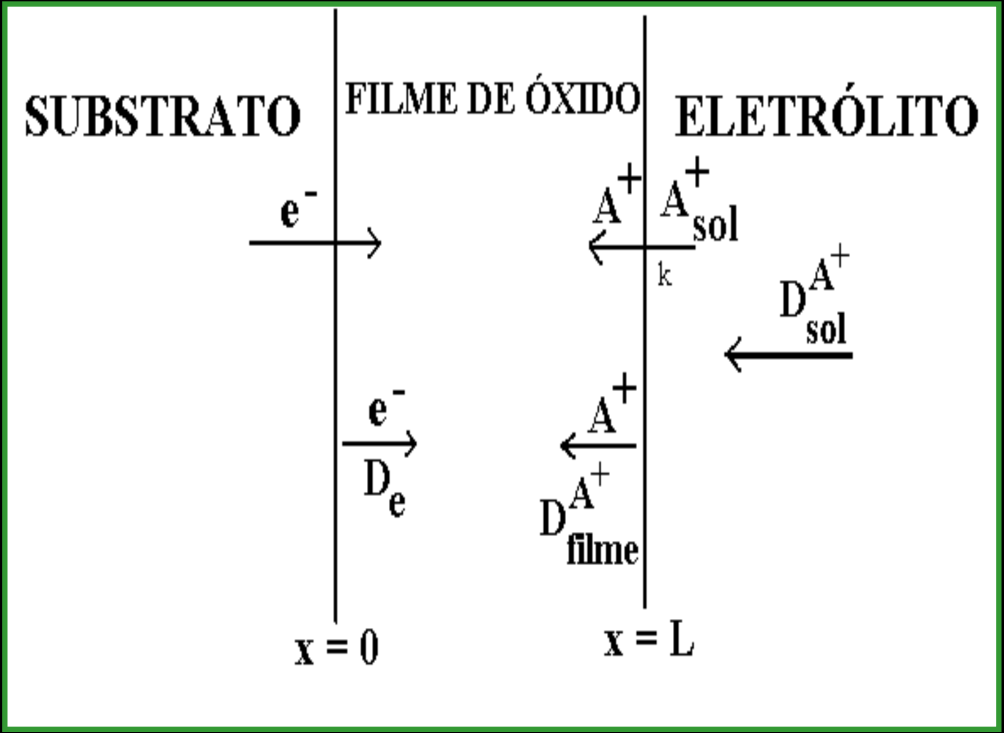
$$t_{ss} \approx \frac{\pi\, a^2}{16\, D}$$

$n = 2$, $F = 96485$ C mol^{-1}
$D = 2.16\times10^{-5}$ cm^2 s^{-1},
$c^* = 2.2\times10^{-7}$ mol cm^{-3}

a / μm	t_{ss} / ms
10	9.1
5	2.3
2.5	0.6
1	0.1



Exemplo difusão finita



- Suposições:
  - $D^{A+}_{sol} > D^{A+}_{filme}$
  - Rápida incorporação das espécies A^+ no filme de óxido
  - Formação do par iônico (A^+ e^-) na interface óxido-eletrólito
  - Difusão do par iônico através do óxido
  - Par iônico encontra sítios M^{+n} originando sítios $M^{(+2n-1)}$

Leis de Fick

$$D\frac{\partial C}{\partial x} = -J \qquad \frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

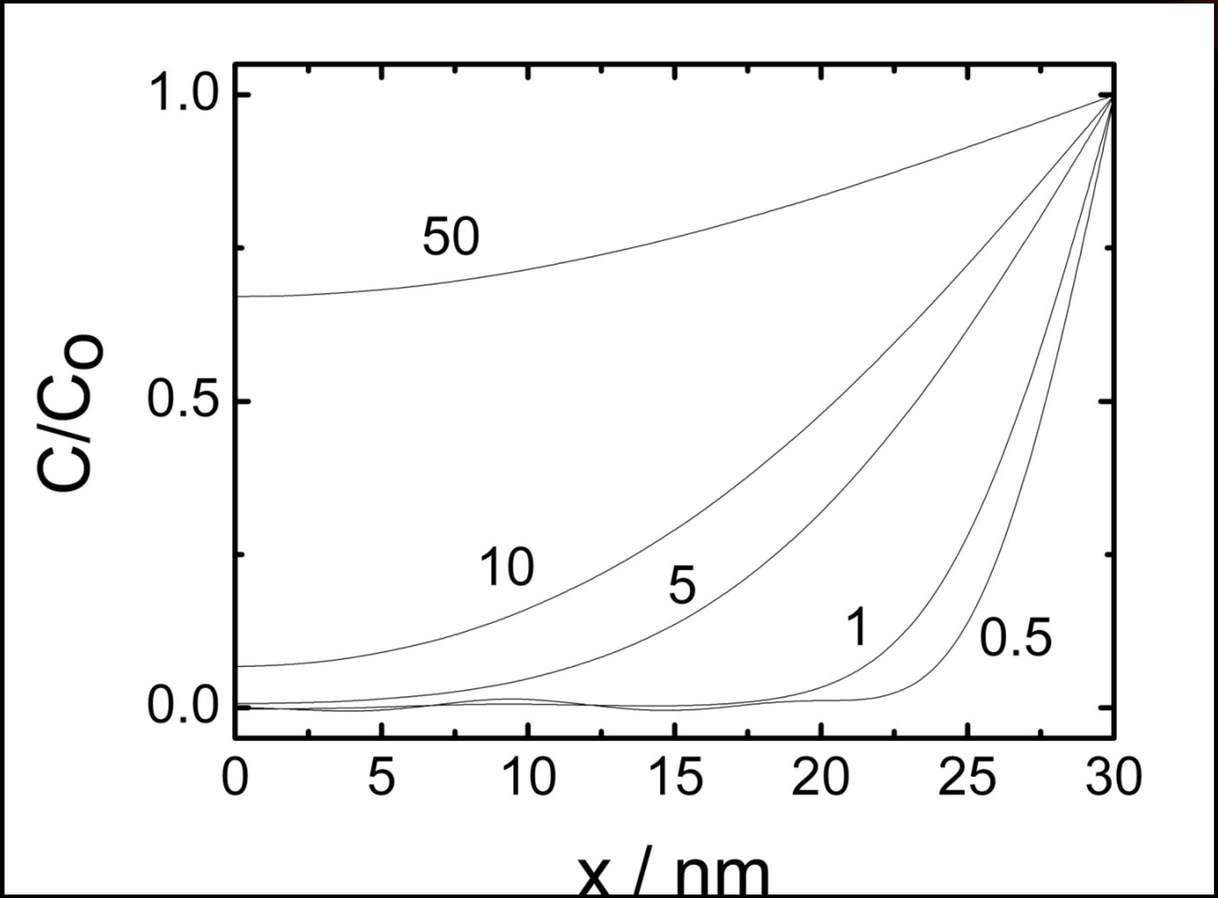
Condições de contorno:

$$C = C_o \text{ para } x = L \text{ e } t \geq 0 \qquad \frac{\partial C}{\partial x} = 0 \text{ para } x = 0 \text{ e } t \geq 0$$

$$J = -D\left(\frac{\partial C}{\partial x}\right)_{x=L} \qquad j = zFJ = -zFD\left(\frac{\partial C}{\partial x}\right)_{x=L}$$

Leis de Fick

$$C = C_o - \frac{4C_o}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left\{ \frac{-D(2n+1)^2 \pi^2 t}{4L^2} \right\} \cos\left[\frac{(2n+1)\pi x}{2L} \right]$$



L = 30 nm

D = 1x10^{-13} cm^2 s^{-1}

Leis de Fick

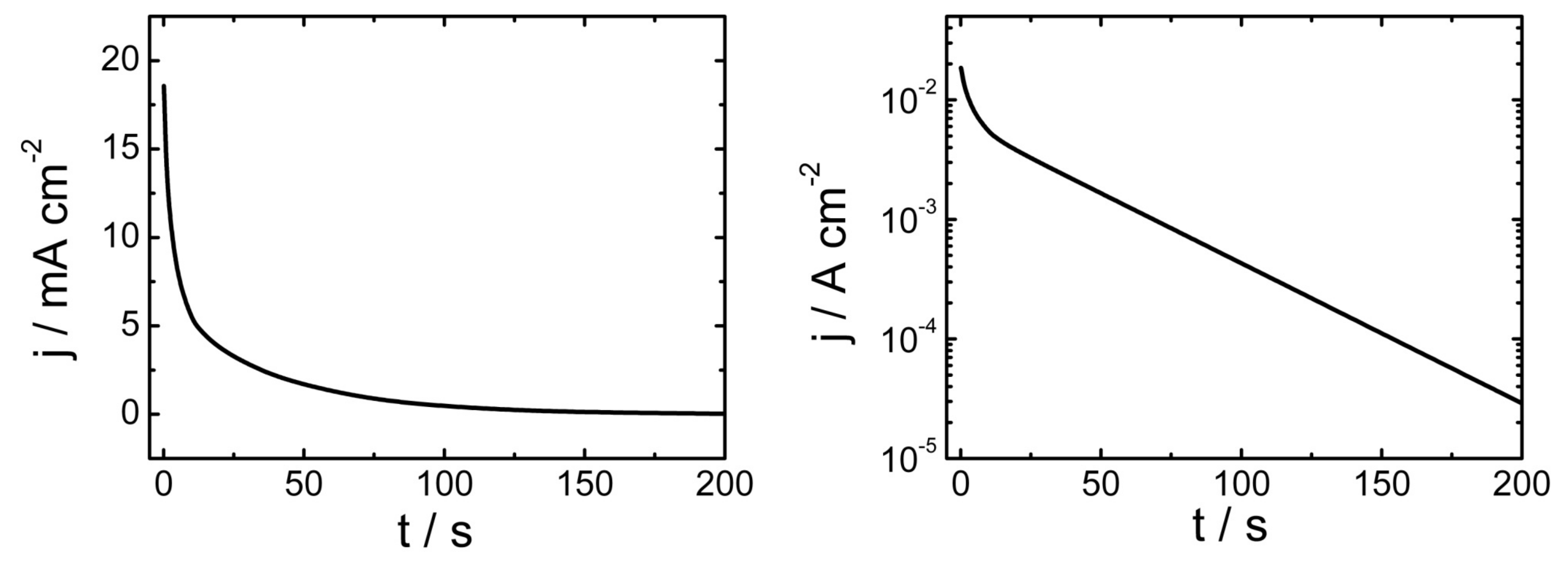
$$C = C_o - \frac{4C_o}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left\{\frac{-D(2n+1)^2 \pi^2 t}{4L^2}\right\} \cos\left[\frac{(2n+1)\pi x}{2L}\right]$$

$$\left(\frac{\partial C}{\partial x}\right)_{x=L} = \frac{2C_o}{L} \sum_{n=0}^{\infty} \exp\left\{\frac{-D(2n+1)^2 \pi^2 t}{4L^2}\right\}$$

$$j = zFD\frac{2C_o}{L} \sum_{n=0}^{\infty} \exp\left\{\frac{-D(2n+1)^2 \pi^2 t}{4L^2}\right\}$$

Leis de Fick

$$j = zFD\frac{2C_o}{L}\sum_{n=0}^{\infty}\exp\left\{\frac{-D(2n+1)^2\pi^2 t}{4L^2}\right\}$$



L = 30 nm - D = 1x10^{-13} cm^2 s^{-1}
C_o = 1 mol cm^{-3}

Exemplo difusão semi-infinita

$$D\frac{\partial C}{\partial x} = -J$$

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

Condições de contorno:

$C = C_o$ para x e $t = 0$

$C = 0$ para $x = 0$ e $t > 0$

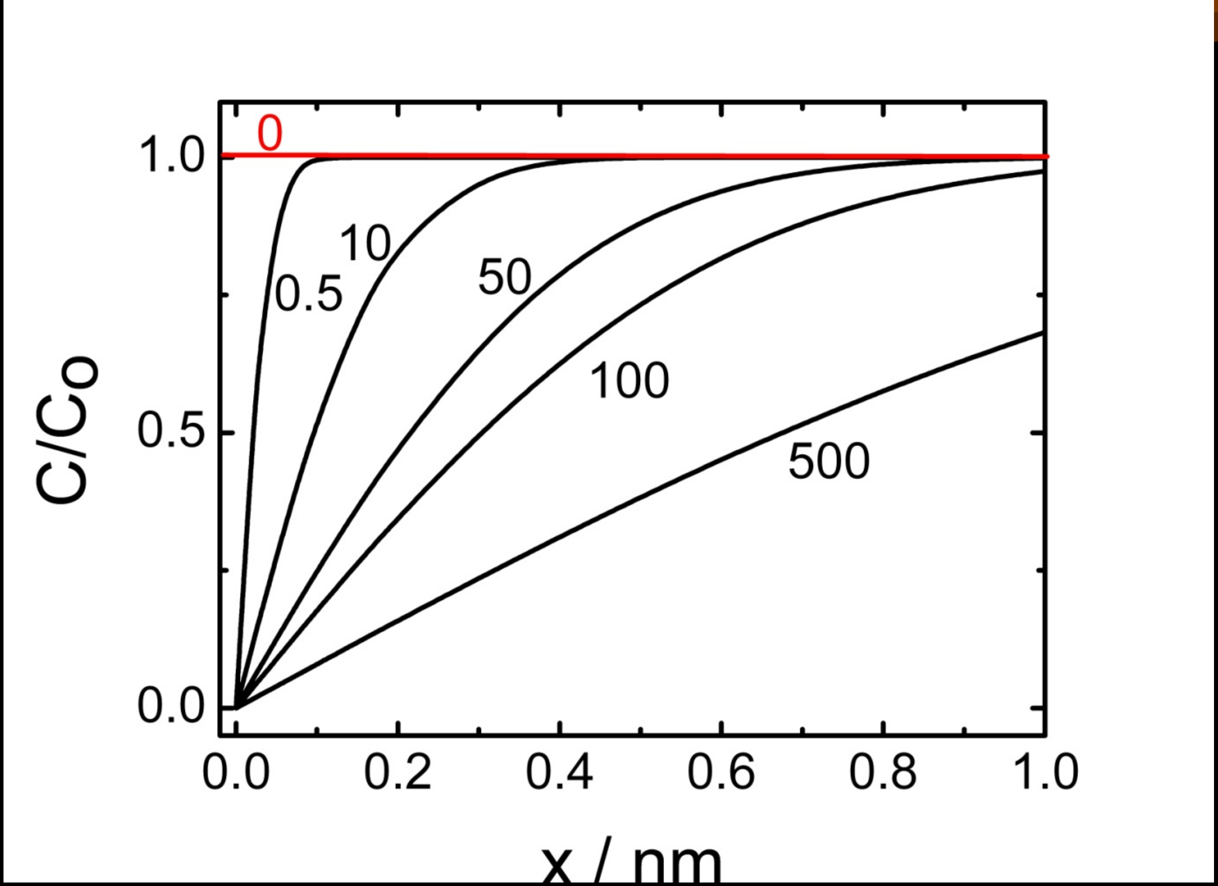
$C = C_o$ para $x \to \infty$ e $t > 0$

$$J = -D\left(\frac{\partial C}{\partial x}\right)_{x=0}$$

$$j = zFJ = -zFD\left(\frac{\partial C}{\partial x}\right)_{x=0}$$

Leis de Fick

$$C = C_o \operatorname{erf}\left[\frac{x}{2\sqrt{D\,t}}\right]$$



Leis de Fick

$$C = C_o \operatorname{erf}\left[\frac{x}{2\sqrt{D\,t}}\right]$$

$$\left(\frac{\partial C}{\partial x}\right)_{x=0} = \frac{C_o}{\sqrt{\pi\,D\,t}}$$

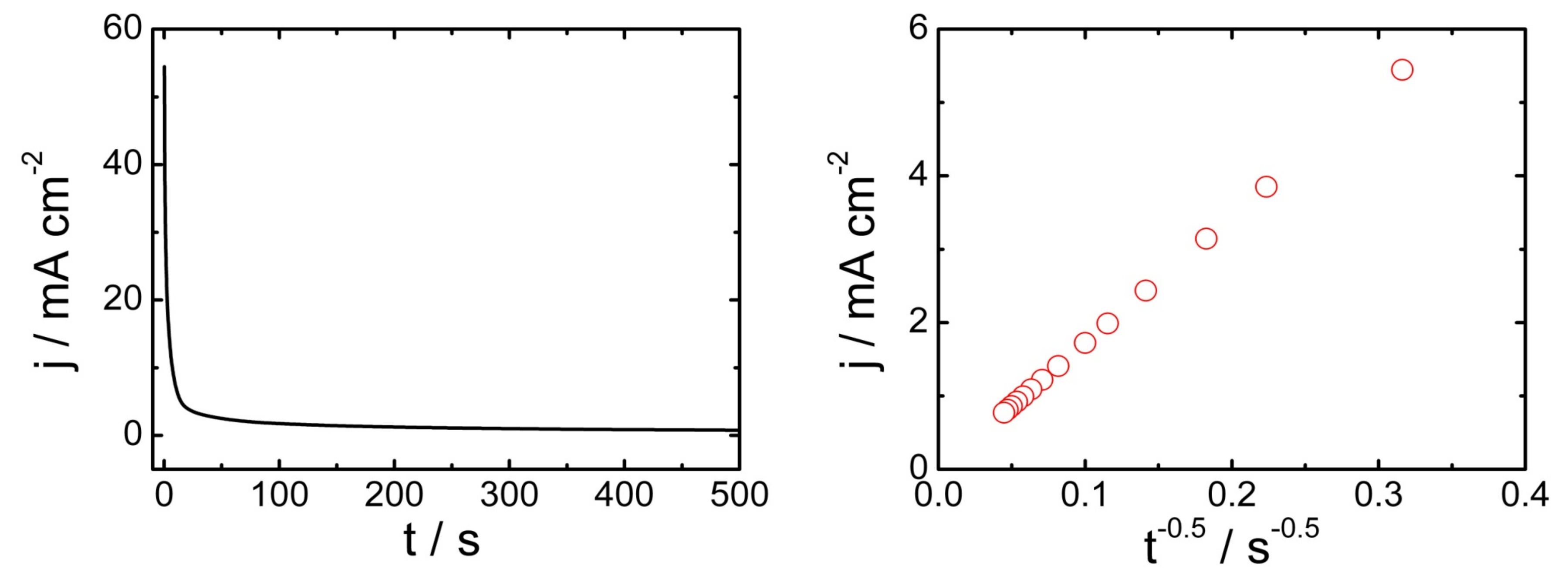
$$j = zF\frac{\sqrt{D}\,C_o}{\sqrt{\pi\,t}}$$

Leis de Fick

$$j = zF\frac{\sqrt{D}\,C_o}{\sqrt{\pi\,t}}$$

$D = 1x10^{-5}\ cm^2\ s^{-1}$

$C_o = 1x10^{-5}\ mol\ cm^{-3}$



Comparação difusão finita/semi-infinita