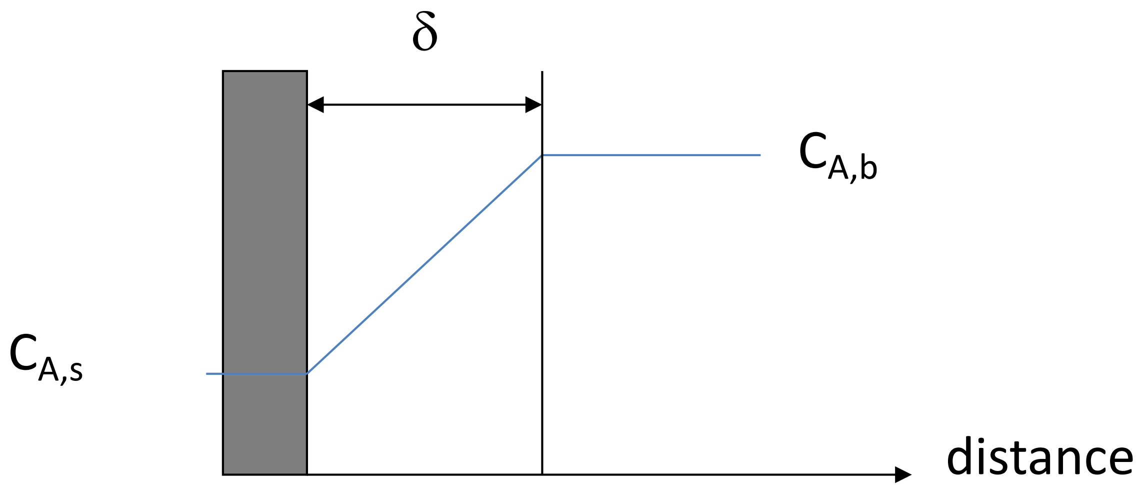
Electrochemistry for materials technology

Chapter 5

Effect of convection on mass transport

not diffusion only (=concentration gradient)
but also a pressure gradient (convection)
= stirring of the solution, e.g. rotating disk

Flux N_A of species A normal to the electrode surface



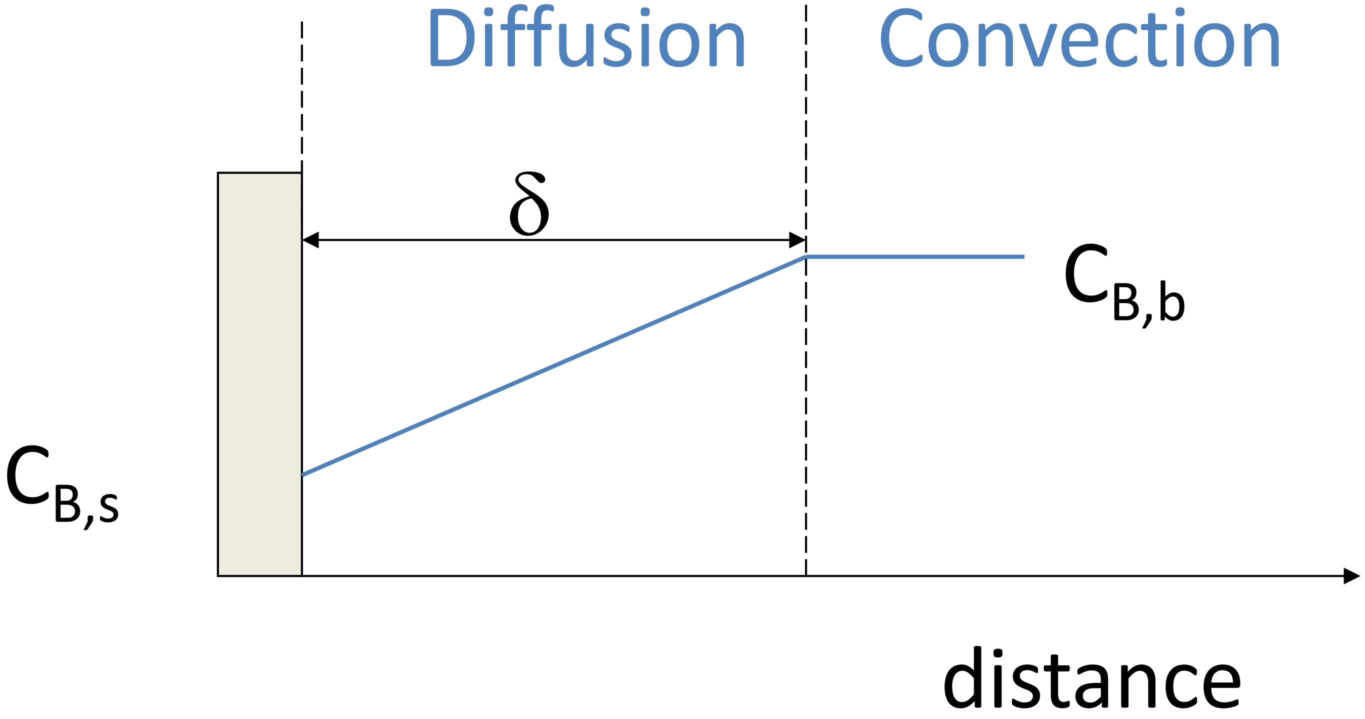
$$\boxed{N_A = -D_A \frac{C_{A,b} - C_{A,s}}{\delta} \qquad (\mathrm{mol/m^2\ s})}$$

D_A : coefficient of diffusion (m^2/s)

δ : thickness of Nernst diffusion layer (m)

$i_{lim} = +/- \, n \, F \, D_A \, c_{A,b} / \delta$

Galvanostatic and potentiostatic polarisation curves



The Sherwood number *Sh*

$i_{lim} = +/- \, n \, F \, D_A \, c_{A,b} / \delta$

$$\mathbf{Sh} = \frac{|\, i_l \,| \, L}{n \, F \, D_b \, c_b} = L / \delta$$

convective
vs
diffusive (D)
mass transfer

Nernst characteristic diffusion length

Sh = f (Re, Sc)

for fluid subjected to relative internal movement due to different fluid velocities, e.g. boundary layer at a surface (pipe, vessel,…)

Reynolds number: $Re = u \, L / \nu$ (inertial forces (speed) vs viscous forces)

Schmidt number: $Sc = \nu / D_b$ (viscous forces vs diffusion transfer)

for fluid where viscosity and mass transfer play simultaneous roles
(=the mass transfer equivalent to the Prandtl number)

L: characteristic (convection) length (m)

u: linear flow rate (m/s)

ν: kinematic viscosity (m^2/s)

= dynamic viscosity divided by fluid density

= absolute viscosity = resistance of a fluid to flow

D_b: diffusion coefficient (m^2/s)

Transport correlations in forced convection systems

Geometry	**Flow**	**Characteristic Length L**	**Sh (mean value, Sc>1000))**
Pipe, smooth walls	turbulent: $Re > 3000$	diameter D_h	$0.0115\ Re^{7/8}Sc^{1/3}$
Pipe, smooth walls	laminar: $Re < 2000$ fully developed velocity profile: $D_h/L_x > 1.85$	diameter D_h	$1.85\ Re^{1/3}Sc^{1/3}(D_h/L_x)^{1/3}$ (L_x= electrode length)
Pipe, smooth walls	laminar, $Re < 2000$ fully developed velocity profile: D_h/L_x --> 0	diameter D_h	3.66
Rotating disk	laminar: $Re < 2.7x10^5$	radius R	$0.62\ Re^{1/2}Sc^{1/3}$ => next slide
Rotating disk	turbulent: $8.9x10^5 < Re < 1.18x10^7$	radius	$0.0117\ Re^{0.896}Sc^{0.249}$
Rotating hemisphere	laminar: $Re < 1.5x10^4$	radius	$0.474\ Re^{1/2}Sc^{1/3}$
Rotating cylinder	turbulent: $10^3 < Re < 2.7x10^5$	radius	$0.079\ Re^{0.7}Sc^{0.35}$

Rotating disk electrode (RDE)

$Sh = 0.62\, Re^{0.5}\, Sc^{0.333}$

$Re = u R / \nu$ $Sc = \nu / D_b$

$Sh = |i_{lim}|\, R / (n F D_b c_b)$

(characteristic length L=R for a disc)

Levich equation:

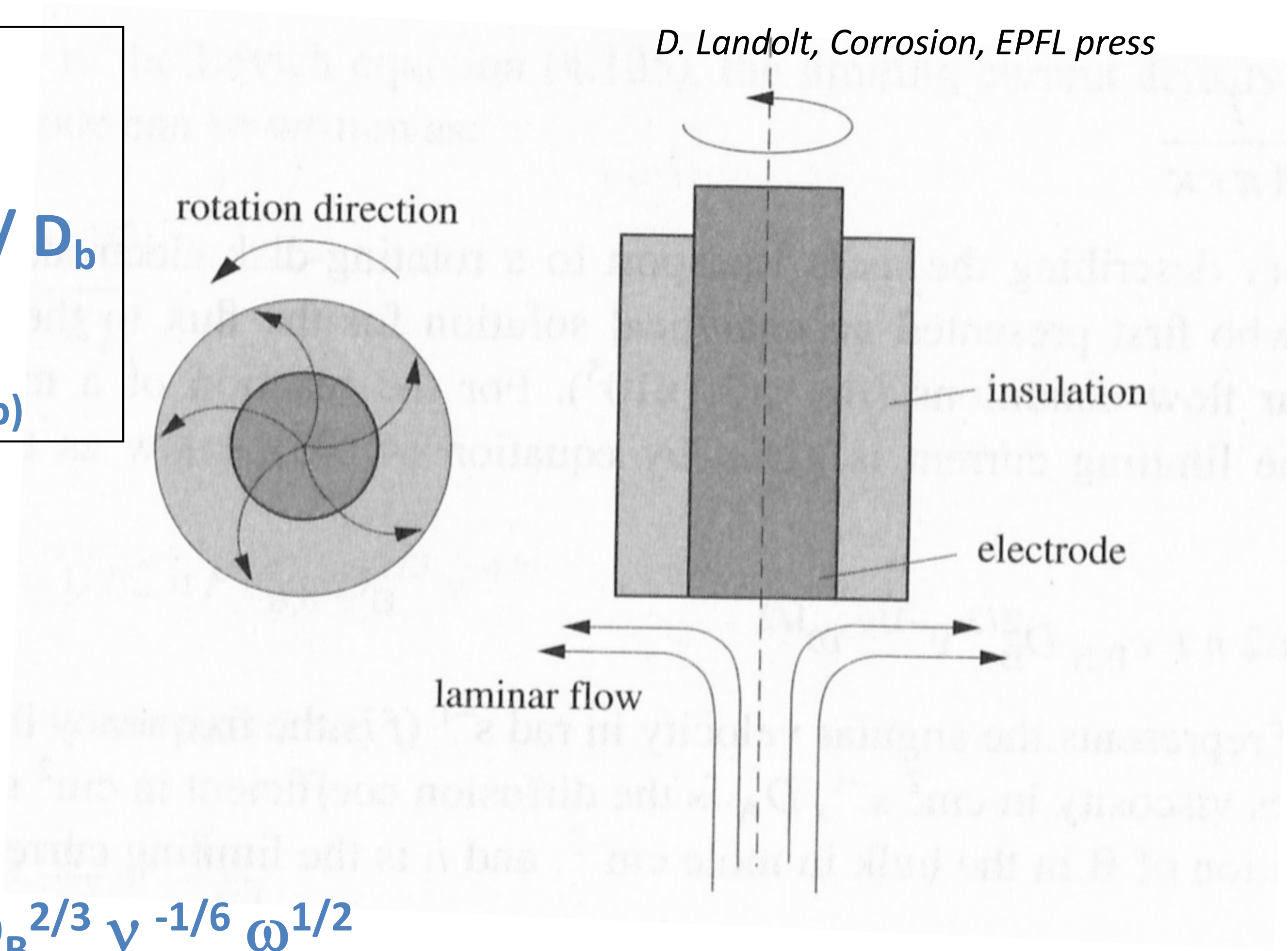
$$|\, i_{lim}\,| = 0.62\, n F C_{B,b} D_B^{2/3} \nu^{-1/6} \omega^{1/2}$$

$\Rightarrow \delta = 1.61\, D_B^{1/3} \nu^{1/6} \omega^{-1/2}$

(with $i_{lim} = n F D_A c_{A,b} / \delta$)

plot i_{lim} vs ω

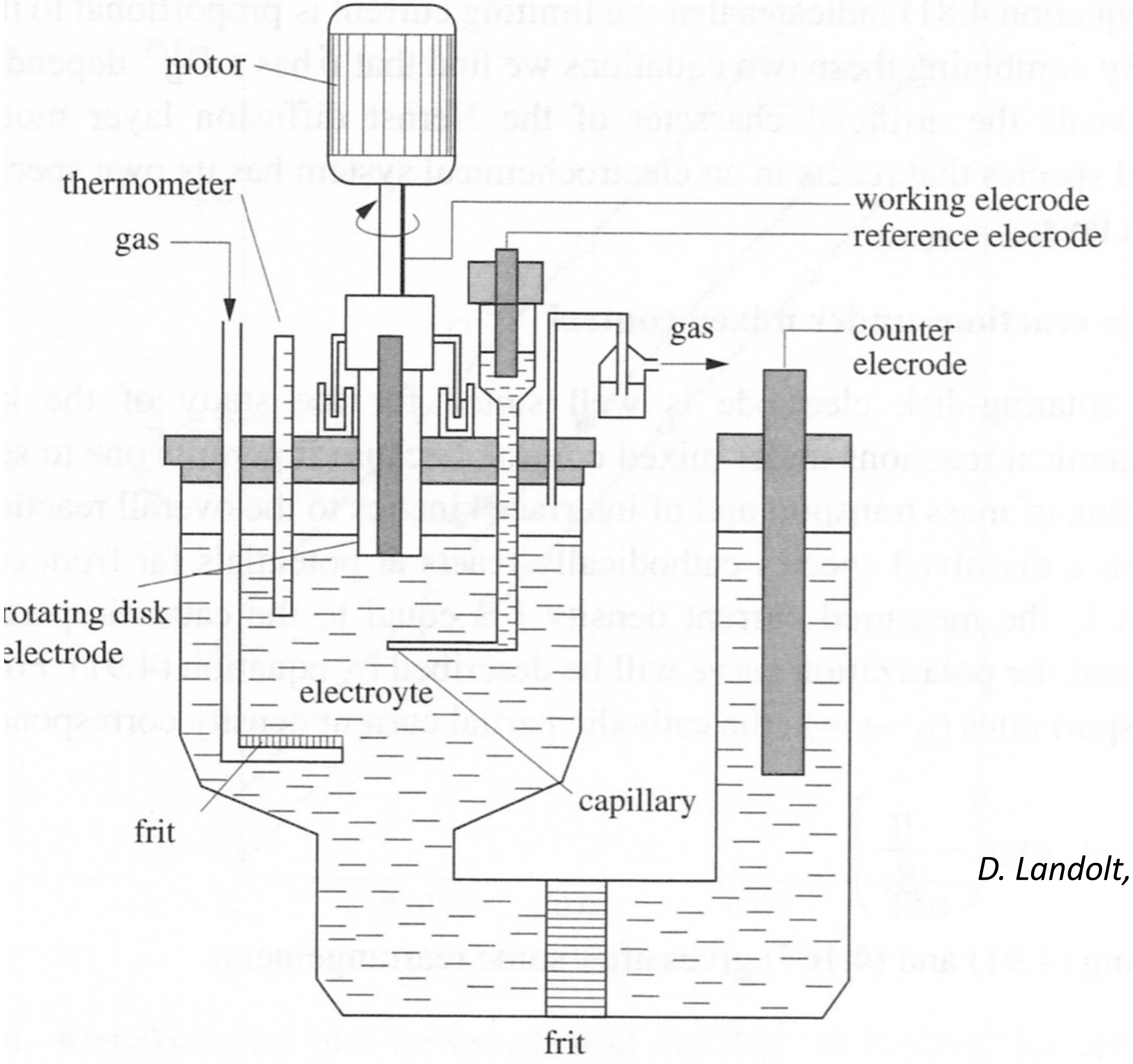
D. Landolt, Corrosion, EPFL press



Rotating disk electrode (RDE)

- The RDE is a method to achieve steady state conditions that allows accurate measurement of diffusion and kinetic parameters under controlled hydrodynamic conditions.
- It has the advantage over stationary electrodes (e.g. cyclic voltammetry - CV) that suffer from random convection caused by gravity and temperature gradients.
- CV gives accurate results at fast scan rate (>100mV s^{-1}) but is liable to error at slower scan rates.
- Common practice: do CV on the stationary RDE and afterwards start the disc rotating and see the effect on the CV: at some point, steady state kicks in and there is no more hysteresis in the CV.
- The two methods are complimentary. Do both to get a completer picture.
- Other forced convection methods are
  - rotating cylinder electrode (easier to make than rotating discs and popular for corrosion experiments where multi samples might need to be studied)
  - wall-jet (impingement) : similar to the RDE but easier to make as the electrode is stationary and the electrolyte is forced through a small nozzle to create the jet impingement (popular for corrosion studies)
  - thin layer cells in which the electrolyte is forced through a gap between two stationary electrodes.

Rotating disk electrode set-up



D. Landolt, Corrosion, EPFL press

Rotating Disc equipment by Autolab

Complete setup

Example electrodes

Rotator controller and electrode head

Levich Equation - example

Reduction of potassium ferricyanide $K_3[Fe(CN)_6]$

($Fe^{3+} \rightarrow Fe^{2+}$)

Concentration C_0 = 0.81 mM in 0.1 M KCl

$$i_L = 0.620\, nFAD^{\frac{2}{3}} \omega^{\frac{1}{2}} \nu^{-\frac{1}{6}} C_0$$

F = Faraday constant
A = area of the electrode
n = number of electrons transferred
ν = kinematic viscosity = 9.913×10^{-3} $cm^2\ s^{-1}$ for 0.1 M KCL

=> calculated diffusion coefficient from the slope
$D = 7.6 \times 10^{-6}\ cm^2\ s^{-1}$

Example of experimental data

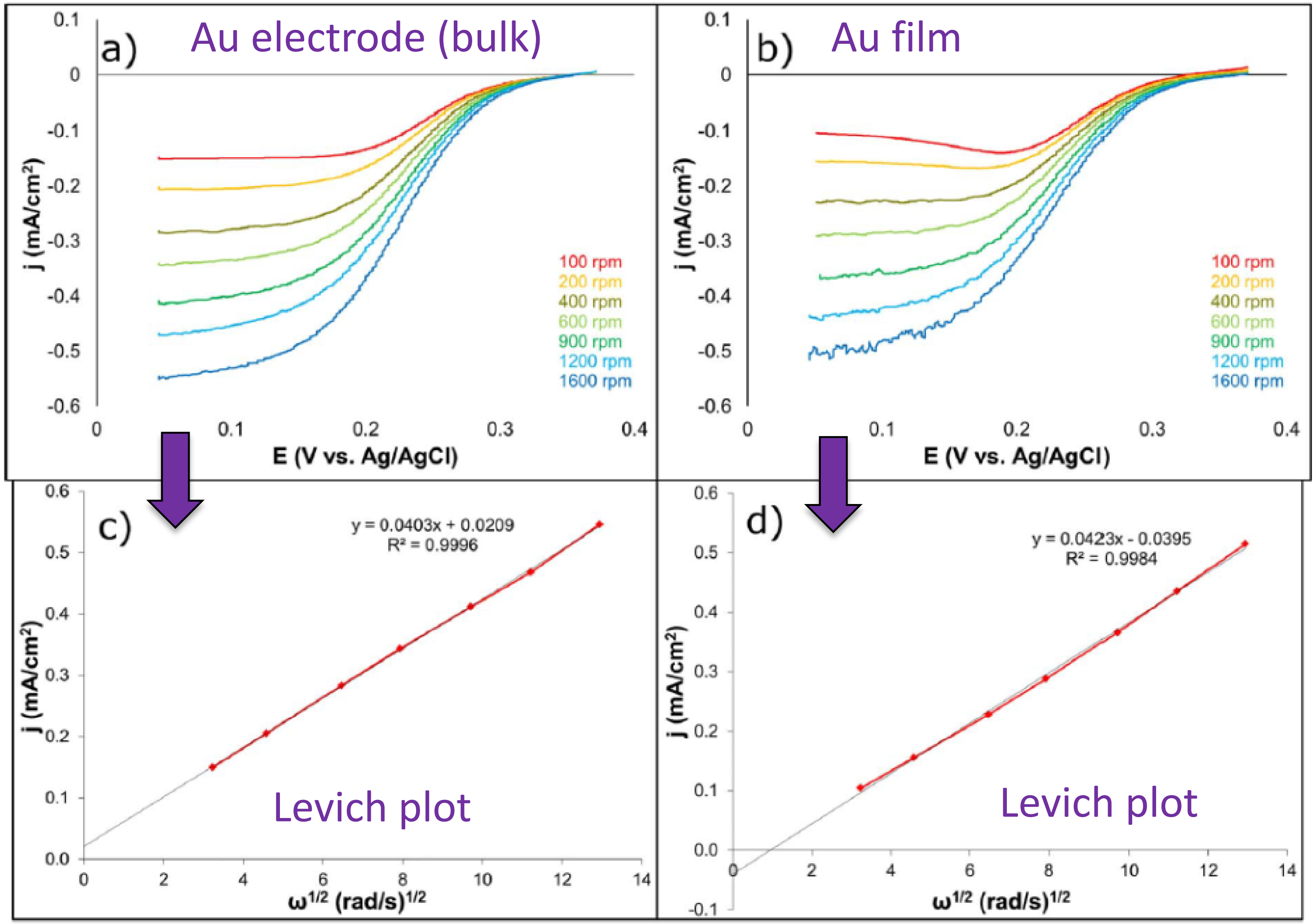


Figure 6. Rotating disk electrode voltammetery of 0.81 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl on bulk Au (a) and Au film (b). (c) Levich plots at 0.06 V vs. Ag/AgCl of bulk Au and Au film (d).

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Koutecky–Levich equation

Add the kinetic term:

$$\frac{1}{i_L} = \underbrace{\frac{1}{i_K}}_{\text{kinetic term}} + \underbrace{\left(\frac{1}{0.620nFAD^{2/3}\nu^{-1/6}C}\right)}_{\text{mass transport term (forced convection)}}\omega^{-1/2}$$

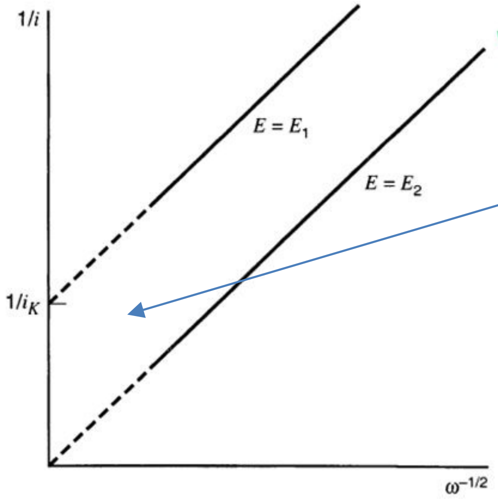
i_L = measured current
i_K= kinetic current

Experiment

Measure the current over a range of rotation speeds, as a function of applied electrode potential as additional parameter, to obtain a series of linear plots – the intercept determines the kinetic parameter and the slope the diffusion parameter

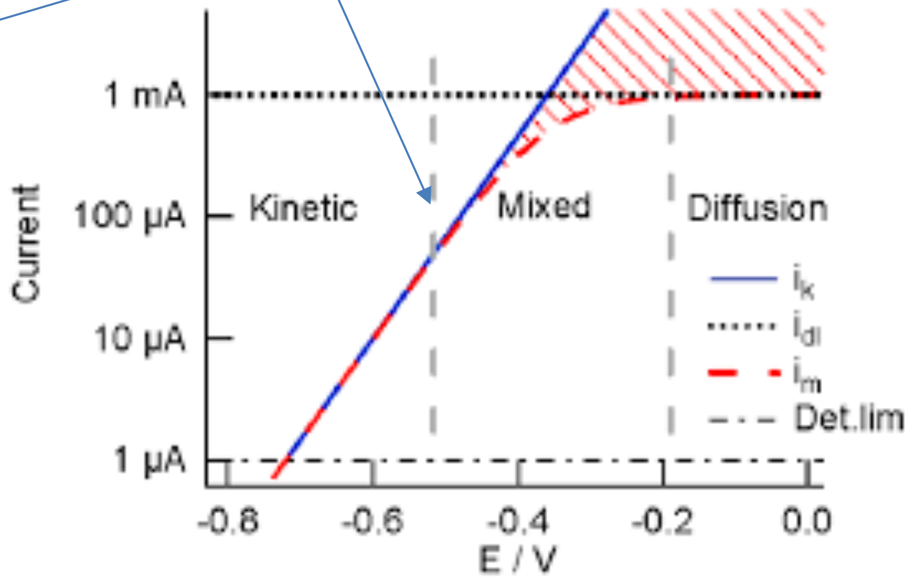
Kouteckỳ-Levich Equation

As the electrode potential is increased, the control switches from kinetic to diffusion



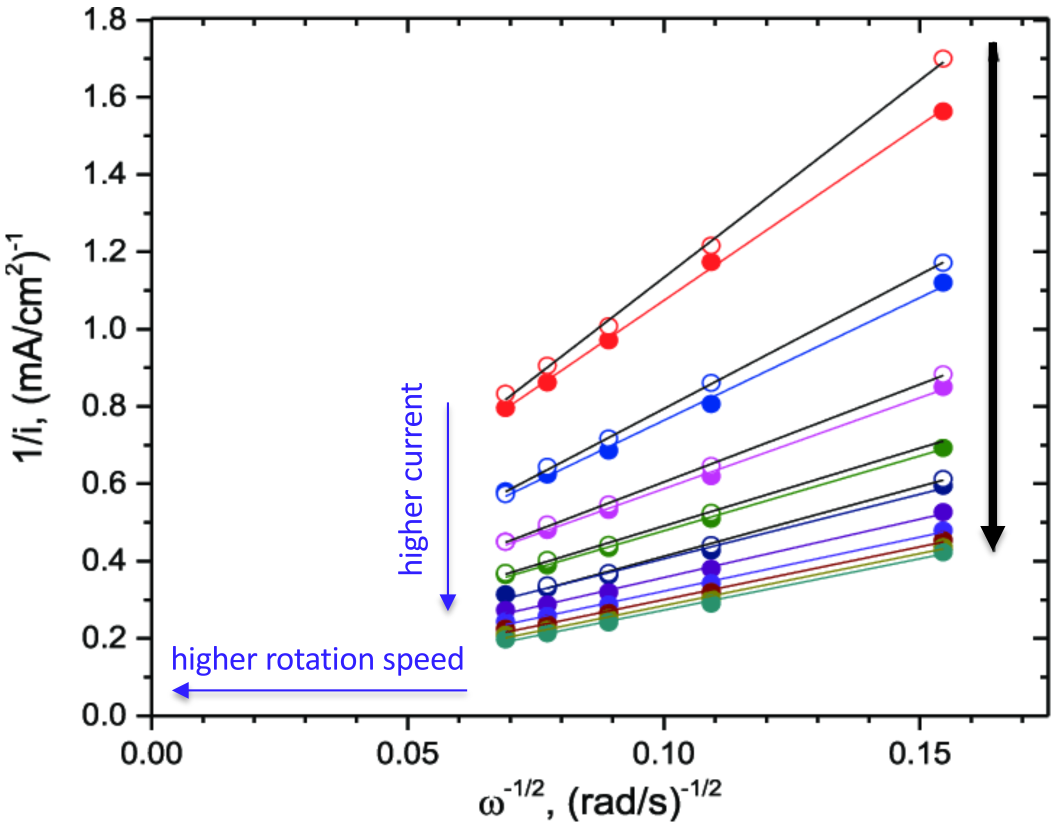
Where E2 < E1 (reduction)
E2>E1 (oxidation)

As expected, i_K grows larger ($1/i_K$ grows smaller) as the overpotentials is increased.



(The higher the rotation speed, the higher the i_{LIM}
Hence the smaller $1/\omega$, the smaller $1/i$)

Example: oxidation of bromide Br^-



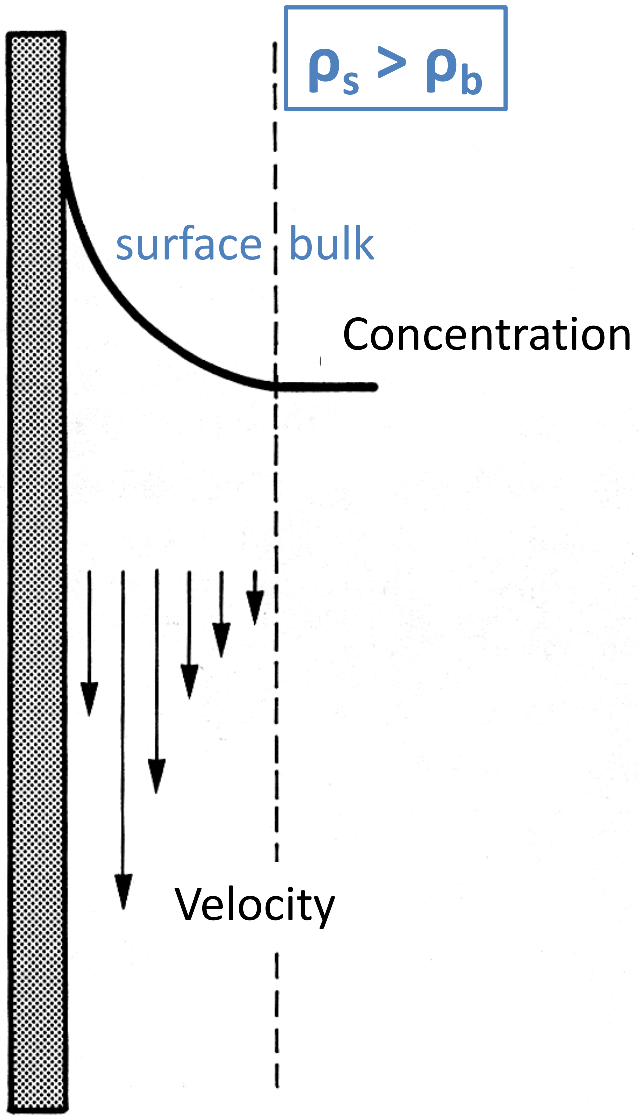
Increasing electrode potentials from 1.21 to 1.3 V in steps of 0.01 V

Oxidation: 1.3 V is more oxidizing than 1.2 V and will produce a higher current.
=>
higher V of 1.3 V is the point plotted lowest in a 1/i scale (higher current).

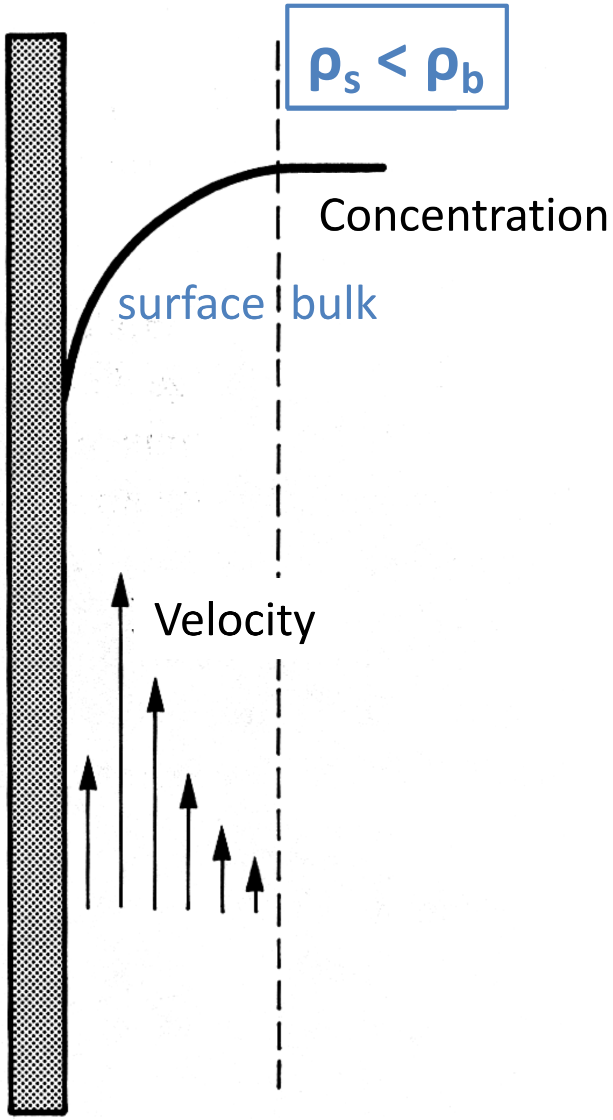
Koutecky-Levich plots for the oxidation of bromide Br^- at a rotating Pt disk electrode. The solid and open circles represent data collected in two fully independent runs and the arrow points in the direction of increasing potentials from 1.21 to 1.3 V in steps of 0.01 V.

The oxidation of Bromide on Platinum Electrodes in aqueous acidic solutions: electrochemical and in situ spectroscopic studies
Journal of The Electrochemical Society 161(6):H392-H398 · April 2014

Free convection at vertical electrodes



a)



b)

Transport correlations for free convection systems

Geometry	**Flow**	**Characteristic length L**	**Sh (mean value: Sc>1000))**
vertical plane electrode	laminar $Gr < 10^{12}$	height	$0.67\,(ScGr)^{1/4}$
vertical plane electrode	turbulent $Gr > 10^{13}$	height	$0.31\,(ScGr)^{0.28}$
horizontal plane electrode facing upwards	laminar $Gr < 10^{7}$	surface/perimeter	$0.54\,(ScGr)^{1/4}$
horizontal plane electrode facing downwards	turbulent $Gr > 10^{7}$	surface/perimeter	$0.15(ScGr)^{1/3}$

Grashof number $Gr = g\,\Delta\rho\,L^3 / \rho_b \nu^2$

The Grashof number approximates the ratio of gravity (buoyancy) to viscous force acting on a fluid.
It arises in situations involving natural convection and is analogous to the Reynolds convection (=forced convection).