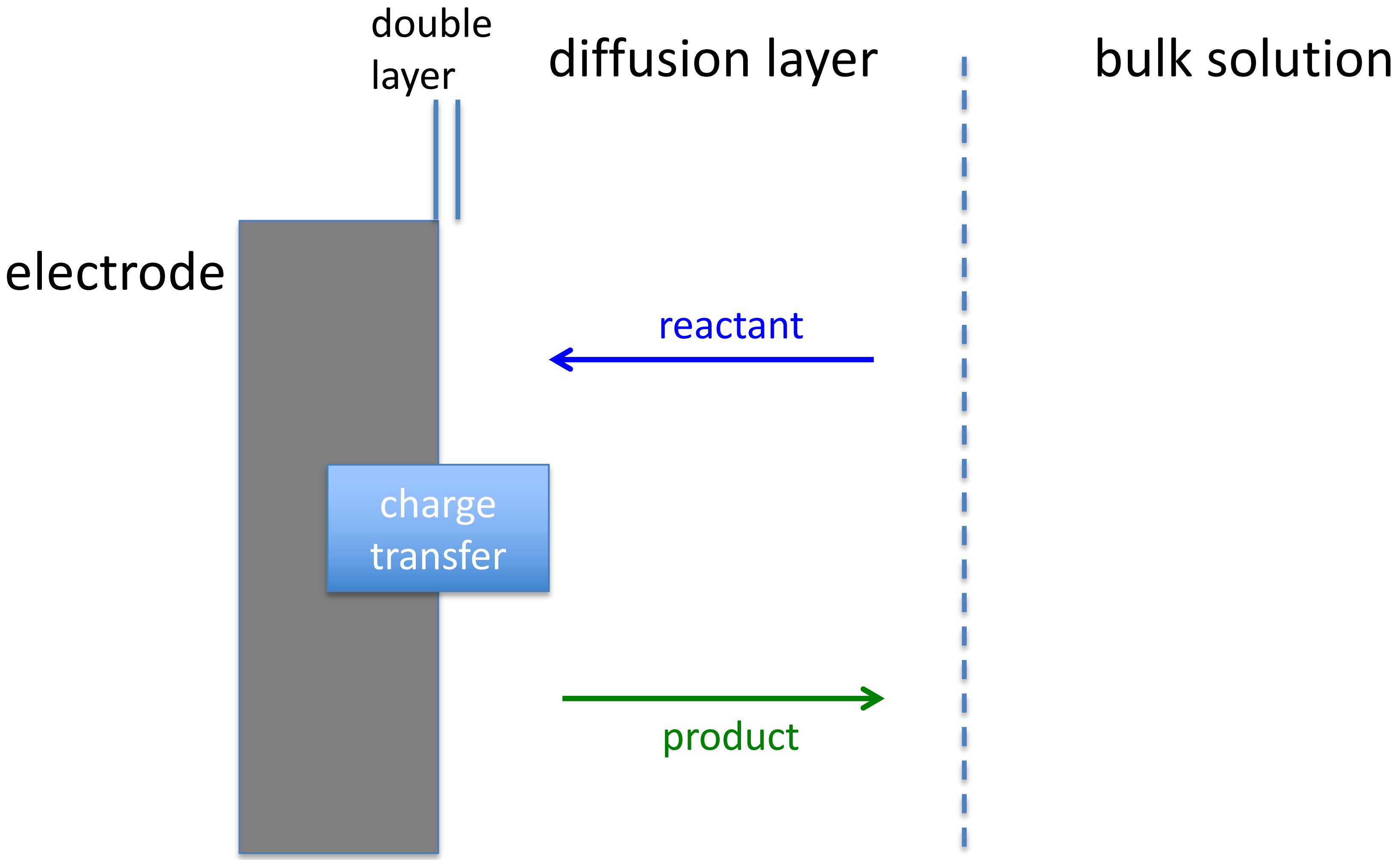
Electrochemistry for materials technology

Chapter 4

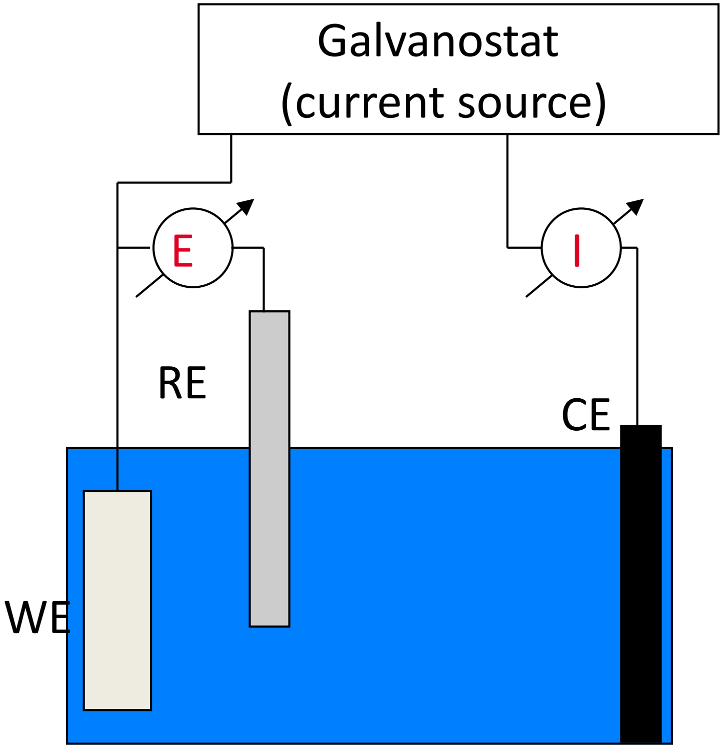
Electrode kinetics

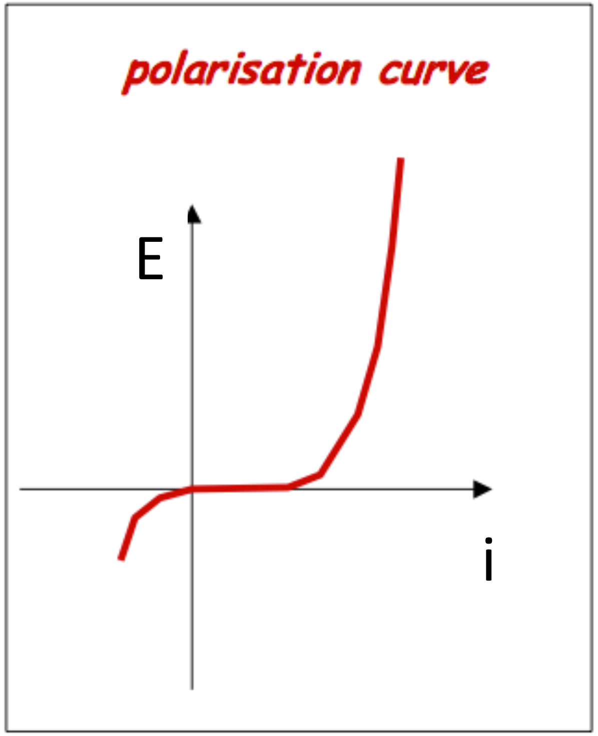
Rate determining steps in electrochemical reactions



Galvanostatic method for measurement of polarisation curves

GALVANOSTAT: current source that forces a selected current I to pass from the working electrode WE (i.e. the electrode under investigation) to the counter electrode CE. The resulting potential E is measured using a reference electrode RE.

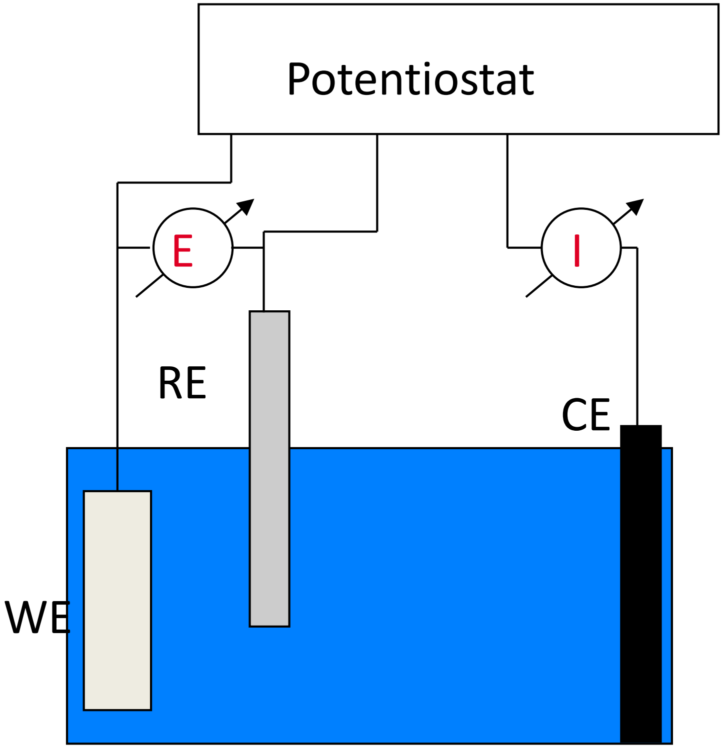


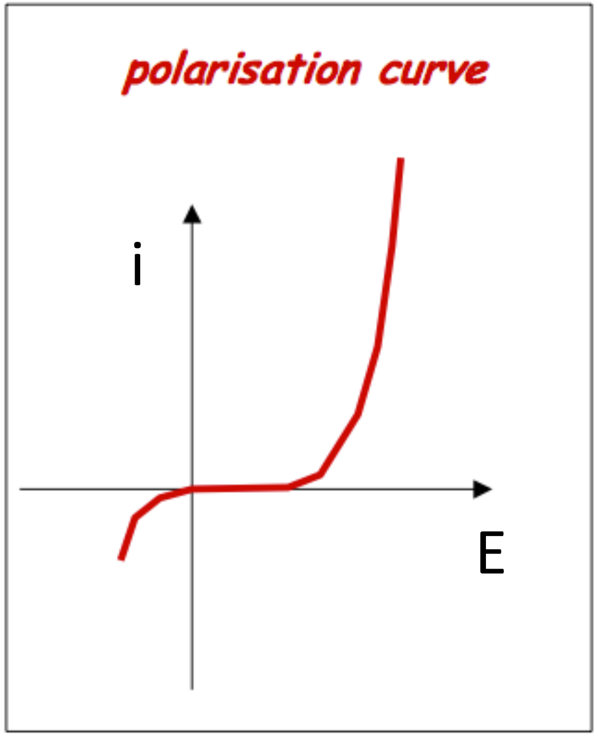


Potentiostatic method for measurement of polarisation curves

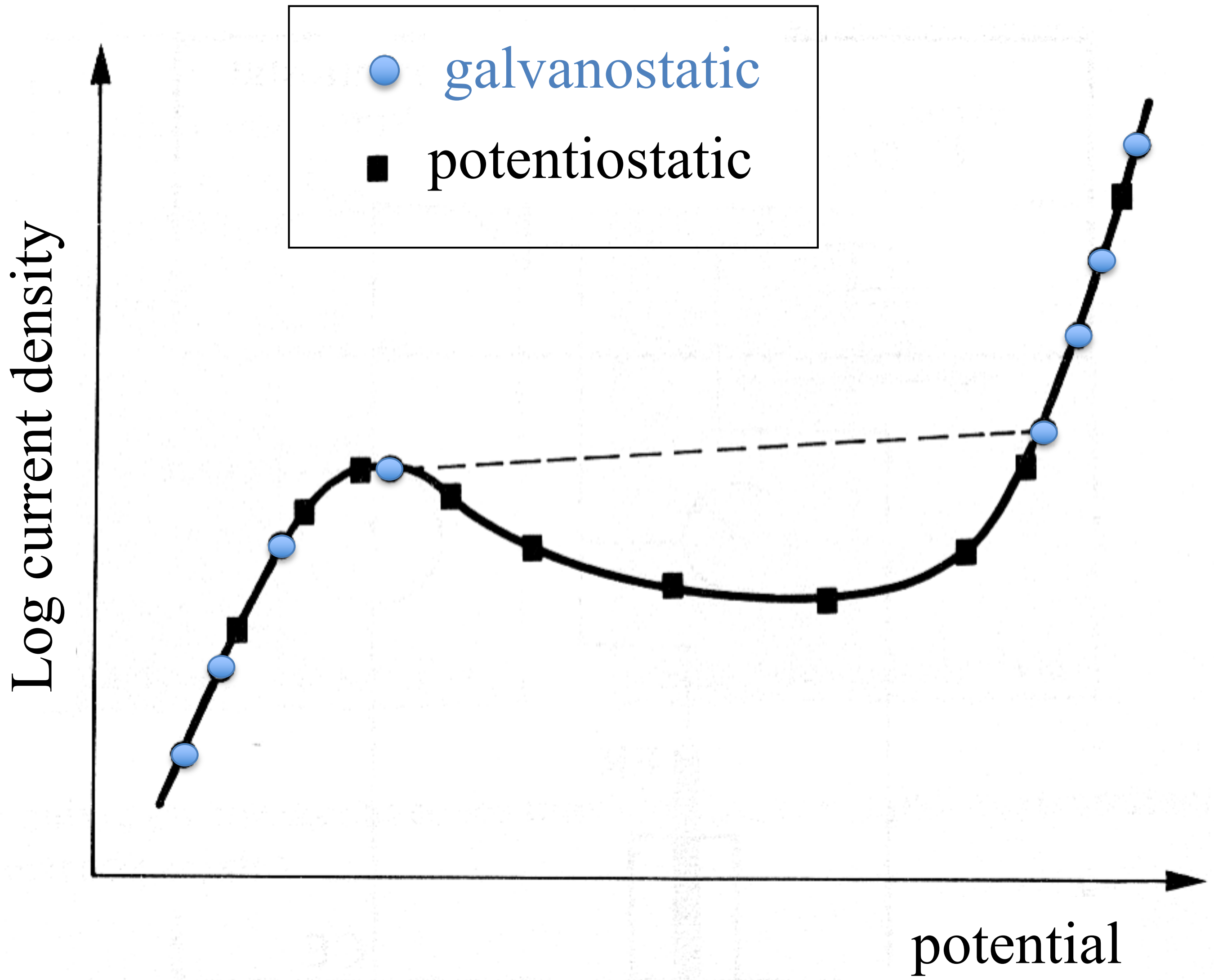
POTENTIOSTAT: electronic device that maintains a selected potential E between RE and WE by passing an appropriate current I between WE and CE.

RE: reference electrode, CE: counter electrode, WE: working electrode





Galvanostatic and potentiostatic polarisation curves



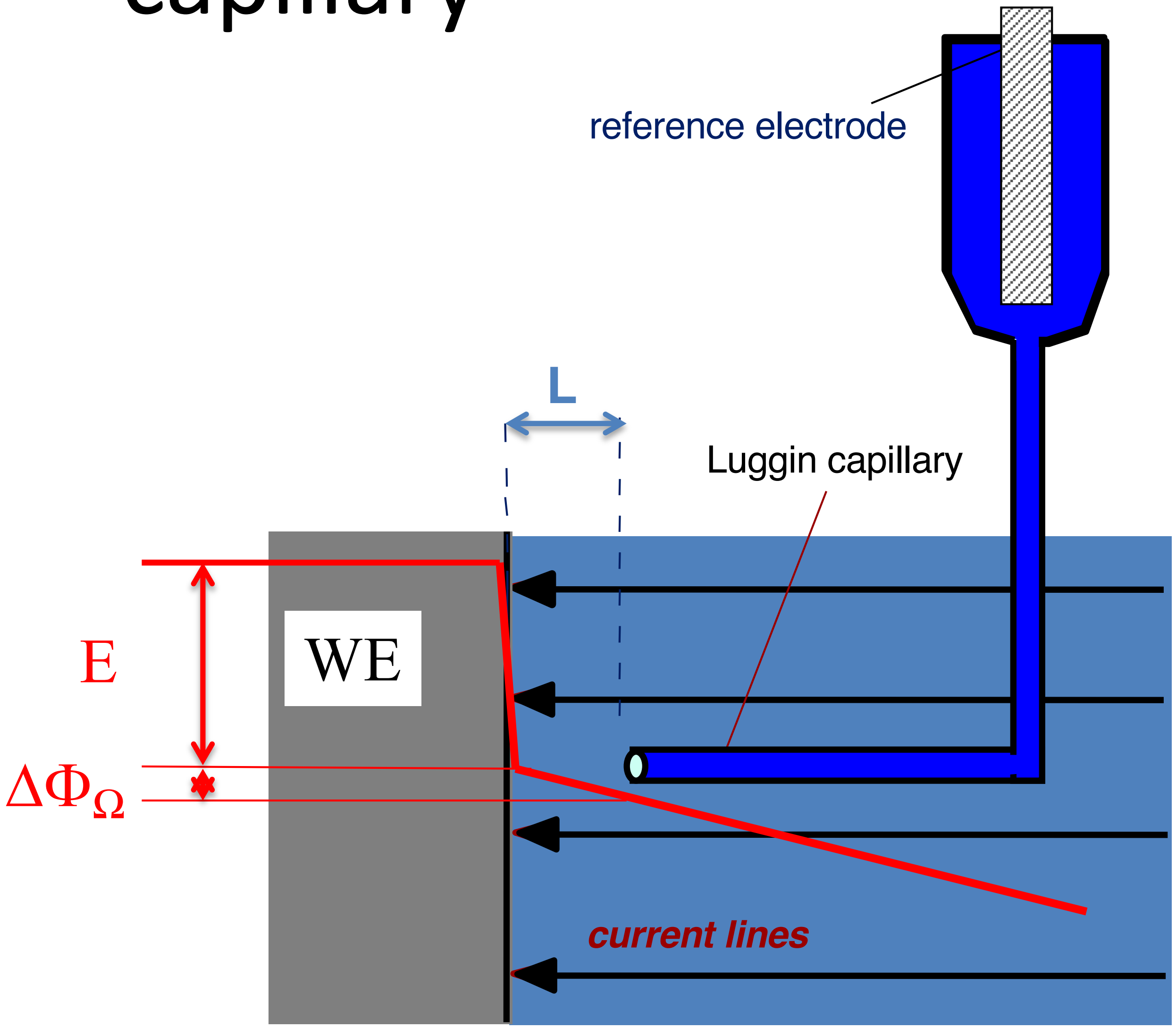
Reference electrode with Luggin capillary

Ohmic drop $\Delta\Phi_\Omega$

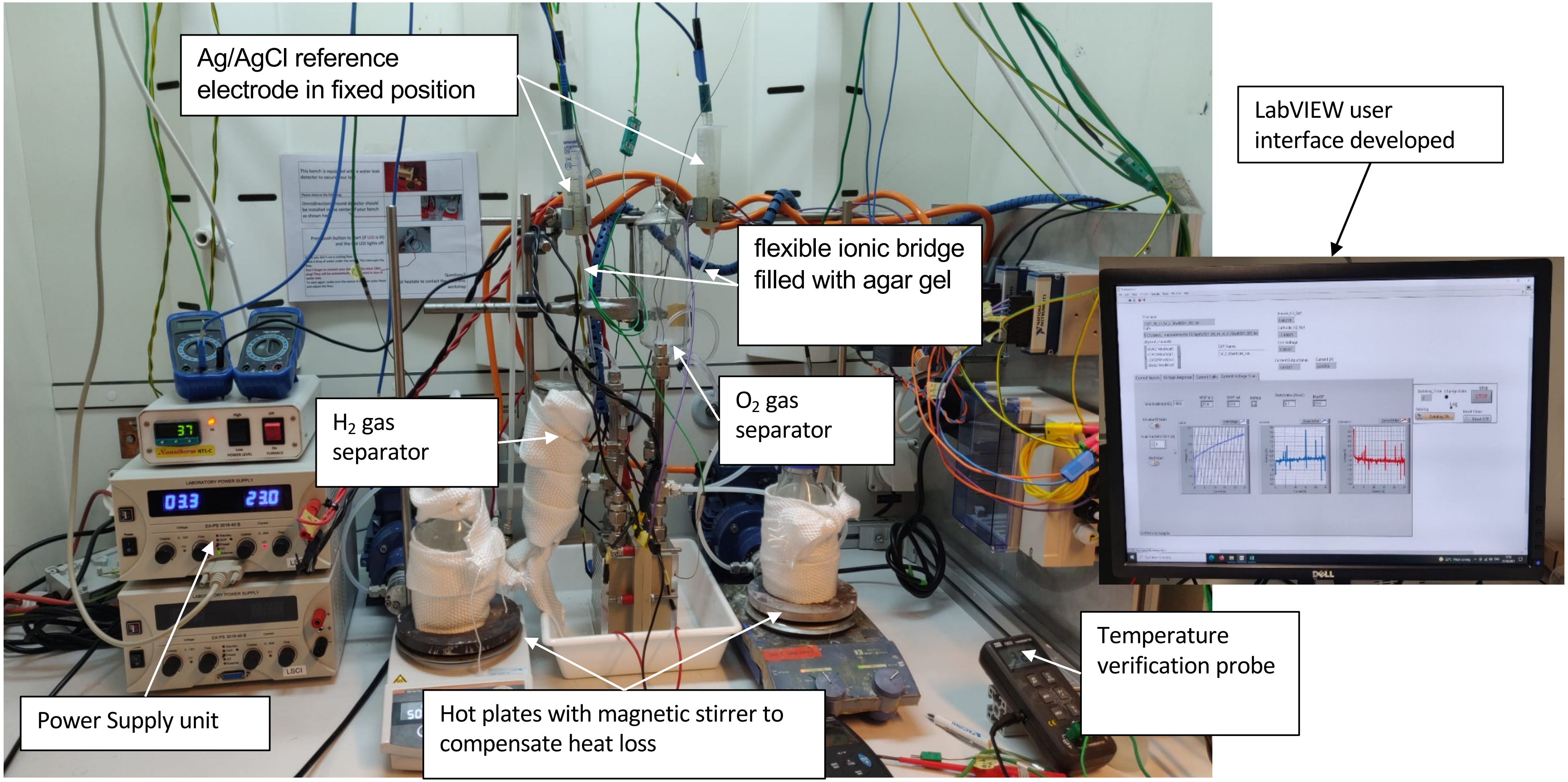
$$E_{measured} = E + \Delta\Phi_\Omega$$

$$\Delta\Phi_\Omega = i\,L / \kappa$$

κ = electrolyte conductivity



Example from actual test rig at GEM lab (water electrolysis)



Ag/AgCl reference electrode in fixed position

LabVIEW user interface developed

flexible ionic bridge filled with agar gel

O_2 gas separator

H_2 gas separator

Power Supply unit

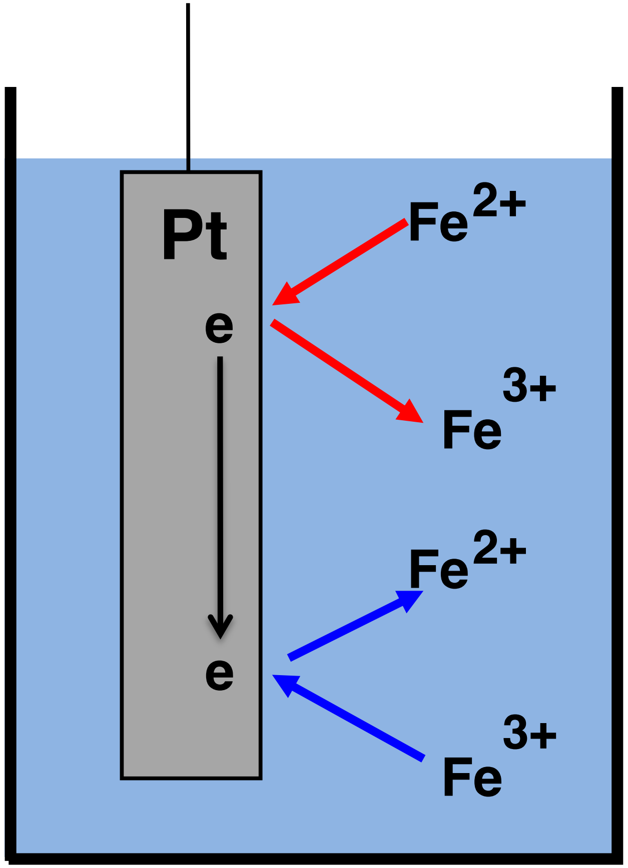
Hot plates with magnetic stirrer to compensate heat loss

Temperature verification probe

Butler-Volmer equation for **charge transfer** reactions

$$Fe^{2+} \underset{v_c}{\overset{v_a}{\rightleftarrows}} Fe^{3+} + e$$

V_a: anodic reaction rate
V_c: cathodic reaction rate



Hypotheses:

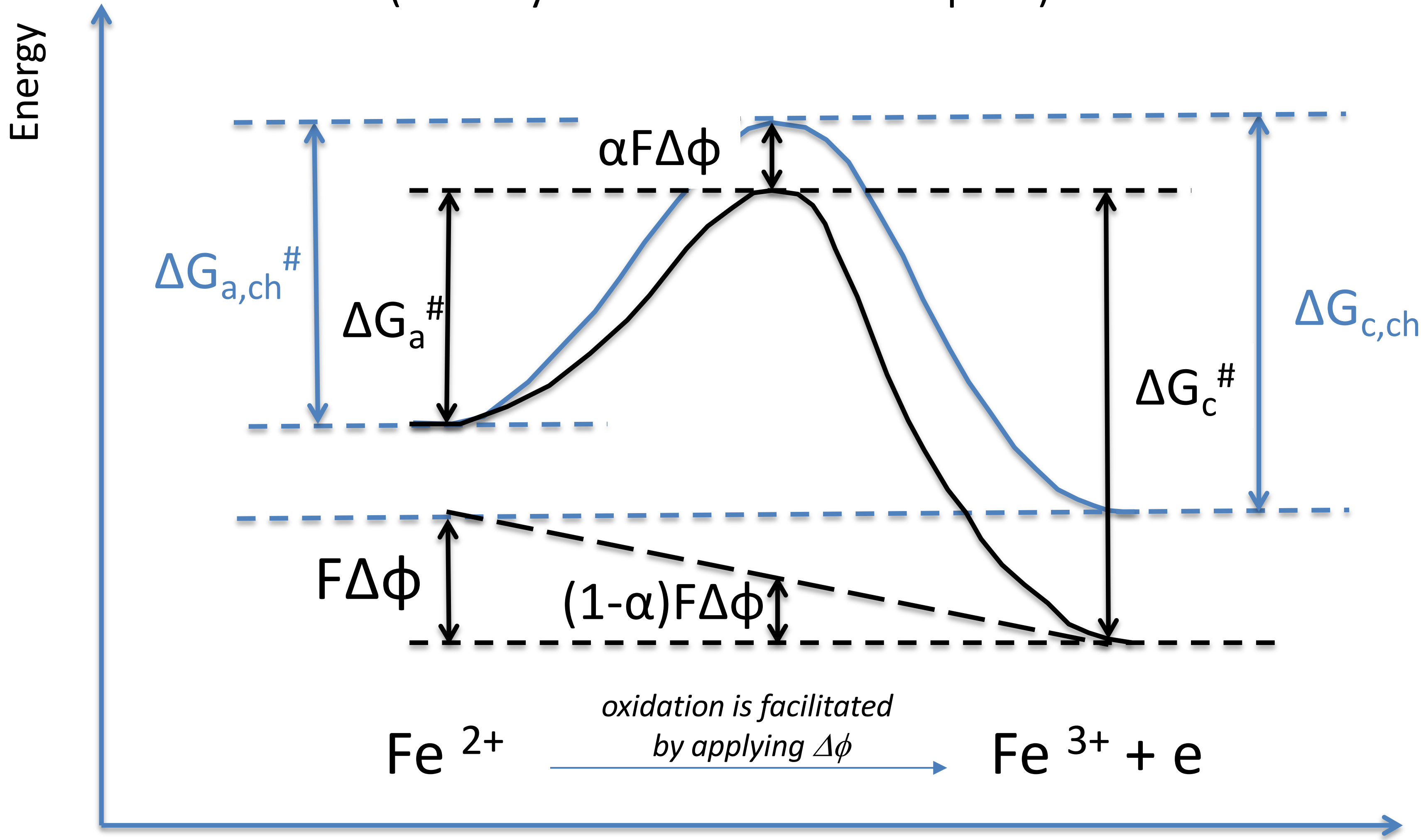
- first order kinetics (v ∝ concentration)
- Arrhenius law

$$v_a = k_a' \, c_{Fe^{2+}} \exp\left(-\Delta G_a^{\#} / RT\right)$$

$$v_b = k_b' \, c_{Fe^{3+}} \exp\left(-\Delta G_c^{\#} / RT\right)$$

Activation energy for charge transfer at electrode-electrolyte interface

('Theory of the activated complex')



Explanations:

1. Blue is for an oxidation of a Fe^{2+} ion in solution (e.g. by oxygen from air).
2. **Black** is for the redox reaction at a solid interface electrode that provides a potential difference to the solution, i.e. $\Delta\phi$.
3. The applied potential is positive (anodic*) since the oxidation of Fe^{2+} to Fe^{3+} is facilitated, the final energy of the right hand side is lowered: the final state at the right is shifted down by $F\Delta\phi$ due to the applied potential.

   (*The electrode takes up an electron from the solution Fe^{2+} , hence it is an oxidation, thus anodic, thus positive potential.)
4. This distorts the reaction path from the blue to the **black** curve, changing the activation energy E_A ($\Delta G^{\#}$) in both directions.
5. The E_A for the reduction (from right to left) is increased by a factor $(1-\alpha)F\Delta\phi$ (more difficult to reduce than before), the E_A for oxidation is lowered by a factor $\alpha F\Delta\phi$ (easier to oxidize thanks to the applied potential).
6. The relative ease depends on the transfer number α, which usually is taken as 0.5 for a 'symmetrical' reaction.

Butler-Volmer equation for a simple electrode (surface conc. c_s = bulk conc. c_b)

= pure charge transfer; no concentration limitations

$i_a = i_0 \exp(\eta / \beta_a)$ anodic current density

$i_c = - i_0 \exp(- \eta / \beta_c)$ cathodic current density

$i = i_a + i_c = i_0 \exp(\eta / \beta_a) - i_0 \exp(- \eta / \beta_c)$

η : *overvoltage*$= E - E_{rev}$

$\beta_a = RT / \alpha n F$ *(units of V)*

$\beta_c = RT / (1-\alpha) n F$ *(units of V)*

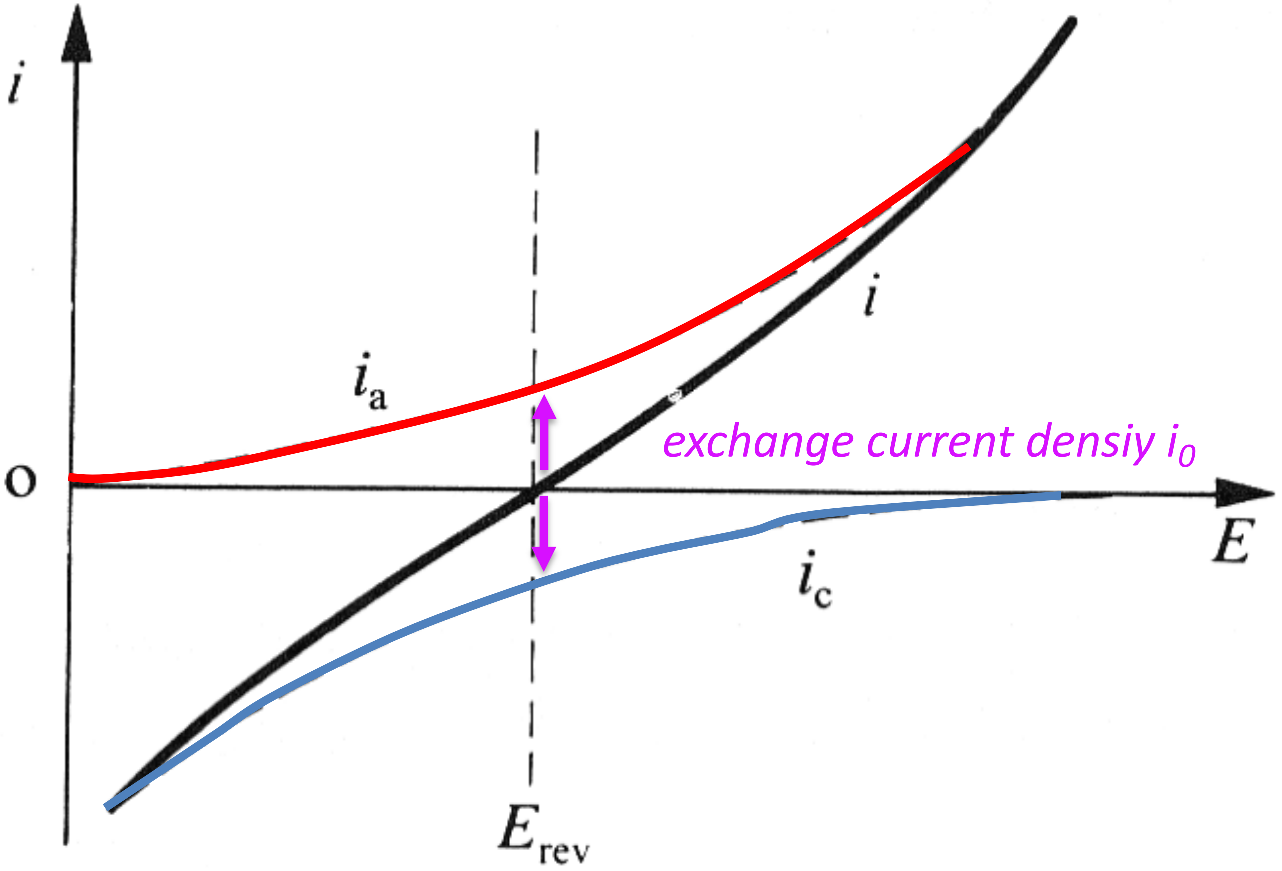
i_0 : *exchange current density*

(reaction speed v is in mol/s.cm^2
=> multiply with F (C/mol) to convert to A/cm^2)

More general: $i_0 = nFk_a c_{red,b} \exp\left(\frac{\alpha nF}{RT} E_{rev}\right) = nFk_c c_{ox,b} \exp\left(-\frac{(1-\alpha)nF}{RT} E_{rev}\right)$

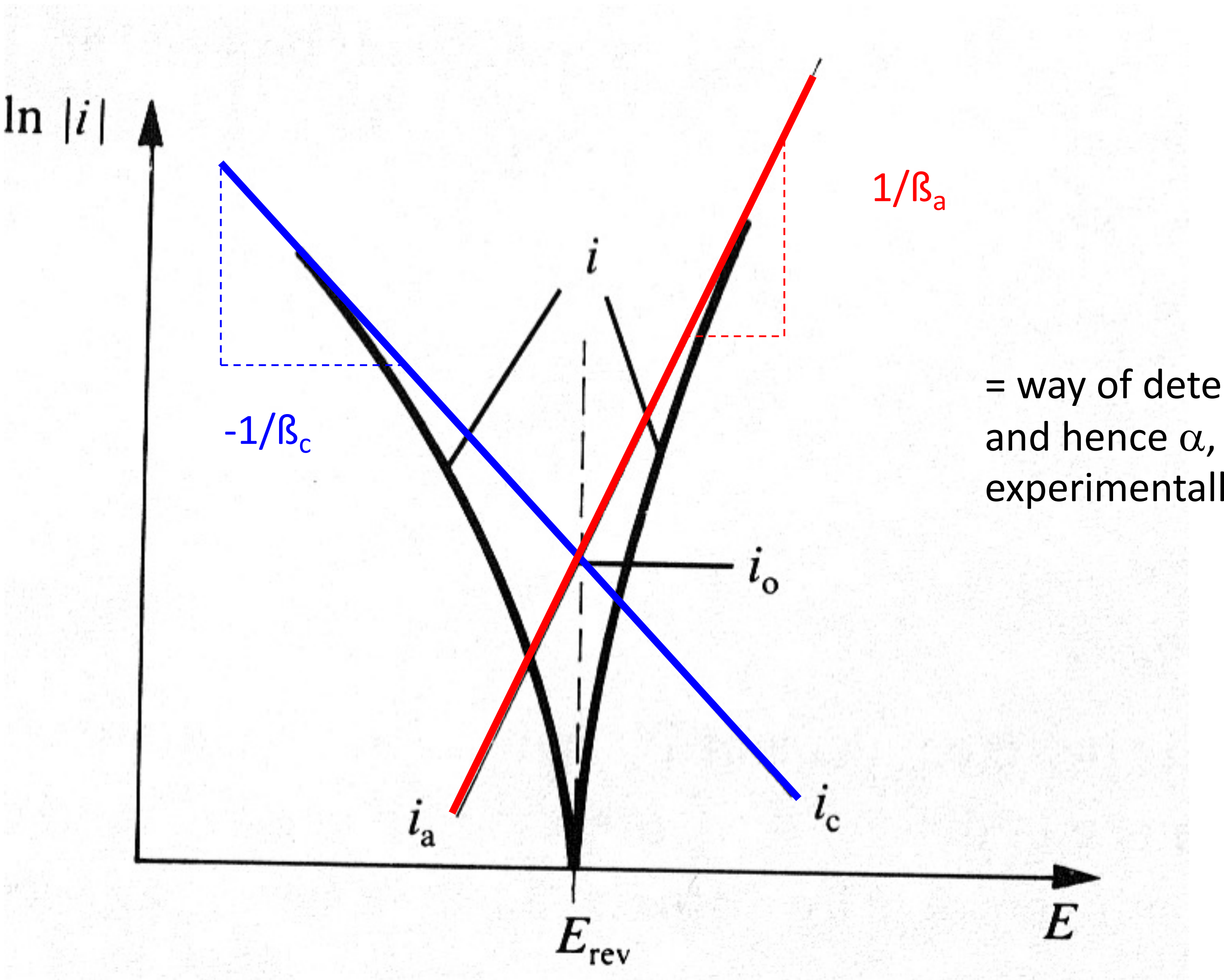
Partial current densities and total current density near equilibrium potential

$$i = i_a + i_c = i_0 \exp(\eta / \beta_a) - i_0 \exp(-\eta / \beta_c)$$



(At large η (+ or -), one branch becomes dominant, the other negligible => Tafel plots)

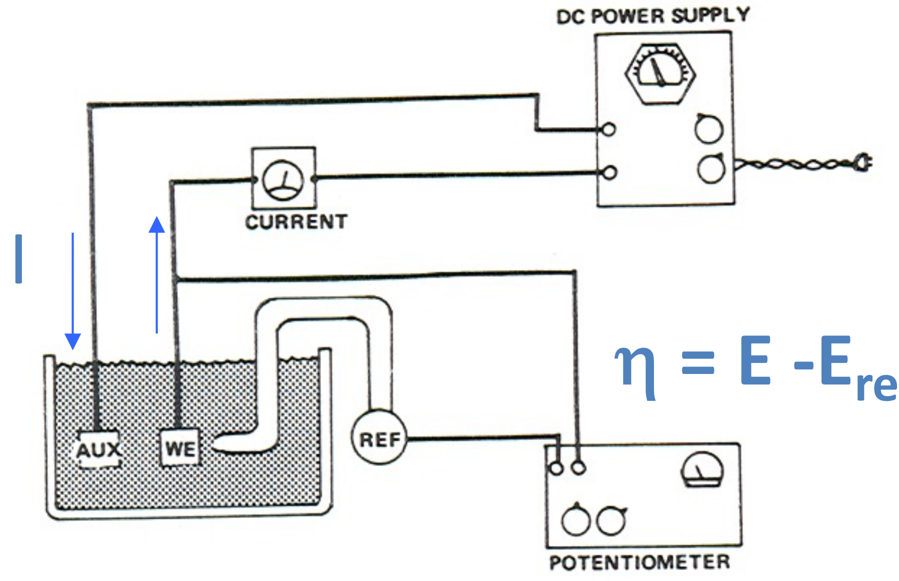
Evans diagram showing partial and total current densities



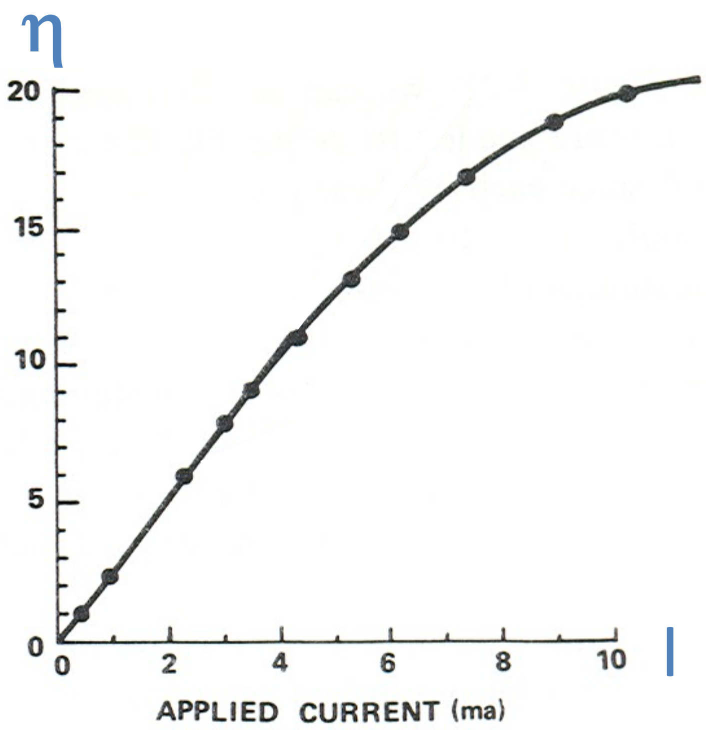
= way of determining β, and hence α, experimentally

Tafel experiment (galvanostatic polarisation curve) at low current densities

($\exp(x) = 1 + x$ for small x)



$\eta = E - E_{rev}$



$\eta = a_a + b_a \log i$ anodic

$\eta = a_c - b_c \log | i |$ cathodic

a, b : Tafel constants (units in V)

a relates to i_0

b relates to Tafel slope in mV per decade of current increase

Conversion Tafel constants (a, b) to Tafel coefficients ($ß_c$, $ß_a$)

$\eta = a_a + b_a \log i$ anodic

$\eta = a_c - b_c \log | i |$ cathodic

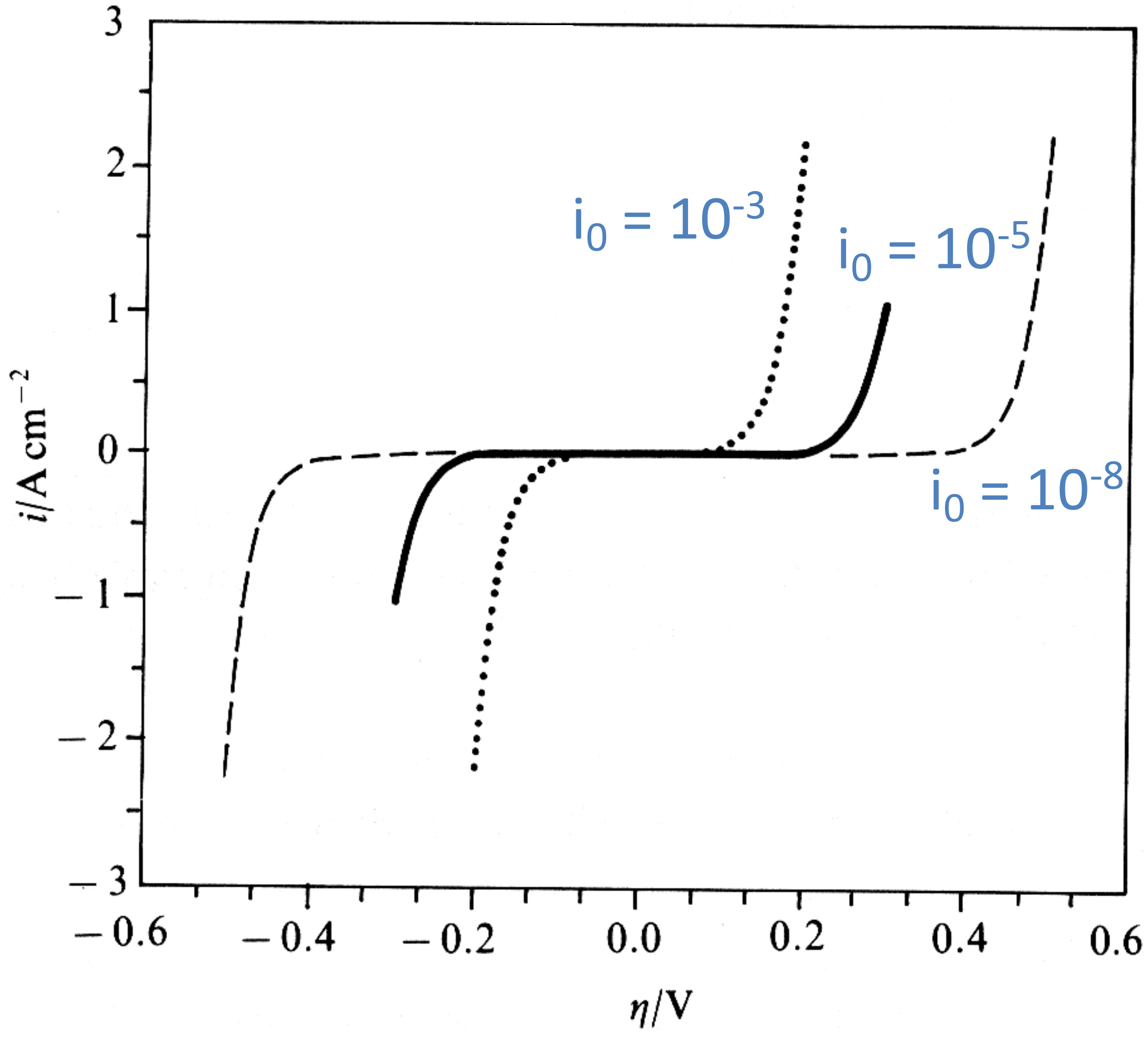
a, b : Tafel constants (units : V)

Conversion Tafel <-> Butler-Volmer

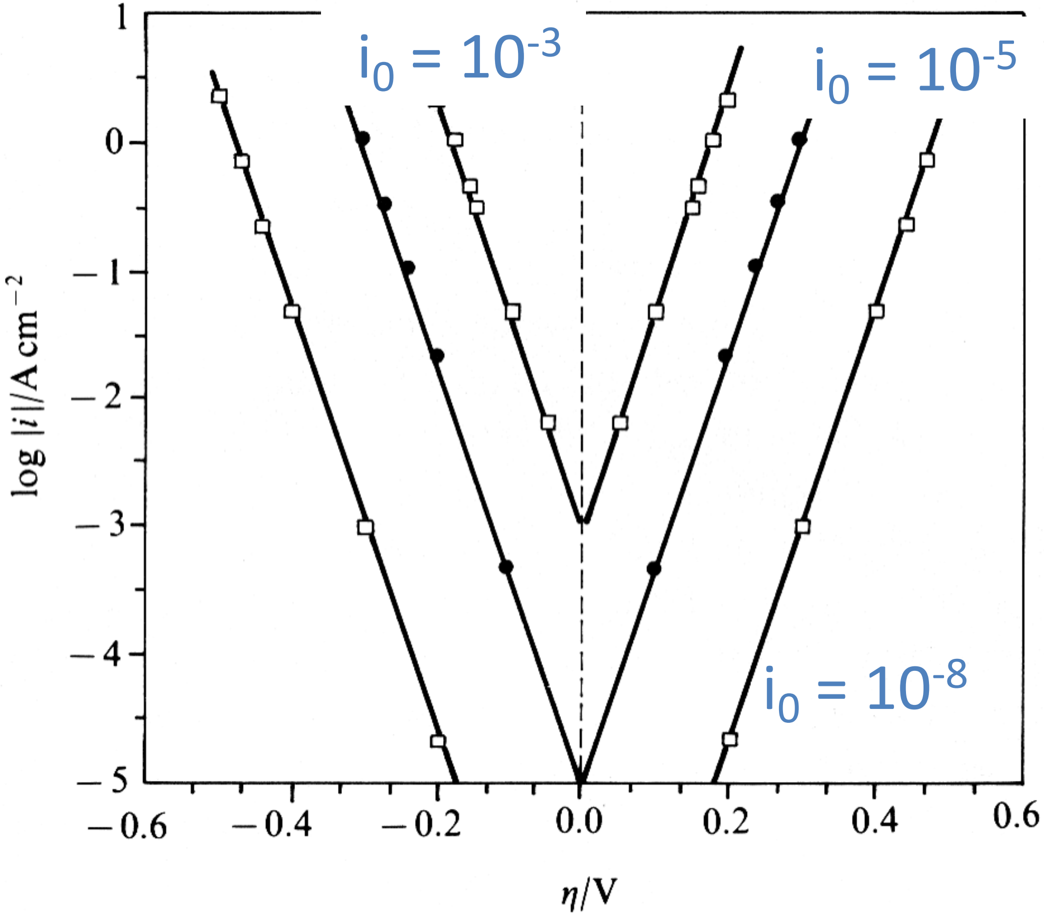
$a_a = - 2.303\, ß_a \log i_0$ (units: V) $a_c = 2.303\, ß_c \log i_0$ (units: V)

$b_a = 2.303\, ß_a$ (units: V) $b_c = 2.303\, ß_c$ (units: V)

Effect of exchange current i_0 on polarisation behaviour (**linear** scale)



Effect of exchange current i_0 on polarisation behaviour (**log** scale)



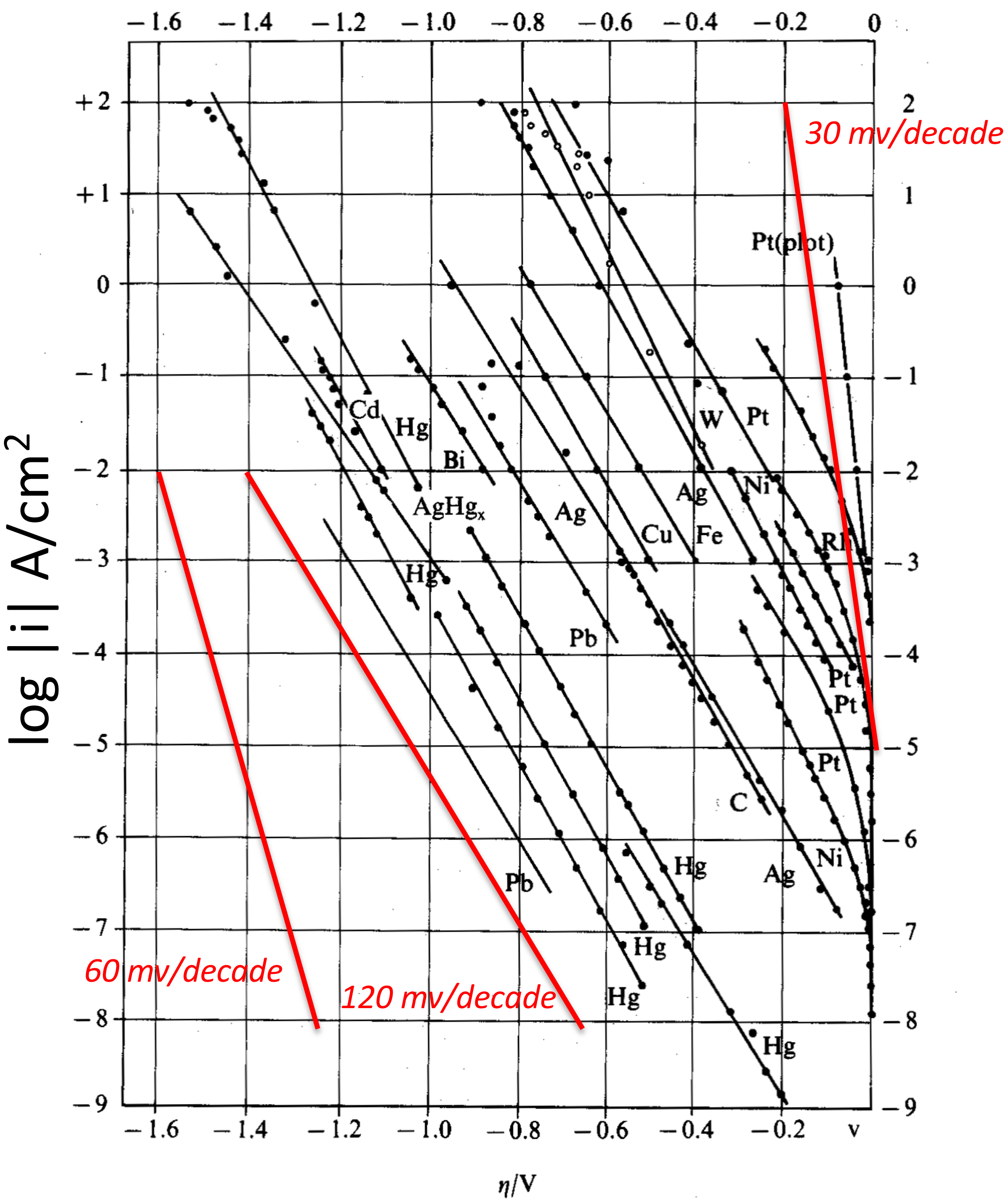
Parameters affecting charge transfer current densities

Exchange current density i_0 of the reaction

$2H^+ + 2e^- \Rightarrow H_2$ (20°C)

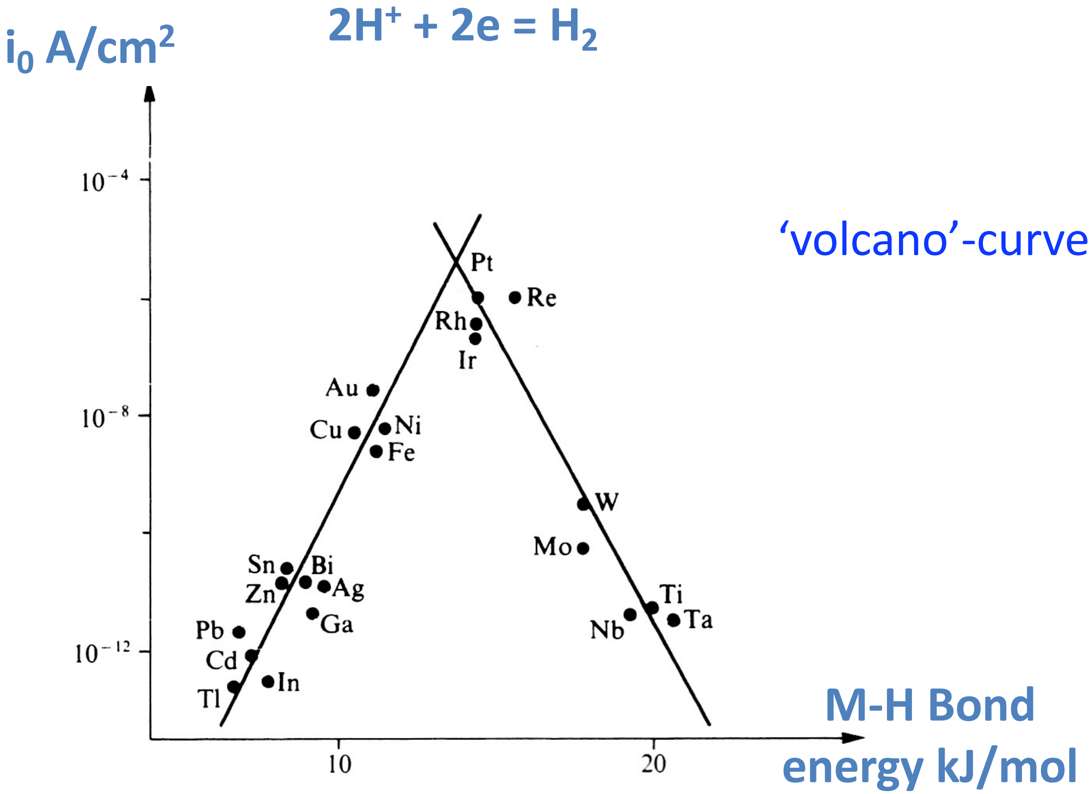
Metal	Solution	i_0 [A/cm^2]
Pt	1 M HCl	1. 10^{-3}
Pb	1 M HCl	2. 10^{-13}
Cu	0.14 M HCl	2. 10^{-7}
Cu	0.15 M NaOH	1. 10^{-6}

Tafel coefficients: β_a and $\beta_c \approx 30 - 60$ mV



Cathodic polarization curves of hydrogen evolution on different metals in sulfuric acid

Exchange current i_0 of hydrogen half cell on different metals M



Reaction mechanisms hypotheses for H^+ reduction to H_2

Volmer-Heyrovsky mechanism (for low coverage H_{ads}):

Step 1 (Volmer): $H^+ + e \rightarrow H_{ads}$

Step 2 (Heyrovsky): $H^+ + H_{ads} + e \rightarrow H_2$

a proton reacts with an adsorbed H to H_2

1 + 2: $2H^+ + 2e \rightarrow H_2$ ($\beta_c = 52$ mV)

Volmer-Tafel mechanism (at high coverage H_{ads}):

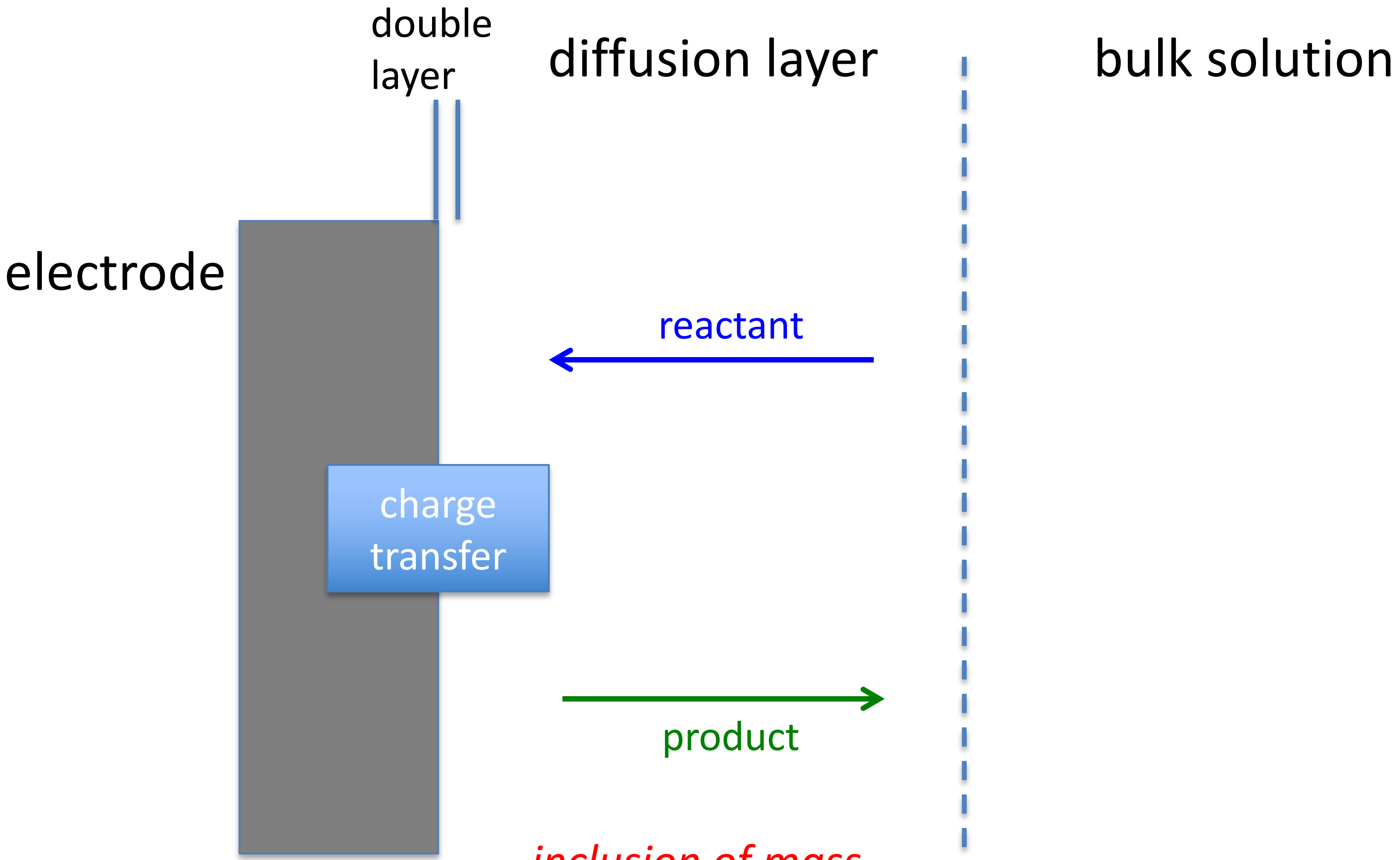
Step 1 (Volmer): $H^+ + e \rightarrow H_{ads}$

Step 2 (Tafel): $H_{ads} + H_{ads} \rightarrow H_2$

2 adsorbed H react to H_2

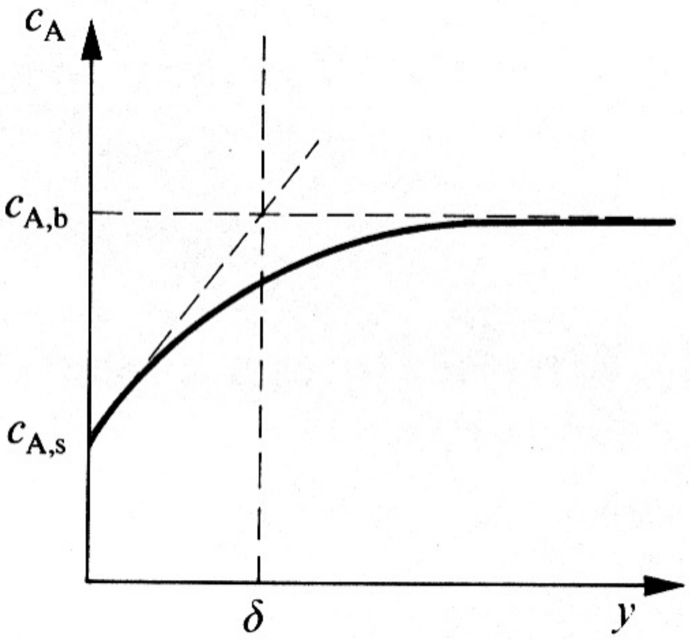
1 + 2: $2H^+ + 2e \rightarrow H_2$ ($\beta_c = 13$ mV)

Rate determining steps in electrochemical reactions

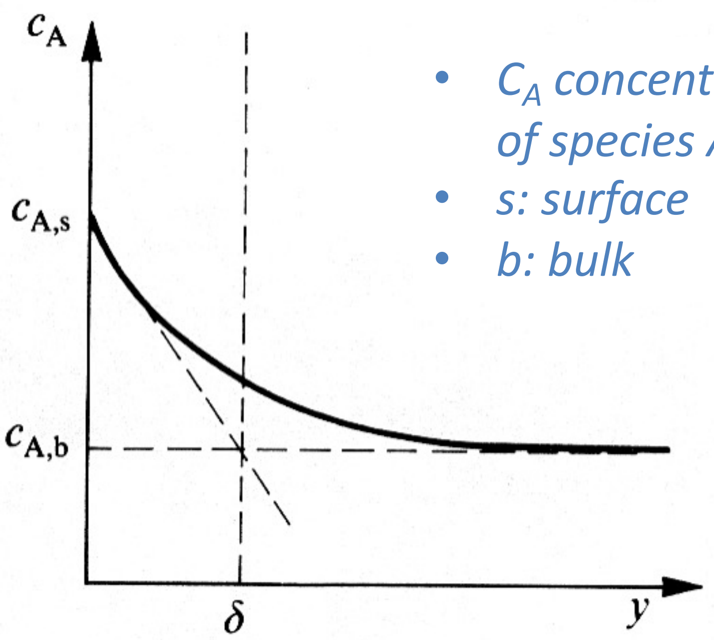


inclusion of mass transfer phenomena => concentration profiles

Concentration profiles near the electrode surface



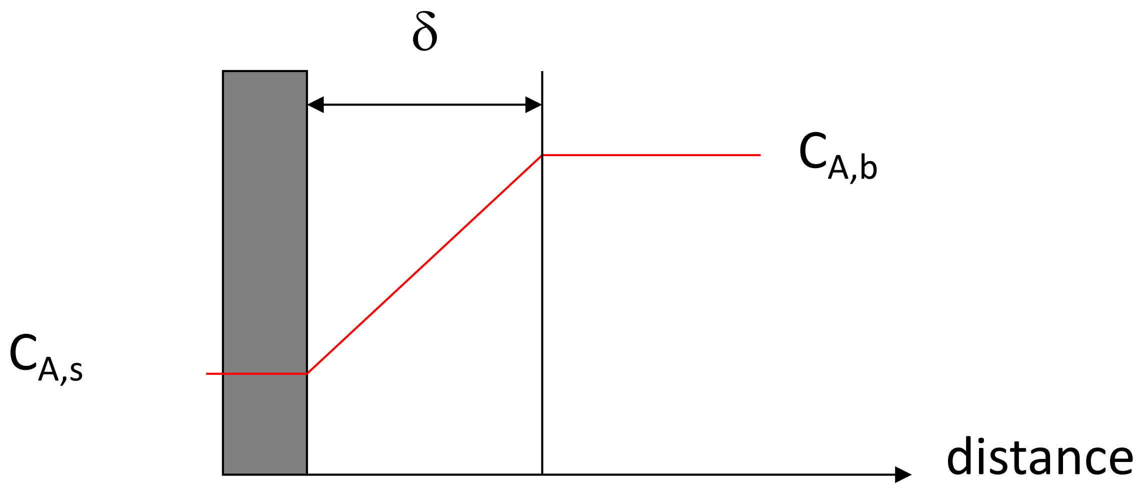
mass transport of reactant A



mass transport of product A

- *C_A concentration of species A*
- *s: surface*
- *b: bulk*

Flux N_A of species A normal to the electrode surface



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

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

δ : thickness of Nernst diffusion layer (m)

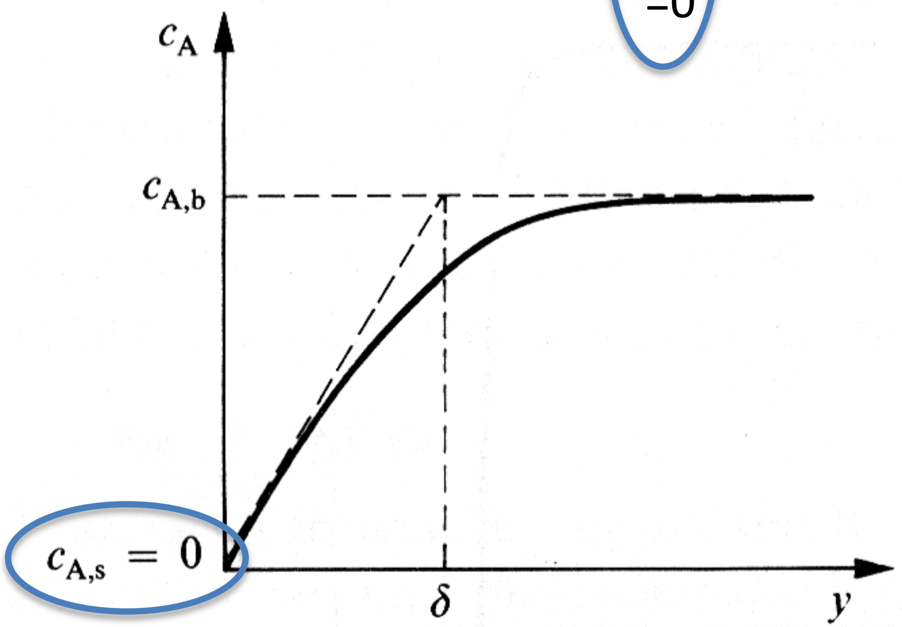
Cathodic and anodic current densities in case of mass transport-limited reactions

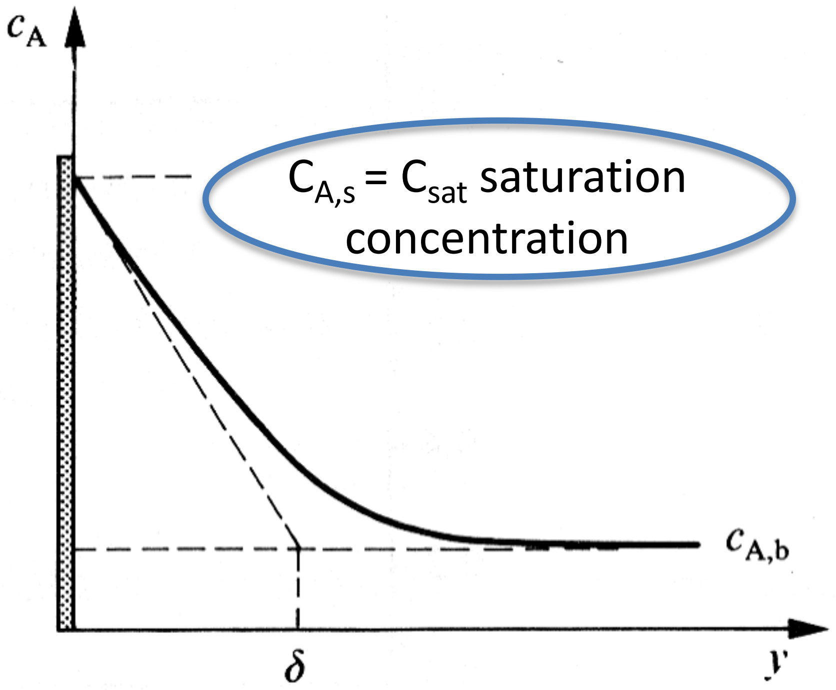
Current density	Transport of
$i_a = - n F N_A$	reactant
$i_a = + n F N_A$	product
$i_c = + n F N_A$	reactant
$i_c = - n F N_A$	product

with $N_A = -D_A (C_{A,b} – C_{A,s}) / \delta$

Concentration profiles near electrode surface at the limiting current

with $N_A = -D_A (C_{A,b} - \underset{=0}{C_{A,s}}) / \delta$





$C_{A,s} = C_{sat}$ saturation concentration

$i_a = - n F N_A$

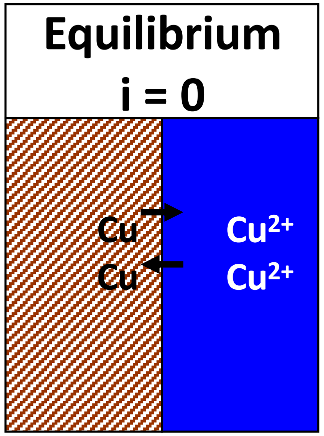
reactant

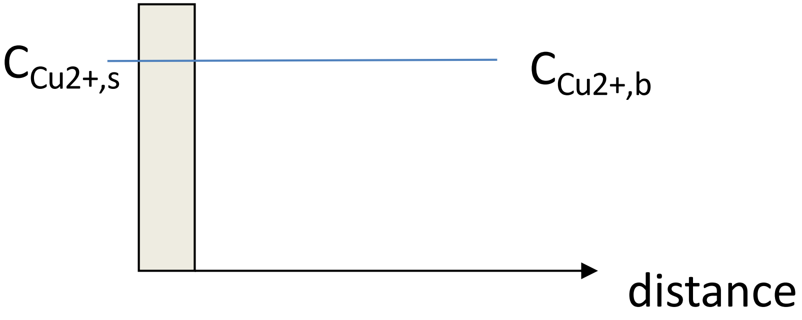
product

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

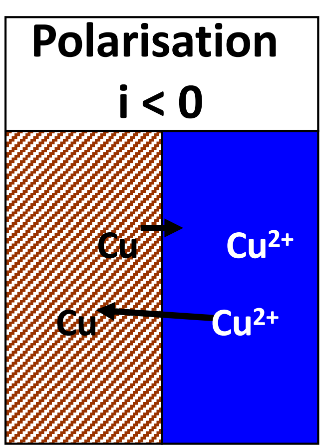
$i_l = +/- n F D_A (c_{sat} - c_{A,b}) / \delta$

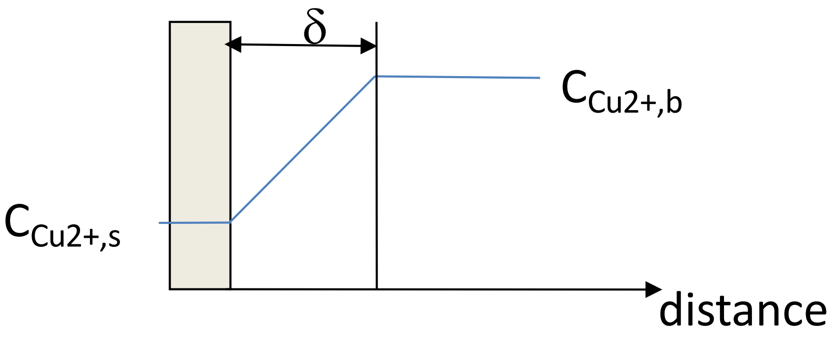
Origin of **concentration overvoltage**





$$E_{I=0} = E^0 + RT/2F \ \ln c_{Cu,b}$$





$$E_{I<0} = E^0 + RT/2F \ \ln c_{Cu,s}$$

Concentration overvoltage

Overvoltage $\eta = E - E_{rev} = RT/2F \ \ln \boxed{(c_{Cu2+,s} / c_{Cu2+,b})}$

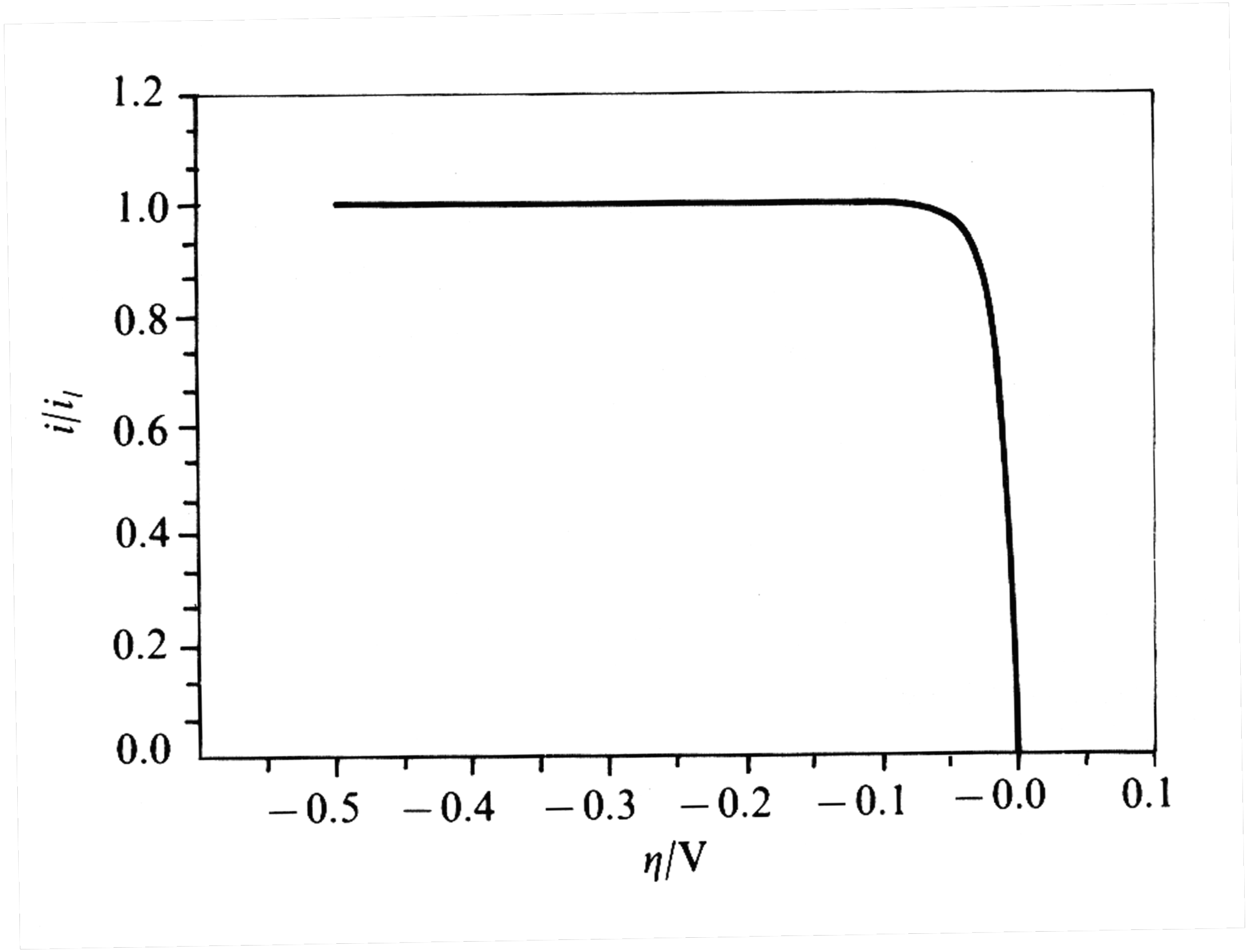
$i = n\,F\,N_{\,Cu2+} = -\,n\,F\,D_{Cu2+}\,(c_{Cu2+,b} - c_{Cu2+,s}) / \delta$

$i_{lim} = n\,F\,N_{max,\ Cu2+} = -\,n\,F\,D_{Cu2+}\,c_{Cu2+,b} / \delta \qquad (c_{Cu2+,s}{=}0)$

$i / i_{lim} = 1 \boxed{-\ (c_{Cu2+,s} / c_{Cu2+,b}}\,)$

$\mathbf{i = i_{lim}\,(\,1 - \ exp\,(\,2F/RT\,\eta\,)\,\,)}$

Theoretical polarization curve for cathodic deposition with only concentration overvoltage



Formalism for **mixed** control: charge transfer ***and*** mass transport

Butler-Volmer (cathodic) – only charge transfer limited

$$i_{c,\ Cu2+} = -\ i_{0,\ Cu2+}\ \boxed{\frac{c_{Cu2+,\ s}}{c_{Cu2+,\ b}}}\ \exp\ (-\ \eta\ /\ \beta_c)$$

see slide 11 for more generalised Butler-Volmer

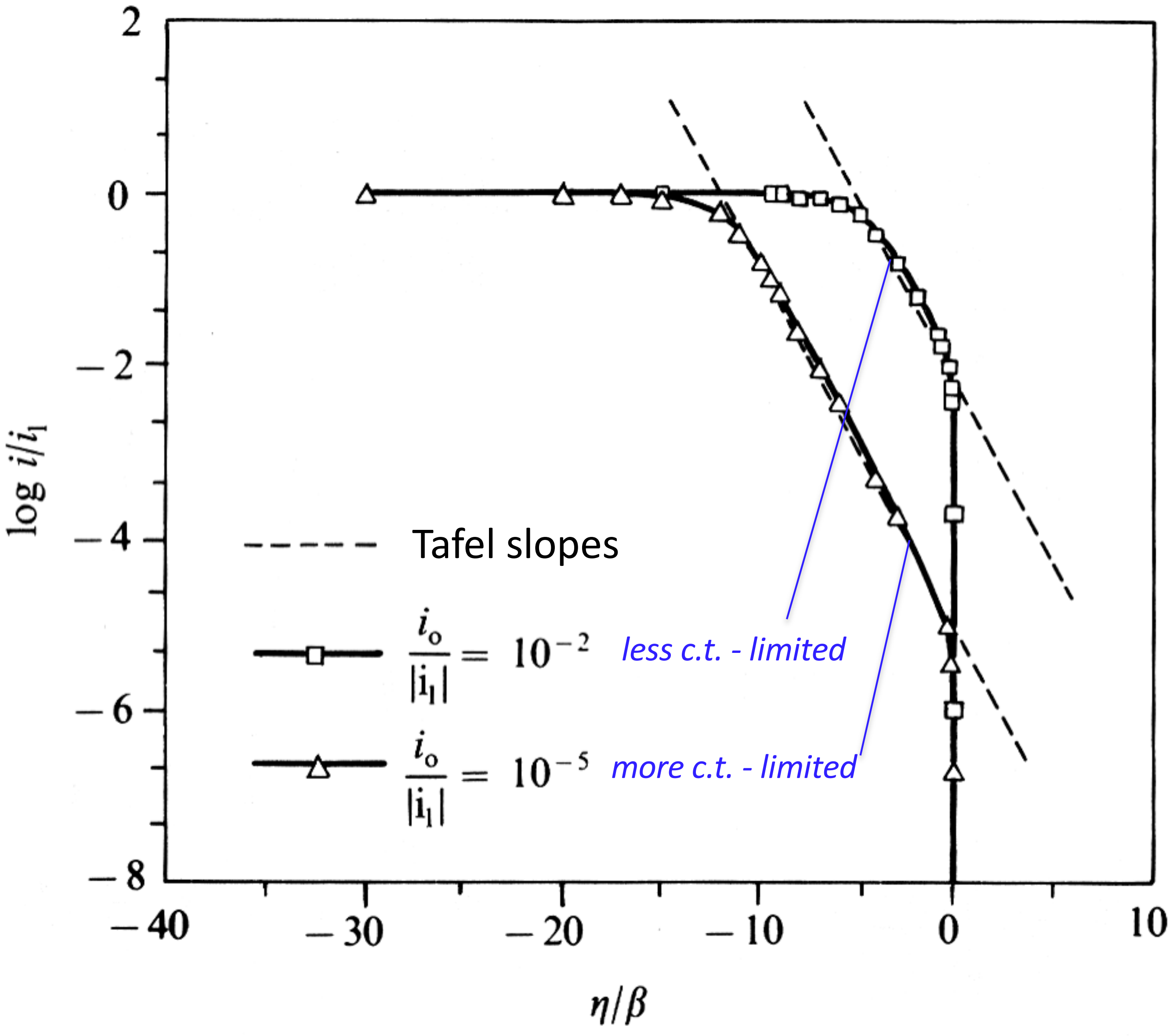
Mass transport – only concentration limited

$$i_c\ /\ i_{lim} = 1 - \boxed{\frac{c_{Cu2+,\ s}}{c_{Cu2+,\ b}}}$$

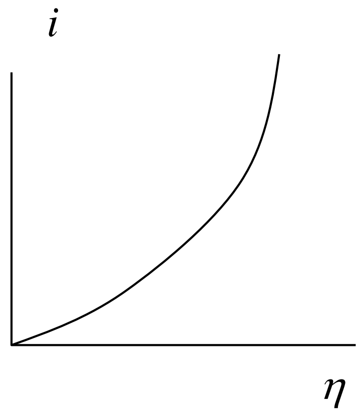
Mixed : both charge transfer and concentration limited

$$i_c\ /\ i_{lim} = -\ \frac{(i_0\ /\ i_{lim})\ \exp\ (-\ \eta\ /\ \beta_c)}{1 - (i_0\ /\ i_{lim})\ \exp\ (-\ \eta\ /\ \beta_c)}$$

Theoretical polarization curves for a cathodic reaction under mixed control



Charge transfer overpotential summary



Exponential relation i-η:

dynamic exchange current at the interface

« transfer coefficient » = 0.5

$$i_{net,cathode\ or\ anode} = \overrightarrow{i} + \overleftarrow{i} = i_0\left[\exp\left(\frac{\alpha.nF.\eta}{RT}\right) - \exp\left(\frac{(1-\alpha).nF.\eta}{RT}\right)\right]$$

BUTLER – VOLMER equation, fundamental current-overpotential relationship for a charge transfer-dominated electrochemical interface

- for large η : → "TAFEL plot"
  (1 exponential branch becomes negligible)

$$i = i_0.\exp\left[\frac{\alpha nF\eta}{RT}\right] \quad ou \quad \ln i = \ln i_0 + \frac{\alpha nF\eta}{RT}$$

- for small η : → resistance R_{ct}
  (exp(x)=1+x, for small x)

$$i = i_0.\frac{nF}{RT}.\eta \qquad ou \qquad \frac{d\eta}{di} = \frac{RT}{nFi_0} = R_{ct}$$

→ Their experimental application allows to **measure i_o and α**

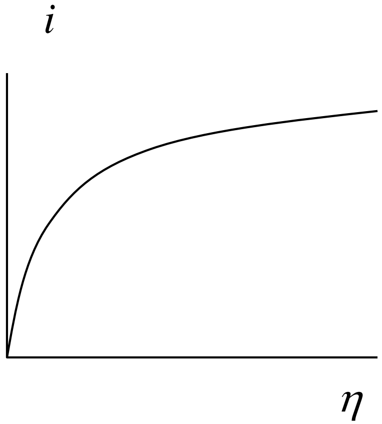
The **exchange current i_o** governs the loss (="quality" of the interface)

- ≈ 1 mA/cm^2 for reactions with H_2
- only ≈ 1 μA/cm^2 for reactions with O_2

} *at 25° C*

- this explains why 'all' loss occurs at the cathode of an ambient T fuel cell (PEFC)

Mass transfer
overpotential summary



Limiting current at high η :

Examples :

a) diffusion :

- H_2 in H_2O (steam)
- O_2 in N_2 (air)

concentration at the interface ($<c^0$)

$$\eta_{diff} = \left|\frac{RT}{nF}\ln\left(\frac{c^S}{c^0}\right)\right| = \frac{RT}{nF}\ln\left(1-\frac{i}{i_{\lim}}\right)$$

concentration in the bulk (gas)

b) slow chemical reaction :

- acid HA -> H^+ + A-

  (supplier of H^+)

concentration of protons in mol/cm³

Diffusion coefficient in cm²/s

$$i_{\lim,reaction} = nFD_{H^+}\frac{c_{H^+}}{\delta_R}$$

Diffusion layer thickness(µm)

c) slow adsorption or desorption :

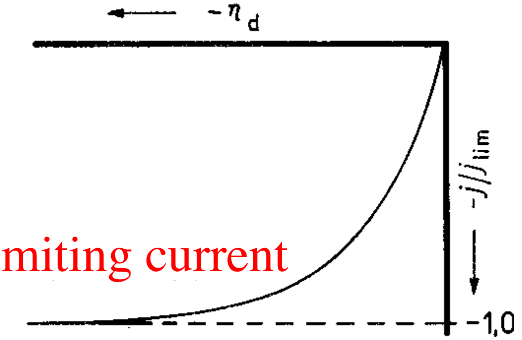
- H_2, CO on anode
- O_2 on cathode
- evacuation of H_2O

$$i_{cath} = -i_{\lim}^{ads} = -nFk_{ads}$$

$$i_{an} = i_{\lim}^{des} = nFk_{des}$$

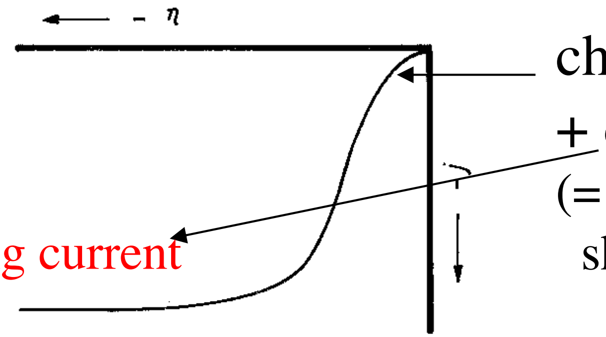
Reaction speed constant (mol/s.cm²)

Examples i-η with limitation



Limiting current

diffusion only

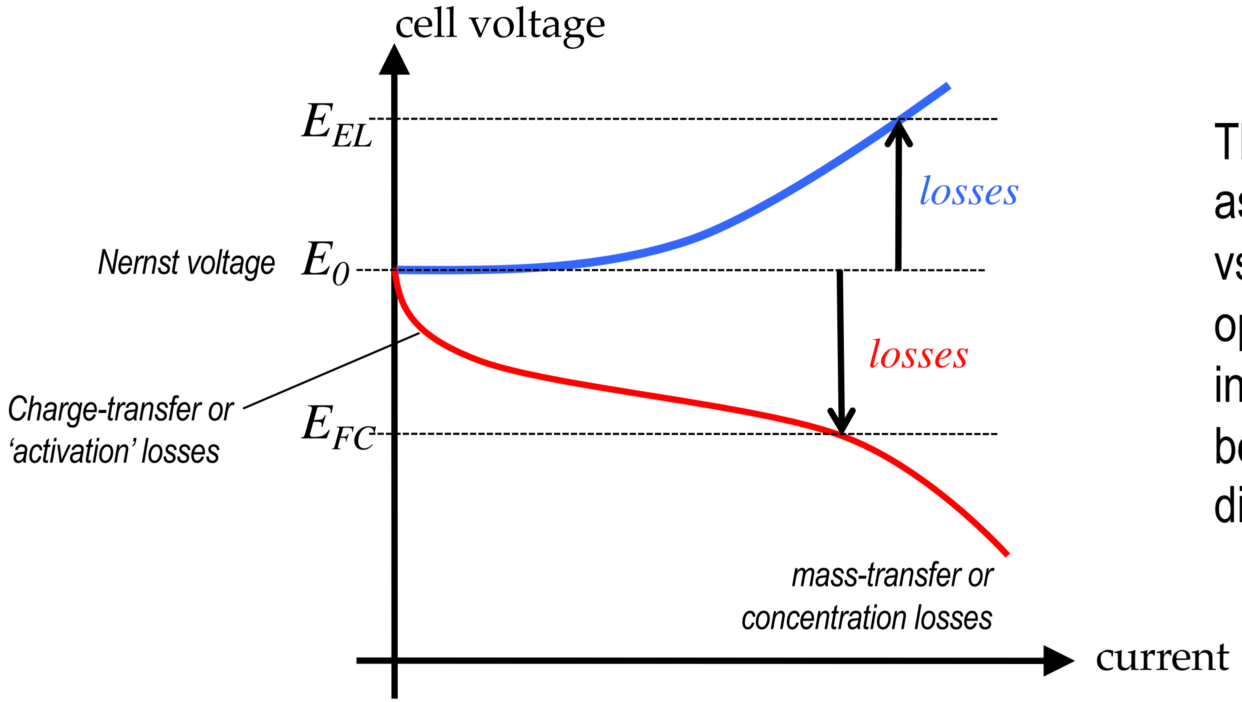


Limiting current

charge transfer
+ diffusion (mix)
(= general case, “S”-
shaped curve)

Characteristic i-V (current-voltage curve)
(“electrolysis mode ” and “galvanic mode”)

fuel cell



The curves are clearly asymmetric for fuel cell vs. electrolyser operation, as the interface reactions in both directions are distinct.