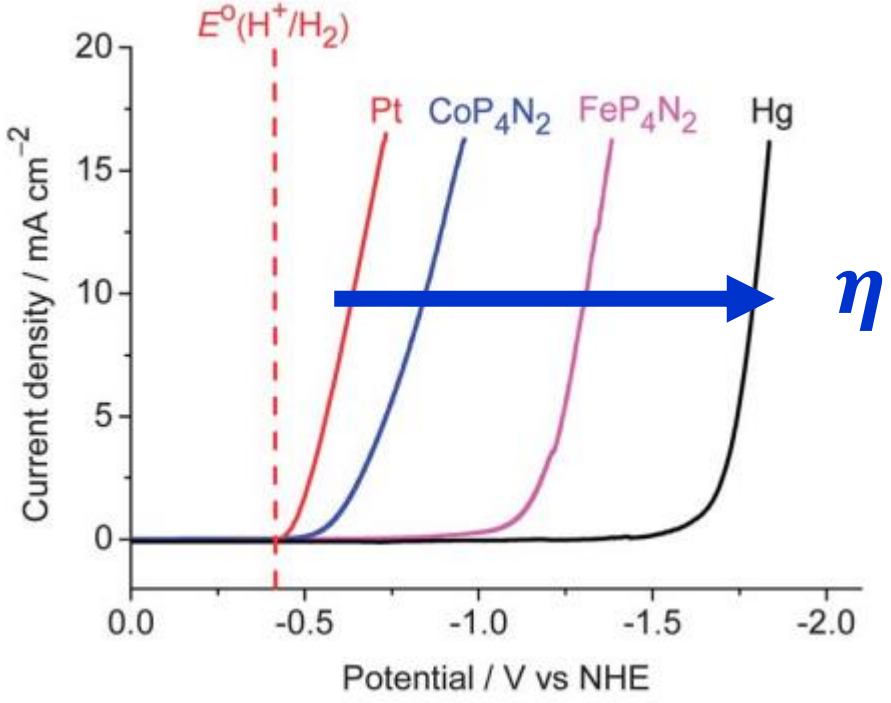
The overpotential (η)

Overpotential (η): deviation from the equilibrium potential (thermodynamic) required to drive a reaction at a certain rate (faradaic current density)

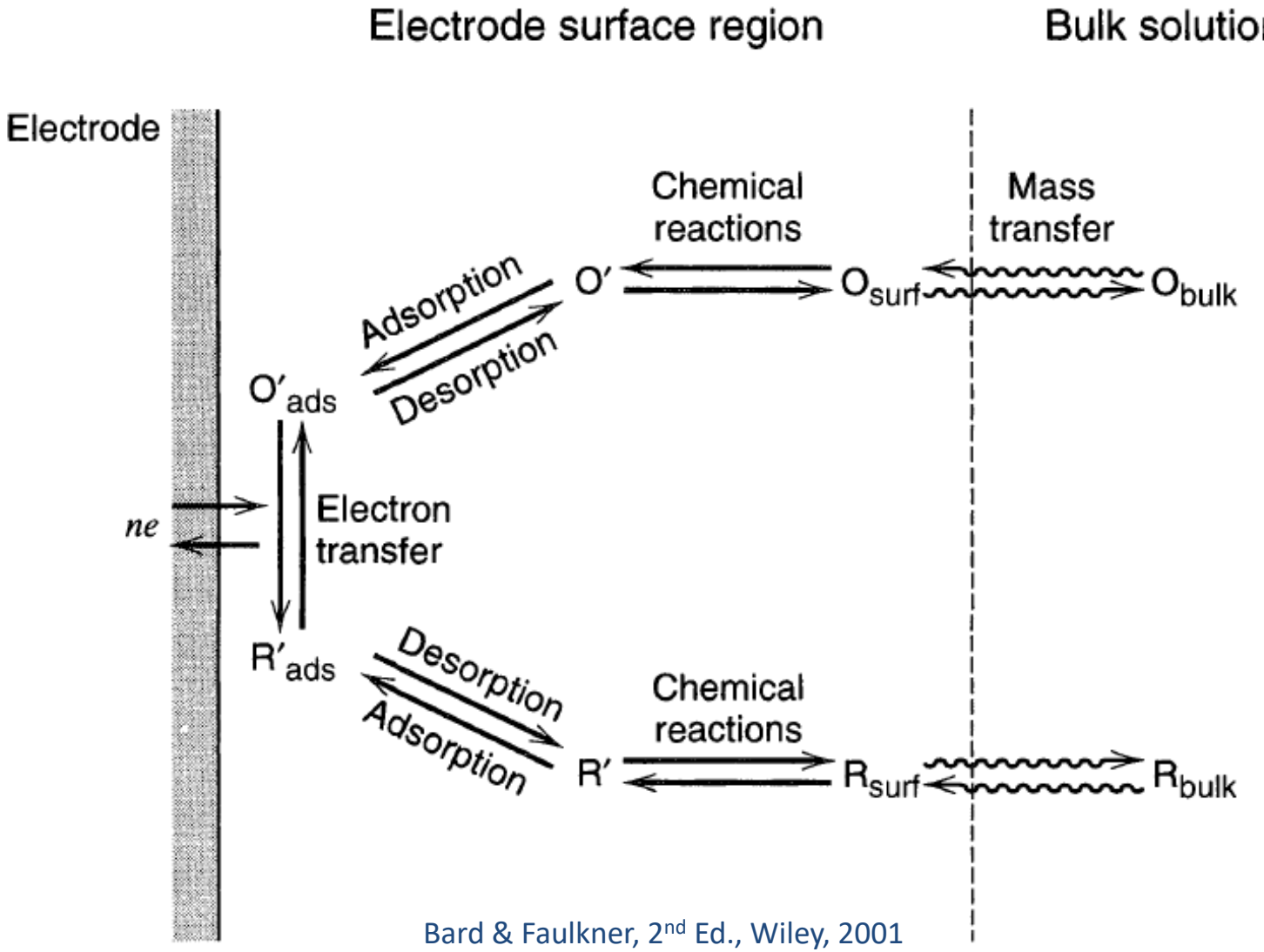


L. Chen et al., *Energy Environ. Sci.*, **2014**, *7*, 329–334

$$\eta = E - E_{eq}$$

- It is an indicator of the **efficiency** of an electrochemical system (the energetic cost required to drive a reaction at a certain rate)
- The rate constant for a heterogeneous electron transfer process is dependent on the applied potential

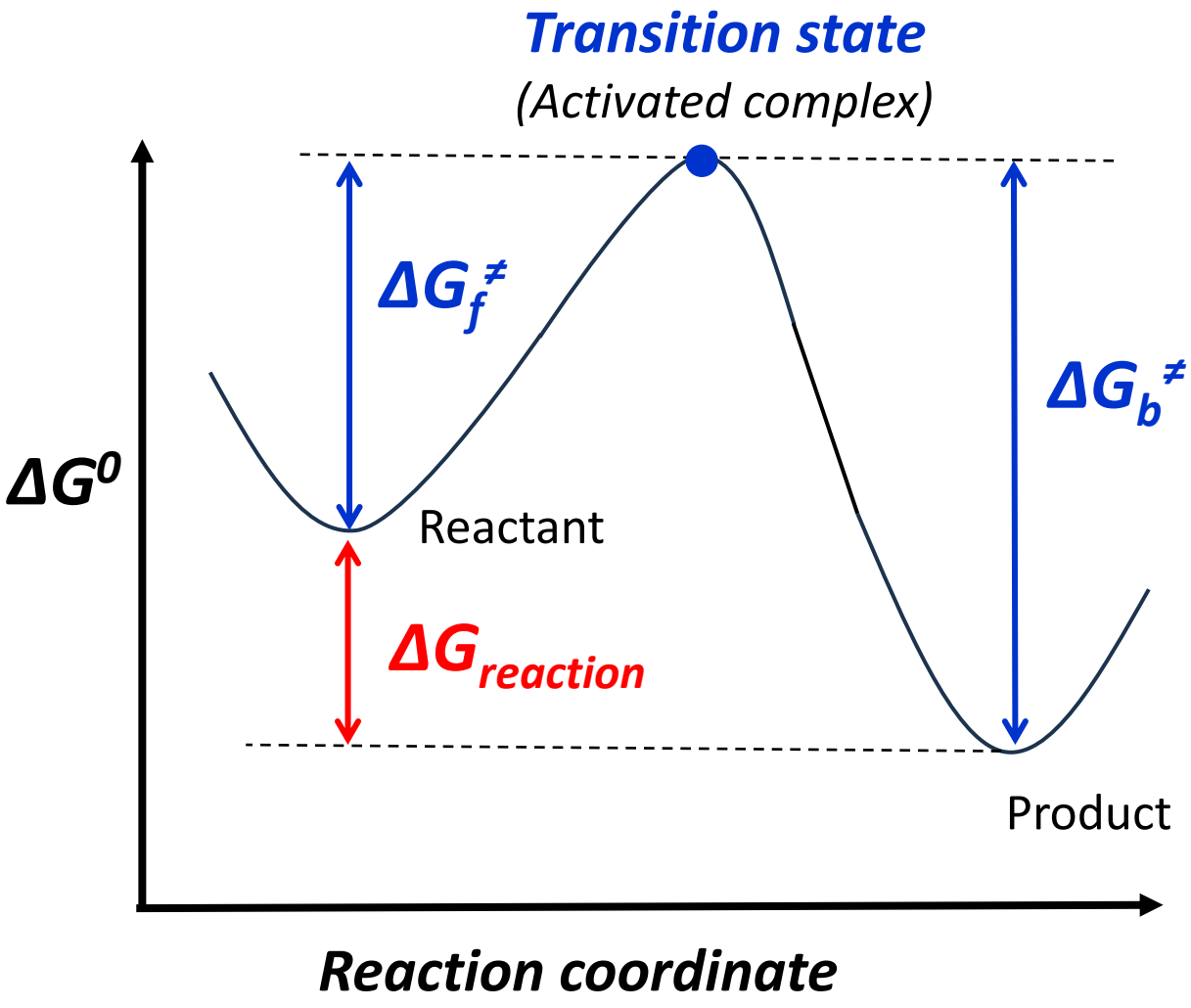
The origin of the overpotential



Bard & Faulkner, 2nd Ed., Wiley, 2001

The **overall η** of an electrode reaction at a given j is the sum of η terms associated to single elementary reaction steps (e. g. mass transport, charge transfer, coupled chemical reactions…)

Transition state theory



Arrhenius equation

$$k = Ae^{-E_a/RT}$$

Pre-exponential factor
(frequency or collision factor *)*

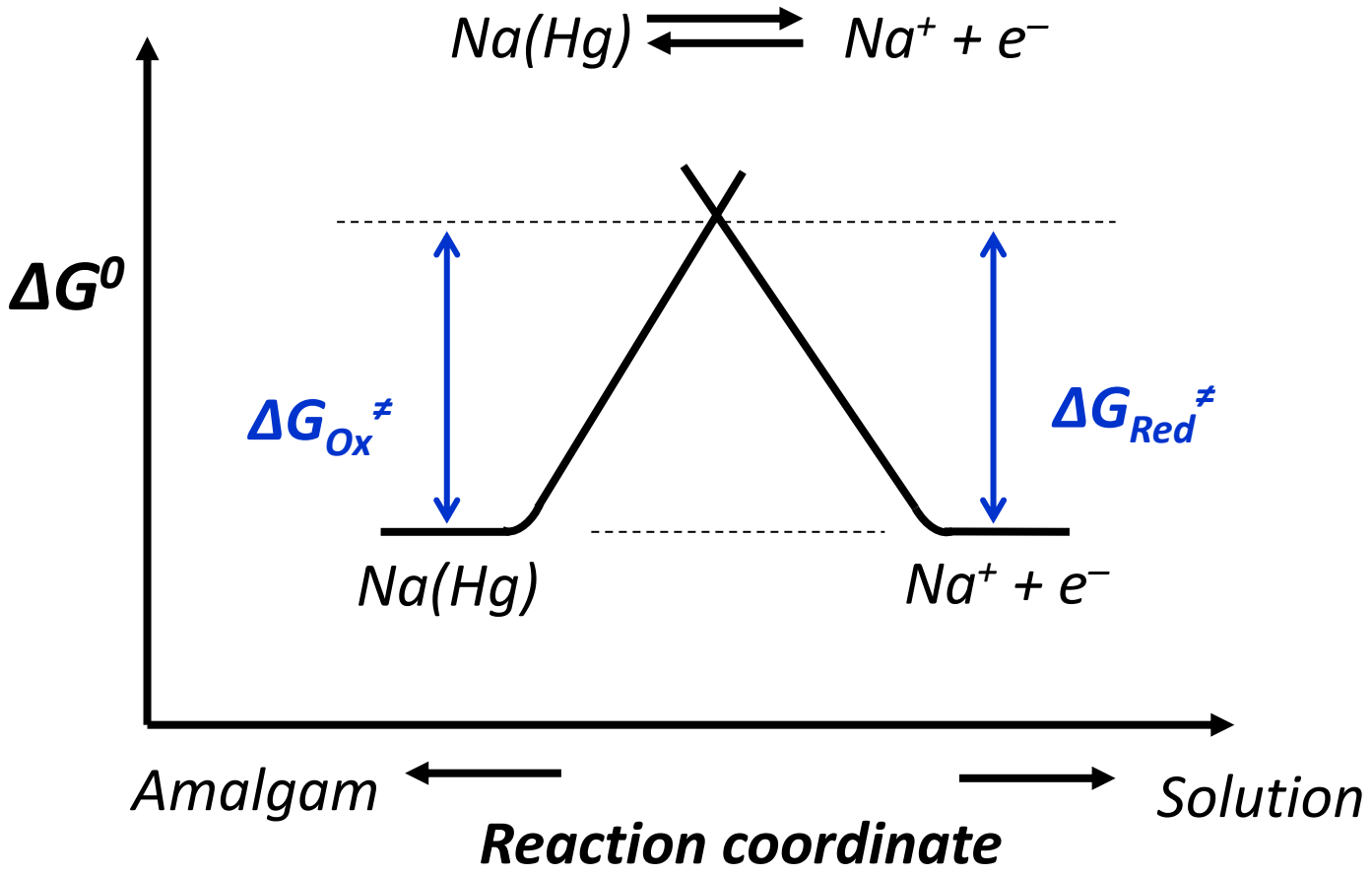
Activation energy
(energy barrier)

Eyring-Polanyi equation

$$k = \kappa \frac{k_B T}{h} e^{-\Delta G^{\neq}/RT}$$

Electrode kinetics: The effect of potential

- Analogous description of the energetic pathway on an electrode reaction through a **reaction coordinate**
- The energetics of electrode processes are dependent on the **applied potential**



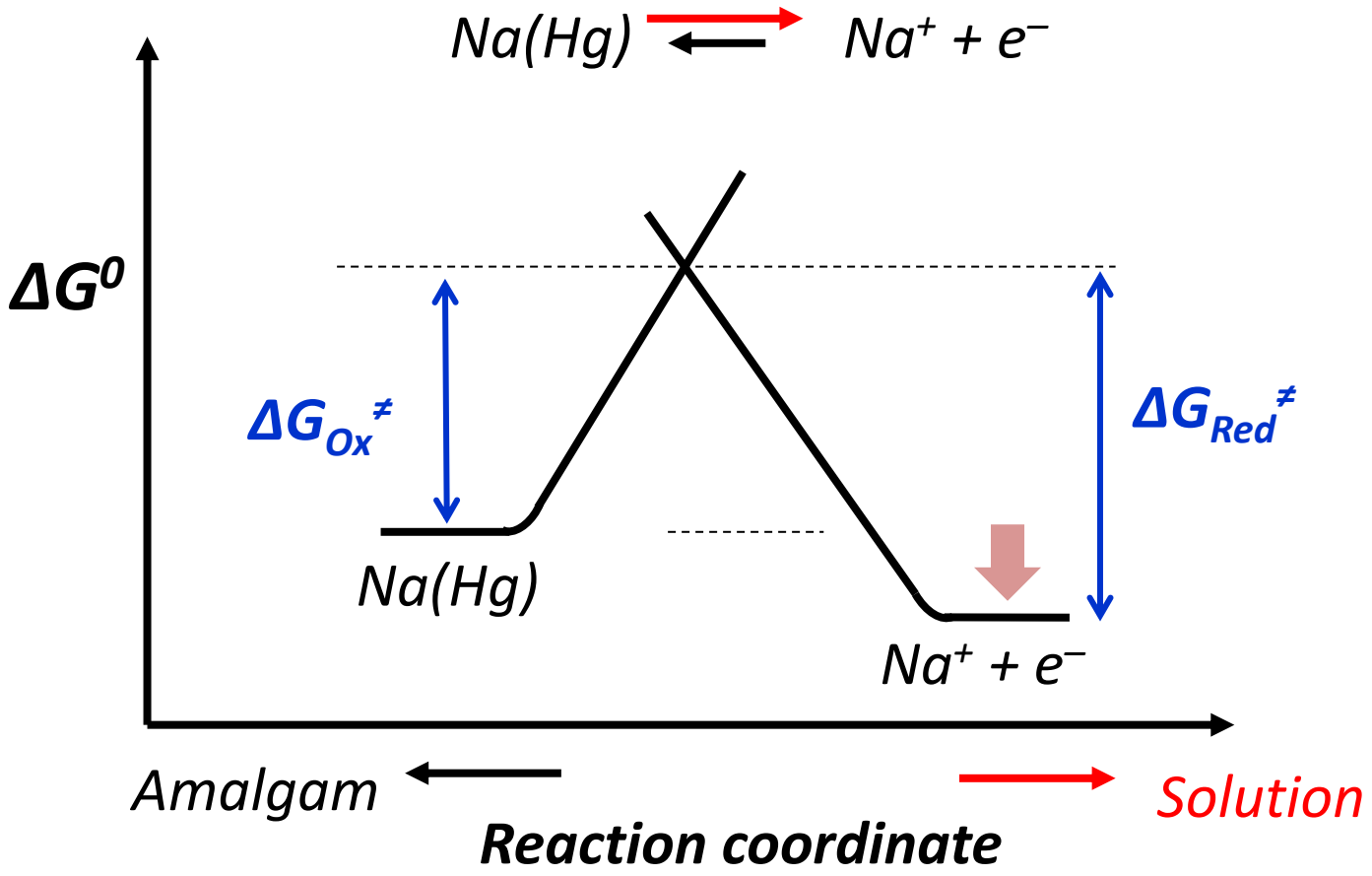
Equilibrium

$$E = E_{eq}$$

$$\Delta G_{Ox}^{\neq} = \Delta G_{Red}^{\neq}$$

Electrode kinetics: The effect of potential

- Analogous description of the energetic pathway on an electrode reaction through a **reaction coordinate**
- The energetics of electrode processes are dependent on the **applied potential**



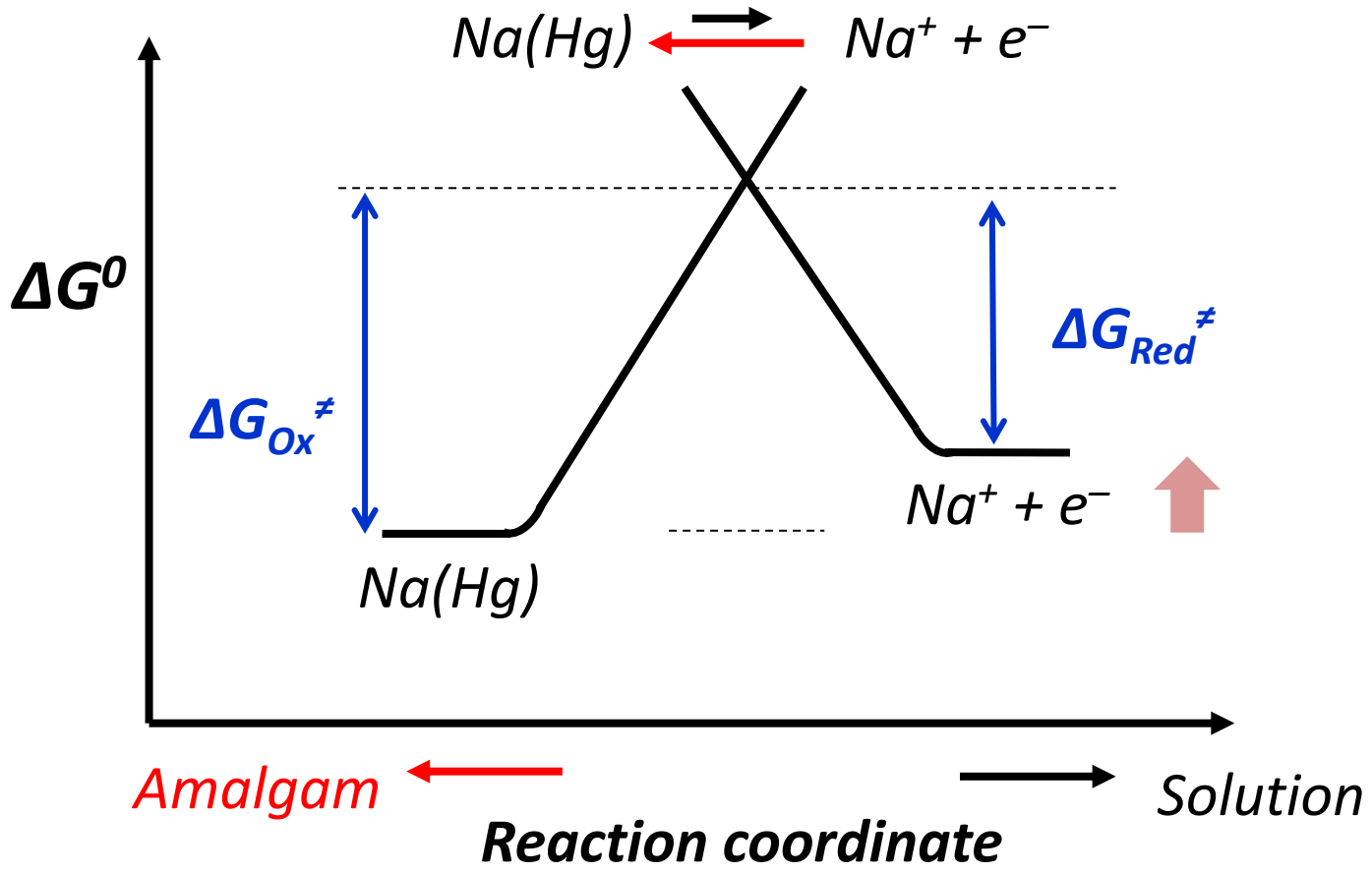
Oxidation

$$E > E_{eq}$$

$$\Delta G_{Ox}^{\neq} < \Delta G_{Red}^{\neq}$$

Electrode kinetics: The effect of potential

- Analogous description of the energetic pathway on an electrode reaction through a **reaction coordinate**
- The energetics of electrode processes are dependent on the **applied potential**



Reduction

$$E < E_{eq}$$

$$\Delta G_{Ox}^{\neq} > \Delta G_{Red}^{\neq}$$

Kinetics of electrode reactions

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

[cm s^{-1}]

[mol s^{-1} cm^{-2}]

Cathodic current

$$v_{Red} = k_{Red} \cdot C_{Ox}(0,t) = \frac{i_c}{nFA}$$

Surface concentration (x = 0)

Anodic current

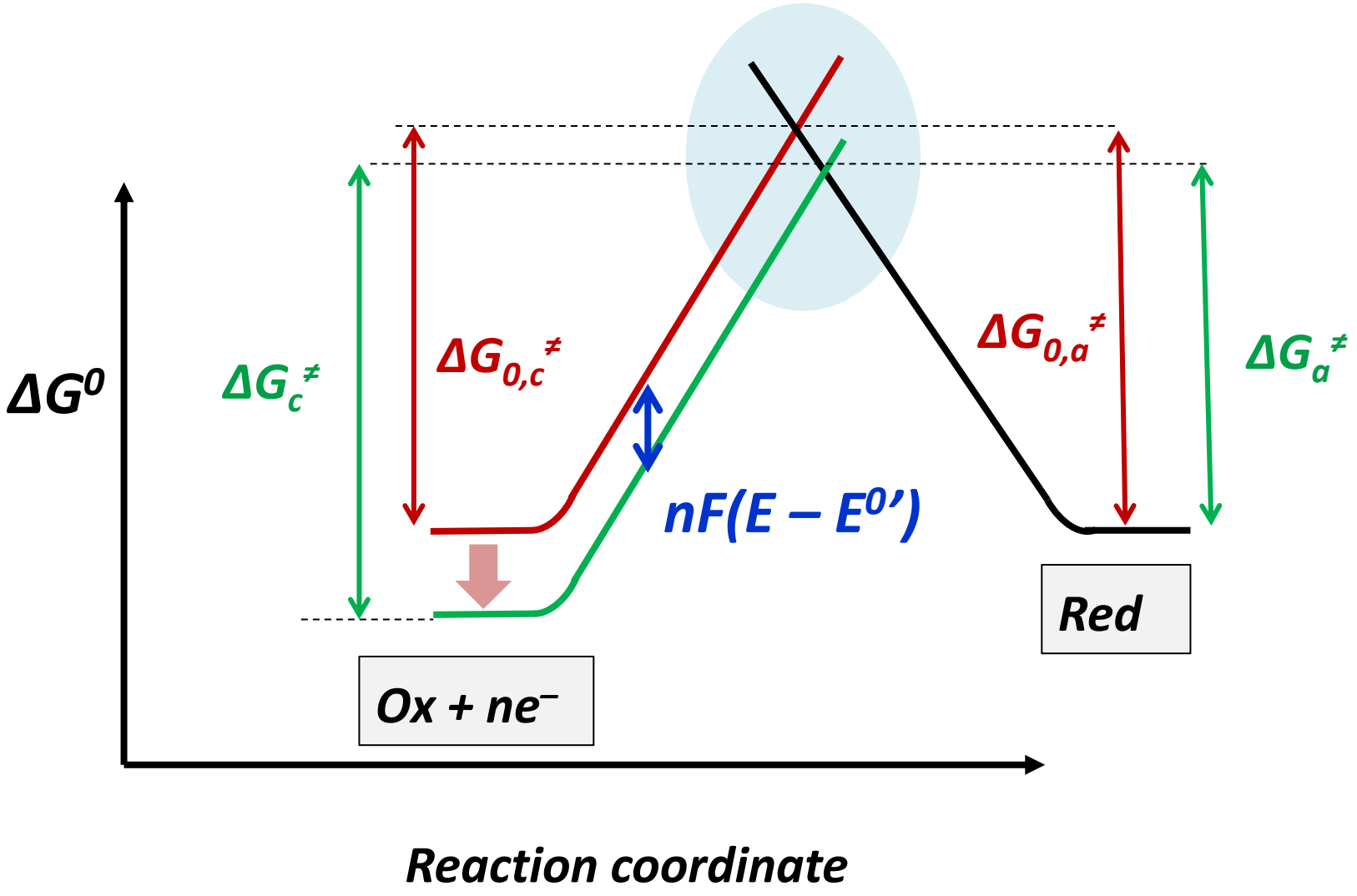
$$v_{Ox} = k_{Ox} \cdot C_{Red}(0,t) = \frac{i_a}{nFA}$$

Surface concentration (x = 0)

$$v_{tot} = v_{Red} - v_{Ox} = k_{Red} \cdot C_{Ox}(0,t) - k_{Ox} \cdot C_{Red}(0,t) = \frac{\overbrace{(i_c - i_a)}^{\boldsymbol{i}}}{nFA}$$

$$\boldsymbol{i} = i_c - i_a = nFA\,[k_{Red} \cdot C_{Ox}(0,t) - k_{Ox} \cdot C_{Red}(0,t)]$$

Kinetics of electrode reactions



At ***Equilibrium:***

$E = E^{0\prime}$

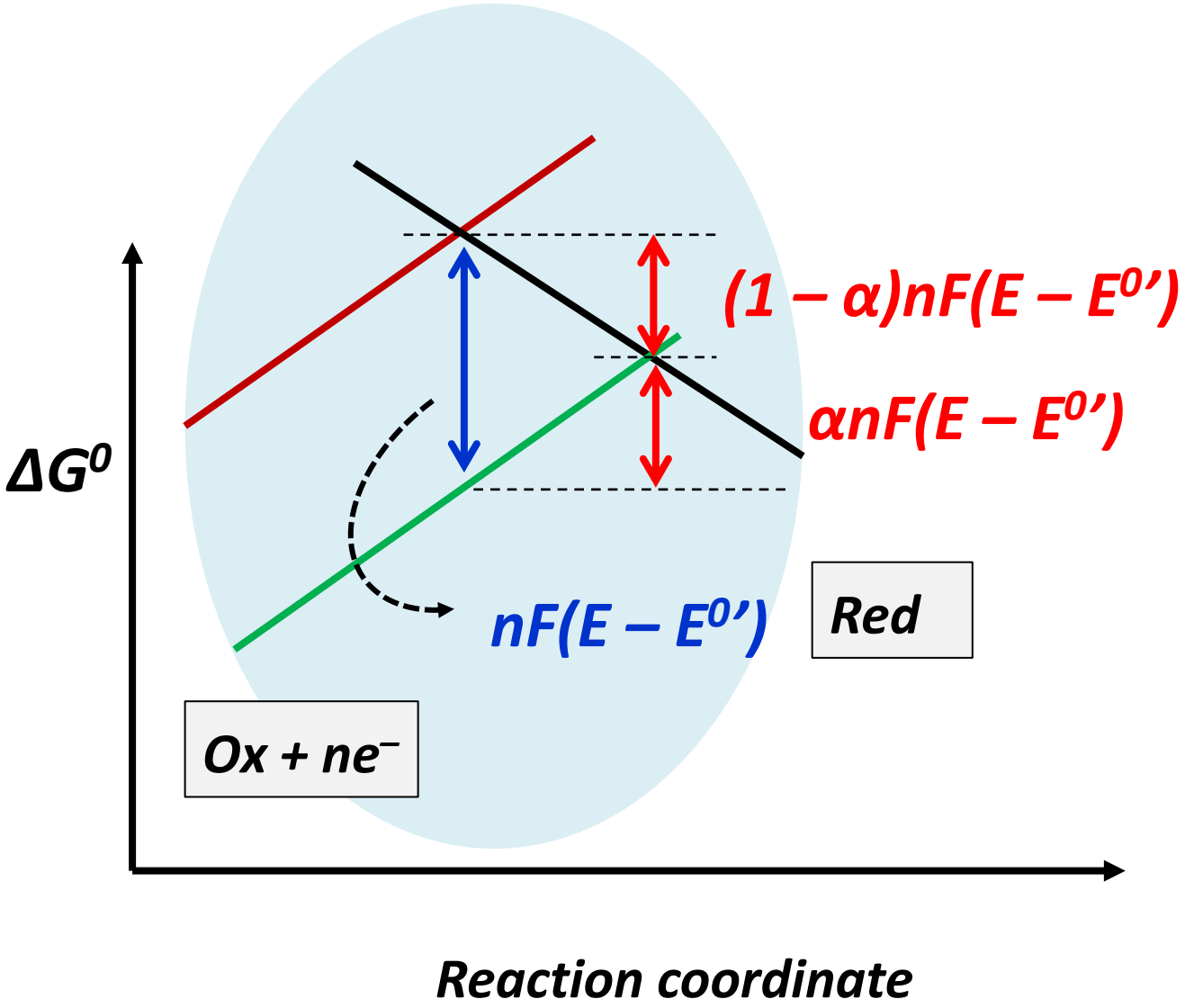
$$\Delta G^{\neq}_{0,c} = \Delta G^{\neq}_{0,a}$$

Upon ***oxidation:***

$E > E^{0\prime}$

$$\Delta G^{\neq}_{c} > \Delta G^{\neq}_{a}$$

Electrode kinetics: The effect of potential



$$\Delta G_a^{\neq} = \Delta G_{0,a}^{\neq} - (1-\alpha)nF(E - E^{0'})$$

$$\Delta G_c^{\neq} = \Delta G_{0,c}^{\neq} + \alpha nF(E - E^{0'})$$

α = transfer coefficient

Electrode kinetics: The effect of potential

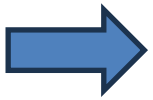
$$\Delta G_c^{\neq} = \Delta G_{0,c}^{\neq} + \alpha nF(E - E^{0'}) \qquad \Delta G_a^{\neq} = \Delta G_{0,a}^{\neq} - (1-\alpha)nF(E - E^{0'})$$

$$k_{Red} = A_{Red}\, exp\left(-\frac{\Delta G_c^{\neq}}{RT}\right) = A_{Red}\, exp\left(-\frac{\Delta G_{0,c}^{\neq}}{RT}\right) \exp\left[-\alpha \frac{nF}{RT}(E - E^{0'})\right]$$

$$k_{Ox} = A_{Ox}\, exp\left(-\frac{\Delta G_a^{\neq}}{RT}\right) = A_{Ox}\, exp\left(-\frac{\Delta G_{0,a}^{\neq}}{RT}\right) \exp\left[(1-\alpha) \frac{nF}{RT}(E - E^{0'})\right]$$

Potential-independent *Potential-dependent*

At equilibrium
with $C_{Ox}^* = C_{Red}^*$
(E = E⁰')



$k_{red} C_{Ox}^* = k_{Ox} C_{Red}^*$ *(C* = bulk concentration)*

$\boldsymbol{k_{red} = k_{Ox} = k^0}$ ***standard rate constant (heterogeneous)***

Electrode kinetics: The Butler-Volmer equation

$$k_{Red} = \boldsymbol{k^0}\exp[-\boldsymbol{\alpha}\frac{nF}{RT}(E - E^{0'})]$$

$$k_{Ox} = \boldsymbol{k^0}\exp[\boldsymbol{(1-\alpha)}\frac{nF}{RT}(E - E^{0'})]$$

Recalling …

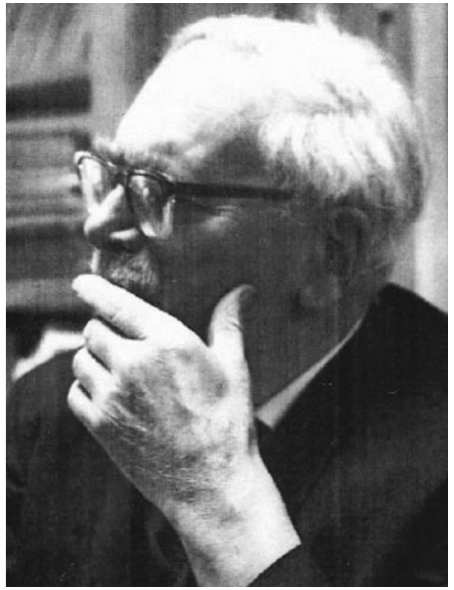
$$\boldsymbol{i} = i_c - i_a = nFA\,[k_{Red}\cdot C_{Ox}(0,t) - k_{Ox}\cdot C_{Red}(0,t)]$$

we obtain …

$$\boldsymbol{i} = nFA\boldsymbol{k^0}[C_{Ox}(0,t)e^{-\boldsymbol{\alpha}\frac{nF}{RT}(E-E^{0'})} - C_{Red}(0,t)e^{\boldsymbol{(1-\alpha)}\frac{nF}{RT}(E-E^{0'})}]$$

Butler-Volmer equation *(current-potential)*

Electrode kinetics: The Butler-Volmer equation



J. A. V. Butler (1899 – 1977)

M. Volmer (1885–1965)

Max Volmer's paper published in 1930

Zur Theorie der Wasserstoffüberspannung.

Von

T. Erdey-Grúz und M. Volmer.

(Mit 3 Figuren im Text.)

(Eingegangen am 31. 7. 30.)

Betrachtungen über die Ursache der Überspannung. — Kinetische Theorie der elektrolytischen Wasserstoffentwicklung und Erklärung der TAFELschen Gleichung. — Das Abklingen der Überspannung.

Um Wasserstoff an einer Metallelektrode zu entwickeln, benötigt man bekanntlich ein unter Umständen viel negativeres Elektroden-

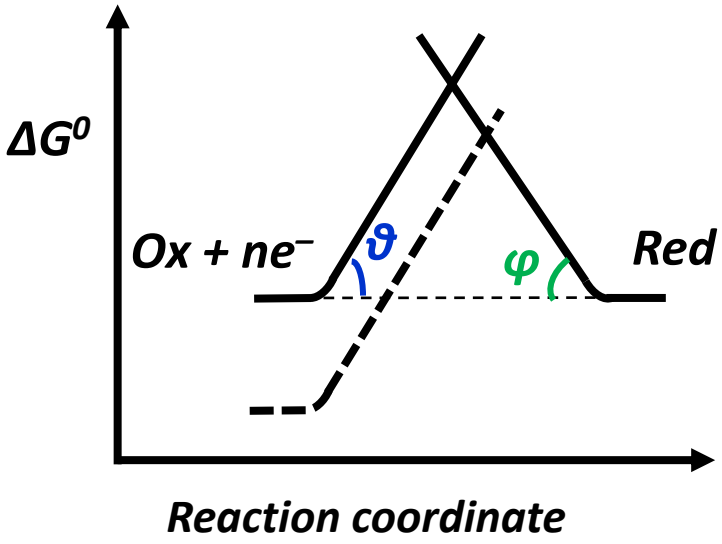
The Standard Rate Constant (k^0)

- Measures the **intrinsic kinetics of heterogeneous electron transfer** of a redox couple (intrinsic ability of a redox couple to exchange electrons with the electrode)
- **Large k^0** indicate **fast** heterogeneous electron transfer (short timescale, $k^0 \approx$ *1-10 cm/s*), usually observed for redox processes that **do not involve significant molecular reorganization** (only e^- transfer + resolvation, e.g. aromatic hydrocarbons)
- **Small k^0** indicate **sluggish** heterogeneous electron transfer ($k^0 < 10^{-9}$-10^{-11} *cm/s*), typically being accompanied by significant molecular rearrangement and/or involving complicated mechanisms (multistep, e.g. ORR, HER)
- Extreme variability in the k^0 range
- **Even for systems with small k^0, the electrode reaction kinetics (k_{Ox}, k_{Red}) can be increased by applying $E >> E^{0'}$ or $E << E^{0'}$!!!**

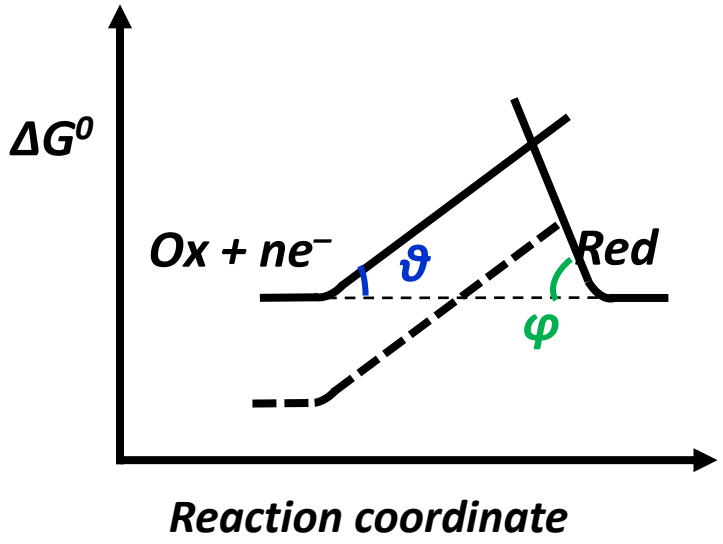
what's the extent of the potential effect on electrode reaction kinetics??

The transfer coefficient (α)

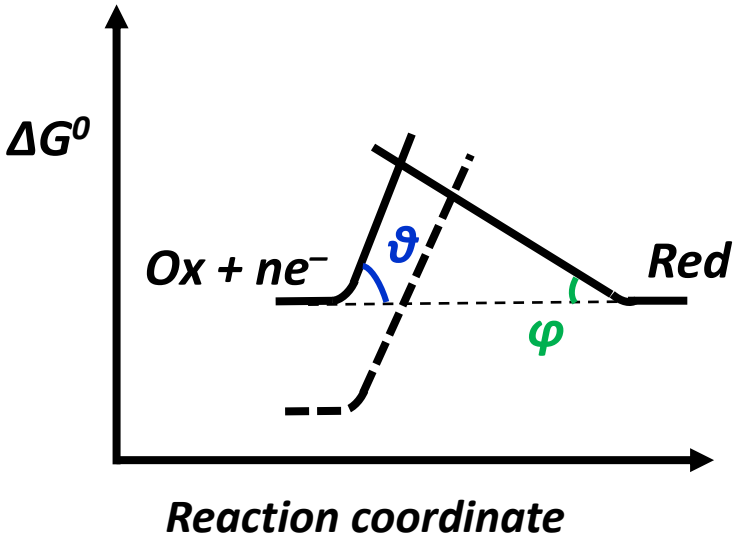
- Measures the **symmetry of the energetic barrier** for a redox process (**$0 \leq \alpha \leq 1$**)
- It can be obtained experimentally and is generally considered equal to **0.5**
- **$\alpha = 0.5$** for a **symmetrical** barrier, **$\alpha \neq 0.5$** for **asymmetrical** barriers (angles ϑ and φ)
- Dissects the effect of change in potential on the barriers to the cathodic ($\Delta G_c^{\neq}$) and anodic reaction ($\Delta G_a^{\neq}$)



$\vartheta = \varphi \quad \alpha = 0.5$



$\vartheta < \varphi \quad \alpha < 0.5$



$\vartheta > \varphi \quad \alpha > 0.5$

Verification of the Butler-Volmer model: the equilibrium

Equilibrium: $\boldsymbol{i = 0}$ $\boldsymbol{i_c = i_a}$ $\boldsymbol{E = E_{eq}}$

$$0 = nFA\boldsymbol{k^0}[C_{Ox}(0,t)e^{-\boldsymbol{\alpha}\frac{nF}{RT}(\boldsymbol{E_{eq}}-E^{0'})} - C_{Red}(0,t)e^{\boldsymbol{(1-\alpha)}\frac{nF}{RT}(\boldsymbol{E_{eq}}-E^{0'})}]$$

$$\cancel{nFA\boldsymbol{k^0}}\underbrace{C_{Ox}(0,t)}_{=C_{Ox}^*}e^{-\boldsymbol{\alpha}\frac{nF}{RT}(\boldsymbol{E_{eq}}-E^{0'})} = \cancel{nFA\boldsymbol{k^0}}\underbrace{C_{Red}(0,t)}_{=C_{Red}^*}e^{\boldsymbol{(1-\alpha)}\frac{nF}{RT}(\boldsymbol{E_{eq}}-E^{0'})}$$

$$e^{\frac{nF}{RT}(\boldsymbol{E_{eq}}-E^{0'})} = \frac{C_{Ox}^*}{C_{Red}^*} \quad \Rightarrow \quad \boldsymbol{E_{eq}} = E^{0'} + \frac{RT}{nF}ln\left(\frac{C_{Ox}^*}{C_{Red}^*}\right)$$

Nernst Equation

The exchange current (i_0)

Equilibrium: $\boldsymbol{i = 0}$ $\boldsymbol{i_c = i_a = i_0}$ $\boldsymbol{E = E_{eq}}$

$$i_0 = nFAk^0 C_{Ox}^* e^{-\alpha \frac{nF}{RT}(E_{eq} - E^{0'})}$$

substitution

$$e^{\frac{nF}{RT}(E_{eq} - E^{0'})} = \frac{C_{Ox}^*}{C_{Red}^*}$$

elevate to –α

$$e^{-\alpha \frac{nF}{RT}(E_{eq} - E^{0'})} = \left(\frac{C_{Ox}^*}{C_{Red}^*}\right)^{-\alpha}$$

Exchange current (bidirectional)

$$i_0 = nFAk^0 C_{Ox}^{*\,(1-\alpha)} C_{Red}^{*\,\alpha}$$

$$i_0 \propto k^0$$

It reflects the intrinsic rate of the electron transfer for a redox couple (k^0)

$$j_0 = \frac{i_0}{A}$$ ***Exchange current density***

Exercise: derive the i_0 equation from i_a instead of i_c

The current – overpotential relationship

$$i = nFAk^0[C_{Ox}(0,t)e^{-\alpha\frac{nF}{RT}(E-E^{0\prime})} - C_{Red}(0,t)e^{(1-\alpha)\frac{nF}{RT}(E-E^{0\prime})}]$$

Butler-Volmer

Exchange current

$$i_0 = nFAk^0 C_{Ox}^{*\,(1-\alpha)} C_{Red}^{*\,\alpha}$$

By dividing i/i_0 and recalling the Nernst equation and the definition of ***overpotential (η)*** *…*

$$e^{\frac{nF}{RT}(E_{eq}-E^{0\prime})} = \frac{C_{Ox}^*}{C_{Red}^*}$$

$$\eta = E - E_{eq}$$

we obtain …

The current – overpotential relationship

Current-overpotential equation

$$i = i_0\left[\frac{C_{Ox}(0,t)}{C^*_{Ox}}\, e^{-\alpha\frac{nF}{RT}\eta} - \frac{C_{Red}(0,t)}{C^*_{Red}}\, e^{(1-\alpha)\frac{nF}{RT}\eta}\right]$$

Cathodic *component current (**i_c**)*

Anodic *component current (**i_a**)*

Current is a function of the *potential* and the *amount of reagent available* at the electrode surface with respect to its bulk concentration

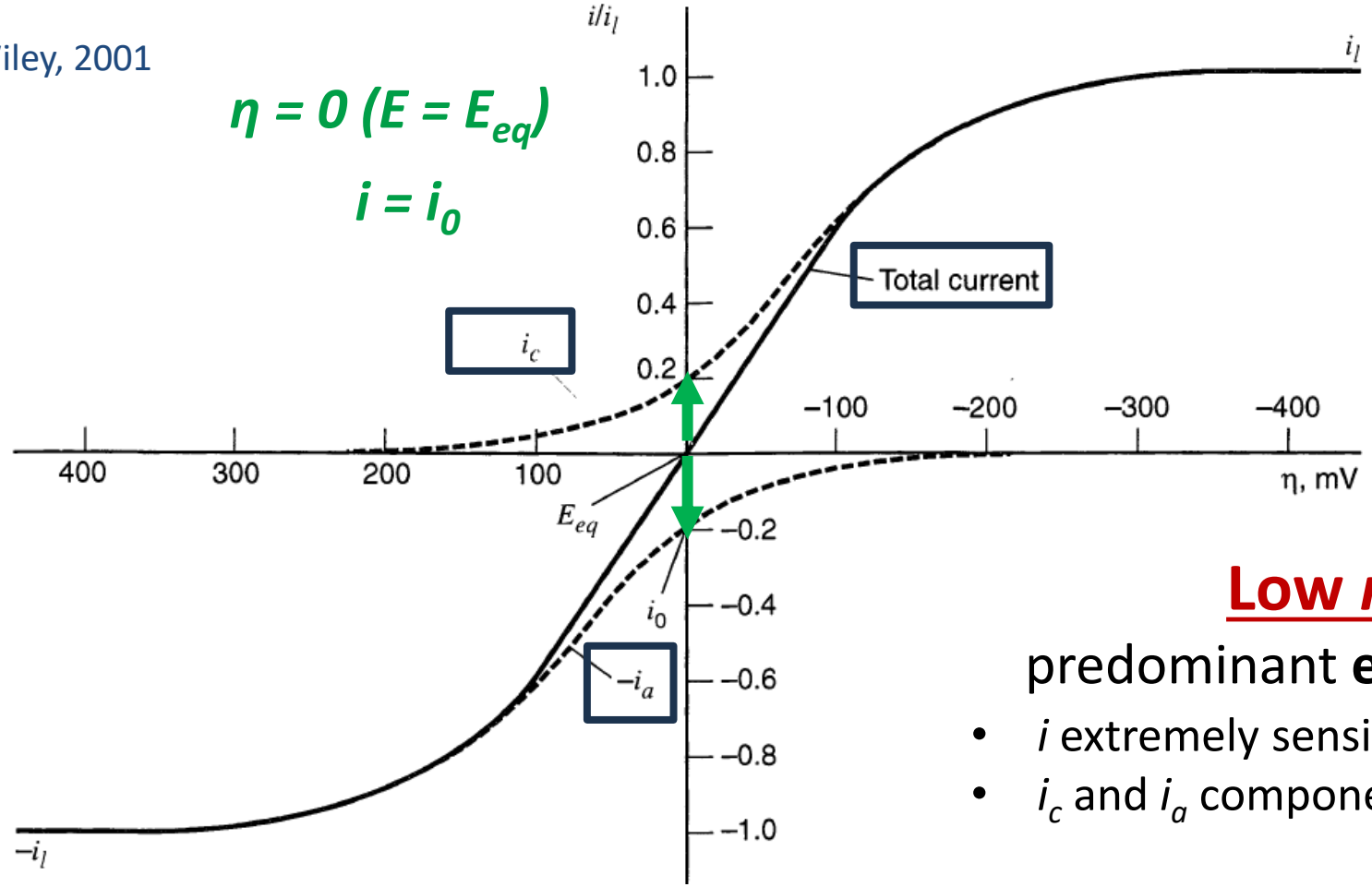
*Exercise: derive the **i (η)** equation*

The current – overpotential relationship

$$i = i_0\left[\frac{C_{Ox}(0,t)}{C^*_{Ox}}e^{-\alpha\frac{nF}{RT}\eta} - \frac{C_{Red}(0,t)}{C^*_{Red}}e^{(1-\alpha)\frac{nF}{RT}\eta}\right]$$

$\alpha = 0.5$

Bard & Faulkner, 2nd Ed., Wiley, 2001



$\eta = 0\ (E = E_{eq})$

$i = i_0$

Low η region

predominant **exponential terms**

- i extremely sensitive to E changes
- i_c and i_a components are not negligible

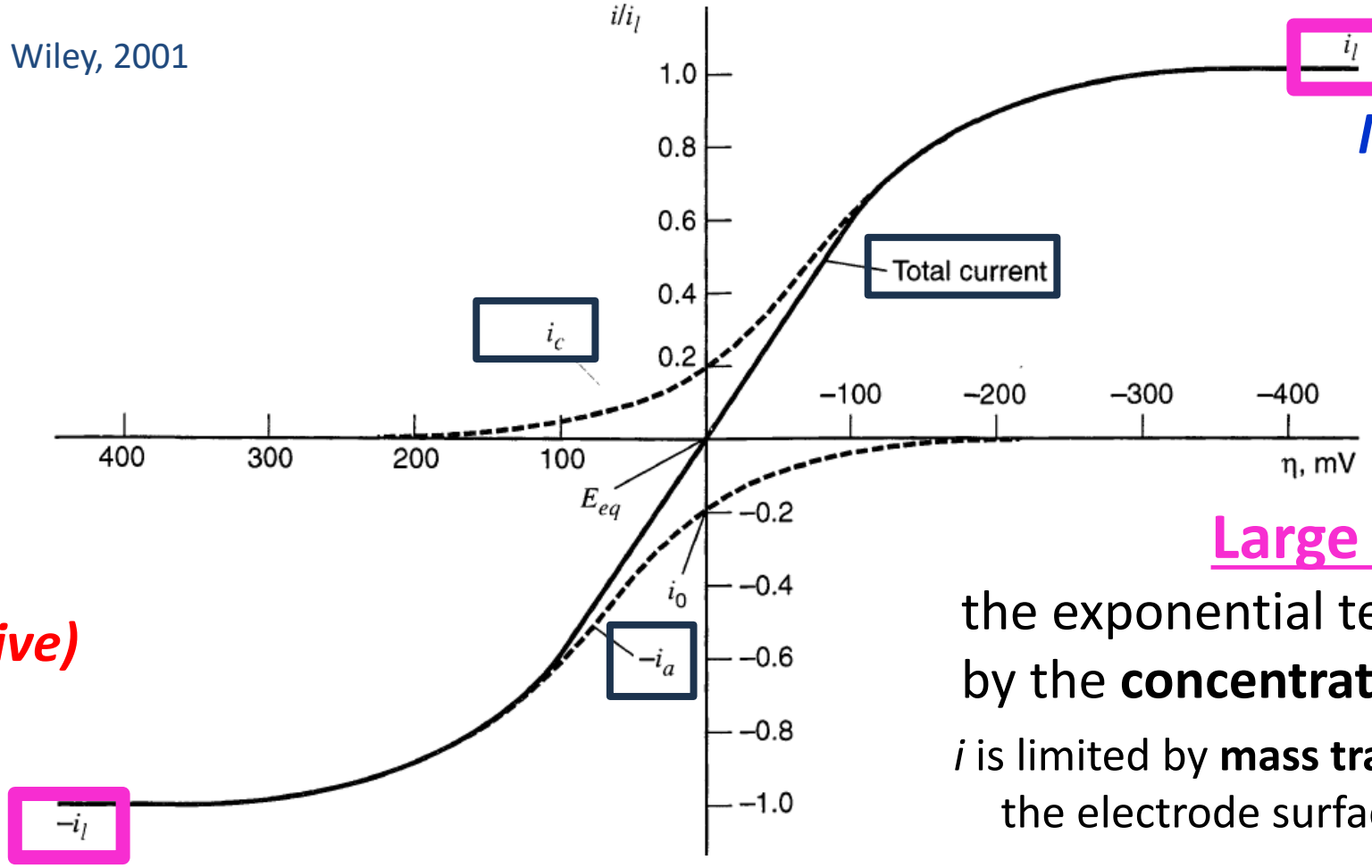
The current – overpotential relationship

$$i = i_0\left[\frac{C_{Ox}(0,t)}{C^*_{Ox}}e^{-\alpha\frac{nF}{RT}\eta} - \frac{C_{Red}(0,t)}{C^*_{Red}}e^{(1-\alpha)\frac{nF}{RT}\eta}\right]$$

Mass transfer-limited current (i_L)

$\alpha = 0.5$

Bard & Faulkner, 2nd Ed., Wiley, 2001



large η (negative)

$i \approx i_c$

$i_a \approx 0$

large η (positive)

$i \approx i_a$

$i_c \approx 0$

Large η region

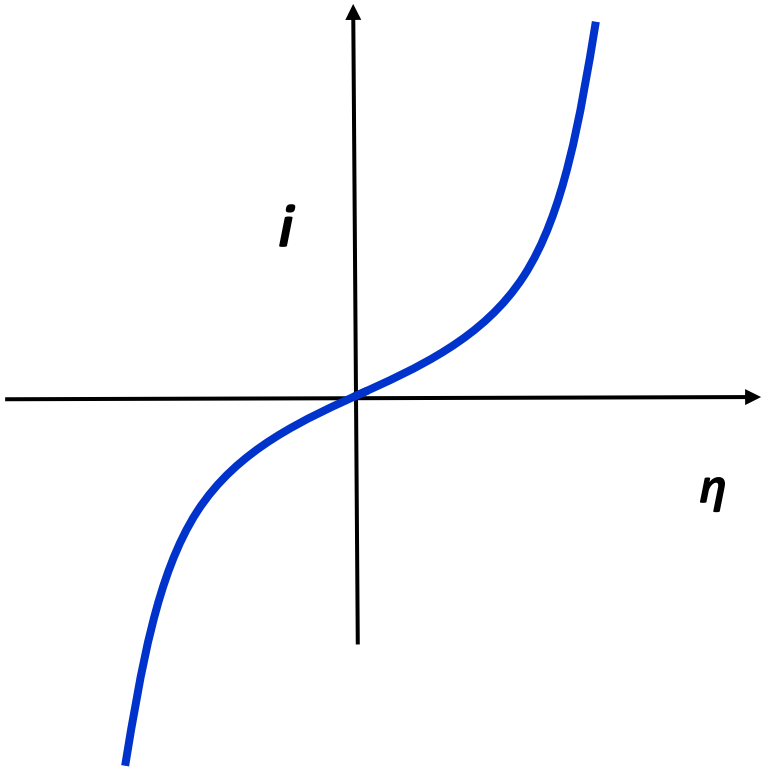
the exponential terms are moderated by the **concentration factors**

i is limited by **mass transport** of the reagent at the electrode surface (***limiting i_L plateau***)

Approximate *i-η* equation: negligible mass transfer effects

No mass transfer
(stirred solution and/or very low current)

$$C_{Ox/Red} \approx C^*_{Ox/Red}$$



$$i = i_0\left[e^{-\alpha\frac{nF}{RT}\eta} - e^{(1-\alpha)\frac{nF}{RT}\eta}\right]$$

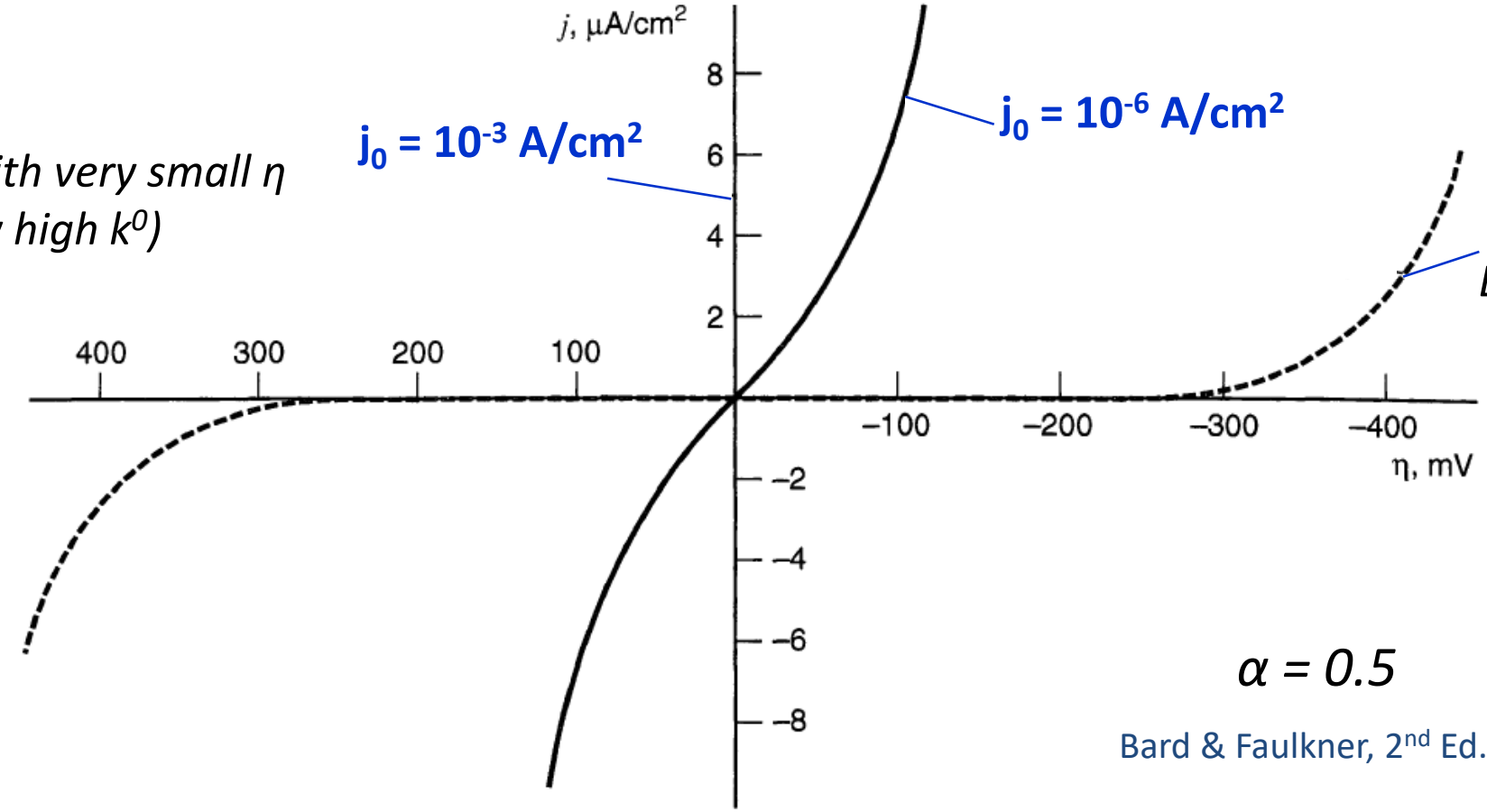
Simplified Butler-Volmer equation

- Exponential curves
- No limiting current
- **Charge-transfer control** (kinetics of the heterogeneous electron transfer is the only contribution to the overpotential at a given current)

The effect of the exchange current

$$i = i_0\left[e^{-\alpha\frac{nF}{RT}\eta} - e^{(1-\alpha)\frac{nF}{RT}\eta}\right]$$

Large currents with very small η (very high k^0)



Large activation η (very low k^0)

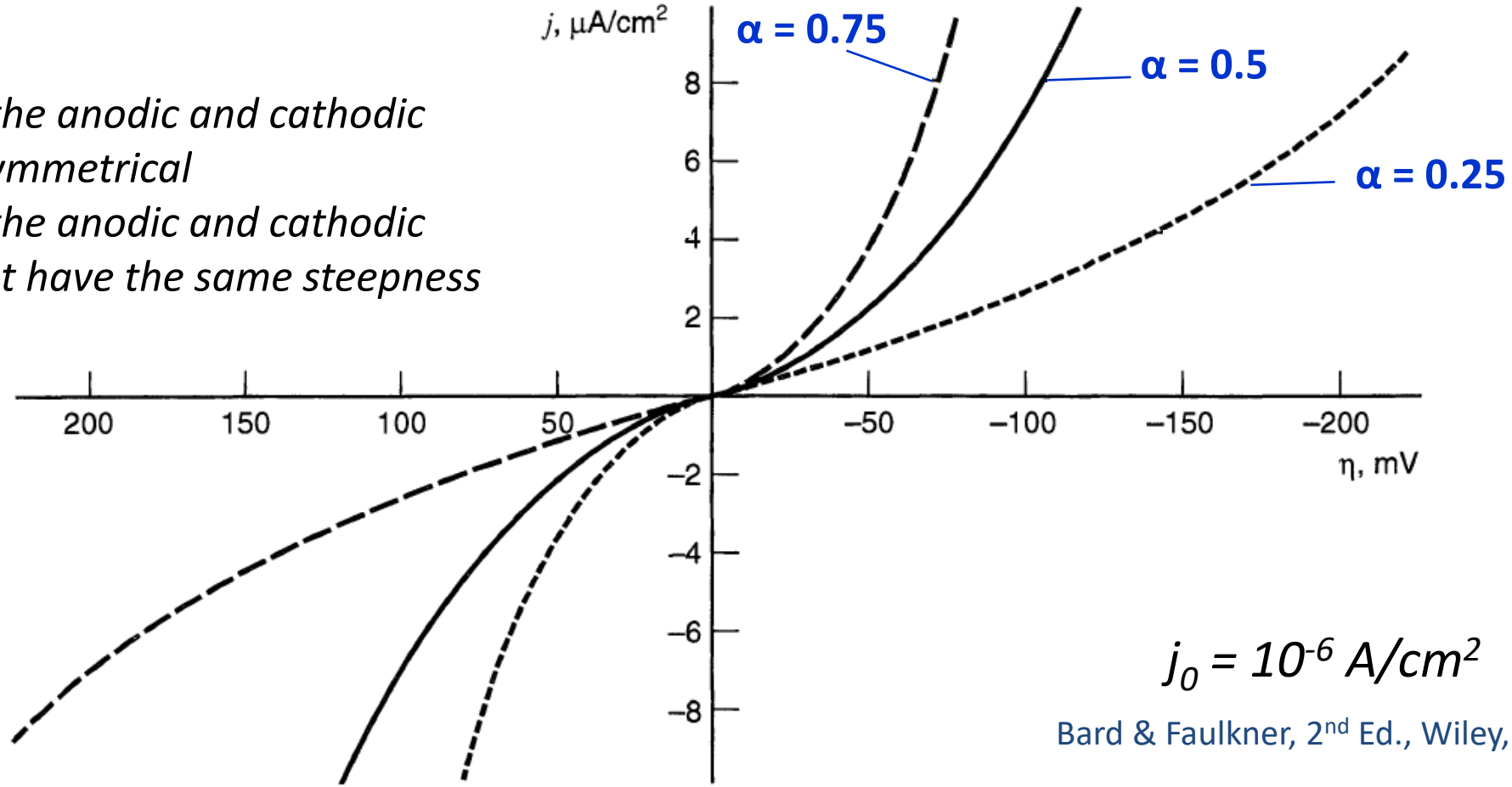
$\alpha = 0.5$

Bard & Faulkner, 2nd Ed., Wiley, 2001

The effect of the symmetry factor

$$i = i_0\left[e^{-\alpha\frac{nF}{RT}\eta} - e^{(1-\alpha)\frac{nF}{RT}\eta}\right]$$

- *For α = 0.5, the anodic and cathodic curves are symmetrical*
- *For α ≠ 0.5, the anodic and cathodic curves do not have the same steepness*



$j_0 = 10^{-6}$ A/cm²

Bard & Faulkner, 2nd Ed., Wiley, 2001

Limiting case: The low overpotential region

$$\boldsymbol{i} = \boldsymbol{i_0}\left[e^{-\boldsymbol{\alpha}\frac{nF}{RT}\boldsymbol{\eta}} - e^{(\mathbf{1}-\boldsymbol{\alpha})\frac{nF}{RT}\boldsymbol{\eta}}\right]$$

For low *η* values ⇒ $e^x \approx 1 + x$

$$\boldsymbol{i} = -\boldsymbol{i_0}\left(\frac{nF}{RT}\boldsymbol{\eta}\right)$$

- **Linear relationship between *i* and *η*** in a small potential range near E_{eq} (< 100 mV)
- According to the Ohm's law, the **–*η*/*i* ratio** has units of resistance (i.e. the negative slope of the *i*-*η* curve) and is called as **charge-transfer resistance**:

$$R_{ct} = -\frac{\boldsymbol{\eta}}{\boldsymbol{i}} = \left(\frac{RT}{nF\boldsymbol{i_0}}\right)$$

$R_{ct} \rightarrow 0$ for i_0 (k^0) $\rightarrow \infty$

Limiting case: The high overpotential regions

For $\eta << 0$:

(cathodic)

$$i = i_0\left[e^{-\alpha\frac{nF}{RT}\eta} - e^{(1-\alpha)\frac{nF}{RT}\eta}\right] \approx i_0\left[e^{-\alpha\frac{nF}{RT}\eta}\right]$$

$$ln\, i = ln\, i_0 - \alpha\frac{nF}{RT}\eta \quad \Rightarrow \quad \boldsymbol{\eta = \frac{RT}{\alpha nF} ln\, i_0 - \frac{RT}{\alpha nF} ln\, i}$$

J. Tafel (1862-1918)

$$\boldsymbol{\eta = \frac{2.3RT}{\alpha nF} log\, i_0 - \frac{2.3RT}{\alpha nF} log\, i}$$

$$\boldsymbol{\eta = a + b\, log\, i}$$

Tafel equation

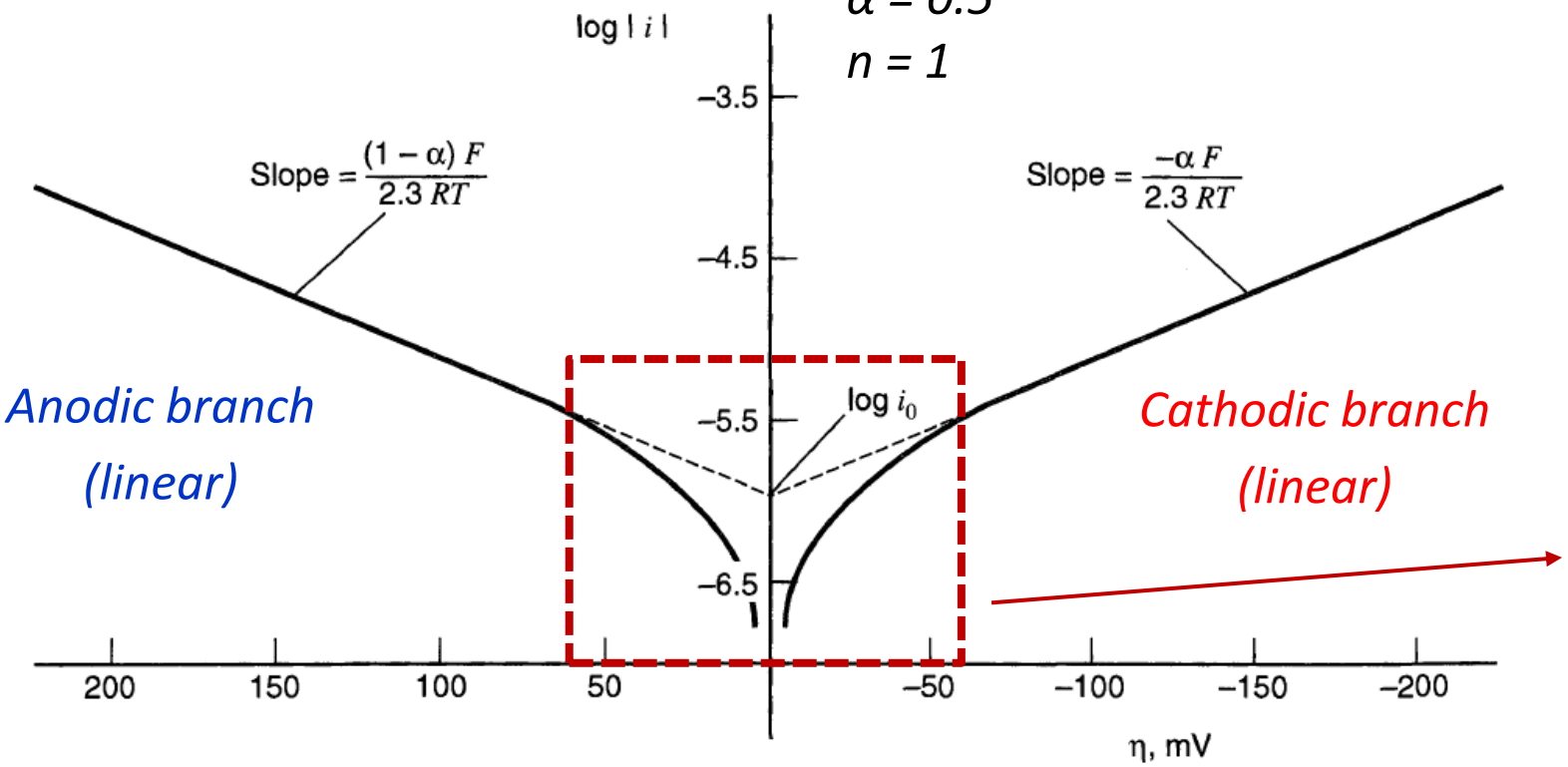
(empirical)

$$\boldsymbol{a = \frac{2.3RT}{\alpha nF} log\, i_0} \qquad \boldsymbol{b = -\frac{2.3RT}{\alpha nF}}$$

The Tafel plots

Log |i| vs. η plots

$j_0 = 10^{-6}$ A/cm^2
$\alpha = 0.5$
$n = 1$



Anodic branch (linear)

Cathodic branch (linear)

- **α** (from the **slope**) and **i_0** (from the **intercept**) can be experimentally obtained
- Symmetrical branches for α = 0.5
- Linear region of the Tafel plots takes place at large η

*Deviation from linearity (in low η region, **contribution from backward reaction is not negligible**)*

Bard & Faulkner, 2nd Ed., Wiley, 2001

The Tafel plots: some considerations

- Linear Tafel relations require a negligible *i* contribution (less than 1%) of the backward reaction (i.e. anodic) (**large η**):

$$\frac{e^{(1-\alpha)\frac{nF}{RT}\eta}}{e^{-\alpha\frac{nF}{RT}\eta}} = e^{\frac{nF}{RT}\eta} \leq 0.01 \qquad |\eta| > 118\ mV \quad (n=1,\ T=298\ K)$$

- Linear Tafel plots require the **absence of mass-transfer effects** on current
- **Negative deviations from linearity are experimentally observed for very large η, due to mass transfer limitations**
- Good Tafel plots are usually obtained for **totally irreversible electrode kinetics** (sluggish ET kinetics, large activation η)

Fast electron transfer kinetics (reversible systems)

$$\frac{i}{i_0} = \left[\frac{C_{Ox}(0,t)}{C^*_{Ox}} e^{-\alpha\frac{nF}{RT}\eta} - \frac{C_{Red}(0,t)}{C^*_{Red}} e^{(1-\alpha)\frac{nF}{RT}\eta}\right]$$

very large i_0 (k^0) ⇒ $\frac{i}{i_0} \to 0$

$$\frac{C_{Ox}(0,t)}{C_{Red}(0,t)} = \frac{C^*_{Ox}}{C^*_{Red}} e^{\alpha\frac{nF}{RT}\eta} e^{(1-\alpha)\frac{nF}{RT}\eta}$$

$$\frac{C_{Ox}(0,t)}{C_{Red}(0,t)} = e^{\alpha\frac{nF}{RT}(\boldsymbol{E}-\boldsymbol{E^{0\prime}})}$$

substitution

$$e^{\frac{nF}{RT}(E_{eq}-E^{0\prime})} = \frac{C^*_{Ox}}{C^*_{Red}}$$

Nernst equation

Electrode potential — *Surface Ox/Red concentration*

$$\boldsymbol{E} = E^{0\prime} + \frac{RT}{nF} ln\left(\frac{C_{Ox}(0,t)}{C_{Red}(0,t)}\right)$$

Nernst-type Equation

- Does not depend on kinetic parameters (ET kinetics too fast)
- **Reversible or nernstian electrochemical systems** (charge-transfer interface always at equilibrium)