

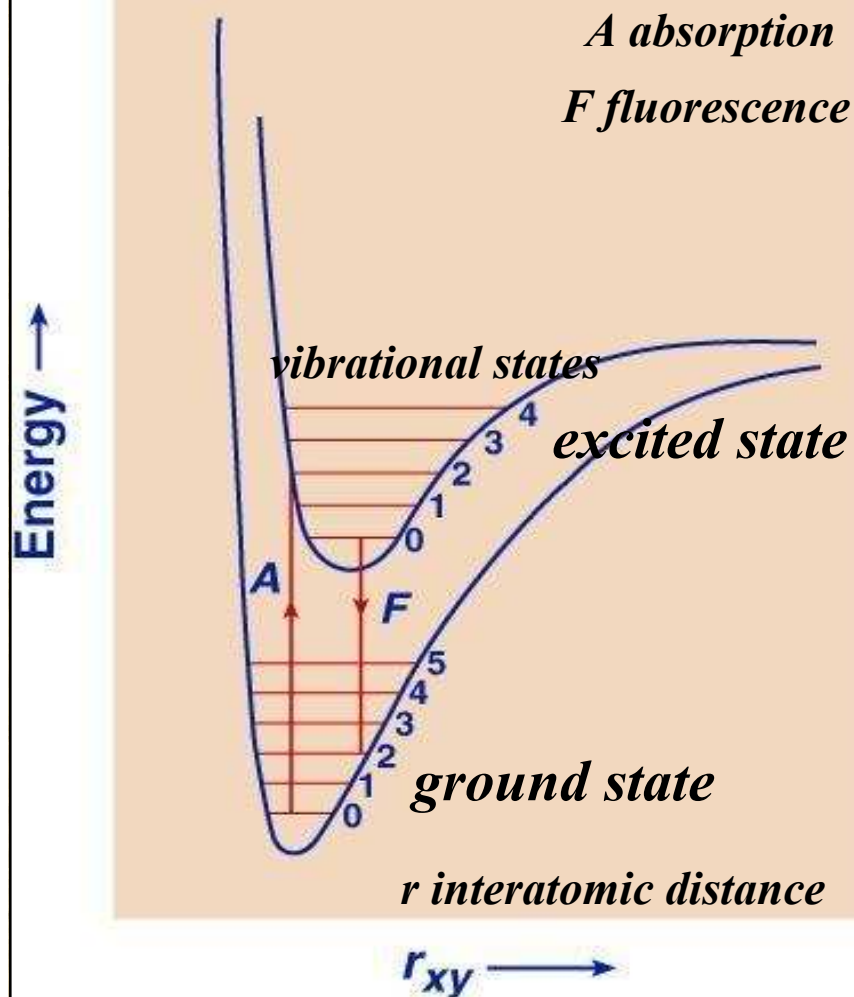


# **BASIC PRINCIPLES OF ELECTRODE PROCESSES**

## **Heterogeneous kinetics**

### **II**

# Electron Transfer Reactions



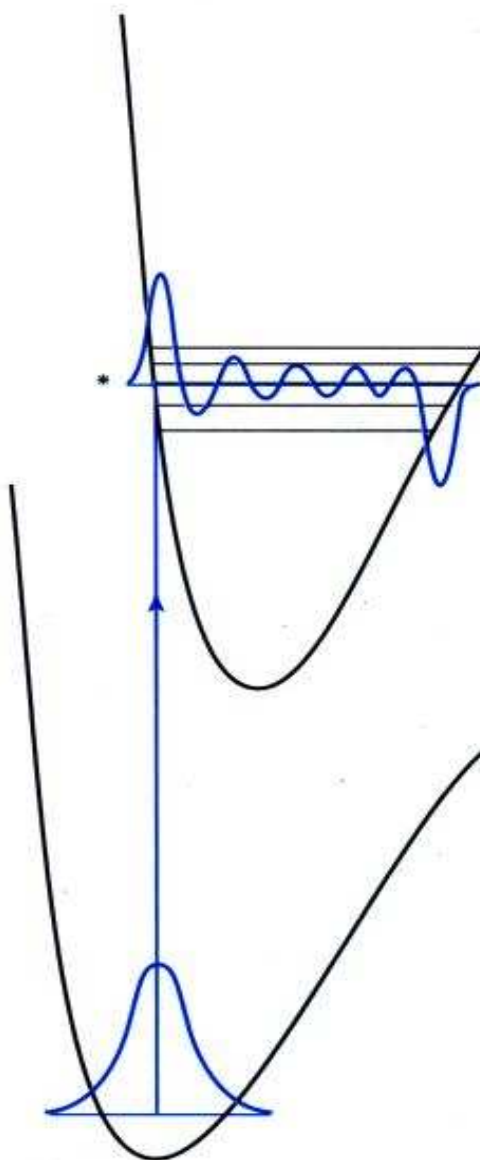
*Potential energy curves for the ground state and an excited state of a diatomic molecule*

## Franck-Condon principle

Electron-transfer processes must satisfy the **Frank-Condon restrictions**, i.e.

- the act of electron transfer (**ET**) is much shorter than atomic motion, **femto-seconds**
- the consequences are that no angular momentum can be transferred to or from the transition state during electron transfer, there is also **restrictions in changes in spin**.

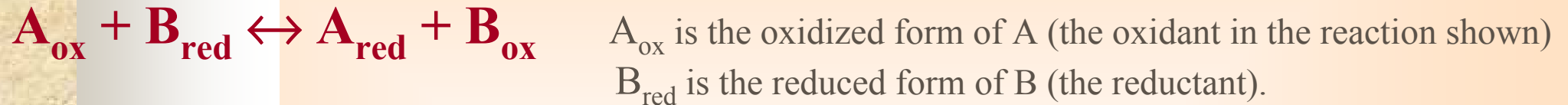
# The Franck-Condon Principle



According to the Franck-Condon principle, the most intense vibronic transition is from the ground vibrational state to the vibrational state lying vertically above it. Transitions to other vibrational levels also occur but with lower intensity

In the QM version of the FC-principle, the molecule undergoes a transition to the upper vibrational state that 'most closely resembles' the vibrational wavefunction of the vibrational ground state of the lower electronic state. The two wavefunctions shown here have the greatest overlap integral of all the vibrational states of the upper electronic state

# Electron transfer in biochemistry



For such an electron transfer, one may consider two half-cell reactions:



For each half reaction:

$$E = E^{\circ'} - RT/zF (\ln [\text{red}]/[\text{ox}])$$

e.g., for the first half reaction:

$$E = E^{\circ'} - RT/zF (\ln [a_{\text{red}}]/[a_{\text{ox}}])$$

$$[a_{\text{red}}] = [a_{\text{ox}}], \dots E = E^{\circ'}$$

$E^{\circ'}$  is the **mid-point potential**, or standard redox potential. It is the potential at which [oxidant] = [reductant] for the half reaction.

For an electron transfer:

$$\Delta E^{\circ'} = E^{\circ'}_{(\text{oxidant})} - E^{\circ'}_{(\text{reductant})} = E^{\circ'}_{(e^- \text{ acceptor})} - E^{\circ'}_{(e^- \text{ donor})}$$

$$\Delta G^{\circ'} = - nF \Delta E^{\circ'}$$



Exercise: Consider ET of 2 electrons from NADH to oxygen:

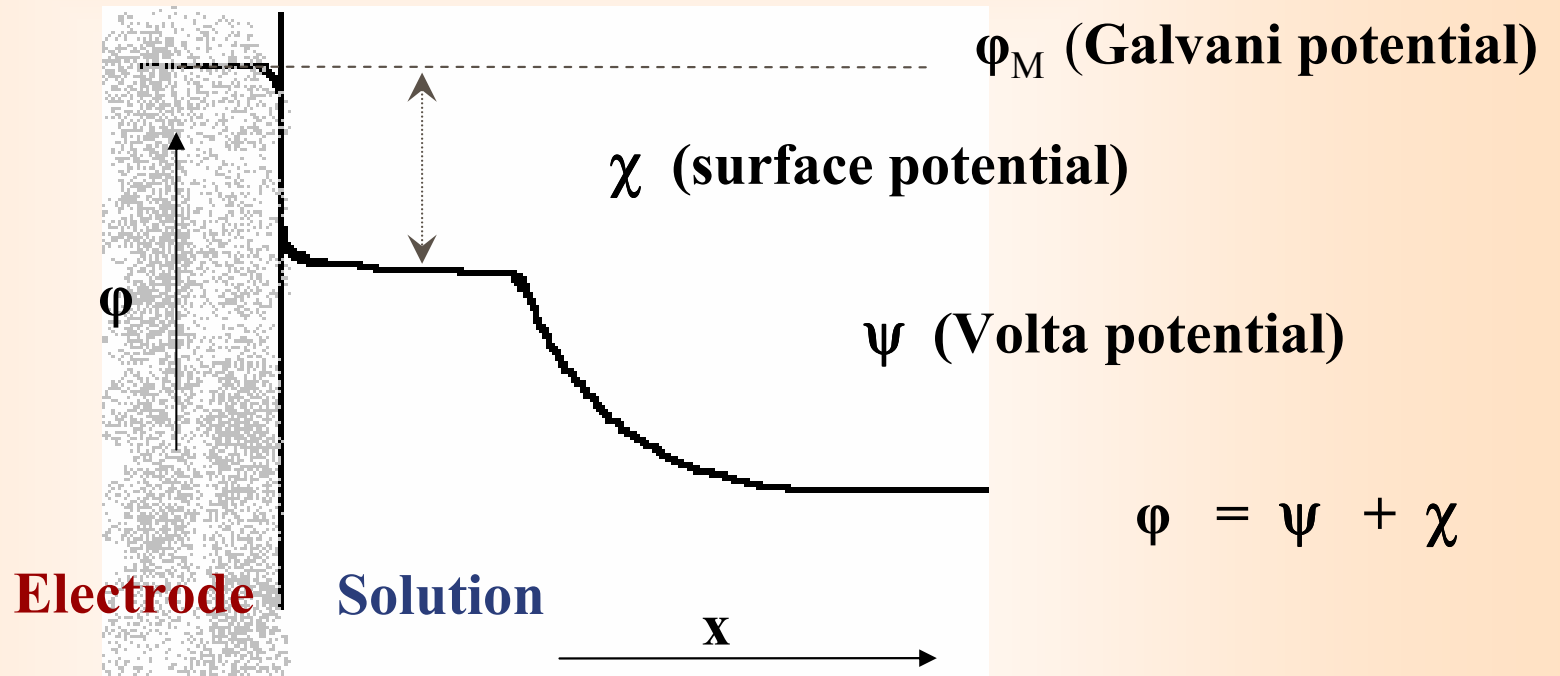


Subtracting reaction **b** from reaction **a**:



$$\Delta G^{\circ'} = - nF\Delta E^{\circ'} = - 2(96485 \text{ Joules/Volt} \cdot \text{mol})(1.13 \text{ V}) = - 218 \text{ kJ/mol}$$

## The solid metallic electrode



$\phi_M$  (Galvani potential – inner potential) is associated with  $E_F$

$\psi$  (Volta potential – outer potential) is associated with the potential outside the electrode's electronic distribution

$\chi$  (surface potential)  $E_F = E_{\text{redox}} - e \chi$

**From without potential insertion on solid phase**

**over / below  $E_r$       more positive / more negative**

**$\Rightarrow$  electrode polarization, overpotential**

$$\Rightarrow \eta = E_p - E_r$$

$$E_p = E_{\text{polarization}} = E_{\text{polarizační}}$$

$$E_r = E_{\text{equilibrium}} = E_{\text{rovnovážný}}$$

**$\Rightarrow$  begins lead an electrode process**

**As well as each electrode process, it consists of more**

**follow steps – levels**

**rds - rate determining step**

**a most slow step**

$\eta$  = overpotential = přepětí

# Electrode reactions steps

Substance crossing from within of electrolyte to a level of maximal approximation  $\Rightarrow$  transport (diffusion) overpotential three transport mechanisms

- **migration** – movement of ions through solution by electrostatic attraction to charged electrode
- **diffusion** – motion of a species caused by a concentration gradient
- **convection** – mechanical motion of the solution as a result of stirring or flow

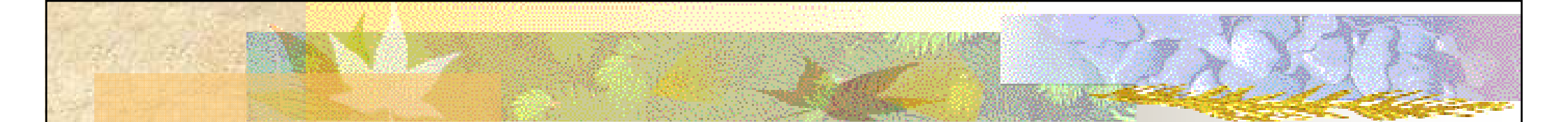
2. **Adsorption** (localization) of ions or molecules in space of electric double layer

3. **Dehydration (desolvation)**

- **absolute**
- **partial**
- **none**

$\eta$  = overpotential = přepětí





**4. Chemical reactions on a metal surface**, coupled with making of intermediates capable of obtaining or losing of electrons

⇒ **reaction overpotential**

**5. Electrode reaction** - solitary electron crossing through interface

⇒ **activation overpotential**

**6. Adsorption of primary product of electrochemical process on a metal surface**



**7. Desorption of a primary product**

**8. Transport of product from a metal surface**

a) Soluble product – by diffusion

(the most used style)

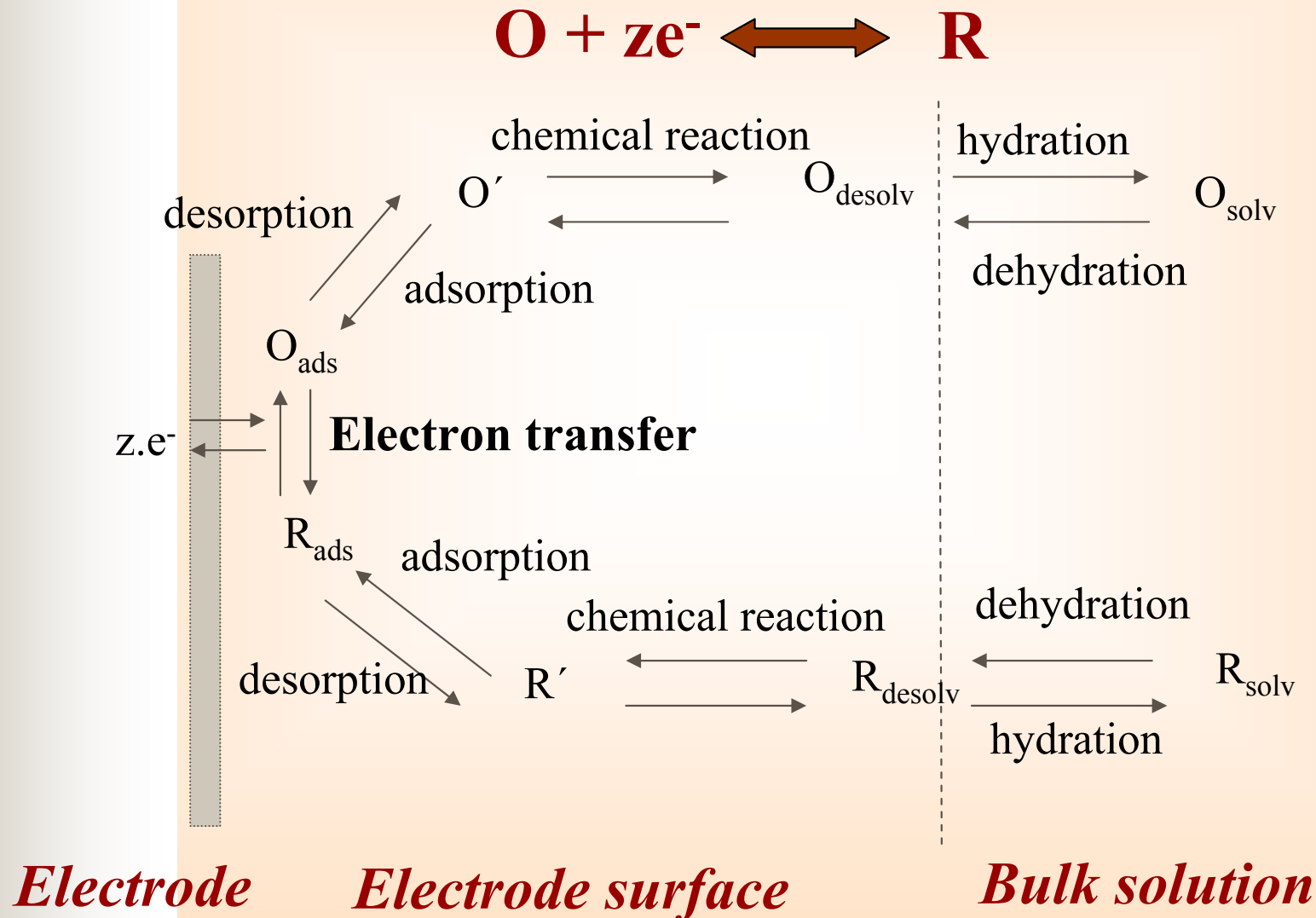
b) Gas products – by bubbling

c) Products can be integrated to an electrode crystal lattice

⇒ **crystalization ( nucleation) overpotential**

g) By diffusion to inside of electrode (for ex. amalgam)

# DYNAMIC ELECTROCHEMISTRY



Electrode kinetics - can be controlled by electrode potential

## Velocity of electrode process

$$v = \frac{dN}{dt}$$

$$\text{Faraday : } I t = N n F = Q$$

= for transformation of *1 mol* of substance with a charge of *z*, charge of *nF* coulomb is consumed ; *F* = 96484 coulomb/mol  
For transformation of *dn mol* of substance at time *dt*, a current *I* is consumed

$$I = nF \frac{dN}{dt} = nFv$$

**Heterogeneous reactions – velocity to surface unit:**

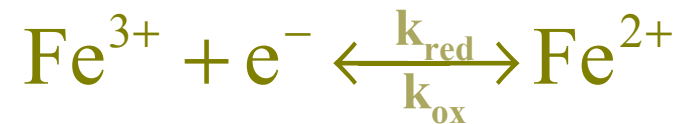
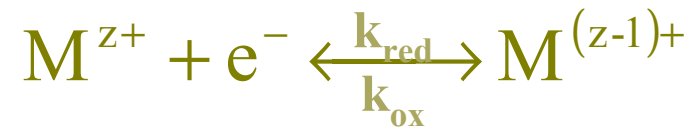
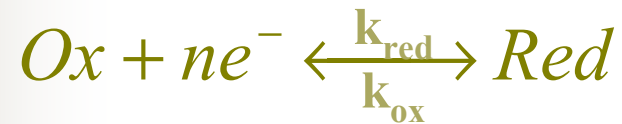
Current density  $j = \frac{I}{A} = nF \frac{dN}{dt} \frac{1}{A}$   $A = \text{area}$

Experimental dependences:

$\eta = f(j)$   
polarization curves

$j = f(\eta)$   
current-potential curves

# Activation overpotential



$$v_{ox} = k_{ox} C_{red}$$

$$v_{red} = k_{red} C_{ox}$$

$$j_{red} = n F \frac{dN_{ox}}{dt} = n F v_{red}$$

$$j_{ox} = n F \frac{dN_{red}}{dt} = n F v_{ox}$$

# An expression for the rate of electrode reaction

## Arrhenius

$$k = A' \exp \left( -\frac{\Delta H^\ddagger}{RT} \right) \quad A' = A \exp \left( \frac{\Delta S^\ddagger}{R} \right)$$

## Gibbs-Helmholtz

$$k = A \exp \left[ -\left( \frac{\Delta H^\ddagger - T\Delta S^\ddagger}{RT} \right) \right] = A \exp \left( -\frac{\Delta G^\ddagger}{RT} \right)$$



# An expression for the rate of electrode reaction

$\alpha$  is a coefficient of charge transfer =  
symmetry coefficient

$$\alpha_a + \alpha_c = 1$$

$$\alpha_c = \alpha;$$

$$\alpha_a = 1 - \alpha$$

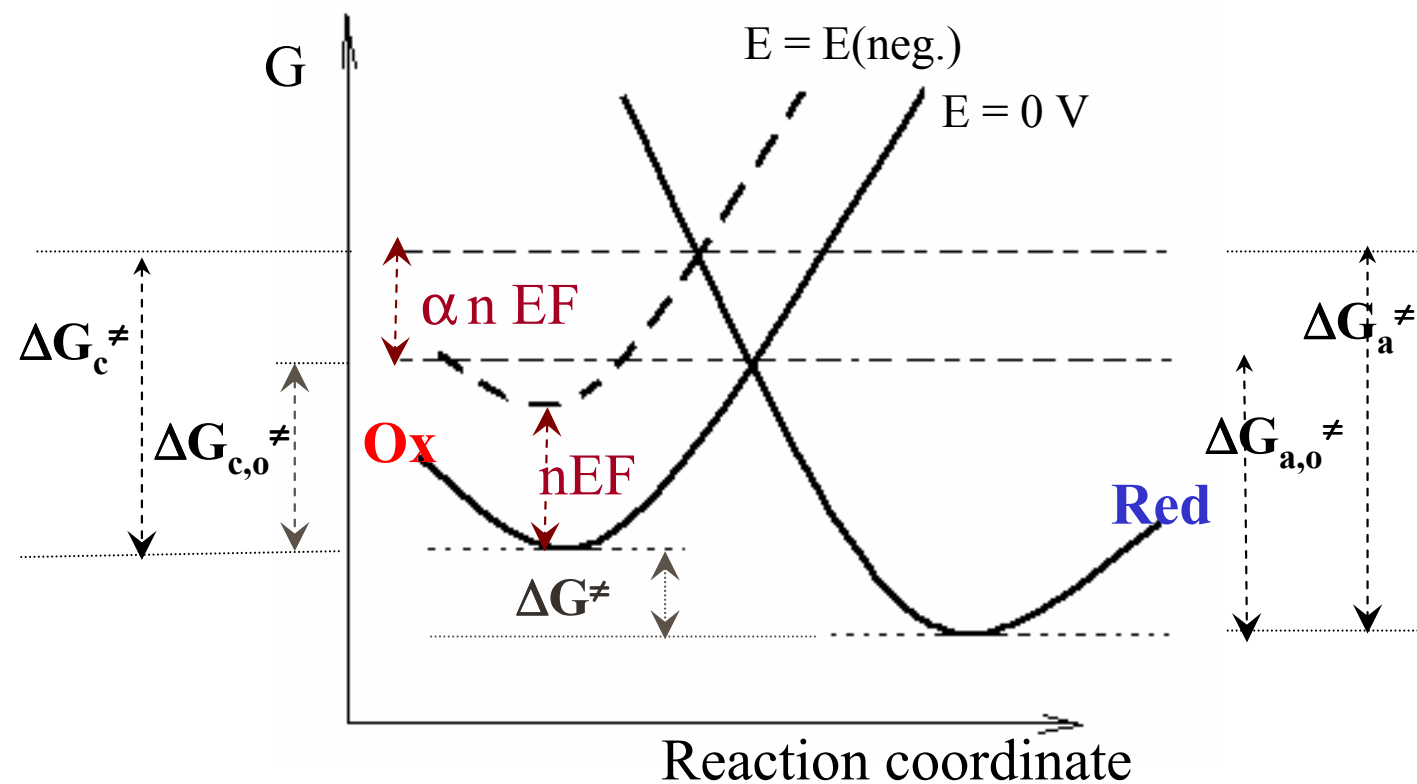
$$\Delta G_c^\ddagger = \Delta G_{c,0}^\ddagger + \alpha_c n F E$$

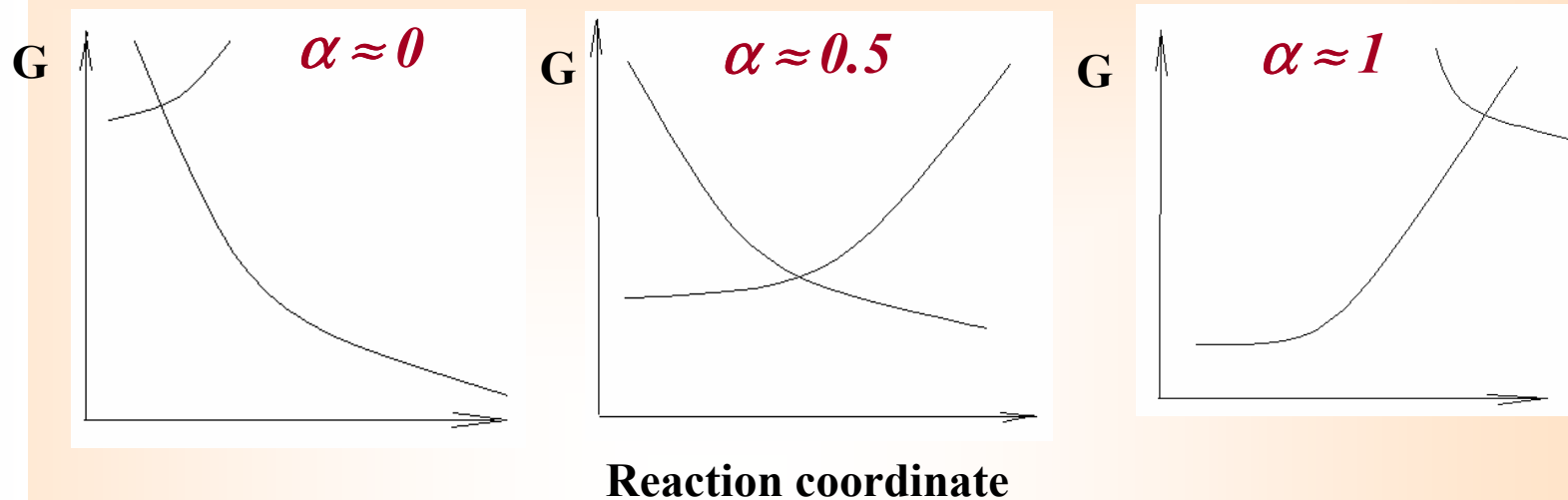
$$\Delta G_a^\ddagger = \Delta G_{a,0}^\ddagger - \alpha_a n F E$$

$\Delta\phi$  for reduction ....  $\alpha_c E$

$\Delta\phi$  for oxidation ....  $\alpha_a E = (1 - \alpha_c) E$

Effect of a change in  
applied electrode  
potential on the  
reduction of **Ox** to **Red**





In many cases electrode processes involving the transfer of more than one electron take place in consecutive steps. The symmetry of the activation barrier referred to the rate-determining step.

$\alpha n$

$\alpha n = 1.5 \Rightarrow \alpha = 0.75$   
*rds* .....rate - determining step



## Balance of electrode process

$$|j_{ox}| = |j_{red}| = j_0$$

$j_0$  is charge current density

$$v_{ox} = v_{red}$$

$$j_0 = j_{red} = n F c_{ox} A_{red} \exp \left[ -\frac{\Delta G_{red}^\ddagger + \alpha n F (E - E^0)}{RT} \right]$$

$$j_0 = j_{ox} = n F c_{red} A_{ox} \exp \left[ -\frac{\Delta G_{ox}^\ddagger - (1 - \alpha) n F (E - E^0)}{RT} \right]$$

**$k^0$  = standard velocity constant  
(members independence on  $E$ )**

$$k^0 = A_{red} \exp \left[ -\frac{\Delta G_{red}^\ddagger - \alpha n F E^0}{RT} \right] = A_{ox} \exp \left[ -\frac{\Delta G_{ox}^\ddagger + (1-\alpha) n F E^0}{RT} \right]$$

$$j_0 = n F c_{ox} k^0 \exp \left[ -\frac{\alpha n F E_{eq}}{RT} \right] = n F c_{red} k^0 \exp \left[ \frac{(1-\alpha) n F E_{eq}}{RT} \right]$$

$$j_{red} = j_c$$

-

$$k = A \exp \left( -\frac{\Delta G^\ddagger}{RT} \right)$$

$$j_{ox} = j_a$$

+

determination of  $E_{eq}$

## Current - overpotential $\eta$ crossing

$$j = |j_{ox}| + |j_{red}| = n F (v_{ox} - v_{red}) = n F k_{ox} c_{red} - n F k_{red} c_{ox}$$

$$= j_0 \exp \left[ \frac{(1-\alpha)nF\eta}{RT} \right] - j_0 \exp \left[ -\frac{\alpha nF\eta}{RT} \right]$$

$$j_{ox} = j_a$$

$$j_{red} = j_c$$

$$j = j_0 \left\{ \exp \left[ \frac{(1-\alpha)nF\eta}{RT} \right] - \exp \left[ -\frac{\alpha nF\eta}{RT} \right] \right\}$$

**Butler- Volmer equation for electrode process,  
where **rds** is charge transfer**

## Butler-Volmer equation

$$\ln j_c = \ln j_0 - \frac{\alpha n F \eta}{RT} \qquad \ln j_a = \ln j_0 + \frac{(1 - \alpha) n F \eta}{RT}$$

- ♥  $j$ ,  $k_a$  and  $k_c$  depends exponentially on potential
- ♥ linear free energy relationship the parameters:  $I$  and  $E$
- ♥  $E_{\text{eq}}$  gives the exchange current  $I_0 = j_0 A \Rightarrow$  standard rate constant
- ♥ electrode as a powerful catalyst
- ♥ for transport the Tafel law must be corrected

♥ the observed current is proportional to the difference between the rate of the oxidation and reduction reactions at the electrode surface

$$I = nFA(k_a [Red]_* - k_c [Ox]_*)$$

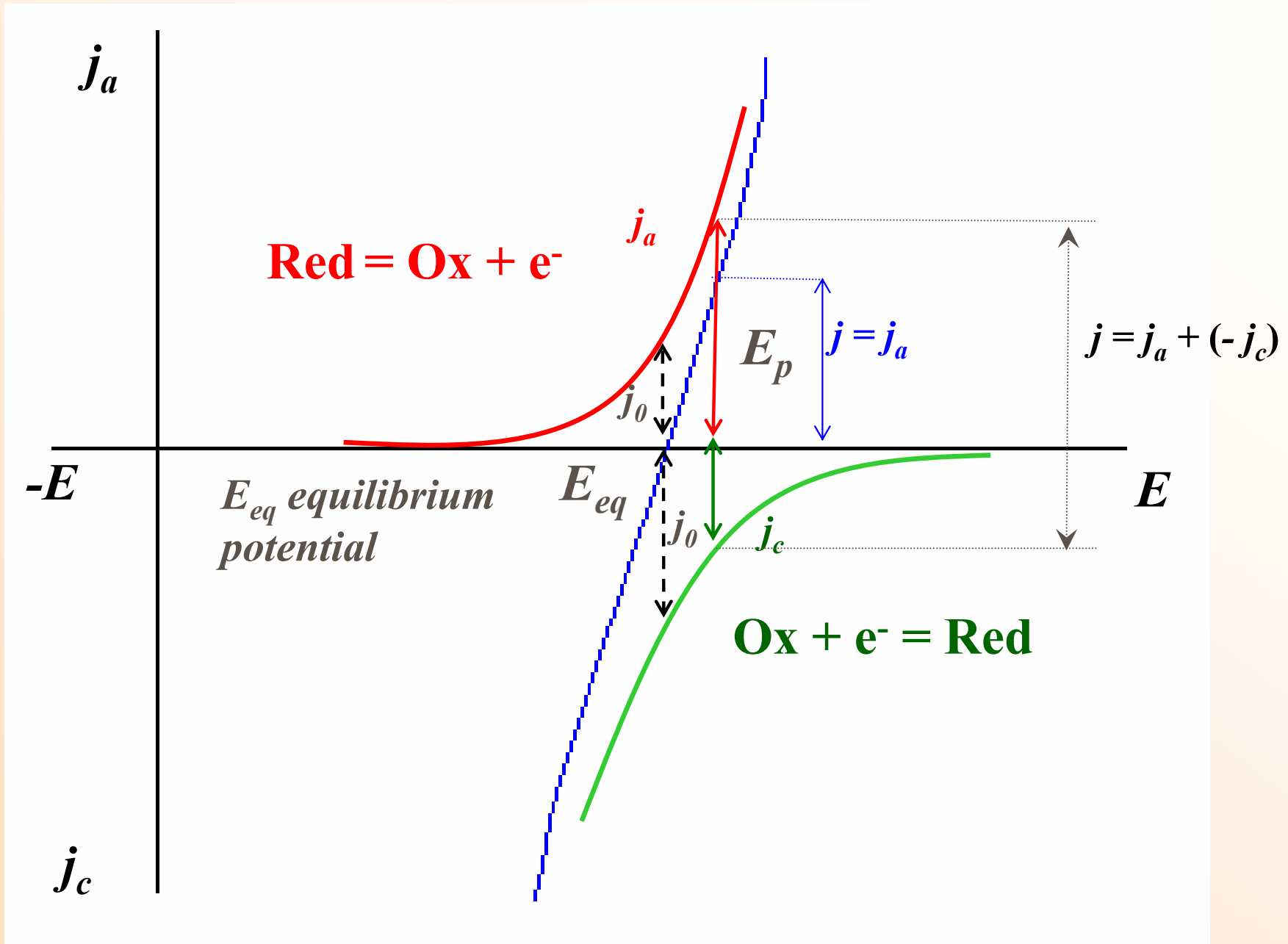
$[Red]_*$   
 $[Ox]_*$  concentrations of Red and Ox next to the electrode

$$v = k_a [Red]_* - k_c [Ox]_*$$

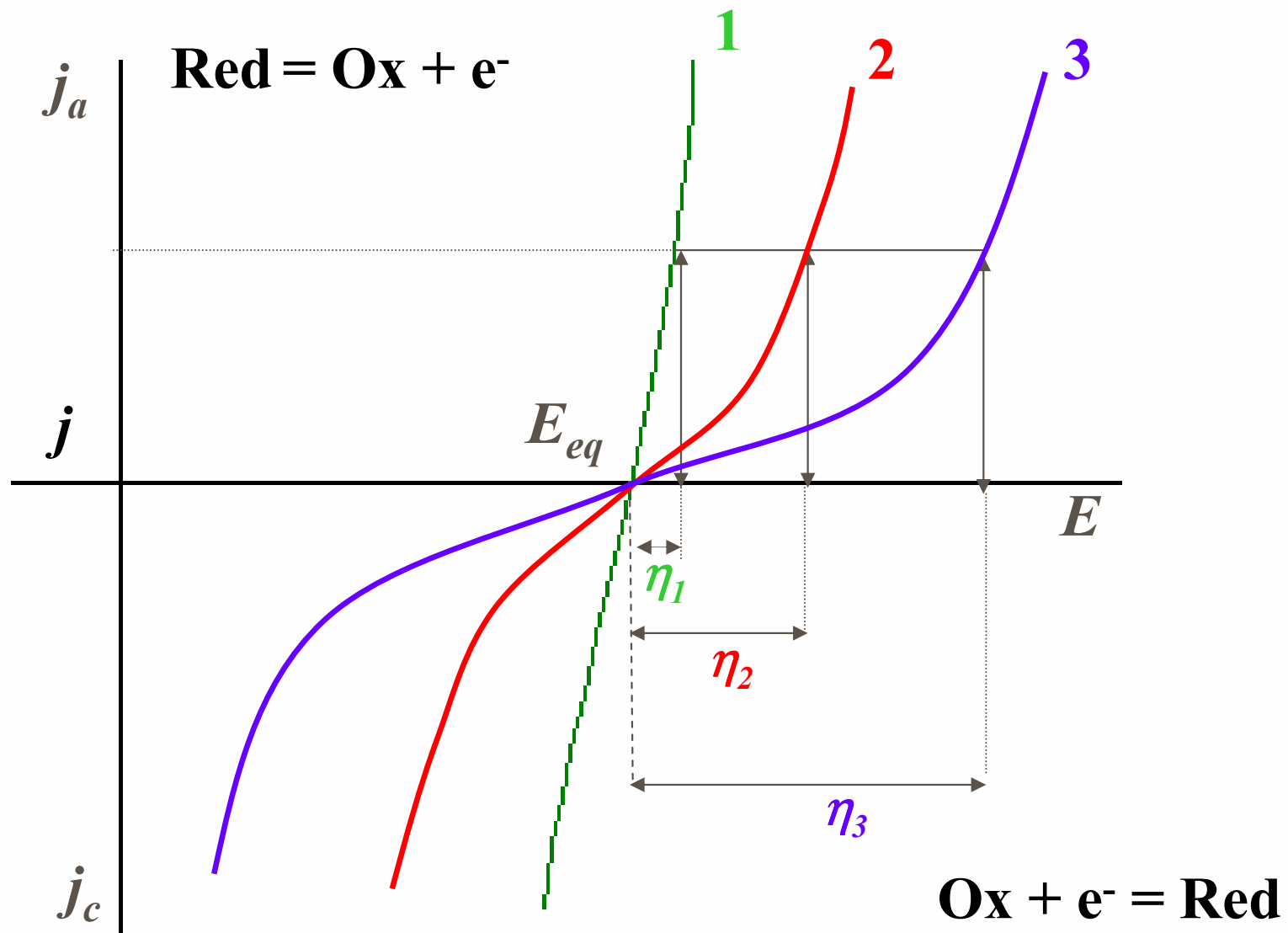
$k_a [Red]_*$  ;  $k_c [Ox]_*$  do not grow indefinitely – limited by the transport of species to electrode

$I_d$  diffusion-limited current

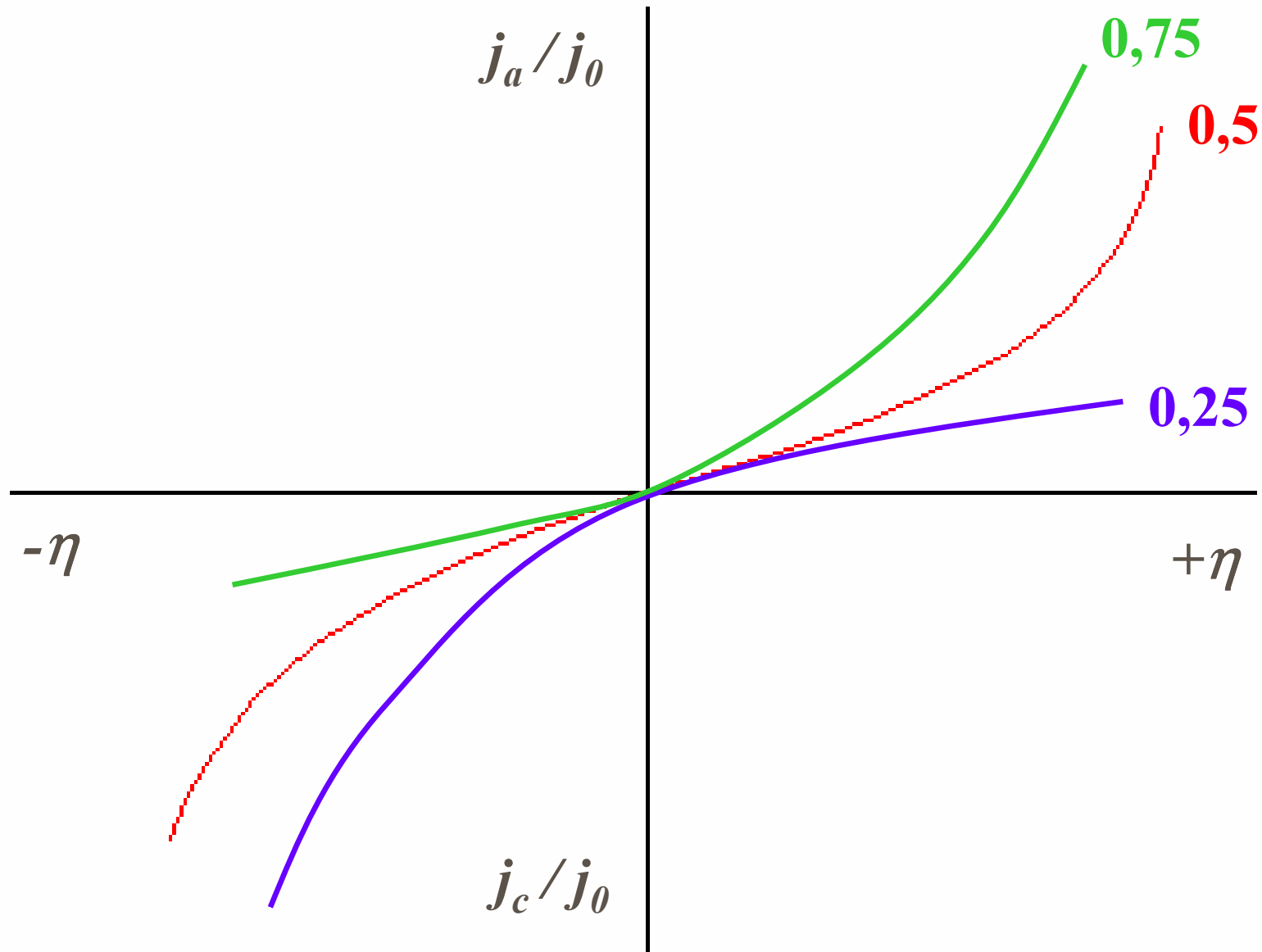
# Polarization curves without overpotential



# Polarization curves with activation overpotential



# Ratio dependence of current density and change current density on overpotential for different $\alpha$ values





## Polarization curve: $\eta = f(j)$ or I-E curves: $j = f(\eta)$

a) Small values of overpotential  $j = j_0 \frac{nF}{RT} \eta$  Development of  $e^{-x}$  function

$$\left( \frac{\partial j}{\partial \eta} \right)_{\eta \rightarrow 0} = \frac{j_0 n F}{R T} \quad \left( \frac{\partial \eta}{\partial j} \right) = \frac{R T}{j_0 n F} = R_p \quad R_p = \text{polarization resistance}$$

b) Large values of overpotential

negative  $\eta \rightarrow$  process of reduction  $\ln j_c = \ln j_0 - \frac{\alpha n F \eta}{R T}$

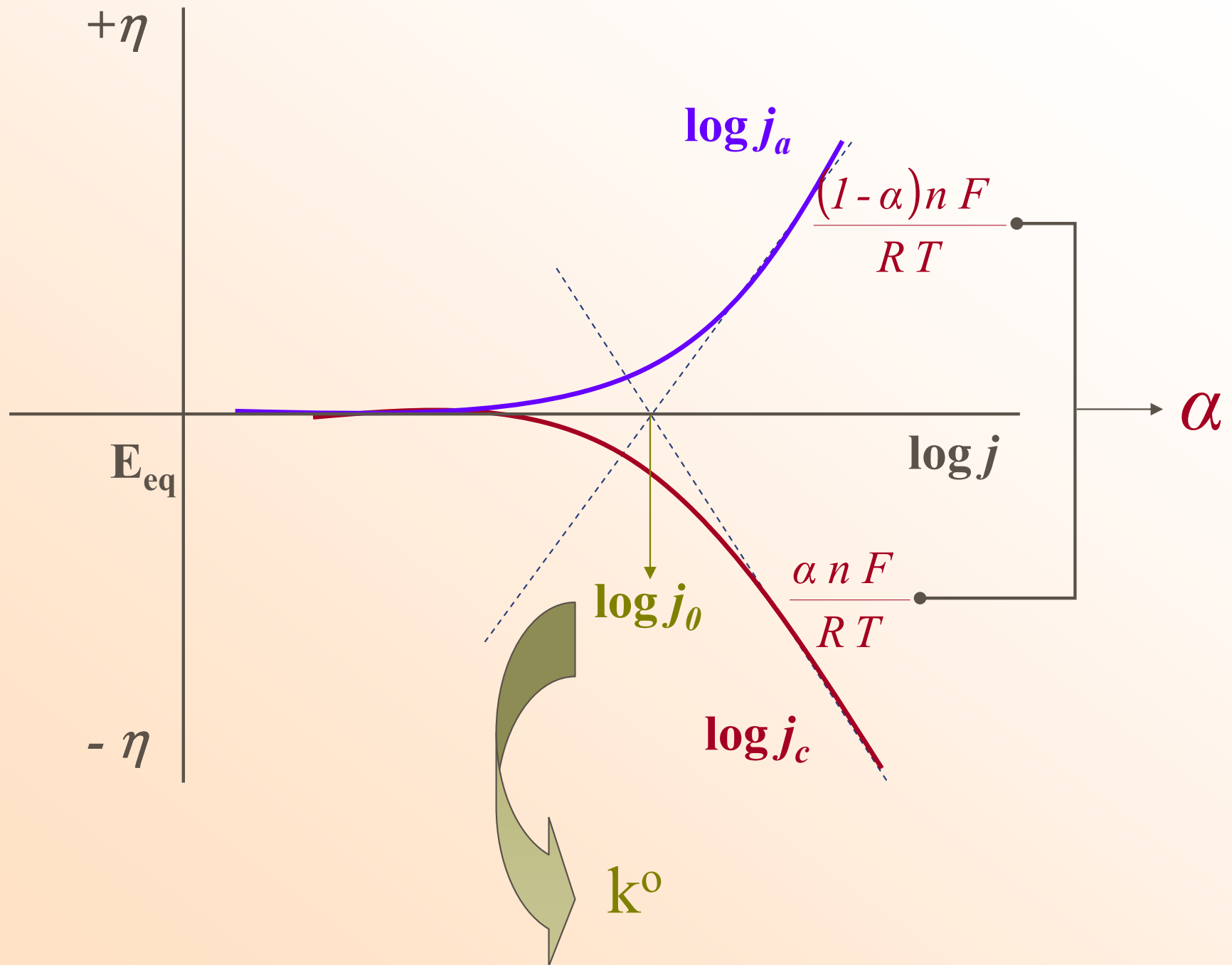
positive  $\eta \rightarrow$  process of oxidation  $\ln j_a = \ln j_0 + \frac{(1 - \alpha) n F \eta}{R T}$

### Tafel relations

$$\eta = a + b \ln |j| \quad \eta = a' + b' \log |j|$$

# Tafel diagram for cathode and anode current density

$$\alpha = 0,25 \quad j_0 = 0,1 \text{ mA}$$



$$\eta = f(k')$$

$$j = 10^{-6} \text{ A.cm}^{-2}; n = 1; c_{\text{Ox}} = 1 \text{ mM}; \alpha = 0.5; T = 298 \text{ K}$$

$k'$ (cm.s <sup>-1</sup> )	10 <sup>-3</sup>	10 <sup>-4</sup>	10 <sup>-6</sup>	10 <sup>-10</sup>	10 <sup>-14</sup>
$\eta$ (V)	0.0002	0.003	0.12	0.59	1.06

reversible **x** irreversible process ↗ current density ↗  $j$

metal	$\eta_{\text{hydrogen}}$ (V)	$\eta_{\text{oxygen}}$ (V)
Ag	0.48	0.58
Au	0.24	0.67
Cu	0.48	0.42
Hg	0.88	-
Ni	0.56	0.35
Pt(smoothed)	0.02	0.72
Pt(platinized)	0.01	0.40

$$j = 10^{-3} \text{ A.cm}^{-2} \quad T = 298 \text{ K}$$

**DIFFUSION:** the natural movement of species in solution without the effects of the electrical field

**I. Fick law:** the natural movement of species in solution without the effects of the electrical field

$$J = -D \frac{dc}{dx} \qquad \frac{dN_i}{dt} = -DA \frac{dc_i}{dx}$$

$\frac{dc_i}{dx}$  ..... concentration gradient

$D$  diffusion coefficient [ $\text{cm}^2\text{s}^{-1}$ ] ;  $10^{-5}$ -  $10^{-6}$  in aqueous solutions

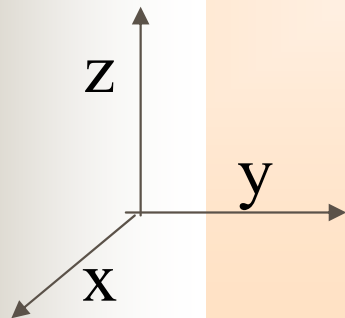
**II. Fick law:** What is the variation of concentration with time ???

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c_i}{\partial x^2} \qquad D = \text{const.}$$

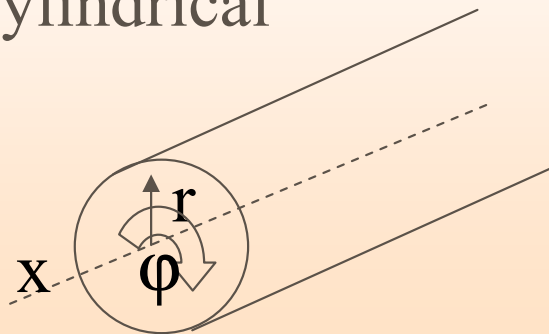
# Laplace operator in various coordinate systems

Coordinates	Laplace operator
Cartesian	$\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}$
Cylindrical	$\frac{\partial}{\partial r} + \frac{1}{r} \frac{\partial}{\partial \varphi} + \frac{\partial}{\partial x}$
Spherical	$\frac{\partial}{\partial r} + \frac{1}{r} \frac{\partial}{\partial \varphi} + \frac{1}{r \sin \varphi} \frac{\partial}{\partial \Theta}$

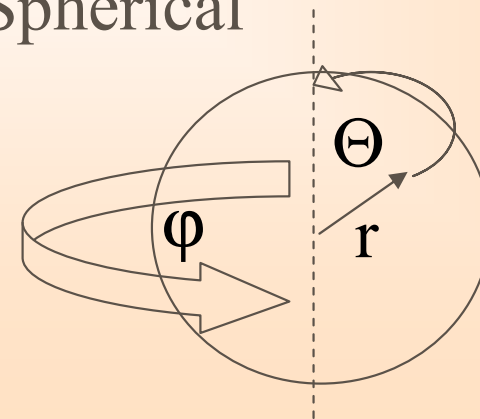
Cartesian



Cylindrical



Spherical



For any coordinate system

$$J = -D\nabla c \quad \nabla \text{ Laplace operator}$$

$$\frac{\partial c}{\partial t} = D\nabla^2 c \quad \text{Laplace transformation} = \text{LT}$$

LT for Fick's second law under conditions of pure diffusion control

$I_d$

- ♣ the potential is controlled, the current response and its variation in time is registered  
**chronoamperometry**
- ♣ the current is controlled and the variation of potential with time is registered  
**chronopotentiometry**

# Diffusion-limited current: planar and spherical electrodes

Mass transport

Reaction of all species reaching the electrode

$I_d$

Potential step to obtain a diffusion-limited current of the electroactive species

No reaction

$E$

$t$

$t = 0$

planar electrode ..... semi-infinite linear diffusion

$$I = nFAD \left( \frac{dc}{dx} \right)_0$$

Boundary conditions

$t = 0$

$c_0 = c_\infty$

no electrode reaction

$t \geq 0$

$\lim c = c_\infty$

bulk solution

$t > 0$  and  
 $x = 0$

$c_0 = 0$

diffusion -limited current  $I_d$

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

$$c = c_{\infty} \left\{ 1 - \operatorname{erfc} \left[ \frac{x}{x(Dt)^{1/2}} \right] \right\}$$

## Cottrell equation

$$I(t) = I_d(t) = \frac{nFAD^{1/2} c_{\infty}}{(\pi t)^{1/2}}$$

to planar electrode

linear diffusion

$$I(t) = I_d(t) = nFAD c_{\infty} \left[ \frac{1}{(\pi Dt)^{1/2}} + \frac{1}{r_0} \right]$$

to spherical electrode

spherical diffusion



$$I(t) = I_d(t) = nFADc_\infty \left[ \frac{1}{(\pi Dt)^{1/2}} + \frac{1}{r_0} \right]$$

- ♣ small t (spherical diffusion  $\longrightarrow$  linear diffusion)
- ♣ large t (the spherical diffusion dominates, which represents a steady state current)

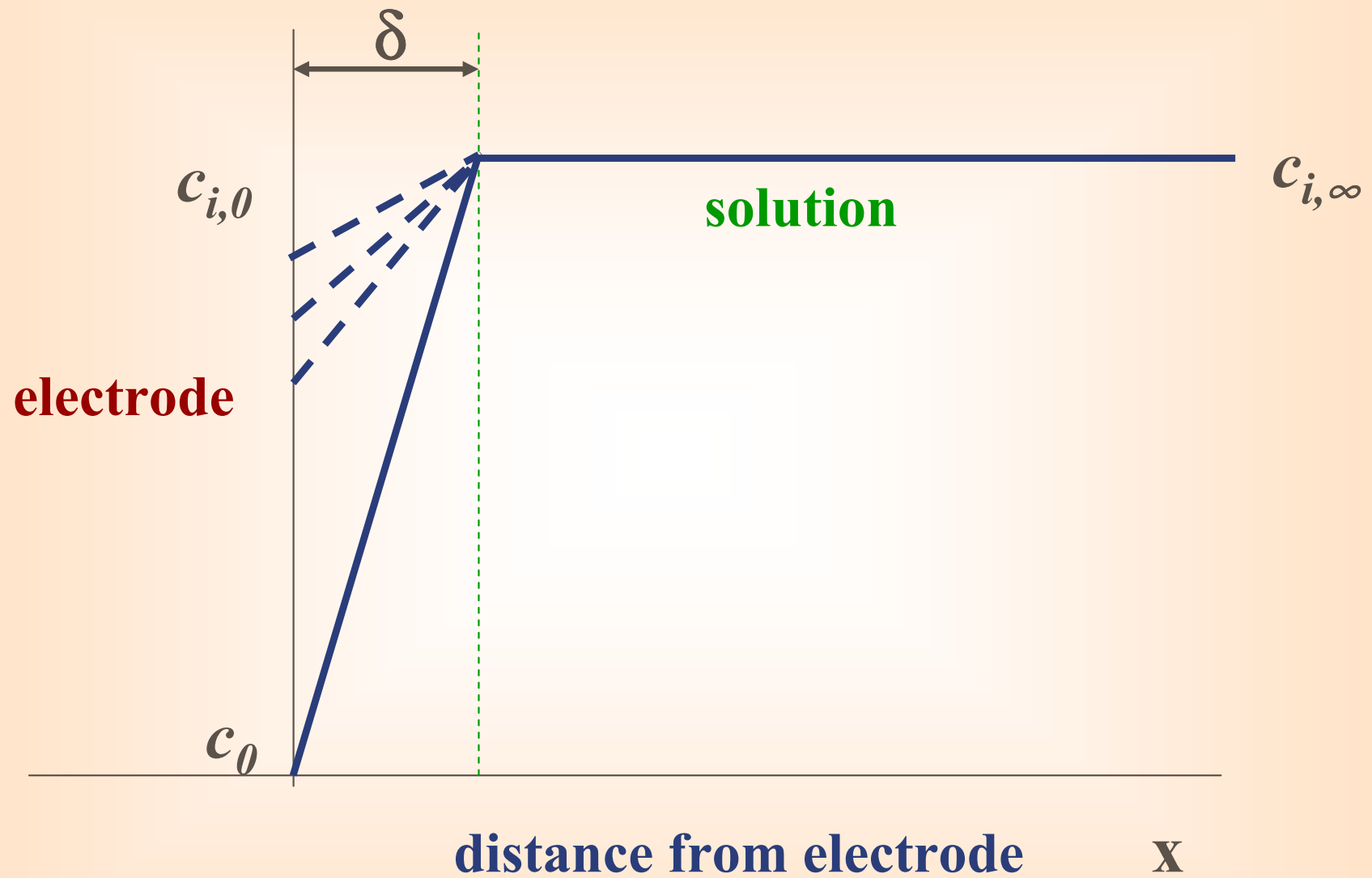
## Microelectrodes

### $\mu$ -electrodes and ultra- $\mu$ -electrodes

- ♣ small size at least one dimension 0.1-0.5  $\mu\text{m}$
- ♣ steady state
- ♣ high current density
- ♣ low total current (% electrolysis is small)
- ♣ interference from natural convection is negligible (supporting electrolyte)

$$I_d = \frac{nFADc_\infty}{r_0} = 2\pi nFr_0Dc_\infty$$

# Diffusion overpotential



## Diffusion overpotential

Solitary electrode process is in balance

$$E_{c_i} = E_i^0 + \frac{RT}{n_i F} \ln c_i \quad (\gamma = 1 \Rightarrow a_i = c_i)$$

$$E_{c_i,0} = E_i^0 + \frac{RT}{n_i F} \ln c_{i,0} \quad (E_i^0 = \text{standard potential})$$

overpotential required for getting over of concentration difference

$$\eta_d = E_{c_i,0} - E_{c_i} = \frac{RT}{n_i F} \ln \frac{c_{i,0}}{c_i}$$

**I. Fick law:**

$$\frac{dN_i}{dt} = -DA \frac{dc_i}{dx}$$

**Nernst diffusion layer  $\delta$  in stationary state**

$$\frac{dN_i}{dx} = konst. \Rightarrow \frac{dN_i}{dt} = -DA \frac{c_i - c_{i,0}}{\delta}$$

**Faraday:**

$$j_c = \frac{I}{A} = -n_i F \frac{1}{A} \frac{dN_i}{dt} = |n_i| F D \frac{c_i - c_{i,0}}{\delta}$$

$$\kappa_{Red} = \frac{n F D_{Red}}{\delta_{Red}}$$

$$\kappa_{Ox} = \frac{n F D_{Ox}}{\delta_{Ox}}$$

in limit:  $c_{i,0} = 0 \Rightarrow j_{k\lim} = n_i F D (c_i / \delta)$

$$\frac{j}{j_{d,l}} = \frac{c_{i,0} - c_i}{c_{i,0}} = 1 - \frac{c_i}{c_{i,0}} \quad \frac{c_i}{c_{i,0}} = 1 - \frac{j}{j_{d,l}}$$

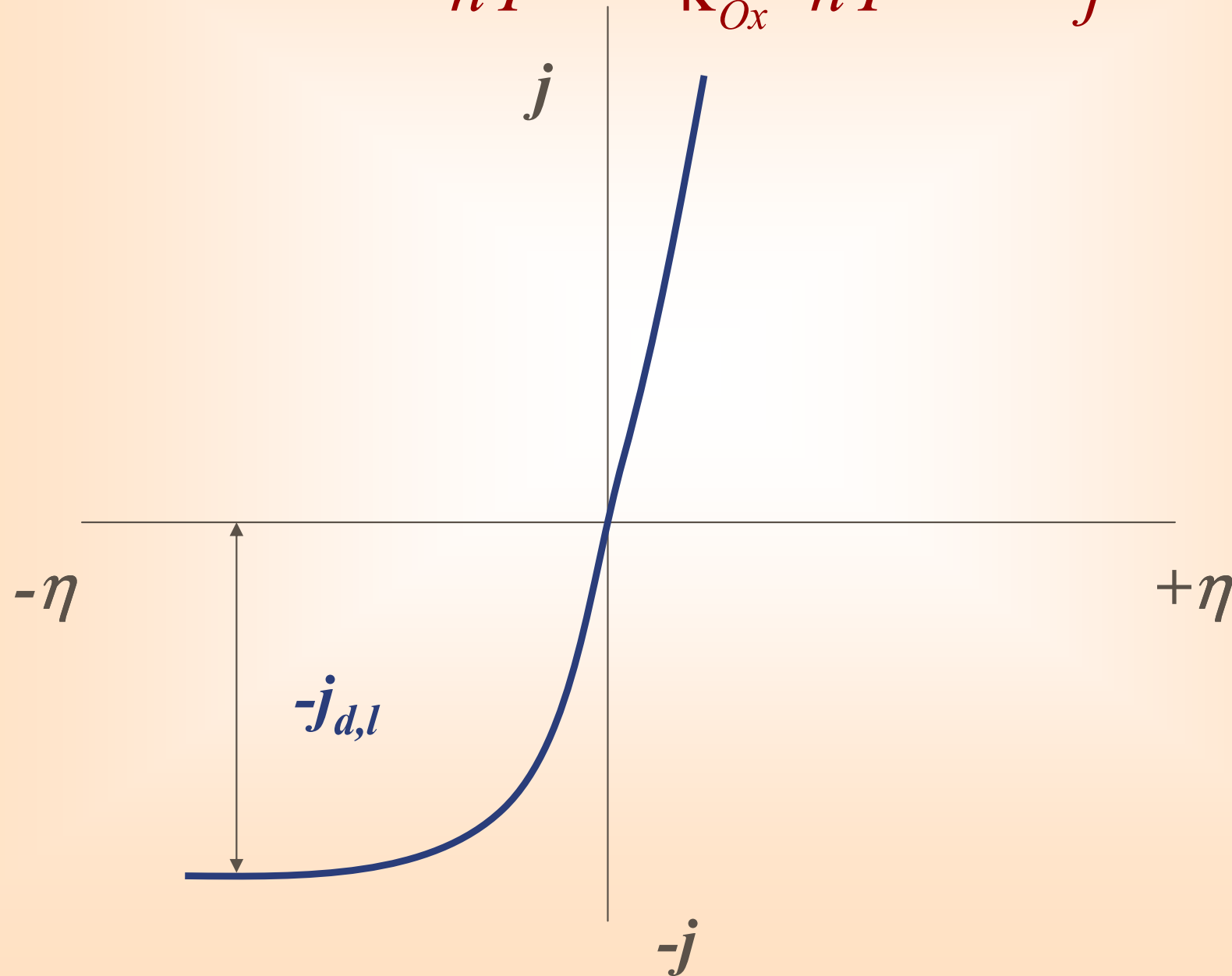
### Diffusion overpotential

$$\eta_d = E_{c_{i,0}} - E_{c_i} = \frac{RT}{n_i F} \ln \frac{c_{i,0}}{c_i}$$

$$\eta_d = -\frac{RT}{n_i F} \ln \left( 1 - \frac{j}{j_{d,l}} \right)$$

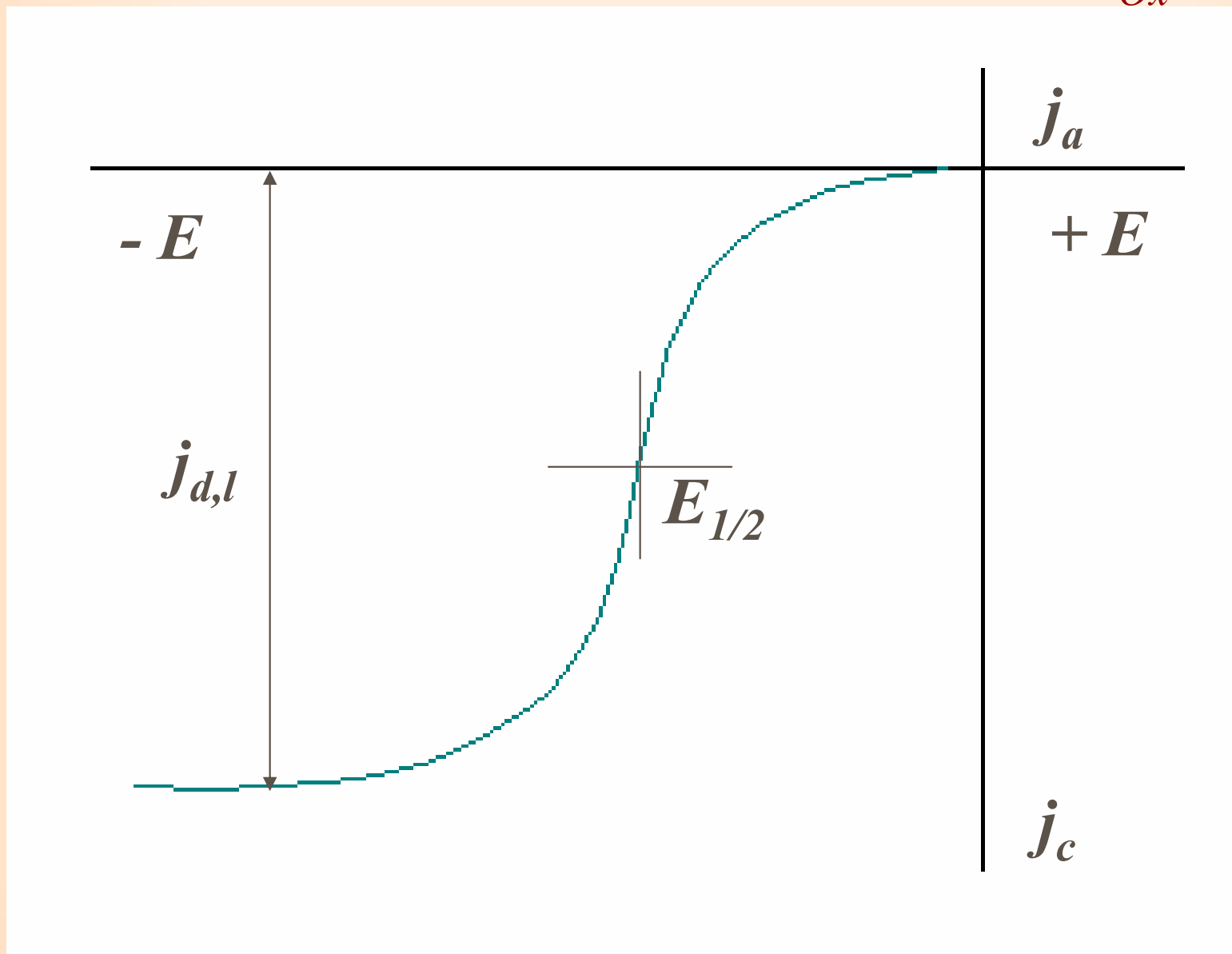
# Polarization curves for diffusion controlled processes

$$E = E_c^o + \frac{RT}{nF} \ln \frac{\kappa_{Red}}{\kappa_{Ox}} - \frac{RT}{nF} \ln \frac{j_{dl} - j}{j}$$

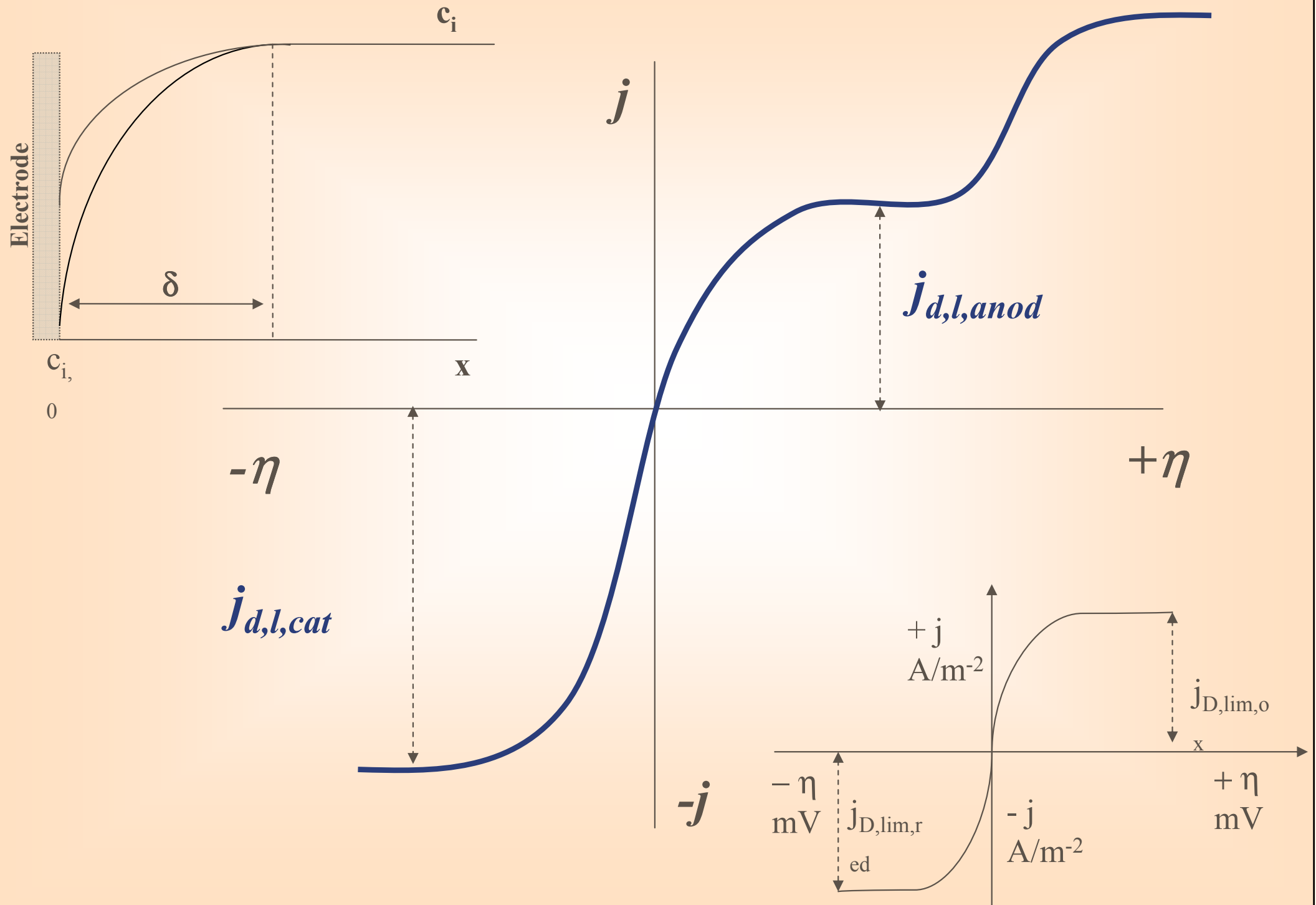


## Diffusion overpotential - polarography

$$j = j_{dl} / 2 \qquad E_{1/2} = E_c^o + \frac{RT}{nF} \ln \frac{\kappa_{Red}}{\kappa_{Ox}}$$



# Polarization curves for diffusion controlled processes





## Jaroslav Heyrovský

\* Dec. 20, 1890, Prague, Bohemia, Austro-Hungarian Empire [now Czech Rep.]

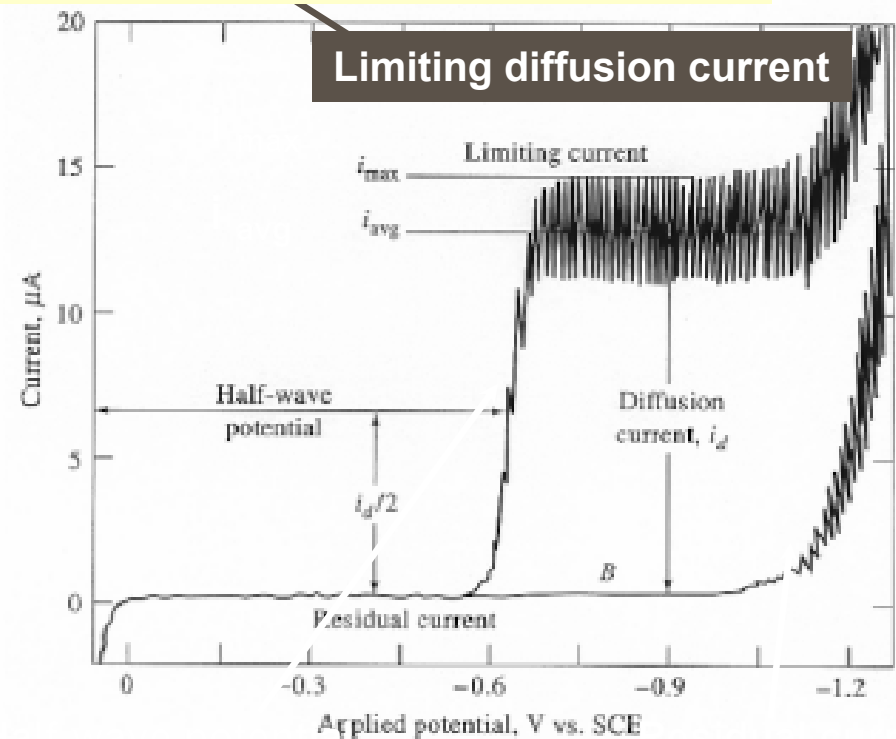
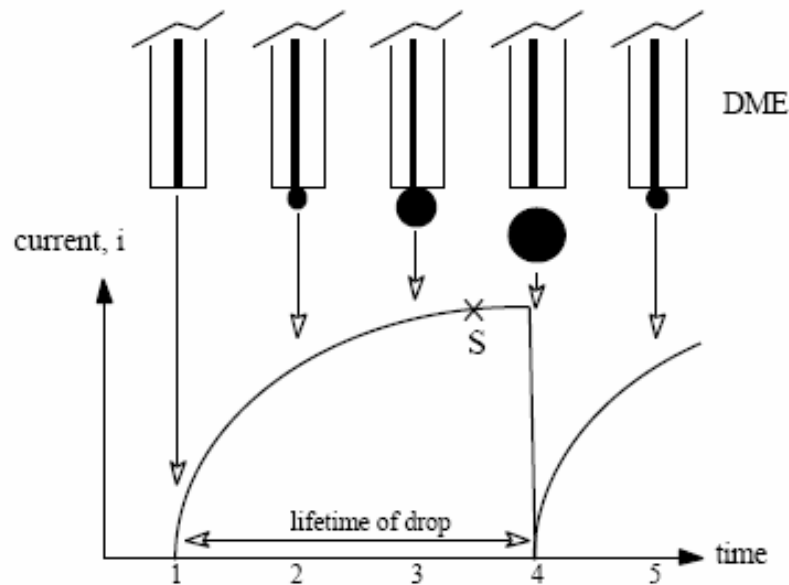
† March 27, 1967, Prague, Czechoslovakia



*J. Heyrovský*

Jaroslav Heyrovský was an inventor of the polarographic method, father of electroanalytical chemistry, recipient of the Nobel Prize (1959). His contribution to electroanalytical chemistry can not be overestimated. All voltammetry methods used now in electroanalytical chemistry originate from polarography developed by him.

# Half-wave potential, limited diffusion current



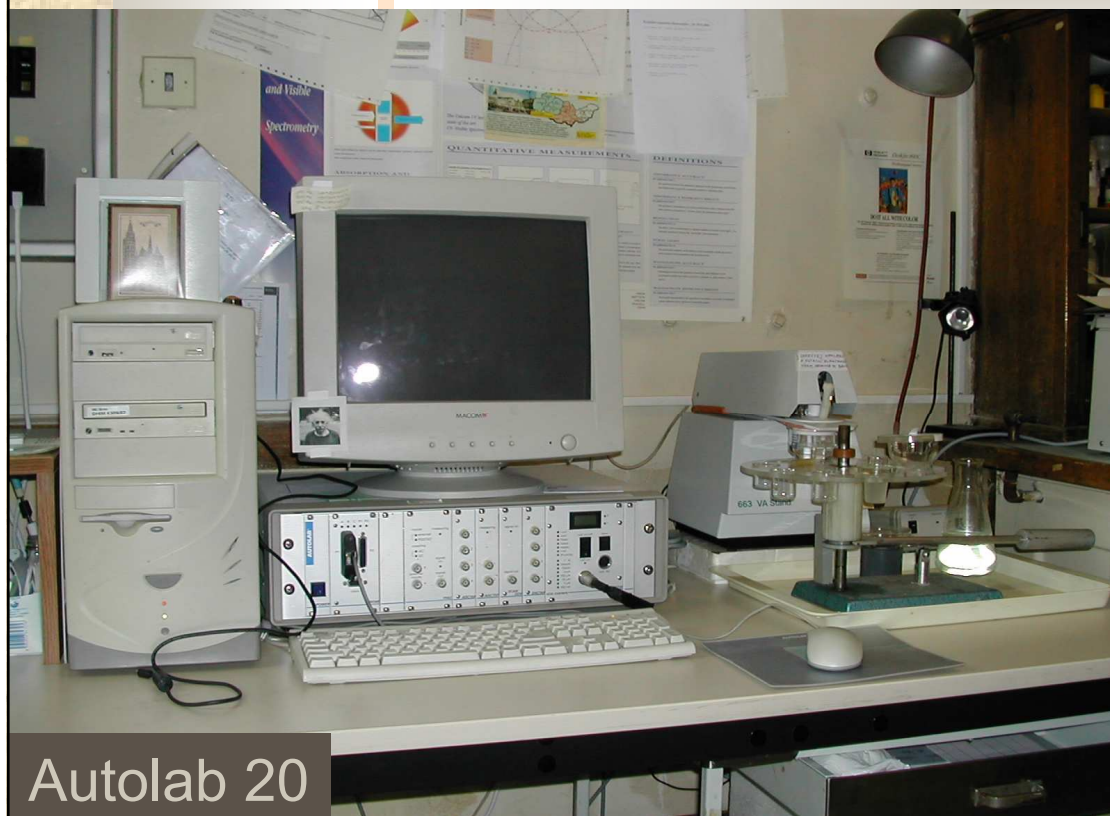
- ½ wave potential ( $E_{1/2}$ ) characteristic of  $\text{M}^{n+}$
- height of either average current maxima ( $i_{\text{avg}}$ ) or top current max ( $i_{\text{max}}$ ) is  $\sim$  analyte concentration
- size of  $i_{\text{max}}$  is governed by
  - rate of growth of DME > drop time ( $t$ , sec)
  - rate of mercury flow ( $m$ , mg/s)
  - diffusion coefficient of analyte ( $D$ ,  $\text{cm}^2/\text{s}$ )
  - number of electrons in process ( $n$ )
  - analyte concentration ( $c$ , mol/ml)

## **Ilkovič equation**

$$(i_d)_{\text{max}} = 0.706 n D^{1/2} m^{2/3} t^{1/6} c$$

$$(i_d)_{\text{avg}} = 0.607 n D^{1/2} m^{2/3} t^{1/6} c$$

# Instrumentation, common techniques

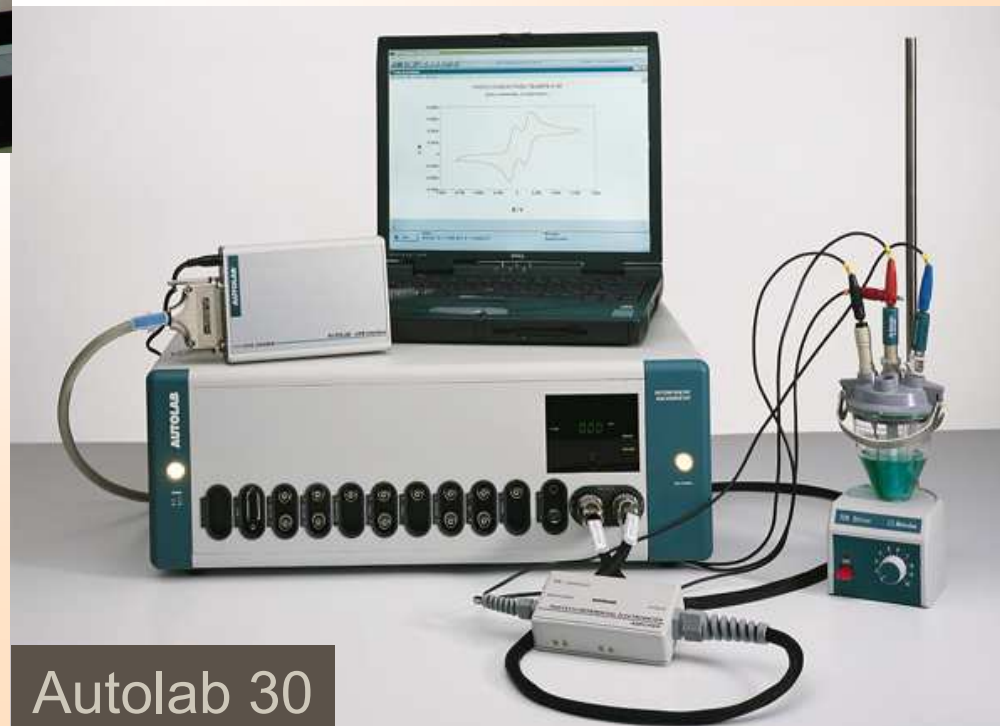


Autolab 20

## Electrochemical analyzer AUTOLAB

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The Netherlands

VA-Stand 663  
Metrohm  
Zurich  
Switzerland



Autolab 30



**Thank you for your attention**