



# **BASIC PRINCIPLES OF ELECTRON TRANSFER**

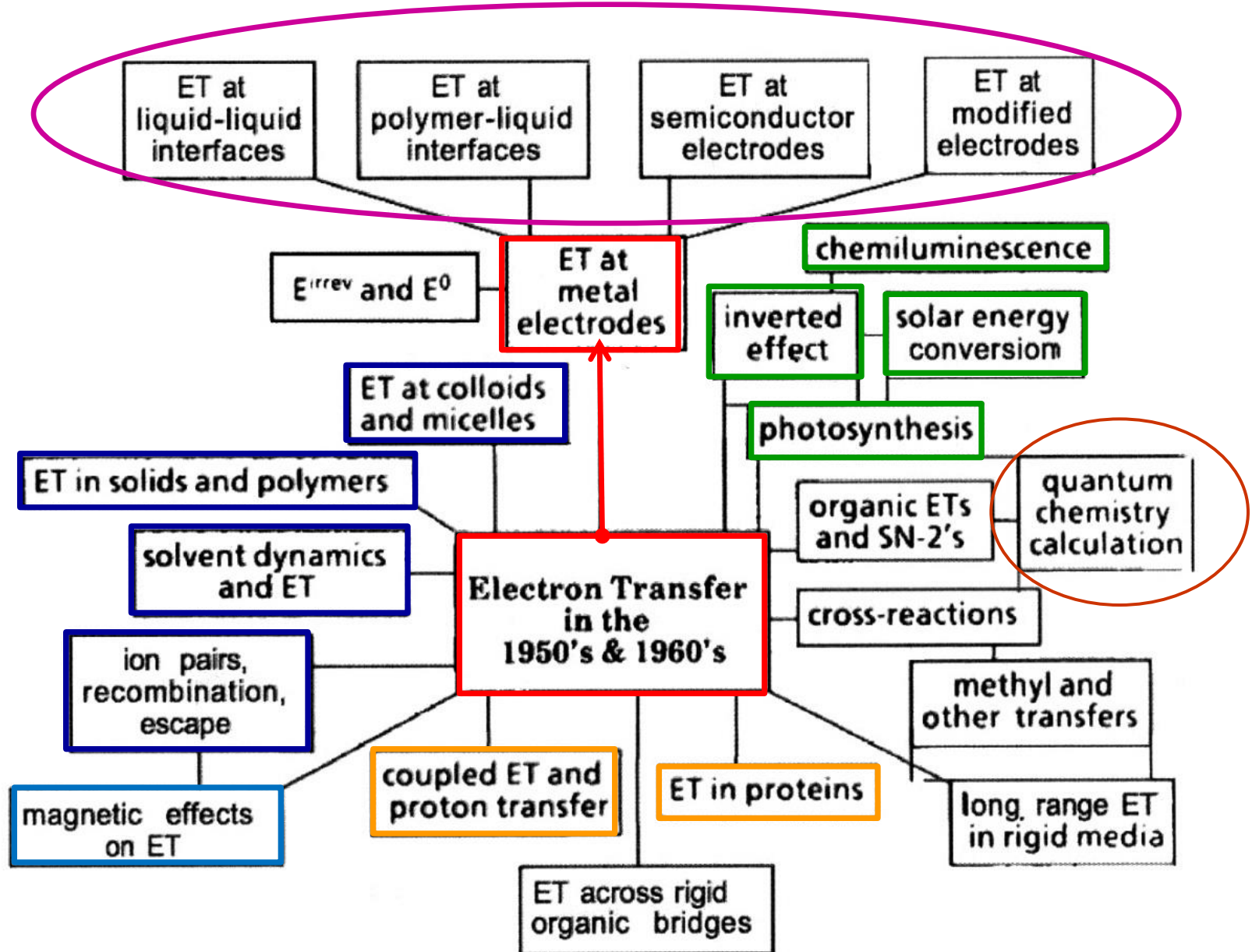


# Electron Transfer

**Electron transfer (ET)** is one of the most important chemical process in nature and it plays a central role in many biological, physical and chemical systems.

- **ET** may be one of the most basic forms of chemical reaction but without it life cannot exist.
- **ET** is one of the simplest forms of a chemical reaction!?!
- **ET** occurs in photosynthetic reaction center where transfer of electrons is used to create charge imbalance across a membrane, originating a proton pumping mechanism to produce ATP
- **ET** respiration and detoxification
- **ET** at the metal surface with oxygen is responsible of the corrosion.
- **ET** in solid state electronics (the control of the ET in semiconductors) - the new area of molecular electronics depends critically on the understanding and the control of the transfer of electrons in and between molecules.

# some fields related to the ET



# Rudolph A. Marcus



Born: July 21, 1923 (age 91)  
Montreal, Quebec

American, Canadian  
Alma mater: McGill University

**Nobel Prize in Chemistry: 1992**

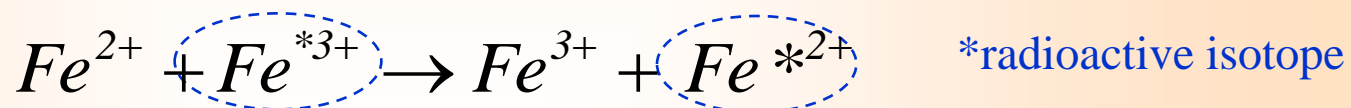
outer-sphere electron transfer was  
based on a transition-state theory  
approach

The Marcus theory of electron transfer was then extended to include  
inner-sphere electron transfer (is ET) by Noel Hush and Marcus



# Marcus theory of ET

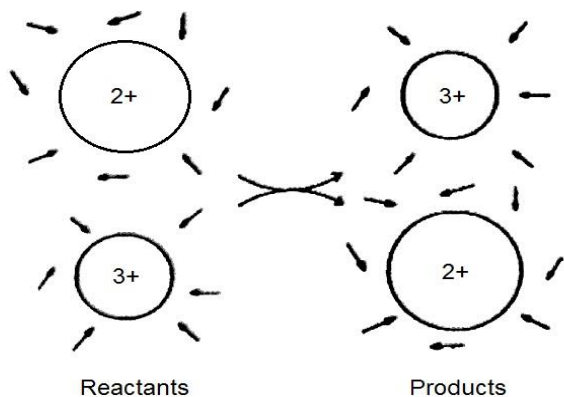
- Nobel Prize in 1992 (the first formulation in 1956)
- “isotopic exchange reactions” (self-exchange reactions) and later “cross reactions”



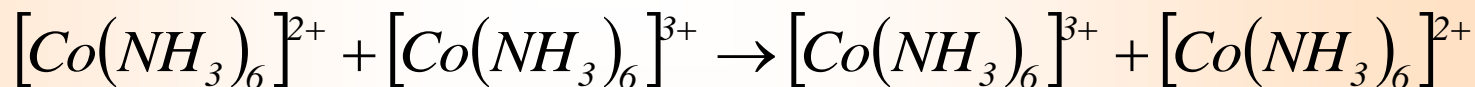
simple ET reactions

- for the reaction-rate of electron transfer: **AB + C → A + BC**
- Bill Libby 's publication (Franck-Condon principle)
- in an **ET** from one reacting ion or molecule to another, the two new ions or molecules formed are in the wrong environment of the solvent molecules since the nuclei do not have time to move during the fast electron jump
- “solvation energy barrier” for the **ET** process

# Marcus theory of ET

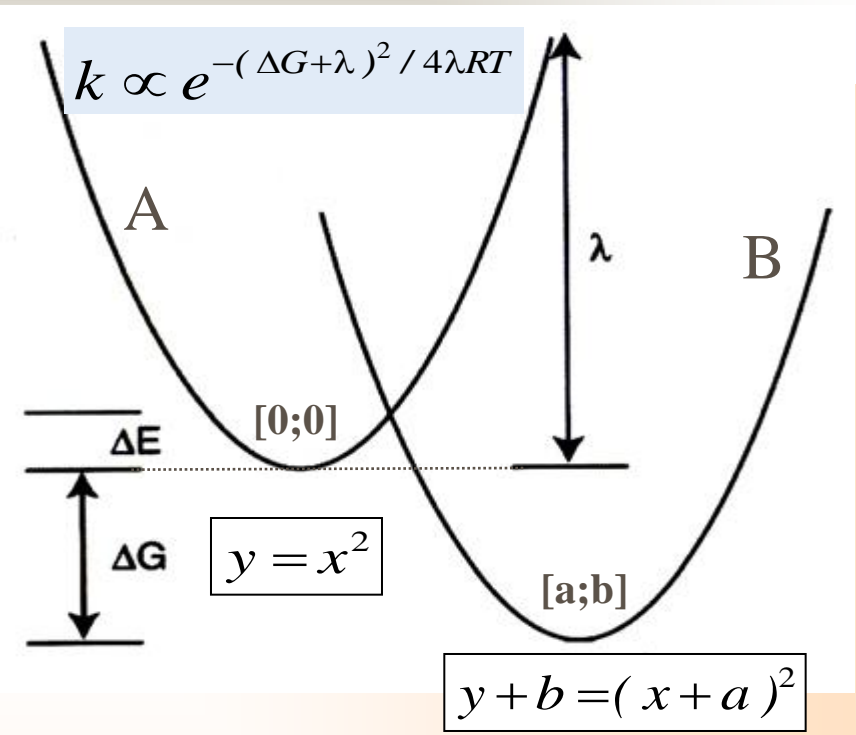
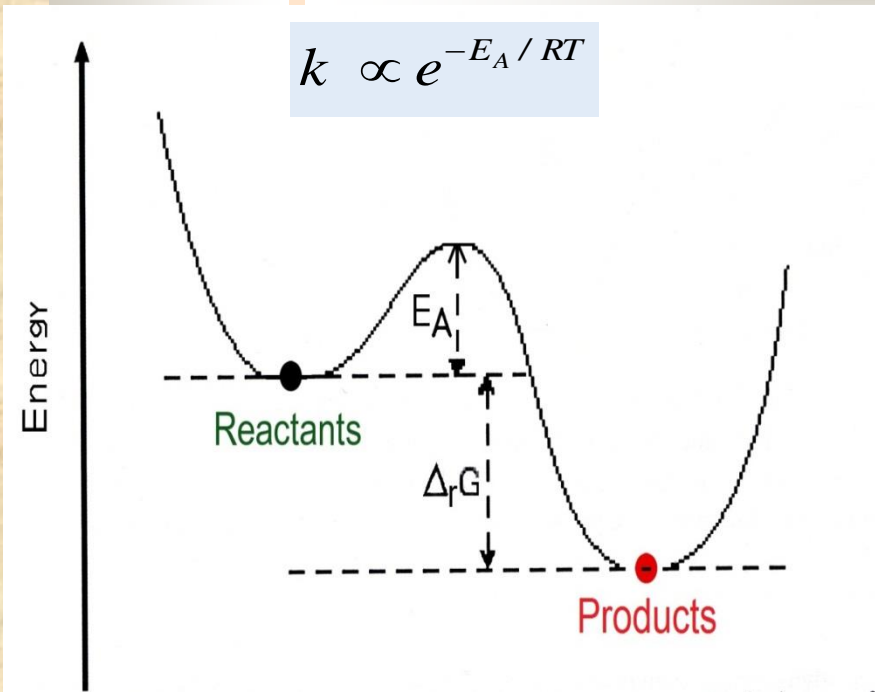


Typical nuclear configurations for reactants, products and surrounding solvent molecules in reaction. The longer M-OH<sub>2</sub> bond length in the state +2 is indicated schematically by the larger ionic radius.



- the reaction is really slow, in contrast to the picture of a **ET** governed by the “**solvation energy barrier**”
- there is a dramatic difference in the equilibrium Co-N bond length in the 3<sup>+</sup> and 2<sup>+</sup> ions so that each ions would be formed in a very “**foreign**”**configuration** of the vibrational coordinates
- **ET** implies **changing in the chemical structure of the reactants**
- the foreign environment for the new electronic state after the electronic jump can be seen as an **energetic barrier for the ET** process.

# Classical theory of ET



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

$$y = x^2 = x^2 + 2ax + a^2 - b$$

$$x = \frac{b - a^2}{2a}$$

$$y = x^2 = \frac{(b - a^2)^2}{4a^2}$$

$$k = ce^{-\beta r} e^{-(\Delta G + \lambda)^2 / 4\lambda RT}$$

$$\Delta E = \frac{(\Delta G - \lambda)^2}{4\lambda}$$

$\beta$ .....the interaction between A and D

$r$  .....the distance between A and D

$\lambda$ .....the reorganization energy

- transfer from a donor (D) to an acceptor (A) during a transition state
- distance between the D and A
- the probability that an ET will decrease with increasing distance
- factors that control the rate constant ( $k_{ET}$ ) involved in a unimolecular ET
- the probability of ET is identified by the term  $kT/h$ , include: the distance D-A complex; the Gibbs energy of activation ( $\Delta G$ ); and the reorganization of energy ( $\lambda$ ).

## Questions:

- The physical meaning of the reorganization energy  $\lambda$ ?
- The relationship between changes in  $\Delta G$  and  $\lambda$ , when the rate constant is the maximum.
- The increase of the rate constant when we go to more negative values of  $\Delta G$ ?
- If we increase the distance between the electron donor and the acceptor of 5 angstroms, we find that the rate constant (ET) decreased 10 times. What is the value of  $\beta$ ?
- At 37° C the rate constant was twice 0° C. Assuming that the equilibrium constant of the reaction is about 100 (in favor of product) and in the temperature range of approximately independent of temperature, which is the reorganization energy of reaction ( $\Delta G = \Delta G_0$ )?



# Odpovědi:

The physical meaning of the reorganization energy  $\lambda$ ?

...konfigurace jader reaktantů – konfigurace jader produktů bez ET...

The relationship between changes in  $\Delta G$  and  $\lambda$ , when the rate constant is the maximum

.....

$$k = ce^{-\beta r} e^{-(\Delta G + \lambda)^2 / 4\lambda RT}$$

$$\Delta G < 0$$

$$\lambda > 0$$

The increase of the rate constant when we go to more negative values of  $\Delta G$ ?

$$\Delta G < 0$$

$$\lambda > 0$$

spontánní ET

If we increase the distance between the electron donor and the acceptor of 5 angstroms, we find that the rate constant (ET) decreased 10 times. What is the value of  $\beta$ ?

$$k = ce^{-\beta r} e^{-(\Delta G + \lambda)^2 / 4\lambda RT}$$

$$k = ce^{-\beta(r+5)} e^{-(\Delta G + \lambda)^2 / 4\lambda RT}$$

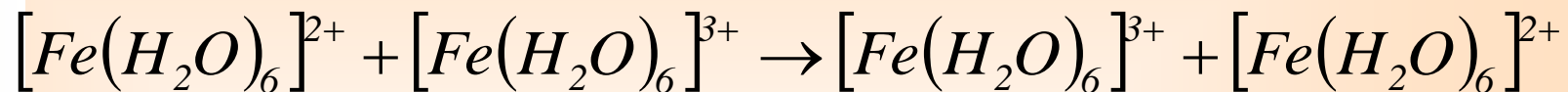
V oblasti ET v proteinech a dalších biochemických materiálech.....charakterizace ET

At 37° C the rate constant was twice 0° C. Assuming that the equilibrium constant of the reaction is about 100 (in favor of product) and in the temperature range of approximately independent of temperature, which is the reorganization energy of reaction ( $\Delta G = \Delta G_0$ )?

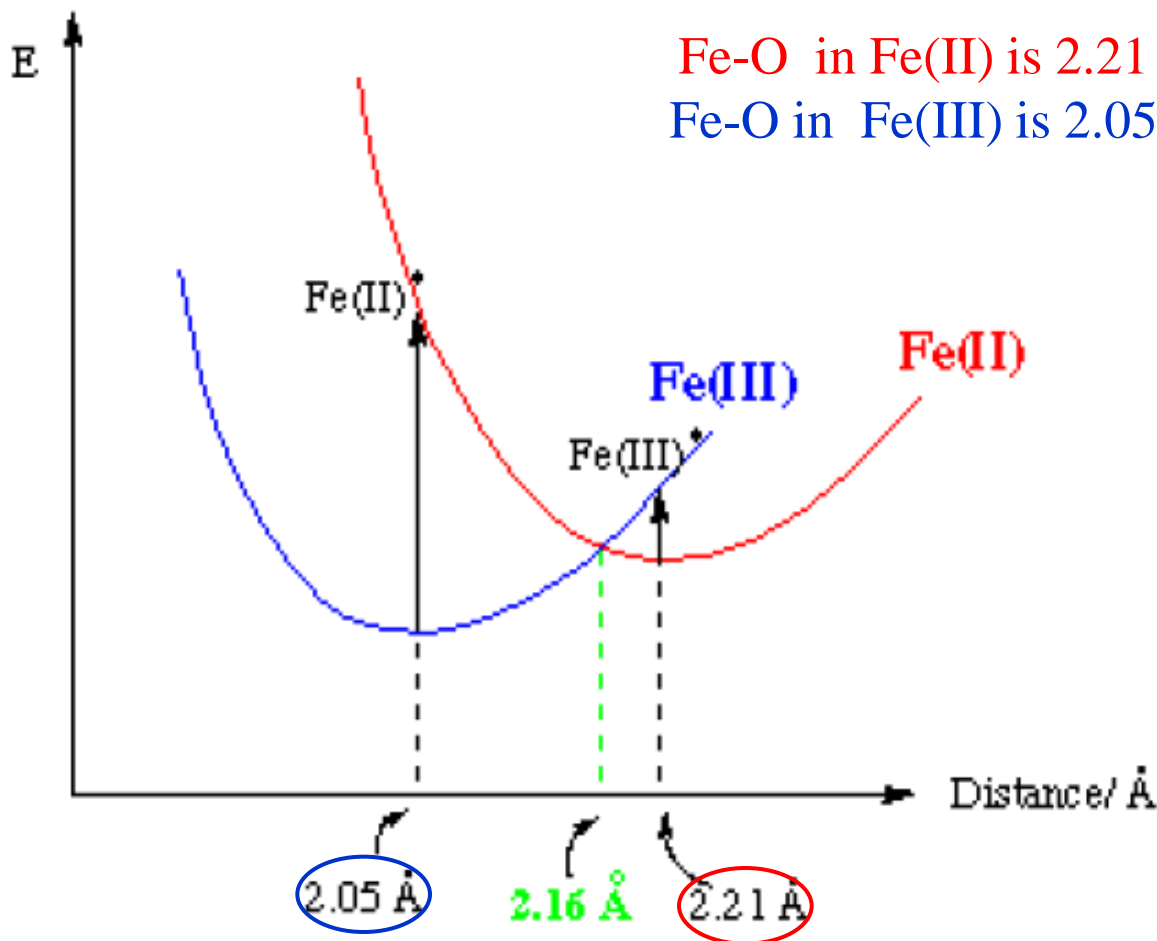
$$k = ce^{-\beta r} e^{-(\Delta G + \lambda)^2 / 4\lambda RT_1}$$

$$k = ce^{-\beta r} e^{-(\Delta G + \lambda)^2 / 4\lambda RT_2}$$

# Marcus theory of ET



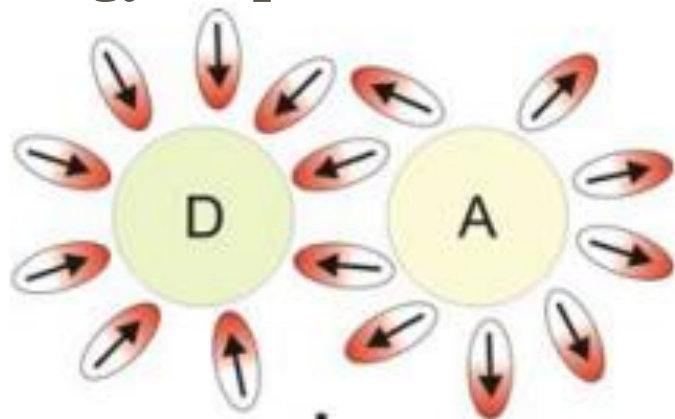
PARABOLIC  
CURVES



# Marcus theory of ET

Displaced Harmonic Oscillator (DHO)  
Energy Gap Hamiltonian (EGH)

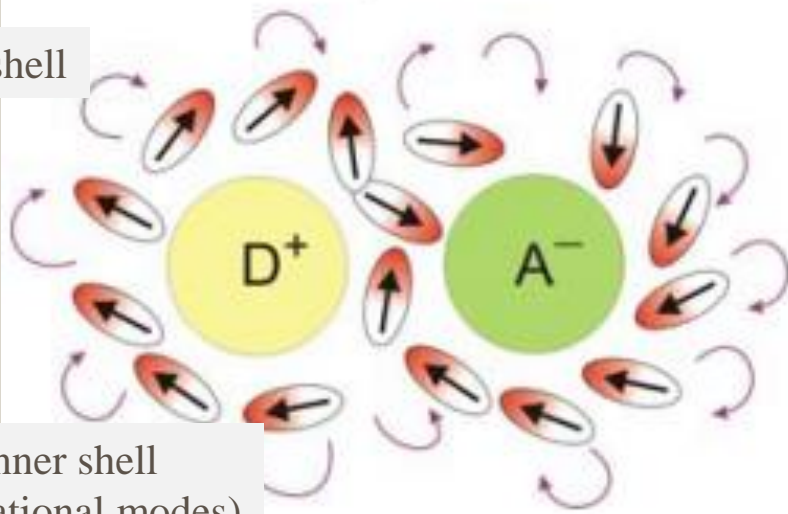
**Describing ET**  
( $e^-$  and  $H^+$ )



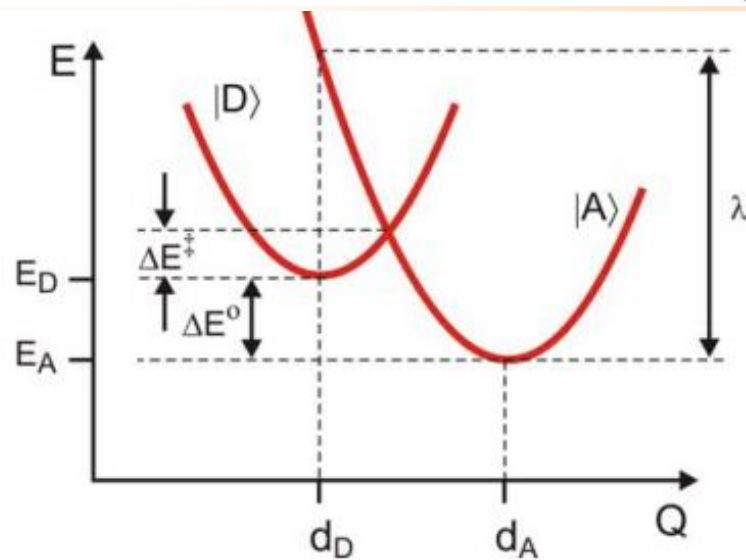
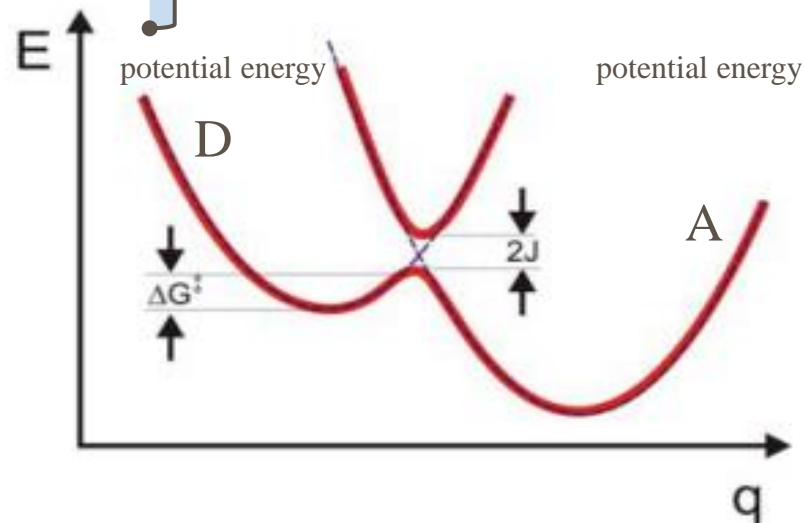
D – donor

A – akceptor

outer shell



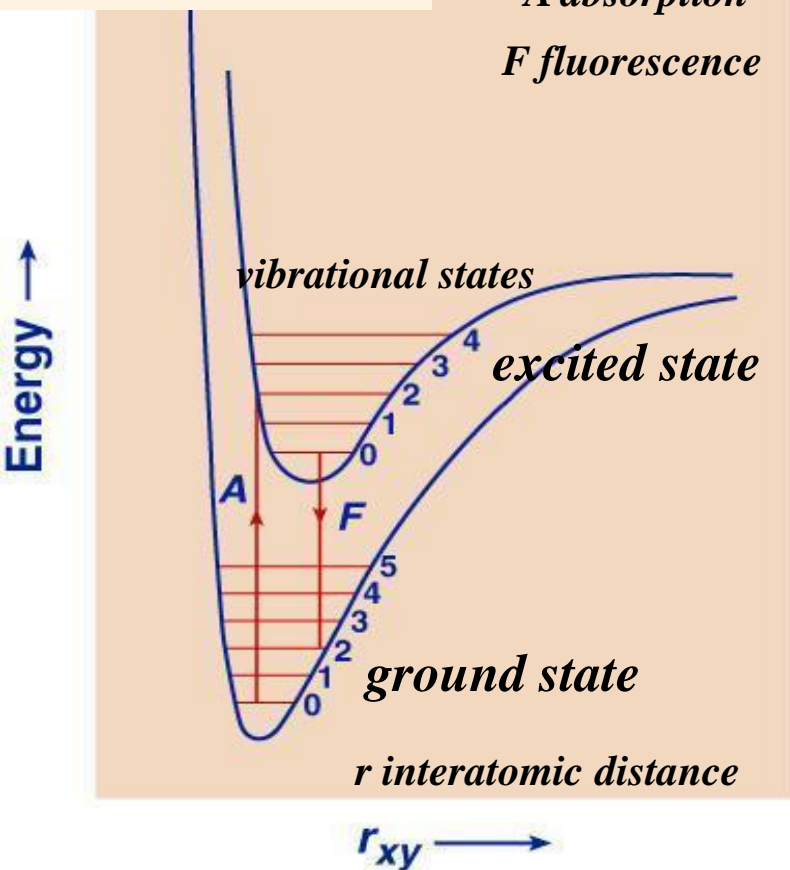
inner shell  
(vibrational modes)



# Electron Transfer Reactions

Jablonski diagram

*A* absorption  
*F* fluorescence



## Franck-Condon principle

ET processes must satisfy the **Franck-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**.
- an electronic transition is most likely to occur without changes in the positions of the nuclei in the molecular entity and its environment. The resulting state is called a **Franck-Condon state**, and the transition involved, a **vertical transition**

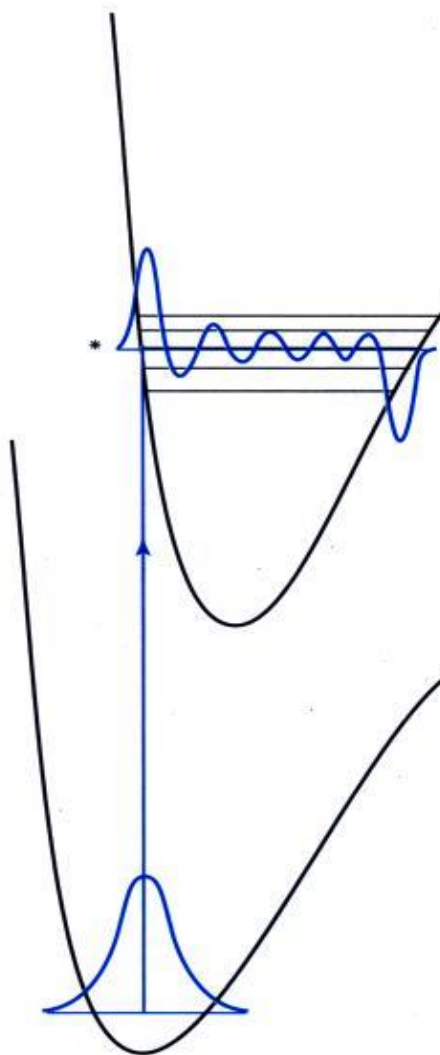
*Potential energy curves for the ground state and an excited state of a diatomic molecule*



# 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



**most closely resembles**



# Marcus theory of ET

- provides a thermodynamic and kinetic framework for describing one electron outer-sphere electron transfer
- **ET** is a mechanistic description of the thermodynamic concept of redox wherein the oxidation states of both reaction partners change

## Classes of electron transfer

- **Inner-sphere electron transfer**  
redox centers are covalently linked via any bridge during the ET
- **Outer-sphere electron transfer**  
redox centers are not covalently linked via any bridge during the ET

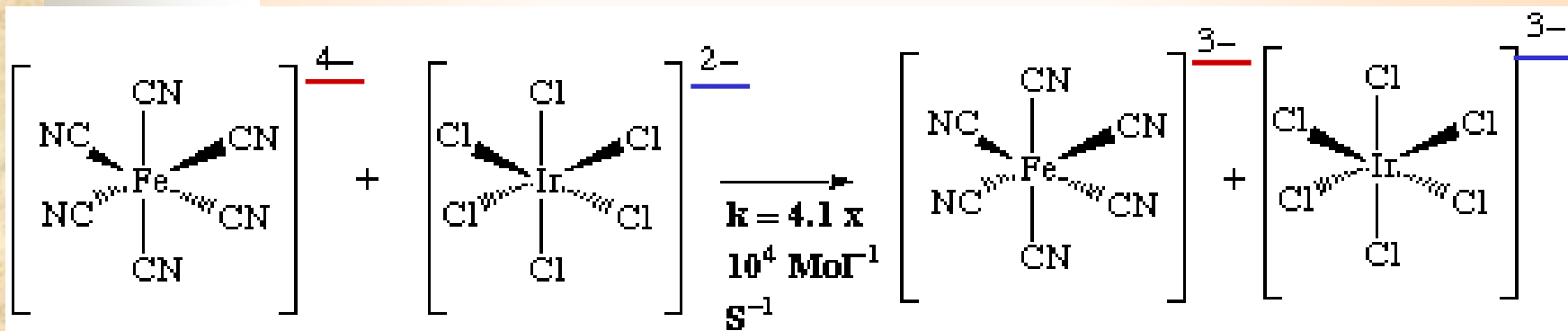
### Five steps of an outer sphere reaction

1. reactants diffuse together out of their solvent shells => precursor complex  
(requires work =  $w_r$ )
2. changing bond lengths, reorganize solvent => activated complex
3. Electron transfer
4. Relaxation of bond lengths, solvent molecules => successor complex
5. Diffusion of products (requires work =  $w_p$ )

# Electron Transfer Reactions in Solutions

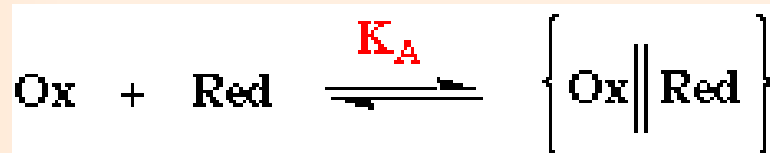
## Outer Sphere Electron-Transfer

In principle all **outer sphere mechanism** involves electron transfer (**ET**) from reductant to oxidant with the coordination shells or spheres of each staying intact. That is one reactant becomes involved in the outer or second coordination sphere of the other reactant and an electron flows from the reductant to oxidant. Such a mechanism is established when rapid **ET** occurs between two substitution complexes.



# Elementary Steps in the Outer Sphere Mechanism

## a) Formation of a precursor (cage) complex



this step is always considered to be fast

## b) Chemical activation of the precursor, electron transfer (ET) and relaxation of the successor complex



Important factors are:

- (i) Solvent reorganization
- (ii) Electronic structure
- (iii) M-L reorganization small

## c) Dissociation to the separated products



$$k_{\text{obs}} = K_A k_{el}$$

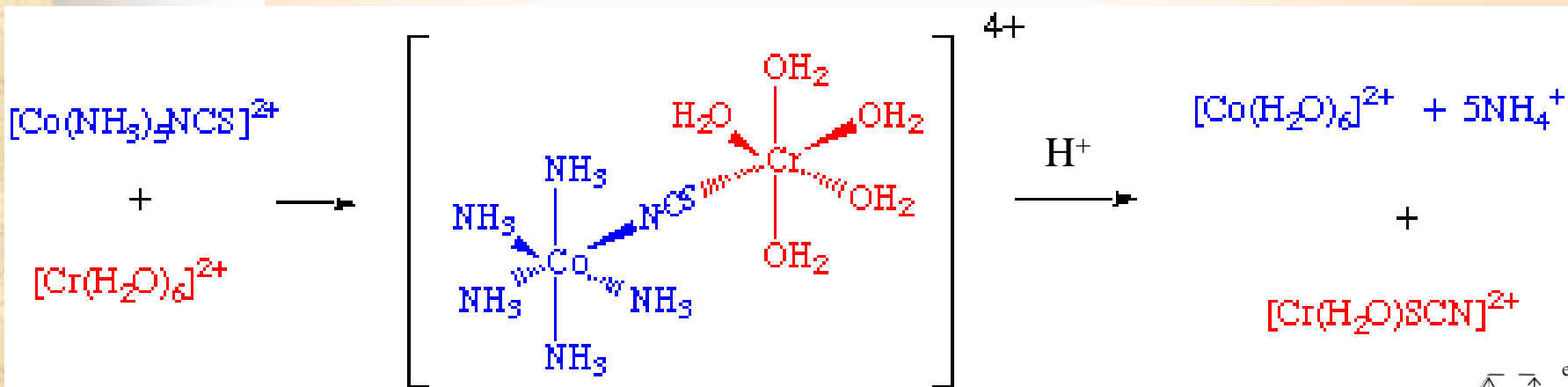
the rate observed is determined by  $K_A$  and  $k_{el}$



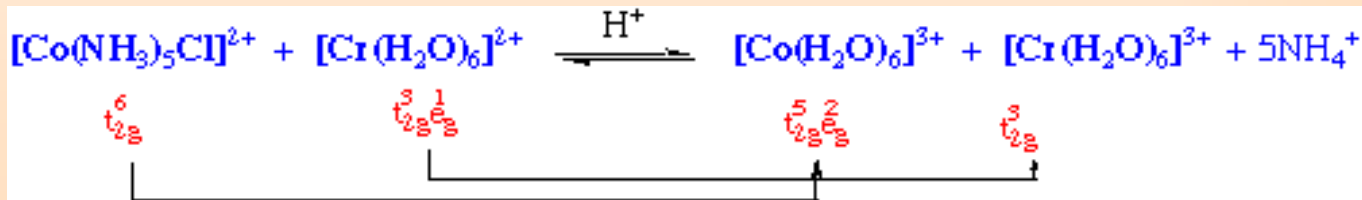
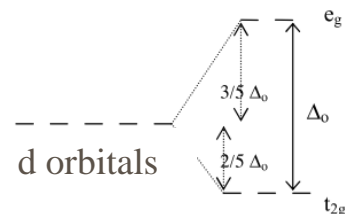
# Electron Transfer Reactions in Solutions

## Inner Sphere Electron-Transfer

An inner sphere mechanism is one in which the reactant and oxidant share a ligand in their inner or primary coordination spheres the electron being transferred across a bridging group.

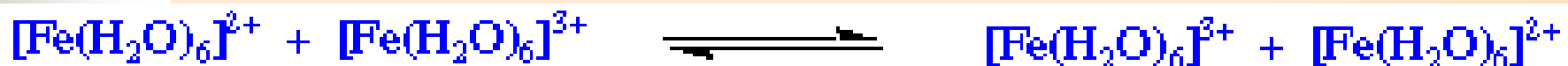


$t_{2g}$  ... the representations of the d-orbitals of transition metals



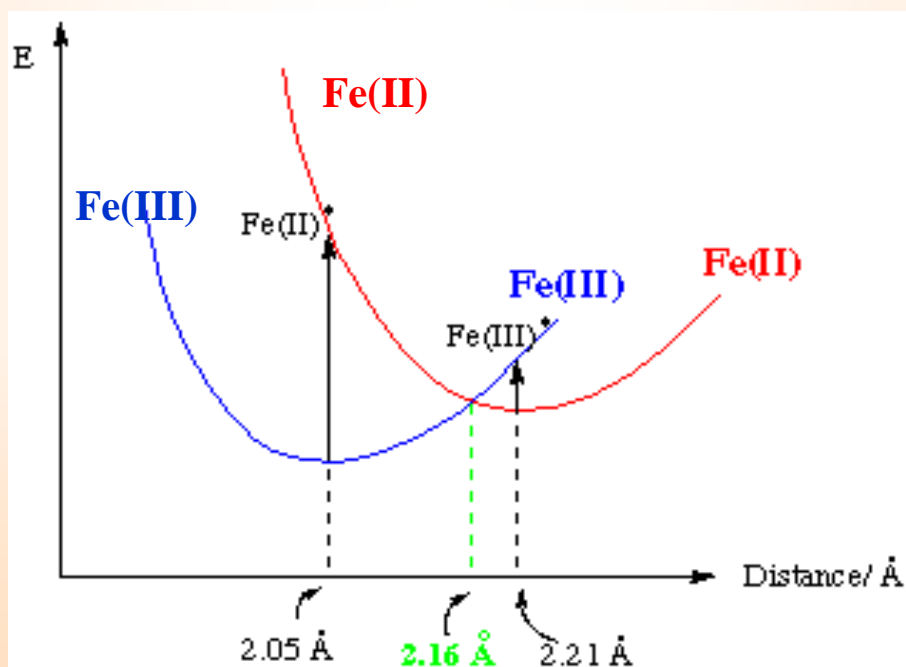
$e_g$  and  $t_{2g}$  .... 2- en 3-dimensional representations in the 48-fold cubic point group  $O_h$ . The g in the subscript denotes inversion symmetry.

# Franck-Condon principle

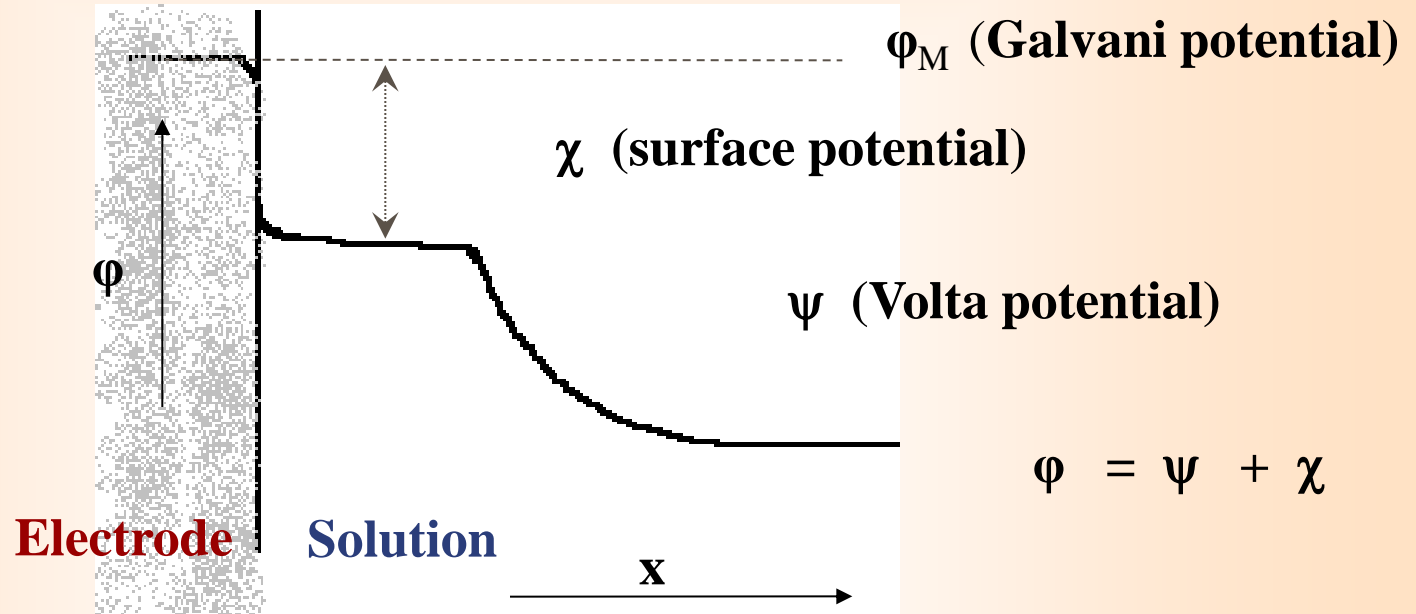


Fe—O = 2.21 Å

Fe—O = 2.05 Å



## The solid metallic electrode

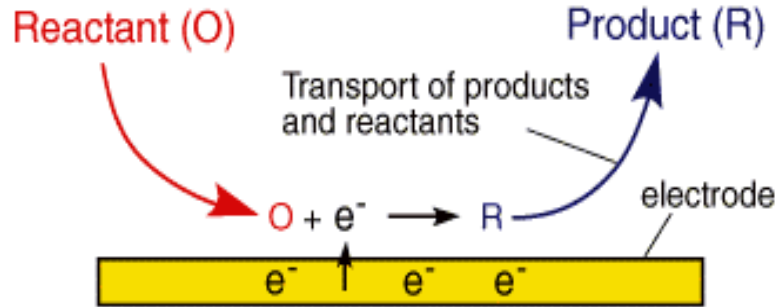


$\phi_M$  (Galvani potential – inner potential) is associated with  $E_F$

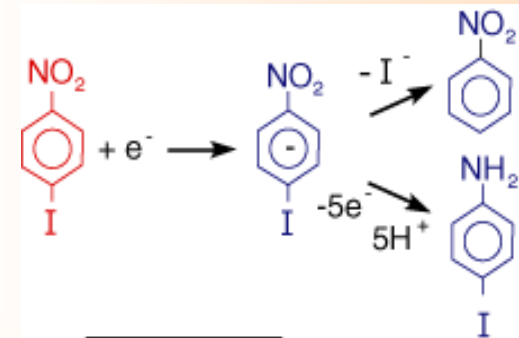
$\psi$  (Volta potential – outer potential) is associated with the potential outside the electrode's electronic distribution

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

# Electrode reactions

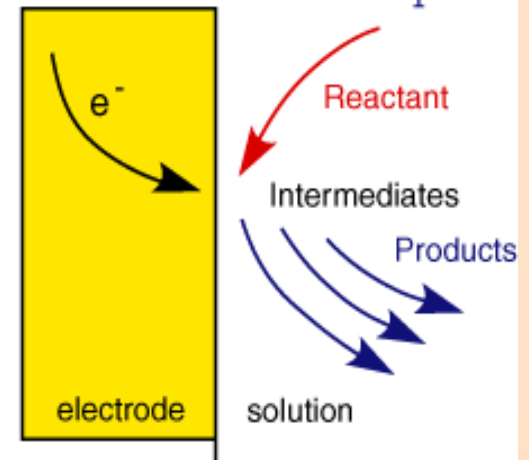
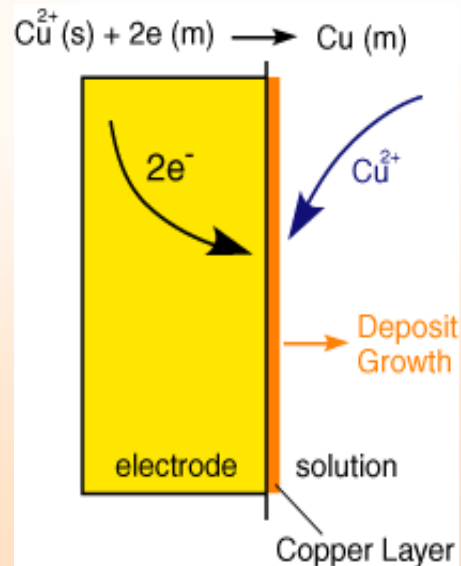
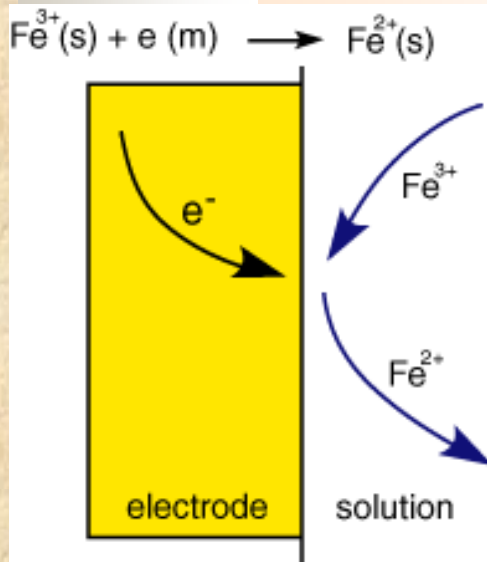


*Electron transfer followed by chemical reaction*



*A single electron transfer reaction*

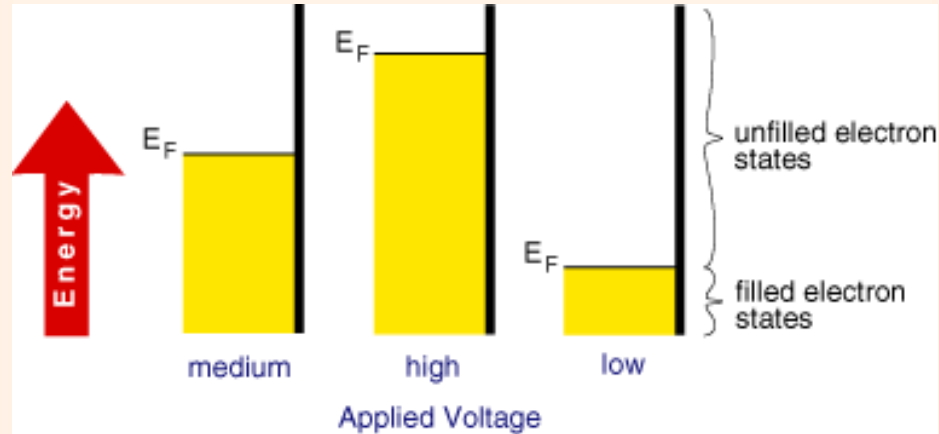
*Copper deposition at a Cu electrode*



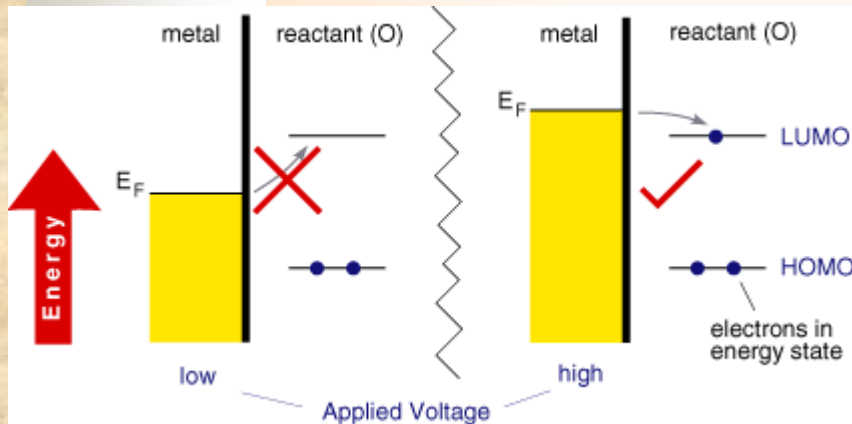


# Applied voltage

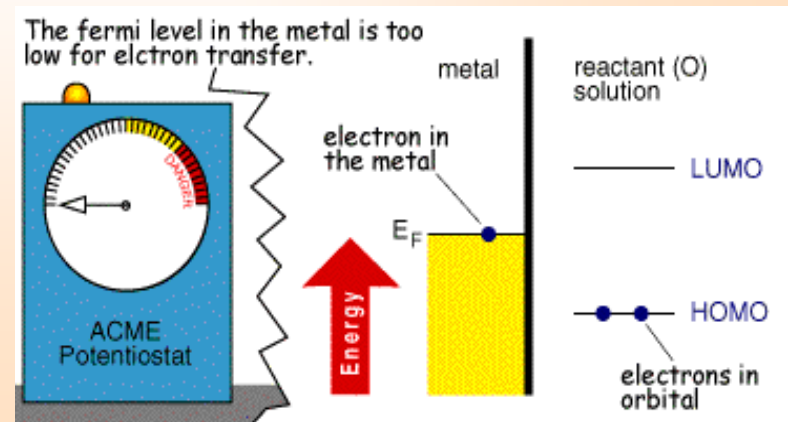
*Representation of the Fermi-level in a metal at three different applied voltages*



*Schematic representation of the reduction of a species (O) in solution*

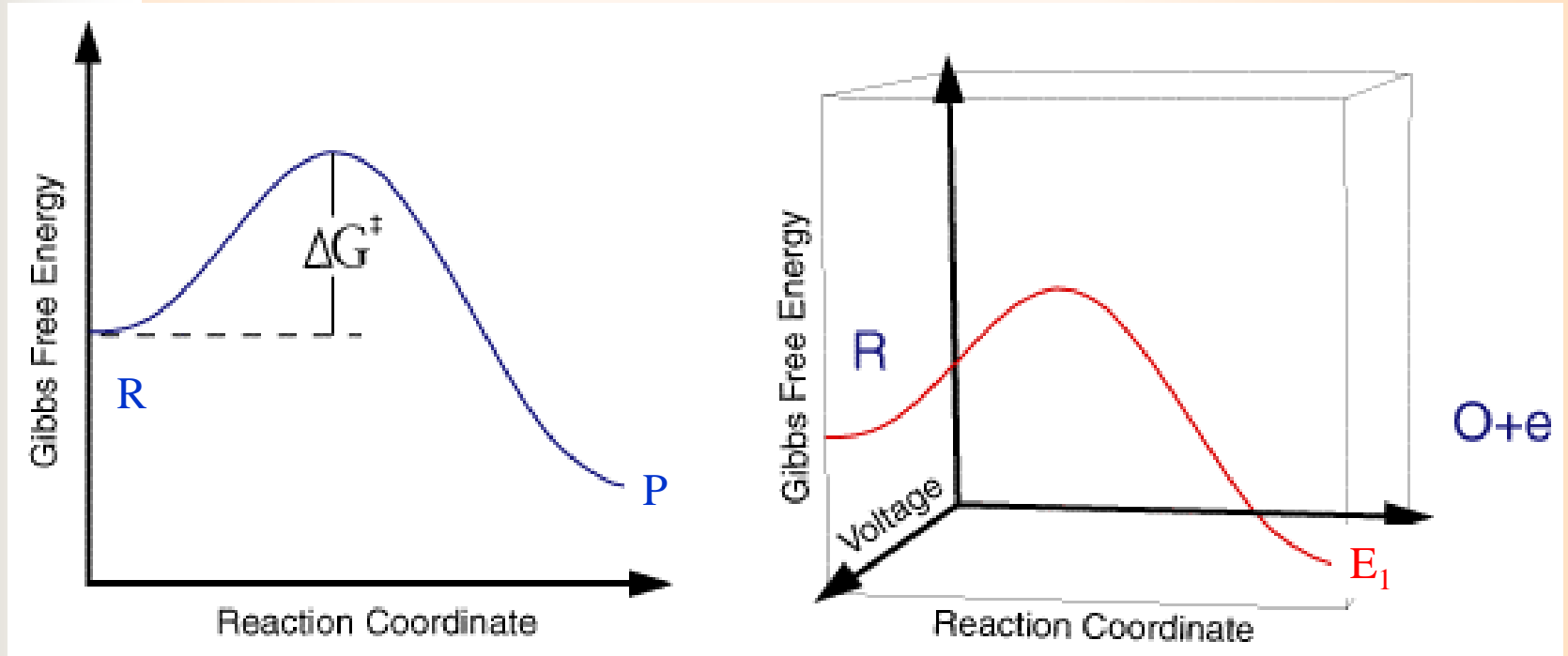


*Animation of the reduction of a species (O) in solution*



# Applied voltage

At voltage E the formation of the species O is thermodynamically favored



The key to driving an electrode reaction is the application of a potential

$$\text{energy} = \text{charge} * \text{potential}$$

$$[J] = [C] * [V]$$

$$[V] = \frac{[J]}{[C]}$$

# Overvoltage - Overpotential

**From without potential insertion on solid phase**

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

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

$$\Rightarrow \eta = E_p - E_r \quad \begin{array}{l} E_p = E_{\text{polarization}} = E_{\text{polarizační}} \\ E_r = E_{\text{equilibrium}} = E_{\text{rovnovážný}} \end{array}$$

**$\Rightarrow$  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)

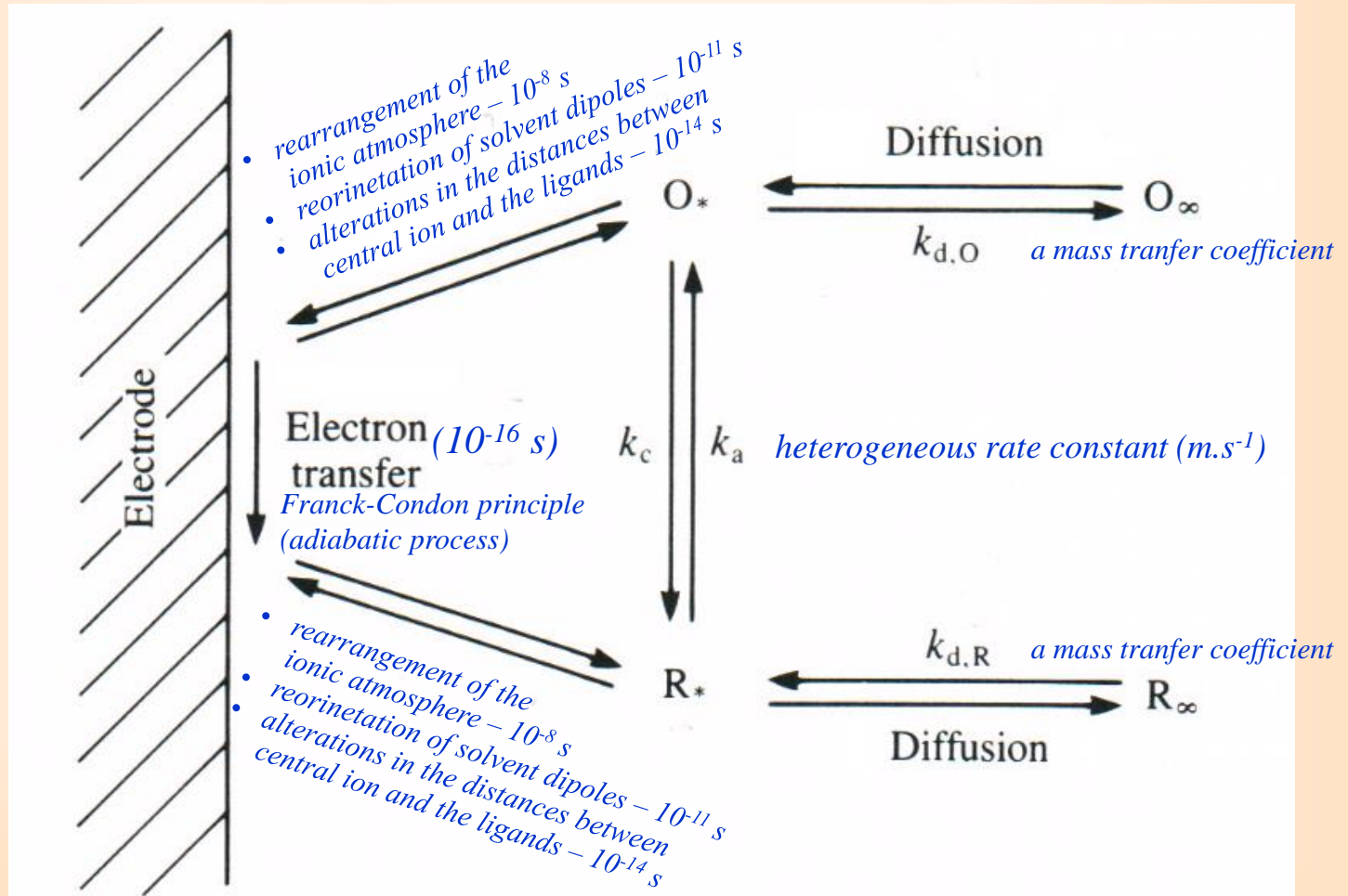
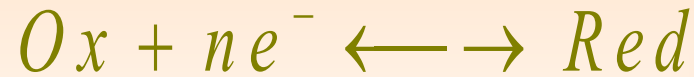
b) Gas products – by bubbling

c) Products can be integrated to an electrode crystal lattice

⇒ **crystallization ( nucleation) overpotential**

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

# Scheme of electron transfer at an electrode



without chemical transformation or breaking chemical bonds

# Electrode kinetics

Phenomenological electrode kinetics: the **Butler-Volmer equation**

John Alfred Valentine **Butler**



Max **Volmer**



**ET reactions at electrode/solution interfaces are activated processes.**

- **ET rate effected by:**
  - Applied electrode potential
  - Temperature
- **Activation energy barrier** height can be effected by applied potential. This is in contrast to ordinary chemical reactions.

$$j = j_0 \{ \exp [(1 - \alpha) f\eta] - \exp [-\alpha f\eta] \} = j_{ox} - j_{red}$$

$$f = \frac{nF}{RT}$$





# Electrode kinetics

**We seek an answer to the following questions:**

- How can we quantitatively model the rate of an ET process which occurs at the interface between a metallic electrode and an aqueous solution containing a redox active couple?
- How can kinetic information about ET processes be derived?

We shall also investigate the influence of material transport, and double layer structure on interfacial ET processes.

<http://www.ceskatelevize.cz/porady/10121359557-port/501-pribeh-kapky/video/>





# Basic concepts of electrode kinetics

For an interfacial ET process:

- current flow is proportional to reaction flux (rate)
- reaction rate is proportional to reactant concentration at interface.

As in chemical kinetics:

- the constant of proportionality between reaction rate  $v$  ( $\text{mol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ ) and reactant concentration  $c$  ( $\text{mol}\cdot\text{cm}^{-3}$ ) is termed **the rate constant  $k$  ( $\text{cm}\cdot\text{s}^{-1}$ )**

**The electrode potential drives ET processes at interfaces**

- generates a large electric field at the el/sol interface
- reduces the height of the activation energy barrier
- increases the rate of the ET reaction
- increases the current

# Electrode kinetics

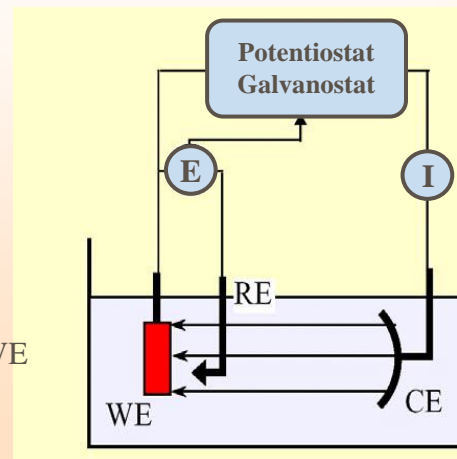
**macroscopic phenomenological approach:** the formal description of electron transfer kinetics in terms of rate equations and current - potential relationships. It is based largely on the activated complex theory of chemical reactions.

**microscopic molecular based approach:** the subject of quantum electrode kinetics. It is based on the molecular interfacial electron transfer with the effects of the molecular structure of the reactant molecules and the electronic band structure of the electrode (GNOME ?)

The  $\text{Fe}^{3+}/\text{Fe}^{2+}$  type of reaction is termed an outer sphere electron transfer process since no bonds are broken or made during the course of the reaction. Consequently, we neglect complicating factors such as diffusional transport of reactants and products, and adsorption effects.

Current is passed between working and counter electrodes. The potential is measured between working and reference electrodes.

Working Electrode – WE



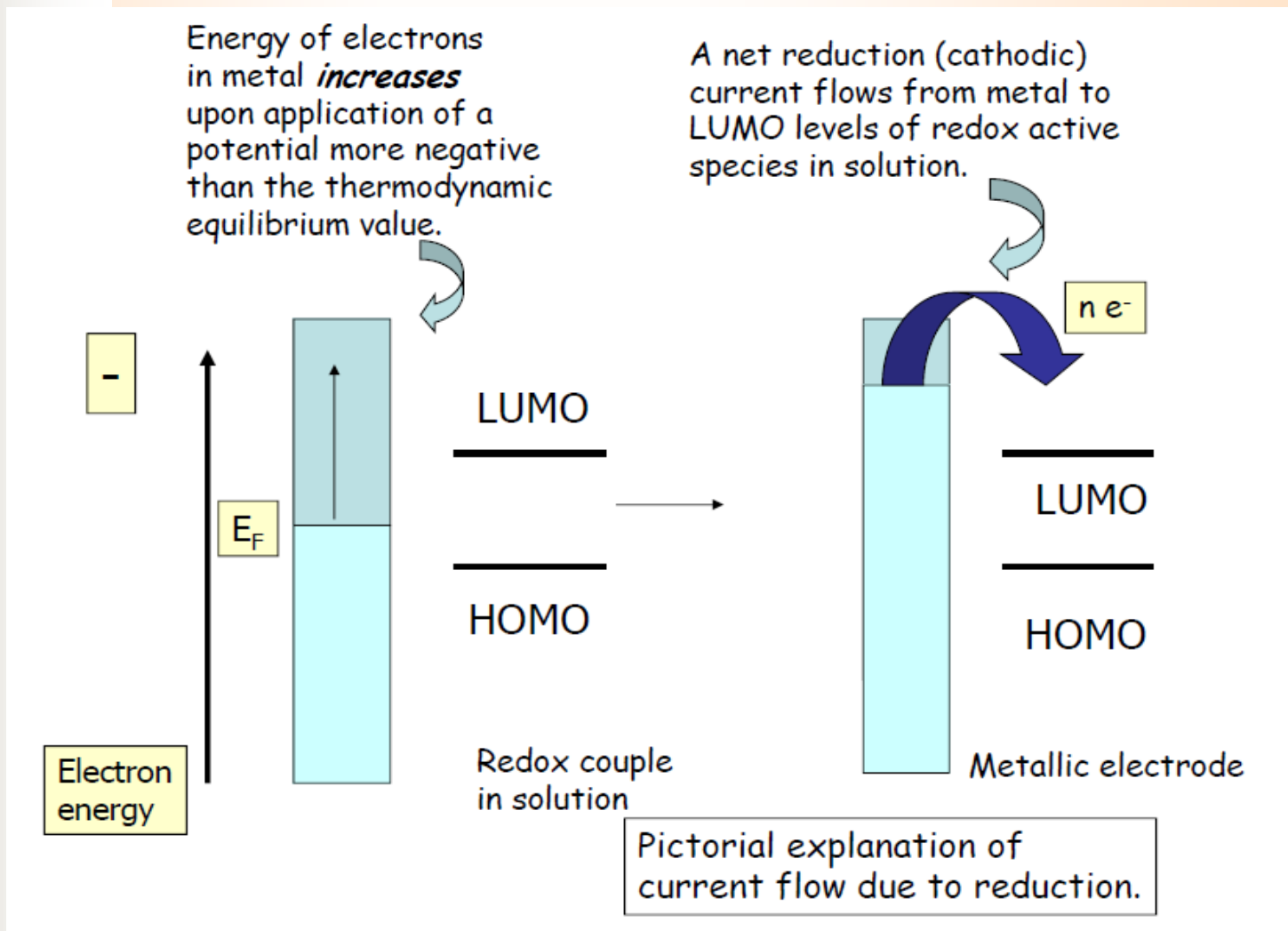
The potential applied to the electrode is controlled using an electronic device called a potentiostat.

Reference Electrode – RE  
(bridge/solution)  
(aqueous/nonaqueous)

Counter Electrode – CE  
Auxillary Electrode – AE

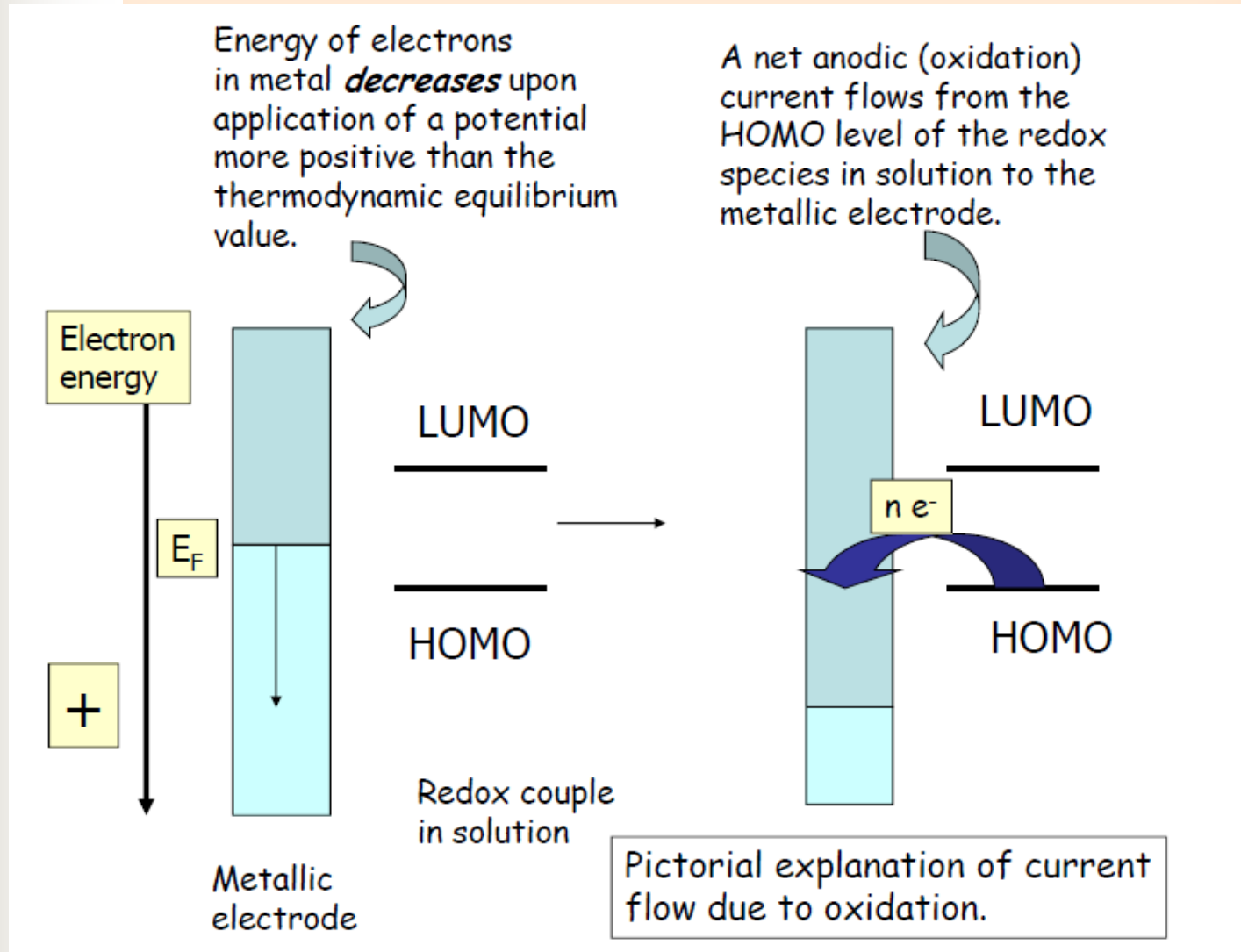
# Electrode kinetics

the electrode acts as an electron source and is termed a cathode



# Electrode kinetics

the electrode acts as an electron sink and is termed an anode



# Electrode kinetics

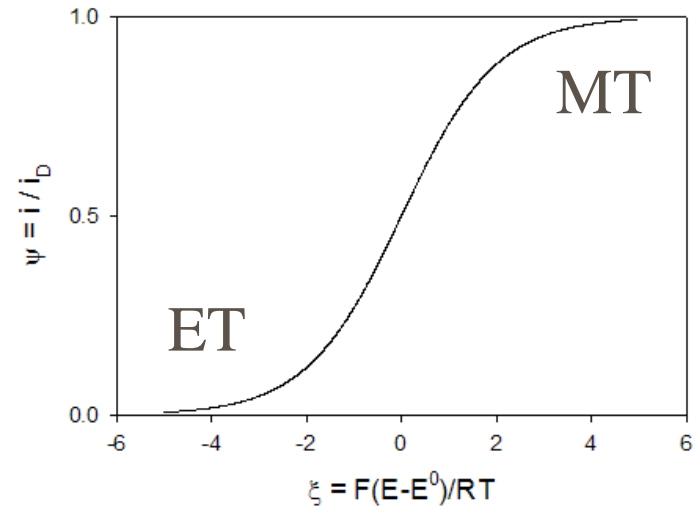
- The current observed at an el/sol interface reflects two quantities:
- Charging of electrical double layer : **non Faradaic charging current  $i_C$**
  - Interfacial ET across interface : **Faradaic current  $i_F$**

at low potentials : arising from **rate determining interfacial ET**,

- at high potentials : arising from **material transport MT** due to diffusion mechanisms.

– These components can be quantified in terms of characteristic rate constants :

$k_0$  (units:  $\text{cm s}^{-1}$ ) for ET and  $k_D$  (units:  $\text{cm s}^{-1}$ ) for MT.



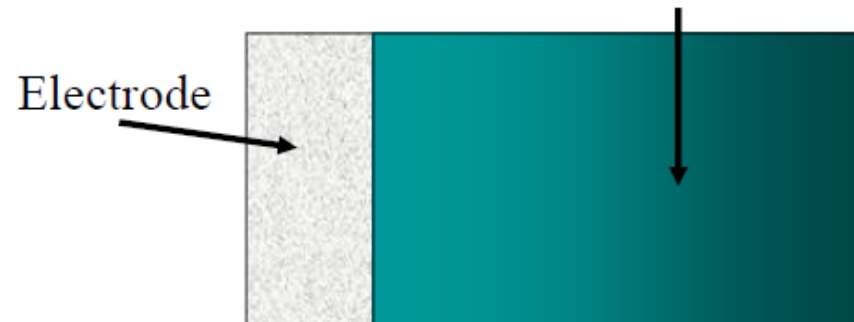
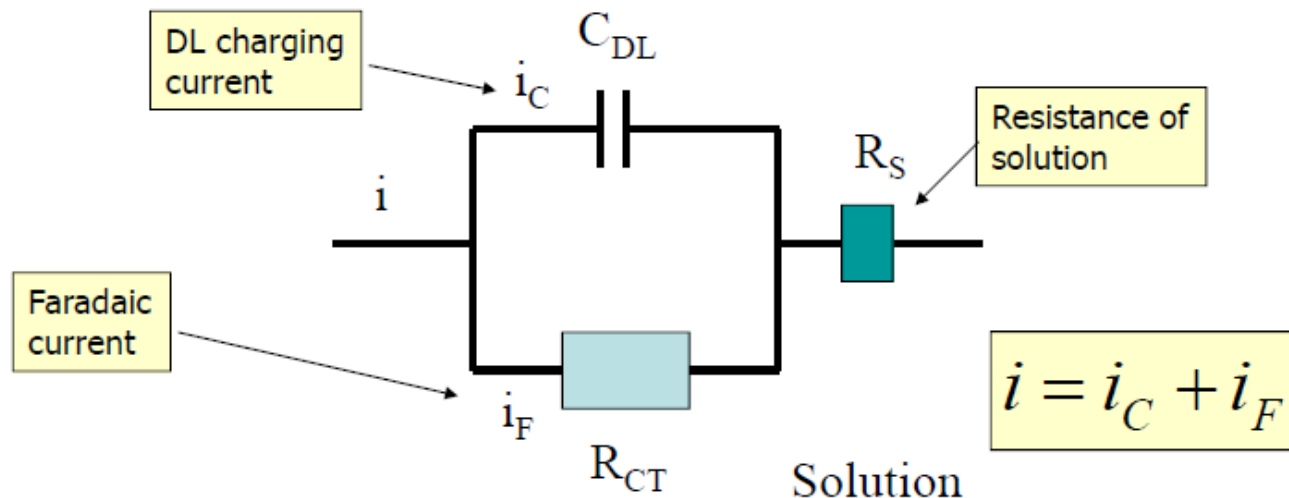


# Electrode kinetics

non Faradaic charging current  $i_C$

Faradaic current  $i_F$

Simple equivalent circuit representation of electrode/solution interface region.



Double layer charging current always present in addition to Faradaic current in electrochemical measurements.

# Velocity of electrode process

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

- for transformation of  $1 \text{ mol}$  of substance with a charge of  $n$  charge of  $nF$  coulomb is consumed ;  $F = 96484 \text{ coulomb/mol}$
- for transformation of  $dN \text{ mol}$  of substance at time  $dt$ , a current  $I$  is consumed

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

$$I = n F S \frac{dN}{dt} = n F S v$$

•  $\xrightarrow{\text{amount of analyt (mols)}}$

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

Current density  $j = \frac{I}{S} = n F \frac{dN}{dt} \frac{1}{S}$   $S = \text{surface (area)}$

Experimental dependences:

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

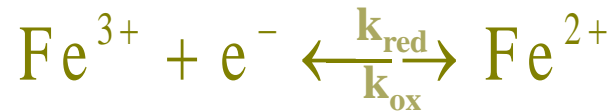
$$\eta = f(j)$$

**polarization curves**

$$j = f(\eta)$$

**current-potential curves**

# Activation overpotential



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

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

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

*S = unit surface*

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

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

# An expression for the rate of electrode reaction

## Arrhenius

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

## Gibbs-Helmholtz

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



QM tunnelling of electrons: time scale is from  $10^{-15}$  to  $10^{-16}$  s

Nuclear motion: about  $10^{-12}$  -  $10^{-13}$  s

# An expression for the rate of electrode reaction

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

$$\alpha_a + \alpha_c = 1$$

$$\alpha_c = \alpha;$$

$$\alpha_a = 1 - \alpha$$

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

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

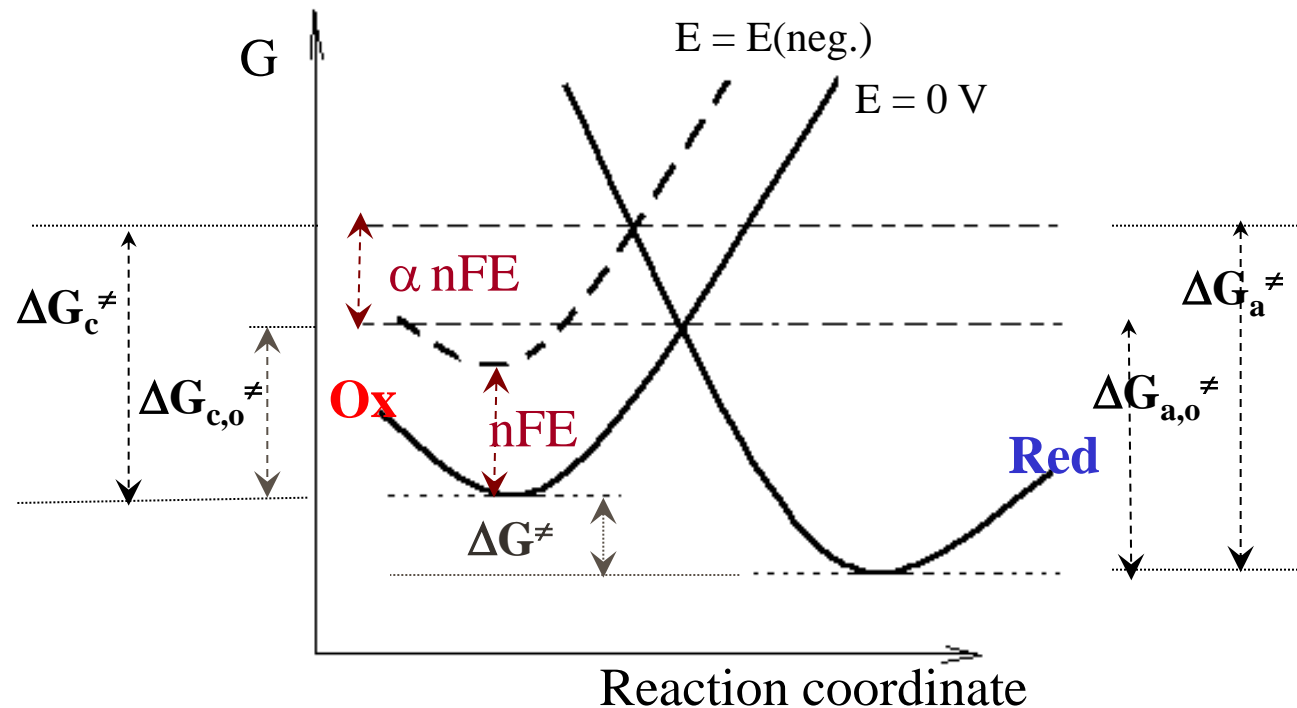
$\Delta\phi$  for reduction ....  $\alpha_c E$

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

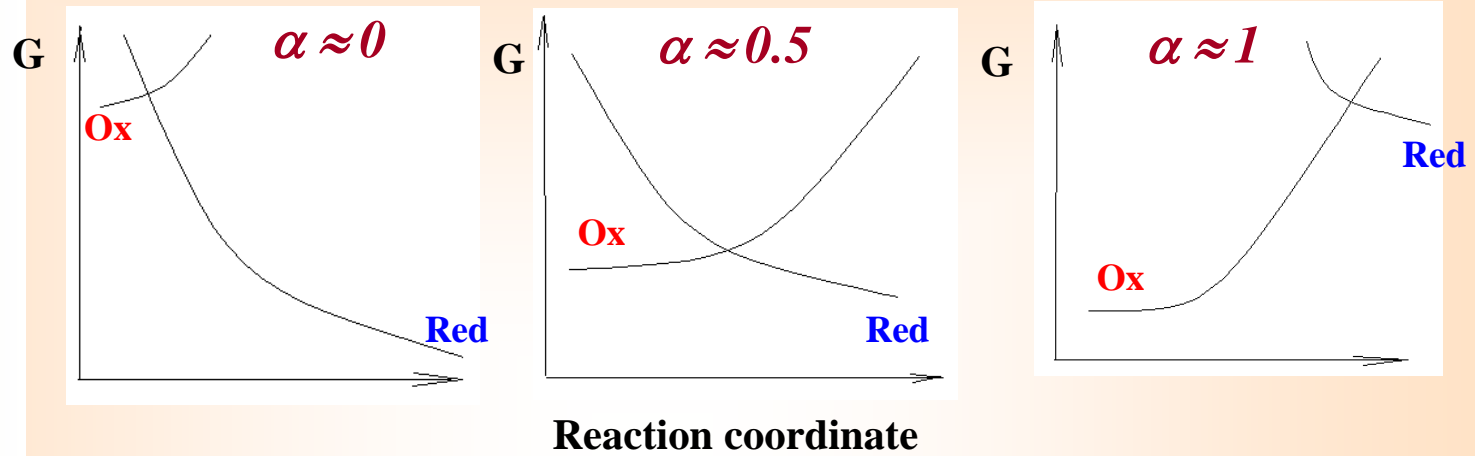
$\alpha_c$  for the cathodic process

$\alpha_a$  for the anodic process

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  $E$ )**

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

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

$$j_{red} = j_c$$

-

$$j_{ox} = j_a$$

+

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

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**

$$f = \frac{nF}{RT}$$

$$j = j_0 \{ \exp [(1-\alpha) f\eta] - \exp [-\alpha f\eta] \}$$

$$f = \frac{nF}{RT}$$

## **Butler- Volmer equation**

$$j = j_0 \{ \exp [(1 - \alpha) f\eta] - \exp [- \alpha f\eta] \}$$



## 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
- ♥  $E_{eq}$  gives the exchange current  $j_0 \Rightarrow$  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

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

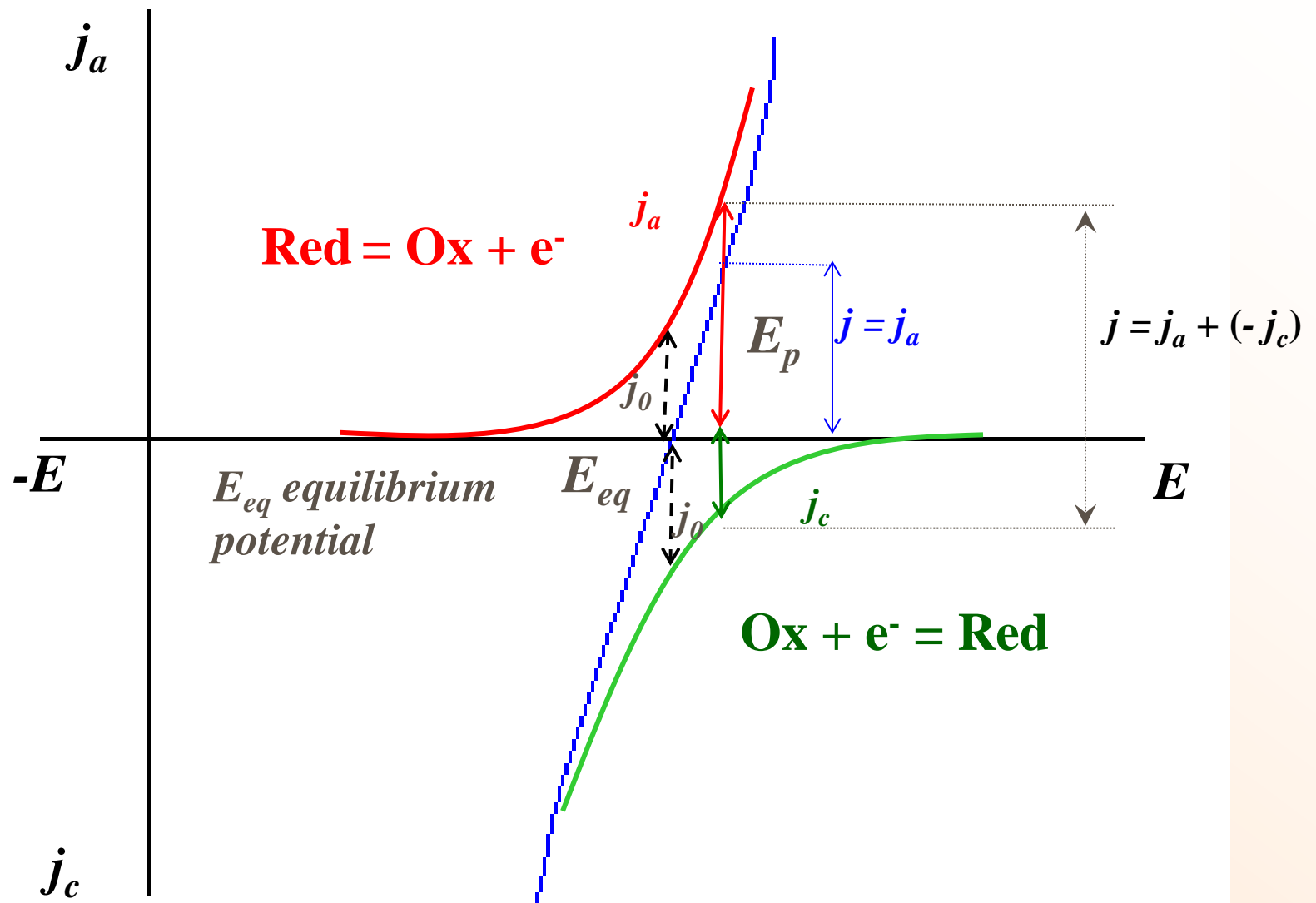
$[Red]_*$   
 $[Ox]_*$  concentrations of Red and Ox next to the electrode

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

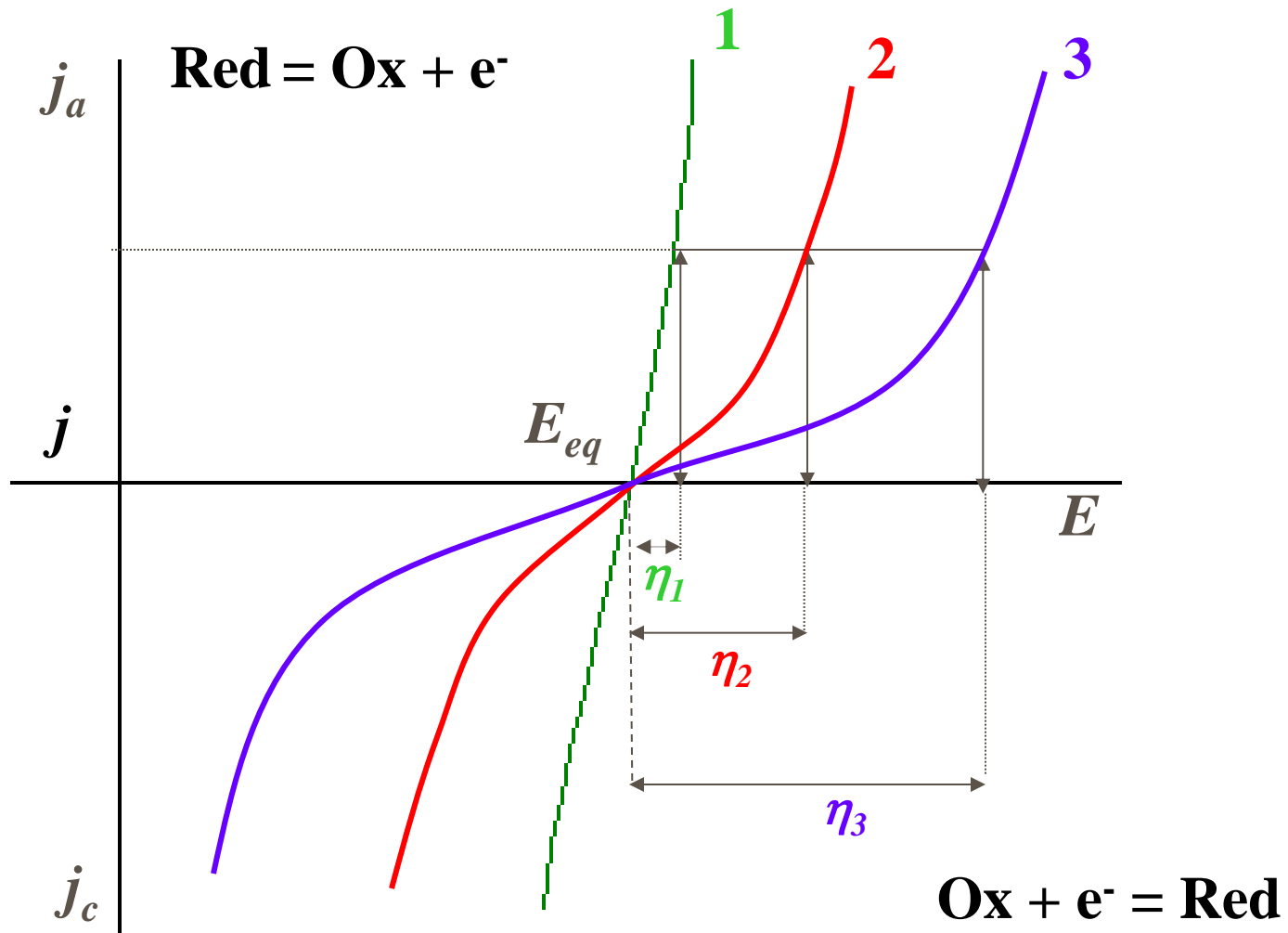
$k_a [Red]_*$  ;  $k_c [Ox]_*$  do not grow indefinitely – limited by the transport of species to electrode

$I_d$  - diffusion-limited current

# Polarization curves without overpotential



# Polarization curves with activation overpotential





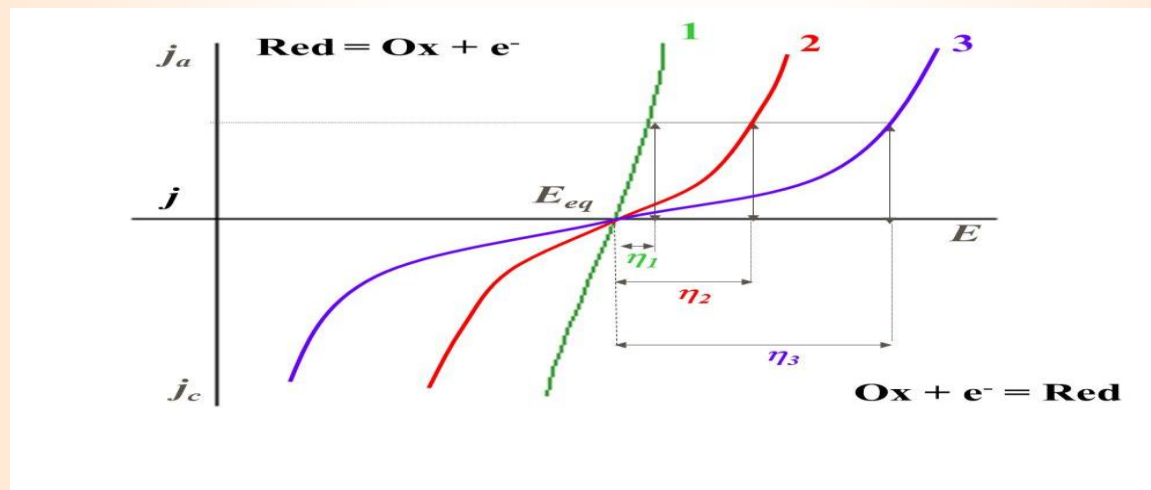
cathodic

Polarization

anodic

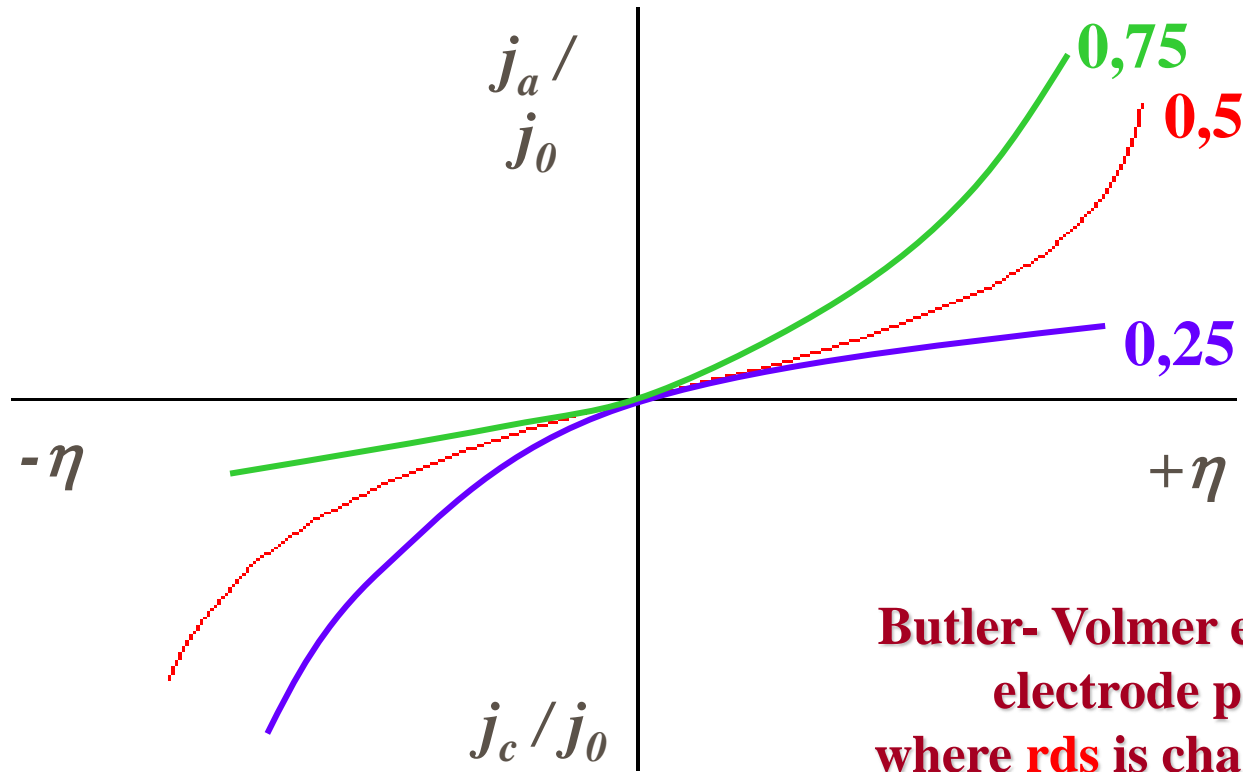
hydrogen overvoltage

oxygen overvoltage



1. Hydrogen ions are absorbed from the solution onto the anode surface.
2. ET occurs from the electrode, the hydrogen ions to form hydrogen.
3. The hydrogen atoms form hydrogen gas molecules.
4. Hydrogen gas bubbles are formed.

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



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

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

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

$$f = \frac{nF}{RT}$$

# Activation Polarization $\eta_{act}$

**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**  $\ln j_a = \ln j_0 + \frac{(1 - \alpha) n F \eta}{R T}$

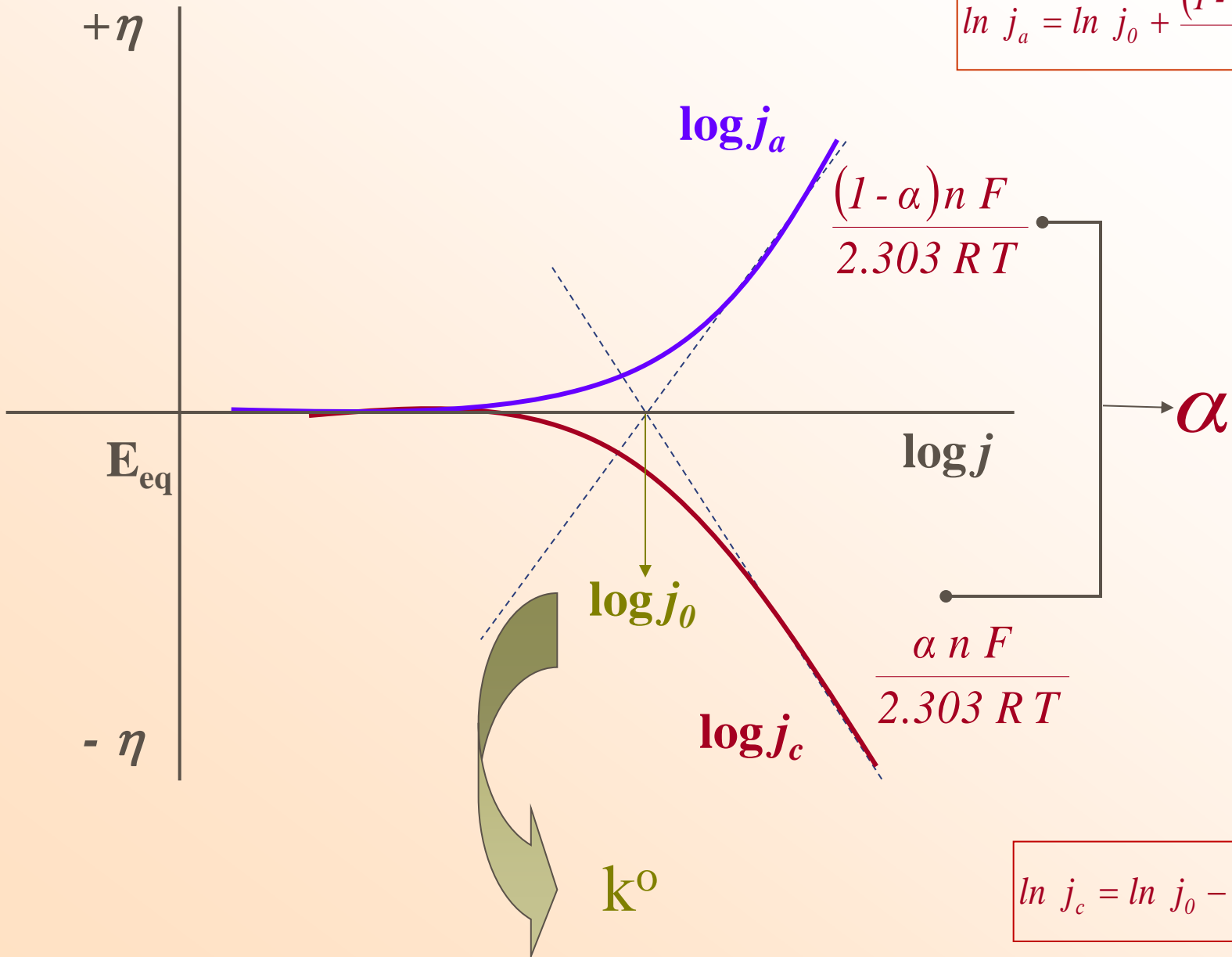
## Tafel relations

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

# Tafel diagram for cathode and anode current density

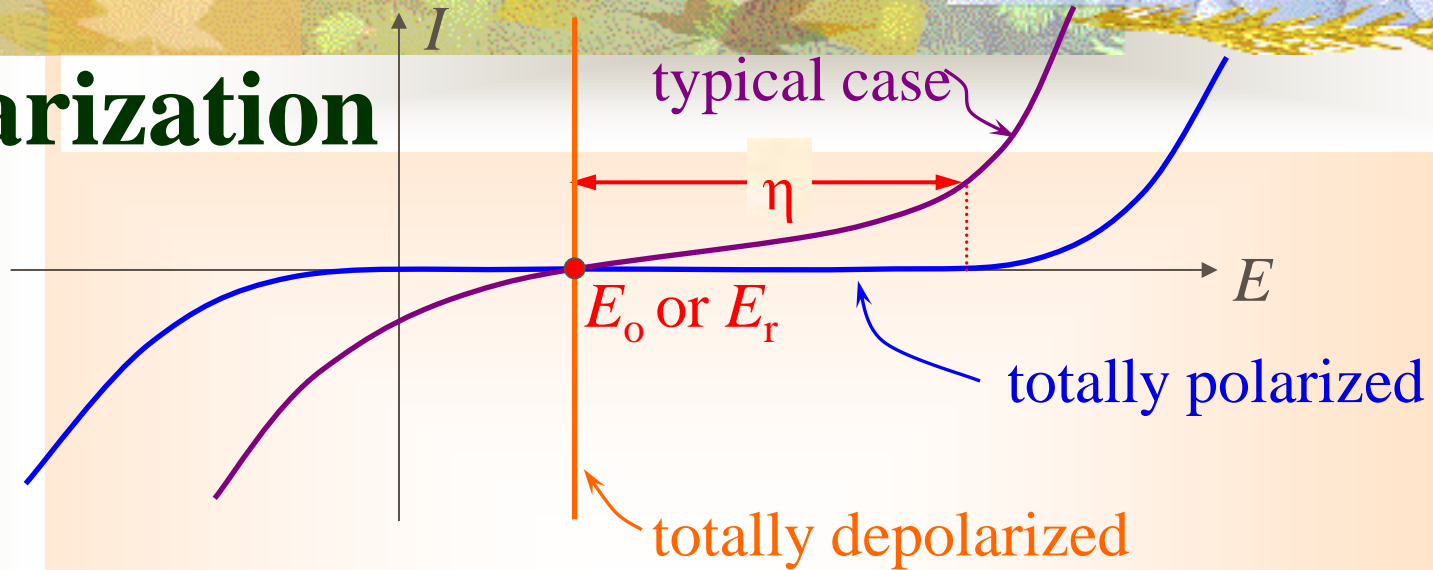
$\alpha = 0.25$        $j_0 = 0.1 \text{ mA}$

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



$$\ln j_c = \ln j_0 - \frac{\alpha n F \eta}{R T}$$

# Polarization



$\eta = \text{overvoltage} = E - E_o \text{ or } E - E_r$   
 (eta)

$\eta = f(I)$

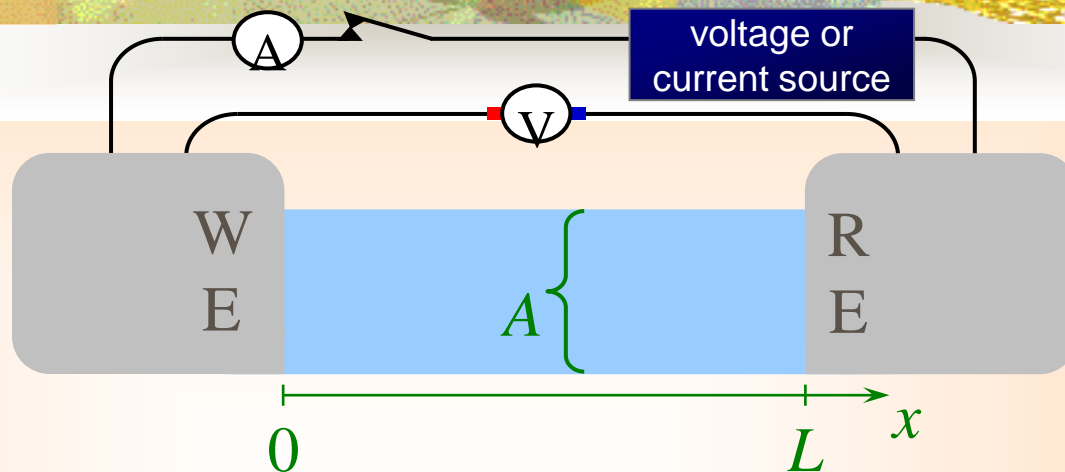
polarization = {  
 ohmic polarization  
 activation polarization  
 concentration polarization

$\eta = \eta_{\text{ohm}} + \eta_{\text{act}} + \eta_{\text{conc}}$



# Resistance (Ohmic) polarization

$\eta_{ohm}$



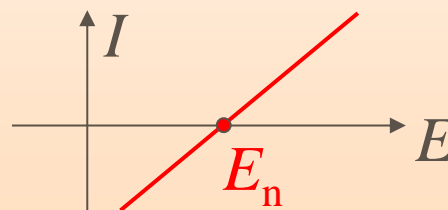
$$\eta_{ohm} = \phi(0) - \phi(L) = - \int_0^L d\phi = \int_0^L \frac{idx}{\kappa} = \frac{I}{\kappa} \int_0^L \frac{dx}{A} = \frac{IL}{\kappa A} = IR$$

$\phi(0)$  and  $\phi(L)$  are potentials in solution.  
 $i = -\kappa \frac{d\phi}{dx}$  is Ohm's Law.  
 $i = \frac{I}{A}$   
 $R = \frac{L}{\kappa A}$

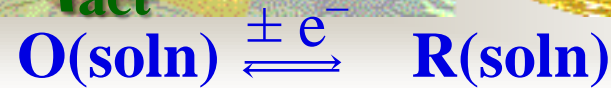


$$\eta_{ohm} = \phi(a) - \phi(\infty) = - \int_a^{\infty} d\phi = \int_a^{\infty} \frac{idr}{\kappa} = \frac{I}{\kappa} \int_a^{\infty} \frac{dr}{A(r)} = \int_a^{\infty} \frac{Idr}{2\pi r^2 \kappa} = \frac{I}{2\pi \kappa A}$$

$\eta_{ohm} = "IR \text{ drop}"$



# Activation polarization $\eta_{act}$



Butler  
Volmer

$$I = AFk^{o'} \left[ c_R^s \exp \left\{ \frac{(1-\alpha)F}{RT} (E - E^{o'}) \right\} - c_O^s \exp \left\{ \frac{-\alpha F}{RT} (E - E^{o'}) \right\} \right]$$

Nernst

$$I = AFk^{o'} (c_O^b)^{1-\alpha} (c_R^b)^\alpha \left[ \frac{c_R^s}{c_R^b} \exp \left\{ \frac{(1-\alpha)F}{RT} (E - E_n) \right\} - \frac{c_O^s}{c_O^b} \exp \left\{ \frac{-\alpha F}{RT} (E - E_n) \right\} \right]$$

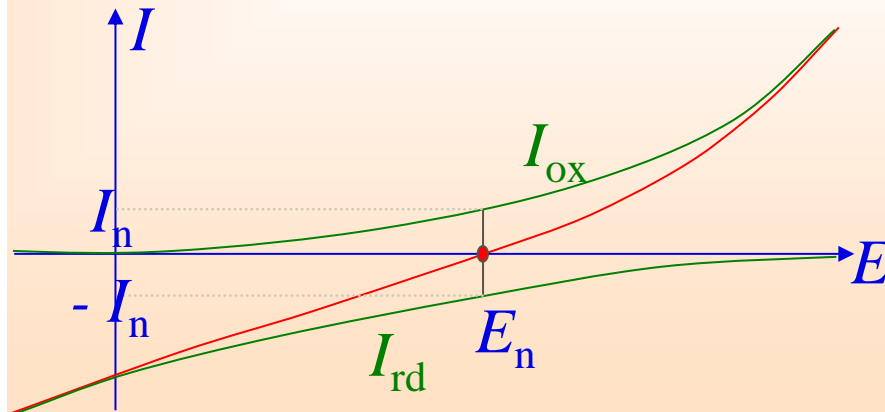
Activation  
only

$$I = AFk^{o'} (c_O^b)^{1-\alpha} (c_R^b)^\alpha \left[ \exp \left\{ \frac{(1-\alpha)F}{RT} \eta_{act} \right\} - \exp \left\{ \frac{-\alpha F}{RT} \eta_{act} \right\} \right]$$

Split

$I_n =$  exchange current

$$I = I_n \exp \left\{ \frac{(1-\alpha)F}{RT} \eta_{act} \right\} - I_n \exp \left\{ \frac{-\alpha F}{RT} \eta_{act} \right\} = I_{ox} + I_{rd}$$



# Activation polarization $\eta_{act}$

At very positive  $E$   $|I_{ox}| \gg |I_{rd}|$

$$I \approx I_{ox} = I_n \exp\left\{\frac{(1-\alpha)F}{RT} \eta_{act}\right\}$$

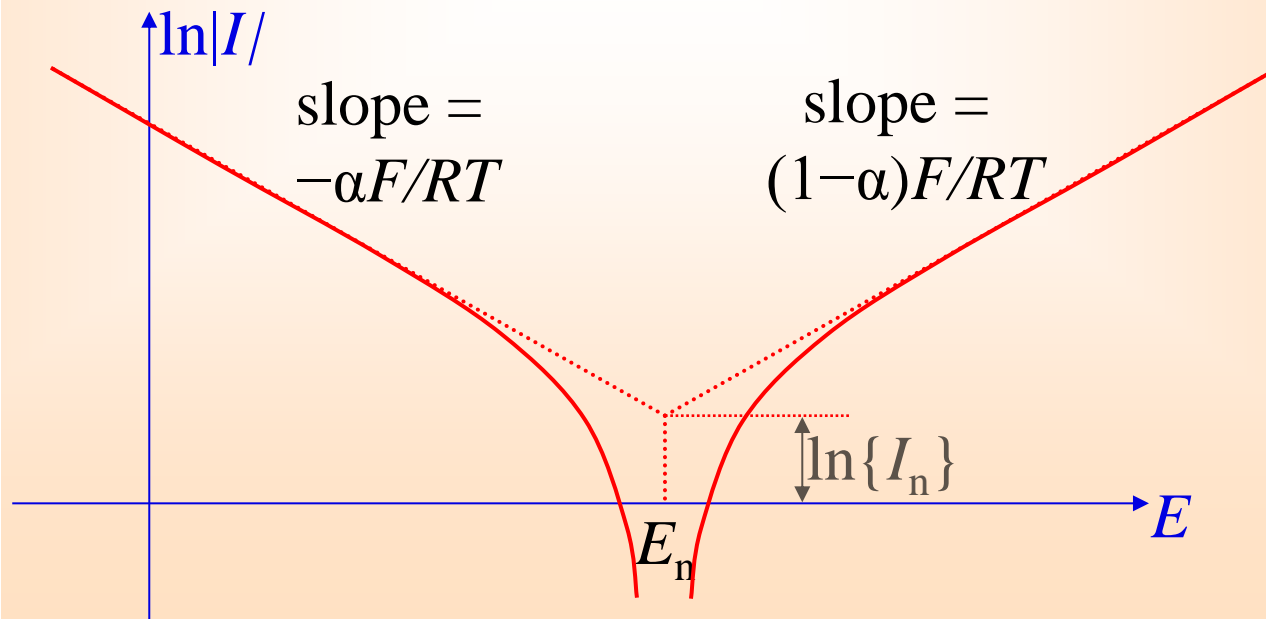
$$\ln\{I\} = \ln\{I_n\} + \frac{(1-\alpha)F}{RT}(E - E_n)$$

$$-I \approx -I_{rd} = I_n \exp\left\{\frac{-\alpha F}{RT} \eta_{act}\right\}$$

Tafel equations

Similarly at very negative  $E$   $|I_{rd}| \gg |I_{ox}|$

$$\ln\{-I\} = \ln\{I_n\} - \frac{\alpha F}{RT}(E - E_n)$$



# Activation polarization $\eta_{act}$

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

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

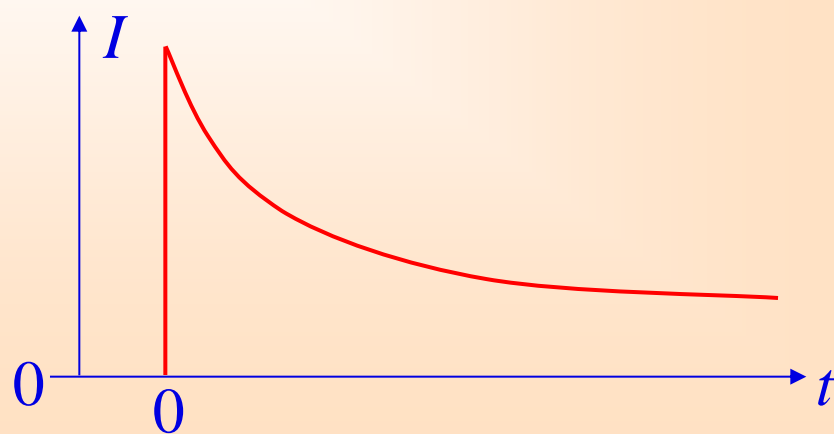
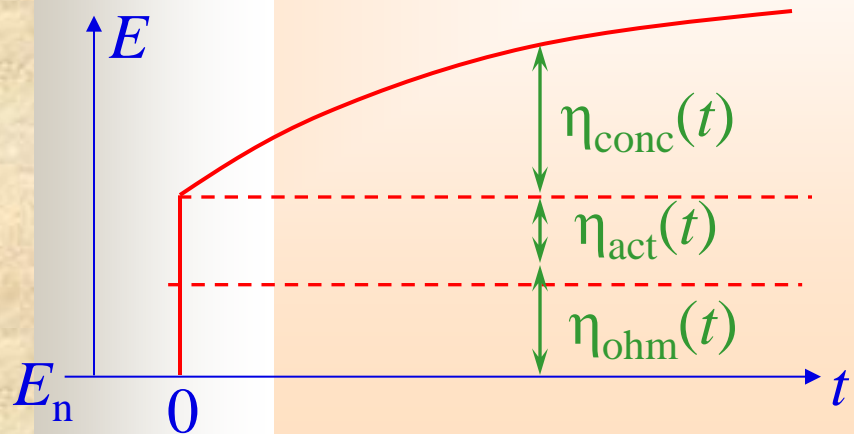
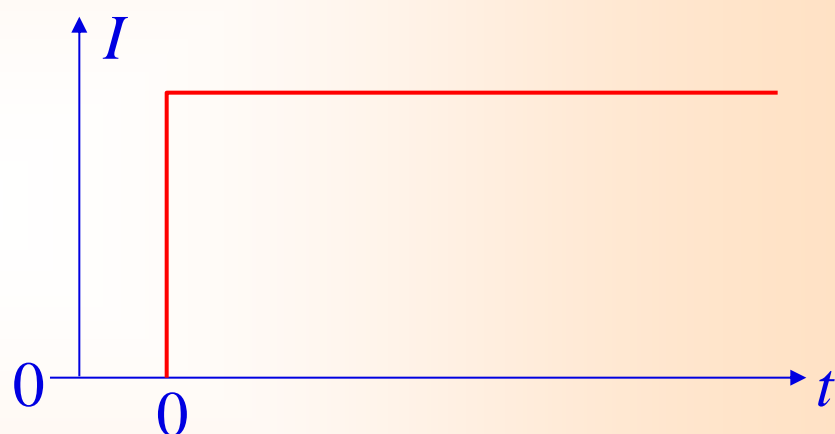
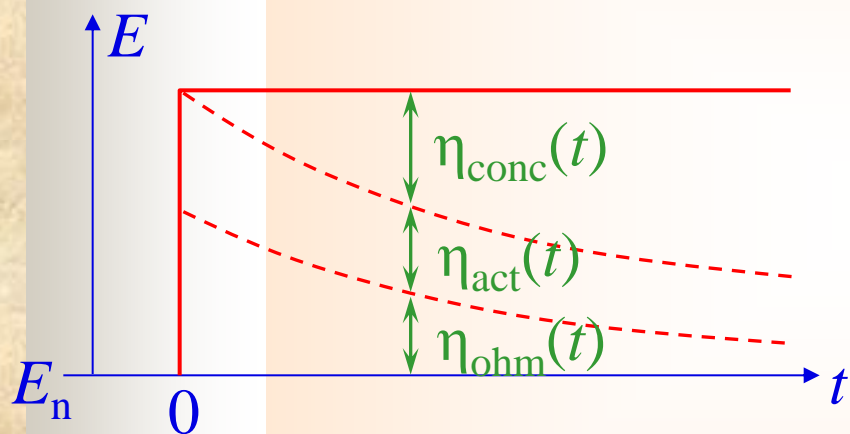
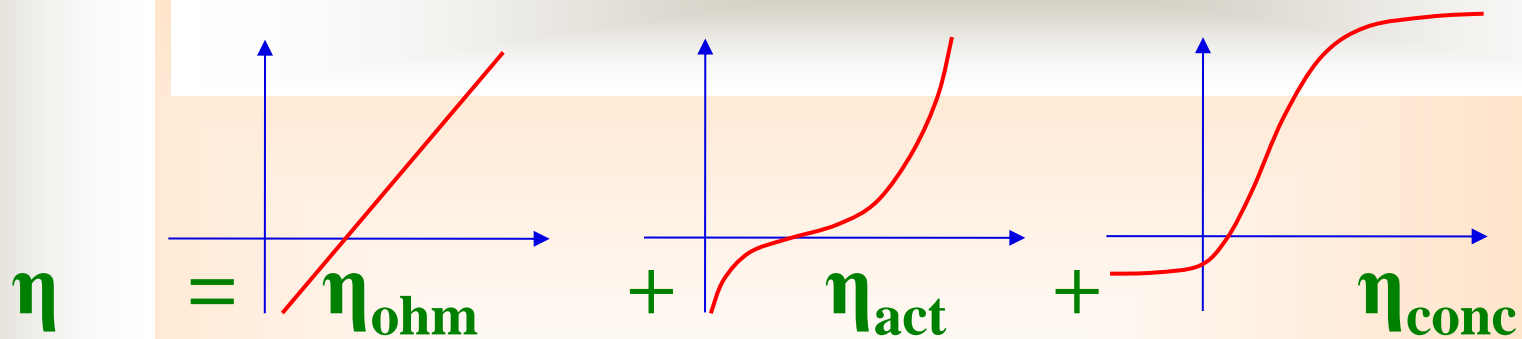
$k'$ (cm.s <sup>-1</sup> )	10 <sup>-3</sup>	10 <sup>-4</sup>	10 <sup>-6</sup>	10 <sup>-10</sup>	10 <sup>-14</sup>
$\eta$ (V)	0.0002	0.003	0.12	0.59	1.06

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

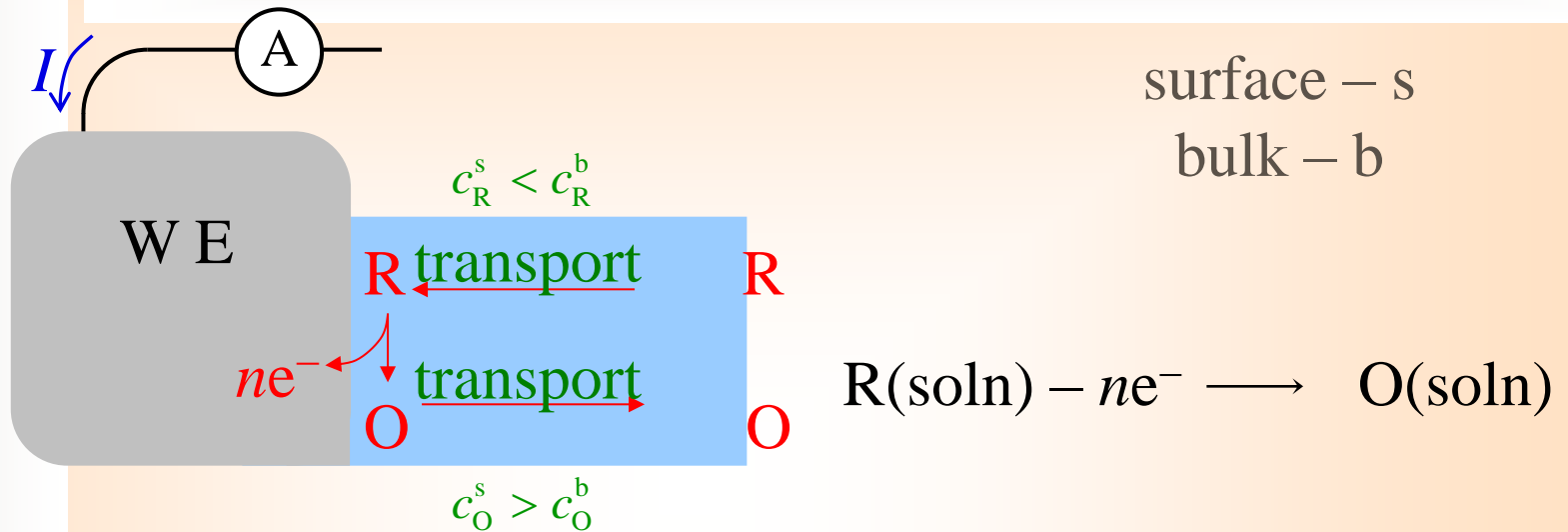
$$j = 10^{-3} \text{ A.cm}^{-2} \quad T = 298 \text{ K}$$

# Three polarizations





# Concentration polarization $\eta_{\text{conc}}$



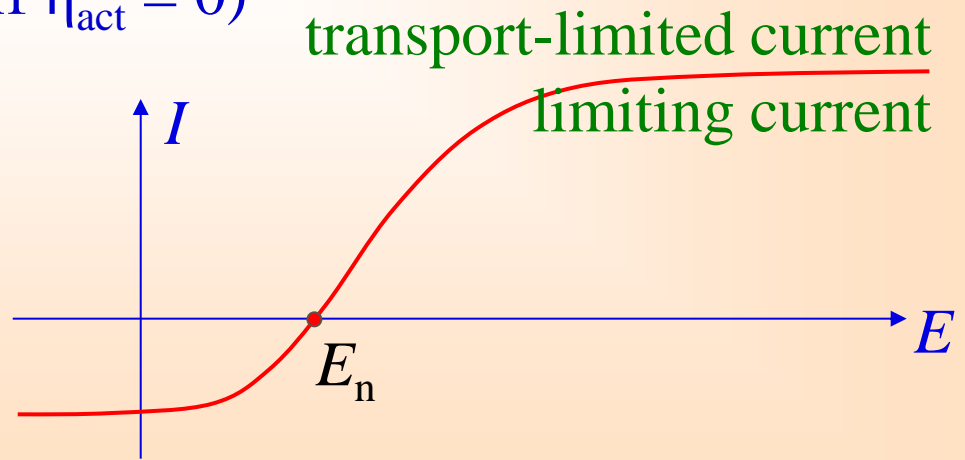
**Nernst's law** (holds for  $I \neq 0$  if  $\eta_{\text{act}} = 0$ )

$$E = E^{o'} - \frac{RT}{nF} \ln \left\{ \frac{c_R^s}{c_O^s} \right\}$$

$I = 0$

$$E_n = E^{o'} - \frac{RT}{nF} \ln \left\{ \frac{c_R^b}{c_O^b} \right\}$$

$$\eta_{\text{conc}} = E - E_n = \frac{RT}{nF} \ln \left\{ \frac{c_R^b}{c_R^s} \frac{c_O^s}{c_O^b} \right\}$$





**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

$$J = -D \frac{dc}{dx}$$

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

$$\frac{dc_i}{dx}$$

..... 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 ???

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

$D = \text{const.}$

## Macroplane Electrode – Universal Solution

$$j = -D \frac{\partial c}{\partial x} \quad \text{Fick's first law}$$

$$\frac{\partial c}{\partial x} = \frac{-\partial j}{\partial r} \quad \text{conservation law}$$

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

$$c = c^s \quad \text{at } x = 0$$

$$c \rightarrow c^b \quad \text{as } x \rightarrow \infty$$

$$\frac{I}{nFA} = \mp j^s = \pm D \left( \frac{\partial c}{\partial x} \right)^s$$

for R and O

$$\frac{M}{nFA} = \sqrt{D_R} [c_R^b - c_R^s] = \sqrt{D_O} [c_O^s - c_O^b]$$

link to  $I$  through  
semidifferentiation

link to  $E$  through  
Nernst or Butler-  
Volmer equation

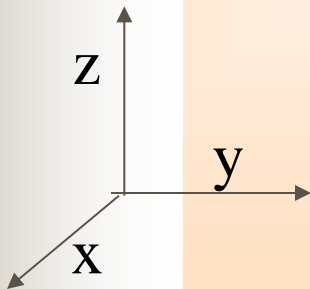
$I \xrightarrow{\text{semiintegration}} M$   
 $M \xleftarrow{\text{semidifferentiation}} I$

$M \xrightarrow{\text{semiintegration}} Q$   
 $Q \xleftarrow{\text{semidifferentiation}} M$

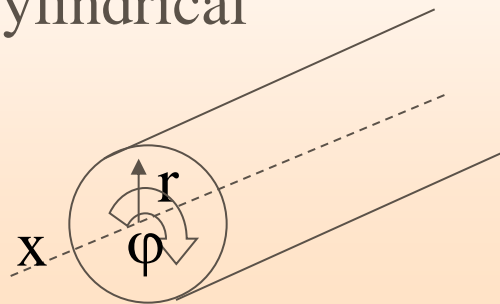
# Laplace operator in various coordinate systems

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	$\frac{\partial}{\partial r} + \frac{1}{r} \frac{\partial}{\partial \varphi} + \frac{1}{r \sin \varphi} \frac{\partial}{\partial \Theta}$

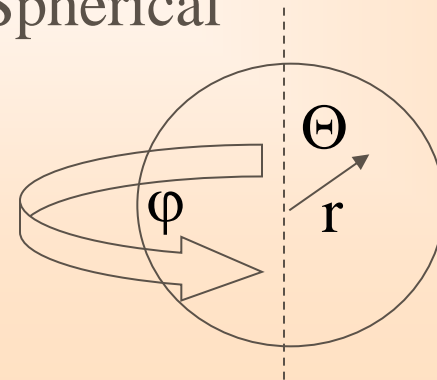
Cartesian



Cylindrical



Spherical





For any coordinate system

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

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

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

$I_d$

$\uparrow$   
E

No reaction

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

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 ≥ 0

lim c = c<sub>∞</sub>

bulk solution

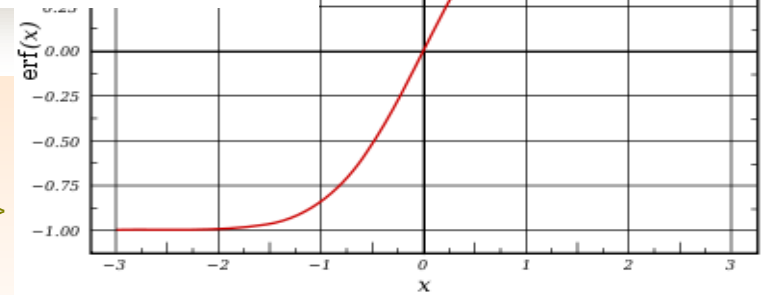
t > 0 and  
x = 0

c<sub>0</sub> = 0

diffusion-limited current  $I_d$

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

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$$



Plot of the error function

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

## 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

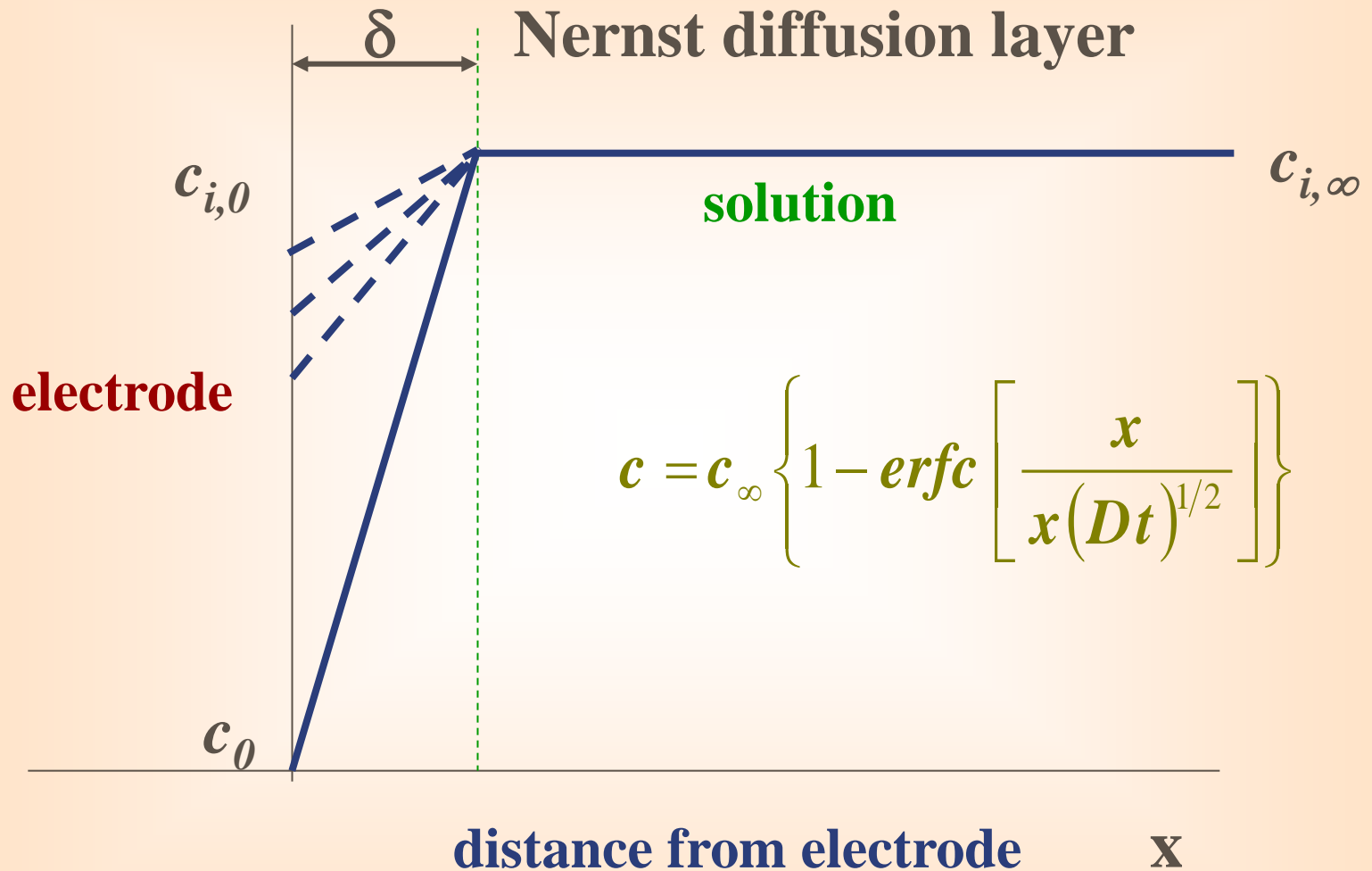
♣ high current density

♣ 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**

**in stationary state**

$\delta$

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

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

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

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

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

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

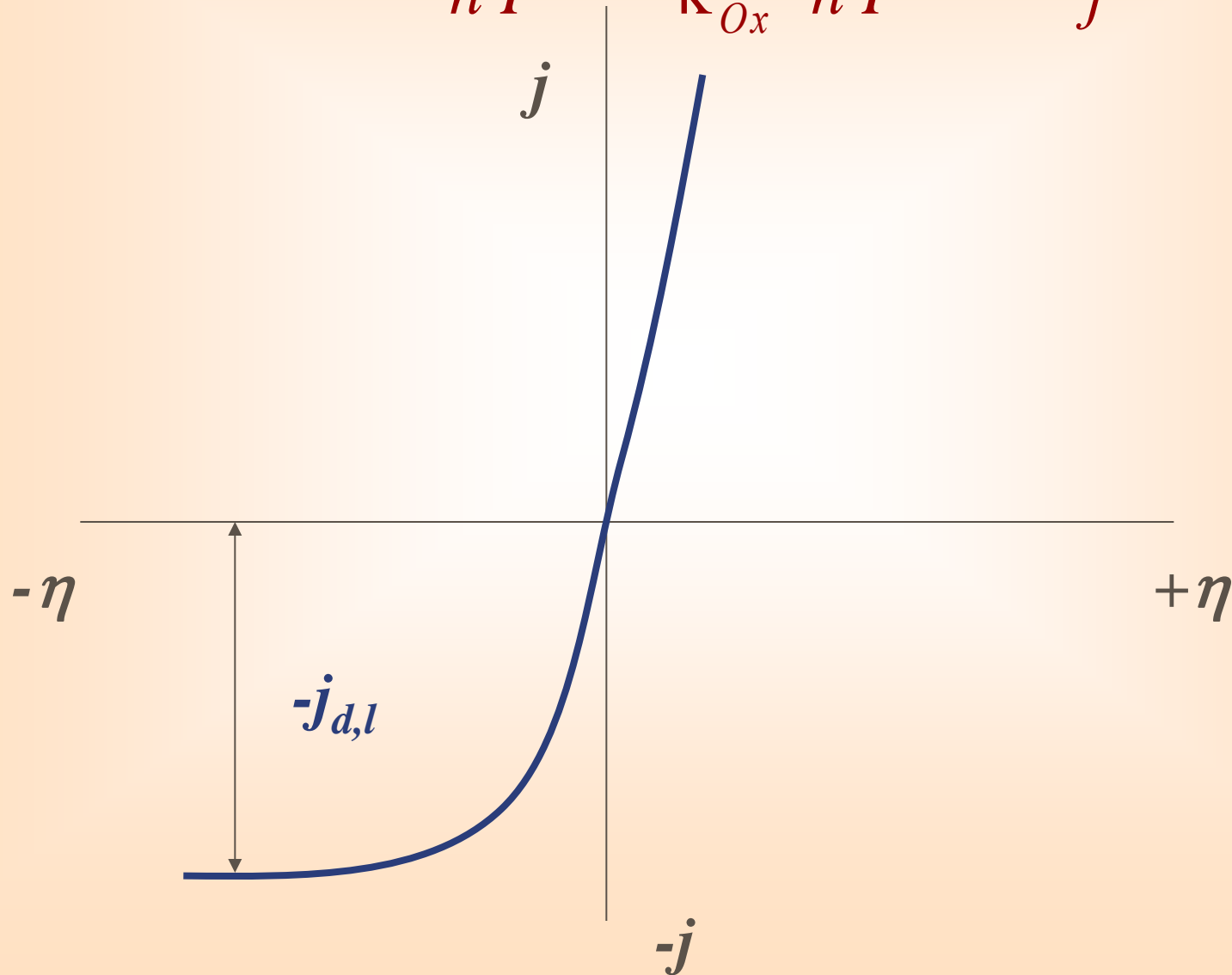
### Diffusion overpotential

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

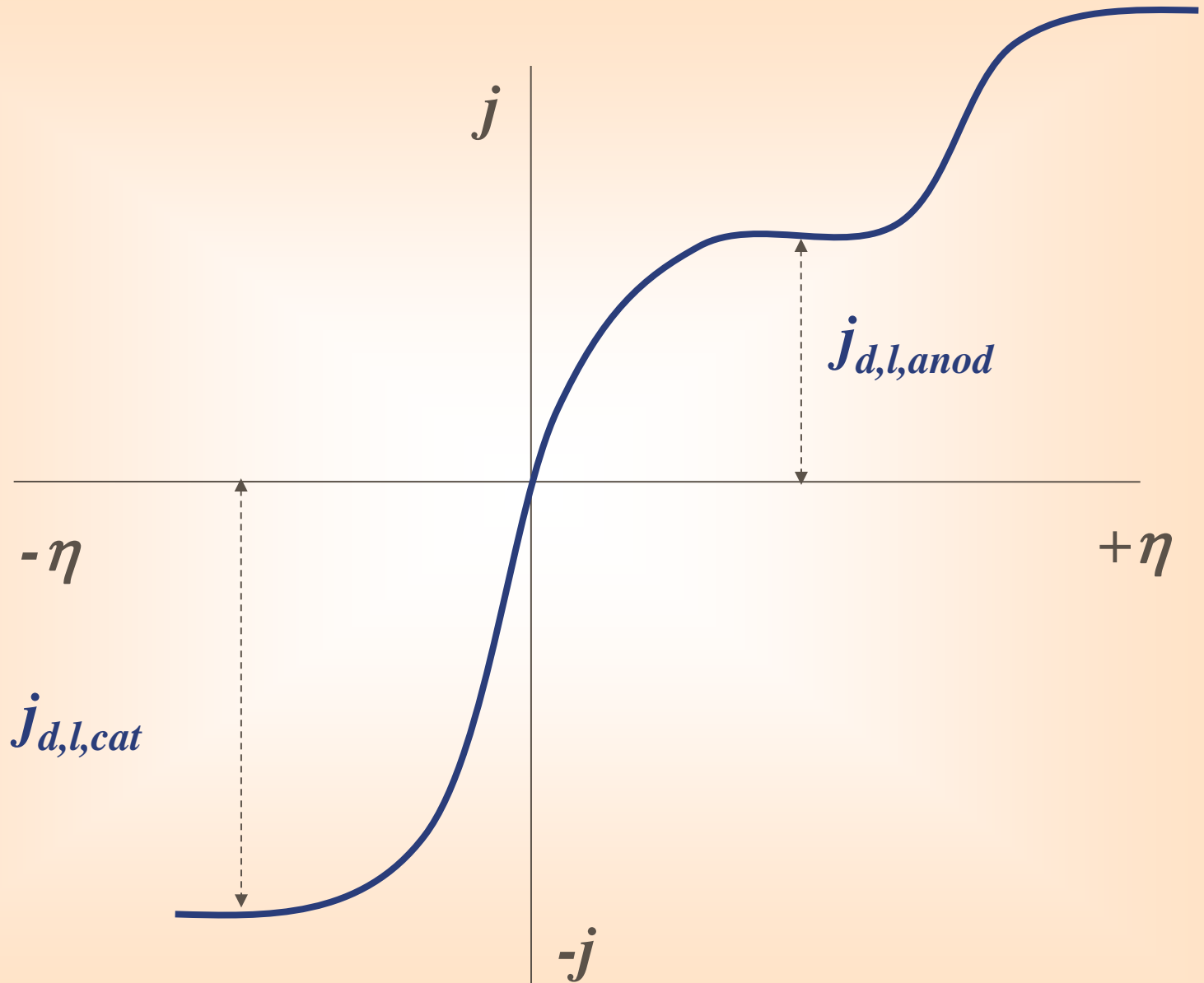
$$\eta_d = - \frac{RT}{n_i F} \ln \left( 1 - \frac{j}{j_{d,l}} \right)$$

# Polarization curves for diffusion controlled processes

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



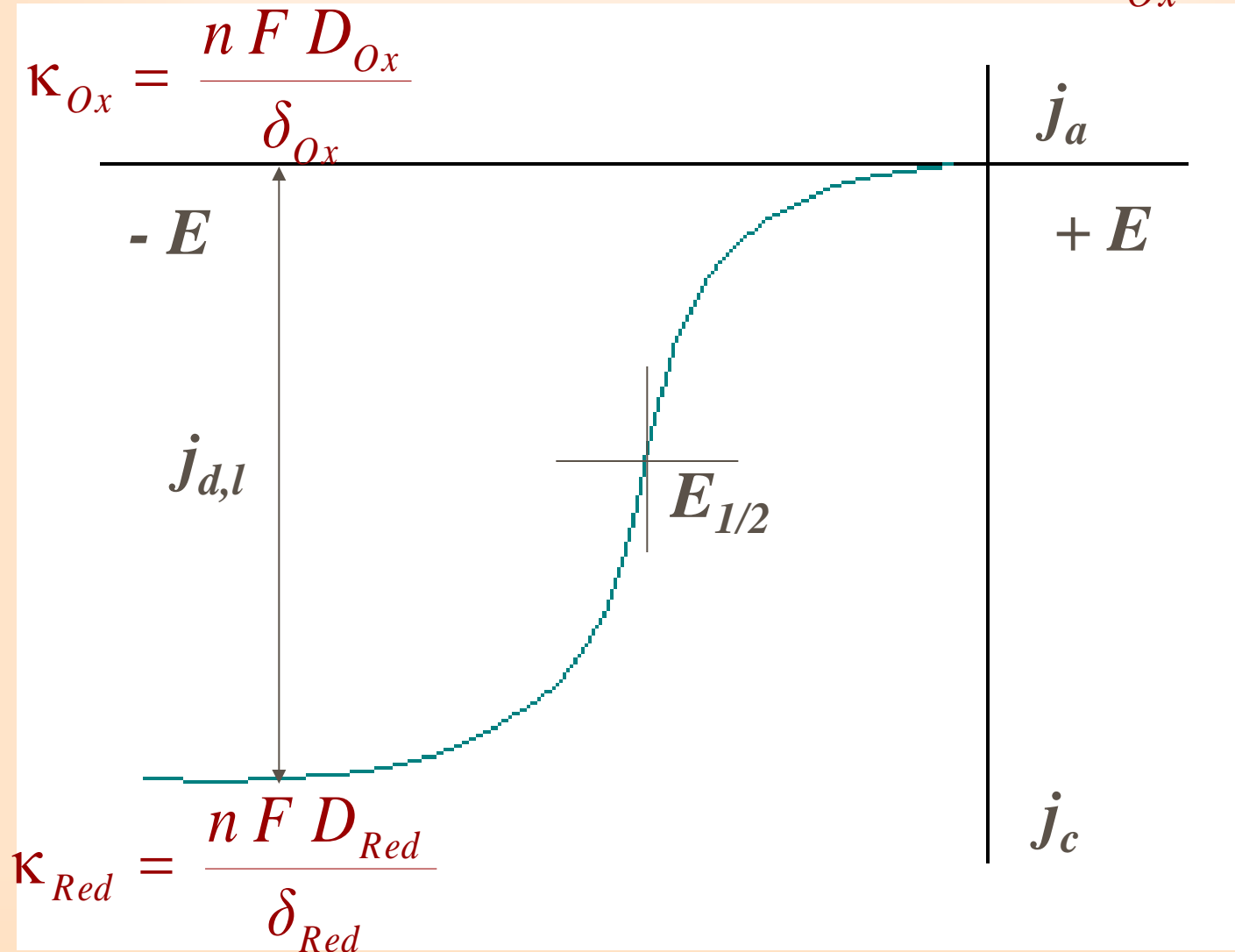
# Polarization curves for diffusion controlled processes



# Diffusion overpotential - polarography

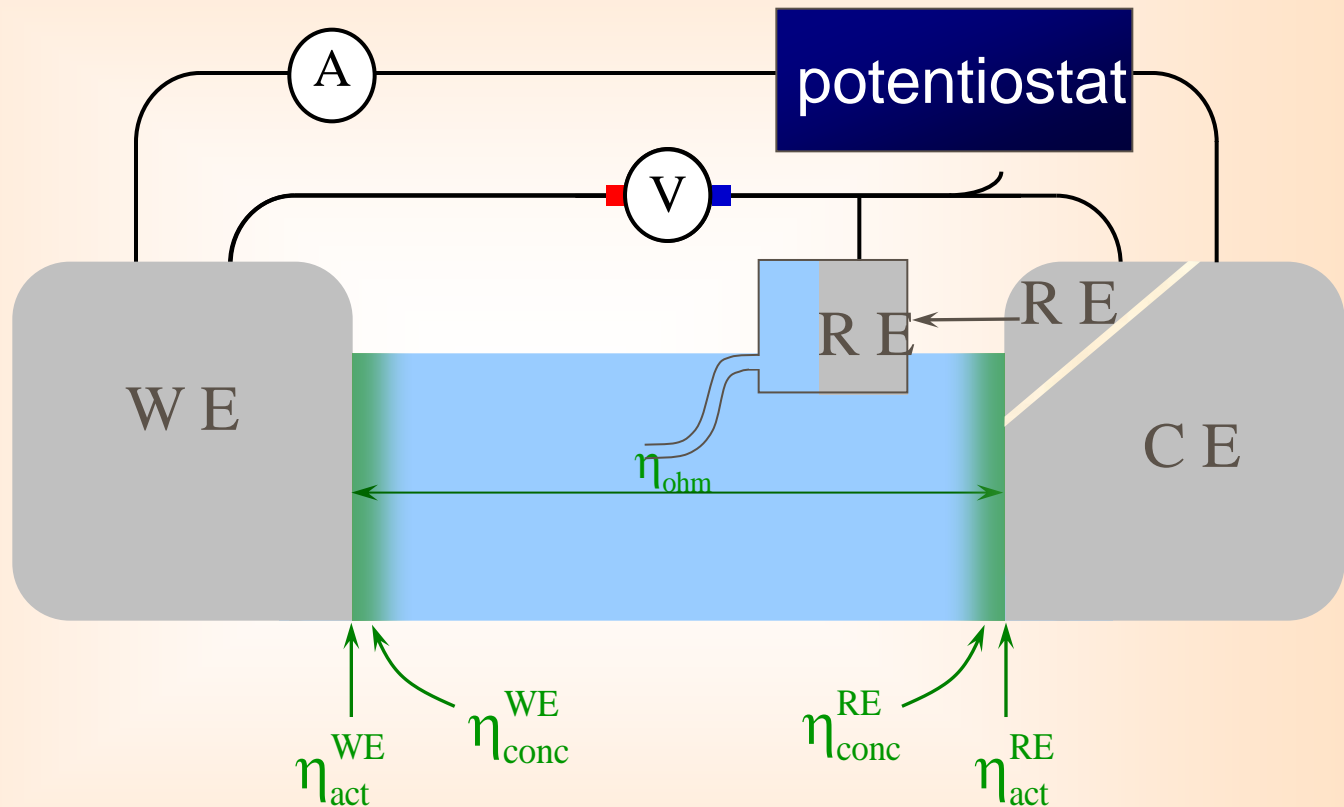
$$j = j_{dl} / 2$$

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





# Three electrodes set in voltammetry



$$E - E_n = \eta = \eta_{act} + \eta_{conc} + IR_u$$



# Methods for studying electrode reactions

- ♥ *Steady state methods* (hydrodynamic electrodes, increasing convection, microelectrodes)
- ♥ *Linear sweep voltammetry* (increasing sweep rate)
- ♥ *Step and pulse techniques* (increasing amplitude and/or frequency)
- ♥ *Impedance methods* ( increasing perturbation frequency)

**timescale of electrode reactions**