I^3N Innovative Integrated Instrumentation for Nanoscience

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High Resolution Electronic Measurements in Nano-Bio Science

The interface between solid & liquid:

how to transfer charge through the electrode

Giorgio Ferrari

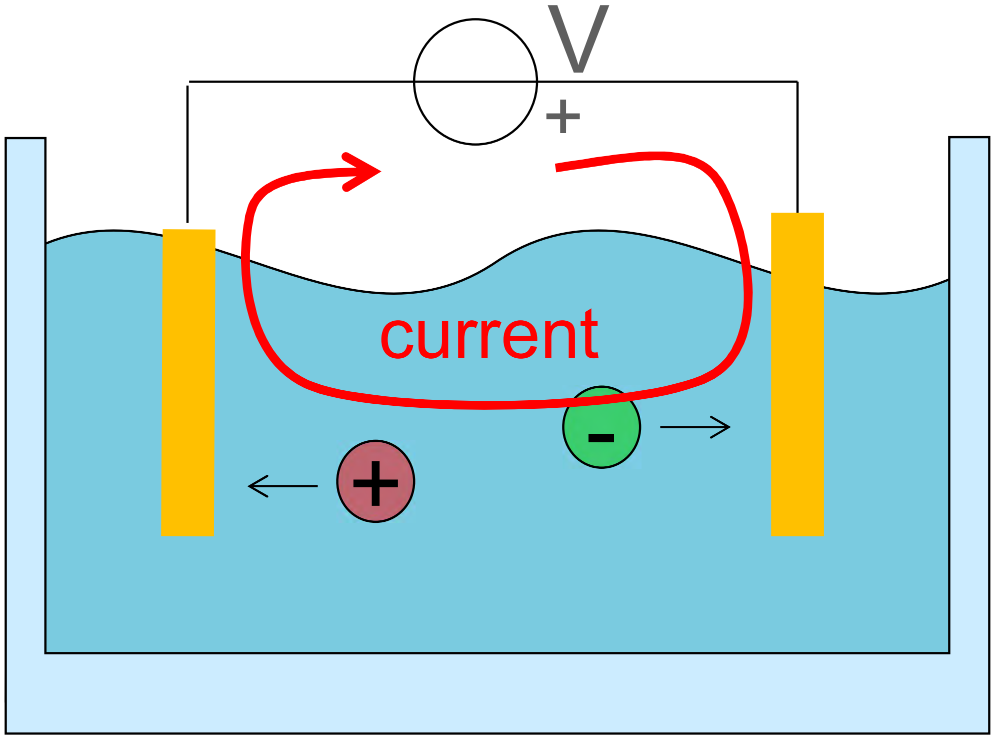
Milano, June 2025

Outline

- The electrical behavior of the bulk liquid
- Metal – liquid interface: double-layer capacitance

- Potential drop across the electrode-liquid interface
- Charge transfer at the interface
- Current-Voltage relation

Electrical current in ionic conductors



Ions move in the liquid

Electrons move in the electrodes

⬇

electron transfer at the metal/liquid interface to sustain a DC current

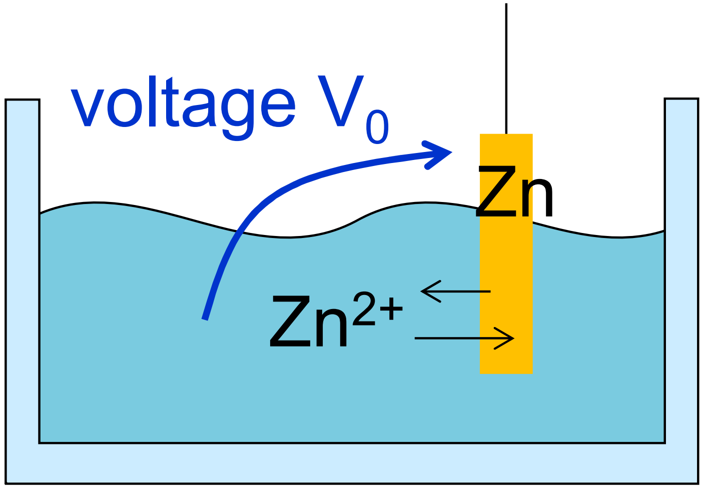
The electron transfer is controlled by the potential difference between the liquid and the electrode:

what are the voltages in our electrochemical cell?

Equilibrium at the interface

Ex.: Zn electrode immersed in a solution with Zn^{2+} ($C_{Zn^{2+}}$):

$$Zn_{solid} \underset{\text{dissolve}}{\overset{\text{deposit}}{\leftrightarrows}} Zn^{2+}_{liquid} + 2e^{-}$$



Dynamic equilibrium

Zn^{2+} deposit → V_0 increases → Zn^{2+} repulsed

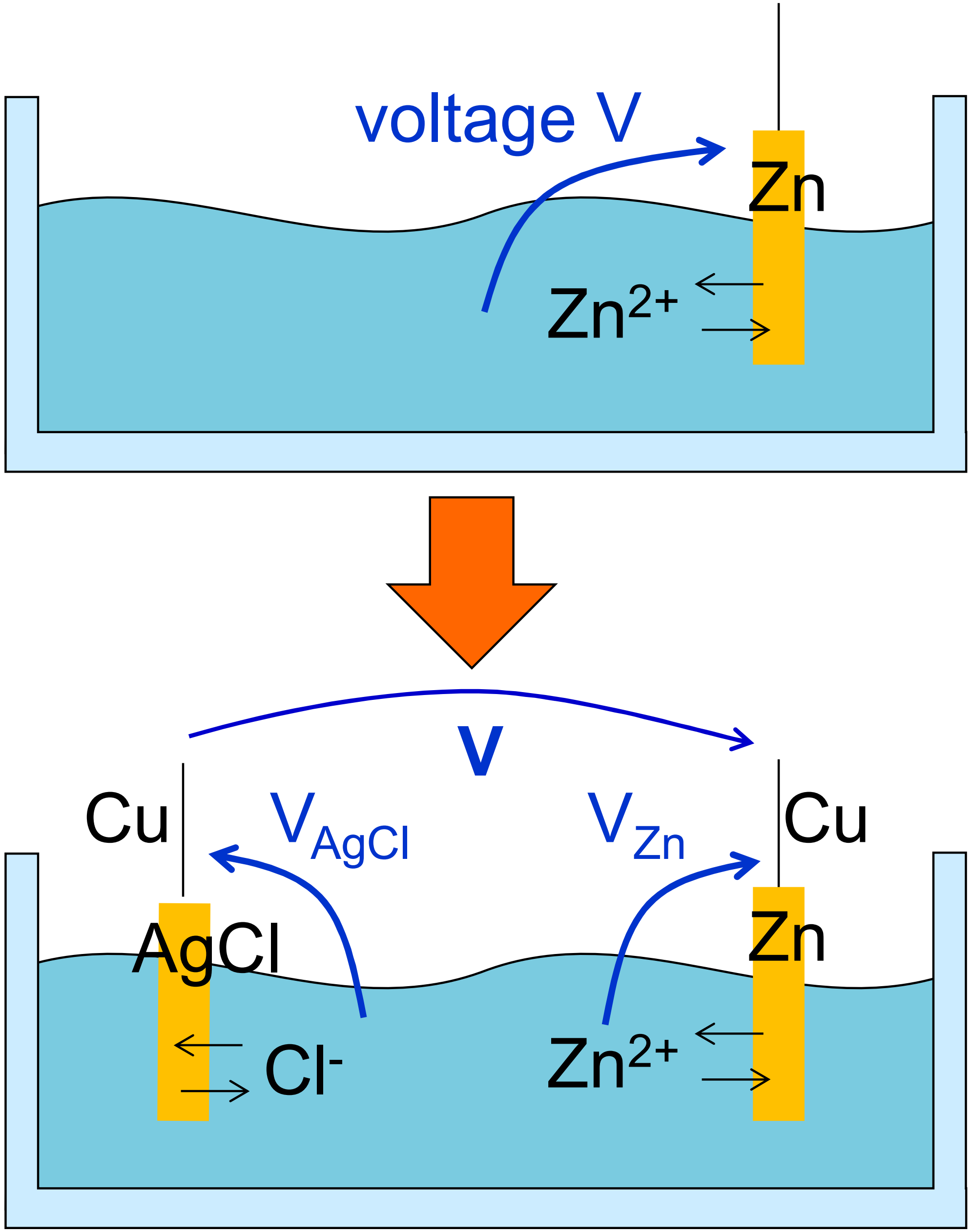
Zn dissolve → V_0 decreases → Zn^{2+} attracted

The equilibrium condition (no corrosion/deposition, no net charge transfer) is reached with a voltage V_0 determined by:

- metal involved
- ions in solution
- solution
- temperature,…

V_0 is typically not equal to zero.

Electrochemical cell



Voltage V is **not** directly measurable using a voltmeter

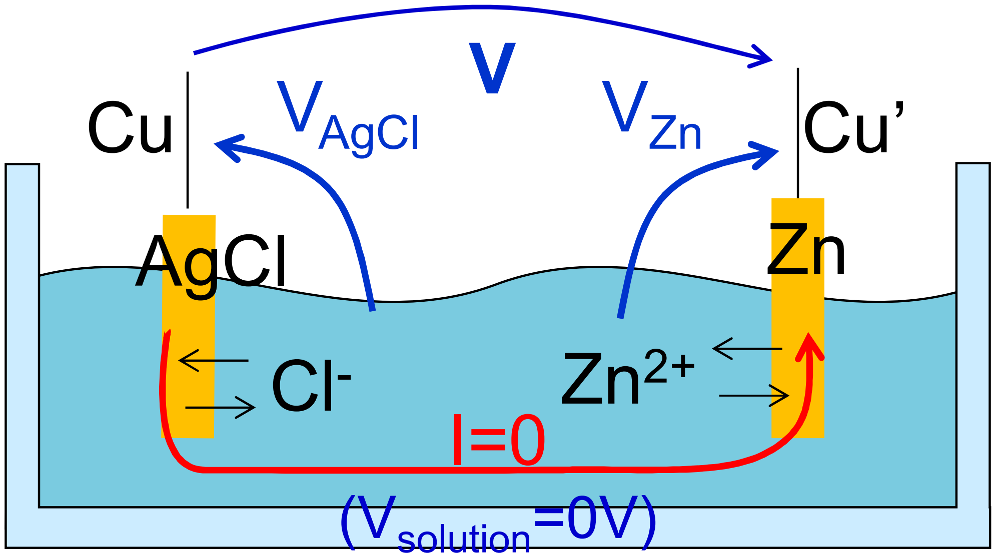
A 2nd electrode is required!

$$\mathbf{V} = V_{Zn} - V_{AgCl}$$

$$AgCl_{(s)} + e^- \leftrightarrows Ag_{(s)} + Cl^-_{(l)}$$

$$Zn_{(s)} \leftrightarrows Zn^{2+}_{(l)} + 2e^-$$

Eq. potential of a electrochemical cell



At the equilibrium I=0
(no voltage drop in solution)

Depends on Zn, C_{Zn}

Depends on AgCl, C_{Cl}

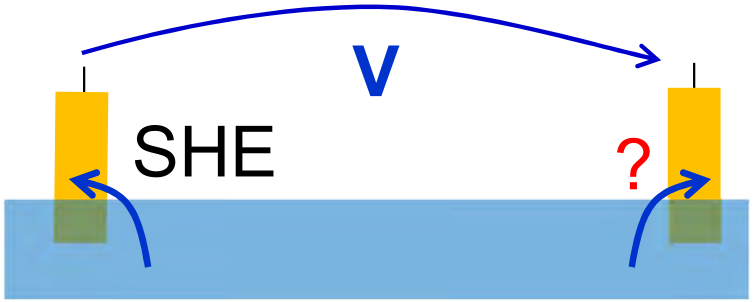
$$V = V_{Zn} - V_{AgCl}$$

Equilibrium may require **V≠0V** (battery!)

Standard electrode potentials

Aqueous Solutions at 25°C in V vs. SHE (standard hydrogen electrode), 1atm, **C^0=1M**

$1/2F_2 + H^+ + e \leftrightarrows HF$	+3.050	$2H^+ + 2e \leftrightarrows H_2$	0.0000
$Au^+ + e \leftrightarrows Au$	+1.83	$Fe^{2+} + 2e \leftrightarrows Fe$	-0.44
$O_2 + 4H^+ + 4e \leftrightarrows 2H_2O$	+1.229	$Zn^{2+} + 2e \leftrightarrows Zn$	-0.762
$Pt^{2+} + 2e^- \leftrightarrows Pt$	+1.188	$2H_2O + 2e \leftrightarrows H_2 + 2OH^-$	-0.828
$Ag^+ + e^- \leftrightarrows Ag$	+0.799	$Na^+ + e \leftrightarrows Na$	-2.714
$Fe^{3+} + e \leftrightarrows Fe^{2+}$	+0.771	$Ca^{++} + 2e \leftrightarrows Ca$	-2.87
$O_2 + 2H_2O + 4e \leftrightarrows 4OH^-$	+0.401	$K^+ + e \leftrightarrows K$	-2.93
$Fe(CN)^{3-}_6 + e \leftrightarrows Fe(CN)^{4-}_6$	+0.361	$Li^+ + e \leftrightarrows Li$	-3.04
$Cu^{2+} + 2e \leftrightarrows Cu$	+0.340		
$AgCl + e \leftrightarrows Ag + Cl^-$	+0.222		



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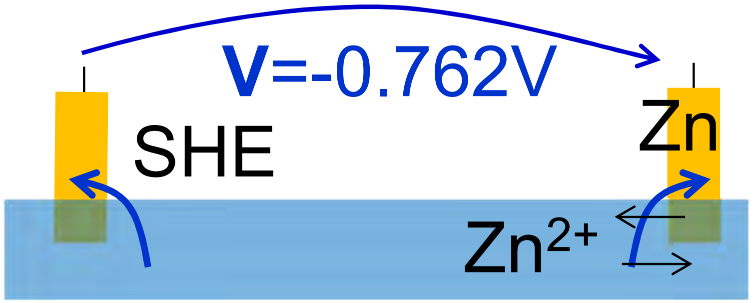

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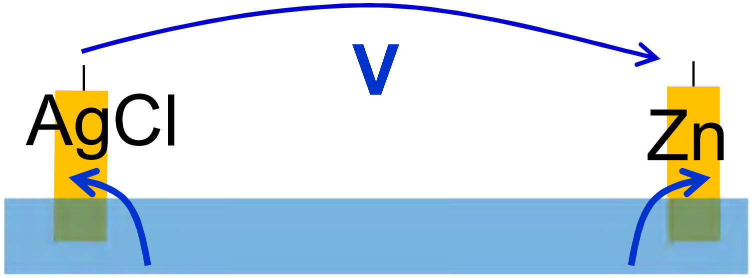


For the previous case:

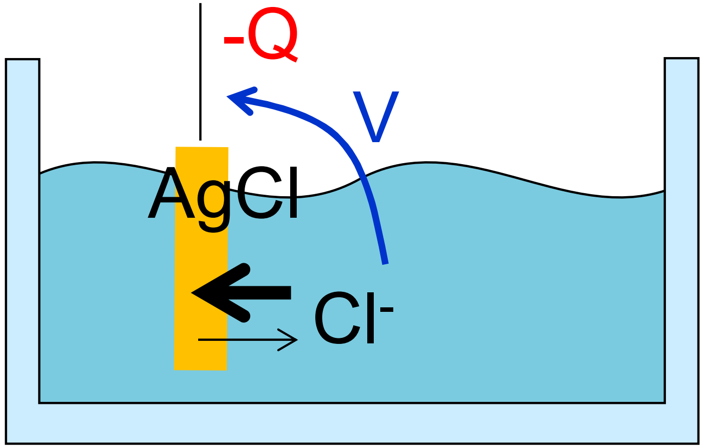
$$V = (-0.762V) - (+0.222V) = -0.984V$$

Eq. potential: role of the concentration

Ex.: AgCl electrode immersed in a solution with Cl^- (c_{Cl^-}):
$AgCl_{(s)} + e^- \leftrightarrows Ag_{(s)} + Cl^-_{(l)}$

$c_{Cl^-} > c_{Cl^-,0}$

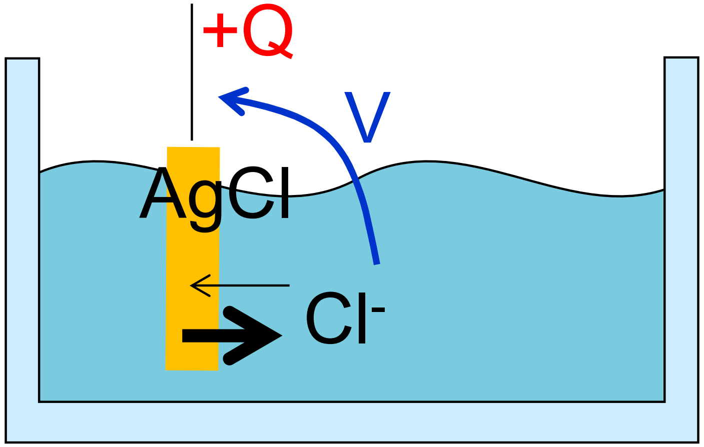
(AgCl production)



equilibrium
condition:
$V<V_0$

$c_{Cl^-} < c_{Cl^-,0}$

(AgCl dissolves)



equilibrium
condition:
$V>V_0$

Assuming a Boltzmann dist.: $V = V_0 \boxed{-} \frac{kT}{q} \log\left({}^{c_{Cl^-}}/{}_{c_{Cl^-,0}}\right)$

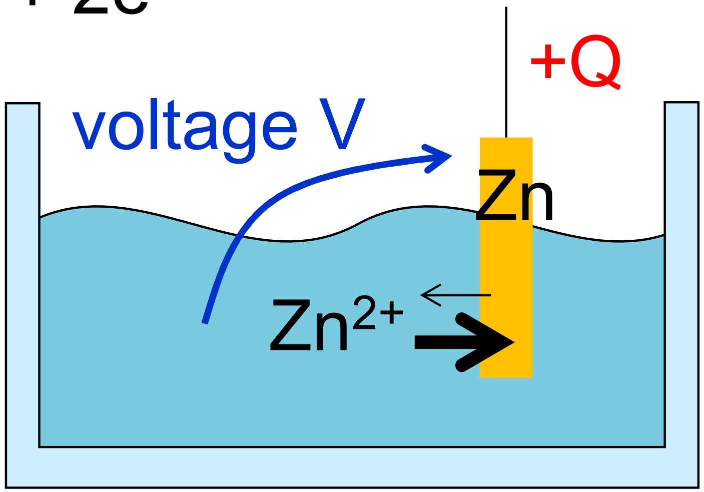
Eq. potential: role of the concentration

Ex.: Zn electrode immersed in a solution with Zn^{2+} ($C_{Zn^{2+}}$):

$Zn_{solid} \leftrightarrows Zn^{2+}_{liquid} + 2e^-$

$C_{Zn^{2+}} > C_{Zn^{2+},0}$

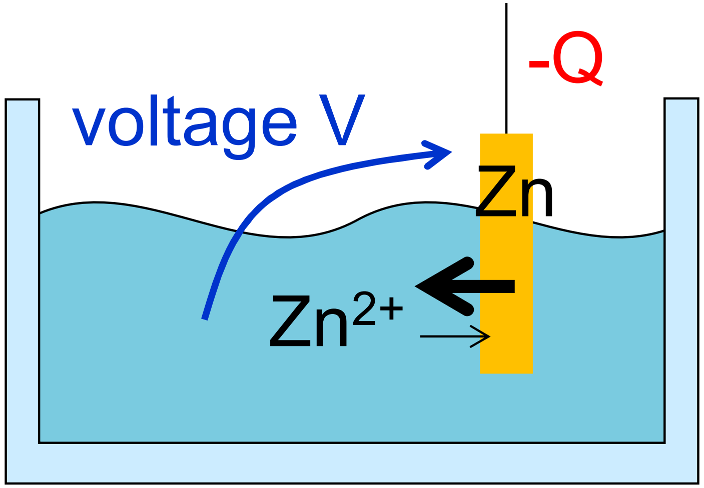
(Zn deposition)



equilibrium condition:
$V > V_0$

$C_{Zn^{2+}} < C_{Zn^{2+},0}$

(Zn dissolves)



equilibrium condition:
$V < V_0$

Assuming a Boltzmann dist.: $V = V_0 \boxed{+ \frac{kT}{2q}} \log\left({}^{C_{Zn^{2+}}}/_{C_{Zn^{2+},0}}\right)$

Nernst equation

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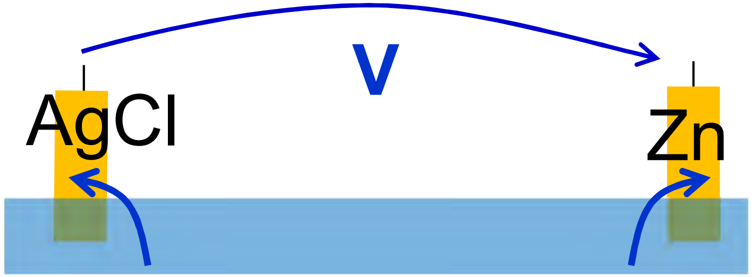
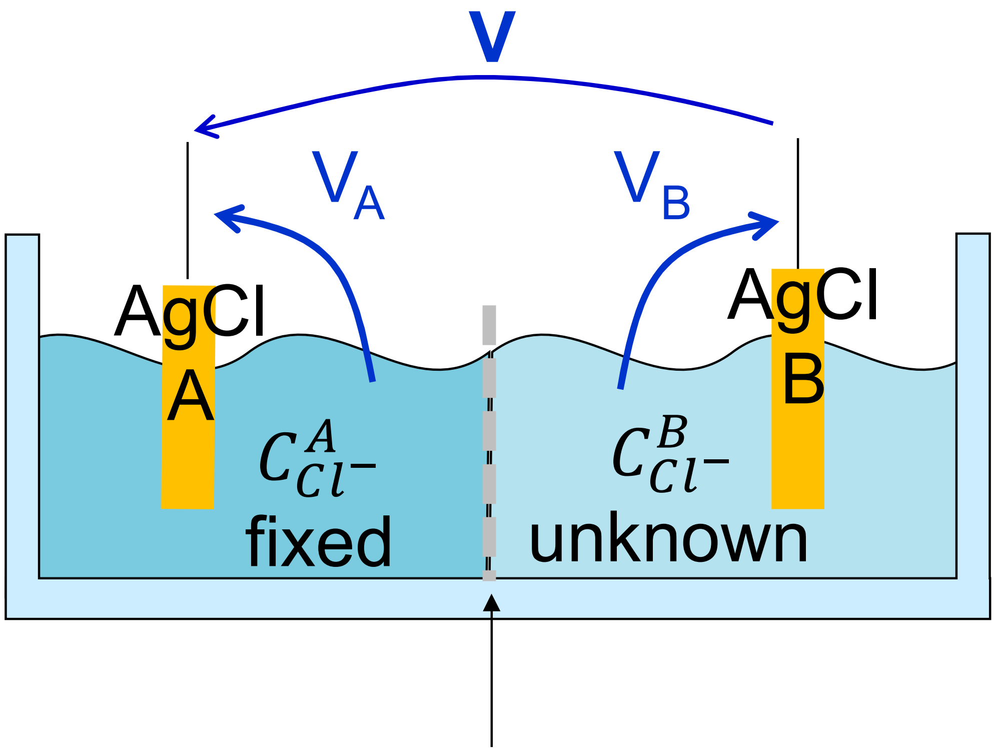


For the previous case:

$$V = -0.762V \underset{\uparrow}{+} \frac{kT}{2q}\ln\left(\frac{C_{Zn^{2+}}}{C^0}\right) - \left[+0.222V \underset{\uparrow}{-} \frac{kT}{q}\ln\left(\frac{C_{Cl^-}}{C^0}\right)\right]$$

Potentiometric sensor

Measure of concentration:



ion-selective membrane

equilibrium condition (I=0)

$$V_A = V_0 - \frac{kT}{q}\ln\left(\frac{C^A_{Cl^-}}{C^0}\right)$$

$$V_B = V_0 - \frac{kT}{q}\ln\left(\frac{C^B_{Cl^-}}{C^0}\right)$$

$$V = V_A - V_B = \frac{kT}{q}\ln\left(\frac{C^B_{Cl^-}}{C^A_{Cl^-}}\right)$$

$$\boxed{V \propto \ln\left(C^B_{Cl^-}\right)}$$

Standard electrode potentials

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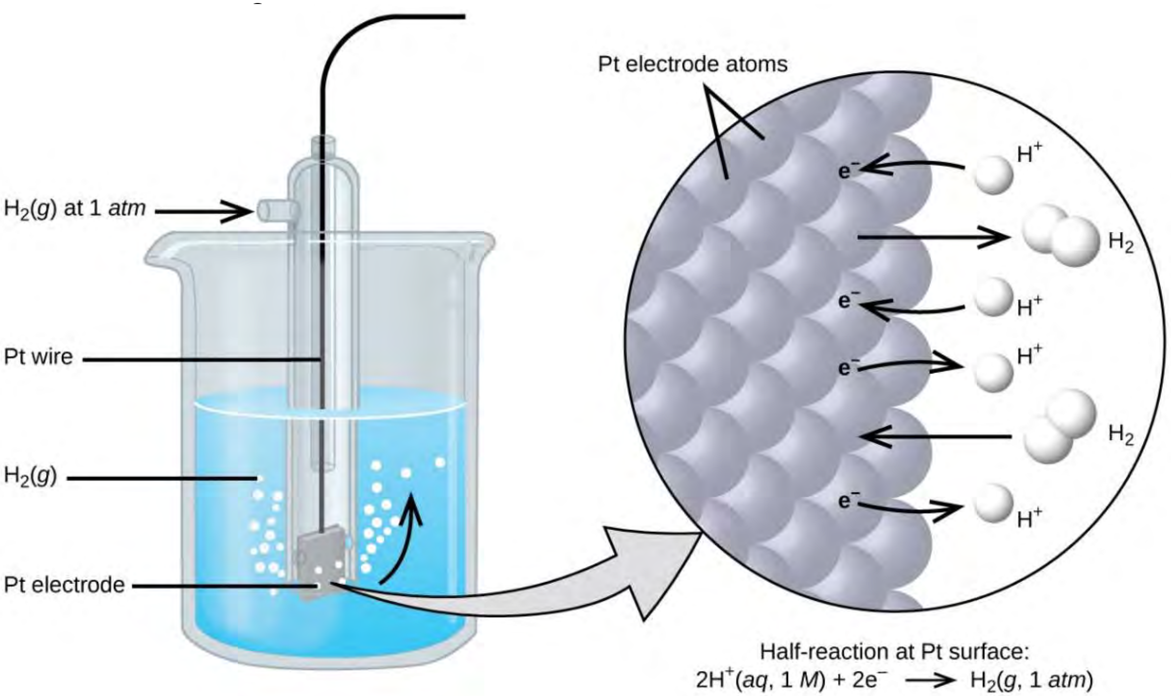
$\boxed{2H^+ + 2e \leftrightarrows H_2 \qquad 0.0000}$



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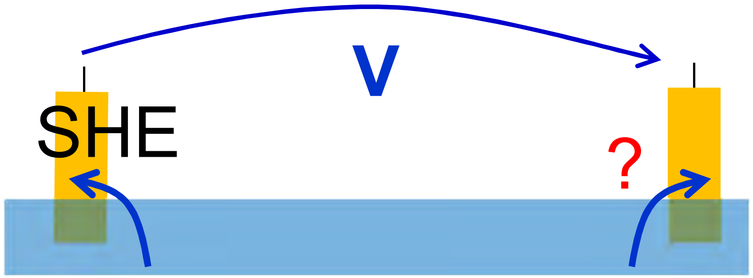

Reference electrodes

Purpose: provide a stable potential against which other potentials can be reliably measured

Criteria:

- stable in potential (time, temperature)
- chemical reactions at the surface are reversible
- potential shouldn’t be altered by passage of small current = not polarizable
- reproducible
- easy fabrication and handling
- convenient for use

Reference electrodes

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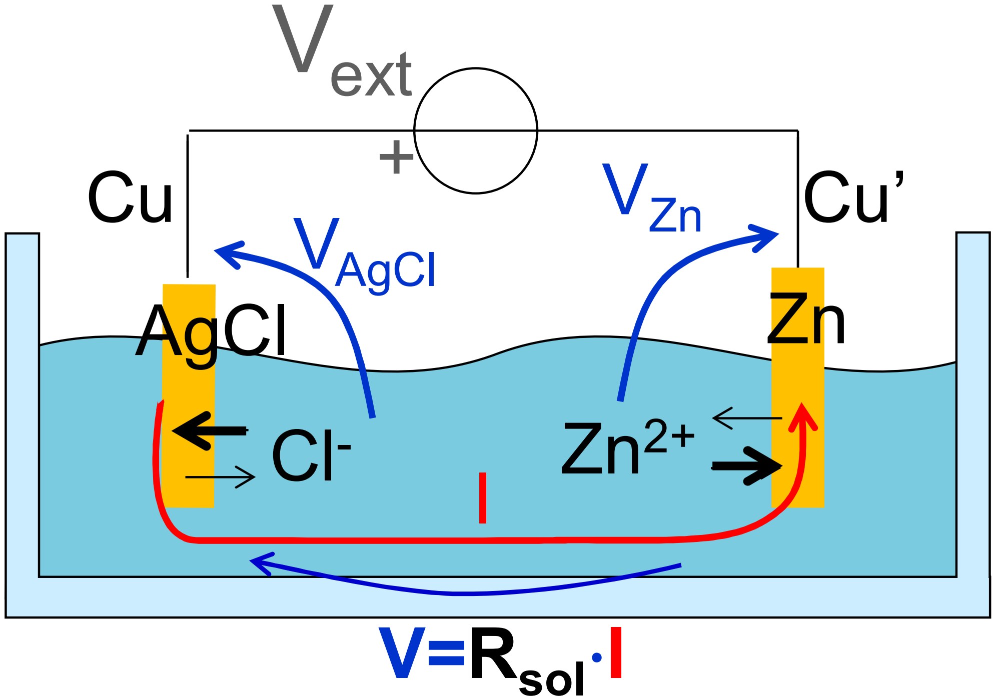
$Fe(CN)^{3-}_6 + e \leftrightarrows Fe(CN)^{4-}_6$	+0.361	$Li^+ + e \leftrightarrows Li$	-3.04
$Cu^{2+} + 2e \leftrightarrows Cu$	+0.340	Saturated Calomel Electrode (SCE):	+0.244
$AgCl + e \leftrightarrows Ag + Cl^-$	+0.222		

Ag wire coated with AgCl(s), immersed in NaCl or KCl solution. It is stable in a solution with a large quantity of Cl^- such as the biological fluid (e.g. PBS).

Out-of-equilibrium condition



$Zn_{solid} \leftrightharpoons Zn^{2+}_{liquid} + 2e^-$

$AgCl_{(s)} + e^- \leftrightharpoons Ag_{(s)} + Cl^-_{(l)}$

$$V_{ext} = V_{AgCl} + R_{sol}\cdot I - V_{Zn}$$

By forcing V_{ext} > equilibrium voltage

→ more Cl^- are attracted on the left (V_{AgCl} ↑)

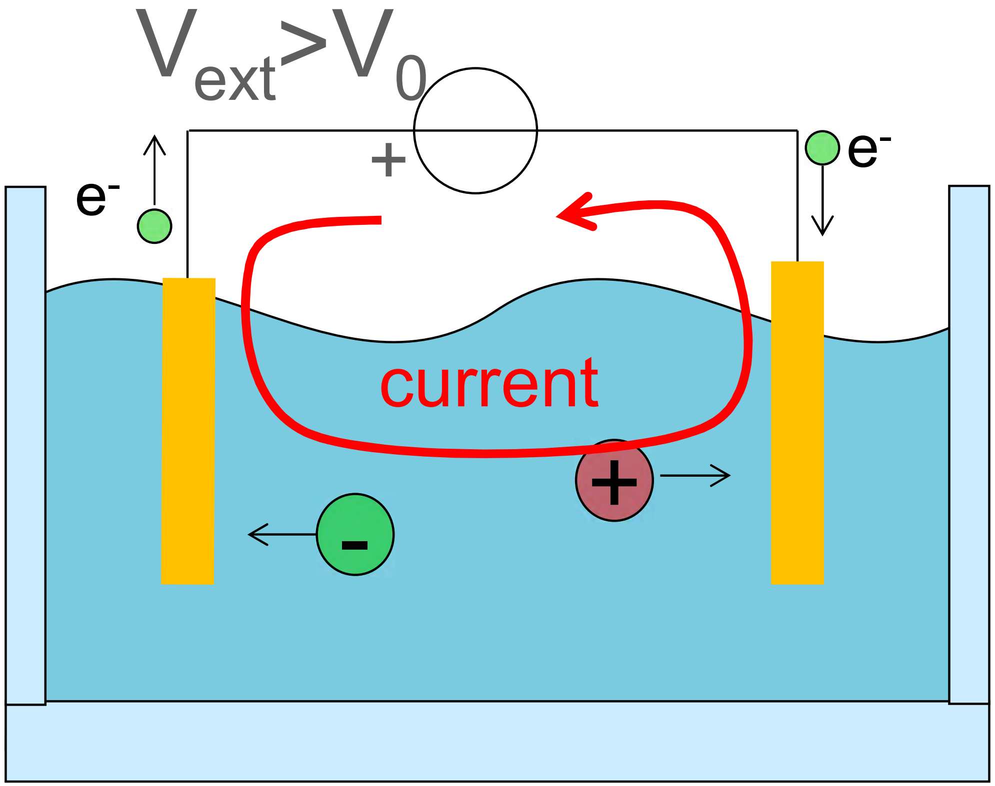
more Zn^{2+} are attracted on the right (V_{Zn} ↓)

→ chemical equilibrium is broken

→ current

Note: no direct control of the voltage drop at metal-liquid interface

Electrical current in ionic conductors

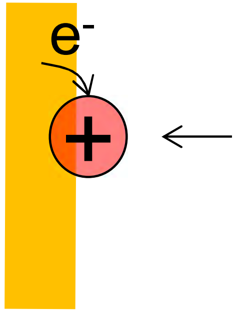


Ions move in the liquid

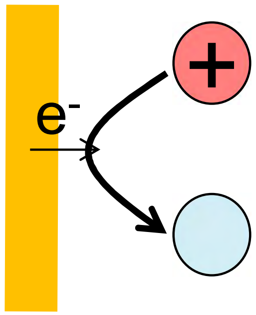
Electrons move in the electrodes

Chemical reactions
with **electron transfer**
at the metal/liquid interfaces

Two main cases:

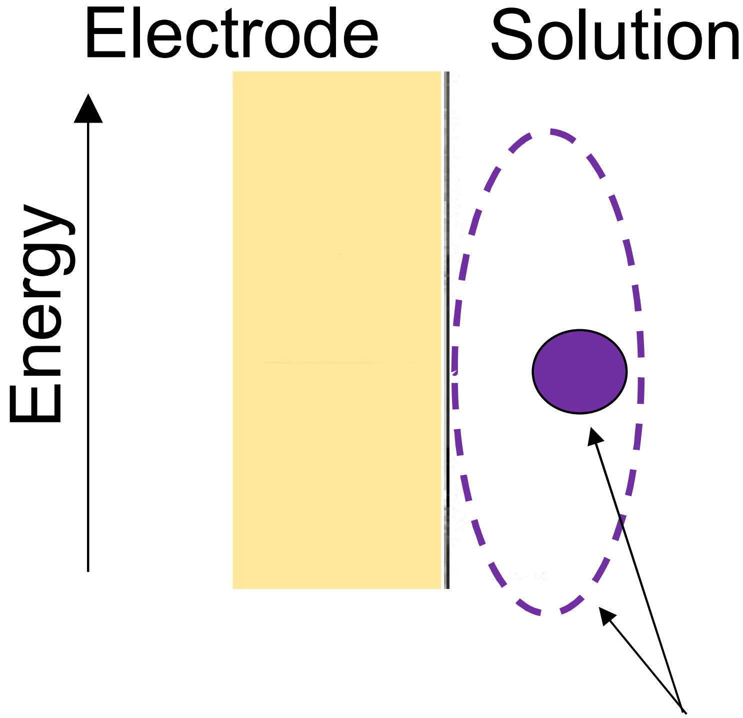


«consumable» electrode:
metal becomes less (more) as a function of time
Corrosion / deposition



«nonconsumable» electrode: reduction-oxidation (redox) reaction of ions or molecules in liquid

Electron Transfer



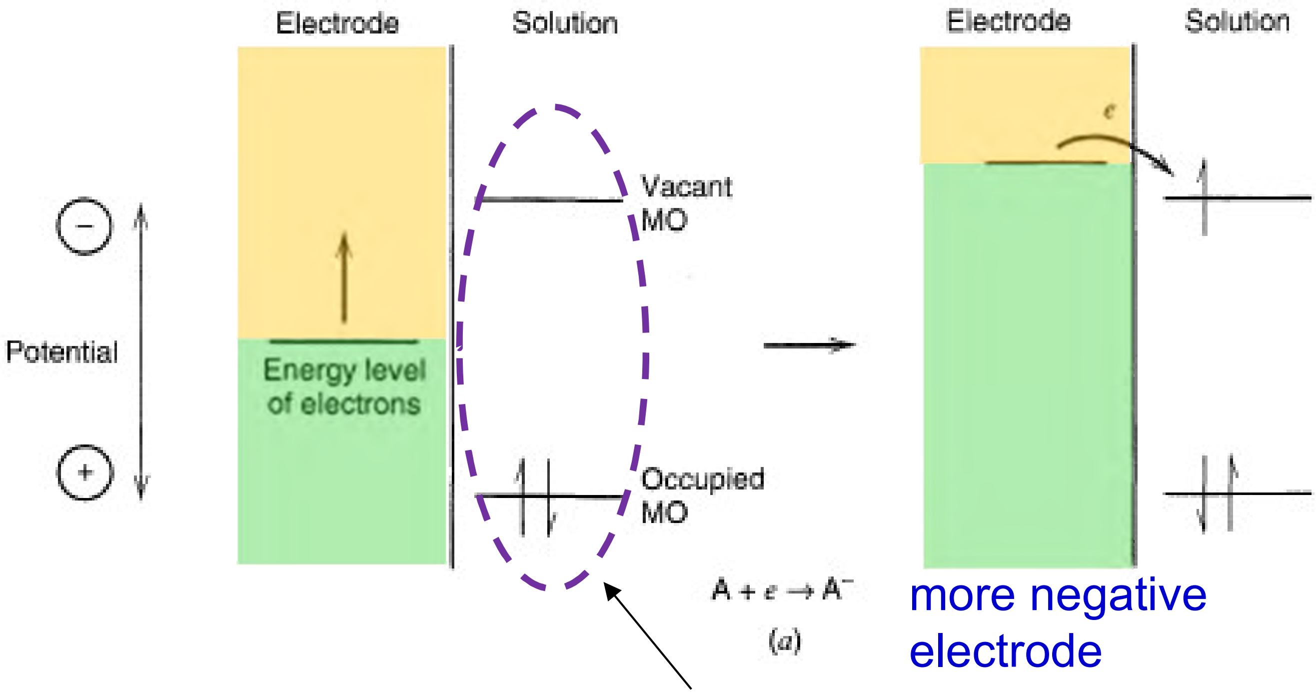
lowest unoccupied molecular orbital

highest occupied molecular orbital

atom/ion/molecule in solution

Bard, Electrochemical methods.
Fundamentals and applications

Electron Transfer



more negative electrode

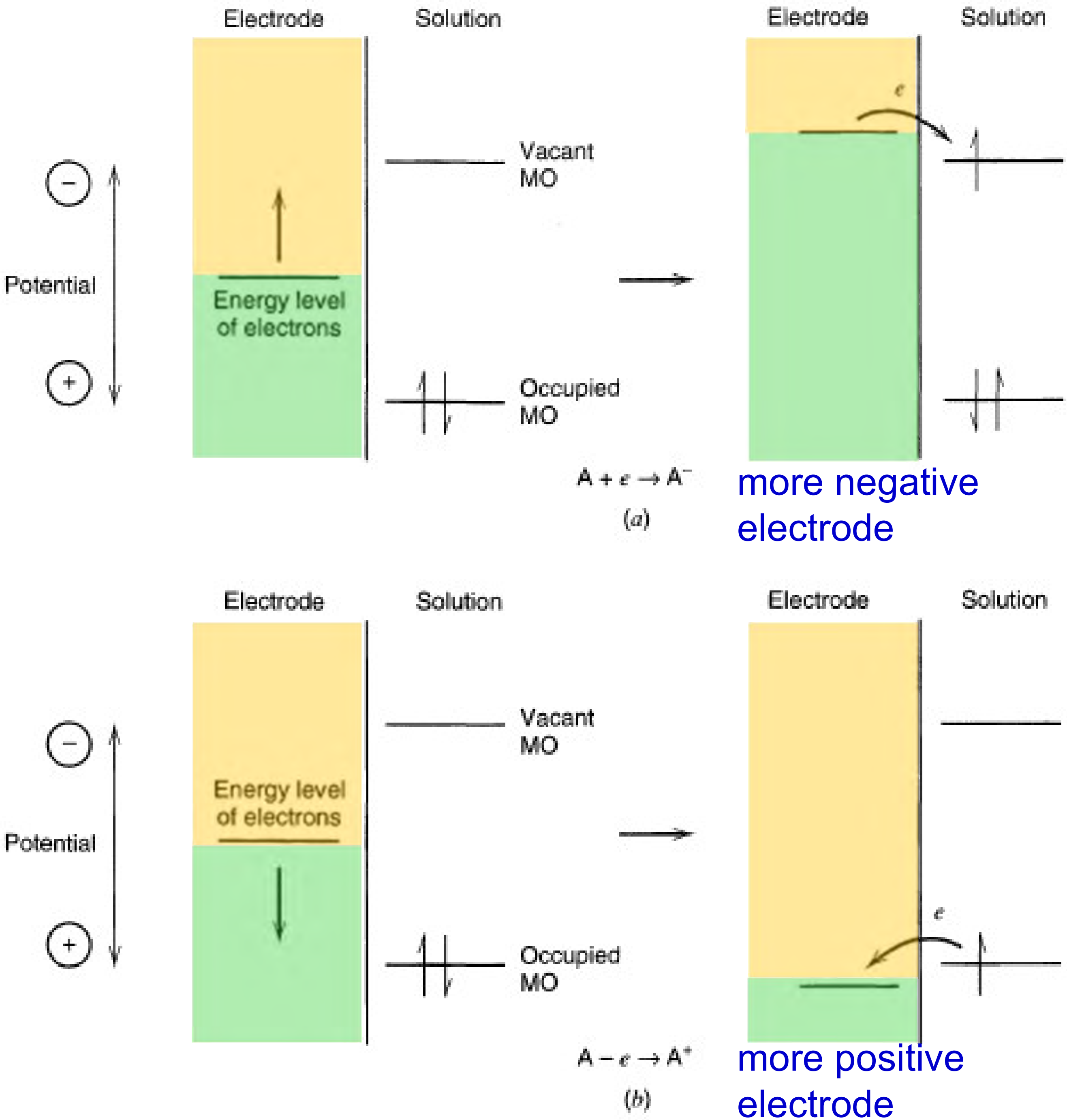
atom/ion/molecule in solution

Reduction: atom/ion/molecule gains an electron

reaction controlled by the potential drop **across the interface**

Bard, Electrochemical methods. Fundamentals and applications

Electron Transfer



more negative electrode

more positive electrode

Reduction:
atom/ion/molecule gains an electron

reaction controlled by the potential drop **across the interface**

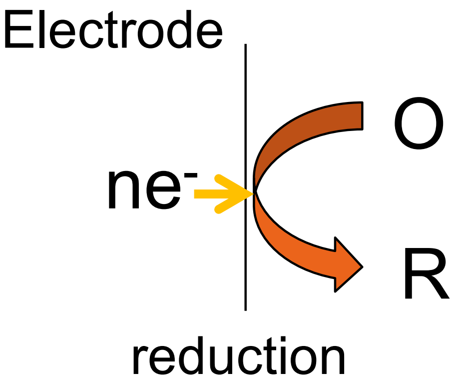
Oxidation:
atom/ion/molecule loses an electron

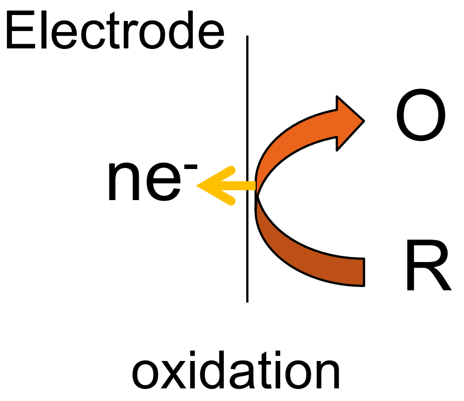
Bard, Electrochemical methods. Fundamentals and applications

The Kinetics of Electron Transfer

Consider:

$$O + ne^- \underset{k_b}{\overset{k_f}{\rightleftarrows}} R$$





Assume:

- O and R are stable, soluble
- no competing chemical reactions occur

number of reductions per second $\propto \underbrace{N_{Av} C_0\, A}$ → $= k_f N_{Av} C_0\, A$

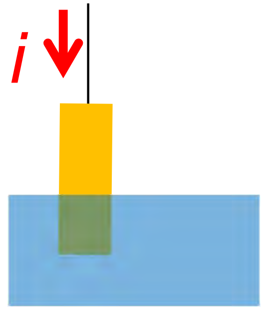
A=area of the electrode [cm^2]

number of O *near the electrode* ***$[C_O]=[mol/cm^3]$***

rate constant (cm/s)

number of oxidations per second $= k_b N_{Av} C_R\, A$

Sign convention:



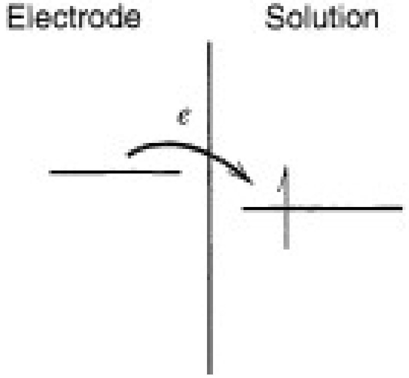
$$\boxed{i = i_b - i_f = nq\left[k_b N_{Av}\, A C_R(0) - k_f N_{Av}\, A C_O(0)\right]}$$

x=0 (at the surface)

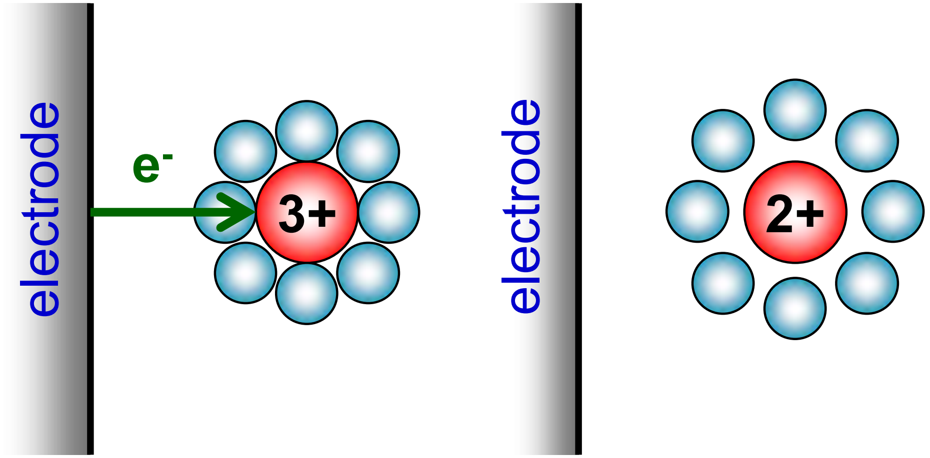
Marcus / Gerischer microscopic model

(1992 Nobel prize in chemistry)

- ***Tunneling*** between states in the electrode and those of the ion/molecule

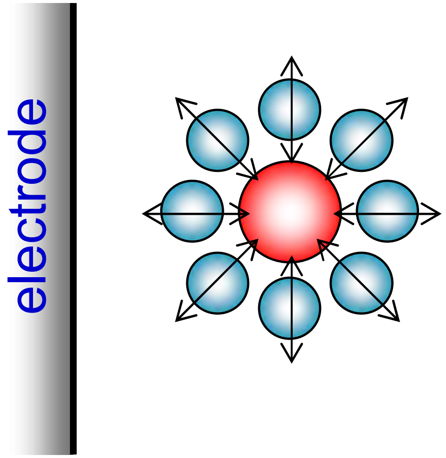


- reorganization energy (λ)



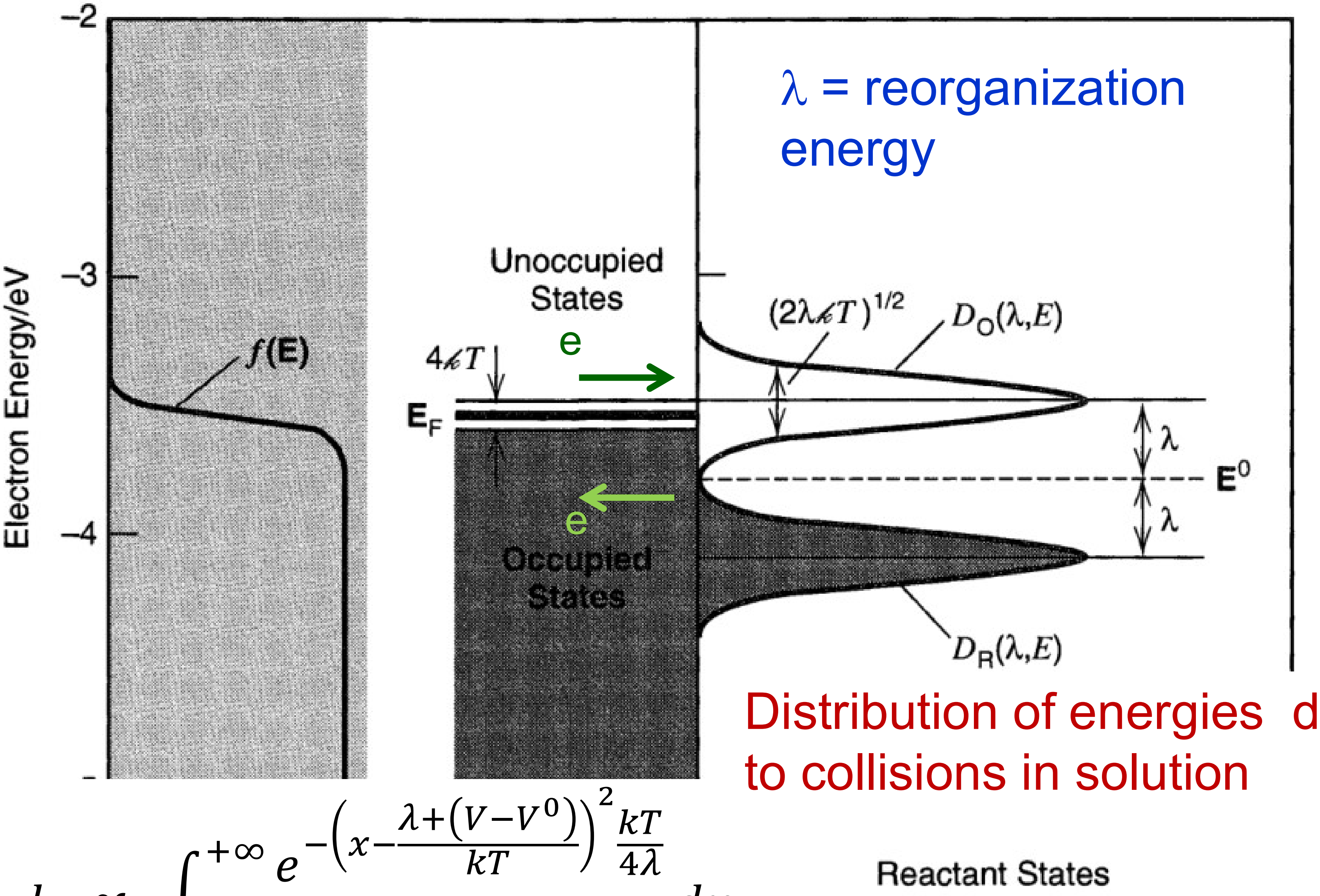
Two different energy levels

- fluctuations of the solvent molec.



Distributions of energy states

Electron Transfer: Gerischer view



λ = reorganization energy

Distribution of energies due to collisions in solution

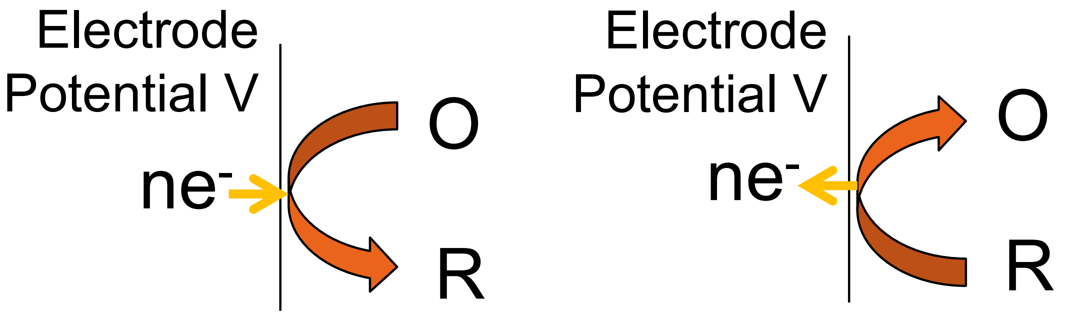
$$k_f \propto \int_{-\infty}^{+\infty} \frac{e^{-\left(x-\frac{\lambda+\left(V-V^0\right)}{kT}\right)^2 \frac{kT}{4\lambda}}}{1+e^x}\,dx$$

Bard, Electrochemical methods. Fundamentals and applications

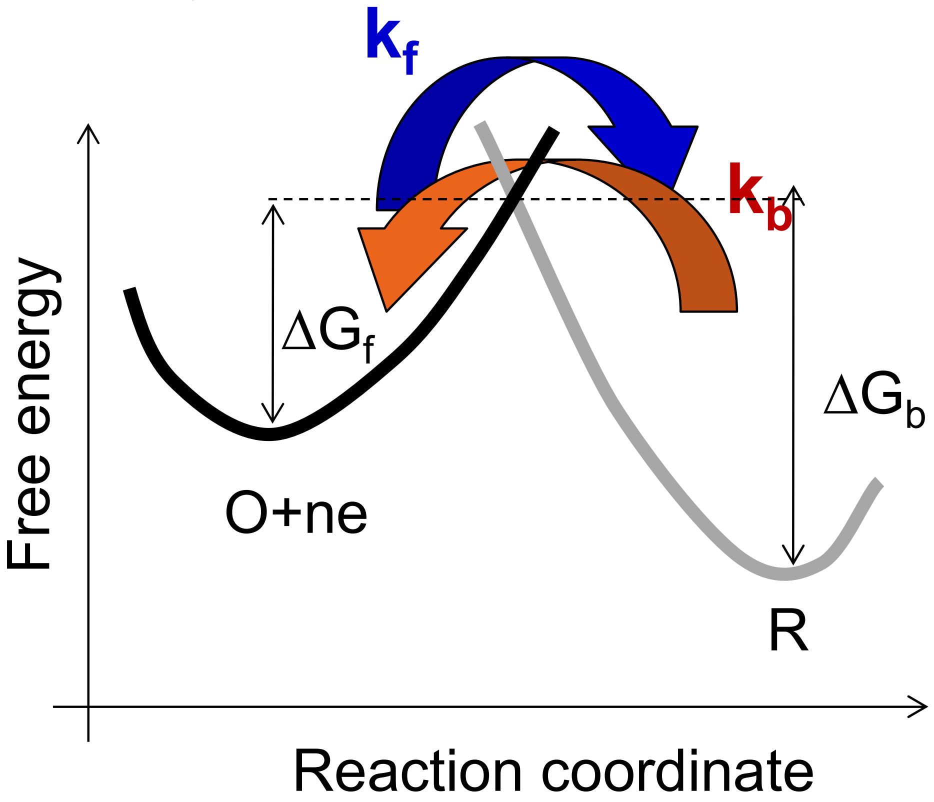
The Thermodynamics of Electron Transfer

Consider:

$$\mathrm{O} + ne^- \underset{k_b}{\overset{k_f}{\rightleftarrows}} \mathrm{R}$$



Arrhenius theory: an energy barrier has to be surmounted by the reactants before they can be converted to product

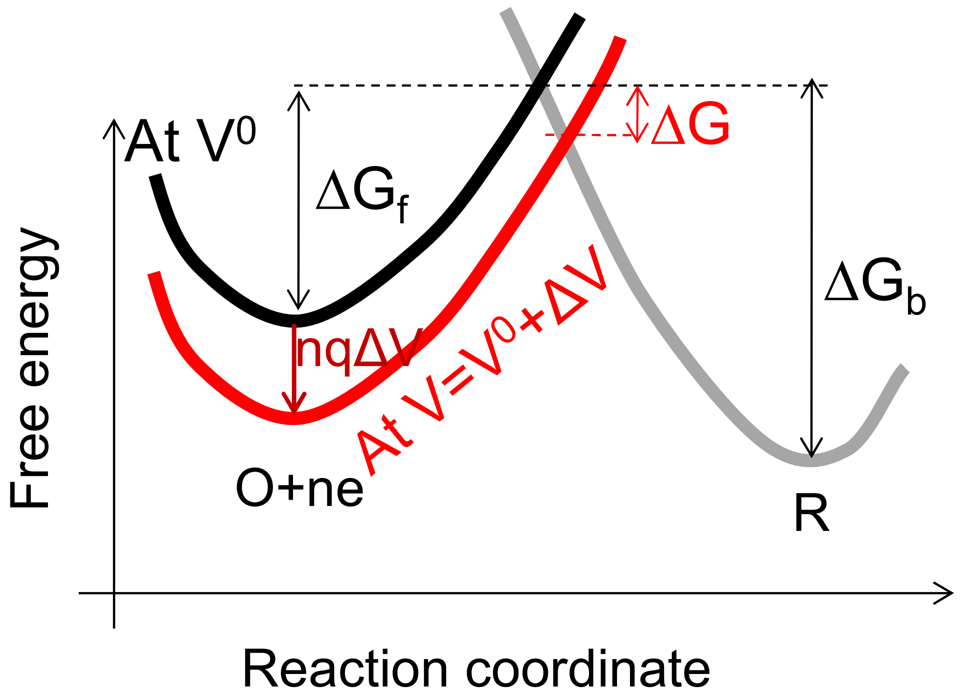


Arrhenius equation:

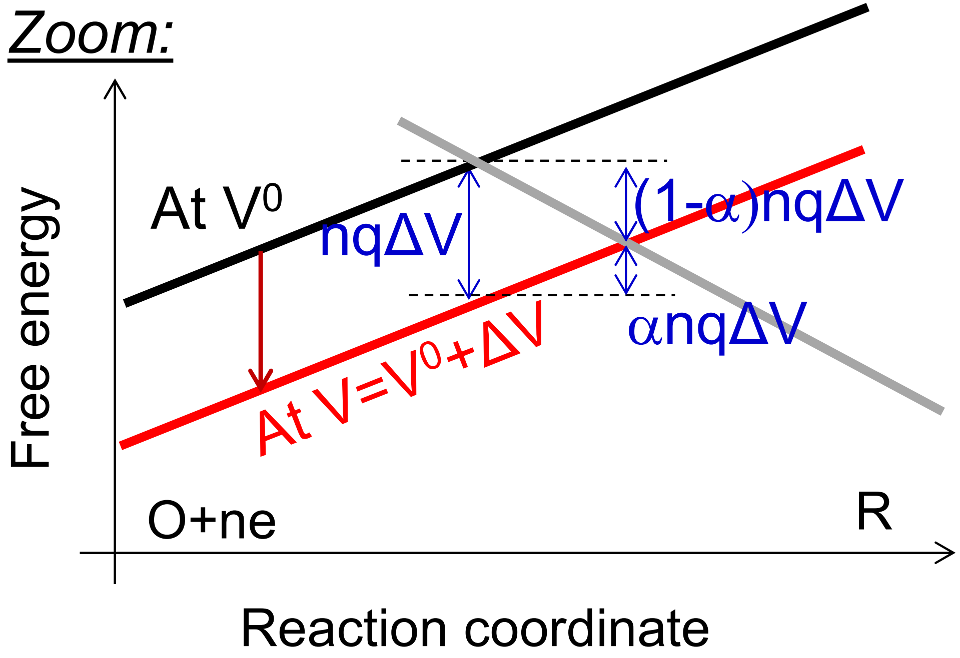
$$k_f = A_f e^{-\frac{\Delta G_f}{kT}}$$

$$k_b = A_b e^{-\frac{\Delta G_b}{kT}}$$

Effect of the voltage on the energy barrier



Zoom:



Linearization of curves:
ΔG is prop. to ΔV

$$\Delta G_f = \Delta G_f^0 + nq\Delta V - (1-\alpha)nq\Delta V$$
$$\Delta G_b = \Delta G_b^0 - (1-\alpha)nq\Delta V$$

$$k_f = k_0 e^{-\frac{\alpha nq\left(V-V^{0'}\right)}{kT}}$$

$$k_b = k_0 e^{\frac{(1-\alpha)nq\left(V-V^{0'}\right)}{kT}}$$

α= transfer coefficient, about 0.5
$V^{0'}$= formal potential of the reaction: $k_f=k_b$
k_0 = standard rate constant

Electronic current

$$O + ne^- \underset{k_b}{\overset{k_f}{\longleftrightarrow}} R$$

$$i = i_b - i_f = nqN_{Av}\,A\left[k_b C_R(0) - k_f C_O(0)\right]$$

A= surface area
C(0)= concentration
at the electrode

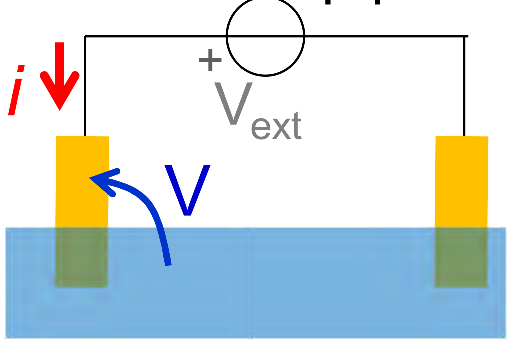
$$\boxed{i = nqN_{Av}Ak_0\left[C_R(0)e^{(1-\alpha)nq\left(V-V^{0'}\right)/kT} - C_O(0)e^{-\alpha nq\left(V-V^{0'}\right)/kT}\right]}$$

Butler-Volmer formulation of electrode kinetics

Typical values:

- $\alpha \approx 0.5$
- k_0 : 1-10 cm/s for simple electron transfer
  10^{-6} cm/s or less for multistep process with molecular rearrangement

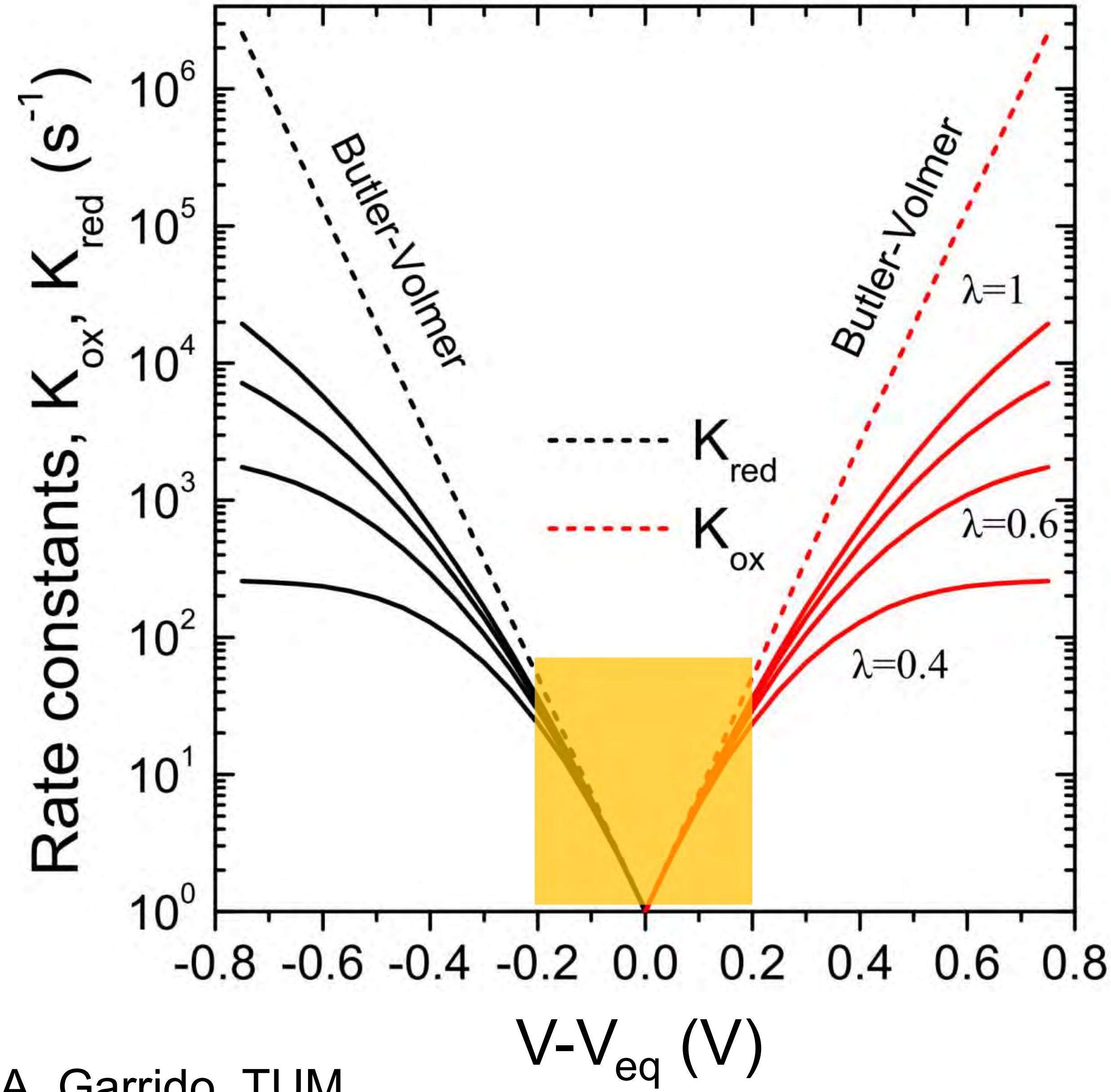
Sign convention:



$V = V_{ext} - R_{sol}\cdot i - V_{2nd\ electrode}$

(see Carminati's lesson on how to better control V using V_{ext})

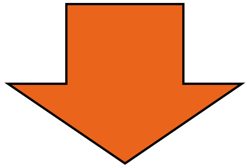
Marcus / Gerischer model vs Butler-Volmer



J.A. Garrido, TUM

typical λ: 0.5eV – 1eV

measurable kinetics usually corresponds to a ΔV_{max} of 50-200mV



Butler-Volmer is accurate enough

…kinetic is not the only parameter controlling the current ! (next lesson)

Equilibrium condition

$$i = nqN_{Av}Ak_0\left[C_R(0)e^{(1-\alpha)nq\left(V-V^{0'}\right)/kT} - C_O(0)e^{-\alpha nq\left(V-V^{0'}\right)/kT}\right]$$

At equilibrium, no net current flows: i =i_b - i_f= 0

$$\boxed{V_{eq} = V^{0\prime} + \frac{kT}{nq}\ln\left(\frac{C_O}{C_R}\right)}$$

Nernst equation

Dynamic equilibrium : O + ne⁻ → R, R - ne⁻ → O

both processes will occur at equal rates:

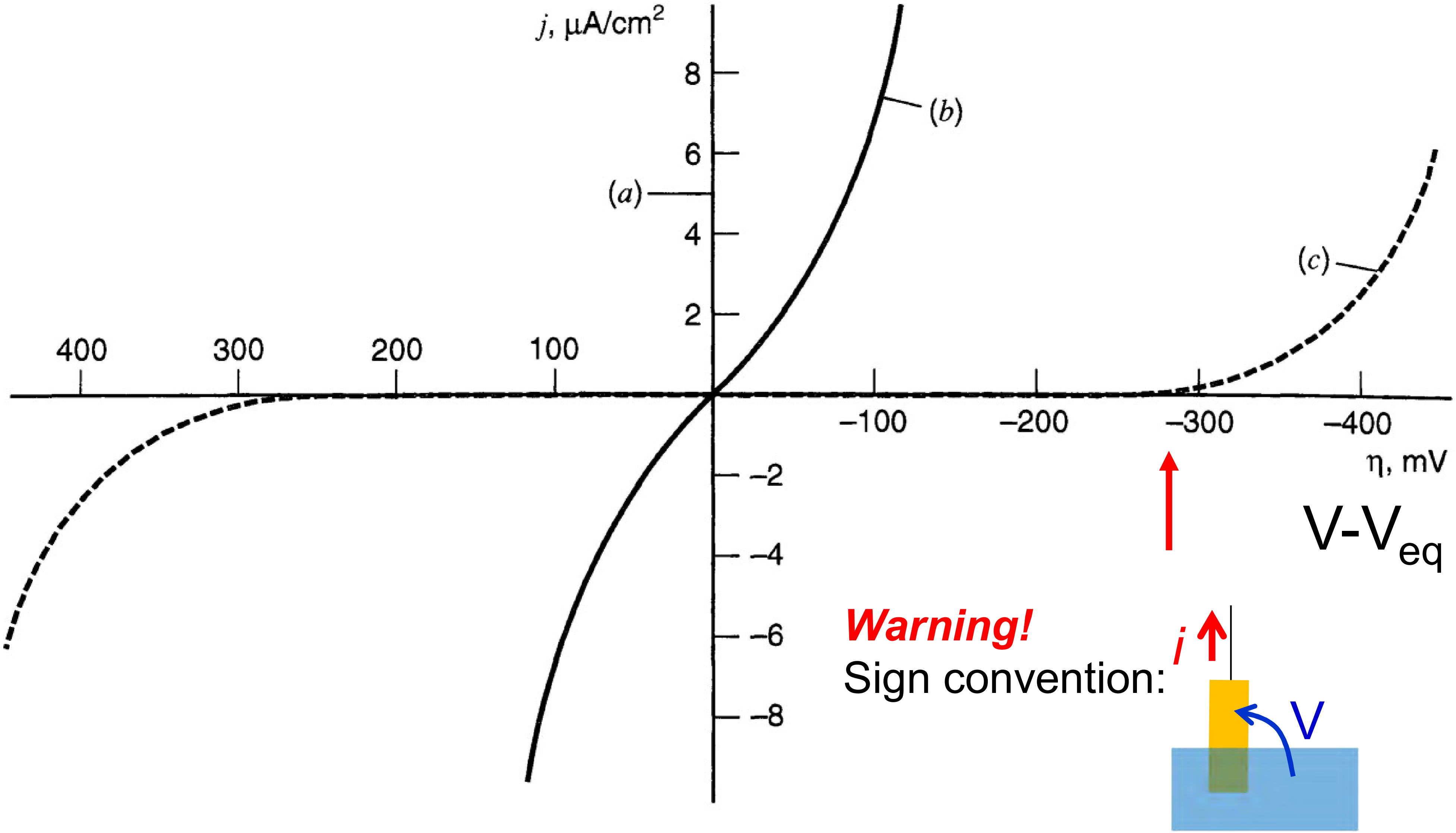
$$i_f = i_b = i_0 = nqN_{Av}Ak_0C_Oe^{-\alpha nq\left(V_{eq}-V^{0'}\right)/kT} = nqN_{Av}Ak_0C_O^{1-\alpha}C_R^{\alpha}$$

$i_0 =$ *exchange current*

$$\boxed{\boldsymbol{i = i_0\left(e^{(1-\alpha)nq(V-V_{eq})/kT} - e^{-\alpha nq(V-V_{eq})/kT}\right)}}$$

(it is the same equation!)

Kinetic controlled current



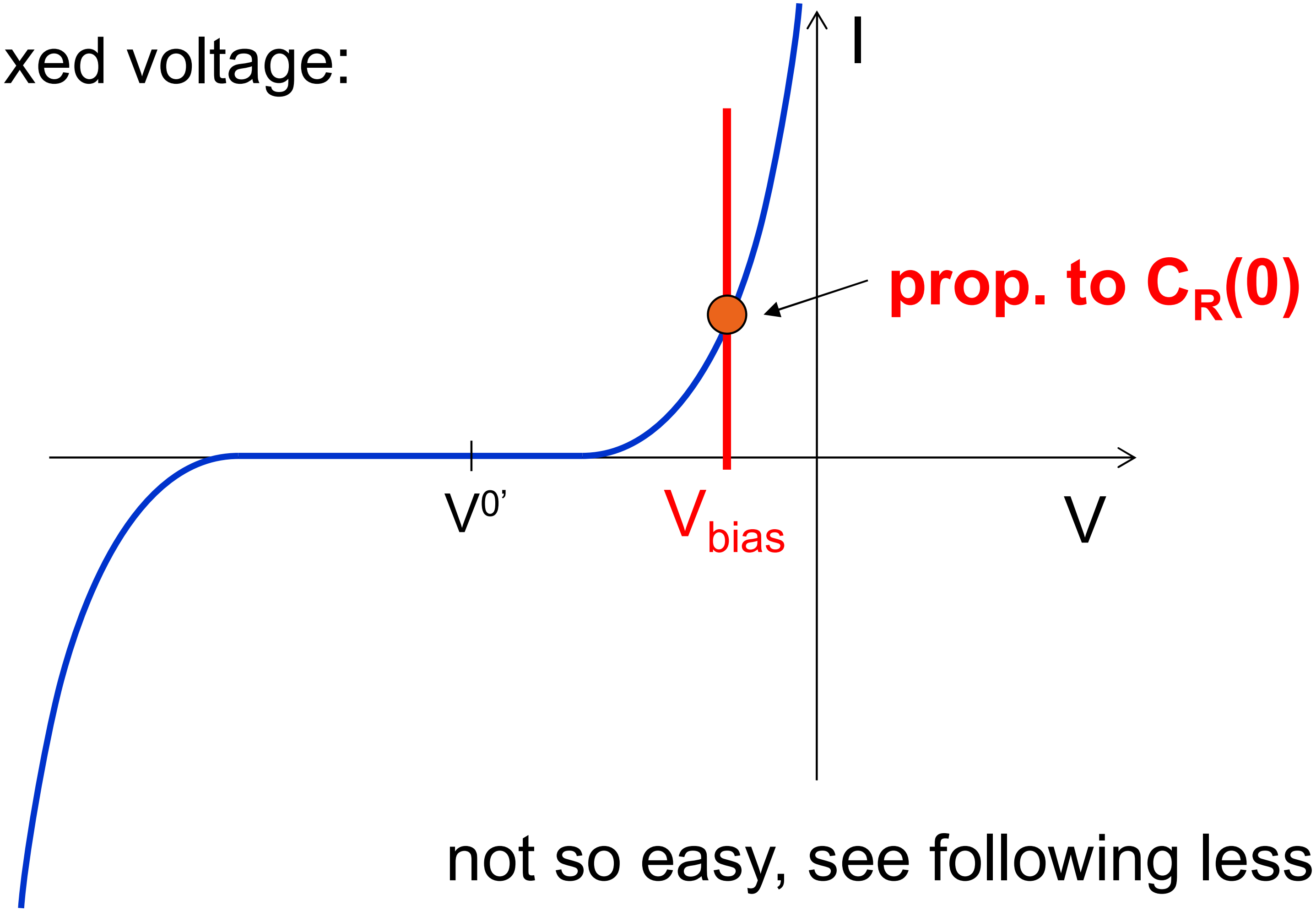
Warning!
Sign convention:

α=0.5; (a) i_0= 10^{-3} A/cm^2; (b) i_0= 10^{-6} A/cm^2; (c) i_0= 10^{-9} A/cm^2

Bard, Electrochemical methods. Fundamentals and applications

Amperometric sensor

Operating at fixed voltage:



not so easy, see following lessons!

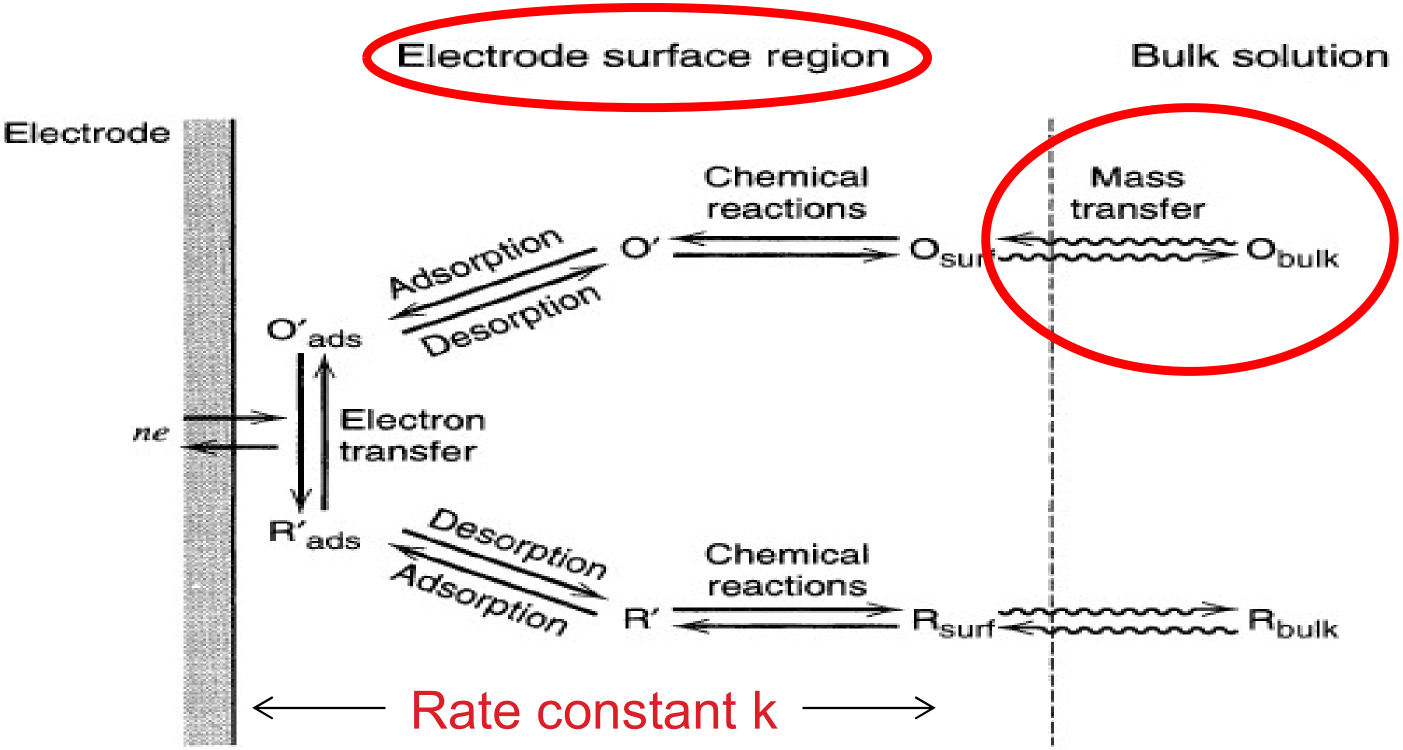
Butler-Volmer equation: concentrations at the surface

$$i = nqN_{Av}Ak_0\left[C_R(0)e^{(1-\alpha)nq\left(V-V^{0'}\right)/kT} - C_O(0)e^{-\alpha nq\left(V-V^{0'}\right)/kT}\right]$$

An Interfacial Process

For: **O + ne$^-$ ↔ R** 5 separate events must occur:

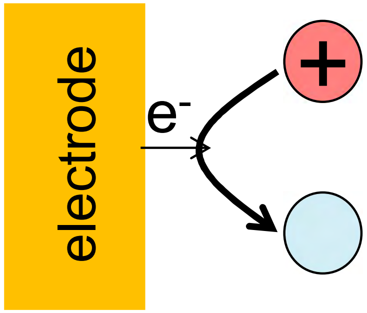
- O must be successfully transported from bulk solution (mass transport)
- O must adsorb transiently onto electrode surface (non-faradaic); Chemical reactions preceding or following the electron transfer (e.g., protonation or dimerization or catalytic decomposition) on the electrode surface.
- CT must occur between electrode and O (faradaic)
- R must desorb from electrode surface (non-faradaic)
- R must be transported away (mass transport)



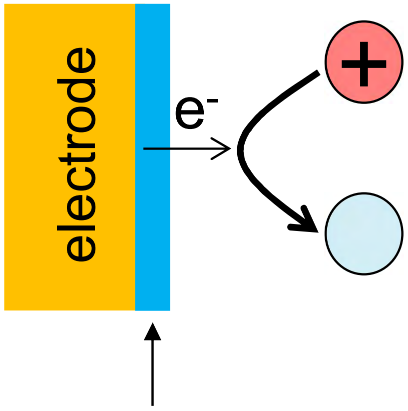
Next lesson

Bard, Electrochemical methods. Fundamentals and applications

Do not forget electrode pretreatments!



The electron transfer of a redox reaction is a tunneling process



Contaminants on the electrode surface

The rate constant is exponentially related to the electrode – molecule distance

↓

≈ nm thick contaminant can drastically reduce the electron transfer rate

Cleanliness is fundamental

Kinetics (and double layer) are controlled by the surface

→ electrodes must be carefully cleaned before each experiment:

- Mechanical polishing (alumina), ultrasonic cleaning, plasma
- Chemical
  - Sonicate in acetone
  - Soak in HNO_3, aqua regia
  - …
- Electrochemical
  - Oxidation/reduction cycles in 0.5 M H_2SO_4 (Pt)
  - Oxidation/reduction cycles (-0.2V – +1.2V vs Ag/AgCl) in 50mM KOH (Au)
  - …

Oxygen reduction can interfere with the measurement

→ removal by purging with an inert gas

Limited electrochemical window

Aqueous Solutions at 25°C in V vs. SHE, 1atm, C^0=1M

$1/2F_2 + H^+ + e \leftrightarrows HF$	+3.050
$Au^+ + e \leftrightarrows Au$	+1.83
$O_2 + 4H^+ + 4e \leftrightarrows 2H_2O$	+1.229
$Pt^{2+} + 2e^- \leftrightarrows Pt$	+1.188
$Ag^+ + e^- \leftrightarrows Ag$	+0.799
$Fe^{3+} + e \leftrightarrows Fe^{2+}$	+0.771
$O_2 + 2H_2O + 4e \leftrightarrows 4OH^-$	+0.401

oxygen and pH can interfere!

$Cu^{2+} + 2e \leftrightarrows Cu$	+0.340
$AgCl + e \leftrightarrows Ag + Cl^-$	+0.222

$2H^+ + 2e \leftrightarrows H_2$	0.0000
$Fe^{2+} + 2e \leftrightarrows Fe$	-0.44
$Zn^{2+} + 2e \leftrightarrows Zn$	-0.762
$2H_2O + 2e \leftrightarrows H_2 + 2OH^-$	-0.828

water electrolysis!

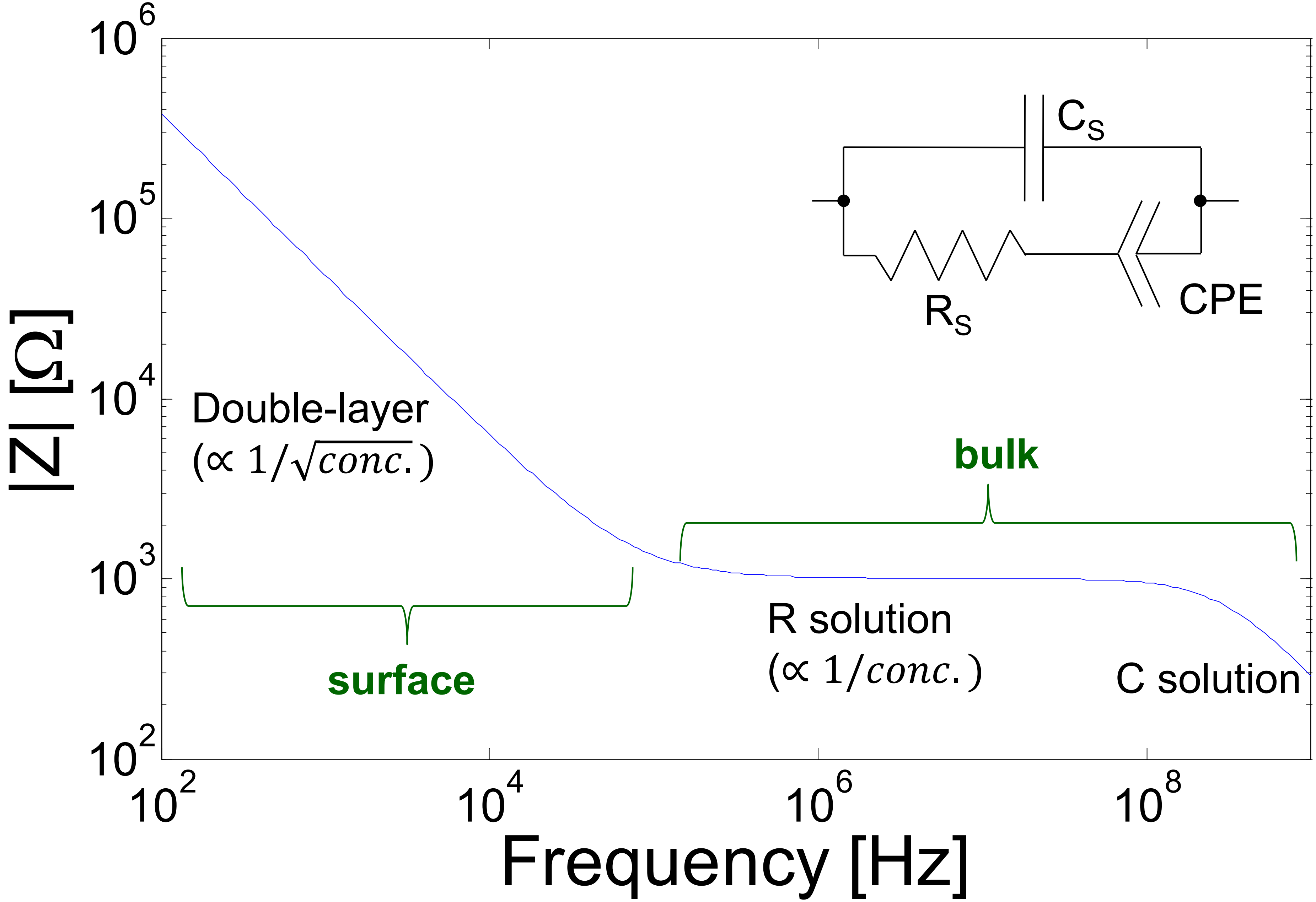
	-2.714
$Ca^{++} + 2e \leftrightarrows Ca$	-2.87
$K^+ + e \leftrightarrows K$	-2.93
$Li^+ + e \leftrightarrows Li$	-3.04

Experiment in water are typically limited at ΔV less than 2V

($\approx -1V < V < \approx 1V$ vs AgCl)

What about impedance spectra?

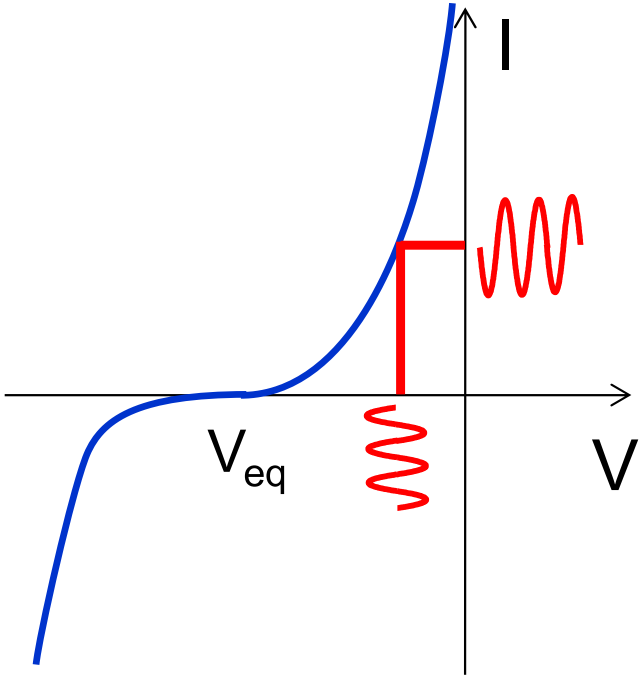
From the previous lesson WITHOUT charge transfer



Equivalent Circuit: Charge Transfer

The impedance concept requires a linear system
Electrode kinetics gives a non-linear behavior

Small signal → linearization



Charge transfer resistance:

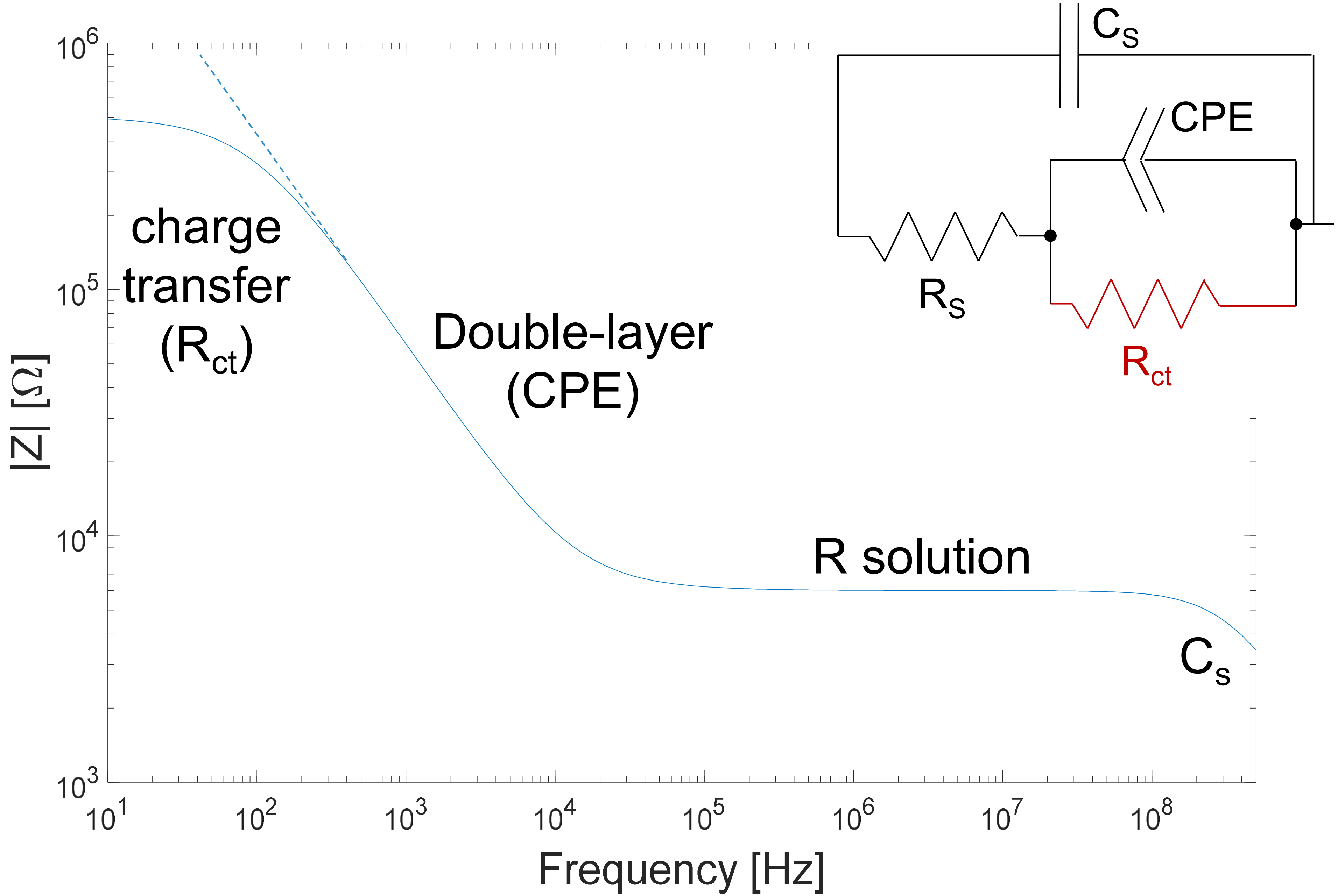
$$\boxed{R_{ct} = \left.\frac{\partial V}{\partial i}\right|_{working\ point}}$$

$$i = i_0\left(e^{(1-\alpha)nq\left(V-V_{eq}\right)/kT} - e^{-\alpha nq\left(V-V_{eq}\right)/kT}\right)$$

$$i_0 = nqN_{Av}Ak_0C_O^{1-\alpha}C_R^{\alpha}$$

A stationary condition is more easily obtained with V≈V_{eq} → $R_{ct} \approx \frac{kT}{nq}\frac{1}{i_0}$

Impedance spectrum



Summary

- Equilibrium potential at the electrode-liquid interface
  - I=0 does not imply external voltage = 0V!
  - Equilibrium potential depends on metals involved, ion species and ion concentrations → standard potentials, Nernst equation
  - You never measure the single liquid-metal potential → at least two electrodes → reference electrode (AgCl)

- Electron transfer at the interface is possible:
  - Corrosion / deposition of the metal or **redox process at the metal-liquid interface**
  - Exponential current-voltage characteristic controlled by $V-V^0$ and by concentrations of species O and R at the surface
  - Empiric Butler-Volmer relation is accurate enough in many cases
  - Impedance: charge transfer resistance in parallel to C_{dl}