



I³N
for *Innovative
Integrated
Instrumentation
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*

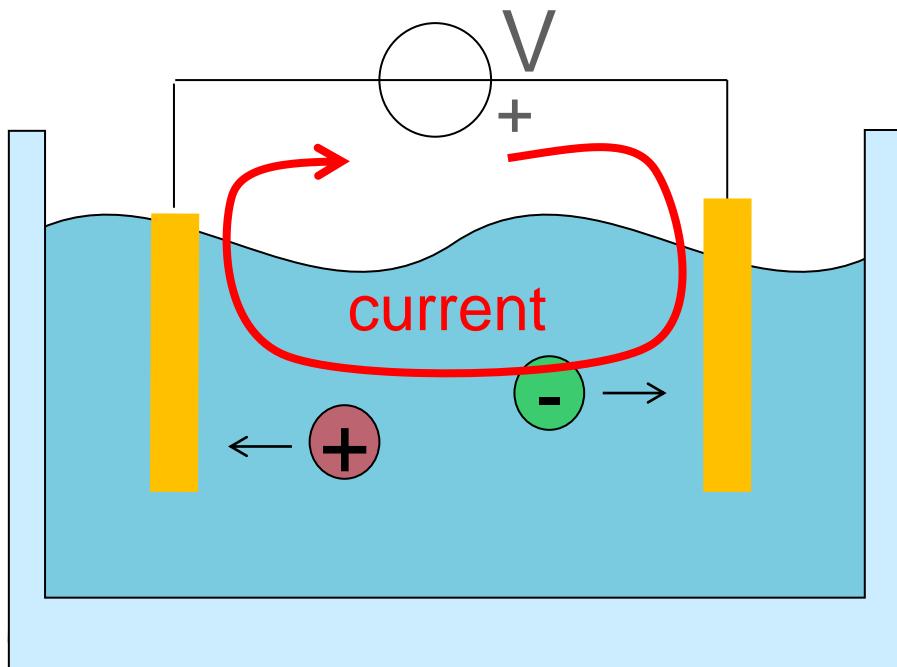
Giorgio Ferrari

Milano, June 2023

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

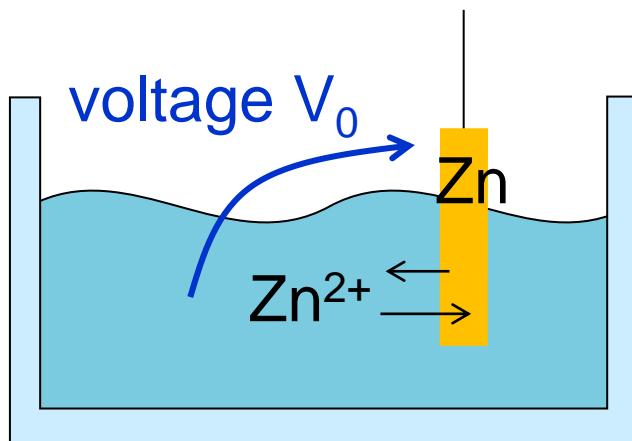
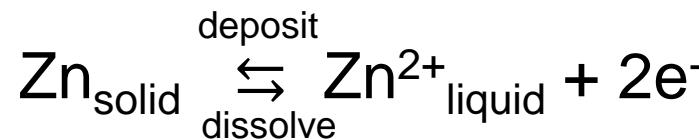


electron transfer at the metal/liquid interface to sustain a DC current

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^{2+} deposit $\rightarrow V_0$ increases $\rightarrow Zn^{2+}$ repulsed

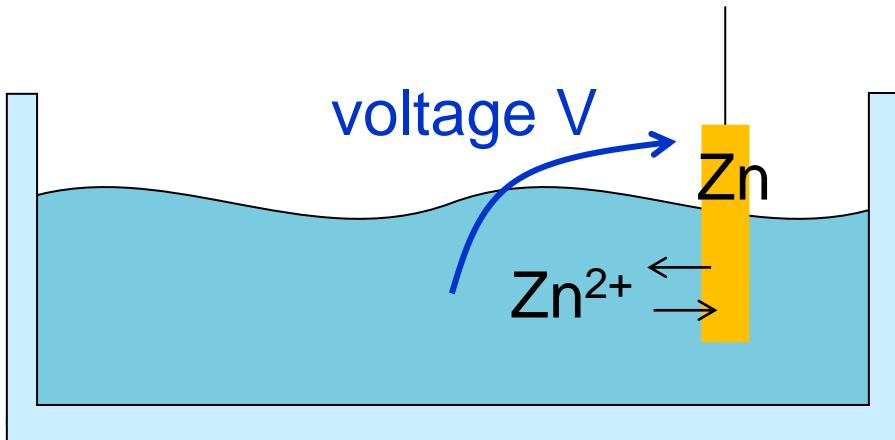
Zn dissolve $\rightarrow V_0$ decreases $\rightarrow Zn^{2+}$ attracted

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,...

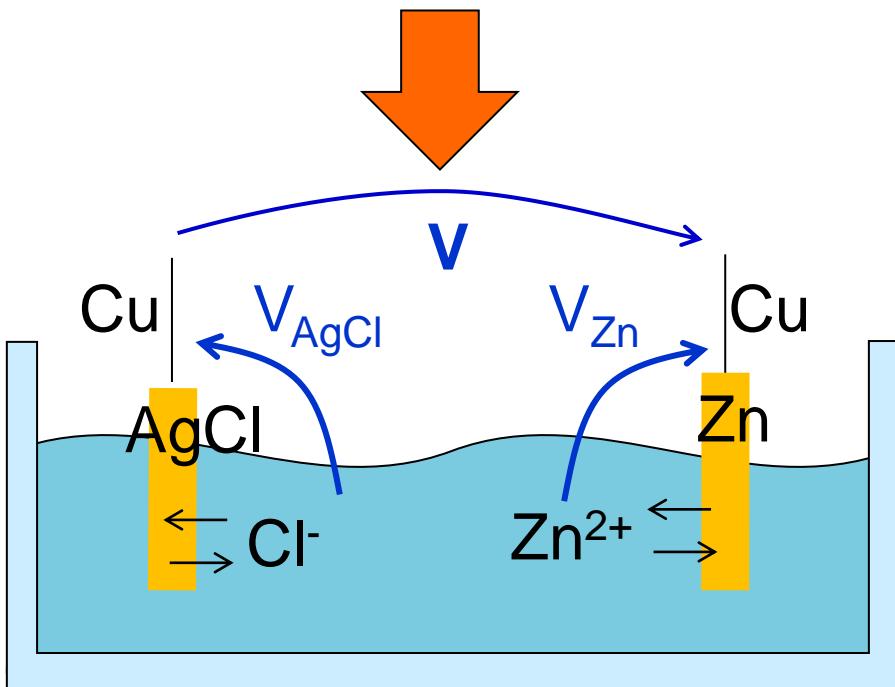
Dynamic equilibrium

Electrochemical cell

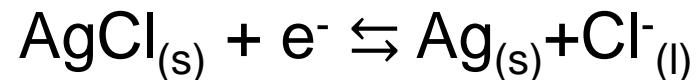


Voltage V is **not** directly measurable using a voltmeter

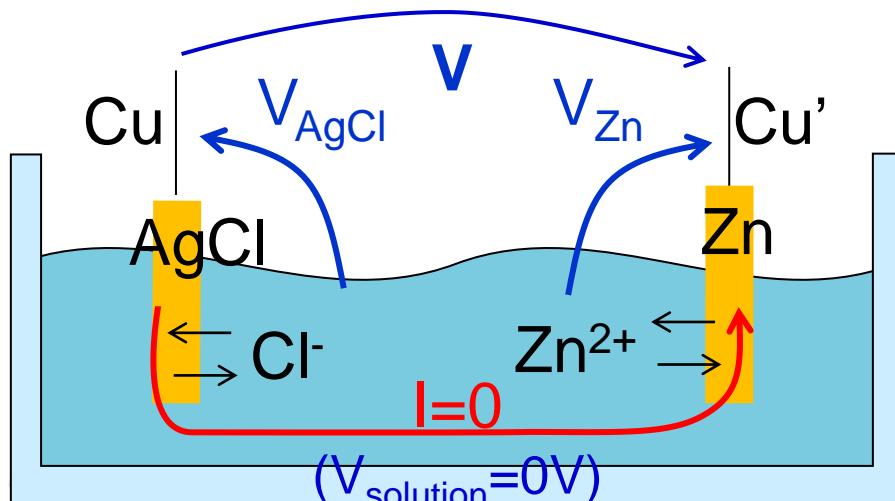
A 2nd electrode is required!



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



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}

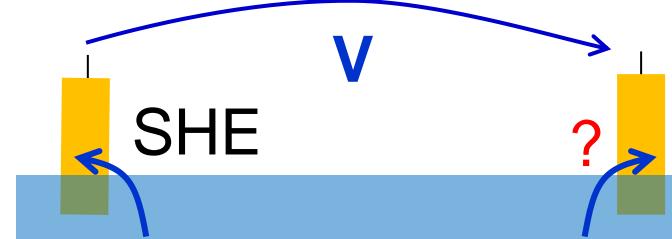
$$V = V_{\text{Zn}} - V_{\text{AgCl}}$$

Equilibrium may require $V \neq 0V$ (battery!)

Standard electrode potentials

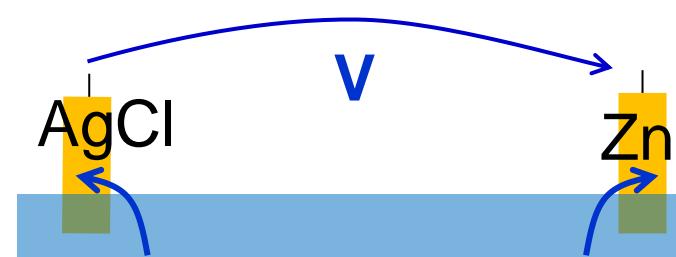
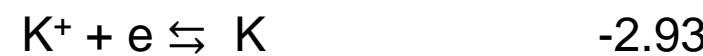
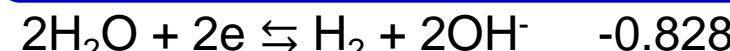
Aqueous Solutions at 25°C in V vs. SHE (standard hydrogen electrode), 1atm, C⁰=1M

$\frac{1}{2}\text{F}_2 + \text{H}^+ + \text{e} \rightleftharpoons \text{HF}$	+3.050	$2\text{H}^+ + 2\text{e} \rightleftharpoons \text{H}_2$	0.0000
$\text{Au}^+ + \text{e} \rightleftharpoons \text{Au}$	+1.83	$\text{Fe}^{2+} + 2\text{e} \rightleftharpoons \text{Fe}$	-0.44
$\text{O}_2 + 4\text{H}^+ + 4\text{e} \rightleftharpoons 2\text{H}_2\text{O}$	+1.229	$\text{Zn}^{2+} + 2\text{e} \rightleftharpoons \text{Zn}$	-0.762
$\text{Pt}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pt}$	+1.188	$2\text{H}_2\text{O} + 2\text{e} \rightleftharpoons \text{H}_2 + 2\text{OH}^-$	-0.828
$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$	+0.799	$\text{Na}^+ + \text{e} \rightleftharpoons \text{Na}$	-2.714
$\text{Fe}^{3+} + \text{e} \rightleftharpoons \text{Fe}^{2+}$	+0.771	$\text{Ca}^{++} + 2\text{e} \rightleftharpoons \text{Ca}$	-2.87
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e} \rightleftharpoons 4\text{OH}^-$	+0.401	$\text{K}^+ + \text{e} \rightleftharpoons \text{K}$	-2.93
$\text{Fe}(\text{CN})_6^{3-} + \text{e} \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}$	+0.361	$\text{Li}^+ + \text{e} \rightleftharpoons \text{Li}$	-3.04
$\text{Cu}^{2+} + 2\text{e} \rightleftharpoons \text{Cu}$	+0.340		
$\text{AgCl} + \text{e} \rightleftharpoons \text{Ag} + \text{Cl}^-$	+0.222		



Standard electrode potentials

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

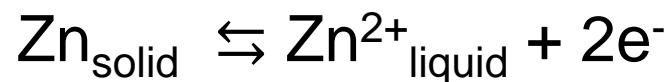


For the previous case:

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

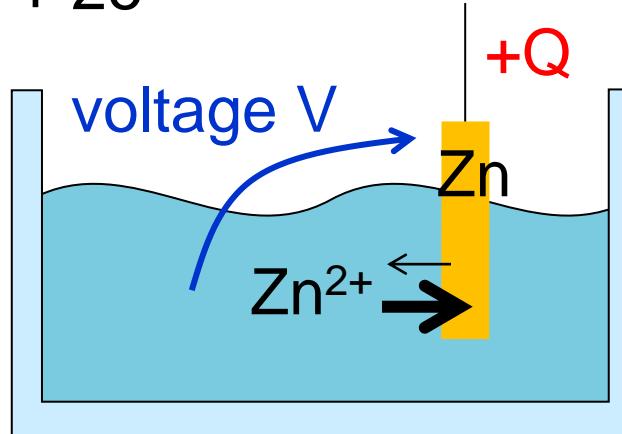
Eq. potential: role of the concentration

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



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

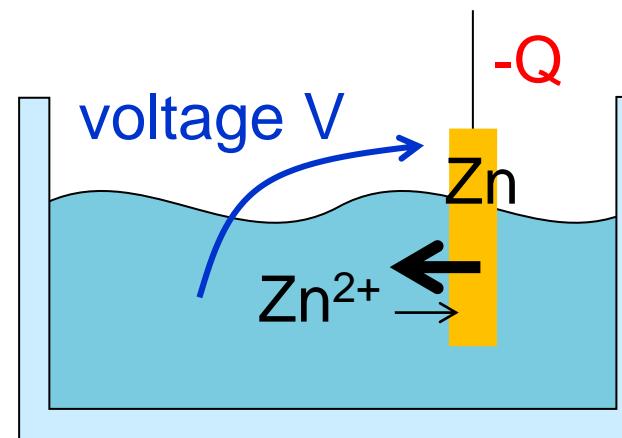
(Zn deposition)



equilibrium condition:
 $V > V_0$

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

(Zn dissolves)

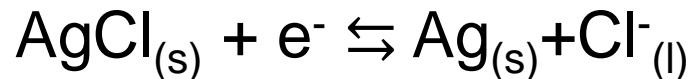


equilibrium condition:
 $V < V_0$

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

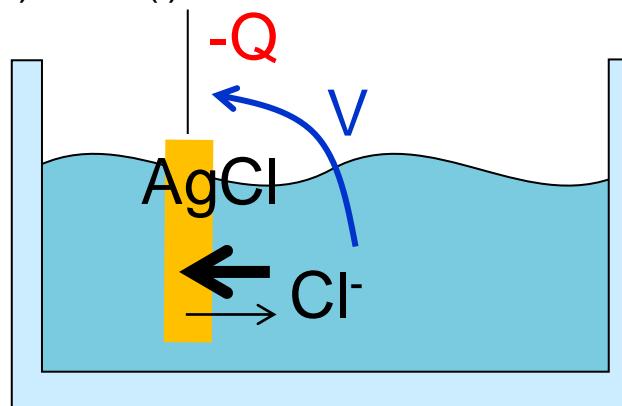
Eq. potential: role of the concentration

Ex.: AgCl electrode immersed in a solution with $\text{Cl}^- (C_{\text{Cl}^-})$:



$$C_{\text{Cl}^-} > C_{\text{Cl}^-,0}$$

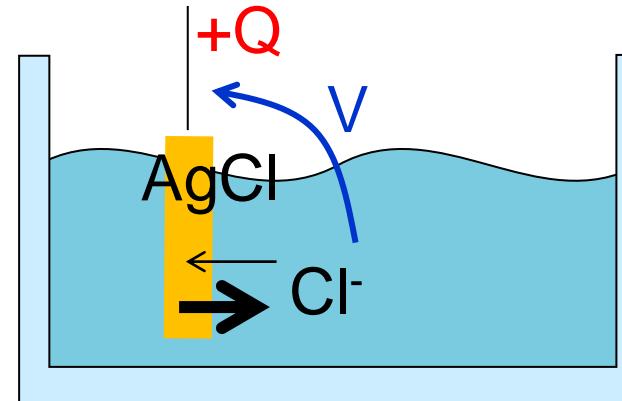
(AgCl production)



equilibrium condition:
 $V < V_0$

$$C_{\text{Cl}^-} < C_{\text{Cl}^-,0}$$

(AgCl dissolves)



equilibrium condition:
 $V > V_0$

Assuming a Boltzmann dist.: $V = V_0 - \frac{kT}{q} \log(C_{\text{Cl}^-}/C_{\text{Cl}^-,0})$

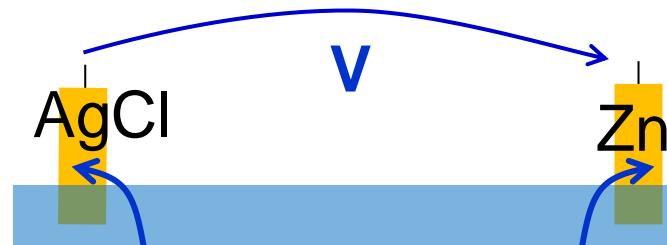
Nernst equation

Aqueous Solutions at 25°C in V vs. SHE, 1atm, C⁰=1M

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$\text{Au}^+ + \text{e} \rightleftharpoons \text{Au}$	+1.83	$\text{Fe}^{2+} + 2\text{e} \rightleftharpoons \text{Fe}$	-0.44
$\text{O}_2 + 4\text{H}^+ + 4\text{e} \rightleftharpoons 2\text{H}_2\text{O}$	+1.229	$\text{Zn}^{2+} + 2\text{e} \rightleftharpoons \text{Zn}$	-0.762
$\text{Pt}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pt}$	+1.188	$2\text{H}_2\text{O} + 2\text{e} \rightleftharpoons \text{H}_2 + 2\text{OH}^-$	-0.828
$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$	+0.799	$\text{Na}^+ + \text{e} \rightleftharpoons \text{Na}$	-2.714
$\text{Fe}^{3+} + \text{e} \rightleftharpoons \text{Fe}^{2+}$	+0.771	$\text{Ca}^{++} + 2\text{e} \rightleftharpoons \text{Ca}$	-2.87
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e} \rightleftharpoons 4\text{OH}^-$	+0.401	$\text{K}^+ + \text{e} \rightleftharpoons \text{K}$	-2.93
$\text{Fe}(\text{CN})_6^{3-} + \text{e} \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}$	+0.361	$\text{Li}^+ + \text{e} \rightleftharpoons \text{Li}$	-3.04
$\text{Cu}^{2+} + 2\text{e} \rightleftharpoons \text{Cu}$	+0.340		
$\text{AgCl} + \text{e} \rightleftharpoons \text{Ag} + \text{Cl}^-$	+0.222		

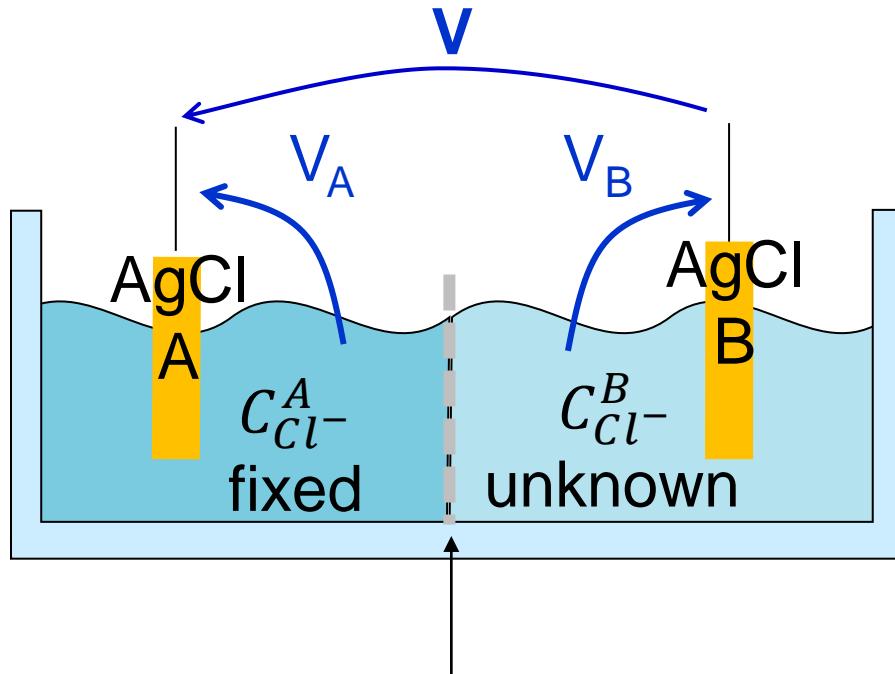
For the previous case:

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



Potentiometric sensor

Measure of concentration:



ion-selective membrane

equilibrium condition ($I=0$)

$$V_A = V_0 - \frac{kT}{q} \ln \left(\frac{C_{Cl^-}^A}{C^0} \right)$$
$$V_B = V_0 - \frac{kT}{q} \ln \left(\frac{C_{Cl^-}^B}{C^0} \right)$$
$$V = V_A - V_B = \frac{kT}{q} \ln \left(\frac{C_{Cl^-}^B}{C_{Cl^-}^A} \right)$$

$$V \propto \ln(C_{Cl^-}^B)$$

Standard electrode potentials

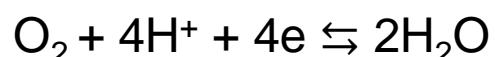
Aqueous Solutions at 25°C in V vs. SHE (standard hydrogen electrode), 1atm, C⁰=1M



+3.050



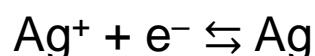
+1.83



+1.229



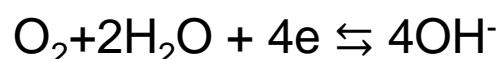
+1.188



+0.799



+0.771



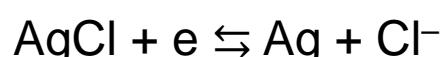
+0.401



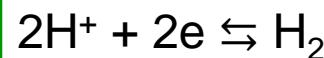
+0.361



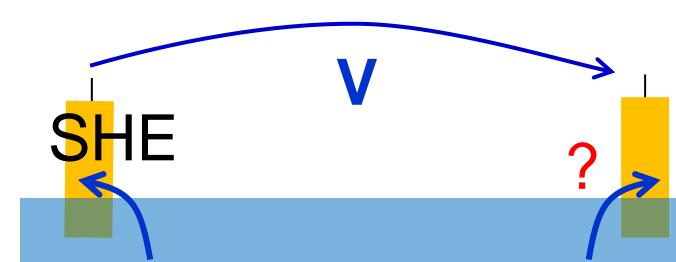
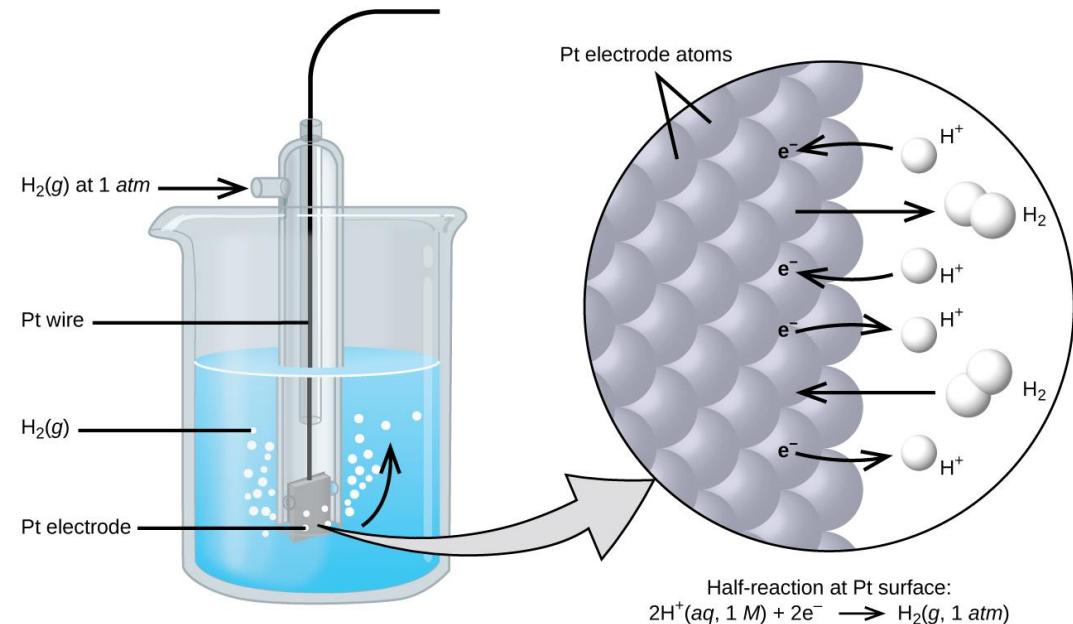
+0.340



+0.222



0.0000



Reference electrodes

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

Criteria:

- stable in potential (time, temperature)
- reversible
- reproducible
- potential shouldn't be altered by passage of small current = not polarizable
- easy fabrication and handling
- convenient for use

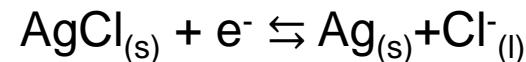
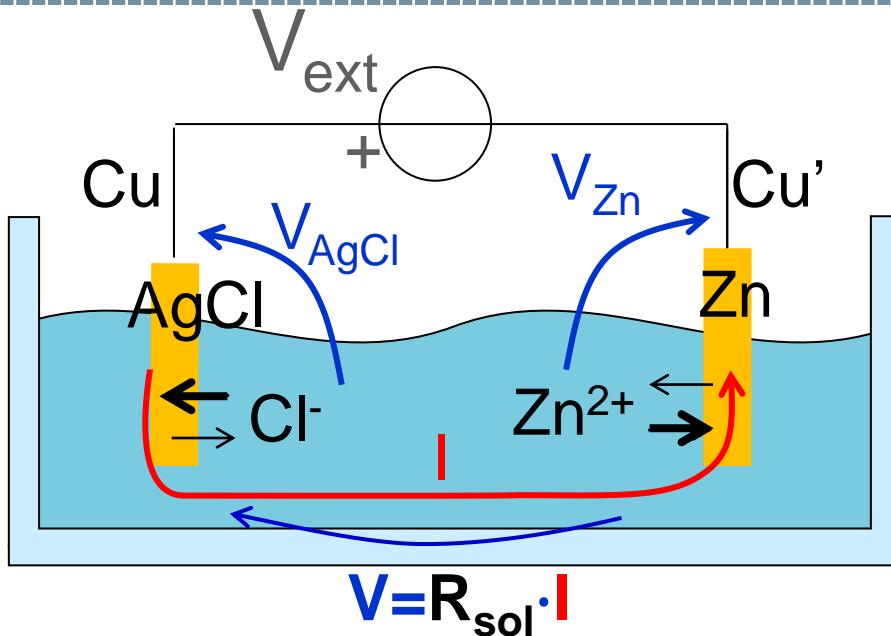
Reference electrodes

Aqueous Solutions at 25°C in V vs. SHE, 1atm, C⁰=1M

$\frac{1}{2}\text{F}_2 + \text{H}^+ + \text{e} \rightleftharpoons \text{HF}$	+3.050	$2\text{H}^+ + 2\text{e} \rightleftharpoons \text{H}_2$	0.0000
$\text{Au}^+ + \text{e} \rightleftharpoons \text{Au}$	+1.83	$\text{Fe}^{2+} + 2\text{e} \rightleftharpoons \text{Fe}$	-0.44
$\text{O}_2 + 4\text{H}^+ + 4\text{e} \rightleftharpoons 2\text{H}_2\text{O}$	+1.229	$\text{Zn}^{2+} + 2\text{e} \rightleftharpoons \text{Zn}$	-0.762
$\text{Pt}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pt}$	+1.188	$2\text{H}_2\text{O} + 2\text{e} \rightleftharpoons \text{H}_2 + 2\text{OH}^-$	-0.828
$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$	+0.799	$\text{Na}^+ + \text{e} \rightleftharpoons \text{Na}$	-2.714
$\text{Fe}^{3+} + \text{e} \rightleftharpoons \text{Fe}^{2+}$	+0.771	$\text{Ca}^{++} + 2\text{e} \rightleftharpoons \text{Ca}$	-2.87
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e} \rightleftharpoons 4\text{OH}^-$	+0.401	$\text{K}^+ + \text{e} \rightleftharpoons \text{K}$	-2.93
$\text{Fe}(\text{CN})^{3-}_6 + \text{e} \rightleftharpoons \text{Fe}(\text{CN})^{4-}_6$	+0.361	$\text{Li}^+ + \text{e} \rightleftharpoons \text{Li}$	-3.04
$\text{Cu}^{2+} + 2\text{e} \rightleftharpoons \text{Cu}$	+0.340	Saturated Calomel Electrode (SCE): +0.244	
$\text{AgCl} + \text{e} \rightleftharpoons \text{Ag} + \text{Cl}^-$	+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



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

By forcing $V_{\text{ext}} >$ equilibrium voltage

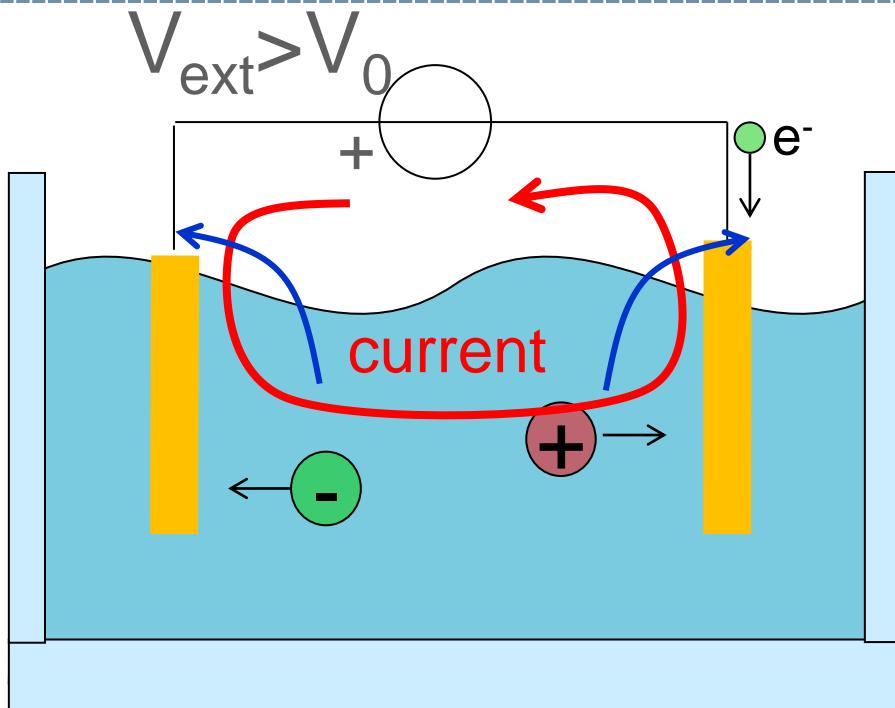
→ more Cl^- are attracted on the left ($V_{\text{AgCl}} \uparrow$)

more Zn^{2+} are attracted on the right ($V_{\text{Zn}} \downarrow$)

→ chemical equilibrium is broken

→ current

Electrical current in ionic conductors



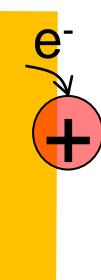
Ions move in the liquid

Electrons move in the electrodes

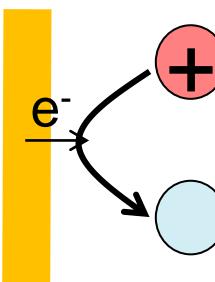


**Chemical reactions
with electron transfer
at the metal/liquid interfaces**

Two main cases:

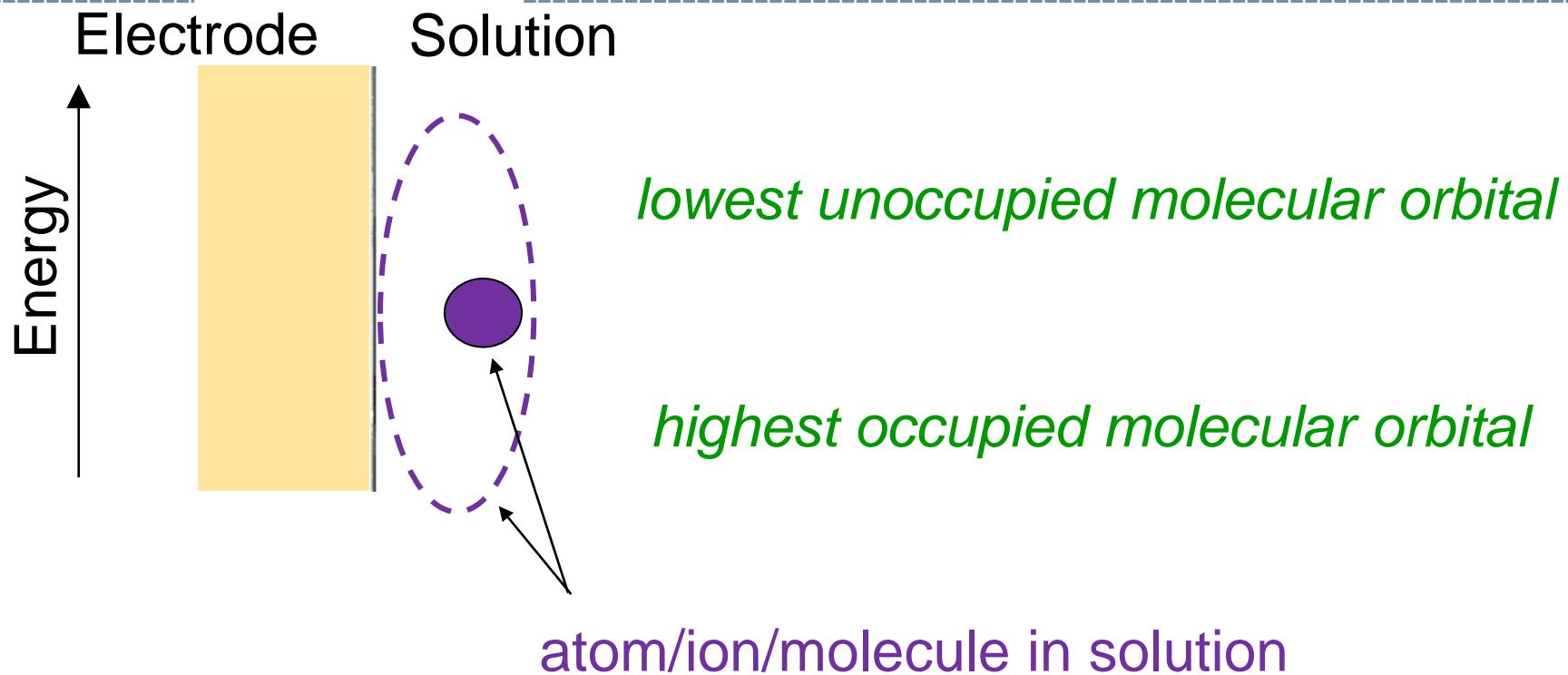


«consumable» electrode:
metal becomes less (more)
as a function of time
Corrosion / deposition



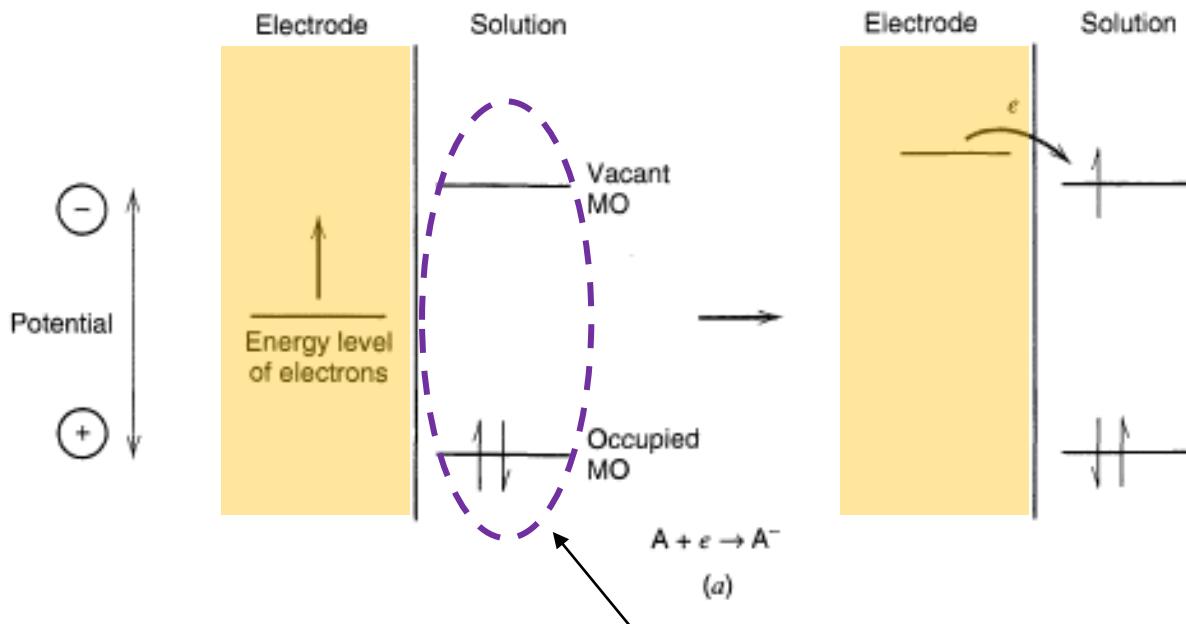
**«nonconsumable»
electrode:** reduction-
oxidation (redox)
reaction of ions or
molecules in liquid

Electron Transfer



Bard, Electrochemical methods.
Fundamentals and applications

Electron Transfer



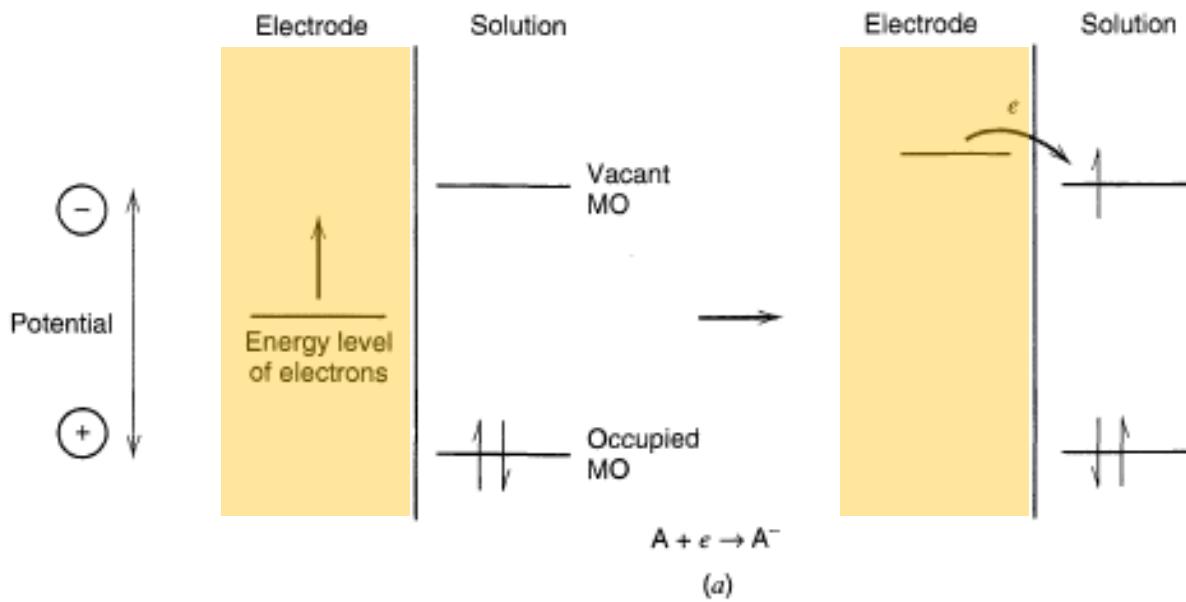
atom/ion/molecule in solution

Reduction:
atom/ion/molecule
gains an electron

reaction controlled by
the potential drop
across the interface

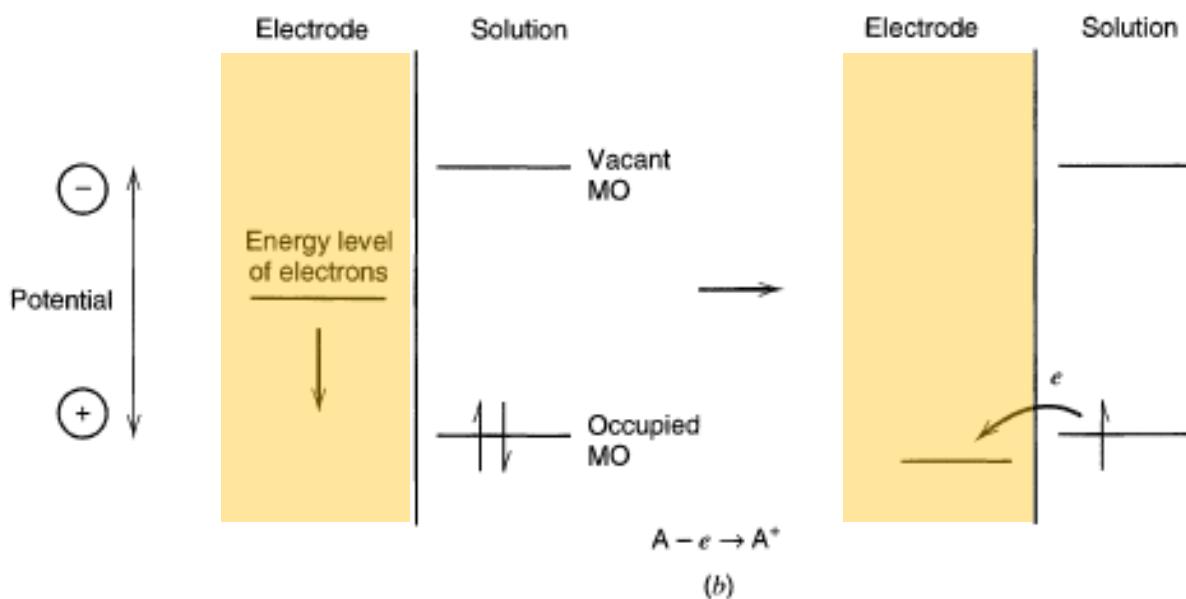
Bard, Electrochemical methods.
Fundamentals and applications

Electron Transfer



Reduction:
atom/ion/molecule
gains an electron

reaction controlled by
the potential drop
across the interface

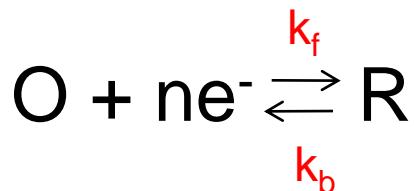


Oxidation:
atom/ion/molecule
loses an electron

Bard, Electrochemical methods.
Fundamentals and applications

The Kinetics of Electron Transfer

Consider:

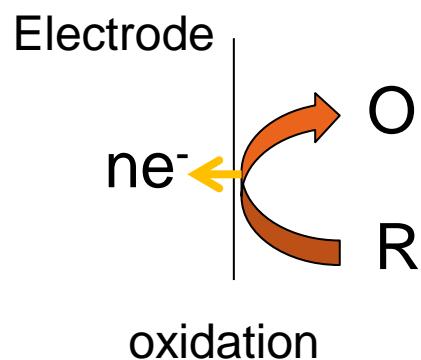
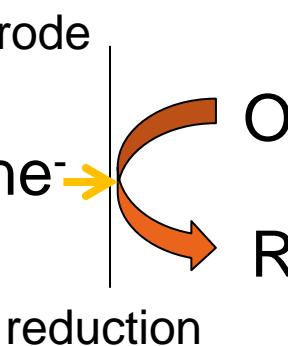


Assume:

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

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

A=area of the electrode [cm²]



**rate constant
(cm/s)**

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

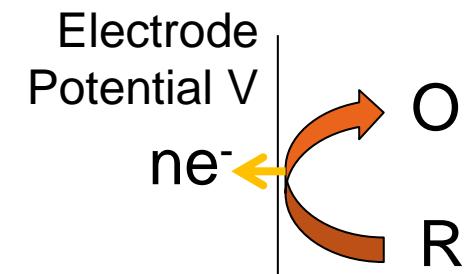
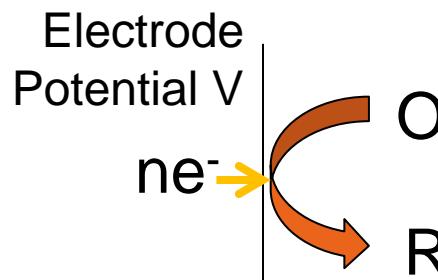
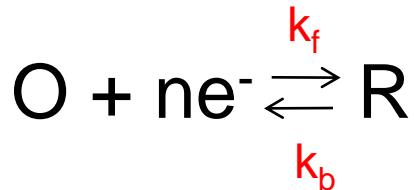
$$i = i_b - i_f = nq [k_b N_{Av} A C_R(0) - k_f N_{Av} A C_O(0)]$$

Sign convention:

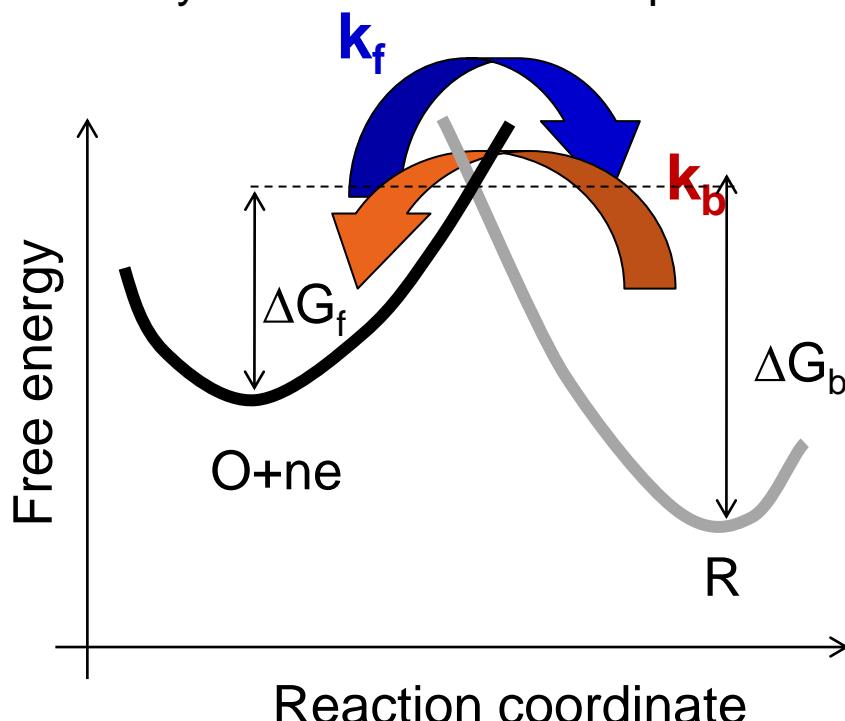


The Kinetics of Electron Transfer

Consider:



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

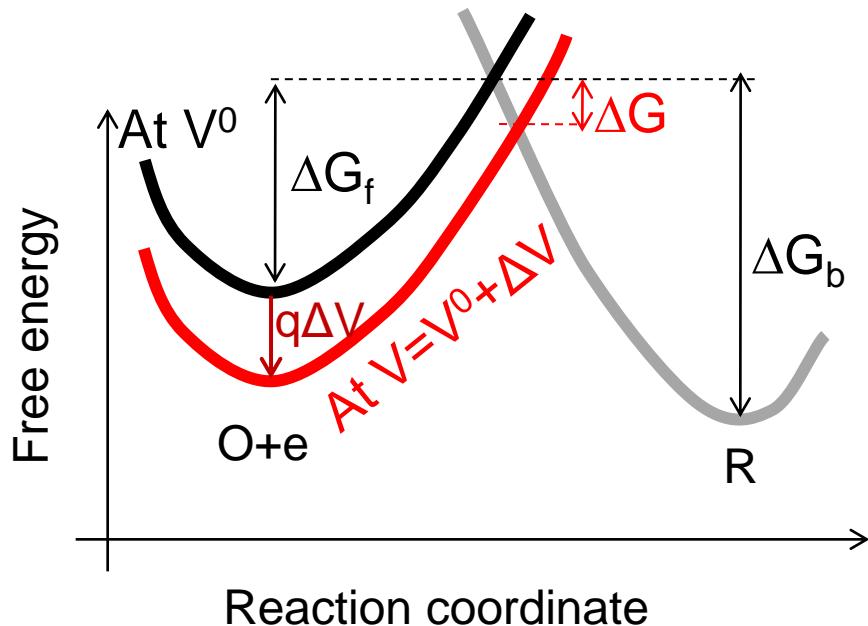


Arrhenius equation:

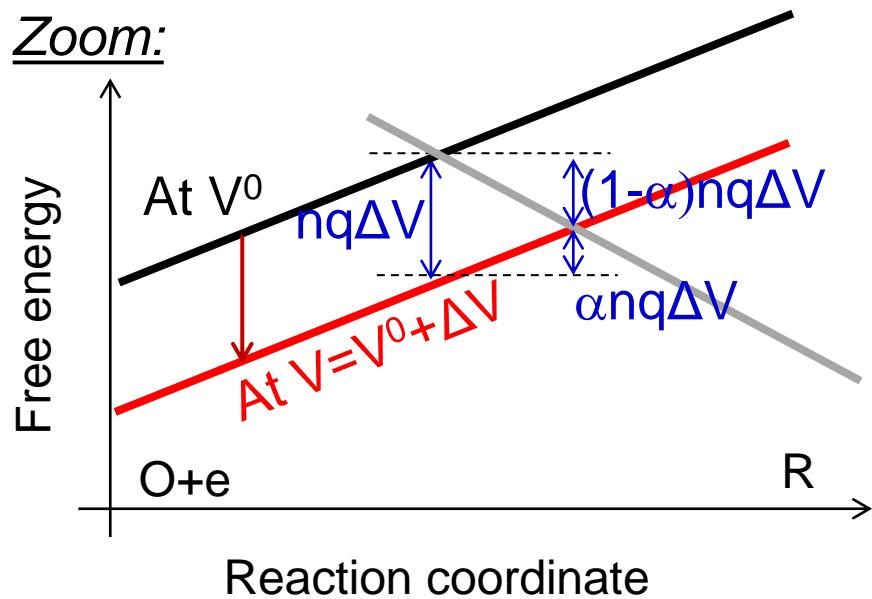
$$k_f = A_f e^{-\frac{\Delta G_f}{kT}}$$

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

Effect of the voltage on the energy barrier



Zoom:



Linearization of curves:
 ΔG is prop. to ΔV

↓

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

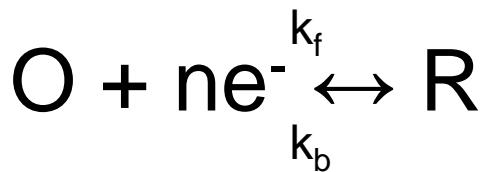
$$\Delta G_b = \Delta G_b^0 - (1 - \alpha)nq\Delta V$$

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

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

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

Electronic current



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

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

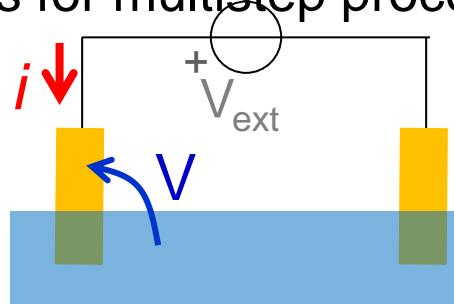
$$i = nqN_{Av}A k_0 \left[C_R(0) e^{(1-\alpha)nq(V-V^0')/kT} - C_O(0) e^{-\alpha nq(V-V^0')/kT} \right]$$

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:



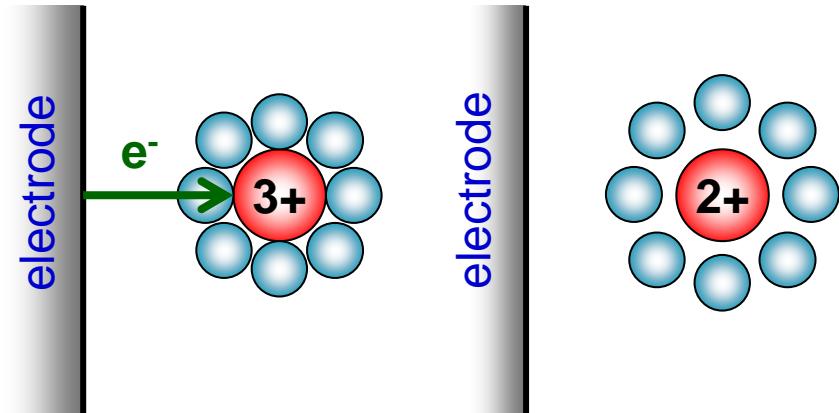
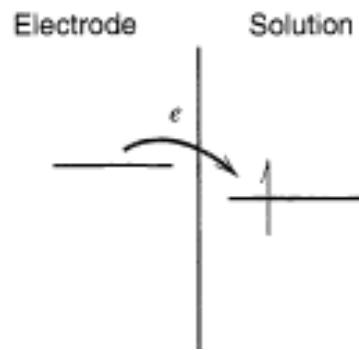
$$V = V_{ext} - R_{sol} \cdot i - V_{2nd\ electrode}$$

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

Marcus/Gerischer microscopic model

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

- reorganization energy (λ)



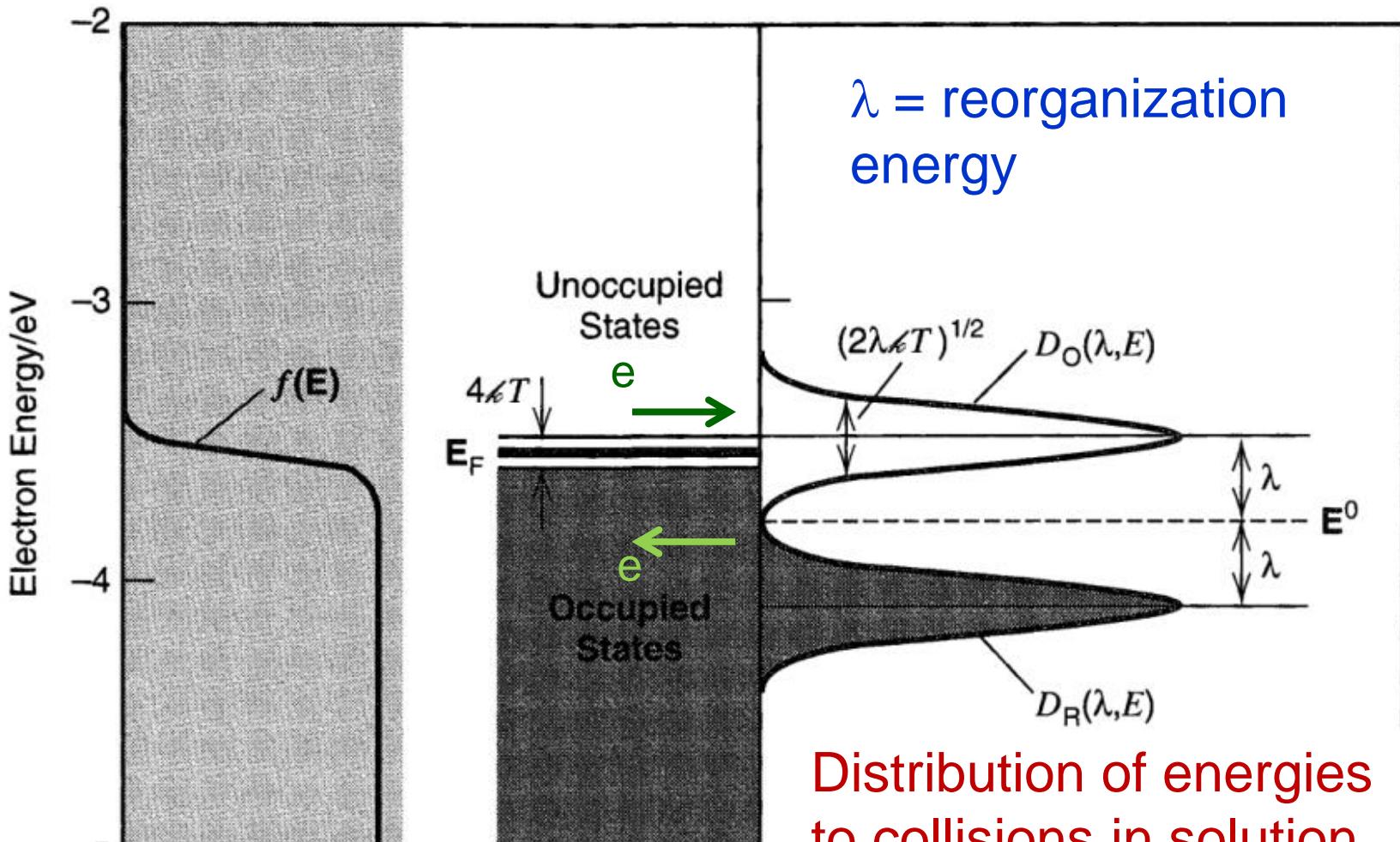
Two different energy levels

- fluctuations of the solvent molec.



Distributions of energy states

Electron Transfer: Gerischer view

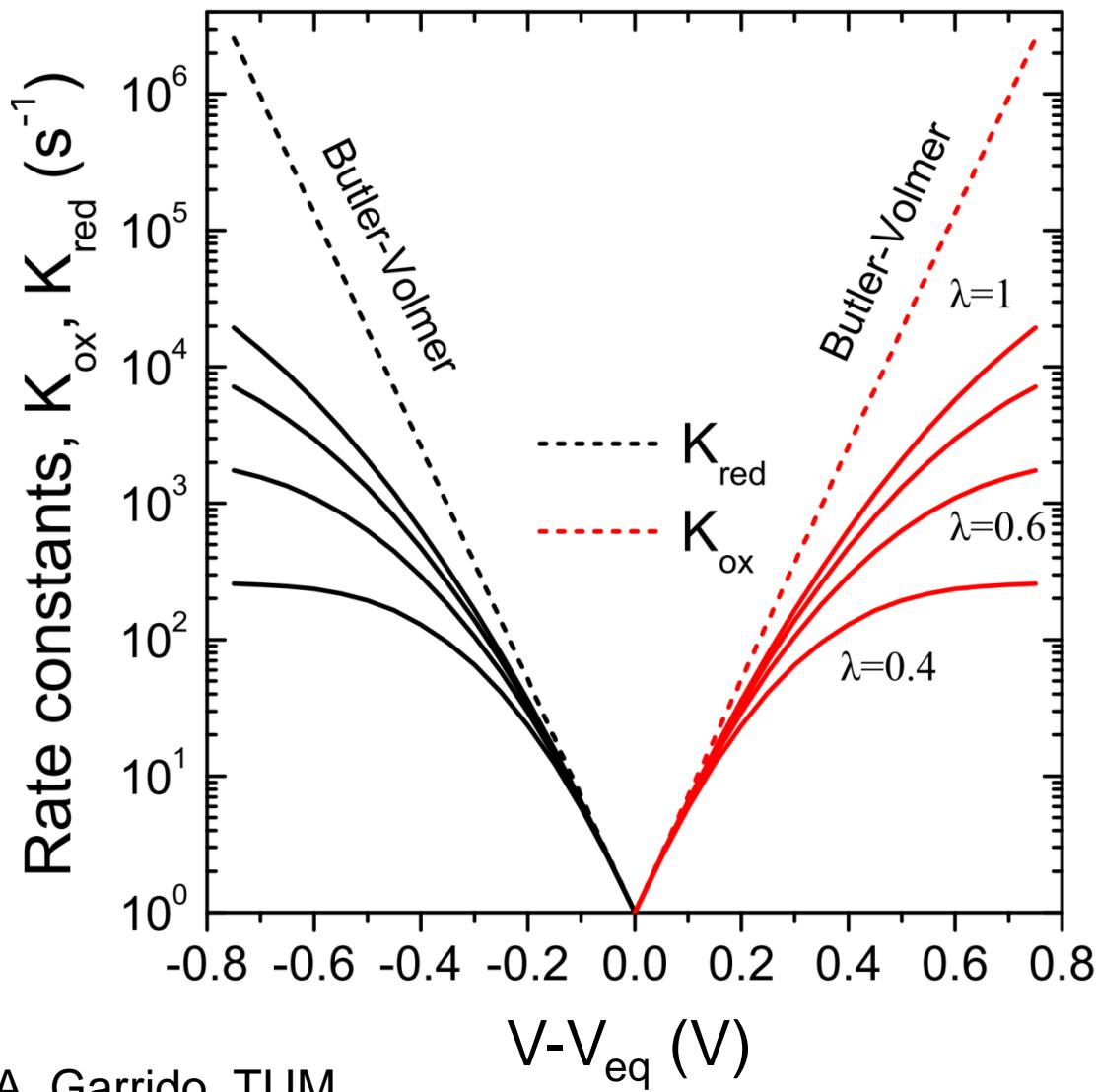


Distribution of energies due
to collisions in solution

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

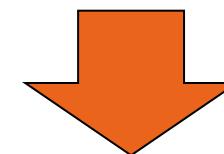
Reactant States

Marcus / Gerischer model



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 !

Equilibrium condition

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

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


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

Nernst relation

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

both processes will occur **at equal rates**:

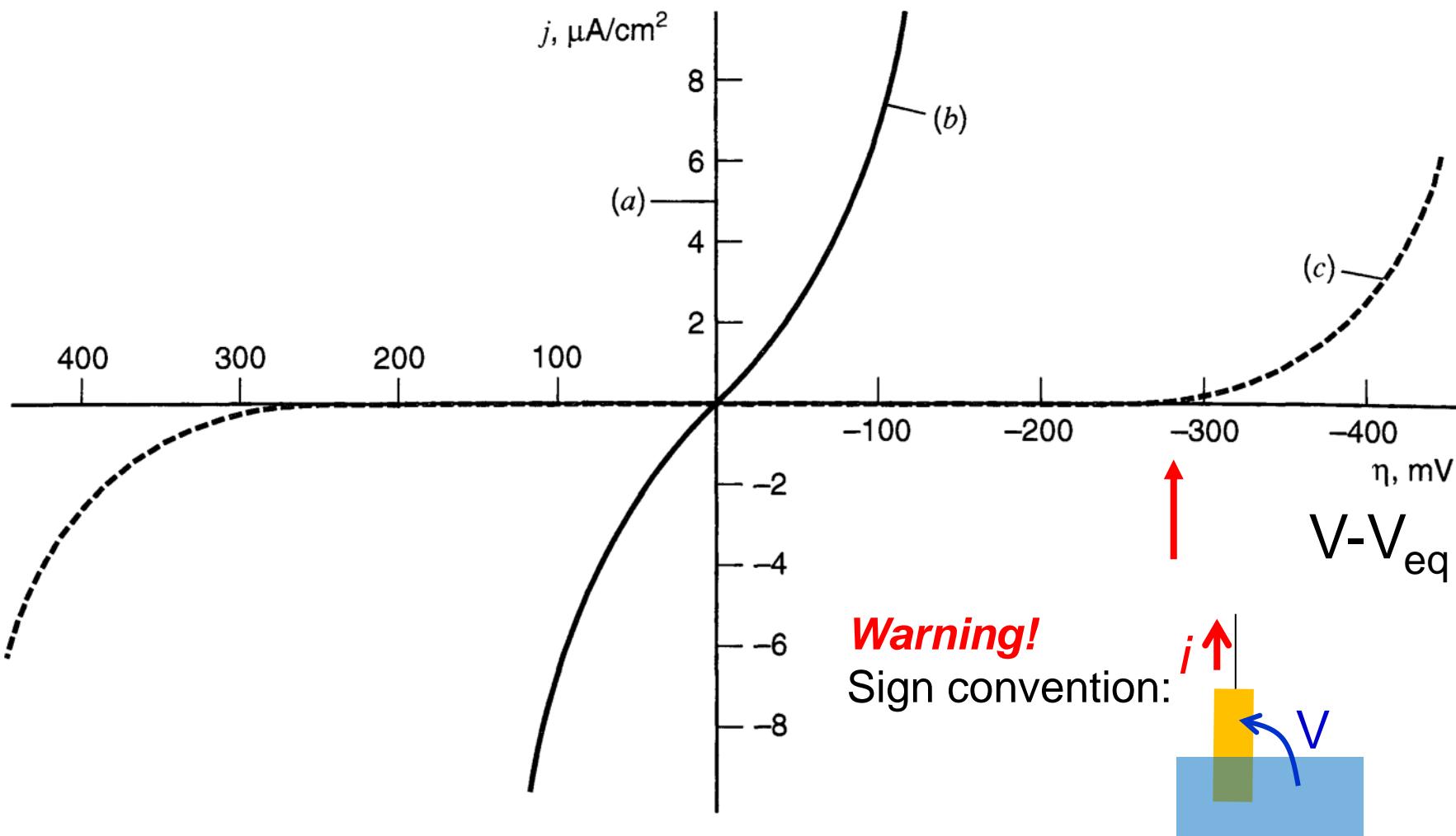
$$i_f = i_b = i_0 = nqN_{Av}Ak_0 C_O e^{-\alpha nq(V_{eq}-V^0')/kT} = nqN_{Av}Ak_0 C_O^{1-\alpha} C_R^\alpha$$

i_0 = exchange current

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

(it is the same equation!)

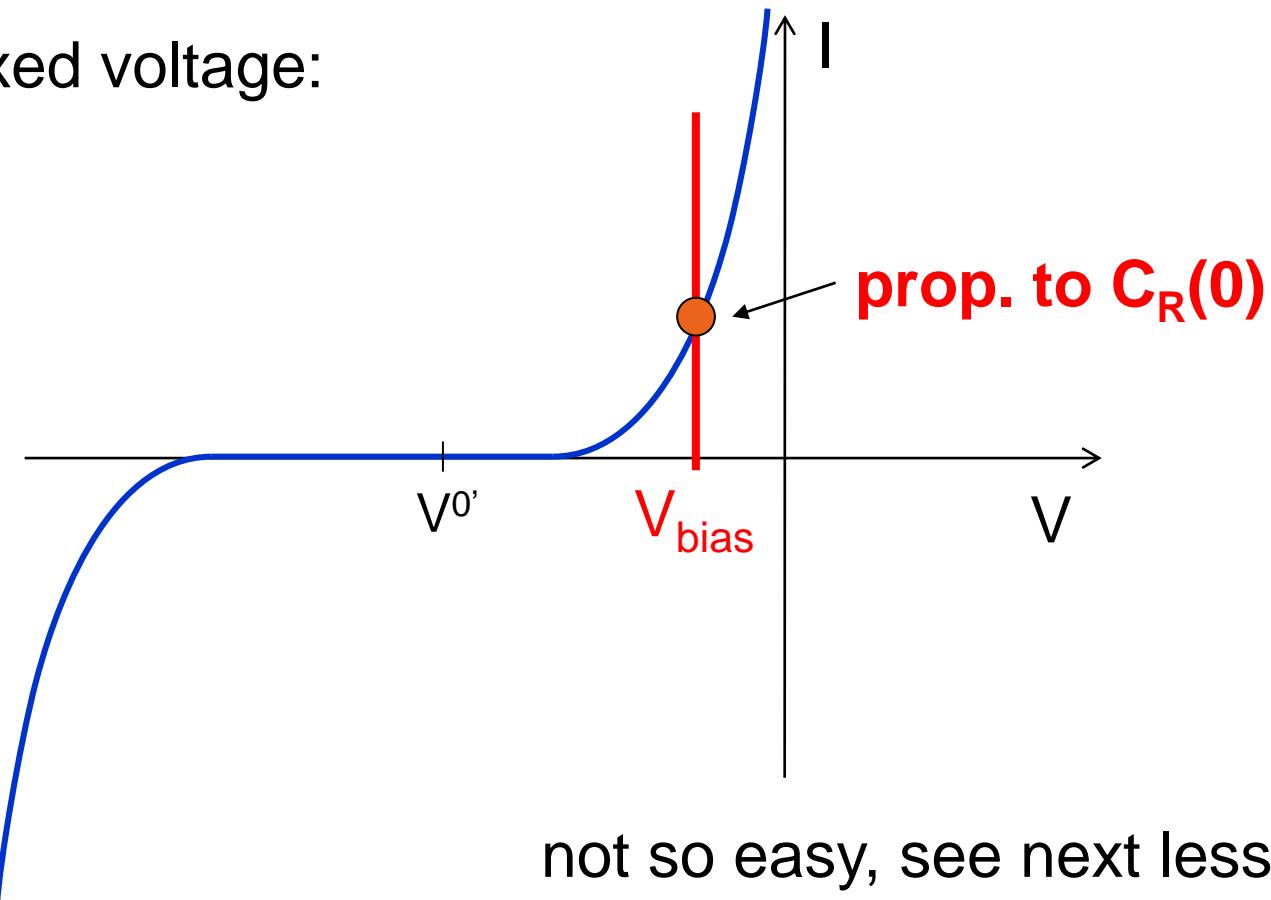
Kinetic controlled current



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

Amperometric sensor

Operating at fixed voltage:



not so easy, see next lesson!

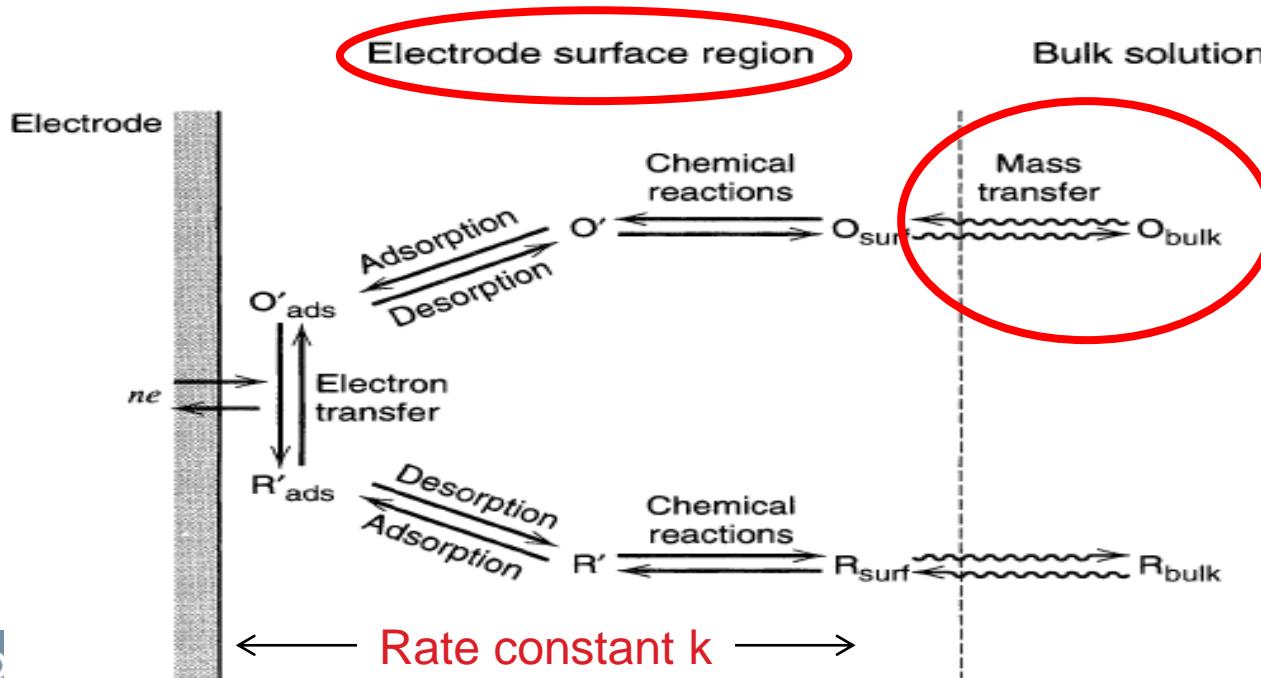
Butler-Volmer equation: concentrations at the surface

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

An Interfacial Process

For: $O + ne^- \leftrightarrow R$ 5 separate events must occur:

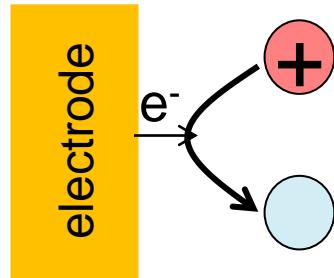
- O must be successfully transported from bulk solution (mass transport)
- O must adsorb transiently onto electrode surface (non-faradaic); Chemical reactions preceding or following the electron transfer (e.g., protonation or dimerization or catalytic decomposition) on the electrode surface.
- CT must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



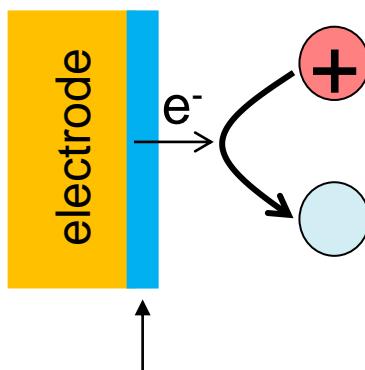
Next lesson

Bard, Electrochemical methods. Fundamentals and applications

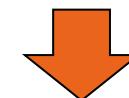
Do not forget electrode pretreatments!



The electron transfer of a redox reaction is a tunneling process



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) controlled by the surface

→ electrode must be carefully cleaned before each experiment:

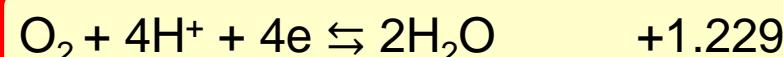
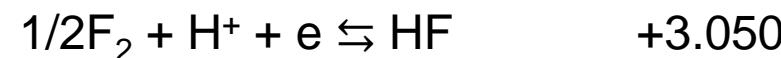
- Mechanical polishing (alumina) and ultrasonic cleaning
- Chemical
 - Sonicate in acetone
 - Soak in HNO_3 , aqua regia
 - ...
- Electrochemical
 - Oxidization/reduction cycles in 0.5 M H_2SO_4 (Pt)
 - ...

Oxygen reduction can interfere with the measurement

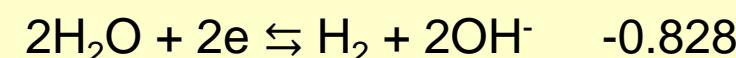
→ removal by purging with an inert gas

Limited electrochemical window

Aqueous Solutions at 25°C in V vs. SHE, 1atm, C⁰=1M



oxygen and pH can interfere!



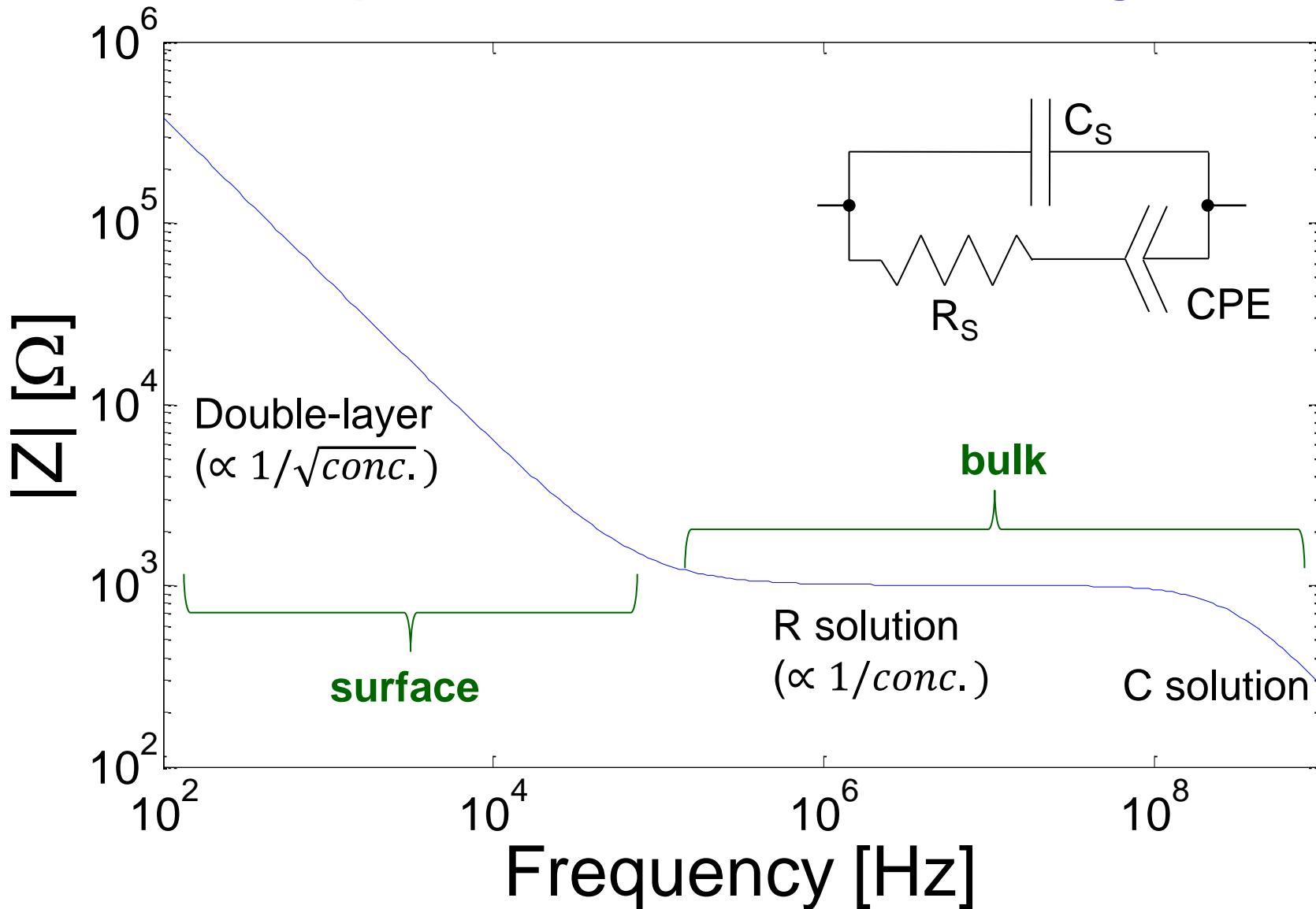
water electrolysis! -2.714



Experiments in water are typically limited at ΔV less than 2V
(-1V < V < 1V vs AgCl)

What about impedance spectra?

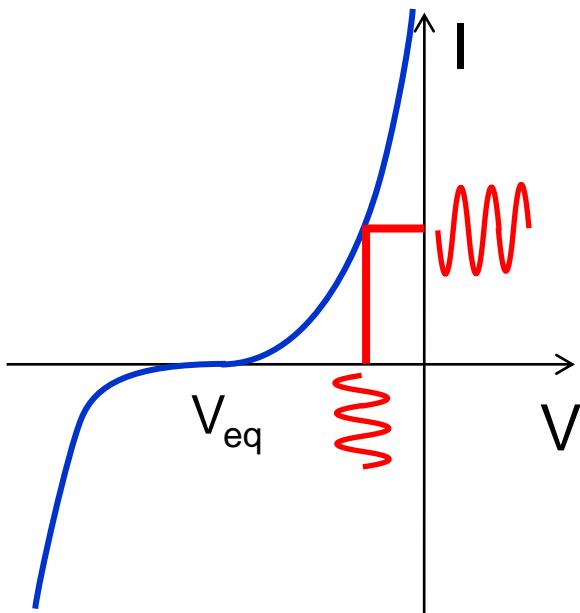
From the previous lesson WITHOUT charge transfer



Equivalent Circuit: Charge Transfer

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

Small signal
linearization



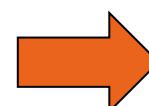
Charge transfer resistance:

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

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

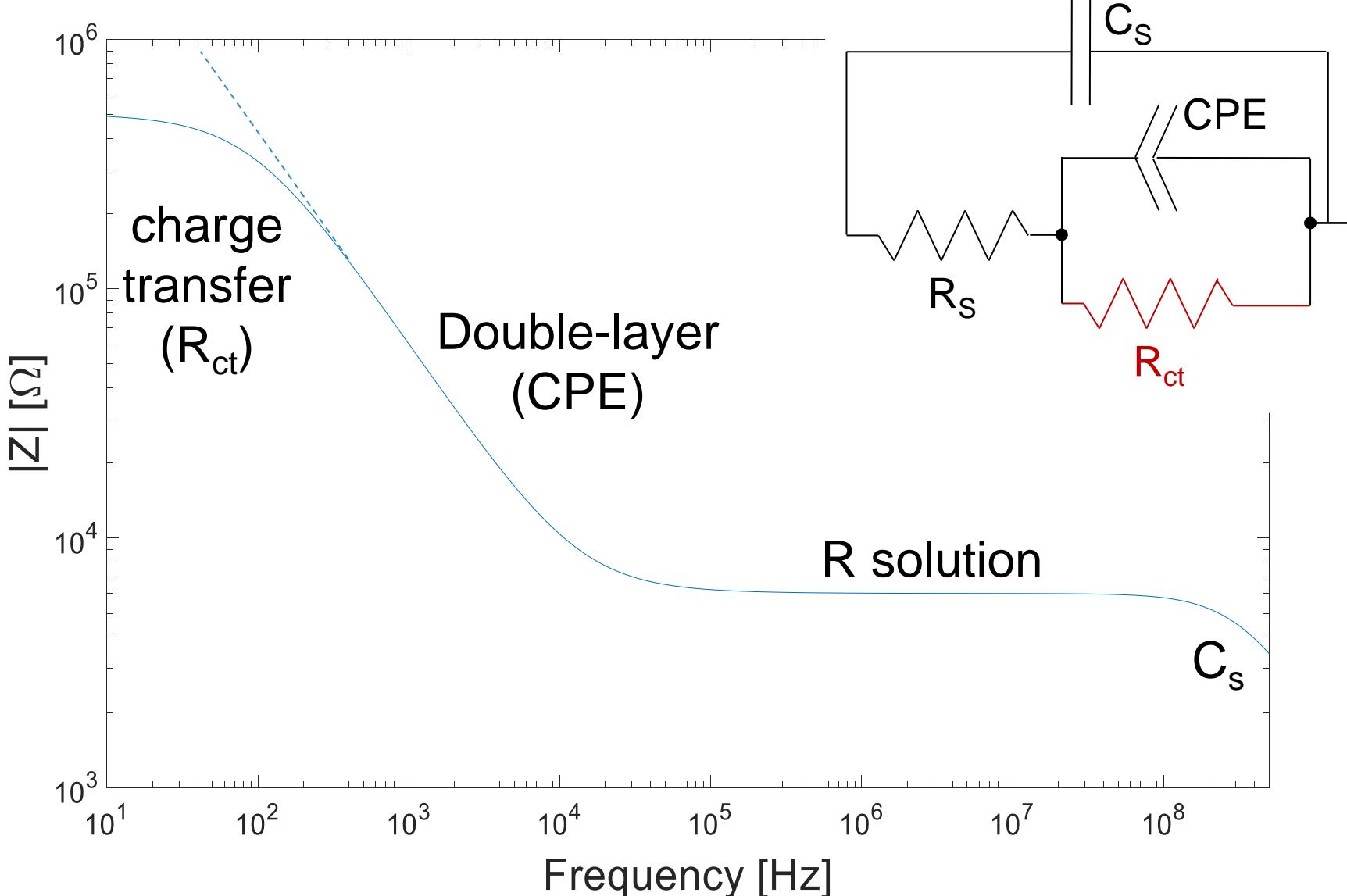
$$i_0 = nqN_A v A k_0 C_O^{1-\alpha} C_R^\alpha$$

A stationary condition is more easily obtained with $V \approx V_{eq}$



$$R_{ct} \approx \frac{kT}{nq} \frac{1}{i_0}$$

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
 - 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}