The interface between solid & liquid:
how to transfer charge through the electrode

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Outline

• 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

Two main cases:

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

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

e-

What is the voltage applied to the solution?
**Equilibrium at the interface**

Ex.: Zn electrode immersed in a solution with Zn\(^{2+}\) (C\(_{Zn^{2+}}\)):

\[ \text{Zn}_{\text{solid}} \rightleftharpoons \text{Zn}^{2+}_{\text{liquid}} + 2e^- \]

No deposition / corrosion for \(V_0\) determined by:
- metal involved
- ions in solution
- solution
- temperature,…

Assuming a Boltzmann dist.:
\[ V - V_0 \propto \frac{kT}{q} \log\left(\frac{C_{Zn^{2+}}}{C_{Zn^{2+},0}}\right) \]
Electrochemical cell

Voltage $V \neq 0$ is not directly measurable using a voltmeter

A 2\textsuperscript{nd} electrode is required!

AgCl(s) + e\textsuperscript{-} ⇌ Ag(s) + Cl\textsuperscript{-}(l)

Zn(s) ⇌ Zn\textsuperscript{2+}(l) + 2e\textsuperscript{-}

Equilibrium potential of a electroc. cell

At the equilibrium $I=0$

(no voltage drop in solution)

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

Equilibrium requires $V \neq 0V!$

Electrochemical potentials:

$Zn(s) ⇌ Zn^{2+}(l) + 2e\textsuperscript{-}$

$2AgCl(s) + 2e\textsuperscript{-} ⇌ 2Ag(s) + 2Cl\textsuperscript{-}(l)$
Standard electrode potentials

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

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Potential (V)</th>
</tr>
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<tbody>
<tr>
<td>( \frac{1}{2}F_2 + H^+ + e \rightleftharpoons HF )</td>
<td>+3.050</td>
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<td>( Au^+ + e \rightleftharpoons Au )</td>
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<td>( 2H^+ + 2e \rightleftharpoons H_2 )</td>
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</tr>
<tr>
<td>( Fe^{2+} + 2e \rightleftharpoons Fe )</td>
<td>-0.44</td>
</tr>
<tr>
<td>( Zn^{2+} + 2e \rightleftharpoons Zn )</td>
<td>-0.762</td>
</tr>
<tr>
<td>( 2H_2O + 2e \rightleftharpoons H_2 + 2OH^- )</td>
<td>-0.828</td>
</tr>
<tr>
<td>( Na^+ + e \rightleftharpoons Na )</td>
<td>-2.714</td>
</tr>
<tr>
<td>( Ca^{2+} + 2e \rightleftharpoons Ca )</td>
<td>-2.87</td>
</tr>
<tr>
<td>( K^+ + e \rightleftharpoons K )</td>
<td>-2.93</td>
</tr>
<tr>
<td>( Li^+ + e \rightleftharpoons Li )</td>
<td>-3.04</td>
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For the previous case:

\[
V = +0.222V - \frac{kT}{q} \ln \left( \frac{c_{Cl^-}}{c_0} \right) - \left( -0.762V + \frac{kT}{2q} \ln \left( \frac{c_{Zn^{2+}}}{c_0} \right) \right)
\]

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

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Saturated Calomel Electrode (SCE): +0.244

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).

Consequences of electrode potentials

- Zero current does not mean zero voltage!
- Limited electrochemical window:
  
  \[
  \begin{align*}
  \text{O}_2 + 4\text{H}^+ + 4e & \rightleftharpoons 2\text{H}_2\text{O} \quad +1.229\text{V} \\
  2\text{H}^+ + 2e & \rightleftharpoons \text{H}_2 \quad 0.0000\text{V}
  \end{align*}
  \]
  Acqueous solutions limited at \(\approx 1.5\text{V}\) (-0.5V – 1V, AgCl)

- Batteries, fuel cells
- Sensors: voltage related to the concentration
**Potentiometric sensor**

Measure of concentration:

\[
\Delta \Phi_1 = \Delta \Phi^0 + \frac{RT}{nF} \ln[Ox]_1
\]

\[
\Delta \Phi_2 = \Delta \Phi^0 + \frac{RT}{nF} \ln[Ox]_2
\]

\[
\Delta V \equiv \Delta \Phi_1 - \Delta \Phi_2 = \frac{RT}{nF} \ln \left( \frac{[Ox]_1}{[Ox]_2} \right)
\]

\([Ox]_1 \rightarrow \text{known!}\)

\[
\Delta V = C_1 + C_2 \ln[Ox]_2
\]

Ion-selective electrodes:

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**Electrical current in ionic conductors**

Electrons move in the electrodes

electron transfer at the metal/liquid interface

Two main cases:

- **«consumable» electrode:** metal becomes more (less) as a function of time
  Deposition / corrosion

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

- **Reduction:** atom/ion/molecule gains an electron
  - reaction controlled by the potential drop across the interface
- **Oxidation:** atom/ion/molecule loses an electron

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**The Kinetics of Electron Transfer**

Consider:

\[ O + ne^- \rightleftharpoons R \]

Assume:
- \( O \) and \( R \) are stable, soluble
- no competing chemical reactions occur

\[ k_f, k_b = \text{rate constant (cm/s)} \]

\[ k_f N_A v C_0 A = \text{number of reductions per second} \]

\( A = \text{area of the electrode} \)
**Effect of potential on energy barriers**

- **Arrhenius equation:**
  \[ k_f = A_f \exp(-\Delta G_f/kT) \]
  \[ k_b = A_b \exp(-\Delta G_b/kT) \]

- **Linearization of curves:**
  \[ \Delta G \text{ is prop. to } E - E^0 \]

- \[ k_f = k_0 \exp[-\alpha q(E - E^0)/kT] \]
- \[ k_b = k_0 \exp[(1-\alpha) q(E - E^0)/kT] \]

- \( \alpha \) = transfer coefficient, about 0.5
- \( k_0 \) = standard rate constant
- \( E^0 \) = equilibrium potential (formal potential of the reaction): \( k_f = k_b \)

**Electronic current**

- \[ O + e^- \leftrightarrow R \]
  \[ i = i_f - i_b = qN_A A \left[ k_f C_O(0) - k_b C_R(0) \right] \]

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

- \[ i = qN_A A k_d \left[ C_O(0)e^{-\alpha q(E - E^0)/kT} - C_R(0)e^{(1-\alpha)q(E - E^0)/kT} \right] \]

**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:**
At equilibrium, no net current flows:

\[ i = i_f - i_b = 0 \]

\[ E_{eq} = E^0' + \frac{kT}{q} \ln \left( \frac{C_O}{C_R} \right) \]

\[ \Rightarrow \]

Nernst relation

However, there will be a dynamic equilibrium at electrode surface:

\[ O + e^- \rightarrow R \]

\[ R - e^- \rightarrow O \]

both processes will occur at equal rates so no net change in solution composition

\[ i_f = i_b = i_0 = qN_AvAk_0C_Oe^{-\alpha q(E_{eq} - E_0')/kT} = qN_AvAk_0C_O^{1-\alpha} C_R^\alpha \]

\[ i = i_0 \left( e^{-\alpha q(E-E_{eq})/kT} - e^{-(1-\alpha)q(E-E_{eq})/kT} \right) \]

\[ i_0 = \text{exchange current} \]

### Marcus microscopic model

- Tunneling between states in the electrode and those of the ion/molecule
- Isoenergetic electron transfer
- Reactants and products do not change their configurations during the actual act of transfer.
- reorganization energy (\( \lambda \))
**Electron Transfer: Gerischer view**

The $E_{\text{ox}}$ level captures an $e^-$
- Reorientation of solvent dipoles (removal of negative poles)
- Ion potential becomes higher (more attractive to $e^-$)
- Electronic level moves to a lower level $E_{\text{red}}$

Two different energy levels

$\lambda = \text{reorganization energy}$

Distribution of energies due to collisions in solution
Marcus / Gerischer model

Typical $\lambda$: 0.5eV – 1eV

Measurable kinetics usually corresponds to a $\Delta E_{\text{max}}$ of 50-200mV

Butler-Volmer is accurate enough

J.A. Garrido, TUM

Kinetic controlled current

...kinetic is not the only parameter controlling the current!
An Interfacial Process

For: \( \text{O} + \text{ne}^- \leftrightarrow \text{R} \) 5 separate events must occur:

- \( \text{O} \) must be successfully transported from bulk solution (mass transport)
- \( \text{O} \) 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.
- \( \text{CT} \) must occur between electrode and \( \text{O} \) (faradaic)
- \( \text{R} \) must desorb from electrode surface (non-faradaic)
- \( \text{R} \) must be transported away (mass transport)

Parameters in Electrochemical Cells

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Do not forget electrode pretreatments!
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 HNO₃, acqua regia
    • …
  ▪ Electrochemical
    • Oxidization/reduction cycles in 0.5 M H₂SO₄ (Pt)
    • …

Oxygen reduction can interferes with the measurement
→ removal by purging with a inert gas

Summary

• Equilibrium potential at the electrode-liquid interface
  • I=0 does not mean external voltage = 0V!
  • Equilibrium potential depends by metals involved and ion concentrations

• Electron transfer at the interface is possible:
  • Corrosion / deposition of the metal or redox process at the interface metal-liquid
  • Exponential current-voltage characteristic controlled by E-E⁰
  • Exponential current-voltage characteristic controlled by E-E⁰
  • Exponential current-voltage characteristic controlled by E-E⁰
  • Empiric Butler-Volmer relation is accurate enough in many cases