Advanced Electroanalytical Chemistry

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**Analytical Chemistry**

- Electrophoresis
- Electroanalysis
- Mass Spectrometry
- Electrochemical Microscopy

**Physical Chemistry**

- Energy Conversion
- Supercritical \( \text{CO}_2 \) Reduction
- Electron Transfer at Soft Interfaces
- Redox Flow Batteries
A reaction is electrochemical if the reaction Gibbs energy depends not only on temperature and pressure, but also on a potential difference, for example between an electrode and an electrolyte solution.

Additionnal parameter:

Electric field at the interface
Nernst Equations

- Electrochemical potential
- Nernst equation & Absolute potential
- Fermi-Dirac Statistics
- Batteries
- Ion selective electrodes

Homework highlighted in the slides
Chemical potential

Internal energy

\[ U = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{el}} + E_{\text{int}} + E_{\text{mass}} \]

Chemical potential

\[ \mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{V,S,n_j \neq i} \]

Extensive variables

\[ dU = -pdV + TdS + \sum_i \mu_i \, dn_i \]
Chemical potential

\[ \mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,p,n_{j \neq i}} = \bar{G}_i \]

Intensive physical variables

Work to transfer a species at rest in vacuum to a phase at constant pressure and temperature
Thermochemistry

\[ aA + bB + \ldots \xleftrightarrow{} xX + yY + \ldots \]

\[ \Delta G_{\text{reaction}} = \sum_{\text{products}} v_i \mu_i + \sum_{\text{reactants}} v_i \mu_i \]

Work of a reaction: Work to add the products + work to remove the reactants

\[ \Delta G_{\text{reaction}} = \left( \frac{\partial G}{\partial \xi} \right)_{T,p} \]

\[ \xi = \frac{n_i - n_i^0}{v_i} \]

Gibbs energy variation by mole of advancement of the reaction
Chemical potential

Gas phase

\[ \mu(T, p) = \mu^\Theta(T) + RT \ln \left( \frac{p}{p^\Theta} \right) + RT \ln \varphi = \mu^\Theta(T) + RT \ln \left( \frac{f}{p^\Theta} \right) \]

Standard state:
Pressure 1 bar

Répulsions
Attractions
entre les molécules

\[ \ln \left( \frac{p}{p^\Theta} \right) \]
Chemical potential

Solution phase - Ideal solution solvent

\[ \mu_A(T, p) = \mu_A^{\text{ideal}}(T) + RT \ln x_A + RT \ln \gamma_A \]

Solution phase - Solute - Molar fraction scale

\[ \mu_B(T, p) = \mu_B^{\text{ideal dil}}(T) + RT \ln x_B + RT \ln \gamma_B \]

Solution phase - Solute - Molality scale

\[ \mu_B(T, p) = \mu_B^{\text{mol}}(T) + RT \ln \left( \gamma_B^m \frac{m_B}{m^\ominus} \right) \]

Solution phase - Solute - Molarity scale

\[ \mu_B(T, p) = \mu_B^{\text{c}}(T) + RT \ln \left( \gamma_B^c \frac{c_B}{c^\ominus} \right) \]
Exercise

Express the equilibrium constant for the dissolution of zinc in a solution of hydrochloric acid.
The flux of the electric field through a closed surface is to the sum of the charges inside it divided by the permittivity.

\[
\int\int_S E \cdot \hat{n} \, dS = \frac{\sum q_i}{\varepsilon_0}
\]
Gauss’ theorem

Charged sphere in vacuum

Spherical Gauss surface

\[ V = \frac{Q}{4 \pi \varepsilon_0 r} \]

\[ V_S = \frac{Q}{4 \pi \varepsilon_0 R} \]

\[ 4 \pi r^2 E \cdot \hat{r} = \frac{Q}{\varepsilon_0} \]

\[ V(r) = \frac{Q}{4 \pi \varepsilon_0 r} \]

Outer potential

As if all the charge was located in the center
Electrochemistry Golden rule

All phases are neutral inside

Excess charges are always located at the surface
Coulomb’s theorem

Electric field at the surface of a metal

No electric field inside at equilibrium

By symmetry, the field is normal to the surface

\[ E = \frac{\sigma}{\varepsilon_0} \hat{n} \]
Frequency response

Rotation et reorientation des dipoles

Libration

Vibration

Polarisation électronique

Permittivité relative

Micro-ondes Infrarouge Visible-UV

log ν
Exercise

Show that the potential at the surface of a conducting sphere of radius $R$ carrying a charge $Q$, covered by a dielectric layer of thickness $h$ and of relative permittivity $\varepsilon_c$ and placed in a medium of relative permittivity $\varepsilon_m$ is equal to

\[ V_S = \frac{Q}{4\pi \varepsilon_0 \varepsilon_c} \left( \frac{1}{R} - \frac{1}{R + h} \right) + \frac{Q}{4\pi \varepsilon_0 \varepsilon_m (R + h)} \]

Application: Gold nanoparticle coated by a self-assembled monolayer
Gold liquid mirrors
Surface of a polar liquid

Surface potential

\[ \chi > 0 \]

\[ p = q d \]

Observed orientational preferences and the illustration of the possible hydrogen-bonding patterns in the case of water

Calculate the surface potential of water

Dipole moment in the gas phase = 1.85 D = 6.17 \times 10^{-30} \text{ C}\cdot\text{m}

Relative permittivity of a layer of aligned water molecules = 5.2

Compare with the experimental value of 0.13V.
Jellium Model

"Electron spill-over"
Potentials

- **Surface potential**: Potential difference due to the anisotropy of surface force fields

- **Outer potential**: Potential difference between the surface of the phase and infinity due to the presence of excess surface charges

- **Inner potential**: Potential difference between the core of the phase and infinity
Inner, Outer & Surface Potentials

The potential is constant inside a phase that is neutral by definition

\[ \phi = \chi + \psi \]
Potential differences

- A difference of outer potentials is called a **Volta** potential difference

- A difference of inner potentials is called a **Galvani** potential difference
Victor Frankenstein
born in Geneva...

Mary Shelley

Biography of Aldini by Francesco Panese

Electrochemical potential

\[ \tilde{\mu}_i = \mu_i + z_i F \chi + z_i F \psi = \mu_i + z_i F \phi \]

\[ = \mu_i^\Theta + RT \ln a_i + z_i F \phi \]

\( \mu_i \) : Chemical contribution

All short range interactions including electrostatic

\( z_i F \psi \) : Approach work to a charged phase

\( z_i F \chi \) : Surface crossing work

“Real chemical potential”

\[ \alpha_i = \mu_i + z_i F \chi \]
Fermi level

Electron in a metal

\[ \tilde{\mu}_e^M = \mu_e^M - F\phi^M = (\mu_e^M - F\chi^M) - F\psi^M \]
\[ = \alpha_e^M - F\psi^M = -\Phi^M_e - F\psi^M \]

Electron in a metallic nanoparticle

\[ IE_{\psi^{NP},z_e}^{V} = \Phi_{\text{Bulk}} + \psi_{c}^{z\to z+1} \]
\[ = \Phi_{\text{Bulk}} + \frac{(2z + 1)e^2}{8\pi\varepsilon_0 r} \]
Band Structure

N sodium atoms

Solid sodium containing N atoms

Fermi level

$3s$

$2p$

$2s$

$1s$
Fermi-Dirac

\[ P(E) = f(E) dE = \frac{dE}{1 + \exp \left[ \frac{(E - \mu^M_{e^-} / pze)}{kT} \right]} \]

\( T = 298 \text{ K} \)

\( P(E) \) vs. \( (E - E_f) / \text{eV} \)
Density of states

Atom projected $d$-band for bulk Pd

The shaded area corresponds to the occupied states below the Fermi level.
Work function

Zero energy in vacuum

Potential energy

Work function

\[ \Phi_{e^-}^M = -\alpha_{e^-}^M \]

Chemical term

\[ \mu_{e^-}^M \]

Electrochemical potential measured from vacuum

\[ \tilde{\mu}_{e^-}^M \]

Electrochemical potential measured from the pze

\[ \tilde{\mu}_{e^-}^M / \text{pze} \]

Fermi level

Point of zero energy

Potential energy

Kinetic energy

\[ -F\chi \]

\[ E_f \]
Contact Potentials

The electron at rest in vacuum is shown with potentials $\Phi_{Au}$ and $\Phi_{Ag}$.

Volta potential difference:

$$\psi^\text{Au} - \psi^\text{Ag} = -\left(\Phi^\text{Au} - \Phi^\text{Ag}\right) / e$$
Exercise

Calculate the Volta potential difference when a gold piece is placed in contact with a silver piece. Work functions: Au = 5.32 eV and Ag = 4.30 eV.
Contact Potentials

Electron at rest in vacuum

\[ \Phi_{Au} \]

\[ \Phi_{Ag} \]

\[ E_{F}^{Au} \]

\[ E_{F}^{Ag} \]

\[ e^- \]

\[ \psi_{Au} \]

\[ \psi_{Ag} \]

\[ \psi = 0 \]

\[ \chi_{Au} \]

\[ \chi_{Ag} \]

\[ \phi_{Au} \]

\[ \phi_{Ag} \]

\[ \psi_{Au} = -0.5V \]

\[ \psi_{Ag} = 0.5V \]
Contact Potentials

Electron at rest in vacuum

$\Phi_{Au}$

$E_{F}^{Au}$

$e^{-}$

$\Phi_{Ag}$

$E_{F}^{Ag}$

$\psi_{Au}$

$\chi_{Au}$

$\phi_{Au}$

$\psi_{Ag}$

$\chi_{Ag}$

$\psi_{Ag} = 0$

$\phi_{Ag}$
Exercise

Work functions: \( \text{Au} = 5.32 \text{ eV} \) and \( \text{Ag} = 4.30 \text{ eV} \).

What is the Fermi level of this Janus particle?

What is the charge distribution?
Core Shell?

Does the core affects the Fermi energy of the shell?
A p–n junction in thermal equilibrium with zero-bias voltage applied. Electron and hole concentration are reported with blue and red lines, respectively. Gray regions are charge-neutral. Light-red zone is positively charged. Light-blue zone is negatively charged. The electric field is shown on the bottom, the electrostatic force on electrons and holes and the direction in which the diffusion tends to move electrons and holes (reprinted from http://en.wikipedia.org/wiki/P–n_junction)
Kelvin probe

\[ \psi^\alpha = \psi^\beta \]
Kelvin Probe

Compensation voltage

\[ E = \phi^{Cu_2} - \phi^{Cu} = \left( \tilde{\mu}^{Cu}_e - \tilde{\mu}^{Cu_2}_e \right) / F \]

\[ E = \left( \tilde{\mu}^\beta_e - \tilde{\mu}^\alpha_e \right) / F = \left( \alpha^\beta_e - \alpha^\alpha_e \right) / F - \left( \psi^\beta - \psi^\alpha \right) \]

Work function difference

\[ E = \left( \Phi^\alpha - \Phi^\beta \right) / F \]
Surface modification

One can modify metal α by passing a gas, e.g. CO on Pt

Before

\[ E^I = \left( \frac{\alpha \beta}{\alpha I} - \frac{\alpha \alpha I}{\alpha I} \right) / F \]

After

\[ E^{\Pi} = \left( \frac{\alpha \beta}{\alpha I} - \frac{\alpha \alpha \Pi}{\alpha I} \right) / F \]

\[ E^{\Pi} - E^I = \chi^{\alpha \Pi} - \chi^{\alpha I} \]
Kelvin mode based on the two-pass technique. In the first pass the topography is acquired using standard **Semicontact mode** (mechanical excitation of the cantilever). In the second pass this topography is retraced at a set lift height from the sample surface to detect the electric surface potential $\Phi(x)$. During this second pass the cantilever is no longer excited mechanically but electrically by applying to the tip the voltage $V_{\text{tip}}$ containing dc and ac components.

Scan size: 6 x 6 um
Topography (upper picture) and surface potential distribution (lower picture) of two component Langmuir-Blodgett film
Kelvin probe II

\[\begin{align*}
A & \quad \text{Cu} \\
\text{Cu} & \quad \text{Cu}_2 \\
E & \quad \text{Vibrator} \\
\beta & \\
\alpha & \quad \beta_2
\end{align*}\]
Au nanoparticles multilayers

Poly-Lysine

![Graph showing CPD (in V) versus Number of layers (0 to 20)]
Nernst Equation

- Electrochemical potential
- Nernst equation & Absolute potential
- Fermi-Dirac Statistics
- Batteries
- Ion selective electrodes

Homework highlighted in the slides
Redox reactions

$$\text{o}x^S + n e^{-M} \rightleftharpoons \red^S$$

Electrochemical reaction Gibbs energy

$$\Delta \tilde{G} = \tilde{\mu}_{\text{red}}^S - (\tilde{\mu}_{\text{o}x}^S + n \tilde{\mu}_{e^{-}}^M) = 0$$
Redox reactions

Expressing the electrochemical potentials

\[
\left[ \mu^{\text{red},S} + RT \ln a^{\text{red}}_S + z_{\text{red}} F \phi^S \right] - \left[ \mu^{\text{ox},S} + RT \ln a^{\text{ox}}_S + z_{\text{ox}} F \phi^S \right] - n \left[ \mu^M_e - F \phi^M \right] = 0
\]

Number of exchanged electrons

\[ n = z_{\text{ox}} - z_{\text{red}} \]

Galvani potential difference and Gibbs chemical energy

\[
nF \left( \phi^M - \phi^S \right) = \left[ \mu^{\text{ox},S} - \mu^{\text{red},S} + n \mu^M_e \right] + RT \ln \left( \frac{a^{\text{ox}}_S}{a^{\text{red}}_S} \right)
\]

\[ = - \Delta G^{\text{red}} + RT \ln \left( \frac{a^{\text{ox}}_S}{a^{\text{red}}_S} \right) = - \Delta G \]
Redox reactions

The equilibrium constant depends on the Galvani potential difference between the two phases

$$K_e = \frac{a_{\text{red}}}{a_{\text{ox}}} = \exp^{-\Delta G^\circ / RT} \exp^{-nF(\phi^M - \phi^S) / RT}$$

Electrochemists control the equilibrium by adjusting the electrode potential
Redox potential on the SHE scale

\[ E_{\text{SHE}} = \left[ E_{\text{ox/red}}^{\ominus} \right]_{\text{SHE}} + \frac{RT}{nF} \ln \left( \frac{a_{\text{ox}}^S}{a_{\text{red}}^S} \right) \]
Hydrogen under standard conditions is passed along the electrode.
(Redox) Nernst equation

Standard redox potential

\[
E_{\text{SHE}} = \left[ E_{\text{ox/red}}^\Theta \right]_{\text{SHE}} + \frac{RT}{nF} \ln \left( \frac{a_{\text{ox}}^S}{a_{\text{red}}^S} \right)
\]

Formal redox potential (apparent standard)

\[
\left[ E_{\text{ox/red}}^{\Theta/} \right]_{\text{SHE}} = \left[ E_{\text{ox/red}}^\Theta \right]_{\text{SHE}} + \frac{RT}{nF} \ln \left( \frac{\gamma_{\text{ox}}}{\gamma_{\text{red}}} \right)
\]

Nernst equation

\[
E_{\text{SHE}} = \left[ E_{\text{ox/red}}^{\Theta/} \right]_{\text{SHE}} + \frac{RT}{nF} \ln \left( \frac{c_{\text{ox}}}{c_{\text{red}}} \right)
\]
Thermodynamic approach

Working electrode

Reference electrode

“Virtual reaction”

This reaction is not at equilibrium as the electrons are blocked by the high impedance of the voltmeter

\[
\Delta G_r = \Delta G_r^\Theta + RT \ln \left[ \frac{a_{\text{red}}^S \left( a_{H^+}^S \right)^n \left( p^\Theta \right)^{n/2}}{a_{\text{ox}}^S f_{H_2}^{n/2}} \right]
\]
Thermodynamic approach

Electrode potential = – Gibbs energy of the reduction by hydrogen / $nF$

$$E_{\text{SHE}} = -\frac{\Delta G_r}{nF} = -\frac{\Delta G_r^\ominus}{nF} + \frac{RT}{nF} \ln \left[ \frac{a_{\text{ox}}^{S} f_{\text{H}_2}^{n/2}}{a_{\text{red}}^{S}(a_{\text{H}^+}^{S})^{n}(p^{\ominus})^{n/2}} \right]$$

Standard redox potential

$$\left[ E_{\text{ox/red}}^\ominus \right]_{\text{SHE}} = -\frac{\Delta G_r^\ominus}{nF} = \left[ \mu_{\text{ox}}^{\ominus, S} - \mu_{\text{red}}^{\ominus, S} - n \mu_{\text{H}^+}^{\ominus, S} + \frac{n}{2} \mu_{\text{H}_2}^{\ominus} \right] / nF$$
If we close the circuit, zinc will dissolve as it is in direct contact with the acid

\[ \Delta G_d = -\Delta G_r = 2FE = 2F(V_a - V_c) \]

For a 1 M solution, we have \( \Delta G_d = -2 \cdot 10^5 \cdot 0.75 = -150 \text{ kJ}\cdot\text{mol}^{-1} \)
Reactions in solution

\[ \text{O}_1 + \text{R}_2 \quad \leftrightarrow \quad \text{R}_1 + \text{O}_2 \]
\[ \text{Ce}^{4+} + \text{Fe}^{2+} \quad \leftrightarrow \quad \text{Ce}^{3+} + \text{Fe}^{3+} \]

Show that the standard Gibbs energy of the redox reaction is given by:

\[ \Delta G_{\text{r}}^\ominus = nF \left( \left[ E_{\text{O}_2/\text{R}_2}^\ominus \right]_{\text{SHE}} - \left[ E_{\text{O}_1/\text{R}_1}^\ominus \right]_{\text{SHE}} \right) \]
Spectroelectrochemistry

Record UV-vis spectra as a function of the electrode potential
Thin layer electrochemistry

\[ E_{\text{SHE}} = \left[ E_{\text{oxy/Red}}^{\ominus} \right]_{\text{SHE}} + \frac{RT}{nF} \ln \left( \frac{c_{\text{ox}}}{c_{\text{red}}} \right) \]

Cathodic reaction \hspace{1cm} Standard state equilibrium \hspace{1cm} Anodic reaction

\[ E < E^{\ominus} \quad c_{\text{O}} < c_{\text{R}} \]

\[ E = E^{\ominus} \quad c_{\text{O}} = c_{\text{R}} \]

\[ E > E^{\ominus} \quad c_{\text{O}} > c_{\text{R}} \]
**OS Cl₆⁻ /**

**OS Cl₆²⁻**

<table>
<thead>
<tr>
<th>Potentiel/V</th>
<th>Absorbance à 410 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 0.750</td>
<td>45</td>
</tr>
<tr>
<td>2 0.875</td>
<td>52</td>
</tr>
<tr>
<td>3 0.900</td>
<td>61</td>
</tr>
<tr>
<td>4 0.925</td>
<td>80</td>
</tr>
<tr>
<td>5 0.950</td>
<td>117</td>
</tr>
<tr>
<td>6 0.975</td>
<td>146</td>
</tr>
<tr>
<td>7 1.100</td>
<td>178</td>
</tr>
</tbody>
</table>

**TOTALE REDUCED**

**TOTALE OXIDIZED**
## OTTLE

<table>
<thead>
<tr>
<th>Potentiel / V</th>
<th>( \frac{c_{ox}}{c_{red}} )</th>
<th>( \log \left( \frac{c_{ox}}{c_{red}} \right) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.875</td>
<td>( \frac{(52 - 45)}{(178 - 52)} = 0.055 )</td>
<td>-1.255</td>
</tr>
<tr>
<td>0.9</td>
<td>( \frac{(61 - 45)}{(178 - 61)} = 0.1367 )</td>
<td>-0.864</td>
</tr>
<tr>
<td>0.925</td>
<td>( \frac{(80 - 45)}{(178 - 80)} = 0.357 )</td>
<td>-0.447</td>
</tr>
<tr>
<td>0.95</td>
<td>( \frac{(117 - 45)}{(178 - 117)} = 1.80 )</td>
<td>0.072</td>
</tr>
<tr>
<td>0.975</td>
<td>( \frac{(146 - 45)}{(178 - 146)} = 3.15 )</td>
<td>0.499</td>
</tr>
</tbody>
</table>

\[
E^\circ = 0.948 \text{ V} \\
Pente = 1
\]

\[
RT/F \ \ln \left( \frac{c_{ox}}{c_{red}} \right) / \text{mV}
\]
Absolute standard redox potential

Oxidised state in water
+ electron at rest in vacuum
\[ \left[ E_{\text{ox/red}}^\Theta \right]_{\text{abs}} = -\frac{\Delta G_r^\Theta}{nF} = \frac{\tilde{\mu}_{\text{ox}}^S - \tilde{\mu}_{\text{red}}^S}{nF} = \frac{\alpha_{\text{ox}}^S - \alpha_{\text{red}}^S}{nF} + \psi^S \]

Reduced state in water

\[ \text{Ox}^S + ne^{-V} \Leftrightarrow \text{Red}^S \]

\[ \left[ E_{\text{ox/red}}^\Theta \right]_{\text{abs, } \psi^S=0} = \left( \alpha_{\text{ox}}^S - \alpha_{\text{red}}^S \right) / nF \]
Ionisation energy

Oxidised state
+ electron at rest in vacuum

Ionisation energy

Reduced state

Gas Phase
Absolute redox potential

Reduced state in the gas phase

$-\Delta G_{\text{hyd}}(R)$

Oxidised state in gas phase + electron at rest in vacuum

Ionisation energy

$F[E_{O/R}]_{\text{abs}} = \Delta G_{\text{hyd}}(O) - \Delta G_{\text{hyd}}(R) + E_I$

Reduced state in water

$F[E_{O/R}]_{\text{abs}}$

Oxidised state in water + electron at rest in vacuum

$\Delta G_{\text{hyd}}(O)$
Absolute redox potential

\[
\frac{1}{2} \text{H}_2 \quad \text{gas} \quad \rightarrow \quad \text{H}^+ \quad \text{in gas phase} \quad + \quad \text{electron at rest in vacuum} \quad \rightarrow \quad \frac{1}{2} \text{H}_2 \quad \text{gas}
\]

\[
\begin{align*}
\left[ E^\ominus_{\text{H}^+/\frac{1}{2}\text{H}_2} \right]_{\text{abs}} &= \left[ \Delta G^\ominus_{\text{hyd}}(\text{H}^+) + E_{\text{I},\text{H}} + \frac{1}{2} E_{\text{laison}}(\text{H}_2(\text{g})) \right] / F \\
\left[ E^\ominus_{\text{H}^+/\frac{1}{2}\text{H}_2} \right]_{\text{abs}} &\approx 4.44 \pm 0.05 \text{ V}
\end{align*}
\]

\[
\Delta G_{\text{hyd}}(\text{H}^+) \quad \rightarrow \quad \text{H}^+ \quad \text{aqueous} \quad + \quad \text{electron at rest in vacuum}
\]
Absolute redox potential

\[ -\Delta G_{\text{hyd}}(\text{Fe}^{2+}) = \left[ E^{\ominus}_{\text{Fe}^{3+}/\text{Fe}^{2+}} \right]_{\text{abs}} \]

\[ = -\left( \Delta G^{\ominus}_{\text{hyd}}(\text{Fe}^{2+}) - \Delta G^{\ominus}_{\text{hyd}}(\text{Fe}^{3+}) - E_{\text{I,Fe}^{2+}} \right) \]

\[ = -(-1930 + 4385 - 2957) / 96.485 = 5.20 \text{V} \]

\[ \left[ E^{\ominus}_{\text{Fe}^{3+}/\text{Fe}^{2+}} \right]_{\text{abs}} = 4.44 + 0.77 = 5.21 \text{V} \]

\[ \Delta G_{\text{hyd}}(\text{Fe}^{3+}) \]

\[ \text{Fe}^{3+} \text{ in gas phase} + \text{electron at rest in vacuum} \]

\[ \text{Fe}^{2+} \text{ in gas phase} \]

\[ \text{Fe}^{2+} \text{ aqueous} \]

\[ \text{Fe}^{3+} \text{ aqueous} + \text{electron at rest in vacuum} \]
Electrochemical potential of the electron in solution

\[
\begin{align*}
\Delta E &= \mu_e - \mu_{Fe^{2+}} \\
&= E_{Fe^{3+/Fe^{2+}}}^{abs} - \tilde{\mu}_{Fe^{3+}} - \tilde{\mu}_{Fe^{2+}}
\end{align*}
\]
Fermi level of the electron in solution

\[-\alpha_{e^-}^S = e \left[ E_{\text{ox/red}} \right]_{\text{AVS, } \psi^S = 0}^S = \alpha_{\text{ox}}^S - \alpha_{\text{red}}^S\]
Fermi level in solution

Electrochemical potential of the electron in solution

\[ \tilde{\mu}_{e^-}^{\oplus, S} = \left[ E_{\text{ox/red}}^{\oplus} \right]_{\text{abs}, \psi^S = 0} \]

Electron at rest in vacuum

- \( \tilde{\mu}_{e^-}^M \)
- Fermi level
- Solution
- \( \tilde{\mu}_{e^-}^{\oplus, S} \)
- Absolute standard redox potential
- Conduction band
- \( \tilde{\mu}_{e^-}^{SC} \)
- Fermi level
- Valence band
- Depends on doping
- Semiconductor
Figure 2.17  Position of energy bands of various semiconductors in the dark (d) and in the light (l) with respect to the SHE and SCE electrochemical scales \( U \) and the vacuum reference energy level \( E \).
Electron electrochemical Potential

Electron in a metal

\[ \tilde{\mu}_{e^-}^M = \mu_{e^-}^M - F\phi^M = (\mu_{e^-}^M - F\chi^M) - F\psi^M \]
\[ = \alpha_{e^-}^M - F\psi^M = -\Phi_{e^-}^M - F\psi^M \]

Electron in solution

\[ \alpha_{e^-}^S = \alpha_{\text{red}}^S - \alpha_{\text{ox}}^S \]
Nernst Equations

- Electrochemical potential
- Nernst equation & Absolute potential
- Fermi-Dirac Statistics
- Batteries
- Ion selective electrodes

Homework highlighted in the slides
Oxidation Energy

\[\Delta G_{\text{hyd}}(\text{Fe}^{3+}) \rightarrow \Delta G_{\text{hyd}}(\text{Fe}^{2+}) \]

\[\text{Fe}_{(g)} + e^{-}(v) \rightarrow E_I \]

\[\text{Fe}_{(g)}^{2+} \rightarrow \text{Fe}_{(g)}^{3+} \]

\[\Delta E_O \]
Solvent Polarisation

Harmonic dependence

\[ E_{\text{Fe}^{2+}} - E_{\text{Fe}^{2+}}^o = \frac{K_{\text{Fe}^{2+}}}{2} \left( P - P_{\text{Fe}^{2+}}^o \right)^2 \]

Solvent re-organisation energy

\[ \lambda_{\text{Fe}^{2+}} = \frac{K_{\text{Fe}^{2+}}}{2} \left( P_{\text{Fe}^{3+}}^o - P_{\text{Fe}^{2+}}^o \right)^2 \]
Solvent reorganisation energy

Fe\(^{3+}\) aqueous badly solvated + electron at rest in vacuum

Fe\(^{3+}\) aqueous + electron at rest in vacuum

Fe\(^{3+}\) aqueous + electron at rest in vacuum

Fe\(^{2+}\) aqueous

Ideally solvated

Oxidation with frozen solvation shell

\[ E^0_O \]

\[ \lambda \]
Energy-Energy diagram

\[ E_{\text{Fe}^{3+}} - E_{\text{Fe}^{3+}}^0 = \frac{\left(\Delta E_O - \Delta E_O^0 + \lambda\right)^2}{4\lambda} \]

\[ E_{\text{Fe}^{2+}} - E_{\text{Fe}^{2+}}^0 = \frac{\left(\Delta E_O - \Delta E_O^0 - \lambda\right)^2}{4\lambda} \]

\[ W_{\text{Fe}^{3+}}(\Delta E_O) = \frac{e^{\frac{-\left(\Delta E_O - (\Delta E_O^0 + \lambda)\right)^2}{4kT\lambda}}}{\sqrt{4\pi kT\lambda}} \]
Gerisher’s diagram for oxidation

$\Delta E_O$  

$W_{\text{red}}(\Delta E_O)$  

$\Delta E_O^o + \lambda$  

Energy fluctuation for the reduced state  

$\Delta E_O^o$  

$W_{\text{ox}}(\Delta E_O)$  

$\Delta E_O^o - \lambda$  

Energy fluctuation for the oxidised state  

Distribution function of energy state
Two-state Fermi-Dirac statistics

Two energy levels of energy $0$ et $E$

\[
\begin{align*}
\text{n}_0 &= \frac{1}{1 + e^{-E_f/kT}} \\
\text{n}_1 &= \frac{1}{1 + e^{(E-E_f)/kT}}
\end{align*}
\]

One particle system

\[
\text{E}_f = \frac{E}{2}
\]

The Fermi level is in the middle of the energy gap

\[
\text{n}_0 + \text{n}_1 = 1
\]
Fermi level for oxidation

Standard state \[ c_O = c_R \]

Fermi level for oxidation

Energy state probability density

\[ D_{\text{Fe}^{2+}}(\Delta E_O) = c_{\text{Fe}^{2+}} W_{\text{Fe}^{2+}}(\Delta E_O) \]

\[ D_{\text{Fe}^{3+}}(\Delta E_O) = c_{\text{Fe}^{3+}} W_{\text{Fe}^{3+}}(\Delta E_O) \]
Fermi level for oxidation

General case: $c_O \neq c_R$

Energy state probability density

$D_{Fe^{2+}}(\Delta E_O) = c_{Fe^{2+}} W_{Fe^{2+}}(\Delta E_O)$

$D_{Fe^{3+}}(\Delta E_O) = c_{Fe^{3+}} W_{Fe^{3+}}(\Delta E_O)$

Fermi level for oxidation:

$E_f = \Delta E_O^0 + kT \ln \left( \frac{c_O}{c_R} \right) \leq \Delta E_O^0$
Gerischer’s diagram

\[ \Delta E_R \]

\[ W_{\text{ox}}(\Delta E_R) \]

\[ \Delta E_R^o + \lambda \]

\[ \Delta E_R^o - \lambda \]

\[ W_{\text{red}}(\Delta E_R) \]

Energy fluctuation for the oxidised state

\[ \Delta E_{F_R} = \Delta E_R^o + kT \ln \left( \frac{c_{\text{Fe}^{2+}}}{c_{\text{Fe}^{3+}}} \right) \]

Energy fluctuation for the reduced state

Electrochemical potential for the electron in solution

\[ \tilde{\mu}_{e^-}^S = \Delta E_{F_R} \]

\[ \tilde{\mu}_{e^-}^{\phi,S} = \mu_{e^-}^{\phi,S} - F \chi^S - F \psi^S = \Delta E_R^o = \Delta E_{F_R}^{\phi} \]
Concentration

Fermi-Dirac statistics

\[
\frac{c_{\text{ox}}}{c_{\text{red}}} = \frac{e^{-\frac{\Delta E_{FR} - \Delta E_{R}^{\circ}}{RT}}}{c_{\text{tot}}}
\]

Nernst equation

\[
\Delta E_{FR} - \Delta E_{R}^{\circ} = -nF \left[ E - E_{\text{ox/red}}^{\Theta/} \right]_{\text{SHE}}
\]
Fermi levels

Electrochemical potential for the electron on the metal

Electrochemical potential for the electron in solution

\[ \tilde{\mu}_{e^-}^S = \Delta E_{FR} \]

Oxydation

Equilibre

Réduction
HOMO-LUMO-Fermi Levels...

A generally applicable linear correlation relationship exists between the calculated HOMO energies and the experimental/calculated IPs.

Linear correlation relationships between the calculated LUMO energies and experimental/calculated EAs (for the bound anionic states)
Summary

Absolute redox potential

$$\left[ E_{\text{ox/red}}^{\oplus} \right]_{\text{abs}, \psi^S=0} = \left( \alpha_{\text{ox}}^{\oplus} - \alpha_{\text{red}}^{\oplus} \right) / nF$$

$$F \left[ E_{\text{O/R}} \right]_{\text{abs}} = \Delta G_{\text{hyd}}(O) - \Delta G_{\text{hyd}}(R) + E_I$$

Electrochemical potential of the electron in solution

$$\tilde{\mu}_{e^-}^{\Phi,S} = -\left[ E_{\text{ox/red}}^{\oplus} \right]_{\text{abs}, \psi^S=0}$$

Solvent reorganisation energy

$$\lambda = \frac{e^2}{4\pi\varepsilon_0} \left( \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_s} \right) \left( \frac{1}{2r_A} + \frac{1}{2r_D} - \frac{1}{r} \right)$$
Metallic Nanoparticles

Figure 3. (a) Equivalence of a single-electron oxidation process in a solvent phase to a cycle of an ionization process in the vacuum preceded and followed by transfer of a charged-state couple of MPC between the vacuum and the solvent phase; (b) Born’s model of the solvation of MPC$^z$.

Figure 4. (a) A typical DPV response of MPCs in the 1,2-dichloroethane electrolyte solution (ca. 0.02 mM MPCs and 0.01 M BTPPATPFB) measured at a 25-μm Pt electrode: scan rate 20 mV s$^{-1}$, pulse height 50 mV, pulse width 60 ms, and period 200 ms. (b) The corresponding $Z$-plot of $E_{Z-1}^{abs}$ vs the adjacent valence states.
Nernst Equations

- Electrochemical potential
- Nernst equation & Absolute potential
- Fermi-Dirac Statistics
- Batteries
- Ion selective electrodes

Homework highlighted in the slides
Zinc dissolution - Hydrogen evolution

\[ E_{\text{SHE}} = E_{\text{Zn}^{2+}/\text{Zn}}^{\ominus} + \frac{RT}{2F} \ln a_{\text{Zn}^{2+}}^S \]

Discharging mode

Zinc plating - Hydrogen oxidation

Charging mode (Electrolysis)

\[ V < E_{\text{SHE}} \]

\[ a_{\text{Zn}^{2+}}^S \downarrow \]
Batteries

In **primary** batteries, the electrode reactions are not “reversible” and the cells are therefore not rechargeable, i.e. after one discharge, they are discarded.

In **secondary** batteries, the electrode reactions are “reversible” and the cells are rechargeable.
Leclanché Battery

In the wooden phone case…
1880

Discharge reactions:
Anode = Oxidation: \( Zn \rightarrow Zn^{2+} \)
Cathode = Reduction: \( \text{Mn(IV)} \rightarrow \text{Mn(III)} \)
\[ \text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 \]

Low current intermittent use, e.g. pocket lamp.
Lead acid Battery

12 V = 6 in series

Gaston Planté, 1859

Discharge reactions

Pôle +, Cathode = Reduction :
\[ \text{PbO}_2 + 3\text{H}^+ + \text{HSO}_4^- + 2e^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O} \]

Pôle –, Anode = Oxidation :
\[ \text{Pb} + \text{HSO}_4^- \rightarrow \text{PbSO}_4 + \text{H}^+ + 2e^- \]
Lithium-Ion Battery

- **Anode**: carbon etc. (graphite)
  - Vacant site for Li^+ during discharge
- **Cathode**: transition metal oxides (LiCoO_2, LiMn_2O_4)
  - Li^+ ions and e^- during charge

- **Wiring** conveys power and data from the protection circuit to the device.
- **Fuse** and **Protection circuit**
- **Positive terminal**
- **Negative terminal**

- **Current flows** as lithium ions move between electrodes and electrons move through an external circuit. During charging, they reverse course.
### Redox Potentials

<table>
<thead>
<tr>
<th>Electrode Potential (V)</th>
<th>Reaction</th>
<th>Lithium-Ion Battery</th>
</tr>
</thead>
<tbody>
<tr>
<td>-3.045</td>
<td>$\text{Li}^+ + e^- \leftrightarrow \text{Li}$</td>
<td>Ni-MH Battery</td>
</tr>
<tr>
<td>-2.9</td>
<td>$\text{Na}^+ + e^- \leftrightarrow \text{Na}$</td>
<td></td>
</tr>
<tr>
<td>-2.714</td>
<td>$\text{Mg}^{2+} + 2e^- \leftrightarrow \text{Mg}$</td>
<td></td>
</tr>
<tr>
<td>-2.363</td>
<td>$\text{Be}^{2+} + 2e^- \leftrightarrow \text{Be}$</td>
<td></td>
</tr>
<tr>
<td>-1.968</td>
<td>$\text{Al}^{3+} + 3e^- \leftrightarrow \text{Al}$</td>
<td></td>
</tr>
<tr>
<td>-1.68</td>
<td>$\text{ZnO}_2^- + 3e^- \leftrightarrow \text{Zn}$</td>
<td></td>
</tr>
<tr>
<td>-1.22</td>
<td>$2\text{H}_2\text{O} + 2e^- \leftrightarrow 2\text{OH}^- + \text{H}_2$</td>
<td>Ni-MH Battery</td>
</tr>
<tr>
<td>-0.828</td>
<td>$\text{Cd}^{2+} + 2e^- \leftrightarrow \text{Cd}$</td>
<td></td>
</tr>
<tr>
<td>-0.825</td>
<td>$\text{Zn}^{2+} + 2e^- \leftrightarrow \text{Zn}$</td>
<td></td>
</tr>
<tr>
<td>-0.763</td>
<td>$\text{S} + 2e^- \leftrightarrow \text{S}^{2-}$</td>
<td></td>
</tr>
<tr>
<td>-0.447</td>
<td>$\text{PbSO}_4 + 2e^- \leftrightarrow \text{Pb}$</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>$2\text{H}^+ + 2e^- \leftrightarrow \text{H}_2$</td>
<td></td>
</tr>
<tr>
<td>0.337</td>
<td>$\text{Cu}^{2+} + 2e^- \leftrightarrow \text{Cu}$</td>
<td></td>
</tr>
<tr>
<td>0.480</td>
<td>$\text{NiOOH} + \text{H}_2\text{O} + e^- \leftrightarrow \text{Ni(OH)}_2 + \text{OH}^-$</td>
<td>Ni-MH Battery</td>
</tr>
<tr>
<td>0.536</td>
<td>$\text{I}_2 + 2e^- \leftrightarrow 2\text{I}^-$</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>$\text{Li}_{1-x}\text{NiO}_2 + x\text{Li}^+ + xe^- \leftrightarrow \text{LiNiO}_2$</td>
<td>Ni-MH Battery</td>
</tr>
<tr>
<td>0.9</td>
<td>$\text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^- \leftrightarrow \text{LiCoO}_2$</td>
<td>Ni-MH Battery</td>
</tr>
<tr>
<td>1.0</td>
<td>$\text{Li}_{1-x}\text{Mn}_2\text{O}_4 + x\text{Li}^+ + xe^- \leftrightarrow \text{LiMn}_2\text{O}_4$</td>
<td>Ni-MH Battery</td>
</tr>
<tr>
<td>1.065</td>
<td>$\text{Br}_2 + 2e^- \leftrightarrow 2\text{Br}^-$</td>
<td></td>
</tr>
<tr>
<td>1.23</td>
<td>$\text{O}_2 + 4\text{H}^+ + 2e^- \leftrightarrow 2\text{H}_2\text{O}$</td>
<td>Ni-MH Battery</td>
</tr>
<tr>
<td>1.36</td>
<td>$\text{Cl}_2 + 2e^- \leftrightarrow 2\text{Cl}^-$</td>
<td></td>
</tr>
<tr>
<td>1.685</td>
<td>$\text{PbO}_2 + 2e^- \leftrightarrow \text{PbSO}_4$</td>
<td></td>
</tr>
<tr>
<td>2.87</td>
<td>$\text{F}_2 + 2e^- \leftrightarrow 2\text{F}^-$</td>
<td>High Energy Density</td>
</tr>
</tbody>
</table>

**Li shows**
- the lowest redox potential among the elements
- the lowest electrochemical equivalent weight among metals

**High voltage cell**
- light anode
Redox potentials

Electronic density of states and Fermi energies for an oxide-based electrode (Li$_x$Ni$_{0.5}$–yMn$_{1.5}$–yCr$_2$O$_4$ spinel material)

SEI:
Solid electrolyte interface
The energy vs. density of states showing the relative Fermi level of the Ni$^{4+/3+}$ and Co$^{4+/3+}$ redox couples for Li$_x$Ni$_y$Mn$_y$Co$_{1-2y}$O$_2$ during the charge, for three states of charge determined by the Li concentration $x$; (a) $x = 1$; (b) $x = 0.5$; (c) $x = 0$. 

Redox potentials
Crystal structure of the three lithium-insertion compounds in which the Li\(^+\) ions are mobile through the 2-D (layered), 3-D (spinel) and 1-D (olivine) frameworks.
Influence of the anion

Figure 8. NASICON framework of Li$_x$M$_2$(XO$_4$)$_3$ that is built with MO$_6$ octahedra linked by corners to XO$_4$ tetrahedra and vice versa. Adapted from ref 70.
Influence of the cation

Figure 10. Olivine structure of LiFePO$_4$ showing Li in 1D channels. Adapted from ref 74.
# Lithium-Ion Battery

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Material</th>
<th>Abbreviation</th>
<th>Short form</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium Cobalt Oxide (^1) (60%) Co</td>
<td>LiCo(_2)</td>
<td>LCO</td>
<td>Li-cobalt</td>
<td>High capacity; for cell phone laptop, phone, laptop, camera</td>
</tr>
<tr>
<td>Lithium Manganese Oxide (LiMn_2O_4)</td>
<td>LMO</td>
<td>Li-manganese, or spinel</td>
<td></td>
<td>Most safe; lower capacity than Li-cobalt but high specific power and long life. Power tools, e-bikes, EV, medical, hobbyist.</td>
</tr>
<tr>
<td>Lithium Iron Phosphate (LiFePO_4) (^1)</td>
<td>LFP</td>
<td>Li-phosphate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lithium Nickel Manganese Cobalt Oxide (LiNiMnCoO_2) (10-20%) Co</td>
<td>NMC</td>
<td>NMC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lithium Nickel Cobalt Aluminum Oxide (LiNiCoAlO_2) (9%) Co</td>
<td>NCA</td>
<td>NCA</td>
<td></td>
<td>Gaining importance in electric powertrain and grid storage</td>
</tr>
<tr>
<td>Lithium Titanate (^2)</td>
<td>Li(_4)Ti(<em>5)O(</em>{12})</td>
<td>LTO</td>
<td>Li-titanate</td>
<td></td>
</tr>
</tbody>
</table>

Figure 10: Typical energy densities of lead, nickel- and lithium-based batteries
Lithium-cobalt enjoys the highest specific energy; however, manganese and phosphate are superior in terms of specific power and thermal stability.

Courtesy of Cadex
Nernst Equations

- Electrochemical potential
- Nernst equation & Absolute potential
- Fermi-Dirac Statistics
- Ion selective electrodes

Homework highlighted in the slides
Equality of the ion electrochemical potentials

$$\tilde{\mu}_i^w = \tilde{\mu}_i^o$$

with

$$\tilde{\mu} = \mu^\oplus + RT \ln a + zF \phi$$

Nernst equation for an ion transfer

$$\Delta_o^w \phi = \phi^w - \phi^o = \Delta_o^w \phi_i^o + \frac{RT}{z_i F} \ln \left( \frac{a_i^o}{a_i^w} \right)$$
Standard transfer potentials

\[ \Delta G_{tr,i}^{\Theta,w\rightarrow o} = \mu_{i}^{\Theta,o} - \mu_{i}^{\Theta,w} \]

Gibbs transfer energy

\[ \Delta G_{tr,i}^{\Theta,w\rightarrow o} = \Delta G_{tr,i}^{\Theta,w\rightarrow o} \]

Standard transfer potential

\[ \Delta_{o}^{w} \phi_{i}^{\Theta} = \frac{\Delta G_{tr,i}^{\Theta,w\rightarrow o}}{z_{i}F} \]
Distribution potential

Nernst equations for the cation and the anion

\[
\Delta_o^w \phi = \Delta_o^w \phi_{C^+}^\Theta + \frac{RT}{F} \ln \left( \frac{a_o^{C^+}}{a_w^{C^+}} \right) \\
\Delta_o^w \phi = \Delta_o^w \phi_{A^-}^\Theta - \frac{RT}{F} \ln \left( \frac{a_o^{A^-}}{a_w^{A^-}} \right)
\]

Distribution potential independent of the phase ratio

\[
\Delta_o^w \phi_{\text{dis}} = \frac{\Delta_o^w \phi_{C^+}^\Theta \prime + \Delta_o^w \phi_{A^-}^\Theta \prime}{2} = \frac{\Delta_o^w \phi_{C^+}^\Theta + \Delta_o^w \phi_{A^-}^\Theta}{2} + \frac{RT}{2F} \ln \left( \frac{\gamma_o^{C^+} \gamma_w^{A^-}}{\gamma_w^{C^+} \gamma_o^{A^-}} \right)
\]
Exemple

\[ \Delta G_{\text{tr,Na}^+}^{\text{H}_2\text{O} \rightarrow \text{DCE}} = 56 \text{ kJ} \cdot \text{mol}^{-1} \]

\[ \Delta G_{\text{tr,Cl}^-}^{\text{H}_2\text{O} \rightarrow \text{DCE}} = 50 \text{ kJ} \cdot \text{mol}^{-1} \]

\[ \Delta G_{\text{tr,TBA}^+}^{\text{H}_2\text{O} \rightarrow \text{DCE}} = -22 \text{ kJ} \cdot \text{mol}^{-1} \]

\[ \Delta G_{\text{tr,TPB}^-}^{\text{H}_2\text{O} \rightarrow \text{DCE}} = -33 \text{ kJ} \cdot \text{mol}^{-1} \]

Distribution potential imposed by TBACl?

\[ \Delta \phi_{\text{H}_2\text{O} \rightarrow \text{DCE}}^{\text{TBA}^+} = -360 \text{ mV} \]
Exemple

\[ \Delta G_{\text{tr,Na}^+}^{\Theta, \text{H}_2\text{O}\rightarrow \text{DCE}} = 56 \text{ kJ} \cdot \text{mol}^{-1} \]
\[ \Delta G_{\text{tr,Cl}^-}^{\Theta, \text{H}_2\text{O}\rightarrow \text{DCE}} = 50 \text{ kJ} \cdot \text{mol}^{-1} \]
\[ \Delta G_{\text{tr,TBA}^+}^{\Theta, \text{H}_2\text{O}\rightarrow \text{DCE}} = -22 \text{ kJ} \cdot \text{mol}^{-1} \]
\[ \Delta G_{\text{tr,TPB}^-}^{\Theta, \text{H}_2\text{O}\rightarrow \text{DCE}} = -33 \text{ kJ} \cdot \text{mol}^{-1} \]

Distribution potential imposed NaTPB?

\[ \Delta \phi_{\text{NaTPB}} = 445 \text{ mV} \]
Ionic distribution coefficient

Ion distribution depends on the potential

\[
P_i = \frac{a_i^o}{a_i^w} = \exp\left[z_i F \left(\Delta_o^w \phi - \Delta_o^w \phi_i^\Theta\right) / RT\right]
\]

\[
P_i = \frac{a_i^o}{a_i^w} = P_i^\Theta \exp\left[z_i F \Delta_o^w \phi / RT\right]
\]

with

\[
\ln P_i^\Theta = -\frac{\mu_{i^\Theta, o} - \mu_{i^\Theta, w}}{RT} = -\frac{\Delta G_{tr, i}^{\Theta, w \rightarrow o}}{RT} = -\frac{z_i F}{RT} \Delta_o^w \phi_i^\Theta
\]
Distribution coefficient of a salt

Salt chemical potential

\[ \mu_{\text{salt}} = \mu_{\text{salt}}^{\ominus} + \nu RT \ln(\gamma_{\pm} \nu_{\pm} c_{\text{salt}}) = \mu_{\text{salt}}^{\ominus} + RT \ln a_{\text{salt}} \]

\[ \mu_{\text{salt}}^{\ominus} = \nu^+ \mu_{C^{z+}}^{\ominus} + \nu^- \mu_{A^{z-}}^{\ominus} \]

Salt distribution

\[ \ln P_{\text{salt}}^{\ominus} = \ln \left( \frac{a_{\text{salt}}^o}{a_{\text{salt}}^w} \right) = \ln \left( \frac{\gamma_{\pm}^o c_{\text{salt}}^o}{\gamma_{\pm}^w c_{\text{salt}}^w} \right)^\nu = - \frac{\mu_{\text{salt}}^{\ominus, o} - \mu_{\text{salt}}^{\ominus, w}}{RT} = - \frac{\Delta G_{\text{tr, salt}}^{\ominus, w \rightarrow o}}{RT} \]

\[ \ln P_{\text{salt}} = \nu^+ \ln P_{C^{z+}}^{\ominus} + \nu^- \ln P_{A^{z-}}^{\ominus} \]
Acid distribution

\[
K^o_a = \frac{a^o_{A^-}a^o_{H^+}}{a^o_{AH}} = K^w_a \frac{P_{A^-}P_{H^+}}{P^{\ominus}_{AH}} = K^w_a \frac{P^{\ominus}_{A^-}P^{\ominus}_{H^+}}{P^{\ominus}_{AH}}
\]
Partition of 3 ions

\[
\Delta_o \phi = \Delta_o \phi_I^+ + \frac{RT}{F} \ln \left( \frac{a_I^o}{a_I^w} \right)
\]

\[
\Delta_o \phi = \Delta_o \phi_{A^-} - \frac{RT}{F} \ln \left( \frac{a_{A^-}^o}{a_{A^-}^w} \right)
\]

\[
\Delta_o \phi = \Delta_o \phi_{X^-} - \frac{RT}{F} \ln \left( \frac{a_{X^-}^o}{a_{X^-}^w} \right)
\]

Mass conservation

\[
c_I^w + c_I^o = c_I^{tot}
\]

\[
c_{A^-}^w + c_{A^-}^o = c_{A^-}^{tot}
\]

\[
c_{X^-}^w + c_{X^-}^o = c_{X^-}^{tot}
\]

6 équations, 6 variables to calculate the Galvani potential difference
Influence of the concentration distribution potential of IA

\[ \Delta \phi_d^{IA} = -60 \text{ mV} \]
\[ \Delta \phi_d^{IA} = -120 \text{ mV} \]

\[ \Delta \phi_d^{IX} = 60 \text{ mV} \]
\[ \Delta \phi_d^{IX} = 120 \text{ mV} \]
\[ \Delta \phi_d^{IX} = 180 \text{ mV} \]
\[ \Delta \phi_d^{IX} = 240 \text{ mV} \]

\[ \log(c_{IX}/c_{IA}) \]

\[ \frac{c_{tot}^{I^+}}{1 + re} \frac{F(\Delta_o \phi - \Delta_o \phi^{\oplus /} I^+/)}{RT} \]
\[ \frac{c_{tot}^{X^-}}{1 + re} \frac{-F(\Delta_o \phi - \Delta_o \phi^{\oplus /} X^-)}{RT} \]
\[ \frac{c_{tot}^{A^-}}{1 + re} \frac{-F(\Delta_o \phi - \Delta_o \phi^{\oplus /} A^-)}{RT} \]

= 0
Potential determining ion

If IA is very hydrophilic

\[ c_{I^+}^w = c_{IA}^w \]

If IX is very lipophilic

\[ c_{I^+}^o = c_{IX}^o \]

The Galvani potential difference is given by the Nernst equation for the ion I

\[
\Delta_o^w \phi = \Delta_o^w \phi_{I^+} + \frac{RT}{F} \ln \left( \frac{a_{I^+}^o}{a_{I^+}^w} \right) = \Delta_o^w \phi_{I^+} + \frac{RT}{F} \ln \left( \frac{a_{IX}^o}{a_{IA}^w} \right)
\]
Ion Selective Electrode
Ion Selective Electrodes

\[ \Delta \phi \]

Reference electrodes

Membrane

Analyte

Reference analyte
ISE response

Equilibrium between 3 phases

\[ \tilde{\mu}_i^{\text{Analyte}} = \tilde{\mu}_i^{\text{Membrane}} = \tilde{\mu}_i^{\text{Reference}} \]

Measured voltage

\[ \phi^R - \phi^A = \left( \phi^R - \phi^M \right) + \left( \phi^M - \phi^A \right) \]

\[ \phi^R - \phi^A = \Delta^R_M \phi_i^\Theta + \frac{RT}{z_i F} \ln \left( \frac{a_i^M}{a_i^R} \right) + \Delta^M_A \phi_i^\Theta + \frac{RT}{z_i F} \ln \left( \frac{a_i^A}{a_i^M} \right) = \frac{RT}{z_i F} \ln \left( \frac{a_i^A}{a_i^R} \right) \]

An ideal ISE includes a very lipophilic salt IX that should not leach out

Aqueous solutions contain very hydrophilic salts that should not diffuse through the membrane
Ionophores

Dibenzo-18-crown-6

Ligands to “solvate” cations in organic phases
## Applications

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Measuring Range / M</th>
<th>Interfering species</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺</td>
<td>10⁻¹⁴ ... 1</td>
<td>Li⁺</td>
<td>Measurement of pH and titrations</td>
</tr>
<tr>
<td>Na⁺</td>
<td>10⁻⁵ ... 1</td>
<td>pH&gt;pNa +4, Ag⁺, Li⁺, K⁺</td>
<td>Water, clinical analysis, ...</td>
</tr>
<tr>
<td>K⁺</td>
<td>10⁻⁶ ... 1</td>
<td>Cs⁺, NH₄⁺⁺, H⁺, Na⁺</td>
<td>Soil, fertilizer, wine, clinical analysis ...</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>5 10⁻⁷ ... 1</td>
<td>Na⁺⁺, Pb²⁺⁺, Fe²⁺⁺, Zn²⁺⁺ Mg²⁺</td>
<td>Soil, food, milk</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>7 10⁻⁶ ... 1</td>
<td>Br⁻, NO₂⁻, Cl⁻, OAc⁻</td>
<td>Soil, vegetables, water, food, ...</td>
</tr>
<tr>
<td>BF₄⁻</td>
<td>7 10⁻⁶ ... 1</td>
<td>NO₃⁻, SO₄²⁻, ClO₄⁻, F⁻, OAc⁻</td>
<td>Surface active agents, plating baths....</td>
</tr>
</tbody>
</table>

Table 2.2: Applications of glass and membrane ion selective electrodes (Copyright, Metrohm CH).
Interfering ion

\[ E_{\text{ISE}} = \frac{RT}{z_I F} \ln \left( \frac{a_I^A + K_{ij}^{\text{pot}} (a_J^A)^{\frac{z_I}{z_J}}}{a_I^R} \right) \]
Ion selective Electrodes

- Ionometry Na⁺, K⁺ in blood
- pH measurement
- Coordination chemistry

Synchron LX4210
2880 samples per hour
pH Glass Electrodes

Micro pH electrode

Combination pH electrode
pH electrode

Co-axial cable

Liquid junction

Inner reference electrode

Outer reference electrode

Outer reference solution, e.g. KCl

Inner buffer solution
Proton, oxonium, etc…

- $\text{H}_3\text{O}^+$
- $\text{H}_9\text{O}_4^+$
- $\text{H}_5\text{O}_2^+$

Zundel’s cation

Eigen’s cation
Glass electrode

Analyte

Buffer

Hydrated glass

Glass

H+  Na+

H+  Na+

H+  Na+

H+  Na+
Describe and explain a pH-FET
DNA Sequencing

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