Chemical vs. thermodynamic reversibility

- **Chemical reversibility:** if reversal of the cell current solely results in a reversal of the cell reaction, a process is termed as **chemically reversible**. Conversely, if current reversal causes the appearance of different electrode reactions and/or leads to a different net reaction, a process is termed as **chemically irreversible**. The same distinction applies for *half-cell reactions*.

Es. $\mathbf{ArX + 1e^- \longrightarrow ArX^{\bullet -} \xrightarrow{fast} Ar^{\bullet} + X^-}$

The observation of chemical irreversibility / reversibility may depend on the experiment timescale!!

- **Thermodynamic reversibility:** a thermodynamically reversible transformation is reversed by an infinitesimal reversal in a driving force, since it proceeds through a series of **equilibrium states**.

In electrochemistry, an electrode reaction following the **Nernst equation** (termed as *nernstian*) is often said to be **thermodynamically or electrochemically reversible**

The Electrochemical equilibrium: Nernst equation

W. H. Nernst (1864 – 1941)
Nobel Prize 1920

$$a\mathrm{Ox}_1 + b\mathrm{Red}_2 \rightleftharpoons a\mathrm{Red}_1 + b\mathrm{Ox}_2$$

$$a\mathrm{Ox}_1 + ze^- \rightleftharpoons a\mathrm{Red}_1 \qquad b\mathrm{Ox}_2 + ze^- \rightleftharpoons b\mathrm{Red}_2$$

$$E_{eq,1} = E_1^0 + \frac{RT}{nF} ln \frac{a_{Ox_1}^a}{a_{Red_1}^a} \qquad E_{eq,2} = E_2^0 + \frac{RT}{nF} ln \frac{a_{Ox_2}^b}{a_{Red_2}^b}$$

Nernst equations for the two half-cell reactions (equilibrium)

$$E_{cell} = E_{cell}^0 + \frac{RT}{nF} ln \frac{a_{Ox_1}^a a_{Red_2}^b}{a_{Red_1}^a a_{Ox_2}^b}$$

Cell potential (or voltage)

Standard Cell potential

The formal potentials

$$Ox + e^- \rightleftharpoons Red$$

$$E = E^0 + \frac{RT}{nF} ln \frac{a_{Ox}}{a_{Red}} = E^0 + \frac{RT}{nF} ln \frac{\gamma_{Ox} \cdot [Ox]}{\gamma_{Red} \cdot [Red]}$$

$$E = E^{0\prime} + \frac{RT}{nF} ln \frac{[Ox]}{[Red]} \quad \text{with} \quad \boxed{E^{0\prime} = E^0 + \frac{RT}{nF} ln \frac{\gamma_{Ox}}{\gamma_{Red}}}$$

Formal potential

- incorporates the terms for **E^0 and the activity coefficients** of the species involved in the process (γ are typically unknown)
- Dependent on the ionic strength of the medium

Gibbs free energy and cell electromotive force (EMF)

$$a\mathrm{Ox}_1 + b\mathrm{Red}_2 \rightleftharpoons b\mathrm{Ox}_2 + a\mathrm{Red}_1$$

$$\boxed{\Delta G = -n \cdot F \cdot E_{cell}} \qquad \Delta G^0 = -n \cdot F \cdot E^0_{cell} \quad (a = 1)$$

Electromotive force (EMF) of the cell reaction (galvanic cells): potential difference between the two half-cells, measured under reversible conditions, at **zero current (open-circuit)**

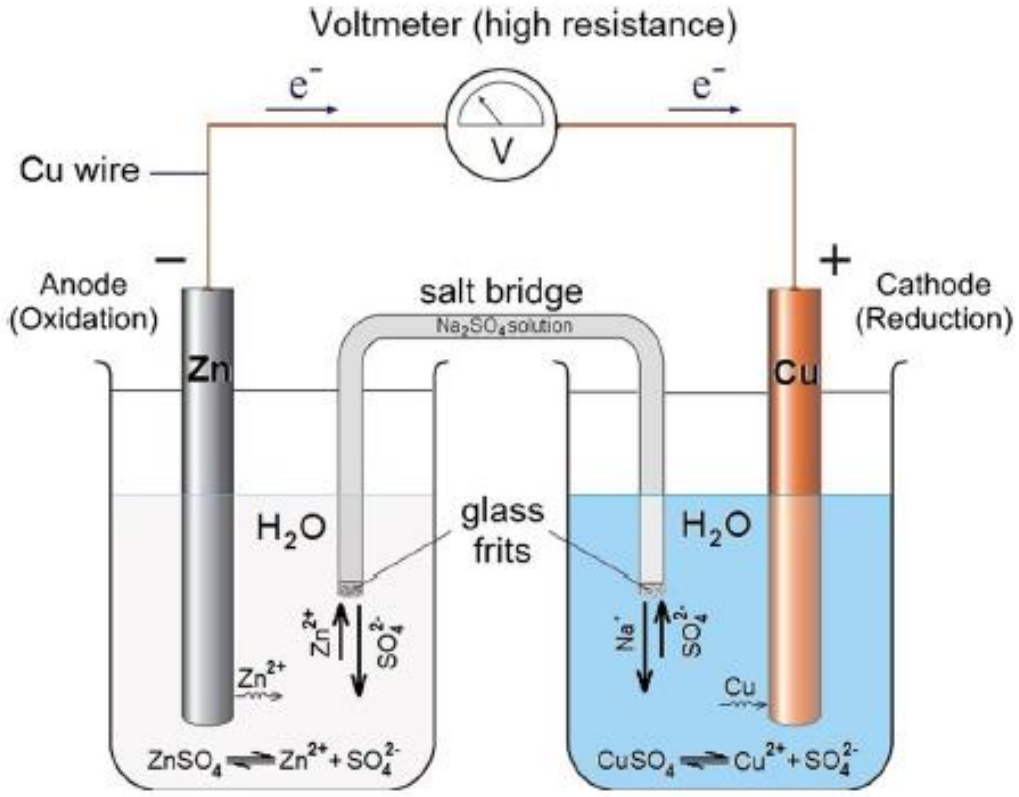
$E_{cell} < 0$ $\quad \Delta G > 0$ **Non-spontaneous cell reaction**

$E_{cell} > 0$ $\quad \Delta G < 0$ **Spontaneous cell reaction**

The larger the value of E_{cell}, the larger is the tendency of a cell reaction to proceed

Gibbs free energy and cell electromotive force (EMF)

- **EMF** is a directional quantity and is related to the **cell reaction** (not to the physical cell)
- It depends on the **concentration of the species** involved and on the **nature of the electrodes**



G. Inzelt, ChemTexts (2014) 1:2

$$Cu^{2+}\ (1\ M)|Cu\|Zn|Zn^{2+}\ (1\ M)$$

Standard conditions (T =298 K)

$$\text{Anode:}\quad Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$$

$$\text{Cathode:}\quad Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

$$EMF = E°_{cathode} - E°_{anode} = 0.34 - (-0.76) = 1.10\ V$$

Standard reduction potentials

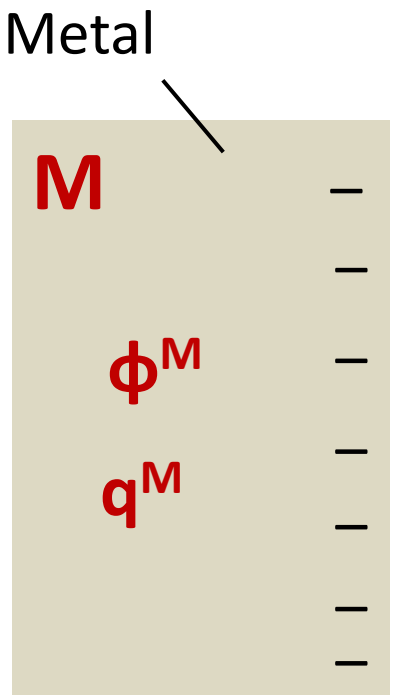
TABLE C.1 Selected Standard Electrode Potentials in Aqueous Solutions at 25°C in V *vs.* NHE[a]

Reaction	Potential, V
$Ag^+ + e \rightleftarrows Ag$	0.7991
$AgBr + e \rightleftarrows Ag + Br^-$	0.0711
$AgCl + e \rightleftarrows Ag + Cl^-$	0.2223
$AgI + e \rightleftarrows Ag + I^-$	−0.1522
$Ag_2O + H_2O + 2e \rightleftarrows 2Ag + 2OH^-$	0.342
$Al^{3+} + 3e \rightleftarrows Al$	−1.676
$Au^+ + e \rightleftarrows Au$	1.83
$Au^{3+} + 2e \rightleftarrows Au^+$	1.36
p-benzoquinone $+ 2H^+ + 2e \rightleftarrows$ hydroquinone	0.6992
$Br_2(aq) + 2e \rightleftarrows 2Br^-$	1.0874
$Ca^{2+} + 2e \rightleftarrows Ca$	−2.84
$Cd^{2+} + 2e \rightleftarrows Cd$	−0.4025
$Cd^{2+} + 2e \rightleftarrows Cd(Hg)$	−0.3515
$Ce^{4+} + e \rightleftarrows Ce^{3+}$	1.72
$Cl_2(g) + 2e \rightleftarrows 2Cl^-$	1.3583
$HClO + H^+ + e \rightleftarrows \frac{1}{2}Cl_2 + H_2O$	1.630
$Co^{2+} + 2e \rightleftarrows Co$	−0.277
$Co^{3+} + e \rightleftarrows Co^{2+}$	1.92
$Cr^{2+} + 2e \rightleftarrows Cr$	−0.90
$Cr^{3+} + e \rightleftarrows Cr^{2+}$	−0.424
$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftarrows 2Cr^{3+} + 7H_2O$	1.36
$Cu^+ + e \rightleftarrows Cu$	0.520
$Cu^{2+} + 2CN^- + e \rightleftarrows Cu(CN)_2^-$	1.12
$Cu^{2+} + e \rightleftarrows Cu^+$	0.159
$Cu^{2+} + 2e \rightleftarrows Cu$	0.340
$Cu^{2+} + 2e \rightleftarrows Cu(Hg)$	0.345
$Eu^{3+} + e \rightleftarrows Eu^{2+}$	−0.35
$1/2F_2 + H^+ + e \rightleftarrows HF$	3.053
$Fe^{2+} + 2e \rightleftarrows Fe$	−0.44
$Fe^{3+} + e \rightleftarrows Fe^{2+}$	0.771
$Fe(CN)_6^{3-} + e \rightleftarrows Fe(CN)_6^{4-}$	0.3610
$2H^+ + 2e \rightleftarrows H_2$	0.0000
$2H_2O + 2e \rightleftarrows H_2 + 2OH^-$	−0.828
$H_2O_2 + 2H^+ + 2e \rightleftarrows 2H_2O$	1.763
$2Hg^{2+} + 2e \rightleftarrows Hg_2^{2+}$	0.9110
$Hg_2^{2+} + 2e \rightleftarrows 2Hg$	0.7960
$Hg_2Cl_2 + 2e \rightleftarrows 2Hg + 2Cl^-$	0.26816
$Hg_2Cl_2 + 2e \rightleftarrows 2Hg + 2Cl^-$ (sat'd. KCl)	0.2415
$HgO + H_2O + 2e \rightleftarrows Hg + 2OH^-$	0.0977
$Hg_2SO_4 + 2e \rightleftarrows 2Hg + SO_4^{2-}$	0.613
$I_2 + 2e \rightleftarrows 2I^-$	0.5355
$I_3^- + 2e \rightleftarrows 3I^-$	0.536
$K^+ + e \rightleftarrows K$	−2.925
$Li^+ + e \rightleftarrows Li$	−3.045
$Mg^{2+} + 2e \rightleftarrows Mg$	−2.356
$Mn^{2+} + 2e \rightleftarrows Mn$	−1.18
$Mn^{3+} + e \rightleftarrows Mn^{2+}$	1.5
$MnO_2 + 4H^+ + 2e \rightleftarrows Mn^{2+} + 2H_2O$	1.23
$MnO_4^- + 8H^+ + 5e \rightleftarrows Mn^{2+} + 4H_2O$	1.51
$Na^+ + e \rightleftarrows Na$	−2.714
$Ni^{2+} + 2e \rightleftarrows Ni$	−0.257
$Ni(OH)_2 + 2e \rightleftarrows Ni + 2OH^-$	−0.72
$O_2 + 2H^+ + 2e \rightleftarrows H_2O_2$	0.695
$O_2 + 4H^+ + 4e \rightleftarrows 2H_2O$	1.229
$O_2 + 2H_2O + 4e \rightleftarrows 4OH^-$	0.401
$O_3 + 2H^+ + 2e \rightleftarrows O_2 + H_2O$	2.075
$Pb^{2+} + 2e \rightleftarrows Pb$	−0.1251
$Pb^{2+} + 2e \rightleftarrows Pb(Hg)$	−0.1205
$Pd^{2+} + 2e \rightleftarrows Pd$	0.915
$Pt^{2+} + 2e \rightleftarrows Pt$	1.188
$PtCl_4^{2-} + 2e \rightleftarrows Pt + 4Cl^-$	0.758
$PtCl_6^{2-} + 2e \rightleftarrows PtCl_4^{2-} + 2Cl^-$	0.726
$Ru(NH_3)_6^{3+} + e \rightleftarrows Ru(NH_3)_6^{2+}$	0.10
$S + 2e \rightleftarrows S^{2-}$	−0.447
$Sn^{2+} + 2e \rightleftarrows Sn$	−0.1375
$Sn^{4+} + 2e \rightleftarrows Sn^{2+}$	0.15
$Tl^+ + e \rightleftarrows Tl$	−0.3363
$Tl^+ + e \rightleftarrows Tl(Hg)$	−0.3338
$Tl^{3+} + 2e \rightleftarrows Tl^+$	1.25
$U^{3+} + 3e \rightleftarrows U$	−1.66
$U^{4+} + e \rightleftarrows U^{3+}$	−0.52
$UO_2^+ + 4H^+ + e \rightleftarrows U^{4+} + 2H_2O$	0.273
$UO_2^{2+} + e \rightleftarrows UO_2^+$	0.163
$V^{2+} + 2e \rightleftarrows V$	−1.13
$V^{3+} + e \rightleftarrows V^{2+}$	−0.255
$VO^{2+} + 2H^+ + e \rightleftarrows V^{3+} + H_2O$	0.337
$VO_2^+ + 2H^+ + e \rightleftarrows VO^{2+} + H_2O$	1.00
$Zn^{2+} + 2e \rightleftarrows Zn$	−0.7626

From Bard, Faulkner, "Electrochemical Methods. Fundamentals and Applications", Wiley, 2001

The interfacial potential

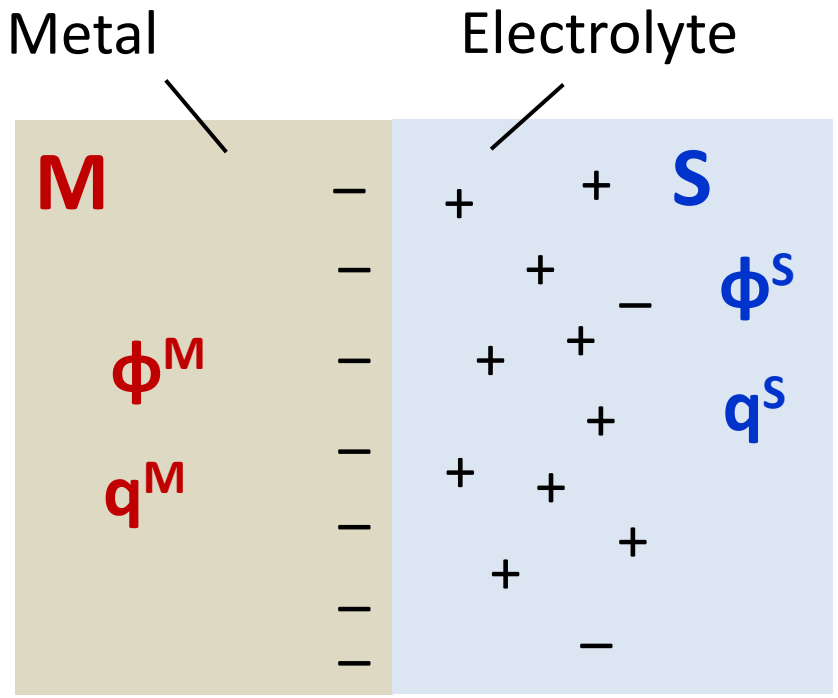
Conducting phases



- Changes in the charge distribution inside or around a phase induce changes in its potential
- The charge carriers of a conducting phase (metal) operate in a way to fully distribute changes in its excess charge over the **entire phase boundary (q^M)**
- The inner part of the phase experiences a constant potential, **ϕ**

The interfacial potential

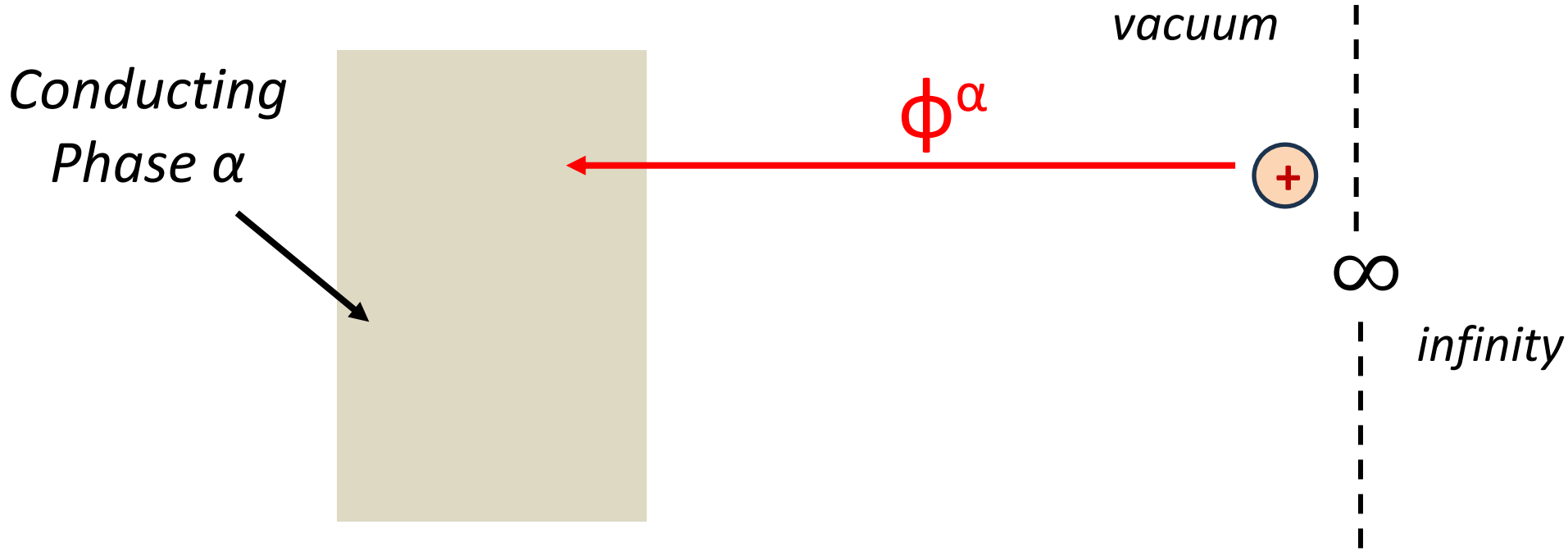
Conducting phases



$$-q^M = q^S$$

- Electrostatic interactions between two conducting phases (M/S) in contact to each other (excess of charge causes inter-dependent potential changes)
- The excess positive charge in the electrolyte ($\mathbf{q^S}$) exactly counterbalances q^M and resides at the metal-electrolyte interface (double layer)
- $\mathbf{(\phi^M - \phi^S)}$ is called the **interfacial potential difference** and depends on the charge imbalance at the M/S interface and the physical size of the interface

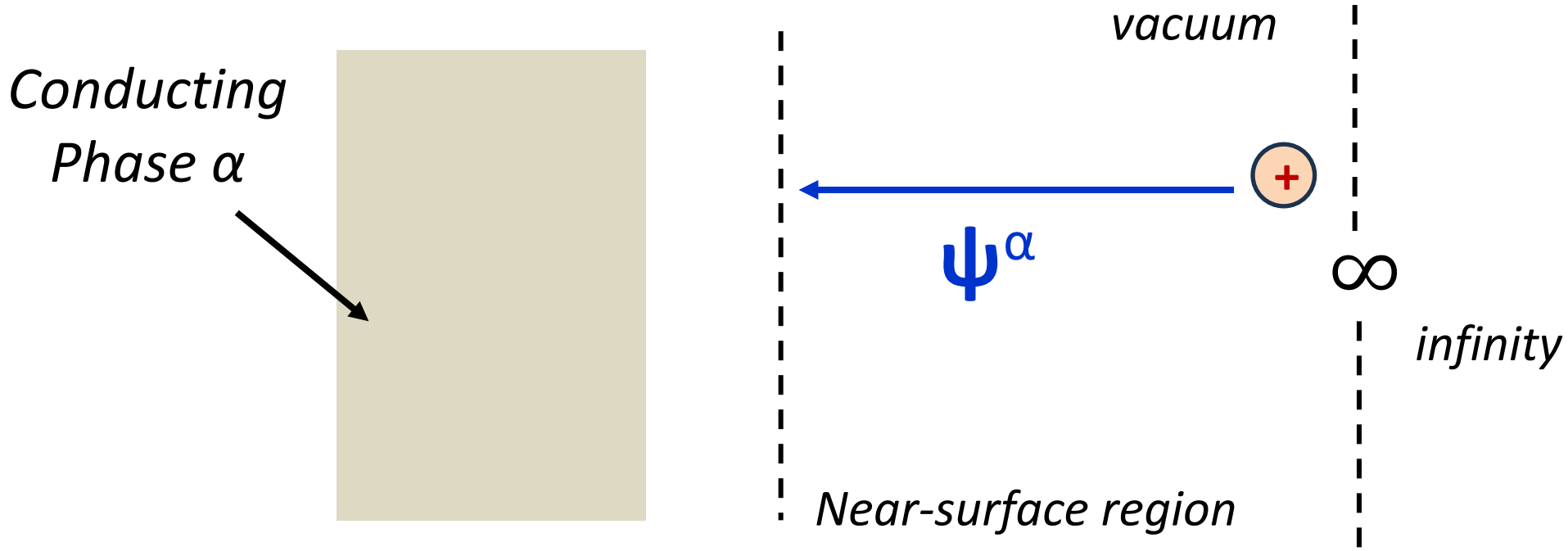
The inner potential (ϕ)



Inner potential or Galvani potential (ϕ^{α}): *the work required to bring a unit point charge ("test charge") from infinite distance to a point inside a conducting phase α.*

It represents the **electrostatic potential** experienced by a charged particle inside the phase

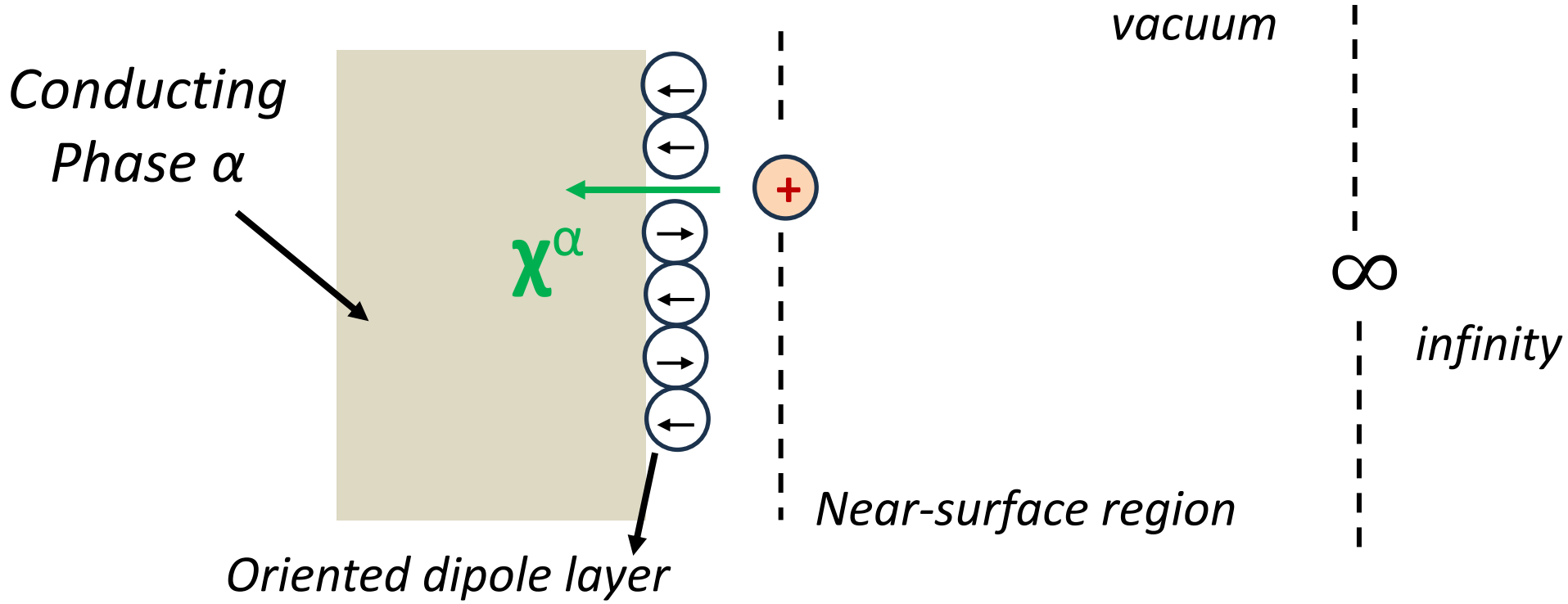
The outer potential (ψ)



Outer or Volta potential (ψ^{α}): *the work required to bring a unit point charge from infinite distance to a point outside the surface of the phase* (very close to the surface, ≈ 10^{-5} - 10^{-3} cm)

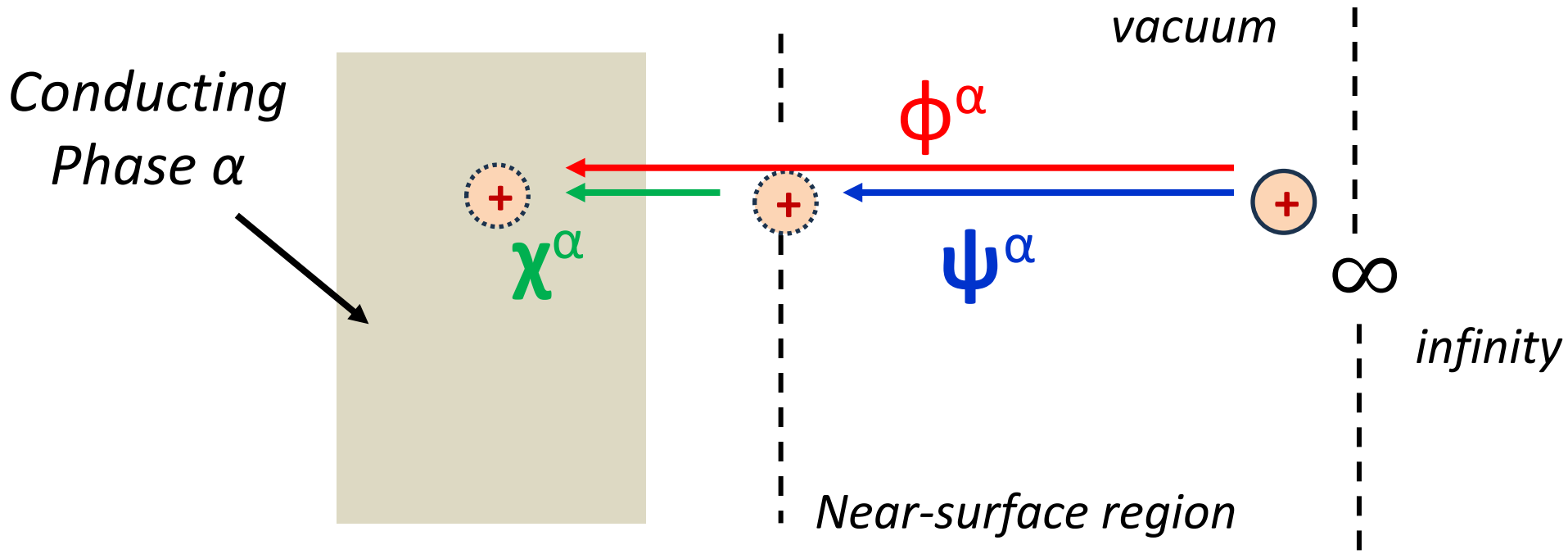
This potential is purely determined by the **charge** on the electrode (and independent on distance).

The surface potential (χ)



Dipole or Surface potential (χ^{α}): *the work required to bring a unit point charge just across the* ***oriented dipole layer*** *at the surface of an uncharged electrolyte (and an uncharged metal).*

Potential difference at the electrified interface



Total potential

$$\phi^\alpha = \psi^\alpha + \chi^\alpha$$

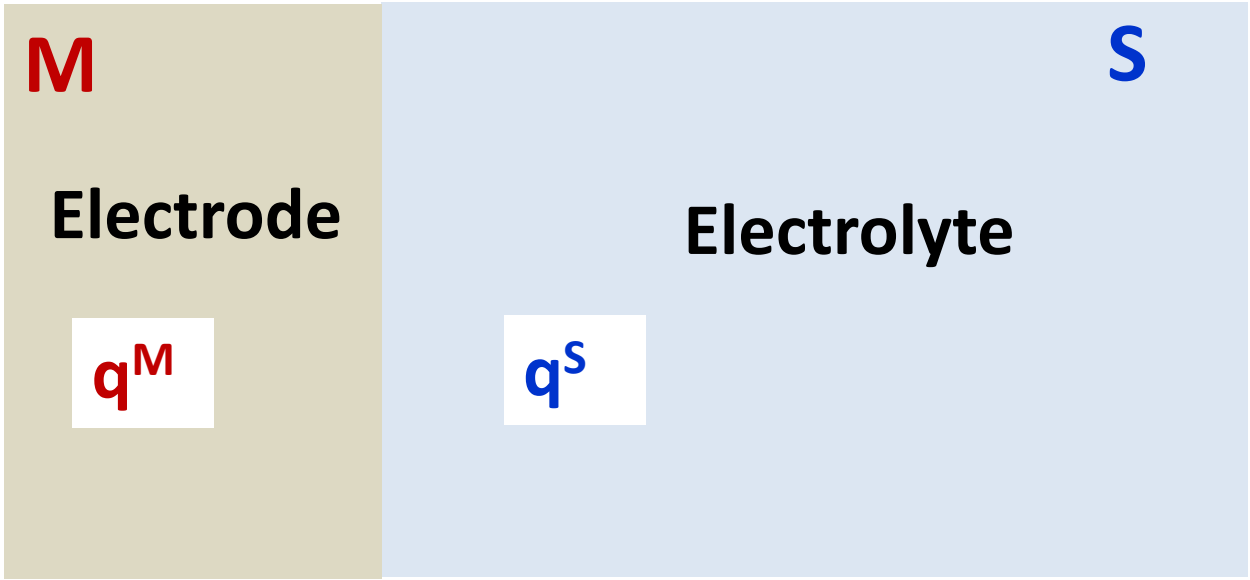
Charge *contribution*

Dipole *contribution*

$$\Delta\phi = \Delta\psi + \Delta\chi$$

Inner potential difference

Potential difference at the electrified interface



$$\Delta\phi^{M/S} = \phi^M - \phi^S$$

Chemical vs. electrochemical potential

$\boldsymbol{\mu_i^\alpha}$ = chemical potential

$$\mu_i^\alpha = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}}$$

$\boldsymbol{\overline{\mu}_i^\alpha}$ = electrochemical potential

$$\overline{\mu}_i^\alpha = \left(\frac{\partial \overline{G}}{\partial n_i}\right)_{T,p,n_{j\neq i}}$$

$$\boldsymbol{\overline{W}} = W_{chem} + W_{el} \quad \Rightarrow \quad \boldsymbol{\overline{G}} = G_{chem} + G_{el}$$

Chemical work ***Electrical work*** ***Electrochemical Gibbs free energy***

The electrochemical potential

$$\overline{\boldsymbol{\mu}}_{\boldsymbol{i}}^{\boldsymbol{\alpha}} = \mu_i^{\alpha} + \underbrace{z_i F \phi^{\alpha}} = \mu_i^{\alpha} + \underbrace{z_i F (\psi^{\alpha} + \chi^{\alpha})}$$

Carica **X** Potenziale elettrico

$\overline{\boldsymbol{\mu}}_{\boldsymbol{i}}^{\boldsymbol{\alpha}} = \boldsymbol{\mu}_{\boldsymbol{i}}^{\boldsymbol{\alpha}}$ for uncharged species

$\overline{\boldsymbol{\mu}}_{\boldsymbol{i}}^{\boldsymbol{\alpha}} = \boldsymbol{\mu}_{\boldsymbol{i}}^{\boldsymbol{0\alpha}}$ for a pure phase at $\alpha = 1$

$$\frac{\partial \overline{\boldsymbol{\mu}}_{\boldsymbol{i}}^{\boldsymbol{\alpha}}}{\partial \boldsymbol{x}} = \frac{\partial \mu_i^{\alpha}}{\partial x} + z_i F \frac{\partial \phi^{\alpha}}{\partial x}$$

Gradient of electrochemical potential

Gradient of chemical potential (diffusion)

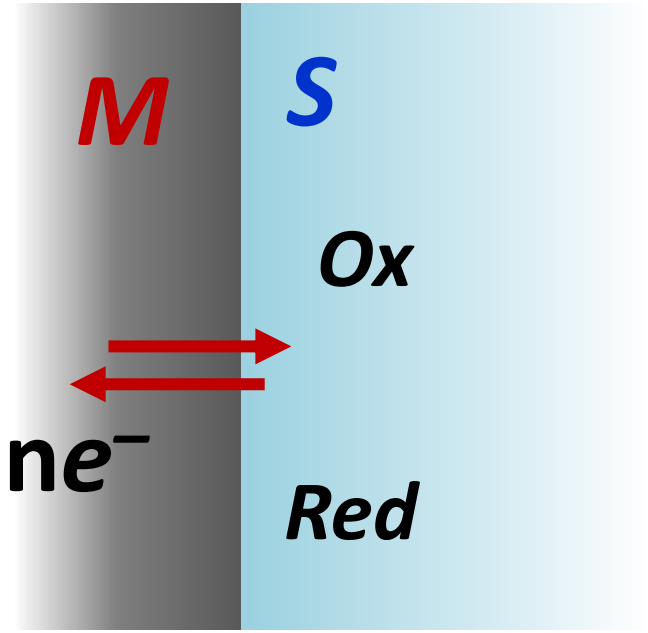
Gradient of electric potential (migration)

The electrochemical potential and the equilibrium

Interface in thermodynamic equilibrium
(α and β phases)

$$\overline{\mu}_i^{\alpha} = \overline{\mu}_i^{\beta} \Rightarrow \overline{\mu}_i^{M} = \overline{\mu}_i^{S}$$

at metal-solution interface



$$Ox^{S} + ne^{-\,M} \rightleftharpoons Red^{S}$$

$$\overline{\mu}_{Ox}^{S} + n\overline{\mu}_{e}^{M} = \overline{\mu}_{Red}^{S}$$

$$(\mu_{Ox}^{S} + z_{Ox}F\,\phi^{S}) + n(\mu_{e}^{0\,M} - F\,\phi^{M}) = (\mu_{Red}^{S} + z_{Red}F\,\phi^{S})$$

For any species in phase α: $\mu_i^{\alpha} = \mu_i^{0\,\alpha} + RT \ln a_i^{\alpha}$

For electrons in metal (z = -1): $\overline{\mu}_e^{M} = \mu_e^{0\,M} - F\,\phi^{M}$

The electrochemical potential and the equilibrium

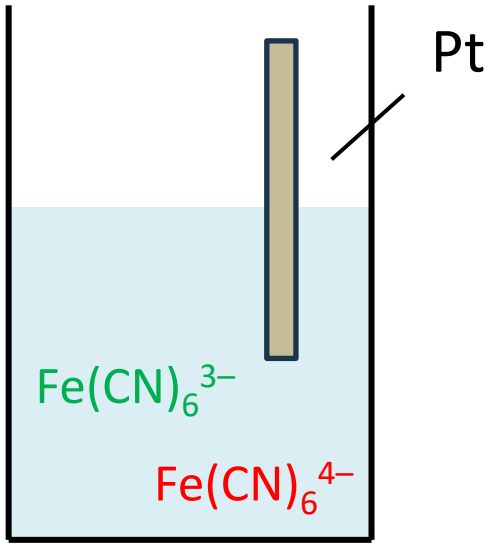
$$(\mu_{Ox}^{0\,S} + RT \ln a_{Ox}^{S} + z_{Ox} F \phi^{S}) + n(\mu_{e}^{0\,M} - F \phi^{M}) = (\mu_{Red}^{0\,S} + RT \ln a_{Red}^{S} + z_{Red} F \phi^{S})$$

$$\underbrace{(\mu_{Ox}^{0\,S} + n\mu_{e}^{0\,M} - \mu_{Red}^{0\,S})}_{\Delta\mu_{Ox/Red}^{0}} + RT \ln \frac{a_{Ox}^{S}}{a_{Red}^{S}} = nF \phi^{M} - \underbrace{(z_{Ox} - z_{Red})}_{n} F \phi^{S}$$

$$\frac{\Delta\mu_{Ox/Red}^{0}}{nF} + \frac{RT}{nF} \ln \frac{a_{Ox}^{S}}{a_{Red}^{S}} = [\phi^{M} - \phi^{S}]_{eq} = E_{Ox/Red}$$

Electrode potential

An example



$$Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-}$$

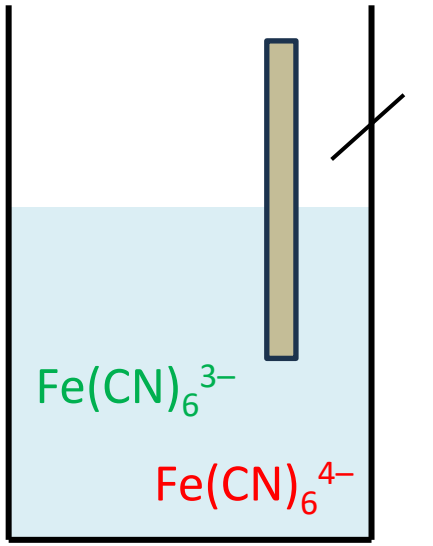
$$\overline{\mu}_{Fe(III)}^{S} + \overline{\mu}_e^{M} = \overline{\mu}_{Fe(II)}^{S}$$

$$(\mu_{Fe(III)}^{S} + 3F\,\phi^{S}) + (\mu_e^{0\,M} - F\,\phi^{M}) = (\mu_{Fe(II)}^{S} + 2F\,\phi^{S})$$

$$(\mu_{Fe(III)}^{0\,S} + RT\ln[Fe(CN)_6^{3-}] + 3F\phi^{S}) + \mu_e^{0\,M} - F\phi^{M} =$$

$$= \mu_{Fe(II)}^{0\,S} + RT\ln[Fe(CN)_6^{4-}] + 2F\phi^{S})$$

An example



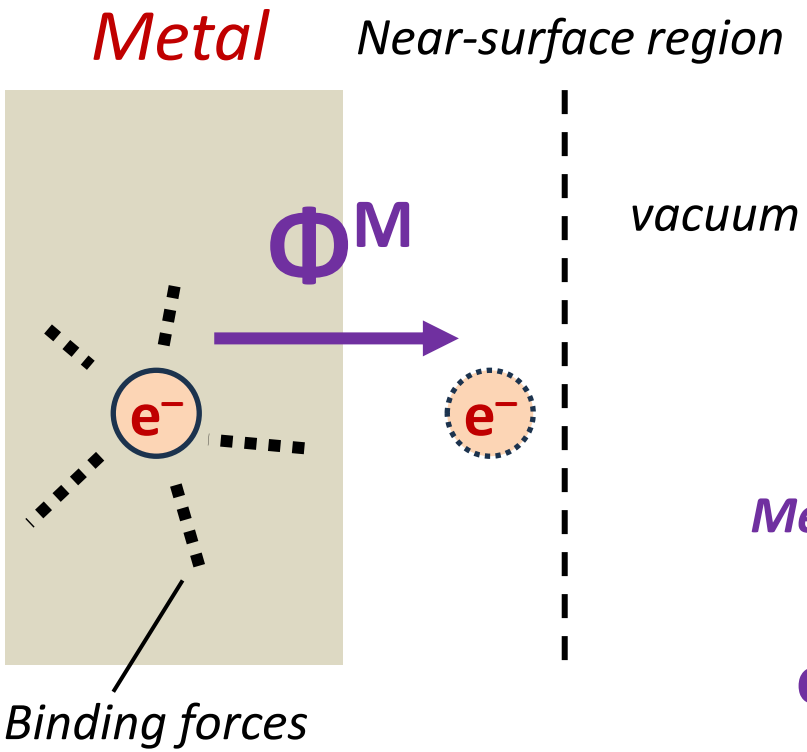
$$\underbrace{(\mu_{Fe(III)}{}^{0\,S} + \mu_e{}^{0\,M} - \mu_{Fe(II)}{}^{0\,S})}_{\Delta\mu^0} + RT \ln \frac{[Fe(CN)_6^{3-}]}{[Fe(CN)_6^{4-}]} =$$

$$= F\phi^M - 3F\phi^S + 2F\phi^S$$

$$(\phi^M - \phi^S) = \frac{\Delta\mu^0}{F} + \frac{RT}{F} \ln \frac{[Fe(CN)_6^{3-}]}{[Fe(CN)_6^{4-}]}$$

Nernst equation for a single electrode-solution interface

The Electron Work Function (Φ)



Energy involved in the ejection of an electron from the metal to a point "just outside" the surface

$$\Phi^M = -\mu_e^M - z_e F \chi^M = -\mu_e^M + F\chi^M$$

Metal work function

Short-range chemical interactions

Dipole or electrical effects

Φ^M are fingerprints of a given conducting material (metal, semiconductor…)

- $\overline{\mu_e}^{\alpha}$ is called the **Fermi level** and corresponds to an electron energy $\mathcal{E}_f^{\alpha}$
- Electrical equilibrium for an inert metal in contact with a solution is given by matching of the Fermi levels of the two phases, $\mathcal{E}_F^M = \mathcal{E}_F^S$