Electrochemical Thermodynamics

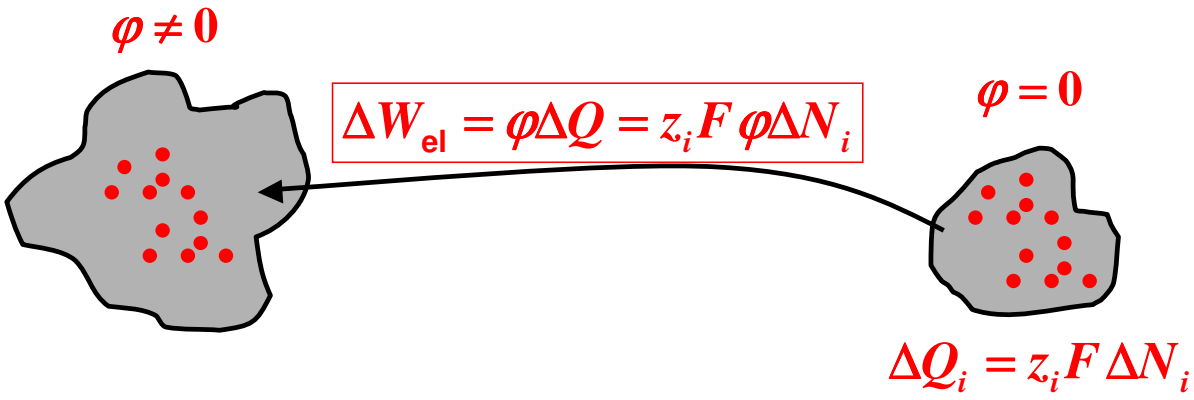
– Interfaces and Energy Conversion

Where does the energy contribution $F\sum_i z_i\varphi\ \mathrm{d}N_i$ come from?

First law of thermodynamics (conservation of energy):

$$\Delta U = T\Delta S + \Delta W$$

Move small amount of charge (ΔQ) of species i through electrical potential difference φ.



Work on charge against inner potential difference.

Corresponding differential of the internal energy:

$$\mathrm{d}\tilde{U} = T\mathrm{d}S - p\mathrm{d}V + \sum_i \mu_i \mathrm{d}N_i + F\sum_i z_i\varphi\ \mathrm{d}N_i$$

Corresponding differential change of Gibbs free energy

$$\mathrm{d}\tilde{G} = -S\mathrm{d}T + V\mathrm{d}p + \sum_i \mu_i \mathrm{d}N_i + F\sum_i z_i\varphi\ \mathrm{d}N_i$$

Important observation: Only differences

$$\tilde{\mu}_i^{\beta} - \tilde{\mu}_i^{\alpha} = \left(\mu_i^{\beta} - \mu_i^{\alpha}\right) + z_i F\left(\varphi^{\beta} - \varphi^{\alpha}\right)$$

between phases α and β are experimentally available.

<u>Gibbs, conclusion of fundamental importance:</u>

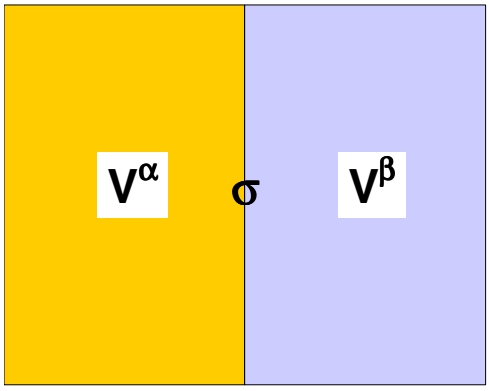
Electrical potential drop can be measured only between points which find themselves in the phases of one and the same chemical composition, i.e. $\mu_i^{\alpha} = \mu_i^{\beta}$ **, and thus,**

Galvani potential $$\Delta_{\alpha}^{\beta}\varphi = \varphi^{\beta} - \varphi^{\alpha} = \frac{\tilde{\mu}_i^{\beta} - \tilde{\mu}_i^{\alpha}}{z_i F}$$

Otherwise, when the points belong to two different phases, $\mu_i^{\alpha} \neq \mu_i^{\beta}$ **, experimental determination of** $\Delta_{\alpha}^{\beta}\varphi$ **is impossible!**

<u>Recall:</u>

- **general situation considered in electrochemistry: phases in contact**



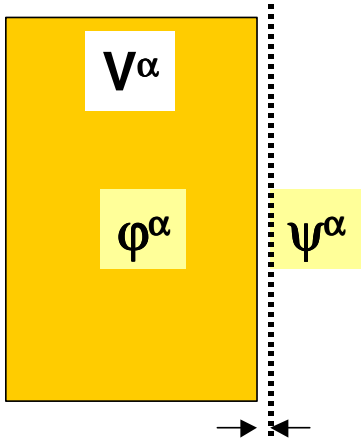
- **potential differences** $\Delta_{\alpha}^{\beta}\varphi$ **control equilibrium between phases and rates of reaction at interface**

The problem is: $\Delta_{\alpha}^{\beta}\varphi$ **is not measurable!**

What is the electrostatic potential of a phase?

Related to work needed for bringing test charge into the phase.

$$\varphi^{\alpha} = \psi^{\alpha} + \chi^{\alpha}$$



φ^{α} : **inner or Galvani potential; work required to bring a unit point charge from ∞ to a point inside the phase α; electrostatic potential that is actually experienced by a charged particle in that phase.**

Unfortunately: φ^{α} cannot be measured! Why not?????

- **Involves transfer across interface with its inhomogeneous charge distribution**
- **Real charged particles interact with other particles in that phase, e.g.: bring an electron into metal**

  ⇒ not only electrostatic work (potential of other charges),

  but: work against exchange and correlation energies (Pauli exclusion principle).

ψ^α : outer or Volta potential; work required to bring a unit point charge from ∞ to a point just outside the surface of phase α; "just outside": very close to surface, but far enough to avoid image interactions (induction effects in metal), 10^{-5} – 10^{-3} cm from surface.

ψ^α can be measured! Why can this be measured????

e.g.: no free charges, metal, uncharged ⇒ $\psi^\alpha = 0$

Why is a metal uncharged? Why is $\psi^\alpha = 0$?

Inner and outer potentials differ by surface potential:

$$\chi^\alpha = \varphi^\alpha - \psi^\alpha$$

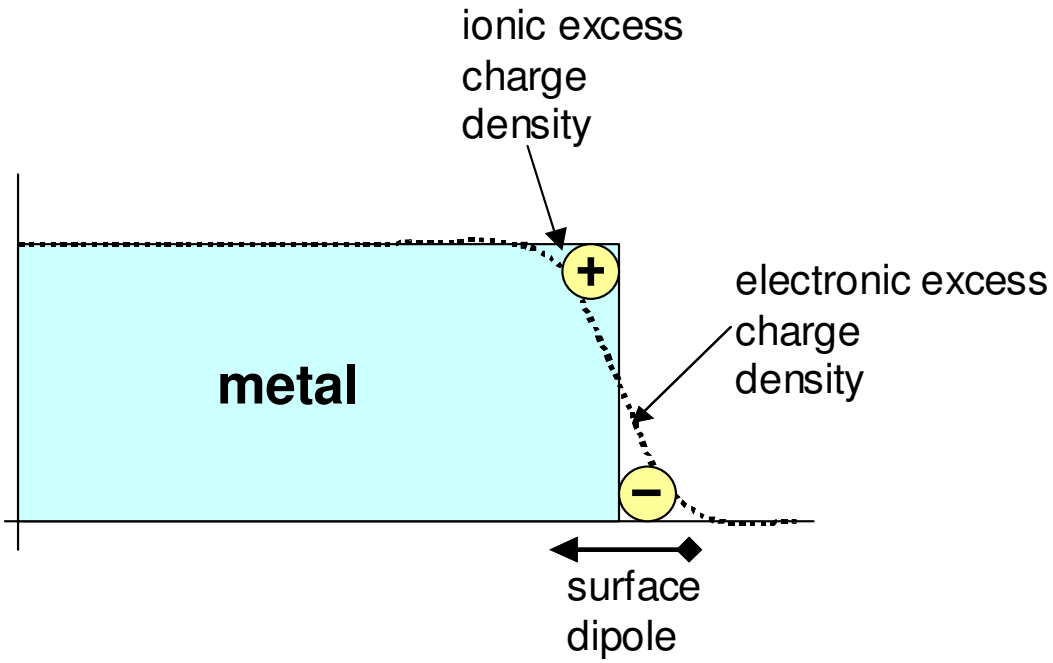
Uncharged phase (metal): $\chi^\alpha = \varphi^\alpha$

$\chi^\alpha \neq 0$ due to inhomogeneous charge distribution at surface

Metal: $\chi^{\alpha} = \varphi^{\alpha}$ **, electroneutrality inside of metal**

positive charge resides on metal ions, fixed at lattice sites,

electronic density decays over ~ 1 Å from bulk value to 0



⇒ **resulting surface dipole potential: ~ a few Volts**

(smaller surface potentials at surfaces of polar liquids)

Different surface planes of metal single crystal: different χ^{α}

Bring charged particles (species i) into uncharged phase α:

Electrochemical potential:

$$\tilde{\mu}_i^{\alpha} = \mu_i^{\alpha} + z_i F \chi^{\alpha}, \; \psi^{\alpha} = 0$$

metal: $$\tilde{\mu}_e^{M} = \mu_e^{M} - F\chi^{M}, \; z_e = -1$$

Electrons in metal:

Highest occupied energy level is the Fermi level E_F **,**

At T = 0: $$E_F = \tilde{\mu}_e^{M}$$

Finite T: $$\tilde{\mu}_e^{M} = E_F \left[1 - \frac{1}{3} \left(\frac{\pi k_B T}{2 E_F} \right)^2 \right]$$

Correction ~0.01% at room T → negligible in most cases!

Work function, Φ^M : **minimum work required to take an electron from inside the metal to a place just outside**

⇒ extract an electron from Fermi-level

~ half the ionization energy of a free metal atom,

(Caesium: ionization energy 3.9 eV, work function 2.0 eV)

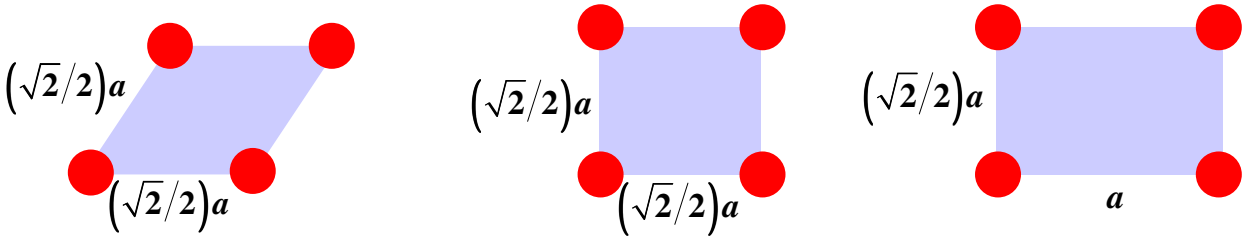
measured by photoemission experiment

contains a surface term – different for different surfaces,

more specifically: Φ^M **increases with density of atoms on metal surface**

$\Phi^M(111) > \Phi^M(100) > \Phi^M(110)$ **for fcc metals, e.g. Pt**

a = 3.9 Å



Pt(111) Pt(100) Pt(110)

reference point for E_F **just outside metal:**

$$E_F = -\Phi^M$$

What would be relation between E_F **and** Φ^M**, if reference point for Fermi energy is taken at inifinity?**

$$E_F = -\Phi^M - e_0\psi$$

Element	Work function (eV)
Caesium (Cs)	1.96
Sodium (Na)	2.06
Zinc (Zn)	3.08
Beryllium (Be)	3.17
Cadmium (Cd)	3.68
Antimony (Sb)	4.01
Tungsten (W)	4.25

Summary:

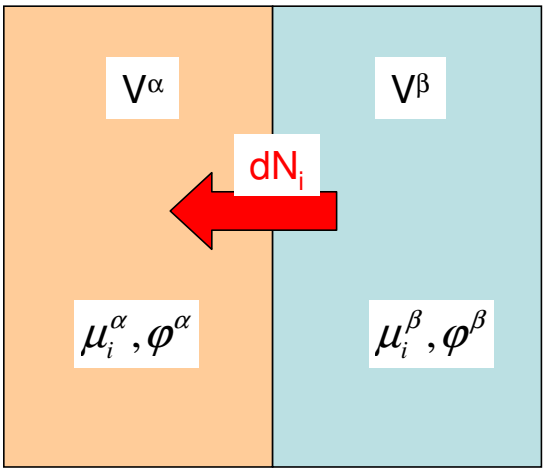
Energy of a particle in a phase:

measurable: $\tilde{\mu}_i^{\alpha}$, ψ^{α} **and for neutral species:** μ_i^{α}

not measurable: $\varphi^{\alpha}, \chi^{\alpha}$ **and for charged species:** μ_i^{α}

Electrochemical equilibrium between two phases α and β

Equality of electrochemical potentials for all components in the contacting phases – species can freely cross the interface



Equilibration: transfer of chemical species between phases

Electrochemical equilibrium (in system at constant p and T):

$\Delta_r \tilde{G} = 0$ for any small $\Delta N_i \quad \Rightarrow \tilde{\mu}_i^\alpha = \tilde{\mu}_i^\beta$, where $\tilde{\mu}_i^\alpha = \mu_i^\alpha + z_i F \varphi^\alpha$

[Note: system not in chemical equilibrium! What does it mean?]

after rearranging: $\varphi^\beta - \varphi^\alpha = \dfrac{\mu_i^\alpha - \mu_i^\beta}{z_i F}$ $\qquad$ $\Delta_\alpha^\beta \varphi = -\dfrac{\Delta_\alpha^\beta \mu_i}{z_i F}$

In words:

Electrical forces **balance** **chemical forces**

$\Delta_\alpha^\beta \varphi \neq 0$ [re-action] $\qquad$ $\Delta_\alpha^\beta \mu \neq 0$ [initial action]

Dependence of Galvani-potential on the activities of the involved ions can be determined. This represents the Nernst-equation for a certain Galvani potential.

Electrochemical Equilibrium – Electromotive Force

Relation between chemical and electric driving forces

Electrochemical system at constant T and p: consider $\tilde{G}$

Consider electrochemical reaction (involving transfer of e^-):

(1) $$|\nu_A|A + |\nu_B|B + |\nu_e|e_R^- \rightarrow |\nu_C|C + |\nu_D|D + |\nu_e|e_L^-$$

reactants **products**

Note:

Stoichiometric coefficients (ν_i) of reactants (A, B) have negative sign, those of products (C,D) are positive

Electrons are written explicitly in this equation since they will appear in the condition of electrochemical equilibrium!

Objective: use thermodynamic arguments to derive electrical potential (the so-called electromotive force, EMF) of a cell and relate this EMF to the composition of electrochemical cells