A few notes on EMF

$$E = E^0 - \frac{RT}{|\nu_e| F} \ln Q \qquad \text{with} \qquad Q = \frac{a_C^{|\nu_C|} \, a_D^{|\nu_D|}}{a_A^{|\nu_A|} \, a_B^{|\nu_B|}}$$

- $\frac{RT}{F}$ important parameter in electrochemistry!

  has units of Volt (V); at 25ºC: $\frac{RT}{F} = 0.0257 \text{ V} \approx \frac{1}{40} \text{ V}$

- effect of concentration changes:

  if concentration of one species changes by factor 10

  → Q changes by factor 10

  → E is shifted by ~60 mV

Literature for next part:

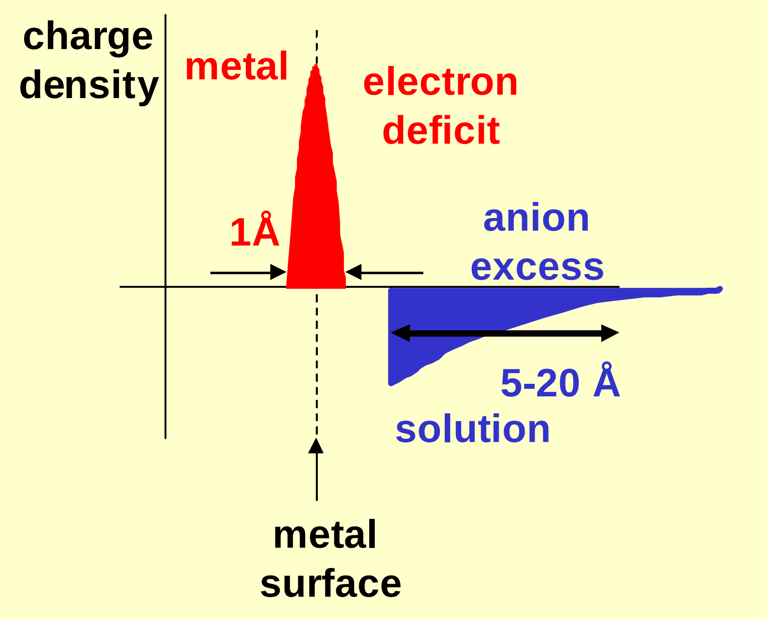
- Chapter 3 in “Brett/Brett”
- Chapter 10 in “Bagotzky”
- Chapter 3 in “Schmickler”

The Electrode/Electrolyte Interface

Charged solid surfaces in liquids:

- **the most important liquid is water**
- **high dielectric constant – good solvent for ions**
- **most surfaces in water are charged**

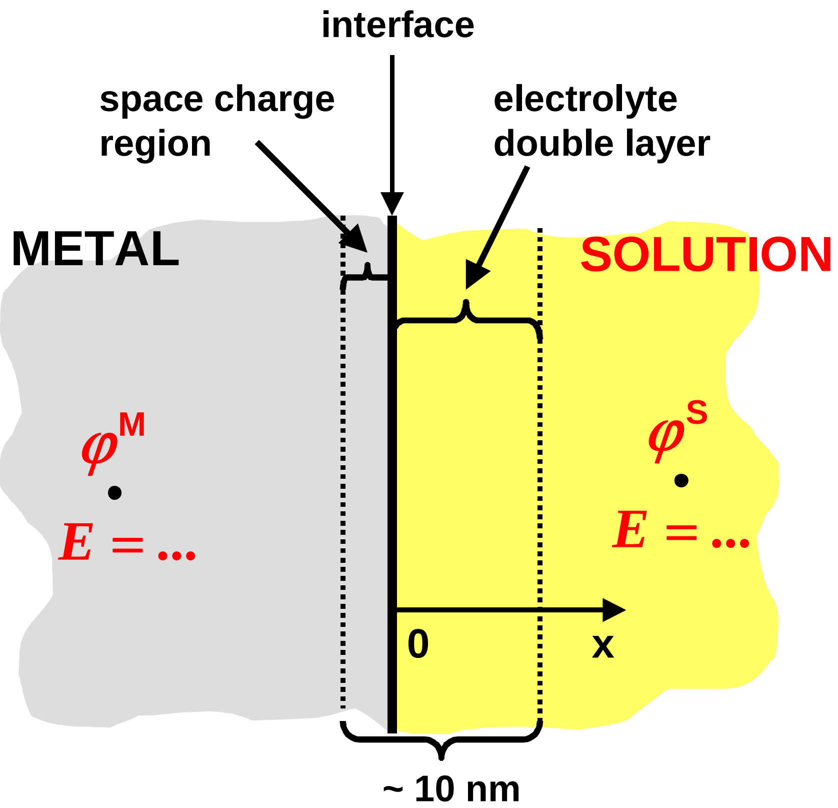
Remember:



Here: external electric potential between the considered metal|electrolyte interface and a counterelectrode can be applied (see previous topic: electrochemical cell and EMF).

Whenever two dissimilar phases are in direct contact with each other, forces become active:

- **Short-range forces (chemical forces, dispersion forces)**
- **Long-range forces (electrostatic interactions)**



Structure? – EXPERIMENTS, MODELS!

Far away from interface

- uniform phases
- bulk potentials, φ^{M}, φ^{S}

Close to interface

- Excess charge on metal surface, σ^{M} → internal electric field at metal|electrolyte interface
- Complex ion distribution in electrolyte, $\rho(x)$ → potential distribution, $\varphi(x)$, non-uniform!
- How to control σ^{M}?

Surface potential corresponding to σ^M causes

- formation of so-called “Electric Double Layer” (EDL) (counter-ions attracted, co-ions repulsed)
- adsorption of ions (physi- and chemisorption)
- metal deposition
- solvent adsorption – ordered arrangement
- charge transfer (difference in electron energies)

Experimental techniques in surface electrochemistry:

- Traditional:
  - cyclic voltammetry
  - impedance spectroscopy
  - step- and pulse techniques
  - electrocapillary measurements

  no spatial resolution of structures and processes, indirect information
- Modern techniques:
  - spectroscopy (IR reflection, X-ray diffraction and absorption, second harmonic generation)
  - microscopy (e.g. scanning tunneling microscopy)

  structure and processes at molecular/atomistic resolution

We will see some characteristic experimental data for the capacitance at the interface. Employing some ideas about the distributions of ions in solution will help to rationalize these data and understand in more detail the nature of the interfacial region.

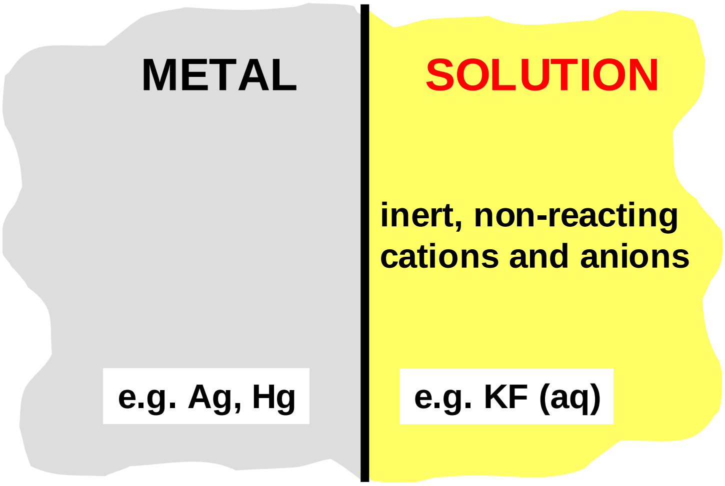
In summary (more precise definition of electrochemistry):

In any electrochemical experiment one applies a potential to the electrode and measures the electronic charge flowing to the electrode surface. This charge generates an electric field that drives fluxes of ions and dipolar molecules to and across the interface. We want to understand in more detail the effects of this electric field.

We start first with the purely electrostatic effects. Later on, we will consider specific adsorption and charge transfer processes.

For the studies of the pure electrostatic effects (i.e. no specific adsorption, no charge transfer for the time being), we need suitable model systems. These are called...

Ideally polarizable electrodes



No electrochemical reactions

(no charge transfer).

Potential range:

no decomposition of solvent

(i.e. for aqueous solution

$E > E_{\text{hydrogen evolution}}$

$E < E_{\text{oxygen evolution}}$

no oxidation or corrosion).

Double layer of equal and opposite charges at the interface:

$$Q^{\mathrm{M}} = -Q^{\mathrm{S}} \quad \text{(electroneutrality!)}$$

Potential drop at interface:

$$E = \Delta_{\mathrm{S}}^{\mathrm{M}}\varphi = \varphi^{\mathrm{M}} - \varphi^{\mathrm{S}}$$

Difference in Galvani potentials between bulk of metal and bulk of solution – controlled in experiment!

Electric fields:

$$\delta \approx 10\ \mathrm{nm} \Rightarrow \Delta_{\mathrm{S}}^{\mathrm{M}}\varphi / \delta \approx 10^{7}\ \mathrm{V\ cm^{-1}}$$

Assumptions for this part:

- No specific adsorption at interface
- Solvent is treated as a medium with a certain dielectric constant, but the molecular nature is ignored

General definition of double layer capacity:

applied potential E

↓

charge accumulation σ^{M}

↓

double layer capacity C_{diff}

Proportionality constant between accumulated charge, σ^{M}, and applied potential, E:

double layer capacity C_{d}.

Usually, we consider the differential double layer capacity:

$$C_{diff} = \left(\frac{\partial \sigma^{M}}{\partial E} \right)$$

What is going on at the interface?

- **Excess charge on metal tightly packed against interface**
- **Excess charge on electrolyte side**
  - **electrostatic interaction of ions with metal surface**
  - **ion-ion interactions**
  - **thermal motion of ions**

We would like to know potential distribution, $\varphi(x)$, and distribution of ions in the interfacial region, which could not be measured by any means! We need appropriate models and theoretical concepts and correlate them with experimental data.

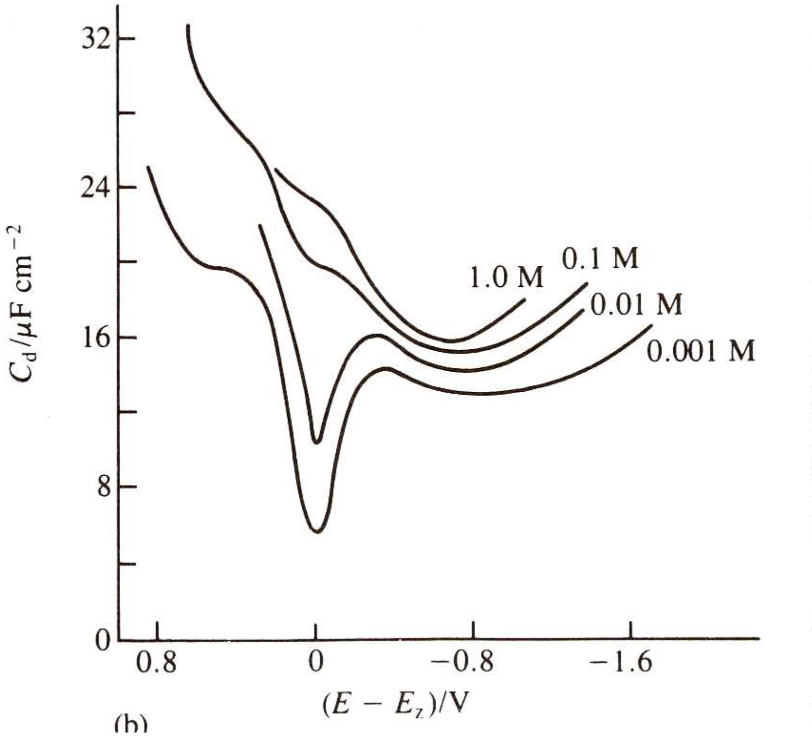
Typical experimental data:

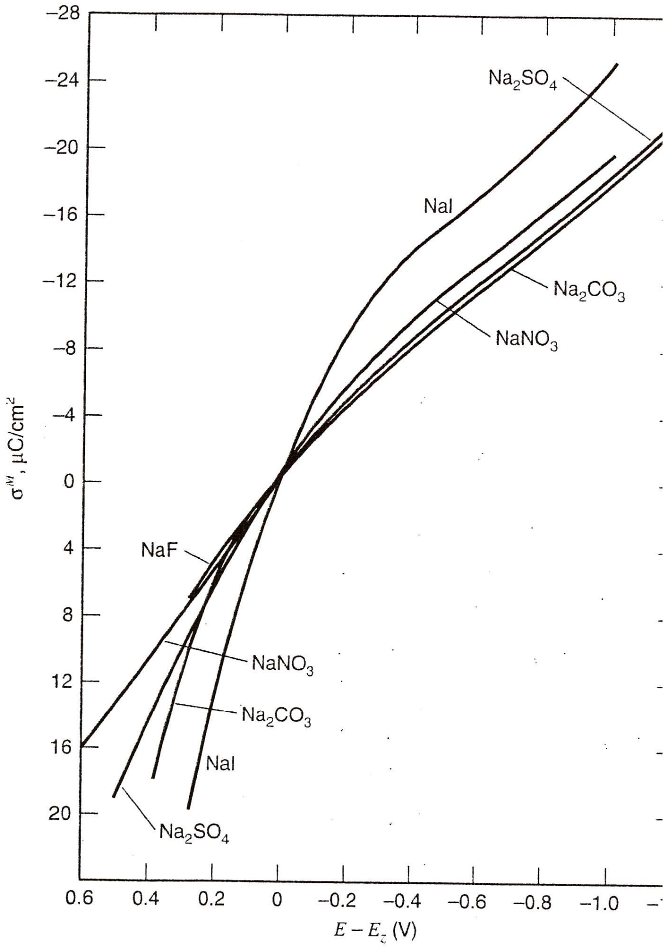
Differential capacity of various electrolytes at ideally polarizable Hg (liquid) electrode, D.C. Grahame, Chem. Rev. 41, 441, 1947.

Method (electrocapillary measurements) described in Appendix.

Left figure: variation of differential capacity with E and electrolyte concentration (NaF).

Right figure: charge density on the electrode for 1 M solutions of the indicated electrolytes (axes labels: E increases from right to left, σ^M from top to bottom!)





Problem: explain typical values and shape of curves (minimum at E_{pzc})

Potential of zero charge (pzc, definition):

At the potential of zero charge, $E = E_{\text{pzc}}$, no excess charge accumulates on the metal surface:

$$E = E_{\text{pzc}} \Leftrightarrow Q^{\text{M}} = 0 \text{, i.e. } \sigma^{\text{M}} = 0$$

This value of potential corresponds to the minimum of DL capacity.

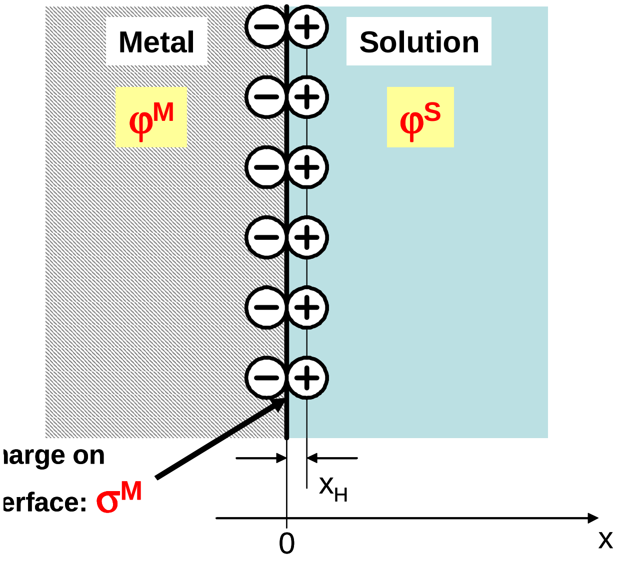
The pzc is a characteristic property of a given metal.

$$E > E_{\text{pzc}} \Rightarrow Q^{\text{M}} > 0 \quad \text{and} \quad E < E_{\text{pzc}} \Rightarrow Q^{\text{M}} < 0$$

Example: for Hg $E_{\text{pzc}} = -0.2$ V (vs. SHE)

What do the data reveal about the structure of the interfacial region? – let's explore the pertinent models

Helmholtz Model (1879)



- Simplest model of double layer
- Preceded discovery of electrons
- Purely phenomenological

(i.e. not based on fundamental understanding, but suitable to reproduce important experimental findings)

Assumptions:

- **Rigid ordering** of positive and negative charges
- Metal charges, σ^M, localized directly on interface, at $x = 0$
- Opposite charges in solution, $\sigma^S = -\sigma^M$, fixed at plane

  $x = x_H$

  → this is the so-called Helmholtz-plane, corresponding to distance of closest approach of ions to interface

  → given by radius of ions, including solvation shells.

Exploit analogy with parallel-plate capacitor:

The Helmholtz double layer capacity (per unit surface area)

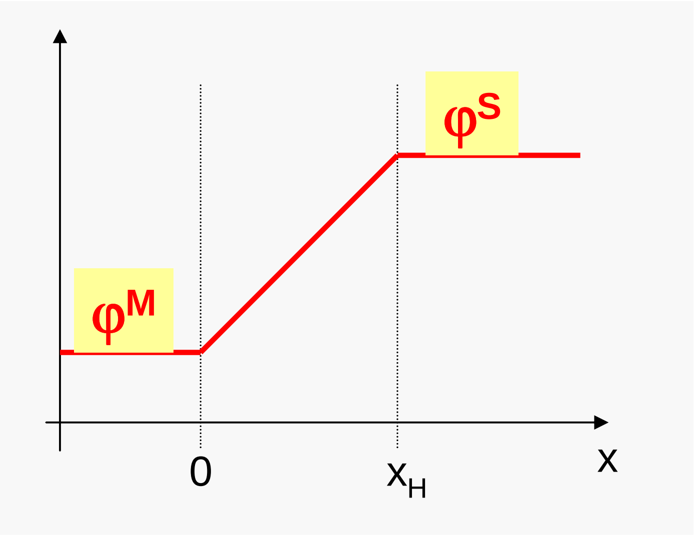
$$C_{D,H} = \frac{\varepsilon\varepsilon_0}{x_H}, \quad \sigma^M = \frac{\varepsilon\varepsilon_0}{x_H}\left(E - E_{pzc}\right)$$

- direct proportionality between σ^M and E
- capacity is independent of E and of ion concentration

Example: ε_r □ 6-7 (oriented water dipoles, not fully polarizable), x_H = 5-10 Å

$$C_{D,H} \approx 10\ \mu F\ cm^{-2}$$

Helmholtz model has discrete charge distribution □



potential distribution in interfacial region: linear, i.e. constant electric field, between x = 0 and x = x_H

Comparison with experiment: magnitude of capacity is OK, but experimental values vary with *E* and ion concentration

□ need a better model!