Electric double layer: Not this way!

Let’s have NaCl between electrodes (plates). Elst. intensity = \( \varepsilon \), Ions do not interact with the plates.
Concept of Na+ a Cl- between the plates?

**Naive solution:**
- Elst. potential = \( \phi(x) = -\xi \)
- cation pot. energy = \( \phi_+ \)
- \( \phi(H^+) \) = cation pot. energy
- \( \phi_+ = -e\xi \)
- anion pot. energy = \( \phi_- = e\xi \)
- \( \phi_+ = -e\xi \)

**Example:** 0.1 M \( \text{NaCl} \), plate distance = 50 nm, voltage = 50 mV
- Neutral (zero potential) in the middle
- \( \phi = \frac{1}{2} eV = 96.485 \text{ J/mol} \)

### Diffuse layer: Gouy-Chapman

| 1:1 salt (NaCl) at concentration \( c \) |
| electric pot. \( \phi \) far away is \( \phi(\infty) = 0 \) |
| electric pot. at the electrode is \( \phi_0 \) (now do not care about its origin) |
| ions = charged points, electrode = hard wall |
| no interaction/adsorption of ions at the electrode |
| ion concentrations replaced by an averaged charge density (no ion-ion correlation) |
| solvent is a dielectric continuum (permittivity = \( \varepsilon = \varepsilon_{\infty} \)) |

Poison equation: \( \frac{\partial^2 \phi}{\partial x^2} = \frac{\rho}{\varepsilon} \)

**Charge density:** \( \rho = \sum \rho_i \rho_+ - \rho_- \), where

\[ \rho_+ = e \exp \left( \frac{\phi(x)}{k_B T} \right) \]
\[ \rho_- = -e \exp \left( \frac{\phi(x)}{k_B T} \right) \]

**Poison–Boltzmann equation for the potential:**

\[ \frac{d^2 \phi}{dx^2} = \frac{\rho}{\varepsilon} \left( e\phi/k_B T - e\phi/k_B T \right) \]

### Diffuse layer: Gouy-Chapman

The Poison–Boltzmann equation:

\[ \frac{d^2 \phi}{dx^2} = \frac{\rho}{\varepsilon} \left( e\phi/k_B T - e\phi/k_B T \right) \]

Linearisation, or approximate solution for weak potentials (\( \phi/k_B T \ll 1 \), \( \xi = 0.26 \text{ mV} \) for 296 K):

\[ \exp(x) \approx 1 + x = \frac{d^2 \phi}{dx^2} = \frac{2e\xi}{k_B T} \phi \Rightarrow \phi = e\phi/k_B T \]

**Debye screening length**:

\[ \lambda = \left( k_B T \right)^{1/2} \]

**Example:** NaCl in water, \( c = 0.1 \text{ mol dm}^{-3} \), 25°C = \( \lambda = 0.96 \text{ nm} \)

**Bjerrum length (energy if a pair of univalent ions = \( k_B T \))**:

\[ \lambda_B = \frac{e^2}{4\pi k_B T} \]

**Example:** 

- \( \phi_0 = 50 \text{ mV} \)
- 0.05 V
- Poisson–Boltzmann eq.
- Linearized PB eq.
- \( \phi_0 = 100 \text{ mV} \)
- 0.1 V
- Linearized PB eq.
- Poisson–Boltzmann eq.

**The potential as a function of the distance from a charged surface**

**Decays exponentially as a consequence of screening (by counterions)**

**Called diffuse layer**, because can be explained by an equilibrium between diffusion and attraction to a charged surface.
### Debye–Hückel theory of electrolyte solutions

**Simplifications:**
- solvent = homogeneous dielectric continuum
- ions (several kinds of) = charged hard spheres of diameter \( \sigma \); other than electric interactions neglected
- distribution of ions described in terms of charged density (or probability of finding an ion); ion-ion correlations neglected
- it holds \( kT \ll kqT \) for ‘most ions’ — for 1:1 \( c < 0.1 \text{ mol dm}^{-3} \) needed
- for \( c > 1 \) even more dilute solutions needed

**Ionic strength**
\[
\mu = \frac{1}{2} \sum_i z_i^2 c_i
\]

the sum is over all ions in the solution

**Surface charge**
\[
\sigma = - \left[ \int_0^\infty (p_+ - p_-) \mathrm{d}x \right] - \left[ \int_0^\infty \sigma \right] \frac{1}{\kappa} \frac{\partial \phi}{\partial x} \mathrm{d}x
\]
Using the linearized theory, \( \phi(x) = 1 + \chi, \) because \( \phi(x)/kqT \ll 1 \)
\[
\sigma \approx 2 \kappa \phi(x) \frac{\chi}{\kappa} \mathrm{d}x = 2 \chi \kappa \rho \approx 2 \chi \kappa \rho = \frac{\varepsilon_0 \varepsilon}{k} \frac{\chi}{\kappa} \rho
\]

**Capacitance of the Gouy–Chapman double layer (as a capacitor):**
\[
C = \frac{\sigma}{\varepsilon_0 \varepsilon} = \frac{\phi(x)}{k} \frac{\chi}{\kappa} \rho
\]

**Strong electrolyte solution**

\[
\text{Al}_2(\text{SO}_4)_3 \rightarrow 2 \text{Al}^{3+} + 3 \text{SO}_4^{2-}
\]

In general:
\[
K_{\text{W}, \text{A}_2\text{Y}_3} = \frac{\nu_{\text{A}_2}^3 \nu_{\text{Y}_3}}{\nu_{\text{W}}^3}
\]

Electroneutrality (\( z_\oplus > 0, z_\ominus > 0 \)):
\[
\nu_{\text{A}_2}^3 \nu_{\text{Y}_3} = \nu_{\text{W}}^3
\]

Mean activity (\( \nu = \nu_{\oplus} + \nu_{\ominus} \))
\[
\nu_{\oplus} \Delta \mu_{\oplus} = \nu_{\ominus} \Delta \mu_{\ominus}
\]

\[
\text{Strong electrolyte solution}
\]

**Mean activity coefficient**
\[
\ln \gamma_{\text{Y}_2} = \frac{1}{2} \ln \frac{\nu_{\text{Y}_2}^3}{\nu_{\text{W}}^3} = \frac{1}{2} \ln \frac{\nu_{\text{Y}_2}^3}{\nu_{\text{W}}^3} - \frac{1}{2} \ln \left( \frac{\nu_{\text{Y}_2}^3}{\nu_{\text{W}}^3} \right)
\]

where \( A = 1.176 \text{ dm}^3/\text{mol} \cdot 1/2; a = 1 \text{ dm}^3/\text{mol} \cdot 1/2 \)

Test for \( \ominus \) NaCl:

**Activity coefficients of ions**

**Calculate:**
- mean activity coefficient of ions in \( \ominus \) CaCl\(_2\), \( c = 0.01 \text{ mol dm}^{-3} \)
- mean activity coefficient in \( \ominus \text{CH}_3\text{COOH}, c = 0.1 \text{ mol dm}^{-3} \), dissociation degree \( \alpha = 0.013 \)
- activity coefficient of protons in \( \ominus \text{H}_2\text{SO}_4, c = 0.01 \text{ mol dm}^{-3} \), ionized 100% to the 1st degree, 60% to the 2nd degree

**Solubility of an insoluble salt (e.g., BaSO\(_4\)).**
- drops in a \( \ominus \) containing one of the ions (e.g., Ba(NO\(_3\))\(_2\) or Na\(_2\)SO\(_4\))
- increases in presence of other (noninteracting) ions, because the activity coefficient of Ba\(^{2+}\) and SO\(_4^{2-}\) decrease

**Example.** The solubility product of barium sulfate is \( 1 \times 10^{-10} \). Calculate the solubility BaSO\(_4\) \( a \) in pure water, and \( b \) in 0.01 M \( \ominus \) of NaCl.

- may change due to pH change in case of hydrolysis (calcium oxalate in oxalic acid, calcium carbonate and carbon dioxide)