Instituto de Química

Double layer capacitance

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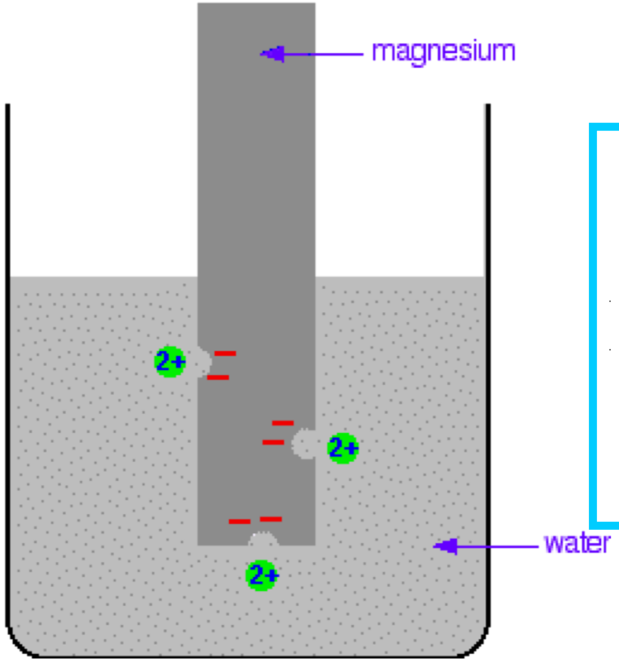
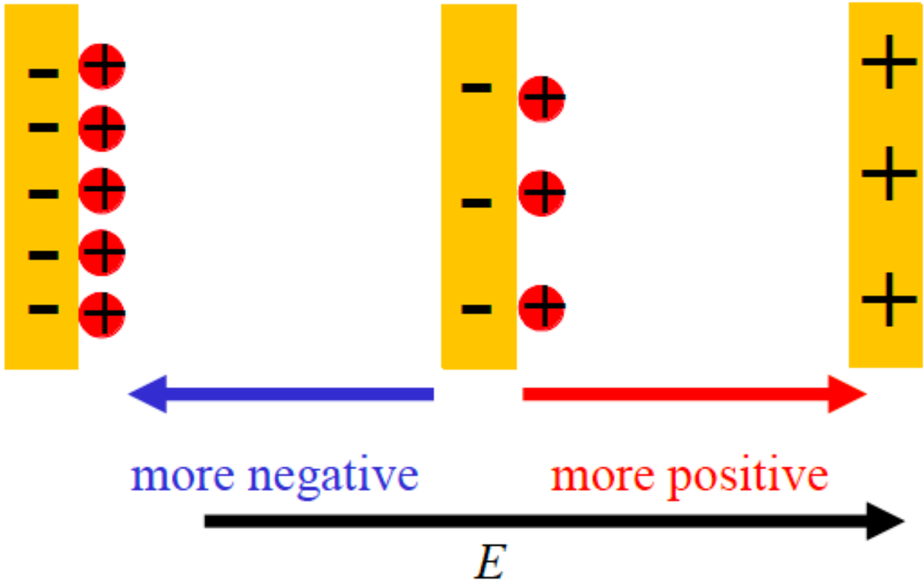
Origin of the Electrode potential



Can occur

$$\begin{cases} Mg^{2+}_{(aq)} + 2e^{-}_{metal} \rightarrow Mg \\ Mg \rightarrow Mg^{2+}_{(aq)} + 2e^{-}_{metal} \end{cases}$$

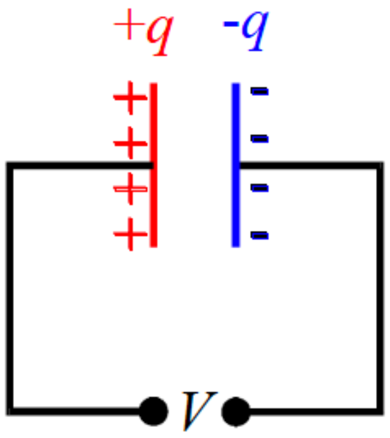
When you change the potential of the electrode you change the charge on the electrode and the distribution of ions in solution close to/at the electrode surface:

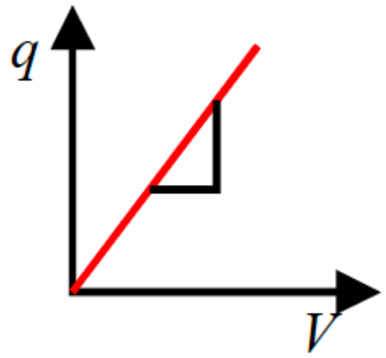


The electrode behaves as a capacitor

Capacitance

For a parallel capacitor





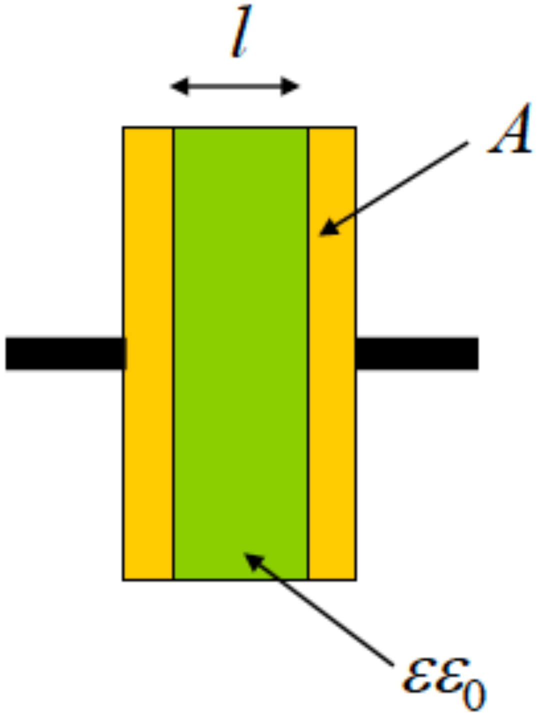
The differential capacitance is defined as:

$$\boxed{C = \frac{dq}{dE}}$$

q is the charge in C
E is the voltage in V
C is the capacitance in F

For a parallel capacitor

$$\boxed{C = \frac{\varepsilon\,\varepsilon_o\,A}{l}}$$



where:

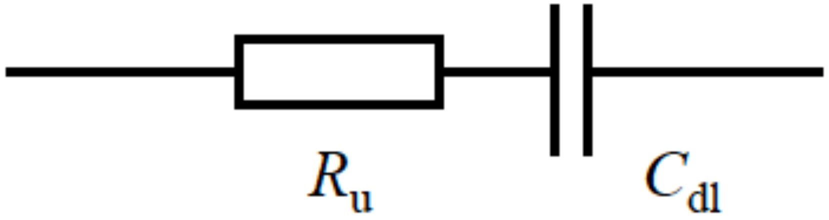
- ❖ ε is the relative permittivity (or dielectric constant) of the material between the plates,
- ❖ ε_o is the permittivity of vacuum (8.854 x 10^{-12} J^{-1} C^{-2} m^{-1}),
- ❖ *A* is the area of the plates
- ❖ *l* is the separation of the plates.

The electrode/electrolyte interface

The electrode/electrolyte interface behaves like a capacitor.

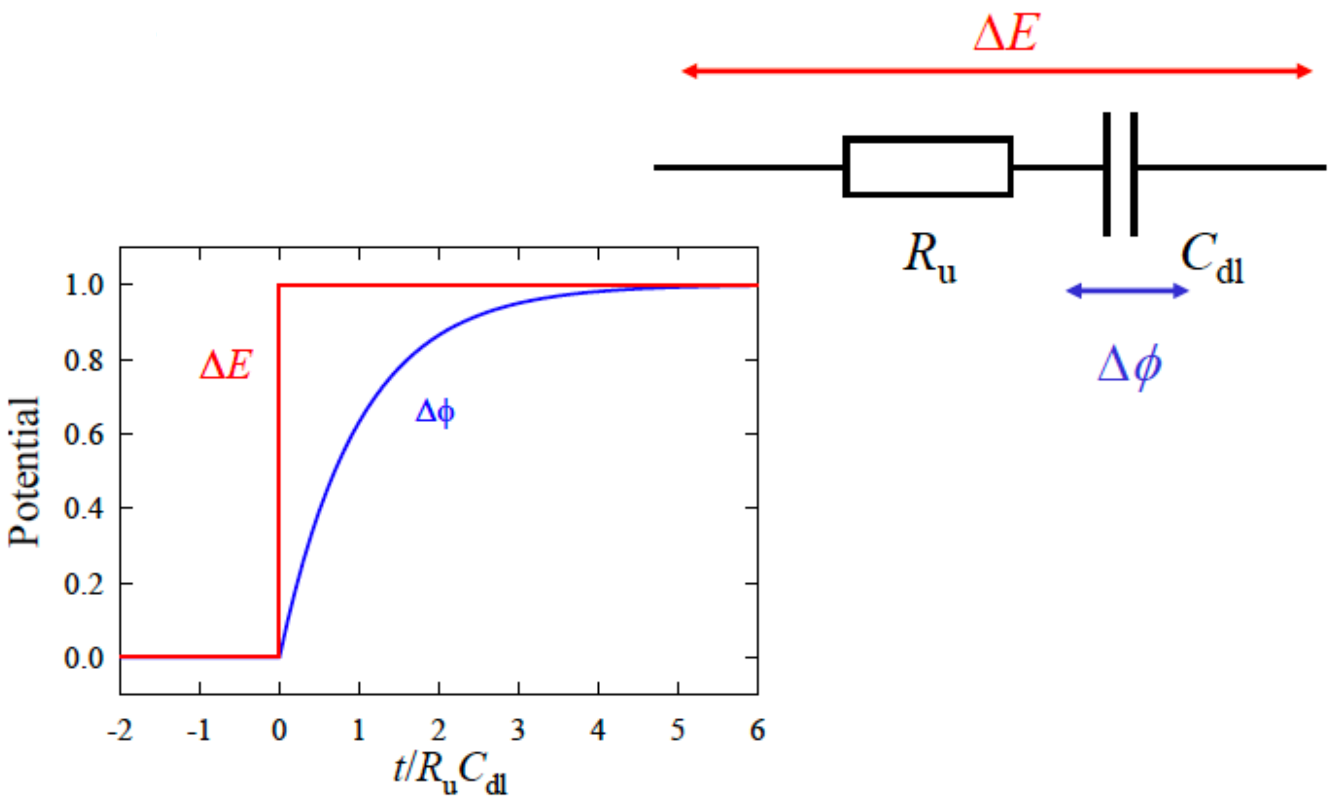
When the electrode potential is changed the amount of charge stored at the electrode/electrolyte interface changes; so, this leads to a charging current.

The simplest equivalent circuit is



Where R_u is the uncompensated solution resistance and C_{dl} is the double layer capacitance.

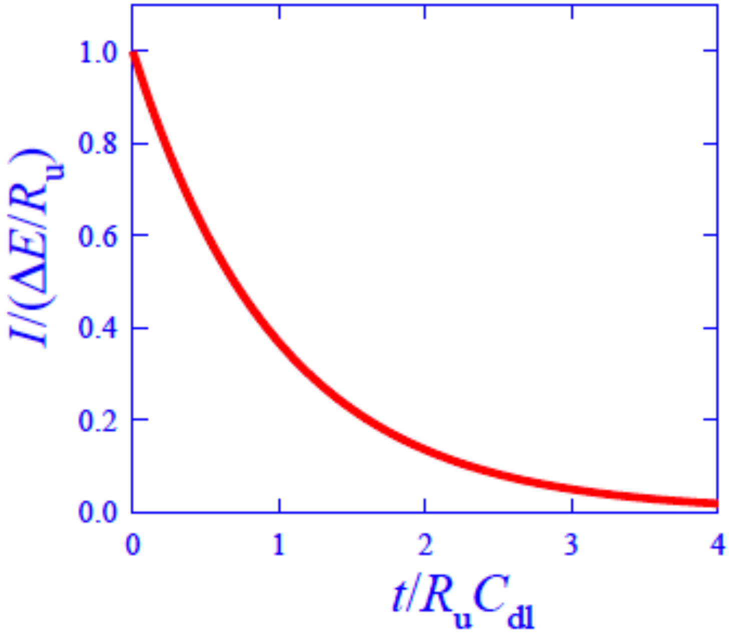
When the applied potential is changed instantaneously by an amount ΔE a transient current will flow through the $R_u C_{dl}$ circuit as the electrode/electrolyte interface is charged and as a result the potential across the electrode/electrolyte interface, $\Delta\phi$, changes exponentially until it reaches the new value.



A current must flow to charge the electrode/electrolyte interface when the applied potential changes. This double layer charging current (or non faradaic current) decays exponentially with the time.

This charging current is given by

$$I = \frac{\Delta E}{R_u} \exp\left(-\frac{t}{R_u C_{dl}} \right)$$

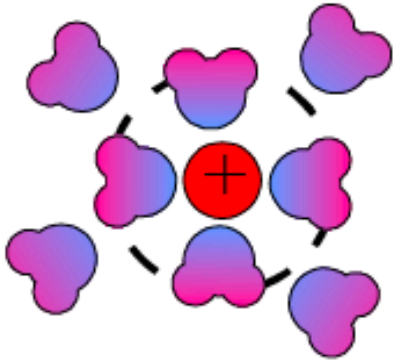


The RC circuit acts like a filter and the response time limits the short time response in chronoamperometry and the maximum sweep rate in cyclic voltammetry

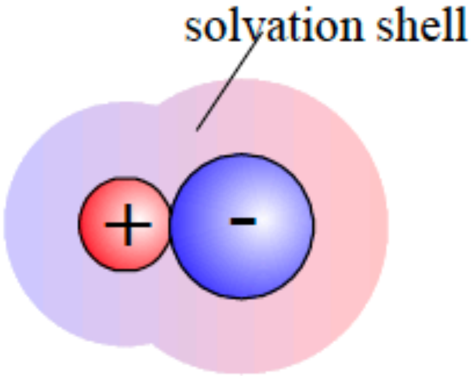
Models of the double layer

Models of the double layer have much in common with models for ions in solution and in many ways the electrode behaves like a “giant ion”.

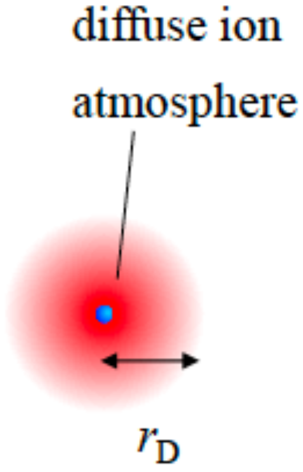
The importante interactions are:



solvation (ion-dipole interaction)



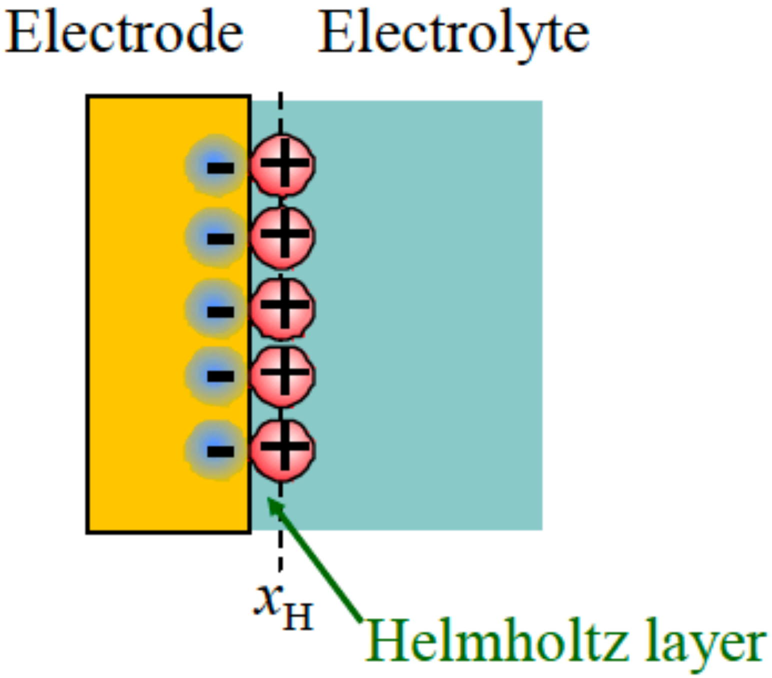
ion pairing

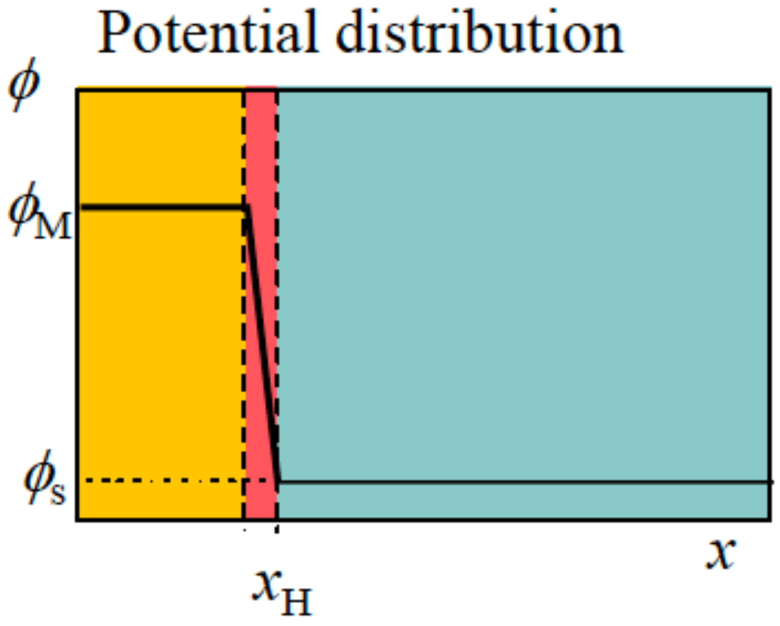


Debye Hückel

(not to scale!)

The Helmoltz model





The solvated ions form a layer at the electrode surface exactly balancing the charge on the electrode.

The capacitance, C_{dl}, of the electrode is independent of the potential, *E.*

Predictions of the Helmoltz model

All the potential is dropped in a very thin (one ion thick) layer at the electrode surface.

- High fields present - typically 106 V m^{-1}.
- The capacitance is independent of the electrode potential and her value is typically 20 μF cm^{-2}.

Gouy-Chapman Theory

Charge density ρ(x) is given by Poisson equation

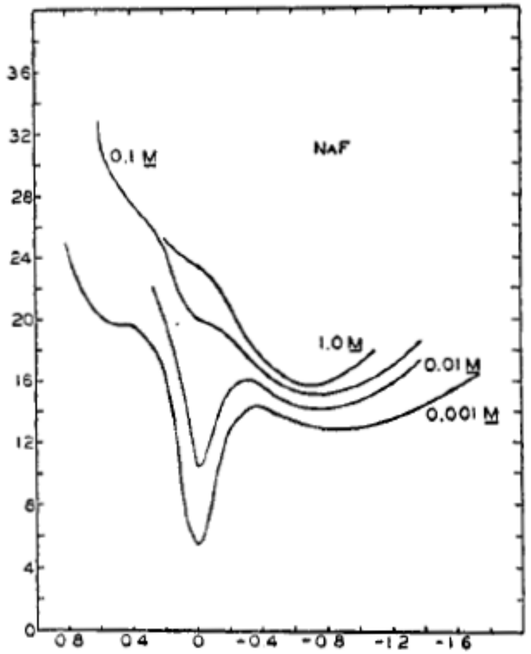
$$\rho(x) = -\varepsilon_r \varepsilon_0 \frac{d^2\phi}{dx^2}$$

Charge density of the solution is obtained summarizing over all species in the solution

$$\rho(x) = \sum_i z_i F c_i(x)$$

Ions are distributed in the solution obeying Boltzmann distribution

$$c_i(x) = c_i^b \exp\left(-\frac{z_i F \phi}{RT}\right)$$



D.C. Grahame, *Chem. Rev.* 41 (1947) 441

Gouy-Chapman Theory

Previous eqs can be combined to yield Poisson-Boltzmann eq

$$\frac{d^2\phi}{dx^2} = -\frac{F}{\varepsilon_r\varepsilon_0}\sum_i z_i c_i^b \exp\left(-\frac{z_i F\phi}{RT}\right)$$

The above eq is integrated using an auxiliary variable *p*

$$\frac{d\phi}{dx} = p \quad \Rightarrow \quad \frac{d^2\phi}{dx^2} = \frac{dp}{dx} = \frac{dp}{d\phi}\frac{d\phi}{dx} = p\frac{dp}{d\phi}$$

$$\int p\,dp = -\frac{F}{\varepsilon_r\varepsilon_0}\int\sum_i z_i c_i^b \exp\left(-\frac{z_i F\phi}{RT}\right)d\phi$$

$$\frac{1}{2}\left(\frac{d\phi}{dx}\right)^2 = \frac{RT}{\varepsilon_r\varepsilon_0}\sum_i c_i^b \exp\left(-\frac{z_i F\phi}{RT}\right) + B$$

Gouy-Chapman Theory

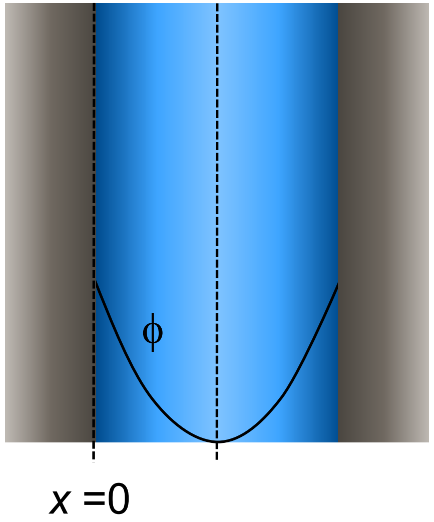
Integration constant B is determined using boundary conditions:

i) Symmetry requirement: electrostatic field must vanish at the midplane → $d\phi/dx = 0$

ii) electroneutrality: in the bulk charge density must summarize to zero → $\phi = 0$

Thus

$$\frac{1}{2}\left(\frac{d\phi}{dx}\right)^2 = \frac{RT}{\varepsilon_r \varepsilon_0}\sum_i c_i^b\left[\exp\left(-\frac{z_i F\phi}{RT}\right)-1\right]$$



Gouy-Chapman Theory

Now it is useful to examine a model system containing only a symmetrical electrolyte

$$\left(\frac{d\phi}{dx}\right)^2 = \frac{2RTc^b}{\varepsilon_r\varepsilon_0}\left(\exp\left(-\frac{zF\phi}{RT}\right)+\exp\left(\frac{zF\phi}{RT}\right)-2\right) = \frac{8RTc^b}{\varepsilon_r\varepsilon_0}\sinh^2\left(\frac{zF\phi}{2RT}\right)$$

$$\Rightarrow \quad \frac{d\phi}{dx} = -\left(\frac{8RTc^b}{\varepsilon_r\varepsilon_0}\right)^{1/2}\sinh\left(\frac{zF\phi}{2RT}\right)$$

The above eq is integrated giving

$$\frac{\tanh(zF\phi/4RT)}{\tanh(zF\phi_0/4RT)} = \exp(-\kappa x)$$

where

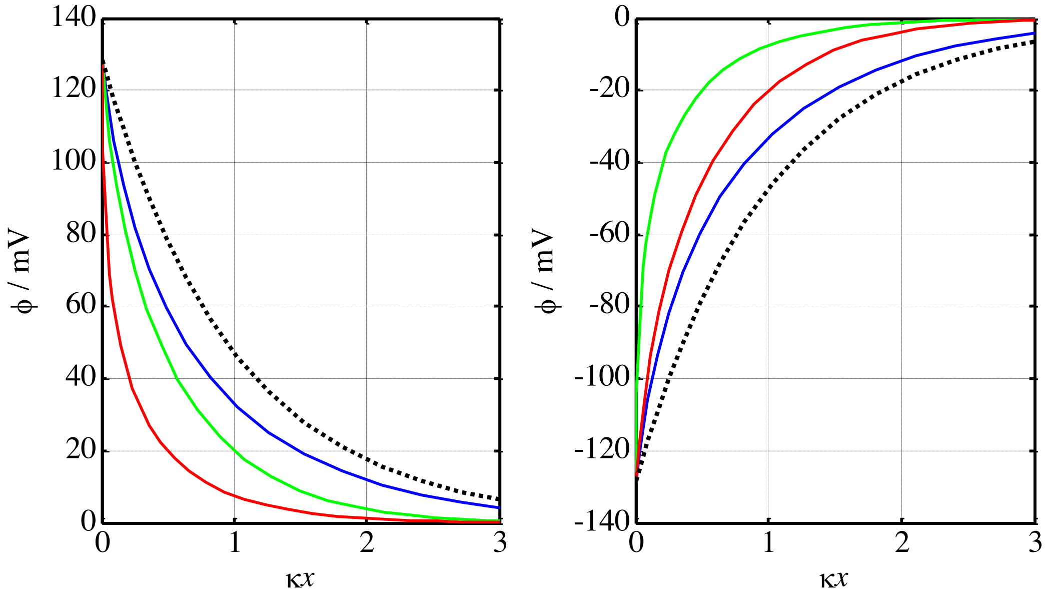
$$\kappa = \left(\frac{2c^b z^2 F^2}{\varepsilon_r\varepsilon_0 RT}\right)^{1/2}$$

potential on the electrode surface, x = 0

Gouy-Chapman Theory – Potential profile

The previous eq becomes more pictorial after linearization of tanh

$$\phi(x) = \phi_0 e^{-\kappa x}$$



$$\frac{1}{2}\left(\frac{d\phi}{dx}\right)^2 = \frac{RT}{\varepsilon_r\varepsilon_0}\sum_i c_i^b\left[\exp\left(-\frac{z_iF\phi}{RT}\right)-1\right]$$

1:1 electrolyte
2:1 electrolyte
1:2 electrolyte
linearized

Gouy-Chapman Theory – ion atmosphere

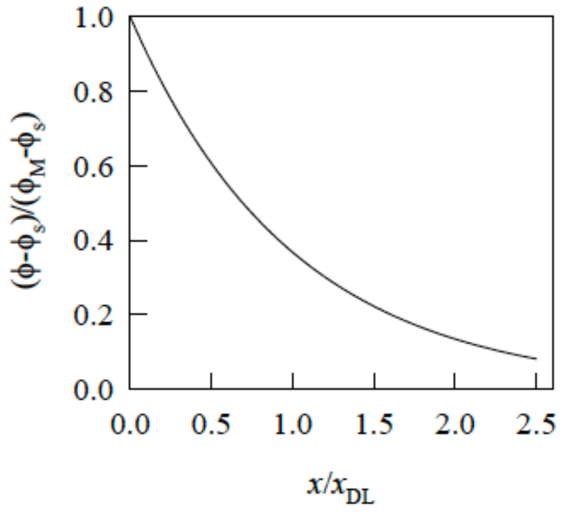
The extent of the ion atmosphere depends on the electrolyte concentration

$$x_{\mathrm{DL}} = \frac{1}{ze}\sqrt{\frac{\varepsilon\varepsilon_0 RT}{2c_\infty}}$$

c_∞ / mol dm^{-3}	10^{-4}	10^{-3}	10^{-2}	10^{-1}
x_{DL} / nm	30	10	3	1

Values for x_{DL} calculated for a 1:1 aqueous electrolyte solution at 298 K.

and the potential is dropped over about two multiples of *x*DL out into the solution.



Gouy-Chapman Theory – Surface charge

Electrical charge q inside a volume V is given by Gauss law

$$q = \varepsilon_r \varepsilon_0 \oint \mathbf{E} \cdot d\mathbf{S}$$

In a one dimensional case electric field strength ***E*** penetrating the surface ***S*** is zero and thus $\boldsymbol{E}\cdot d\boldsymbol{S}$ is zero except at the surface of the electrode ($x = 0$) where it is $(df/dx)_0 dS$. Cosequently, double layer charge density is

$$q = \varepsilon_r \varepsilon_0 \left(\frac{d\phi}{dx} \right)_0$$

After inserting eq (5.42) for a symmetric electrolyte in the above eq surface charge density of an electrode is

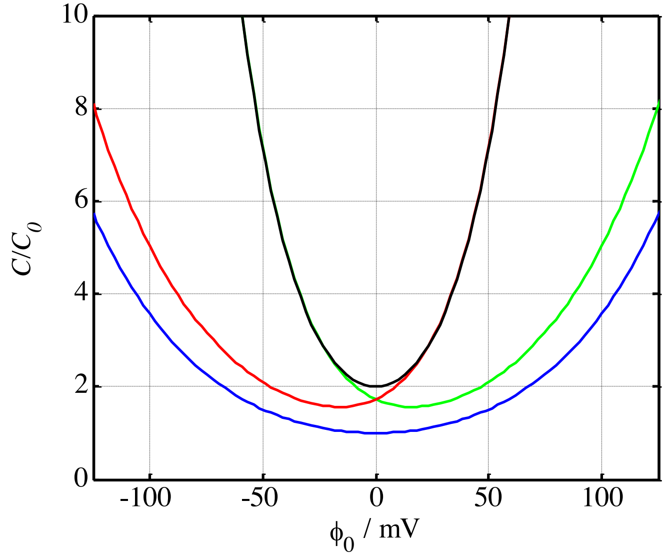
$$\sigma^m = -q = \left(8RTc^b \varepsilon_r \varepsilon_0 \right)^{1/2} \sinh\left(\frac{zF\phi_0}{2RT} \right)$$

Gouy-Chapman Theory – Double layer Capacitance

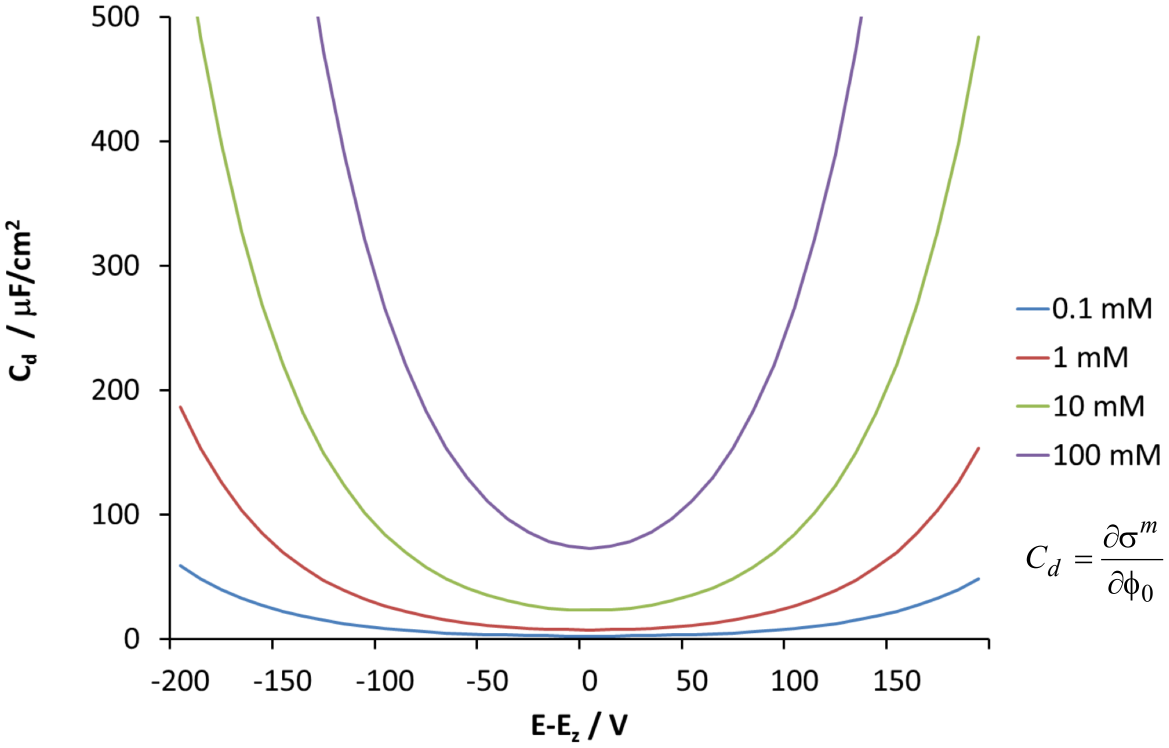
Capacitance of the diffusion layer is obtained by differentiating the surface charge eq

$$C_d = \frac{\partial \sigma^m}{\partial \phi_0} = \left(\frac{2c^b z^2 F^2 \varepsilon_r \varepsilon_0}{RT} \right)^{1/2} \cosh\left(\frac{zF\phi_0}{2RT} \right)$$

1:1 electrolyte
2:1 electrolyte
1:2 electrolyte
2:2 electrolyte

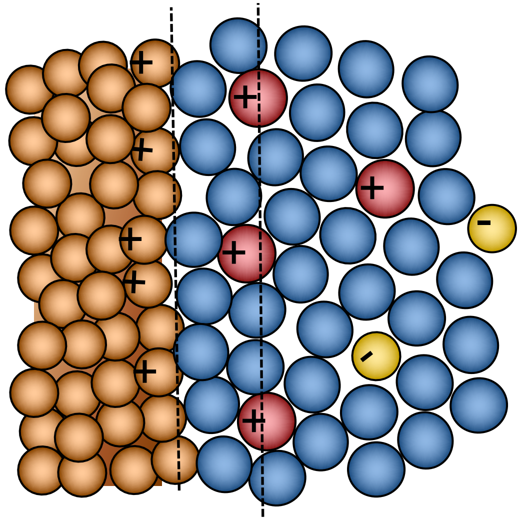


Gouy-Chapman Theory – Double layer Capacitance



$$C_d = \frac{\partial \sigma^m}{\partial \phi_0} = \left(\frac{2c^b z^2 F^2 \varepsilon_r \varepsilon_0}{RT}\right)^{1/2} \cosh\left(\frac{zF\phi_0}{2RT}\right)$$

Inner layer effect on the capacity

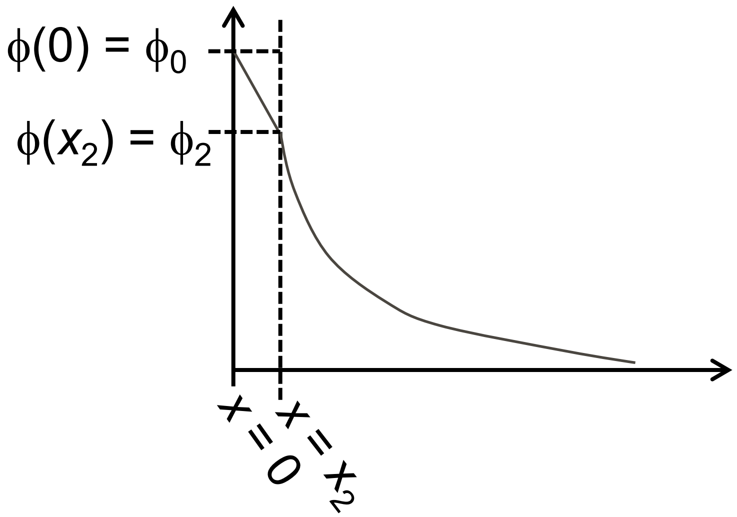


x = 0
ϕ_0

OHL
$x = x_2$
$\phi(x_2) = \phi_2$

If the charge density at the inner layer is zero potential profile in the inner layer is linear:

$$\left(\frac{\partial \phi}{\partial x}\right)_{\text{innerlayer}} = \frac{\phi_2 - \phi_0}{x_2}$$



Inner layer effect on the capacity

Surface charge density is obtained from the Gauss law

$$\sigma^m = -\varepsilon_r \varepsilon_0 \frac{\phi_2 - \phi_0}{x_2} = \left(8RTc^b \varepsilon_r^b \varepsilon_0\right)^{1/2} \sinh\left(\frac{zF\phi_2}{2RT}\right)$$

relative permeability in the inner layer

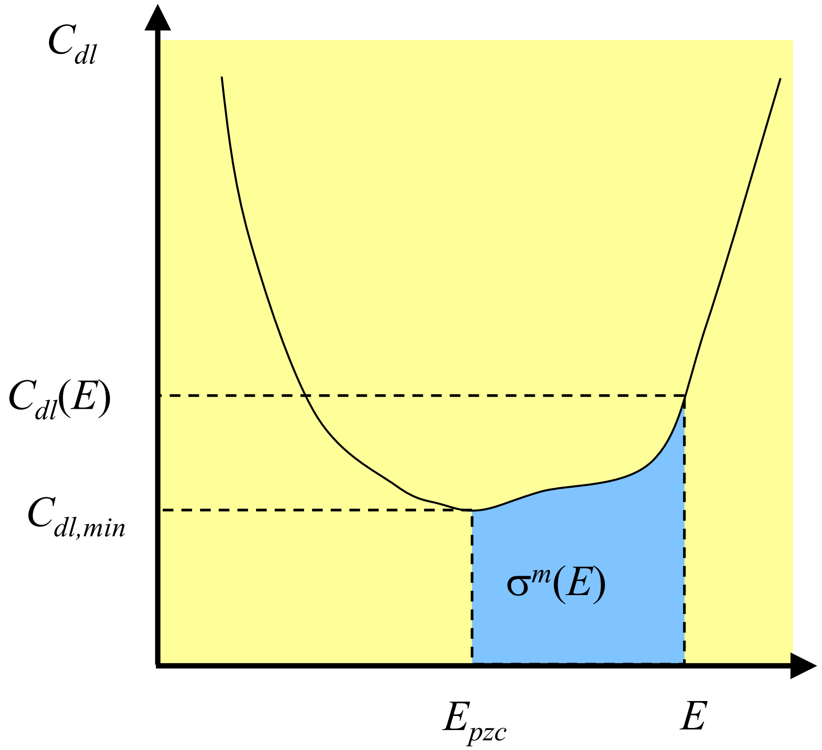
relative permeability in the bulk solution

ϕ_2 is solved from the left hand side eqs and inserted into the right hand side eq and C_{dl} is obtained after differentiating

$$\frac{1}{C_{dl}} = \left(\frac{\partial \sigma^m}{\partial \phi_0}\right)^{-1} = \frac{x_2}{\varepsilon_r \varepsilon_0} + \frac{1}{(2\varepsilon_r^b \varepsilon_0 z^2 F^2 c_b / RT)\cosh\left(zF\phi_2 / 2RT\right)} = \frac{1}{C_2} + \frac{1}{C_d}$$

Surface charge density

$$\sigma^m = \int_{E_{pzc}}^{E} C_{dl}\, dE$$



Effect of specific adsorption on the double layer capacitance

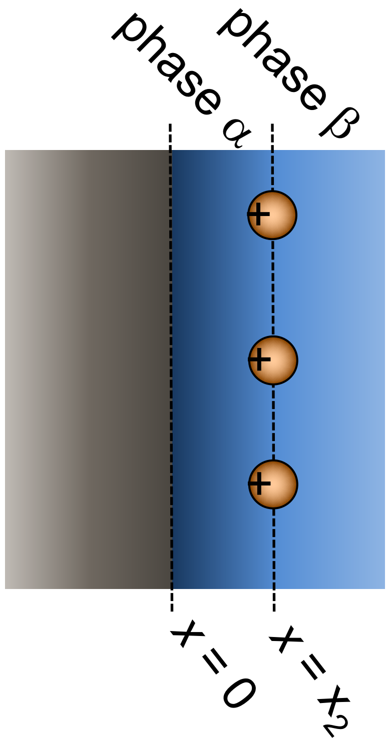
From electrostatistics, continuation of electric field, for $\alpha|\beta$ phase boundary

$$\varepsilon_r^{\alpha}\varepsilon_0\left(\frac{\partial\phi^{\alpha}}{\partial x}\right)-\varepsilon_r^{\beta}\varepsilon_0\left(\frac{\partial\phi^{\beta}}{\partial x}\right)=q'$$

Specific adsorbed species are described as point charges located at point x_2. Thus the inner layer is not charged and its potential profile is linear

$$\varepsilon_r\varepsilon_0\frac{\phi_2-\phi_0}{x_2}+\underbrace{\left(8RTc^b\varepsilon_r^b\varepsilon_0\right)^{1/2}\sinh\left(\frac{zF\phi_2}{2RT}\right)}_{q_d}=q'$$

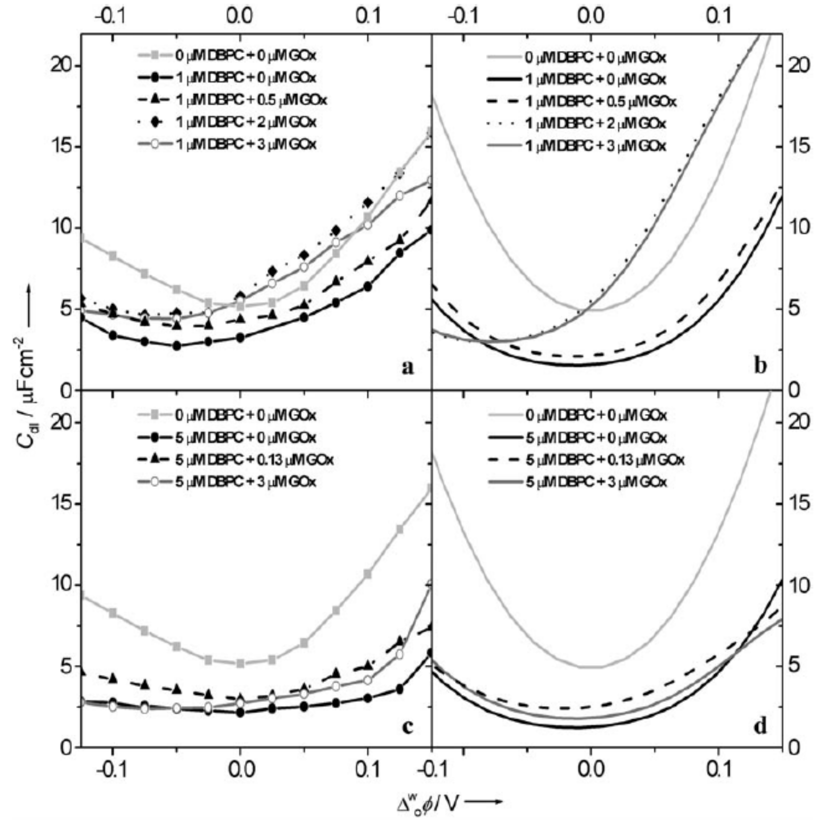
$$\Rightarrow\quad q_d+q'=\varepsilon_r\varepsilon_0\frac{\phi_2-\phi_0}{x_2}=-\sigma^m$$



Effect of specific adsorption on the double layer capacitance

So the total capacitance is

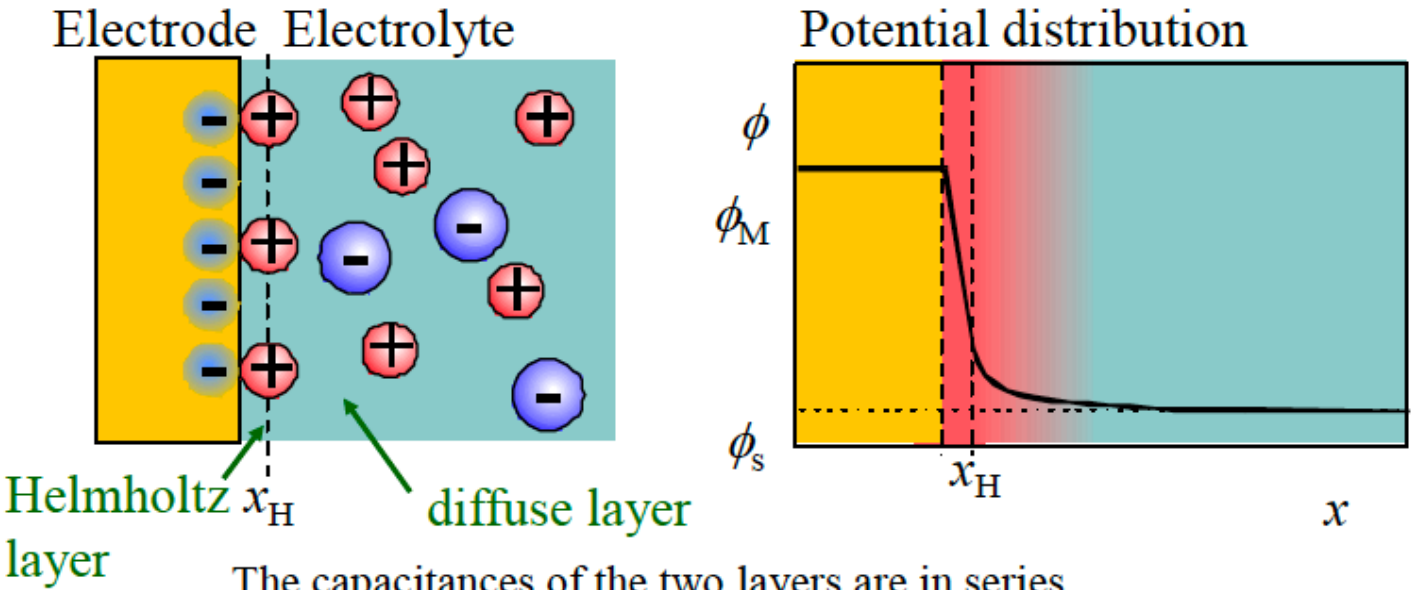
$$C_{dl}^{q'} = -\left(\frac{\partial q_d}{\partial \phi_0}\right) - \left(\frac{\partial q'}{\partial \phi_0}\right) = C_{dl} + C^{q'}$$



H. A. Santos *et al.*, ChemPhysChem8(2007)1540-1547

The Stern Model

The Helmholtz and Gouy-Chapman models are two extreme views. In reality a more realistic model for concentrated electrolyte solutions (e.g. 0.1 M) is a combination of the two in which most of the charge is balanced by ions in the Helmholtz layer and the Gouy-Chapmam diffuse layer makes up the rest.

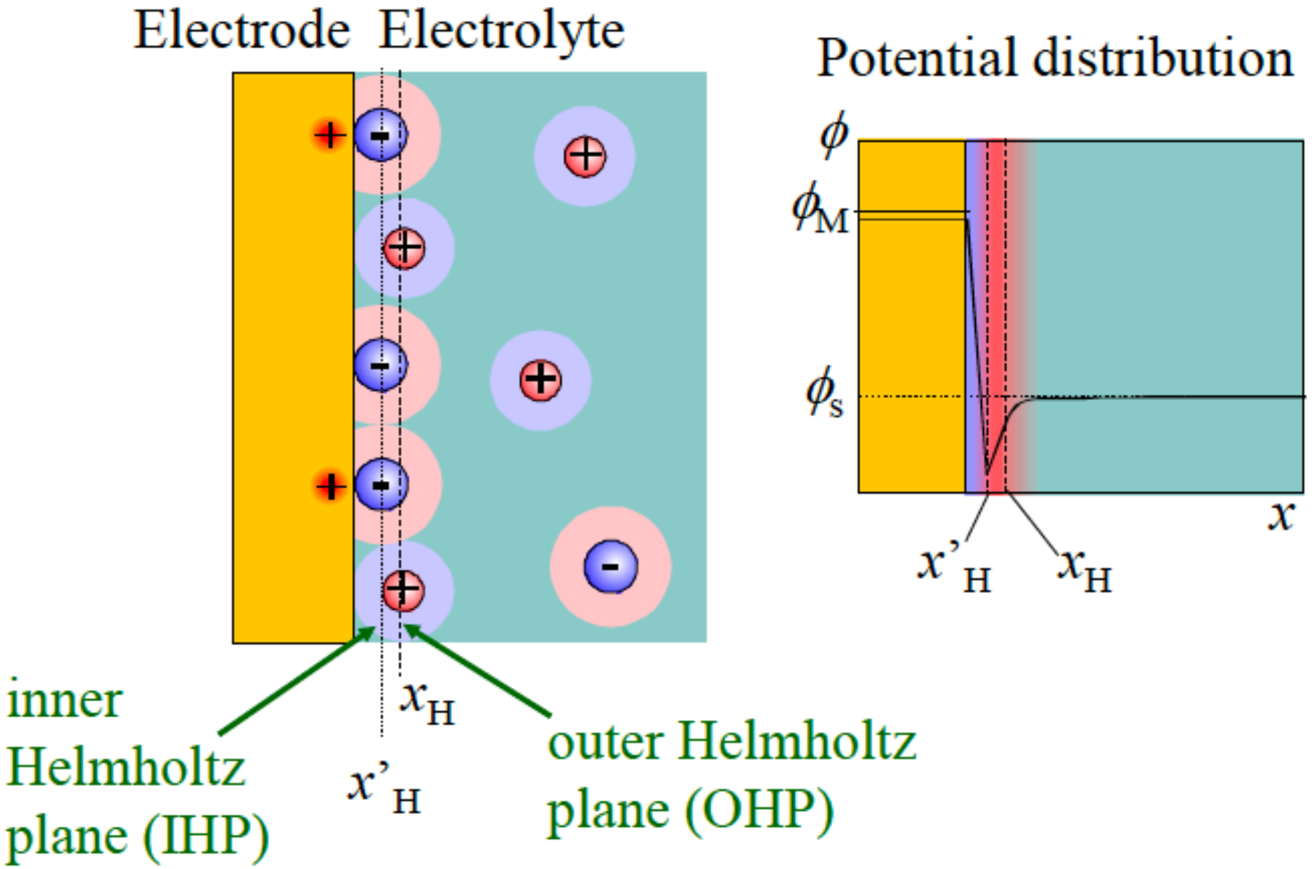


The capacitances of the two layers are in series

$$C_{dl}^{-1} = C_{Helmholtz}^{-1} + C_{diffuse}^{-1}$$

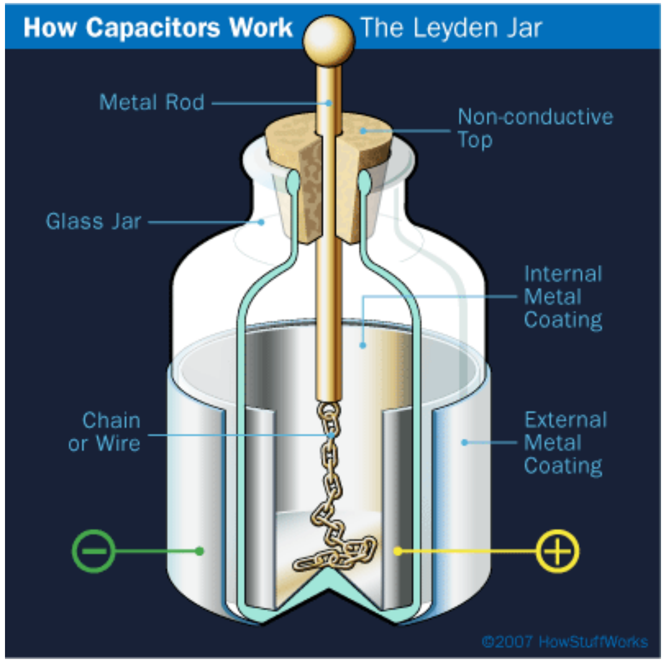
The Triple model

A final refinement is to recognise that the size and strength of solvation of the anions and cations will be different. Therefore there will be two sorts of adsorbed ions.



History of Capacitors

- In 1740, Ewald Georg von Kleist constructed the first capacitor.
- In the same year Pieter von Musschenboek invented the Leyden Jar.
- Ben Franklin soon found out a flat piece of glass can be used in place of the jar model



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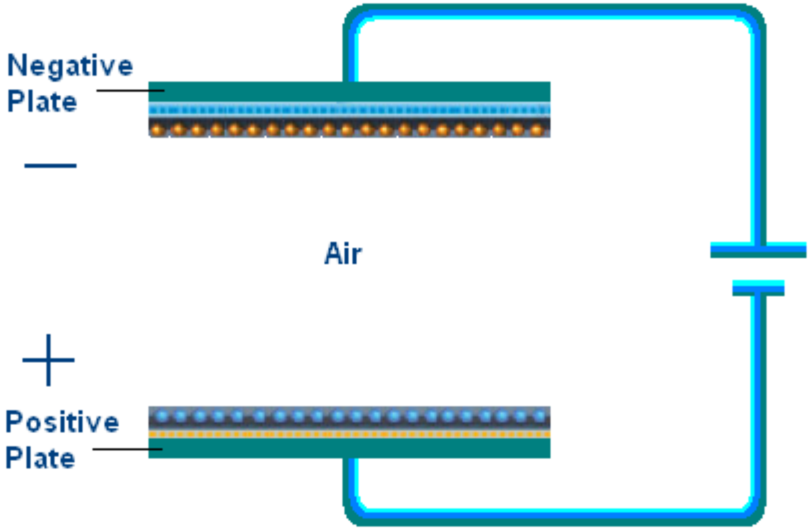
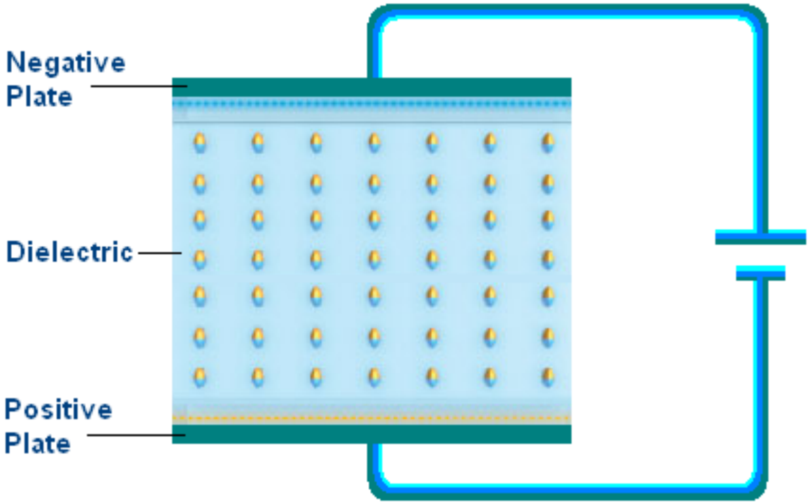
Electrolytic Capacitors

- Two parallel plates with dielectric in between
- Capacitance limited by flat surface area and dielectric properties

$$C = \epsilon_r \epsilon_0 \frac{A}{d}$$

  - *C* is the capacitance
  - *A* is the area
  - ε_r is the relative static permittivity (dielectric constant)
  - ε_0 is the permittivity of free space (8.854x10-12 F/m)
  - *d* is distance





History of Super Capacitors

- The Electric Double Layer Capacitor effect was first noticed in 1957 by General Electric.
- Standard Oil of Ohio re-discovered this effect in 1966.
- Standard Oil of Ohio gave the licensing to NEC, which in 1978 marketed the product as a “supercapacitor”.

Carbon Aerogel

- Aerogel is a low-density solid derived from gel that has had the liquid component replaced with a gas.

- Composed of nanometer sized particles covalently bonded together
- High porosity (>50% under 100 nm)
- Large surface area (400–1000 m²/g)

Activated Carbon:

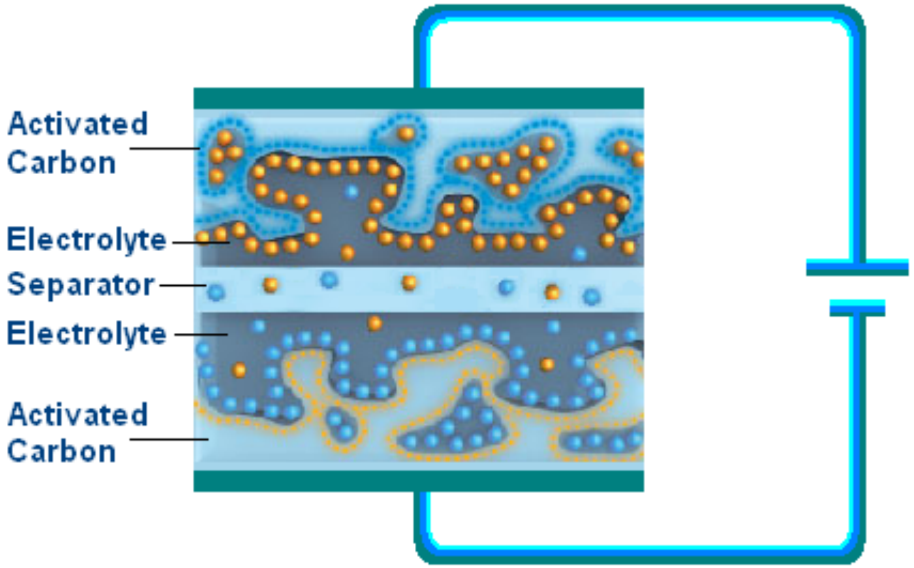
- Extremely porous with a very large surface area.
- Surface resembles a sponge.
- Area allows more electrons to be stored than other conductors.

Activated Carbon

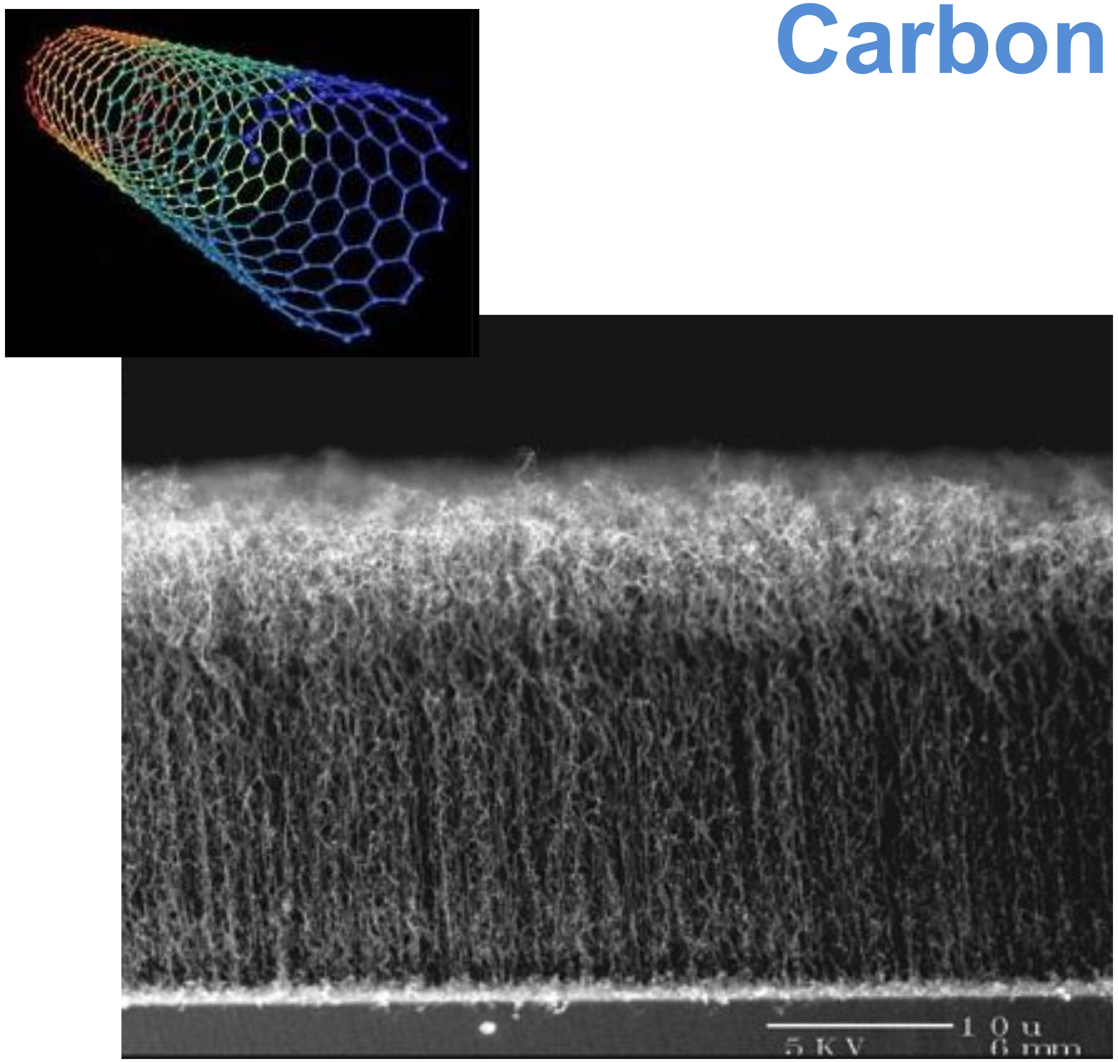
(Activated Charcoal)

Double Layer Electrolytic Capacitors Using Activated Carbon

- Two layers consisting of nanoporous electrodes
- Separator is impregnated with an organic electrolyte
- Thin separator can only withstand low voltages



Carbon Nanotubes



- Approximately 1/50,000th the width of a human hair
- Strongest and stiffest material on earth (>300 X Steal)
- Low density
- Semiconductor

Applications for Supercapacitors

- Back up for uninterruptable power supplies (UPS)
- Light weight power supplies for small aircraft
- Provide short duration power for various vehicle systems such as breaking or steering
- Used to absorb power during short periods of generation such as Regenerative Braking
- Extend range and battery life in Hybrid Electric Vehicles (HEV)