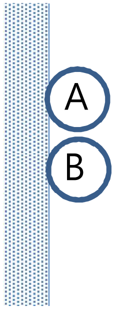
# Solid-Liquid Interface

- **Adsorption** from Solution



At lest 2 competing species

Ⓐ: solute molecules

Ⓑ: solvent molecules

Reaction:
A(solute in solution)+B(adsorbed solvent) $\rightleftharpoons$ A(adsorbed)+B(solution)

At equilibrium $$K = \frac{a_A^S a_B}{a_A a_B^S}$$

Dilute solution $$a_B \approx 1$$

Represent activities by concentration in solution, and mole fractions on surface

$$K = \frac{N_A^S}{N_B^S c_A}$$

If surface has fixed no of sites

$$N_A^S + N_B^S = 1$$

$$K = \frac{N_A^S}{(1 - N_A^S) C_A}$$

$$also \quad N_A^S = \frac{n_A^s}{n^s} = \theta$$

$n_A^s$ : *moles of A on surface*

$n^s$ : *moles of sites on surface*

$$\therefore \frac{\theta}{1-\theta} = KC_A$$

$$or \quad \theta = \frac{KC_A}{1 + KC_A} \quad : \; Langmuir\ Isotherm$$

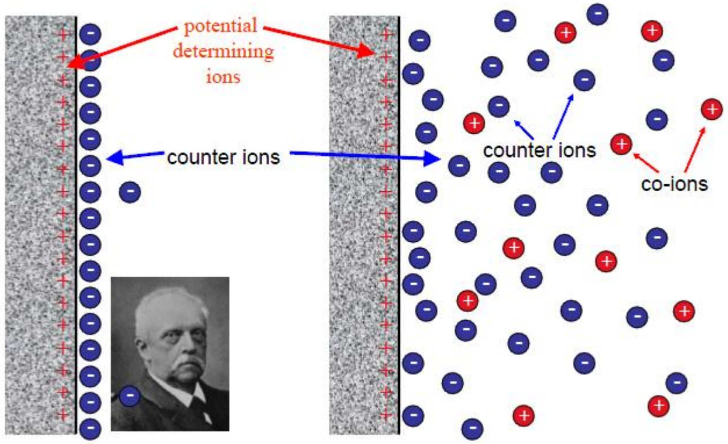
Can also derive BET equation: $C/C_0$ instead of $P/P_0$

$C_0$: saturation concentration, i.e., precipitation of solute at interface

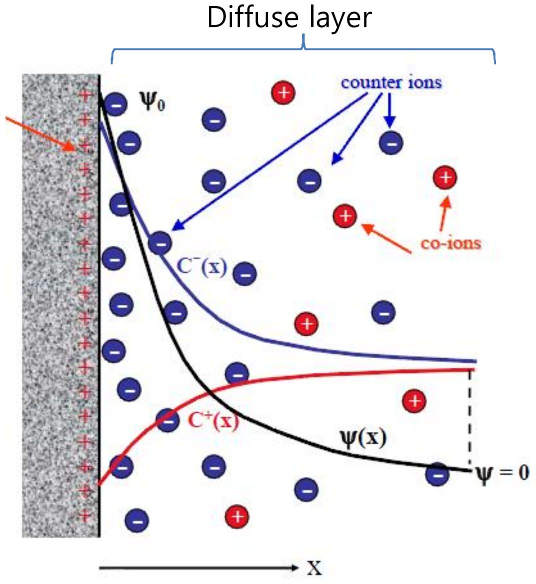
# Electrical Effects at Solid-Liquid Interface

- Charged surface : preferential adsorption of cations or anions

**Electrical double layer**



Helmholtz model (1879)　Gouy-Chapman model (1914)



# Basics of Electrochemistry

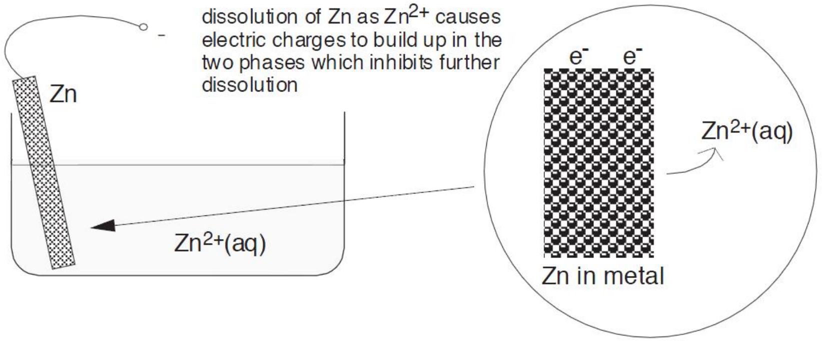


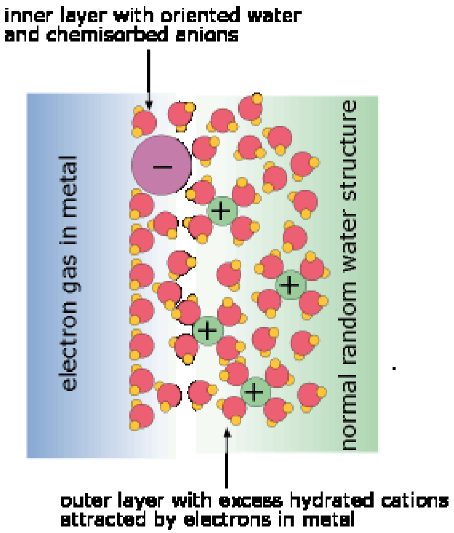
Figure 1: Oxidation of metallic zinc in contact with water

When we immerse a piece of zinc metal in pure water, a small number of zinc atoms go into solution as Zn2+ ions, leaving their electrons behind in the metal:

$$Zn(s) \rightarrow Zn^{2+} + 2e^-$$

As this process goes on, the electrons which remain in the zinc cause a negative charge to build up which makes it increasingly difficult for additional positive ions to leave the metallic phase. A similar buildup of positive charge in the liquid phase adds to this inhibition. Very soon, therefore, the process comes to a halt, resulting in a solution in which the concentration of $Zn^{2+}$ is so low (around $10^{-10}$ M) that the water can still be said to be almost "pure".

# Potential differences at interfaces



The transition region between two phases consists of a region of charge unbalance known as the *electric double layer.*

- inner monomolecular layer of adsorbed water molecules and ions,
- outer diffuse region that compensates for any local charge unbalance that gradually merges into the completely random arrangement of the bulk solution.

In the case of a metal immersed in pure water,

- polar water molecules adsorb to the surface and orient themselves so as to create two thin planes of positive and negative charge.

If the water contains dissolved ions,

- some of the larger (and more polarizable) anions will loosely bond (*chemisorb*) to the metal, creating a negative inner layer which is compensated by an excess of cations in the outer layer.

The slight unbalance in the electric charges of the electrode and the solution give potential differences between the two phase.
These potential differences can be related to the thermodynamics and kinetics of electrode reactions. *In particular, manipulation of the interfacial potential difference affords an important way of exerting external control on an electrode reaction.*

# Interfacial potential differences are not directly observable

- The usual way of measuring a potential difference between two points is to bring the two leads of a voltmeter into contact with them.
- It's simple enough to touch one lead of the meter to a metallic electrode, but there is no way you can connect the other lead to the solution side of the interfacial region without introducing a second electrode with its own interfacial potential, so you would be measuring the sum of *two* potential differences.
- Thus *single electrode potentials*, as they are commonly known, are not directly observable.

# Electrochemical Cells

We can easily measure a potential difference between two such electrodes immersed in a solution. The result will be the sum of the two electrode potentials.

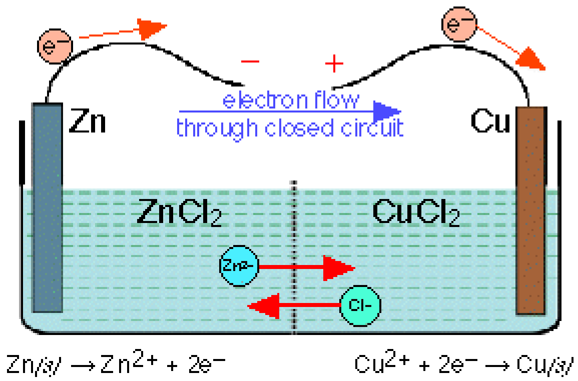


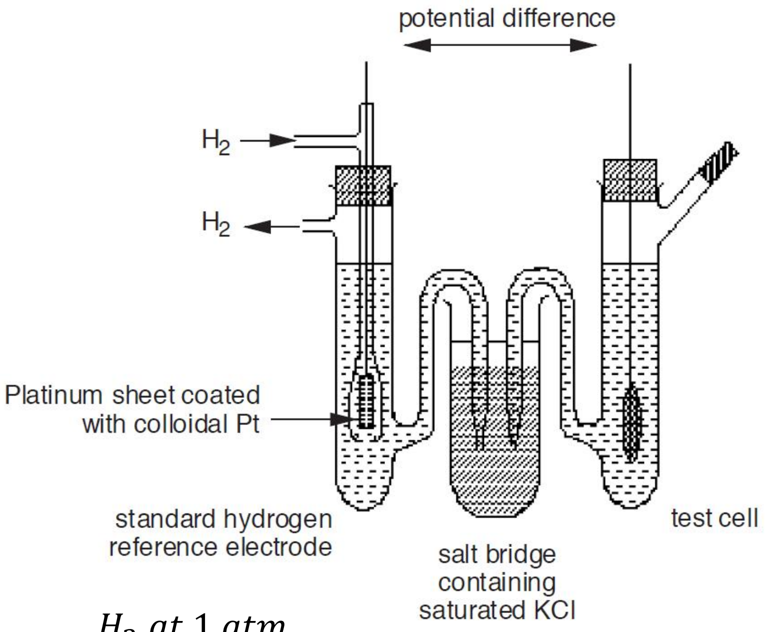
**Fig: A simple electrochemical cell**
The two compartments of this cell are separated by a porous barrier that allows ions to pass through while preventing gross mixing of the two solutions. When the two electrodes are connected, charges flow in the directions indicated. Note that the buildup of positive charge on the left side can be offset either by diffusion of $Zn^{2+}$ to the right or (less efficiently) by $Cl^{-}$ to the left.

anode: oxidation   cathode: reduction

$$\begin{aligned} E_{cell} = \Delta V &= E_{right} - E_{left} \\ &= V_{Cu} - V_{soln} + V_{soln} - V_{Zn} \end{aligned}$$

# Standard Half-cell Potentials

Measure the potential in relation to the potentials of other half cells. In particular, if we adopt a reference half-cell whose potential is arbitrarily defined as zero, and measure the potentials of various other electrode systems against this reference cell, we are in effect measuring the half-cell potentials on a scale that is relative to the potential of the reference cell.



$H_2$ at 1 atm,
$H^+$ at 1 molar

$$H_2(g) \rightarrow 2H^+ + 2e^-$$

$$\frac{Zn^{2+} + 2e^- \rightarrow Zn(s)}{Zn^{2+} + H_2(g) \rightarrow Zn(s) + 2H^+}$$

Chemical Work

$$\Delta G = \Delta G^0 + RT \frac{a_{Zn}^{2+} P_{H_2}}{a_{Zn} [H^+]^2} \quad a_{Zn} \approx 1$$

Electrical Work

$$= zF \cdot E$$

$z$: no. of charge
$F$: Faraday constant

At equilibrium $\Delta G + zF \cdot E = 0$

*For Zn system*

$$2F \cdot E = -\Delta G^0 - RT \ln a_{Zn}^{2+}$$

$$If\ components\ are\ in\ standard\ state\ [\,a_{Zn}^{2+}\,] = 1$$

$$2F \cdot E^0 = -\Delta G^0$$

$$E = E^0 - \frac{RT}{2F} \ln a_{Zn}^{2+}$$

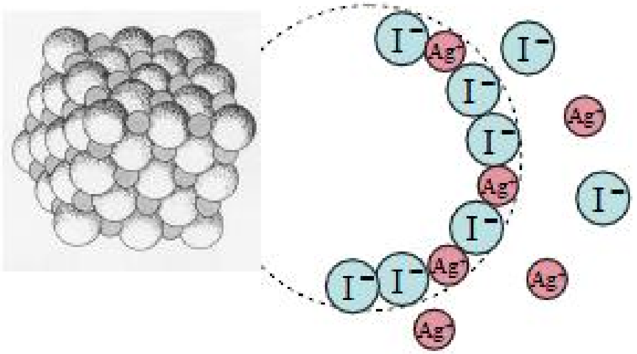
In general

$$E = E^0 - \frac{RT}{zF} \ln a_M^{z+} \quad : \quad Nernst\ Eq.$$

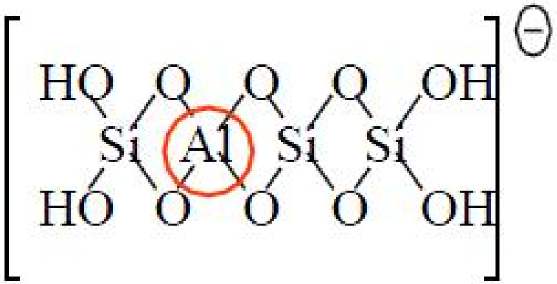
$M^{z+}$ : *some metal ion*

# Sources of interfacial charge at the solid/aqueous solution interface

(1) Differential ion solubility;
Some ionic crystals have a slight imbalance in number of lattice cations or anions on surface,
*eg*. AgI, $BaSO_4$, $CaF_2$, NaCl, KCl

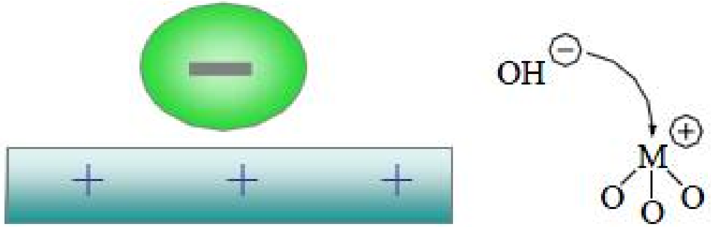


(2) Substitution of surface ions
*eg*. lattice substitution in kaolin

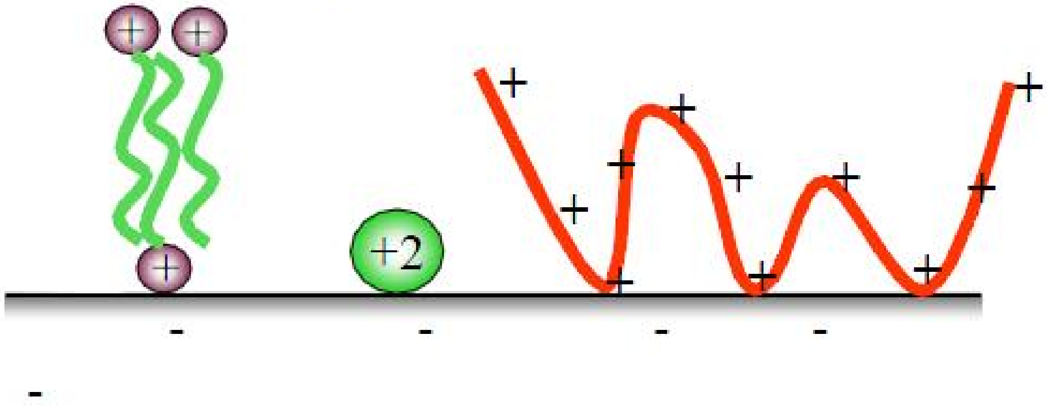


# Sources of interfacial charge
# at the solid/aqueous solution interface

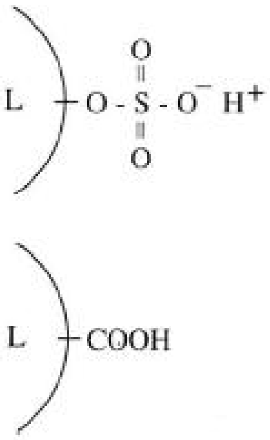
## (3) Specific ion adsorption



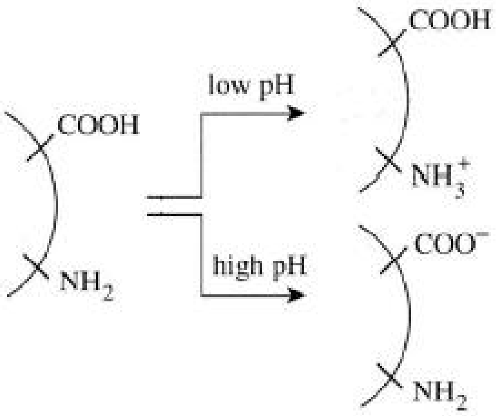
- $OH^-$ and $H^+$ ions
- multivalent ions: $Ca^{+2}$, $Mg^{+2}$, $La^{+3}$, $SO_4^{2-}$,
- ionic surfactants, polyelectrolytes



# 4) Ionization of surface groups, cont.



Strong acid sites (indep. of pH)
Weak acid sites (dep. on pH)

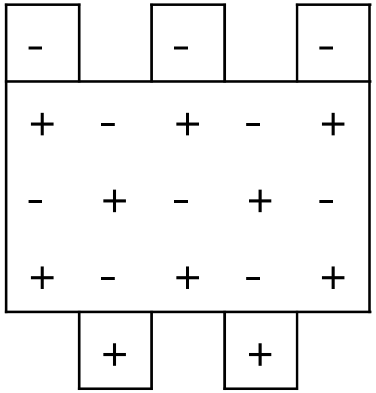


Mixed acid and basic sites;
(dependent on pH)

# Differential Ion Solubility

Excess $I^-$, - charge

eg. AgI



Excess $Ag^+$, + charge

solution
$Ag^+$, $I^-$

$$K_{sp} = [Ag^+][I^-] = 10^{-16}$$

$$Ag^+_{\text{soln}} \Leftrightarrow Ag^+_{surf}$$

$$\Delta G = \Delta G^0 + RT\ln\frac{a_{Ag^+surf}}{a_{Ag^+\text{soln}}} = -F\psi_0$$

$\psi_0$ = *potential difference across the* interface
(*surface potential*)

$a_{Ag^+surf} \approx 1$ *because* $Ag^+_{surf}$ *is a constituent of the solid*

Define a standard state as $a^{0}_{Ag^{+}}$ *when* $\Psi_{0} = 0$

- called the Point of Zero Charge (PZC)

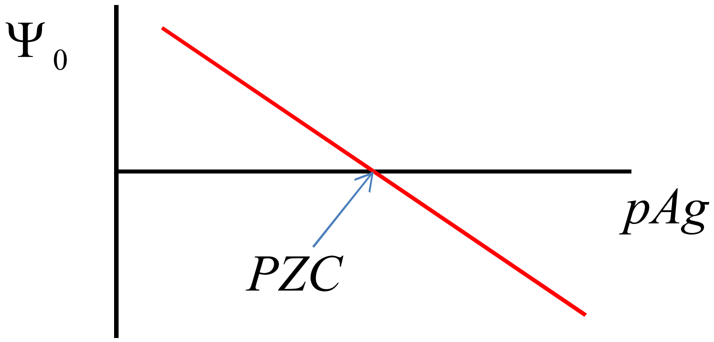
At the PZC $\Delta G^{0} = RT \ln a^{0}_{Ag^{+}\mathrm{soln}}$

$$\psi_{0} = \frac{RT}{F} \ln \frac{a_{Ag^{+}\mathrm{soln}}}{a^{0}_{Ag^{+}\mathrm{soln}}} : \quad \textit{potential fixed by solution composition}$$

$$a^{0}_{Ag^{+}\mathrm{soln}} = \textit{activity at PZC}$$

$$pAg = -\log a_{Ag^{+}}$$

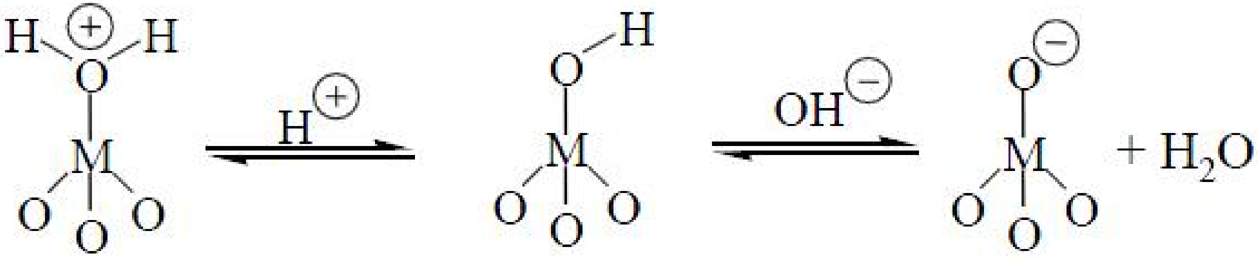
$$\psi_{0} = \frac{2.303RT}{F}(pAg^{0} - pAg)$$



Ag$^{+}$ and I$^{-}$ are called potential determining ions (PD ions) for AgI

$$pAg + pI = pK_{sp}$$

## (4) Direct Ionization of surface groups (oxide surfaces)



$MOH_2^+ \Leftrightarrow H^+ + MOH$
(+ charge)

Hydroxylation of surface

$MOH + OH^- \Leftrightarrow MO^- + H_2O$
(- charge)

(H$^+$ and OH$^-$ act like p.d. ions)

Reaction

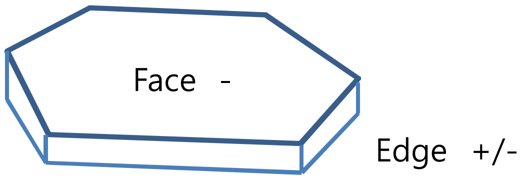
$H^+_{\mathrm{soln}} \Leftrightarrow H^+_{surf}$

$$\Delta G = \Delta G^0 + RT\ln\frac{a_{H^+surf}}{a_{H^+\mathrm{soln}}} = -F\psi_0$$

$if\ \ a_{H^+_{surf}} = 1$

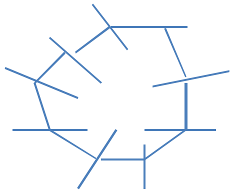
$$\psi_0 = \frac{2.303RT}{F}(pH^0 - pH)$$

# Clay Minerals

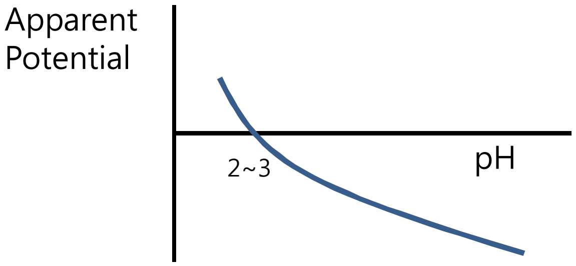


Two sources of change

- Face charge (fixed by substitution): always –
- Edge (like oxide surface): + at low pH, - at high pH



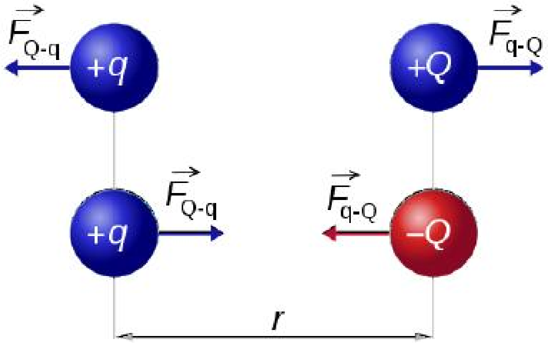
Card house structure



PZC edge appears to be ~pH7

# Coulomb's Law

$$F = \frac{1}{4\pi\epsilon_0}\frac{|q_1 q_2|}{r^2}$$



$\epsilon_0 \cong 9\times 10^{-12} C^2/(Nm^2)$ Permittivity of free space

$$\frac{1}{4\pi\epsilon_0} \cong 9\times 10^{9} Nm^2/C^2 \approx 10^{10} Nm^2/C^2$$

This formulation suggests ***instantaneous*** interaction ("*spooky action at a distance*" Einstein).
Thus, this law must be modified in electrodynamics .

- In the presence of dielectric medium

$$F = \frac{1}{4\pi\epsilon_0\varepsilon_r}\frac{|Q|}{r^2} = \frac{1}{4\pi\varepsilon}\frac{|Q|}{r^2}$$

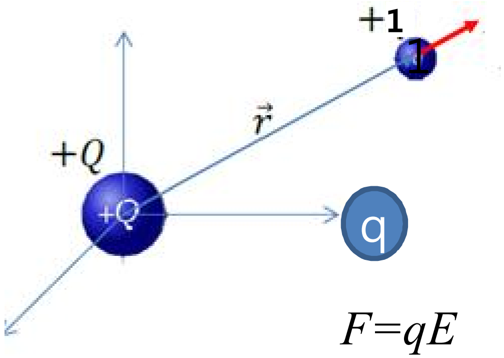
$\varepsilon = \epsilon_0\varepsilon_r$ $\quad$ $\varepsilon_r$ : relative permittivity
~80 for water at 20°C

# The electric field

- How can one charged particle exert a force on another?
  - We deduce that every charge creates around it a disturbance
  - We call this disturbance an electric field
    - **E**-field, units volts per meter (V/m)
  - An electric field, **E**, exerts a force on a charge ***q***

$$\mathbf{F} = q\,\mathbf{E}$$

    - the force is in the same direction as the field



$$F = qE$$

$$F = \frac{1}{4\pi\epsilon_0}\frac{|Q|}{r^2}$$

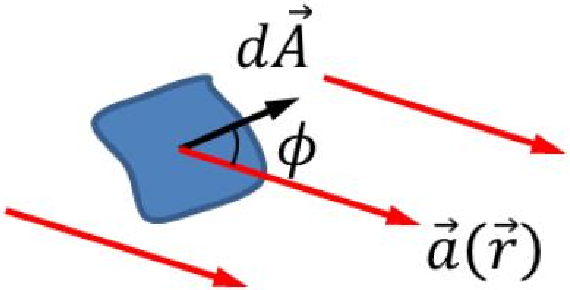
$$\vec{E} = \frac{1}{4\pi\epsilon_0}\frac{Q}{(\vec{r})^2}\hat{r}$$

Force per unit charge

# Concept of Flux

Let's consider a ***vector field*** $\vec{a}(\vec{r})$ (the velocity vectors in a flow of fluid, the electric field vectors, etc.). Locally the field is uniform.

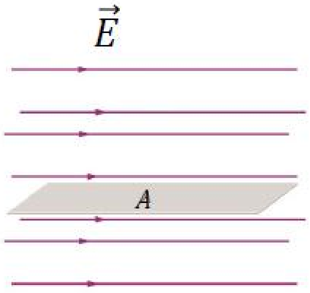
Also consider a ***small*** element of surface $d\vec{A}$: the length of this vector is proportional to the area, the direction is normal to the surface (i.e. to two non-parallel tangent lines to the surface at a given point).



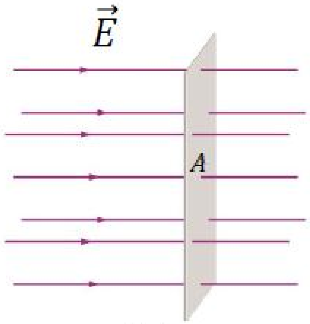
By definition, the flux of this field through the small element of surface $d\vec{A}$ :

$$\Phi_a = \vec{a}(\vec{r}) \cdot d\vec{A} = a(r)A \cdot cos\phi$$

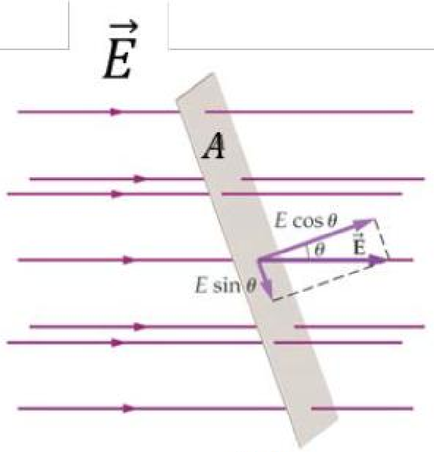
↑ scalar !



(a)

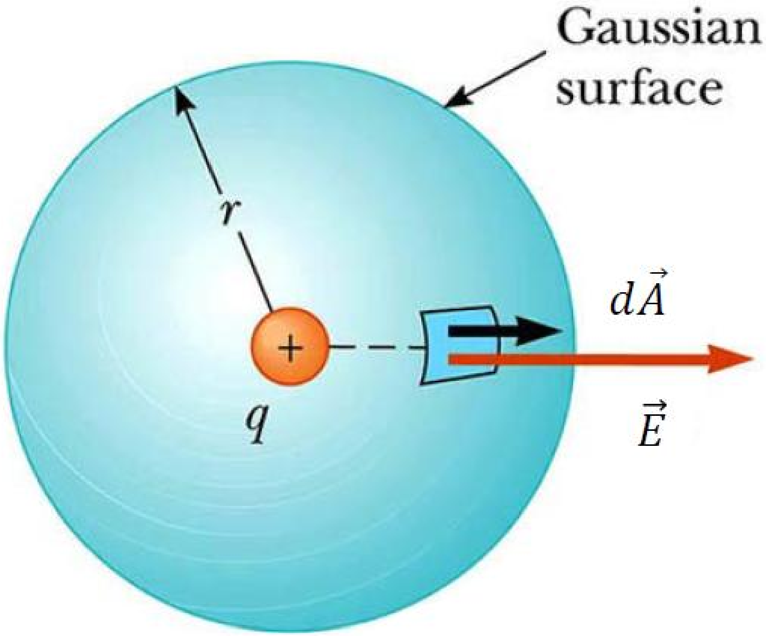


(b)



(c)

# Flux through Closed Surfaces

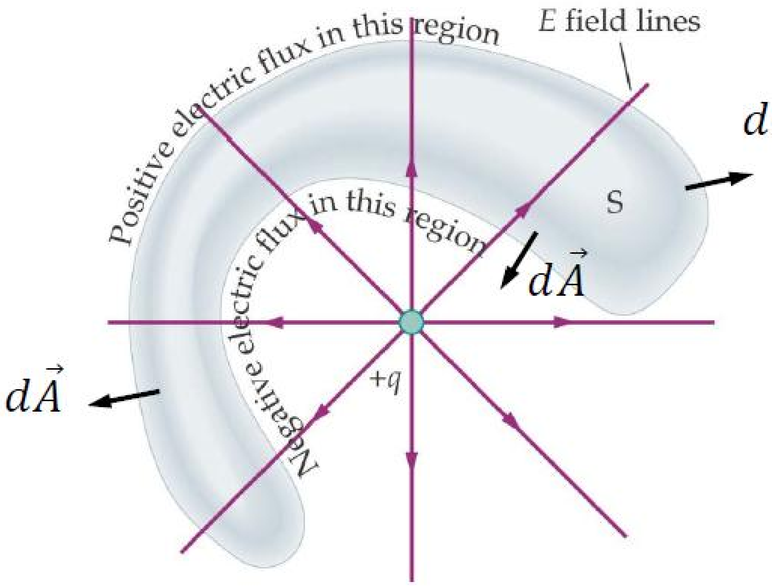


The net flux of the electric field through the closed surface:

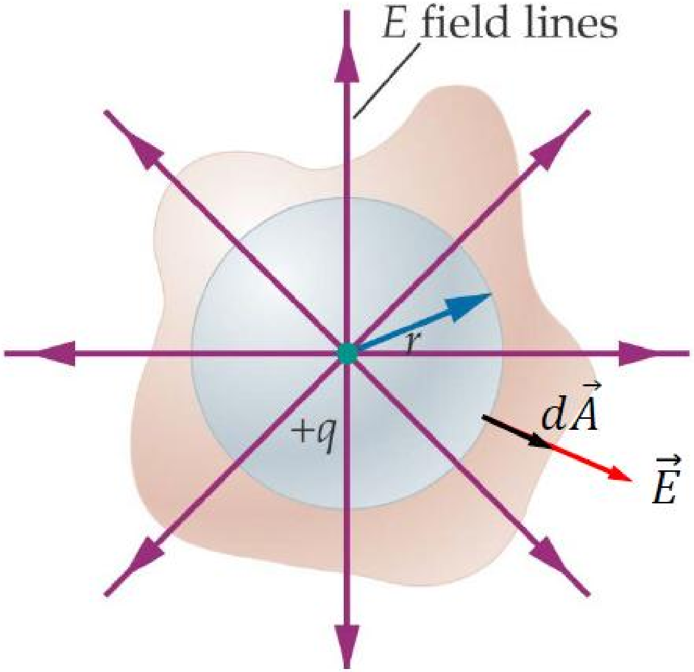
$$\Phi_E = \oint \vec{E}(\vec{r}) \cdot d\vec{A}$$

the integral is taken over the whole surface

Convention: the vector normal to the surface points outward.



# Example: Point Charge at the Center of a Spherical Surface



At each point of the surface $\vec{E} \parallel d\vec{A}$ ($\cos\phi$=1)

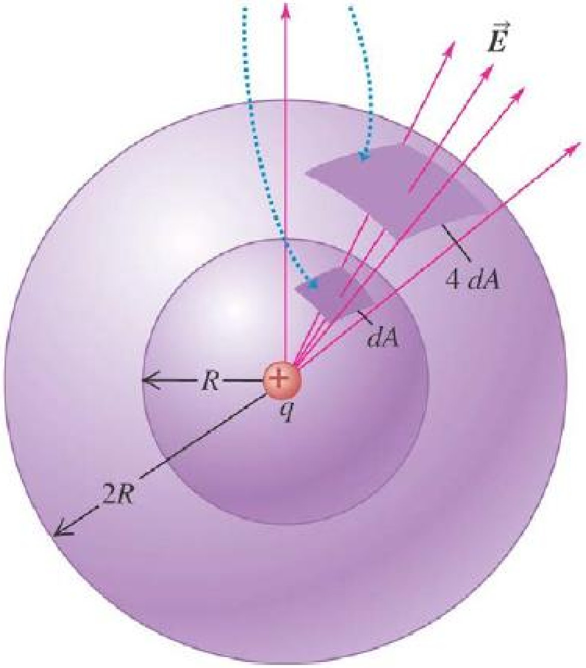
$$\Phi_E = \oint \vec{E}(\vec{r}) \cdot d\vec{A} = E(r) 4\pi r^2$$

$$= \frac{1}{4\pi\varepsilon_0} \frac{q}{r^2} 4\pi r^2 = \frac{q}{\varepsilon_0}$$

- doesn't depend on *r*

!

This is the case for any vector field of a point source whose strength $\propto 1/r^2$.
(electrostatic, gravitational, etc.)

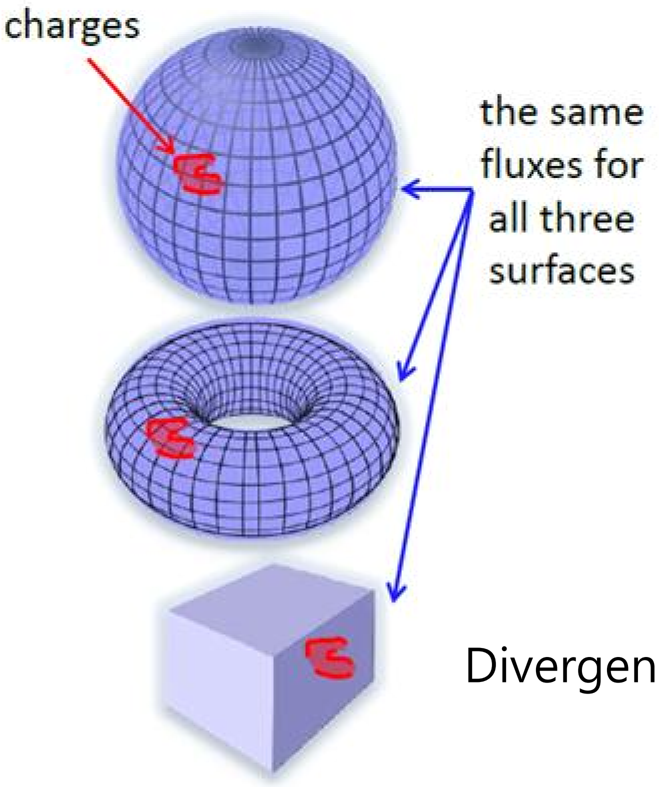


# Gauss' Law

The total flux of the electric field though ***any closed*** surface is proportional to the ***total*** charge inside the surface.

$$\Phi_E \equiv \oint \vec{E}(\vec{r}) \cdot d\vec{A} = \frac{1}{\varepsilon_0} \sum_i q_i$$

(the proportionality coefficient: $1/\varepsilon_0$)



The total charge:

$$Q = \sum_i q_i \qquad Q = \oint_{volume} \underset{\text{charge density}}{\rho(r)}\, \underset{\text{element of volume}}{dv}$$

$$\oiint E \cdot dA = \frac{1}{\varepsilon_0} \oiiint \rho d\mathrm{v} = Q_{enclosed}$$

Divergence (or Gauss Theorem): $\iint F \cdot dS = \iiint \nabla \cdot F dV$

$$\boxed{\nabla \cdot E = \frac{\rho}{\varepsilon_0}}$$

# Bringing two charges close together

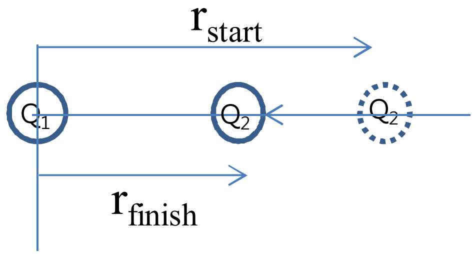
- How much work is required to bring two charges together, starting at $r=\infty$ and finishing at $r$

$$WD = -\int_{r_{start}}^{r_{finish}} \mathbf{F} \bullet d\mathbf{r} = -\int_{r_{start}}^{r_{finish}} \frac{Q_1 Q_2}{4\pi\varepsilon r^2}.dr$$

$$WD = \frac{Q_1 Q_2}{4\pi\varepsilon}\int_{r_{start}}^{r_{finish}} \frac{-1}{r^2}.dr$$

$$WD = \frac{Q_1 Q_2}{4\pi\varepsilon}\left[\frac{1}{r}\right]_{r_{start}}^{r_{finish}} = \frac{Q_1 Q_2}{4\pi\varepsilon}\left[\frac{1}{r}\right]_{\infty}^{r} = \frac{Q_1 Q_2}{4\pi\varepsilon r}$$

$$WD = \frac{Q_1 Q_2}{4\pi\varepsilon r}$$



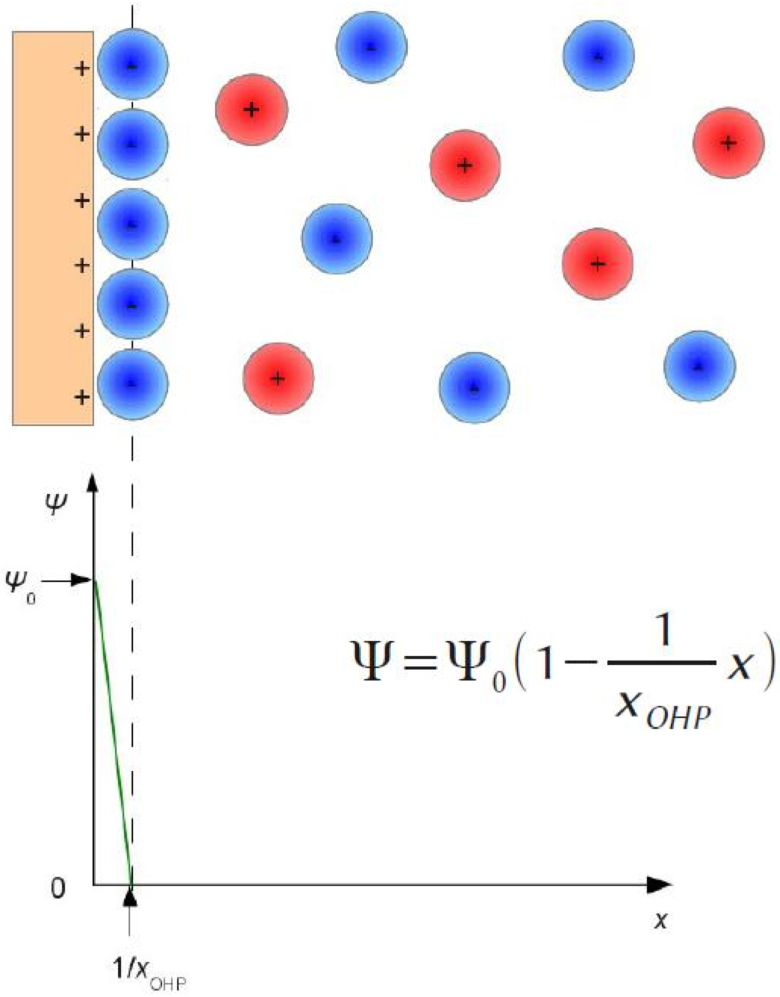
Electric Potential at r: work required to bring unit charge from infinity to r

$$\Psi = -\int_{\infty}^{r} E \cdot dr = \frac{Q}{4\pi\varepsilon r} \qquad E = -\frac{d\Psi}{dr} = -\nabla\Psi$$

$$\nabla \cdot E = \frac{\rho}{\varepsilon_0} \qquad \nabla \cdot (\nabla\Psi) = \nabla^2\Psi = -\frac{\rho}{\varepsilon}$$

Poisson's Eq.

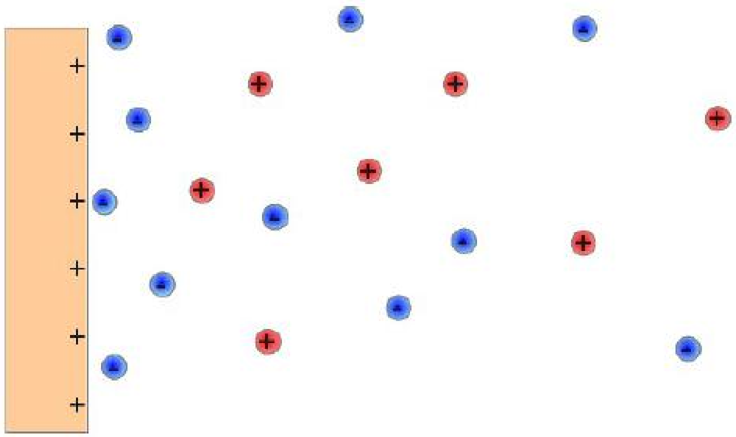
# The Helmholtz model

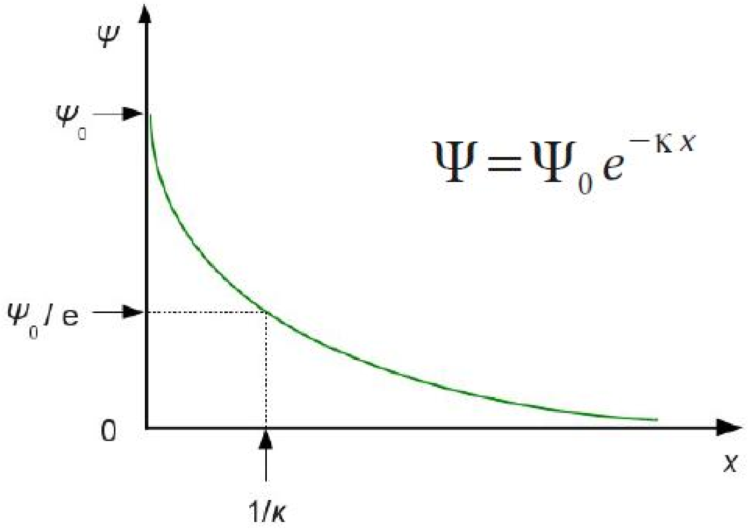


$$\Psi = \Psi_0 \left(1 - \frac{1}{x_{OHP}} x\right)$$

- Helmholtz, 1850s
- Electrostatic interaction between the surface and counter-ions of the solution
- Electric double layer forms (capacitor)
- Linear potential drop from the surface to the outer Helmholtz plane (OHP)
- Does not take into account
  - thermal motion
  - ion diffusion
  - adsorption onto the surface
  - solvent/surface interactions

# The Gouy-Chapman model





$$\Psi = \Psi_0 e^{-\kappa x}$$

- Gouy & Chapman, 1909-1913
- Flat, infinite, uniformly charged surface
- Ions considered as point charges
- Boltzmann statistical distribution near the surface
- Accounts for thermal motion
- Counter-ion concentration decreases, co-ion concentration increases from the surface (in the bulk solution the two concentrations become equal)
- Exponential potential decrease
- Debye length (1/κ): "thickness of the diffuse double layer" or thickness of an equivalent plane capacitor

# Derivation of the Gouy-Chapmann Model

- In solution phase, potential at any point is given by the Poisson Eq.

$$\nabla^2\Psi = -\frac{\rho}{\varepsilon} \qquad \rho(x,y,z){:}\ space\ charge\ density\ (\frac{coulombs}{m^3})$$

$$\rho = \sum_i z_i e n_i$$

$z_i$ = valance of ionic species *i*
$e$ = charge of an electron
$n_i$ = no. concentration (ions/$m^3$) of *i*

- Distribution of ions at a point with potential Ψ is given by Boltzmann Distribution

$$n_i = n_i^0 \exp\left(\frac{-z_i e\Psi}{kT}\right)$$

$n_i^0$: *bulk concentrat ion*
$k$ : *Boltzmann const.*
$T$ : *absolute Temp.*

$$\nabla^2\Psi = -\frac{1}{\varepsilon}\sum z_i e n_i^0 \exp\left(\frac{-z_i e\Psi}{kT}\right)$$

Poisson-Boltzmann Eq.

$$\nabla^2\Psi = \frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2}$$

- Can be simplified if $\frac{z_i e\Psi}{kT}$ is small (<<1) everywhere
- For $z_i$=1 at room temp. $\Psi_0 << 25.6\ mV$

$$\frac{z_i e\Psi}{kT} = 1$$

$$\Psi = \frac{kT}{z_i e} = \frac{(1.38\times10^{-23} J/K)(298 K)}{(1)(1.6\times10^{-19} C)} = 0.0256V$$

$$\exp\left(\frac{-z_i e\Psi}{kT}\right) = 1 - \frac{z_i e\Psi}{kT}$$

$$\nabla^2\Psi = -\frac{1}{\varepsilon}\sum z_i e n_i^0\left(1 - \frac{z_i e\Psi}{kT}\right)$$

$$= -\frac{1}{\varepsilon}\left[\sum z_i e n_i^0 - \sum \frac{z_i^2 e^2 n_i^0 \Psi}{kT}\right]$$

- For electric neutrality $\sum z_i e n_i^0 = 0$

$$\nabla^2\Psi = \kappa^2\Psi \qquad \kappa^2 = \frac{e^2}{\varepsilon kT}\sum z_i^2 n_i^0$$

*Derbyie-Hückel Approximation*

$\kappa$ *has dimensions of 1/length*

*1/*$\kappa$ *= length*

$\kappa$ *: Derbyie-Hückel reciprocal length parameter*

- For infinite flat plate: one dimensional, $\nabla^2\Psi = \frac{\partial^2\Psi}{\partial x^2}$

$$\frac{d^2\Psi}{dx^2} = \kappa^2\Psi$$

- Solution

$$\Psi = Ae^{-\kappa x}$$

$$\Psi = \Psi_0 \;\; at \;\; x = 0 \;\rightarrow\;\; A = \Psi_0$$

$$\Psi = \Psi_0 e^{-\kappa x} \qquad alternately, \;\; \kappa x = \ln\left(\frac{\Psi_0}{\Psi}\right)$$

- Complete solution without approximation for z:z electrolyte

$$\nabla^2\Psi = -\frac{1}{\varepsilon}\sum z_i e\, n_i^0 \exp\left(\frac{-z_i e\Psi}{kT}\right)$$

$$\Psi_0 > 25.6 \; mV$$

$$\kappa x = \ln\left(\frac{(e^y+1)(e^{y_0}+1)}{(e^y-1)(e^{y_0}-1)}\right)$$

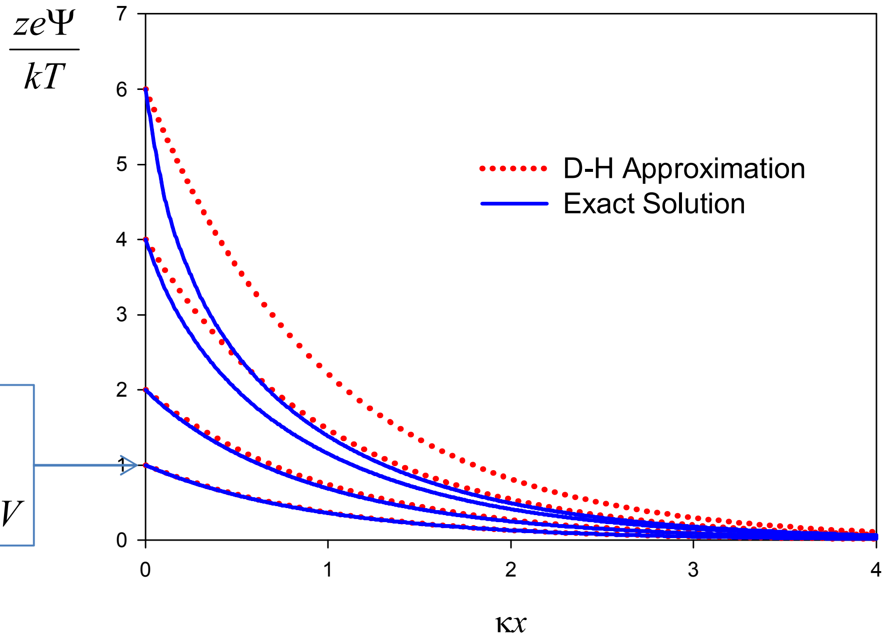
$$y = \frac{ze\Psi}{2kT}, \quad y_0 = \frac{ze\Psi_0}{2kT}$$

$$\Psi = \frac{2kT}{ze}\ln\left(\frac{1+\chi\exp(-\kappa x)}{1-\chi\exp(-\kappa x)}\right)$$

$$\chi = \frac{\exp(y_0)-1}{\exp(y_0)+1}$$

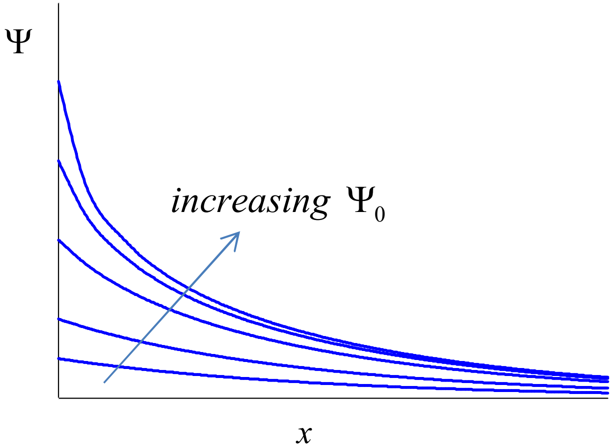
$$\frac{ze\Psi_0}{kT} = 1$$

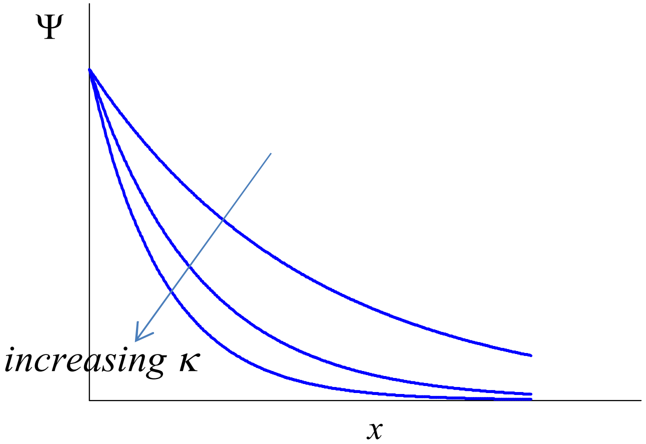
$$\Psi_0 = 25.6\,mV$$



D-H approximation works better than expected even when

$$\Psi_0 > 25.6\,mV$$





$$\kappa x = \ln\left(\frac{(e^{y}+1)(e^{y_0}+1)}{(e^{y}-1)(e^{y_0}-1)}\right) \qquad y = \frac{ze\Psi}{2kT}, \quad y_0 = \frac{ze\Psi_0}{2kT}$$

$$\Psi = \frac{2kT}{ze}\ln\left(\frac{1+\chi_0\exp(-\kappa x)}{1-\chi_0\exp(-\kappa x)}\right) \qquad \chi_0 = \frac{\exp(y_0)-1}{\exp(y_0)+1}$$

$$\chi = \chi_0\exp(-\kappa x) \qquad \chi = \frac{\exp(y)-1}{\exp(y)+1}$$

For large $x$, $y$ is small $\quad \chi = \frac{1+y-1}{1+y+1} = \frac{y}{2} = \frac{ze\Psi}{4kT}$

$$\frac{ze\Psi}{4kT} = \chi_0\exp(-\kappa x)$$

$$\Psi = \frac{4kT}{ze}\chi_0\exp(-\kappa x)$$

For very large values of $\Psi_0, \quad \chi_0 \rightarrow 1$

$$\Psi = \frac{4kT}{ze}\exp(-\kappa x)$$

The potential in the outer region is independent of the surface potential for large potentials

- Symmetric electrolyte: $Na^+Cl^-$, $Mg^{2+}SO_4^{2-}$ $\quad |z^+| = |z^-|$

$$\kappa^2 = \frac{e^2}{\varepsilon kT}\sum z_i^2 n_i^0 = \frac{2z^2e^2n_i^0}{\varepsilon kT} = \frac{2z^2e^2N_{av}\cdot c\times 1000}{\varepsilon_0\varepsilon_r kT} \quad c: moles/L$$

$$= \frac{2z^2(1.6\times 10^{-19}C)^2(6\times 10^{23})\cdot c\times 1000}{(9\times 10^{-12}C^2/Nm^2)(80)(1.38\times 10^{-23}J/K)(298K)}$$

$$\kappa \approx 3\times 10^9\,|z|\sqrt{c} \quad (unit: 1/m)$$

- For 1:1 electrolytes: |z|=1

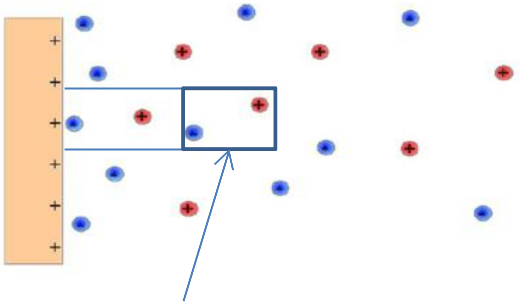
| $c$ (moles/L) | $\kappa(cm^{-1})$ | $1/\kappa$ |
|---|---|---|
| $10^{-7}$ | $10^4$ | 1 μm |
| $10^{-5}$ | $10^5$ | 0.1 μm |
| $10^{-3}$ | $10^6$ | 100 Å |
| $10^{-1}$ | $10^7$ | 10 Å |

- Increasing total ionic conc. increases $\kappa$
  - compresses double layer
- Aqueous solution: min. ionic conc.=$2\times10^{-7}$ (pH=7)

  $1/\kappa \approx 1\,\mu m$ – max. thickness
- Indifferent ions: only electrostatic interactions between ions and surface
- P.D ions: change $\Psi_0$, also affect $\kappa$
- Specially adsorbed ions: non-electrostatic interactions –affect $\Psi_0$ and $\kappa$

# Surface Charge

- Fixed by adsorption of P. D. ions or by lattice substitution



Space charge $\rho$

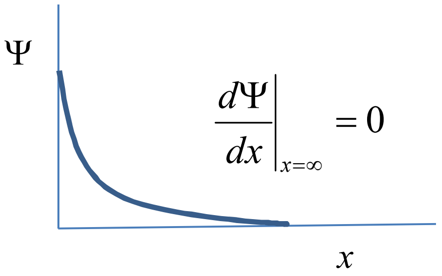
Electroneutrality: $\sigma_s = -\sigma_d$

$\sigma_s$: surface charge, $\sigma_d$: double layer charge

$$\sigma_d = \int_0^\infty \rho dx = -\sigma_s$$

Poisson Eq. $\rho = -\varepsilon \frac{d^2\Psi}{dx^2}$

$$\sigma_d = -\varepsilon \int_0^\infty \frac{d^2\Psi}{dx^2} dx = -\varepsilon \left[ \frac{d\Psi}{dx} \right]_0^\infty$$



$$\left.\frac{d\Psi}{dx}\right|_{x=\infty} = 0$$

$$\sigma_d = \varepsilon \left( \frac{d\Psi}{dx} \right)_{x=0} \qquad \sigma_s = -\varepsilon \left( \frac{d\Psi}{dx} \right)_{x=0}$$

## At low potentials (D-H Approx.)

$$\Psi = \Psi_0 e^{-\kappa x}$$

$$\frac{d\Psi}{dx} = -\kappa\Psi_0 e^{-\kappa x}$$

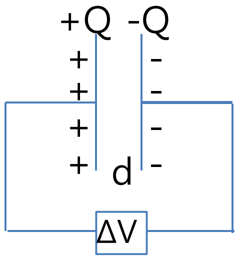
$$\left(\frac{d\Psi}{dx}\right)_{x=0} = -\kappa\Psi_0$$

$$\sigma_s = \varepsilon\kappa\Psi_0$$

*complete solution*

$$\sigma_s = \sqrt{8\varepsilon kTn_0}\,\sinh\left(\frac{ze\Psi_0}{2kT}\right)$$

## Capacity of Double Layer



Analogous to a capacitor

$$Q = C\Delta V \quad C = \frac{Q}{\Delta V}$$

$$C = \frac{\varepsilon A}{d} \quad \frac{Q}{A} = \frac{\varepsilon}{d}\Delta V$$

Differential capacity: $c = \dfrac{\partial\sigma}{\partial\Psi_0}$

Integral capacity: $C = \dfrac{\sigma}{\Psi_0}$

$$D - H : \frac{\partial\sigma_s}{\partial\Psi_0} = \varepsilon\kappa = \frac{\sigma_s}{\Psi_0}$$

$$c = C = \varepsilon\kappa = \frac{\varepsilon}{\kappa^{-1}}$$

$$\equiv \textit{capacity with plate } \kappa^{-1} \textit{ apart}$$

$$\textit{At high potential}, \ c \neq C \neq \textit{constant}$$

# Problems with Gouy-Chapmann Model

- Calculated capacity >> measured values because size of ions is not considered.
- Calculated ionic concentrations are sometimes ridiculous.

✓ Surface with $\Psi_0$=-200 mV in presence of NaCl

$$n_i = n_i^0 \exp\left(\frac{-z_i e\Psi}{kT}\right)$$

- Adjacent to surface $\Psi \approx \Psi_0$

$$n_{Na^+} = n_{Na^+}^0 \exp(8)$$

$$if\ n^0 = 0.1M \qquad n = 300M$$

$$= 0.01M \qquad = 30M$$

$$NaCl\ crystal = \sim 37M$$