La Interfase Electrizada

Tema 8

La Interfase Electrizada

1. Introducción
2. Termodinámica de la I. E.
3. Estructura de la I. E.
   - 3.1. Modelo Doble Capa Rígida o Helmholtz-Perrin
   - 3.2. Modelo Doble Capa Difusa o Gouy-Chapman
   - 3.3. Modelo de Stern
4. Doble Capa y Coloides

La Interfase Electrizada

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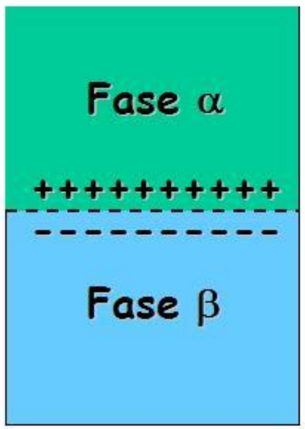
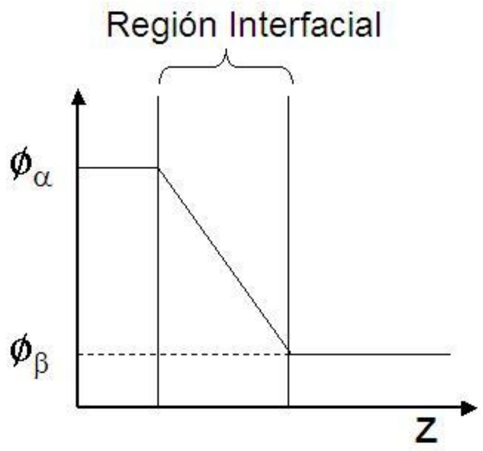
‘Química Física’ (6ª ed.) P. W. Atkins

1. Introducción

$$dU = TdS - PdV + \gamma dA + \sum_i \mu_i dn_i$$

Y = Potencial Eléctrico
X = Carga Eléctrica





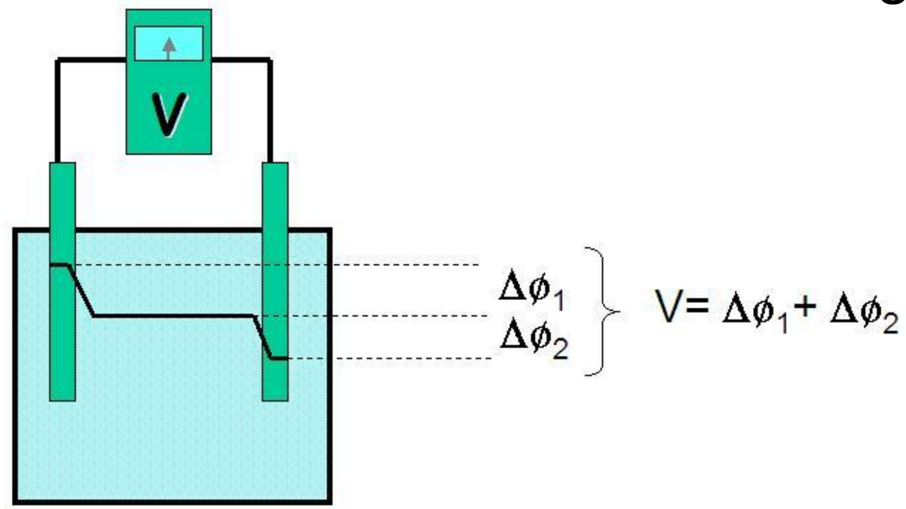
Caída Potencial $\Delta\phi = \phi_\alpha - \phi_\beta$

1. Introducción

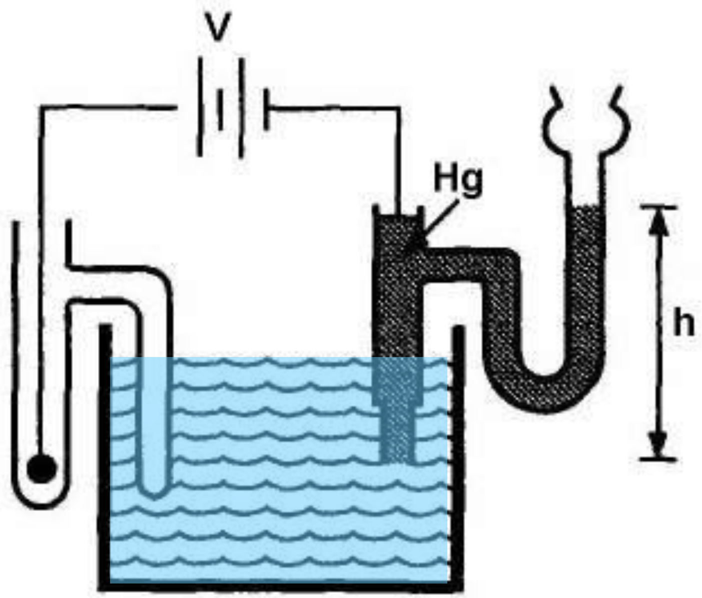
$$dU = TdS - PdV + \gamma dA + \sum_i \mu_i dn_i + \sum_j Y_j dX_j$$

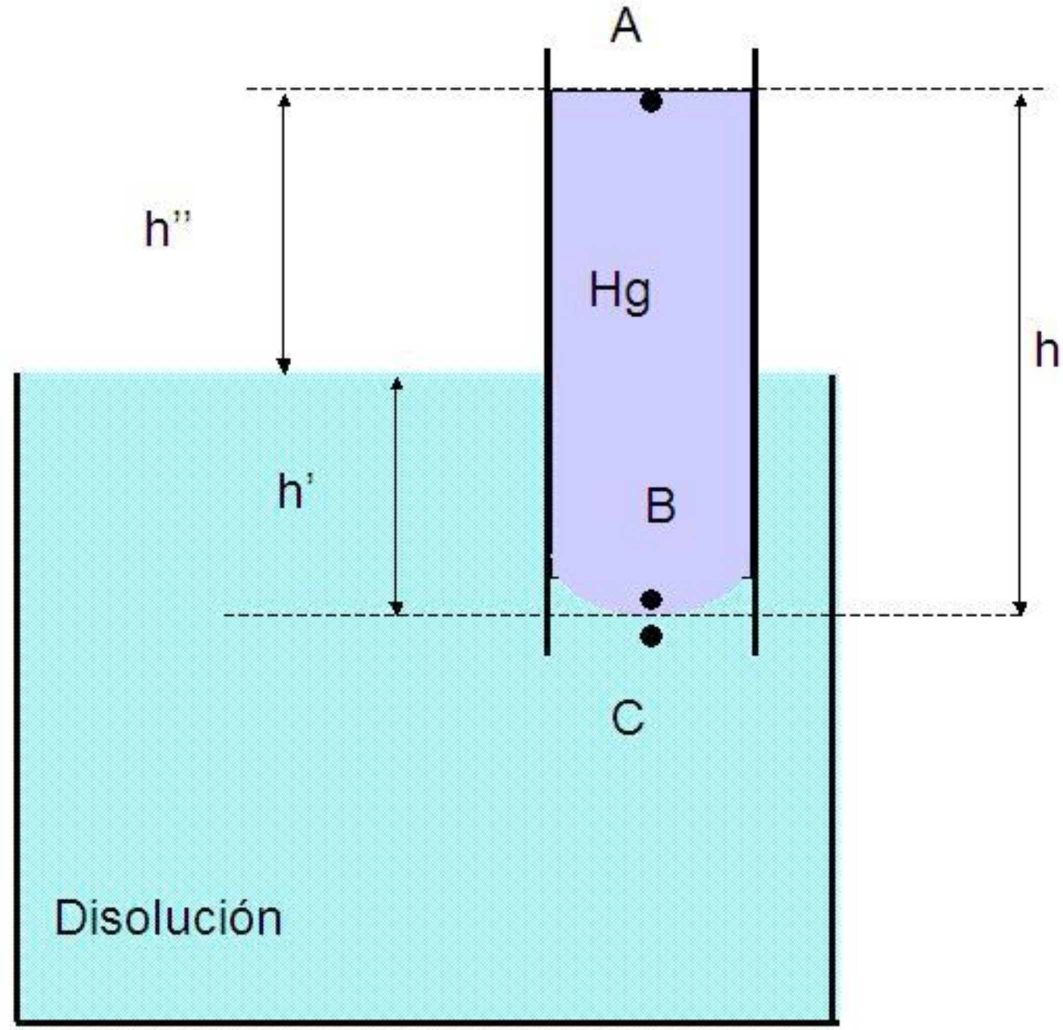
Y = Potencial Eléctrico

X = Carga Eléctrica



1. Introducción





1. Introducción

$$P_B - P_C = \frac{2\gamma}{r} = \frac{2\gamma\cos\theta}{R}$$

$$P_B = P_A + \rho_{Hg} g h$$

$$P_C = P_A + \rho_{aire} g h'' + \rho_{dis} g h'$$

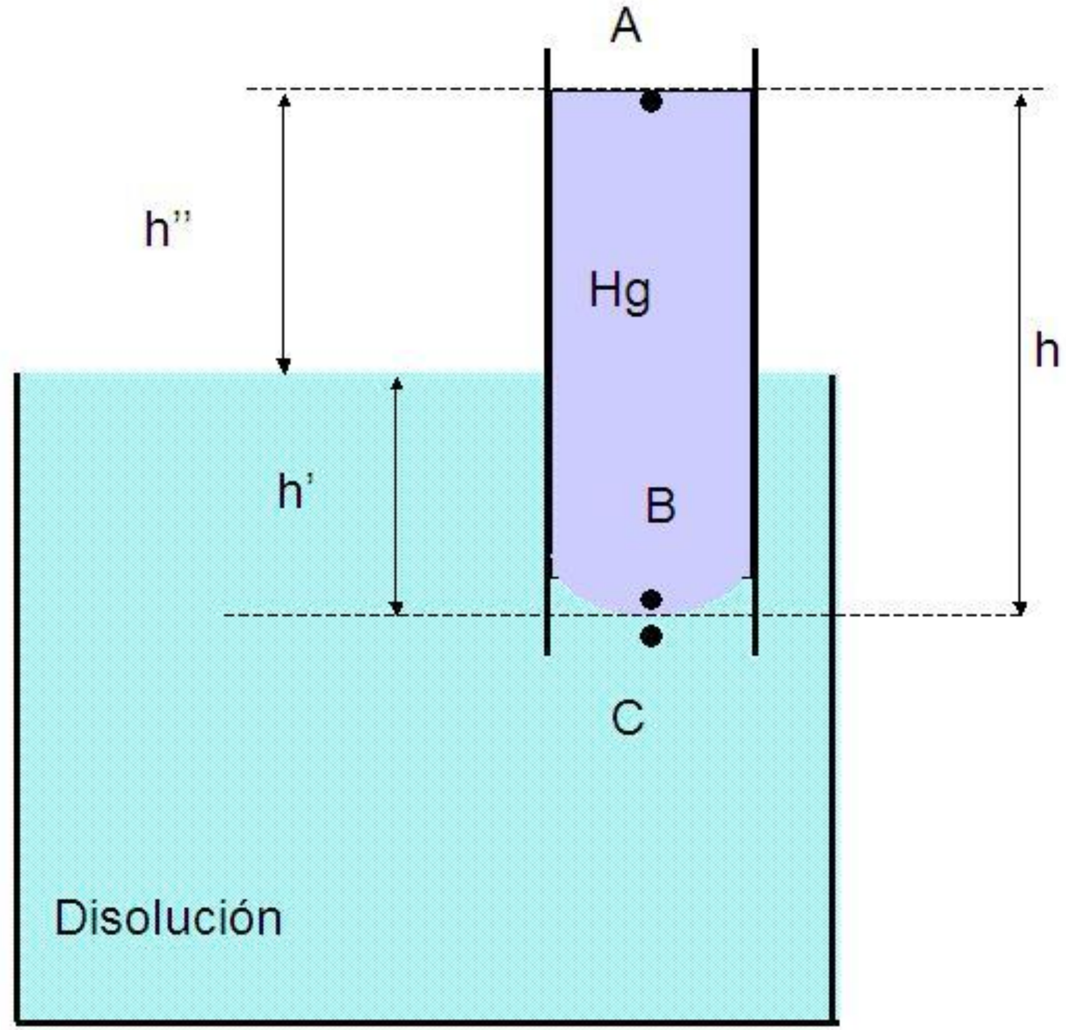
$$P_A + \rho_{Hg} g h - P_A - \rho_{aire} g h'' - \rho_{dis} g h' = \frac{2\gamma\cos\theta}{R}$$

$$\left[\rho_{Hg} h - \rho_{aire} h'' - \rho_{dis} h'\right] \cdot g = \frac{2\gamma\cos\theta}{R}$$

$\rho_{Hg} >> \rho_{aire}$ $\quad$ $\rho_{Hg} >> \rho_{dis}$

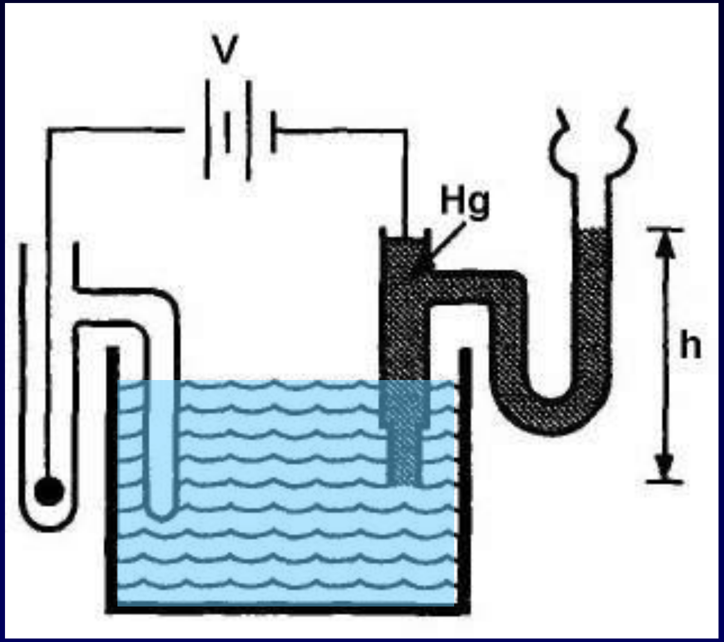
$\cos\theta \approx 1$

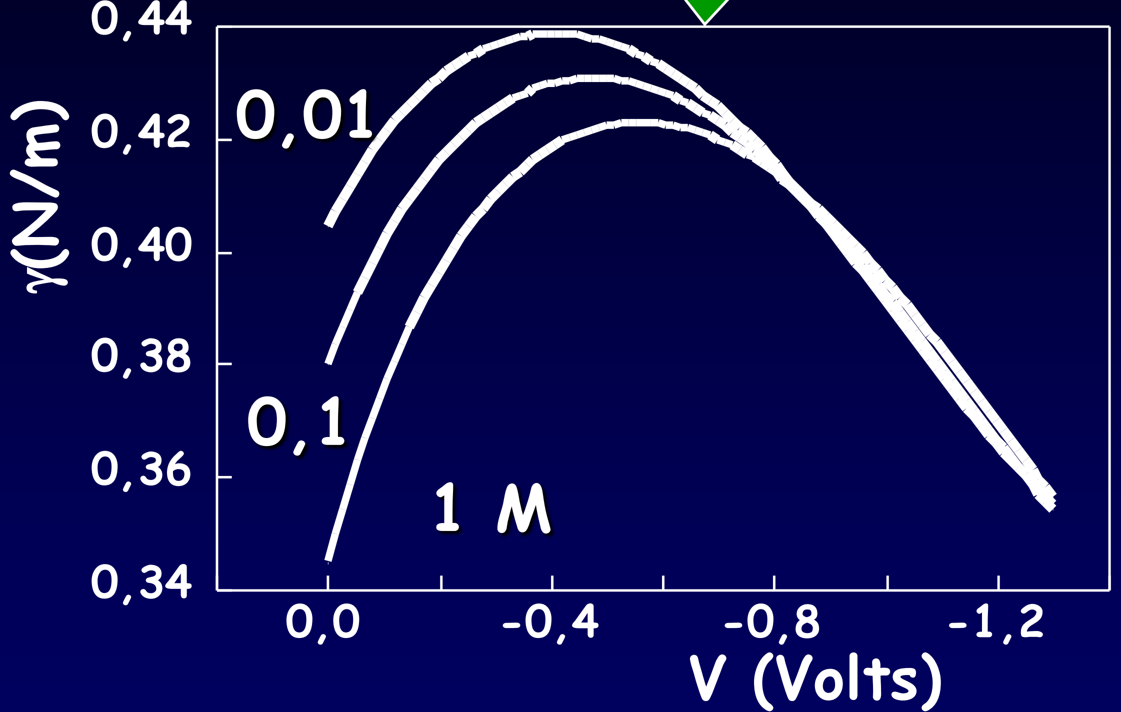
$$\gamma = \frac{\rho_{Hg} g h R}{2}$$



1. Introducción

$$\gamma = \rho g h R/2$$





$V = \Delta\phi_{Hg} + \Delta\phi_{ref}$

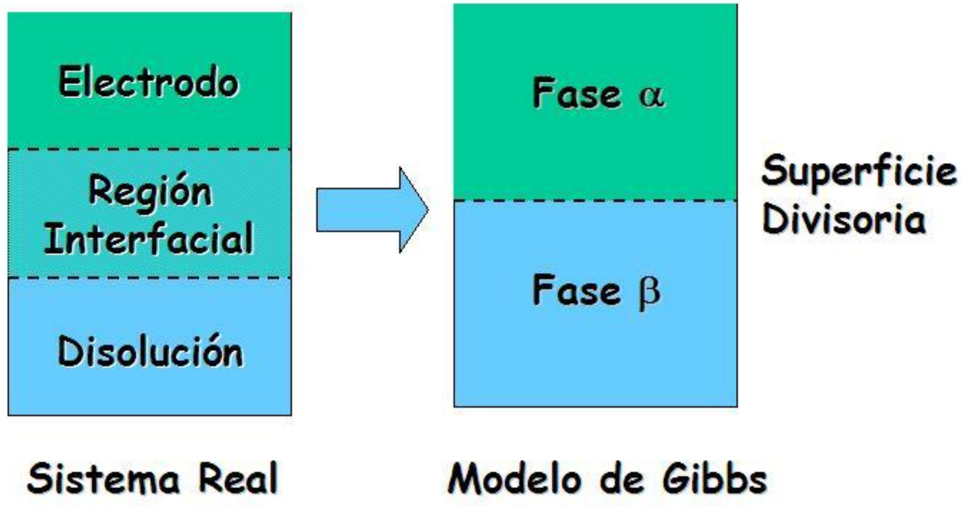
$\Delta V = \Delta\Delta\phi_{Hg} + \Delta\Delta\phi_{ref}$

Ref = No polarizable

Hg= Polarizable

$\Delta V = \Delta\Delta\phi_{Hg}$

2. Termodinámica



$$dU = TdS - PdV + \gamma dA + \sum_i \mu_i dn_i + \phi dQ$$

$$dU = TdS - PdV + \gamma dA + \sum_i \mu_i dn_i + \phi dQ$$

$$Q = \sum_i z_i F n_i$$

$$dU = -PdV + TdS + \gamma dA + \sum_i \mu_i dn_i + \sum_i z_i F \phi dn_i$$

$$= -PdV + TdS + \gamma dA + \sum_i \left(\mu_i + z_i F \phi\right) dn_i = -PdV + TdS + \gamma dA + \sum_i \bar{\mu}_i dn_i$$

$$d\gamma = -\sum_i \Gamma_i d\mu_i$$

Isot. Adsorción Gibbs

$$d\gamma = -\sum_i \Gamma_i d\bar{\mu}_i$$

Isot. Adsorción Gibbs
Interfases Electrizadas

2. Termodinámica

$$d\gamma = -\sum_i \Gamma_i d\bar{\mu}_i = -\sum_i \Gamma_i d\mu_i - \sum_i \Gamma_i z_i F d\phi$$

$$d\gamma = -\sum_i \Gamma_i d\mu_i - \sum_j^{\alpha} \Gamma_j z_j F d\phi^{\alpha} - \sum_k^{\beta} \Gamma_k z_k F d\phi^{\beta}$$

$$\left\{ \begin{array}{l} \sum_i^{\alpha} \Gamma_i z_i F = \sum_i^{\alpha} \frac{n_i^S}{A} z_i F = \sigma^{\alpha} \\ \sum_k^{\beta} \Gamma_k z_k F = \sum_k^{\beta} \frac{n_k^S}{A} z_k F = \sigma^{\beta} \end{array} \right.$$

$$d\gamma = -\sum_i \Gamma_i d\mu_i - \sigma^{\alpha} d\phi^{\alpha} - \sigma^{\beta} d\phi^{\beta} = -\sum_i \Gamma_i d\mu_i - \sigma^{\alpha} d\phi^{\alpha} + \sigma^{\alpha} d\phi^{\beta}$$

$$= -\sum_i \Gamma_i d\mu_i - \sigma^{\alpha} d(\phi^{\alpha} - \phi^{\beta}) = -\sum_i \Gamma_i d\mu_i - \sigma^{\alpha} d(\Delta\phi)$$

$$d\gamma = -\sum_i \Gamma_i d\mu_i - \sigma^\alpha d(\Delta\phi)$$

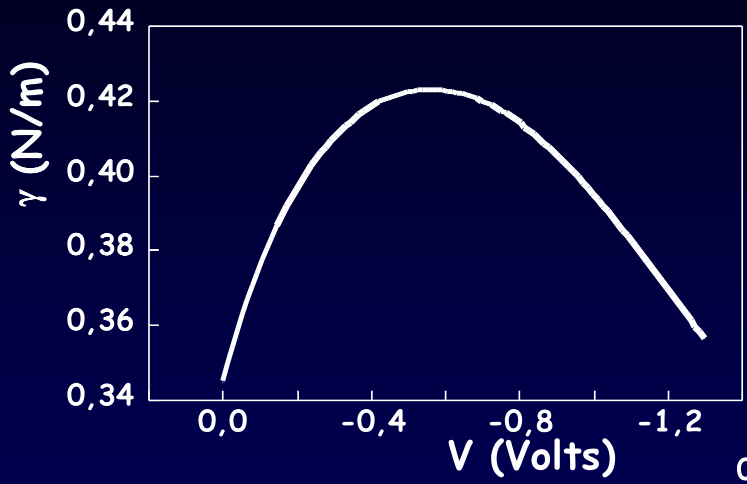
$\Delta\phi = cte$ $\qquad$ $d\gamma = -\sum_i \Gamma_i d\mu_i$

$\mu = cte$ $\qquad$ $d\gamma = -\sigma^\alpha d(\Delta\phi)$

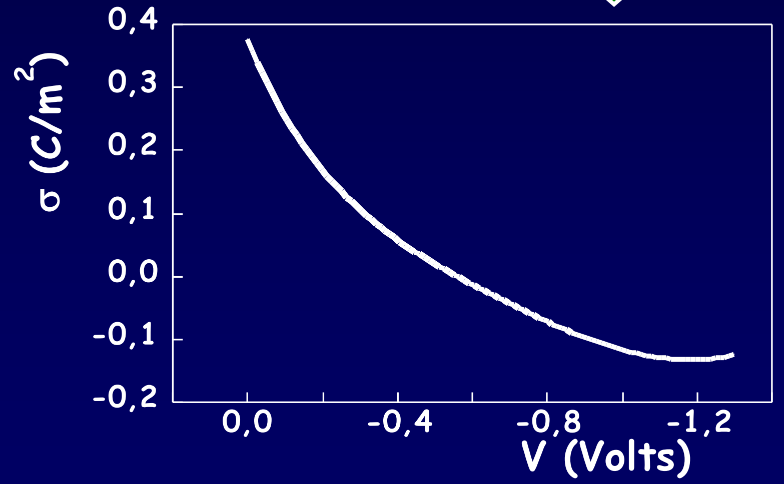
$$\left(\frac{\partial\gamma}{\partial V}\right)_{T,\mu} = -\sigma$$

Ecuación de Lippmann

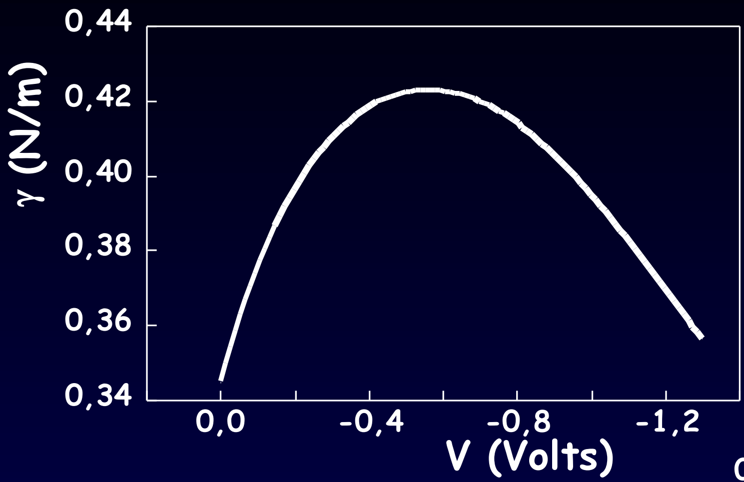
2. Termodinámica



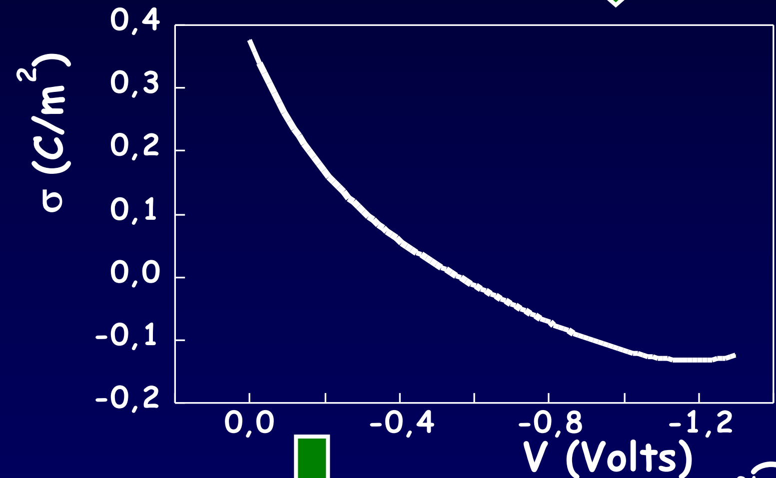
$$\left(\frac{\partial \gamma}{\partial V}\right)_{T,\mu} = -\sigma$$



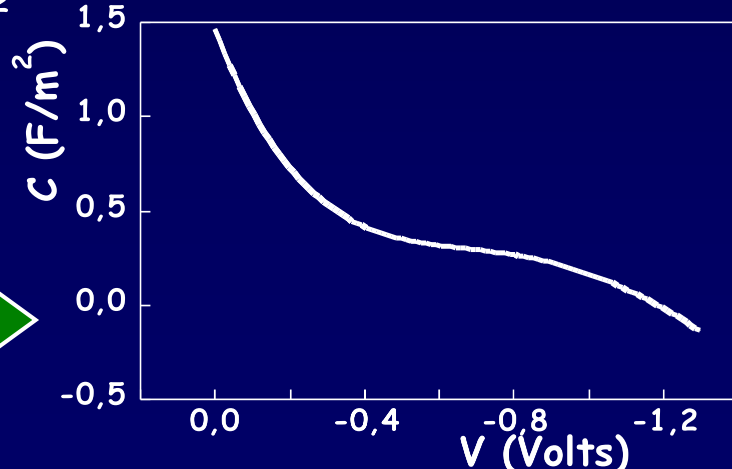
2. Termodinámica



$$\left(\frac{\partial \gamma}{\partial V}\right)_{T,\mu} = -\sigma$$

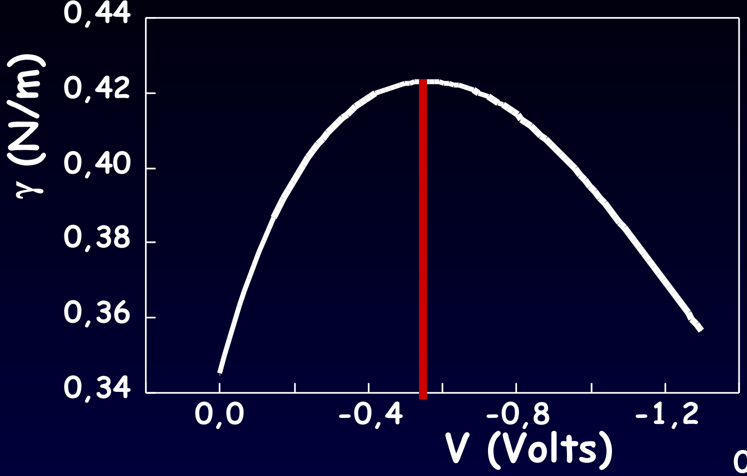


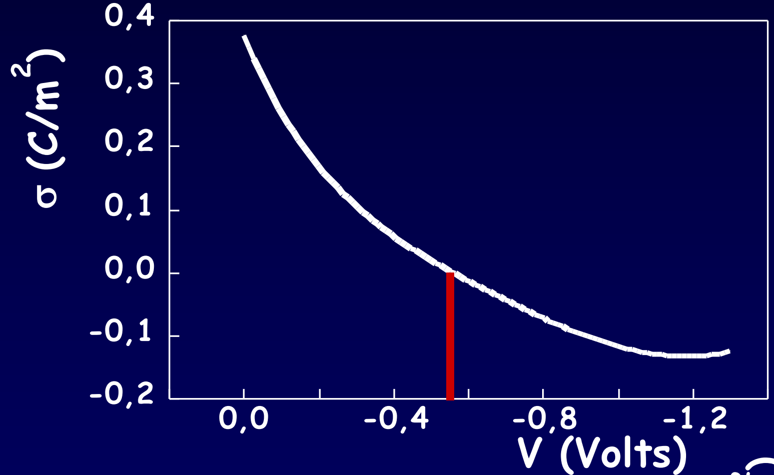
$$C = \frac{d\sigma}{dV} = -\left(\frac{\partial^2 \gamma}{\partial V^2}\right)_{T,\mu}$$

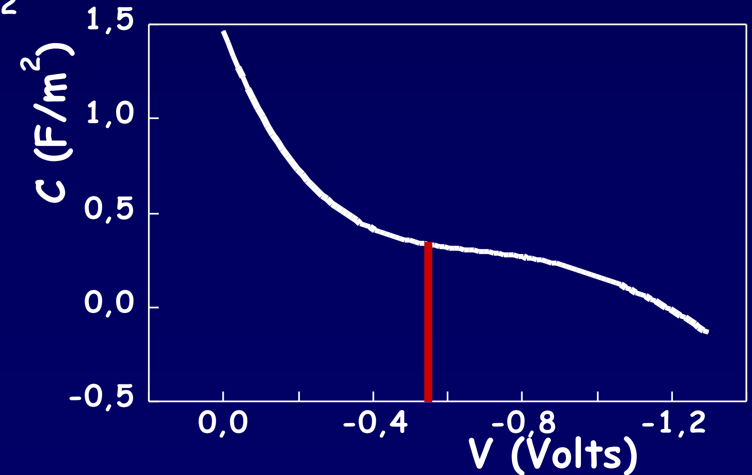


2. Termodinámica

$$\gamma^{max} \Rightarrow \left(\frac{\partial \gamma}{\partial V}\right)_{T,\mu} = -\sigma \Rightarrow \sigma = 0$$







3. Estructura de la Interfase

- Electrodo plano e infinito $\phi = \phi(x)$
- Disolvente como continuo (ε)
- Sólo consideran la contribución de los iones

$$\Delta\phi = \phi_e - \phi_d = \phi_e$$

3. Estructura de la Interfase

1. Ecuación de Poisson

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

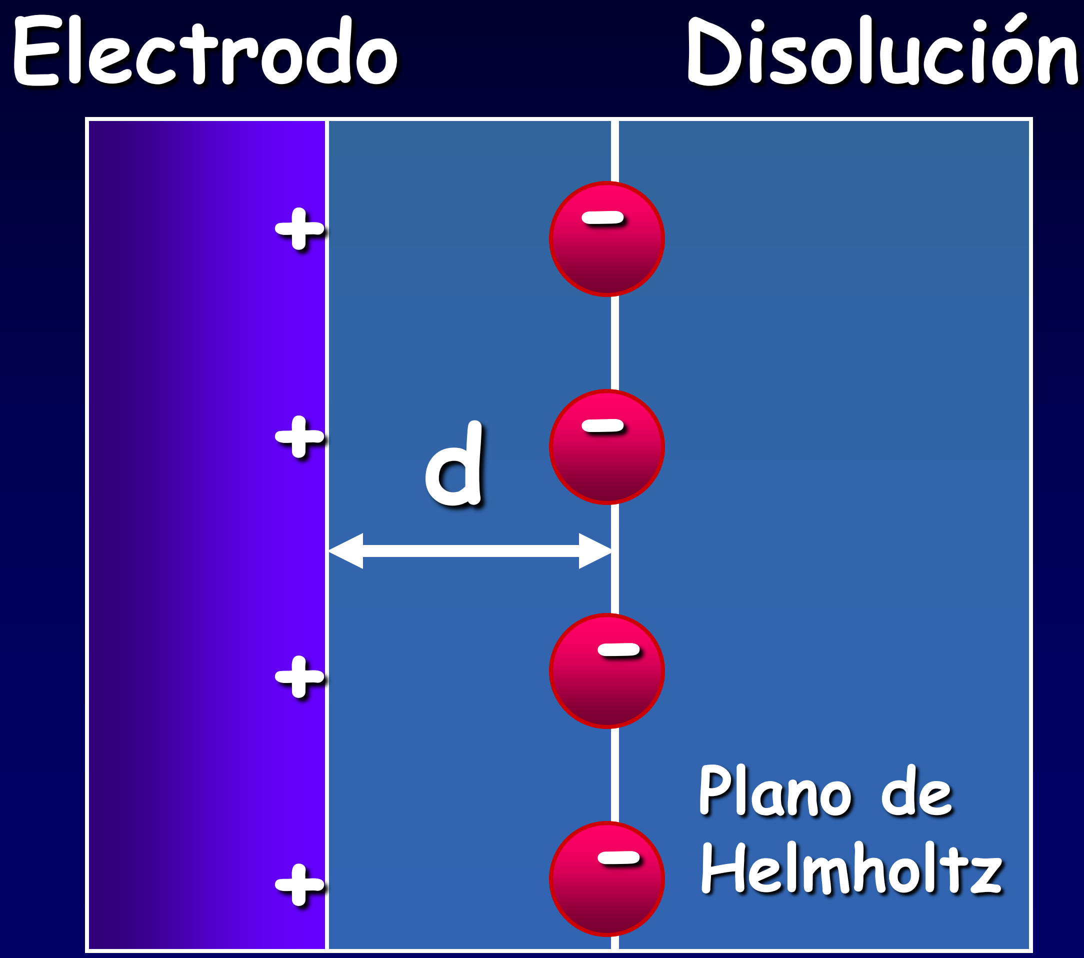
2. Teorema de Gauss

$$\sigma = -\varepsilon\left(\frac{d\phi(x)}{dx}\right)_{x=0}$$

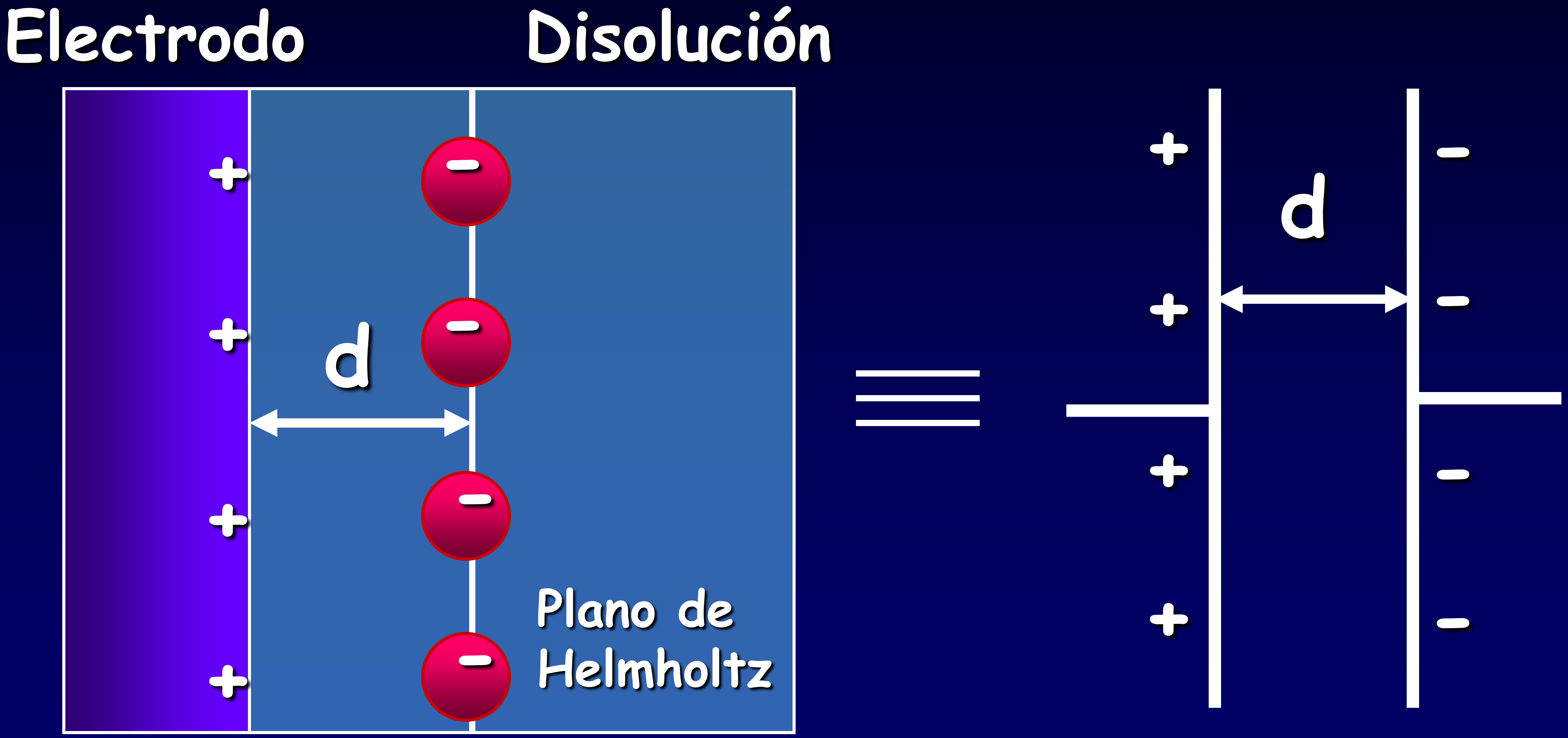
3. Ecuación de Lippmann

$$\int d\gamma = -\int \sigma \cdot d\phi_e$$

Modelo de Helmholtz-Perrin



Modelo de Helmholtz-Perrin

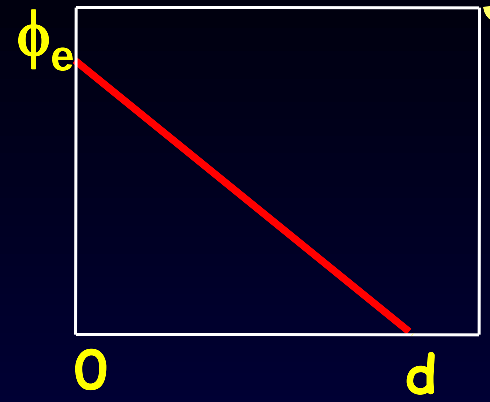


3. Estructura

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

Ec. Poisson

$$\phi(x) = \phi_e\left(1 - \frac{x}{d}\right)$$



$$\sigma = -\varepsilon\left(\frac{d\phi}{dx}\right)_{x=0} = \frac{\varepsilon}{d}\phi_e$$

Teorema de Gauss

$$\int d\gamma = -\int \sigma \; d\phi_e$$

Ec. Lippmann

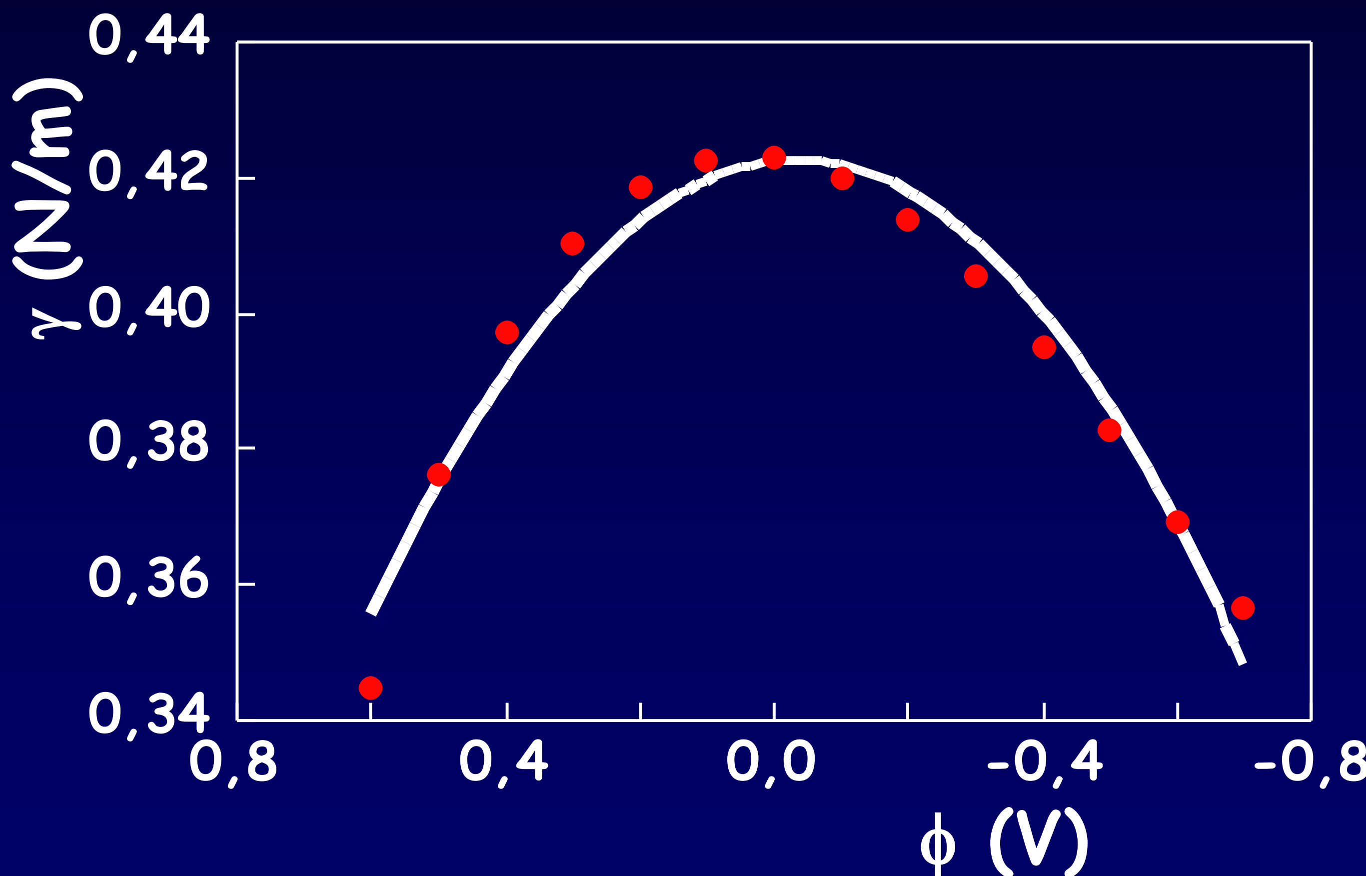
$$\gamma = -\frac{\varepsilon}{2d}\phi_e^2 + cte$$

$$\left(\phi_e = 0 \rightarrow \sigma = 0 \rightarrow \gamma = \gamma^{max}\right)$$

$$\gamma = \gamma^{max} - \frac{\varepsilon}{2d}\phi_e^2$$

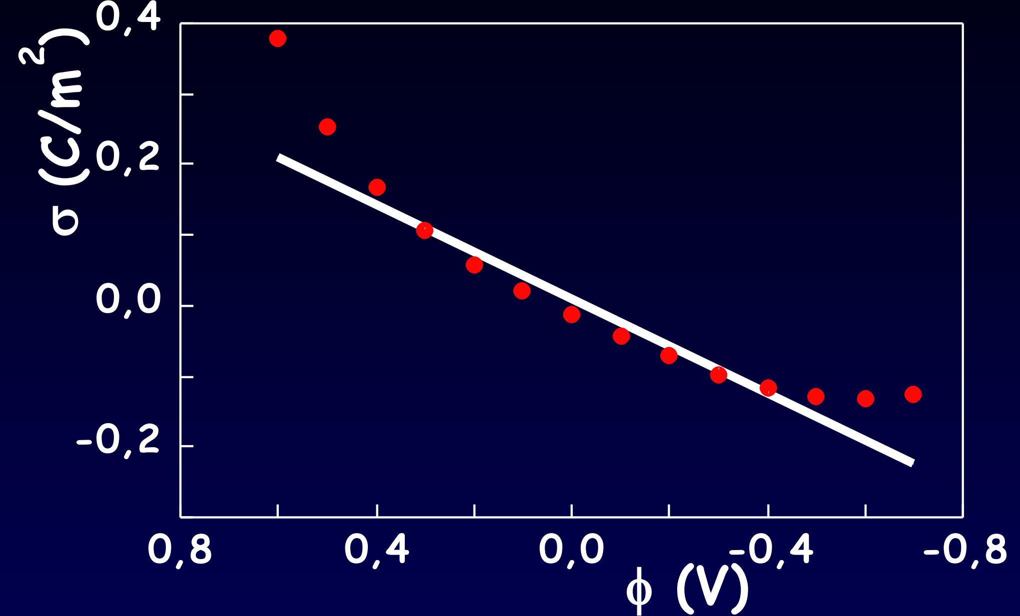
3. Estructura

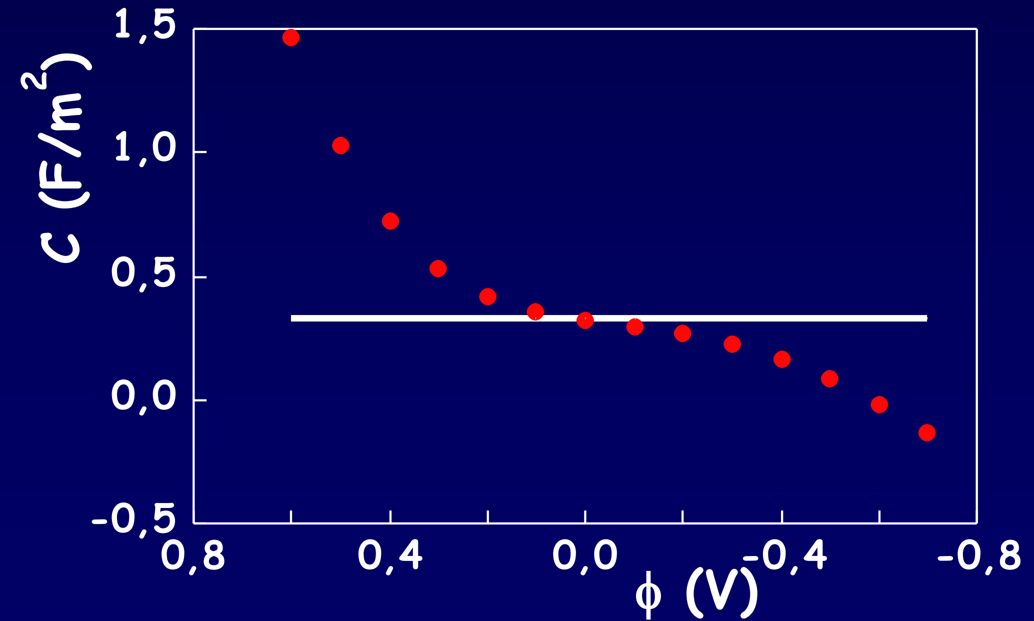
$$\gamma = \gamma^{max} - \frac{\varepsilon}{2d}\phi_e^2$$



$$\sigma = \frac{\varepsilon}{d}\phi_e$$

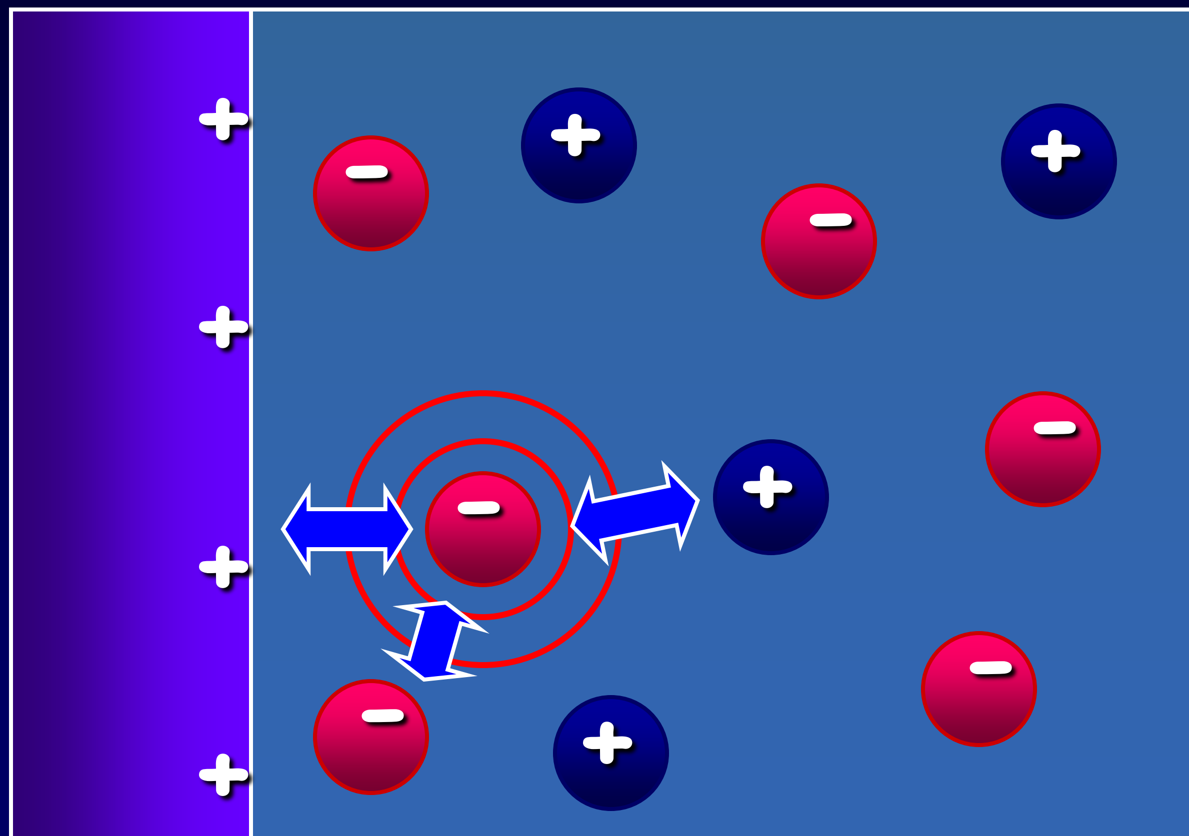
$$C = \left(\frac{d\sigma}{d\phi_e}\right) = \frac{\varepsilon}{d}$$





Modelo de Gouy-Chapman

Electrodo Disolución



3. Estructura

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

Ecuación de Poisson

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

Carga iónica

$$\frac{C_i(x)}{C_i^0} = \exp\left(-\frac{E_i(x) - E_i(x=\infty)}{RT}\right)$$
$$= \exp\left(-\frac{z_i F\phi(x) - z_i F\phi(\infty)}{RT}\right) = \exp\left(-\frac{z_i F\phi(x)}{RT}\right)$$

Distribución Boltzmann

$$\frac{d^2\phi}{dx^2} = -\frac{F}{\varepsilon}\sum_i z_i C_i^0 \exp\left(-\frac{z_i F\phi(x)}{RT}\right)$$

Ecuación de Poisson-Boltzmann

3. Estructura

$$\frac{d^2\phi}{dx^2} = -\frac{F}{\varepsilon}\sum_i z_i C_i^0 \exp\left(-\frac{z_i F\phi(x)}{RT}\right)$$

Ecuación Poisson-Bolztmann

Si el campo eléctrico no es muy fuerte (aprox. de campo débil):

$$\exp\left(-\frac{z_i F\phi}{RT}\right) = \left(1 - \frac{z_i F\phi}{RT} + \ldots\right) \approx 1 - \frac{z_i F\phi}{RT}$$

La ec. de Poisson-Bolztmann queda: Vale 0, por electroneutralidad

$$\frac{d^2\phi(x)}{dx^2} = -\frac{F}{\varepsilon}\sum_i z_i C_i^0\left(1 - \frac{z_i F\phi}{RT}\right) = -\frac{F}{\varepsilon}\left[\sum_i z_i C_i^0 - \sum_i \frac{z_i^2 C_i^0 F\phi}{RT}\right]$$

La ec. de Poisson-Bolztmann linealizada bajo la aprox de campo débil es:

$$\frac{d^2\phi(x)}{dx^2} = \frac{F^2\phi}{\varepsilon RT}\sum_i z_i^2 C_i^0$$

$$I = 1/2\sum z_i^2 C_i^0$$

Fuerza iónica

$$\frac{d^2\phi(x)}{dx^2} = \frac{2IF^2\phi(x)}{\varepsilon RT}$$

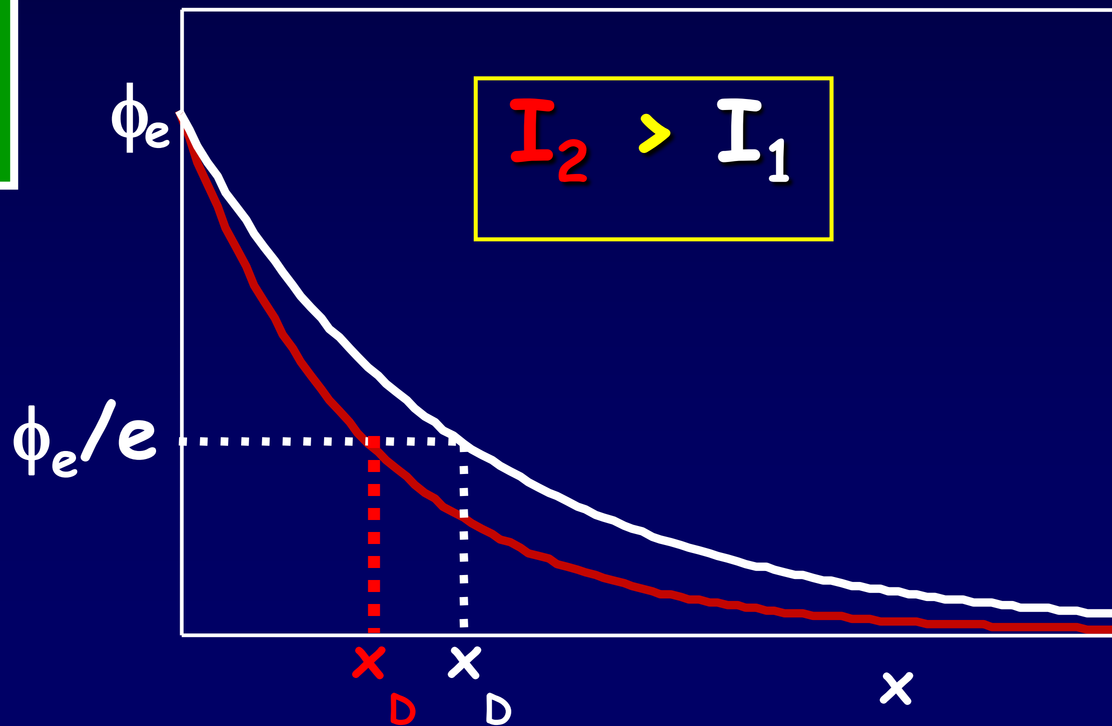
3. Estructura

$$\frac{d^2\phi(x)}{dx^2} = \frac{2IF^2\phi(x)}{\varepsilon RT}$$

$$\frac{d^2\phi(x)}{dx^2} = \frac{\phi(x)}{x_D^2}$$

$$x_D = \left(\frac{\varepsilon RT}{2F^2 I}\right)^{1/2}$$

$$\phi(x) = \phi_e \exp\left(-\frac{x}{x_D}\right)$$



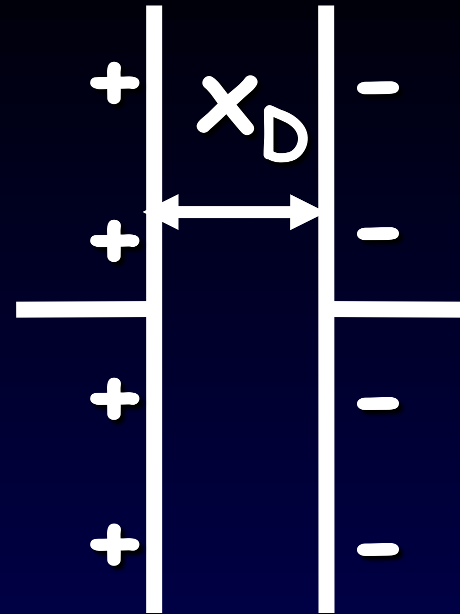
$$\phi(x) = \phi_e \exp\left(-\frac{x}{x_D}\right)$$

Aproximación Campo Débil

$$\sigma = -\varepsilon\left(\frac{d\phi}{dx}\right)_{x=0} = \frac{\varepsilon}{x_D}\phi_e$$

$$\gamma = \gamma^{max} - \frac{\varepsilon}{2x_D}\phi_e^2$$

$$C = \left(\frac{d\sigma}{d\phi_e}\right) = \frac{\varepsilon}{x_D}$$



x_D (nm)

C (M)	1:1	1:2	2:2
0.0001	304	176	152
0.01	30,4	19,2	15,2
0.1	0,96	0,78	0,68

Aproximación Campo Débil

$$\sigma = -\varepsilon\left(\frac{d\phi}{dx}\right)_{x=0} = \frac{\varepsilon}{x_D}\phi_e$$

$$\gamma = \gamma^{max} - \frac{\varepsilon}{2x_D}\phi_e^2$$

$$C = \left(\frac{d\sigma}{d\phi_s}\right) = \frac{\varepsilon}{x_D}$$

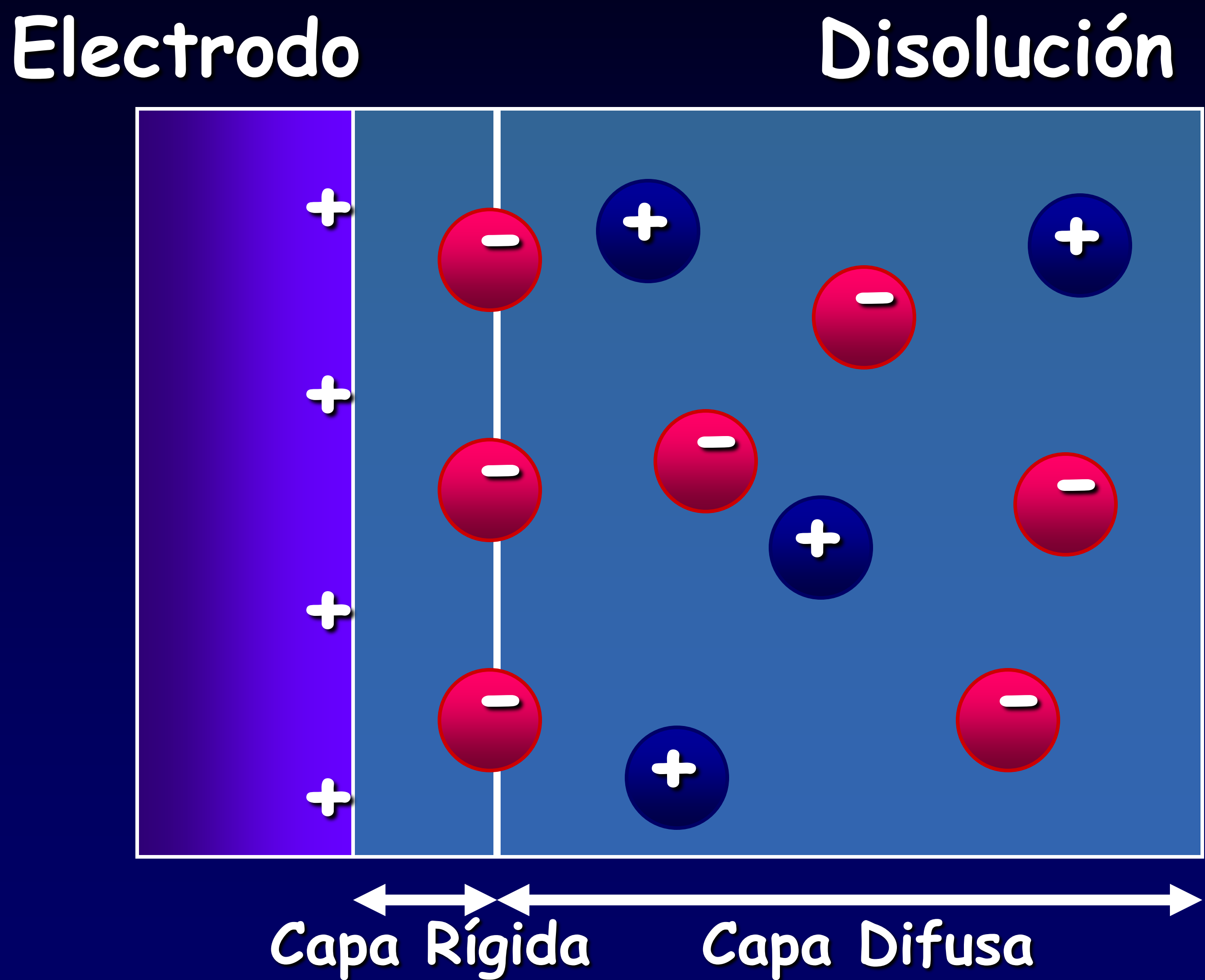
Un solo Electrolito z-z

$$\sigma = \left(8RTC^0\varepsilon\right)^{1/2}\operatorname{senh}\left(\frac{zF}{2RT}\phi_e\right)$$

$$\gamma = \gamma^{max} - \frac{8\varepsilon}{x_D}\left(\frac{RT}{zF}\right)^2\operatorname{senh}^2\left(\frac{zF}{4RT}\phi_e\right)$$

$$C = \frac{\varepsilon}{x_D}\cosh\left(\frac{zF}{2RT}\phi_e\right)$$

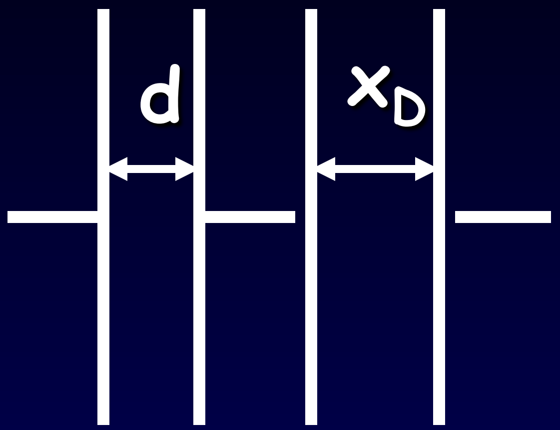
Modelo de Stern

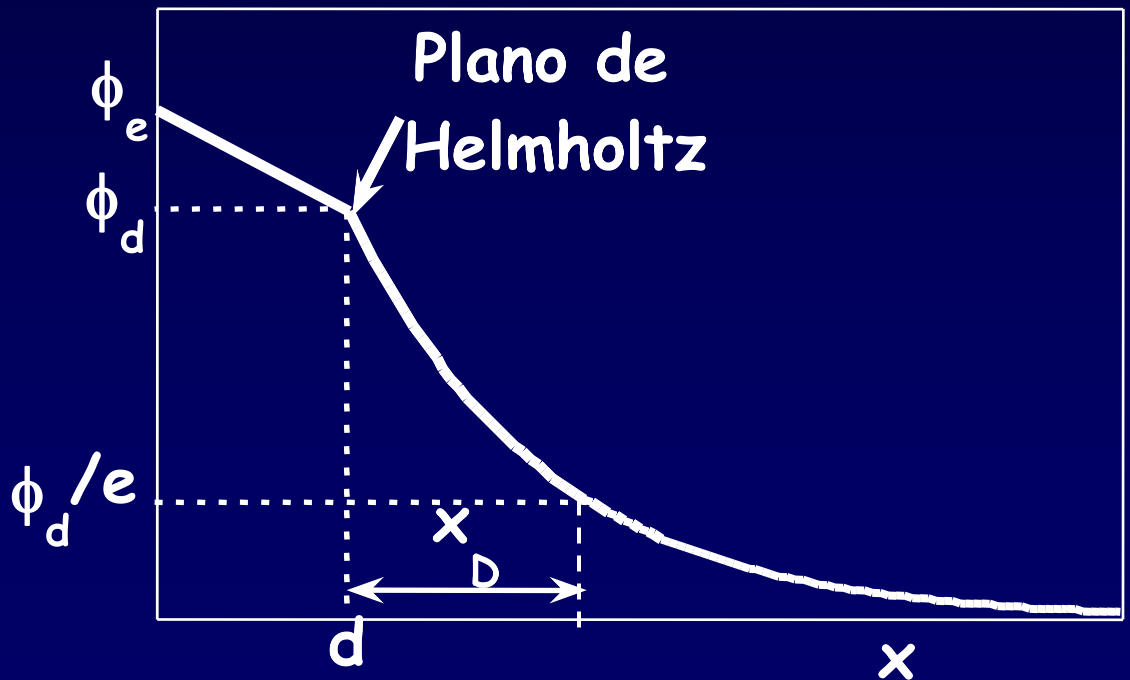


3. Estructura

$$\phi(x) = \phi_e\left(1 - \frac{x}{d}\right) + \phi_d\left(\frac{x}{d}\right) \qquad x < d$$

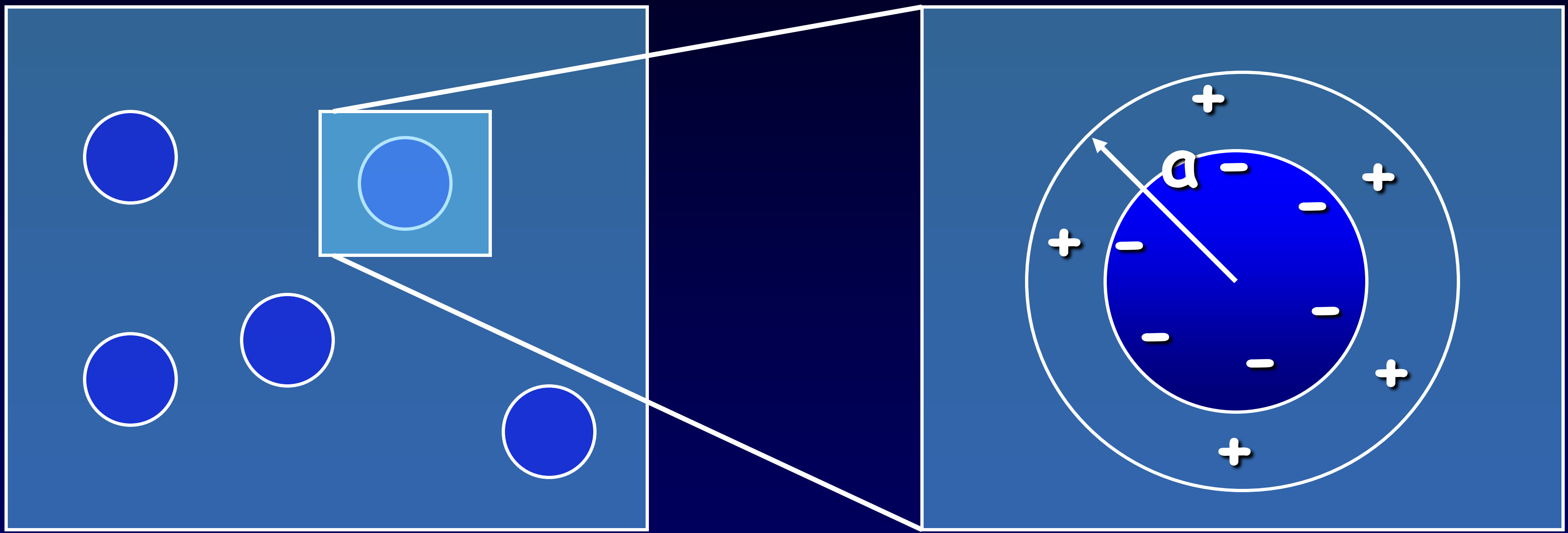
$$\phi(x) = \phi_d \exp\left(\frac{-x+d}{x_D}\right) \qquad x > d$$





$$\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_G}$$

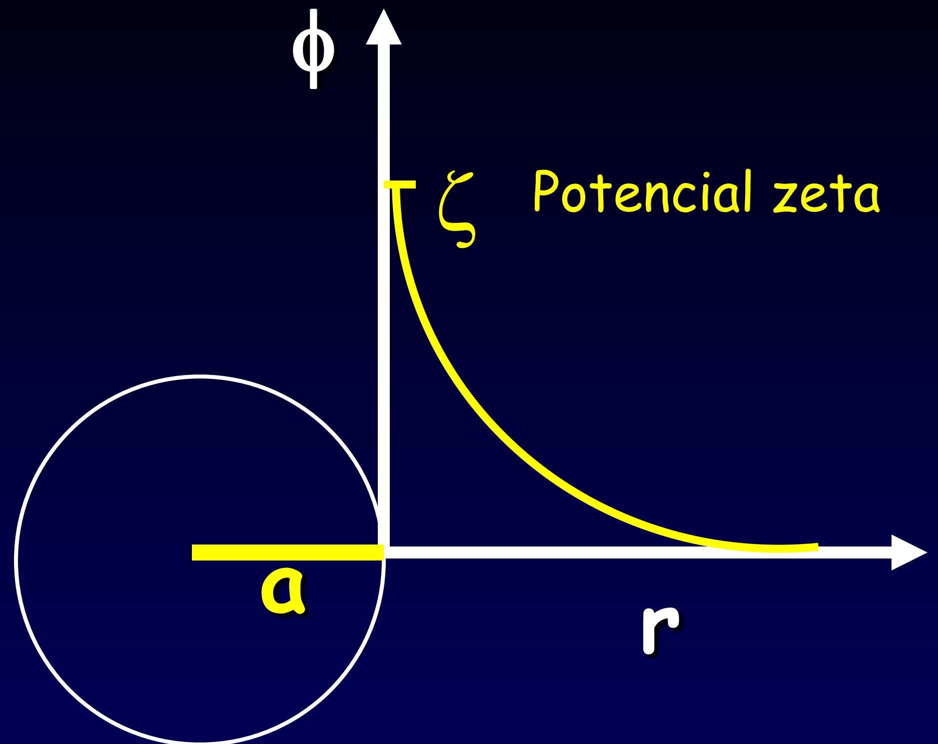
4. Doble Capa y Coloides



- Movilidad ➡ Electroforesis
- Estabilidad ➡ Coagulación

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\phi(r)}{dr}\right) = \frac{\phi(r)}{x_D^2}$$

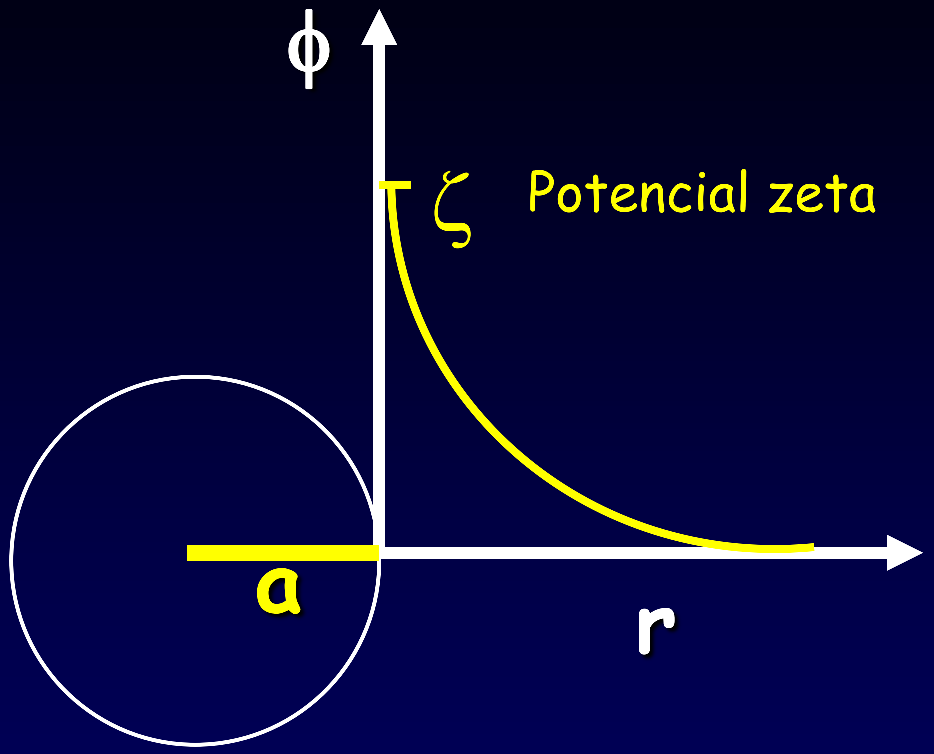
$$\phi(r) = \zeta\left(\frac{a}{r}\right)\exp\left(\frac{a-r}{x_D}\right)$$



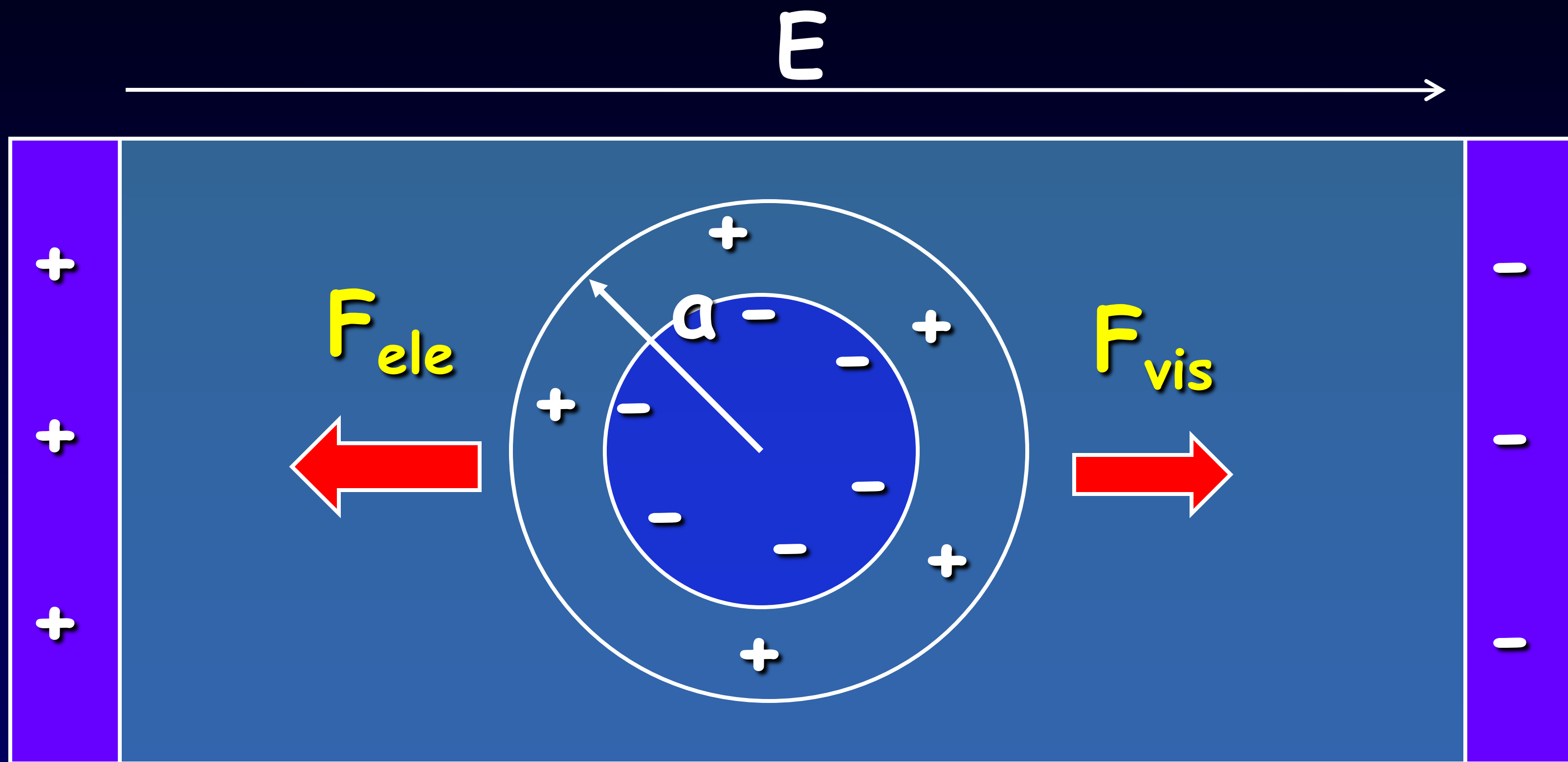
$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\phi(r)}{dr}\right) = \frac{\phi(r)}{x_D^2}$$

$$\phi(r) = \zeta\left(\frac{a}{r}\right)\exp\left(\frac{a-r}{x_D}\right)$$

$$\sigma = -\varepsilon\left(\frac{d\phi(r)}{dr}\right)_{r=a} = \frac{\varepsilon\zeta}{a}\left(1+\frac{a}{x_D}\right)$$



Electroforesis



Régimen estacionario $F_{ele} = F_{vis}$ ➡ Velocidad cte

Se define la movilidad electroforética (u) como el cociente v/E

$$F_{ele} = qE = (\sigma A)E = 4\pi a^2 E \frac{\varepsilon\zeta}{a}\left(1 + \frac{a}{x_D}\right)$$

$$F_{vis} = 6\pi a \eta v$$

$$F_{ele} = F_{vis}$$

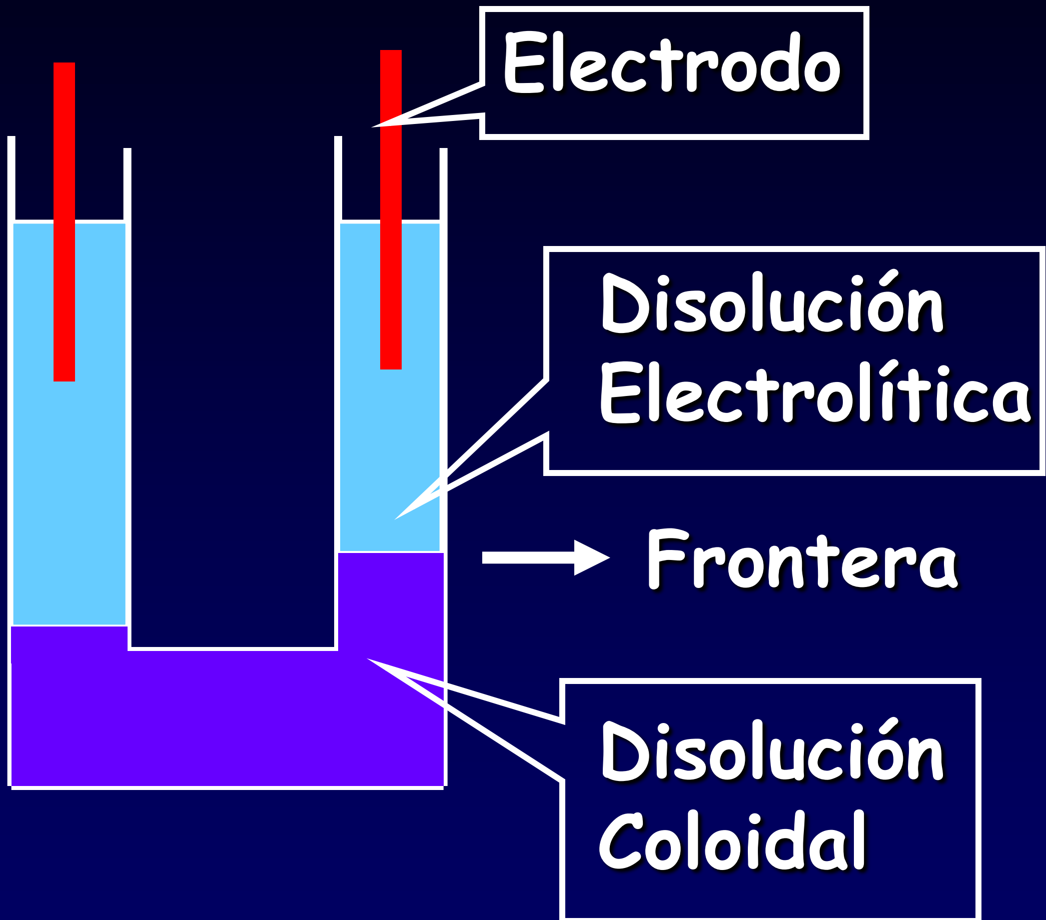
$$u = \frac{v}{E}$$

$$u = \frac{2}{3}\left(1 + \frac{a}{x_D}\right)\frac{\varepsilon\zeta}{\eta}$$

$$u = f\,\frac{\varepsilon\zeta}{\eta}$$

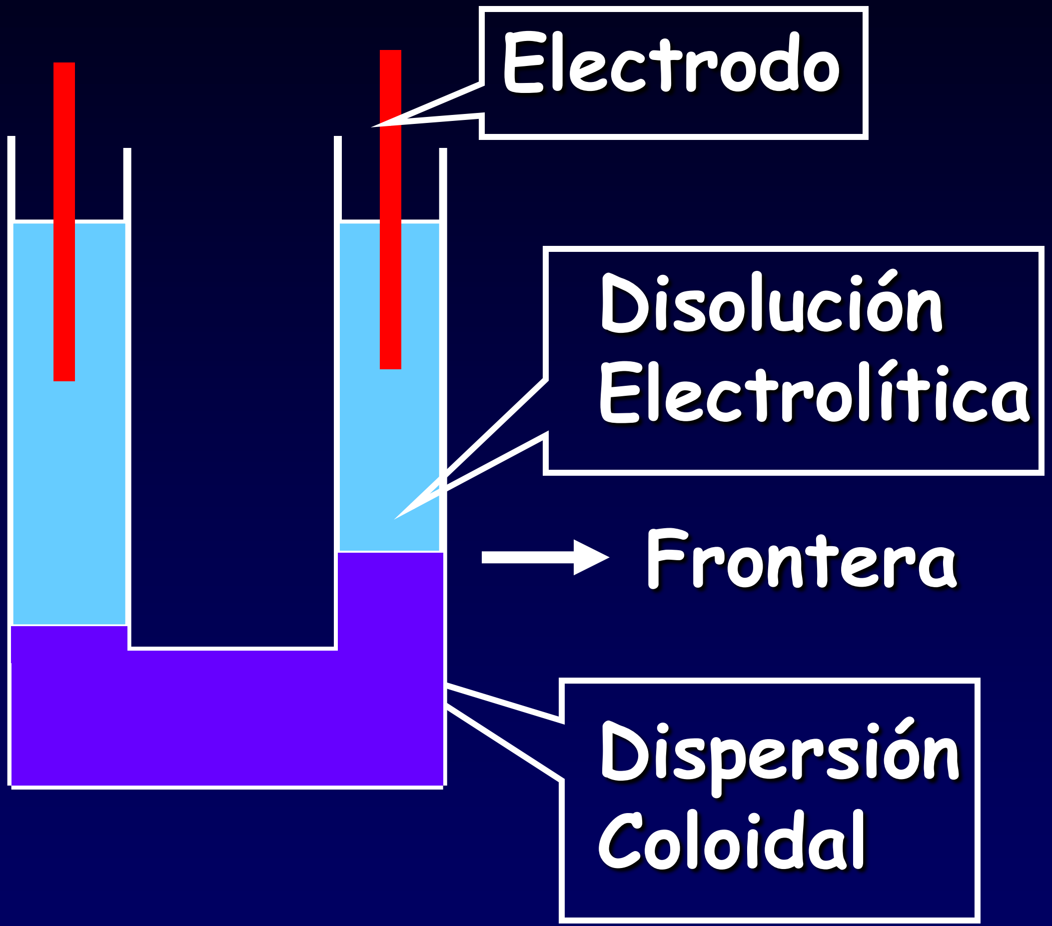
Ecuación de la Movilidad Electroforética

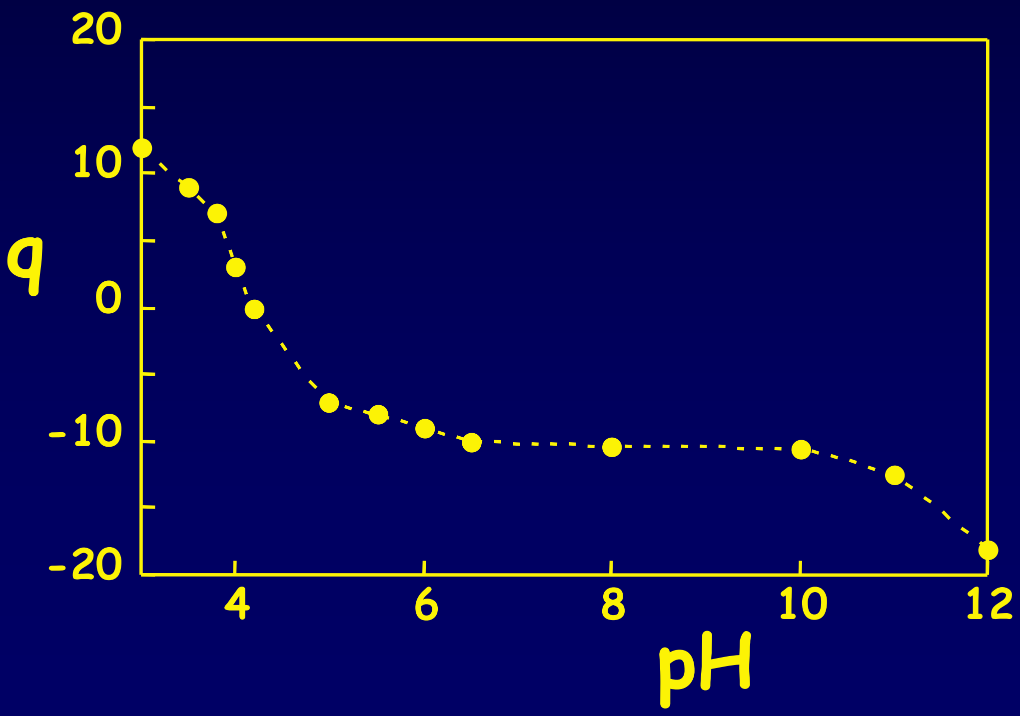
Electroforesis Práctica



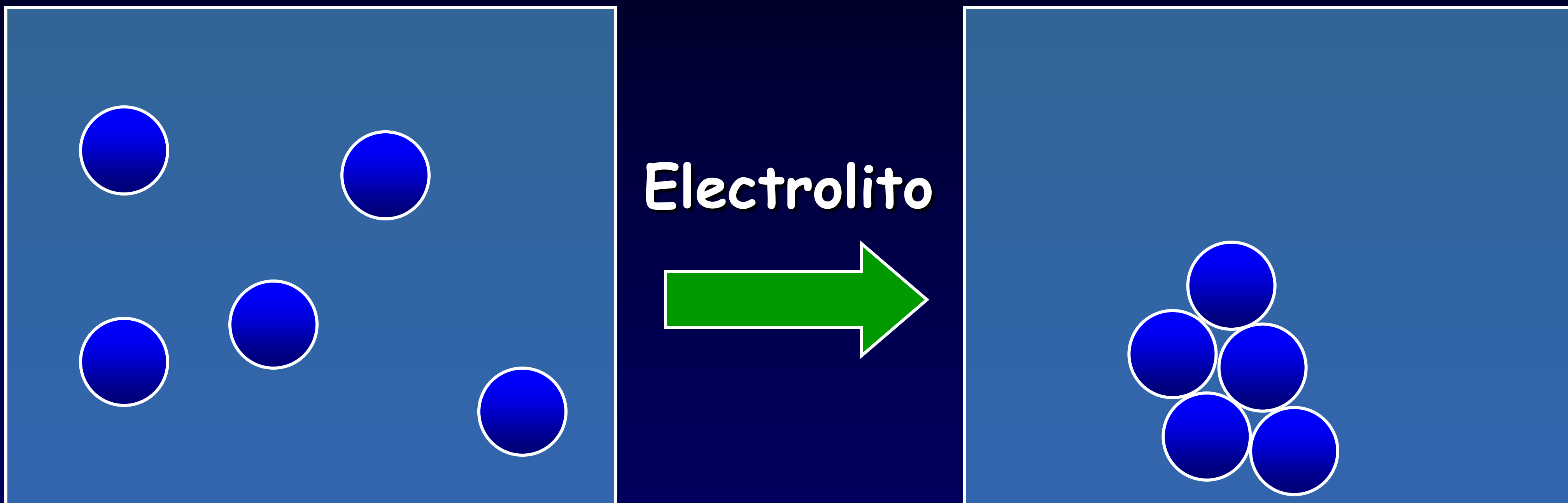
Electroforesis Práctica

$u \Rightarrow \zeta \Rightarrow q$



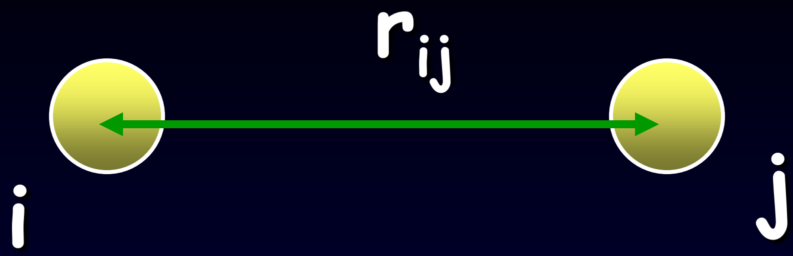


Estabilidad Dispersiones Coloides



$$U = U_{ele} + U_{dis} + U_{rep}$$

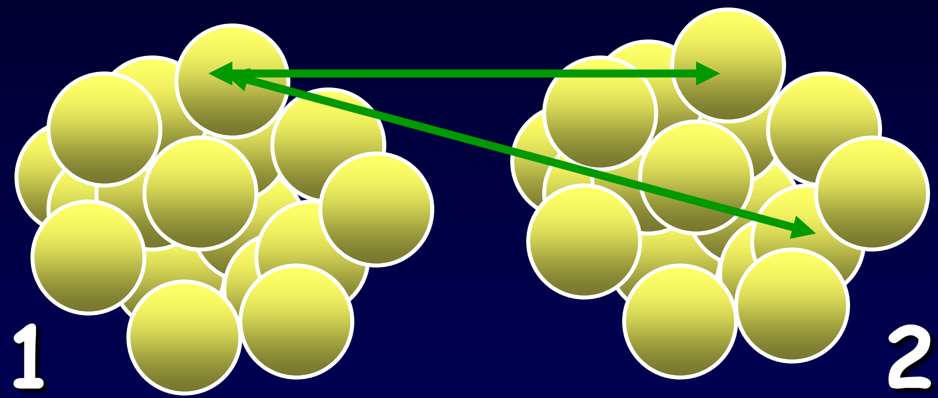
4. Coloides



$$U_{dis} = -\frac{C_{ij}}{r_{ij}^{6}}$$

4. Coloides

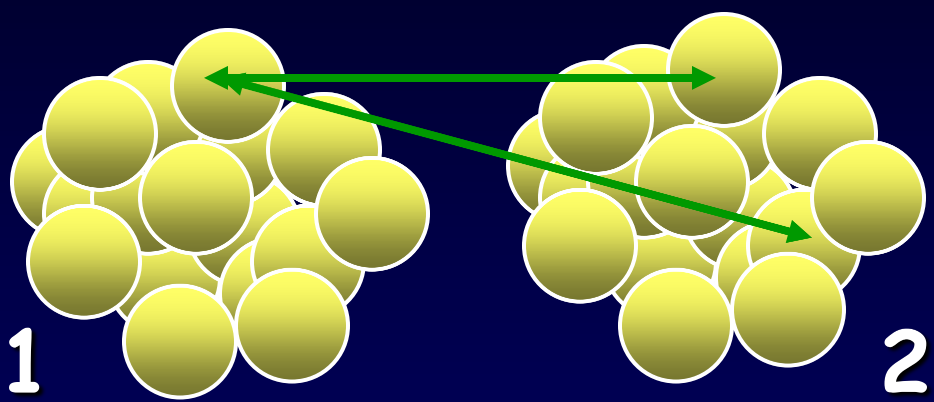
$$U_{dis} = -\frac{c_{ij}}{r_{ij}^6}$$



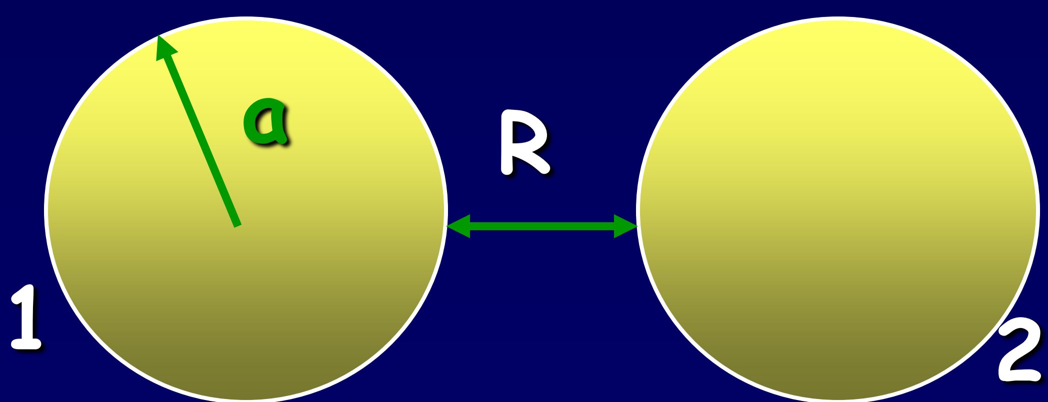
$$U_{dis} = -\sum_{i\in 1}\sum_{j\in 2}\frac{c_{ij}}{r_{ij}^6}$$

4. Coloides

$$U_{dis} = -\frac{C_{ij}}{r_{ij}^{6}}$$



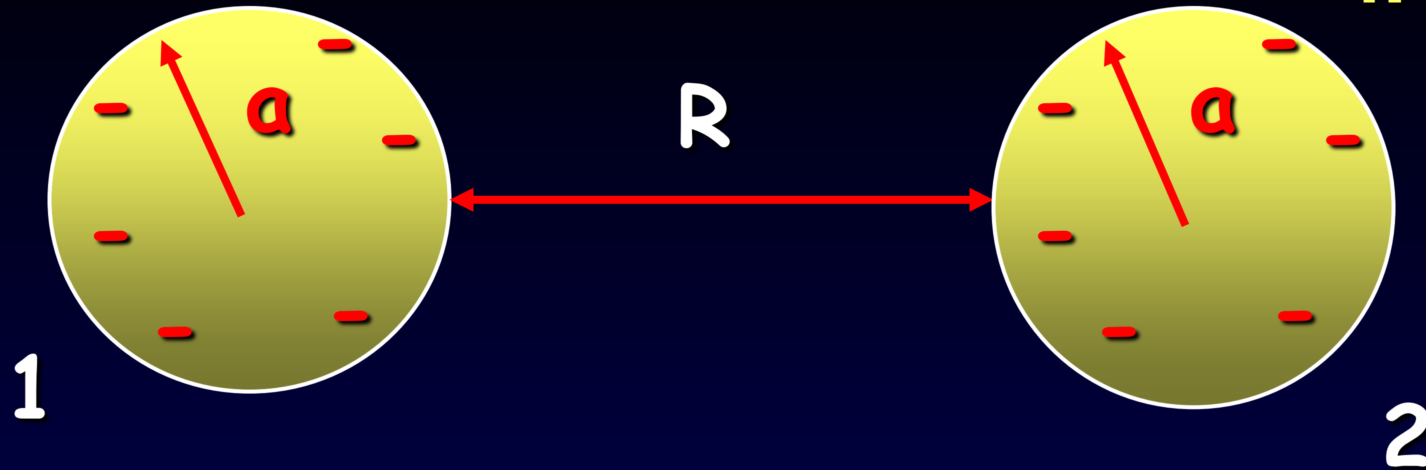
$$U_{dis} = -\sum_{i\in 1}\sum_{j\in 2}\frac{C_{ij}}{r_{ij}^{6}}$$

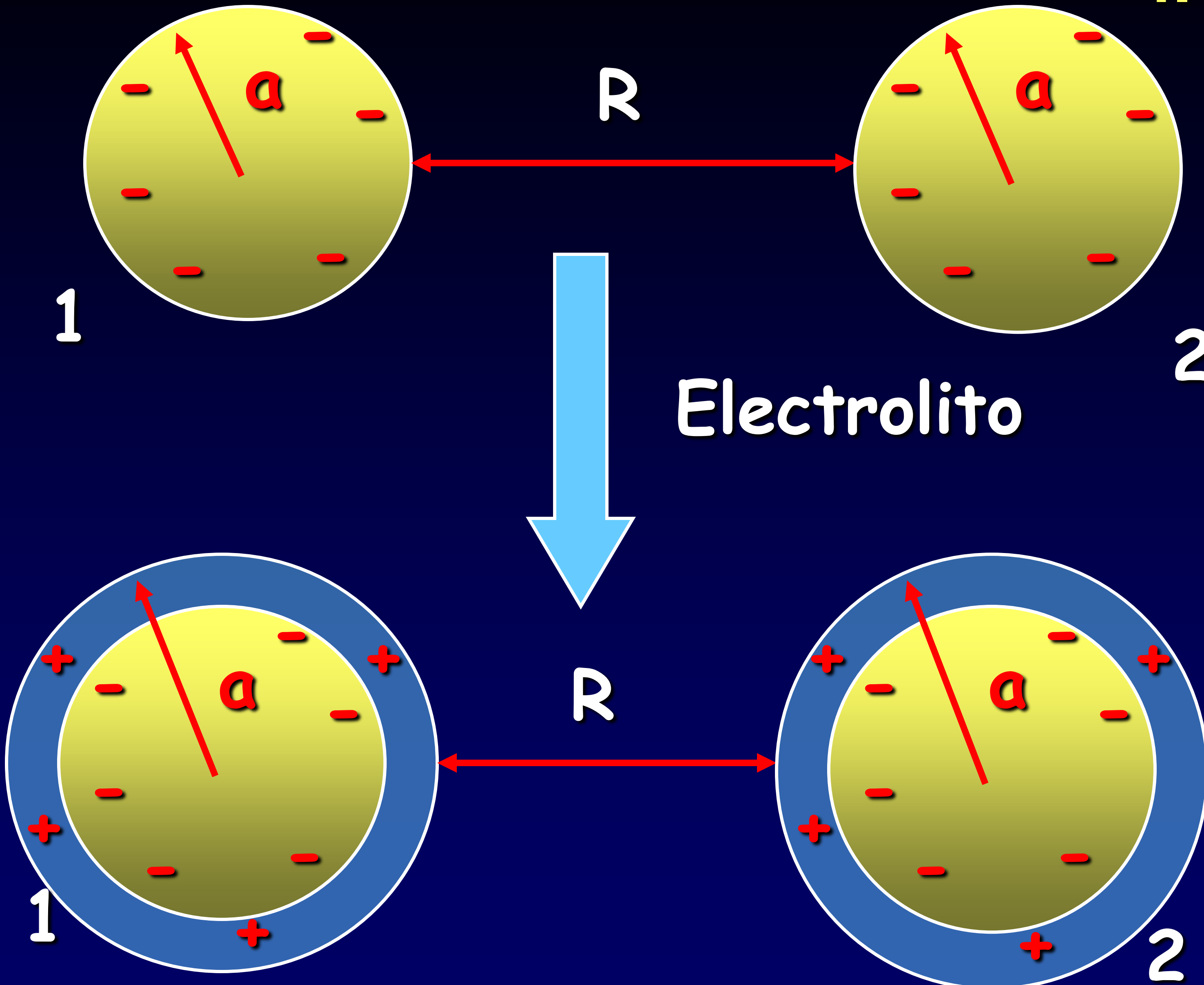


$$U_{dis} = -C\rho^{2}\int_{\tau_1} d\tau(1)\left[\int_{\tau 2}\frac{d\tau(2)}{r^{6}}\right] =$$

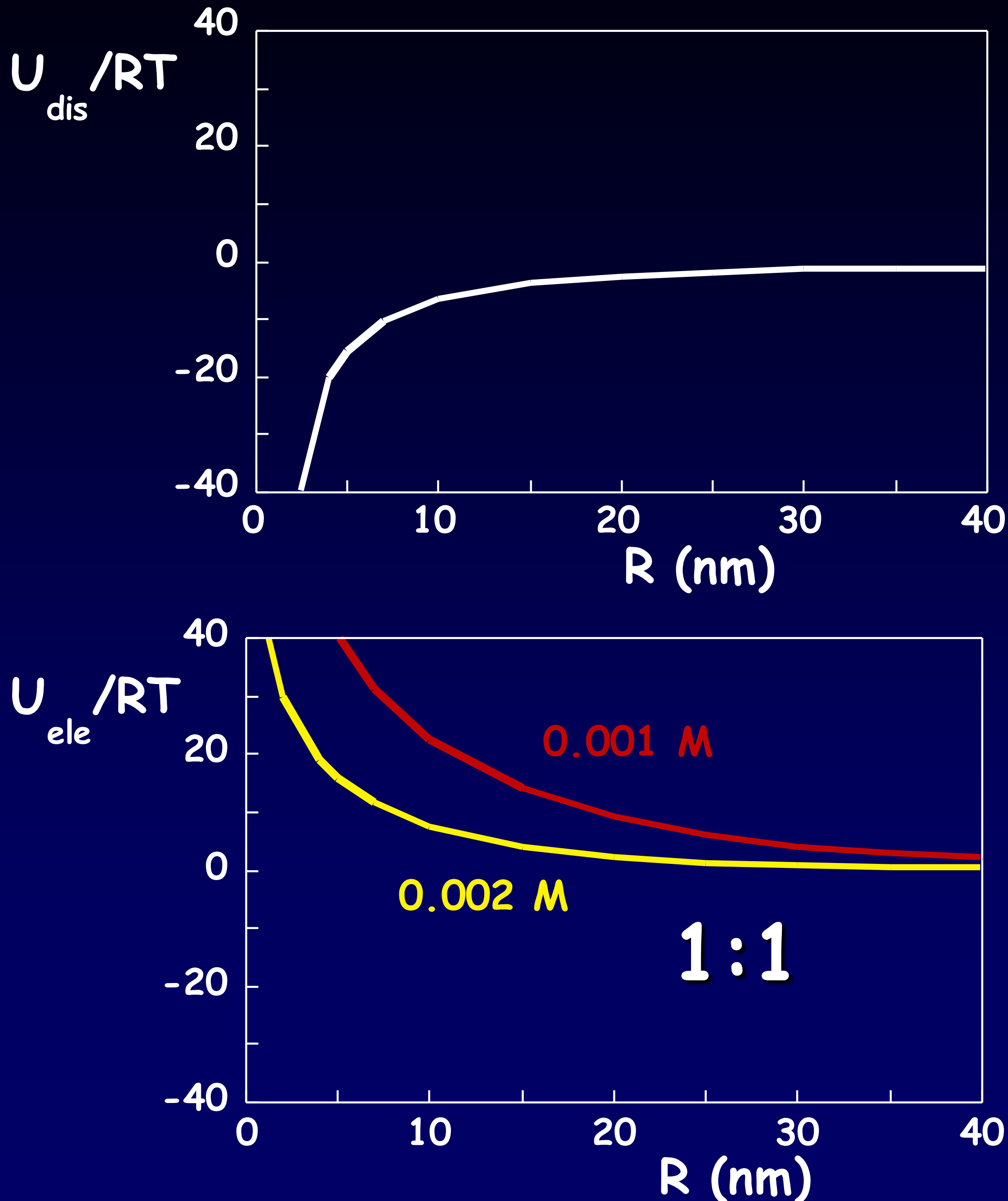
$$= -\frac{A}{12}\left[\frac{8a^{2}(R+a)}{R(R+2a)^{2}} + 2Ln\left(\frac{R(R+4a)}{(R+2a)^{2}}\right)\right]$$

4. Coloides



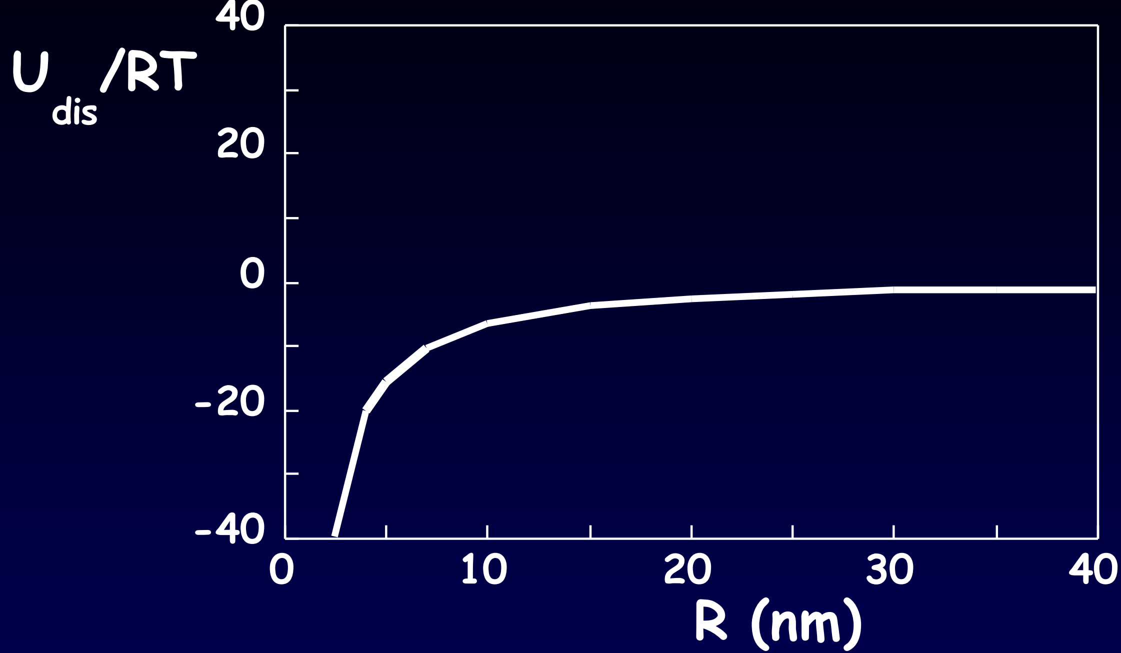

a
R
a
1
2
Electrolito
a
R
a
1
2

4. Coloides

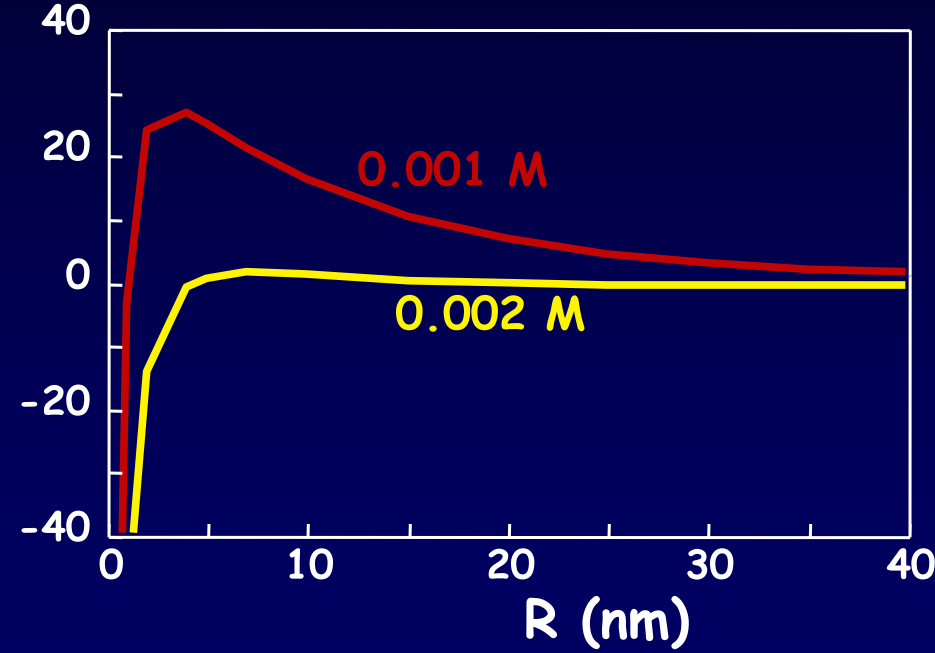


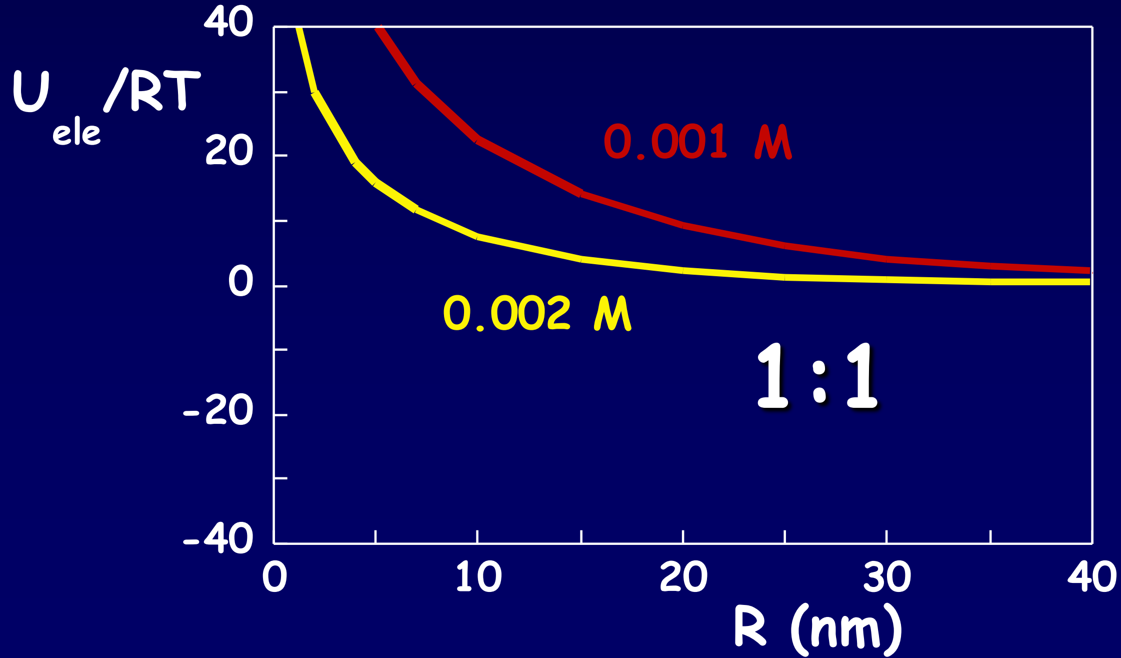
40
U_{dis}/RT
20
0
-20
-40
0
10
20
30
40
R (nm)
40
U_{ele}/RT
20
0.001 M
0
0.002 M
1:1
-20
-40
0
10
20
30
40
R (nm)

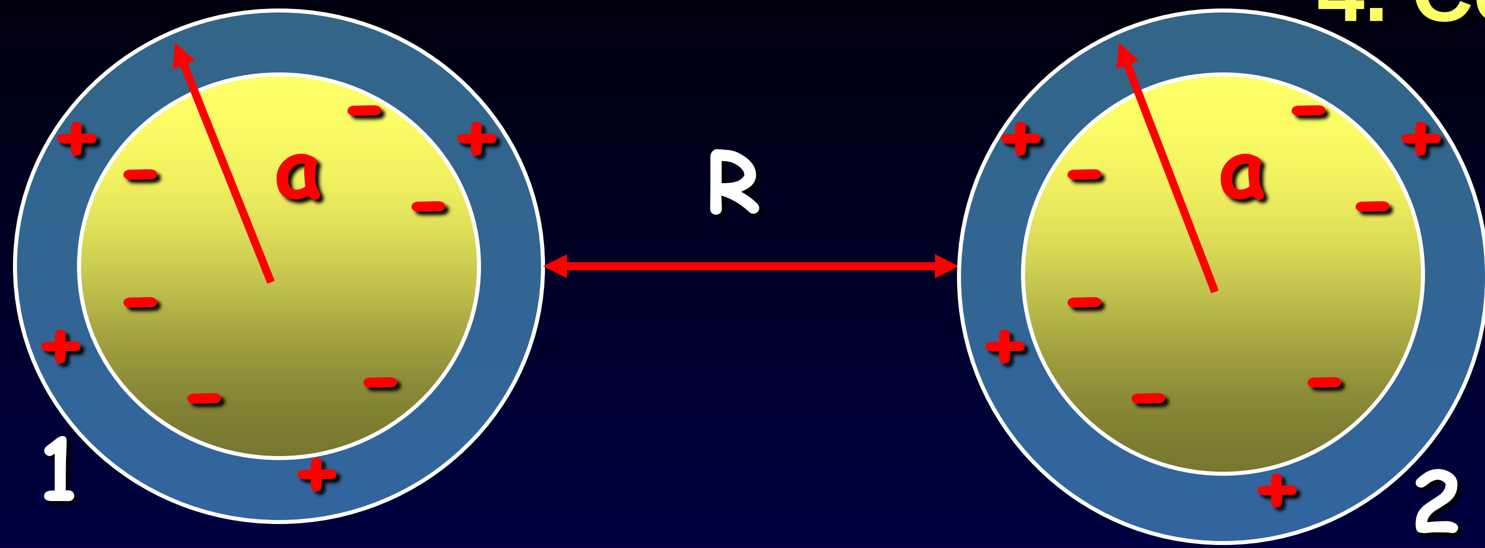
4. Coloides



$$U = U_{dis} + U_{ele}$$







$$U_{ele} = \int_{\tau 2} \phi_1(r)\rho_2(r)d\tau_2 = \int_{S_2} \phi_1(r)\sigma_2 dS_2$$

$$U_{ele} = -\frac{2\pi a^3}{\left(1+\frac{a}{x_D}\right)^2}\frac{\sigma^2}{\varepsilon}Ln\left[1-\exp\left(-\frac{R}{x_D}\right)\right] \qquad (a>>x_D)$$